SERIES C

Experimental petrology and petrology of lunar basalts, identification of primitive or parental magmas and use of high pressure experimental studies to deduce the nature of lunar sources.


SERIES D

Application of experimental petrology to understanding of the composition, mineralogy, melting relations, physical properties and evolution of the Earth's upper mantle. Includes spinel and garnet peridotite stability relationships and geothermometry and geobarometry, role of pargasitic amphibole in controlling melting relations, role of water and C-H-O fluids with particular emphasis on important roles for fO2 variation in effects of CH4 + H2O ± CO2 fluids and H2O ± CO2 fluids.


D8 Mori, T. and Green, D.H., 1975: Pyroxenes in the system Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ at high pressure. *Earth Planet. Sci. Lett.* 26: 277-286.


**SERIES E**

Experimental petrology related to crustal rocks, including subduction of oceanic crust, nature of crust/mantle boundary, mineral assemblages of granulite facies and geothermometry and geobarometry applied to crustal rocks.


Experimental petrology and petrogenesis of Apollo 12 basalts

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Abstract—Experimental studies at 1 bar and up to 30 kb establish the crystallization sequences for basalts 12021, 12065, 12022, 12009, and 12040. Olivine is the liquidus phase at low pressures. Minor chromium spinel and pigeonitic clinopyroxene either join the olivine at lower temperatures or accompany the olivine in the less magnesian basalts (12021, 12065). At higher pressures, subcalcic clinopyroxene becomes the liquidus phase except in the most magnesian basalt (12040), in which orthopyroxene joins the olivine and becomes the liquidus phase at pressures of 25 kb. Integration of experimental studies with observed mineralogy of natural rocks shows conclusively that the basalt compositions studied do not lie on a plagioclase + pyroxene + spinel + olivine cotectic nor have these rocks been derived by accumulation of olivine or pyroxene into such a low temperature cotectic liquid. The Apollo 12 basalts provide clear evidence for the genesis of olivine-rich basalts in the lunar interior. The nature of the source rock is deduced to be pyroxenite or olivine-bearing pyroxenite in which orthopyroxene is probably the major phase with lesser subcalcic or pigeonitic clinopyroxene. The 100 Mg/(Mg + Fe) ratio of the source region in the deep lunar interior is 75–80.

INTRODUCTION

The mineralogies of five examples of Apollo 12 basalts have been examined quantitatively, using polished thin sections of the natural rocks. The electron microprobe was used for analysis of olivine, pyroxenes, feldspar, spinels, ilmenite, and metallic iron, both as they occurred in the natural rocks and where synthesized in the experimental study. The samples studied were:

1. Well-crystallized pigeonite basalt (12040) rich in normative olivine (28% normative olivine);
2. Quenched olivine-rich augite basalt (12022) (19% normative olivine) with rather high TiO$_2$ content and low Mg/(Mg + Fe) ratio;
3. A remarkable chilled basalt (12009), containing only olivine and spinel as well crystallized phases set in glass or devitrified glass. This rock contains 11% normative olivine and is particularly significant for discussions of petrogenesis since its modal mineralogy shows that this composition existed at the lunar surface as a liquid or liquid with ~ 7% skeletal olivine phenocrysts;
4. Quartz-normative pigeonite basalt (12065) with low modal olivine and indication of a reaction relation between olivine and pigeonite;
5. Quartz-normative pigeonite basalt (12021) or dolerite, lacking olivine, and containing large pigeonite crystals with relatively unzoned cores.

The crystallization sequence of each of these compositions was studied experimentally at atmospheric pressure and high pressure, and the compositions of phases precipitated experimentally were determined with the electron probe. Accuracy of electron probe analysis is estimated as ±3% of the amount of an element present.
Most of the above-solidus experiments were carried out on glass prepared by melting 0.3 to 0.5 gm of the powdered, homogenized lunar sample. In addition, investigations were made of subsolidus mineral assemblages displayed by 12009, 12040, and 12021, glasses prepared from oxide mixes were used. No differences were detected in results from the glasses prepared in the two different ways. Experimental techniques were similar to those of RINGWOOD and ESSENE (1970). Experiments were carried out in metallic Fe capsules and redox conditions closely matching those present during the crystallization of Apollo 12 rocks were achieved—this is confirmed by the close matching of Cr, V, and Ni contents of both the experimental and natural olivines and spinel. For certain key relationships, such as the appearance of plagioclase in the melting interval and the incoming of garnet in the subsolidus assemblages, the phase boundaries were reversed.

Subsolidus Relationships

Results of subsolidus experiments on 12040 and 12009 are shown in Fig. 1. In both rocks, the low pressure olivine + pyroxene + plagioclase + ilmenite assemblage reacts at 7–8 kb, 1200°C to yield slightly different pyroxenite assemblages. In 12009, both olivine and plagioclase are eliminated by this reaction, yielding an assemblage of over 95% pyroxene (Ca_{23}Mg_{39}Fe_{38}, 9 weight % Al_2O_3) with minor ilmenite and rutile. Spinel may occur at lower temperatures (< 1100°C) in the pyroxenite assemblage if the pyroxene is unable to accommodate 9% Al_2O_3; the assemblage will then be pyroxene + spinel + rutile + quartz, the latter three phases being very minor constituents. In 12040, reaction between olivine and anorthitic plagioclase eliminates the latter phase producing an assemblage of olivine pyroxenite, [80% pyroxene (Ca_{23}Mg_{46}Fe_{31}; 9% Al_2O_3), 15.5% olivine, 4.5% ilmenite]. At lower temperatures, spinel may occur in place of olivine, the pyroxene then becoming less aluminous.

The reaction by which garnet is produced in both 12040 and 12009 involves the breakdown of aluminous pyroxene (9% Al_2O_3) to less aluminous pyroxene + garnet with increasing pressure. This reaction occurs over a broad pressure interval; theoretical garnet contents of 37% (with 59% pyroxene, 2.5% ilmenite, 1.5% rutile in 12009) and 32% (with 15.5% olivine, 48% pyroxene, 4.5% ilmenite in 12040) being reached at the highest pressures.

In comparison with the Apollo 11 compositions (RINGWOOD and ESSENE, 1970) the disappearance of plagioclase occurs at considerably lower pressure in 12009 and 12040; this is a direct result of the incompatibility between olivine and anorthitic plagioclase (GREEN and HIBBERSON, 1970) in the Apollo 12 compositions. In the Apollo 11 basalts, it is the reaction of plagioclase with ilmenite and quartz which first yields garnet and begins to eliminate the plagioclase. The appearance of garnet in Apollo 12 basalts at 1200°C also occurs at a slightly lower pressure than the appearance of garnet in Apollo 11 basalt, because of the different reactions involved. The relationships are exactly as would be predicted from the study of a variety of terrestrial basalts, pyroxenites and olivine + anorthite assemblages (GREEN and RINGWOOD 1967; IRVING and GREEN, 1970; and GREEN and HIBBERSON, 1970). At lower temperatures (~ 900 or 800°C) the pyroxenite field of 12040 and 12009 may be
The rocks are discussed in order of decreasing normative olivine content except for 12022, which differs in other respects and is treated last.

**12040**

The liquidus olivine at 1400°C is Fo$_{82}$ and olivine becomes more iron rich and more abundant at lower temperatures. Spinel (titaniferous chromite) is the second phase to appear and pigeonite the third phase at 1190°C. Some of the early formed magnesian olivine then reacts with the liquid to precipitate pigeonite. Plagioclase does not appear until near 1140°C and ilmenite (probably a product of reaction of the prior-formed...
titaniferous spinel with residual liquid) appears at about 1100°C. Comparison of the natural olivine (≤ Fo65), pigeonite (Ca7.5Mg66.5Fe26) and spinel crystals with the experimental phases shows that the earliest phases within the natural rock record a crystallization temperature of 1150 ± 10°C and crystallization proceeded to lower temperatures without equilibration of early precipitated phases with the interstitial liquid. Thus, if 12040 represents a magma composition, then the magma had cooled slowly from a liquidus of ~ 1400°C during its movement to the lunar surface and only entered the stage of rapid cooling (extrusive stage?) when approximately 50–60% crystallization had occurred. On the other hand, it can be shown (COMPSTON et al., 1971) that the major element composition of 12040 can be closely matched by the addition of 21.2% olivine (Fo74.4) to liquid of 12009 composition. Trace element data rule out this particular genetic relationship (COMPSTON et al., 1971), but a parent...
similar to 12009 in major elements but with lower Ba, Rb, Sr, Zr, and REE could yield 12040 composition by olivine accumulation. The observations on the natural rock would then require that the ~ 20% accumulative olivine continued to equilibrate with the liquid from ~ 1230°C to 1150°C so that all Fo_{74.4} olivine was converted to olivine ≤ Fo_{65}. In brief, chemical data (Compston et al., 1971) show that 12040 cannot be simply related to any of 12009, 12018, 12020, 12052, 12065, 12022, 12035, by processes of olivine accumulation. However, it could be so related to a parent magma, not represented in the Apollo 12 samples, which is less olivine rich than 12040. However, 12040 natural rock contains no intrinsic evidence of olivine accumulation (no large olivines with homogeneous magnesian cores, no olivine of Fo_{74.4} composition). Thus, the possibility remains that 12040 represents a liquid composition or a liquid + ~ 10% olivine crystals. The implications of this possibility will be further explored.

12009

The liquidus olivine at 1230°C is Fo_{75} and the crystallization sequence at lower temperatures parallels that of 12040 with spinel, pigeonite, plagioclase, and ilmenite appearing at the same temperatures (within experimental error) in the two compositions. It is to be noted particularly that the olivine composition at the temperature of plagioclase appearance is Fo_{55} and at this temperature the rock would be 40–60% crystallized. The natural rock 12009 was very rapidly chilled from T ~ 1190°C so that there was no opportunity for pigeonite to crystallize. The composition of the natural olivine (cores) in 12009 is up to Fo_{71} and thus matches with the liquidus olivine determined for the 12009 composition. It is emphasized that if any of the olivine occurring naturally in 12009 were of accumulative origin, precipitated from liquid (A) less olivine-rich than 12009 bulk composition, then experimental remelting of this (liquid A + accumulate) must produce liquidus olivine of more magnesian composition than that in equilibrium with the liquid A. Thus the combination of data from the natural rock and the experiments shows unequivocally that the bulk composition 12009 existed as a liquid at or close to the lunar surface. This liquid could thus itself be a primary magma from the lunar interior or the primary magma could have been richer in olivine (≥ Fo_{75}) than 12009.

12065

Olivine, pigeonite, and spinel occur together on the liquidus of 12065 at 1180°C. Olivine reacts out at 1150°C if equilibrium is maintained during cooling and plagioclase appears at 1130°C. The composition of the olivine on the experimental liquidus is Fo_{67} but the cores of the natural olivines range up to Fo_{71}. We may exclude as improbable that the olivine was accidentally incorporated as xenocrysts into the magma. Then, because the most magnesian olivine that will crystallize from 12065 is Fo_{67}, the presence of the Fo_{71} cores must be interpreted as metastably preserved from an earlier higher temperature precipitation from a more magnesian liquid. Separation of most but not all the early formed olivine from the parental liquid produced 12065 as a derivative liquid with a few relict olivines which had failed to equilibrate with the
fractionating liquid. It may be noted that the most magnesian olivines in 12065, as in 12040, are grains partly or completely enclosed in large pigeonite crystals.

Thus the combination of experimental data and analytical data on the natural rock provides evidence for the origin of 12065 as a derivative composition produced by olivine \((\sim \text{Fo}_{71})\) extraction from a more olivine-rich, more magnesian parent magma. Compston et al. (1971) show that a composition (12052) closely similar to 12065 can be produced from 12009 by extraction of \(\sim 12\%\) olivine [composition averaging \(\text{Fo}_{73}\)] and 0.24\% spinel.

12021

Olivine, pigeonite and spinel also occur on the liquidus, at 1155\(^\circ\)C, in this composition. The olivine is \(\text{Fo}_{66}\) and is consumed by reaction with liquid to precipitate pigeonite by \(\sim 1140\)\(^\circ\)C. The natural rock contains no olivine and the most magnesian cores of the pigeonite are less magnesian than the pigeonites coexisting with olivine in the highest temperature experimental runs. The pigeonite compositions thus indicate temperatures of crystallization of 1140\(^\circ\)C for the highest temperature pyroxenes of the natural rock. It may be noted that rock 12021 is the only one of the rocks examined by us in which plagioclase could have been co-precipitating with pyroxene at or prior to the onset of rapid cooling or quenching of the rock (at \(\sim 1120\)\(^\circ\)C for 12021). In the other rocks plagioclase appeared during rapid cooling and not during the stage of equilibrium crystallization.

12022

The liquidus phase of 12022 is olivine of composition \(\text{Fo}_{77}\). Pyroxene (pigeonite) does not appear until a temperature of about 1150\(^\circ\)C and ilmenite and plagioclase a little lower at 1130\(^\circ\)C. The natural rock contains olivine of composition \(\text{Fo}_{69}\), spinel with low Mg/(Mg + Fe) ratio, but contains no pigeonite, only quench augite. Although the rock was rapidly cooled, there is no evidence of early precipitation of olivine, \(\text{Fo}_{77}\), or the near-liquidus spinel.

The compositions of the cores of the olivine phenocrysts are \(\text{Fo}_{67} - \text{Fo}_{69}\) and correspond to compositions in equilibrium with spinel + liquid at temperatures of \(\sim 1170\)\(^\circ\)C in the 12022 bulk composition. Thus 12022 may be partially an accumulate with accumulation of olivine (\(\text{Fo}_{69} - \text{Fo}_{67}\)) in a liquid less olivine-rich than 12022 and crystallizing spinel + olivine on or slightly below its liquidus. This liquid + accumulate was very rapidly chilled from a temperature of \(\sim 1170\)\(^\circ\)C, allowing no opportunity for nucleation of pigeonite (at \(\sim 1150\)\(^\circ\)C) but instead producing quench augite, quench plagioclase and quench ilmenite. The very small size of the olivine crystals (most of 0.3–0.5 mm diameter, rarely to 0.9 mm) suggests that crystal settling could not have been rapid and it is likely that the olivine is locally concentrated within a fluid lava prior to rapid quenching of the particular portion sampled.

Deviations of Magmas from Plagioclase Cotectic Compositions

In the previous section we have shown that 12009 composition existed as a liquid at the lunar surface at temperatures of 100\(^\circ\)C above the olivine-pigeonite-plagioclase-spinel cotectic, and that approximately 50\% of 12009 would crystallize before this
cotectic was reached. The natural rock was quenched from a temperature 60–70°C above this 4-phase cotectic. Similarly, we have shown that 12022 was quenched from about 40°C above the olivine-pyroxene-plagioclase-spinel cotectic and, prior to quenching, was precipitating only olivine + spinel. Basalts 12065 and 12021 represent derivative liquids from more olivine-rich magnesian basalts such as 12009 and both bulk compositions lie on the olivine + pigeonite + spinel cotectic. The data indicate that basalt 12065 was rapidly cooled from 40°C above the plagioclase cotectic and would have had to crystallize about 30–40% of pyroxene + spinel and react all olivine away before reaching the pyroxene + plagioclase + spinel cotectic. Rapid cooling or quenching of 12021 began only 10–15°C above the temperature for plagioclase appearance and 20–30% crystallization of pyroxene occurs before plagioclase appears. In 12040, the liquid was in equilibrium with olivine, pigeonite and spinel at the onset of rapid cooling and was 10–15°C above the temperature marking the appearance of plagioclase.

Of the Apollo 12 basalts which we have studied not one has a bulk composition corresponding to a liquid lying along a pyroxene + plagioclase + spinel ± olivine cotectic. Furthermore, chemical compositions of other Apollo 12 rocks (Compston et al., 1971; Kushiro and Haramura, 1971), with the exception of 12038, indicate that they also have this characteristic. Biggar et al. (1971) interpret these compositions as mixtures of a liquid of (pyroxene + plagioclase + spinel + olivine) cotectic composition with added cognate accumulative olivine or pyroxene. This hypothesis, that almost all surface-collected samples are partial accumulates rather than primary or derivative liquids, is of low intrinsic plausibility. It should be based on direct supporting evidence adduced from each sample. Our experimental studies, integrated in the previous sections with the natural mineral data, provide definitive evidence that this hypothesis is invalid for each of the compositions on which we have worked. We emphasize that, whilst our studies of both Apollo 11 and Apollo 12 rocks contradict the specific O'Hara et al. (1970) and Biggar et al. (1971) hypothesis involving the accumulation of cognate olivine etc., into a low temperature, highly fractionated cotectic (pyroxene + plagioclase + spinel ± olivine) liquid, they do not rule out limited (∼ 20%) fractionation involving olivine, accessory spinel and possibly minor pyroxene in liquids which themselves depart from the plagioclase cotectic.

The difference in our own interpretation of Apollo 12 basalts from that of Biggar et al. is not due to any major differences in experimental results. Indeed, the actual observations on experimental crystallization of lunar samples by Muñ et al. (1971), Biggar et al. (1971), and our own data are in substantial agreement. On the determination of the temperature for incoming of plagioclase, our results on 12021, 12065, 12022, and 12040 are identical within experimental limits with those of Muñ et al. (1971). Biggar et al. (1971) record appearance of plagioclase at 1160°C in 12040, 12018, and 12020, but Muñ et al. (1971) note plagioclase appearance between 1125°C and 1150°C, and in our data on 12040 we also find plagioclase disappears at 1150°C. The distinction which Biggar et al. (1971) make between their group I and group II basalts with plagioclase appearing at 1160° and 1140°C, respectively is not substantiated by our own or Muñ et al.'s data. In their experiments, Muñ et al. used the natural crystalline basalts and most runs were carried out for 3 days or more
to reach equilibrium. We used glass (made from natural rocks) as starting material for most runs of 1–6 hours \((T \geq 1100^\circ\text{C})\) but we confirmed the temperature of disappearance of plagioclase in both Apollo 12 basalts and Apollo 11 basalts by using glass previously crystallized to a very fine grained olivine + pyroxene + plagioclase assemblage. The latter reversal experiments refute the contention of Biggar et al. (1971) that the nonappearance of plagioclase on the liquidus of the Apollo 11 composition studied by Ringwood and Essene was due to metastability and failure of plagioclase to nucleate from the glass.

It must be concluded therefore that most Apollo 11 and Apollo 12 rock compositions are substantially removed from the pyroxene + plagioclase coticetic compositions to be expected if they represent residual liquids (from 80% crystallization, Biggar et al. (1971)) produced by near-surface crystal fractionation in large lava lakes as advocated by O'Hara et al. (1970) and Biggar et al. (1971). It can be further stated that the observed mineralogies of Apollo 12 basalts show that these rock compositions are not produced by accumulation of cognate olivine and/or pyroxene into a low temperature \((\sim 1140^\circ\text{C})\) liquid fractionating along the plagioclase + pyroxene + spinel \pm olivine coticetic. The particular model discussed by Biggar et al. is unfortunate because 12038, the composition regarded as the coticetic liquid in which accumulative olivine gave rise to rocks 12018, 12020, and 12040, has trace element and Sr-isotopic characteristics which show conclusively that the proposed relationships are invalid (Compston et al., 1971). Similar objections apply to the other postulated coticetic composition 12064 and the postulated derivative compositions 12021, 12065, and 12052. Also, the data of Biggar et al. (1971) and Muñoz et al. (1971) show that the liquidus of 12064 is 30–40°C above the appearance of plagioclase.

**MELTING RELATIONSHIPS AT HIGH Pressures**

The data and discussion presented in previous sections argue that the Apollo 12 basalts are samples of a number of separate, apparently independent lava flows produced within the lunar interior and having undergone only minor crystal fractionation (extraction and accumulation of olivine mainly) at or near the lunar surface. It is thus relevant to examine the melting behavior and subsolidus mineralogy of the Apollo 12 basalts to attempt deductions on their origin and on the nature of the lunar interior.

Although olivine is a liquidus phase in all compositions studied at atmospheric pressure, the load pressure at which olivine disappears from the liquidus is very dependent on bulk composition. In 12021, olivine disappears from the liquidus at less than 2 kb, in 12065 it disappears at slightly greater than 2 kb, in 12009 it disappears between 7 and 9 kb, in 12022 between 14 and 15 kb, and in 12040 between 20 and 25 kb. Spinel, on or near the liquidus, shows a sensitive increase in \(\text{Al}_2\text{O}_3\) with increasing pressure. The near-liquidus pyroxene in all cases is low-calcium clinopyroxene (pigeonite) at atmospheric pressure (Table 1). Low-calcium clinopyroxenes also occur at higher pressures but with increasing degree of crystallization at a given pressure or with increasing pressure for a given degree of crystallization the pyroxene becomes more calcium-rich and slightly more aluminous. The effect is most marked in 12021 and 12065, i.e., the basalts with lowest MgO contents, and in 12022, possibly as a
result of the higher normative Di/Hy ratio of this composition. In 12009, the near-liquidus pyroxene at 5 kb, 1280°C contains 2.5% CaO and 1.8% Al₂O₃ (Ca₅.0Mg₇.5Fe₂.6), at 10 kb, 1300°C the liquidus pyroxene contains 4.2% CaO and 2.3% Al₂O₃ (Ca₈.7Mg₆.7Fe₂.8), and at 15 kb, 1390°C the liquidus pyroxene contains 7.2% CaO and 4.1% Al₂O₃ (Ca₁₅.₃Mg₅₈.₄Fe₂₆.₄).

<table>
<thead>
<tr>
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<td>38.70</td>
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<td>&lt; 0.03</td>
<td>4.61</td>
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<tr>
<td>Al₂O₃</td>
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<td>&lt; 0.03</td>
<td>12.14</td>
<td>12.24</td>
<td>12.32</td>
</tr>
<tr>
<td>FeO</td>
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<td>25.56</td>
<td>27.62</td>
<td>28.20</td>
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<td>0.20</td>
<td>0.40</td>
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<tr>
<td>MgO</td>
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<td>38.13</td>
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<td>8.38</td>
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<td>0.54</td>
<td>48.88</td>
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<td>44.26</td>
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<td>V₂O₃</td>
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<td>1.02</td>
<td>1.02</td>
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<table>
<thead>
<tr>
<th>12021</th>
<th>1. Most Mg-rich pigeonite core in natural rock</th>
<th>2. Pigeonite, accompanied by olivine, at 1150°C, 1 bar</th>
<th>3. Pigeonite, not accompanied by olivine, at 1140°C, 1 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.85</td>
<td>52.32</td>
<td>52.39</td>
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<tr>
<td>TiO₂</td>
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<td>0.79</td>
<td>0.96</td>
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<td>Al₂O₃</td>
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<td>1.10</td>
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<td>FeO</td>
<td>17.92</td>
<td>17.10</td>
<td>20.00</td>
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<td>MnO</td>
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<tr>
<td>MgO</td>
<td>21.78</td>
<td>22.62</td>
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<td>CaO</td>
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<td>4.55</td>
<td>4.85</td>
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<td>0.06</td>
<td>0.05</td>
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<td>Cr₂O₃</td>
<td>0.84</td>
<td>0.75</td>
<td>0.69</td>
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High pressure pyroxenes

<table>
<thead>
<tr>
<th>1. Clinopyroxene from 12009, 15kb, 1390°C (near liquidus)</th>
<th>2. Orthopyroxene from (12009 + 10% olivine) at 15kb, 1440°C (coexists with olivine Fo₇₄)</th>
<th>3. Orthopyroxene from 12040, 15kb, 1460°C (coexists with olivine Fo₇₈)</th>
<th>4. Orthopyroxene from 12040, 20kb, 1480°C (coexists with clinopyroxene)</th>
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<tr>
<td>SiO₂</td>
<td>51.70</td>
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<td>7.19</td>
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<tr>
<td>Cr₂O₃</td>
<td>1.04</td>
<td>0.78</td>
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In 12022, the first pyroxenes to appear vary as follows:

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature</th>
<th>CaO (%)</th>
<th>Al₂O₃ (%)</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Atmosphere</td>
<td>1150°C</td>
<td>3.7%</td>
<td>1.7%</td>
<td>Ca₇.₈Mg₇₂.₃Fe₁₉.₉ with olivine</td>
</tr>
<tr>
<td>5 kb</td>
<td>1280°C</td>
<td>2.9%</td>
<td>1.2%</td>
<td>Ca₆.₀Mg₇₃.₁Fe₂₀.₉</td>
</tr>
<tr>
<td>13 kb</td>
<td>1360°C</td>
<td>4.5%</td>
<td>3.7%</td>
<td>Ca₉.₁Mg₆₉.₁Fe₂₁.₈</td>
</tr>
<tr>
<td>15 kb</td>
<td>1370°C</td>
<td>6.5%</td>
<td>6.2%</td>
<td>Ca₁₃.₇Mg₆₃.₄Fe₂₂.₉ no olivine</td>
</tr>
</tbody>
</table>

In 12040, pigeonite is the second phase to appear up to 10 kb but at 12–20 kb orthopyroxene joins olivine on or near the liquidus, clinopyroxene appearing at lower temperatures and replacing orthopyroxene. Orthopyroxene becomes the liquidus phase at 25 kb, olivine is absent and clinopyroxene is the second phase to appear. Although the orthopyroxene is optically very distinctive and easily distinguished from the clinopyroxene, the difference in chemical composition is remarkably small. Orthopyroxenes (Table 1) analyzed from runs at 12 kb and 15 kb contain 1.8–1.9% CaO, 1.8–2.2% Al₂O₃, and have compositions near Ca₄.₀Mg₇₆.₅Fe₁₉.₅ (compared with clinopyroxene at 5 kb, 1280°C which contains 3.0% CaO, 1.9% Al₂O₃ and Ca₇Mg₷₁Fe₂₃). The pressure required for disappearance of olivine as a liquidus phase (20–25 kb) and the relative roles of olivine, orthopyroxene and clinopyroxene in 12040 basalt are closely analogous to those of terrestrial olivine-rich tholeiite to tholeiitic picrite as summarized in GREEN (1970).

It was shown in the section on atmospheric pressure melting studies that 12009 composition was originally completely liquid at or very near the lunar surface. However, this conclusion permits 12009 to be itself a derivative liquid at or near the lunar surface. The experimental results show that as olivine alone (or with a trace of metallic iron) occurs on the liquidus of 12009 then any possible parental liquid to 12009 must be along the 12009 olivine Fo₇₅ compositional join. In major elements, 12040 lies almost on this join possibly representing addition of 21% olivine, Fo₇₄₄, to 12009 (COMPSTON et al., 1971). A second composition was prepared corresponding to 90.9% basalt 12009 + 9.1% olivine (Fo₇₅). Experiments on this composition gave a liquidus temperature of 1440 ± 10°C at 15kb (compared with 1390 ± 10°C for 12009); both olivine (Fo₇₄₄) and orthopyroxene (2.0% CaO, 2.3% Al₂O₃ Ca₄.₀Mg₇₆.₀Fe₂₀) occurred on the liquidus. Sub-calcic clinopyroxene joined the olivine and orthopyroxene at lower temperature (1420°C).

**IMPLICATIONS OF EXPERIMENTAL STUDY OF APOLLO 12 BASALTS**

*Limitations on lunar composition arising from subsolidus results*

Calculated densities of the low pressure gabbroic mineral assemblages of rocks 12009 and 12040 are 3.37 and 3.40 g/cm³, respectively. With increasing pressure these rocks transform successively through a transitional pyroxenite facies lacking feldspar (3.55–3.52 g/cm³) and ultimately to eclogitic facies (3.67–3.63 g/cm³). At similar temperatures, feldspar disappears at a much lower pressure than in Apollo 11 and garnet appears also at a slightly lower pressure. Using analogous arguments to those used in the case of Apollo 11 basalts (RINGWOOD and ESSENE, 1970) it can be demonstrated conclusively that the internal composition of the moon cannot resemble those...
of rocks 12009 and 12040. Because of the initial high density of these rocks and transformations to much denser pyroxenite and eclogite, a moon composed of such material would be much denser than is observed.

It follows that the magmas from which rocks 12009 and 12040 crystallized have been differentiated from more primitive source material possessing a higher \( \text{Mg/(Mg + Fe)} \) ratio. The large degree of low pressure crystallization necessary before the appearance of plagioclase combined with the high Cr and V abundances in these rocks, demonstrate that extensive low pressure fractional crystallization has not been a major factor. The role of limited (\( \sim 20\% \)) separation of olivine, accessory spinel, and possibly minor pigeonite has previously been discussed. Following arguments introduced by Ringwood and Essene (1970) and Ringwood (1970) in the case of Apollo 11 basalts, it is inferred that the Apollo 12 basalts have also formed by a partial melting process within the lunar interior. Ages of Apollo 12 basalts are more than 1 billion years less than that of the moon and during this period extensive cooling of the lunar lithosphere by conduction would have extended to depths of more than 200 km. Accordingly, the source region lay below this depth. By studying the nature of phases on and near the liquidus of Apollo 12 basalts, inferences regarding the nature of this source region may be drawn.

Role of crystal fractionation at or near the lunar surface in Petrogenesis of Apollo 12 basalts

The atmospheric pressure melting studies, together with the chemical and mineralogical data on the natural basalts, clearly demonstrates the role of olivine addition and subtraction, possibly accompanied by minor chromium spinel, in those lunar basalts which have normative olivine or < 2% normative quartz. The role of olivine extraction and accumulation is confirmed by the detailed chemical studies (Compton et al., 1971). In all the Apollo 12 basalts studied, pigeonitic pyroxene precedes plagioclase and the degree of crystallization increases markedly with the appearance of pyroxene, inhibiting the possibility of mechanical separation of crystals during cooling.

It can be firmly stated using the experimental crystallization sequences and the chemical data, that the compositions of the various Apollo 12 basalts studied cannot have been derived one from another by any process of crystal fractionation involving extraction or addition of plagioclase. On the other hand, basalts like 12021 and 12065 may be derivative from olivine basalts such as 12009 by extraction of olivine, trace of spinel and possibly, for 12021, minor pigeonitic pyroxene. The olivine-rich basalt 12022 is distinctive in its composition and crystallization sequence and cannot be genetically related to 12009 (12021, 12065) by processes of low pressure crystal fractionation. This rock probably contains some accumulative olivine and is transitional towards Apollo 11 basalts in its higher TiO\(_2\) content, higher normative Di/Hy and rather low \( \text{Mg/(Mg + Fe)} \) ratio. Although the major element composition of basalt 12040 is consistent with derivation by olivine (Fo\(_{74}\)) accumulation into liquid of a 12009 composition, this is inconsistent with the very low trace element abundance (Zr, Rb, REE, etc.) in 12040. Conversely, 12009 (and thus 12065, 12021) is consistent in major element content with derivation from 12040 as the parental magma, by separation of olivine formed at the lunar surface or during ascent above 300 km.
Thus 12040 must either represent a different magma or magma + accumulative olivine composition—the magma would have higher Mg/(Mg + Fe), lower TiO$_2$, and much lower Zr, Rb, REE (Compton et al., 1971) than 12009 and appears to continue a chemical trend: Apollo 11 basalts $\rightarrow$ 12022 $\rightarrow$ 12009 (12065, 12021) $\rightarrow$ 12040. This chemical variation or trend is not produced by processes acting at the lunar surface and may be a consequence of variation in the melting process in the lunar interior.

**Nature of source region**

It has been argued previously that all the Apollo 12 basalts examined must originate by partial melting rather than complete melting of their source region. The experimental studies at high pressure provide information on the possible residual phase(s) from this partial melting process, and thus on the possible total composition of the source region. The basalts 12065, 12021, like the Apollo 11 basalts, have olivine as a liquidus phase only at $\leq$ 2 kb; at higher pressures, the liquidus role of pigeonitic pyroxene (3–4% CaO, 1–2% Al$_2$O$_3$ in 12065; 5–6% CaO, 3% Al$_2$O$_3$ in 12021) suggests the possibility of a pyroxenitic source. The Mg/(Mg + Fe) ratio of the liquidus phase is $\approx$ 66, and if these liquids were direct melts from a source pyroxenite, then this pyroxenite would have 100Mg/(Mg + Fe) $\approx$ 66. However, the density of this pyroxenite ($\approx$ 3.45) is higher than that of the moon and source material of this kind could not be characteristic of the lunar interior. It is more probable that these basalts have been modified by fractional crystallization of 10–30% of olivine in near-surface lunar conditions from parental basalts like 12009 or 12040.

Basalt 12009 could be a direct melting product of olivine clinopyroxenite at pressures up to 8 kb, in which case the source region would have 100Mg/(Mg + Fe) $\leq$ 75. At higher pressures, 12009 again has pigeonitic pyroxene alone on the liquidus (9 kb, 1310°C pyroxene with 4.66% CaO, 2.61% Al$_2$O$_3$ and 100Mg/(Mg + Fe) = 75). The Al$_2$O$_3$/CaO ratio of a source region combining 12009 composition with pigeonite of the above composition would be < 1 and the arguments of Ringwood and Essene (1970, p.781) for the presence of significant orthopyroxene in the source region remain relevant. Basalt 12009 is clearly very nearly saturated with orthopyroxene at 10 kb and the studies of terrestrial olivine tholeiites, of 12040 and of 12009 + 10% olivine allow the prediction that the addition of 5–7% of olivine ($\approx$ Fo$_{75}$) to 12009 would produce a basalt with orthopyroxene + clinopyroxene + olivine on the liquidus at 11–14 kb. Such a basalt would be a potential derivative from a pyroxenite or an olivine pyroxenite source rock (100Mg/(Mg + Fe) $\approx$ 75) at depths of 200–400 km.

Basalt 12040, if accepted as a magma composition, would provide unambiguous evidence for the presence of orthopyroxene in the source region as orthopyroxene is near or on the liquidus from 12 kb to 20–25 kb (250–500 km). Olivine accompanies the orthopyroxene (but would not be present at the higher pressures (> 14 kb) for a magma composition intermediate between 12009 and 12040, i.e. with $\approx$ 20% normative olivine) and clinopyroxene appears at lower temperatures. Basalt 12040 could thus be derived from a pyroxenite (olivine pyroxenite) source at 250–500 kms depth provided the degree of melting was sufficiently high to eliminate clinopyroxene leaving only major orthopyroxene (1.7% CaO, 1.5–3% Al$_2$O$_3$) and minor olivine as residual phases. The temperature of melting would be 1420 $\pm$ 20°C at 250 km or 1540 $\pm$ 20°C.
at 500 km. The source region, if 12040 is a direct partial melt, would have 100Mg/(Mg + Fe) = 82 ± 2.

In summary, we consider that the Apollo 12 basalts provide strong evidence for the derivation of olivine-rich magmas containing 20–30% normative olivine and derived by partial melting of a pyroxenite or olivine pyroxenite source region at depths of 200–500 km. The observed variation in the lunar basalts in TiO₂, K₂O, Na₂O, P₂O₅, and in the trace elements which are strongly partitioned into a melt fraction implies either large differences in degrees of partial melting or large inhomogeneity in the source regions in the abundances of these elements. Alternatively, both factors may operate. If differences in degree of partial melting are important then we maintain that the Apollo 11 basalts were derived by very small degrees of partial melting of the source pyroxenite. Basalt 12022 was derived by a higher degree of melting than the Apollo 11 basalts, and 12009 and 12040 were derived by still higher degrees of melting which caused dilution of the trace element-rich early melt by large amounts of orthopyroxene and low-Ca clinopyroxene.

The source region of lunar basalts is inferred to differ from the source region for terrestrial basalts in having a lower 100Mg/(Mg + Fe) ratio of 75–80 (earth's upper mantle 100Mg/(Mg + Fe) ∼ 89). In addition, the much lower Al₂O₃ contents of the clinopyroxenes and orthopyroxenes on the liquidus of the lunar basalts in the 10–25 kb range, when compared with those of terrestrial basalts, implies that the residual pyroxenes of the source region are similarly low in Al₂O₃. It is inferred that the Al₂O₃/pyroxene ratio of the lunar source region is considerably lower than that of the source region for terrestrial basalts.

Europium anomaly

The presence of a negative europium anomaly (relative to other rare earths) may be either a characteristic of the source region, or, assuming chondritic RE abundances in the source region, it may be a consequence of crystal-liquid fractionation during formation of lunar basalt. To explore the latter possibility, preliminary experiments upon the partition of Eu²⁺, Sr²⁺ and Gd³⁺ between feldspars, pyroxene, calcium phosphate and liquid have been carried out (results are summarized in Table 2).

The significance of the feldspar-liquid partition coefficients has been previously discussed (RINGWOOD, 1970). The negative europium anomaly cannot readily be explained by crystallization of calcic plagioclase from a parent basaltic magma possessing chondritic initial relative abundances. (See also HASKIN et al., 1970.) The partition coefficients for Gd³⁺ and Eu²⁺ between pyroxene and liquid are both small, the coefficient for Eu²⁺ being even smaller than for Gd³⁺. These values (Table 2) confirm previous expectations (e.g., HASKIN et al., 1970) that the negative europium anomaly also cannot be explained by either partial melting or fractional crystallization processes involving equilibrium partition of rare earths between pyroxene and liquid.

Unfortunately, it was not possible to determine the partition coefficient for Eu²⁺ in the diopside-whitlockite system, as this ion did not appear to be stable relative to Eu³⁺. In all runs in sealed iron capsules where substantial amounts of phosphate were present, partial reduction of phosphate occurred, with phosphorus dissolving in the iron, as shown by electron probe analysis. This process apparently caused an increase
Table 2. Experimentally determined crystal-liquid partition coefficients $K^1$.

<table>
<thead>
<tr>
<th>System</th>
<th>Element</th>
<th>Crystalline Phase</th>
<th>$K_{\text{Crystal-liquid}}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apollo 11 basalt</td>
<td>Eu$^{2+}$</td>
<td>Plagioclase</td>
<td>1.20 ± 0.10</td>
<td>This work</td>
</tr>
<tr>
<td>Apollo 11 basalt + 25%</td>
<td>Eu$^{2+}$</td>
<td>Plagioclase</td>
<td>1.00 ± 0.10</td>
<td>Ringwood (1970)</td>
</tr>
<tr>
<td>additional normative</td>
<td>Sr$^{2+}$</td>
<td>Plagioclase</td>
<td>1.50 ± 0.10</td>
<td>Ringwood (1970)</td>
</tr>
<tr>
<td>anorthite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Eu$^{2+}$</td>
<td>Augite (16% CaO)</td>
<td>0.10 ± 0.04</td>
<td>This work, liquidus phase at 1250°, 10kb</td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Gd$^{3+}$</td>
<td>Augite (16% CaO)</td>
<td>0.17 ± 0.05</td>
<td>This work, liquidus phase at 1250°, 10kb</td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Gd$^{3+}$</td>
<td>Augite (19% CaO-liquid)</td>
<td>0.35 ± 0.11</td>
<td>Near-liquidus phase, atmospheric pressure</td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Gd$^{3+}$</td>
<td>Olivine</td>
<td>&lt;0.02</td>
<td>Near-liquidus phase, atmospheric pressure</td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Eu$^{2+}$</td>
<td>Armalcolite</td>
<td>0.11 ± 0.05</td>
<td>Near-liquidus phase, atmospheric pressure</td>
</tr>
<tr>
<td>Apollo 11 basalt</td>
<td>Gd$^{3+}$</td>
<td>Armalcolite</td>
<td>0.05 ± 0.03</td>
<td>Near-liquidus phase, atmospheric pressure</td>
</tr>
<tr>
<td>D60 W20</td>
<td>Gd$^{3+}$</td>
<td>Diopside</td>
<td>0.06 ± 0.04</td>
<td>Near eutectic composition</td>
</tr>
<tr>
<td>D60 W40</td>
<td>Gd$^{3+}$</td>
<td>Whitlockite$^2$</td>
<td>3.44 ± 0.18</td>
<td>$T = 1280°$ atmospheric pressure</td>
</tr>
<tr>
<td>D60 W40</td>
<td>Sr$^{2+}$</td>
<td>Diopside</td>
<td>0.09 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>D60 W40</td>
<td>Sr$^{2+}$</td>
<td>Whitlockite</td>
<td>1.00 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>D60 W40 + 2% Al$_2$O$_3$</td>
<td>Gd$^{3+}$</td>
<td>Diopside</td>
<td>0.16 ± 0.05</td>
<td>$T = 1260°$ atmospheric pressure</td>
</tr>
<tr>
<td>D60 W40 + 2% Al$_2$O$_3$</td>
<td>Gd$^{3+}$</td>
<td>Whitlockite</td>
<td>3.67 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>D60 W40 + 2% Al$_2$O$_3$</td>
<td>Sr$^{2+}$</td>
<td>Diopside</td>
<td>0.08 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>D60 W40 + 2% Al$_2$O$_3$</td>
<td>Sr$^{2+}$</td>
<td>Whitlockite</td>
<td>1.00 ± 0.10</td>
<td></td>
</tr>
</tbody>
</table>

1 Melts were doped with 1\% each of Eu$_2$O$_3$, Gd$_2$O$_3$, or SrO and Gd$_2$O$_3$. Runs were carried out in sealed iron capsules and samples were carefully pre-reduced before melting. Redox states so obtained were believed to maintain europium in the divalent state and gadolinium in the trivalent state. Partition coefficients were determined with electron probe microanalyzer.

2 The term "whitlockite" is applied to the Ca$_3$(PO$_4$)$_2$ phase.

3 D = diopside, CaMgSi$_2$O$_6$; W = whitlockite, Ca$_3$(PO$_4$)$_2$.

in the oxygen fugacity of the system, accompanied by oxidation of Eu$^{2+}$ to Eu$^{3+}$. All partition coefficients for Eu and Gd which have been measured for several phases in the presence of phosphate were found to be identical, indicating that europium was present as Eu$^{3+}$.

However, the partition coefficients for Sr$^{2+}$ and Gd$^{3+}$ between diopside and Ca$_3$(PO$_4$)$_2$ are of considerable interest. Gd$^{3+}$ is enriched in Ca$_3$(PO$_4$)$_2$ relative to liquid by a factor of 3.4–3.7, whereas the corresponding strontium coefficient is unity. The data in Table 2 show that calcium phosphate in equilibrium with diopside is enriched by factors of 2 to 5 in Gd$^{3+}$ compared to Sr$^{2+}$.

In view of their similar ionic radii and crystal chemical properties, it seems that the partition coefficients for Eu$^{2+}$ will be generally similar to those of Sr$^{2+}$. This has been demonstrated to be the case for feldspar (Table 2). If so, these results suggest that in the source regions of lunar basalts, accessory phosphate minerals will be enriched in trivalent rare earths relative to Eu$^{2+}$ and will thus display a negative europium anomaly. With a small degree of partial melting of the source region, under conditions of local or surface equilibrium, the phosphate minerals would be expected to dissolve
completely at the earliest stage of melting, thereby imposing their negative europium anomaly upon the resultant liquid.

The hypothesis has been discussed in greater detail by RINGWOOD (1970). The present results provide only a crude model of the proposed mechanism, and it will be necessary to measure the partition coefficients at lower temperatures, below the $\alpha \rightarrow \beta$ transition temperature in $\text{Ca}_3(\text{PO}_4)_2$. It is conceivable that the partition coefficients of trivalent rare earths are even higher at lower temperatures. Nevertheless, the present limited results are distinctly favourable to the hypothesis.

REFERENCES


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PART 1, SAMPLE 12009

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EXPERIMENTAL PETROLOGY OF APOLLO 12 BASALTS:
PART 1, SAMPLE 12009

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The lunar sample, 12009, is a rapidly quenched basalt with microphenocrysts of olivine (~7%) and spinel in a cryptocrystalline matrix with many small microlites. The rock is olivine-normative (11%) and comparison of the olivine microphenocryst compositions with the experimentally determined liquidus olivine compositions shows that the rock was originally entirely liquid and that none of the observed olivine results from crystal accumulation.

The magma (12009) began crystallizing olivine at $-1230^\circ C$, spinel joined the olivine at $-1210^\circ C$, and pigeonitic clinopyroxene would have appeared at $-1190^\circ C$ but sudden quenching of the magma occurred before this temperature was reached. Experimental studies at high pressure on 12009 magma show that olivine ceases to be a liquidus phase at pressures above 8kb and the liquidus clinopyroxene becomes more Ca and Al rich with increasing pressure. Although 12009 is not saturated with orthopyroxene at any pressure, a composition of 12009 + 10% olivine ($\text{Fo}_{\text{eq}}$) has olivine and orthopyroxene as liquidus phases at 15kb. The data are used to infer partial melting of olivine pyroxenite [orthopyroxene + clinopyroxene + olivine, 100 Mg/Mg + Fe = 75–80] at depths >200 km within the lunar interior, as the primary source of the maria-filling magmas.

1. Introduction

The mineralogy of five examples (12009, 12021, 12022, 12065 and 12040) of Apollo 12 basalts has been examined quantitatively using the electron microprobe for chemical analysis of olivine, pyroxenes, feldspar, spinels and ilmenite. The crystallization sequence and compositions of precipitated phases for each of these basalts have been determined experimentally at atmospheric pressure and at high pressure. The purpose of a study of this nature is to obtain information on the temperature of extrusion of the basalt, on its cooling history, and on the crystallization sequence and subsolidus mineralogy of the basalt under the higher pressure conditions of the lunar interior. The latter information places constraints on the possible chemical and mineralogical comparison of the lunar interior provided that it can be shown that the rock composition studied represents a liquid composition unmodified by near-surface differentiation processes.

2. Mineralogy of basalt 12009

Basalt 12009 is a rapidly chilled rock in which olivine and spinel occur as medium-sized, euhedral crystals (up to 1 mm) set in dark cryptocrystalline or glassy matrix containing acicular, skeletal, olivine quench-crystals, small spinel crystals and microlites of pyroxene and olivine. The specimen is particularly significant in that the bulk composition of the rock clearly must be very close to an actual liquid. The larger olivine crystals are skeletal with entrapped glass inclusions and rarer included spinel grains. Based on textural criteria alone it is possible that about 7% olivine could be accumulative from another part of the flow, but even this is unlikely considering the small size and the skeletal form of the olivine.

It will be shown in later sections that this possibility can be eliminated by experimental and analytical data.

The chemical composition of 12009 (table 1) reveals the very low Na,K contents, low Al content and
Table 1
Chemical composition and CIPW norm of basalt 12009 (from Chappell (1971), pers. comm.).

<table>
<thead>
<tr>
<th></th>
<th>12009</th>
<th>12009 + 10% Foʻʻ</th>
<th>12009</th>
<th>12009 + 10% Foʻʻ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.03</td>
<td>44.56</td>
<td>CIPW norms</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.90</td>
<td>2.64</td>
<td>Or</td>
<td>0.35</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.59</td>
<td>7.83</td>
<td>Ab</td>
<td>1.95</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.55</td>
<td>0.50</td>
<td>An</td>
<td>22.2</td>
</tr>
<tr>
<td>FeO</td>
<td>21.03</td>
<td>21.23</td>
<td>Di</td>
<td>20.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.28</td>
<td>0.26</td>
<td>Hy</td>
<td>37.4</td>
</tr>
<tr>
<td>MgO</td>
<td>11.55</td>
<td>14.07</td>
<td>01</td>
<td>11.3</td>
</tr>
<tr>
<td>CaO</td>
<td>9.42</td>
<td>8.59</td>
<td>Chr</td>
<td>0.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.23</td>
<td>0.21</td>
<td>Im</td>
<td>5.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.06</td>
<td>0.05</td>
<td>Ap</td>
<td>0.15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07</td>
<td>0.06</td>
<td>Normative olivine</td>
<td>Fo₂₂.7</td>
</tr>
<tr>
<td></td>
<td>99.71</td>
<td>100.00</td>
<td>Normative plagioclase</td>
<td>An₉₅.₆</td>
</tr>
<tr>
<td>100 Mg</td>
<td>49.5</td>
<td>54.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg + Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Al/Ca ratio, and high Fe, Mg contents observed in other lunar compositions. When compared with terrestrial basalts of similar 100 Mg/Mg + Fe⁺² ratio, the low SiO₂ and high normative olivine contents are notable. Examples of terrestrial basaltic rocks also with 100 Mg/Mg + Fe = 50–55 such as some Hawaiian tholeiites [6], some oceanic tholeiites [7] and continental dolerites [8] have >2% normative quartz. The very high Cr content also contrasts with the much lower Cr-content of terrestrial basalts of similar 100 Mg/Mg + Fe ratio.

Selected compositions olivine and spinel in 1209, determined by electron probe microanalyzer, are given in tables 2 and 3. These represent the extremes of 100 Mg/Mg + Fe observed in the minerals analyzed. The magnesian composition in the cores of larger crystals represents a stage of relatively slower cooling and crystal growth but the more iron-rich and rapidly zoned outer rims and small quench crystallites result from cooling and probably metastable, non-equilibrium crystallization during quenching of the matrix melt.

3. Experimental crystallization of 12009 basalt

3.1. Techniques

A 300 mgm sample of the powdered natural basalt was mixed with 6 mgm finely divided metallic iron, fused in an argon atmosphere and quenched to a glass. A platinum crucible was used but care was taken that small drops of metallic iron were present in the glass after melting — these were magnetically extracted after fine crushing and the Fe⁺², Fe⁺³ and total Fe contents of the glass checked by chemical analyses — Fe⁺³ was found to be zero. A second (1gm) batch of glass was prepared from Analar reagents when the bulk composition of 12009 became available — results on the natural rock and the compositionally identical synthetic mix were mutually consistent. For 1 atm pressure runs, 15–20 mgm samples were placed in iron capsules with close fitting lids. For some runs these capsules were sealed in evacuated SiO₂-tubes and suspended in a vertical cylindrical furnace. For other runs, the technique described by Ringwood and Essene [1] was used. Consistent results were obtained with both techniques. Temperatures
were controlled within ± 5°C with accuracy of sample temperature estimated at ± 10°C (the measuring thermocouple is not actually in contact with the sample capsule). Runs were held at temperature for 1–12 hr.

In experiments above 1 atm, a piston cylinder apparatus of Boyd-England design was used and the sample enclosed in an iron capsule with close-fitting lid. A pressure correction of −10% has been applied to the nominal load pressure. Temperature variation is ± 5° about the control point with absolute accuracy estimated at ± 10°C, or possibly ± 20°C at higher pressures due to possible pressure effects on thermocouple emf.

In most of our 1 atm pressure runs and all the above-solidus high pressure runs, the starting material was powdered glass. In the 1 atm runs this material yielded crystals which were unusually too small for microprobe analysis when there was more than 30–40% crystallization. For lower degrees of crystallization, olivine and pyroxene, and occasionally spinel, were large enough for analysis. The technique of using glass as starting material establishes a minimum temperature for the appearance of a phase in the crystallization sequence. This technique allows the possibility that a given phase should have appeared at higher temperature but failed to nucleate in the run-time chosen. To eliminate this possibility, while avoiding the problems of metastable persistence of relic crystals from the coarse-grained natural rock, we have reversed critical boundaries such as the appearance of plagioclase by first crystallizing* the glass to an entirely crystalline but extremely fine-grained (<3μ) subsolidus assemblage (eg. of pyroxene + plagioclase + ilmenite ± olivine ± spinel). This assemblage was then run at increasingly higher temperature to determine the maximum temperature for persistence of plagioclase or pyroxene. In fact, in 12009 composition it was demonstrated that both techniques gave identical results for the appearance of plagioclase and pyroxene. This aspect of our technique has been discussed in detail in view of the criticism of Biggar et al. [2].

The techniques of the latter authors do not provide a reversal of the incoming of a phase in the melting interval and the use of the coarse-grained natural rocks, with all the attendant difficulties of fine and uniform crushing, allows the probability of metastable persistence of phases to higher temperature. In this respect it is important to note that Muan et al. [3] found much longer run times (1–30 days compared with 1–5 hr by Biggar et al. [2]) were necessary when using the crystalline natural rock as starting material. The results of Muan et al. [3] are consistent within experimental limits with our own data where the same rocks have been studied by both groups.

3.2. Subsolidus mineral assemblages

To locate the pressure required for incoming of garnet (fig. 1) at higher pressures, a mixture of powdered glass + 10% seed material was run. The seed material was a garnet + pyroxene assemblage crystallized at 1200°C, 20 kb. Garnet was absent at 8 and 10 kb, 1200°C and 7 kb, 1150°C but present as minor

* At 4kb, 1150°C for 2 hr.
Fig. 1. Experimental crystallization of basalt 12009 at 1 atm and higher pressures. Boundaries for disappearance of plagioclase and incoming of garnet are approximate only.

4. Melting relationships

4.1. Atmosphere

The sequence of appearance of phases at 1 atm pressure is olivine (1230°C), spinel (1210°C) pigeonite (1190°C) plagioclase (1130°C) and ilmenite (fig. 1). The presence of plagioclase at 1130°C and its absence at 1140°C was confirmed in runs using the powdered glass starting material and using the finely crystalline, synthesized pyroxene + plagioclase + olivine + ilmenite assemblage. Although the clinopyroxenes present at 1190°C and 1180°C could be analyzed, pyroxenes in equilibrium runs at 1170°C, and lower temperatures, have so far proved too small for quantitative analysis so that we have not been able to determine the temperature of apperance of augitic clinopyroxene or whether a cotectic or reaction relation exists between pigeonite and augite in this composition under equilibrium conditions.

A similar uncertainty applies to spinel and ilmenite for we have not been able to identify spinel at temperatures below the incoming of ilmenite at about 1100°C.
Table 2

Electron microprobe analysis of olivines occurring in sample 12009; (a) and (b) respectively are the most magnesian and most iron-rich compositions found in the cores of larger olivines; (c) is an outer rim composition to such an olivine and (d) is the composition of a small skeletal, 'quench' olivine. Columns (e) and (f) give the compositions of olivines crystallized from 12009 at 1230°C and 1130°C at 1 atm.

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
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<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
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<td>0.54</td>
<td>0.41</td>
<td>0.45</td>
<td>0.45</td>
<td>0.20</td>
</tr>
<tr>
<td>FeO</td>
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<td>35.88</td>
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<td>37.23</td>
</tr>
<tr>
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<td>0.36</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
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<td>29.71</td>
<td>26.36</td>
<td>38.13</td>
<td>26.00</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.28</td>
<td>0.32</td>
<td>0.45</td>
<td>0.31</td>
<td>0.41</td>
</tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>99.71</td>
<td>99.56</td>
<td>100.16</td>
<td>99.67</td>
<td>100.45</td>
</tr>
</tbody>
</table>

Molecular proportions

- Forsterite: 74.5, 69.6, 61.2, 55.9, 74.6, 54.7
- Fayalite: 24.5, 29.1, 37.4, 42.5, 24.2, 44.0
- Mn-olivine: 0.25, 0.3, 0.4, 0.4, 0.4, 0.4
- Ca-olivine: 0.3, 0.4, 0.5, 0.7, 0.4, 0.6
- Cr²⁺-olivine: 0.5, 0.6, 0.5, 0.5, 0.5, 0.3

\[
\frac{100 \text{ Mg}}{\text{Mg} + \text{Fe}} = 75.3, 70.2, 62.0, 56.7, 75.6, 55.4
\]

* Limit of detection for TiO₂, Al₂O₃, Na₂O, NiO < 0.03.

The compositions of selected olivines within the natural rock are compared with olivines from the experimental runs in table 2 and fig. 2. The most significant point of this comparison is that the liquids olivine found experimentally at 1230°C (where there are <1% crystals present) is identical within analytical precision with the most magnesian olivine found in the natural rock. The composition of olivine cores in the microphenocrysts of the natural rock ranges from 100 Mg/Mg + Fe = 72–76 implying a temperature range for nucleation and growth of these crystals. Magnesian, chrome-rich spinels were also crystallizing in the natural rock along with olivine, and

---

Fig. 2. Comparison of compositions of natural olivines in 12009 with olivines crystallized at various conditions. • = Olivine microphenocryst cores, o = olivine skeletal, quench crystals, x = olivine crystallized at 1 atm, and + = olivine crystallized at > 2 kb.
some grains were included in olivine microphenocrysts. Pyroxene had not begun to crystallize before the rock was suddenly quenched. During the quench-cooling there was overgrowth of iron-rich olivine, nucleation and growth of feathery and acicular olivine and pyroxene and continued growth of zoned spinel grains.

The experimental study clearly demonstrates that the rock 12009 was initially completely liquid. If any olivine microphenocrysts were accumulative in 12009 then the bulk composition of the rock would be that of liquid (A) + 0-10% accumulative olivine. Experimental melting of this composition would thus yield a liquidus olivine which was more magnesian than that in equilibrium with liquid A and more magnesian than olivine occurring as the postulated accumulate crystals. The experimental demonstration that the liquidus olivine of 12009 and the most magnesian olivine microphenocrysts are matched in composition is a direct demonstration that the composition of 12009 is the composition of an actual liquid which was quenched on the moon's surface.

The 12009 liquid began crystallizing olivine at 1230°C and olivine was joined by spinel near 1210°C. The compositions of the experimental olivines closely match the natural olivine an Mg/Mg + Fe, in Cr content and Ca content but are higher in Mn content (fig. 2). The high Mn is a consequence of exchange of Mn between the sample and the iron used for the sample capsule which contained about 1% Mn. The marginally higher Ca content of all the experimental olivines probably results from matrix interference during microprobe analysis of these small crystals. The agreement in CrO content (0.4 to 0.5%) between experimental and natural olivines is particularly important as the Cr content in olivine is probably present as Cr²⁺ and implies highly reducing conditions [13] which have apparently been closely matched by the experimental technique used.

The compositions of spinels in 12009 define two groups, particularly on the basis of 100 Mg/Mg + Fe, and the more iron-rich spinels are probably formed during rapid quenching (fig. 3). The experimental spinels formed at temperatures above 1150°C are very similar to the more magnesian natural spinels but are about 10% lower in Cr content and higher in Mg, Fe and Mn contents (cf. table 3, fig. 3).

Table 3

| Column (a) is an example of the most magnesian spinel found. Column (b) is the rim composition on a large spinel similar to (a) and column (c) is the composition of a very small spinel associated with the quench olivine laths. Column (d) is the composition of spinel in the run at 1190°C, 1 atm. |
|---|---|---|---|
| (a) | (b) | (c) | (d) |
| SiO₂ | 0.05 | 0.08 | 0.22 | 0.20 |
| TiO₂ | 4.84 | 5.02 | 7.38 | 3.80 |
| Al₂O₃ | 12.40 | 12.76 | 12.01 | 12.24 |
| Cr₂O₃ | 50.16 | 47.40 | 41.37 | 45.46 |
| V₂O₃ | 0.98 | 1.02 | 0.96 | 1.02 |
| FeO | 24.59 | 26.68 | 35.14 | 27.39 |
| MnO | 0.37 | 0.39 | 0.41 | 0.63 |
| MgO | 7.26 | 6.53 | 3.05 | 8.38 |
| CaO | 0.04 | 0.08 | 0.19 | 0.27 |
| Total | 100.69 | 99.96 | 100.73 | 99.39 |

Structural formulae

<table>
<thead>
<tr>
<th>Cations to 4 oxygens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>Fe</td>
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<td>Mn</td>
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<td>Mg</td>
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<tr>
<td>La</td>
</tr>
<tr>
<td>Total cations</td>
</tr>
<tr>
<td>100 Mg/Mg + Fe</td>
</tr>
</tbody>
</table>

* Low cation totals and high 'B' totals in the AB₂O₄ spinel structure result in part from the assumption that all Cr is present as Cr²⁺ in (Mg, Fe) Cr₂O₄. There is probably Cr²⁺ present in the spinel, as in the olivine (table 2).
The clinopyroxenes crystallized at 1190°C and 1180°C (fig. 4 and table 4) form elongate laths and roughly rectangular blocky crystals, occasionally showing simple twinning and with inclined extinction. We obtained no evidence of the presence of two co-existing pyroxenes at 1190°C or 1180°C and the compositions of the pyroxenes crystallized can be matched with almost identical compositions in the natural pigeonites occurring in rocks 12040 and 12065 particularly (TiO₂ is lower at 0.5–0.6 in the natural pigeonites and MnO is higher in the experimental pyroxenes as a consequence of Mn exchange with the iron capsule). For these reasons we have no hesitation in designating these pyroxenes as pigeonite in spite of their very close similarity in composition to pyroxene which Biggar et al. [2] found in a run at 1179°C, 1 atm on 12040 composition and which they called protohypersthene (inverted). These ‘protohypersthenes’ are probably relict pigeonite cores from the crushed natural rock used as starting material, for their composition matches perfectly within experimental precision (except for Cr₂O₃ reported as 0.06% compared with 0.68%) with the most magnesian pigeonite which we have observed in 12040 natural rock.

The cooling experiments on 12009 composition in which the charge was cooled over 5–15 min from 1250°C to the run temperature produced quench pyroxene compositions lying between the pigeonites at 1190°C and 1180°C and the ‘normative pyroxene’ composition of 12009 (fig. 4). These pyroxenes were not homogeneous and the analyses plotted represent the cores of crystals. Similarly coexisting olivines and spinels range in composition from the phases in the highest temperature runs to more Fe-rich olivine and more Fe and Ti-rich spinels.
4.2. Conclusions from 1 atm melting studies

It has been shown definitively by the matching of natural olivine micro-phenocrist compositions with the liquidus olivine for the 12009 composition that this composition was once completely liquid at a temperature > 1230°C. Further, the comparison of natural rock and experimental data show that the liquid cooled with precipitation of small olivine and spinel crystals to a temperature between 1210 and 1190°C and from the temperature was quenched to glass + microlites. The liquid began crystallizing at a temperature 100°C above the temperature for plagioclase appearance and it is estimated that about 40% of the rock would have crystallized as olivine, pyroxene and spinel before plagioclase appeared [4, fig. 1].

This is supported by the comparison of the olivine composition analyzed at 1130°C (Mg\(_{55.4}\), table 1) and the normative olivine composition (Mg\(_{52.7}\)) implying that a high proportion of the ferromagnesian phases had already precipitated from the magma at 1130°C.

There is no doubt, from the combination of experimental data and the observed mineralogy of the natural rock that 12009 liquid extruded on the moon’s surface with composition and temperature far removed from plagioclase + pyroxene ± olivine ± spinel cotectic. The only possible crystal fractionation which could have affected 12009 before the beginning of crystallization of olivine (Mg\(_{75}\)) and the quenching which followed, was extraction of more magnesian olivine. The data show that in 12009 we have an example of a lunar magma which is either itself a 'primary magma' or has been derived from such a primary magma by precipitation and extraction of olivine of composition Mg\(_{75}\) during movement from the source conditions of the primary magma. O’Hara et al. [5] and Biggar et al. [2] have postulated extensive loss of 'volatiles', principally Na, K, P, H\(_2\)O and oxygen, both during a postulated existence in a turbulently 'convecting' lava lake and during eruption of late stage liquids (which the Apollo 11 and 12 lavas are considered to be by these authors) onto the surface of the lava lake. It is apparent by comparison of 12009 composition and that of its liquidus olivine, with those of more slowly cooled Apollo 12 rocks [9] that the rapid chilling of 12009 did not cause it to retain any higher alkali, P or H\(_2\)O content than the slowly cooled rocks nor preserve any quenched-in evidence of higher P\(_2\)O\(_5\) during initial crystallization. The detailed investigation of 12009 shows that this rock is quite incompatible with an origin as a late stage liquid from a large differentiating lava lake and thus saturated at low pressure with olivine, clinopyroxene, plagioclase and spinel. It is equally incompatible with an origin as a mixture of such a cotectic liquid enriched in either olivine or pyroxene as accumulate crystals. The hypotheses of O’Hara et al. [15] and Biggar et al. [2] are thus shown to be incompatible with the observations on 12009 basalt. The only escape from the deduction that 12009 indeed represents a primary lunar magma from the lunar interior or a liquid obtained from a primary magma by olivine separation alone is to assume that it is an impact melt. This way out of the impasse raises more problems than it would solve in view of the evidence for co-genetic character of samples 12009, 12018, 12020, 12052, 12065 [9], and the evidence for varied cooling rates and local fractionation controlled by olivine and spinel separation. There is no evidence in the mineralogy or texture of 12009 to support an impact melt assumption.

5. Melting relationships at high pressures

5.1. Experimental results

It has been inferred in previous sections that 12009 is a primary magma from the lunar interior. Elsewhere [1, 4] it has been argued that 12009 and the other lunar basalts are products of partial melting and not of complete melting in the lunar interior. Thus; by a study of the nature of the liquidus phases, of 12009 over the pressure range existing in the lunar interior, it is possible to place constraints on the nature of possible residual minerals and thus on the mineralogy and chemistry of the lunar interior in the basalt source region. The results of the high pressure melting studies are presented in fig. 1 with olivines and pyroxenes plotted in figs. 2 and 4 and analyses of selected pyroxenes given in table 4.

Clinopyroxene joins olivine on the liquidus near 7 kb and olivine is absent in the melting interval at 9 kb and higher pressures. The clinopyroxene on or near the liquidus becomes progressively more calcium-rich with increasing pressure above 6 kb and this effect is quite marked between 9 kb and 15 kb. The
Table 4
Compositions of pyroxenes crystallized at various pressures from basalt 12009.

<table>
<thead>
<tr>
<th>Clinopyroxenes from 1209</th>
<th>Clinopyroxene 1209 + 2% enstatite (Mg$_{80}$)</th>
<th>orthopyroxene 1209 + 10% olivine (Mg$_{10}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 atm 1190°C 1 atm 1180°C 5 kb 1260°C 5 kb 1250°C 7 kb 1290°C 7 kb 1310°C 9 kb 1300°C 9 kb 1390°C 15 kb 1390°C 15 kb 1360°C 15 kb 1390°C 15 kb 1440°C 15 kb 1400°C</td>
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</tr>
<tr>
<td>SiO$_2$</td>
<td>54.04 51.54 53.41 53.07 52.88 52.85 52.77 52.87 51.70 48.06 48.94 54.03 53.41</td>
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</tr>
<tr>
<td>TiO$_2$</td>
<td>1.05 1.04 0.78 0.83 0.56 0.82 0.62 0.48 0.84 1.00 0.52 0.34 0.24</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.55 2.21 1.84 2.28 2.06 2.95 2.61 2.39 4.06 6.30 5.91 2.30 2.24</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.62 0.94 1.20 1.06 0.99 1.08 0.79 0.79 1.04 0.87 0.83 0.78 0.69</td>
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</tr>
<tr>
<td>MnO</td>
<td>0.48 0.78 0.30 0.35 0.26 0.33 0.30 0.27 0.29 0.18 0.39 0.29 0.16</td>
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</tr>
<tr>
<td>MgO</td>
<td>26.16 24.15 26.67 25.76 24.62 22.27 23.37 22.38 19.69 13.77 22.71 27.69 27.04</td>
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<tr>
<td>CaO</td>
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<td>Na$_2$O</td>
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<td>Mg + Fe</td>
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</tr>
</tbody>
</table>

| 100 Mg Mg + Fe | 77.5 72.5 77 76 74.5 72 74.5 72.5 69 55 72 79.5 77 |
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Fig. 4. Compositions of pyroxenes crystallized from 12009 at various pressures, plotted in Ca-Mg-Fe (mol. proportions) diagram. Symbols as shown in legend, with $\varnothing$ = clinopyroxene from 12009 + 2% enstatite (table 4), $\bigodot$ = normative (CIPW) pyroxene for 12009, $\bigodot$ = normative (CIPW) pyroxene for 12009 + 10% Ol, and # = theoretical pyroxene calculated for pyroxenite assemblage (see text) stable at moderate pressures.

Pyroxenes crystallized at 1 atm and those at 5 kb are very similar in spite of 80–90°C difference in their temperature of crystallization. All coexist with olivine and the only compositional difference may be very slightly higher Al content and lower Ca content in the 5 kb pyroxenes. In general the high pressure pyroxenes have lower TiO$_2$ content than the 1 atm phases but this effect is not large in this composition. We find no evidence for any compositional break between pyroxenes which are clearly pigeonite at 1 atm and pyroxenes which appear to range, in terms of composition, from 'pigeonite' (table 4, columns 1–8, 11) to 'sub-calcic augite' (table 4, column 10) at 15 kb. This is not to say that there are not compositional breaks at any one pressure (cf. following discussion on orthopyroxene) but to illustrate the problematical nature of relationships between pigeonite and sub-calcic augite at pressures above 1 atm. At all pressures the CaO and Al$_2$O$_3$ contents of the pyroxenes increase with increasing degree of crystallization and this is most marked at 15 kb.

Although orthopyroxene did not crystallize as a liquidus or near liquidus phase from 12009, the very sub-calcic character of the high pressure clinopyroxenes suggests that the liquid must be close to saturation with orthopyroxene. To test the possibility of nucleation difficulties, two percent of enstatite (Mg$_{80}$) was added as seed crystals to 12009 and the mixture run at 15 kb, 1400°C (above liquidus) and 15 kb, 1390°C (clinopyroxene + liquid). The clinopyroxene (fig. 4, table 4) is slightly more calcium-poor and more magnesian than that crystallizing from 12009 but the experiment showed that clinopyroxene and not orthopyroxene is stable at the liquidus of 12009 at 15 kb.

In a previous section it was argued that if 12009 was not in itself a primary magma in the sense of a direct partial melt from the lunar interior then it could have been derived from such a primary magma by extraction of olivine (>Mg$_{75}$) by crystal settling at shallow depths. To examine the consequences of this possibility, high pressure runs on the composition 12009 + 10% olivine (Mg$_{75}$) (table 1) were carried out at 15 kb. In this composition, with 19.4% normative olivine, olivine remains on the liquidus at 15 kb but is joined by orthopyroxene. The orthopyroxene
is optically easily characterized and distinguished from clinopyroxene which indeed coexists with olivine and orthopyroxene at lower temperatures at 15 kb (1420°C, 1400°C). Chemically the orthopyroxene has lower CaO (though only very slightly lower than that of the 1 atm and 5 kb pigeonite compositions) TiO₂, Cr₂O₃ and Al₂O₃ contents than clinopyroxenes crystallized at 15 kb. Unfortunately the finer-grain size of the clinopyroxene at 15 kb, 1420 and 1400°C has so far prevented analysis of coexisting orthopyroxene/clinopyroxene pairs. However, it may be noted that the clinopyroxenes from 12009 + 2% enstatite show that clinopyroxene coexisting with orthopyroxene at (100 Mg/Mg + Fe) = 72 must contain < 5.1% CaO and > 2.3% CaO. This should be compared with orthopyroxene/clinopyroxene pairs analyzed from runs on terrestrial olivine basalt 13.5 kb, 1320°C in which orthopyroxene contains 2.3% CaO coexisting with clinopyroxene with 5.1% CaO (100 Mg/Mg + Fe = 83–86) [14]. These data indicate that a very narrow pyroxene miscibility gap persists to higher temperatures and more Fe-rich compositions at 13–15 kb than was previously known but also illustrate the complex nature of the pyroxene diagram for natural basalts at high pressure and temperature. In table 4 it is apparent that a clinopyroxene at 5 kb 1280°C is compositionally almost indistinguishable from orthopyroxene at 15 kb 1390°C yet optically the two minerals could not be more distinctive (in extinction, birefringence and crystal habit).

The data on the relative roles of olivine, orthopyroxene and clinopyroxene in 12009 and 12009 + 10% olivine are similar to and consistent with the roles of these phases in terrestrial olivine tholeiites and quartz tholeiites [10–12]. In the terrestrial basalts the clinopyroxenes coexisting with olivine at lower pressures are much more calcium-rich ("augites" rather than "pigeonites") than those from 12009. This is probably largely due to the very low normative diopside/hypersthene ratio of the lunar rocks in comparison with terrestrial basalts.

5.2. Conclusions from high pressure melting studies

The experimental studies show that if 12009 or 12009 + olivine (< 10%) magmas are produced by partial melting in the lunar interior then the mineralogy of the residual material may include olivine (Mg₇₅–Mg₈₀) orthopyroxene (~Mg₈₀, 2–2.5% Al₂O₃) or clinopyroxene (Mg₁₀–₈₀, up to 6.5% Al₂O₃). Plagioclase is not a near-liquidus phase at any pressure in these compositions and thus cannot be a residual phase in the source regions. Basalt 12009 could be a partial melting product of olivine clinopyroxenite at 7–8 kb (130–150 km) in which case the source region would have 100 Mg/Mg + Fe ~ 75. Since the subsolidus mineralogy of a pyroxenite or olivine pyroxenite at these pressures would probably contain minor plagioclase [1,4] a sufficient degree of melting would be required to eliminate plagioclase from the residue. At higher pressures, 12009 could be a partial melt leaving residual clinopyroxenite and the analytical data on the pyroxenes show that the pyroxene would be pigeonitic in composition. The Al₂O₃/CaO ratio of a source region combining 12009 liquid with residual clinopyroxenite or olivine clinopyroxenite would be < 1 and the arguments of Ringwood and Essene [1] for the presence of significant orthopyroxene in the source region remain relevant. The studies of terrestrial tholeiites, 12009, 12009 + 10% olivine, and 12040 compositions allow the prediction that a composition of 12009 + 5–7% olivine (> Mg₇₅) would produce a basalt with orthopyroxene + clinopyroxene ± olivine on the liquidus at 11–14 kb (200–300 km). Combining 12009 + 5–7% olivine composition with major orthopyroxene, minor clinopyroxene (low calcium) and minor olivine could yield an overall olivine pyroxenite composition with 100 Mg/Mg + Fe = 77–80, Ca/Al ratio ~ 1 and with density distribution (olivine + plagioclase pyroxenite at low pressures, garnet-poor pyroxenite at high pressures) suitable for the overall density and moment of inertia of the moon [11].

In support of the suggestion that 12009 may have lost up to 10% of olivine by minor crystallization and crystal settling in its movement from depths > 200 km to the moon's surface, it may be noted that there are other compositions among the Apollo 12 rocks which are richer in normative olivine than 12009 (12040, 12004, 12018, 12020, 12022, 12035) [9]. Also Champness et al. [15] have reported olivine up to Fo₉₈ in composition from rock 12075. Brett et al. [16] report compositions ranging from "fayalite₂₃" to "fayalite₄₅" for olivines from 12004, 12009 and 12022. These data suggest that the detailed study of the composition of olivine cores...
in rapidly quenched Apollo 12 rocks may yield evidence that liquids more olivine-rich and more magne- 
sian than 12009 existed at the lunar surface.

The experimental study of 12009 in particular and 
of the Apollo 12 rocks in general, demonstrates the 
importance of olivine-rich basalts in forming the 
lar maria. Basalts such as 12009 crystallize olivine 
first, joined by chrome-spinel, at or near the lunar 
surface and Compston et al. [9] have presented 
chemical arguments for the derivation of less olivine- 
rich Apollo 12 rocks by extraction of olivine from 
basalt 12009 or similar magma. The experimental and 
analytical data on 12009 show this to be a very im-
portant sample in relation to lunar genesis, preserving 
equivocal evidence of the presence on the lunar 
surface of olivine-rich liquids which could produce 
the olivine-poor basalts (12065, 12021, 12052) by 
local settling out of olivine with minor spinel and pos-
sibly pigeonite. The high pressure melting studies of 
12009 provide support for a model composition of 
the lunar interior (> 200 kms depth) with orthopyrox-
e, clinopyroxene and olivine as major phases and 
posing a ratio 100 Mg/Mg + Fe = 75–80.

Acknowledgements

We wish to thank Prof. A.E. Ringwood for reading 
the manuscript and E. Kiss and E.H. Pedersen for 
technical assistance.

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CRYSTALLIZATION OF PLAGIOCLASE IN LUNAR BASALTS
AND ITS SIGNIFICANCE

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CRYSTALLIZATION OF PLAGIOCLASE IN LUNAR BASALTS
AND ITS SIGNIFICANCE

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A new series of crystallization experiments upon an average high K, Rb type Apollo 11 basalt has been carried out in order to check the suggestion [7] that earlier results by several groups of investigators were invalid because of failure to achieve equilibrium. The new experiments on samples which initially contained plagioclase confirm the earlier conclusion that plagioclase is not a liquidus phase in this magma, and indeed, does not separate until more than 30% of the magma has crystallized as olivine, pyroxene and ore minerals. The magma is thus demonstrated to be of a decidedly non-cotectic character. A suggestion that departure from the plagioclase-pyroxene cotectic is a consequence of loss of alkalis by volatilization is also checked experimentally and found to be invalid. Implications of the non-cotectic character of Apollo 11 and 12 magmas are discussed.

1. Introduction

Petrologists have recently offered differing interpretations of the experimental crystallization behaviour of maria basalts returned by the Apollo 11 and 12 missions. O'Hara et al. [1] studied Apollo 11 basalts and stated that they “have compositions similar to those of liquids in equilibrium with crystals of olivine, two clinopyroxenes, feldspar and iron-titanium oxide”. They concluded from the inferred near-cotectic nature of the Apollo 11 basalts that the latter represented “the residual liquids of advanced near-surface crystal fractionation, most probably in a vast lava lake”. On the other hand, Ringwood and Essene [2], Roedder and Weiblen [3], Smith et al. [4] and Weil et al. [5] found that average Apollo 11 basalts were not saturated with plagioclase, which did not begin to crystallize until 30 to 50% of the magma had already crystallized as olivine, pyroxene and ore minerals. The Apollo 11 magmas were thus found to exhibit strong departures from the low-pressure cotectic compositions in which plagioclase would necessarily appear on the liquidus. From this behaviour, and also from other geochemical characteristics, it was concluded that Apollo 11 magmas had been performed deep in the lunar interior by a small degree of partial melting and had not undergone extensive near-surface crystallization differentiation [2, 6].

It is important that these differences be finally resolved if further progress is to be made towards an understanding of the origins of the maria. Biggar et al. [7] have recently claimed that the source of the conflict was that other workers had not achieved equilibrium in their experiments. These authors [7] also qualified their position by suggesting that if perhaps some Apollo 11 magmas indeed displayed a limited departure from cotectic compositions, this may have been the result of loss of alkalis by volatilization (p. 871).

2. Crystallization of Apollo 11 basalts

The above proposition are readily amenable to testing by direct experiments. Biggar et al. [7] claim firstly that the results of three other groups of workers [2, 4, 5] are invalid because they used synthetic glasses as starting materials in their experiments which resulted in the delayed non-equilibrium crystallization of plagioclase. On the other hand, Biggar et al. [7] used natural crystalline basalts in their experiments in which the presence of plagioclase was believed to
pressure cotectic character which are displayed by Apollo 11 and Apollo 12 lavas" ([7], p. 871).

We have tested this postulate by adding 2% Na\textsubscript{2}O and 0.5% K\textsubscript{2}O to the average K,Rb-rich Apollo 11 basalt type. This composition was crystallized to a sub-solidus assemblage (plagioclase + pyroxene + olivine + opaque oxides) at 1050°C, 1 atm. The fine-grained plagioclase-rich assemblage was then crystallized at various temperatures to determine the melting relationships. The comparison of results given in table 2 demonstrates that addition of Na\textsubscript{2}O + K\textsubscript{2}O suppressed rather than enhanced the initial appearance of plagioclase. The alkali-enriched composition is further from cotectic character than the natural, low alkali lunar basalt. These experiments effectively refute the argument that alkali-loss is responsible as a liquidus phase. Inspection of the norms of table 1 illustrates that the addition of alkalis enriches the rocks in normative olivine and diopside, decreases the normative anorthite content and changes the normative plagioclase to andesine rather than bytownite. These changes would be expected to result in depression of the temperature of plagioclase appearance relative to ferromagnesian minerals.

4. Non-cotectic character of Apollo 12 basalts

An analogous controversy also developed when Apollo 12 rocks were studied. Interpretations in this case were complicated by possible segregation of olivine and pyroxene phenocrysts. Biggar et al. [7] claimed that all deviations from simple cotectic behaviour could be explained by the assumption of variable degrees of segregation of pyroxene and olivine within a cotectic liquid. On the other hand, Green et al. [10, 11] compared the experimental crystallization behaviour of five different basalt specimens under controlled laboratory conditions with the record of crystallization preserved in the minerals of the natural rocks. Whilst noting the important role of olivine extraction and accumulation in specific Apollo 12 basalts, these investigations succeeded in demonstrating that none of the basalts was crystallizing plagioclase prior to the onset of rapid quenching, and that therefore, these basalts could not be derivative liquids from prolonged crystal fractionation involving plagioclase at or near the lunar surface. The experimental data on which these conclusions were based were criticised by Biggar et al. [7] on the assumed basis that use of glass starting material gave non-equilibrium metastable assemblages under experimental conditions. Their assumption was without foundation however since key runs relating to plagioclase occurrence had been repeated using previously crystallized specimens containing well-crystallized plagioclase. As with Apollo 11 specimens, these confirmed that use of glass starting materials under the particular experimental conditions employed yielded equilibrium results. So far, only one of the Apollo 12 rocks (12038) seems, on the basis of experiments by Biggar et al. [7] to represent a liquid crystallizing at the plagioclase—pyroxene cotectic. This specimen was not studied by Green et al. [10].

5. Conclusion

Experimental investigations have clearly established that the majority of Apollo 11 and 12 magmas were not crystallizing at the plagioclase—pyroxene cotectic, and indeed, were highly undersaturated with respect to plagioclase when erupted at the lunar surface. If these liquids represented the end-products of extensive near-surface crystallization differentiation involving the separation of vast amounts of plagioclase, pyroxene and ore minerals [1, 7], then the basalts would necessarily have been saturated with plagioclase which should have appeared on the liquidus. Likewise, if Apollo 11 and 12 basalts had been formed by partial melting in the lunar interior from a source material which contained plagioclase (and some residual plagioclase remained behind in the source after extraction of the basalt) then the magmas which reached the surface would necessarily also have been saturated with plagioclase. The effect of pressure in the lunar interior serves only to enhance this effect [2, 6]. Likewise, loss of alkalis by volatilization can only contribute in the direction of oversaturation of plagioclase, as demonstrated in this paper.

The absence of plagioclase on the liquidus of most Apollo 11 and 12 rocks is therefore taken to imply that these magmas are not the products of extensive near-surface crystal fractionation in huge, lava lakes nor have they been formed by partial melting of a plagioclase-bearing region of the lunar interior. On the contrary, it implies that Apollo 11 and 12 magmas
were formed at depths below those at which plagioclase was present as a stable phase in the lunar interior. On this, and on other ground, it was concluded that Apollo 11 and 12 magmas were formed by small and varying degrees of partial melting from a pyroxene-rich source region at depths of 200–500 km [2, 6, 10, 11]. Perhaps this is true of maria basalts generally. A possible explanation of the europium anomaly in Apollo 11 and 12 basalts in terms of a mechanism which does not involve plagioclase has recently been offered [12].

On the other hand, our preliminary studies on Apollo 14 and 15 highland rock compositions show that these magmas indeed have plagioclase on their liquidus at atmospheric pressure, and furthermore, are not parental to or divided from Apollo 11 and 12 type basalts by any process of low-pressure crystal fractionation. Other geochemical evidence indicates that they were formed by partial melting rather than by fractional crystallization [9]. It appears therefore that Apollo 14 or 15 rocks (and perhaps highland basalts generally) represent magmas formed by partial melting in a region of the moon where plagioclase was a stable phase. This suggests that the source region of highland basalts (plagioclase present) was shallower than the source region of maria basalts (plagioclase absent). Since the maria are believed to be younger than the highlands, this suggests that on the average, the depth of magma generation on the moon increased with time [6, 9].

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References

Table 1

Compositions of Apollo 11 basalts and synthetic analogues on which experimental crystallization studies have been carried out.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.7</td>
<td>39.8</td>
<td>40.7</td>
<td>41.6</td>
<td>40.8</td>
<td>43.0</td>
<td>43.4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>11.6</td>
<td>11.3</td>
<td>11.9</td>
<td>10.3</td>
<td>9.8</td>
<td>10.0</td>
<td>11.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.8</td>
<td>8.6</td>
<td>7.8</td>
<td>10.6</td>
<td>9.8</td>
<td>10.0</td>
<td>7.8</td>
</tr>
<tr>
<td>FeO</td>
<td>19.7</td>
<td>19.2</td>
<td>19.5</td>
<td>17.2</td>
<td>20.7</td>
<td>19.0</td>
<td>21.3</td>
</tr>
<tr>
<td>MgO</td>
<td>7.7</td>
<td>7.5</td>
<td>7.5</td>
<td>8.0</td>
<td>7.0</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>CaO</td>
<td>10.5</td>
<td>10.2</td>
<td>10.8</td>
<td>10.6</td>
<td>11.1</td>
<td>9.7</td>
<td>9.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.52</td>
<td>2.46</td>
<td>0.51</td>
<td>0.51</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.30</td>
<td>0.78</td>
<td>0.30</td>
<td>0.15</td>
<td>0.16</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
</tr>
</tbody>
</table>

a Average composition (recalculated to 100%) of K,Rb-rich Apollo 11 basalt type (from Hubbard and Gast [9]).
b Composition derived from a by the addition of 2.0% Na₂O, 0.5% K₂O and recalculation to 100%.
c Composition of basalt 10017 (Compston et al. [8]). This is the basalt used by O'Hara et al. in their experimental studies [1].
d Average composition of Apollo 11 basalt used by Ringwood and Essene [2].
e Composition of inclusion in olivine of rock 10020. Crystallization behaviour studied experimentally by Roedder and Weiblen [3].
f Synthetic analogue of Apollo 11 basalt studied experimentally by Smith et al. [4].
g Synthetic analogue of Apollo 11 basalt studied experimentally by Weill et al. [5].

prevent the delayed nucleation which they attribute to other experimenters.

To place the issue beyond dispute, we have carried out a further series of melting experiments upon a previously crystallized, plagioclase-bearing sample of high-Rb Apollo 11 basalt [8, 9]. A glass of this composition (table 1) was first prepared from Analar reagents using standard procedures. A 100 mg sample of this was then crystallized at 1050°C, 1 atm, 24 hrs in an iron capsule sealed in an evacuated silica tube to obtain a fine-grained assemblage of pyroxenes, plagioclase and ilmenite. The plagioclase occurred in grains up to 2-μm in size, in intimate intergrowth with pyroxene and ilmenite. Fifteen milligram charges of this material were then sealed in small iron capsules placed in evacuated silica tubes and re-run at various temperatures for 3 hours to determine the position of plagioclase in the crystallization sequence.

The results are presented in table 2. Plagioclase is a major phase at 1120°C and is present in minor amounts (< 10%) at 1130°C, accompanied by about 40% of clinopyroxene and ilmenite. At 1140°C, plagioclase is absent, the rock consisting of about 30% crystalline phases (mainly clinopyroxene) and 70% glass. These results thus confirm those of earlier workers [2, 4, 5] who used glass starting materials with compositions slightly different from the present (table 1). The conclusion that plagioclase does not begin to crystallize from most Apollo 11 magmas until about 30 to 50% of the magmas has already crystallized as olivine, pyroxene and ore minerals is also in agreement with the results of Roedder and Weiblen [3] on the crystallization of natural Apollo 11 magmas containing nuclei of all major phases, including plagioclase.

Biggar et al. [7] ignored the significance of this latter work. The above experiments thus demonstrate that under the experimental conditions employed, there is no
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Table 2

Experimental results on average Apollo 11 basalt (high K,Rb type) (table 1, column a) and an alkali-enriched basalt (table 1, column b). Length of all runs was 3 hours.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. [°C]</th>
<th>Starting material</th>
<th>Run products</th>
<th>Est. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A253</td>
<td>1160</td>
<td>Cpx + Pl + Ilm</td>
<td>GL + Ol + Arm + rare Cpx</td>
<td>90</td>
</tr>
<tr>
<td>A256</td>
<td>1150</td>
<td>Cpx + Pl + Ilm</td>
<td>GL + minor Ol + Arm + major Cpx</td>
<td>75</td>
</tr>
<tr>
<td>A252</td>
<td>1140</td>
<td>Cpx + Pl + Ilm</td>
<td>GL + Arm + Cpx + Ilm + minor Pl</td>
<td>65</td>
</tr>
<tr>
<td>A255</td>
<td>1130</td>
<td>Cpx + Pl + Ilm</td>
<td>GL + Cpx + Ilm + major Pl</td>
<td>50–60</td>
</tr>
<tr>
<td>A254</td>
<td>1120</td>
<td>Cpx + Pl + Ilm</td>
<td>GL + Cpx + Ilm + minor Pl</td>
<td>30–40</td>
</tr>
<tr>
<td>A264</td>
<td>1170</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + Ol + rare Arm</td>
<td>95</td>
</tr>
<tr>
<td>A260</td>
<td>1150</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + Ol + Arm</td>
<td>95</td>
</tr>
<tr>
<td>A258</td>
<td>1130</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + minor Ol + Arm + major Cpx + Ilm</td>
<td>70</td>
</tr>
<tr>
<td>A263</td>
<td>1120</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + minor Ol + Arm + major Cpx + Ilm</td>
<td>60</td>
</tr>
<tr>
<td>A259</td>
<td>1110</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + possible Ol + Arm + Cpx + Ilm + Pl</td>
<td>50</td>
</tr>
<tr>
<td>A262</td>
<td>1100</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + possible Ol + ?Arm + Cpx + Ilm + Pl</td>
<td>30</td>
</tr>
<tr>
<td>A261</td>
<td>1090</td>
<td>Cpx + Pl + Ilm + minor Ol</td>
<td>GL + Cpx + Ilm + Pl (very fine-grained run)</td>
<td>10</td>
</tr>
</tbody>
</table>

Abbreviations: Cpx = clinopyroxene; Ilm = ilmenite; Arm = armalcolite; Pl = plagioclase; Ol = olivine; GL = glass.

significant difference between results obtained using glasses, or finely crystalline starting materials. There is a simple reason for this. The glass sample requires a couple of minutes to reach the equilibrium temperature after being placed in the furnace and we have found that it devitrifies to a very finely crystalline plagioclase-bearing assemblage whilst it is warming up to chosen run temperature between solidus and liquidus. Crystalline nuclei of major phases are therefore present at the beginning of the experiment and there is no reason to doubt that equilibrium is finally achieved.

Ironically, the experimental results of O'Hara et al. [1] on the crystallization of Apollo 11 basalt 10017 (table 1) actually agree with the findings of all other workers [2–5] that plagioclase is not a liquidus phase in average Apollo 11 basalt. O'Hara et al. [1] table 1, p. 696, report olivine + minor clinopyroxene + opaque phases at 1162°C (1 atm., iron-Wüstite buffer, Mo capsule), minor olivine + major clinopyroxene + ilmenite at 1133°C and clinopyroxene, plagioclase and ilmenite at 1099°C. Thus, plagioclase appeared between 1133°C and 1099°C compared to the occurrence of minor plagioclase at 1130°C and major plagioclase at 1120°C in our present experiments. In fig. 1 of O'Hara et al. [1] the key run at 1162°C is not illustrated and the boundary marking the incoming of clinopyroxene is drawn too low in temperature.

3. Alkali volatilization

Although they repeatedly make the unqualified generalization that Apollo 11 basalts lie on the plagioclase-pyroxene-ilmenite ± olivine cotectic [1, 7] Biggar et al. [7] elsewhere implicitly admit that this may not hold strictly for some specific basalts. They suggest that the deviation of these basalts from the cotectic compositions may be connected with loss of alkalis through volatilization at the lunar surface. They hypothesized that the primary Apollo 11 magma may have resembled terrestrial alkali-olivine basalts or tholeiites and only acquired their characteristic highly-reduced and alkali-depleted composition on eruption [1]. Loss of alkalis was claimed to cause an expansion in the primary fields of crystallization of mafic minerals. "Any volatilization losses will displace the erupted magma composition towards these (mafic) mineral compositions rather than away from them. These are precisely the types of departure from atmospheric
Experimental petrology and petrogenesis of Apollo 14 basalts

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Abstract—Sample 14310 and a model KREEP composition have been studied experimentally as examples of the nonmare basaltic compositions that are represented at the Fra Mauro landing site.

Results of experimental melting studies at 1 atmosphere, compared with the observed mineralogy in 14310, show that the mineralogy of 14310 formed during crystallization at or near the lunar surface. Detailed study of the roles of plagioclase, olivine, pigeonite, and orthopyroxene crystallization in experiments and in the natural rock leads to the inference that 14310 cooled relatively slowly to \( \sim \) 1180°C and then was more rapidly quenched, eliminating evidence for early transient olivine precipitation but preserving magnesian pigeonite (in part inverted to orthopyroxene) cores in zoned pyroxenes crystallized at \( T < 1180°C \).

It is inferred that 14310 was an impact melt of pre-Imbrian regolith. High-pressure studies of 14310 and KREEP composition suggest primary derivation of nonmare basaltic compositions from a plagioclase-bearing source region in the outer 200 km of the moon. It is concluded that the moon is chemically zoned, the outer 200 km having significantly higher \( \frac{\text{MgO}}{\text{MgO + FeO}} \) and \( \text{U/K} \) ratios together with a higher abundance of \( \text{Al} \) and perhaps \( \text{Ca} \), relative to the region below 200 km which was the source of mare basalts. This chemical zonation appears to be a primary feature established during the accretion process.

INTRODUCTION

The breccia samples collected on the Apollo 14 mission contain rock fragments of mare-basalt type resembling examples of the Apollo 12 rock suite in texture and mineralogy. They include also fragments of plagioclase-rich basalt, distinctive in the textural dominance of plagioclase laths and in the common presence of orthopyroxene and absence or rarity of olivine. Sample 14310 is a large example of this rock type and, because of its differences from the Apollo 11 or 12 samples, has been studied experimentally to determine crystallization characteristics as functions of \( P \) and \( T \).

In addition, a model composition, designated KREEP (Meyer et al., 1971) has been studied experimentally as a representative of the same class of nonmare basalts exemplified by 14310, but less rich in plagioclase. Compositions of the rocks studied are given in Table 1.

SUBSOLIDUS HIGH PRESSURE MINERALOGY

Experiments on 14310 composition used glass seeded with 10\% Ga + Px + Qz + Rutile ± Kyanite (run at 25 kb, 1,100°C). High-pressure experiments used “piston-in” and a pressure correction of (−10\%) of nominal load pressure. Techniques were the same as previously described (Ringwood and Essene, 1970; Green et al., 1971). At 1,100°C, garnet disappeared from runs at 7 kb and 8 kb but occurred as minor but euhedral, well formed crystals at 9 kb and 10 kb. Plagioclase remained the major phase at 9 and 10 kb but showed a large decrease at 15 kb, with accompanying
increase in garnet and pyroxene. Ilmenite was present below 9 kb but at 10 kb was accompanied by rutile, which became more abundant at 15 kb and higher pressures. Plagioclase persisted to 21–22 kb but was absent at higher pressures. Quartz was present and kyanite tentatively identified as minor phases at >20 kb. At 1,300°C plagioclase was a minor phase at 20 kb but absent at 25 kb; garnet and pyroxene were the major phases at both pressures.

Subsolidus experiments on the KREEP composition were carried out using glass as starting material. At 1,100°C, 9 kb, rare garnet crystallized; garnet remained a very minor phase at 13 kb but increased markedly in a 15 kb run. Plagioclase crystallized as a minor phase at 17 kb but was absent at 18 kb. Minor quartz was present at 18 kb. The garnet which crystallized from KREEP composition at high pressures was lower in grossular content than that crystallized from 14310.

In comparison with Apollo 11 and 12 compositions, the pressure required for the first appearance of garnet resembles that of the olivine-bearing Apollo 12 basalts and may be attributed to reaction of anorthitic plagioclase with ferromagnesian minerals (ilmenite + hypersthene) in a quartz-free mineral assemblage. Very little garnet forms from this reaction and only above ~14 kb, with hypersthene and plagioclase reacting to yield garnet + clinopyroxene + quartz, does garnet noticeably increase in amount. The very high anorthite content and high normative plagioclase/hypersthene + olivine ratio for these basalts cause plagioclase to coexist with increasing garnet and clinopyroxene to much higher pressures than for Apollo 11 and 12 compositions. These effects of chemical composition on the conditions of appearance and disappearance of garnet and plagioclase are consistent with compositional effects observed in terrestrial basalts (Ringwood and Green, 1966; Green and Ringwood, 1972).
mean lunar density and moment of inertia shows that a moon composed of rocks of compositions like 14310 or KREEP would have a substantially lower coefficient of moment of inertia than is observed (Ringwood and Essene, 1970), demonstrating that such compositions are not representative of the lunar interior.

**Melting Relationships at 1 Atmosphere**

In experiments at one atmosphere, charges were held in iron capsules sealed in evacuated silica tubes. (See Figs. 1 and 2.) The starting material for most runs on 14310 was a finely crystalline (pyroxene + plagioclase + ilmenite) charge crystallized from glass at 1,050°C, 1 atmosphere. Runs were also carried out using glass as starting material particularly to obtain a reversal on the liquidus temperature and to grow phases sufficiently large for microprobe analyses. Starting glasses were prepared, by melting at 1,400–1,450°C for 1–2 mins. in an induction heater (argon atmosphere), from a homogenized 300 mg sample of the natural rock and from an oxide mix prepared to the 14310 composition provided by B. W. Chappell (personal

![Fig. 1. Results of experimental crystallization studies at one atmosphere and up to 10 kb on sample 14310. Compositions of phases, where analyzable, are indicated in molecular proportions: 100 An

\[
\begin{align*}
\text{An} & = \frac{100 \text{ An}}{	ext{An} + \text{Ab} + \text{Or}} \\
\text{Fo} & = \frac{100 \text{ Fo}}{\text{Fa} + \text{Fo}} \\
\text{Mg} & = \frac{100 \text{ Mg}}{\text{Wo} + \text{Ens} + \text{Fs} + \text{Mg} + \text{Fe}}
\end{align*}
\]
communication). After preparation of the glasses and devitrification at 1,050°C and 1 atmosphere, it was found by analysis that FeO was 8.2% and the Fe₂O₃ was not measurable (see Table 1). For runs on the KREEP composition, glass (see Table 1) was used as the starting material.

For 14310 composition, plagioclase (An₉₂, Ab₇.₅, Or₀.₅) was the liquidus phase at 1,320°C, joined by olivine (Fo₉₈) at 1,230°C after approximately 10–15% plagioclase had crystallized. Olivine continues to crystallize with plagioclase down to temperatures of <1,200°C, but between 1,200°C and 1,180°C olivine reacts with liquid to precipitate low-calcium clinopyroxene (Table 2), and olivine is not detectable in lower temperature runs. The solidus was not determined but lies above 1,050°C.

For the KREEP composition, olivine (Fo₈₀) occurs on the liquidus at 1,225°C and is joined by plagioclase (An₈₉.₅, Ab₈.₅, Or₂.₀) at very slightly lower temperature (see Table 3). These minerals continue to precipitate together to 1,180°C, where minor clinopyroxene appears. Runs below 1,180°C consisted of very fine-grained pyroxene and plagioclase; the presence of olivine could not be confirmed and pyroxene and plagioclase were too fine grained for microprobe analysis.

**MELTING RELATIONSHIPS AT HIGH PRESSURES**

For 14310 composition, plagioclase remains the liquidus phase to at least 10 kb. (See Figs. 1 and 2.) At 5 kb, the second phases to appear are olivine and orthopyroxene...
Table 2. Compositions of natural and experimentally produced pyroxenes in 14310 and KREEP compositions (wt%).

<table>
<thead>
<tr>
<th></th>
<th>Natural Pyroxenes–14310</th>
<th>Experimentally crystallized pyroxenes–14310</th>
<th>Experimental pyroxenes–KREEP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Opx Opx Cpx Cpx</td>
<td>1 Atm. 5kb 5kb 6kb 7kb 7kb 7kb 7kb 7kb</td>
<td>1,180°C 1,260 1,260 1,260 1,260 1,240 1,240 1,280</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 Atm. 5kb 5kb 6kb 7kb 7kb 7kb 7kb 7kb</td>
<td>1,220 1,220 1,210 1,260 1,260 1,280</td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.1 53.8 54.6 53.2</td>
<td>53.3 50.8 53.3 51.3 50.8 49.7 49.5</td>
<td>50.3 53.0 50.1 54.2 47.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5 0.7 0.5 0.7</td>
<td>0.8 0.4 0.7 1.0 0.6 1.1 0.9</td>
<td>0.9 1.1 1.5 0.5 1.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.6 2.2 2.1 1.4</td>
<td>2.4 8.5 3.4 7.4 8.0 8.2 9.2</td>
<td>5.8 3.4 7.6 3.2 9.8</td>
</tr>
<tr>
<td>FeO</td>
<td>11.0 14.1 12.5 14.8</td>
<td>10.4 9.4 9.9 9.5 10.3 12.1 9.1</td>
<td>11.2 12.2 9.9 11.4 9.7</td>
</tr>
<tr>
<td>MnO</td>
<td>0.2 0.2 0.2 0.3</td>
<td>0.2 0.2 0.2 0.3 0.3 0.3 0.2</td>
<td>— — — — —</td>
</tr>
<tr>
<td>MgO</td>
<td>28.0 26.8 27.7 25.6</td>
<td>28.3 28.4 27.9 23.8 23.9 19.7 21.4</td>
<td>23.9 26.2 20.7 25.2 19.1</td>
</tr>
<tr>
<td>CaO</td>
<td>2.5 2.3 2.5 2.9</td>
<td>2.8 2.4 3.3 6.0 6.0 8.9 9.3</td>
<td>8.3 4.7 10.7 5.0 12.3</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.6 0.4 0.4 0.5</td>
<td>1.1 0.6 1.1 0.6 0.7 0.6 0.5</td>
<td>— — — — —</td>
</tr>
<tr>
<td></td>
<td>100 Mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg + Fe</td>
<td>81.5 77 80 75 83 84 83 82 81 75 81 79 79 78.5 80 77.5</td>
</tr>
</tbody>
</table>

Table 3. Compositions of natural and experimental phases from 14310 and KREEP compositions (wt%).

<table>
<thead>
<tr>
<th></th>
<th>Plagioclase</th>
<th>Ulvöspinel</th>
<th>Experimentally crystallized spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14310</td>
<td>14310</td>
<td>14310</td>
</tr>
<tr>
<td></td>
<td>1 Atm. 5kb 5kb 1,260</td>
<td>1 Atm. 5kb 7kb 1,260 1,240</td>
<td>1 Atm. 5kb 7kb 1,260 1,240</td>
</tr>
<tr>
<td></td>
<td>plagioclase faths</td>
<td>1230°C 1,260</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>44.9 46.5 45.6 46.3</td>
<td>46.3 47.6 47.6</td>
<td>29.4 0.7 0.4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>35.1 33.3 34.2 32.3</td>
<td>33.0 31.6 32.0</td>
<td>4.3 48.3 54.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1 0.2 0.1 0.5</td>
<td>0.1 1.0 0.6 0.8 0.7 0.7 0.8 0.7 FeO</td>
<td>59.2 13.6 12.9</td>
</tr>
<tr>
<td>MgO</td>
<td>19.1 18.4 18.5 18.1</td>
<td>17.8 17.5 17.9</td>
<td>4.4 15.1 9.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.5 0.8 0.8 1.2</td>
<td>0.95 1.4 1.1</td>
<td>0.2 — — —</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.05 0.12 0.09 0.16</td>
<td>0.31 0.6 0.5</td>
<td></td>
</tr>
<tr>
<td>Or</td>
<td>0.3 0.7 0.5 0.9</td>
<td>1.8 3.3 3.1</td>
<td></td>
</tr>
<tr>
<td>Ab</td>
<td>4.8 7.3 7.6 10.9</td>
<td>8.7 12.1 9.6</td>
<td></td>
</tr>
<tr>
<td>An</td>
<td>94.9 92.0 91.9 88.2</td>
<td>89.5 84.6 87.3</td>
<td></td>
</tr>
</tbody>
</table>

at 1,260°C, but the field of crystallization of orthopyroxene is very small, being replaced at 1,250°C by low-calcium clinopyroxene. Olivine is not detectable below 1,250°C and clinopyroxene + plagioclase are the major phases. Spinel is a minor phase below 1,250°C at 5 kb and at 1,260°C, 7 kb. At 7 kb neither orthopyroxene nor olivine appears, and the first clinopyroxene observed (at 1,260°C) is both more calcic and more aluminous than that crystallized at lower pressures. This trend continues at 10 kb (see Fig. 1 and Table 2).

At 5 kb for the KREEP composition, olivine, clinopyroxene, and plagioclase crystallize within 10°C of the liquidus, although olivine appears to be the actual liquidus phase. At 7 kb, clinopyroxene is the liquidus phase and plagioclase the second phase to appear. Olivine does not appear in the melting interval at this pressure. Clinopyroxene at 1 atmosphere was too fine grained for analysis, but at 5 kb, 1,220°C two coexisting clinopyroxenes, “pigeonite” and “subcalcic augite,” were observed. Almost identical pairs were observed in two runs at 1,220°C, one of which was heated first to 1,260°C for 2 minutes and then rapidly cooled to 1,220°C.
and the other of which was heated to and held at 1,220°C. Quench clinopyroxenes observed in some runs were very different (>10% Al$_2$O$_3$, >1.2% TiO$_2$, $\frac{100\text{Mg}}{\text{Mg} + \text{Fe}} \sim 60$) from either of the two clinopyroxenes at 5 kb, 1,220°C. The experiments are consistent with the existence of a miscibility gap at low pressure between pigeonite and subcalcic augite compositions (see Fig. 3). This is not to be confused with an apparent reaction relationship between orthopyroxene and pigeonite at low pressure (cf. 14310 composition with orthopyroxene at 5 kb, 1,260°C and "pigeonite" at 5 kb, 1,250°C). At 5 kb and 1,210°C only one pyroxene (subcalcic augite) is present in the KREEP composition system, and at 7 kb there appears to be a sudden change from a "pigeonite" composition in equilibrium with liquid at 1,260°C to a subcalcic augite composition in equilibrium with liquid at 1,220°C. No evidence for the coexistence of two pyroxenes was found at this pressure.

**INTERPRETATION OF CRYSTALLIZATION HISTORY AND GENESIS OF BASALT 14310 IN THE LIGHT OF EXPERIMENTAL STUDIES**

The plagioclase observed on or very close to the liquidus at 1,320°C and 1 atmosphere is slightly less calcic (An$_{92}$) than the most calcium-rich natural plagioclase present in 14310 (An$_{95}$). The difference is not large enough for one to state with certainty that the most calcic plagioclases must be exotic or xenocrystal in relation to 14310 liquid, but the data are sufficient to show that the phenocrystal or larger plagioclase crystals did not precipitate from a liquid with a higher Na/Ca ratio than observed at present in 14310 (cf. Brown and Peckett, 1971). Olivine is the first ferro-

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**Fig. 3.** Pyroxene diagram indicating compositions of natural and experimentally crystallized pyroxenes from 14310. □ Orthopyroxene cores in natural rock; ○ low-calcium clinopyroxenes in natural rock; ● high-calcium clinopyroxene in natural rock; ○ orthopyroxene crystallized at 5 kb; ★ clinopyroxenes crystallized at 1 atm, 5 kb, 7 kb, and 10 kb; × olivines crystallized at 1 atm.
magnesian phase to appear in experiments at 1 atmosphere, and orthopyroxene does not appear. These observations appear to conflict with the natural rock in which the most Mg-rich phases are orthopyroxene and low-Ca, magnesian pigeonite. However, the olivine at 1,230°C has \( \frac{100\text{Mg}}{\text{Mg + Fe}} = 88 \) and that at 1,200°C has \( \frac{100\text{Mg}}{\text{Mg + Fe}} = 84 \), whereas the most magnesian orthopyroxenes observed in the natural rock have \( \frac{100\text{Mg}}{\text{Mg + Fe}} = 81.5 \). Between 1,200°C and 1,180°C olivine (\( < \text{Mg}^{84} \)) reacts with liquid to precipitate low-calcium pigeonite (\( \text{Mg}^{83} \) at 1,180°C). The low-calcium pigeonite is slightly more magnesian but otherwise almost identical in composition to orthopyroxene and magnesian pigeonite occurring in the natural rock (see Fig. 1 and Table 2). It is inferred that the orthopyroxene of 14310, at least that with the composition given in Table 2, has inverted from low-calcium pigeonite, the latter phase being in equilibrium with plagioclase + liquid (14310 bulk composition) at 1,180°C or slightly lower temperature. The zoned pigeonite and augite of the natural rock crystallized during relatively rapid cooling at \( T < 1,180°C \). Thus, 14310 preserves a record of crystallization in which there is no evidence in the ferromagnesian phases of crystallization in the 1,230–1,180°C temperature interval, but in contrast the rock contains plagioclase that is too calcic to have been in equilibrium with liquid in 14310 below 1,320°C (plagioclase in 14310 composition at 1,180°C would be \( < \text{An}^{88} \). See Fig. 2.).

These internal inconsistencies in the crystallization of 14310 cannot be explained by the hypothesis that 14310, at the time of crystallization of the larger euhedral plagioclase, contained ~70% higher \( \text{Na}_2\text{O} + \text{K}_2\text{O} \) contents (Brown and Peckett, 1971). This would enlarge the crystallization field of olivine at the expense of pyroxene and plagioclase and would ensure that the earliest plagioclase to crystallize was much more sodic than even \( \text{An}^{92} \) (Green, Ware, and Hibberson, in preparation).

Two interpretations of the experimental results in relation to the observed petrology of the natural rock might be considered:

(a) 14310 was once completely liquid but cooled relatively slowly from >1,320°C to 1,180°C, allowing time for all olivine precipitated between 1,230°C and 1,200°C to react with liquid but permitting only limited reequilibration of large, early-formed plagioclase crystals. This hypothesis is permissible whether 14310 was ultimately an impact melt or of internal lunar origin.

(b) 14310 is an impact melt of preexisting crystalline material in which calcic plagioclase and orthopyroxene were important and more refractory phases. Thus, 14310 may not have been completely molten nor homogenized in the impact event, and some pyroxene and plagioclase may be “xenocrysts” (with overgrowths) in an inhomogeneous impact melt.

If the second interpretation of 14310 crystallization history is correct, then the rock allows no further conclusions about the nature of the lunar interior except insofar as the composition of various samples of the regolith* may be used to infer

* The term “regolith” is used in a broad sense to denote the outermost layer of the pre-Imbrian crust which probably was shattered, crushed, or shock melted and repeatedly mixed by the intense (meteoritic?) bombardment responsible for the highland craters. This “regolith” may be as much as 20 km thick.
the processes that operated in producing the pre-Imbrian regolith. If the first interpretation is correct, then either impact melting or internal partial melting to produce 14310 liquid remain possible processes. However, the chemical composition and high-pressure crystallization characteristics of 14310 do not support an origin by one-stage partial melting of the lunar interior. The high $K$ and $P$ and incompatible trace element abundances of 14310 in comparison with Apollo 12 mare basalts or relative to chondritic abundances, coupled with the high $\frac{Mg}{Mg + Fe^{++}}$ ratio and Cr content, indicate that 14310 composition could only be a product of very small degrees of melting, unless the source region possessed extremely high incompatible trace element contents. However, the wide field of plagioclase crystallization below the liquidus at 0–10 kb unaccompanied by other phases, shows that 14310, if postulated as a partial melt, would be derived by a sufficiently high degree of melting to eliminate all phases but plagioclase from the residue. It has previously been argued that plagioclase is absent from the source region (below approximately 200 km) of mare basalts (Ringwood and Essene, 1970; Ringwood, 1971; Green et al., 1971). A further difficulty with derivation of 14310 by partial melting of the lunar interior is that temperatures in excess of 1,320°C in the outer 200 km of the moon would be required at $T \sim 3.9$ b.y. (Turner et al., 1971), 0.6 b.y. after formation of the moon. During this time interval, cooling and formation of a “rigid” crust make such high temperatures, at shallow depths, rather improbable.

These constraints on the hypothesis of origin of 14310 as a direct partial melt of the lunar interior can be reconciled only by postulating that 14310 was produced by very small (probably $<5\%$) degrees of melting of an anorthosite source rock ($>95\%$ anorthite) as shallow depths in the moon. Our prejudice is that such a source rock and origin for 14310 are improbable and we adopt as a preferred hypothesis that 14310 was produced as an impact melt of the pre-Imbrian regolith, the particular regolith sample that was melted being enriched in plagioclase.

NATURE OF THE LUNAR INTERIOR AS INFERRED FROM THE PETROGENESIS OF MARE AND NONMARE BASALTS

Our preferred hypothesis interprets 14310 as an impact melt of pre-Imbrian regolith. The composition of 14310 relates it to the component recognized in Apollo 11, 12, and 14 soils and breccias and referred to as KREEP, norite, or nonmare basalt (Hubbard, et al., 1971; Meyer et al., 1971; Apollo Soil Survey, 1971; Fuchs, 1971; Lindsay, 1971). In the following discussion we will examine the significance of this component with respect to the nature of the outer layers of the moon and the early stages of lunar evolution.

The composition and mineralogy of nonmare basalt as defined by the above investigators demonstrate its overall basaltic character (e.g. “Fra Mauro basalts” Types B, C, and D of Apollo Soil Survey, 1971 or average KREEP basalt of Hubbard et al., 1971). The nonmare basalt compositions possess high abundances of incompatible elements, including K, U, Th, Ba and the rare earths, coupled with high
Experimental petrology and petrogenesis of Apollo 14 basalts

Table 4. K/U ratios of mare and nonmare basalts.*

<table>
<thead>
<tr>
<th></th>
<th>Mare</th>
<th>Nonmare</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apollo 11</td>
<td>2800</td>
<td>—</td>
</tr>
<tr>
<td>Apollo 12</td>
<td>2200</td>
<td>1230 (KREEP)</td>
</tr>
<tr>
<td>Apollo 14</td>
<td>—</td>
<td>1200</td>
</tr>
<tr>
<td>Apollo 15</td>
<td>2700</td>
<td>1600</td>
</tr>
</tbody>
</table>

*Data from LSPET reports.

Mg ratios and high Cr content. These characteristics may result from efficient fractionation in a partial melting process (implying a very small degree of partial melting) but are inconsistent with an origin by high degrees of crystal fractionation of some parental magma.

The relative abundance of plagioclase in the "KREEP" or "nonmare basalt" compositions, coupled with the experimental demonstration of the importance of near-liquidus plagioclase in 14310 and KREEP at high pressures, argues that plagioclase must have been present in the source region and left as a residual phase, accompanied by low-calcium, aluminous pyroxene(s) and possibly olivine. In comparison with the source region for mare basalts, the relative composition and nature of the phases on the liquidus of 14310 and KREEP compositions show that the source region for nonmare or KREEP basalt had higher Al$_2$O$_3$/pyroxene ratio and higher

$$\frac{100\text{Mg}}{\text{Mg} + \text{Fe}^{++}}$$

ratio ($> 80$) than the source region for mare basalts (with $\frac{100\text{Mg}}{\text{Mg} + \text{Fe}} < 80$).

Another significant difference between mare and nonmare basalts is the higher K/U ratios of the former (Table 4); this difference would also be characteristic of their respective source regions. To summarize, the source region of nonmare basalts is inferred to occur at depths <200 km (because of the role of plagioclase in the source region; see also Ringwood, 1971) and to differ chemically from the source region for mare basalts in having higher Al$_2$O$_3$ content and $\frac{\text{Mg}}{\text{Mg} + \text{Fe}^{++}}$ and U/K ratios than the source region for mare basalts. This chemical inhomogeneity is inferred to be of primary origin and may be indicative of zonal chemical variation in the moon's outer layers established during accretion (Hubbard and Gast, 1971; Ringwood, 1972).

Evaluation of the significance of the nonmare or KREEP basaltic composition depends to a large extent on the abundance and distribution of this component on the lunar surface. The orbital gamma-ray spectrometer data (Metzger et al., 1972) and orbital x-ray fluorescence spectrometer data (Adler et al., 1972) both provide evidence that the characteristic or dominant (compositional) rock type of the highlands is related to gabbroic anorthosite and that KREEP is only locally (particularly near Mare Imbrium and Oceanus Procellarum) a major component. Although such conclusions are highly tentative, it appears that the dominance of plagioclase-rich compositions, low in incompatible element contents, in the highland regions may result from a primitive stage of complete melting or high degrees of melting of the outermost layers in which pronounced crystal fractionation produced a dominance of near-surface plagioclase-rich rocks. The identification of a seismically fast horizon
at depths > 60 km (Toksóz et al., 1972) may possibly be correlated with olivine-rich accumulated complementary to the plagioclase-rich near surface layers.

Acknowledgments—We wish to acknowledge the technical assistance of E. Kiss and E. H. Pedersen.

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SIGNIFICANCE OF A PRIMITIVE LUNAR BASALTIC COMPOSITION PRESENT IN APOLLO 15 SOILS AND BRECCIAS

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Distinctive spherules and fragments of ‘Green Glass’ previously described from Apollo 15 soils, have olivine-rich (30%) magnesian (100 Mg/ Mg + Fe = 61) picritic compositions. ‘Green Glass’ has been interpreted as a representative composition of a significant lunar rock unit, the actual glass being produced by melting of this unit. Experimental studies of high pressure melting relations in a compositionally similar Apollo 12 basalt (12040) lead to prediction of the nature of liquidus phases of Apollo 15 Green Glass at various pressures. It is argued that the Apollo 15 Green Glass unit was a product of very high degrees of partial melting (30-60%) of pyroxenite (olivine-poor, dominated by sub-calcic clinopyroxene) source rock with magma segregation (from residual olivine and orthopyroxene only) occurring at 15 kb, T = 1450°C. The source rock is similar to that predicted for Apollo 11, 12 and 15 mare basalts but the degree of melting is much greater than that postulated for even the more olivine rich mare basalts (e.g. 12009 — 10% melting, magma segregation 10 — 12 kb).

1. Introduction

Ridley et al. [1] have described and analyzed distinctive green glass fragments and spherules occurring in Apollo 15 breccias and soils. They have shown that this material is remarkably constant in composition, and argue that these glasses are representative of a significant petrological unit present in the Apennine Front. Other workers have also identified and characterized this type of glass [2, 3]. The composition is rich in normative olivine and pyroxene and may be described as picritic. It is distinguished from all other lunar basaltic compositions in its very low abundances of Ti, rare earths [1] and other incompatible elements such as U, Th, Zr, Hf, Ba, Nb [2]. This entire group appears to be present at only about 4—5 times the chondritic levels. There is also a very small negative europium anomaly [1, 2]. The green glass thus appears to represent the most primitive material yet recovered from the moon. Ridley et al. [1] suggest that the green glass may have been derived from deep-seated ultramafic rocks of the type that formed the source region for mare basalts.

We concur in the importance of this rock composition in discussions to mare basalt genesis and in this paper use information obtained from our high pressure melting studies of lunar compositions to discuss possible origins for this material and its implications for the composition of the lunar interior.

2. Comparison of Apollo 15 Green Glass with Apollo 12 basalt compositions

In table 1, we have compared the Apollo 15 Green Glass composition with those of an olivine-rich Apollo 12 basalt (12040), and an olivine basalt (12009) shown to be entirely liquid at the lunar surface [5, 6]. It has been argued [5, 6] that 12009 or a more olivine (> Fo75) enriched liquid (e.g. 12009 + 10% olivine, table 1) was a primary melt from the lunar interior and derived by partial melting leaving orthopyroxene, olivine, and sub-calcic clinopyroxene as residual phases. It was not possible to demonstrate that 12040 composition was that of a primary melt because this composition and the mineralogy of the natural rock are also consistent with local accumulation, mainly of olivine, at low pressure, enriching a liquid such as 12009 or its derivatives in olivine and minor chromespinel [5, 7].

The comparison in table 1 demonstrates great similarity in major element compositions between
D.H. Green, A.E. Ringwood, Primitive lunar basaltic composition present in Apollo 15 soils

### TABLE 1
Comparisons of compositions of Apollo 15 Green Glass [1] and Apollo 12 compositions which have been studied experimentally [5, 6].

<table>
<thead>
<tr>
<th></th>
<th>Green Glass from soil 15101 (av. of 28 analyses)</th>
<th>Column 1 less 25% olivine (Fo75)</th>
<th>12040</th>
<th>12009+10% olivine (Fo75)</th>
<th>12009</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
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<tr>
<td>SiO2</td>
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<td>47.4</td>
<td>44.08</td>
<td>44.56</td>
<td>45.03</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.43</td>
<td>0.57</td>
<td>2.41</td>
<td>2.64</td>
<td>2.90</td>
</tr>
<tr>
<td>Al2O3</td>
<td>7.63</td>
<td>10.2</td>
<td>7.18</td>
<td>7.83</td>
<td>8.59</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.43</td>
<td>0.44</td>
<td>0.55</td>
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<td>0.55</td>
</tr>
<tr>
<td>FeO</td>
<td>19.73</td>
<td>18.9</td>
<td>21.27</td>
<td>21.23</td>
<td>21.03</td>
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<tr>
<td>MnO</td>
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<td>0.25</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>MgO</td>
<td>17.89</td>
<td>11.2</td>
<td>16.21</td>
<td>14.07</td>
<td>11.55</td>
</tr>
<tr>
<td>CaO</td>
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<td>10.8</td>
<td>8.10</td>
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<tr>
<td>K2O</td>
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<td>0.00</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
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<tr>
<td>Mg/Mg+Fe (mol)</td>
<td>0.62</td>
<td>0.51</td>
<td>0.58</td>
<td>0.54</td>
<td>0.50</td>
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</table>

**CIPW norms**

<table>
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<tr>
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<td>Feldspar</td>
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<td>17.4</td>
<td>18.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Hypersthene</td>
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<td>38.6</td>
<td>29.5</td>
<td>34.1</td>
<td>37.4</td>
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<tr>
<td>Olivine</td>
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<td>8.7</td>
<td>27.5</td>
<td>19.4</td>
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</tr>
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<td>Chromite</td>
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<td>1.1</td>
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</tr>
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</table>

12040 and Apollo 15 Green Glass and this is also apparent in normative mineralogy. There are significant differences in that the TiO$_2$ and REE contents [1, 8, 9, 13] of 12040 or 12009 are about 5 times those of the Apollo 15 Green Glass. These differences are extremely important in the genesis of these compositions and will be discussed in a later section. However, the similarities in major elements in table 1 are sufficient to be able to confidently predict the crystallization behaviour of Apollo 15 Green Glass at depth in the lunar interior and to be able to discuss hypotheses relating this composition to the source region for mare basalts.

### 3. High pressure phase relationships in Apollo 15 Green Glass

The following behaviour for Apollo 15 Green Glass is predicted from our data on 12040, 12009 + 10% olivine and 12009 [5, 6].

- **Liquidus temperature:**
  - 1 Atmosphere: $1420^\circ C \pm 20^\circ C$
  - 15 kb: $1470 \pm 20^\circ C$
  - 25 kb: $1540 \pm 20^\circ C$

- **Liquidus phase:**
  - Olivine to $13 \pm 2$ kb
  - Olivine+orthopyroxene from $13 \pm 2$ kb to $22 \pm 2$ kb
TABLE 2
Compositions of phases observed on or very close to the liquidus of 12040 and predicted compositions for phases on the liquidus of Apollo 15 Green Glass at 15 kb to 25 kb.

<table>
<thead>
<tr>
<th></th>
<th>1 atm</th>
<th>15 kb</th>
<th>20 kb</th>
<th>15 kb</th>
<th>20 kb</th>
<th>25 kb</th>
<th>15 kb</th>
<th>20 kb</th>
<th>25 kb</th>
<th>25 kb</th>
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<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>39.7</td>
<td>40.5</td>
<td>39.2</td>
<td>40.6</td>
<td>55.4</td>
<td>55.5</td>
<td>53.9</td>
<td>56.1</td>
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<td>0.1</td>
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<tr>
<td>Al₂O₃</td>
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<td>0.1</td>
<td>0.0</td>
<td>2.1</td>
<td>2.0</td>
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<td>2.6</td>
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</tr>
<tr>
<td>Cr₂O₃</td>
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<td>0.4</td>
<td>0.7</td>
<td>1.0</td>
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<tr>
<td>FeO</td>
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<td>11.9</td>
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</tr>
<tr>
<td>MnO</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
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<td>0.1</td>
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<tr>
<td>MgO</td>
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<td>CaO</td>
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<td>0.4</td>
<td>1.8</td>
<td>2.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>78</td>
<td>84</td>
<td>81</td>
<td>80</td>
<td>79</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>77</td>
</tr>
<tr>
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<td>Opx</td>
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<td>Cpx</td>
<td>Ol</td>
<td>Ol</td>
<td>Cpx</td>
<td>Ol</td>
<td>Opx</td>
</tr>
</tbody>
</table>

D.H. Green, A.E. Ringwood, Primitive lunar basaltic composition present in Apollo 15 soils.
Orthopyroxene and/or sub-calcic clinoxyroxene > 22 ± 2 kb
Garnet may become the liquidus phase at pressure > 30 kb.
Clinopyroxene will be the second silicate phase to appear up to 10 kb and at this pressure will appear ~ 50°C below the liquidus. Clinopyroxene will be the third phase to appear from 12–25 kb approx. and at lower temperatures, orthopyroxene reacts out, apparently replaced by the increasingly abundant sub-calcic clinoxyroxene.

The compositions of liquidus and near-liquidus phases for Apollo 15 Green Glass can also be deduced from the compositions of phases crystallized from 12040, 12009, etc. There are two important differences. Firstly, the higher value of 100Mg/Mg+Fe (62 compared with 57.5) means that liquidus olivine at low pressure for Apollo 15 Green Glass will be Fo85±1 rather than Fo82±1 and liquidus orthopyroxene will also have higher 100Mg/Mg+Fe [2, 3, 15]. Secondly, the lower TiO2 content of Apollo 15 Green Glass compared with 12040 means that liquidus pyroxenes, assuming the same partition coefficients for (TiO2)px/(TiO2)liq, will have <0.1% TiO2. The predicted compositions for liquidus phases of Apollo 15 Green Glass are given in table 2, and are compared with the appropriate phase compositions from 12040 [5, 10].

Under subsolidus conditions, the Apollo 15 Green Glass composition will react to an olivine eclogite or garnet pyroxenite mineralogy (olivine + garnet + pyroxene) at pressures varying from 10 kb at 1100°C to 20 kb at 1350°C [5, 6, 10].

4. Implications of high pressure phase relationships

The previous study [5] of subsolidus relationships in 12040 composition showed that the relatively high density of the pyroxenite (~ 3.52 g/cm) and olivine eclogite (~ 3.63 g/cm) high pressure mineral assemblages precluded this composition from being representative of the deep lunar interior. Because of the lower TiO2 content and higher Mg/Mg+Fe ratio, the Apollo 15 Green Glass composition would have slightly lower densities than 12040. Nevertheless, following arguments presented previously [11, 12, 15] it is inferred that a moon in which the mean subcrustal composition was close to that of Apollo 15 Green Glass would have mean density and coefficient of moment of inertia inconsistent with the moon's observed parameters.

We infer therefore that Apollo 15 Green Glass composition is derived by a partial melting process or by some combination of partial melting followed by crystal accumulation processes from a more primitive source material possessing a higher Mg/Mg+Fe ratio and lower incompatible element (including TiO2, alkalis, rare-earths) contents. We have no information on the age of the deduced partial melting event(s) but note that if this glass should represent a major unit within the Apennine Front, then the partial melting may have occurred prior to the very early stages of the mare-filling magmatic processes.

In the following sections, we explore in greater detail two alternative, but closely related, models for the genesis of the parental "Green Glass" rock type, and their implications for lunar mantle composition. We have previously shown that the compositions of Apollo 11, 12 and 15 maria basalts can be explained by increasing degrees of partial melting of an approximately uniform source material at pressures of 10–20 kb [5, 6, 11, 12, 14–16]. In view of the close chemical relationships between Green Glass and maria basalts (discussed elsewhere), a reasonable assumption would be that the parental green glass magma was also derived by partial melting from the same source region. In Model A, we shall examine the hypothesis that the parent rock of Apollo 15 Green Glass was once a completely liquid magma ultimately derived by a large degree of partial melting, in the lunar interior, of the same source material which produced Apollo 11, 12 and 15 basalts. In Model B, we shall test the hypothesis that the antecedent of Green Glass represented not a completely molten magma, but rather, an accumulation of mafic phases (chiefly olivine) in a magma resembling 12009 in major element composition.

4.1. Model A

The complete absence of plagioclase as a near-liquidus phase either at low or high pressure, contrasts with the importance of this phase in the "non-mare basalt" type represented by the 14310 and KREEP compositions [17] and suggests that this
composition has no genetic relationship with the presumed magmatic processes occurring within the outer 200 km of the moon, possibly during very primitive crust-formation or late accretionary stages [12]. The dominance of olivine and hypersthene and the major and minor element compositions all suggest a genetic relationship between Apollo 15 Green Glass composition and the compositions of mare basalts, particularly as represented by Apollo 12 and 15 mare basalts. It has previously been suggested [5] that there is a chemical trend (Apollo 11 basalts \( \rightarrow 12022 \rightarrow 12009 \rightarrow 12040 \rightarrow 12035 \)), defined by decreasing incompatible element (Ti, Zr, Rb, REE) contents and increasing Mg/Fe+Fe ratios, which is not produced by processes acting at or near the lunar surface but may be a consequence of variation in the melting process in the lunar interior [5, 6]. The Apollo 15 Green Glass continues this chemical trend. Comparison with 12009 and 12040 compositions shows that, if differences in incompatible element contents are due to partial melting, then the partial melting process enriched 12009 and 12040 in incompatible elements by a factor 4–6 times greater than Apollo 15 Green Glass composition. This implies, on the simple partial melting model, that if 12009 was derived by, say, 10% melting of the source composition then Apollo 15 Green Glass was derived by 40–60% melting of the source composition. The previous studies [5, 6, 10] have shown that the mineralogy of the source region for basalts 12009, 12009 + 10% olivine or 12040 must be dominated by low-calcium pyroxenes and may have orthopyroxene, sub-calcic clinopyroxene and probably olivine as major phases and/or residual phases after magma extraction. It is predicted in a previous section that the same phases would be present in the source region for Apollo 15 Green Glass with the important differences that after magma extraction, olivine would be a residual phase up to \( \sim 25 \) kb, clinopyroxene would only be a residual phase near to 25 kb and residual orthopyroxene would be more magnesian and much lower in TiO\(_2\) than that left after extraction of Apollo 12 parental basalts. We conclude that, to a first approximation, the same source rock which yielded parental basalt for the Apollo 12 basalts (particularly 12009, 12040) by \( x\% \) melting at \( \sim 12–20 \) kb could have also produced Apollo 15 Green Glass as a direct partial melt by \( 4x–6x\% \) melting at 12–20 kb or slightly higher pressures (17–25 kb). We further note that if this hypothesis is correct, then the source region originally had 100Mg/Mg+Fe = 75–80 (and with small (<10%) degrees of partial melting the residual phases changed only slightly in 100 Mg/Mg+Fe value) but with high degrees of melting (~30–60%) to produce Apollo 15 Green Glass as a magma, the residual phases became more magnesian (to 100Mg/Mg+Fe \( \approx 85 \)). The similarities and differences in chemical composition between 12009, 12040 and Green Glass show that if these compositions reflect an increase in degree of melting from production of 12009 to the production of Apollo 15 Green Glass, then this must have occurred largely by an incongruent melting or reaction relationship in which sub-calcic clinopyroxene + resid-ual orthopyroxene + olivine + liquid (with higher CaO/SiO\(_2\), Al\(_2\)O\(_3\)/SiO\(_2\) ratio than original pyroxene). This process is entirely compatible with the near-liquidus relationships observed at high pressure in 12009, 12009 +10% olivine and 12040 (and in terrestrial olivine-rich basalts [18, 19]) where with decreasing temperature, liquidus orthopyroxene is joined by and then replaced by sub-calcic clinopyroxene. The requirement, in terms of self-consistency, for this type of melting is apparent from the similar CaO and Al\(_2\)O\(_3\) contents of 12009, 12040 and Apollo 15 Green Glass and the much lower CaO, Al\(_2\)O\(_3\) contents present in the liquidus pyroxenes for 12009, 12009+10% olivine and 12040 [5, 6, 10]. The incompatible trace-elements and TiO\(_2\) contents require a difference of a factor of 4–6 in degree of partial melting but adding the observed near-liquidus phases of 12009 or 12040 in the required proportions would grossly reduce CaO and Al\(_2\)O\(_3\) contents unless the magma is formed largely by incongruent melting of sub-calcic clinopyroxene to residual orthopyroxene + olivine.

We conclude that it is possible to erect an internally self-consistent hypothesis which identifies 12009 and similar “primitive” or “parental” Apollo 12 basalts as small (~10%) melt fractions (\( T \approx 1320^\circ C \)) from the lunar mantle at depths \( \geq 250 \) km (\( \geq 12 \) kb) and Apollo 15 Green Glass as a large degree of melting (40–60% probably, \( T \sim 1450^\circ C \)) of the same source.
rock at similar or greater depths (250–500 km). This hypothesis requires that the lunar mantle, prior to melting or after small degrees (<10%) of melting, is mainly composed of sub-calcic (~5–8% CaO), aluminous (4–6% Al₂O₃) clinopyroxene (with lesser orthopyroxene+olivine), and that residual, highly refractory mantle after extraction of magma such as Apollo 15 Green Glass, consists dominantly of orthopyroxene (2% Al₂O₃, 1–2%CaO) and olivine (>Fo₈₄).

### 4.2. Model B

Model B accepts the constraint of constancy of source composition for Apollo 12, Apollo 15 and Apollo 15 Green Glass magmas but postulates that Apollo 15 Green Glass composition is not that of a primary magma but rather, that of magma + crystals. There is evidence for near-surface crystallization of olivine and fractionation of lavas controlled by olivine separation [5, 7, 10, 16] in both Apollo 12 and Apollo 15 mare basalts. Thus it is possible that Apollo 12 Green Glass is an impact melt of a rock unit containing accumulative olivine in a less olivine-rich magma, perhaps resembling 12009 in major element chemical composition. This hypothesis permits an extrusion temperature for the postulated parent basalt of ~1250°C compared to ~1420°C required if Apollo 15 Green Glass parent was an entirely liquid magma extruded on the lunar surface.

To evaluate this hypothesis we first discuss the chemical composition of a liquid component assuming Apollo 15 Green Glass composition contains 25% accumulative olivine. In table 1, column 2 lists the composition of a hypothetical liquid which, if it contained 25% of accumulative olivine of composition Fo₇₅, would give the bulk composition of Apollo 15 Green Glass. This composition would have olivine (Fo₇₆–₇₇) as liquidus phase, and it is reasonable that such a liquid might locally produce a more olivine-rich (<Fo₇₆–₇₇) accumulate. This composition would have a similar liquidus temperature to that of 12009 but there are marked differences in composition (compare columns 2 and 5). SiO₂, Al₂O₃ and CaO are higher in the composition derived from Apollo 15 Green Glass and there is a factor of 5 difference in TiO₂ content. The REE and other incompatible elements in 12009 are present at about 20 times the chondritic abundances whereas in the composition derived from Apollo 15 Green Glass these elements are present at 4 to 6 times the chondritic abundances [1, 4].

It is again possible to predict the high pressure liquidus phases for the composition in table 1, column 2 from previous studies in lunar and terrestrial basalts. Olivine will not be a liquidus phase at pressures >6–7 kb, and orthopyroxene will probably not occur on the liquidus at all. The liquidus phase at pressures >6–7 kb will be sub-calcic clinopyroxene with a higher CaO, and Al₂O₃ content than the pyroxene on the liquidus of 12009.

The TiO₂ and REE abundances in the olivine-depleted Apollo 15 Green Glass again require (within the framework of a constant source composition) that if 12009 was produced by x% melting, then this magma was produced by 4x–5x% melting. However, the residual clinopyroxene in the source region would have significantly higher CaO and Al₂O₃ content than that left after extraction of 12009 magma but only marginally higher Mg/Mg+Fe value. These constraints may be incompatible with one another or at least would require that x be very small, i.e. 1–2% melting for 12009, 5–10% melting for the olivine-depleted Apollo 15 Green Glass composition. The formation of 12009 and Green Glass by such small degrees of partial melting appears implausible however, since it implies that the abundance of involatile incompatible elements in the source region is lower than in chondrites by a factor of 2 to 5. A number of arguments can be advanced against this [15].

Whilst this version of model B is rejected, it would nevertheless be possible to construct a modified version in which the proportion of accumulative olivine was smaller, say, about 10–15%. For example, a magma composition between those of columns 1 and 2, table 1 (say, with 15–20% normative olivine) might be specified, having olivine, orthopyroxene ± clinopyroxene on the liquidus at ~15 kb and 1370°C (compared with 20–25 kb and 1450–1500°C for Green Glass). The liquidus temperature of such a magma at the lunar surface would be about 1300°C, and it would have an Mg/Mg+Fe value of about 0.55 with liquidus olivine ~Fo₈₀. This version of Model B, however, is only marginally distinct from Model A in that it implies that if 12009 magma is produced by
Self-consistent models can be constructed which show that if parental Apollo 12 magmas were produced by $x\%$ partial melting of a source region in the lunar interior at depths greater than 200 km, as implied by experimental evidence [5, 6, 12] then a magma plus crystals of Apollo 15 Green Glass composition can be formed by 4x to 6x percent partial melting of the same source region. The most probable value of $x$ is believed to be about 10%.

The igneous precursor to Green Glass may have been emplaced at temperatures of 1300–1350°C if mobilized as a crystal mush or at temperatures as high as 1400–1450°C if erupted as a completely liquid magma. The models require a source region for mare basalts dominated by sub-calcic, low alumina clinopyroxene (3–5% $\text{Al}_2\text{O}_3$, $\text{CaO}$; 100Mg/Mg+Fe = 75–80), with lesser orthopyroxene and olivine, and melting behaviour in which the clinopyroxene melts incongruently yielding orthopyroxene + olivine + liquid. The Model B has an important difference from A in that the temperature of extrusion of the magma giving rise to Apollo 15 Green Glass would be $\sim 1300°C$ rather than $1420°C$. It may also be relevant that a magma reaching the surface at $\sim 1300°C$ and containing $\sim 15\%$ olivine ($\text{Fo}_{35} - \text{Fo}_{80}$ composition) crystals may have begun its movement to the lunar surface as a diapiric crystal mush at $\sim 15\, \text{kb}$, $T \sim 1330°C$ consisting of liquid (composition not known) + sub-calcic clinopyroxene $\pm$ orthopyroxene $\pm$ olivine crystals. The degree of melting would increase as the diapir rose under adiabatic conditions and, if equilibrium was maintained, the suspended olivine crystals may have been formed by incongruent melting of the pyroxenes.

**Summary**

Self-consistent models can be constructed which show that if parental Apollo 12 magmas were produced by $x\%$ partial melting of a source region in the lunar interior at depths greater than 200 km, as implied by experimental evidence [5, 6, 12] then a magma plus crystals of Apollo 15 Green Glass composition can be formed by 4x to 6x percent partial melting of the same source region. The most probable value of $x$ is believed to be about 10%.

The igneous precursor to Green Glass may have been emplaced at temperatures of 1300–1350°C if mobilized as a crystal mush or at temperatures as high as 1400–1450°C if erupted as a completely liquid magma. The models require a source region for mare basalts dominated by sub-calcic, low alumina clinopyroxene (3–5% $\text{Al}_2\text{O}_3$, $\text{CaO}$; 100Mg/Mg+Fe = 75–80), with lesser orthopyroxene and olivine, and melting behaviour in which the clinopyroxene melts incongruently to yield basaltic liquid + residual orthopyroxene + olivine.

**References**


CHEMICAL COMPOSITIONS AND PETROGENETIC RELATIONSHIPS IN APOLLO 15 MARE BASALTS

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Major element analyses, together with selected trace element analyses, of fourteen Apollo 15 mare basalt samples show that these basalts fall into two distinctive groups. On a normative basis these two groups have been designated Apollo 15 olivine basalts and Apollo 15 quartz basalts; previous identification of these groups on a modal basis led to the names porphyritic olivine basalt and porphyritic pyroxene basalt respectively [1]. The Apollo 15 olivine basalts include genetically related flow units in which there has been near-surface fractionation controlled mainly by movement of olivine. It is also shown that these olivine basalts cannot be genetically related to Apollo 15 quartz basalts, nor to Apollo 12 olivine basalts nor to Apollo 11 basalts by any process of near-surface crystal fractionation. Evaluation of known and predictable high pressure crystallization sequences leads to a model of magma genesis in which the source rock (lunar mantle) is olivine-bearing pyroxenite and distinctive parental mare basalt magmas are formed by variable degrees of partial melting and different depths of magma segregation.

1. Introduction

The Apollo 15 mission returned a large number of fragments of basalt of mare type from the vicinity of Hadley Rille. These basalts were subdivided into four petrographic types on the basis of texture and mineralogy [1]. In this paper we report the compositions, in terms of major elements and some trace elements, of thirteen basalts, including examples of the four petrographic types. These basalts are compared with Apollo 11 and 12 mare basalts. Knowledge of the crystallization behaviour of the basalts at both high and low pressures is used to discuss possible genetic relationships among the Apollo 15 basalts themselves and the more general problems of petrogenesis and source region for mare basalt.

The major and trace element analyses were made by X-ray fluorescence spectrometry using the same methods as for previous Apollo samples [2].

2. Analytical data

Table 1 contains analyses and CIPW norms of thirteen individual basalt fragments including examples of petrographic types 1 (15475), 2 (15499, 15597), 3 (15555, 15545) and 4 (15016) [1]. The samples are dominantly from locality 9A at the edge of Hadley Rille but also include representatives from localities 2, 3 and 4.

Examination of the data in table 1, together with the plotting of analytical data on variation diagrams (figs. 1, 2) leads to grouping of the samples and provides evidence for genetic relationships. First, the four quartz-normative samples of table 1 are distinctive in their low TiO2 contents, and relatively high 100 Mg/(Mg + Fe) values accompanying high SiO2 and the presence of normative quartz. Two other published analyses [1], 15058 and 15076, also have affinities with this group although 15076 has even
lower TiO₂ and higher 100 Mg/(Mg + Fe) (47.6) with 1.8% normative quartz. This chemical group includes both petrographic groups 1 and 2 [1] and the distribution and variation in grain size and texture of samples of this type suggests that these samples represent fragments of a widely distributed rock unit (?flow) in which there existed wide variations in cooling rate but very limited superimposed chemical variation due to crystal settling. If the very low TiO₂, low P₂O₅ and relatively Mg-rich character of 15076 are not due to non-representative sampling, then this sample must be from a different unit than 15475, 15499, 15595, 15597 and 15058. The chemical characteristics of 15076 suggest closer affinities with this group of Apollo 15 samples rather than Apollo 11, 12, or the other analyzed Apollo 15 basalts (affinities 2–7, table 1).

The remaining analyses of table 1 display significant variation in chemical composition but all are olivine basalts and are chemically distinctive from the Apollo 11 or Apollo 12 olivine basalts. Among the rake samples from the edge of Hadley Rille (Station 9A) there are two groups (15622, 15636 and 15658, 15668, 15674 respectively) within which the similarity in chemical compositions suggests that these samples are chips of the same rock. In the following petrogenetic discussion the compositions of these two groups have been averaged. There is a significant difference between the two analyses given for sample 15555 in table 1. This is a relatively coarse-grained
B.W. Chappell, D.H. Green. Apollo 15 mare basalts

Fig. 2. Variation of TiO$_2$ versus MgO for Apollo 12 and Apollo 15 basalts. Symbols as for fig. 1.

olivine basalt and the compositional differences are probably due to sample inhomogeneity. The second analysis [3] is from a chip weighing only 0.56 g and the high TiO$_2$, FeO and lower SiO$_2$, Al$_2$O$_3$ and CaO possibly represent a non-representative concentration of ilmenite. The analysis of this sample given in the PET report [1] is intermediate between the analyses given in table 1.

The variation diagrams (figs. 1, 2) suggest that the olivine-normative Apollo 15 basalts form a coherent group distinct from the Apollo 12 basalts but displaying a parallel chemical variation dominated by variability in those elements concentrated in ferromagnesian minerals. It has been demonstrated [4-7] that a major chemical variation in the Apollo 12 basalts is due to crystal fractionation controlled by olivine separation under near-surface conditions. In fig. 1 we have plotted the line joining those compositions in which separation of olivine (of composition appropriate to that crystallizing from the magma) produces a fractionation trend consistent with major element, trace element and isotopic variations observed between the basalts [4]. Not all Apollo 12 basalts fit this trend; in particular 12035 has anomalously high

normative olivine relative to 100 Mg/(Mg + Fe), a lower TiO$_2$ content, and also the lowest REE abundances of the Apollo 12 basalts [8]. It is transitional towards Apollo 15 olivine normative basalts. On the other hand 12022 has a high TiO$_2$ content and is possibly transitional towards the Apollo 11 basalts [7]. In samples 12040 or 12051, olivine fractionation is consistent with major element differences but inconsistent with trace element abundances. These differences led to the conclusion that the Apollo 12 basalts included samples from different flows representing separate episodes of partial melting in the lunar interior [4, 10, 11]. A similar conclusion is suggested for the Apollo 15 olivine normative basalts. The variation illustrated in figs. 1 and 2 and the calculations presented in table 2 show that a principal variation among Apollo 15 basalts is due to olivine fractionation possibly accompanied in some samples by minor chrome spinel (note the high Cr$_2$O$_3$ content of 15016 and 15622 suggesting accumulation of spinel). From experimental crystallization studies of lunar and terrestrial basalts, and particularly from studies of the Apollo 12 basalts, it can be predicted that olivine is the liquidus phase for all olivine-normative
Table 2
Calculated amounts and compositions of olivines which when added to or subtracted from Apollo 15 basalt compositions will give derived compositions with MgO and FeO values corresponding to those of other Apollo 15 basalts

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Derived compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>15475</td>
<td>15499</td>
</tr>
<tr>
<td>15595</td>
<td>15597</td>
</tr>
<tr>
<td>15016</td>
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<tr>
<td>15658</td>
<td>15668</td>
</tr>
<tr>
<td>15674</td>
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</table>

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Derived compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>15475</td>
<td>(+16.4%Fo55.1)</td>
</tr>
<tr>
<td>15499</td>
<td>(Si,Ti)</td>
</tr>
<tr>
<td>15595</td>
<td>(+15.3%Fo55.1)</td>
</tr>
<tr>
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<td>(Si,Ti)</td>
</tr>
<tr>
<td>15016</td>
<td>(-13.9%Fo50.1)</td>
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<tr>
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<td>15119</td>
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<td>15119</td>
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<td>(-9.4%Fo45.9)</td>
</tr>
<tr>
<td>15555</td>
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</tr>
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<td>(-14.5%Fo55.6)</td>
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<td>15668</td>
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<td>(Si,Ti)</td>
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<tr>
<td>15674</td>
<td>(Si,Ti)</td>
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Olivine data in brackets are those with compositions inappropriate to either the 'parental' or 'derivative' compositions. Elements listed in brackets are those with anomalous abundances in the derived compositions relative to observed abundances.
Table 3
Examples of calculations testing possible genetic relationships between Apollo 15 basalts. A 'derivative' composition is calculated from a 'parent' composition by finding the amount and composition of olivine which on addition to or subtraction from the parent composition will give FoO and MgO values exactly matching those observed in the second sample. This table makes a direct comparison of other elements both as calculated and occurring in the natural sample.

<table>
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<tr>
<th>Parent</th>
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<th>Process</th>
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<tr>
<td>15555</td>
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<td>-7.1% Fo</td>
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<tr>
<td>15016</td>
<td>15622,636</td>
<td>-4.4% Fo</td>
</tr>
<tr>
<td>15658.668,674</td>
<td>+7.3% Fo</td>
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<table>
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<tr>
<th>SiO₂</th>
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<th>Calc.</th>
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<th>Calc.</th>
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<td>93</td>
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<td>Y</td>
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<th>Yes</th>
<th>No</th>
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<th>No</th>
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<tr>
<td>Elements inconsistent with genetic relationship</td>
<td>Cr*</td>
<td>?Y</td>
<td>Na, Cr* (olivine composition)</td>
<td>Cr*</td>
<td>Si, Ti, Al, Ca (olivine composition)</td>
</tr>
</tbody>
</table>

* Differences in Cr content could be adjusted by assuming minor chromium spinel accompanying olivine.
basalts of fig. 1. Furthermore the composition of olivine on the liquidus of 15119 is Fo$_{75}$, and that on the liquidus of (15622, 15636) is Fo$_{72}$, [7, 9].

To quantitatively evaluate the role of olivine fractionation in relating any pair of rock compositions we have calculated the amount and composition of olivine which must be added to or removed from one composition to give a derivative composition with identical MgO and FeO contents to the second composition. The calculated and actual compositions may then be compared for similarities or differences in components other than MgO and FeO. The method also shows whether the calculated olivine is of a composition consistent with crystallization from either the 'parent' or derivative basalt. The general results of these calculations are given in table 2 and in table 3 typical results are given in detail for several pairs of analyses.

We infer that most of the Apollo 15 olivine-basalts have compositions consistent with derivation from a single rock unit (flow) in which there has been local differentiation controlled by the crystallization and separation of olivine (possibly with minor chromite spinel). Sample 15545 appears to be derived from a different rock unit relative to the other olivine-normative basalts but this sample does display affinities to the olivine-normative Apollo 15 basalts rather than to Apollo 11 or 12 basalts. We also conclude that it is not possible to derive Apollo 11 or Apollo 12 basalts from Apollo 15 olivine-basalts (or conversely) by any process of crystal fractionation at low pressures involving near-liquidus phases (olivine, spinel, pigeonite). The data also demonstrate that the Apollo 15 quartz-normative basalts are not related to Apollo 11, 12 or 15 basalts by processes of crystal fractionation involving those minerals.

3. Petrogenesis of Apollo 15 basalts

3.1. Olivine basalts

It is not yet possible, from the data available to us, to determine where a possible parent magma might lie within the chemical trend of the Apollo 15 olivine basalts. Thus it is uncertain whether the most olivine-rich and Mg-rich basalt (15622, 15636) is a parent magma composition and gave rise to the other compositions by settling out of olivine crystals or whether the parental magma composition is less olivine-rich and the more olivine-rich samples are partly accumulative. When full data on olivine compositions are available it will be possible to place some constraints on the parent magma composition. If the most magnesian olivine observed in any of these rocks is Fo$_{75}$ then it must have crystallized from a liquid of composition near (15622, 15636). However if the most magnesian olivine is only Fo$_{70}$ then there is no unequivocal evidence for a liquid more olivine-rich than 15119.

Thus if the Apollo 15 basalts include examples of liquids which have been so rapidly quenched that they preserve olivine (cores of zoned crystals) which crystallized at the liquidus (cf. 12009 [10, 11]), it will be possible to deduce the probable parent composition for these basalts. In samples 15555 (and 15557) the most magnesian olivines observed are Fo$_{60}$, indicating equilibration of olivine well below the liquidus of those particular bulk compositions [3].

In the following discussion we will examine the petrogenetic implications based on the assumption that the source region for the Apollo 15 parent basalt has 100 Mg/(Mg + Fe) = 75-80, i.e., the value deduced for the source region for both the Apollo 11 and Apollo 12 mare basalts. This implies that the parent basalt to the Apollo 15 basalts resembles composition 15622 but will be richer in normative olivine (>21% olivine) and with 100 Mg/(Mg+Fe) > 49. In comparison with 12009, a possible parent magma for Apollo 12 basalts with 100 Mg/(Mg+Fe) = 49.5 [10, 11], the Apollo 15 parent basalt would have almost identical CaO, Al$_2$O$_3$ and Cr$_2$O$_3$ contents but lower SiO$_2$ (44:45), TiO$_2$ (2.2:2.9), higher Na$_2$O (0.29:0.22) FeO and MgO contents. The high pressure crystallization behaviour of such a composition is predictable from the extensive data on Apollo 12 and terrestrial tholeitic basalts [7, 10-12]. Olivine will occur on the liquidus at ~15 kb but will be joined by orthopyroxene and/or subcalcic clinopyroxene on the liquidus at ~15 kb or below the liquidus at 10-15 kb. We infer that a parent magma to Apollo 15 olivine basalts could be derived by partial melting of a source rock containing olivine (Fo$_{75}$-80), subcalcic clinopyroxene. This is the same source mineralogy postulated for parent magma for Apollo 11 and 12 basalts [10, 11, 13, 14]. However, to account for the higher Ol content, Ol/Hy and Ol/Di ratios for a given 100 Mg/(Mg+Fe) value in the Apollo 15 basalts, we
infer that the Apollo 15 parental olivine basalts result from magma extraction at 15–17 kb, whereas the Apollo 12 basalts represent extraction at 10–12 kb. The liquids temperature of Apollo 12 parental basalt would be ~1350–1370°C, that of Apollo 15 parental basalt would be ~1400–1420°C. The difference in TiO$_2$ content between Apollo 12 and Apollo 15 olivine basalts (fig. 2) suggests that the Apollo 15 parental basalt is formed by a higher degree of partial melting than Apollo 12 basalt, since TiO$_2$ is apparently as strongly partitioned into the liquid in partial melting at 15–17 kb as at 10–12 kb. This is consistent with lower Zr, Rb and particularly Y abundances in the Apollo 15 basalts, but is not supported by their apparently higher Na content and by similar Sr contents. REE data on a single sample (15555) [15] are consistent with the lower Y contents of the Apollo 15 olivine basalts, indicating REE abundances of about 10X chondrites compared with 20X chondrites for olivine-rich Apollo 12 basalts. Basalt 12035 is transitional between the groups in REE abundances and also in the components represented in fig. 1.

From the relative abundances of minor and trace elements strongly partitioned into the liquid we infer that the Apollo 15 parent basalt was the product of a higher degree of partial melting than that producing the Apollo 12 parental basalts. The very small negative europium anomaly in 15555, if this is general to Apollo 15 basalts, may be a direct consequence of the higher temperature and greater degree of melting postulated for the Apollo 15 parent basalt. These differences could cause the partial melting process to more closely approach an equilibrium partial melting in terms of incompatible element partition between liquid and residual crystals rather than the surface equilibrium process proposed to account for the large negative europium anomaly in Apollo 11 and 12 basalts [10, 14, 16]. Alternatively, since the Apollo 12 and Apollo 15 parental olivine basalts are inferred to be derived by magma segregation at different depths in the lunar interior, the differences in TiO$_2$, Na$_2$O, REE abundances and in the magnitude of the europium anomaly, may be referred to differences in minor and trace element abundances occurring within the lunar mantle.

3.2. Pyroxene basalts (quartz basalts)

The basalts 15475, 15499, 15595, 15597 of table 1 and the previously analyzed [1] samples 15058 and 15076 are petrographically [1] distinctive in the absence of normative olivine, abundance of phenocrystal pigeonite and rarity of modal olivine. The data listed in tables 1, 2 and 3 and plotted in figs. 1 and 2, demonstrate that this group of basalts is chemically distinctive and cannot be derived by olivine fractionation from parental olivine basalt of Apollo 11, 12 or 15 type. Although experimental data on basalts such as 12021, 12038 and 12065 are adequate to show that olivine will be a liquidus phase in Apollo 15 pyroxene basalts at the lunar surface, the Mg-rich composition (relative to their quartz-normative character) determines that the liquidus olivine would be Fo$_{73}$. Pigeonite would either occur on the liquidus with the olivine (c.f. 12021 [10, 12]) or begin crystallizing soon after the olivine. As both phases became more Fe-rich with increasing degree of crystallization, olivine would react with liquid to precipitate pigeonite pyroxene (c.f. 12065, 12021 [10]). These conclusions are supported by observations on 15499 basalt, a pyroxene porphyritic vitrophyre. This sample contains large pigeonite-cored phenocrysts and very rare olivine grains in a glass and devitrified glass matrix. The olivine is Fo$_{68}$ and the most magnesian pigeonite has 100 Mg/(Mg + Fe) = 72 (Ca$_5$Mg$_{68}$Fe$_{26}$). The olivine composition is not appropriate to liquidus olivine but would be in equilibrium in this bulk composition at only about 20°C below the liquidus.

Examination of fig. 1 shows that a composition of Apollo 15 olivine basalt type which has olivine of Fo$_{73}$ on the liquidus would have 12% normative olivine whereas a composition of Apollo 12 olivine basalt type with olivine of Fo$_{23}$ on the liquidus would have 4% normative olivine. Alternatively we may compare the 100 Mg/(Mg + Fe) values of liquids which are just saturated (neither normative quartz nor olivine) in the different basalt groups. For Apollo 12 basalts such a composition would have 100 Mg/(Mg + Fe) = 41–42; for Apollo 15 olivine basalts 100 Mg/(Mg + Fe) = 37 at saturation and for Apollo 15 quartz basalts 100 Mg/(Mg + Fe) = 44 at saturation. Similarly, the low TiO$_2$ content of the quartz basalts prohibit their derivation by any process of extraction of olivine, pyroxene or spinel (with
B. W. Chappell, D. H. Green. Apollo 15 mare basalts compositions corresponding to liquidus phases of the quartz or olivine basalts) from Apollo 15 or Apollo 12 olivine basalts.

The chemical and mineralogical data thus demonstrate that the Apollo 15 quartz basalts cannot be genetically related by processes of low pressure crystal fractionation to parent basalts of Apollo 12, Apollo 15 olivine basalts or Apollo 11 basalt types. The data do not preclude the possibility that the quartz basalts are near-surface fractionation products from parental olivine basalt. Indeed we favour the hypotheses that a parental basalt composition to Apollo 15 quartz basalt is to be found along an olivine-controlled fractionation trend. Such a parental composition might have 10% normative olivine and 100 Mg/(Mg + Fe) = 53 (cf. fig. 1). This interpretation leads to the suggestion that the parent basalt would have been the product of magma segregation at P7-9 kb with a higher degree of partial melting than that producing Apollo 12 parent basalt. Since the TiO₂ content of Apollo 15 quartz basalt is about half that of Apollo 12 olivine basalts of similar degree of saturation or of similar 100 Mg/(Mg + Fe) value, the parental magma could be a product of approximately twice as much partial melting — the REE abundance data will provide a critical test of this but yttrium abundance data (42 ppm in average of 12051, 12052, 12064, 12065 quartz basalts [4] compared with 25 ppm in average of 15475, 15499, 15595, 15597) (table 1) support this relationship and Rb and Zr, though more variable, give moderate support. This interpretation would probably require that the partial melting to yield parent magma for Apollo 15 quartz basalt would be sufficient to eliminate clinopyroxene from the residue and change the 100 Mg/(Mg + Fe) rate of residual olivine and orthopyroxene from ~76 (for Apollo 12 (12009) genesis) to ~79.

Evidence for or against this hypothesis for genesis of Apollo 15 quartz basalts may be found in further analytical data on olivine-rich samples of Apollo 15 basalts since the hypothesis suggests that there should exist basalts (which may or may not have reached the lunar surface in undifferentiated state) with TiO₂ < 1.5%, ~10% normative olivine, 100 Mg/(Mg + Fe) ~53 and with about 8.5% Al₂O₃ and 9.5% CaO.

4. Conclusions

The samples of mare basalts collected from the Apollo 15 landing site fall into two very distinctive chemical, petrographic and petrogenetic groups, designated Apollo 15 olivine basalts and Apollo 15 quartz basalts. Within the olivine basalt group there is evidence for differentiation controlled by extraction or accumulation of olivine, accompanied by minor chromian spinel, leading to a spectrum of compositions ranging from 8% normative olivine to 20% normative olivine. There are differences in trace element and minor element abundances within the group of Apollo 15 olivine basalts which show that the samples were derived from more than one (flow) unit but such differences are subordinate to the differences which exist between this group of lavas and the Apollo 12 mare basalts or between the Apollo 15 olivine basalts and Apollo 15 quartz basalts respectively. The Apollo 15 quartz basalts are distinctive in their low TiO₂ content and relatively high Mg-value (100 Mg/(Mg + Fe) = 44) coupled with high SiO₂ (48%) and quartz-normative character. Further sampling may reveal more magnesian and slightly olivine-normative samples genetically related to the quartz basalts, if there has been any near-surface fractionation by olivine separation in this suite (as there has in the Apollo 12 and Apollo 15 olivine basalt suites) [5, 10].

Knowledge of high pressure crystallization behaviour of lunar and terrestrial basalts [7,9-13] permits the prediction of source mineralogy and conditions of partial melting of the lunar mare basalts. It is inferred that the parental basalts of the Apollo 15 olivine basalt group were derived by ~15% melting of a source rock containing major sub-calcic clinopyroxene, orthopyroxene and minor olivine (Fo₅₉₋₆₃) and further, that the depth of magma segregation was 300–350 km (15–17 kb). These conditions may be compared with the deduced conditions of magma segregation, from a similar source rock, for Apollo 12 olivine basalts as ~10% melting at 200–250 km [10, 11, 13, 14]. The Apollo 15 quartz basalts may result from olivine extraction from a more magnesian and olivine normative (~5% olivine) parental magma. Such a parental magma could result from magma segregation at depths of 130–180 km (7–9 kb), again from a similar olivine pyroxenite source rock. The nature of this parental magma and abundances of incompatible
elements (Ti, Y, Rb, Zr) suggest that the degree of partial melting of the source rock would be about 20%. The inference that variable depths of magma separation and variable degrees of partial melting are involved in lunar mare basalt genesis gives support to suggestions that large scale diapiric ('convective') movements in the lunar mantle accompanied the filling of the mare basins [17].

References

EXPERIMENTAL PETROLOGY OF LUNAR HIGHLAND BASALT COMPOSITION AND APPLICATIONS TO MODELS FOR THE LUNAR INTERIOR

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ABSTRACT

Lunar Highland Basalt (gabbroic anorthosite) composition transforms with increasing pressure through assemblages of spinel + clinopyroxene + anorthite, and garnet + clinopyroxene + anorthite + quartz to eclogitic assemblages of garnet + clinopyroxene + kyanite + quartz (p = 3.51 — 3.52). Estimates of the lunar thermal gradient allow evaluation of the mineralogical variation with depth in the moon and thus allow calculation of mean lunar density and coefficient of moment of inertia for several models for the moon. These calculations show that the simplest models of Highland Basalt as the mean lunar composition and Highland Basalt as comprising the outer 250-270 km (formed as a partial melt from a Ca, Al-rich lunar interior) fail to meet the lunar density constraint but could do so if the hypotheses were modified towards more Fe-rich compositions. The geochemical constraints are much stronger and show that it is not possible for Highland Basalt to act as a source rock for mare basalt magmas under any conditions of melting in the lunar interior. It is further shown that Highland Basalt cannot be a partial melt from a mean lunar composition matching the Ca, Al-rich inclusions of the Allende meteorite (Anderson 1973) leaving the residual deep lunar interior of diopside + merwinite + spinel mineralogy.

INTRODUCTION

Studies of the soil and glass spherule compositions from all lunar landing sites (e.g., Reid, Ridley et al. 1972; Reid, Warner et al. 1972; Ridley et al. 1973) and data from the orbiting X-ray spectrometer experiments (Adler et al. 1973) demonstrate the importance in the lunar highland region of bulk compositions rich in Al2O3 and, in normative mineralogical terms, classifiable as gabbroic anorthosite or anorthositic gabbro. It is relevant to use experimental petrology to examine an hypothesis that such highly aluminous compositions are either partial melts from, or representative of, the composition of the deep lunar interior. A previous study (Green et al. 1972) has briefly reported a subsolidus mineralogy at high pressures for moderately aluminous compositions 14310 and KREEP but there has been no study of the more aluminous “Highland Basalt” or gabbroic anorthosite composition (table 1), apart from studies on more sodic terrestrial gabbroic anorthosite and grosspydite compositions (T. H. Green 1967). The need for a direct study of the high pressure phase equilibria for the lunar “gabbroic anorthosite” or “highland basalt” composition is also apparent in a recent paper by Mason (1972) where it is argued that a lunar interior of this composition will yield mean density and coefficient of moment of inertia consistent with those values determined for the moon. A different approach, stemming from a specific hypothesis of lunar condensation and accretion, has led Anderson (1972, 1973) to argue that the deep lunar interior is highly enriched in Ca, Al, Mg, Ti and associated refractory (in terms of volatility in a gas of solar composition) trace elements and depleted in SiO2, FeO, and alkalis. Anderson (1973) suggests that the deep lunar interior contains iron-free diopside, spinel, merwinite and mellilitite as major phases and further suggests that the Ca-Al-rich compositions of the lunar highlands (particularly the gabbroie anorthosite composition) represent products of partial melting, followed by crystal fractionation, from the deep lunar interior. The methods of experimental petrology

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TABLE 1
COMPOSITION OF HIGHLAND BASALT (Reid et al. 1972) AND COMPARISON WITH SEVERAL COMPOSITIONS WHICH ANDERSON (1973) SUGGESTED WERE FORMED AS MELT FRACTION DERIVED FROM A Ca, Al-RICH DEEP LUNAR INTERIOR

<table>
<thead>
<tr>
<th>Composition</th>
<th>Table 5/3</th>
<th>Table 5/4</th>
<th>Table 7/1</th>
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<td>SiO₂</td>
<td>45.2</td>
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<td>45.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25.9</td>
<td>25.9</td>
<td>27.6</td>
</tr>
<tr>
<td>FeO</td>
<td>5.4</td>
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</tr>
<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
<td>14.8</td>
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<td>15.1</td>
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<tr>
<td>Na₂O</td>
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<td>—</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>—</td>
<td>100.7</td>
<td>101.2</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Σ</td>
<td>99.9</td>
<td>100.7</td>
<td>101.2</td>
</tr>
</tbody>
</table>

can provide a test of the internal consistency of this model by establishing whether the high pressure liquidus phases of the gabbroic anorthosite composition are those minerals postulated as major phases in the lunar interior.

EXPERIMENTAL METHODS

The composition selected for experimental study (table 1) is the average of the five very similar median compositions of high alumina glasses derived by Reid, Warner et al. (1972) from Apollo 11, 12, 14, and 15 and Luna 16 samples, respectively. These authors have argued the significance of this compositional grouping and its distinction from other non-mare compositions designated as Fra Mauro basalts and anorthosite or plagioclase glasses. The composition also occurs in the Luna 20 (Reid 1973) and Apollo 16 glasses.

The “Highland Basalt” composition of table 1 was prepared from AR grade reagents, fused at 1,450°C in platinum crucible with 5% excess metallic iron and the excess metallic iron extracted magnetically after repeated crushing and elutriation to obtain a grain size < 10μ (about 75% < 5μ). Semi-microanalysis of the glass by E. Kiss gave negligible Fe₂O₃ (< 0.5%) and electron probe analysis of both the glass and experimental runs confirmed the composition of table 1. Detailed studies of Fe-distribution in the charges showed that in some above-solidus runs—for example, 18 kb, 1,420°C—there had been addition of iron (~1 wt%) within 100–200μ of the capsule wall leading to crystallization of garnet rather than spinel in the more Fe-rich areas. In all cases however, and particularly in the subsolidus runs, the central part of the change preserved the starting composition with neither addition or loss of Fe. The glass prepared as described above contained 5–10% of fine (< 5μ long) feathery plagioclase microlites but no other crystalline phases. Three different starting mixes were used for experimental runs:

1. Starting mix A: Glass + 5–10% of plagioclase microlites; used to confirm that the minimum pressure required for the incoming of garnet at 1,100°C, as determined on mix B, was correct and not due to metastable persistence of garnet seeds. Mix A was also used for runs above the solidus.

2. Starting mix B: 90% Mix A + 10% high pressure assemblage of garnet + pyroxene + kyanite + quartz. The latter was prepared in large capacity (50 mgm) Ag₇₅Pd₂₅ capsules at 30kb, 1,100°C, 17 hr, yielding a fine-grained charge of grossular-
rich garnet, pyroxene, kyanite and quartz. Mix B was used to determine the incoming of garnet on the basis of growth or disappearance of the garnet seeds and on the composition of the garnet in the run in comparison to that of the seed garnet.

3. Starting mix C: Consisted entirely of the fine-grained garnet + pyroxene + kyanite + quartz assemblage from 30 kb, 1,100°C. This mix, which did not contain plagioclase, was used to reverse the subsolidus plagioclase-out boundary defined by mix B.

Experimental runs were carried out using a piston-cylinder apparatus and samples were enclosed in iron capsules with close-fitting lids. Temperature variation is ± 5°C about the control point with an accuracy estimated as ± 10°C. A pressure correction of minus 10% of the nominal pressure has been applied (T. H. Green et al. 1966). At 1,000°C, experiments were run for 49 ± 7 hrs using mix A or B but for 96 ± 10 hrs using mix C. At 1,100°C experiments were run for 24 hr on mix A or B and 72 hr on mixes A and C. At 1,200°C and 1,250°C experimental runs were given 6 hr and at 1,300°C they were given 4 hr. Runs between the solidus and liquidus were given from 3 hr to 10 min, depending on the degree of melting. Experimental runs were examined optically, by X-ray powder diffraction and by electron microprobe. The use of the finely focused electron beam and the non-dispersive X-ray detector of the TPD electron probe (Reed and Ware 1973; Green 1973) permit complete analysis of finer-grained phases than previously possible. The data on mineral chemistry and element partition between coexisting minerals under experimental conditions are comparable in accuracy with those data obtained from natural eclogites and granulites and permit calculations of modal abundances from the bulk composition and specific mineral compositions. The densities of the minerals have been estimated using linear interpolations between densities for end members of the solid solutions (Tröger 1959; Clark 1966) and thus the densities of the total mineral assemblage were determined with an estimated accuracy of ± 0.005.

**Subsolidus experimental data**

The low-pressure gabbroic anorthosite assemblage mainly consists of plagioclase + orthopyroxene + clinopyroxene ± olivine and has a calculated density of 2.93 g/cc (Unless otherwise specified, densities are given for room temperature and pressure conditions; NTP conditions =20°C 1 atm.) for a low-temperature assemblage assuming negligible Al₂O₃ solid solution in pyroxene and the presence of minor olivine. At pressures of 7–8 kb, 1,100°C, olivine is eliminated from the assemblage by reaction with anorthite, yielding aluminous pyroxene and aluminous spinel. (At pressures > 7 kb, orthopyroxene could not be firmly identified by either X-ray or optical means. However, the pyroxene composition e.g., 10 kb, 1,300°C contains a very high content of the \((\text{Mg, Fe})\text{SiO}_3\) molecule (figs. 2-3)). This reaction would produce an assemblage with density of 2.99 g/cc. At 9 kb, 1,100°C garnet is stable (fig. 1). Garnet increases in abundance and changes composition, becoming more pyrope-rich between 9 and 12 kb (fig. 2, table 2) but with little change in grossular content. Calculated density at 11 kb is 3.07 g/cc based on compositions of bulk rock, analyzed garnet at 11 kb, and on estimated pyroxene and anorthite. From 13–17 kb, garnet increases only slightly in grossular content but pyroxene decreases in Mg + Fe (enstatite and/or Mg, Fe Tschermak’s silicate) solid solution as reaction with anorthite proceeds to yield increasing garnet content, Ca-Tschermak’s silicate in pyroxene and minor quartz. These changes at 1,100° are partially illustrated in figures 2 and 3 by the differences in pyroxene composition between 15 kb and 17 kb but the analogous changes at T ≥ 1,300°C (illustrated in figs. 2 and 3) more clearly demonstrate the very marked changes in pyroxene
Fig. 1.—Experimental data on highland basalt composition showing data points and nature of mineral assemblages, lines between liquidus and solidus mark the upper temperature limit of the different phases. Points immediately below the point marked Liquidus contain <1% crystalline phases. Symbol with dashed square = plagioclase present in runs using seeded glass starting material (mix B), but absent in runs using Ga + Px + Ky + Qz starting material (mix C).

Composition as a function of pressure (tables 2 and 3). From the mineral analyses at 15 kb and 17 kb, 1,100°C, calculated densities are 3.195 g/cc at 15 kb and 3.125 at 17 kb. A rather more rapid increase in density with pressure may occur between 12 kb and 13 kb due essentially to the enstatite + anorthite reaction but this cannot be divorced entirely from other coupled reactions involving the pyroxene and garnet solutions. Anorthite persists as a major phase at 1,100°C to between 17 and 18 kb but is absent at higher pressures in the eclogitic assemblage (garnet + clinopyroxene + kyanite + quartz). The breakdown in anorthite produces a sharp change in garnet composition (see figs. 2 and 3) and the appearance of kyanite as a major phase. Since anorthite is a major mineral even at 17 kb, 1,100°C this breakdown results in a sharp density increase, to 3.50 g/cc (20 kb assemblage). With further increase in pressure at 1,100°C garnet becomes more grossular-rich and pyroxene becomes lower in Ca-Tschermak’s silicate content (figs. 2 and 3). A coupled reaction of clinopyroxene + kyanite + garnet + quartz is also present between 20 and 30 kb, the net results being that the 30 kb assemblage has
The changes in mineralogy as a function of pressure at 1,100°C are summarized in figure 4 in the form of a density (NTP) versus pressure diagram. This diagram, together with the data on the detailed changes in pyroxene and garnet composition (figs. 2 and 3) (table 3) illustrates the mineralogical complexity of the metamorphic reactions from the gabbroic anorthosite mineral assemblage to the eclogitic high pressure assemblage. The higher garnet and kyanite contents and higher density (3.515) than the 20 kb assemblage (table 4).
distinctive, non-basaltic chemical composition of the "Highland Basalt," particularly the very high normative anorthite content and extremely low normative albite and diopside contents, has the effect of giving more abrupt mineralogical and density changes than for normal terrestrial basalt compositions (Green and Ringwood 1967, 1972; Ito and Kennedy 1971). In particular, increase of olivine + pyroxene relative to plagioclase content would have the effect of decreasing the relative importance of the simple anorthite breakdown reaction, and sufficiently high (olivine + pyroxene):anorthite contents would eliminate this reaction altogether.

**FIG. 3.**—Al-Ca-(Mg + Fe) (Atomic proportions) diagram showing compositional changes in garnet and pyroxene at 1,100°C (left diagram) and 1,300-1,400°C (right diagram). Note the extremely Al-rich pyroxene at 20 Kb, 1,400°C and the sub-calcic nature of the 10 Kb/1,300°C pyroxene, co-existing with spinel + anorthite.

**TABLE 3**

MINERAL COMPOSITIONS, SUBSOLIDUS, 1,300°C

<table>
<thead>
<tr>
<th></th>
<th>Cpx (10 kb)</th>
<th>Sp (10 kb)</th>
<th>Ga (12 kb)</th>
<th>Cpx (12 kb)</th>
<th>Ga (21 kb)</th>
<th>Ga (23 kb)</th>
<th>Cpx (23 kb)</th>
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<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Σ       | 100.2       | 100.0      | 100.2      | 99.9        | 99.8       | 99.6       | 99.2        |

Density (g/cm³) | — | — | — | — | — | 3.73 | 3.35 |
<table>
<thead>
<tr>
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<th>Before Breakdown of Olivine</th>
<th>After Breakdown of Olivine</th>
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<tr>
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<td>8 kb (1,100°)</td>
<td>9 kb (1,100°)</td>
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<tr>
<td>Ilm</td>
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</tr>
<tr>
<td>Ab</td>
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<td>1.6</td>
</tr>
<tr>
<td>An</td>
<td>69.9</td>
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</tr>
<tr>
<td>Di</td>
<td>2.9</td>
<td>13.0</td>
</tr>
<tr>
<td>Hy</td>
<td>17.0</td>
<td>21.5</td>
</tr>
<tr>
<td>Of</td>
<td>7.7</td>
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<td>Density (g/cm³)</td>
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<td>Conditions for above density corrections</td>
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</table>
3.4 - 3.2 - 3.1 - 3.0 - 2 9

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3.5 -

10 15 20 2

193 194

PRESSURE Kb

4.—Variation of density (calculated for standard conditions \(T = 20^\circ{}C, P = 1\) Atmos.) vs. Pressure for Highland Basalt, illustrating effects of mineralogical changes.

Higher normative diopside contents would increase the density of the low pressure assemblage and have a “smoothing” effect on all density steps. Normative albite contents which are typically basaltic would similarly smooth the low-pressure density steps, and, particularly if coupled with basaltic diopside contents, would smooth or eliminate the plagioclase-breakdown step. The mineralogical details of the gabbro to eclogite transformation obtained in the present study accentuate the importance of chemical composition in determining the high pressure assemblages and reactions (Green and Ringwood 1972). A similarly detailed experimental study of the mineralogical changes in typical terrestrial basalts has not as yet been carried out but the present study illustrates that the mineralogical details of the complex coupled reactions can be monitored in an experimental study.

The gradient \(dP/dT\) for the boundary between plagioclase-bearing and plagioclase-free assemblages is approximately 20 bars/°C using starting mix C (Ga + Px + Ky + Qz) and 10 bars/°C using starting mix B (90% (Glass + plagioclase microlites) + 10% seed crystals (Ga + Px + Ky + Qz)]. At 1,300°C the disappearance of plagioclase lies between 21 and 22 kb for both starting mixes i.e. the plagioclase-out boundary has been reversed within 1 kb. At 1,100°C and 1,000°C, the reversal brackets are \(\sim 3\) kb and \(\sim 4\) kb respectively (fig. 1). The tendency for glass starting material to nucleate plagioclase outside its stability field (Ostwald’s Step Rule) has previously been noted (Green and Ringwood 1967) and our preferred interpretation of the data is that the plagioclase-out boundary is at or very close to the 20 bars/°C slope shown in figure 1. The composition of the garnet at 18 kb 1,100°C (starting mix B) is considered to be metastable (fig. 2) due to metastable persistence of plagioclase. The stable garnet composition should be close to that for 20 kb. Confirmation of equilibrium in the 20–30 kb runs at 1,100°C, and 23 kb run at 1,300°C in the eclogite field is provided by the observation that Ga–Px tie lines in the Ca–Mg–Fe plot (fig. 2) pass through the bulk composition point. At lower pressures the bulk composition point lies in the three-phase Ga + Px + Plag or Sp + Px + Plag fields (fig. 2).

APPLICATION OF SUB-SOLIDUS EXPERIMENTAL DATA TO LUNAR MODELS

Suggested model compositions for the lunar interior must satisfy a number of geophysical constraints, among them the mean lunar density \((\rho \approx 3.36; \text{Kaula 1970})\) and coefficient of moment of inertia. Several recent papers have suggested that the Highland Basalt composition (or composition very close to it) may be representative of the interior lunar composition (Mason 1972) or representative of the outer 250–270 km (Anderson 1973). It is possible
to evaluate these models using the $P-T$ stability fields of various mineral assemblages determined in the present work. We require for this purpose knowledge of the lunar thermal gradient. Recent data on the electrical conductivity of olivine and pyroxene under redox conditions matching those appropriate to returned lunar samples, have led to revision of early estimates of a "cold" moon and have yielded models in which the present lunar temperature is near the basalt solidus at depths of 600–900 km (Duba and Ringwood 1973). Anderson and Hanks (1972) have also argued for high, near-solidus temperatures for the lunar interior. In figure 5 we have used the high temperature gradient of Anderson and Hanks (1972) and the low temperature limit of Ringwood and Essene (1970) as limiting cases of possible lunar temperature distributions.

The mean lunar density and coefficient of moment of inertia have been calculated for three different lunar models:

(a) Moon composed of material of composition of the Highland Basalt (Mason 1972).

(b) Anderson’s (1973) model I: Highland Basalt in the outer 250 km and the inner moon of refractory Ca–Al-rich residue (as given in Anderson 1973, table 5, col. 7). This model postulates an overall com-
position of the moon matching that of the Ca-Al-rich inclusions in the Allende meteorite, with the moon then partially melting to yield a low melting fraction, postulated to be of Highland Basalt (gabbroic anorthosite) composition, which forms the outer 250–270 km.

(c) Anderson (1973) model II: as for model I, but the inner moon of composition given in Anderson (1973, table 7, col. 5).

The calculated modal mineralogy (from known bulk composition and mineral composition) and calculated densities (at NTP) for assemblages stable at various $P, T$ conditions are shown in tables 4 and 5. Corrections for compressibility and thermal expansion effects along the model lunar thermal gradients are approximate due to the limited mineral data (Clark 1966) but show clearly that thermal expansion effects dominate over the effects of compressibility. As a result, the mean lunar densities discussed below and calculated using the NTP data for densities of various mineral assemblages (table 4 and 5) should be lowered by about 3% if thermal expansion and compressibility effects were incorporated. The mean density (NTP) for a moon of Highland Basalt composition (assumption (a)) throughout is 3.21 g/cc for mineral assemblages intersected along the highest temperature thermal gradient of figure 5 and 3.35 g/cc along the lowest temperature gradient of figure 5. D. L. Anderson's (1973) models (designated I and II herein) give mean densities 3.22 g/cc (I), 3.20 g/cc (II) along the high temperature thermal gradient and 3.23 g/cc (I) 3.20 g/cc (II) along the low geothermal gradients respectively.

When compared with the observed lunar density of 3.36 g/cc (Kaula 1970) the above densities, particularly when corrected for thermal expansion and compressibility, are low and particularly low for the "hot moon" temperature distribution.

Coefficients of moment of inertia for the various models and temperature distributions are as follows:

(a) Highland Basalt

<table>
<thead>
<tr>
<th>High thermal gradient</th>
<th>Low thermal gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I = 0.388$</td>
<td>$I = 0.390$</td>
</tr>
</tbody>
</table>

(b, c) Anderson’s Ca–Al-rich moon

<table>
<thead>
<tr>
<th>High thermal gradient</th>
<th>Low thermal gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I = 0.393$</td>
<td>$I = 0.393$</td>
</tr>
</tbody>
</table>

An earlier estimate of the coefficient of moment of inertia as $0.402 \pm 0.002$ (Kaula 1970) has since been revised to $0.395 + 0.006(−0.010)$ (Bender et al. 1973) and the above coefficients are within the revised observational uncertainty.

The mean lunar density calculated from Anderson's lunar models are too low to match the real moon but it is clear that these simple models could be modified by addition of more FeO to the chosen compositions, presence of an iron core, greater role of mare basalt or presence of a mare basalt source layer, etc., and that such modifications, although destroying the simplistic
charm of the matching of the model lunar composition with that of the Ca, Al rich inclusions in the Allende meteorite, would satisfy the density constraint and yet retain a lunar composition that is dominated by Ca, Al, Si, O, Mg as the major elements.

We confirm (c.f., Mason 1972; Anderson 1973) that the high pressure experimental studies of postulated lunar interior compositions do not allow the lunar density or coefficient of moment of inertia constraints to be used to eliminate slightly modified versions of models A, B, or C or the lunar pyroxenite model (Ringwood and Essene 1970). However, the experimental studies do conclusively eliminate the hypothesis (Anderson and Kovach 1972) that the possible increase of seismic velocity at depths of ~ 70 km to values of 9 km/sec could be caused by appearance of major grossular-rich garnet in the Highland Basalt composition. At its first appearance with increasing pressure, the garnet is of pyrope-almandine composition and is a minor phase which would not dominate the seismic velocity in the manner postulated.

EXPERIMENTAL DATA ON MELTING RELATIONSHIPS

The positions of the solidus and liquidus for the Highland Basalt composition were determined by optical and microprobe examination of the quenched charges (fig. 1, table 6). Spinel is the liquidus phase from 5 kb to > 20 kb but is accompanied by anorthite at 5 kb and by corundum and clinopyroxene at 20 kb. Garnet may join clinopyroxene and corundum on the liquidus at 5 to 25 kb. Garnet may join clinopyroxene and corundum on the liquidus at ≥ 25 kb. In three runs above the solidus (15 kb, 1,360°C; 18 kb, 1,420°C and 20 kb, 1,440°C) and one subsolidus run (12 kb, 1,300°C) the experimental mounts were zoned with garnet + clinopyroxene ± plagioclase or corundum or liquid present in the outer part of the sample adjacent to the Fe-capsule wall, and spinel + clinopyroxene ± plagioclase or corundum or liquid, present in the core of the sample. The mineralogical inhomogeneity may be a response to small temperature or compositional (Fe addition from the capsule wall?) gradients across the sample but these runs clearly lie on or very near to the equilibrium boundary making the first appearance of garnet for this composition.

APPLICATION OF EXPERIMENTAL STUDY OF MELTING RELATIONSHIPS

Highland Basalt as source rock for mare basalts.—The hypothesis that mare basalts could be derived by partial melting of source rocks of Highland Basalt composition in the lunar interior requires that the minerals occurring on the liquidus of mare basalts at high pressures should match those on or above the solidus of the Highland Basalt composition at similar P, T conditions. The absence of plagioclase and/or corundum from the liquidus of mare basalts at either low or high pressure and the presence of one or both of these phases throughout the melting interval of the Highland Basalt is inconsistent with the above hypothesis. Similarly the role of highly aluminous and magnesian spinel, the dominance of high-Ca clinopyroxenes at P > 10 kb and the extremely high Al2O3 contents of the pyroxenes in the melting interval of the Highland Basalt are all sharply contrasted with the liquidus phases of mare basalts at similar P, T conditions.

At 10 kb, 1,300°C the pyroxene at the solidus of the Highland Basalt is sub-calcic (table 3, figs. 2 and 3) and has 100 Mg/(Mg + Fe2+) = 76. In these respects it is very close to compositions of sub-calcic pyroxenes on the liquidus of mare basalt compositions in the pressure range 7-15 kb (Ringwood and Essene 1970; Green, Ware, Hibberson and Major 1971; Green, Ringwood, Ware, Hibberson, Major and Kiss 1971). However the mare basalt pyroxenes contain 2-4% Al2O3 in contrast to 10.3% Al2O3 in the solidus pyroxene of the Highland Basalt. Mare basalts from Apollo 11, 12, 15, 17 collections can be related one to another on the basis of
TABLE 6
EXPERIMENTAL RUNS UNDER PARTIAL MELTING CONDITIONS (WITH COMPOSITIONS OF PHASES)

<table>
<thead>
<tr>
<th>Pressure (Kb)</th>
<th>Temperature (°C)</th>
<th>Time (mins)</th>
<th>Phases Crystallized* (With Glass Unless Stated Otherwise)</th>
<th>100 Mg Al₂O₃</th>
<th>100 Mg Mg + Fe³⁺</th>
<th>Garnet Composition (Ca : Mg : Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1,400</td>
<td>10</td>
<td>Pi (An₉₂Pb₃Or₇) + Sp (Al₂₉Mg₈₃)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>1,420</td>
<td>10</td>
<td>Sp (Al₂₉Mg₈₃)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>1,400</td>
<td>30</td>
<td>Pi + Sp</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>1,380</td>
<td>30</td>
<td>Pi + Sp (Al₂₉Mg₈₃)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>1,360</td>
<td>30</td>
<td>Pi + Sp</td>
<td>82</td>
<td>29 : 59 : 12</td>
<td>11.6</td>
</tr>
<tr>
<td>10</td>
<td>1,340</td>
<td>180</td>
<td>Pi + Px + Sp (Al₂₉Mg₈₃)</td>
<td>76</td>
<td>8 : 70 : 22</td>
<td>10.3</td>
</tr>
<tr>
<td>10</td>
<td>1,330</td>
<td>180</td>
<td>Pi + Px + Sp (Al₂₉Mg₈₃)</td>
<td>82</td>
<td>45 : 47 : 8</td>
<td>13.3</td>
</tr>
<tr>
<td>10</td>
<td>1,300</td>
<td>180</td>
<td>Pi + Px + Sp (Al₂₉Mg₈₃)</td>
<td>82</td>
<td>46 : 44 : 10</td>
<td>16.0</td>
</tr>
<tr>
<td>15</td>
<td>1,440</td>
<td>10</td>
<td>Sp (Al₂₉Mg₈₃)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>1,420</td>
<td>30</td>
<td>Sp</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>1,400</td>
<td>30</td>
<td>Pi + Sp (Al₂₉Mg₈₃)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>1,380</td>
<td>30</td>
<td>Pi + Px + Sp (Al₂₉Mg₈₃)</td>
<td>86</td>
<td>45 : 47 : 8</td>
<td>13.3</td>
</tr>
<tr>
<td>15</td>
<td>1,360</td>
<td>30</td>
<td>Pi + Px + Sp (Al₂₉Mg₈₃)</td>
<td>82</td>
<td>46 : 44 : 10</td>
<td>16.0</td>
</tr>
<tr>
<td>15</td>
<td>1,340</td>
<td>25</td>
<td>Px + Sp (Subsolidus)</td>
<td>78</td>
<td>50 : 59 : 11</td>
<td>21.2</td>
</tr>
<tr>
<td>18</td>
<td>1,440</td>
<td>25</td>
<td>Px + Sp (Subsolidus)</td>
<td>73</td>
<td>26 : 53 : 20</td>
<td>—</td>
</tr>
<tr>
<td>18</td>
<td>1,420</td>
<td>25</td>
<td>Px + Sp (Subsolidus)</td>
<td>73</td>
<td>26 : 53 : 20</td>
<td>—</td>
</tr>
<tr>
<td>20</td>
<td>1,460</td>
<td>15</td>
<td>Px + Ga + Cor</td>
<td>87</td>
<td>53 : 41 : 6</td>
<td>20.9</td>
</tr>
<tr>
<td>20</td>
<td>1,440</td>
<td>15</td>
<td>Px + Ga + Cor</td>
<td>86</td>
<td>57 : 37 : 6</td>
<td>22.3</td>
</tr>
<tr>
<td>20</td>
<td>1,420</td>
<td>30</td>
<td>Px + Ga + Cor</td>
<td>84</td>
<td>54 : 39 : 7</td>
<td>21.4</td>
</tr>
<tr>
<td>22</td>
<td>1,400</td>
<td>120</td>
<td>Px + Ga + Cor</td>
<td>77</td>
<td>52 : 37 : 11</td>
<td>21.4</td>
</tr>
</tbody>
</table>

* Abbreviations used: Pi = plagioclase; Sp = spinel; Px = Pyroxene; Ga = garnet; Cor = Corundum; Ab = albite; An = anorthite; Or = orthoclase; Al₂₉ = (100 Al)/(Al + Cr) = 99 (atomic proportions); and Mg₈₃ = (100 Mg)/(Mg + Fe²⁺) = 85 (atomic proportions).
major and trace element abundances (Chappell and Green 1973; Green and Ringwood 1973). Those basalts which, on the basis of their low content of incompatible elements (REE, Na, Ti), require the highest degrees of melting of the source rock, have low-Al orthopyroxene + olivine as liquidus phases but with falling temperature sub-calcic pyroxene joins or replaces orthopyroxene. In contrast with these relationships among mare basalts, melting of the Highland Basalt at 10 kb produces liquids which, as temperature is increased, are in equilibrium with pyroxenes with increasing CaO and Al₂O₃ contents, and with coexisting plagioclase and spinel. The data show that there are no conditions at which the solidus or above-solidus phases of the Highland Basalt composition resemble the liquidus or near-liquidus phases of mare basalts and furthermore, that variation of partial melting of Highland Basalt, with consequent variation of residual phases and of liquid composition, bears no relation to deduced and experimentally tested petrogenetic relationships among mare basalts. The experimental data at high pressure on mare basalt and Highland Basalt compositions demonstrate, when considered together, that there are no P, T conditions at which mare basalt magmas could be derived by partial melting of Highland Basalt source rock.

**Highland Basalt as a partial melt of the lunar interior.**—The hypothesis that the Highland Basalt composition is that of a partial melt from the lunar interior requires that the source composition within the lunar interior can be calculated as a combination of the Highland Basalt composition and the composition(s) of liquidus phase(s) at the conditions of melting, these phases being combined in chosen proportions. Since spinel is the liquidus phase from 10-20 kb, the potential source rock assuming ≥ 35% melting would be dominated by spinel (ρ = 3.7) and a moon dominantly of this mineralogy would not satisfy the lunar density constraint. At 20 kb, spinel, corundum and a pyroxene rich in Ca-Tschermak’s silicate (CaAl₂SiO₆) occur on the liquidus of the Highland Basalt and some combination of these four phases is a potential lunar interior composition. If clinopyroxene is the dominant residual phase then the deduced interior composition will be very rich in Ca and Al. The data obtained in this study may be used to evaluate Anderson’s (1973) model of a Ca, Al-rich moon with gabbroic anorthosite (Highland Basalt) outer layer and refractory Ca, Al-rich interior.

Anderson suggests that the bulk composition of the moon was that of early, high temperature condensates from the solar nebula and rich in Ca, Al, and Ti compounds (gehlenite, spinel, perovskite, Ca-Al rich pyroxenes and anorthite). Accepting the suggestions that the Ca-Al rich inclusions in the Allende meteorite are examples of high temperature condensates from the solar nebula (Larimer and Anders 1970 and Marvin et al. 1970), Anderson suggested that their composition is similar to the bulk composition of the lunar interior. The model has been further developed to postulate melting of the lunar interior to yield a high-alumina gabbroic anorthosite (0.22 basalt + 0.78 anorthosite or 0.14 basalt + 0.86 anorthosite) melt fraction (34.6%) segregating to form the outer 270 km of the moon, leaving a residual interior of melilite or merwinite, diopside and spinel. The postulated melt is very close to the Highland Basalt composition (table 1) and the experimental data on the latter may be used to test Anderson’s model. Firstly, neither melilite nor merwinite occur on or near the liquidus of the Highland Basalt to 20 kb, and at sufficiently high pressure above 20 kb the probable liquidus phases will be garnet, Ca-Al rich pyroxene and either spinel or corundum. Attempts to match the postulated parental Allende composition by 35% melting to yield Highland Basalt + 65% of the observed liquidus phases (and thus potential residual phases) result
TABLE 7

EVALUATION OF ALLENDE Ca, Al-RICH INCLUSIONS AS SOURCE COMPOSITIONS FOR HIGHLAND BASALT PARTIAL MELT AND RESIDUE MADE UP OF LIQUIDUS PHASES OF HIGHLAND BASALT AT HIGH PRESSURE

<table>
<thead>
<tr>
<th>Allende*</th>
<th>Liquidus Phases of Highland Basalt (20 kb; 400 km lunar depth)</th>
<th>Possible Lunar Interior Compositions, Based on 35% Highland Basalt and the Liquidus Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cpx</td>
<td>Sp</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>----</td>
</tr>
<tr>
<td>SiO₂</td>
<td>34.1</td>
<td>43.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.0</td>
<td>20.9</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>FeO</td>
<td>2.3</td>
<td>3.1</td>
</tr>
<tr>
<td>MgO</td>
<td>13.3</td>
<td>11.4</td>
</tr>
<tr>
<td>CaO</td>
<td>21.9</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Highland Basalt</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Cpx</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Sp</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cor</td>
<td>1</td>
</tr>
</tbody>
</table>

* Allende Single aggregate; Clarke et al. 1970.

in compositions unlike the Allende inclusion compositions (table 7). Use of garnet, pyroxene and corundum (as at 20 kb 1,440°C) as the residual phases also does not give a reasonable match with the Allende inclusions composition. Potential source compositions capable of yielding a partial melt fraction (35% melting) of Highland Basalt composition are richer in FeO, SiO₂ or Al₂O₃ and lower in CaO, MgO and TiO₂ than the Allende Ca-Al rich inclusion. Anderson's model for the lunar interior could of course be modified by postulating some other Ca-Al rich composition (different from that of the Allende inclusion and similar to table 7, columns 5-7) as the composition of the lunar interior prior to partial melting to yield a "gabbroic anorthosite" zone in the outer ~ 270 km. Modification of the model along these lines appears arbitrary, abandons the Allende "touchstone" and would require some justification for the new composition in terms of a condensation model. In addition, modification of Anderson’s models by addition of FeO to fit the constraints of mean density or mare-basalt genesis, contravenes the basic conclusions of Grossman (1972) inferring the absence of oxidized iron in early high temperature condensates from a solar nebula. Complete absence of FeO in the early condensates, and thus by Anderson’s model, in the lunar interior would yield even lower densities than predicted herein and such material could not possibly act as source for either mare basalt or "highland basalt" rock types.

CONCLUSIONS

Experimental study of the Lunar Highland Basalt (gabbroic anorthosite) composition at high pressures at both subsolidus and partial melting conditions yields mineralogical data of petrogenetic significance in its own right. In particular, the detailed mineralogical changes in pyroxene and garnet composition through the gabbro to eclogite transformation further demonstrate the control of chemical composition, as well as P and T, on the nature of mineral assemblages. Within the eclogite field at high temperature the garnet + pyroxene + kyanite + quartz
assemblage increases in both garnet and kyanite content with increasing pressure as the garnet becomes more grossular-rich and the pyroxene decreases in Ca-Tschermak’s molecule and approaches diopside composition.

Using the high pressure experimental data and the constraints of lunar mean density and coefficient of moment of inertia, it has been shown that simple models of a moon of Highland Basalt composition throughout (Mason 1972) or Highland Basalt (250-270 km overlying refractory Ca-Al rich residue (Anderson 1973) give mean lunar densities that are too low but coefficient of moment of inertia within the range of uncertainty. It might be possible to modify the Ca-Al rich moon models to fit these constraints and the high pressure subsolidus experimental data cannot eliminate lunar models invoking a Ca-Al rich mean lunar composition. However the experimental studies firmly refute suggestions that the appearance of Ca-rich garnet as a major phase in rocks of Highland Basalt composition at 60-100 kms is responsible for seismic P-velocities of > 9 km/sec (Anderson and Kovach 1972).

Experimental studies of melting relations of Highland Basalt effectively show that:

1. Partial melting of Highland Basalt as source rocks cannot yield liquids of the compositions of mare basalts under any lunar P, T conditions.

2. Hypotheses suggesting that Highland Basalt or similar gabbroic anorthosite compositions are partial melts from the deep lunar interior leaving residual mineralogy of spinel + merwinite + diopside (Anderson 1973) are not in accord with the liquidus relationships of the Highland Basalt at high pressures.

3. A model lunar composition matching the composition of the Ca, Al rich inclusions of the Allende meteorite is not satisfactory as a source composition for either mare basalt or “Highland Basalt” partial melts. Experimental studies of observed lunar compositions demonstrate internal inconsistencies in the hypothesis of origin and composition of the moon based on the Allende Ca, Al rich inclusions (Anderson 1973) and provide arguments against that model.

ACKNOWLEDGMENTS.—We would like to thank Prof. A. E. Ringwood, Dr. F. E. M. Lilley and Dr. R. C. Liebermann for helpful discussion during the project.

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Experimental petrology of Apollo 17 mare basalts

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Abstract—Equilibrium crystallization experiments on 70215, 74275, and 74220 orange glass demonstrate the existence at the lunar surface of titanium-rich (>13% TiO$_2$) and olivine-rich liquids at temperatures $\geq$1250°C. Limited near-surface crystal fractionation, of olivine, armalcolite, and ilmenite principally, yields derivative liquids approaching plagioclase saturation (75035, 75055). High-pressure experimental studies show that parental titanium-rich magmas are not saturated in an Fe-Ti oxide phase at any pressure and are not partial melts of a source region in which ilmenite was a residual phase. The most primitive liquids among the Apollo 17 samples are 74275 (74245) and 74220 Orange Glass. Magma of 74275 composition is multiply saturated (olivine + low-Ca clinopyroxene + high-Ca clinopyroxene) at 12–13 kbar, 1320 ± 10°C. Magma of 74220 Orange Glass composition is multiply saturated at $\sim$20–25 kbar, 1470–1500°C (olivine + orthopyroxene) and at 30 kbar, 1520°C (orthopyroxene and low-Ca clinopyroxene). Mare basalts of both low-Ti and high-Ti character have compositions consistent with partial melting of an olivine pyroxenite source (100 Mg/Mg + Fe$^{2+}$ = 80 ± 1) at temperatures and pressures close to the three pyroxene (orthopyroxene + low-Ca clinopyroxene + high-Ca clinopyroxene) field. However, although experimental studies indicate the same mineralogy and Mg value for the source regions (olivine + low-Ca clinopyroxene + high-Ca clinopyroxene) for low-Ti and high-Ti mare basalts, it is not possible to derive the observed TiO$_2$, CaO, and Al$_2$O$_3$ variations among the mare basalts by different degrees of melting of the same olivine pyroxenite source at 200–400-km depth. Analogous relationships exist between Apollo 15 Green Glass and Apollo 17 Orange Glass; both are consistent with derivation by partial melting from olivine + orthopyroxene (Mg$_{95\text{max}}$) residue at $\geq$400 km but require the TiO$_2$ contents of the source regions to be different prior to partial melting. The lunar mantle is inhomogeneous in TiO$_2$ (and other minor and trace elements) over the depth range at least from 200 to 400 km yet essentially constant in Mg value (81 ± 2, possibly varying from 79 to 83 with depth) and of olivine + calcium-poor pyroxene mineralogy. Processes which may have determined this character for the lunar mantle are briefly discussed.

INTRODUCTION

The aims of our investigation of Apollo 17 mare basalts include the following:

1. The characterization of the mineralogy of the Apollo 17 mare basalts with particular attention to analyses of the highest temperature, early formed phases.

2. The identification of those rock compositions which existed as liquids at the lunar surface and those, if any, which may represent liquid + accumulate crystals.

3. The determination of liquidus temperatures and oxidation states of mare basalt liquids prior to and during crystallization.

4. The identification of possible genetic relationships amongst mare basalts and of parental or primitive basalts.

5. The experimental study of melting relationships of "parental" basaltic compositions at high pressure to establish the nature of their liquidus phases and,
thus, to place constraints on the mineralogy and $P$–$T$ conditions of the source regions for mare basalts.

Our selection and allocation of samples (apart from the initial sample 70035) was based on thin section examination and choice of those basalts classifiable as vitrophyres or with textures indicating very rapid quenching. Such basalts should preserve in their mineralogy the compositional characteristics of near-liquidus phases. In contrast, as will be seen later, in more slowly cooled basalts such as 70035, the minerals present have equilibrated at temperatures below the liquidus for that bulk composition and such rocks may have attained their observed bulk compositions by crystal accumulation.

**MINERALOGY OF APOLLO 17 BASALTS**

We have obtained electron microprobe analyses of major phases in eight rapidly quenched Apollo 17 basalts. All have olivine phenocrysts with skeletal pyroxene and ilmenite and are within the Type IA classification of Brown et al. (1975). In all samples the ferromagnesian silicates and titanium-rich phases are strongly chemically zoned from magnesian cores to iron-rich margins. For our purposes, the most significant information is given by the most magnesian [i.e. highest Mg value = $100\frac{Mg}{(Mg+Fe^{2+})}$] analyses of each mineral since the crystallization path for liquid and all coexisting phases is from magnesian to iron-rich composition with decreasing temperature. This basic principle could only be invalidated if Fe$^{2+}$ was removed from the system by either oxidation (not observed) or reduction to Fe metal (not observed in other than trace amounts, insufficient to affect Mg values).

The mineralogical data are summarized in Table 3 together with modal olivine abundances (from Brown et al., 1975) and total rock Mg value where rock analyses are available. The latter data pose some problems as variations in whole-rock compositions reported by various groups are quite large (Table 3; Fig. 2) and probably include real inhomogeneity in sample splitting as well as analytical differences.

Sample 72135 is a monomict basaltic breccia in which individual fragments range from fine-grained, quenched basalt (mineralogical data in Table 3) to spheres and irregular shards of orange glass. Analyses of 18 such glass fragments give a tightly clustered composition (Table 1) differing from Apollo 17 Orange Glass [74220] in composition. Small euhedral olivine and armalcolite in one such glass fragment match closely in composition with the most magnesian phases of the crystallized basalt fragment. Although we do not have whole-rock analyses of the breccia or of the crystallized basalt fragments, the uniformity of the mineral compositions is significant. We infer that 72135 is a volcanic breccia or welded tuff due to lava fountaining of a liquid of composition of the glass fragments (Table 1).
EXPERIMENTAL STUDIES AT 0 kbar

For these studies we have used standard vertical quenching furnaces, Pt–Pt 13% Rh thermocouples calibrated against the melting point of gold and samples enclosed in iron minicapsules (20-mg capacity) with close-fitting lids, within evacuated silica tubes. The choice of sample capsule is of importance as the capsule equilibrates or approaches equilibrium with the charge during the experiment and may cause compositional changes in the charge. In earlier studies of Apollo 12 basalts (Green et al., 1971a; Green et al., 1971b) we had used both “Spec-Pure” iron (Johnson-Matthey Grade 1) and various mild steels leading in some cases to satisfactory results and in other cases to either iron loss (metallic iron precipitation) or iron addition, manganese addition or chromium addition (all minor and monitored by microprobe analyses). In the study of Apollo 17 basalts we found that use of “high-purity nonmagnetic iron” [as used in the telecommunications industry] while free of metallic impurities (but not of carbon) resulted (in long runs) in reduction of the charge and precipitation of metallic iron globules. Use of “Spec-Pure” iron gave satisfactory results in most short runs (≤ 1 hr) but in longer runs resulted in addition of iron as FeO to the charge. One batch of mild steel capsules gave superior data to runs using “Spec-Pure” iron for basalt 70215. This is apparent when both sets of runs are tested by mass-balance calculations (see below). In short, we have found no perfect sample container and have found that use of Spec-Pure iron capsules (cf. Longhi et al., 1974; Kesson, 1975) may yield erroneous results. We have found it necessary to confirm that iron (FeO) has neither increased, decreased nor oxidized (Fe' to Fe'') in a given experiment by electron microprobe analyses of all phases and use of mass-balance calculations to check bulk composition and mineral analyses to confirm $f_{O_2}$-sensitive parameters such as Cr' in olivine, Cr'/Cr' in spinel or Ti'/Ti'' in armalcolite. The quality and internal consistency of our data can be judged from Table 2.

The samples used for experiments were glasses prepared from Analar-grade reagents and checked for iron content and oxidation state [<0.5% Fe$_2$O$_3$] by spectrophotometric methods (E. Kiss, analyst).

Table 1. Composition of glass in 72135 breccia and electron microprobe analyses of glasses prepared for experimental runs.

<table>
<thead>
<tr>
<th></th>
<th>Mean (18 analyses)</th>
<th>Standard deviation</th>
<th>70215</th>
<th>74275</th>
<th>Orange glass from 74220</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>38.90 ± 0.29</td>
<td>37.7</td>
<td>37.9</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>12.29 ± 0.26</td>
<td>13.4</td>
<td>12.6</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.12 ± 0.09</td>
<td>8.8</td>
<td>8.3</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.37 ± 0.05</td>
<td>0.45</td>
<td>0.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>20.10 ± 0.11</td>
<td>19.3</td>
<td>19.1</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.24 ± 0.04</td>
<td>0.3</td>
<td>0.2</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>7.51 ± 0.17</td>
<td>8.7</td>
<td>10.4</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>11.09 ± 0.11</td>
<td>10.5</td>
<td>10.2</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.30 ± 0.08</td>
<td>0.4</td>
<td>0.4</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.08 ± 0.02</td>
<td>—</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>100 Mg + Fe'</td>
<td>40.0 ± 0.55</td>
<td>44.5</td>
<td>49.3</td>
<td>54.5</td>
<td></td>
</tr>
</tbody>
</table>

(a) Composition modeled from Rhodes (1973).
(b) Composition based on glass bead (30 mg) fusion of 74275 sample and electron probe analysis of bead. Compare also with analyses by Compston et al. (unpublished data) and Duncan et al. (1974).
(c) Composition modeled from Reid et al. (1973).
Glasses were prepared to match compositions reported for the whole-rock sample and are given in Table 1. We have avoided use of natural rock starting materials because of possible errors due to composition change or oxidation by fine crushing or to sample inhomogeneity due to small sample size if samples are not finely crushed. We also wished to avoid the possibility that coarse mineral grains present in the natural rock may persist above their equilibrium solution temperature because of compositional gradients around such crystals and very sluggish intracrystalline diffusion rates. Use of coarser-grained natural materials also requires long run times and this increases the iron-exchange problems noted above. To eliminate the possibility of sluggish nucleation of pyroxene and plagioclase in the lower temperature runs we have initially sintered 100-mg batches at 1080-1100°C, confirmed the presence of pyroxene and plagioclase (at 1-3-μm grain size) by X-ray diffraction and used this material in higher temperature runs seeking the disappearance or persistence of these phases. Phases were analyzed using the TPD electron microprobe with energy dispersive analytical system (Reed and Ware, 1973).

**EXPERIMENTAL RESULTS**

Experimental data are presented in Fig. 1 showing the temperature and sequence of appearance of all crystalline phases together with the Mg value of ferromagnesian phases and the An content of plagioclase. In Fig. 2, the compositional variation of the liquids with increasing degree of crystallization is illustrated for all three compositions in a simple MgO versus TiO\(_2\) plot. In this diagram, as in more complex projections, changes in trend of the liquid fractionation path denote appearance and disappearance of phases. Olivine crystallization alone, at and immediately below the liquidus (74275 and 74220 glass), gives rapidly decreasing MgO and increasing TiO\(_2\). The appearance of spinel has little effect because of its minor abundance but it does prevent Cr\(_2\)O\(_3\) contents from rising above ~0.45%; marked depletion in Cr\(_2\)O\(_3\) does not occur until ilmenite (0.4-0.5% Al\(_2\)O\(_3\), 2.5-1.9% Cr\(_2\)O\(_3\)) becomes a major phase. Clinopyroxene (16-18% CaO, 2.5-5% TiO\(_2\), 2-6% Al\(_2\)O\(_3\), 0.6-1.0% Cr\(_2\)O\(_3\)) also results in Cr\(_2\)O\(_3\) depletion. The appearance of armalcolite (2-2.2% Al\(_2\)O\(_3\), 2.0% Cr\(_2\)O\(_3\)), joining olivine and spinel; prevents TiO\(_2\) enrichment above 13.5% TiO\(_2\) (approx.) at 0 kbar in these liquids, but marked depletion in TiO\(_2\) does not occur until the appearance of ilmenite. Armalcolite becomes more Fe-rich and reacts with ilmenite and liquid with decreasing temperature and the trend of rapid TiO\(_2\) depletion is slowed below 1140°C by the disappearance of armalcolite and particularly by the appearance of first clinopyroxene and then plagioclase (An\(_{86}\)) at 1140°C and 1130°C respectively in 70215 and 74275. Clinopyroxene and plagioclase have not been identified and analyzed in 74220 at 1130°C and 1120°C and the glass compositions do not show a deflection of the liquid trend (Fig. 2).

Table 2 lists the liquid compositions from 1180°C to 1120°C for 70215 compositions and the calculated modal phase assemblage and corresponding bulk composition. The latter calculation serves as a check on any effects of iron exchange with the sample container. The use of "Spec-Pure" iron capsules in the 1120°C and 1135°C runs listed has resulted in addition of iron to the sample, decreasing the degree of crystallization, suppressing clinopyroxene crystallization at 1135°C and possibly increasing the amount of olivine present at 1120°C. The data of Table 2 establish a closed system crystallization path from liquidus to
Experimental petrology of Apollo 17 mare basalts

Fig. 1. Experimental data showing mineral assemblage and composition of phases [100 Mg/(Mg + Fe²⁺) for ferromagnesian minerals, 100 An/(Ab + An) for plagioclase] at 0 kbar. For 70215, the experimental data for the Harvard group (Longhi et al., 1974) are in the left columns (headed H) and are compared with our own data (headed A). See text for further discussion. (Abbreviations: * indicates absence of a phase; + indicates phase present but not analyzable; ol—olivine; arm—armalcolite; cpx—clinopyroxene; sp—spinel; ilm—ilmenite; plag—plagioclase.)

1130°C (and with lesser accuracy to 1120°C) for the bulk composition (particularly FeO content) actually observed in 70215 rock. As a further check that the experimental conditions have reproduced the same or closely similar redox conditions as experienced by lunar sample 70215 during its crystallization we can examine redox-sensitive parameters such as the oxidation state of Cr (Cr²⁺ and
Fig. 2. Oxide variation diagram illustrating equilibrium liquid compositions along the fractionation path for crystallization of 70215, 74275, and 74220 Orange Glass at 0 kbar. For 70215, the glass compositions listed in Table 2 which have not exchanged appreciable iron with the capsule (i.e. in mild steel capsules) are shown as + connected by a heavier line. The glass compositions from runs in “Spec-Pure” capsules (iron added) are shown by + connected by a lighter line. The glass compositions in 70215 from the Harvard group (Longhi et al., 1974) are shown by x. The bulk rock compositions for various Apollo 17 basalts are plotted as larger symbols (legend on figures). Sources of data are noted by number: (1) Compston (unpublished data), (2) Rose et al. (1975), (3) Rhodes (1973), (4) Duncan et al. (1974), (5) Table 1 (this paper), and (6) Nava (1974). Arrows against some experimental glasses at high temperatures indicate some Fe loss or gain from the sample due to reaction with the capsule. (Abbreviations as in Fig. 1.)

Cr$^{3+}$) in spinel and olivine and of Ti (Ti$^{3+}$ and Ti$^{4+}$) in armalcolite (cf. Kesson and Lindsley, 1975). The olivines of the experimental runs contain Cr(0.2–0.4% Cr$_2$O$_3$) such that (Cr)olivine/(Cr)liquid = 0.5 ± .1 (for olivine ≦ Mg$_{65}$) to (Cr)olivine/(Cr)liquid = 0.9 ± .1 (for olivine ≦ Mg$_{85}$) and the natural olivines of 70215 contain 0.3% Cr$_2$O$_3$ (Mg$_{74}$) to 0.2% (Mg$_{65}$). In both the natural rock and the experiments neither spinel nor armalcolite have stoichiometric compositions if it is assumed that Cr and Ti are present only as Cr$^{3+}$ and Ti$^{4+}$, respectively.

The calculation of structural formulae of spinel choosing all Ti as Ti$^{4+}$ but allocating Cr to Cr$^{2+}$Cr$_2$$^{3+}$O$_4$, and of armalcolite by choosing all Cr as Cr$^{3+}$ but allocating Ti to Ti$_2$$^{3+}$Ti$^{4+}$O$_4$, allows calculation of Cr$^{2+}$/(Total Cr) and Ti$^{3+}$/(Total Ti) for spinel and armalcolite in natural and experimental assemblages. For 70215 and 74275 spinels, Cr$^{2+}$/(Total Cr) = 0.27 (in mild steel) and 0.21 (in “Spec-Pure” iron), respectively at 1170°C and 1180°C. The natural, most magnesian, spinels in these rocks have higher total Cr contents and lower TiO$_2$ contents with
Table 2. Liquid fractionation path for equilibrium crystallization of 70215 and evaluation of degree of crystallization and mass balance (i.e. constant bulk composition) of charges. Capsule materials were mild steel (A) or "Spec-Pure" iron (B). Columns headed L are analyses of glass; those headed CB are calculated bulk compositions from calculated mode and the phase analyses.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Capsule</th>
<th>L</th>
<th>L</th>
<th>CB</th>
<th>L</th>
<th>L</th>
<th>CB</th>
<th>L</th>
<th>L</th>
<th>CB</th>
<th>L</th>
<th>L</th>
<th>CB</th>
<th>L</th>
<th>L</th>
<th>CB</th>
</tr>
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<tbody>
<tr>
<td>1180</td>
<td>0.25</td>
<td>A</td>
<td>38.0</td>
<td>38.3</td>
<td>37.6</td>
<td>39.0</td>
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<td>37.9</td>
<td>42.6</td>
<td>38.0</td>
<td>41.4</td>
<td>37.0</td>
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<td>13.0</td>
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<td>12.3</td>
<td>13.4</td>
<td>9.7</td>
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<td>9.4</td>
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<tr>
<td>1160</td>
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<td>9.0</td>
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<td>9.6</td>
<td>8.65</td>
<td>9.5</td>
<td>8.2</td>
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<tr>
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<td>A</td>
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<td>0.45</td>
<td>0.55</td>
<td>0.35</td>
<td>0.4</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td></td>
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</tr>
<tr>
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<td>A</td>
<td>19.2</td>
<td>18.9</td>
<td>19.1</td>
<td>18.9</td>
<td>19.2</td>
<td>17.2</td>
<td>18.8</td>
<td>17.6</td>
<td>19.3</td>
<td>20.5</td>
<td>20.6</td>
<td>20.2</td>
<td>21.6</td>
<td></td>
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<tr>
<td>1120</td>
<td>4</td>
<td>B</td>
<td>3.3</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
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</tr>
<tr>
<td>1135</td>
<td>4</td>
<td>B</td>
<td>8.1</td>
<td>8.0</td>
<td>8.6</td>
<td>7.5</td>
<td>8.7</td>
<td>6.7</td>
<td>8.9</td>
<td>6.4</td>
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<td>5.85</td>
<td>8.5</td>
<td>6.7</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| S<sub>2</sub>O<sub>2</sub> | 38.0 | 38.3 | 37.6 | 39.0 | 37.7 | 42.0 | 37.9 | 42.6 | 38.0 | 41.4 | 37.0 | 39.5 | 36.5 |    |
| TiO<sub>2</sub> | 13.3 | 13.0 | 13.4 | 12.3 | 13.4 | 9.7 | 13.5 | 9.4 | 13.5 | 9.2 | 13.1 | 11.0 | 13.4 |    |
| Al<sub>2</sub>O<sub>3</sub> | 9.0 | 9.1 | 8.8 | 9.5 | 8.8 | 11.0 | 9.0 | 10.7 | 8.9 | 9.6 | 8.65| 9.5 | 8.2 |    |
| Cr<sub>2</sub>O<sub>3</sub> | 0.45| 0.45| 0.55| 0.35| 0.4 | 0.3 | 0.5 | 0.2 | 0.4 | 0.3 | 0.5 | 0.3 | 0.4 |    |
| FeO | 19.2 | 18.9 | 19.1 | 18.9 | 19.2 | 17.2 | 18.8 | 17.6 | 19.3 | 20.5 | 20.6 | 20.2 | 21.6 |    |
| MnO | 0.3 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |    |
| MgO | 8.1 | 8.0 | 8.6 | 7.5 | 8.7 | 6.7 | 8.9 | 6.4 | 8.7 | 5.85| 8.5 | 6.7 | 8.5 |    |
| CaO | 10.9 | 11.1 | 10.7 | 11.5 | 10.6 | 12.1 | 10.5 | 12.0 | 10.4 | 12.2 | 10.8 | 11.8 | 10.3 |    |
| Na<sub>2</sub>O | 0.4 | (0.6) | (0.6) | 0.6 | 0.5 | 0.6 | 0.5 | 0.6 | 0.5 | 0.6 | 0.5 | 0.5 | 0.5 |    |
| K<sub>2</sub>O | 0.1 | 0.1 | 0.1 | — | — | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | <0.1 | 0.1 |    |

100 Mg Mg + Fe | 43.0 | 43.0 | 41.3 | 40.9 | 39.4 | 33.7 | 37.3 | 37.3 |    |

| Liq | 97–98 | 96.5 | 92.5 | 79.0 | 74.5 | 53 | 86.5 |    |
| Ol | ~2% | 2.0 | 4.5 | 6.0 | 6.5 | 8 | 6.5 |    |
| Sp | Trace | 0.5 | — | — | — | — | — |    |
| Arm | <1% | 1.0 | 2.0 | 0.5 | — | — | — |    |
| IIm | — | — | 1.0 | 9.5 | 11.0 | 13.5 | 7.0 |    |
| Px | — | — | — | 5.0 | 6.0 | 16.5 | — |    |
| P1 | — | — | — | 2.0 | 9.0 | — | — |    |

Notes: (a) Slight iron loss (2.5% of amount present).
(b) Addition of iron (1.6% FeO, i.e. 8% of amount originally present).
(c) Addition of iron (2.8% FeO, i.e. 14.5% of amount originally present).
Temperatures ±5°.
Cr\(^{2+}/(\text{Total Cr})\) = 0.02–0.21 (70215) and 0.05–0.21 (74275). Both natural and experimental armalcolites have Ti\(^{3+}/(\text{Total Ti})\) = 0.08 ± .01. The comparisons suggest that experiments in iron capsules have closely similar but slightly more reducing redox conditions than those which applied for the natural rocks.

The partitioning of iron and magnesium between olivine solid solution and liquid can be used to test for equilibrium between observed olivine crystals and potential parent bulk compositions (Roeder and Emslie, 1970). From our data we have measured \((\text{Fe}/\text{Mg})_{\text{ol}}/(\text{Fe}/\text{Mg})_{\text{liq}}\) for 28 olivine (Mg\(_{81–82}\)) and glass pairs over the temperature range 1320–1120°C and obtain \(K_{\text{D}^{\text{ol/liq}}} = (\text{Fe}/\text{Mg})_{\text{ol}}/(\text{Fe}/\text{Mg})_{\text{liq}} = 0.283 ± 0.013\) (mean and standard deviation). We observed evidence for a variation of \(K_{\text{D}^{\text{ol/liq}}}\) with temperature or composition (or both) in that the value increased from 0.26–0.27 for 74275 at 1200–1240°C to 0.29–0.30 at 1100–1140°C. This effect is not well displayed in the 74220 data (1320–1120°C, lower TiO\(_2\) liquids) and requires further study. For the purpose of discussion olivine/liquid relationships in the mare basalts, we use the mean value \(K_{\text{D}^{\text{ol/liq}}} = 0.28\) (\(T = 1100–1250°C\), high-Ti mare basalt bulk compositions).

APPLICATIONS OF 0 kbar EXPERIMENTAL DATA TO PETROGENESIS OF APOLLO 17 MARE BASALTS

We first address the proposition (O’Hara and Humphries, 1975) that Apollo 17 mare basalt “hand specimens were derived by crystal sinking and floating within a plagioclase saturated average magma composition” and examine the 70215 and 74275 data in this context. Our data show that a magma bulk composition 70215 in the correct redox conditions will have (between 1140°C and 1130°C) the character described by the proposition, i.e. it will consist of 74.5–79% liquid, 6–6.5% olivine, 0–0.5% armalcolite, 9.5–11% ilmenite, 5–6% calcic clinopyroxene, and 0–2% plagioclase. The liquid will have a composition near those shown in Table 2 and close to the compositions of 75035 and 75055 amongst the analyzed mare basalts. However, if this were, indeed, the origin of 70215, i.e. accumulate crystals in equilibrium with (and concentrated in) a plagioclase-saturated liquid, then the rock would not contain spinel and the most magnesian olivine and armalcolite would be Mg\(_{21.5}\) and Mg\(_{45.3}\), respectively (Fig. 1). Furthermore, the equilibrium ilmenite and clinopyroxene crystals should be Mg\(_{72–72.5}\) and Mg\(_{72–72.5}\), respectively. In fact, the basalt contains olivine as magnesian as Mg\(_{71.2}\) and Mg\(_{63.3}\), respectively (Fig. 1). Furthermore, the equilibrium ilmenite and clinopyroxene crystals should be Mg\(_{72–72.5}\) and Mg\(_{72–72.5}\), respectively. In fact, the basalt contains olivine as magnesian as Mg\(_{71.8}\), armalcolite to Mg\(_{67.6}\) and spinel (to Mg\(_{27.6}\)) providing clear evidence of a crystallization sequence from its liquidus at 1180 ± 5°C. The most magnesian ilmenite (Mg\(_{61,0}\)) and clinopyroxene (Mg\(_{66.7}\), 5.6% TiO\(_2\), 7.7% Al\(_2\)O\(_3\)) in the rock are not equilibrium compositions as predicted by the O’Hara and Humphries proposition, but are unequilibrated quench compositions precipitated as the magma cooled rapidly from its liquidus through the (armalcolite + liquid, → ilmenite + liquid) reaction, spinel reaction, and pyroxene and plagioclase crystallization fields.

Specimen 74275 is even more inconsistent with the proposition than 70215 and the experimental study confirms that this bulk composition also existed at the
lunar surface as an entirely liquid magma (at $T \geq 1250^\circ C$). The composition of the most magnesian olivine is $Mg_{79.5}$ which is identical to the liquidus olivine predicted for 74275 composition [using $K_\gamma^{ol/liq} = 0.26$ ($T = 1250^\circ C$)] and more magnesian than the olivine ($Mg_{77.6}$) analyzed at 1240$^\circ C$ in the 74275 experiments (slight Fe addition $\sim 0.5\%$ FeO, occurred in this run). The magma quenched from its liquidus temperature too rapidly to allow re-equilibration of olivine or for spinel, armalcolite, ilmenite, or pyroxene to crystallize at compositions appropriate to their equilibrium, most magnesian compositions—all phases in the natural rock other than rare olivine phenocrysts are quench phases. Sample 74275 is thus most significant among the high-Ti mare basalts in that it is the most magnesian and olivine-rich and highest temperature ($1250^\circ C$) magma yet identified (neglecting 74220 Orange Glass for the moment.)

Our data establish that 70215 and 74275 both represent liquids existing at the lunar surface and of the two, 74275 is the more “primitive” or parental. There are small compositional differences between the magmas which, accepting the accuracy of the analytical data, argue against derivation of 70215 from parental 74275. The compositions and mineralogical data (Table 3) on other high-Ti mare basalts allows us to comment on their significance in the light of the experimental studies.

Basalt 70017 has a bulk composition very similar to 74275 or 74275 less 1-2% olivine (Fig. 2 and references therein), but its mineralogy (Longhi et al., 1974) does not retain phases more magnesian than olivine of $Mg_{69}$, armalcolite of $Mg_{44}$, and clinopyroxene of $Mg_{73}$. This rock is consistent in major-element chemistry and mineralogy with slow-cooling and equilibration of 74275 magma to $1140-1150^\circ C$ and more rapid disequilibrium cooling below $1140^\circ C$. Basalts 79155 and 71055 (Fig. 2) are very high-Ti basalts, but we have no mineral data to assess whether these compositions were liquids. Basalt 70035 lies close to 74275 and 70215 in bulk composition, but is distinctly lower in CaO content. The most magnesian cores of all ferromagnesian phases and the plagioclase cores ($An_{89}$) are consistent with equilibration at $1140-1130^\circ C$ (i.e. on the plagioclase saturation surface) and the rock preserves no evidence (except possibly in the rare Cr--Ti spinel) of cooling from a higher temperature. The mineralogy and composition relationships for this rock are consistent with the O'Hara and Humphries (1975) proposition quoted previously, but are, of course, equally consistent with slow cooling, without crystal accumulation, of a liquid of its own bulk composition.

Basalts 71569 and 74235 have bulk compositions which are very similar and suggestive of an olivine fractionation control with either 74235 being the parent liquid or consisting of 71569 liquid with 2-4% accumulate olivine crystals. These compositions are such that they are not related by 0 kbar crystal fractionation to either the very high-TiO$_2$ liquids (70215) or to the lower TiO$_2$ (74220) Orange Glass trend (Fig. 2) but lie between these trends. The mineralogy of 71569 (Table 3) shows that this rock was entirely liquid with olivine ($Fo_{73}$) and without armalcolite (contrast 70215) on its liquidus at $T = 1170 \pm 10^\circ C$. Armalcolite, ilmenite, and pyroxenes have compositions appropriate to growth during quenching from $1170^\circ C$. Basalt 74235, although a more magnesian bulk composition, contains less
Table 3. Mineralogical data for Apollo 17 mare basalts and (in right-hand column) Mg values of whole rocks as analyzed (key 1, 2, 3, 4 refers to sources listed in Fig. 2) and predicted liquidus olivine for each bulk composition assuming that $K_D^{\text{oliv}} = 0.28$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Olivine</th>
<th>Spinel</th>
<th>Armalcolite</th>
<th>Ilmenite</th>
<th>Pigeonite</th>
<th>Augite</th>
<th>Maximum An content of plagioclase</th>
<th>Modal olivine (Brown et al., 1975)</th>
<th>Mg/Mg + Fe for total rock and equilibrium liquidus olivine ($K_n = 0.28$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70035,7</td>
<td>66.3</td>
<td>26.9</td>
<td>44.5</td>
<td>27.1</td>
<td>71.8</td>
<td>75.1</td>
<td>89.1</td>
<td>&lt;1.0</td>
<td>47.5 49.0 76.4 77.4</td>
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<td>70215,144</td>
<td>73.8</td>
<td>21.8</td>
<td>47.6</td>
<td>18.1</td>
<td>n.f.</td>
<td>66.7</td>
<td>n.a.*</td>
<td>10.1</td>
<td>43.6 41.7 46.5 44.5</td>
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<tr>
<td>70275,38</td>
<td>72.2</td>
<td>n.f.†</td>
<td>25.2</td>
<td>n.f.</td>
<td>70.0</td>
<td></td>
<td></td>
<td>88.0</td>
<td>73.2 71.9 75.6 74.0</td>
</tr>
<tr>
<td>71135,31</td>
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<td>n.f.</td>
<td>11.5</td>
<td>62.3</td>
<td>68.0</td>
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<td></td>
<td>88.5</td>
<td>trace</td>
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<tr>
<td>71569,57</td>
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<td>42.6</td>
<td>11.8</td>
<td>64.7</td>
<td></td>
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<td>85.1</td>
<td>7.8 43.2 73.0</td>
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<tr>
<td>72135,45</td>
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<td>25.8</td>
<td>46.7</td>
<td>12.5</td>
<td>n.f.</td>
<td>n.a.</td>
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<td>n.a.</td>
<td>trace</td>
</tr>
<tr>
<td>72135</td>
<td>71.8</td>
<td>n.f.</td>
<td>47.0</td>
<td>n.f.</td>
<td>n.f.</td>
<td>n.f.</td>
<td></td>
<td>n.f.</td>
<td>trace or none 40.0 70.5</td>
</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>72155</td>
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<td>n.f.</td>
<td>10.2</td>
<td>60.9</td>
<td>72.6</td>
<td></td>
<td></td>
<td>85.2</td>
<td>3.5 45.6 75.0</td>
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<tr>
<td>74235</td>
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<td>n.a.</td>
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<td>n.a.</td>
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<td>n.a.</td>
<td>10.1 45.6</td>
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<tr>
<td>74275</td>
<td>79.5</td>
<td>28.5</td>
<td>45.1</td>
<td>19.5</td>
<td>n.f.</td>
<td>68.3</td>
<td></td>
<td>n.a.</td>
<td>13.8 50.5 50.6 50.8 49.3</td>
</tr>
<tr>
<td>17 Orange</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>78.4 (79.5)* 78.5 (79.6) (79.9) (79.0) 77.6</td>
</tr>
<tr>
<td>Glass</td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*n.a. = not analyzed. †n.f. = not found. ‡Olivine composition for $K_D = 0.26$. 

$K_D^{\text{oliv}} = 0.28$. 

$K_n = 0.28$. 

$K_D^{\text{oliv}} = 0.28$.
magnesian olivine, armalcolite in equilibrium with olivine \((T = 1150-60^\circ C)\) and quench clinopyroxene. The absence of olivine compositions up to \(\text{Mg}_{75}\) means that some of the olivine may be accumulative.

The monomict breccia (72135) has been discussed previously—its composition, petrography, and mineralogy demonstrate the existence of magma (and lava fountain?), possibly derived from 70215 or 74275 by olivine and armalcolite separation, at \(T = 1160^\circ C\). We do not have whole-rock chemical compositions of 70275, 71135, or 72155, so cannot interpret the mineralogical data in relation to the bulk rock composition. Basalt 70275 contains olivine which is too magnesian to be in equilibrium with the most magnesian ilmenite and pyroxene observed so that this rock is probably also a quenched liquid (from \(T = 1170 \pm 10^\circ C\)). A similar conclusion applies to 72155, but in this rock the presence of very magnesian clinopyroxene (\(\text{Mg}_{72.6}\) \% \(\text{TiO}_2\), \(5.5\% \text{Al}_2\text{O}_3\) cores and apparent absence of armalcolite or magnesian ilmenite warrants further study. Basalt 71135 contains rare relatively iron-rich olivine (\(\text{Mg}_{80}\)) and may be a liquid close to plagioclase and pyroxene saturation. The absence of armalcolite and magnesian ilmenite are again curious but without the bulk rock composition further speculation is not justified.

Two other basalts, 75035 and 75055, plotted on Fig. 2 are classed by Brown et al. (1975) as Type II Apollo 17 basalts. Their compositions are appropriate to the liquid fraction of 70215 magma at \(T = 1145-1150^\circ C\) (Table 2), i.e. immediately prior to crystallization of pyroxene. Thus, although these are compositionally distinct rocks from the high-Ti, olivine-normative basalts, they are most probably genetically related by near-surface crystal fractionation. Liquids of 75035 and 75055 composition should crystallize olivine (\(\text{Mg}_{71}\)), ilmenite (\(\text{Mg}_{27}\)), possibly armalcolite (minor) as liquidus phases followed closely by crystallization of pyroxene (\(\text{Mg}_{72-3}\)). The natural basalts do not preserve near-liquidus mineralogy (Brown et al., 1975); and have evidently cooled slowly, possibly in the interior of thick lava flows or lava lakes of 74275 or 70215 magma compositions.

When re-examined in the light of the Apollo 17 data, Apollo 11 lavas show a sequence of compositions including more primitive olivine-bearing magmas such as 10045 (olivine to \(\text{Mg}_{25}\)) (Compston et al., 1970; Agrell et al., 1970). These magmas were of composition and extrusion temperature such that they were not saturated in plagioclase. Other more evolved liquids such as 10047 have bulk compositions either at or very close to plagioclase saturation at liquidus temperature. It is to be noted, however, that such plagioclase-saturated liquids are most reasonably interpreted as fractionates of more primitive, parental olivine-rich high-Ti basalts such as 10045 for Apollo 11 or more generally to 74275 and 70215, etc.

The parental magmas for both Apollo 11 (low-K) and Apollo 17 high-Ti basalts were olivine-rich, relatively magnesian (\(\text{Mg}_{49-50}\)) with \(\text{TiO}_2 \approx 12.5\%\) and their distinctive chemical characteristics (including the europium anomaly) were present prior to the limited and variable near-surface crystal fractionation which has modified some liquids. In seeking constraints on the genesis of these basalts in the lunar interior we attach most significance to basalt 74275 and the more magnesian 74220 Orange Glass.
Experimental Studies at High Pressures

In our experimental studies at high pressure we have used the standard 1-in. piston-cylinder apparatus and samples contained in iron capsules. The experiments on 74275 composition were carried out in "Spec-Pure" iron capsules. Those for 70215 and 74220 composition were carried out in mild steel capsules. Since we are principally concerned with liquidus or near-liquidus phases at high pressure and nucleation and growth of crystals are very rapid in these compositions, length of runs has varied from 5 min (≥1400°C) to 1 hr (≤1150°C for mild steel capsules but ≤1300°C for "Spec-Pure" iron capsules). In some very high temperature runs in 74220 glass, chromium has migrated from the mild steel capsule into marginal areas of the melt. Pyroxenes crystallizing from the melt in these regions show higher and variable Cr2O3 contents (1–2%) than those from the centers of the samples (~0.7% Cr2O3). We have used only mineral analyses from these central, uncontaminated parts of the samples. In general, runs quenched at pressures ≥15 kbar show extensive crystallization of quench clinopyroxene and it has not been possible to analyze derivative liquids at these pressures.

70215

Our experimental data for 70215, 74275, and 74220 are summarized in Figs. 3–5. For 70215 our data appear to be in good agreement with those of Kesson.
Experimental petrology of Apollo 17 mare basalts

At 10 kbar, a run at 1300°C is above the liquidus whereas that at 1280°C is below the liquidus with olivine (Mg75) and clinopyroxene (Mg76, 1.8% TiO₂, 2.3% Al₂O₃, 5.8% CaO) in equilibrium with liquid (Mg₄₄) which resembles 70215 in having higher TiO₂ (13.3%) and lower SiO₂ (37.2%) than 74275. This fractionation trend of increasing TiO₂ and decreasing SiO₂ continues to 1260°C where ilmenite

(1975) except that we do not observe ilmenite actually on the liquidus at 8 or 10 kbar. We obtained a run at 8 kbar, 1250°C in which olivine, ilmenite, and clinopyroxene were in equilibrium with liquid but at 8 kbar, 1260°C ilmenite was no longer present. The clinopyroxene contained lower TiO₂, Al₂O₃, and CaO content and had higher Mg value (Table 4). Similarly at 10 kbar, 1275°C we obtained clinopyroxene + liquid without ilmenite. Our data show that 70215 liquid does not have a TiO₂-rich phase on its liquidus at high pressure and is only doubly saturated (with olivine and low-calcium pyroxene) at 8 kbar, 1260°C. There is no condition at which 70215 liquid could have been derived as a partial melt of an ilmenite-bearing source rock, leaving ilmenite as a residual phase. However, 70215 is less significant for this type of analyses than the more magnesian and olivine-rich basalt 74275.

74275

At 10 kbar, a run at 1300°C is above the liquidus whereas that at 1280°C is below the liquidus with olivine (Mg₇₅) and clinopyroxene (Mg₇₆, 1.8% TiO₂, 2.3% Al₂O₃, 5.8% CaO) in equilibrium with liquid (Mg₄₄) which resembles 70215 in having higher TiO₂ (13.3%) and lower SiO₂ (37.2%) than 74275. This fractionation trend of increasing TiO₂ and decreasing SiO₂ continues to 1260°C where ilmenite

Fig. 4. Experimental crystallization of 74275 at high pressure. See Fig. 3 for key to symbols. (Abbreviations as in Fig. 1.)
Table 4. Selected pyroxene analyses illustrating low-Ca and high-Ca compositions and compositions of orthopyroxene. Also glass of derivative liquid at 10 kbar, 1260°C and 1320°C after pyroxene separation from 74275.

<table>
<thead>
<tr>
<th>Sample</th>
<th>70215</th>
<th>70215</th>
<th>70215</th>
<th>74275</th>
<th>74275</th>
<th>74220</th>
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<tbody>
<tr>
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<td>cpx</td>
<td>cpx</td>
<td>cpx</td>
<td>cpx</td>
<td>cpx</td>
<td>low-Ca cpx</td>
<td>high-Ca cpx</td>
<td>opx</td>
<td>opx</td>
<td>low-Ca cpx</td>
</tr>
<tr>
<td>Pressure (kbar)</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>10</td>
<td>12</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1260</td>
<td>1250</td>
<td>1275</td>
<td>1280</td>
<td>1310</td>
<td>1470</td>
<td>1430</td>
<td>1520</td>
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<table>
<thead>
<tr>
<th>Component</th>
<th>70215</th>
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<th>70215</th>
<th>74275</th>
<th>74275</th>
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<td>53.8</td>
<td>52.6</td>
<td>54.5</td>
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<td>TiO₂</td>
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<td>2.2</td>
<td>1.8</td>
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<td>2.4</td>
<td>1.1</td>
<td>1.1</td>
<td>1.5</td>
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<tr>
<td>Al₂O₃</td>
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<td>3.4</td>
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<td>4.0</td>
<td>1.8</td>
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<td>1.8</td>
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<td>Cr₂O₃</td>
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<tr>
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<td>11.5</td>
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<td>0.3</td>
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<td>MgO</td>
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<tr>
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</tr>
<tr>
<td>Na₂O</td>
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<td>—</td>
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</tr>
<tr>
<td>K₂O</td>
<td>—</td>
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<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
</tbody>
</table>

| Mg        | Mg₀⁺ | Mg₇⁷⁺ | Mg₇₂⁺ | Mg₇₆⁺ | Mg₇₉⁺ | Mg₇₂⁺ | Mg₆₁⁺ | Mg₆₀⁺₂⁺ | Mg₆₄⁺₆⁺ | Mg₆₈⁺ | Mg₇₄⁺₅⁺ | 39.7  | 39.5  |
| Coexisting* |      |       |       |       |       |       |       |       |       |       |       |       |
| olivine   | +     | Mg₉₀⁺₃⁺ | —     | Mg₇₃⁺ | Mg₅₃⁺ | Mg₇₉⁺ | Mg₇₇₅⁺ | —     | —     | —     | Mg₉₀⁺ | —     |
| ilmenite* | —     | Mg₇₇⁺ | —     | —     | —     | —     | —     | —     | —     | —     | —     | Mg₇₉⁺ | —     |
| Glass*    | Mg₄₁⁺ | Mg₄₂⁺ | Mg₄₃⁺ | Mg₄₅⁺ | Mg₄₅⁺₅⁺ | ?     | ?     | ?     | —     | —     | —     | —     |

*(+*) denotes phase present but not analyzed, (—) denotes phase absent.
Experimental petrology of Apollo 17 mare basalts

Fig. 5. Experimental crystallization of 74220 Orange Glass at high pressure. See Fig. 3 for key to symbols other than those for garnet and orthopyroxene. (Abbreviations as in Fig. 1.)

(Mg_{22}) joins olivine (Mg_{70}) and clinopyroxene (Mg_{71.5}, 1.8% TiO_2, 2.2% Al_2O_3, 7.1% CaO). The liquid composition at 1260°C is given in Table 4. Olivine is absent at 1240°C and the ilmenite composition (Mg_{22}) at this temperature implies a high degree of crystallization of the bulk composition between 1260°C and 1240°C. At 12 kbar, 1310°C, 74275 is triply saturated with olivine (Mg_{73.4}) and two clinopyroxenes (Table 4) occurring in glass (Mg_{46}). Similarly at 12 kbar, 1300°C, olivine (Mg_{72.9}) and two clinopyroxenes (Table 4) are observed. At 13 kbar, 1330°C, the liquid (Mg_{46}) contains only one clinopyroxene, similar to the more calcic pyroxene present at 12 kbar, but at 1320°C and 1310°C both low-Ca and higher Ca clinopyroxenes are present, without olivine or ilmenite.

At 15 kbar, 1340°C, only clinopyroxene is present at the liquidus and becomes more calcic (8.3% CaO at 1340°C, 12.1% CaO at 1330°C) but then less calcic (9.7% CaO at 1320°C). The glass at 1320°C (Table 4) shows marked enrichment in TiO_2, depletion in SiO_2 and depletion in CaO demonstrating very clearly that at 10–15 kbar, liquids such as 74275 are not saturated with a TiO_2-rich phase and consistently give partition coefficients (TiO_2)liquid/(TiO_2)pyroxene = 5 ± 0.5 for clinopyroxenes with 8–12% CaO. Ilmenite (Mg_{44}) and clinopyroxene (Mg_{46}) are
present at 15 kbar, 1300°C and the clinopyroxene in equilibrium with ilmenite contains 4.0% TiO₂, 7.3% Al₂O₃, and 13.2% CaO.

In an attempt to establish whether 74275 was nearly saturated with orthopyroxene at 15 kbar, a mix of 98% 74275 glass + 2% enstatite (Mg₆₆) was run at 15 kbar, 1340°C. The charge consisted of glass (Mg₄₆) + two clinopyroxenes, of more magnesian compositions and with a wider composition gap than those present in 74275 composition at 1330°C.

At 17 kbar, 1350°C, the clinopyroxene coexisting with glass has Mg₇₁, 2.4% TiO₂, 3.6% Al₂O₃, and 11.5% CaO. Separation of the clinopyroxene leads to TiO₂ enrichment and SiO₂ and CaO depletion in the liquid as at 10–15 kbar.

**74220 Orange Glass**

For this composition olivine (Fo₇₉–₈₀) remains the liquidus phase up to 20 Kb, 1480°C and at this pressure orthopyroxene (Table 4) joins olivine at 1470°C. These two phases are joined by low-Ca clinopyroxene at 1430°C (Table 4) and by 1420°C orthopyroxene reacts out in favor of the olivine and low-Ca clinopyroxene assemblage. A similar relationship probably holds at 25 kbar and again at 30 kbar except that at this pressure, olivine is not a liquidus phase and orthopyroxene (Mg₆₀.₅) and low-Ca clinopyroxene (Mg₇₅.₃) occur together close to the liquidus (1520°C). At 1500°C, olivine (Mg₇₄) and more calcic clinopyroxene (Mg₇₂) occur and are joined by garnet at 1480°C.

The compositions of orthopyroxene and low-Ca clinopyroxene at 20–30 kbar are such that (TiO₂)liquid/(TiO₂)orthopyroxene ≈ 8 and (TiO₂)liquid/(TiO₂)low-Ca clinopyroxene ≈ 6.5–7. The Al₂O₃:CaO contents of both orthopyroxene and low-Ca clinopyroxene are approximately 1:1 in the 20–30-kbar pressure range (cf. Ringwood and Essene, 1970) but < 1:1 in the 10–15-kbar pressure range (Table 4).

**Conclusions from High-Pressure Studies**

The high-pressure experimental data on Apollo 17 basalts and 74220 Orange Glass, when combined with the evidence for actual liquid compositions at the lunar surface presented in the previous section, place constraints on genesis of these liquids by process of partial melting or crystal fractionation in the lunar interior. We have shown that liquids of the most primitive (parental) character amongst the Apollo 17 high-Ti basalts are not saturated with ilmenite or other Fe–Ti oxide at any pressure. This statement is marginally true of 70215, emphatic for 74275 (and by implication similar rocks such as 74245, 70017, 70035, and 75075 if these compositions also existed as liquids) and more emphatic for 74220 Orange Glass. There is no direct basis from experimental data to support the hypothesis that high-Ti mare basalts originate by partial melting of an olivine, pyroxene, Fe–Ti oxide source region at 100–150 km (Longhi et al., 1974) or an olivine, pyroxene, and ilmenite source region at ≥170 km (Kesson, 1975). These earlier conclusions are based primarily on 70215 but are particularly at variance with
Experimental petrology of Apollo 17 mare basalts

74275 (and similar compositions) and 74220 Orange Glass. It is still possible to adhere to this hypothesis provided it is accepted that the postulated source region has melted sufficiently to eliminate ilmenite leaving only olivine (Mg$_{75}$) and clinopyroxene in the residue for generation of 70215 magma. Furthermore, it must then be postulated that a higher degree of melting, leaving only residual olivine (Fo$_{89}$), yielded 74275 magma, and still further melting leaving olivine (Fo$_{62}$), yielded 74220 magma. This model, generally applied to the Apollo 17 olivine-rich basalts, would not explain the differences in REE contents and Eu anomaly amongst the basalts, the small variations in TiO$_2$ content and relatively large variations in Mg value (note that if the melt fraction is less than 30% and olivine is the only residual phase then it takes a large increment of melt to change the olivine composition from Mg$_{75}$ → Mg$_{79}$ → Mg$_{62}$).

We prefer to adhere to the model which locates the depth of origin of a particular liquid to the pressure and temperature where that liquid is in equilibrium with two or more crystalline phases, i.e. the liquid is a potential partial melt in cotectic relationship with a residual multiple phase assemblage. This is also the rationale which led to the previously discussed hypothesis and if adhered to in the light of the new data on 70215, 74275, and 74220 Orange Glass, requires that these liquids be generated at $\geq$170 km for 70215 (olivine + low-Ca clinopyroxene residue), at $\geq$230 km for 74275 (olivine + low-Ca clinopyroxene + high-Ca clinopyroxene residue) and at $\geq$400 km for 74220 Orange Glass (olivine + orthopyroxene ± low-Ca clinopyroxene residue). Since 70215 could result from olivine extraction from a more olivine-rich parental basalt such as 74275, 75075, 70017, and 74245 there is no convincing case for derivation of this basalt from depths as low as 170 km.

The experimental studies at 10–15 kbar on 74275 showed that a spectrum of basalts with increasing TiO$_2$, SiO$_2$ and only minor changes in CaO, Al$_2$O$_3$, etc. could be generated by addition and subtraction of crystals dominated by clinopyroxenes. We consider that small variations in the degree of partial melting in this depth interval could account for the variations in TiO$_2$ content among Apollo 17 basalts which in other respects are of similar primitive character (contrast 71569 and 74235 with 79155 or 71055; Table 1, Fig. 2). However, REE elements (Shih et al., 1975; Philpotts et al., 1974) vary in total abundance and magnitude of Eu anomaly in rocks whose bulk composition is Ti-rich and olivine-rich (i.e. like 70215–74275 and unlike 75035 and 75055) and thus this variation is unlikely to be due to crystal fractionation at low pressure [which could account for differences for 75035 and 75055 (cf. Shih et al. (1975)]. We thus have the same dilemma within “parental” or “primitive” Apollo 17 high-Ti mare basalts as has been emphasized in the Apollo 11, 12, and 15 basalts and Apollo 15 Green Glass studies; namely, that either the variations in REE abundances and magnitude of the Eu anomaly are generated in partial melting from a common source by processes not involving plagioclase or these variations are intrinsic to the source regions and developed in some earlier lunar chemical fractionation (cf. Green et al., 1971; p. 613).

This question is reviewed in the wider context in the next section in which we
seek to evaluate whether a common source or chemically and mineralogically different sources, are required to generate the major-element compositions of the whole spectrum of mare basalts.

**Mare Basalt Petrogenesis**

The Apollo 17 mare basalt data has provided evidence that the phase equilibria controlling the major-element chemistry of Ti-rich mare basalts include olivine and three pyroxenes—orthopyroxene, low-Ca clinopyroxene ("pigeonite" or high-pressure equivalent) and high-Ca clinopyroxene (subcalcic augite). Compositional relationships between these three pyroxenes and the $P-T$ dependence of compositions defining the pyroxene three phase field in the system CaO–MgO–FeO–SiO$_2$ have been studied at $T = 1000$–$1400^\circ$C, $P = 0$–$30$ kbar (Mori and Green, unpublished data). These studies confirm that the lunar mare basalts have liquidi appropriate to intersection of the pyroxene phase diagram at or very close to, the critical three phase assemblage. Discussions of equilibrium partition of trace elements depend on knowledge of partition coefficients at high pressure between liquid and these three pyroxenes and particularly between liquid and low-Ca clinopyroxene (3–5% CaO) + high-Ca clinopyroxene (9–10% CaO) for most mare basalts. Appropriate partition data do not exist but it nevertheless seems unlikely that equilibria involving pyroxenes of appropriate composition and at appropriate $P-T$ and redox conditions could account for the observed relative depletions and total abundances of REE (Shih et al., 1975; Philpotts et al., 1974). The Rb/Sr and U-Th-Pb systematics of mare basalts and the Sm/Nd systematics of at least one Apollo 17 basalt (Lugmair et al., 1975) argue that variations in Rb/Sr, U-Th-Pb, and Sm/Nd existed in the source regions for mare basalts prior to the magma extraction events at 3.8–3.2 b.y. (Compston et al., 1971; Tera and Wasserburg, 1974). In earlier studies of Apollo 11, 12, and 15 basalts we have been able to infer that for major-element composition (and thus mineralogy) of the deep lunar interior, there was no requirement from phase equilibria studies for major inhomogeneity in the source regions. In particular we have advocated an olivine pyroxenite source region (Mg$_{75-80}$) for mare basalts and accounted for differences in TiO$_2$ content, normative olivine, etc., amongst Apollo 11, 12, and 15 basalts (and Green Glass) by different degrees of melting and $P-T$ conditions of melting (Ringwood and Essene, 1970; Green et al., 1971; Green and Ringwood, 1973; Chappell and Green, 1973). This model has been in agreement with the simplest (i.e., homogeneous lunar mantle) model consistent with the phase equilibria and major-element data but has required additional modifications to account for REE data particularly (Ringwood, 1970, 1974, 1975).

The experimental data presented in this paper, apart from the isotopic and trace-element constraints noted above, convince us that major-element and mineralogical inhomogeneity is required in the source regions for mare basalts and our data place some constraints on the depths and nature of the mineralogical variations.
There are remarkable "coincidences" in the source region constraints set by the mare basalts. The new data on Apollo 17 mare basalts do not support a shallower depth of origin for these basalts than Apollo 12 or 15, but rather define a source region of the same mineralogy (olivine + calcium-poor pyroxenes), the same 100 Mg/Mg + Fe2+ (80 ± 1 in olivine), and the same depth range (>200 km) as those required by Apollo 12 and 15 basalts (Green et al., 1971; Grove et al., 1973; Green and Ringwood, 1973; Chappell and Green, 1973). Similarly the two distinctive and very different glasses, Apollo 15 Green Glass and Apollo 17 Orange Glass, each representing disaggregation and chilling of a larger body of liquid just saturated with olivine [Fo82 in Green Glass (Dymek et al., 1974), Fo84 in Orange Glass (Reid et al., 1974)] can be derived from an olivine pyroxenite source region at ~400 km leaving residual olivine (~Mg81-83) and orthopyroxene.

From the data in this and our previous papers on the compositions of pyroxenes and olivines in equilibrium with mare basalt liquids, we can define partition relationships for TiO2, CaO, Al2O3, etc., between residue and liquids to set up models for partial melting. If we use Apollo 17 Orange Glass and assume it to be 1% melt of an olivine pyroxenite (ol ≪ opx) source rock then that model source rock contains too much TiO2 to act as the source rock (even for complete melting) for Apollo 15 Green Glass using appropriate partition coefficients from the analyzed phases. TiO2 mass balance could be achieved by assuming ol ≫ opx in the Orange Glass source region (i.e. a harzburgite to dunite source region for 1% melting to yield Orange Glass) but then melting would not yield correct Al2O3 and CaO concentrations in Green Glass. Similar arguments applied to primitive mare basalts such as 12009 (2.9% TiO2), 12040 (2.4% TiO2), 12022 (4.6% TiO2), Apollo 15 olivine basalts (2.2% TiO2), postulated parents for Apollo 15 pyroxene–phyric basalts (~1.5% TiO2; Chappell and Green, 1973), and Apollo 17 olivine basalts (74275, 12–13.5% TiO2) also show that a single source composition cannot provide this variety of liquids using the partition relationships for TiO2, CaO, and Al2O3 defined by the experimental studies. Yet, most remarkably, all parental basalts are consistent with a source region of the same Mg/Mg + Fe and residual mineralogy of olivine + calcium-poor pyroxenes.

We conclude that the lunar mantle, acting as source for mare basalts at depths from ~200 km to ≥ 400 km, consists of olivine and calcium-poor pyroxenes (2 or 3 coexisting pyroxenes depending on P–T, composition) of constant Mg/Mg + Fe = 80 ± 1 but throughout this depth range is inhomogeneous in TiO2 content of pyroxene solid solutions and in REE relative abundances, Rb/Sr, etc. This inhomogeneity, the local enrichment in TiO2, development of large Eu anomaly, etc., is not restricted to shallow depths and, from the Sr and Nd isotopic studies, was relict from some earlier process of chemical fractionation occurring within the moon or in the material accreting to form the moon at T > 3.9 b.y. A model of relict accretion inhomogeneity (Ringwood, 1974, 1975) appears capable of explaining the mare basalt characteristics. We do not consider that the various differentiation models, as currently formulated (Taylor and Jakeš, 1974; Wood, 1975; Smith et al., 1970; Smith and Steele, 1975) are consistent with or capable of accounting for the mare basalt source region characteristics but accept the attractions and
plausibility of the models in relating the anorthite-rich crust and mare basalt source regions. A model requiring deep stirring (to \( \geq 400 \text{ km} \)) of the lunar mantle with flotation of a plagioclase-rich crust (Wood, 1975) may provide the foundations of a satisfactory model. However, if deep stirring is postulated in order to prevent iron enrichment, etc., in the Ti-rich residual liquids by re-equilibration and homogenization of ferromagnesian minerals, then it should also homogenize TiO\(_2\) partition since TiO\(_2\) does partition into pyroxenes at high pressures with a partition coefficient of 0.1–0.2 (px/liq). One process which might permit local enrichment in TiO\(_2\), etc. without Mg/Fe fractionation would be to postulate buffering of Fe activity in the melt by metallic iron either disseminated through or settling through the mantle from highly reducing conditions at the primitive lunar surface. We note our experimental studies in "nonmagnetic pure iron" where the high-C content of the iron caused reduction of charges in long runs, producing a reversed fractionation trend of SiO\(_2\), TiO\(_2\), etc. enrichment with increasing Mg value and increasing degree of crystallization. Disseminated metallic iron, if present in mare basalt source regions, would settle out during any later melting processes. Sensitive tests for this suggestion may be found in the f\(_{fo}\)-sensitive parameters such as Cr\(^{2+}/Cr^{3+}\), Ni/Ni\(^{2+}\), and Ti\(^{3+}/Ti^{4+}\). The petrogenesis of mare basalts appears to strongly constrain the composition and equilibrium mineralogy of the lunar mantle but cannot, as yet, be unequivocally fitted into a model for overall lunar composition and differentiation.

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**REFERENCES**


APPENDIX. DETAILS OF EXPERIMENTAL RUNS ON 70215 AND 74275 MARE BASALTS

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74275 + 2% Ens (Mgs)  
| 15             | 1340       | 1         | Fe      | g + Ens            | px + glass                |

Notes:  
1. Capsule of mild steel (S) or “Spec-Pure” iron (Fe); 2. Starting material of glass (g) or sintered, fine-grained pyroxene + plagioclase + ilmenite ± olivine (c) (sintered at 1050°C); 3. Abbreviations: ol—olivine; arm—armalcolite; sp—spinel; ilm—ilmenite; px—pyroxene; plag—plagioclase.
Mineral Assemblages in a Model Mantle Composition

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Department of Geophysics
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Abstract. The primary chemical composition of the undifferentiated upper mantle is believed to be equivalent to that of a mixture of three parts of dunite to one part of basalt. Rocks approaching this model composition are herein called 'pyrolites.' A study is made of the mineralogy and geological environment of naturally occurring pyrolites. Such rocks occur as xenoliths in kimberlites and basalts and also in some intrusive peridotites. They are observed to crystallize in one of four distinct mineral assemblages: (1) olivine + amphibole, (2) olivine + plagioclase + pyroxenes, (3) olivine + aluminous pyroxenes + spinel, or (4) olivine + pyrope garnet + pyroxenes. Evidence regarding the geological occurrence and experimental stability of these assemblages is reviewed, and the relative P-T stability fields of the different assemblages are inferred. The ability of the pyrolite model composition to crystallize in a number of very distinct mineral assemblages controlled by pressure and temperature would lead to large-scale mineralogical zoning in the upper mantle. Such zoning will have an important effect on many properties of this region, particularly including the seismic velocities.

1. Introduction. In a model for the upper mantle proposed by Ringwood [1962a, b], observed variations in seismic velocity were attributed to different mineral assemblages exhibited by a hypothetical primitive rock type which he named 'pyrolite.' It was suggested that pyrolite possessed the mean chemical composition of the upper mantle–crust system, being approximately equivalent to a mixture of four parts of dunite or peridotite to one part of basalt. Fractional melting of this parental material could therefore yield a basaltic magma, leaving residual dunite or peridotite.

The suggested 4:1 ratio was derived from a consideration of the chemical compositions of chondritic meteorites and their bearing on the chemical composition of the earth's mantle and core. This ratio is somewhat flexible, however, since it depends sensitively upon the amounts of Ca and Al which are assumed to remain in the residual dunite or peridotite after fractionation. If the residual ultramafic component should be of dunitic composition, and therefore very low in Ca and Al, then a 3:1 ratio would be more applicable. On the other hand, if the residual ultramafic component should be of peridotitic composition, somewhat higher in Ca, Al, and Si, than a ratio of 4:1 or 5:1 would be appropriate.

The suggested composition of pyrolite and its complementary components are set out in Table 1. We have chosen dunite, rather than peridotite, as the refractory ultramafic component. The basalt composition used is the mean composition between the averaged normal tholeiite (column 2a) and normal alkali basalt (column 2b) [Nockolds, 1954]. These compositions of dunite and basalt have been combined in a 4:1 and a 3:1 ratio (columns 3 and 4, Table 1). For comparison, a mantle composition derived from a consideration of chondritic meteorites [Ringwood, 1959] is also tabulated (column 5). It is seen that the 3:1 ratio gives a closer match to the chondritic composition.
TABLE 1. Derivation of the Hypothetical Mantle Composition

<table>
<thead>
<tr>
<th></th>
<th>Average Basalt</th>
<th>Pyrolite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2a)</td>
</tr>
<tr>
<td></td>
<td>Average Anhydrous Dunite*</td>
<td>Normal Tholeite [Nockolds, 1954]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>41.32</td>
<td>50.83</td>
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<tr>
<td>MgO</td>
<td>49.81</td>
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<tr>
<td>FeO</td>
<td>5.91</td>
<td>9.06</td>
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<tr>
<td>Fe₂O₃</td>
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<tr>
<td>Al₂O₃</td>
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<td>14.07</td>
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<td>CaO</td>
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<td>MnO</td>
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<tr>
<td>P₂O₅</td>
<td>Trace</td>
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</tr>
<tr>
<td>H₂O₆⁺</td>
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<td>0.91</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Trace</td>
<td>2.03</td>
</tr>
</tbody>
</table>

|                  | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

* Normative composition: 91.6% olivine; 5.3% enstatite; 3.1% spinel.

Discussion: We shall adopt the 3:1 mixture in column 4 as the composition of pyrolite.

In the model previously referred to, it was pointed out that material of pyrolite composition could occur in a number of distinct mineral assemblages under the P-T conditions existing in the upper mantle. The intersection of geotherms with the stability fields for these mineral assemblages would have an important effect upon the seismic velocity distributions and particularly upon the formation of a low-velocity zone.

In the previous paper the different mineral assemblages were inferred from rather limited experimental and petrographic data. In the present paper we draw attention to naturally occurring peridotitic rocks which possess chemical compositions very similar to the postulated pyrolite composition. These rocks exhibit several distinct mineral assemblages, despite their similarity in chemical composition, and these assemblages correspond closely to those suggested in the previous model. A consideration of the geologic occurrence of these assemblages, combined with experimental data, permits their relative stability to be established as a function of temperature and pressure, thereby leading toward a concept of mineral zoning in the upper mantle.

2. Natural mineral assemblages in rocks of pyrolitic composition. We have assembled Table 2 a series of analyses taken from the literature. These analyses are extremely similar one another and compare closely with the postulated pyrolite composition. Their main differences lie in having lower Na₂O, K₂O, and TiO₂ than the pyrolite. These analyses have been grouped according to the mineralogy displayed by the rock, available mineralogical information also being summarized in Table 2.

Table 2 demonstrates that from essentially the same bulk composition, four distinct mineral assemblages may form as follows:

1. Olivine + amphibole (edenite, pargasite) + accessory chromian spinel.
2. Olivine + plagioclase + enstatite + clinopyroxene + accessory chromite.
3. Olivine + aluminous enstatite + aluminous diopside + spinel.
4. Olivine + pyrope garnet + pyroxene(s).

These different assemblages, which give every indication of representing equilibrium, must
<table>
<thead>
<tr>
<th>'Pyroxite' Composition</th>
<th>Olivine + Amphibole</th>
<th>Olivine + Pyroxene + Plagioclase</th>
<th>Olivine + Aluminous Pyroxene ± Spinel</th>
<th>Olivine + Pyroxene + Garnet</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>California (Johann-</td>
<td>Cyprus In-</td>
<td>St. Paul's</td>
<td>Kimberite</td>
</tr>
<tr>
<td></td>
<td>sen)</td>
<td>trusive (</td>
<td>Nodule (</td>
<td>Nodule (</td>
</tr>
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<td></td>
<td></td>
<td>Gas)</td>
<td>Nodule (</td>
<td>Nodule (</td>
</tr>
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<td></td>
<td></td>
<td>(Brown)</td>
<td>He)</td>
<td>He)</td>
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<td>(Tilly)</td>
<td>(Stan-</td>
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<td></td>
<td></td>
<td>Nodul</td>
<td>ley)</td>
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<td>(He)</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
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<td>44.89</td>
<td>43.98</td>
<td>45.12</td>
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<tr>
<td>MgO</td>
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<tr>
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<td>(8.15)</td>
<td>(8.49)</td>
<td>(8.56)</td>
<td>(7.87)</td>
</tr>
<tr>
<td>FeO</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>Na₂O</td>
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<td>K₂O</td>
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<tr>
<td>Cr₂O₃</td>
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<td></td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
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</tr>
</tbody>
</table>

* All Fe calculated as FeO in the moderately serpentinized Lizard rocks.
† Average Ni and Co contents, determined spectrographically, of Lizard peridotites are 0.20 and 0.01%, respectively.
‡ Major constituent, >30%.
§ Minor constituent, >5%, <30%.
¶ Accessory constituent, <3%.

**Note:** Analyses have been calculated to 100% anhydrous, but no adjustment has been made to the Fe**2/Fe**3 ratio.
indicative of widely differing pressure and temperature conditions of crystallization. In the following sections, evidence relating to the relative P-T stability fields of these assemblages is discussed.

3. The assemblage olivine + amphibole + accessory chromian spinel. Descriptions of granulitic or gneissic terrains containing metamorphosed ultrabasic bodies [Howie, 1955; Davidson, 1943; Eskola, 1952; Carstens, 1920] refer to assemblages of olivine + amphibole ('hornblende,' 'edenite') with, in addition, possibly orthopyroxene, clinopyroxene, or spinel, depending upon specific rock composition. These rocks, where analyzed, are richer in CaO, SiO₂, and FeO than the chosen pyrolite composition. Nevertheless, they strongly suggest that in conditions equivalent to granulite and higher-grade amphibolite facies metamorphism in the crustal environment, ultramafic rocks of pyrolite composition may be characterized by the assemblage olivine + magnesian hornblende.

Two analyses of amphibole + olivine rocks possessing the pyrolite composition are recorded in Table 2. One is a partial analysis of an edenite olivinite from California [Johannsen, 1938, p. 411]. The other analysis quoted is from the Lizard (Cornwall) peridotite [Green, 1963]. This peridotite was emplaced as a high-temperature crystalline diapir during low-grade regional metamorphism. The assemblage olivine + amphibole characteristically occurs at contacts with hornblende granulite or brown hornblende amphibolite of the metamorphic aureole and in local retrogressive alteration of plagioclase-bearing peridotite (cf. next section).

Tilley [1947] describes peridotite mylonites from St. Paul's rocks (mid-Atlantic ridge) which contain olivine + green-brown amphibole. Older analyses (quoted by Tilley) of the assemblage olivine + amphibole show essentially the same rock composition as is given in Table 2, column 8. Tilley notes that relics of an unmylonitized intergrowth of olivine + amphibole occur locally within the mylonite. Thus, in the coarsely crystalline rocks from which the mylonites were derived, there appear to have been representatives of both the assemblage olivine + amphibole and the assemblage olivine + pyroxene + spinel (cf. section 5). Hess [1960b] has suggested that these mylonites from St. Paul's rocks may be tectonically exposed parts of the suboceanic mantle.

The examples quoted above show clearly that rocks of pyrolite composition may crystallize a stable assemblage consisting of olivine + amphibole. An upper limit to the thermal stability of this assemblage is imposed by the dehydration of the amphibole. Under conditions where \( P_{H₂O} = \) load pressure, this may be as high as 1000°C. Where the water-vapor pressure is much less than the load pressure, i.e. in a water-deficient environment, the stability field of the assemblage olivine + amphibole will be displaced to lower temperatures. Ringwood [1962b] has pointed out that these conditions may be realized in the uppermost suboceanic mantle.

If material of primitive pyrolite composition should exist below the oceanic Mohorovicic discontinuity, and, furthermore, if this region should be water deficient, containing between 0.5 and 0.7 per cent of water, then the assemblage olivine + amphibole would probably remain stable at levels of lower temperature (< 500°C).

4. The assemblage olivine + plagioclase enstatite + clinopyroxene + accessory chromian spinel. There are very few analyzed rocks of approximate pyrolite composition which display the mineral assemblage olivine + plagioclase + pyroxenes (hereinafter called 'plagioclase pyrolite'). Two such rocks are from the Lizard peridotite [Green, 1963] (Table 2, columns 4 and 5). This intrusive provides a particular instructive example of the relationships between plagioclase pyroline and pyroxene pyroline. The assemblage olivine + aluminous pyroxenes is previously been called 'transitional pyroline' [Ringwood, 1962a, 6], but the term 'pyroline' is preferred as more explicit.)

The Lizard peridotite consists of a coarse-grained, primary core, characterized by the assemblage olivine + aluminous enstatite (6.5 per cent Al₂O₃) + aluminous diopside (6.5 per cent Al₂O₃) + aluminous spinel. Detailed field and petrographic investigations [Green, 1963] lead to the conclusion that the body was derived from the mantel and that the coarse primary mineral assemblage mentioned above was formed in an initial, deep-seated crystallization of the body. The peridotite was subsequently intruded at a high temperature, perhaps between 800° and 1000°C, to a high
crustal level, resulting in the formation of a high-grade metamorphic aureole in the country rock. During this diapiric intrusion, a marginal sheath of the peridotite was mylonitized and recrystallized. The resultant mineral assemblage consists of olivine + enstatite (2 per cent Al₂O₃) + diopside (3 per cent Al₂O₃) + calcic plagioclase + chrome diopside. This assemblage, corresponding to the 'plagioclase pyrolite' of Ringwood's [1962a] model, has clearly crystallized as an equilibrium assemblage at moderate crustal depth and at a temperature probably in the range 700° to 1000°C. The plagioclase-bearing peridotite locally, under lower temperature and/or higher water pressure conditions, shows partial or complete retrogressive alteration to the assemblage olivine + amphibole.

The plagioclase has formed from lime, alumina, and soda, which were originally present in solid solution in the pyroxenes of the primary assemblage. The change in mineralogy has clearly been caused by recrystallization in the crust at a lower pressure than that under which the primary assemblage olivine + aluminous pyroxenes formed, probably in the mantle.

Brown's [1957] analysis of average peridotite accumulate in the Rhum complex comes close to the pyrolite composition but is distinctly higher in FeO, CaO, and Al₂O₃ contents. Mineralogically it differs from the Lizard assemblages in lacking enstatite. Although the minerals in the Rhum peridotite are accumulated from a basaltic magma, it is considered that their retention at a high temperature during the accumulation of the overlying peridotite and olivine would have caused reaction between the phases if the accumulated assemblage were not stable at a high temperature, at shallow or moderate crustal depths, and in an anhydrous low P₆H₅O environment.

The intrusive ultrabasic rock from Cyprus [Gus, 1958] consists of olivine phenocrysts set in plagioclase, diopside, and hypersthene (see Table 2, column 6). Again a sequence of crystallization is involved, and the composition of the magma during precipitation of each phase is not known. The rock as a whole is much higher in Al₂O₃ and lower in MgO than the other examples. The evidence from olivine gabbronorritolites, and norites, although departing considerably from the rock composition proposed for pyrolite, is that the assemblage magnesian olivine + plagioclase + orthopyroxene + clinopyroxene is a stable one at high temperatures at crustal levels, particularly in an anhydrous environment.

The occurrence of a plagioclase pyrolite assemblage in the mantle will be limited by the breakdown of plagioclase at higher pressures—as exemplified (in reverse) by the Lizard peridotite. Breakdown occurs in favor of jadeite and Tschermak's silicate, (CaMg)Al₂SiO₆, which go into solid solution in pyroxenes, forming highly aluminous varieties.

The experimental results of Robertson et al. [1957], Yoder and Chinner [1960, p. 80], Yoder and Tilley [1961], and Clark and de Neufville [1962] set an upper limit to the maximum pressure at which olivine + plagioclase + pyroxenes would be stable. It is improbable that this assemblage can exist above 20 kilobars, and the maximum pressure may be substantially less than this figure. Uncertainty arises because most experimental results deal only with the stability of end members of the plagioclase series. Anorthite and albite break down to different reaction products. Accordingly, intermediate plagioclase will be somewhat stabilized by the free energy mixing of the end members of the series.

On the balance of available evidence, it appears that plagioclase pyrolite may be stable at depths less than 50 km and temperatures in excess of 600° to 700°C in an environment of low water-vapor pressure. This assemblage may therefore occur in a rather small zone in the oceanic upper mantle as suggested by Ringwood [1962b]. The assemblage may be more important in regions of high heat flow, where the temperatures beneath the Mohorovicic discontinuity are higher than usual.

5. The assemblage olivine + aluminous enstatite + aluminous diopside ± spinel. The constant mineralogy of the peridotite nodules in basalt has drawn comment from a number of authors, notably Ross et al. [1954], Hess [1960a], Wilshire and Birns [1961], and these authors, among others, have argued for their derivation from the mantle. The nodules contain dominant olivine, less abundant enstatite and diopside, and accessory spinel. Analyses of these minerals [Ross et al., 1954] from the nodules demonstrate the characteristic high Al₂O₃ content of both ortho- and clinopyroxene and also the high MgAl₂O₄ content of the spinels.
The compositions of a typical nodule from California [Hess, 1960a], a nodule from olivine basalt at Mount Gambier, South Australia [Stanley, 1910], and of two averages of several nodules from each of two new South Wales localities [Wilshire and Binns, 1961] are given in Table 2. These analyses are strikingly similar in both major and minor constituents.

As discussed in the preceding section, the Lizard peridotite contains a primary core having a 'pyroxene pyrolite' assemblage (Table 2, column 9) and differs from the nodule compositions only in its higher AlO3 content. A detailed comparison [Green, 1963] of the compositions of the minerals of the Lizard peridotite with those of peridotite nodules argues convincingly for similar conditions of crystallization.

Except for its low K2O and Na2O contents the dunite mylonite from St. Paul’s rocks [Tilley, 1947] has nearly the same composition as the peridotite nodules and garnet peridotites. The analysis given in column 8, Table 2, is of a mylonite containing both enstatite and diopside augen in fine, recrystallized olivine and brown, translucent spinel. Data on the AlO3 contents of the large pyroxenes would be particularly welcome, but, bearing in mind the rock composition and mineralogy, we can compare the rock most closely with the 'pyroxene pyrolite' assemblage.

From the experimental and field evidence discussed in the preceding section, it is clear that the characteristic assemblage olivine + aluminous pyroxenes + aluminous spinel has crystallized under greater load pressure than the plagioclase pyrolite assemblage. As implied by Ringwood’s [1962b] model, this assemblage may well occupy an extensive region in the upper mantle. As would be expected, the calculated density of the pyroxene pyrolite assemblage (about 3.22 g/cm³) is significantly higher than that of the corresponding plagioclase pyrolite assemblage (3.24 g/cm³).*

6. The assemblage olivine +pyrope garnet + pyroxene(s). The three analyses of garnet peridotites given in Table 2 include two inclusions in African kimberlites [Dawson, 1962; Holmes, 1936] and one analysis from a garnet peridotite lens occurring in association with eclogite as lenses in gneiss in Switzerland [Johannsen, 1938, p. 422]. From their mineralogy, some of the garnet + diopside + enstatite peridotites within dunite in Amklovdalen, Nor [Eskola, 1921], may also approach this composition.

The Swiss garnet peridotite differs from other two analyses in having a higher CaO content, and it differs mineralogically in its enstatite. Nevertheless, the analyses are remarkably similar to the analyses of peridotite nodules in basalt and to the pyrolite model composition.

The contrast in mineralogy between aluminous pyroxene-bearing assemblage and garnet-bearing assemblage must be attributed to different P-T conditions of crystallization. The absence of the assemblage olivine + pyrope garnet + pyroxene(s) (garnet pyrolite) in the Lizard peridotite sequence, and as nodules in basaltic rocks, compared with its characteristic occurrence in the diamond-bearing peridotite lenses, suggests that garnet pyrolites derive from greater depths in the mantle than the aluminous pyroxene + olivine assemblages.

Such a relationship would be expected from crystallographic and general mineralogical grounds. Thompson [1948] has pointed out that high pressure strongly favors mineral assemblages in which aluminum lies in octahedral coordination. Minerals in which aluminum occurs in tetrahedral coordination appear to be unstable at high pressure. The change in coordination from tetrahedral to octahedral is accompanied by a substantial increase in density due to closer packing.

In aluminous pyroxenes, approximately half of the Al atoms lie in tetrahedral coordination. A change in coordination with resultant increase in density can be obtained if, under high pressure, the highly aluminous pyroxene breaks down into a low alumina pyroxene and pyrope rich garnet. Transition from the pyroxene to garnet pyrolite appears to be due to this effect. The calculated density of garnet pyrolite is 3.37 g/cm³ as compared with 3.22 g/cm³ for pyroxene pyrolite.

The P-T conditions governing the transition from pyrope pyrolite to garnet pyrolite are not known. Ringwood [1962b] has pointed out that garnet pyrolite requires higher pressure for its stability than eclogites, at corresponding temperatures. A possible boundary between the two assemblages, derived from indirect seismic evidence, was outlined in that paper. Hence, 8
Table 3. Calculated Modal Compositions and Densities for Ideal Pyrolite Composition of Table 1

<table>
<thead>
<tr>
<th>Assemblage</th>
<th>Olivine + Amphibole a (%)</th>
<th>Plagioclase Pyrolite</th>
<th>Pyroxene Pyrolite a (%)</th>
<th>Garnet Pyrolite b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine + Amphibole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Normal Al$_2$O$_3$</td>
<td>65.0</td>
<td>71.9</td>
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<td>Enstatite</td>
<td>17.6</td>
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<td>15.6</td>
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<td>High Al$_2$O$_3$</td>
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<tr>
<td>Diopside</td>
<td>4.7</td>
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<td>Amphibole</td>
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<tr>
<td>Hornblende</td>
<td>31.3</td>
<td>13.6</td>
<td>5.9</td>
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<td>Plagioclase (Ab$<em>{41}$An$</em>{24}$)</td>
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<tr>
<td>Spinel (high MgAl$_2$O$_4$ content)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>70% pyrope</td>
<td></td>
<td>12% almandine</td>
<td>6% grossular</td>
<td>6% uvarovite</td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
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</tr>
<tr>
<td>Rutile</td>
<td>0.6</td>
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<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
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<tr>
<td>Density, g/cm$^3$</td>
<td>3.25</td>
<td>3.28</td>
<td>3.24</td>
<td>3.30</td>
</tr>
<tr>
<td>H$_2$O (wt %) in rock</td>
<td>0.7%</td>
<td>0.5%</td>
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</tbody>
</table>

In Table 3 two olivine + amphibole assemblages are calculated, one on the basis that plagioclase, clinopyroxene, and enstatite have been completely replaced by an amphibole (composition in mole per cent of 12% soda-tremolite, 12% cummingtonite, 12% wehrlite, and 64% tremolite). The second assemblage is calculated using as a basic control the composition of an analyzed hornblende from the Lizard olivine + amphibole assemblage (high in edenite substitution, with some cummingtonite and wehrlite substitution) and the presence of enstatite as in some examples of the Lizard peridotite.

Two pyroxene pyrolite assemblages are possible, depending on whether the pyroxenes, particularly the enstatite, can accommodate a high Al$_2$O$_3$ content or whether this appears as spinel.

The calculated composition of the garnet compares well with that observed by Dawson in the garnet peridotite xenolith in lamellae previously discussed.

According to the model, garnet pyrolite would occupy an extensive region in the upper mantle, directly underlying a zone of pyroxene pyrolite. According to the model, garnet pyrolite would occupy an extensive region in the upper mantle, directly underlying a zone of pyroxene pyrolite.

2. Olivine + plagioclase + enstatite + clinopyroxene + accessory chromian spinel.
3. Olivine + aluminous enstatite + aluminous clinopyroxene + spinel.
4. Olivine + pyrope garnet + pyroxene(s).

All these assemblages are possible, depending on the P-T conditions and in rock compositions close to that suggested for the mantle. In Table 3 we give the calculated modal compositions (weight per cent) and rock densities for analogous assemblages in the chosen mantle composition of Table 1. The high content of Fe$_2$O$_3$ in the chosen composition (cf. footnote, Table 2) and its calculation as magnetite, together with the calculation of TiO$_2$ as rutile, introduce a bias toward slightly high values in the calculated densities. However, this is consistent for all the assemblages and does not affect the relative densities.

8. Discussion. The data we have collected show conclusively that rocks of peridotitic composition with low but essential Al$_2$O$_3$, CaO, and Na$_2$O crystallize in four distinct mineral assemblages, dependent upon the P-T conditions of crystallization.

1. Olivine + amphibole + accessory chromian spinel.
2. Olivine + plagioclase + enstatite + clinopyroxene + accessory chromian spinel.
3. Olivine + aluminous enstatite + aluminous clinopyroxene + spinel.
4. Olivine + pyrope garnet + pyroxene(s).
temperature conditions of formation of the assemblages are qualitatively consistent with that model. Significant aspects of that model may therefore now be considered verified by the evidence of the natural mineral assemblages discussed herein.

The primitive 'pyrolite' chemical composition of the mantle has been taken (somewhat arbitrarily) to be equivalent to a mixture of one part of basalt to three parts of dunite. The rocks discussed in this paper possess chemical compositions closely approaching that model. It should be emphasized, however, that any parent rock characterized by basalt-dunite ratios between 1:1 and 1:10 would probably be capable of crystallizing in each of the four mineral assemblages, according to the specific P-T conditions.

Accordingly, if ultrabasic rocks in this composition-range do, in fact, predominate in the upper mantle, large-scale mineralogical zoning controlled by the P-T distribution will be inevitable. The upper mantle cannot, therefore, be regarded as a homogeneous region possessing a characteristic set of physical parameters (such as density and seismic velocity). Implications of this mineralogical zoning with respect to the presence or absence of a low-velocity zone, and to regional variations in seismic velocity profiles and surface heat flow, were outlined in previous papers [Ringwood, 1962a, b]. Further progress now awaits the direct experimental determination of the P-T fields of the four assemblages, as well as a better knowledge of the elastic properties of the individual minerals of these assemblages, as a function of temperature and pressure.

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THE STABILITY FIELDS OF ALUMINOUS PYROXENE PERIDOTITE AND GARNET PERIDOTITE AND THEIR RELEVANCE IN UPPER MANTLE STRUCTURE

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An experimental study of the stability fields at high pressure of garnet peridotite and aluminous pyroxene peridotite has been carried out in compositions matching estimates of the average, undifferentiated upper mantle (pyrolite). The appearance of garnet at higher pressures in the pyrolite compositions results from either of two reactions:

(I) spinel + orthopyroxene + olivine + garnet
(2) aluminous pyroxene + garnet + pyroxene (lower alumina).

The role of spinel in the lower pressure assemblages is sensitively dependent on temperature and bulk composition. For the pyrolite composition preferred for the upper mantle, spinel is absent above 1300°C and the first appearance of garnet at pressures of 24 kb (1300°C) to 31 kb (1500°C) is due to reaction (2). In this composition garnet does not appear on the pyrolite solidus nor in its melting interval at pressures below 31.5 kb.

At temperatures less than 1300°C, garnet appears at 21 kb (1100°C) to 24 kb (1300°C) and develops by reaction (1) at the expense of spinel. The amount of garnet formed by this reaction is dependent on the alumina content of the pyroxenes and throughout the temperature range 1100-1500°C the amount of garnet present increases markedly with increasing pressure within the garnet peridotite field. Microprobe analyses of orthopyroxenes demonstrate that this is matched by decreasing Al₂O₃ content of the pyroxenes and allow preliminary estimation of P-T-dependent curves of constant Al₂O₃ content for orthopyroxene in garnet peridotite assemblages.

The experimental data are applied to estimate density and seismic velocity variations along oceanic and continental geothermal gradients in a pyrolite upper mantle. It is emphasized that seismic velocity distributions are sensitively affected by variations in geothermal gradient and by mantle chemical composition, e.g. by variation from pyrolite to residual, refractory, dunite-peridotite. It is suggested that seismic velocity (Vₛ) variation in an oceanic upper mantle of pyrolite composition may be characterized by two low-velocity channels:

(1) a narrow, but sharply defined low-velocity zone at 60-70 km depth caused by mineralogical zoning in the upper mantle;
(2) a broader low velocity zone at 120-150 km depth defined primarily by the critical gradient for Vₛ in the upper mantle but accentuated by mineralogical variations in pyrolite.

INTRODUCTION

In previous papers we have advanced arguments for specific model compositions for the peridotite upper mantle [1-4] and have used the term "pyrolite" for these deduced mantle compositions. On theoretical grounds and on the evidence of natural rocks approaching the pyrolite composition, it has been demonstrated that pyrolite may crystallize in four different mineral assemblages within the P,T conditions of the upper mantle. These mineral assemblages are as follows [2-4]:

a. Olivine + amphibole + enstatite ("amphibolite")

b. Olivine + pyroxenes + plagioclase ("plagioclase pyrolite")

c. Olivine + aluminous pyroxenes + spinel ("pyroxene pyrolite")

d. Olivine + pyroxenes + garnet ("garnet pyrolite").

The stability relationships of these assemblages in model pyrolite composition have been experimentally investigated in our laboratory and the present letter explores the implications of this study on mineralogical and seismic velocity variations in the upper mantle.

2. EXPERIMENTAL METHOD

The ultramafic compositions used in the investigation are listed in table 1.
Table I
Chemical compositions and CIPW norms of model pyrolic compositions used in experimental runs.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SiO₂</strong></td>
<td>43.20</td>
<td>43.95</td>
<td>45.20</td>
</tr>
<tr>
<td><strong>TiO₂</strong></td>
<td>0.58</td>
<td>0.57</td>
<td>0.71</td>
</tr>
<tr>
<td><strong>Al₂O₃</strong></td>
<td>4.01</td>
<td>3.88</td>
<td>3.54</td>
</tr>
<tr>
<td><strong>Cr₂O₃</strong></td>
<td>0.42</td>
<td>0.41</td>
<td>0.43</td>
</tr>
<tr>
<td><strong>Fe₂O₃</strong></td>
<td>0.35</td>
<td>0.75</td>
<td>0.48</td>
</tr>
<tr>
<td><strong>FeO</strong></td>
<td>7.88</td>
<td>7.50</td>
<td>8.04</td>
</tr>
<tr>
<td><strong>MnO</strong></td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>NiO</strong></td>
<td>0.39</td>
<td>0.39</td>
<td>0.20</td>
</tr>
<tr>
<td><strong>MgO</strong></td>
<td>39.54</td>
<td>39.00</td>
<td>37.48</td>
</tr>
<tr>
<td><strong>CaO</strong></td>
<td>2.67</td>
<td>2.60</td>
<td>3.08</td>
</tr>
<tr>
<td><strong>Na₂O</strong></td>
<td>0.61</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td><strong>K₂O</strong></td>
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<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td><strong>100 Mg</strong> atom ratio</td>
<td>89.9</td>
<td>90.3</td>
<td>89.2</td>
</tr>
<tr>
<td><strong>Mg + Fe⁺⁺</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CIPW Norm</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Or</td>
<td>1.1</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Ab</td>
<td>5.2</td>
<td>5.2</td>
<td>5.0</td>
</tr>
<tr>
<td>An</td>
<td>7.5</td>
<td>7.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Di</td>
<td>4.6</td>
<td>4.3</td>
<td>6.8</td>
</tr>
<tr>
<td>Hy</td>
<td>3.8</td>
<td>9.4</td>
<td>15.8</td>
</tr>
<tr>
<td>Ol</td>
<td>75.6</td>
<td>69.8</td>
<td>62.5</td>
</tr>
<tr>
<td>Ilm</td>
<td>1.1</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Mt</td>
<td>0.5</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Chr.</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Pyrolite I and pyrolite III refer to the model compositions calculated by Green and Ringwood [2] and Ringwood [3], respectively. They differ principally in their MgO/SiO₂ ratios and thus in pyroxene/(Al₃Cr₂)O₃ and pyroxene/olivine ratios. Pyrolite II is a composition intermediate between the two in which the enstatite/olivine ratio of Pyrolite I was increased without appreciable change in the R₂O₃ content. The experimental compositions were prepared from AR grade chemicals, carefully ground and reacted together under high temperature reducing conditions and then analyzed for FeO and Fe₂O₃ contents. The initial mixes were extremely finegrained (≤ 1 micron) and consisted of olivine, clinopyroxene, orthopyroxene and plagioclase. To facilitate identification of minor phases and of the presence or absence of small degrees of partial melting, compositions were prepared which are equivalent to the pyrolite compositions of table 1 after extraction of 50% olivine [Mg₉₁.₆Fe₈.₁Ni₀.₂Mn₀.₁] from pyrolites I and II and after extraction of 40% olivine [Mg₉₉.₆Fe₈.₁Ni₀.₂Mn₀.₁] from pyrolite III. In all experiments conducted with these modified pyrolite compositions, excess olivine was present as a stable phase. Hence the above procedure did not affect in any way the equilibrium relationships which are discussed below.

Crystallization of the experimental compositions was carried out using a single-stage, piston-cylinder apparatus [5,6] and a pressure correction of -10% was applied to the nominal pressure for all runs [7]. Samples were run in both platinum capsules and in graphite capsules. In seeking to determine the solidus for the pyrolite composition it was found that the graphite capsules, while preventing Fe-loss from the sample to capsule walls, gave poorly reproducible results and indicated anomalously low temperatures for the beginning of melting. Using the dry furnace assemblies with talc + boron nitride pressure media [6,8] welded platinum capsules gave satisfactory results for the
solidus determinations. The magnitude of Fe-loss from the sample in these runs, was quantitatively determined and found to be of minor importance. In subsolidus experiments the results of runs in graphite and in platinum capsules were mutually consistent. Samples were examined optically and by X-ray powder diffraction. Orthopyroxene forms quite large tabular porphyroblasts; garnet is commonly subhedral but contains many inclusions at lower temperatures and olivine and clinopyroxene form small anhedral grains. Spinel occurs as small, equant, green, isotropic grains and differs from ilmenite (ilmenite + geikielite solid solution) in that the latter is commonly elongate, brown, translucent and with high birefringence. The orthopyroxene crystals are readily analyzed by electron microprobe techniques and some data have been obtained on olivine, clinopyroxene and garnet compositions. Microprobe analyses for Fe, Ca, Al and Cr were carried out by the methods previously reported [9] using glasses of orthopyroxene composition, analyzed olivines and analyzed garnets as standards.

3. EXPERIMENTAL RESULTS

The results of the determination of the stability field for garnet pyrolite are presented in fig. 1. The data points denote the phase assemblages present in pyrolite III composition. Plagioclase pyrolite is stable under dry conditions on the low pressure side of AB. Between AB and ELF, both garnet and plagioclase are absent and the mineral assemblage is dominated by aluminous pyroxenes. Within this field, spinel is present as a minor phase at temperatures below the line marked K but only olivine, aluminous pyroxenes and accessory ilmenite are present at higher temperatures. Garnet first appears in trace amounts along the line ELF and, at a given temperature, steadily increases in abundance as pressure increases. The data points for pyrolites I and II are not shown in fig. 1 but in these compositions the first appearance of garnet is along EJ and spinel remains a stable phase up to solidus temperatures on the low pressure side of EJ. Garnet and spinel co-exist together over a very small pressure interval on the high pressure side of EJ. The triangular P,T field FLJ is one in which the olivine + aluminous pyroxenes assemblage is stable in pyrolite III but olivine + aluminous pyroxenes + garnet is stable in pyrolites I and II. The microprobe analyses so far carried out clearly demonstrate the important role that (Ca,Mg)42Si06 solid solution in the pyroxenes plays in determining the phase assemblages. The Al2O3 contents of orthopyroxene in some of the runs are listed in table 2. The orthopyroxene at 1500°C also contains 0.7 - 0.9% Cr2O3 in solid solution. Co-existing clinopyroxene contains higher Al2O3 and Cr2O3 content but this is largely due to NaR++Si2O6 solid solution in the clinopyroxene. Neglecting the sodic pyroxene component, the orthopyroxene and clinopyroxene have very similar degrees of (Ca,Mg)Al2Si06 solid solution. The orthopyroxenes crystallizing above 1300°C and lying on the boundary LF contain 6.0 ± 0.2% Al2O3.
Table 2
Alumina content of orthopyroxene in equilibrium with garnet in high pressure experimental runs.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature (°C)</th>
<th>$\text{Al}_2\text{O}_3^*$ content of orthopyroxene (weight percent)</th>
<th>Garnet content of assemblage</th>
<th>Spinel content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolite III</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.8</td>
<td>1350</td>
<td>6.1</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>25.9</td>
<td>1350</td>
<td>5.5</td>
<td>minor</td>
<td>nil</td>
</tr>
<tr>
<td>27.0</td>
<td>1350</td>
<td>4.9</td>
<td>minor</td>
<td>nil</td>
</tr>
<tr>
<td>36.0</td>
<td>1300</td>
<td>2.6</td>
<td>common</td>
<td>nil</td>
</tr>
<tr>
<td>40.5</td>
<td>1300</td>
<td>2.2</td>
<td>common</td>
<td>nil</td>
</tr>
<tr>
<td>30.4</td>
<td>1500</td>
<td>5.9</td>
<td>trace</td>
<td>nil</td>
</tr>
<tr>
<td>31.5</td>
<td>1500</td>
<td>5.6</td>
<td>minor</td>
<td>nil</td>
</tr>
<tr>
<td>33.8</td>
<td>1500</td>
<td>4.8</td>
<td>minor</td>
<td>nil</td>
</tr>
<tr>
<td>36.0</td>
<td>1500</td>
<td>4.2</td>
<td>common</td>
<td>nil</td>
</tr>
<tr>
<td>Pyrolite I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.8</td>
<td>1400</td>
<td>5.9</td>
<td>trace</td>
<td>minor</td>
</tr>
</tbody>
</table>

* Estimated accuracy, ±5% of amount present.

Preliminary curves denoting the maximum $\text{Al}_2\text{O}_3$ content of orthopyroxene in equilibrium with garnet in pyrolite compositions may be derived from the data of table 2 and have been shown in fig. 2.

The cause of the break in slope of the boundary ELF lies in the different equilibria involved in the formation of garnet along the curve. At temperatures below L, aluminous spinel is present in the assemblage and is in equilibrium with orthopyroxene containing $\text{Al}_2\text{O}_3 < 6.0\%$. The first appearance of garnet from this assemblage involves reaction between spinel and pyroxenes [10] and the idealized reaction is as follows:

$$\text{(1)} \quad \text{MgA}_2\text{O}_4 + 4 \text{MgSiO}_3 \rightleftharpoons \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$$

spinel   entstatite  pyrope

$$+ \text{Mg}_2\text{Si}_4\text{O}_9$$

forsterite

In contrast, spinel is absent above 1300°C in pyrolite III composition and the $\text{Al}_2\text{O}_3$ content of the mix is entirely in solid solution in the pyroxenes. In this assemblage the orthopyroxene contains $6\%$ $\text{Al}_2\text{O}_3$ (weight percent) and the clinopyroxene contains $>6\% \text{Al}_2\text{O}_3$. Garnet appears from this assemblage when the load pressure is sufficient to cause the aluminous pyroxenes to break down in favour of garnet + less-aluminous pyroxene [11, 12]. Thus the simplified reaction for the appearance of garnet in pyrolite III composition along LF is as follows:

$$\text{(2)} \quad m \text{MgSiO}_3 \cdot n \text{MgAl}_2\text{SiO}_6 \rightleftharpoons \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$$

aluminous entstatite solid solution

$$+ (m-2)\text{MgSiO}_3 \cdot (n-1)\text{MgAl}_2\text{SiO}_6$$

entstatite solid solution

The different roles of reactions involving spinel and those involving aluminous pyroxenes are in harmony with previous work on simple systems [10-14]. The boundary EF (fig. 1) is almost identical to that established by MacGregor [10] for reaction (1) in the pure spinel + 4 entstatite system, provided that a -10% pressure correction is applied to MacGregor's data. The boundary LF representing assemblages containing garnet in equilibrium with orthopyroxene (6.0% $\text{Al}_2\text{O}_3$) is similar in slope to analogous boundaries in the pure magnesian system, entstatite + pyrope [12] and the natural, simple system entstatite + chromiferous pyrope garnet [11]. However, at a given pressure and temperature, the $\text{Al}_2\text{O}_3$-content of orthopyroxene in equilibrium with garnet in the complex pyrolite composition is substantially less than that obtained in the
simple 2-component systems. This effect is attributed to differences in garnet and pyroxene composition, possibly relating particularly to Ca and Cr contents and the presence of clinopyroxene, between the two component and complex systems. The persistence of spinel to around 1300°C in the pyrolite composition contrasts with its anticipated absence above 1000°C predicted by Ringwood et al. [13] and is also attributed to chemical or coupled reaction effects in the complex composition.

4. MINERALOGY IN A PYROLITE UPPER MANTLE.

In the following discussion, it is assumed that the average composition of the upper mantle beneath oceanic and geologically “young” regions is that of pyrolite. In continental regions and particularly in Precambrian shield regions, there is probably a much greater proportion of refractory residual peridotite at shallower levels and the upper mantle may be chemically zoned [3,4]. Mineralogical variation in the upper mantle is determined by the intersection of geothermal gradients with the stability fields of fig. 1. The variation of temperature in the continental and oceanic crusts and upper mantle has been discussed by Clark [15] and Clark and Ringwood [16]. It is clear from these papers that there is a large difference between oceanic and stable shield geotherms and that this difference takes the form illustrated in fig. 2. Nevertheless, the specific form of the curves, particularly their “convexity” and their closeness of approach to the pyrolite solidus, depend sensitively on knowledge of
the magnitude of radiative heat transfer in the upper mantle. Clark and Ringwood [16] assumed an opacity of about 5 cm\(^{-1}\) and obtained geotherms about 200°C lower at 150-200 km and 100°C lower at 100 km than those in fig. 2. Ringwood, MacGregor and Boyd [13] and Ringwood [4] assumed a higher opacity for the upper mantle and qualitatively obtained the geotherms which we illustrate in fig. 2. No unique solution for geothermal gradients is currently possible but a general evaluation of the role of mineralogical zoning in the upper mantle can best be obtained by consideration of the two examples in fig. 2.

Along the Precambrian shield geotherm, the probability of chemical zoning [1,3] would limit the possible phase assemblages. If rocks of composition approaching pyrolite composition occur locally, then there may be an extremely limited zone near the base of the crust where these would crystallize to olivine + orthopyroxene (1% Al\(_2\)O\(_3\)) + clinopyroxene + spinel assemblages. Similar compositions below about 35-40 km would yield olivine + orthopyroxene (1-2% Al\(_2\)O\(_3\)) + clinopyroxene + garnet assemblages and it may be noted that the garnet content would be relatively high (e.g. 12% garnet in pyrolite III composition). No regular change in mineralogy would occur for rocks of pyrolite composition along the Precambrian shield geotherm (c.f. refs. [13,14]).

The picture is very different along the oceanic geotherm. The olivine + orthopyroxene + clinopyroxene + spinel assemblage is stable in pyrolite composition to depths of 60-70 km [14]. Within this interval the amount of spinel would decrease and the Al\(_2\)O\(_3\) content of pyroxenes would increase with increasing depth (reaction 3):

\[(3) \text{MgAl}_2\text{O}_4 + m \text{MgSiO}_3 \rightarrow (m-2)\text{MgSiO}_3 + \text{MgAl}_2\text{Si}_6\text{O}_{16} + \text{Mg}_2\text{SiO}_4 \]

Prior to the incoming of garnet at 60-70 km in the oceanic mantle probably occurs over a relatively small depth interval (5-15 km). With further penetration along the geotherm into the garnet pyrolite field the amount of garnet may actually decrease - this will occur for temperature gradients steeper than the lines of constant Al\(_2\)O\(_3\) content of orthopyroxene shown in fig. 2. For the gradient shown, pyrolite III will contain about 5% garnet at depths between 90 and 120 km and the mineralogy will remain constant over this interval. At depths greater than 120 km the geothermal gradient becomes increasingly transgressive to the lines of constant Al\(_2\)O\(_3\) content for orthopyroxene. Thus, along this part of the geothermal gradient, the aluminous pyroxenes will gradually break down to yield an increasing garnet content and low-alumina pyroxenes. At depths of 200-250 km the assemblage of pyrolite III will probably contain 11-12% of garnet.

The transition from aluminous pyroxenes + spinel pyrolite to garnet pyrolite at depths of 60-70 km in the oceanic mantle is in agreement with MacGregor's data [10] and with the conclusions of Ito and Kennedy [17] on the stability of spinel and garnet-bearing peridotite. Although the present work does not support earlier conclusions [13, 14] that garnet pyrolite would not in general be stable until depths of 120-150 km, it provides excellent confirmation of the importance of this depth interval of the breakdown of
uminous pyroxenes to garnet + low alumina pyrox-
ines, the reactions on which these earlier conclusions
ere based. It should be pointed out that for pyrol-
e-like compositions with higher pyroxene/
11, (Cr)2O3 ratios than pyrolites I, II and III, the
eld of garnet pyrolite may not be entered until
phs in excess of 120 km are reached - this is parti-
sarily relevant for mantle regions from which basal-
c fractions have been removed. Geothermal gradients
er than that illustrated will have a similar effect
: diminishing the amount of garnet produced at
0-70 km depth by reaction (1) and increasing the
ount of garnet produced at deeper levels from reac-
on (2).

This brief discussion serves to illustrate the applica-
on of our experimental data to a more flexible range
f mantle compositions and geothermal gradients than
plied in fig. 2.

1. VARIATION OF SEISMIC VELOCITY WITH
DEPTH IN THE UPPER MANTLE

Seismic velocity distributions in the upper mantle
ill be principally determined by
1. The effects of pressure and temperature changes
along the geothermal gradient. Previous authors;
18-21 have discussed the opposing effects of
perature increase (causing seismic velocity to
decrease) and pressure increase (causing seismic ve-
locity to increase) along a geothermal gradient and
cluded that, in homogeneous upper mantle ma-
terial, seismic velocities V_s and V_p should initially
decrease to a minimum and then increase with in-
creasing depth in the upper mantle.
2. The effects of mineralogical variation in the upper
mantle. Although later data on the solidus curves
or basalts and peridotite have removed some of the
asons for Ringwood’s [1] postulate of
inarol rating in the upper mantle, experim-
tal evidence on mineral reactions in peridotitic
ositions has confirmed the high probability of
uch effects in the upper mantle.
3. The effects of vertical chemical fractionation of the
upper mantle such that some regions may be main-
ly residual, refractory dunite and peridotite, de-
leted of low melting components now residing in
overlying crustal levels. These effects have been dis-
cussed elsewhere [1,3,16] and are probably of
greatest significance in mantle regions beneath
able continental shields.

From the data presented in previous sections it is
ossible to examine qualitatively the effects of the
irst and second factors in determining seismic velo-
ity along the oceanic geotherm illustrated in fig. 2. It
emphasized that this exercise is of an illustrative
ature and no special significance is claimed for the
oethern assumed for fig. 2 or the absolute values of
ismic velocities (V_s) estimated in fig. 3.

Fig. 3a is a quantitative expression of the change
in mineralogy along the oceanic geotherm, as dis-
cussed in the previous section. At depths less than 30
km it is assumed that amphibole may be an important
ase in the oceanic upper mantle [2,4]. The effects
f these assemblages on density (room T and P) and
ismic velocity (V_s) are qualitatively estimated in
bs. 3b and 3c. A principal reason for suggesting an
mphibolite zone (U1) at the top of the oceanic
mantle is the seismological evidence for an initial in-
crease in seismic velocity with depth just below M
18, 22.

In estimating seismic velocity variation with depth
it is necessary to know the critical temperature gradi-
(∂T/∂P)V_s for which the seismic velocity V_s re-
ains constant, the opposing pressure and temper-
ature effects just cancelling each other. In the past,
critical gradients for V_s of around 6-10°C/km have
en predicted on theoretical grounds but Schreiber
nd Anderson [23] have recently measured critical
gadients for V_s in MgO of 2.7°C/km and in Al2O3
 of 2.1°C/km, values which are considerably lower
han those previously assumed for the silicate min-
als of the upper mantle. It is possible that the criti-
gradient for olivine may be somewhat higher than these
 values. In fig. 3c, a critical gradient for V_s of 4.5°C/
k m has been assumed, this being the value which
would produce a velocity minimum in homogeneous
aterial at a depth of about 130 km along the oceanic
goethernal gradient of fig. 2. The assumption of a
smaller critical gradient would have the effect of in-
creasing the depth of the velocity minimum. The
uperimposition of the mineralogical zoning effects
 and the P,T effects on V_s suggest a “fine structure” in
he oceanic upper mantle seismic velocity distribution
as follows:

a) Zone U1. A zone in which the mineralogical varia-
tion due to decreasing amphibole content produces
an increase in seismic velocity. This is sufficiently large to overcome the temperature effect tending to produce a decrease in seismic velocity.

b) Zone $U_2$. The mineralogical effect of decreasing spinel content produces a density decrease which augments the temperature effect, leading to relatively rapid decrease in $V_s$ with depth.

c) Zone $U_3$. A velocity increase is caused by the relatively large density change over a small depth interval caused by the reaction of spinel and pyroxene to yield garnet and olivine. This is sufficient to cancel the temperature effect in decreasing $V_s$ and leads to the narrow but rather sharply defined velocity minimum ($M_1$) between zones $U_2$ and $U_3$.

d) Zone $U_4$. The temperature effect on $V_s$ is dominant but is augmented by slight decrease in garnet content and increase in aluminous pyroxene content (a density decrease). $V_s$ thus decreases to a minimum value with the location of this determined by the critical temperature gradient $(\partial T/\partial P)_{V_s} = 4.5^\circ C/km$. 

e) Zone $U_5$. This is below the critical depth for the geotherm illustrated and increasing depth leads to increase in seismic velocity, even in a homogeneous medium. This is augmented by the mineralogical change in $U_5$ giving increased garnet content. Thus the rate of increase in seismic velocity with depth is more rapid, leading to a more sharply defined “floor” to the low velocity minimum between $U_4$ and $U_5$.

f) Zone $U_6$. This is homogeneous in mineralogy and the seismic velocity increase is that determined by the $P,T$ effect on $V_s$ alone. Zone $U_6$ extends to about 350 km where a more rapid increase in seismic velocity marks the beginning of the Transition Zone of the mantle and may be attributed to increase of garnet at the expense of pyroxene by solid solution of pyroxene in garnet [24].
The above discussion illustrates the principle that both mineralogical changes and $P,T$ effects on $V_s$ are of prime importance in determining the seismic velocity distribution within the upper mantle. Even without any effects of chemical zoning within the upper mantle it is apparent that variations in geothermal gradients will considerably affect the velocity distributions, particularly the depth of velocity minima, the magnitude of velocity differences and the presence of one or two low velocity channels in the upper mantle. Assuming a critical gradient of 4.5°C/km for $V_s$ a broad low velocity channel at about 150-170 km depth might be expected along the shield geotherm of fig. 2. Similar models may be set up from fig. 2 by assuming various geothermal gradients and also including the additional complexity of chemical variation from pyrolite to refractory peridotite and dunite.

6. CONCLUSIONS

An experimental study of the equilibrium relations between pyroxene pyrolite and garnet pyrolite demonstrates that pyroxene + spinel pyrolite is stable in the sub-oceanic mantle to depths of 60-70 km. At this depth spinel and pyroxene react to form garnet and olivine. The amount of garnet formed from this reaction depends sensitively upon the temperature at which the geotherm intersects the spinel + pyroxene = garnet + olivine boundary. At temperatures in excess of 1000°C, less than half the potential garnet in the pyrolite composition forms by this reaction, the rest remaining in solid solution in aluminous orthopyroxene ($> 3\% Al_2O_3$) and aluminous clinopyroxene. At depths between 60-70 km and about 120 km, the garnet content of the pyrolite remains roughly constant or may decrease slightly as more $Al_2O_3$ goes into solid solution in the pyroxenes. At depths greater than 120-130 km the geothermal gradient enters a region in which, with increasing depth, the amount of garnet gradually increases as $(Ca, Mg)Al_2SiO_6$ solid solution in the pyroxenes decreases.

It is demonstrated that mineralogical variation on geothermal gradients, particularly in oceanic regions, may be expected to strongly influence the seismic velocity distribution in the upper mantle. In particular, mineralogical zoning of the upper mantle may yield two low velocity channels (for $V_s$) at depths of about 65 km and between 100 and 150 km respectively. No unique model of mineralogical or seismic velocity distribution in the upper mantle is presented, rather it is argued that regional variations in chemical composition (from pyrolite to refractory peridotite), and in geothermal gradients will produce significant, regional differences in seismic velocity distributions.

REFERENCES


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THE INSTABILITY OF PLAGIOCLASE IN PERIDOTITE AT HIGH PRESSURE

D. H. GREEN & W. HIBBERSON


Experimental crystallization of forsterite + anorthite (2.2:1 molar ratio) in a piston-cylinder solid-media apparatus shows that forsterite and anorthite are stable at less than 8.5 ± 0.5 kb at 1250°C, but forsterite + orthopyroxene + clinopyroxene + spinel is the stable assemblage at higher pressures. The fayalite + anorthite assemblage is stable to 7-7.5 kb at 1050°C and to 6-6.5 kb at 900°C, and at higher pressure is replaced by almandine-grossular garnet. Reactions between magnesian olivine (Fo92) and labradorite (An59), and between olivine and plagioclase in a complex peridotite composition (pyrolite), show that there is a 5-phase field of olivine + orthopyroxene + clinopyroxene + plagioclase + alumino-spinel between 9 kb and 11-14 kb (depending on composition) at 1200°C. At higher pressures plagioclase is absent and at lower pressures pyroxenes are absent or present in smaller amounts, and alumina-rich spinel is absent. The experimental data are applied in discussions of corona formation and of the stability of plagioclase in peridotite compositions.

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Introduction

Olivine and plagioclase are in reaction relationship at high pressure and are replaced by assemblages including garnet or pyroxenes + spinel. These reactions are well illustrated by corona textures in troctolitic and anorthositic rocks, and experimental studies of olivine and plagioclase reactions are desirable for interpretation of such coronas. Kushiro & Yoder (1966) have studied reactions between the end members forsterite and anorthite, but there is uncertainty in applying these data to the natural rocks, in which olivines are more iron-rich; the plagioclase (even in very magnesian peridotites) is usually labradorite or bytownite. Reactions between the olivine and plagioclase in complex basaltic compositions have been studied by Green & Ringwood (1967a), T. H. Green (1967), Ito & Kennedy (1968), Irving & Green (1969), and in a nephelinitic composition by Bultitude (1968). These studies show that the reactions between olivine and plagioclase cannot be considered independently of the presence of other phases, notably clinopyroxene and nepheline, and that the conditions of reaction and the nature of the products are sensitive to bulk composition. The reactions in basaltic compositions eliminate olivine from the low pressure assemblages and plagioclase persists to higher pressures in assemblages with pyroxenes + spinel or garnet. In peridotite compositions, however, olivine will persist at high pressure and plagioclase disappear. A knowledge of the pressure
required for elimination of plagioclase, particularly near the peridotite solidus, is most important for the hypothesis of partial melting in the upper mantle and variations in upper mantle mineralogy. The present investigation began as an attempt to ascertain the limits of stability of plagioclase in 'pyrolite' composition, i.e. a complex peridotite composition suggested as the mean composition of the upper mantle (Ringwood 1962, 1966a, b; Green & Ringwood 1963). The simple systems forsterite (Fo_{100}) + anorthite, fayalite (Fo_{0}) + anorthite, and olivine (Fo_{90}) + labradorite (An_{99}) were studied to throw further light on the complex reactions in the pyrolite composition.

Experimental methods

Experiments were carried out in a solid-media apparatus similar to that described previously (Boyd & England, 1960; Green & Ringwood, 1967a). Sample capsules were of either platinum or graphite, the former having the advantage that sealing by welding can exclude water, but the disadvantage that some iron may be lost from the sample due to solid solution in the platinum. For this reason, runs on the fayalite + anorthite mix were carried out in graphite capsules. In runs in graphite capsules, water vapour from dehydration of the talc pressure medium cannot be entirely excluded and may result in lowering of solidus temperatures, particularly in long runs. No reduction of fayalite to metallic iron was observed in any of the runs: any such reduction would be also accompanied by appearance of pyroxene in the fayalite + anorthite mix.

Reactants and products were identified by optical examination and X-ray powder diffraction. Experimental difficulty was experienced in the simple Fo ± An and Fa ± An systems in the sluggish nucleation and growth of phases and in the metastable persistence of low pressure phases. Runs were thus seeded with 10–15% of the synthesized high pressure assemblage containing garnet or spinel + pyroxene. Experiments close to the reaction boundaries required identification of rather small degrees of growth or corrosion of the seed phases. Runs were not seeded with the low pressure assemblages in all cases, since it was shown that olivine and plagioclase nucleated rapidly from the glass within the first few minutes at pressures near their stability limits.

Equations (1), (3) and (9) on the following pages illustrate the expected reactions, and to ensure the presence of an excess of olivine in all high pressure assemblages, the olivine: anorthite mixtures were prepared in the molecular ratio 2.2 : 1, i.e. 10% excess olivine over that required for equation 1 with \( x = 0 \). Similarly, olivine is present in excess (in relation to equation (9)) in the olivine + labradorite mix (olivine (Fo_{90}) : labradorite (An_{99}) = 1.8 : 1 mol.ratio) and in the pyrolite mix (Table 1).

The fayalite and anorthite used in the experiments were pure synthetic phases (from Tem-Pres. Inc.); forsterite was synthesized at high tempera-
ture, olivine (Fo$_{90}$) and labradorite (An$_{39}$) were natural analyzed minerals, and the pyrolite mixture was prepared from reacted oxides. As with previously reported experiments on the pyrolite composition, the masking of minor phases by abundant olivine was avoided by using a composition (Table 1) equivalent to 'pyrolite less 40% olivine (Fo$_{91.0}$)' (Green & Ringwood 1967c, p. 152).

Experimental data

*Forsterite + Anorthite*
Using glass seeded with 10% of the higher pressure assemblage of orthopyroxene$_{ss}$ + clinopyroxene$_{ss}$ + spinel + olivine, the experiments yielded forsterite + anorthite assemblage at 8.1 kb at 1250°C, but yielded the orthopyroxene$_{ss}$ + clinopyroxene$_{ss}$ + forsterite assemblage at 9 kb, 1250°C. In the experiments in which no seed of the spinel + pyroxenes assemblage was added, the forsterite + anorthite assemblage persisted at 9 kb, 1250°C, and yielded pyroxenes + spinel at 9.9 kb, 1250°C. A similar result was obtained using unseeded glass at 1300°C. The data demonstrate the unsuitability of using unseeded glass or low pressure assemblages in runs up to 3 hrs at $T = 1250°C$ to establish the boundary between olivine + anorthite and pyroxenes + spinel assemblages. This is important in evaluating the data of Kushiro & Yoder (1966), who used glass or finely crystalline Fo + An in their studies on the forsterite + anorthite join, and only used the seeding technique (5% Ga + Cpx ± Fo added to the Fo + An crystalline mix) in runs near the garnet boundary. The present study, using solid media apparatus with a −10% pressure correction applied (Green, Ringwood & Major 1966), gives a reversal across the reaction boundary between 8.1 kb and 9.0 kb at 1250°C, i.e. consistent with Kushiro and Yoder's boundary. The reaction may be written as follows (Kushiro & Yoder 1966):

\[(1) \ 4\text{Mg}_2\text{Si}_2\text{O}_4 + 2\text{CaAl}_2\text{Si}_2\text{O}_8 \equiv (2-x)\ \text{CaMgSi}_2\text{O}_6 \cdot x\ \text{CaAl}_2\text{Si}_2\text{O}_6 + (4-2x)\text{MgSiO}_3 \cdot x\text{MgAl}_2\text{Si}_2\text{O}_6 + (2-2x)\text{MgAl}_2\text{O}_4 + 2x\ \text{Mg}_2\text{Si}_2\text{O}_4\]

If further experiments in gas apparatus could demonstrate the stability relations suggested by Kushiro and Yoder's synthesis runs, then comparison with the solid media apparatus data would confirm the validity of the (−10%) pressure correction for the solid media apparatus ('$\frac{1}{2''}$ piston) at or near 10 kb.

The boundary between An + Fo and Cpx + Opx + Sp ± An or Fo, as drawn by Kushiro & Yoder (1966, Figs. 1 & 2), has a steep slope (dT/dP), and it has been suggested by Kushiro & Yoder (1966, p. 347–8) that this may intersect the boundary for the incoming of garnet at lower temperatures (estimated near 6 kb and 700°C) leading to an invariant point in the Fo + An system at which six phases (Fo, An, Sp, Ga, Opx$_{ss}$, Cpx$_{ss}$) may coexist. MacGregor (1967) also illustrated (Fig. 12.2) such an invariant point. This has important implications for metamorphic petrology, but it
Table 1. Column 1: Model 'pyrolite'; Column 2: 'Pyrolite minus 40% olivine' used in experimental runs. Both compositions retain excess olivine in the high pressure assemblages

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>C.I.P.W. Norm</th>
<th>1</th>
<th>2</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>45.20</td>
<td>47.84</td>
<td></td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.71</td>
<td>1.18</td>
<td></td>
<td>Ab</td>
<td>5.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.54</td>
<td>5.90</td>
<td></td>
<td>An</td>
<td>6.6</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.43</td>
<td>0.72</td>
<td></td>
<td>Di</td>
<td>6.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.48</td>
<td>0.80</td>
<td></td>
<td>Hy</td>
<td>15.8</td>
</tr>
<tr>
<td>FeO</td>
<td>8.04</td>
<td>8.21</td>
<td></td>
<td>Ol</td>
<td>62.5</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
<td>0.13</td>
<td></td>
<td>Ilm</td>
<td>1.3</td>
</tr>
<tr>
<td>NiO</td>
<td>0.20</td>
<td>0.18</td>
<td></td>
<td>Mt</td>
<td>0.7</td>
</tr>
<tr>
<td>MgO</td>
<td>37.48</td>
<td>28.73</td>
<td></td>
<td>Ap</td>
<td>0.6</td>
</tr>
<tr>
<td>CaO</td>
<td>3.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

should be pointed out that the experimental evidence for intersection of the two boundaries is subject to doubt. The persistence of Fo + An (1 : 1 mix) in a 2 hr run at 1200°C 8 kb was taken by Kushiro & Yoder 1966 (Fig. 1, Table 1) as indicating stability of that assemblage, but in the light of the present experiments showing the necessity of seeding with pyroxenes + spinel at 1250°C, 3 hr runs, the Fo + An may have been metastable. Other data on the Fo + An, (1 : 1 or 2 : 1) mixes, permit a much smaller slope (dT/dP). Similarly, in their studies on the appearance of garnet in the Fo + An (1 : 1 and 2 : 1) mixes, Kushiro & Yoder used (Fo + An) glass or (Fo + An) finely crystallized material and seeded some runs with 5% Ga + Cpx ± Fo. However, the (Fo + An) assemblage is metastable on the low pressure side of the reactions under study, i.e.:

(2) Opₓss + Cpxₓss + An ⇔ Garnet ± Cpx (1 : 1 mix)
(3) Opₓss + Cpxₓss + Fo ⇔ Garnet + Fo ± Cpx (2 : 1 mix)

Thus, the metastable growth of garnet seeds instead of Cpxₓss + Opₓss + Sp is possible. It should be noted that Kushiro & Yoder (1966, Figs. 1 & 2, Tables 1 & 2) obtained Opₓss + Cpxₓss + Sp + Fo from runs, seeded with garnet, at 1160°C, 14 kb, 4 hrs (1 : 1 mix) and from runs at 1175°C, 18 kb, 1½ hrs and 1225°C, 18½ kb, 1½ hrs (2 : 1 mix). These results were regarded as erroneous by the authors, but, if valid, they imply a steeper slope (dT/dP) for the boundaries marking the incoming of garnet.

Thus it is emphasized that neither the previous studies nor the present study are adequate to define dT/dP for the reaction between forsterite and anorthite to yield pyroxenes and spinel, nor of the latter assemblage to yield garnet ± olivine. Petrological application of the experimental data in the Fo + An system must recognize the experimental uncertainties and difficulty. The authors consider that at present there is no evidence either from natural highly magnesian peridotites nor from the experimental study, that reactions (1) and (3) intersect under geologically significant conditions.
**Fayalite + Anorthite (Table 2)**

Melting occurs in the Fe-rich system at much lower temperatures than in the Mg-rich system so that experiments were run only at 1100°C, 1050°C, and 900°C. In the 1100°C runs there was minor melting at pressures above 8 kb and a large amount of melting at 7.2 kb. Using a mix of glass + 10% seed (garnet + fayalite), garnet increased in amount in the 8.1 kb run. In the unseeded mixes garnet crystallized from glass and from crystalline (An + Fa) mix at 9 kb, 1100°C, but was absent at 8.1 kb, 1100°C. Neither magnetite, pyroxene nor metallic iron was observed in any of the runs, and residual or excess fayalite was present in all runs.

At 1050°C the problems of minor melting were avoided, and garnet disappeared from the seeded mix in the run at 6.3 kb, formed a major phase at 8.1 kb, and a minor phase in both the 7.2 kb, 3 hr and 7.2 kb, 24 hr runs. The coarser grain size of the garnet in the 24 hr run compared with that in the 3 hr run is taken to indicate stability of this phase, but also run conditions very close to the reaction boundary.

At 900°C, run times were of 24 hrs, and in one case, of 88 hrs. Seeded mixes were used in all cases. The marked increase in garnet in the 7.2 kb and 8.1 kb runs contrasts with its decrease and corroded nature at 5.4 kb, and the decrease in the 88 hr run at 6.3 kb. Knowledge of the bulk composition and the observation that pyroxene or spinel do not occur amongst the products in any of the subsolidus runs, shows that the reaction occurring to yield garnet (assuming no significant larnite solid solution in fayalite) is as follows:

\[
2\text{Fe}_2\text{SiO}_4 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{CaFe}_2\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Fe}_2\text{SiO}_4 \quad \Delta V = -28.5\text{cm}^3
\]

The specific garnet composition was confirmed by determination of \(a_0\) (11.64 ± 0.01 Å) and refractive index (1.800 ± 0.005).

**Olivine + Labradorite**

Unlike the end member anorthite, reaction between labradorite and olivine is controlled by coupled reactions involving changes in plagioclase solid solution and will occur over a range of pressures at a given temperature. Kushiro (1965a) has presented preliminary data in the system forsterite + nepheline + silica suggesting that forsterite + albite is stable up to approximately 11 kb at 1100°C, but is replaced by nepheline + enstatite and then by enstatite + jadeite at higher pressures (reactions (5) & (6)).

\[
2\text{Mg}_2\text{SiO}_4 + \text{NaAlSi}_3\text{O}_8 \rightleftharpoons 4\text{MgSiO}_3 + \text{NaAlSiO}_4
\]

\[
\text{Mg}_2\text{SiO}_4 + \text{NaAlSi}_3\text{O}_8 \rightleftharpoons 2\text{MgSiO}_3 + \text{NaAlSi}_2\text{O}_6
\]
Table 2. Results of experiments on the stability of plagioclase in olivine-rich compositions. Unless otherwise stated (see footnotes), the identification of olivine, pyroxenes, garnet and plagioclase is based on X-ray diffraction data. Spinel was readily identified optically and confirmed by X-ray data in most cases.

Abbreviations: Fo — forsterite, Fa — fayalite, Ol — olivine, Px — pyroxene, Sp — spinel, An — anorthite, Pl — plagioclase, Ga — garnet

<table>
<thead>
<tr>
<th>Corrected Pressure Kb</th>
<th>Temperature °C</th>
<th>Time Hrs.</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORSTERITE + ANORTHITE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>1250</td>
<td>4</td>
<td>Glass + 10% Seed (Px + Sp) Fo + An</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>1250</td>
<td>4</td>
<td>&quot;</td>
<td>Fo + Px' + Sp</td>
</tr>
<tr>
<td>9.0</td>
<td>1250</td>
<td>3</td>
<td>Glass + quench Fo</td>
<td>Fo + An</td>
</tr>
<tr>
<td>9.9</td>
<td>1300</td>
<td>1</td>
<td>Glass + quench Fo</td>
<td>Fo + An</td>
</tr>
<tr>
<td>9.9</td>
<td>1300</td>
<td>1</td>
<td>&quot;</td>
<td>Fo + Px' + Sp</td>
</tr>
<tr>
<td>FAYALITE + ANORTHITE (runs in graphite capsules)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>1100</td>
<td>6</td>
<td>Fa + An</td>
<td>Fa + An + glass</td>
</tr>
<tr>
<td>9.0</td>
<td>1100</td>
<td>6</td>
<td>&quot;</td>
<td>Fa + Ga + glass</td>
</tr>
<tr>
<td>8.1</td>
<td>1100</td>
<td>6</td>
<td>Glass</td>
<td>Fa + An + glass</td>
</tr>
<tr>
<td>9.0</td>
<td>1100</td>
<td>6</td>
<td>&quot;</td>
<td>Fa + Ga + glass</td>
</tr>
<tr>
<td>9.0</td>
<td>1100</td>
<td>1</td>
<td>&quot;</td>
<td>Fa + Ga + An + glass</td>
</tr>
<tr>
<td>7.2</td>
<td>1100</td>
<td>6</td>
<td>Glass + 10% Seed (Ga + Fa) Hercynite + glass</td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>1100</td>
<td>2</td>
<td>&quot;</td>
<td>Fa + Hercynite + glass</td>
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<td>8.1</td>
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<td>&quot;</td>
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</tr>
<tr>
<td>6.3</td>
<td>1050</td>
<td>3</td>
<td>&quot;</td>
<td>Fa + An No garnet</td>
</tr>
<tr>
<td>7.2</td>
<td>1050</td>
<td>3</td>
<td>&quot;</td>
<td>Fa + An + Ga Minor garnet</td>
</tr>
<tr>
<td>7.2</td>
<td>1050</td>
<td>24</td>
<td>&quot;</td>
<td>Fa + An + Ga Minor garnet. Coarser grained but similar in garnet content to 3 hr run</td>
</tr>
<tr>
<td>8.1</td>
<td>1050</td>
<td>3</td>
<td>&quot;</td>
<td>Fa + An + Ga Common garnet, minor anorthite</td>
</tr>
<tr>
<td>5.4</td>
<td>900</td>
<td>24</td>
<td>&quot;</td>
<td>Fa + An (+ Ga) Garnet rare and crystals corroded</td>
</tr>
<tr>
<td>6.3</td>
<td>900</td>
<td>24</td>
<td>&quot;</td>
<td>Fa + An + minor garnet</td>
</tr>
<tr>
<td>6.3</td>
<td>900</td>
<td>88</td>
<td>&quot;</td>
<td>Fa + An + trace garnet, less garnet than in 24 hr run</td>
</tr>
<tr>
<td>7.2</td>
<td>900</td>
<td>24</td>
<td>&quot;</td>
<td>Fa + Ga + An. Garnet common, minor anorthite</td>
</tr>
<tr>
<td>8.1</td>
<td>900</td>
<td>26</td>
<td>&quot;</td>
<td>Fa + Ga No pyroxene or anorthite</td>
</tr>
</tbody>
</table>

If equation 5 represents a stable equilibrium relation, then it is possible that the olivine + labradorite mix could yield assemblages of orthopyroxene + olivine + plagioclase + nepheline at intermediate pressures. However, Bultitude (1968) has demonstrated the instability of nepheline + plagioclase + pyroxene + olivine assemblages relative to plagioclase + spinel + pyroxene in complex olivine nephelinite at very low pressure — probably due to combination of reactions (7), (8).
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<table>
<thead>
<tr>
<th>Corrected Pressure (Kb)</th>
<th>Temperature (°C)</th>
<th>Time (Hrs.)</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OLIVINE</strong> (Fo&lt;sub&gt;92&lt;/sub&gt;) + <strong>LABRADORITE</strong> (An&lt;sub&gt;92&lt;/sub&gt;) (runs in platinum capsules)</td>
<td></td>
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</tr>
<tr>
<td>9.0</td>
<td>1100</td>
<td>4</td>
<td>Ol + Pl</td>
<td>Ol + Pl</td>
</tr>
<tr>
<td>11.2</td>
<td>1100</td>
<td>4</td>
<td>Ol + Pl</td>
<td>Ol + Pl + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
</tr>
<tr>
<td>4.5</td>
<td>1100</td>
<td>2</td>
<td>Glass</td>
<td>Ol + Pl</td>
</tr>
<tr>
<td>6.7</td>
<td>1100</td>
<td>4</td>
<td>&quot;</td>
<td>Ol + Pl</td>
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<tr>
<td>9.0</td>
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<td>Ol + Pl</td>
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<tr>
<td>11.2</td>
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<td>3</td>
<td>&quot;</td>
<td>Ol + Pl + Px&lt;sup&gt;2&lt;/sup&gt; + minor Sp</td>
</tr>
<tr>
<td>13.5</td>
<td>1100</td>
<td>4</td>
<td>&quot;</td>
<td>Ol + Pl + Px&lt;sup&gt;1&lt;/sup&gt; + Sp Weak plagioclase reflections</td>
</tr>
<tr>
<td>9.0</td>
<td>1150</td>
<td>2</td>
<td>Ol + Pl</td>
<td>Ol + Pl</td>
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<tr>
<td>11.2</td>
<td>1200</td>
<td>1</td>
<td>Ol + Pl</td>
<td>Ol + Pl + minor Px&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>11.2</td>
<td>1200</td>
<td>2</td>
<td>Glass</td>
<td>Ol + Pl + Px&lt;sup&gt;1&lt;/sup&gt; + Sp Moderately strong plagioclase, weak orthopyroxene and spinel reflections.</td>
</tr>
<tr>
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<td>1200</td>
<td>2</td>
<td>Ol + Px + Sp&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Ol + Pl + Px&lt;sup&gt;1&lt;/sup&gt; + Sp Weak but definite plagioclase reflections</td>
</tr>
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<td>12.4</td>
<td>1200</td>
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<td>Glass</td>
<td>Ol + Pl + Px&lt;sup&gt;1&lt;/sup&gt; + Sp Weak plagioclase reflections</td>
</tr>
<tr>
<td>13.5</td>
<td>1200</td>
<td>2</td>
<td>Glass</td>
<td>Ol + ? P&lt;sub&gt;3&lt;/sub&gt; + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
</tr>
<tr>
<td>15.7</td>
<td>1200</td>
<td>1</td>
<td>Glass</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
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<tr>
<td>15.7</td>
<td>1200</td>
<td>4</td>
<td>Ol + Pl</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
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<td>1200</td>
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<tr>
<td>20.2</td>
<td>1200</td>
<td>4</td>
<td>Ol + Pl</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Ga Very weak orthopyroxene reflections</td>
</tr>
<tr>
<td>18.0</td>
<td>1300</td>
<td>1</td>
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<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
</tr>
<tr>
<td>20.2</td>
<td>1300</td>
<td>1</td>
<td>Ol + Pl</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Sp + minor Ga Very weak orthopyroxene reflections</td>
</tr>
<tr>
<td><strong>PYROLITE</strong> (runs in platinum capsules)</td>
<td></td>
<td></td>
<td></td>
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<td>2</td>
<td>Ol + Px&lt;sup&gt;2&lt;/sup&gt; + Pl</td>
<td>Ol + Px&lt;sup&gt;2&lt;/sup&gt; + Pl + ? Sp</td>
</tr>
<tr>
<td>4.5</td>
<td>1100</td>
<td>4</td>
<td>Ol + Px&lt;sup&gt;2&lt;/sup&gt; + Pl</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Pl + Sp minor orthopyroxene and rare green-brown spinel</td>
</tr>
<tr>
<td>6.7</td>
<td>1100</td>
<td>2</td>
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<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Pl + Sp minor orthopyroxene</td>
</tr>
<tr>
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<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + P&lt;sub&gt;3&lt;/sub&gt; + Sp More orthopyroxene than previous runs</td>
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<td>Ol + Px&lt;sup&gt;2&lt;/sup&gt; + ? P&lt;sub&gt;3&lt;/sub&gt; + Sp + glass</td>
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<td>2</td>
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<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + P&lt;sub&gt;3&lt;/sub&gt; + Sp + glass Enstatite laths with included plagioclase and spinel</td>
</tr>
<tr>
<td>9.0</td>
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<td>2</td>
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<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + P&lt;sub&gt;3&lt;/sub&gt; + Sp</td>
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<td>1</td>
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<tr>
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<td>2</td>
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<td>15.8</td>
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<td>Ol + Px&lt;sup&gt;2&lt;/sup&gt; + Pl</td>
<td>Ol + Px&lt;sup&gt;1&lt;/sup&gt; + Sp</td>
</tr>
</tbody>
</table>

**Footnotes:**

1. Pyroxene includes clinopyroxene and orthopyroxene, the latter identifiable on X-ray diffraction pattern.
2. Pyroxene mainly clinopyroxene. Orthopyroxene not identifiable by X-ray diffraction.
3. Plagioclase probably present in amount below detection limit by X-ray diffraction. Discontinuous grains of low (< 1.65) refractive index phase observed optically.
4. Synthesized at 15.7 kb, 1200°C.
In the light of this study it appears unlikely that nepheline and enstatite will coexist at moderate pressures in either basaltic compositions or in the olivine + labradorite mix.

There is no evidence amongst natural enstatites of high pressure origin nor from experimental studies, for significant solid solution of jadeite in enstatite or vice versa. Thus, the minimum conditions required for reaction (6) are those delimiting the jadeite stability field (Robertson, Birch & MacDonald 1957), i.e. approximately 21.5 kb at 1100°C or 23 kb at 1200°C. However, in the olivine + labradorite mix, reaction between olivine and anorthite molecule at lower pressures according to reaction (1) yields diopside. Diopside-jadeite solid solution (omphacite) is stable at lower pressures than pure jadeite (Kushiro 1965b), and reaction between olivine and labradorite to eliminate plagioclase will occur at lower pressures than reaction (6). The reaction between olivine and labradorite may be approximated as follows:

(9) \[ 3\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{Mg}_2\text{SiO}_4 \rightleftharpoons 3\text{CaMgSi}_2\text{O}_6 + 2\text{NaAlSi}_2\text{O}_6 \]

Extrapolation of the experimental data of Kushiro (1965b) and Birch & LeComte (1960) on omphacite + quartz and on jadeite and jadeite + quartz stability, suggests approximately 15 kb at 1100°C or 17 kb at 1200°C for elimination of plagioclase from the olivine + labradorite mix by equation (9). This is an approximation since the effects of Al-pyroxene solid solution and enstatite solid solution on the nature and stability of the clinopyroxene phase have not been considered.

The experimental data of Table 2 show that the first observable pyroxene + spinel occurs at 11.2 kb at both 1100°C and 1200°C. The data suggest that a slightly higher pressure is required for the beginning of reaction between magnesian olivine and labradorite than between forsterite and anorthite. However, this conclusion should be treated with some caution as the runs were not seeded with the high pressure assemblage, and metastable persistence of the olivine + labradorite assemblage in the 9 kb runs is possible. The data demonstrate the persistence of plagioclase to a higher pressure than for the Fo + An and Fa + An mixes, and the existence of
a five phase (olivine + orthopyroxene + clinopyroxene + plagioclase + spinel) stability field. At 1100°C plagioclase is present in the 13.5 kb run, and at 1200°C plagioclase disappears between 13.5 kb and 15.7 kb. Since the reactants were either glass or crystalline olivine + labradorite, metastable persistence of plagioclase to a higher pressure is possible in these runs, and the boundary for the stability field for plagioclase could not be very tightly located by reversals (i.e. growth of plagioclase from Ol + Px + Sp assemblages), because of the difficulty of distinguishing small amounts of plagioclase from possible incipient melting. However, a reversal was obtained in a run at 11.2 kb, 1200°C in which reactants of the Ol + Px + Sp assemblage were re-run and yielded the plagioclase-bearing, 5-phase assemblage. In contrast, anorthite is absent at pressures greater than 8.5 kb at 1200°C in the Fo + An mix.

In the higher pressure experiments on the olivine + labradorite mix, garnet appears from reactions involving spinel and pyroxene solid solution. Garnet first appears in minor amounts in the 18 kb, 1200°C run and between 18 kb and 20.2 kb at 1300°C. These conditions are similar to those at which garnet crystallized in the system Fo + An (2 : 1 mol.ratio) (Kushiro & Yoder 1966), and in diopside + enstatite + spinel systems (MacGregor 1965), but at considerably lower pressure than the appearance of garnet in the pyrolite composition (Green & Ringwood 1967c, 1969). The latter boundary has been confirmed by reversals, and the data illustrate the difficulty in extrapolation from simple to complex system — the presence of chromite solid solution in the spinel probably stabilizes the spinel bearing assemblage to higher pressures.

**Pyrolite**

The pyrolite composition, even at low pressures, contains the five phase assemblage olivine + orthopyroxene + clinopyroxene + plagioclase + spinel. However, at low pressures the orthopyroxene is a minor phase, olivine is a major phase and the uncommon spinel grains are brown in colour (with the presence of 0.72% Cr₂O₃, in the experimental mix the brown spinel is regarded as chromite-rich). The reaction between plagioclase and olivine yields a marked increase in orthopyroxene and spinel and a decrease in plagioclase; the spinel also changes to pale green in colour as it becomes more abundant. The highest pressure run in which plagioclase is considered to be stable is at 11.2 kb; this is based on the constancy of the Ol/Opx ratio (as deduced from relative intensities of characteristic X-ray reflections), and on the absence of low R. I. grains at higher pressures. Definitive plagioclase X-ray reflections could not be observed in any runs at pressure of 9 kb or more.

It may be inferred that the plagioclase (normative labradorite) in the pyrolite composition should disappear at lower pressures than in the olivine + labradorite mix, because of the presence of diopside in the low pressure
assemblage. The clinopyroxene solid solution formed at the highest pressures in the pyrolite mix would thus have a lower jadeite/diopside ratio than that of the olivine + labradorite mix. Consideration of the experimental data and comparison with the Fo + An and olivine + labradorite mixes leads to the conclusion that plagioclase persists to 11–12 kb at 1200°C, but the interval 8–11 kb is one in which plagioclase decreases in amount with increasing pressure. The decrease in plagioclase is accompanied by increase in spinel and pyroxene.

At higher pressures the olivine + pyroxenes + spinel assemblage gives way to olivine + pyroxenes + garnet ± spinel assemblage (Green & Ringwood 1967c, 1969).

Effect of Fe/Mg variation in olivine
The extrapolation, assuming positive dT/dP, of the boundaries between high and low pressure assemblages in both the Fa + An and Fo + An systems suggests that there is little pressure difference at a given temperature between the high pressure stability limit of iron-rich olivine and anorthite and magnesian olivine and anorthite. There is, however, a very large difference in the pressure required to form garnet — the almandine-grossular garnet (Alm$_{67}$Gross$_{33}$) appearing directly from olivine + anorthite reaction at 7 kb, 1000°C, whereas the pyrope-grossular garnet would appear at 13–15 kb, 1000°C from the olivine + pyroxenes + spinel assemblage in the magnesian composition (Kushiro & Yoder 1966). Reconnaissance studies on reactions between anorthite and olivine of various Fe/Mg values confirm the general conclusion that at temperatures near 1000°C the high pressure stability limit of plagioclase + olivine is relatively insensitive to Fe/Mg, but the nature of the reaction products is very sensitive. For olivines of intermediate Fe/Mg ratio, the olivine + anorthite assemblage gives way at higher pressures to olivine + spinel + Fe-rich garnet + pyroxenes. The spinel decreases whereas garnet increases in amount and becomes more magnesian with increasing pressure.

Applications of experimental data
The experimental data presented have their main application in evaluating the near-solidus stability of plagioclase in olivine-rich, peridotitic compositions. In the olivine-normative basaltic compositions studied previously (Green & Ringwood 1967a), reaction between olivine and plagioclase occurred mainly between 8 kb and 11 kb, resulting in elimination of olivine, but persistence of plagioclase in px + pl + sp or px + pl + ga ± qz assemblages to higher pressures. In the ultramafic composition it is plagioclase which is eliminated, and olivine persists to higher pressures with spinel and aluminous pyroxenes. At high temperatures (>1000°C) the olivine + orthopyr-
oxene + clinopyroxene + spinel assemblage in ultramafic rocks overlaps the stability field of the intermediate pressure granulites (opx + cpx + plag ± ga, opx + cpx + plag + qz) and high pressure granulites (cpx + ga + plag ± qz), and in some compositions such as the pyrolite (Green & Ringwood 1967c), overlaps into the eclogite field at high temperatures. (Facies terms are used in the sense of Green & Ringwood 1967a).

The reliable extrapolation of the boundary between plagioclase-bearing and plagioclase-free peridotite to lower temperatures is not possible from the data presented. Assuming a moderate to large slope (dT/dP) for the boundary in pyrolite composition, the intersection of estimated geothermal gradients with this boundary would allow some estimation of the potential role of plagioclase peridotite ('plagioclase pyrolite') in the upper mantle (Ringwood 1966b, Green & Ringwood 1967c). It is clear from the present data and these earlier papers that plagioclase pyrolite could only occur beneath a normal continental crust (25-40 km) under conditions of extremely high geothermal gradient, and even then would be limited to a zone of <10 km thickness. In oceanic regions, plagioclase pyrolite is potentially more important at depths from 10-40 km, but uncertainty of the extrapolation to low pressure prevents firm conclusions. In regions of very high heat flow, such as mid-oceanic ridges, plagioclase pyrolite is probably present but restricted to levels above 40 km.

The data also permit some further deductions on the conditions of crystallization of the uncommon high temperature peridotite intrusions, such as Lizard (Green 1964a, 1967), Tinaquillo (MacKenzie 1960) and Serrania de la Ronda (Dickey 1969). In the Lizard peridotite, accepting a temperature of 1000°C-1200°C for the body during diapiric emplacement, the movement of the body from the field of stability of the olivine + aluminous pyroxenes + aluminous spinel to stability of olivine-pyroxenes + plagioclase (labradorite) implies movements from depths of at least 35 km to depths of 25-30 km or less. In the Tinaquillo example, accepting a similar temperature of crystallization, the absence of plagioclase and presence of spinel porphyroblasts and zoned pyroxenes (Green 1963) implies final equilibration of the peridotite mineralogy at depths of at least 35 km. Final crystallization at lower temperatures (800-900°C) would allow crystallization at somewhat shallower depths (≈ 30 km). The nature of the basic granulites of the aureoles of the two peridotites provides interesting comparisons in that the Lizard aureole does not contain almandine-pyrope garnet, but the granulites are characteristically opx + cpx + plag, locally with olivine (Green 1964b). The Lizard metamorphics are thus 'low-pressure granulites'. On the other hand, the Tinaquillo peridotite has granulites with cpx + ga + plag ± hornblende at the outer margin and cpx + opx + ga (minor) ± hornblende in included blocks. The Tinaquillo metamorphics are thus intermediate pressure granulites. The experimental data on basic and ultramafic rocks at high pressures provides confirmation of the compatibility of the recrystallized assemblages in the ultramafic bodies.
and their aureoles, and allows some estimation of their conditions of crystal-
ization (Green 1967, O'Hara 1967).

An olivine tholeiitic or picritic magma, crystallizing in the lower crust at
depths corresponding to 6–10 kb, might yield accumulates containing
olivine, pyroxenes and plagioclase. Cooling of such accumulates at constant
pressure would result in incompatibility of olivine and plagioclase, while
temperatures were quite high (≈ 800–1000°C). The extent of reaction
would be kinetically controlled largely by the cooling rate of the body. It
is considered that these conditions would lead to corona formation, often of
concentric multistage type (Griffin & Heier 1969, Griffin 1970), as the
olivine and plagioclase passed successively through stability fields of pyrox-
enes + spinel, pyroxenes + spinel + garnet, pyroxenes + garnet. The
widespread occurrence of corona textures in basic rocks of the metamorphic
terrains of western Norway (Gjelsvik 1952) may reflect the high pressure
cooling histories of varied igneous intrusives emplaced in a pre-Caledonian,
metamorphic lower crust. The occurrences of high pressure coronas and
assemblages (including eclogites and garnet peridotites) in the 'axial' Cale-
donide zone may thus be a consequence of tectonic exposure of pre-Cale-
donian lower crust, rather than indicative of particularly high pressure
during later Caledonian regional metamorphism. Corona textures with
pyroxenes + spinel around magnesian olivine or garnet + clinopyroxene
around more Fe-rich olivine are considered to imply falling temperatures
in the range 1100–800°C at pressures of 6–10 kb (depths of 20–35 km).

The experimental data are also relevant to melting studies on peridotitic
compositions. The pressure interval of 8–12 kb, at solidus temperatures, is
also the pressure range over which melting of pyrolite composition produces
liquids of high-alumina type in equilibrium with residual olivine, aluminous
orthopyroxene and clinopyroxene (Green, Green & Ringwood 1967, Green
& Ringwood 1967b). In the 5-phase subsolidus assemblage, the minor
plagioclase enters the basaltic liquid at temperatures only slightly above the
solidus, and this is a major factor in producing the high alumina liquids.

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MINERALOGY OF PERIDOTITIC COMPOSITIONS
UNDER UPPER MANTLE CONDITIONS

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MINERALOGY OF PERIDOTITIC COMPOSITIONS
UNDER UPPER MANTLE CONDITIONS

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experimental study of the stability fields at high pressure of diopside peridotite, aluminous pyroxene (+ spinel) peridotite, garnet peridotite, has been carried out in compositions ching estimates of the average undifferentiated upper mantle (pyrolite). The appearance of garnet at high pressures results from one of two complex reactions:

spinol + pyroxene ⇌ olivine + garnet,
(solid solutions)

luminous pyroxene ⇌ garnet + pyroxene (lower Al₂O₃).
(solid solution)

The model pyrolite composition, garnet appears at 21 kb (0°C) to 24 kb (1300 °C) by reaction (a) but at temperatures over 1300 °C spinel is absent from the low pressure assemblage garnet develops by reaction (b) at pressures of 24 kb (0°C) to 31 kb (1500 °C). Reactions (a) and (b) have very different P, T gradients. In the garnet peridotite field, the amount of garnet is inversely proportional to the alumina content of the pyroxenes. This is confirmed by microprobe analyses of orthopyroxene (ranging from 6.0 to 2.2% Al₂O₃, 0.7-0.9% Cr₂O₃) coexisting with garnet, olivine and clinopyroxene. Coexisting clinopyroxenes have higher R₂O₃ content and exhibit a variable, temperature dependent enstatite solid solution.

The experimental data are applied to estimate mineralogical, density and seismic velocity variations along oceanic and continental geothermal gradients in a pyrolite upper mantle. Although the mineralogical variation may produce a low velocity zone, the alternate explanation of incipient or minor partial melting is preferred. Experimental data on the maximum stability limit of amphibole in pyrolite (with 0.1-0.2% water) are presented showing that amphibole breaks down to olivine + pyroxenes + garnet + fluid phase at approximately 29 kb, 1000 °C. The instability of amphibole at depths >80-90 km is considered to result in a zone of incipient or minor melting in a pyrolite upper mantle with 0.1-0.2% water. The nature of the liquid in this zone is considered to be highly undersaturated olivine basanite or olivine nephelinite.

Introduction

The uppermost region of the Earth's mantle acts as immediate source region for basaltic magmas and one part of the mantle "sampled" by magmatic petrotectonic processes and, in certain circumstances, exceeded for direct petrological and geochemical investigation. The properties of the upper mantle can also be more closely defined by geophysical methods, particularly by seismological and gravity studies. The weight of evidence and geophysical evidence on upper mantle position favours an overall peridotitic composition arguments against an alternative of eclogitic composition have previously been presented (RINGWOOD, 1966; RINGWOOD, 1966a). Other authors (ITO and KENNEDY, 1967; KUSHIRO and KUNO, 1963; KUSHIRO et al., 1968; HESS, 1964; HARRIS et al., 1967) have derived possible upper mantle compositions on other grounds or have selected specific samples of peridotite xenoliths. These compositions also have essential Al₂O₃, CaO and Na₂O and, like the pyrolite compositions, may crystallize in four different mineral assemblages within the P, T conditions of the upper mantle (minor accessory minerals such as ilmenite, apatite, phlogopite are omitted):

a. Olivine + amphibole ± enstatite ("ampholite"),
b. Olivine + pyroxenes + plagioclase + chromite, ("plagioclase pyrolite")
c. Olivine + aluminous pyroxenes ± spinel, ("pyroxene pyrolite")
d. Olivine + pyroxenes + garnet ("garnet pyrolite").

2. Previous investigations

Experimental investigations of the stability relationships of these assemblages have been undertaken by several authors using either complex systems or simple, end member systems. Reactions between olivine and plagioclase to yield aluminous pyroxenes + spinel have been studied for the system Fo—An (KUSHIRO and YODER, 1966) and for the systems Fo—An, olivine (Fo92)-labradorite (Ab41An39), and for pyrolite composition (GREEN and HIBBERSON, 1969). These investigations show that plagioclase pyrolite will not occur as the stable mantle assemblage along typical geothermal gradients in either continental or oceanic regions but may be present in areas of particularly high heat flow and thin crust, e.g. if near-solidus temperatures are reached at depths of 25–35 km beneath mid-oceanic ridges. More interest centres on the conditions for the incoming of garnet and the role of garnet pyrolite and pyroxene pyrolite assemblages in upper mantle mineralogy.

MACGREGOR (1964, 1965) studied the reaction

\[
\text{pyroxene + spinel } \rightleftharpoons \text{ garnet + olivine} \tag{1}
\]

in the system MgO—Al$_2$O$_3$—SiO$_2$ and in the system MgO–CaO–Al$_2$O$_3$–SiO$_2$. In the latter system MACGREGOR (1965) used pyroxene proportions (enstatite/diopside) of 75/25, 25/75 and 0/100. KUSHIRO and YODER (1965) studied the analogous reaction for enstatite: diopside = 50:50 and established a boundary for the incoming of garnet close to that found by MACGREGOR for the enstatite + diopside bearing mixtures. MACGREGOR (1964) did not report olivine on the low pressure side of the reaction (1) in the system MgAl$_2$O$_4$ + 4MgSiO$_3$ but did observe olivine in the low pressure assemblages (Ol + Al-pyroxene(s) + spinel) in the systems 2MgAl$_2$O$_4$ + CaMgSi$_2$O$_6$ + 6MgSiO$_3$ and 2MgAl$_2$O$_4$ + 3CaMgSi$_2$O$_6$ + 2MgSiO$_3$. The appearance of olivine results from a reaction

\[
\text{pyroxene + spinel } \rightleftharpoons \text{ aluminous pyroxene + olivine} \tag{2}
\]

The apparent absence of reaction (2a) (MACGREGOR, 1964) contrasts with other data showing high solubility of Al$_2$O$_3$ in enstatite and with the presence of reaction (2b) (or an analogous reaction involving (CaAl$_2$Si$_2$O$_6$) solid solution) in the Ca-bearing system. The study of reaction (1) in the system MgO–CaO–Al$_2$O$_3$–SiO$_2$ MACGREGOR (1965) utilized mixes containing both high and low pressure assemblages and the position of the reaction boundary was determined by changes in the intensity of garnet and pyroxene reflections. However, the metastable growth of garnet from aluminous pyroxene (e.g. reaction (3))

\[
\text{mMgSiO}_3 + \text{nMgAl}_2\text{O}_4 \rightleftharpoons \text{Mg}_3\text{Al}_3\text{Si}_3\text{O}_{12} + (m-2)\text{MgSiO}_3 + (n-1)\text{Mg}_2\text{SiO}_4
\]

may have proceeded more rapidly than reaction of aluminous pyroxene with olivine to yield less aluminous pyroxene and spinel. A difficulty involving metastable growth of garnet may account for some results of KUSHIRO and YODER (1966, fig. 2) in which, using a mix of An + Fo seeded with Ga + Fo + Cpx, they obtained some runs in which garnet and plagioclase appeared in favour of Cpx + Opx + Fo + Sp but other runs at lower pressure in which the seed phases, Ga + Fo + Cpx, increased at the expense of An + Fo. Although there are no true reversals, it would seem that the boundary for reaction (1) should lie at higher pressures at 1100°–1300 °C, than shown by KUSHIRO and YODER (1966).

Other apparent discrepancies exist in the experimental data attempting to define the conditions for reaction (3), i.e. the breakdown of aluminous enstatite to garnet and less aluminous pyroxene. BOYD and ENGLA (1964) and MACGREGOR and RINGWOOD (1964) carried out experiments homogenizing different garnet + pyroxene mixtures to a single pyroxene phase using pyrope and enstatite and natural pyrope-rich garnet and enstatite respectively. The natural enstatite in equilbrium with garnet contained 1.5–2 mol% molar (Al, Cr, Fe)$_2$O$_3$ in solid solution than the enstatite.
MgO–Al₂O₃–SiO₂ system. Ringwood et al. (1964) and Ringwood (1966) integrated the data from the olivine + pyrope studies with the pyrolite (Ringwood, 1966a) composition* to infer stability fields for the assemblages olivine + pyroxenes + spinel, olivine + aluminous pyroxenes, and olivine + pyroxenes + garnet. Direct experimental study (Green and Ringwood, 1967a) on the pyrolite III revealed a much lower solubility of Al₂O₃ in orthopyroxene than that predicted from the study of the simple systems—this resulted in persistence of spinel to higher temperature (≈1200 °C, 11 kb or ≈1300 °C, 23 kb) than the 900 °C predicted by Ringwood et al. (1964) and in appearance of garnet from breakdown of aluminous pyroxene at lower pressures (≈26.5 kb at 1400 °C) than previously predicted (39 kb at 1400 °C). These surprisingly large differences imply that the presence of coexisting olivine or clinopyroxene considerably alters the solubility of Al₂O₃ in orthopyroxene—this can readily occur if the coexisting phases can enter solid solution in either garnet or orthopyroxene. The addition of clinopyroxene to the assemblage obviously establishes new partition relations involving grossular solid solution in garnet and diopside solid solution in enstatite. However MacGregor and Ringwood (1964) found higher solubilities of garnet in orthopyroxene for the natural enstatite (52% CaO) + garnet (5.21% CaO) mixes than for the enstatite + pyrope system. MacGregor and Ringwood (1964) homogenized mixtures of 50% garnet, 50% enstatite to a pyroxene phase at 30 kb, 1500 °C implying that the pyroxene contained 3.0% CaO (by weight)—this either exceeds or is very close to saturation in diopside solid solution for these compositions. More detailed work is required, attempting to eliminate the possibility of metastable reactions or other experimental uncertainties. From the data already obtained, it is clear that the reaction (1) is one in which the pyroxene will vary in composition along the reaction boundary. This boundary is actually the locus of intersections of reactions (2) and (3) which define the coordinates of reactions (1), (2) and (3), either in simple systems or in complex natural peridotitic compositions. More detailed work is required, attempting to eliminate the possibility of metastable reactions or other experimental uncertainties. From the data already obtained, it is clear that the reaction (1) is one in which the pyroxene will vary in composition along the reaction boundary. This boundary is actually the locus of intersections of reactions (2) and (3) which define the curves of constant Al₂O₃ content of pyroxene in peridotitic compositions. The position of reaction (1) will also depend sensitively on the spinel composition.

From the preceding summary of published data, it is apparent that there is as yet no general agreement on the P, T coordinates of reactions (1), (2) and (3), either in simple systems or in complex natural peridotitic compositions. More detailed work is required, attempting to eliminate the possibility of metastable reactions or other experimental uncertainties. From the data already obtained, it is clear that the reaction (1) is one in which the pyroxene will vary in composition along the reaction boundary. This boundary is actually the locus of intersections of reactions (2) and (3) which define the curves of constant Al₂O₃ content of pyroxene in peridotitic compositions. The position of reaction (1) will also depend sensitively on the spinel composition.

* This agreement may be fortuitous as Green and Ringwood (1967a) applied a (−10%) pressure correction while Ito and Kennedy (1967) applied no pressure correction. It should also be noted that MacGregor (1964, 1965, 1967) did not apply a pressure correction.

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(Cr$_2$O$_3$/Al$_2$O$_3$ ratio) in complex compositions and this will vary due to coupled reaction (2) with pyroxene.

With the complexity of the reactions in mind, there is much to be said for the direct experimental testing of model pyrolite compositions. In the following sections the data obtained on the model pyrolite compositions of Green and Ringwood (1963) and Ringwood (1966a) are summarized and emphasis is placed on the attempts to establish reaction boundaries by unequivocal reversals.

3. Experimental data on the incoming of garnet in pyrolite

3.1. Experimental methods

The experimental compositions (table 1) were prepared from AR grade chemicals, carefully ground and reacted together under high temperature reducing conditions and then analyzed for FeO and Fe$_2$O$_3$ contents. The initial mixes were extremely finegrained ($\leq$1 $\mu$m) and consisted of olivine, clinopyroxene, orthopyroxene, plagioclase and minor chromite and ilmenite. To facilitate identification of minor phases and of the presence or absence of small degrees of partial melting, compositions were prepared which are equivalent to the pyrolite compositions of table 1 after extraction of 50 % olivine (Mg$_{2+}$Fe$_{2-}$) from pyrolites I and II and after extraction of 40 % olivine (Mg$_{91.5}$Fe$_{8.0}$Ni$_{0.4}$Mn$_{0.1}$) from pyrolite III. In all experiments conducted with these modified pyrolite compositions, excess olivine was present. Hence the above procedure did not affect in any way the equilibrium relationships which are discussed below.

Crystalization of the experimental compositions was carried out using a single-stage, piston-cylinder apparatus and a pressure correction of $-10\%$ was applied to the nominal pressure for all runs. Samples were run in both platinum capsules and in graphite capsules. The run conditions using platinum capsules were such that iron loss to the Pt capsule was less than 25% of the amount present. Analyses of samples after experimental runs are listed in table 1a, the average iron content is 5.7% FeO, 0.7% Fe$_2$O$_3$ yielding a normative composition with approx. 33% olivine and 30% enstatite. The worst examples (in table 1a) give normative olivine of approximately 31% and 33% enstatite.

Microprobe analyses across a polished sample (36 kb, 22.5 kb, 20.3 kb, 1500 kb) from pyrolite III less 40% olivine (E. Kiss, analyst).

### Table 1

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<tr>
<th>Pyrolite</th>
<th>Pyrolite</th>
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<th>Pyrolite</th>
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<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>III</td>
</tr>
<tr>
<td>% total Fe as FeO</td>
<td>% FeO</td>
<td>% Fe$_2$O$_3$</td>
<td>% total Fe as FeO</td>
</tr>
<tr>
<td>27 km</td>
<td>1500°C</td>
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</tr>
<tr>
<td>29.3 km</td>
<td>1500°C</td>
<td>0.33</td>
<td>5.18</td>
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<tr>
<td>30.4 km</td>
<td>1500°C</td>
<td>0.33</td>
<td>5.11</td>
</tr>
<tr>
<td>29.3 km</td>
<td>1400°C</td>
<td>1.00</td>
<td>5.10</td>
</tr>
<tr>
<td>30.4 km</td>
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<td>24.8 km</td>
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</tr>
<tr>
<td>20.3 km</td>
<td>1200°C</td>
<td>2.00</td>
<td>6.89</td>
</tr>
<tr>
<td>22.5 km</td>
<td>1100°C</td>
<td>4.00</td>
<td>7.17</td>
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MINERALOGY OF PERIDOTITIC COMPOSITIONS UNDER UPPER MANTLE CONDITIONS

In the experiments on the stability of amphibole, the methods used should outline the maximum stability of amphibole at 1000 °C and were designed to specifically test the model that pyrolite contains 0.1-0.2% H₂O at shallow mantle depths. The use of a very small water content also avoids the problems of large degrees of melting and depression of the solidus, and of the possibility of solubility of components in a vapour phase. The starting material for these runs was prepared by adding 0.3% H₂O to the “pyrolite III less 40% olivine” mix. This mix was run at 10.8 kb, 900 °C for 4½ hrs yielding a fine-grained assemblage of olivine, pyroxenes and amphibole (≈15%). This was then rerun at 1000 °C and at pressures of 18 kb to 29 kb and examined carefully by optical and X-ray methods for the disappearance of amphibole and the appearance of garnet.

3.2. Experimental results

The results of the determination of the synthesis fields for garnet pyrolite and pyroxene pyrolite are presented in fig. 1. The data points denote the phase assemblages present in pyrolite III composition. Plagioclase pyrolite is stable under dry conditions on the low pressure side of AB. Between AB and ELF, both garnet and plagioclase are absent and the mineral assemblage is dominated by aluminous pyroxenes. Within this field, spinel is present as a minor phase at temperatures below the line marked K but only olivine, aluminous pyroxenes and accessory ilmenite are present at higher temperatures. Garnet first appears in trace amounts along the line EJ and spinel remains up to solidus temperatures on the low pressure side of EJ. Garnet and spinel co-exist together over a very small pressure interval on the high pressure side of EJ. The triangular P, T field FLJ is one in which the olivine + aluminous pyroxenes assemblage occurs in pyrolite III but olivine + aluminous pyroxenes + garnet occurs in pyrolites I and II.

The boundary for the appearance of garnet was apparently defined by different reactions at low and high temperatures and it was desirable to obtain reversals.
Fig. 1. Experimental runs on pyrolite III composition. Garnet is absent on the low pressure and present on the high pressure side of ELJ. Spinel is absent on the high temperature side of the line K. In pyrolites I and II garnet is present on the high pressure side of ELJ. (From Green and Ringwood, 1967a).

across these boundaries as previous data (Boyd, 1960) had demonstrated difficulty in nucleation of magnesian garnet near its low pressure stability limit. Reversals involving complete disappearance of garnet on the low pressure side of the boundary, were achieved at 1400 °C and 1200 °C (table 2). The starting mix for the 1400 °C reversals was a large capacity run at 36 kb, 1000 °C, 3 hrs yielding fine grained olivine and pyroxene and a very poikilitic garnet. For the 1200 °C reversal, the starting material was a 50:50 mix of runs carried out at 1200 °C, 18 kb, 2 hrs and 1200 °C, 27 kb, 2 hrs. The reversals at 1400 °C and 1200 °C confirm the position of the boundaries established from the olivine + pyroxenes + plagioclase + chromite starting mixtures. The analysis of the roles of spinel and aluminous pyroxene gives a theoretical explanation for the change in slope of the boundary marking the appearance of garnet in pyrolite III and the absence of such a change in slope of the boundary in pyrolites I and II. Microprobe analyses of orthopyroxene (table 4) show regular variations in Al$_2$O$_3$ and CaSiO$_3$ solid solution which are themselves very good evidence that the experimental assemblages closely approach equilibrium.

In the runs (table 3) on the olivine + amphibole + pyroxenes mix, amphibole breaks down finally between 27 kb and 28.8 kb at 1000 °C. There is a transition assemblage of olivine + pyroxenes + garnet + amphibole from 23.5 kb to 28 kb. In this assemblage the amount of garnet is less than in lower pressure runs. Experiments on the stability of amphibole in basaltic compositions (Essene et al., 1970) have demonstrated that amphibole may form readily from (glass + H$_2$O) mixtures and persist metastably at high pressures and temperatures. This possibility has not been fully tested in the

Table 2

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Capsule</th>
<th>Pressure (kb)</th>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Starting material</th>
<th>Products</th>
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<tr>
<td>1096</td>
<td>Graphite</td>
<td>27.0</td>
<td>1450</td>
<td>1</td>
<td>OI+Opx+Cpx+Ga</td>
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<td>OI+Opx+Cpx+Ga</td>
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<tr>
<td>1099</td>
<td>Graphite</td>
<td>25.9</td>
<td>1400</td>
<td>1</td>
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<td>OI+Opx+Cpx</td>
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<td>1055</td>
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<td>1400</td>
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<td>OI+Opx+Cpx+Plag+Chromite</td>
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<tr>
<td>1100</td>
<td>Graphite</td>
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<td>OI+Opx+Cpx+Ga</td>
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<tr>
<td>1016</td>
<td>Pt</td>
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<td>1400</td>
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<td>OI+Opx+Cpx+Rare Ga</td>
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<tr>
<td>2289</td>
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<td>20.7</td>
<td>1200</td>
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<td>50% (OI+Opx+Cpx+Ga)</td>
<td>OI+Opx+Cpx+Rare Spinel</td>
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<tr>
<td>2290</td>
<td>Pt</td>
<td>22.5</td>
<td>1200</td>
<td>4</td>
<td>50% (OI+Opx+Cpx+Sp)</td>
<td>OI+Opx+Cpx+Ga</td>
</tr>
</tbody>
</table>

(minor garnet but with euhedral form)
Table 3

<table>
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<tr>
<th>Run no.</th>
<th>Pressure (kb)</th>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Starting material</th>
<th>Products</th>
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<tr>
<td>2170</td>
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<td>1100</td>
<td>7</td>
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<td>Ol+Amph+Px</td>
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<td>2171</td>
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<td>1000</td>
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<td>2189</td>
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<tr>
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<td>Ol+Px+minor Ga+trace amphibole</td>
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<td></td>
<td></td>
<td></td>
<td>10% Ol+Px+Ga</td>
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</table>

The present experiments although the higher temperature of the runs and the persistence of amphibole in a 48 hr run seeded with garnet + pyroxene + olivine at 25.2 kb, 1000 °C suggest that the effect may be small. Another difference from the experiments on basaltic amphibolite is that the experiments on pyrolite are devised with specific model i.e. mantle composition with 0.1-0.2% water (RINGWOOD, 1969), in mind and the problem of partial melting at low temperatures for $P_{H_2O} = P_{total}$ has been avoided. KUSHIRO et al. (1968) reported data on melting of a lherzolite nodule under anhydrous and hydrous conditions and found the solidus to be 1100 °C for $P_{H_2O} = P_{total}$ at 20-30 kb. They did not report amphibole at 26 kb, 980 °C but apparently used optical methods only in identification of phases and minor amphibole may have been missed.

Partial analyses by electron probe micro-analyser are listed in table 4. The orthopyroxenes, because of their porphyroblastic habit, could be analysed with similar accuracy to those in partial melting runs (GREEN and RINGWOOD 1967b) but the finer grain size of olivine and clinopyroxene and the poikilitic nature of the garnet made analysis more difficult. The figures given in table 4 include only those grains where two or more consecutive analyses (2-3 μ steps) gave consistent analytical data. The data show a very clear pattern of increasing $Al_2O_3$ solubility in orthopyroxene with increasing pressure within the garnet pyrolite field. The $Al_2O_3$ content of orthopyroxene from pyrolite III at the incoming of garnet (boundary LF, fig. 1) is 1.0 ± 0.2%. Coexisting clinopyroxene contains approximately 7.7% $Al_2O_3$ and the $Cr_2O_3$ contents are 0.9% $Cr_2O_3$ (orthopyroxene) and ≥1.0% $Cr_2O_3$ (clinopyroxene). The higher $Al_2O_3 + Cr_2O_3$ content of the clinopyroxene is due to NaR$_3$Si$_2$O$_6$ solid solution. The minimum $Al_2O_3$ content of analyzed orthopyroxene is 2.2% at 40.5 kb, 1300 °C. Clinopyroxene contains 4.6% at 36 kb, 1300 °C in equilibrium with orthopyroxene with 2.6% $Al_2O_3$. The degree of mutual solid solution between pyroxenes shows a consistent pattern although the difficulty of analysing the small clinopyroxenes prevents any confident statement on limits of pyroxene solid solution in the complex composition. Orthopyroxene (∼En$_{90}$) coexisting with clinopyroxene contains approximately 2.4% CaO at 1500 °C, 2.2% CaO at 1400 °C, 2.0% CaO at 1350 °C and 1-5% CaO at 1300 °C. Coexisting clinopyroxene contains ≥11.4% CaO at 1400 °C and ≥14.5% CaO at 1350 °C – this is a higher CaO content than in clinopyroxene obtained at similar temperatures at 9-18 kb from more iron-rich basaltic compositions (GREEN and RINGWOOD, 1967b, p. 136-8). The garnets are more Fe-rich than coexisting clinopyroxene and olivine and contain 4.5-5.0% CaO and ≈1.7% $Cr_2O_3$. Higher values of CaO (6.9% and 5.6%) are probably due to small clinopyroxene inclinations.

The experimental data on pyrolite III composition are summarized in fig. 2 in which we have plotted curves showing maximum solubility of $Al_2O_3$ (with ≈0.8% $Cr_2O_3$ in addition) in orthopyroxene coexisting with garnet, olivine and clinopyroxene. Data are inadequate to draw similar curves in the olivine + py-
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (kb)</th>
<th>Time (hrs)</th>
<th>Sample capsule</th>
<th>Phase analysed</th>
<th>Garnet content</th>
<th>Remarks</th>
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<tr>
<td>1500</td>
<td>22.5</td>
<td>0.33</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>≈ 50% melting, OI + Opx + Quench, Opx &gt; OI</td>
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<tr>
<td>1500</td>
<td>27.0</td>
<td>0.33</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>Minority melting, OI + Opx + Cpx + Quench</td>
</tr>
<tr>
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<td>29.3</td>
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**Pyrolite III less 40% olivine**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (kb)</th>
<th>Time (hrs)</th>
<th>Sample capsule</th>
<th>Phase analysed</th>
<th>Garnet content</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450</td>
<td>27.0</td>
<td>0.66</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>No identifiable melting, OI + Opx + Cpx</td>
</tr>
<tr>
<td>1400</td>
<td>22.5</td>
<td>1.0</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>Local patchy melting, OI + Opx + Cpx</td>
</tr>
<tr>
<td>1400</td>
<td>24.8</td>
<td>1.0</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>Minor melting, water access, OI + Opx + Cpx</td>
</tr>
<tr>
<td>1400</td>
<td>25.9</td>
<td>1.0</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>No identifiable melting, OI + Opx + Cpx</td>
</tr>
<tr>
<td>1400</td>
<td>27.0</td>
<td>1.0</td>
<td>Pt</td>
<td>Opx</td>
<td>Nil</td>
<td>No identifiable melting, OI + Opx + Cpx + Ga</td>
</tr>
</tbody>
</table>

**Pyrolite I less 50% olivine**

| Temperature (°C) | Pressure (kb) | Time (hrs) | Sample capsule | Phase analysed | Garnet content | Remarks       |
|-----------------|--------------|------------|----------------|---------------|---------------|---------------|--------------|
| 1400            | 22.5         | 1          | Pt             | Opx           | Minor         | No melting, OI + Opx + Cpx + Ga |
| 1400            | 24.8         | 1          | Pt             | Opx           | Minor         | No melting, OI + Opx + Cpx + Ga |
| 1350            | 24.8         | 2.0        | Graphite       |               | Nil           | No garnet, no melting, OI + Opx + Cpx |
| 1350            | 25.9         | 2.0        | Graphite       |               | Minor         | No melting, OI + Opx + Cpx + Ga |
| 1350            | 27.0         | 2.0        | Graphite       |               | Minor         | No melting, OI + Opx + Cpx + Ga |
| 1300            | 36.0         | 4          | Graphite       |               | Minor         | OI + Opx + Cpx + Ga |
| 1300            | 40.5         | 4          | Graphite       |               | Minor         | OI + Opx + Cpx + Ga |

**Remarks**

- Nil: No garnet
- Minor: OI + Opx + Cpx
- Common: OI + Opx + Cpx + Ga
Mineralogy of peridotitic compositions under upper mantle conditions

In the following discussion, it is assumed that the average composition of the upper mantle beneath oceanic and geologically “young” regions is that of pyrolite III. In continental regions and particularly in Precambrian shield regions, there is probably a much greater proportion of refractory residual peridotite at shallower levels and the upper mantle may be chemically zoned. Mineralogical variation in the upper oceanic mantle is thus determined by the intersection of geothermal gradients with the stability fields of fig. 1.

The variation of temperature in the continental and oceanic crusts and upper mantle has been discussed by Clark (1962) and Clark and Ringwood (1964). It is clear from these papers that there is a large difference

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**Fig. 2.** Diagram illustrating the $P$, $T$ fields of different mineral assemblages in pyrolite III composition. The figures $1\% Al_2O_3$, $Al_2O_3$ etc. refer to the $Al_2O_3$ content of orthopyroxene in equilibrium with garnet in the garnet pyrolite field. The oceanic and Precambrian shield geotherms are those illustrated by Ringwood et al. (1964). (From Green and Ringwood, 1967a.)

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4. Mineralogy in a pyrolite upper mantle

In the following discussion, it is assumed that the average composition of the upper mantle beneath oceanic and geologically “young” regions is that of pyrolite III. In continental regions and particularly in Precambrian shield regions, there is probably a much greater proportion of refractory residual peridotite at shallower levels and the upper mantle may be chemically zoned. Mineralogical variation in the upper oceanic mantle is thus determined by the intersection of geothermal gradients with the stability fields of fig. 1.

The variation of temperature in the continental and oceanic crusts and upper mantle has been discussed by Clark (1962) and Clark and Ringwood (1964). It is clear from these papers that there is a large difference
between oceanic and stable shield geotherms and that this difference takes the form illustrated in fig. 2. Nevertheless, the specific form of the curves, particularly their “convexity” and closeness of approach to the pyrolite solvus, depend sensitively on knowledge of the magnitude of radiative heat transfer in the upper mantle. No unique solution for geothermal gradients is currently possible but a general evaluation of the role of mineralogical zoning in the upper mantle can best be obtained by consideration of the two examples in fig. 2.

Along the Precambrian shield geotherm, the probability of chemical zoning would limit the possible phase assemblages. If rocks of composition approaching pyrolite occur locally, then there may be an extremely limited zone near the base of the crust where these would crystallize to olivine + orthopyroxene (1% \( \text{Al}_2\text{O}_3 \)) + clinopyroxene + spinel assemblages. Similar compositions below about 35–40 km would yield olivine + orthopyroxene (1–2% \( \text{Al}_2\text{O}_3 \)) + clinopyroxene + garnet assemblages and it may be noted that the garnet content would be relatively high (e.g. 12% garnet in pyrolite III composition). No regular change in mineralogy would occur for rocks of pyrolite composition along the Precambrian shield geotherm.

The picture is very different along the oceanic geotherm. The olivine + orthopyroxene + clinopyroxene + spinel assemblage is stable in pyrolite composition to depths of 60–70 km. Within this interval the amount of spinel would decrease and the \( \text{Al}_2\text{O}_3 \) content of pyroxenes would increase with increasing depth (reaction (2)). Prior to the incoming of garnet at about 60–70 km and about 1000 °C, aluminous spinel would coexist with orthopyroxene containing about 3% \( \text{Al}_2\text{O}_3 \). An intersection of the geotherm with the phase boundary at a higher temperature than that illustrated in fig. 2 would yield assemblages with less spinel and with orthopyroxene of higher \( \text{Al}_2\text{O}_3 \) content (4–5% \( \text{Al}_2\text{O}_3 \)).

An extremely steep geothermal gradient, possibly realized only in regions actively producing basaltic magmas, would be required to enter the olivine + aluminous enstatite (6% \( \text{Al}_2\text{O}_3 \)) + aluminous clinopyroxene field. In regions of partial melting and magma generation, such gradients must be attained and it may be noted that garnet does not appear on the pyrolite III (anhydrous) solvus until depths > 100 km are reached.

At depths of 60–70 km on the oceanic geotherm, garnet appears from reaction (1) and is in equilibrium with orthopyroxene containing about 3% \( \text{Al}_2\text{O}_3 \). It is estimated that about 6% garnet would appear in pyrolite III composition at 60–70 km on the geothermal gradient illustrated. If the geothermal gradient intersected the boundary at a higher temperature, the amount of garnet appearing would be correspondingly less, e.g. about 3–4% garnet coexisting with orthopyroxene containing about 4.5% \( \text{Al}_2\text{O}_3 \).

The incoming of garnet due to reaction (1) at about 60–70 km in the oceanic mantle probably occurs over a relatively small depth interval (5–15 km). With further penetration along the geotherm into the garnet pyrolite field the amount of garnet may actually decrease – this will occur for temperature gradients steeper than the lines of constant \( \text{Al}_2\text{O}_3 \) content of orthopyroxene shown in fig. 2. For the gradient shown, pyrolite I will contain about 5% garnet at depths between 90 and 120 km and the mineralogy will remain constant over this interval. At depths greater than 120 km the geotherm gradient becomes increasingly transgressive with the lines of constant \( \text{Al}_2\text{O}_3 \) content for orthopyroxene. Thus, along this part of the geothermal gradient, the aluminous pyroxenes will gradually break down and yield an increasing garnet content and low-alumina pyroxenes. At depths of 200–250 km the assemblage pyrolite III will probably contain 11–12% of garnet.

The transition from aluminous pyroxenes + spinel pyrolite to garnet pyrolite at depths of 60–70 km in the oceanic mantle is in agreement with MacGregor (1964) data and with the conclusions of Ito and Kennedy (1967) on the stability of spinel and garnet-bearing peridotite. Although the present work does not support earlier conclusions (Ringwood et al., 1964; MacGregor and Boyd, 1964) that garnet pyrolite would not in general be stable until depths of 120–150 km, it provides excellent confirmation of the importance of this depth interval of the breakdown of aluminous pyroxenes to garnet + low alumina pyroxenes, the reactions on which these earlier conclusions were based. It should be pointed out that for pyrolite-like compositions with higher pyroxene/(Al, Cr)_2O_3 ratios than pyrolites I, II and III, the field of garnet pyrolite may not be entered until depths in excess of 120 km are reached – this is particularly relevant for mantle regions from which basaltic fractions have been removed (cf. MacGregor, 1967). Geothermal gradients steeper than that
Illustrated will have a similar effect in diminishing the amount of garnet produced at 60-70 km depth by reaction (1) and increasing the amount of garnet produced at deeper levels from reaction (3).

This brief discussion serves to illustrate the application of our experimental data to a more flexible range of mantle compositions and geothermal gradients than applied in fig. 2. The effects of the mineralogical variations along the oceanic geothermal gradient in causing variations of seismic velocity have been previously discussed by Green and Ringwood (1967a) and fig. 3 is produced from this paper.

The previous discussion and the data presented in fig. 3 illustrate the principle that both mineralogical changes and $P$, $T$ effects on $V_s$ are of primary importance in determining seismic velocity distributions in the upper mantle and may in themselves produce velocity minima in the upper 200 km of the mantle. Variations in the seismic velocity distributions illustrated in fig. 3 may be set up from fig. 2 by assuming various geothermal gradients and including the complexity of chemical variation from pyrolite to refractory peridotite and dunite.

5. Amphibole stability, partial melting and the low velocity zone

The mineralogical variations illustrated in fig. 3 may produce $V_s$ variations of approximately 2% but these are inadequate to account for a low velocity zone with a $V_s$ minimum of 4.1 km/sec below the uppermost mantle “lid” with $V_s \approx 4.6$ km/sec (Anderson, 1967; Berry and Knopoff, 1967). Other analyses of seismic data have inferred high values of seismic attenuation in the low velocity zone (Anderson, 1962, 1967), or have inferred very low values of shear modulus for the low velocity zone (Hales and Doyle, 1967). These considerations have led a number of authors to suggest that the low velocity zone of the mantle owes its existence to partial or incipient melting (Anderson, 1962, 1967; Oxburgh and Turcotte, 1968; Aki, 1967). Lambert and Wyllie (1968) carried out experiments aimed at establishing the high pressure stability limit
of amphibole for \( P_{\text{H}_2\text{O}} = P_{\text{total}} \) and suggested that the existence of interstitial amounts of water-rich fluid phase or water-rich silicate melts at depths below the stability limit of amphibole would lead to low seismic velocities. At greater depths, incorporation of water into high pressure hydrous magnesian silicates and hydroxylated pyroxenes (RINGWOOD and MAJOR, 1967; SCLAR et al., 1967) would produce a lower depth limit to this feature. The temperature of formation of magmas in the zone of amphibole instability and free water would be considerably below the anhydrous pyrolite solidus.

The data on maximum amphibole stability in pyrolite presented here support this hypothesis and suggest that amphibole would be stable along the shield geotherm of fig. 2 to depths of approximately 100–120 km and along the oceanic geotherm to depths of 80–90 km. The latter estimates derive from the data of table 3 and appearance of amphibole in pyrolite runs at 1200 °C, 18 kb and 22.5 kb, unless stringent precautions against drying of furnace components are observed.

RINGWOOD (1969) inferred a water content for the upper mantle of around 0.1 % and \( \text{CO}_2 \) contents may also be significant. The presence of a fluid phase, even if \( P_{\text{H}_2\text{O}} < P_{\text{total}} \), will depress the beginning of melting of pyrolite, probably by as much as 200 °C. RINGWOOD (1969) has presented arguments that a limited water content of around 0.1 % will have the effect of buffering a condition of incipient melting (≈1 % melting) so that comparatively large changes in temperature will have little effect on the amount or nature of the melt formed – this condition would not apply for melting of anhydrous pyrolite (GREEN and RINGWOOD, 1967a). The nature of hydrous magmas in equilibrium with olivine, orthopyroxene, clinopyroxene and garnet has been shown to be highly undersaturated olivine-rich basanite (GREEN, 1969, 1970) or possibly olivine-rich nephelinite and olivine melilite nephelinite (BULTITUDE and GREEN, 1968). Thus it is inferred that regions with a relatively shallow (80–120 kms) low velocity zone with proportionately large velocity decrease owe these characteristics to the presence of very small amounts of partial melting. The liquids formed by degrees of melting up to about 5% are highly undersaturated basalts and nephelinites and extraction of such liquids will leave regions of the low velocity zone selectively depleted in elements strongly partitioned into the initial liquid.

Movement of magma batches through overlying mantle may lead to breakdown of hydrous phases and selective element depletion by “wall rock reaction” process (GREEN and RINGWOOD, 1967b; GREEN, 1970). Models of mantle evolution such as those of OXBURGH and TURCOTTE (1968) and RINGWOOD (1969) would also lead to regions of the mantle overlying the low velocity zone which were partially or completely depleted in basaltic components.

6. Conclusions

Reactions producing garnet or garnet + olivine from assemblages with aluminous pyroxenes or pyroxenes + spinel are complex, involving sensitively \( P, T \) dependence of solid solution of \( \text{R}_2\text{O}_3 \) components in pyroxene. There is a need for further experiments to confirm data presented for several simple systems and natural assemblages and to evaluate the role of \( \text{Cr}_2\text{O}_3 \) and other components on the phase boundaries. The experimental study of the relations between pyroxene pyrolite and garnet pyrolite for the model mantle composition (RINGWOOD, 1966a) has established reversals for this boundary at key temperatures and enables application of these studies to evaluation of upper mantle mineralogy.

Pyroxene + spinel pyrolite is stable to depths of 60–70 km along an estimated sub-oceanic geotherm gradient. At this depth spinel and pyroxene react to form garnet and olivine. The amount of garnet formed from this reaction depends sensitively upon the temperature at which the geotherm intersects the spinel + garnet boundary. At temperatures in excess of 1000 °C, less than half the potential garnet in the pyrolite compositions forms by this reaction, the rest remaining in solid solution in aluminous orthopyroxene (>3% \( \text{Al}_2\text{O}_3 \)) and aluminous clinopyroxene. It has been demonstrated that mineralogical variation along geothermal gradients, particularly in oceanic regions, may be expected to strongly influence the seismic velocity distribution in the upper mantle.

No unique model of mineralogical or seismic velocity distribution in the upper mantle is presented, rather it is argued that regional variations in chemical composition (from pyrolite to refractory peridotite), and geothermal gradients will produce significant, regional differences in seismic velocity distributions.

Although mineralogical variation in anhydrous py
lithite may cause the existence of a low velocity zone, the alternate explanation of a zone of incipient or minor partial melting is preferred. The presence of this zone inferred to result from the presence of small (≈0.1%) quantities of water in the mantle, and from the instability of the hydrous phase amphibole at depths greater than about 80 km. The presence of a fluid, water-rich phase in limited quantity produces incipient melting well below the anhydrous pyrolite solidus. Liquids produced in this way are highly undersaturated sananes and nephelinites.

References

Kushiro, I., Y. Syono and S. Akimoto (1968) J. Geophys. Res. 73, 6023.
CONTRASTED MELTING RELATIONS IN A PYROLITE UPPER MANTLE UNDER MID-OCEANIC RIDGE, STABLE CRUST AND ISLAND ARC ENVIRONMENTS

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(Accepted for publication November 7, 1972)

ABSTRACT


The pyrolite model composition provides a satisfactory source composition for mantle-derived magmas insofar as major elements and "compatible" trace elements are concerned but there is evidence for mantle inhomogeneity in the abundances of "incompatible" minor and trace elements (e.g., K, Ti, P, Rb, Sr, light rare earth elements etc.). The composition of a magma, assuming a constant source composition, varies according to the pressure, temperature and water pressure or water content of the source region. The latter two variables essentially determine the degree of partial melting of the source region and in considering the chemical composition of the melt and nature of the residual phases, this parameter is of prime importance.

For high degrees (> 20% approx.) of partial melting of a pyrolite source region, magmas are of tholeiitic character but are of increasingly undersaturated and alkaline type for lower degrees of partial melting and high pressures. For any chosen degree of melting and fixed water content of the source region, magmas are more olivine-rich at higher pressures. For any chosen pressure and chosen degree of partial melting, magmas are less olivine-rich at high water contents (and thus lower temperatures). Quartz tholeiite magmas may be derived by ~ 30% melting of pyrolite under water-saturated conditions at pressures up to between 17 kbar and 20 kbar. These generalizations may be applied to understand the characteristic magmatism of mid-oceanic ridges, island chains, oceanic islands and orogenic regions.

INTRODUCTION

The hypotheses of continental drift and plate tectonics require an understanding of the petrological processes occurring in the creation of new oceanic crust in areas once covered by sialic crust and an understanding of the petrological processes occurring in the destruction or modification of oceanic crust in areas where this is apparently carried down into the mantle (Benioff zone of orogenic regions). Up to the present time, experimental petrologists have obtained a great deal of data which integrates very well with the plate-tectonics model.

Studies of P, T dependent subsolidus metamorphic reactions such as gabbro to eclogite and amphibolite to eclogite, and phase transformations such as olivine to spinel structure, pyroxene to garnet structure etc., have demonstrated the probable role of gravitational in-
stability as a driving force in the plate-tectonics model. Taken as a whole, plate tectonics can be seen as continuing, irreversible, chemical differentiation of the earth's upper mantle. The upper mantle, by processes of partial melting, yields magmas which rise to the earth's surface, leaving the more refractory residue as the peridotitic lithosphere. There is compelling evidence that the parental mantle composition is itself peridotitic (pyrolite) and that magmas derived by equilibrium partial melting are broadly basaltic in composition. In this paper I shall review the evidence that an upper mantle of pyrolite composition is capable of yielding a wide variety of magma types under diverse conditions of melting. Knowledge of petrogenetic processes responsible for the diversity of magma types, when coupled with their characteristic tectonic environments, places important constraints on the dynamics of the lithosphere and mantle.

EXPERIMENTAL STUDIES OF PERIDOTITE MELTING RELATIONSHIPS

The philosophical basis for the calculation of a model mantle composition (pyrolite) by combining the compositions of natural basalts and of residual, refractory peridotite, has been presented previously (Green and Ringwood, 1963; Ringwood, 1966; Green and Ringwood 1967a; Green 1970, 1971, 1972a). The specific pyrolite composition calculated by Ringwood (1966) has been extensively studied experimentally and on the basis of these experiments and the known chemical compositions and crystallization behaviour of mantle-derived basalts, this particular composition (Table I) remains appropriate as a mean composition for the source region of basaltic magmas (to the level of precision currently possible) (Green, 1971, 1972a; Frey and Green, 1972).

The subsolidus mineralogy of pyrolite varies as a function of pressure, temperature and water content (Green and Ringwood, 1967a, 1970; Green and Hibberson, 1970; Green 1972b, c) and the position of the pyrolite solidus is particularly sensitive to water content (Green 1970, 1971, 1972a, b, c). The stability relationships of amphibole (pargasite) in the pyrolite composition exercise a most important control on both the melting relations and sub-solidus mineralogy of pyrolite. Because of the composition of pargasite and the limited Ca, Na and Al contents of pyrolite, the maximum amount of pargasitic amphibole which can form in pyrolite is approximately 30%, giving a water content in pyrolite of approximately 0.4% H₂O. Pargasite is unstable at pressures > 29 ± 1 kbar at 1000°C and breaks down to the denser assemblage olivine + pyroxenes + garnet + phlogopite + (water) (Green 1970, 1972 b, c).

The K₂O content (0.13%) of pyrolite in Table I permits the formation of < 1.5% of phlogopite assuming no other K-bearing phase. Thus at P > 29 ± 1 kbar the model pyrolite will contain free water if the water content is > 0.06% H₂O, and the beginning of melting will be approximately at the pyrolite solidus for water-saturated conditions. At lower pressures, the solidus for pyrolite will lie at the water-saturated position (Fig. 1) for water contents in pyrolite > 0.4% (approximately) but for 0 < H₂O < 0.4% (approximately) the pyrolite solidus is at higher temperature (Kushiro et al., 1968; Green, 1970, 1971; Wyllie, 1971 a, b) and is determined by the intersection of the pyrolite solidus for a given P_H₂O with the amphibole dehydration curve for the same P_H₂O. The solidus for pyrolite with ~ 0.2% H₂O has been experimentally determined. Although amphibole is
TABLE I
Composition of pyrolite (Ringwood, 1966), in column 1; compositions of analyzed glasses from experimental runs on pyrolite +6% H₂O at 10 kbar (column 3) and 20 kbar (column 4) compared with calculated melt in equilibrium with olivine (Fo₉₀) at 10 kbar, 1200°C and glass analyzed by Kushiro et al. (1972) from a melting experiment on a spinel herzolite

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tr>
<td></td>
<td>Pyrolite</td>
<td>10 kbar and 1200°C</td>
<td>1100°C</td>
<td>Glass</td>
<td>Glass</td>
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<tr>
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<td>calculated melt</td>
<td>analyzed glass</td>
<td>at 20 kbar, 1100°C</td>
<td>(Green, 1972c)</td>
<td>(Kushiro et al., 1972)</td>
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<tr>
<td>SiO₂</td>
<td>45.2</td>
<td>54.6</td>
<td>59.7</td>
<td>68.9</td>
<td>67.8</td>
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<td>0.6</td>
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<td>Al₂O₃</td>
<td>3.5</td>
<td>10.7</td>
<td>13.7</td>
<td>19.6</td>
<td>16.1</td>
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<td>0.1</td>
<td>0.4</td>
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<td>—</td>
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<tr>
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<td>—</td>
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<td>Na₂O</td>
<td>0.6</td>
<td>1.9</td>
<td>&gt;1.4*</td>
<td>&gt;1.8*</td>
<td>(3.1*)</td>
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<td>K₂O</td>
<td>0.13</td>
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<td>0.6</td>
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<td>—</td>
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<td>Water content</td>
<td>—</td>
<td>~9%</td>
<td>~12%</td>
<td>~15%</td>
<td>~13%</td>
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<tr>
<td>100 Mg/ (Mg+Fe²⁺)</td>
<td>89</td>
<td>72</td>
<td>64</td>
<td>58</td>
<td>49</td>
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<td>olivine</td>
<td>Olivine, ortho-pyroxene, clinopyroxene, quench phases</td>
<td>Olivine, ortho-pyroxene, clinopyroxene</td>
</tr>
<tr>
<td></td>
<td>+ trace chromite</td>
<td>(+quench olivine?)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 Mg/ (Mg + Fe²⁺)</td>
<td>in coexisting olivine</td>
<td>90</td>
<td>90</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>Approximate % melting</td>
<td>—</td>
<td>33</td>
<td>?</td>
<td>~20</td>
<td></td>
</tr>
</tbody>
</table>

* Sodium is volatilized by the electron beam from these water-rich glasses. The values in columns 2 and 3 were measured using a continuously traversing beam and the TNO electron probe (Green, 1972a), the value in column 4 was estimated.
Fig. 1. Experimentally determined solidi for pyrolite with various water contents. —— = solidus for anhydrous pyrolite (Green and Ringwood, 1967a); —— = solidus for water-saturated conditions (6% H$_2$O) (Green, 1972a, c); —— = solidus for $P_{H_2O} < P_{TOTAL}$, (0.2% H$_2$O) (Green, 1972c).

This is also the curve for amphibole disappearance for pyrolite + 0.2% H$_2$O; .... = curve for amphibole disappearance for pyrolite + 6% H$_2$O; stippled area = schematic geothermal gradients illustrating the difference in the depth of beginning of partial melting for $P_{H_2O} = P_{TOTAL}$ and $P_{H_2O} < P_{TOTAL}$.

stable up to the solidus at $P < 29 \pm 1$ kbar; the melting relationships show that liquids derived by partial melting of pyrolite with $0 < H_2O < 0.4\%$ are not in equilibrium with amphibole except possibly for low degrees of melting within $\sim 10^\circ$C of the solidus (Green, 1972a, c).

If H$_2$O $> 0.4\%$ then, depending on the solubility of water in the magma and the total water content of pyrolite, amphibole will persist above the solidus and play an important role in buffering the liquid composition. As H$_2$O content decreases to approach the "critical" value near 0.4% amphibole will persist through an increasing temperature interval above the solidus, tending towards the amphibole-breakdown curve (and solidus) for $0 < H_2O < 0.4\%$ (Fig. 1) (Green 1972 a, c; unpublished data for pyrolite + 1.2% H$_2$O).

As well as exerting a sensitive control on the position of the pyrolite solidus and stability field of amphibole, the percentage of water in the source pyrolite controls the degree of partial melting at any given pressure and temperature (Green, 1972a, fig. 3, 4). If the degree of melting at a given P, T condition is varied by change in water content the nature of the liquid and nature and proportions of the residual phases are changed. The complexity
of the three major controls on partial melting \((T, P_{\text{dry}}, pH_2O^*)\) when coupled with the chemical complexity of both pyrolite and natural basalts, suggests that direct melting studies on the pyrolite composition may be necessary to establish the composition of magma for any pressure, temperature and water content of the source region.

**EXPERIMENTAL MELTING STUDIES OF PYROLITE AND OTHER PERIDOTITES**

Green and Ringwood (1967b, 1970) and Ito and Kennedy (1967) reported above-solidus runs under anhydrous conditions at pressures up to 40 kbar for pyrolite and garnet peridotite compositions respectively. No attempt was made to directly determine the composition of the quenched liquid phase, a principal reason in the case of pyrolite being the presence of quench clinopyroxene outgrowths on orthopyroxene and consequent uncertainty in the real liquid composition. Kushiro et al. (1968) reported melting relations for a spinel lherzolite composition under anhydrous, water-saturated and water-undersaturated conditions and in some of their runs obtained sufficiently large areas of quenched glass for microprobe analysis. Reference to these data; and similar data from quenched runs from the Fo—Di—SiO\(_2\) system, as demonstrating production of very silica-rich melts (andesitic to dacitic) from peridotitic source rock in the presence of water was made by Kushiro (1969), Yoder (1969), and Wyllie (1971a, b). These experiments favoured the hypothesis that andesitic or even dacitic melts could be primary magmas, formed by direct partial melting of mantle peridotite under conditions of high \(P_{H_2O}\). The analytical data (Kushiro et al., 1972) from experiments on spinel lherzolite provided compositions of co-existing pyroxenes, olivine and glass. The authors considered that these compositions represented equilibrium between crystals and liquid. An apparent non-equilibrium partition of \(Fe/Mg\) between olivine \((100 \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 92)\) and pyroxenes on the one hand and liquid \((100 \text{Mg}/(\text{Mg} + \text{Fe}) = 49)\) on the other (Green and Ringwood, 1967b; Green, 1970; Roeder and Emslie, 1970) was not commented upon, and could be explained only if the liquid contained high \(Fe^{3+}\) content, thus increasing \(100 \text{Mg}/(\text{Mg} + \text{Fe}^{2+})\) to approximately 75.

Green (1972c) has reported similar quenching studies of pyrolite with high water contents (6%) in which melting under water-saturated conditions at 10 kbar and 20 kbar produced homogeneous crystals and areas of glass sufficiently large for microprobe analysis. The energy-dispersive microprobe technique used allowed simultaneous analysis of 11 elements at each given point and demonstrated inhomogeneity in the glass composition.

In addition it was possible to identify and analyze quench clinopyroxene and quench amphibole. For example in an experiment at 20 kbar, 1100°C it was demonstrated that the

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* It is recognized that the partial pressure or activity of other volatile components which may be present and also, like water, readily soluble in basaltic melt will also sensitively control the degree and nature of partial melt products. In particular \(CO_2\) may be quite soluble in basaltic melt at \(p > 20\) kbar (Hill and Boettcher, 1970; Green, unpublished data on basanitic composition). In the absence of sufficient experimental data the present discussion is limited to \(H_2O\) as the major volatile phase in the earth's upper mantle.
analyzed glass, Table I, with $100 \frac{\text{Mg}}{\text{Mg} + \text{Fe}} = 58$, was not in equilibrium with primary olivine and pyroxenes but had fractionated to variable degrees by separation of quench amphibole, clinopyroxene and probably mica (not analyzable) and olivine (possible as thin rims on primary crystals).

In melting experiments on pyrolite at 10 kbar, very similar silica-rich glasses (Table I) were observed but again the presence of analyzable quench phases shows that the glass compositions cannot be interpreted as compositions of the equilibrium melt phase formed by melting of pyrolite. In two runs at 10 kbar in which high degrees of melting yielded olivine + liquid ($1200^\circ \text{C}$) and olivine + minor clinopyroxene + liquid ($1100^\circ \text{C}$) as the only primary phases, it was possible to use the Mg/Fe partition relationship for olivine/liquid equilibrium (Roeder and Emslie, 1970) and compositions of the pyrolite and of analyzed crystals to calculate the composition of the equilibrium liquid, prior to fractionation by metastable quench phases. It was shown that the equilibrium liquid was basaltic (quartz tholeiite to basaltic andesite) rather than andesitic or dacitic. The experiments demonstrate the extreme difficulty and unavoidable uncertainty in direct determination of equilibrium liquid compositions by direct analyses of glass in experimental charges in which there is a large proportion of primary crystalline phases (with consequent opportunity for zonal outgrowth during quenching*) and in which there is any crystallization of quench phases (amphibole, mica, clinopyroxene).

Because of these uncertainties it is not sufficient to determine the nature of partial melting products by experimental study of the postulated source composition. It must also be demonstrated that the liquid suggested as a partial melt has as its liquidus phases, at the postulated P, T conditions of melting, minerals identical in both species and composition to those observed in the postulated source rock at the same P, T conditions. Nicholls and Ringwood (1972b) evaluated the crystallization behaviour of a composition matching that of the glass produced at 26 kbar, $1190^\circ \text{C}, 30\% \text{H}_2\text{O}$ on a spinel lherzolite composition and analyzed by Kushiro et al. (1972). Nicholls and Ringwood found that this composition was above its liquidus when held at 26 kbar, $1190^\circ \text{C}, 15$ and $30\% \text{H}_2\text{O}$. The water-saturated liquidus temperature was $940^\circ \text{C}$ at 26 kbar with clinopyroxene as the liquid phase (L.A. Nicholls, personal communication, 1972). Neither olivine nor orthopyroxene occurred on or near the liquidus of the glass composition. These data, coupled with the identification of similar glass compositions in pyrolite melting studies accompanied by quench amphibole and clinopyroxene as well as primary olivine, orthopyroxene and clinopyroxene, demonstrate that the silica-rich glasses, of composition broadly classified as andesitic or dacitic, are not equilibrium partial melting products of peridotitic source compositions at pressures > 10 kbar. These glasses are products of fractionation along a metastable, quench-cooling path from parental (equilibrium) liquids of more magnesian and silica-poor character (olivine tholeiites to quartz tholeiites; Nicholls and Ringwood, 1972a, b, see also following discussion).

* Such zonal outgrowth may be volumetrically very significant yet not resolved by the electron probe, e.g., a "shell" of 0.5 μ thickness on a 10 μ diameter olivine crystal results in > 33% volume increase of crystallized olivine.
INTEGRATED STUDIES OF BASALT AND PERIDOTITE MELTING RELATIONSHIPS

In previous papers (Green, 1970, 1971) experimental studies under anhydrous and hydrous conditions on the pyrolite composition and on compositions ranging from olivine tholeiite to olivine nepheline were integrated to present a petrogenetic grid. In this grid a mantle of pyrolite composition containing approximately 0.1% H$_2$O was inferred to yield a very wide variety of magmas depending on the degree of partial melting (i.e., temperature) and depth of magma segregation (pressure). The choice of a water content of 0.1% in the source region was arbitrary, but the form of the solidus and nature of the melts would be little different provided H$_2$O < 0.4%, as discussed above. A more recent paper (Green, 1972b) demonstrates an experimental testing of one part of the petrogenetic grid by parallel studies on the near-liquidus phases of olivine-rich basanite composition and on the position of the solidus and nature of the phases above the solidus for pyrolite containing 0.2% H$_2$O. An internally consistent relationship between the pyrolite and olivine-rich basanite was established in which the olivine-rich basanite was derived by 6% melting of pyrolite + (0.2–0.4)% H$_2$O at ~ 30 kbar, 1250°C, leaving a residual, more refractory peridotite consisting of 60% olivine, 18% orthopyroxene, 14% clinopyroxene and 8% garnet. The data also supported the earlier conclusion that with smaller degrees of partial melting the melt would be increasingly undersaturated and of olivine nepheline to olivine melilitite character. With higher degrees of melting, phases such as garnet or clinopyroxene (depending on pressure) are absent (Fig. 3, 4; Green, 1972a) and liquids become less undersaturated and tend towards olivine tholeiite or tholeiitic picrite compositions.

The experimental testing of the basalt petrogenetic grid (Green, 1970, 1971) by direct study of the sequence of disappearance of phases during melting of pyrolite + 0.2% H$_2$O has already shown that the field in which garnet co-exists with liquid extends down to ~ 20 kbar (Fig. 1) rather than 25 kbar (Green, 1970, 1971) at the solidus and also that for water contents of ~ 0.2% the persistence of amphibole above the solidus is very limited so that this phase will not play a significant role in buffering liquid compositions at P < 20 kbar. Experiments in progress with pyrolite + 1.2% H$_2$O show greater persistence of amphibole above the solidus and illustrate melting conditions where this phase may have a greater role in buffering the chemical compositions of the melt phase.

In studies of melting relations with even higher water contents i.e., “pyrolite + 6% H$_2$O” (Fig. 1; Green, 1972c) it has been shown that at ~ 33% melting the liquid co-existing with residual olivine (Fo$_{90.5}$) at 10 kbar, 1200°C has the composition of a magnesian, silica-rich, quartz tholeiite (100Mg/(Mg + Fe) = 72). For lower degrees of melting (~ 28%) at 10 kbar, 1100°C the liquid coexists with olivine (Fe$_{89}$) and calcic clinopyroxene and the composition of the liquid is estimated as that of a quartz-rich tholeiite (100 Mg/(Mg + Fe$^{++}$) = 70). In both cases the liquid is saturated in water. In parallel studies on silica-saturated tholeiite (i.e., neither olivine nor quartz in the norm), Nicholls and Ringwood (1972b) have shown that at 10 kbar, 1040°C, a quartz tholeiite liquid (100 Mg/(Mg + Fe) < 65) has olivine and clinopyroxene on its water-saturated liquidus. Allowing for difference in liquidus temperature due to differences in 100Mg/(Mg + Fe) value, it is considered that the data effectively demonstrate that melting of pyrolite in the presence of large water contents produces water-saturated quartz tholeiite liquids at depths of ~ 35 km, T ~ 1100°C, leaving residual wehrlite. At lower temperatures (1020°C, 1050°C)
at this depth, orthopyroxene is also present as a residual phase in pyrolite and amphibole
is present at 1000°C, approximately 20°C above the solidus. The nature of the liquid in
equilibrium with these residual phases is at present uncertain but it will have higher con-
tents of alkalis and other incompatible elements. Further experiment is required to deter-
mine whether liquids formed at lower degrees of melting pass through a field of
“hawaiite” (low normative hypersthene) to nepheline normative compositions or remain
quartz normative but with higher Na/Ca and SiO₂ contents.

The experimental studies of melting relations of tholeiitic compositions under water-
saturated conditions by Nicholls and Ringwood (1972a, b) demonstrate a much larger ex-
pansion of the field of olivine crystallization with increasing water pressure in these com-
positions relative to that observed for olivine-rich and highly undersaturated
basanite (Green, 1972b). In particular they provide evidence that, under water-saturated
conditions, liquids of quartz tholeiite compositions can form in equilibrium with residual
olivine and orthopyroxene up to pressures between 17 kbar and 20 kbar. At higher pres-
ures, liquids in equilibrium with olivine and orthopyroxene would be olivine-normative
but would contain less normative olivine than those derived by melting of dry or water-
undersaturated pyrolite. The new data show that the mutually exclusive inferences of
Green (1970, 1972a) that quartz-normative liquids could not be derived by partial melting
of peridotite at high water pressure at pressures > 10 kbar P_{TOTAL}, and that of Kushiro
(1969) and Kushiro et al. (1972) that quartz-normative liquids including andesites, could
be derived by partial melting of peridotite at water pressures up to at least 26 kbar were
both in error. They demonstrate that direct partial melting to produce quartz tholeiite
liquids is apparently limited to P < 17–20 kbar for water-saturated conditions.

Fig. 2. Approximate solubility of water in magma in equilibrium with olivine and orthopyroxene. Note
that the nature of magma changes from quartz-normative at low pressure to olivine-normative at high
pressure. Estimated from data obtained in the ANU laboratory on magma ranging from quartz tho-
leitic to olivine-rich basanite and peridotitic liquids.
Fig. 3. Diagram illustrating the effect of varying water content of pyrolite source rock on the conditions (pressure and % melting) at which magmas change from water-oversaturated to water-under-saturated ($P_{H_2O} < P_{TOTAL}$). The surface on which water-saturated magmas lie is contoured for water contents from 0.1% $H_2O$ to 7% $H_2O$ in the source region. The petrogenetic grid (Green, 1970, 1971) forms the front face (0.1% $H_2O$) of the figure. Fig. 4 presents a section through the diagram at ~ 25% melting.

An attempt to summarize these new data and inter-relate them with earlier data on melting of dry and water-undersaturated pyrolite requires the consideration of an additional variable in the upper mantle, i.e., variation in the concentration of water in the source region. In Fig. 2 a general relationship between pressure and maximum solubility of water in magmas is presented; this is based on experimental data on a number of rock types but, for simplicity, the variation in solubility with basalt composition at a given pressure is ignored in using an "average" solubility for "basalts". As a consequence of the relationship illustrated in Fig. 2 the inter-relationships of the three variables, pressure, % melting, % $H_2O$ in source (Fig. 3) show the existence of a surface of water-saturated melting ($P_{H_2O}$)$_{melt} = P_{TOTAL}$ which divides conditions of magma genesis in the absence of an $H_2O$-rich vapour phase from those in which a vapour phase ($H_2O$-rich) is present. As experimental data accumulate it may be possible and useful to present petrogenetic grids such as fig. 6 of Green (1970) for various water contents in the source region. Available data allow the presentation of schematic sections through Fig. 3 for high degrees of melting only, e.g., Fig. 4. Fig. 4 illustrates the variation in magma type for ~ 25% melting of the mantle source material and since for this degree of melting amphibole, phlogopite or omphacitic clinopyroxene (at pressures > 20 kbar) are not residual phases, those elements which are not present in olivine, orthopyroxene or clinopyroxene (with low jadeite content) must be entirely partitioned into the liquid. Thus all liquids lying on the 25% melting plane will have, when recalculated anhydrous, about 2.3% $Na_2O$, 0.5% $K_2O$, 0.25% $P_2O_5$, 2.8% $TiO_2$, and < 12% CaO, < 14% $Al_2O_3$ assuming a source composition of pyrolite (Table 1). The concentration of these elements, particularly of the incompatible elements $TiO_2$, $K_2O$ and $P_2O_5$, will vary if the source compositions are themselves variable in these components.
Fig. 4. The ~ 25% melting plane (Fig. 3) for pyrolite is divided by a line along which magmas are saturated with water but change from probably basaltic andesite at very low pressure to olivine-poor tholeiites at high pressure. The field of water-undersaturated magmas may be approximately contoured for normative olivine content and for the planes of silica-saturation dividing quartz normative from olivine normative and hypersthene normative from nepheline normative compositions.

PLATE TECTONICS AND BASALT PETROGENESIS

Studies in experimental petrology and in geochemistry of basalts have shown that the constraints of source composition, depth of partial melting and degree of partial melting are of primary importance in determining the chemical characteristics of a magma. To a first approximation it is inferred that the source composition can be considered constant in terms of major elements and compatible trace elements (such as Ni, Co, Mn, Cr, Ga, Y, heavy rare-earth elements). The model pyrolite composition of Ringwood (1966) represents a satisfactory composition for these elements. However the group of minor and trace elements designated as incompatible elements on the basis of their failure to substitute in the major minerals of pyrolite under upper-mantle conditions (e.g., Ti, P, Rb, Sr, light rare-earth elements, Zr) are considered to be inhomogeneously distributed within the low-velocity zone and the lithosphere (Green, 1968, 1971, 1972). In the low-velocity zone, these elements vary with proportions of a melt phase and accessory minerals such as phlogopite and apatite. In the lithosphere they vary with the proportions of amphibole, phlogopite and apatite (Frey and Green, 1972). Inhomogeneity in incompatible elements in the source region has greatest effect in modifying magma chemistry for small degrees of partial melting.

Because of the inferred constancy in major-element composition of the source region it is also important to consider the effect of other variables on magma generation. The de-
MELTING OF PYROLITE IN VARIOUS ENVIRONMENTS

degree of partial melting is sensitively controlled by water content* in the source region and by temperature. Experimental studies have shown that for high degrees of melting (> 20% approximately) magmas are of tholeiitic character (i.e., hypersthene normative). Magmas are of increasingly alkaline and undersaturated type for lower degrees of melting, ranging to olivine nephelinites, olivine melilitites and possibly kimberlites for extremely small degrees of melting and depths of > 50–70 km. For any chosen degree of melting and fixed water content in the source region, magmas are more olivine-rich at higher pressures (Fig. 3, 4). For any chosen pressure and chosen degree of partial melting, magmas are less olivine-rich and are of lower liquidus temperatures for higher water content in the source region.

These generalizations may be applied to analyze the characteristic magmatism of mid-oceanic ridges and continental rift systems, island chains (e.g., Hawaii) and oceanic islands, and of orogenic regions. The concept of diapiric upwelling of mantle source rock, either from the low-velocity zone, or, in orogenic regions, within seismically anomalous mantle (Karig, 1971), above the Benioff zone, is of fundamental importance for this process and leads to increasing degrees of melting at shallow depth and the production of voluminous and rather chemically homogeneous basaltic eruptions. A model of magma genesis (Green, 1971, 1972a) for mid-oceanic ridge and continental rift systems, and for island-chain volcanism, with the low-velocity zone as the primary source of magmas, appears to be in good agreement with geochemical and geophysical data and is consistent with plate tectonic models. However, the complexity of volcanic associations of island arc and orogenic regions appears to reflect the complexity of the source region. Recent work has convincingly demonstrated that the input of large amounts of water (probably derived by dehydration reactions in the down-going slab) to the peridotitic upper mantle overlying the Benioff zone can lead to the direct derivation of magnesian quartz tholeiite parental magmas from the peridotite source provided the depth of magma segregation is less than ~ 60 km. Olivine-poor tholeiites may be similarly derived if magma segregation occurs at deeper levels or if the water content of the source peridotite is insufficient to saturate magmas separating at < 60 km (Nicholls and Ringwood, 1972a, b). These water-rich magmas will partially crystallize and commonly fractionate by precipitation of olivine, pyroxene and amphibole as they move to the surface, giving rise to derivative magmas of quartz tholeiite, basaltic andesite and possibly andesitic character (Nicholls and Ringwood, 1972a, b). It is probable that this process is primarily responsible for the parental magmas of the rock series designated island-arc tholeiites (Jakes and White, 1969; Jakes and Gill, 1970; Jakes and White, 1971, 1972; T.H. Green, 1972; Nicholls and Ringwood, 1972a, b). However, the subducted oceanic crust of the lithosphere in the downgoing slab must also go through dehydration reactions, solid—solid metamorphic reactions and partial melting as it is carried into the upper mantle (Ringwood and Green, 1966; T.H. Green and Ringwood, 1968a). Melts derived from this source are, on the basis of experimental studies under both hydrous and anhydrous conditions, of andesitic to dacitic character (T.H. Green and Ringwood, 1968a; T.H. Green, 1972) and residues are eclogitic. The recent description of

* Water may in some regards be considered as another incompatible component but its role as a separate vapour of fluid phase under geological conditions sets it apart.
melting in mixed acid-basic gneissic terranes undergoing eclogite-facies metamorphism (Green and Mysen, 1972) and of the presence of CaO-rich garnet xenocrysts* in andesitic lavas (Brousse et al., 1972) supports the hypothesis that crustal rocks, carried to deep levels in a subduction zone, may act as source material for andesitic and dacitic magmas. These magmas may play a part in the origin of the "calc-alkaline" magma series, as opposed to the island arc tholeiitic series discussed previously. The complexity of the orogenic situation does not at present permit detailed understanding of petrogenetic processes but it appears that the upper mantle above the Benioff zone, the subducted oceanic crust and lithosphere, and the lower part of the continental crust are all capable of contributing to the chemical composition of magmas reaching the earth's surface in orogenic and island arc regions.

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* Interpretable as high-pressure phenocrysts or relict minerals in partial melting of the andesite from an eclogite source rock (T.H. Green and Ringwood, 1968b).
MELTING OF PYROLITE IN VARIOUS ENVIRONMENTS


EXPERIMENTAL MELTING STUDIES ON A MODEL UPPER MANTLE COMPOSITION AT HIGH PRESSURE UNDER WATER-SATURATED AND WATER-UNDERSATURATED CONDITIONS

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EXPERIMENTAL MELTING STUDIES ON A MODEL UPPER MANTLE COMPOSITION AT HIGH PRESSURE UNDER WATER-SATURATED AND WATER-UNDERSATURATED CONDITIONS

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The solidus of a model pyrolite composition is sensitively dependent on water content and has been determined experimentally up to 40 kb, for water-saturated (6% H$_2$O) and water-undersaturated (0.2% H$_2$O) conditions. Pargasitic hornblende is a major subsolidus phase to 29 kb and its breakdown at higher pressure has the effect of sharply depressing the solidus for (pyrolite + 0.2% H$_2$O) from \(-1150^\circ C\) to \(-1020^\circ C\) between 25 and 29 kb. Experiments have been carried out above the solidus to determine the nature of the partial melting process, particularly the nature and composition of the residual phases at a specific pressure, temperature and water content. The presence of siliceous (>58% SiO$_2$), low-magnesium glasses, broadly of andesitic or dacitic character, in experiments quenched at both 10 kb and 20 kb, is shown to be due to growth during quenching of olivine, clinopyroxene, amphibole and mica. However, it is possible in some experiments to use the compositions of the starting mix and analyzed residual phases to calculate the composition of the equilibrium liquid and degree of melting at the particular condition. High degrees of melting under water-saturated conditions at \(P > 10\) kb yield magnesian, quartz-normative basaltic andesites \(\approx 10\%\) Qz, \((1100^\circ C, 28\%\) melting) to quartz tholeiite magmas \(5-7\%\) Qz, \((1200^\circ C, 32.5\%\) melting), and at \(20\) kb, yield olivine tholeiite magmas \((1100^\circ C, 27-30\%\) melting). Andesitic or dacitic magmas are not products of equilibrium partial melting of pyrolite at \(P > 10\) kb under water-saturated conditions but may be derived from parental olivine-poor tholeiites, quartz tholeiites or basaltic andesites \((P < 10\) kb) by crystal fractionation. Parental magmas of the island arc tholeiitic magma series may originate by partial melting of upper mantle peridotite (pyrolite or residual peridotite of the lithosphere) under water-saturated conditions at \(\approx 5-20\) kb.

1. Introduction

In a recent paper, Kushiro et al. [1] report the results of experimental melting [7] of a peridotitic composition (herzolite inclusions from Salt Lake Crater, Hawaii) at \(20\) kb and \(26\) kb under water-saturated conditions (30% H$_2$O). With high degrees of melting (\(\approx 20\%\)), glass was obtained among the run products, together with olivine, orthopyroxene and clinopyroxene. The compositions of the latter phases were quite different from those of the starting material, providing evidence that reaction to a new equilibrium assemblage has occurred under the experimental conditions. The composition of the glass, analyzed by electron microprobe, was high in SiO$_2$, Al$_2$O$_3$ and CaO and also apparently contained \(\approx 13\%\) H$_2$O. The authors noted that their glass composition was broadly andesitic or dacitic in character and not basaltic. These experimental data were thus taken to support models of direct derivation of siliceous magmas (\(> 55\%\) SiO$_2$) by partial melting of mantle peridotite under water-saturated conditions [1, 8, 9].

In this laboratory, melting experiments on a model pyrolite composition under water-saturated conditions yielded very similar data to those described above. However, it can be shown that the glass obtained is metastable, with a composition determined by growth of quench amphibole, mica olivine and pyroxene, and does not correspond to the composition of a liquid in equilibrium with olivine, orthopyroxene and clinopyroxene. The data presented in this paper support and are complementary to studies by Nicholls and Ringwood.
[2] which have shown that quartz-normative liquids (including quartz tholeiite, andesite, dacite) do not have olivine as a liquidus phase at pressures > 20 kb, even for water-saturated conditions, and thus cannot be direct partial melts of a peridotitic source rock.

2. Experimental methods

Experiments were carried out in a piston-cylinder apparatus using welded Ag75Pd25 and Ag50Pd50 sample capsules containing known quantities of water. The composition investigated was a model pyrolite [4] as shown in analysis 1, table 1. To diminish the dominance of olivine and consequent high proportions of crystals to liquid under conditions of partial melting, a composition equivalent to pyrolite minus 40% olivine (Mg91.6Fe8.1Mn0.1Ni0.2) was used in all experiments [5, 6]. Sample weights of 15 mg were used with a water content of 10%. The water was added by microsyringe and checked by weighing before and after welding. With such a large water content, piercing of the capsule after the run yielded small droplets of water and drying of the opened sample at 110°C showed that 7–9% water was ‘free’ after quenching of the sample. These techniques also readily identified any runs in which capsule failure has caused loss of water.

TABLE 1

| Composition of pyrolite [16] and pyrolite minus 40% olivine (Olivine of composition Mg91.6Fe8.1Ni0.2Mn0.1), The latter composition is that used in experimental runs |
|---|---|---|---|
| SiO2 | 45.2 | 48.3 |
| TiO2 | 0.7 | 1.2 | 0.2 |
| Al2O3 | 3.5 | 5.9 | 4.9 |
| Fe2O3 | 0.5 | 0.8 | 0.5 |
| FeO | 8.0 | 8.2 | 10.0 |
| MnO | 0.1 | 0.1 | 0.07 |
| MgO | 37.5 | 28.7 | 32.5 |
| CaO | 3.1 | 5.1 | 3.0 |
| Na2O | 0.6 | 0.95 | 0.7 |
| K2O | 0.13 | 0.22 | 0.07 |
| P2O5 | 0.4 | 0.7 | 0.3 |
| Cr2O3 | 0.2 | 0.2 | 0.07 |
| NiO | 0.2 | 0.2 | 0.07 |
| 100Mg | 89.2 | 86.5 | 85.2 |
| Mg + Fe++ | | | |
| 100Mg | 89.2 | 86.5 | 85.2 |

As there is > 10% olivine present in all experiments reported in this paper, the water content of 10% added to the olivine-depleted pyrolite is equivalent to an experimental study of standard pyrolite with 6% water added. In addition to experiments with excess water, the pyrolite solidsus and melting relations for PyH2O < Ptotal were determined using a composition (pyrolite minus 40% olivine plus 0.3% H2O) equivalent to (pyrolite plus 0.2% H2O). In studying the water-under-saturated melting relationships in pyrolite it is necessary to add accurately the very small quantities of water. To overcome the weighing error and practical difficulty of weighing or micropipetting 0.03 mg H2O to a 10 mg sample, large capacity runs [100 mg (pyrolite minus 40% olivine) + 0.3 mg H2O] were carried out at 15 kb, 1000°C for 6 hr. This produced fine-grained assemblages of olivine + amphibole + pyroxenes in which the water is locked in amphibole. This material was finely ground and mixed, and 10 mg portions were re-run under various P, T conditions using sealed Ag75Pd25 Ag50Pd50 or Pt capsules (Pt at T > 1250°C at 30 kb or T > 1150°C at 5 kb). The experimental method is equivalent to a study of pyrolite + 0.2% H2O, or, in mineralogical terms, of hornblende peridotite containing 15–20% paragmatic hornblende (compared with a maximum paragmatic hornblende content of about 30% for pyrolite composition [12] with excess water and subsolidus conditions at about 10 kb).

Experimental charges were examined microscopically in transmitted light and polished mounts were also prepared. The latter method enabled close observation of the textures of melting and subsolidus runs, the recognition of glass by its low reflectivity and interstitial habit, the distinction between quench and primary plagiogope, and the recognition of abundant and evenly distributed gas-phase bubbles. Solid phases were analyzed using an electron microprobe and non-dispersive X-ray analytical system, based on the TPD microprobe [10]. Full details of the instrument and analytical procedures will be described elsewhere by Reed and Ware [30]. Conditions of analyses are as described previously [11] but several features of this instrument are particularly important for the present investigation. Firstly, the specimen current of 3–5 nA is an order of magnitude lower than that for most electron microprobe systems but in spite of this, careful investigation by I.A. Nicholls showed that highly siliceous and water-rich glasses suffered specimen damage and Na-volatilization by the electron beam during 100 sec analysis-time at each point. Thus the analyses of glass were carried out, where possible, by continuously moving the beam on an area of glass or by counting for 10 sec on each of 10 glass spots. This resulted in an increase of apparent Na content from ~ 0.5% to 1.5% Na2O but it is recognized that these figures may still be low. It was possible to analyze simultaneously for Na, Mg, Si, P, K, Ca, Ti, Cr, Mn, Fe at each point and this permitted the identification and analysis of quench amphibole and quench clinopyroxene, as well as primary phases. The analytical method also identified real compositional variations within the glass, although for such “point” analyses, Na-figures are not reliable. In the TPD instrument the high quality optics and ability to view the sample while
TABLE 2

<table>
<thead>
<tr>
<th></th>
<th>Most Fe-rich olivine core of larger crystals *</th>
<th>Most common olivine, cores of small crystals *</th>
<th>Quench border; average of ~1–2 μm rim *</th>
<th>Calculated equilibrium olivine, no Fe-loss *</th>
<th>Chromite included in olivine</th>
<th>Glass</th>
<th>Glass composition</th>
<th>Glass range **</th>
<th>Bulk composition of sample after experiment†</th>
<th>Calculated equilibrium liquid. Starting composition minus [45% olivine (Fo(93)) + 1% chromite]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.3</td>
<td>41.2</td>
<td>39.8</td>
<td>40.9</td>
<td>–</td>
<td>59.7</td>
<td>59.2–60.2</td>
<td>49.2</td>
<td>54.6</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5–2.7</td>
<td>1.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>–</td>
<td>–</td>
<td>0.6</td>
<td>–</td>
<td>10.0</td>
<td>13.7</td>
<td>13.2–14.1</td>
<td>6.1</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>8.2</td>
<td>6.8</td>
<td>14.5</td>
<td>9.7</td>
<td>14.0</td>
<td>4.6</td>
<td>4.4–4.8</td>
<td>6.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>50.4</td>
<td>52.0</td>
<td>45.9</td>
<td>49.3</td>
<td>9.0</td>
<td>4.6</td>
<td>3.9–5.3</td>
<td>30.1</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>0.1</td>
<td>–</td>
<td>0.1</td>
<td>–</td>
<td>12.7</td>
<td>12.4–13.1</td>
<td>5.4</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.4</td>
<td>1.1–1.6</td>
<td>0.8</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.6</td>
<td>0.6</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>64.0</td>
<td>0.4</td>
<td>0.2–1.4</td>
<td>0.7</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(H₂O)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(11%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>100 Mg/(Mg + Fe++)</td>
<td>91.6</td>
<td>93.0</td>
<td>84.5</td>
<td>–</td>
<td>52</td>
<td>64</td>
<td>61–66</td>
<td>89.7</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>100 Mg/(Mg + Fe++)</td>
<td>91.6</td>
<td>93.0</td>
<td>84.5</td>
<td>90.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Run conditions: 10 kb, 1200°C, 1 hr, Ag₅₀Pd₅₀ capsule. 100 Mg/(Mg + 2Fe) of sample after run: 89.7.

* Some large (~30 μm) olivine crystals show reverse zoning reflecting growth of the crystal prior to Fe-loss to the Ag₅₀Pd₅₀ capsule (column 8) and failure of the centres of crystals to readjust to equilibrium as the bulk composition changed. Outer parts of such crystals and centres of smaller (10 μm) crystals have compositions Fo₉₃ (column 2) and are taken to be in equilibrium in the bulk composition of column 8. Analyses of the outermost 1–2 μm of crystals, after correction for partial admixture of glass and high TiO₂ (quench ilmenite?) in the analysed volume, show compositions averaging Fo₈₄.₅, indicating the presence of thin shells of olivine quench outgrowth on the primary crystals (column 3).

** The glass composition was obtained using only data from analyses in which the electron beam was moved over the areas of glass during analysis (100 sec). Data from stationary beam analyses, when corrected for low Na values, yield an almost identical average composition. In this and following tables glass compositions are recalculated to 100% anhydrous. The "H₂O" figure is estimated from the failure of the 11 elements determined to total to 100%, in contrast to totals of 98–101% for olivines and pyroxenes.

† Determined with 30 μm defocussed beam in continuous movement over polished surface of sample.
under the electron beam remove any uncertainty in correlating analytical data with petrographic observation.

To determine the effect of iron loss from the sample to the Ag-Pd capsule, bulk analyses of the samples were carried out using a defocussed (30 μ diameter) electron beam kept in continuous movement over the polished surface of the sample. The resultant analyses (e.g. table 2, column 8) gave excellent agreement with that of the initial mix (table 1, column 2) when corrected for Fe-loss, and thus provided a check on the analytical method. The data showed that there was appreciable iron loss from the 10 kb, 1200°C run (from 100 Mg/(Mg + ΣFe) = 85.2 to 89.7), slight iron loss from the 10 kb, 1100°C run, but no significant loss from 10 kb runs at T < 1100°C or in the 20 kb runs at T < 1100°C (see tables 2-12).

3. Experimental results

3.1. Water-saturated solidus

The experimental data are summarized in fig. 1 showing the results applied to pyrolite + 6% H₂O. The solidus is markedly depressed below the anhydrous solidus and is readily distinguished by textural change and the disappearance of phlogopite and amphibole at the beginning of melting at 30 kb and 20 kb respectively. At 10 kb the preferred solidus is shown as a solid line although the presence of rare, very low-R.I. glass and coarser grain size of the 970°C run relative to the 900°C run suggest that the solidus may lie at the lower-temperature dotted line. The glass at 970°C may however be quenched from the excess, intergranular vapour phase. Examination of the polished surface shows this vapour phase to be evenly distributed throughout the charge. Amphibole is an abundant phase in both the 900°C and 970°C runs accompanied by olivine and orthopyroxene and, at 970°C at least, by minor clinopyroxene*. There is no difference in Mg-value of orthopyroxene between the 900°C and 970°C runs so that the amount of melting at 970°C could only be very small. In addition, the Na/K, Ti/Na and Ti/K ratios of the amphibole at 970°C are close to those of the initial mix so that there are no chemical grounds from which to infer the existence of a low-melting fraction enriched in K, or Ti or Na, in addition to the solid phases at 970°C.

* The compositions and approximate proportions of olivine, orthopyroxene and amphibole also show that there should be another phase present in the pyrolite composition, with higher Ca : Al ratio than either orthopyroxene or amphibole.

There are minor differences between the amphibole, considered to be subsolidus, at 970°C and that at 1000°C, where a minor melt fraction is observed and is considered to have caused the decreased K content and increased Na/K and Ti/Na ratios of the amphibole. The marked difference in Cr₂O₃ content of amphibole between 970°C and 1000°C is probably due to a tiny spinel inclusion in the 970°C amphibole, several other less satisfactory amphibole analyses having about 1% Cr₂O₃. For the above reasons, the solidus at 10 kb is placed between 970°C and 1000°C and not at the lower-temperature dotted line of fig. 1. The order of disappearance of phases with increasing degree of melting is shown in fig. 1. There are minor
D.H. Green, Experimental melting studies

changes from the preliminary diagram previously published [12] and based only on optical examination of crushed samples. Later optical and microprobe examination of polished mounts shows that olivine alone is present as an equilibrium crystalline phase at 10 kb, 1200°C; clinopyroxene and olivine are present at 10 kb, 1100°C and orthopyroxene first appears at 10 kb, 1050°C. The runs at 10 kb, 1000°C and 1020°C contain small euhedral amphibole laths and the crystal habit, textural relations and grain size led to the interpretation that these were primary crystals, in equilibrium with olivine, orthopyroxene and clinopyroxene. However, microprobe analysis of amphibole from runs at 1050°C and 1020°C yielded compositions of silica-rich amphiboles, with low CaO contents and Mg-values* which are much lower than those of the subsolidus amphibole at 970°C or of the coexisting olivine and pyroxenes. On the other hand, the amphibole at 1000°C resembles that at 970°C except for the differences in Na, Ti, and K. The amphiboles at 1050°C and 1020°C are thus either quench amphiboles or largely quench outgrowths of amphibole on small cores of primary amphibole. The amphibole-out curve [13] is placed between 1000°C and 1020°C, i.e. within ~40°C of the solidus rather than 60°C above the solidus as shown in the preliminary diagram [12].

Ilmenite is a minor but distinctive phase, persisting to >40°C above the solidus at 20 kb but for <30°C at 30 kb. Garnet is absent at 20 kb but is an important residual phase at 30 kb where it persists ~100°C above the solidus, i.e. about 50°C higher than the disappearance of clinopyroxene.

3.2. Water-undersaturated solidus

In addition to experiments on pyrolite + 6% H₂O, a programme of melting and subsolidus experiments applicable to pyrolite + 0.2% H₂O has been completed (fig. 2) and a further study on pyrolite + 1.2% H₂O is in progress. The solidus for P_H₂O < P_total has a very different shape from that for P_H₂O < P_total and is determined by the pargasitic hornblende stability field. Colourless, pargasitic hornblende disappears at or very close to the pyrolite solidus for P < 30 kb and neither ilmenite nor phlogopite are observed either for subsolidus conditions at P < 27 kb approximately. Both ilmenite and phlogopite persist however for about 150°C above the solidus at 30 kb and 50—100°C at 40 kb. Rare garnet appears on the solidus at 20 kb but persists for ~350°C above the solidus at 30 kb compared with ~100°C above the solidus for P_H₂O = P_total at 30 kb (fig. 1). Both clinopy-
roxene and orthopyroxene (particularly at 10 kb, figs. 1, 2) also persist over a wide temperature range above the solidus. These differences are directly attributable to the much lower degree of melting at a given \( P_{\text{total}} T \) in pyrolite with low water content. Almost all the partial melting data points of figs. 1 and 2 are below the anhydrous solidus for pyrolite.

4. Melting in the upper mantle

The data of figs. 1 and 2 and that for anhydrous pyrolite [5, 6] provide a firm experimental basis for discussion of melting behaviour in the upper mantle. If the upper mantle is anhydrous then estimates of the geothermal gradient beneath either oceans or continents do not intersect the pyrolite solidus. If, however, there is a small water content (< 0.4% approximately) in an upper mantle of pyrolite composition the solidus for \( P_{H_2O} < P_{\text{total}} \) between 27 and 29 kb produces a situation where a geothermal gradient may pass from subsolidus to above-solidus conditions at depths of ~90 km [6, 12 – 15]. The existence of the low velocity zone (LVZ), particularly in oceanic crustal regions, is considered to be a direct result of the intersection of a normal geothermal gradient with the pyrolite solidus for \( P_{H_2O} < P_{\text{total}} \). The depth of the “roof” of the LVZ, defined by the intersection of geotherm and pyrolite solidus, is relatively insensitive to changes in temperature over a 100°C temperature range or in changes in water content from nearly anhydrous up to about 0.4%. Changes in these parameters in the mantle will, however, affect the degree of partial melting [12, 15] and thus the seismic velocities and attenuation within the LVZ. If the geothermal gradient is very low then it may not intersect the pyrolite solidus at all (LVZ absent and lithosphere “welded” to upper mantle) or may intersect the solidus at \( P > 30 \) kb to produce extremely small degrees of melting and a deep low-velocity zone. If the geothermal gradient is very steep then melting may begin at \( < 27 \) kb and the degree of melting within the LVZ will be proportionately large. This situation would probably be very unstable and diapirism and magmatism from the LVZ would occur.

The possibility of addition of water to the low velocity zone, by dehydration of lithosphere beneath a neighbouring Benioff zone [2, 3, 12, 14, 18, 19] or by upward concentration of water-rich fluid or magma within the LVZ [17], would initially lead to formation of increasing amounts of amphibole in the “roof” (lithosphere). However this can only absorb up to about 0.4% \( H_2O \) [12, fig. 3] — higher water contents would produce conditions of \( P_{H_2O} = P_{\text{total}} \) and the relevant solidus would be that of fig. 1. It is thus possible, without changing the local geothermal gradient, for the depth to the top of the LVZ to change rather abruptly from ~90 km to ~65 km by addition of small quantities of water [12, 13]. The amount of melt formed along the geothermal gradient would again be very sensitively controlled by the amount of water present [12]. It is suggested that melting of mantle peridotite under water-saturated conditions occurs beneath island arcs, caused by access of water from dehydration reactions occurring within the subducted crust and lithosphere of the downgoing slab. Thus the solidus of fig. 1 is relevant to the island arc situation leading to partial melting at very shallow depths along normal geothermal gradients in the upper mantle. Melting due to water access may occur in parts of the mantle that, prior to initiation of the downgoing slab, comprised the lithosphere overlying the LVZ. The latter feature may account for some of the puzzling features of the island arc tholeiitic and basaltic andesite magmas, particularly the observations that \( TiO_2, Na_2O \), rare-earth elements and other incompatible elements are present in lower abundance than in mid-ocean ridge tholeiites, of similar or more magnesian major element composition or even of less fractionated composition [18, 20]. If the oceanic lithosphere is formed at a mid-oceanic ridge, then the peridotite forming the lithosphere must be partially residual in character and depleted in incompatible elements relative to the primary mantle material which, in upwelling at the mid-oceanic ridges, gave rise to basaltic oceanic crust and residual peridotite lithosphere. If, in its later history, a region of depleted lithosphere is remelted above a “subduction zone”, then the products of melting will have their major element chemistry determined by equilibria involving olivine and pyroxene but their incompatible element contents will reflect the residual and depleted character of the “reactivated lithosphere”.
5. Chemical compositions of liquids formed by equilibrium partial melting of pyrolite under water-saturated conditions

5.1. Compositions of quenched glasses and equilibrium liquids in experimental runs at 10 kb

5.1.1. 10 kb, 1200 °C

The experimental run at 10 kb, 1200 °C showed excellent partial melting texture with euhedral olivines (~50%) and uncommon, small chromite crystals in glass. No evidence for quench amphibole or clinopyroxene was found by either optical or X-ray powder diffraction examination. Because of the simplicity of the run products it is possible to deduce a great deal about both the equilibrium partial melting of pyrolite at 10 kb and 1200 °C under water-saturated conditions, and about the nature of the quenching process in recovering the sample for petrographic study. While the optical, microprobe and X-ray diffraction identification of quench amphibole and clinopyroxene in lower temperature runs at 10 kb and in runs at 20 kb casts immediate doubt on the glass compositions as those of an equilibrium liquid, this does not obviously apply to the 10 kb, 1200 °C and 10 kb, 1100 °C runs. Thus these two runs were examined in detail as test cases to establish whether the nature of liquids derived by partial melting of peridotite could be directly determined from the composition of quenched glasses.

Analyses of glass using both stationary beam (giving low Na2O values of 0.4% due to volatilization) and with the electron beam kept continually in motion during analysis within larger "pools" of glass (giving higher Na2O values of 1.4% but very similar values for other elements) showed that the glass is of high SiO2 and Ca, and low Mg and Fe character. The glass is strongly quartz normative (20%) and could be broadly classed as andesitic. However the compositions given in tables 1 and 2 show that it is not possible to obtain a mass balance for the original bulk composition of the charge (table 1) if magnesian olivine (table 2, columns 1 or 2) and glass (table 2, column 6) are the only phases present.

The presence of reverse zoning in some large olivine crystals, and analyses of the bulk composition of the run demonstrate that about 30% of the original iron was lost from the sample to the Ag50Pd50 capsule. If this effect is allowed for a mass balance is attempted using the bulk composition of column 8, table 2 it can be shown that 56% olivine (column 2), 43% glass (column 6), and 1% chromite (column 5) gives reasonable agreement for SiO2, TiO2, Al2O3, CaO, and K2O but gives high MgO and low FeO figures. Careful analysis of the outer rims of olivine crystals reveal Fe-concentrations higher than those in the glass or within the olivine crystals. Analyses of such margins, when corrected for admixture of glass by use of the Ca, Al and Ti contents, yield compositions consistent with thin borders of Fe-rich olivine (e.g. column 3, table 2) as quench outgrowth on the primary crystals. Further evidence for non-equilibrium between glass and olivine crystals is provided by data on Fe/Mg partition between olivine and liquid [21, 22] which predicts that a liquid in equilibrium with olivine (Fo92) should itself have 100 Mg/(Mg + Fe++) ~ 80. The analysed glass has an Mg-value of 64 (table 2). It is considered that the evidence presented establishes the presence of quench outgrowths of more Fe-rich olivine on the primary crystals, resulting from partial crystallization of the equilibrium liquid during quench cooling. The composition of the residual glass is thus not that of the equilibrium liquid.

Although it has been shown that, even in the deceptively simple run products at 10 kb and 1200 °C, it is not possible to determine the composition of the partial melt directly, it remains possible to calculate the equilibrium liquid composition by allowing for the effects of iron loss and using the empirically determined partition coefficient between Fe/Mg in olivine and liquid [21, 22]. Residual chromite (1%) will contain most of the chromium in the charge. Knowing the equilibrium olivine composition (Fo92) and bulk composition Mg-value of 89.7 after the run and the bulk composition Mg-value of 85.2 before the run, the equilibrium olivine composition, had there been no Fe-loss, can be calculated and is Fo90 (column 4, table 2). From the Fe/Mg partition relation for olivine: liquid equilibrium [21, 22], the liquid in equilibrium with olivine of composition Fo92 has 100 Mg/(Mg + Fe++) = 73.5. Assuming olivine (Fo90) chromite (1%) and liquid are the only equilibrium phases in the pyrolite composition at 10 kb and 1200 °C, then the charge would be about 54% molten and the liquid would be of composition similar to that in table 2 (column 9) and would be classed as a magnesian, quartz-rich tholeiite (5–7% normative quartz depending on whether Fe2O3 = 0 or 1.5%, respectively). There is a small uncertainty in calculating 100 Mg/(Mg + Fe++) of the equilibrium liquid because change in the oxidation state may occur during the run. Analyses for Fe++ and Fe+++ for runs in Ag50Pd50 capsules indicate a decrease in Fe2O3/FeO during runs [23]. In table 2 (column 9) the calculated 100 Mg/(Mg + Fe++) value assumes no change in Fe2O3 content and the 100 Mg/(Mg + Fe) value assumes all Fe+++ reduced to Fe++. The value for a liquid in equilibrium with Fo90 is 100 Mg/(Mg + Fe++) = 73.5 and lies between those values obtained using the assumptions on Fe+++ discussed above.

From the data in table 2, it is inferred that a liquid produced by 32.5% melting of pyrolite (i.e. 54% melting of pyrolite minus 40% olivine) under water-saturated conditions would have a composition very similar to that of column 9, table 2, leaving residual olivine (Fo90) and a trace of chromite. The liquid would be a magnesian quartz tholeiite (5–7% quartz). Since olivine is the dominant residual phase, liquids
would become less quartz-normative and then become olivine normative with higher degrees of melting.

5.1.2. 10 kb, 1100°C

Optical examination of this run resulted in identification of euhedral olivine and clinopyroxene in a glassy matrix. Tentative identification of rare tabular crystals, with straight extinction and low birefringence, as orthopyroxene [12] was not confirmed by electron microprobe examination which identified only olivine (Fo$_{89.8}$) and low alumina, chrome diopside (Ca$_{42}$Mg$_{52}$Fe$_6$). A liquid in equilibrium with olivine of this composition has 100 Mg/Mg + Fe$^{++}$ \(\approx 73\) [21, 22] and this is much higher than the Mg-value of the glass (table 3). As in the 1200°C run, the composition of the glass, which is very similar to that at 10 kb and 1200°C, is considered to result from rapid metastable growth of crystalline phases during quenching. As there are two crystalline phases present, it is not possible to use the data on bulk composition, mineral composition and Mg/Fe partition between olivine and liquid, to calculate the equilibrium liquid composition without specifying the relative proportions of olivine and clinopyroxene. Optical, X-ray and microprobe examination shows that clinopyroxene is a very minor phase relative to olivine.

Analysis of the bulk composition showed slight Fe-loss, taking the Mg-value from 85.2 to 86.4. Thus the composition of the equilibrium olivine, assuming no Fe-loss, is calculated as Fo$_{89.0}$ rather than Fo$_{89.8}$ (table 3). A liquid in equilibrium with olivine (Fo$_{89.0}$) has 100 Mg/(Mg + Fe$^{++}$) \(\approx 71\) [21, 22]. In table 3, column 5, the composition of a liquid is calculated by assuming 47% melting of (pyrolite - 40% olivine) and a residual mineralogy of 49% olivine (cf. 45% at 1200°C), 1% chromite, and 3% clinopyroxene. The liquid has an Mg-value of 69.5 - 74, depending on the assumed oxidation state.

The composition of the liquid formed by partial melting of pyrolite at 10 kb 1100°C under water-saturated conditions cannot be specified uniquely by direct melting studies but the composition given in column 5 of table 3 must be a close approximation to the melt composition. It differs from the melt at 10 kb 1200°C in its higher SiO$_2$ content and in lower Ca/Al, lower MgO and higher TiO$_2$ and K$_2$O contents, and has 9–11% normative quartz (i.e. it may be classified as a basaltic andesite composition). Liquids of this character would be produced by ~28% partial melting of pyrolite leaving clinopyroxene-bearing dunite (olivine (Fo$_{89}$) + chrome diopside + accessory chromite) as residue. The absence of orthopyroxene as a residual phase for these conditions is noteworthy. Orthopyroxene would become even-less

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzed olivine</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>SiO$_2$</td>
</tr>
<tr>
<td>TiO$_2$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na$_2$O</td>
</tr>
<tr>
<td>K$_2$O</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>100 Mg</td>
</tr>
<tr>
<td>Mg + Fe$^{++}$</td>
</tr>
<tr>
<td>100 Mg</td>
</tr>
<tr>
<td>Mg + (\Sigma)Fe</td>
</tr>
</tbody>
</table>

Run conditions: 10 kb, 1100°C, 1 hr, Ag$_{850}$Pd$_{50}$ capsule. 100 Mg/(Mg + \(\Sigma\)Fe) of sample after run: 86.4.
important as a residual phase for water-saturated melting at lower pressures but more important at higher pressures (fig. 1). These relationships become important in seeking to interpret very magnesian dunites, wehrlites and harzburgites of the alpine-type ultramafic complexes as possible residues and accumulates from either island arc or mid-oceanic ridge magma genesis.

5.1.3. 10 kb, 1050°C

Olivine, orthopyroxene, clinopyroxene and liquid are primary phases at these run conditions. Analysis of the bulk composition shows that there has been no detectable Fe-loss (table 4). The increasing degree of crystallization of the charge is accompanied by decreasing forsterite content of olivine (Fo$_{88.5}$). The analyses of pyroxene 'pairs' at 10 kb 1020°C and 1000°C, and at 20 kb 1050°C, consistently yielded clinopyroxene with slightly higher Mg-value and slightly higher TiO$_2$ content than coexisting orthopyroxene. It appears probable that the analysis of clinopyroxene in the 10 kb 1050°C run includes a small proportion of quench clinopyroxene outgrowth giving slightly low Mg-value and high Al$_2$O$_3$ and TiO$_2$ contents (tables 4, 5, 6, 9).

The amphibole composition is that of a quench phase, on the basis of the Mg-value (too low for equilibrium with olivine or pyroxenes but probably correct for equilibrium with the glass composition), very high TiO$_2$ and low CaO contents and very high SiO$_2$ contents. In these respects the amphiboles of both the 1050°C and 1020°C runs are similar to one another and markedly different from the subsolidus amphibole at 970°C (table 7) or the amphibole (considered to be an equilibrium phase) at 1000°C (table 6). Because of the presence of quench amphibole, the Mg-value relationships between glass and crystals, and the evidence deduced

### TABLE 4

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
<th>Quench amphibole</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>41.2</td>
<td>56.6</td>
<td>54.0</td>
<td>53.1</td>
<td>65.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>0.2</td>
<td>0.8</td>
<td>3.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.5</td>
<td>3.9</td>
<td>13.3</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>11.1</td>
<td>7.6</td>
<td>4.0</td>
<td>6.4</td>
<td>2.7</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>47.5</td>
<td>32.4</td>
<td>16.3</td>
<td>14.8</td>
<td>1.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
<td>1.3</td>
<td>20.1</td>
<td>5.4</td>
<td>8.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>&gt; 0.9</td>
<td>&gt; 0.8</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

"H$_2$O" (2%) (~13.5)

100 Mg/Mg + SiFe

|        | 88.5 | 88.5 | 88.0 | 80.5 | 51 |

Run conditions: 10 kb, 1050°C, 4 hr, Ag$_{75}$Pd$_{25}$ capsule. 100 Mg/(Mg + SiFe) of sample after run: 85.2.

### TABLE 5

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
<th>Quench amphibole</th>
<th>Glass 1*</th>
<th>Glass 2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>40.5</td>
<td>55.1</td>
<td>53.7</td>
<td>53.5</td>
<td>56.2</td>
<td>64.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>0.2</td>
<td>0.6</td>
<td>2.1</td>
<td>3.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-</td>
<td>1.1</td>
<td>2.0</td>
<td>11.0</td>
<td>17.7</td>
<td>21.0</td>
</tr>
<tr>
<td>FeO</td>
<td>12.3</td>
<td>7.6</td>
<td>3.8</td>
<td>6.4</td>
<td>5.9</td>
<td>2.4</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>46.8</td>
<td>33.8</td>
<td>17.7</td>
<td>15.3</td>
<td>7.4</td>
<td>2.5</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>1.3</td>
<td>21.2</td>
<td>8.8</td>
<td>6.4</td>
<td>8.3</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>&gt; 1.1</td>
<td>&gt; 0.7</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.7</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
<td>0.6</td>
<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
<td>-</td>
</tr>
</tbody>
</table>

100 Mg/Mg + SiFe

|        | 87.2 | 88.8 | 89.3 | 81   | 69   | 65     |

Run conditions: 10 kb, 1020°C, 4 hr, Ag$_{75}$Pd$_{25}$ capsule. 100 Mg/(Mg + SiFe) of sample after run: 85.3.

* Stationary electron beam giving low Na$_2$O value.
TABLE 6

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
<th>Amphibole</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.5</td>
<td>54.5</td>
<td>51.5</td>
<td>44.6</td>
<td>Not analyzable</td>
</tr>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>0.4</td>
<td>1.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>–</td>
<td>4.1</td>
<td>4.6</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>13.3</td>
<td>8.4</td>
<td>4.2</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>46.2</td>
<td>30.8</td>
<td>17.8</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>1.1</td>
<td>19.5</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>–</td>
<td>0.6</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>–</td>
<td>0.8</td>
<td>0.7</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>100 Mg</td>
<td>85.3</td>
<td>86.9</td>
<td>88.4</td>
<td>85.4</td>
<td></td>
</tr>
<tr>
<td>Mg + Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run conditions: 10 kb, 1000°C, 6 hr, Ag₇₅Pd₂₅ capsule.

In this and previous runs for outgrowth of quench clinopyroxene and olivine respectively, the highly siliceous glass is considered to be a non-equilibrium quench product and to bear no relation to the composition of an equilibrium melt at 10 kb 1050°C in water-saturated pyrolite composition.

It is not possible to deduce the composition of the equilibrium melt at 10 kb 1050°C without rather arbitrary assumptions about the degree of crystallization and the proportions of olivine, orthopyroxene and clinopyroxene. The decrease in Mg-value of crystalline phases between 1100°C and 1050°C implies a decrease in the amount of liquid present and the low Na and K values of the pyroxenes imply that these elements are concentrated in the liquid phase. These factors, and the increased proportion of pyroxenes (with 54–57% SiO₂) to olivine, all argue that the equilibrium liquid, with 100 Mg/(Mg + Fe++) = 69–70 will have SiO₂ < 56% and high alkali contents.

5.1.4. 10 kb, 1020°C

This run is similar to the 1050°C run in both the nature and compositions of its phases. Orthopyroxene (Ca₂₋₅Mg₈₋₆.₅Fe₁₁) appears to be slightly high in CaO but the coexisting clinopyroxene (Ca₄₋₃.₅Mg₅₀₋₅Fe₆) has low TiO₂, Al₂O₃ and very low Na₂O contents, and the composition is considered to be free of quench contamination. Both the amphibole and glass compositions show non-equilibrium characteristics as in the 1050°C runs, and the microprobe data, while confirming the presence of amphibole at 1020°C as observed optically [12], demonstrate that it is not an equilibrium phase at 1020°C. The glass appears to be more variable in composition in this run than in the higher temperature runs.

5.1.5. 10 kb, 1000°C

This experimental run contains olivine, orthopyroxene (Ca₂₋₂.₅Mg₈₋₄.₈Fe₁₃₋₀.), clinopyroxene (Ca₄₋₁Mg₅₋₂Fe₁) and amphibole, all as major constituents and all with Mg-values consistent with the four phases being primary and in equilibrium with each other. This con-
clusion is particularly important with respect to amphibole and derives from knowledge of compositions of co-existing amphiboles, olivine and pyroxenes in natural high-temperature ultramafic rocks [24–27]. Glass is a minor component (probably < 10%) of the charge and did not occur in areas large enough for analysis. The observation that the amphibole has lower K/Na ratio than that of the subsolidus amphibole at 970°C has the corollary that the equilibrium liquid is higher in K/Na ratio than either the amphibole or the initial mix.

5.1.6. 10 kb, 970°C, and 10 kb, 900°C

Both these run products are finer grained than for higher temperature runs and satisfactory analyses (as judged by structural formulae) were only possible for orthopyroxene and amphibole at 970°C and orthopyroxene at 900°C. Nevertheless, the increased K/Na ratio of the amphibole compared with that at 1000°C is a clear indication of some melting at 1000°C. The compositions of amphibole and orthopyroxene provide no chemical evidence for an additional melt phase at 970°C.

Comparing orthopyroxene compositions in all 10 kb experimental runs, there is a steady decrease in CaO content with decreasing temperature and it is particularly instructive to compare the 900°C orthopyroxene (Ca1.7Mg64.8Fe13.5) with natural peridotite orthopyroxenes from lherzolite inclusions, high-temperature peridotites, etc. Many such orthopyroxenes contain <0.8% CaO and have equilibrated with clinopyroxene at T < 900°C, on the evidence presented here. The Al2O3 content of orthopyroxene (and of clinopyroxene) increases rather sharply at 1000°C, marking the first appearance of a relatively Al-rich coexisting phase (amphibole). At lower temperatures the Al2O3 content of orthopyroxene decreases whereas TiO2 and Cr2O3 contents are insensitive to temperature changes within this range.

5.2. Compositions of quenched glasses and equilibrium liquids in experimental runs at 20 kb

5.2.1. 20 kb, 1100°C

Under these conditions the experimental charge showed a high degree of melting with euhedral olivine and orthopyroxene being obvious primary phases but broad plates of clinopyroxene in parallel growth to orthopyroxene showed optical characteristics indicative, in part, of quench growth. Some well-formed amphibole crystals were also optically consistent with primary crystallization. However, the chemical analyses in table 8 demonstrate that clinopyroxene was probably absent at 20 kb 1100°C, with orthopyroxene, olivine, accessory chromite and liquid being the equilibrium assemblage for water-saturated melting conditions.

Bulk analysis of the sample shows a very small Fe-loss which would only slightly affect the compositions of the residual phases. The residual olivine is Fo90 compared with the calculated equilibrium olivine (Fo89) at 10 kb 1100°C and Fo90 at 10 kb 1200°C, and this implies that the degree of partial melting at 20 kb 1100°C must be about 30%. Also, since orthopyroxene is present in similar proportion to olivine, and clinopyroxene is absent, the equilibrium liquid at 20 kb 1100°C, relative to that calculated for 10 kb 1100°C (table 3), must be lower in SiO2 and higher in CaO, Na2O and TiO2. Calculated compositions are given in columns 8 and 9 of table 8 and are of olivine tholeiitic character. These calculated equilibrium liquid compositions are not unique solutions because variation in percentage of melting and in the relative proportions of olivine and orthopyroxene would produce solutions also consistent with the olivine: liquid, Mg/Fe partition constraint. However, if the estimate of the degree of partial melting is increased then liquids will become quartz-normative but also have too low 100 Mg/(Mg + Fe') values for equilibrium with olivine Fo90. The latter effect can be countered by decreasing the olivine proportion in the residue but his then makes the liquids increasingly olivine-normative. By reasoning of this type, it can be shown that the composition of liquid derived by partial melting of pyrolite at 20 kb 1100°C, leaving only residual olivine and orthopyroxene, must be very similar to the compositions given in columns 8 and 9 of table 8. These compositions are of olivine tholeiitic character but of lower normative olivine content than for olivine tholeiite magmas produced by melting of dry pyrolite or of pyrolite with low water content [12, 15, 21].
TABLE 8
Analyses of minerals and glasses present in (pyrolite minus 40% olivine) composition at 20 kb. The last two columns contain calculated liquid compositions compatible with equilibrium with olivine of FeO composition and derived using estimated relative proportions of residual olivine and orthopyroxene (3:2).

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Quench*</th>
<th>Quench clino-</th>
<th>Quench clino-</th>
<th>Glass</th>
<th>Calculated equilibrium liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pyroxene</td>
<td>pyroxene</td>
<td></td>
<td>27% melting of pyrolite</td>
</tr>
<tr>
<td>SiO₂</td>
<td>41.5</td>
<td>55.4</td>
<td>51.3</td>
<td>47.6</td>
<td>45.5</td>
<td>68.9</td>
<td>67.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td></td>
<td>1.6</td>
<td>3.3</td>
<td>1.9</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td></td>
<td>1.7</td>
<td>4.4</td>
<td>7.7</td>
<td>14.5</td>
<td>19.6</td>
</tr>
<tr>
<td>FeO</td>
<td>9.7</td>
<td>6.6</td>
<td>5.3</td>
<td>7.9</td>
<td>13.1</td>
<td>1.1</td>
<td>1.1</td>
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<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>48.9</td>
<td>33.9</td>
<td>16.6</td>
<td>13.0</td>
<td>11.6</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td></td>
<td>1.3</td>
<td>19.2</td>
<td>19.5</td>
<td>8.9</td>
<td>6.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.7</td>
<td>2.0</td>
<td>1.8**</td>
</tr>
<tr>
<td>K₂O</td>
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<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr₂O₃</td>
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<td></td>
<td>1.0</td>
<td>1.3</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 Mg</td>
<td>90.0</td>
<td>85.0</td>
<td>74.5</td>
<td>61</td>
<td>58</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Mg + ΣFe</td>
<td>90.0</td>
<td>90.0</td>
<td>85.0</td>
<td>74.5</td>
<td>61</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>100 Mg</td>
<td>72</td>
<td>77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg + Fe**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;H₂O&quot;</td>
<td>(2%)</td>
<td>(~15%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run conditions: 20 kb, 1100°C, 1 hr, Ag₉₅Pd₃₅ capsule.
Run description: Large (> 10 μ euhedral olivine and orthopyroxene. Orthopyroxene with broad clinopyroxene borders with characteristics of quench clinopyroxene (wavy extinction, R1 > Opx). Quench mica, amphibole and common glass also occur. Small brown euhedral spinel crystals are probably also primary rather than quench phases and are occasionally included in olivine and orthopyroxene. 100 Mg/(Mg + ΣFe) of sample after run: 85.7.

* This is the most magnesian clinopyroxene composition analyzed but the differences in TiO₂, Al₂O₃ and 100 Mg/(Mg + ΣFe) contents between orthopyroxene and the clinopyroxene suggest that these phases are not in equilibrium with each other. It is inferred that the two clinopyroxene compositions in the table represent growth stages in quench growth of clinopyroxene. It is possible that primary clinopyroxene occurs as cores to the quench phase and is included in the analysis of the more Mg-rich clinopyroxenes but this cannot be proven on the evidence available.

** Analysis of the small areas of glass required use of a stationary beam. The Na₂O figure has been corrected by the factor found for analyses using both stationary beam (with Na volatilization) and moving beam on the 10 kb, 1200°C and 1150°C runs.
† The Na₂O figure is inferred from the bulk composition and the estimated degree of crystallization. Analysis gave low values due to Na-volatilization.
†† Calculated as 1.8% Fe₂O₃, 8.0% FeO.
‡ Calculated as 1.6% Fe₂O₃, 8.0% FeO.

5.2.2. 20 kb, 1050°C
At these conditions the primary phases are olivine, orthopyroxene and calcium-rich clinopyroxene. Quench clinopyroxene and quench amphibole are both present in the run product and the residual glass is highly siliceous and Al₂O₃-rich. Because of the presence of amphibole and quench clinopyroxene outgrowths on primary crystals and the probability that olivine is also rimmed by quench outgrowth, the composition of the glass is considered to have no similarity to the composition of the original equilibrium liquid under these conditions. The rather large change in Mg-value of olivine and orthopyroxene between 1100°C and 1050°C suggests that there is much less liquid present at 1050°C.
TABLE 9

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Ortho-pyroxene*</th>
<th>Clinopyroxene*</th>
<th>Quench clino-pyroxene</th>
<th>Quench amphibole</th>
<th>Glass 1 **</th>
<th>Glass 2 **</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.7</td>
<td>53.5</td>
<td>53.2</td>
<td>45.6</td>
<td>47.4</td>
<td>70.0</td>
<td>68.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0.2</td>
<td>0.5</td>
<td>3.3</td>
<td>2.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1</td>
<td>2.5</td>
<td>2.3</td>
<td>9.0</td>
<td>15.5</td>
<td>19.3</td>
<td>21.0</td>
</tr>
<tr>
<td>FeO</td>
<td>12.1</td>
<td>8.1</td>
<td>4.1</td>
<td>8.8</td>
<td>10.8</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>46.9</td>
<td>33.9</td>
<td>17.6</td>
<td>17.2</td>
<td>11.2</td>
<td>1.2</td>
<td>0.5</td>
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<tr>
<td>CaO</td>
<td>0.1</td>
<td>1.0</td>
<td>20.8</td>
<td>14.2</td>
<td>8.4</td>
<td>5.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td>0.4</td>
<td></td>
<td>0.8</td>
<td>2.0</td>
<td>&gt; 1.5</td>
<td>&gt; 1.0</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
<td>0.9</td>
<td>1.1</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 Mg/(Mg + Fe)</td>
<td>87.5</td>
<td>88.0</td>
<td>88.5</td>
<td>77.5</td>
<td>65</td>
<td>72</td>
<td>60</td>
</tr>
</tbody>
</table>

"H₂O" (2%) (16%) (15%)

Run conditions: 20 kb, 1050°C, 4 hr, Ag₇₅Pd₂₅ capsule.
Run description: Large (> 10 μm) euhedral orthopyroxene, olivine and clinopyroxene as outgrowths on orthopyroxene and also as separate crystals. Primary crystals enclosed in glass with quench mica and quench amphibole. Estimated ~20% melting.
100 Mg/(Mg + Fe) of sample after run: 85.6.
* Note the similar 100 Mg/(Mg + Fe), Al₂O₃, TiO₂ contents of the two pyroxenes in contrast to the orthopyroxene and quench clinopyroxene of table 8.
** Glass analyses using stationary beam, Na₂O values estimated from 10 kb data evaluating the effect of Na volatilization by the electron beam.

TABLE 10

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
<th>Ilmenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.4</td>
<td>53.9</td>
<td>50.8</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0.2</td>
<td>0.7</td>
<td>59.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1</td>
<td>4.5</td>
<td>6.0</td>
<td>0.7 *</td>
</tr>
<tr>
<td>FeO</td>
<td>12.7</td>
<td>8.0</td>
<td>4.1</td>
<td>25.0</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>45.2</td>
<td>31.6</td>
<td>16.3</td>
<td>12.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2</td>
<td>0.9</td>
<td>20.6</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td></td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td></td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
<td>0.9</td>
<td>0.8</td>
<td>2.4</td>
</tr>
<tr>
<td>NiO</td>
<td>0.4</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>100 Mg/(Mg + Fe)</td>
<td>86.4</td>
<td>87.6</td>
<td>87.8</td>
<td>46.3</td>
</tr>
</tbody>
</table>

Run conditions: 20 kb, 1000°C, 4 hr, Ag₂₅Pd₇₅ capsule.
Run description: Common olivine and orthopyroxene laths and minor clinopyroxene in quench amphibole + mica + glass. Accessory ilmenite and spinel included in some orthopyroxene and olivine. Differs from the 1100°C run in the absence of broad clinopyroxene borders on the orthopyroxene laths.
* Al₂O₃ may be too high from matrix interference.
TABLE 11

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.2</td>
<td>53.2</td>
<td>51.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td>FeO</td>
<td>12.6</td>
<td>8.5</td>
<td>4.4</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>46.7</td>
<td>30.3</td>
<td>16.8</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>1.0</td>
<td>20.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>NiO</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 Mg</td>
<td>86.9</td>
<td>86.5</td>
<td>87.3</td>
</tr>
<tr>
<td>Mg + Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run conditions: 20 kb, 970°C, 6 hr, Ag₇₅Pd₂₅ capsule.
Run description: Common orthopyroxene, olivine and clinopyroxene (commonly as simply-twinned crystals) together with mica (possibly primary) and spinel (and ilmenite) and minor interstitial glass.

TABLE 12

<table>
<thead>
<tr>
<th></th>
<th>Olivine</th>
<th>Orthopyroxene</th>
<th>Clinopyroxene</th>
<th>Amphibole</th>
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<tr>
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<td>53.2</td>
<td>51.3</td>
<td>44.3</td>
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<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.4</td>
<td>0.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>5.4</td>
<td>4.6</td>
<td>13.6</td>
</tr>
<tr>
<td>FeO</td>
<td>13.9</td>
<td>8.8</td>
<td>3.8</td>
<td>5.5</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>45.1</td>
<td>30.5</td>
<td>17.0</td>
<td>19.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>0.8</td>
<td>21.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>2.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>0.7</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>NiO</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 Mg</td>
<td>85.2</td>
<td>86.1</td>
<td>88.9</td>
<td>86.1</td>
</tr>
<tr>
<td>Mg + Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run conditions: 20 kb, 970°C, 6 hr, Ag₇₅Pd₂₅ capsule.
Run description: Common olivine, orthopyroxene, amphibole (small colourless laths), minor clinopyroxene and accessory ilmenite and spinel. No evidence for melting, orthopyroxene does not have borders of (quench) clinopyroxene.

than at 1100°C, and the low Na₂O, K₂O and TiO₂ contents of the primary clinopyroxene shows that the liquid will be enriched in these elements while retaining SiO₂ < 50% (because of the increasing importance of pyroxenes as residual phases).

5.2.3. 20 kb, 1000°C, 970°C and 950°C

In these runs, although quench phases and glass were present at 1000°C and 970°C, only primary phases have been analyzed. With decreasing temperature the Mg-values of olivine and orthopyroxene decrease, with the compositions at 950°C being similar to those at 970°C and 900°C (both subsolidus) at 10 kb. The presence of Mg, Cr-rich ilmenite at 1000°C is noteworthy. This phase is probably present, though not analyzable, in lower temperature runs and would account for the lower TiO₂ content of amphibole at 20 kb 950°C than that at 10 kb 970°C and 10 kb 1000°C. In comparing the subsolidus, primary amphibole at 950°C with quench amphibole at 1050°C and 1100°C the main difference is in Mg-value in CaO, TiO₂ and SiO₂ contents. The K₂O/Na₂O ratio of the amphibole at 950°C is lower than that of the starting mix and this effect is more marked when the Na₂O content (0.7%) of the clinopyroxene is also considered. This comparison suggests the presence of a minor K-rich phase, possibly phlogopite or a trace of K-rich melt phase. If a melt phase is present and thus 950°C is slightly above the solidus, then the amount of melt must be too small to affect Mg-values.

The analysis of coexisting pyroxene pairs in these runs shows a similar temperature dependence of the width of the pyroxene miscibility gap at both 10 kb and 20 kb. There is some suggestion that orthopyroxene shows slightly lower CaO content at a given temperature at 20 kb than at 10 kb. The data at 950°C 20 kb support the view that orthopyroxene-clinopyroxene pairs in lherzolites, in which orthopyroxene has < 0.8% CaO and clinopyroxene has > 20% CaO, have equilibrated at T < 1000°C.

6. Application of the experimental melting studies to models of the upper mantle

6.1. The lithosphere and low velocity zone

The experimental data presented in this paper provide constraints on both geophysical and petrogenetic

* Because of its readiness to form inclusion-free porphyroblasts or phenocrysts, orthopyroxene is the most easily analyzed mineral in the assemblage and thus the best for noting changes in Mg-value, Al₂O₃ content etc.
aspects of the upper mantle. Firstly, the determination of the pyrolite solidus in the presence of small amounts of water (water-undersaturated, \( p_{H_2O} \) determined by equilibrium between pargasitic amphibole and its breakdown products) establishes a firm petrological model for the low velocity zone (LVZ) of the upper mantle. If the water content of the upper mantle is < 0.4% approximately, the petrological model predicts a relatively stable location of the roof to the low velocity zone at depths equivalent to 27–29 kb load pressure (85–95 km approx.) due to intersection of the local geothermal gradient with the pyrolite solidus. Variation in the local geothermal gradient would cause variation in the degree of partial melting (and thus the magnitude of the seismic attenuation) within the LVZ and possibly considerable variation in the depth to the floor of the LVZ, with little change in the depth to the roof of the LVZ (base of the lithosphere). The data on subsolidus mineralogy for (pyrolite + 0.2% \( H_2O \)) also show that the appearance of garnet would occur along an oceanic geotherm at load pressures of approximately 17–19 kb (55–66 km). This mineralogical change would cause a small increase in density and possibly in seismic velocity in the lower part of the lithosphere; similar mineralogical zoning for an anhydrous mantle has been discussed previously [5, 6].

The data illustrating the position of the pyrolite solidus for water-saturated melting show that the base of the lithosphere, if located by the intersection of the geotherm with the pyrolite solidus, may move abruptly from depths of 85–95 km to depths of 60–70 km, without change in the local geothermal gradient, if the water content of the lower part of the lithosphere is increased to exceed ~0.4% \( H_2O \). Addition of water to previously immobile lithosphere may occur from underthrust lithosphere of a subduction zone, and may lead to rather high degrees of partial melting and mantle diapirism from depths of 60–70 km, the degree of partial melting increasing as the diapirs moved towards the surface.

The experimental data provide an explicit model for two different tectonic regimes (fig. 3). The water-undersaturated melting data are applied to yield a model of a relatively stable lithosphere and LVZ, either in oceanic or continental regions, in which volcanism may occur either by simple fracturing of the lithosphere and direct tapping of the small melt fraction in the LVZ, or by tensional thinning of the lithosphere with

D.H. Green, Experimental melting studies

Fig. 3. Diagram summarizing the petrogenetic applications of the melting studies on pyrolite composition. The column to the left illustrates the mineralogical character of the lithosphere and depth to the onset of partial melting in the island arc situation and the normal oceanic crust-mantle situation. In the right side of the diagrams, the character of magma derived by partial melting of pyrolite is plotted as a function of depth of magma segregation and degree of partial melting. Numbers in parentheses adjacent to basalt names refer to the normative olivine content of the partial melt. The hatched areas illustrate the range of conditions over which quartz-normative magmas may be derived by direct partial melting and magma segregation from pyrolite. (A) is compiled for melting under water-undersaturated conditions, with a water content in the source pyrolite of about 0.2%. (B) is compiled for melting under water-saturated conditions. The asterisks denote the specific liquid compositions calculated at 10 kb and 20 kb in this paper.
consequent upwelling and diapirism from the LVZ leading to higher degrees of partial melting and shallower depths of magma segregation. If the latter process develops into large-scale rifting apart of lithospheric plates, then the deeper parts of the LVZ become involved in the upwelling at the rift axis and act as major magma sources. The data of fig. 2 may in this way, be applied to quantify the specific models of basaltic volcanism of mid-oceanic ridge, rift valley, island chain and oceanic island situations which were developed previously [12, 15–17].

In contrast to this tectonic setting, the data on water-saturated melting is applied to yield a model of an unstable situation in which the base of the lithosphere moves to depths of 60–70 km due to access of water (to exceed about 0.4% H₂O) and the higher water contents produce higher degrees of partial melting at depths > 60 km. This setting is one in which mantle diapirism, in some cases from reactivated lithosphere, would lead to high degrees of melting under water-saturated or near-saturated conditions and to magma segregation at rather shallow depths. The tectonic conditions described would occur if there were access of proportionately large amounts of water to the upper 60–150 km of the mantle. Such conditions may occur in the wedge of mantle overlying the Benioff zone in oceanic trench-island arc situations where the source of proportionately large and rapidly released amounts of water can be attributed to dehydration reactions in subducted lithosphere [2, 3, 12, 13, 18, 20].

6.2. Magma genesis in island arcs

As well as defining the $P$, $T$ conditions of melting of a pyrolite upper mantle under water-saturated conditions, the data presented establish the nature of the magmas produced by partial melting under these conditions. It has been shown that with sufficiently high degrees of melting of pyrolite at 10 kb such that olivine (+ accessory chromite) is the only residual phase (~ 32% melting), the melt is of magnesian quartz tholeiite character. For lower degrees of melting (28%) of pyrolite under these conditions, liquids with ~10% normative quartz and ~56% SiO₂ are produced at temperatures of ~1100°C, leaving residual wehrlite (olivine + clinopyroxene ± accessory chromite). For < 25% melting, at 10 kb and $T < 1100^\circ$C, the magma composition cannot as yet be clearly specified but the evidence presented suggests that liquids will have higher alkali-content but retain SiO₂ contents of around 55%. Magmas such as the highly magnesian, low-calcium, quartz-rich "andesites" (56–58% SiO₂) of Cape Vogel, Papua [28, 31] might be products of high degrees of melting of pyrolite under water-saturated conditions with magma segregation occurring at < 10 kb [29].

The data presented in this paper on the experimental melting of pyrolite show that water-saturated, magnesian quartz tholeiites and basaltic andesites may be derived by direct partial melting of pyrolite at ~10 kb but that water-saturated olivine tholeiites are the least undersaturated magmas which may be derived by partial melting of pyrolite at ~20 kb. These conclusions support those of Nicholls and Ringwood [2, 3] who have carried out the necessary complementary study, i.e. the determination of the liquidus phases of olivine tholeiite, quartz tholeiite and basaltic andesite under water-saturated conditions. These studies [2, 3] defined the expansion of the field of olivine as a liquidus phase in quartz-normative natural rock compositions under water-saturated conditions and demonstrated that such liquids could be equilibrium melt products of a peridotite source, leaving residual olivine. The data presented in this paper do not support the conclusion that andesitic or dacitic magmas can be derived by direct partial melting of peridotite at pressures up to 25 or 30 kb [1, 7–9, 29]. More importantly, the data provide clear evidence that the presence of highly siliceous glasses in quenched high-pressure runs containing a large proportion of primary crystals (either with or without readily identifiable quench phases) is a result of metastable fractionation of liquid during quenching, caused by the outgrowth of rims on primary phases and/or nucleation of quench clinopyroxene, amphibole and mica. The compositions of such glasses are not consistent with equilibrium between liquid and primary olivine and pyroxenes of the peridotite source rock and do not constitute evidence for the genesis of siliceous (> 55% SiO₂) liquids by partial melting of peridotite under water-saturated conditions at $P >$ 10 kb.
Acknowledgements

The author acknowledges the skill and assistance of W.O. Hibberson in carrying out the experimental runs. The installation and calibration of the TPD electron probe by S.J.B. Reed and N.G. Ware has added greatly to the usefulness of this technique in experimental petrology. The critical comments of I.A. Nicholls, A.E. Ringwood and T.H. Green on the manuscript, particularly in areas where the present study integrates with their own experiments, resulted in improvements to the data (role of Fe-loss, particularly) and to the manuscript. The comments of the reviewers for the manuscript have materially improved the paper. These contributions are gratefully acknowledged.

References

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Coexisting Garnets and Ilmenites Synthesized at High Pressures from Pyrolite and Olivine Basanite and Their Significance for Kimberlitic Assemblages

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Abstract. Coexisting garnets and ilmenites have been synthesized at high pressure (21–40 kb) within the temperature range between 900 and 1100°C from pyrolite-less-40% olivine and olivine basanite with various water contents. The two compositions yield phases with a range in the 100 Mg/Mg+Fe ratio for both garnet (41–76) and ilmenite (15–47). The distribution coefficient for iron and magnesium (K_{Fe/Mg}) = 4.0±0.5) for coexisting phases does not appear to vary with change in the bulk composition or temperature of synthesis. The synthesized ilmenites are of similar composition to those of kimberlites in 100 Mg/Mg+Fe ratio and Al₂O₃ and Cr₂O₃ solid solution. CO₂ content in ilmenite is dependent on Cr₂O₃ in the bulk composition and also on Fe₃O₄ content of ilmenite. Fe₃O₄ content of ilmenite is very sensitive to O₂ and natural ilmenites from peridotites have formed under low O₂. Al₂O₃ solid solution in ilmenite as well as TiO₂ in coexisting garnet tend to be higher with higher temperature. All the variety of compositions of ilmenites from kimberlites may be obtained from rocks rather close in composition to those used in experiments, within the same range of pressure and temperature but at variable oxygen fugacities.

Introduction
Pyrope—almandine garnets and magnesian ilmenites are among the most common minerals found in a majority of kimberlitic pipes. Garnets occur in xenoliths of various peridotites and eclogites and as discrete nodules and isolated grains in the heavy mineral concentrates from kimberlites. In most cases, garnets do not have a paragenetic relation to ilmenites. Ilmenite is mainly found as nodules of varied size and as isolated grains in concentrates, and more rarely as regular intergrowths with pyroxenes (both diopside and enstatite), (Williams, 1932; Sobolev, 1959, 1964; Frantsesson, 1970; Mitchell, 1973; Milashev et al., 1963). It also occurs rarely within ilmenite-bearing peridotites. The rare occurrences of ilmenite co-existing with other phases such as olivine, pyroxenes and garnet attract special attention in attempts to clarify possible systematic relationships of its formation in kimberlite. (Ringwood and Lovering, 1970; Dawson and Reid, 1970; Boyd and Nixon, 1973; Ponomarenko et al., 1971, 1972).

In experimental studies of several basaltic and peridotitic compositions, mineral assemblages containing co-existing garnet and ilmenite, had been syn-

thesized in studies aimed at determining solidus, liquidus and phase relationships as functions of pressure, temperature and water content. The known variations in composition of natural ilmenite and garnet, particularly in Ti-content of garnet, Al-content of ilmenite etc., suggested that useful constraints on $P$, $T$ conditions of crystallization of the natural minerals might be obtained by analysis of the coexisting mineral pairs synthesized under known $P$, $T$ conditions. The study was of reconnaissance character seeking to isolate $P$, $T$ dependent substitutions or partition relationships which would then repay further detailed study in compositions chosen specifically to calibrate the potential $P$, $T$ indicator (cf. the study by Raheim and Green (1974) of the $K_{\text{Fe}-\text{Mg}}^{\text{Grt}-\text{Cpx}}$ partition coefficient for Fe, Mg in garnet and clinopyroxene).

Experimental Methods

Selection of Compositions

For the present study the composition of pyrolite-less-40% olivine (Green and Ringwood, 1970; Green, 1973b) and also olivine basanite (Green, 1973a) were used. These compositions contain garnet and ilmenite in both subsolidus and above-solidus mineral assemblages and phase relationships have been investigated for a wide range of pressure and temperature conditions and for various water contents (Green 1972, 1973a, b, c).

The comparatively low TiO$_2$ content of the bulk compositions and the appreciable solubility of TiO$_2$ in pyroxenes, amphibole and garnet, meant that ilmenite was a minor phase and though identifiable in many runs, could only be analyzed with sufficient accuracy when crystals were $>$ 3 microns diameter. In several runs (Tables 1 and 2) garnet was analyzable but ilmenite was absent or not confirmed by electron probe (pyrolite composition). These data give information on minimum TiO$_2$ solubility in garnet at the varous temperatures and pressures.

Microprobe Analyses

The analyses of synthesized phases were carried out using the TPD electron probe microanalyzer with energy-dispersive detection and analysis system (Reed and Ware, 1973; Green, 1973a). This instrument is uniquely suited for complete analyses of very small grains ($>$ 3 $\mu$) present in experimental high pressure runs. Some minerals from the kimberlites of Yakutia were analyzed using the MS46 electron probe using the procedure described by Sobolev, Lavrent'iev et al. (1969).

The ten to twenty individual analyses of garnet and ilmenite were carried out on each experimental run and the analyses listed in Tables 1 and 2 were selected as having totals between 98% and 102%, acceptable structural formulae and (for ilmenites only) SiO$_2$ $<$ 1%.

Analytical Data (Tables 1 and 2)

(a) Garnet. At 35 kb, 1500° C in pyrolite composition garnet containing 1.4% TiO$_2$ may not coexist with ilmenite so that the TiO$_2$ content of 1.4% is a minimum value for TiO$_2$ solubility in garnet. Similarly, in the olivine basanite runs at 30 kb, 1280° C and at 25 kb, 1160° C, 1140° C and 1120° C, garnet coexists with liquid and clinopyroxene but not with ilmenite and the TiO$_2$ contents of these garnets are also minimal values. The increase in TiO$_2$ at 25 kb from the 1160° C run (1.2% TiO$_2$), through the 1140° C run (1.6% TiO$_2$) to the 1120° C run (1.8% TiO$_2$) is considered to reflect increasing TiO$_2$ content of the coexisting liquid and possibly changing partition coefficient between liquid and garnet [Mg$_{66}$ to Mg$_{68}$] as the degree of crystallization increases at lower temperatures. At the same
pressure, garnet coexisting with ilmenite at 1040°C contains 1.4% TiO₂ but this decreases through runs at 1020°C, 1000°C to 0.8% TiO₂ at 900°C.

In the pyrolite (less-40%-olivine) composition, garnet coexisting with ilmenite contains 0.9–1.6% TiO₂ at 1100°C, 0.7–1.1% TiO₂ at 1000°C and 0.4% TiO₂ at 950°C (Table 1). The data suggest a decrease in TiO₂ content at lower temperatures but are not sufficient to evaluate possible systematic pressure or compositional effects as opposed to analytical uncertainty in giving rise to the rather large spread in TiO₂ at any one temperature.

We have evidence for compositional control on the amount of TiO₂ soluble in the pyrope-almandine solid solution in that garnet from pyrolite (~Mg₅₀) has lower TiO₂ content than that from basanite (Mg₅₀–₆₀), crystallized at similar P, T conditions (Tables 1, 2 and 5).

(b) Ilmenite. The ilmenites analyzed from both pyrolite and basanite composition are characterized by high (Fe, Mg) TiO₂ contents and low degrees of solid solution of Cr₂O₃, Fe₂O₃, and Al₂O₃. This feature is very well illustrated in the TiO₂ vs MgO diagram utilized by Sobolev (1974) to illustrate variation in natural ilmenites from kimberlite pipes. This diagram can be contoured for Fe₂O₃ content of ilmenite and such contours are approximately correct for (Cr₂O₃+Fe₂O₃) solid solutions because of similar molecular weights of Cr₂O₃ and Fe₂O₃. The analyzed magnesian ilmenites (Mg₄₂–Mg₄₈) from the experimental runs on pyrolite-less-40% olivine composition have <5%Fe₂O₃±Cr₂O₃ and the major substitution is Cr₂O₃ (1.4–2.3% Cr₂O₃) with minor Al₂O₃ and possibly very minor Fe₂O₃. In the basanite composition, Cr₂O₃ is not detectable in ilmenite and the more iron-rich ilmenites (Mg₁₅–Mg₂₈) require low Fe₂O₃ contents to satisfy structural formulae constraints.

In Fig. 1, the experimentally synthesized ilmenites are compared with natural ilmenites of various paragenetic associations occurring within kimberlite pipes. The synthetic magnesian ilmenites most closely resemble these ilmenites occurring in intergrowth with diamond and those occurring in intergrowth with garnet or within garnet peridotite. Most discrete ilmenite crystals within kimberlite have higher Fe₂O₃ contents, implying higher oxygen fugacity at crystallization than the conditions pertaining within the piston-cylinder apparatus. The ilmenite megacrysts occurring in basanite magmas in N.S.W. (Binns, 1969; Wass, 1971) are similar to but have slightly higher Fe₂O₃ contents than those crystallized experimentally from the basanite. One ilmenite megacyrst occurring within a mantle-derived nepheline benmoreite magma (Green et al., 1974) from S.E. Queensland has low MgO content and low Fe₂O₃ content, closely resembling the ilmenite crystallized from basanite at 900°C (i.e. after a moderately high degree of crystallization of the basanite liquid).

The data on ilmenite compositions synthesized in the presence of a water-rich fluid phase or with water dissolved in the silicate melt phase, demonstrate that the experimental techniques used maintain oxygen fugacity at low values, consistent with equilibrium with carbon (graphite or diamond) in the C—H—O system. Experiments in a basalt-H₂O—CO₂ system (Brey and Green, 1975) at 30 kb using the oxygen buffering technique have shown that at 30 kb, 1100 to 1200°C with fO₂ buffered by the magnetite—haematite buffer, titanomagnetite rather than ilmenite coexists with garnet, and the garnet contains andradite solid
Table 1. Compositions of coexisting garnets and ilmenites in the pyrolite less 40% olivine Ag$_{75}$Pd$_{25}$ capsules except

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Mol. proportions

| 100 Mg/Mg + Fe | 83.5 | 76.8 | 45.8 | 47.9 | 77.2 | 47.4 | 75.8 | 45.8 |
| Ca | 12.7 | 13.2 |
| Mg | 72.9 | 60.7 | 45.8 | 47.9 | 63.7 | 47.4 | 62.2 | 45.8 |
| Fe | 14.4 | 20.1 | 54.2 | 52.1 | 18.8 | 52.6 | 19.9 | 54.2 |

K$_{D(Fe,Mg)}^{ilm-ga}$

3.91

3.76

3.70

$^a$ Presence of ilmenite not confirmed by electron probe, garnet coexists with olivine, enstatite.

Table 2. Compositions of coexisting garnets and ilmenites in olivine basanite at various except column 1

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Mol. proportions

| 100 Mg/Mg + Fe | 80.0 | 68.0 | 60.4 | 55.3 | 53.5 | 23.9 | 53.8 | 21.2 |
| Ca | 15.0 | 18.5 | 18.0 | 17.3 | 19.1 | — | 16.5 | — |
| Mg | 68.0 | 55.4 | 49.7 | 45.8 | 43.3 | 23.9 | 44.9 | 21.2 |
| Fe | 17.0 | 26.1 | 32.3 | 36.9 | 37.6 | 76.1 | 38.8 | 78.8 |

K$_{D(Fe,Mg)}^{ilm-ga}$

3.68

4.31

$^a$ No ilmenite present, garnet coexisting with liquid and clinopyroxene.
Coexisting Garnets and Ilminites from Pyrolite and Olivine Basanite composition at various pressures, temperatures and water contents. All experiments in column 1 (Pt capsule)

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Clinopyroxene.

pressures, temperatures and for various water contents. All experiments in Ag₇₅Pd₂₅ capsules (Pt. capsule)

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b Nepheline mugearite bulk composition (Irving and Green, in preparation).

Fig. 1. Plot of MgO vs TiO₂ for experimentally synthesized ilmenites and ilmenites from various associations in kimberlite illustrating the divergence of ilmenites from the simple FeTiO₃—MgTiO₃ solid solution.

1. Ilmenite in kimberlites of Yakutia (Frantsesson, 1970; Milashev et al., 1963; Sobolev, ed., 1959, 1964)
2. Ilmenite in kimberlites of West Africa and South Africa (Danchin, d’Orey, 1972; Kukharenko et al., 1971; Mitchell, 1973; Vladimirov et al., 1971)
3. Ilmenite in intergrowth with clinopyroxene, Yakutia (Ponomarenko et al., 1971; Sobolev, ed., 1964)
5. Ilmenite from garnet peridotites or intergrown with pyrope garnets, Yakutia (Ponomarenko et al., 1971, 1972; Sobolev, ed., 1964, this paper, Table 6)
6. Ilmenite from garnet peridotites or intergrown with pyrope garnets, S. Africa (Boyd, Nixon, 1972, 1973; this paper, Tables 4, 5)
7. Ilmenite intergrown with diamond, Mir pipe, Yakutia (Sobolev, 1974; Sobolev et al., 1971; this paper, Table 6)
8. Inclusions of ilmenite in zoned garnet from Mir pipe, Yakutia (Sobolev et al., 1974)
9. Ilmenites synthesized from pyrolite-40% olivine at T=1100°C (this paper, Table 2)
10. Ilmenites synthesized from pyrolite-40% olivine at T=1000°C (this paper, Table 2)
11. Ilmenites synthesized from pyrolite-40% olivine at T=950°C (this paper, Table 2)
12. Ilmenites synthesized from olivine basanite at T=1100°C
13. Ilmenites synthesized from olivine basanite at T=1000–1050°C
14. Ilmenite synthesized from olivine basanite at T=900°C (data for 12, 13, 14 are from this paper, Table 3)
15. Ilmenite synthesized by Akella and Boyd (1972)
16. Ilmenite megacrysts from basaltic lavas (Green et al., 1974; Wass, 1971)
solution. The experimental syntheses of ilmenite confirm earlier conclusions based on analyses of FeO, Fe₂O₃ in bulk charges and evaluation of buffer assemblages, that the standard experimental techniques used in the piston cylinder apparatus result in fo, conditions considerably lower than the haematite-magnetite buffer, and close to the nickel-nickel oxide or magnetite-wustite buffers (Allen et al., 1972; Green and Ringwood, 1967; Nichols and Ringwood, 1974). Comparison of the natural ilmenites from garnet peridotite parageneses with those synthesized, suggests that the natural assemblages have crystallized at fo, much lower than the magnetite-haematite buffer but within a small range of fo, close to and slightly greater than fo, for the Ni-NiO buffer. Similarly, the analyses of ilmenite megacrysts in basanitic magmas argues that the crystallization and deep seated crystal fractionation processes in which ilmenite plays a role have occurred under conditions of low fo, close to that of the Ni—NiO buffer.

The range of higher Fe₂O₃ contents in discrete ilmenite megacrysts in kimberlite, the crystallization (Table 3) within the garnet peridotite WSS1 of a more Fe₂O₃-rich secondary ilmenite (Fig. 1, Table 3) and the rimming of ilmenite megacrysts in basanitic magmas with titanomagnetite (Green et al., 1974) are all features suggesting that in the transport or eruptive stages of extraction of xenolithic material from the upper mantle, the fo, in the host magma (fluid) increases to higher values than appropriate to the upper mantle source environment.

The synthesized ilmenites show an increase in Al₂O₃ with increasing temperature but with considerable scatter in the data. Natural ilmenites show a similar spread in Al₂O₃ contents but extending to lower values, particularly in ilmenites

### Table 3. Coexisting primary and secondary phases in peridotite xenolith W.S.S.1, Wesselton pipe, South Africa

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Mol. proportions

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ᵃ Calculated from the mineral formula.
ᵇ Total Fe as FeO.
Table 4. Coexisting garnets and ilmenites in Peridotite Xenoliths of Udachnaya pipe, Yakutia (UV-494, Uv-600), and ilmenites from intergrowths with individual diamond (spec. BM-10a), and with polycrystalline diamond aggregate (MR-331) from the Mir pipe, Yakutia

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<tr>
<th></th>
<th>Uv-494</th>
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<th>BM-10</th>
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<td>1.94</td>
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<td>1.41</td>
<td>0.23</td>
<td>0.76</td>
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<td>12.4b</td>
<td>2.4</td>
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<td>5.28</td>
<td>0.01</td>
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Totals 98.37 101.35 99.14 101.56 98.46 100.46

Mol. proportions

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<tr>
<th></th>
<th>100 Mg/Mg+Fe</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
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<td></td>
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<td></td>
<td>38.5</td>
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<td>38.5</td>
<td>61.5</td>
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</tbody>
</table>

a Data from Sobolev et al. (1971).
b Calculated from mineral formulae.

associates with diamond. Al₂O₃ content of ilmenite appears to be independent of Cr₂O₃ and Fe₂O₃ contents of ilmenite.

Element Partition between Coexisting Garnet and Ilmenite

(a) Distribution of Iron and Magnesium

The data of Tables 1 and 2 illustrate correlation between the Mg/Mg+Fe-values, and the Cr₂O₃ contents of both ilmenite and garnet. Ilmenite has much lower Mg-value \( \left( \frac{100 \text{Mg}}{\text{Mg}+\text{Fe}} \right) \) than coexisting garnet and we may define a distribution coefficient.

\[
K_D^{\text{ilm-ga}} = \frac{(\text{Fe}^{++}/\text{Mg})_\text{ilm}}{(\text{Fe}^{++}/\text{Mg})_\text{ga}}
\]

To express the compositional relationships between the coexisting solid solutions. \( K_D^{\text{ilm-ga}} \) will be a function of pressure, temperature and possibly of composition if either garnet or ilmenite solid solutions are non-ideal. Fig. 2 and Tables 1 and 2 show that \( K_D^{\text{ilm-ga}} = 4.0 \pm 0.5 \) for all synthesized assemblages. In pyrolite composition at 1100°C, variation in pressure from 21 kb to 40 kb shows slight increase in \( K_D \) with increasing pressure (3.70 to 3.91) but further data would be required to substantiate this trend. There is no obvious temperature effect on \( K_D \) within the temperature interval 900°C to 1050°C for the basanite composition or within the temperature 950°C to 1100°C for pyrolite composition. The wide range of Mg-values of garnet (41-77) and ilmenite (47 to 15) without systematic change in \( K_D \) suggests that \( K_D \) is dependent
Coexisting Garnets and Ilmenites from Pyrolite and Olivine Basanite

Fig. 2a and b. Partitioning of Fe and Mg between garnet and ilmenite for synthesized samples (a) and for both natural and synthesized ilmenites (b). Symbols (b) as for Fig. 1

of compositional (Mg-value only) variation over the range of compositions of interest for natural ultramafic or basic rocks.

The temperature range over which $K_D$ variation can be examined is not large in the experiments reported and further experiments are required at lower and higher temperatures to evaluate the $K_D$ vs $T$ relationship. It may be noted that $K^{Ga}_{D(Fe, Mg)}$ has values of 4.7 (900°C), 4.0 (950°C), 3.0 (1050°C) and 2.7 (1100°C) at 30 kb (Raheim and Green, 1974) and the data presented herein shows that $K^{Ga}_{D(Fe, Mg)}$ is less sensitively dependent on temperature than $K^{Ga-cpx}_{D(Fe, Mg)}$. Our data  

suggests that Fe/Mg partition between ilmenite and clinopyroxene (or olivine, or orthopyroxene) is likely to be more useful as a petrological tool in deduction of $P$, $T$ conditions of equilibration than Fe/Mg partition between ilmenite and garnet. From Fig. 2 and the data of Raheim and Green (1974) $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ at 900° C, 30 kb and $K_{D}^{\text{lim-cpx}}$ $\text{Fe}^{++}$. For the Wesselton garnet peridotite (Table 4), $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ $\approx$ 8.75; for ilmenite (8.6% Fe$_2$O$_3$) and diopside (sub-calcic) in lamellar intergrowth from Untjes Berg Pipe, $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ $\approx$ 8.02 (Boyd and Nixon, 1973) and for ilmenite (2.61% Fe$_2$O$_3$) and diopside (sub-calcic) from Matsoku Pipe $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ $\approx$ 7.15 (Akella and Boyd, 1973).

We conclude, from the experimental data and the comparison with natural ilmenite/garnet and ilmenite clinopyroxene parageneses that $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ $\approx$ 4.0 ± 0.5 for a range of $P$, $T$ conditions about 20–40 kb, 900–1100° C and is probably not sensitively dependent on $P$, $T$ or Mg-value of the bulk composition. However, $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ is probably sensitively and positively correlated with Fe$_3$O$_4$ substitution in ilmenite. It appears probable that $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ is more sensitively dependent on temperature and it is of interest that two independent parameters (the more sub-calcic pyroxene and lower $K_{D}^{\text{lim-cpx}}$ $\text{Ilm-ga/Fe}^{++}$ indicate that the Matsoku Ol+Cpx+Opx+Ilm assemblage (Akella and Boyd, 1973) is a higher temperature assemblage than the Wesselton example (Table 3).
(b) Chromium Partition between Ilmenite and Garnet

Examination of Tables 1, 3 and 4 shows that coexisting garnet and ilmenite have similar contents of Cr$_2$O$_3$ (weight %) in both the synthesized assemblages and in those of natural garnet-ilmenite associations. Comparison of $(100 \text{ Cr/}R^{VI})_{\text{garnet}}$ vs $(100 \text{ Cr/}R^{VI})_{\text{ilmenite}}$ ($R^{VI} = \text{Ti} + \text{Al} + \text{Cr} + \text{Fe}^{+++}$) reveals a wide spread of Cr content in natural garnet-ilmenite paragenesis and preference by Cr$^{+++}$ for the six-fold co-ordination sites in garnet. The synthesized mineral pairs are similar to the more Cr-rich of the natural assemblages but the Wesselten garnet peridotite WSS1 is exceptionally high in Cr-content. The coexisting ilmenite/garnet analyses from a zoned garnet from Mir pipe (Sobolev et al., 1974) are anomalous in that Cr$^{+++}$ shows preference for ilmenite-haematite sites rather than garnet sites—this exceptional behavior may be directly linked to the very high Fe$_2$O$_3$ content (>20%) of these particular ilmenites. The ilmenites with highest Cr$_2$O$_3$-contents occur within compositional zones of the garnet containing 4.7–4.0% Cr$_2$O$_3$ together with coexisting inclusions of chromite (V. S. Sobolev et al., 1972; N. V. Sobolev et al., 1974). Further evidence of the relationship between Cr$_2$O$_3$ and Fe$_2$O$_3$ content in ilmenite is provided by the secondary ilmenite within alteration zones of the Wesselton peridotite (Table 3). Ilmenite containing 10.4% Fe$_2$O$_3$ and coexisting with chromite, contains 8.6% Cr$_2$O$_3$ and is in addition a much more magnesian (12.2% MgO) ilmenite than the Fe$_2$O$_3$ and Cr$_2$O$_3$-rich ilmenites from zoned garnet in the Mir pipe.

Conclusions

In garnet±ilmenite parageneses, the TiO$_2$ content of garnet appears to be proportional to temperature of equilibration. The synthesized garnet/ilmenite pairs presented support this conclusion over the temperature range 950°C to 1100°C and the similarity of TiO$_2$ contents of natural and synthesized garnets (Tables 2 and 3) argues for similar temperatures of equilibration for most natural ilmenite-bearing peridotite assemblages. The most TiO$_2$-rich natural garnet (2.38% TiO$_2$, Ponomarenko et al., 1971) known from ilmenite-bearing peridotite of Yakutia contains high temperature, sub-calcic clinopyroxene (100 Ca/Cd-Mg = 30) and on the data presented here implies equilibration temperatures above 1150°C.

The synthesized ilmenites from pyrolite and basanite compositions demonstrate that very low $f_{O_2}$ conditions are normally present under the experimental procedures using the piston cylinder apparatus. In particular, $f_{O_2}$ conditions are very close to these under which natural ilmenites coexisting with diamond were formed. Other natural ilmenites from peridotite xenoliths contain a small range of Fe$_2$O$_3$ contents, implying a small range of $f_{O_2}$ conditions in the source region. Ilmenites with considerably higher Fe$_2$O$_3$ contents occur as secondary products in peridotite xenoliths and as discrete crystals within kimberlite breccias. The higher $f_{O_2}$ conditions implied by these ilmenites probably reflect rapidly changing conditions during transport and eruption of the kimberlitic magma. We infer that mantle-derived ilmenite may be used as a sensitive indicator of $f_{O_2}$ conditions within the mantle and furthermore that $f_{O_2}$ conditions close to the magnetite-haematite oxygen buffer are too high, and inappropriate for experiments aimed at highly undersaturated magma genesis. In contrast, experimental conditions of equilibrium
with graphite (system C—H—0) or close to the Ni—NiO oxygen buffer are appropriate for upper mantle conditions.

The distribution of iron and magnesium between coexisting garnet and ilmenite \( (K_{D(Fe^{++}, Mg)}^{ilm-ga}) \) appears to be a relatively insensitive function of temperature of equilibration but may increase with increasing pressure at constant temperature. The partition coefficient \( (K_{D(Fe^{++}, Mg)}^{ilm-px}) \) offers more promise as a temperature-dependent variable of use in estimation of conditions of equilibration of natural ilmenite-bearing assemblages. However, the \( f_O \)-dependent substitution of \( Fe_3O_3 \) in ilmenite markedly affects \( Cr_2O_3 \) solubility relationships and may affect \( Fe^{++}/Mg \) partition relation relationships. Natural ilmenites show sufficient variation in major and minor element composition to warrant further study and initiation of experimental projects specifically designed to investigate ilmenite solid solutions under controlled physical conditions.

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PYROXENES IN THE SYSTEM Mg$_2$Si$_2$O$_6$—CaMgSi$_2$O$_6$
AT HIGH PRESSURE

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The enstatite—diopside solvus in the system Mg$_2$Si$_2$O$_6$—CaMgSi$_2$O$_6$ has been experimentally determined within the pressure range 5–40 kbars and the temperature range 900–1500 °C. Experiments involving reversal of the phase boundaries by unmixing from glass starting material and by reaction of pure clinoenstatite and diopside showed difficulty in achieving equilibration due to persistence of metastable, subcalcic clinopyroxene and to the sluggishness of reaction rate. The experimental data showed that the temperature dependence of the diopside limb is less than previously accepted. At 1500 °C and 30 kbars subcalcic diopside found by Davis and Boyd (1966) is shown to be metastable with respect to enstatite and more calcic diopside of composition En$_{42}$Di$_{57}$. The solvus widens with increasing pressure between 5 and 40 kbars at 1200 °C, but at 900 °C the pressure effect on the solvus is very small. The stability relationships of the four pyroxenes, protoenstatite, enstatite, iron-free pigeonite and diopside are summarized, based on data from the literature and the present study.

1. Introduction

Previous studies [1–7] have shown that the solvus between enstatite and diopside in the system Mg$_2$Si$_2$O$_6$—CaMgSi$_2$O$_6$ narrows with increasing temperature and suggest that the pressure effect on the solvus is small and may be opposite to that of temperature. However, because of the possible uncertainty of measurement and some scattering of the experimental data, the pressure effect on the solvus remains uncertain. A further problem at high pressure and temperature is the strong curvature of the diopside limb above 1400 °C at 30 kbars [4] with diopside becoming subcalcic (En$_{70}$Di$_{30}$ in mole %, at 1500 °C and 30 kbars). Kushiro [3] suggested that these subcalcic clinopyroxenes might be pigeonitic.

In the present investigation we have concentrated our experiments on accurate determination of the pressure effect on the solvus from 5 to 40 kbars at 1200 °C and on delineation of the temperature dependence of the solvus at 30 kbars. The practicability of the project was also dependent on the high accuracy and reproducibility of analysis on small grains, combined with excellent optics and contemporaneous analysis for all elements attainable with TPD electron probe and energy dispersive analytical system [8].

2. Preparation of starting materials

Several kinds of starting materials were prepared.

2.1. En$_{50}$Di$_{50}$ glass

Three separate glasses of the same composition, En$_{50}$Di$_{50}$ (mole %), were prepared from A.R. grade chemicals of SiO$_2$, MgO, and CaCO$_3$. Weighed mixtures of the reagents were melted on an iridium-strip heater and were stirred by a platinum rod to homogenize, then quenched by cutting off the power and simultaneously cooling by compressed air. The glasses were ground to average 25-μm grain size. One piece of glass from each batch was polished and examined by microscope, microprobe and, in some cases, X-ray powder photography. Two batches among the three batches were used for the experiments.
contained a trace amount (<1%) of quench clinopyroxene and olivine. Compositions of quenched clinopyroxene were similar to those of the host glasses. The third glass was free from any crystals. Composition of the three glasses varied from En$_{48.4}$Dis$_{6.6}$ to En$_{49.6}$Di$_{50.4}$ with an inhomogeneity of ±0.2 to ±0.5 mole % end member.

2.2. En$_{80}$Di$_{20}$ glass

A glass with the composition of En$_{80}$Di$_{20}$ was made in the same way as above. A trace amount of crystals (<1%) was found in the glass, but they were not identified because of their scarcity and tiny sizes. Analyzed composition of the glass was En$_{81.6}$Di$_{18.4}$.

2.3. Synthetic pyroxenes

In some homogenization runs, synthetic diopside (CaMgSi$_2$O$_6$) and clinoenstatite (Mg$_2$Si$_2$O$_6$) of TemPres Research Co. were used. Microprobe analysis showed the presence of trace amount of CaO (<0.05 wt.%) in the clinoenstatite.

3. Synthesis and chemical analysis of pyroxenes

The high-pressure apparatus used was a Boyd and England [9] design piston-cylinder device and a pressure correction of −10% of nominal load pressure, using piston-in technique, was applied. This method of correction is based on calibrations on quartz-coesite at 1100°C [10] and albite = jadeite + quartz at 600°C (G. Brey and D.H. Green, unpublished data). Temperature measurement was by Pt/Pt$_{90}$Rh$_{10}$ thermocouple with no correction applied for pressure effect on thermocouple emf. Samples were encased in sealed Pt capsules or in Pt capsules with a crimped end in those cases where the catalytic effect of low water-vapour pressures was desired.

Chemical analyses were by means of the TPD-electron probe, with an analysis area of about 3 μm diameter as judged by fluorescence on periclase. The visible fluorescence of the pyroxenes made positioning for analysis easier and more reliable. All relevant elements were measured simultaneously and at least ten analyses were made on each pyroxene phase in every run. Some analyses with structural formulae deviating from stoichiometry were discarded. These were less than 10% of all the analyses.

In some of the homogenization experiments the capsule was loaded with a layer of clinoenstatite in contact with a layer of diopside. A polished thin section across this contact was prepared after the run and the contact between the two pyroxene types was examined optically and with the electron probe.

4. Experimental results

The run procedures, products and pyroxene compositions are summarized (Table 1 and brief comments in the Appendix). Pyroxene analyses* are shown (Fig. 1) except for the runs 2, 3 and 7 which are of shorter reaction time.

The spread of data in some of the unmixing and homogenization experiments is related to mechanisms and sluggishness of chemical reactions. As shown in run 2, the En$_{50}$Di$_{50}$ glass crystallized both orthopyroxene and clinopyroxene within only 6 minutes at 30 kbars and 1200°C. The glasses found in other experiments with longer run duration are, therefore, not unreacted starting glasses but melts generated by presence of water and equilibrated with pyroxenes. The water-saturated melting point of En$_{50}$Di$_{50}$ is about 1050°C at 30 kbars [7], and water added to or allowed to enter the capsules naturally causes melting at higher temperature. The run duration of 45 minutes at 30 kbars and 1200°C (run 3, Table 1) crystallized orthopyroxene and clinopyroxene of compositions lying between the original bulk composition and the equilibrium compositions. The 4-hour experiment (run 4) gave pyroxenes with a wider composition gap and appears to have reached the equilibrium compositions (see later discussion). Comparison of runs 7 and 8 shows a similar time dependent relationship for pyroxenes crystallizing from glass starting material. Although from these experiments we have no information on the initial steps of crystallization from glass, since even after 6 minutes we have two pyroxenes present, we have obtained further information in Fe-bearing experiments with varying run duration. The crystallization sequence in these runs was firstly

* A list of pyroxene analyses is obtainable by writing to the authors.
### TABLE 1
Details of experiments and chemical ranges of pyroxenes (number of analyses are shown in parentheses)

<table>
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<tr>
<th>Run. No.</th>
<th>P (kbars)</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>Starting composition</th>
<th>H₂O</th>
<th>Products</th>
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<tr>
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<td>1</td>
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<td>1200</td>
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<td>*</td>
<td>EnDi</td>
<td>6.6—5.6 (14)</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1200</td>
<td>0.1</td>
<td>EnsoDiso</td>
<td>*</td>
<td>EnDi</td>
<td>10.0—11.6 (4)</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>1200</td>
<td>0.75</td>
<td>EnsoDiso</td>
<td>*</td>
<td>EnDi</td>
<td>4.8—6.4 (10)</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>1200</td>
<td>4</td>
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<td>*</td>
<td>EnDi</td>
<td>2.2—6.2 (15)</td>
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<td>5</td>
<td>30</td>
<td>1200²</td>
<td>170</td>
<td>synthetic EnDi</td>
<td>*</td>
<td>EnDi</td>
<td>7.4—10.0 (10)</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>1200</td>
<td>4</td>
<td>EnsoDiso</td>
<td>*</td>
<td>EnDi</td>
<td>9.4—12.2 (10)</td>
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<tr>
<td>7</td>
<td>5</td>
<td>1200</td>
<td>4</td>
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<td>*</td>
<td>EnDi</td>
<td>9.6—12.6 (10)</td>
</tr>
<tr>
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<td>5</td>
<td>1200</td>
<td>11</td>
<td>EnsoDiso</td>
<td>*</td>
<td>EnDi</td>
<td>45.6—55.0 (12)</td>
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<tr>
<td>9</td>
<td>30</td>
<td>1500</td>
<td>2.5</td>
<td>EnsoDiso</td>
<td>*</td>
<td>EnDi</td>
<td>5.4—10.0 (11)</td>
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<tr>
<td>10</td>
<td>30</td>
<td>1200/1500</td>
<td>2.5/2.0</td>
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<td>*</td>
<td>EnDi</td>
<td>10.4—11.6 (10)</td>
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<td>anhydrous EnDi</td>
<td>EnDi</td>
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<td>12</td>
<td>30</td>
<td>1200/1500²</td>
<td>2.1/4.2</td>
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<td>EnDi</td>
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</tr>
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<td>13</td>
<td>30</td>
<td>900</td>
<td>23</td>
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<td>a few % 3%¹</td>
<td>EnDi Amph</td>
<td>0.2—1.6 (5)</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>900</td>
<td>214</td>
<td>synthetic EnDi</td>
<td>a few % 4%¹</td>
<td>EnDi Amph</td>
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<td>10</td>
<td>900</td>
<td>72</td>
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<td>a few % 4%¹</td>
<td>EnDi Amph</td>
<td>4.2—6.4 (6)</td>
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<tr>
<td>16</td>
<td>10</td>
<td>900</td>
<td>212</td>
<td>synthetic EnDi</td>
<td>a few % 4%¹</td>
<td>EnDi Amph</td>
<td>1.4—2.8 (9)</td>
</tr>
</tbody>
</table>

* Starting materials were slightly moistened by breathing.

¹ 22% silver oxalate was also added.

² In the middle of the experiment indicated temperature decreased possibly due to chemical contamination of the thermocouple, and temperature was then controlled by maintaining power equal to the earlier condition. In run 5, an accidental "correction" of +70°C occurred for less than 1 hour after 100 hours of the experiment.

In contrast to glasses, starting material of synthetic diopside (CaMgSi₂O₆) and enstatite or clinoenstatite (Mg₂Si₂O₆) react inwards until the solvus limits are reached. This is well demonstrated by the experiments in which layers of diopside and clinoenstatite were allowed to react across their boundary surface. In runs 5, 14 and 16, the CaMgSi₂O₆ content of diopside
30 \mu m from the boundary was 100\%, and rapidly decreased to the boundary zone (10 \mu m) in which orthopyroxene occurred. The CaMgSi_2O_6 content of enstatite decreased away from the boundary zone and approached Mg_2Si_2O_6 at the other end. Additional examples of the inward reaction of natural pyroxenes towards the solvus are found in Hensen [11].

Thus, a pair of unmixing and homogenization experiments establishes or limits the position of a solvus even if chemical hysteresis remains and the data in either of the experiments are themselves scattered between starting composition and equilibrium composition.

Both unmixing and homogenization experiments were done at 30 kbars and 1200°C, 30 kbars and 900°C, 10 kbars and 900°C, and 30 kbars and 1500°C (Fig. 1), the last of which is separately discussed in the next section. The pair of experiments at 30 kbars and 1200°C yielded an overlap of the data by two experiments (Fig. 1). At 30 and 10 kbars at 900°C, the data could limit positions of solvus within analytical error except for the clinopyroxene limb at 10 kbars and 900°C where either the unmixing or homogenization experiments (or both) did not reach solvus and its position was only bracketted between En_{12.2}Di_{8.7.8} and En_{6.8}Di_{9.3.2}.

At 40, 10 and 5 kbars at 1200°C, only unmixing experiments were made. Inferred solvus positions at these conditions are averages of the data.
5. Stability of subcalcic clinopyroxene at 30 kbars and 1500°C

There are four runs which are relevant to the problem of stability of subcalcic clinopyroxene found by Davis and Boyd [4]: runs 9 and 10 are on En50Di50, and runs 11 and 12 are on En80Di20. In runs 10 and 12, the charges were first kept at 1200°C and 30 kbars for a time considered sufficient (runs 2–4) to bring all the pyroxene compositions outside the solvus of 1500°C and 30 kbars, then temperature was increased to 1500°C. Thus, runs 9 and 10, and runs 11 and 12 can be regarded as pairs of unmixing and homogenization experiments. The results of runs 11 and 12 define the solvus very well. Run 9, however, resulted in a single-phase clinopyroxene and is inconsistent with run 10 where two pyroxenes remained and did not homogenize to a single phase. Two analyses of clinopyroxene in run 10 are slightly inconsistent with the solvus defined by runs 11 and 12, but only 15°C difference between them would explain the inconsistency. This choice of the solvus is in agreement with the data of Nehru and Wyllie [7] who carried out synthesis experiments using sintered gel of En50Di50 as starting material (Fig. 2).

Generally, in unmixing runs yielding two pyroxenes, measured chemical ranges may be attributed to incomplete unmixing reactions, but if the single-phase pyroxene in run 9 were stable, there would be no reason for it to show such a wide chemical range as shown in Fig. 1. In run 11, two pyroxenes appeared within 3.2 hours, a slightly longer run duration than run 9, but the difference in run time appears unlikely to explain the absence of orthopyroxene. It is highly probable that En50Di50 is within the metastable composition range where Ca—Mg internal diffusion fails to occur at this P–T condition [12].

Further support for the revised position of solvus at 1500°C and 30 kbars is found in a partial melting experiment on natural garnet lherzolite [13]. In this run, clinopyroxene coexists with orthopyroxene as well as olivine, spinel and glass. The composition of the clinopyroxene (Ca29.3Mg66.2Fe0.5, Al2O3 = 5.3%) is near to the revised solvus. Since Al2O3 solid solution stabilizes a wider solvus [5], correction for the Al2O3 effect in their result will move the composition of the clinopyroxene even closer to the solvus defined above. Thus the experiment in the multicomponent system supports the stability and wide solvus between two pyroxenes at 30 kbars and 1500°C in the simple system.

6. Temperature and pressure effects on the enstatite–diopside solvus

The positions of the solvus determined in preceding sections and shown in Fig. 1 are plotted on the pressure–composition diagram (Fig. 2) and temperature–composition diagram (Fig. 3). Available data from the literature are also shown. These data were obtained by three methods: optical identification of minerals in experimental charges, X-ray calibration of pyroxene composition, and microprobe analysis of pyroxenes. It should be noted that all the data plotted in both the figures are the respective authors' ultimate selections after statistical treatment or simple curve fittings, and are not their raw data which often deviate from the selections.

Accuracy of the first method depends on the quality of identification of minerals and the spacing of the
Fig. 3. The enstatite–diopside solvus at 30 kbars. Solid line: our data, dotted line: Davis and Boyd [4], and dashed line: Nehru and Wyllie [7].

composition grid employed, and that of X-ray method is ±1 to ±3 mole % end member [6,14]. The inconsistency seen among the data including ours should be viewed in relation to the accuracy of the method employed and the type of reaction, i.e. homogenization or unmixing. Particularly, it should be noted that determination of pyroxene composition from homogenization experiments using the X-ray calibration is very uncertain. This is because, in those experiments, chemical hysteresis can hardly be avoided, and the X-ray method will bias towards compositions outside the solvus.

The differences between the various data plotted in Fig. 2 are not entirely within analytical or method-derived error. We will examine particularly the data for the clinopyroxene lim at 1200°C and 30 kbars and at 900°C, 30 kbars to 1 atmosphere. Our reversal experiments at 30 kbars and 1200°C yielded overlapping compositional ranges with the unmixing experiment (run 4) giving strongly clustered data. We consider that the spread of the homogenization (run 5) data to lower diopside contents is due to greater temperature uncertainty in this run (see Table 1). In Fig. 2 we have drawn the solvus at 1200°C as a function of pressure as defined by our own data.

At 900°C and 30 kbars our closely bracketted reversal gives a clinopyroxene composition coincident with that predicted by extrapolation of Nehru and Wyllie’s [7] data (1500—1000°C) and this composition is less calcic than that previously accepted [4]. At 900°C and 10 kbars our data bracket the clinopyroxene limb of the solvus within 5 mole % end member. At 900°C and 2 kbars earlier data [6] led to selection of a more calcic composition but it should be noted that in their unmixing experiments, Warner and Luth [6] did not obtain clinopyroxene more calcic than En₈Di₉₂ (Fig. 2). The clinopyroxene limb at 900°C has been drawn through the reversal brackets at 30, 10 and 2 kbars but its extrapolation is then inconsistent with 1-atmosphere data [1,14]. Boyd and Schairer’s [1] determination was based on optical identification of phases and some of the crucial phase identifications at and below 900°C were reported as doubtful (queried) [1, table 5]. Their data thus permit the interpretation that the clinopyroxene limb at one atmosphere lies between En₈.₃Di₉₄.₇ and En₆.7Di₈₉.₃. We conclude, in the light of this and earlier studies, that there is little or no pressure effect on the diopside limb of the pyroxene solvus at 900°C from 0 to 30 kbars.

To summarize (Fig. 2), at higher temperature (≥1200°C) the pyroxene solvus widens considerably as pressure increases, and at low temperature (≤900°C) there is no perceptible pressure effect on the clinopyroxene limb and a slight pressure effect on the orthopyroxene limb. The pressure dependence of the orthopyroxene limb is of the same character as inferred in the Fe-bearing system [11]. Although pressure effects on emf of the thermocouple have not been corrected for and remain uncertain, the correction would raise indicated temperature to higher real values and would thus enhance the widening of the solvus with increasing pressure.

The temperature dependence of the solvus is shown in Figs. 2 and 3 which reaffirm the well-established increase of mutual solubility with increasing temperature. At 30 kbars, however, the shape of the re-determined solvus is very different from that of Davis and Boyd [4] and similar to that of Nehru and Wyllie [7]. Our new data show that the clinopyroxene limb is less sensitively dependent on temperature between 900 and 1200°C. This means that the
pyroxene geothermometer is less effective between 900 and 1200°C at high pressure than previously accepted.

7. Some problems in petrologic applications to natural pyroxenes

Applying Figs. 2 and 3, one may in theory estimate both pressure and temperature simultaneously from chemistry of coexisting enstatite and diopside. However, this is impractical as the isochemical contour lines for the two pyroxenes are nearly parallel throughout the \( P-T \) field except at temperatures above 1200°C where the two lines cross with a rather high angle between them. Even at high temperature, however, the application of this method to natural pyroxenes requires a full understanding of chemical effects in the multicomponent system. Consequently, the enstatite—diopside solvus can be used as a geothermometer only if the pressure of formation is estimated by another method, except in those cases where temperature is so low that the clinopyroxene limb is independent of pressure.

Application of the present results will necessitate revision of many temperature estimates found in the literature, particularly for assemblages of low-temperature peridotites and granulites and for high-pressure, high-temperature assemblages such as peridotite nodules in kimberlites. For example, estimates of temperature in the range 1200–1400°C at 30 kbars based on Davis and Boyd [4] would be revised upwards by about 100°C based on Fig. 3. An estimate of 1000°C at 30 kbars would be little changed but estimates of 900°C at 30 kbars would be revised downwards by more than 100°C. We emphasize, however, that data on the multi-component pyroxene system are required before unambiguous \( P-T \) determinations can be obtained for natural two-pyroxene assemblages.

8. Phase relations of pyroxenes in the system \( \text{Mg}_2\text{Si}_2\text{O}_6–\text{CaMgSi}_2\text{O}_6 \)

Not only are enstatite and diopside stable in the system \( \text{Mg}_2\text{Si}_2\text{O}_6–\text{CaMgSi}_2\text{O}_6 \), but at least two more

stable phases exist, protoenstatite and pigeonite*. Protoenstatite is restricted to a low-pressure, high-temperature region [2,16]. Recent work by Smyth [17] reported protoenstatite of the composition \( \text{Mg}_2\text{Si}_2\text{O}_6 \) is stable up to melting point at 1 atm. Pigeonite appears over a wide \( P-T \) range from 1 atm to at least 20 kbars [2,18,19].

Three univariant assemblages known to occur are protoenstatite—enstatite—diopside at 1 atm and about 1400°C [1], enstatite—pigeonite—diopside at 17.5 kbars and 1450°C [18], and protoenstatite—pigeonite—diopside at 1 atm and about 1230°C [2]. For conditions for the last assemblage, the temperature, 1276°C [20], was preferred. This choice, in spite of

* This mineral is called iron-free pigeonite in the literature but the term "pigeonite" is used in this paper for convenience.
the presence of Al$_2$O$_3$ in the system studied by Yang [20] was made because the coexistence of protoenstatite, pigeonite and diopside was confirmed at that temperature, and the Al$_2$O$_3$ content of less than 0.5 wt.% in the pyroxenes should have little effect on the temperature of the equilibrium. An invariant assemblage of all the four pyroxenes almost certainly occurs and Warner and Luth [6] estimate this to be at about 2 kbars and 1320°C.

A geometrical arrangement of four univariant lines around the invariant point is obtained following Schreinemakers' method [21]. An assumption here is that the CaMgSi$_2$O$_6$ content of pyroxenes at the invariant point increases in the order protoenstatite, enstatite, pigeonite, diopside. The shaded area in Fig. 4 limits the conditions for the invariant point. This area is partly defined by: (1) demands by the arrangement of the univariant lines, (2) three fixed points noted above, (3) a bracket for the univariant line (Pr) at 5 kbars [18], and (4) stability of enstatite and diopside at 10 and 5 kbars and 1300°C [6].

The nature of the stable assemblage at 2 kbars and 1300°C is confusing: it is enstatite and diopside (homogenization experiment) or pigeonite-bearing assemblage (unmixing experiment) [6,18]. This confusion might imply that a reaction, pigeonite $\rightarrow$ enstatite + diopside, characteristic of the univariant line (Pr), occurs near 2 kbars and 1300°C. If so, the invariant point will be further restricted to less than 2 kbars.

The deviation of the area thus restricted from Warner and Luth's estimate [6] is small but critical: their value implies that (En) is at a higher temperature than 1320°C at 1 atm [6, Fig. 5]. In fact it is not [2,20]. The conditions of the invariant point are hereafter referred to as $P_0$ and $T_0$.

It is now easy to draw the geometry of phase diagram at any $T$–$P$ conditions. Fig. 5A, B shows examples at constant pressure and temperature around $P_0$ and $T_0$. They are only schematic, and partly exaggerated. Fig. 5B is drawn on an assumption that the slope of (En) is negative. A positive slope removes the protoenstatite–diopside solvus from the figure. The detail of the phase relations around $P_0$, $T_0$ must be determined by experiments, which should be concentrated in the shaded area (Fig. 4). However, such experiments will be extremely difficult because of...
the difficulties in fine $P-T$ control, sluggish reaction rate and appearance of metastable phases.

The univariant line (Pr) will be extrapolated to about 1590°C at 30 kbars (Fig. 4), which means that pigeonite becomes stable at this condition. Thus, as Kushiro [3] suggested, some of the subcalcic clinopyroxenes coexisting with orthopyroxene at high temperatures in the phase diagram by Davis and Boyd [4] are possibly pigeonite and the diopside—pigeonite solvus should appear at temperatures higher than about 1590°C. This interpretation is similar to that for pyroxenes in the system Fe$_2$Si$_2$O$_6$–CaFeSi$_2$O$_6$ at 20 kbars [22].

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Appendix. Run details

Run 1 (40 kbars, 1200°C, unmixing from glass). Enstatite and diopside were commonly euhedral, up to 70 µm in grain size and in some cases in parallel growth or as inclusions one within the other.

Run 2 (30 kbars, 1200°C, unmixing). Within 6 minutes, all the starting glass crystallized into pyroxenes. They were identified optically and by X-ray as minor enstatite and common diopside, but were too small for microprobe analysis.

Run 3 (30 kbars, 1200°C, unmixing). Enstatite and diopside grew up to 20 µm.

Run 4 (30 kbars, 1200°C, unmixing). Enstatite (up to 50 µm) and diopside (up to 20 µm) were subhedral to euhedral. About 20% of glass was present.

Run 5 (30 kbars, 1200°C, homogenization). At the interface between diopside and enstatite layers in the capsule, pyroxenes with two different textures were found, i.e. orthoenstatite and diopside crystals as large as the original synthetic pyroxenes (30 µm), and small pyroxenes (<8 µm) interpreted as products of new nucleation of pyroxene. Both types of pyroxene were analyzed.

Run 6 (10 kbars, 1200°C, unmixing). Enstatite and diopside were <30 µm in grain size and there was a small amount of glass.

Run 7 (5 kbars, 1200°C, 4 hours, unmixing). Enstatite, diopside, glass, and probably minor olivine occurred in anhedral texture.

Run 8 (5 kbars, 1200°C, 11 hours, unmixing). Enstatite (<30 µm) and diopside (<15 µm) occurred as subhedral crystals, probably with trace amounts of glass. Some diopside crystals are simply twinned. The diopside is more calcic than that in run 5 (Table 1) and this run is preferred to run 7.

Run 9 (30 kbars, 1500°C, unmixing). Only clinopyroxene was observed optically, as subhedral grains up to 30 µm in grain size.

Run 10 (30 kbars, 1500°C, homogenization). A glass (En$_{50}$Di$_{50}$) was subjected to 30 kbars and 1200°C for 2.5 hours and then the temperature was raised to 1500°C for 2 hours. From runs 2–4 we infer that the charge crystallized to two pyroxenes with a wide composition gap at 1200°C and that these pyroxenes then approached re-equilibration at 1500°C. Euhedral diopside and enstatite (up to 20 µm) and a trace amount of glass were produced.

Run 11 (30 kbars, 1500°C, unmixing). A glass of En$_{80}$Di$_{20}$ yielded euhedral enstatite (up to 50 µm) with small anhedral or subhedral diopside.

Run 12 (30 kbars, 1500°C, homogenization). The same techniques as for run 10 were used for a glass of En$_{80}$Di$_{20}$ composition. Some enstatite crystals were up to 30 µm long and had parallel growth of diopside. Diopside was generally much smaller and anhedral.

Run 13 (30 kbars, 900°C, unmixing). Enstatite was frequently acicular (up to 70 µm long) while diopside was equant and <15 µm. An amphibole (Ca$_3$.8Mg$_{3.8}$Si$_8$.00$_2$.3) occurred and is probably metastable (judged by its unusual composition).

Run 14 (30 kbars, 900°C, homogenization). Originally, in order to try both homogenization and unmixing experiments at one time, layers of synthetic diopside, clinoenstatite and glass (En$_{80}$Di$_{20}$) were loaded successively into the capsule. However, the unmixing experiment in the glass layer proved am-
biguanus and unusable because of mechanical contamination of the synthetic pyroxenes into this layer during loading, and eventually only the homogenization experiment was usable. To minimise the likelihood of amphibole stability in the presence of approximately 3% H₂O, about 22% silver oxalate was mixed into each layer. However, amphibole of similar composition to that in run 13 was formed locally at the boundary between synthetic pyroxene layers, and within the glass layer. Trace amounts of silica mineral and magnesite were formed as well. Very small pyroxenes appeared to have nucleated at the enstatite/diopside boundary but were difficult to distinguish from relict grains.

**Run 15** (10 kbars, 900°C, unmixing). Enstatite (<10μm) and diopside (<5 μm) were so fine grained that it is not clear whether the wide compositional range of diopside (Table 1) is real, and due to incomplete equilibration, or results from enstatite contamination in the diopside analyses.

**Run 16** (10 kbars, 900°C homogenization). The same preparation of the starting material, together with water and silver oxalate, was used as in run 14 and the unmixing experiment was unsuccessful for the same reason. At the boundary between the two synthetic pyroxene layers, the same texture was present as in run 14. Two pyroxenes and a trace of silica mineral were present.

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PHASE EQUILIBRIA AND ELASTIC PROPERTIES OF A PYROLITE MODEL FOR THE OCEANIC UPPER MANTLE

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ABSTRACT


The upper-mantle source regions of basaltic magmas in oceanic regions contain both H$_2$O and CO$_2$. If the water content of the upper-mantle peridotite is <0.4% approx., then its solidus has a distinctive P,T character such that the geotherm for older oceanic regions will enter a zone of incipient (<2%) melting — the low-velocity zone (LVZ) — at depths of 85–95 km. This LVZ is overlain by a lithosphere of subsolidus amphibole-bearing peridotite in which there is a density increase at ~55 km due to the first appearance of garnet. An alternative model in which the LVZ is attributed to the presence of CO$_2$ fluid phase bubbles is incompatible with experimental data showing high solubility of CO$_2$ in basaltic magmas at the P,T conditions of the LVZ. The LVZ contains a small melt fraction as an intergranular film (aspect ratio $<10^{-2}$); this melt is of olivine melilitite (CO$_2$, H$_2$O present) or olivine nephelinite (H$_2$O only present) character and is interstitial to olivine >> orthopyroxene > garnet > clinopyroxene mineralogy. Temperatures at the top of the LVZ are in the range 1000–1150°C. The lithosphere thickens with age and distance from the mid-oceanic ridges, reaching a stable configuration at a thickness of 85–95 km for $t > 80$ m.y. With increasing age of the oceanic crust, the velocities in the lithosphere increase, the LVZ becomes thinner, and the velocity contrast between the lithosphere and the LVZ decreases. The pyrolite petrological model and its velocity profile satisfactorily account for most of the geophysical data for various age provinces in oceanic regions.

INTRODUCTION

The distinction between the lithosphere and low-velocity zone (LVZ) of the earth’s upper mantle is based primarily on interpretations of seismological data. It has been suggested that the LVZ is a region of incipient partial melting (Anderson, 1962; Aki, 1968; Oxburgh and Turcotte, 1968; Anderson and Sammis, 1969; Lambert and Wyllie, 1968). With the current wide acceptance of tectonic models advocating the movement of oceanic and continental plates over subjacent mantle, it has become almost axiomatic that the older geological and tectonic concept of an asthenosphere (region of
geologically rapid flow) beneath a more rigid and brittle lithosphere should be correlated with the divisions based on seismology. Within the framework of the plate-tectonics hypothesis, a number of authors have attempted to model the processes of formation of the oceanic lithosphere beginning from volcanism at mid-oceanic ridges, and have investigated the elevation, heat flow, gravity anomalies and thickness of the lithosphere resulting from cooling of the plate as it moves away from the active ridge crest (Langseth et al., 1966; McKenzie, 1967; Sleep, 1969; Parker and Oldenburg, 1973; Bottinga, 1974). The degree of petrological sophistication or constraint employed in these models has been rather variable, but several authors have attempted to incorporate the details of sub-solidus mineralogy into their models (Forsyth and Press, 1971; Sclater and Francheteau, 1970; Sclater, 1972).

In contrast to the geophysical data and approach, a petrological model for the upper mantle has been built up over recent years based on the constraints provided firstly by the requirement that the upper mantle yields basaltic magma by processes of partial melting and secondly that natural sampling of upper-mantle lithologies consistently points to a dominant lherzolite composition. This composition specifically contains 50—60% olivine, with orthopyroxene > clinopyroxene ≥ aluminous phase (plagioclase, spinel, or garnet) and contains 3—5% $\text{Al}_2\text{O}_3$, 3—5% CaO and 100 Mg/(Mg + Fe$^{2+}$) = 88—89% (mol.%).

This approach has led to the calculation of the "pyrolite" model composition for the upper mantle (Ringwood, 1962a, b; Green and Ringwood, 1963; Ringwood, 1966, 1969). Extensive experimental studies of this composition have established the phase relations as a function of pressure and temperature for dry (Green and Ringwood, 1967b, 1970), water-saturated (Green, 1972, 1973a, b), and water-undersaturated conditions (Green, 1970, 1971, 1973a, b). It is the purpose of this paper to summarize these experimental studies and to develop a model for the lithosphere and asthenosphere which owes its primary formulation to a petrologically derived upper-mantle composition and to a petrological understanding of the magmatic processes occurring at the ridges and at volcanic centres well removed from the ridges. We then translate the petrological model into density and velocity profiles for the lithosphere and asthenosphere along a variety of oceanic geotherms and compare the calculated profiles with observed geophysical data.

However, before embarking on the preferred model, it is desirable to comment on an alternate hypothesis for the existence of the LVZ (H.W. Green, 1972; Green and Gueguen, 1974) in which the low seismic velocities and high seismic attenuation of the LVZ are attributed not to partial melting but to the presence of dispersed bubbles of a CO$_2$-rich fluid phase.

THE ROLE OF CO$_2$ IN THE ASTHENOSPHERE

H.W. Green (1972) considered that bubbles of CO$_2$-rich fluid phase, occurring within and between crystalline phases in a sub-solidus mantle peridotite,
would produce the observed seismological characteristics of the LVZ. In a later paper (Green and Gueguen, 1974) the original CO$_2$-charged asthenosphere model was modified to require the presence of small quantities of water in addition to CO$_2$. Green’s model used simplifying assumptions on solubility of CO$_2$ in silicate magmas which are now known to be invalid. In particular it has been shown that CO$_2$ (as CO$_3^{2-}$) is highly soluble in undersaturated olivine melilitite and olivine basanite magmas at high pressure and indeed mole for mole substitution of CO$_2$ for H$_2$O produces little or no increase of liquidus temperature for $X_{CO_2} = 0$ to $X_{CO_2} = 0.5$ (for H$_2$O = 20 wt.% when $X_{CO_2} \rightarrow 0$) in an olivine melilitite liquid (Brey and Green, 1975). Direct experiments on the position of the pyrolite solidus for $X_{CO_2} = 0.5$, $X_{H_2O} = 0.5$, H$_2$O = 0.1–0.2 wt.% and H$_2$O = 2–3 wt.% show that the presence of CO$_2$ has very little effect on the solidus at $P > 30$ kbar and in particular that estimated geothermal gradients such as those of Clark and Ringwood (1964) which were used by H.W. Green in his model, will necessarily exceed the pyrolite solidus at depths of 85–95 km if both CO$_2$ and H$_2$O are minor components of the pyrolite. Thus, the presence of CO$_2$ and H$_2$O in the upper mantle will not result in fluid phase bubbles at the P,T conditions of the LVZ but will produce a region of partial melting due to the high solubility of CO$_2$ in undersaturated liquids and low solidus temperature of pyrolyte containing traces of water and carbon dioxide. The effect of CO$_2$ in addition to H$_2$O in the LVZ is to change the character of the melt fraction (2–3% melt) from olivine nephelinite (H$_2$O only present, no CO$_2$) to more extremely undersaturated olivine melilitite (H$_2$O + CO$_2$ present, H$_2$O > CO$_2$; Brey and Green, 1975).

The geochemical arguments of Rubey (1951), the observation of H$_2$O and CO$_2$ in volcanic gases and in fluid inclusions in mantle-derived xenoliths, and the presence of hydrous minerals (phlogopite, amphibole, apatite) in mantle-derived xenoliths, all attest to the presence of both H$_2$O and CO$_2$ in the upper mantle and that H$_2$O > CO$_2$. The recent experimental data show that provided temperatures in the earth exceed 1000°C at 100 km, there must be a region of partial melting in a pyrolite mantle at depths around 100–150 km.**

**PETROLOGICAL MODEL FOR THE UPPER MANTLE**

The pyrolite composition of Ringwood (1966) remains suitable as a mantle parent composition for those basalts which we might classify broadly as chemically of Hawaiian type (including Hawaiian olivine tholeiite through Hawaiian olivine melilitite nephelinite; Green, 1973b, c; Brey and Green, 1975) but is too enriched in TiO$_2$, K$_2$O and other incompatible elements to act as a source for mid-oceanic ridge basalts of low K$_2$O type. Mantle inhomogeneity in incompatible elements, particularly enrichment in the elements towards the top of

\[ X_{CO_2} = \frac{CO_2}{CO_2 + H_2O} \]  (mol. proportions).

** See note at the end of this paper.
the LVZ, has been advocated to account for different source region characteristics (Green, 1970, 1971). As models for magma genesis become increasingly constrained, it will be possible to refine the calculation of pyrolite compositions using more stringent internal consistency arguments.

In the continuing experimental studies aimed at determining the conditions at which observed natural basaltic (in the broadest sense) magmas were derived by partial melting of the source pyrolite, it was found that the more undersaturated magmas (basanites, olivine nephelinites) could only be partial melts of pyrolite provided there was some water present in the magma (but not sufficient for water-saturation of the magma). Water contents of 0.1—0.2% in the source region have profound effects on the position of the solidus and on the nature of magmas for low degrees of melting but have little effect on magma composition at >20% melting. Theoretical studies (Green, 1970, 1971) followed by experimental studies (Green, 1972, 1973a, b, c) showed that the solidus for pyrolite containing <0.4% H₂O has a very distinctive form (Fig. 1) with a “shoulder” on the solidus due to the high-pressure instability of amphibole. Intersection of the oceanic geotherm of Clark and Ringwood (1964) with this solidus led to the prediction that the stable oceanic lithosphere should be 85—95 km thick (Green, 1970, 1971, 1973a, b). Thus the indepen-

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Fig. 1. Experimentally determined (see text for references) solidi for pyrolite under anhydrous and water-saturated conditions and for pyrolite + 0.2% H₂O. Figure illustrates the relationship of these solidi to the stable oceanic and Precambrian shield geotherms of Clark and Ringwood (1964). The figure implies partial melting and a consequent LVZ along the oceanic geotherm but no melting along the shield geotherm (calculated assuming fixed continents and subjacent mantle). A = beginning of partial melting if H₂O ≥ 0.5%, B = beginning of partial melting if H₂O ≤ 0.4%.
dent petrological approach led to a highly specific model for a lithosphere of spinel and garnet lherzolite containing 0—0.4% H₂O locked in accessory amphibole overlying a garnet lherzolite asthenosphere at depths of 85—95 km in which there is a small (<5%) melt fraction of hydrous olivine nephelinite to basanite magma.

The position and character of the solidus for pyrolite is sensitively dependent on water content and has the distinctive form illustrated in Fig. 1 only for 0 < H₂O ≤ 0.4%. The more usual, water-saturated solidus in Fig. 1 is that which is appropriate for H₂O ≳ 0.5% approximately. On the ocean floor, water pressures of 0.2—0.4 kbar are sufficient to allow 0.5—1.0% H₂O to remain dissolved in a basaltic liquid. We may use the water contents of glasses quenched from basalts extruded on the ocean floor to indicate the water content of their source region. From data for tholeiitic glasses (Moore, 1970) we thus infer that the source region for mid-ocean ridge, low-K tholeiites contains 0.02—0.1% H₂O whereas the source region for Hawaiian, ocean-island, moderate-K tholeiites contains 0.1—0.2% H₂O. These inferences assume that in each case the major-element chemistry and high-pressure phase relations of the tholeiitic magmas can be used to constrain the degree of partial melting of their source regions as sufficient to eliminate clinopyroxene as a residual phase; i.e., 25—30% melting of a pyrolite source (Green and Ringwood, 1967a; Green, 1970, 1971, 1973b).

The differences in inferred water content for the source region of mid-ocean ridge and Hawaiian tholeiites are also matched by differences in K, Rb, Sr, light rare-earth elements etc.; i.e., those elements which are strongly enriched in liquids relative to olivine, pyroxenes, garnet or spinel ('incompatible elements' of Green and Ringwood, 1967a). These differences in minor and trace-element abundances, particularly the depletion and enrichment (relative to chondritic abundances) patterns of the light rare-earth elements (LREE) amongst basalts with similar major-element chemistry, lead to the conclusion that the source regions for basaltic magmas are inhomogeneous in incompatible element abundances (Gast, 1968; Green, 1968, 1971; Green and Ringwood, 1967a). Inhomogeneity in the minor- and trace-element geochemistry of the source region would have a large effect on calculated velocity profiles for the asthenosphere because these elements are strongly concentrated into the melt phase and even subtle variations in their abundance in the source rock cause large variations in the amount of melting at a given P and T. Thus, if at 1250°C, 30 kbar the melt fraction of pyrolite containing 0.2% water contains 5% H₂O and there are no hydrous residual phases present (Green, 1973b, c) then the degree of melting is 4%. If, however, the pyrolite at 1250°C 30 kbar contains only 0.05% water then the degree of melting is ≲1% and phlogopite may remain as a residual phase.

These effects are illustrated more generally in Fig. 2 where we illustrate the subsolidus mineralogy for pyrolite containing a trace of water, the solidus for pyrolite with 0 < H₂O < 0.4% and have then contoured the above-solidus region for degree of partial melting for pyrolite containing 0.05% H₂O. In addi-
Fig. 2. Detail of solidus and sub-solidus mineralogy for pyrolite with approx. 0.05% H$_2$O (i.e. approx. 5% amphibole within the amphibole stability field). In the above-solidus region the figure is contoured for % partial melting, these contours being semiquantitatively determined from data on melting relationships in pyrolite and liquidus temperatures for a number of basalts with various water contents. Hydrous phases are not present in equilibrium with melt except within $\sim$10–20°C of the amphibole-bearing solidus and for very small degrees of melting and $T < 1200°C$, 30 kbar (phlogopite present, Green 1973b). In the 80–110 km interval, the dashed curves (---3---) show the degree of partial melting for pyrolite containing 0.2% H$_2$O and enriched in incompatible elements (K$_2$O = 0.13% etc., Fig. 3). ---4--- Contour of 4% partial melting, pyrolite +0.05% H$_2$O. ---3--- Contour of 3% partial melting, pyrolite +0.2% H$_2$O. Other boundaries as for Fig. 1.

In the depth range 80–110 km we have superimposed the contours for % partial melting for pyrolite containing 0.2% H$_2$O.

The physical properties of the lithosphere and LVZ as determined by seismological methods, are averaged properties and local inhomogeneities in mineralogy, degree of melting etc. may be masked in the sampling process. However, these inhomogeneities may be of major regional extent. This is implied by models which attribute the distinctive petrochemical character of Hawaiian, Icelandic or Azores-region basalts (moderate-K olivine tholeiites or LREE-enriched tholeiites) to deep ‘mantle plumes’ originating below the LVZ (Schilling, 1975). Similarly, a preferred, alternative model which attributes the distinctive source regions of low-K oceanic tholeiites and moderate-K olivine tholeiites to chemical zoning within the LVZ (Green, 1971, 1973a) carried implications that affect the geophysical properties. In this model (Figs. 2 and 3) the tapping of material deep within the LVZ to yield magmas of the mid-oceanic ridges involves tapping of pyrolite containing <0.1% H$_2$O from
depths >110 km approx. In contrast, tapping of material within the upper part of the LVZ to yield magmas of the oceanic island type either by within-plate volcanism (island chain and single oceanic island volcanism) or by a few centres of oceanic-ridge volcanism (Iceland, ?Azores) involves tapping pyrolite containing >0.1% H₂O from depths of 90—110 km approx. The second model invokes vertical chemical zoning in the LVZ and argues that this is of general occurrence. Thus the distinctive source characteristics of both enriched (in incompatible elements) and depleted source regions are available in all areas,

Fig. 3. Diagrammatic section through lithosphere and LVZ along Clark and Ringwood geotherm of Fig. 2. Also incorporates chemical zoning of the lithosphere as developed following magma segregation at the mid-oceanic ridges and of variants on this by segregation of basalt and retention as eclogite mineralogy in the 30—50 km depth range, or by thick basaltic crest developed beneath island chains such as Hawaii (see text). Chemical zoning in LVZ developed by migration of an intergranular melt fraction towards the top of the LVZ.
both at constructive plate edges and within plates and it is the nature of the magma-tapping process which determines the depth and chemical fingerprint of the source region on the extruded magmas. If this model is correct then the vertical compositional zoning in the LVZ must be incorporated into the general geophysical model for the lithosphere and LVZ.

In Fig. 3, we have illustrated the petrologically derived model for mineralogical and chemical variation in the lithosphere and LVZ at distances well removed from the thermal and dynamic effects of the mid-oceanic ridges. For this purpose, the Clark and Ringwood (1964) oceanic geotherm is adopted as representative of the steady-state temperature beneath oceanic basins. We note the similarity of this geotherm originally constructed for a static, non-convecting mantle, with the geotherms for ocean floor older than 100 m.y. (Fig. 4) estimated by Sleep (1969), Sclater and Francheteau (1970), and Parker and Oldenburgh (1973); i.e. with geotherms for regions approaching a steady-state temperature profile with increasing age and distance from the ridge axis. Our conclusions in this section would remain valid if one of these 'steady-state' temperature profiles were adopted rather than the Clark and Ringwood geotherm.

The steady-state geotherm (Fig. 2) passes from spinel pyrolite to garnet

---

**Fig. 4.** P-T solidi for dry and water-undersaturated (<0.4% H₂O) pyrolite with geotherms for older oceanic regions superimposed. CR64 is steady-state geotherm of Clark and Ringwood (1964) for a static, non-convecting mantle. Other geotherms represent plate models at t = 100 m.y. for different choices of plate thickness (h) and temperature at the bottom of the lithospheric plate (T_b): FP71 — Forsyth and Press (1971), SF70a, b — Sclater and Francheteau (1970), PO73 — Parker and Oldenburg (1973), S69 — Sleep (1969).
pyrolite at 16–17 kbar (~55 km), ~850°C, and since the orthopyroxene in
equilibrium with garnet at this pressure contains ~2% Al₂O₃, the garnet con-
tent of the garnet pyrolite assemblage, assuming <1% amphibole present, will
be ~14%. On the low-pressure side of the boundary, about 4% spinel would
be present. The garnet content decreases slightly (to ~12%) through the gar-
net pyrolite field as more Al₂O₃ enters the pyroxene solid solutions. At ~90
km, the geotherm passes through the amphibole breakdown curve for pyro-
lite with ≤0.4% H₂O and enters a region of partial melting. The model, on the
geochemical and petrological grounds noted above, is characterized by enrich-
ment in incompatible elements in the upper ~20 km of the LVZ. If this re-

gion contains ~0.2% H₂O, 0.13% K₂O and is LREE-enriched relative to chon-
dritic abundances with HREE approx. 2 × chondrites, then it is similar in
composition to the pyrolite of Ringwood (1966) and will contain 2% melt.

Fig. 5. Diagram illustrating diapiric upwelling of pyrolite from the lower part (0.05% H₂O)
of the LVZ with individual diapirs increasing their degrees of partial melting (contours of
Fig. 2) prior to magma segregation at 20–40 km. Magma extruded at 1200–1300°C.  
- - - - - Contour of 3% partial melting, pyrolite +0.05% H₂O. ...... O ...... Diapiric ascent
path and degree of partial melting for pyrolite from upper part of LVZ, i.e. pyrolite +0.2%
H₂O (0.13% K₂O etc.). Upper path illustrates ascent beginning from a geotherm perturbed
by +100°C from Clark and Ringwood geotherm. Lower path illustrates ascent from Clark
and Ringwood geotherm at ~100 km. Diapirs originating at <100 km crystallize com-
pletely on entering the amphibole stability field of H₂O ≤ 0.4%. ...... 4 ...... Diapiric ascent path
and degree of partial melting for pyrolite +0.6% H₂O approx. With this water content the
water-saturated solidus is applicable and such material may ascend diapirically through the
lithosphere.
In contrast, the lower part of the LVZ, depleted in incompatible elements, will contain approx. 0.5% melt at depths >110 km approx. The two source regions defined as above have the chemical characteristics required by the source pyrolite for Hawaiian-type tholeiites (upper part of LVZ) and low-K mid-ocean ridge tholeiites (lower part of LVZ), each magma type being produced by 20–30% melting. It is emphasized that the depths of these source regions are not the same as the depths of magma segregation but only the depths from which diapirs of partially molten pyrolite begin to move towards the surface along adiabatic or near-adiabatic paths, increasing their degree of melting at shallower depths and finally segregating into magma and crystalline residue at 20–60 km depth (depth of magma segregation) (Fig. 5).

The solidus for pyrolite with <0.4% H₂O places several constraints on magma-genesis mechanisms. Referring to the stable oceanic geotherm of Fig. 2 it is apparent that it may be possible, by fracturing through the lithosphere, to tap directly the ~2% melt fraction present in the 90–110 km interval of the LVZ. This melt will be of olivine melilitite or olivine melilite nephelinite character (Green, 1971, 1973b; Brey and Green, 1975). However it is not possible, given this geotherm, for pyrolite from the 90–100 km depth interval to ascend an adiabatic path without the pyrolite crystallizing completely to a subsolidus, amphibole-bearing assemblage at depths of 85–90 km (Fig. 5).

For pyrolite from this depth interval to ascend as a partially molten diapir to shallower levels, it is necessary either to initially perturb the geotherm (Fig. 5) to higher values (i.e. raise the temperature at ~100 km by 60–80°C) or if the water concentration in the upper part of the lithosphere is locally >0.5%, then the solidus for depths <85 km would be the water-saturated solidus (Fig. 1 and Green, 1972, 1973a, b). Pyrolite containing 0.6% H₂O would have approx. 6% melt fraction at ~100 km depth (Fig. 5), and on moving adiabatically to 85 km would contain 15–20% amphibole and ~2% melt. The diapir could continue to move adiabatically to shallower depths, maintaining a small melt fraction to depths of <50 km approx. when the amount of melt present would begin to rise rather rapidly again (Fig. 5).

Geological support for the models of diapiric ascent of pyrolite and for the roles of partial melting and amphibole stability, is provided by the peridotites of St. Pauls Rocks which show characteristics consistent with initial high-pressure crystallization in the spinel peridotite field and partial magma segregation of very undersaturated, water-rich liquids, now observed as brown hornblende mylonites (Melson et al., 1972). High-temperature peridotite intrusions such as Tinaquillo (MacKenzie, 1960), Lizard (Green, 1964), Serrania del Ronda (Dickey, 1970), etc. also provide evidence of ascent through >10 km by largely crystalline peridotite diapirs with chemical compositions which are slightly depleted and refractory, having lost a small, undersaturated, LREE-enriched liquid fraction (Frey, 1969).

In contrast to the special conditions under which the upper part of the LVZ under stable oceanic regions can act as a source for adiabatically ascending peridotite diapirs, the lower part of the LVZ in such regions is at tempera-
tures high enough that adiabatic ascent of diapirs to shallower depths is possible (Fig. 5). The melt fraction of such diapirs will increase rather slowly until it reaches ~5% (~10–20 kbar) and then more rapidly as the P,T conditions exceed the anhydrous solidus of pyrolite.

ELASTIC PROPERTIES OF THE LITHOSPHERE AND LVZ IN STABLE OCEANIC REGIONS

We have used petrological arguments to define a specific model for the lithosphere in regions well removed from mid-oceanic ridges. The left-hand side of Fig. 3 illustrates the "preferred and normal" oceanic model in which the sub-Moho layer of residual harzburgite (i.e., pyrolite less 20–30% olivine tholeiite) is underlain by spinel lherzolite of slightly depleted pyrolite composition (i.e., pyrolite depleted by <10% basaltic magma) and then by zones of spinel pyrolite and garnet pyrolite before entering the LVZ at depths of ~90 km. The LVZ is itself chemically zoned in the manner described in the previous section.

We now use the petrological model to construct velocity and density profiles along the stable oceanic geotherm (Fig. 6). Initial densities ($\rho$) and com-

![Graph showing velocity and density profiles](image_url)
TABLE I

Initial densities (ρ) and compressional (v_p) and shear (v_s) velocities calculated from mineral data in Table II

<table>
<thead>
<tr>
<th>Mineralogy (all wt. %)</th>
<th>Ol</th>
<th>Opx</th>
<th>Cpx</th>
<th>Sp</th>
<th>Ga</th>
<th>IIm</th>
<th>Jad</th>
<th>ρ (g/cm³)</th>
<th>v_p (km/sec)</th>
<th>v_s</th>
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<tbody>
<tr>
<td>Refractory peridotite</td>
<td>80M₉₀</td>
<td>20M₉₁</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.31</td>
<td>8.30</td>
<td>4.86</td>
</tr>
<tr>
<td>Transitional layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eclogite (20)</td>
<td>5M₇₅</td>
<td>20M₈₀</td>
<td>22Di</td>
<td>—</td>
<td>—</td>
<td>40M₅₀</td>
<td>3M₉₀</td>
<td>10</td>
<td>3.55</td>
<td>8.43</td>
</tr>
<tr>
<td>Harzburgite (80)</td>
<td>75M₉₀</td>
<td>25M₉₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.37</td>
<td>8.33</td>
<td>4.88</td>
</tr>
<tr>
<td>Mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinel pyrolite (16 kbar, 720°C)</td>
<td>52</td>
<td>28</td>
<td>16</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.33</td>
<td>8.22</td>
<td>4.84</td>
</tr>
<tr>
<td>Garnet pyrolite (28 kbar, 1120°C)</td>
<td>56</td>
<td>21</td>
<td>11</td>
<td>—</td>
<td>12M₇₁</td>
<td>—</td>
<td>—</td>
<td>3.36</td>
<td>8.32</td>
<td>4.86</td>
</tr>
</tbody>
</table>

* These pressures and temperatures represent the conditions along the Clark and Ringwood (1964) geotherm (Fig. 7) for which the listed mineralogies are appropriate. The calculated densities and velocities are determined at P = 1 bar, T = 25°C.
Presessional \((v_p)\) and shear \((v_s)\) velocities at \(P = 1\) bar, \(T = 25^\circ\)C are calculated from the properties of the constituent minerals for each of the sub-solidus mineral assemblages (see examples in Table I based on mineral data in Table II). The initial \(\rho, v_p,\) and \(v_s\) are then corrected for the effects of pressure and temperature along the geotherm using the derivatives for olivine (Table III).

At the base of the lithosphere, \(\rho, v_p,\) and \(v_s\) are used to calculate the bulk \((K)\) and shear \((\mu)\) moduli of the mineral assemblage. In the LVZ, \(K\) and \(\mu\) of the partially molten material are determined using the Eshelby-Walsh equations (Walsh, 1969) and Birch's (1969) parameters for the molten component \((K_{fluid} = 0.65\) Mbar, \(\mu_{fluid} = 0\)). We have arbitrarily assumed that the aspect ratio \((\alpha = \) ratio of semi-minor to semi-major axes of ellipsoidal melt ‘pools’) of the intergranular fluid is \(\alpha = 10^{-2}\) for all melt concentrations. This assumption may not be valid and all we can offer in support is the qualitative observation that in experimental studies of melting of the pyrolite composition, the melt forms a thin film along grain boundaries at low degrees of melting; tending to broaden at higher degrees of melting to small cuspate segregations at grain-boundary triple junctions. We have not observed any tendency for liquids to form spherical or sub-spherical segregations at low degrees of melting (<5%). Our estimate of the aspect ratio is probably too high for the smallest melt concentrations so that we may have underestimated the decrease of \(v_p\) and \(v_s\) in the LVZ. The dashed segments in the velocity profiles of Fig. 6 within the LVZ depict the effect of the vertical chemically zoning indicated in Fig. 3.

The base of the LVZ cannot be fixed on petrological or experimental pet-

### TABLE II

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Density</th>
<th>Velocity ((km/sec))</th>
<th>(v_p/v_s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(v_p) (v_s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olivine</td>
<td>Mg(_{93})</td>
<td>3.31</td>
<td>8.42 4.89</td>
<td>1.72</td>
<td>Kumazawa and Anderson (1969)</td>
</tr>
<tr>
<td>Bronzite</td>
<td>Mg(_{75})</td>
<td>3.51</td>
<td>8.1   4.7</td>
<td>1.72</td>
<td>Liebermann (1975)</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>Diopside</td>
<td>3.34</td>
<td>7.85 4.76</td>
<td>1.45</td>
<td>Kumazawa (1969)</td>
</tr>
<tr>
<td>Spinel *</td>
<td></td>
<td>4.0</td>
<td>9.2   5.1</td>
<td>1.80</td>
<td>Liebermann (1975)</td>
</tr>
<tr>
<td>Garnet *</td>
<td>Py(<em>{35})Al(</em>{35})Gr(_{30})</td>
<td>3.70</td>
<td>9.0 5.0</td>
<td>1.80</td>
<td>Liebermann (1974)</td>
</tr>
<tr>
<td>Garnet *</td>
<td>Py(<em>{50})Al(</em>{20})Gr(_{30})</td>
<td>3.83</td>
<td>8.9 5.0</td>
<td>1.78</td>
<td>Liebermann (1974)</td>
</tr>
<tr>
<td>Ilmenite *</td>
<td>Mg(_{10})</td>
<td>4.7</td>
<td>8.4   4.4</td>
<td>1.91</td>
<td>Liebermann (1974)</td>
</tr>
<tr>
<td>Jadeite</td>
<td></td>
<td>3.33</td>
<td>9.01 5.35</td>
<td>1.68</td>
<td>Hughes and Nishitake (1963)</td>
</tr>
</tbody>
</table>

* Velocities estimated from compressional velocity-density and bulk sound velocity-density trends in isostructural series and then shear velocity derived (Liebermann, 1974, 1975).
TABLE III

Velocity derivatives. Use values for Fo93 (Kumazawa and Anderson, 1969)

\[
\frac{1}{v_p} \left( \frac{\partial v_p}{\partial P} \right)_T = 1.21 \text{ Mbar}^{-1}
\]

\[
\frac{1}{v_s} \left( \frac{\partial v_s}{\partial P} \right)_T = 0.74 \text{ Mbar}^{-1}
\]

\[
\frac{1}{v_p} \left( \frac{\partial v_p}{\partial T} \right)_P = -0.58 \cdot 10^{-4} \text{ km \cdot sec}^{-1} \cdot ^\circ \text{C}^{-1}
\]

\[
\frac{1}{v_s} \left( \frac{\partial v_s}{\partial T} \right)_P = -0.70 \cdot 10^{-4} \text{ km \cdot sec}^{-1} \cdot ^\circ \text{C}^{-1}
\]

Compressibility \( \beta = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T = 0.79 \text{ Mbar}^{-1} \)

Volume thermal expansion \( \alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P = 3 \cdot 10^{-5} / ^\circ \text{C} \)

rological grounds and may be due to at least three effects (Anderson and Sammis, 1969, 1970): (1) the geotherm and water-saturated solidus intersect at \( P > 40 \text{ kbar} \); (2) the water content of the mantle decreases below \( \sim 150 \text{ km} \) sufficiently so that \( p_{\text{H}_2\text{O}} \ll P_{\text{total}} \) and the solidus moves to higher temperatures to approach the anhydrous solidus; or (3) new hydrous phases, stable at high pressure (> 40 kbar) may act as hosts for water in the deeper mantle (Sclar, 1970; Ringwood, 1970; Yamamoto and Akimoto, 1974), reversing the amphibole breakdown effect and moving the solidus to higher temperatures. In our model, we have arbitrarily assumed that the base of the LVZ is at 150–175 km and used the anhydrous mineralogy of pyrolite to calculate the elastic properties below that depth.

Possible basaltic (eclogitic) segregation in the lithosphere

In the central portion of Fig. 3, the "transitional" layer (\( z = 20–40 \text{ km} \) depth) retains the same bulk chemistry as spinel lherzolite but consists of residual harzburgite with segregations of basaltic composition (Table I) or of composition appropriate to high-pressure accumulates (aluminous pyroxenes ± spinel ± olivine ± garnet ± amphibole) from basaltic magma. At the P,T conditions of the stable geotherm (9–11 kbar, 500–700°C), these compositions would be of eclogite or garnet pyroxenite mineralogy. The higher Mg-value of the refractory harzburgite, the increased percentage of garnet and the presence of jadeite solid solution in pyroxene all tend to increase the velocities, so that this alternative lithology for the transitional region produces slightly higher mean velocities than the spinel lherzolite mineralogy (illustrated by
dashed portions of Fig. 6) We have in this variant of the model thus given quantitative expression to a qualitative suggestion that high $v_p$- and $v_s$-values in the upper mantle may be due to segregation of basalt without eruption to the surface and later cooling of the basaltic segregations to enter the eclogite stability field (Forsyth and Press, 1971).

Possible eclogite layer at the base of the basaltic crust

In the right side of Fig. 3 we have depicted possible lithosphere characteristics for areas of greatly thickened basaltic crust such as beneath the Hawaiian Island or Emperor Seamount volcanic chains. In these regions it has been suggested (Ringwood and Green, 1966; Green, 1972) that the base of the thickened basaltic crust will, given time at appropriate temperature and pressure, convert to eclogite of $\rho = 3.5$ approx. In Fig. 3 we have illustrated the basalt to eclogite reactions occurring at 250–300°C, ~15 km. Any regions of the oceanic crust where this process occurs would be expected to yield high $v_s$- and $v_p$-values at shallow depths and also to be gravitationally unstable. It is of interest to note the high sub-mantle seismic velocities locally reported in the Pacific are, in some cases, in such regions of thickened oceanic crust (Woollard, 1975, fig. 18). A further location where it might be anticipated that the basaltic oceanic crust would convert to eclogite and possibly initiate sinking into the lithosphere due to its gravitational instability, is in areas of very old oceanic crust, marginal to continental regions and depressed to higher P,T levels by loading by thick continent-derived sediment sequences.

Velocity profiles in the oceanic lithosphere

The principal features of the velocity profiles along the stable oceanic geotherm are (Fig. 6):

1. Lithosphere
   - 85 km thick
   - Mean $v_p \approx 8.10$ km/sec  $v_s \approx 4.67$ km/sec
   - Jump at spinel $\rightarrow$ garnet pyrolite transition (50 km)
     $\Delta \rho = 0.03$ g/cm$^3$  $\Delta v_p = 0.13$ km/sec  $\Delta v_s = 0.03$ km/sec

2. LVZ
   - 85–165 km depth
   - Chemically homogeneous (0.5% melt) $v_p = 7.8$ km/sec  $v_s = 4.3$ km/sec
   - Chemically zoned (2% $\rightarrow$ 0.5% melt)
     Enhanced low-velocity channel at top of LVZ with $v_p = 7.2$ km/sec  $v_s = 3.5$ km/sec

3. Sub-LVZ
   - >165–200 km thick
   - $\rho \approx 3.39$ g/cm$^3$  $v_p \approx 8.30$ km/sec  $v_s \approx 4.6$ km/sec

   The sub-Moho $P_n$ velocity in our model is $v_p = 8.25$ km/sec (2 kbar, 160°C) which compares favorably with the bulk of the observed $P_n$ data for the
Pacific oceanic mantle in regions 60–90 m.y. old (Woollard, 1975, fig. 10). Approximately 25% of the data tabulated by Woollard exceed $v_p = 8.5$ km/sec and are too high to be explained by our preferred model. The values of $v_p$ in our model are only slightly increased ($\Delta v_p \lesssim 0.1$ km/sec) in the 20–40 km depth interval if we assume discontinuous segregation of eclogite/garnet pyroxenite in refractory harzburgite residue rather than the more probable spinel lherzolite mineralogy. Even if the postulated eclogite segregation formed a continuous layer at this depth, the $v_p$ for the appropriate eclogite mineralogy would be $v_p \leq 8.40$ km/sec (Table I). It is worth noting that the petrological and geological constraints do not allow arbitrary choice of eclogite mineralogy but limit the bulk composition to possible derivatives of a peridotite source, to reasonable jadeite contents of pyroxene, and to known partition relationships between Fe and Mg for coexisting garnet and clinopyroxene.

The second variant of the pyrolite model allows for an eclogite layer at the base of a thickened basaltic crust (Fig. 3). The basaltic compositions in such a sequence could be quite variable and more flexibility exists for the generation of compositions later crystallizing to quartz eclogites, olivine eclogites or kyanite eclogites. Nevertheless, $v_p$ in such rocks is unlikely to exceed 8.5 km/sec (Manghnani et al., 1974). We see no way within the framework of the pyrolite model and consideration of likely related basaltic compositions of generating velocities at any depth in the lithosphere as high as $v_p = 8.8–9.0$ km/sec (Zverev, 1970; Hales et al., 1970; Woollard, 1975) without postulating a role for pronounced anisotropy in the upper mantle due to preferred orientation of olivine or pyroxene crystals.

Our shear-velocity profile for the lithosphere in stable oceanic regions may be compared with observed seismic models based on travel-times of body waves and surface wave dispersion. Observations of $S_n$ velocities (for a “phase” which travels in the uppermost mantle and samples the highest velocity in the lithosphere) in old oceanic regions indicate $v_s = 4.66–4.79$ km/sec (Molnar and Oliver, 1969; Hart and Press, 1973; Huestis et al., 1973) which is quite compatible with the velocities in our model $v_s = 4.60–4.80$ km/sec. Geophysical models for $v_s$ in the upper mantle (e.g. Knopoff, 1972) based on Rayleigh wave dispersion data often involve a trade-off between velocity contrast [$v_s$ (lithosphere)/$v_s$ (LVZ)] and the thickness of the LVZ (and the depth to the bottom of the lithosphere); many recent models, however, include shear velocities in the lithosphere of $v_s = 4.5–4.7$ km/sec (Knopoff, 1972; Leeds et al., 1974; Weidner, 1974; Yoshii, 1975; Forsyth, 1975).

Due to the ambiguity in the geophysical models for the LVZ and the uncertainty in the assumptions used to derive the velocities in the partially molten zone from our petrological model, it is difficult to make definitive comparisons. Nevertheless, the shear velocity in our LVZ $v_s = 4.3$ km/sec (0.5% melt and $\alpha = 10^{-2}$) is quite consistent with the LVZ channel velocities $v_s = 4.1–4.3$ km/sec used in the inversion of the surface-wave data. The thickness of the lithosphere in the various geophysical models discussed above varies from 60 to 100 km, which is in accord with the ~90 km predicted in our
model. Note that the shoulder in the pyrolite solidus (Fig. 2) implies that the depth to the LVZ beneath old ocean basins is very insensitive to temperature fluctuations and will be between 85 and 95 km for $T = 1020-1160^\circ$C. Lithospheric thickness of circa 100 km are also implied by interpretations of other geophysical data (heat flow, ocean-floor topography, gravity anomalies) for oceanic regions older than 80 m.y. (Sclater et al., 1975).

The sub-LVZ velocities in our model (Fig. 6) are only notional as we do not know the precise mineralogy of the pyrolite composition at those depths (165–200 km, 55–67 kbar, 1400–1450$^\circ$C). The in-situ velocities of $v_p = 8.3$ km/sec and $v_s = 4.6$ km/sec are calculated by a linear extrapolation of the initial values using pressure and temperature derivatives of velocity measured at low pressure and in the neighborhood of room temperature; we may have thus overestimated the pressure correction (positive) and underestimated the temperature correction (negative) so that our calculated velocities may be too high. Furthermore, we may have overestimated the velocity—depth slopes between 155 and 200 km by using the linear extrapolation instead of the more rigorous finite-strain equations (Sammis et al., 1970). It is interesting to compare our calculated velocities, however, with those of Helberger's (Helmberger and Engen, 1974; Helmberger and Wiggins, 1971) model SHR14 for the western United States which is compatible with both travel times and wave forms of the observed seismograms.

At 200 km:

<table>
<thead>
<tr>
<th>Petrological model</th>
<th>SHR14</th>
</tr>
</thead>
<tbody>
<tr>
<td>(67 kbar, 1450$^\circ$C)</td>
<td></td>
</tr>
<tr>
<td>$v_p$ (km/sec)</td>
<td>8.35</td>
</tr>
<tr>
<td>$v_s$ (km/sec)</td>
<td>4.62</td>
</tr>
</tbody>
</table>

The modifications to our calculation procedure discussed above would lower our velocities and make them even more compatible with SHR14 (for which the ambient temperature may be intermediate between shield and oceans).

PETROLOGICAL PROCESSES AT MID-OCEANIC RIDGES AND FORMATION OF THE LITHOSPHERE

The distinctive feature of the mid-ocean ridges is their active basaltic volcanism and associated heat flow, seismic and topographical effects. The nature of the basaltic volcanism places constraints on the processes occurring at the ridges and is the key factor in formulating the conditions present in the lithosphere beneath the ridges.

The effects of variable low-pressure fractionation with extraction of minor olivine, and in some cases plagioclase and/or clinopyroxene, are well documented for ocean-floor basalts (Miyashiro et al., 1970; Frey et al., 1974). Parental, primitive compositions have $100 \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) \sim 70$ and include both high-Al (>15% $\text{Al}_2\text{O}_3$) olivine tholeiites and low-Al (<14% $\text{Al}_2\text{O}_3$) olivine
tholeiites. The former magma types have segregated from olivine, orthopyroxene and minor residual clinopyroxene at $P = 10-15$ kbar, $T = 1300-1350^\circ C$ and by 20–25% melting of source peridotite. The latter magma types have segregated from olivine and orthopyroxene residue at $P = 15-20$ kbar, $T = 1350-1400^\circ C$ by 25–30% melting of source peridotite. More rarely, undersaturated, nepheline-normative basalts occur on or very close to the mid-oceanic ridges. Schilling and Bonatti (1975) report nepheline-normative compositions from the East Pacific Rise and their major- and trace-element chemistry is consistent with small degrees of melting of a depleted pyrolite source (i.e. lower part of LVZ in the preferred model under discussion). Muir and Tilley (1964) described high-K olivine tholeiites from within 4 km of the axis of the mid-ocean rift valley and the trace-element characteristics (Frey et al., 1968; Kay et al., 1970) are those of Hawaiian-type tholeiites or basalts transitional towards alkali olivine basalts. Schilling (1973, 1975) has documented the transitional nature (in REE relative abundances) of basalts dredged from the Reykjanes ridge, south of Iceland, and from the Mid-Atlantic ridge north and south of the Azores. In these areas, the distinction between the implied source characteristics for Hawaiian-type tholeiites (i.e. pyrolite with $\sim 0.13$% $K_2O$, enriched in incompatible elements including LREE) and the implied depleted pyrolite source for mid-oceanic ridge basalts, becomes blurred.

Further complexity in the ridge-forming process is shown by recent data (Bonatti and Honnorez, 1971; Bonatti, 1971; Melson et al., 1972; and Ozima et al., 1976) which shows the existence of geologically old materials (metabasalts, ultramafic rocks, shallow-water sediments) on or close to intersections of the Mid-Atlantic ridge with transverse fracture zones. These data, as yet fragmentary, indicate the inadequacy of a simple, steady-state model in which the entire crust and mantle of the lithosphere is newly formed at the mid-oceanic ridges. It appears more probable that beneath the ridges the cause of volcanism is the episodic and sequential ascent of individual peridotite diapirs, intruding and displacing earlier diapirs and screens of old lithosphere. The existence of fracture zones and the displacement of mid-oceanic ridges along such fracture zones (transform faults) together with the interpretations of sea-floor magnetic anomalies showing that mid-ocean ridges have histories of cessation of activity and displacement to a new locality, suggest that the location and activity of a ridge are effects rather than causes of plate tectonics. There is apparently no primary geochemical or geothermal character of the underlying mantle region which primarily determines the lithosphere-forming process at a ridge.

In the model for development of the lithosphere which we have attempted to analyze, the processes operative at a ridge are considered to develop from any normal steady-state condition of the lithosphere. This allows the position of the ridge to migrate continuously relative to the mantle LVZ and also to migrate discontinuously in response to a new tensional fracturing or thinning of the lithosphere.

In Fig. 5 we illustrate our view of active volcanism at the ridge with diapirs
ascending on adiabatic cooling paths (1–2°C/kbar, increasing slightly as the amount of melt increases and in response to latent heat of melting) to yield magmas segregating with 20–30% melting at 20–40 km. The magmas move through feeder-dyke systems to erupt at the sea floor and the residual material (harzburgite with olivine (Fo90, 70–80%), enstatite (Mg91, 20–25%) minor clinopyroxene (0–5%) and accessory chromite) remains, to be displaced upward and laterally by later diapirs. Using the pyrolite model composition and the compositions of ocean-floor basalts, the model predicts a zone of 20–25 km approx. of refractory harzburgite forming the upper part of the lithosphere (Fig. 3). The process outlined sets the boundary conditions for the initial formation of new lithosphere, i.e. at <1 m.y., the temperature in residual harzburgite at ~30 km depth is 1300°C. Beneath the zone of refractory harzburgite, we infer the presence of a zone in which there has been some minor depletion by extraction of basaltic magma; this layer is probably inhomogeneous varying from pyrolite to harzburgite but with average composition and mineralogy of a spinel lherzolite. Since this region has presumably followed an upwelling path at the near-ridge location it is possible that there has been partial segregation of magma but without movement to the surface — this possibility (cf. Bottinga, 1974) leads to a variant of the mineralogy of the 30–50 km interval (Fig. 3) in which there is up to 20–25% segregations of basaltic compositions (eclogite) in refractory harzburgite. We note, however, that if the high-pressure inclusions in undersaturated basaltic magmas are a reasonably representative sampling of the upper-mantle lithosphere to ~50–60 km depth then they indicate that the model to be preferred for this region is the spinel lherzolite model. Beneath the partially depleted zone, the bulk composition is inferred to be pyrolite, largely of composition appropriate to the lower part of the LVZ (i.e. low water contents and low incompatible element contents). This compositionally layered section (Fig. 3) cools as it moves away from the ridge, leading to crystallization of the melt fraction and reaction of spinel pyrolite to garnet pyrolite, slightly increasing the density in the base of the lithosphere.

Finally we return to the cautionary point that although the attempt to quantify the petrological model for the formation of lithosphere necessarily is an averaging process and treats different regions as compositionally homogeneous, the real processes are more probably discontinuous and episodic. We see no reason to suppose that relics of old lithosphere and subjacent LVZ may not locally persist in the near-ridge environment, particularly where the ridge is offset by transform faults with associated screens of old crust and lithosphere.

ELASTIC PROPERTIES OF SUB-OCEANIC MANTLE AS A FUNCTION OF CRUSTAL AGE

The velocity and density profiles for the lithosphere and LVZ constructed in the earlier section from our petrological model are appropriate to geotherms for stable oceanic regions well removed from the mid-oceanic ridges (t > 80
m.y.). For younger oceanic regions, the geotherm will be perturbed to higher temperatures due to the intrusion of molten material along the ridge axis and subsequent cooling as the new crust moves away from the ridge. Many authors (e.g. Langseth et al., 1966; McKenzie, 1967; Sleep, 1969; Sclater and Francheteau, 1970) have demonstrated that a simple model of a plate of constant thickness 50—100 km with a base temperature between 550° and 1500°C can satisfactorily explain the decay of observed heat flow and ocean-floor topography away from the ridge crest. In these plate models, almost all of the heat due to the intrusion process is lost after 40—50 m.y.

The primary differences in the thermal regimes for the various plate models for the oceanic lithosphere are in the assumed plate thickness \( h \) and the temperature at the base of the plate (invariably related to the solidus temperature \( T_s \)). In Fig. 4 we have plotted the 100-m.y. geotherms of several investigators along with the solidus curve for pyrolite with \(<0.4\%\ H_2\O\). The effect of \( h \) on the geotherm is best illustrated by comparing S69 \((h = 100\ \text{km}, \ T_s = 1200\text{°C})\) with FP71 \((h = 70\ \text{km}, \ T_s = 1230\text{°C})\) and SF70a \((h = 75\ \text{km}, \ T_s = 1300\text{°C})\), with the thicker plates naturally having lower temperatures at all depths. Similarly, models with the same \( h \) and higher \( T_s \) will be hotter at all depths, compare SF 70b \((h = 100\ \text{km}, \ T_s = 1475\text{°C})\) with S69 \((h = 100\ \text{km}, \ T_s = 1200\text{°C})\).

From the viewpoint of our petrological model, a more realistic plate model should have variable thickness defined by the intersection of the geotherms with the solidus (for which \( T_s = 1120\text{°C} \) is a reasonable approximation to depths of 85 km). Parker and Oldenburg (1973; see also Davis and Lister, 1974) have actually developed such a model in which material accretes on to the base of the lithospheric slab as it moves away from the ridge, releasing latent heat that must be carried away by conduction to the surface. As a consequence of this latent heat (100 cal./g), the PO73 geotherms \((h = \text{variable}, \ T_s = 1200\text{°C})\) are displaced to higher temperature (Fig. 7) relative to those for S69 \((h = 100\ \text{km}, \ T_s = 1200\text{°C})\), but both the PO73 and S69 geotherms approach the steady-state geotherm at 60—100 m.y. (Fig. 4). Crough (1975) has recently demonstrated that the heat-flow data can be equally well satisfied by a variable-thickness plate model with no latent heat if it is assumed that there is a constant heat flux \((0.6—0.8\ \text{h.f.u.})\) into the base of the lithosphere from the underlying athenosphere; the thermal models constructed and the plate thicknesses derived by Crough (1975, for \( T_s = 1200\text{°C} \)) are quite similar to those of Parker and Oldenburg (1973) for ages younger than 100 m.y.

The variable-thickness plate models (Parker and Oldenburg, 1973; Davis and Lister, 1974) gave satisfactory fits to the heat-flow data and to the topographic data out to 80 m.y. but imply that the plate thickness continues to increase as \( h \propto t^{1/2} \). From a comparison of the long-wavelength residual elevation and free-air gravity anomalies in the North Atlantic, Sclater et al. (1975) have extended the ocean depth versus age relation from 80 to 150 m.y. They infer from the very small increase of depth with age in the Cretaceous and the
uniform heat flow through old oceanic crust that the oceanic plate approaches a constant thickness in regions older than 80 m.y. In this interpretation (Sclater et al., 1975), the oceanic heat flow consists of two components, one due to conductive cooling of the plate as it moves away from the ridge and a uniform background heat flux provided by small-scale convective flow in the asthenosphere of the type suggested by Richter (1973). The only disturbing aspect of the Sclater et al. (1975) analysis is the difference between the limiting plate thicknesses necessary to match the heat-flow data ($h = 60$ km) and the topographic data ($h = 125$ km) in the older oceanic regions.

From the discussion above, it is clear that the ocean-floor topography, heat flow and gravity-anomaly data can be satisfactorily accounted for by a plate model with an isothermal base temperature ($T_b$) and variable thickness which approaches a constant value ($h \approx 60-125$ km) at least by 100 m.y. (Sclater et al., 1975). We have therefore adopted the Parker and Oldenburg (1973) geotherms for $t < 100$ m.y. and have superimposed them on our petrological phase diagram (Fig. 8). We have then derived a lithosphere–asthenosphere upper-mantle model as a function of age of the oceanic crust (Fig. 9). Similar mantle cross-sectional models have been constructed by Sclater and Francheteau (1970) and Forsyth and Press (1971) using plate models of constant thickness and slightly different phase diagrams.

Our model for the evolution of the oceanic upper mantle (Fig. 9) contains
Fig. 8 P-T solidi and sub-solidus mineralogy for dry and water-undersaturated (<0.4% H₂O) pyrolite. Superimposed are the oceanic geotherms for 0, 20, 60 and 100 m.y. for the plate model of Parker and Oldenburg (1973); portions of these geotherms are schematic. Dotted curves between the dry and water-undersaturated solidi indicate varying degrees of partial melting.

Fig. 9. Mineralogical cross-section of the oceanic crust and upper mantle based on the phase diagram for pyrolite and the geotherms of Parker and Oldenburg (1973) for t ≈ 100 m.y. Dashed curves are isotherms for the same thermal plate model. Symbols (circles, crosses, triangles) represent estimates of lithospheric thickness as a function of age derived by inversion of surface wave dispersion curves. (Leeds et al., 1974; Yoshii, 1975; Forsyth, 1975).
a chemically and mineralogically zoned lithosphere overlying an asthenosphere (LVZ) which may contain vertical chemical zoning beneath the older (> 80 m.y.) oceanic basins. The boundary of the lithosphere and LVZ is defined by the intersection of the PO73 geotherms with the solidus for pyrolite with \( \leq 0.4\% \) \( H_2O \); for \( t > 80 \) m.y. (Fig. 4), there is little or no increase in the thickness of the lithosphere (\( h = 85-95 \) km) because of the shoulder on the pyrolite solidus. Our model for the variation of \( h \) as a function of age is remarkably similar to that constructed by Sclater et al. (1975) using \( T_s = 1120^\circ C \) and assuming a constant thickness for \( t > 80 \) m.y. As mentioned above, Sclater et al. (1975) were unable, for the North Pacific area, to reconcile observed heat flow and topographic data with the same limiting thickness of the lithosphere. However, their topographic estimates did not include the effect of sub-solidus phase boundaries which Sclater and Francheteau (1970) have shown can make an important contribution to the calculated topography for younger regions. By combining our petrological model for the lithosphere (Fig. 9) with the calculations of Sclater and Francheteau (1970, fig. 17b), we estimate that the phase changes in our model may contribute an additional 200–300 meters to the topographic profiles of Sclater et al. (1975, fig. 11 bottom) for \( t < 60 \) m.y. Consideration of this effect would permit the topographic data for \( t > 80 \) m.y. to be satisfied with a lithosphere of 90–100 km thickness, rather than the fit to 125 km illustrated by Sclater et al. (1975, fig. 11).

Following the procedures described previously (Fig. 6), we then use the petrological model (Fig. 9) to construct velocity and density profiles along the geotherms for various ages of oceanic crust (Fig. 8). The principal features of the velocity profiles along the Parker-Oldenburg geotherms are (Fig. 10):

1. Lithosphere — thickness increases from 20 km at 5 m.y. to 90 km at 100 m.y. Both maximum and mean velocities show a systematic increase with age due to:
   a. lower temperatures;
   b. increasing percentage of garnet pyrolite for \( t > 60 \) m.y.
2. LVZ
   - thickness decreases with increasing age
   - velocity contrast \([v(\text{lithosphere})/v(\text{LVZ})]\) decreases with increasing age due to decreasing melt fraction but is enhanced where chemical zoning is present or develops in the LVZ.
3. Sub-LVZ
   - \( h = 165-200 \) km
   - assumed identical for all geotherms
   - \( \rho \approx 3.39 \text{ g/cm}^3 \quad v_p \approx 8.30 \text{ km/sec} \quad v_s \approx 4.61 \text{ km/sec} \)

The maximum velocities of compressional and shear waves in our lithosphere model exhibit a systematic increase with increasing age (Fig. 11). For compressional waves, these velocities should be compared to sub-Moho \( P_n \) velocities observed in oceanic regions; we have already commented that the calculated \( v_p = 8.2–8.3 \) km/sec are consistent with many of the data tabulated by Woollard (1975). However, even in the variant of our model which assumes discontinu-
ous segregation of eclogite in refractory harzburgite at depths of 20–50 km, \( v_p \) does not exceed 8.3 km/sec in the lithosphere. In a recent study of the northeastern Pacific basin using body-wave data recorded on hydrophones, Sutton and Walker (1972) found a wave guide immediately below the Moho which propagates 3–8 Hz energies of compressional and shear phases with velocities of \( v_p = 8.28 \pm 0.03 \) and \( v_s = 4.79 \pm 0.04 \) km/sec, respectively to great distances (observed to 33\(^\circ\)); these observations are almost identical with our calculated velocities for all oceanic regions (Fig. 11).

The maximum shear velocities illustrated in Fig. 11 should be compared with measurements of \( S_n \) velocities in the uppermost mantle. Our model predicts a systematic increase in the maximum \( v_s \) from 4.67 km/sec at 5 m.y. to
4.82 km/sec at 100 m.y. Regionalized Sn velocities determined by Hart and Press (1973) also exhibit a dependence on crustal age with $v_s = 4.58 \pm 0.02$ km/sec for $t = 0-50$ m.y. and $v_s = 4.71 \pm 0.01$ km/sec for $t > 50$ m.y.; the trend to higher velocities is consistent with our model but the calculated velocities are somewhat higher than observed. This is in contrast to the results of Hart and Press (1973, p. 411) who concluded that "no purely peridotitic lithosphere attains velocities as high as those observed under the old sea floor"; their conclusion was based on the calculations of Forsyth and Press (1971, p. 7975) who based their initial shear velocities on the assumption that Poisson's ratio $\sigma = 0.26$ which corresponds to $v_p/v_s = 1.76$. The mineral data in Table II clearly demonstrate that $v_p/v_s = 1.71-1.72$ or $\sigma = 0.24$ for garnet pyrolite which accounts for the higher shear velocities calculated in our model.

Several authors have recently attempted to regionalize variations in Rayleigh wave phase velocities across the Pacific Ocean (Kausel et al., 1974; Leeds et al., 1974; Yoshii, 1975; Forsyth, 1975). In the studies, the surface-wave paths were grouped by age of the oceanic crust using the magnetic-lineation chronology; previous workers had observed regional variations in phase velocities but were able only to divide the paths into ridge and basin categories (e.g. Wu, 1972; Weidner, 1974). In their inversion of the phase-velocity data to obtain shear velocity profiles, Leeds et al. (1974) and Yoshii (1975) assumed a fixed velocity contrast between the lithosphere and LVZ (4.6/4.1 for LKK 74 and 4.6/4.3 for Y75) and adjusted the thickness of the lithosphere ($h$) to fit the data; their determinations of $h$ vs. $t$ are plotted in Fig. 9 and compare favorably with the lithosphere—LVZ boundary out to 100 m.y. in our petrologically derived model. Forsyth (1975) permitted both $h$ and the mean litho-

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Fig. 11. Maximum lithospheric velocities as a function of age for petrological and geophysical model of Figs. 8-10. Data of Hart and Press (1973) are for regionalized $S_n$ studies, of Sutton and Walker (1972) for oceanic refraction studies, and of Forsyth (1975) from inversion of surface-wave dispersion curves.
sphere velocity to vary in his models and observed a systematic increase in both parameters with increasing age (Figs. 9 and 11); both of these trends are in accord with our model.

In a paper presented at this meeting, Forsyth (1975, and personal communication, 1975) showed that the Rayleigh wave data in the Pacific require an increase of $v_s$ within the LVZ (100–150 km) from about 4.10 km/sec beneath young sea floor to about 4.25 km/sec beneath old ($t = 100–135$ m.y.) sea floor. In the lithosphere, the shear velocity over the depth range $h = 20–45$ km is well-resolved and shows an increase with age which cannot be traded off with a change in lithospheric thickness: $v_s$ (lid) increases from $4.43 \pm 0.03$ km/sec ($t = 10–20$ m.y.), to $4.46 \pm 0.03$ km/sec ($t = 20–40$ m.y.), to $4.66 \pm 0.025$ km/sec ($t = 100–135$ m.y.). According to Forsyth's interpretation the lithospheric thickness beneath old sea floor is about 90 km, so that both the thickness and mean shear velocity in the lithosphere are in excellent agreement with our model beneath stable oceanic regions. The numerical disagreement between our model and that derived from the Rayleigh wave data for younger areas (Figs. 9 and 11) may be due to the averaging process of surface waves or velocity anisotropy in the lithosphere (Forsyth, personal communication, 1975). Note that one measure of such anisotropy is the different velocity structures derived from Rayleigh wave and Love wave data; in the Pacific, the average $v_s$ detected by Love waves over the depth range 0–125 km is $0.15 \pm 0.06$ km/sec higher than that detected by Rayleigh waves (Forsyth, 1975).

As mentioned in a previous section of this paper, the inversion of the surface-wave phase-velocity data to obtain a shear-velocity model for oceanic regions involves a tradeoff between the thickness of the LVZ and the velocity contrast with the overlying lithosphere; this tradeoff operates in such a way that a thin LVZ is correlated with a large velocity contrast, and vice versa. One notable feature of the velocity profiles for our petrological model (Fig. 10) is the fact that the thicker low-velocity zones are characterized by higher degrees of partial melting and hence larger velocity contrasts, in marked distinction to the seismic tradeoff. This behaviour is not unique to the pyrolite model but is a general feature of petrological models in which low-velocity zones are produced by partial melting in chemically homogeneous materials having solidi with positive P vs. T slopes. It may be useful in future inversions of such data to invoke the constraints implicit in a petrological model to eliminate some of the non-uniqueness in the geophysical models.

CONCLUDING REMARKS

The pyrolite model for the upper mantle has been developed on petrological and geochemical grounds, particularly on the basis of accounting for the characteristics (major element and trace element) of basalts in both the mid-ocean ridge and off-ridge volcanic environments. The inferred mineralogy and chemical zoning in the LVZ have been translated into estimates of seismic
velocities which are not inconsistent with the observed data in stable oceanic regions. If the estimates of degrees of partial melting in the LVZ based on petrological arguments are accepted, then the matching of predicted and observed values for $v_p$ and $v_s$ has the corollary that the aspect ratio for the melt segregations in the LVZ must be about $10^{-2} - 10^{-3}$.

The processes leading to basaltic volcanism at mid-ocean ridges, predict an uppermost mantle layer beneath stable oceanic regions of $\sim 20$ km thickness of refractory harzburgite, overlying a slightly depleted, probably inhomogeneous, spinel lherzolite layer. The predicted seismic velocities within these layers and in underlying pyrolite range from $v_p = 8.0 - 8.2$ km/sec and $v_s = 4.6 - 4.8$ km/sec. along the stable oceanic geotherm. A small discontinuity with a sharp increase in $v_p$ from 8.0 km/sec to 8.12 km/sec is predicted at $\sim 55$ km depth due to reaction from spinel pyrolite to garnet pyrolite assemblage (14% garnet). The low-velocity zone commences at depths $\sim 90$ km, and most of this region is characterized by $\sim 0.5\%$ partial melt producing decreases in $v_p$ of 2% and in $v_s$ of 8%. Vertical chemical zoning of the LVZ in off-ridge environments produces higher degrees of partial melting ($\sim 2\%$) and larger decreases in $v_p$ and $v_s$ at 90–110 km depth.

We conclude from this attempt to translate our petrological model into a seismological model for the stable oceanic lithosphere and LVZ that the pyrolite model satisfactorily accounts for the presence of the LVZ, the thickness of the lithosphere and the observed velocities in the lithosphere and LVZ.

The preferred pyrolite model (Figs. 3 and 5) does not explain compressional velocities in the lithosphere of $v_p > 8.3$ km/sec. Within the 30–40 km depth interval, quantitative evaluation of the possible role of mixing of eclogite mineralogy and residual harzburgite mineralogy (due to segregation but not eruption of basaltic magma during lithosphere formation) shows that this process may cause small increments in $v_p$ ($\Delta v_p = 0.06 - 0.1$ km/sec) and $v_s$ ($\Delta v_s = 0.05$ km/sec). It might be suggested that a continuous layer of eclogite develops at 30–50 km from segregated basalt. The petrological constraints on the composition of basalt derived by partial melting of pyrolite or lherzolite and the known partition relationships between Fe and Mg in coexisting garnet, clinopyroxene and olivine, lead to the conclusion that the maximum in-situ velocities for such eclogite would be $v_p = 8.4$ km/sec and $v_s = 4.9$ km/sec. The presence of an eclogite layer developing immediately at the base of a thickened oceanic crust would yield somewhat higher maximum velocities of $v_p = 8.5$ km/sec and $v_s = 5.0$ km/sec at 10–20 km depth.

There appears to be no way in either the pyrolite model or its variant incorporating eclogitic segregations to account for the very high values of $v_p = 8.8 - 9.0$ km/sec observed in seismic refraction studies of certain oceanic regions (Hales et al., 1970; Zverev, 1970; Woollard, 1975) without invoking anisotropy due to the preferred orientation of olivine or pyroxene crystals. Appeal to eclogite as the major component of or as layers within the lithosphere also does not produce sufficiently high values of in-situ $v_p$ particularly if the knowledge of likely compositions of natural eclogites and basalts is used
to constrain the eclogite mineralogy. The very high intrinsic velocities of pure pyrope garnet (estimated $v_p = 9.3$ km/sec, STP) or pure jadeite ($v_p = 9.0$ km/sec, STP) are not very relevant in natural peridotite and eclogite where garnets contain $\leq 50\%$ pyrope and clinopyroxene in basaltic compositions contain $\leq 50\%$ jadeite. The petrological approach suggests a need to very critically examine the methodology, assumptions in modelling and the data interpretation in these studies where compressional velocities in the lithosphere of $\geq 8.5$ km/sec have been inferred. In such areas, reversal of refraction profiles and studies to evaluate possible seismic anisotropy are clearly desirable. It appears to us unlikely that uncertainties in knowledge or error in predictions of the elastic properties of minerals and their P,T derivatives are sufficient to permit values of $v_p \geq 8.5$ km/sec in petrologically reasonable rock types under upper-mantle conditions, without appeal to seismic anisotropy.

Our petrological model for the evolution of the oceanic crust and upper mantle predicts a lithosphere which thickens with age as it cools, stabilizing at $h = 85-95$ km for $t > 80$ m.y. The mean compressional and shear velocities in our model lithosphere also increase with age due to lower temperature and higher garnet content. Since the low-velocity zone commences at shallower depths for younger regions and is assumed to terminate at the same depth for all oceanic geotherms, it becomes gradually thinner with increasing age. However, the velocity contrast between the lithosphere and the LVZ decreases with age as a consequence of smaller degrees of partial melting. This petrological model and its velocity profile are compatible with most of the geophysical data for various 'age' provinces in oceanic regions. It is possible that some of the residual discrepancy between our model and the data could be eliminated if constraints implied by the petrological model were incorporated in the inversion of the surface-wave dispersion curves.

ACKNOWLEDGEMENTS

We have profited from discussions with D.L. Anderson, A.L. Hales and R.L. Parker while preparing this paper. We thank D.L. Anderson, D.W. Forsyth and A.E. Ringwood for their comments on the manuscript, D.W. Forsyth for a preprint of his paper and for permission to discuss his Rayleigh wave models in advance of publication and W.O. Hibberson for drafting the figures.

REFERENCES


NOTE ADDED IN PROOF

Recent studies (e.g. Brey, G. and Green, D.H., 1976, Solubility of CO₂ in olivine melilitite and role of CO₂ in the upper mantle. Contrib. Mineral. Petrol., in press) further show that CO₂ occurs under mantle conditions as magnesite or dolomite at subsolidus P,T conditions and not as a free CO₂-rich vapour phase.
Subsolidus equilibria between pyroxenes in the CaO-MgO-SiO$_2$ system at high pressures and temperatures

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Abstract

The extent of pyroxene solid solutions has been experimentally determined in the CaO-MgO-SiO$_2$ system at 30 kbar and 1500°C. The results show the enstatite and diopside mutual solid solutions and also define the limited solid solutions towards olivine and quartz. Although the enstatite-diopside solvus is wider when olivine rather than quartz is a coexisting phase, the difference does not seriously affect the pyroxene solvus as a geothermometer. Thus, this geothermometer can be used without taking the coexisting phases other than pyroxenes into account.

The study of the enstatite-diopside solvus in the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ system has been extended above 1500°C at 20 and 30 kbar. These pyroxenes show almost complete solid solution at solidus temperatures. The iron-free pigeonite-diopside solvus which was previously found at 20 kbar and inferred to be stable at 30 kbar did not appear at these pressures. The phase equilibrium data in this paper are combined with those in the literature to make a compilation of the enstatite-diopside solvus over a wide temperature-pressure range.

Some difficulties in use of the pyroxene solvus geothermometer are discussed, taking the garnet lherzolite nodules from Lesotho kimberlites as examples.

Introduction

The past few years have seen much interest in the phase equilibrium studies of pyroxenes (Lindsley et al., 1974a; Warner and Luth, 1974; MacGregor, 1974; Smyth, 1974; Nehru and Wyllie, 1974; Howells and O’Hara, 1975; Mori and Green, 1975; and Chen and Presnall, 1975). We note particularly Howells and O’Hara’s (1975) treatment of pyroxenes as solid solutions towards forsterite and quartz. The present study, although a continuation of our earlier work, was in part undertaken to evaluate their suggestions.

The enstatite-diopside solvus has long been used as a geothermometer and applied to temperature estimates of natural rocks. An implicit assumption in using the geothermometer is that pyroxenes had no solid solutions towards forsterite and/or quartz. Thus temperatures have been estimated without taking coexisting phases into account. However, Howells and O’Hara (1975) suggested that pyroxenes have solid solutions towards forsterite and quartz and that these solid solutions greatly affect the degree of mutual solid solution. Since all minerals are solid solutions in a strict sense, it is important whether or not the magnitudes of solid solution towards forsterite and quartz are enough to alter the practical application of the solvus as a geothermometer. In this paper we describe experiments made to define these solution limits.

The second problem treated in this paper is a reexamination of the stability of iron-free pigeonite at high pressures. Kushiro (1969) presented a phase diagram in the system Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ at 20 kbar. Pigeonite was thought to be stable above 1450°C, producing two solvi between enstatite and pigeonite, and pigeonite and diopside. Howells and O’Hara (1975) reexamined this system at the same pressure, and contrary to Kushiro’s experiments found homogeneous clinopyroxenes well within the pigeonite-diopside solvus as determined by Kushiro. We have reexamined this system at 20 kbar and obtained

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1 Hereafter, this mineral is called pigeonite for convenience. We use this term for low-calcium clinopyroxene which is distinguished from diopside (high-calcium clinopyroxene) by a solvus between them. This definition is also applicable to iron-bearing pigeonite. Note that if the two minerals have the same crystal structure of C2/c, it is not necessary to call them by different names.
results supporting Howells and O'Hara's conclusions.

The third experimental problem discussed in this paper is the enstatite–diopside solvus at temperatures above 1500°C at 20 and 30 kbar. The data are supplementary to those previously obtained at lower temperatures by us (Mori and Green, 1975).

Throughout this paper we use mole percent rather than weight percent in describing pyroxene compositions in terms of their end members. Data referred to from the literature have also been converted to mole percent.

Experimental method and results
All the starting materials used in the experiments were mechanical mixtures of two or three synthetic minerals among diopside (CaMgSi$_2$O$_6$), clinoenstatite (Mg$_2$Si$_2$O$_6$), forsterite (Mg$_2$SiO$_4$), and quartz (SiO$_2$). The mixtures were dried and loaded into Pt capsules. We used a piston-cylinder pressure apparatus (Boyd and England, 1960a), and the furnace assemblage included alumina sleeve and alumina thermocouple-insulator to minimize thermocouple contamination and pyrex glass instead of boron nitride outside the graphite heater. A pressure correction of —10 percent of nominal load pressure, using piston-in technique, was applied. No pressure correction was made to thermometry by W$_{97}$Re$_3$/W$_{75}$Re$_{25}$ thermocouples.

All the run products were analyzed by means of the TPD-electron microprobe. Phases were almost free from inclusions and were large enough to avoid chemical contamination from surrounding minerals: the sizes of crystals were up to 60, 40, 20, and 20 microns for enstatite, diopside, forsterite, and quartz, respectively, except for quartz in trace amount (grain size around 4 microns).

The details of experiments are listed in Table 1. Chemical analyses of the run products are shown in Tables 2 and 3.

### The extents of pyroxene solid solutions in the CaO–MgO–SiO$_2$ system

Figure 1 is an isothermal, isobaric diagram of the Di(CaMgSi$_2$O$_6$)–Fo(2Mg$_2$SiO$_4$)–Qz(2SiO$_2$) system which is itself a portion of the CaO–MgO–SiO$_2$ system. Though solid solution fields are much exaggerated and are schematic only, two aspects suggested by Howells and O'Hara (1975) are illustrated: firstly, the diopside limb of the enstatite–diopside solvus is less calcic when pyroxenes are coexisting with forsterite rather than with quartz, and secondly, enstatite–diopside tie lines cross the stoichiometric En–Di join from upper left to lower right.

Among the six runs (2B1-2G in Table 1) made at 30 kbar and 1500°C, two had bulk compositions within the three-phase fields, namely, one in the forsterite–enstatite–diopside field and the other in the quartz–enstatite–diopside field, and the remaining

### Table 1. Results of experiments in the systems Di(CaMgSi$_2$O$_6$)–Fo(2Mg$_2$SiO$_4$)–Qz(2SiO$_2$) and En(Mg$_2$SiO$_4$)–Di(CaMgSi$_2$O$_6$)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Starting materials</th>
<th>Bulk compositions (mole %)</th>
<th>P (kb)</th>
<th>T (°C)</th>
<th>hrs</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B1</td>
<td>Fo, C-En</td>
<td>Fo$<em>{65.3}$ Qz$</em>{35.7}$</td>
<td>30</td>
<td>1500</td>
<td>4</td>
<td>Fo, En,</td>
</tr>
<tr>
<td>2B2</td>
<td>C-En, Qz</td>
<td>Fo$<em>{27.1}$ Qz$</em>{72.9}$</td>
<td>30</td>
<td>1500</td>
<td>4</td>
<td>En, Qz</td>
</tr>
<tr>
<td>2B3</td>
<td>Di, Qz</td>
<td>Di$<em>{52.8}$ Qz$</em>{47.2}$</td>
<td>30</td>
<td>1500</td>
<td>4</td>
<td>Di, Qz</td>
</tr>
<tr>
<td>2B4</td>
<td>Fo, Di</td>
<td>D$<em>{1}$32.0, Fo$</em>{27.0}$</td>
<td>30</td>
<td>1500</td>
<td>4</td>
<td>Fo, Di</td>
</tr>
<tr>
<td>2F</td>
<td>Fo, C-En, Di</td>
<td>Di$<em>{1}$29.5, Fo$</em>{40.9}$ Qz$_{29.6}$</td>
<td>30</td>
<td>1500</td>
<td>20</td>
<td>Fo, En, Di</td>
</tr>
<tr>
<td>2G</td>
<td>Qz, C-En, Di</td>
<td>D$<em>{1}$30.0, Fo$</em>{29.3}$ Qz$_{40.7}$</td>
<td>30</td>
<td>1500</td>
<td>24</td>
<td>Qz, En, Di</td>
</tr>
<tr>
<td>3Y1</td>
<td>C-En, Di</td>
<td>En$<em>{66.8}$ Di$</em>{33.2}$</td>
<td>20</td>
<td>1600</td>
<td>6</td>
<td>Di, Qz (tr)</td>
</tr>
<tr>
<td>3A3</td>
<td>C-En, Di</td>
<td>En$<em>{87.0}$ Di$</em>{13.0}$</td>
<td>20</td>
<td>1600</td>
<td>8</td>
<td>En, Di</td>
</tr>
<tr>
<td>3Y2*</td>
<td>C-En, Di</td>
<td>En$<em>{85.1}$ Di$</em>{41.6}$</td>
<td>30</td>
<td>1700</td>
<td>2</td>
<td>En, Di</td>
</tr>
<tr>
<td>3Y3*</td>
<td>C-En, Di</td>
<td>En$<em>{83.1}$ Di$</em>{16.9}$</td>
<td>30</td>
<td>1600</td>
<td>4</td>
<td>En, Di</td>
</tr>
<tr>
<td>3A4</td>
<td>C-En, Di</td>
<td>En$<em>{71.5}$ Di$</em>{91.5}$</td>
<td>30</td>
<td>1600</td>
<td>10</td>
<td>En, Di, Qz (tr)</td>
</tr>
</tbody>
</table>

C-En: clinoenstatite, En: enstatite, Di: diopside, Fo: forsterite, Qz: quartz. The minerals in the starting materials are of synthetic end member components and those in the run products are solid solutions.

*: disequilibrium.
### Table 2. Electron probe analyses of olivine, pyroxenes, and quartz in the system Di–Fo–Qz at 30 kbar and 1500°C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>2B1</th>
<th>2B2</th>
<th>2B3</th>
<th>2B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>En</td>
<td>Fo</td>
<td>En</td>
<td>Qz</td>
</tr>
<tr>
<td>SiO₂</td>
<td>59.55(63)</td>
<td>42.70(20)</td>
<td>60.05(50)</td>
<td>100.37(17)</td>
</tr>
<tr>
<td>MgO</td>
<td>39.98(34)</td>
<td>56.49(13)</td>
<td>39.33(33)</td>
<td>0.41(5)</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>99.53(96)</td>
<td>99.19(12)</td>
<td>99.39(70)</td>
<td>100.78(22)</td>
</tr>
</tbody>
</table>

Number of ions (olivine: 0=4, pyroxene: 0=6, quartz: 0=4):

| Si  | 2.000(3) | 1.007(4) | 2.016(6) | 1.994(1) | 2.003(2) | 1.996(1) | 1.994(5) | 1.001(3) |
| Mg  | 2.001(5) | 1.986(7) | 1.968(12) | 0.012(0) | 0.985(10) | 0.002(1) | 1.047(23) | 1.978(5) |
| Ca  | - | - | - | - | 1.010(9) | 0.006(1) | 0.965(22) | 0.020(3) |

Molecular percent (Di: CaMgSi₂O₆, Fo: 2Mg₂SiO₄, Qz: 2SiO₂):

| Di  | - | - | - | 100.8(9) | 0.6(1) | 96.8(2.3) | 4.0(5) |
| Fo  | 50.0(2) | 98.6(7) | 48.8(5) | 0.3(1) | -0.7(5) | -0.1(1) | 2.1(1.1) | 97.8(5) |
| Qz  | 50.0(2) | 1.4(7) | 51.2(5) | 99.7(1) | -0.1(5) | 99.5(1) | 1.2(1.3) | -1.8(5) |

<table>
<thead>
<tr>
<th>Run No.</th>
<th>2F</th>
<th>2G</th>
<th>11*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>En</td>
<td>Di</td>
<td>Fo</td>
</tr>
<tr>
<td>SiO₂</td>
<td>59.10</td>
<td>56.57</td>
<td>42.79(40)</td>
</tr>
<tr>
<td>MgO</td>
<td>37.96</td>
<td>26.46</td>
<td>56.78(43)</td>
</tr>
<tr>
<td>CaO</td>
<td>2.68</td>
<td>16.13</td>
<td>0.35(2)</td>
</tr>
<tr>
<td>Total</td>
<td>99.74</td>
<td>99.15</td>
<td>99.92(81)</td>
</tr>
</tbody>
</table>

Number of ions:

| Si  | 1.996 | 1.998 | 1.003(2) | 2.000 | 2.012 | 1.995(1) | 2.018 | 2.014 |
| Mg  | 1.911 | 1.393 | 1.985(5) | 1.897 | 1.394 | 0.006(2) | 1.862 | 1.404 |
| Ca  | 0.097 | 0.610 | 0.009(1) | 0.103 | 0.583 | 0.003(1) | 0.103 | 0.568 |

Molecular percent:

| Di  | 9.7  | 61.1 | 1.7(1) | 10.3 | 57.9 | 0.3(1) | 10.2 | 56.4 |
| Fo  | 45.4 | 19.6 | 98.5(5) | 44.8 | 20.2 | 0.1(1) | 43.6 | 20.8 |
| Qz  | 44.9 | 19.3 | -0.2(4) | 44.8 | 21.9 | 99.6(1) | 46.2 | 22.9 |

The numbers in parentheses represent estimated standard errors (1 sigma) and refer to the last decimal place(s). See text for explanations of the data without standard error. *: referred from the supplemental analytical list to Mori and Green (1975). About 10 analyses were obtained for pyroxenes, and 4 for olivine and quartz in each charge.

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four runs were on the edges of the Di–Fo–Qz triangle.

For the analyses in Table 2, synthetic forsterite, clinoenstatite, diopside, and quartz were used as standards additional to the standards used in routine analysis in our laboratory (Reed and Ward 1973). Thus, we could locate phase boundaries more precisely and could also lower the background uncer
Table 3. Electron probe analyses of pyroxenes in the En-Di system

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Y1</th>
<th>2A3</th>
<th>Y2</th>
<th>2A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>P kb</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>T °C</td>
<td>1600</td>
<td>1600</td>
<td>1700</td>
<td>1600</td>
</tr>
<tr>
<td>Phase</td>
<td>Di</td>
<td>En</td>
<td>Di</td>
<td>En</td>
</tr>
<tr>
<td>SiO₂</td>
<td>59.06(50)</td>
<td>59.77(41)</td>
<td>59.28(36)</td>
<td>60.44(35)</td>
</tr>
<tr>
<td>MgO</td>
<td>32.37(83)</td>
<td>36.80(35)</td>
<td>34.42(36)</td>
<td>37.60(36)</td>
</tr>
<tr>
<td>CaO</td>
<td>8.77(87)</td>
<td>2.83(4)</td>
<td>5.54(27)</td>
<td>2.95(17)</td>
</tr>
<tr>
<td>Total</td>
<td>100.19(69)</td>
<td>99.40(73)</td>
<td>99.25(51)</td>
<td>100.99(64)</td>
</tr>
</tbody>
</table>

Number of ions \((O = 6)\)

| Si   | 2.016(3)   | 2.021(3)   | 2.023(3)   | 2.014(3)   | 2.022(3)   | 2.019(5)   |
| Mg   | 1.647(34)  | 1.755(7)   | 1.751(14)  | 1.867(10)  | 1.858(10)  | 1.605(11)  |
| Ca   | 0.321(33)  | 0.103(2)   | 0.203(10)  | 0.105(6)   | 0.098(9)   | 0.359(13)  |
| Di mole % | 32.6(3.4) | 10.48(16)  | 20.8(1.1)  | 10.67(66)  | 10.06(84)  | 36.6(1.2)  |

The numbers in parentheses represent estimated standard errors (1 sigma) and refer to the last decimal place(s).

The solvus is wider when pyroxenes are saturated

The solvus is wider when pyroxenes are saturated

The solvus is wider when pyroxenes are saturated

The solvus is wider when pyroxenes are saturated

The solvus is wider when pyroxenes are saturated

The solvus is wider when pyroxenes are saturated
with forsterite rather than with quartz. This feature is opposite to that inferred by Howells and O'Hara (1975). The difference of the diopside limb in terms of the Di component is about 3 mole percent. This suggests that when the pyroxene solvus is used as a geothermometer at approximately 1500°C and 30 kbar without taking the coexisting phases into account, errors in the temperature estimates of the order of 20°C may result (cf. Nehru and Wyllie, 1974; and Mori and Green, 1975). Thus, silica activity does not seriously affect the pyroxene solvus as a geothermometer.

It should also be noted that the enstatite–diopside tie-lines are almost parallel to the En–Di join. The diopside–forsterite tie-line for a charge with a bulk composition on the Di–Fo join clearly crosses the join, in agreement with observations of coexisting natural forsterite and diopside.

Stability of pigeonite–diopside solvus at high pressures in the Mg₆Si₂O₆–CaMgSi₂O₆ system

Two runs (Y1 and 2A3) at 20 kbar and 1600°C yielded results supporting Howells and O'Hara's (1975) conclusion that there is no stability field of coexisting pigeonite and diopside at this pressure, in contradiction to Kushiro's (1969) phase diagram. The measured compositions of enstatite and diopside grains are shown in Figure 3 and are summarized in Table 3. The synthetic diopside and clinoenstatite loaded into the run Y1 with a bulk composition within Kushiro's (1969) pigeonite–diopside solvus (En₈₂Di₁₈–En₉₀Di₁₀) and within Howells and O'Hara's (1975) diopside field homogenized to clinopyroxene although there is some compositional hysteresis. Enstatite was not found in the charge. The run 2A3 at the same T-P conditions had a less calcic bulk composition. Compositions of enstatite and diopside were well clustered with a definition of the diopside limb which coincides with that of Howells and O'Hara (1975) within estimated errors.

Kushiro's (1969) main reason for deducing the presence of a pigeonite–diopside solvus at 20 kbar was the systematic change in intensities of paired 31 X-ray reflections with bulk composition of starting materials. Thus the solvus was located by observing the presence or absence of the paired reflections. For
example, the diopside limb of the solvus at 1600°C and 20 kbar was estimated to be at En50Di50.

Alternatively, the 2θ angle of the 311 peak can be more directly used in determining the pyroxene compositions (McCallister, 1974). 2θ values read from Kushiro's Figure 4, combined with McCallister's 2θ-composition equation, which we found very satisfactory, allowed us to estimate the diopside limb of the solvus to be on En28Di72, En36Di64, or En31Di69 at 1600°C and 20 kbar, and on En22Di68 at 1650°C and 20 kbar. All the data locate more calcic pyroxenes than the diopside limb as determined by Kushiro at corresponding temperatures. The difference is about 20 mole percent CaMgSi2O6. In addition, according to Kushiro's Figure 3, liquid, instead of clinopyroxene, is stable for the last composition at 1650°C and 20 kbar. These facts show difficulties in the use of paired X-ray reflection to infer the presence or absence of the pigeonite—diopside solvus.

We also cast doubt on the pigeonite—diopside solvus at 17.5 kbar as inferred by Kushiro and Yoder (1970, Fig. 19), which we believe was constructed by an analogy to the solvus at 20 kbar by Kushiro (1969).

Thus, our experiments refute the existence of the pigeonite—diopside solvus at 1600°C and 20 kbar, and the X-ray data of Kushiro (1969), reinterpreted by McCallister's (1974) calibration, can be shown to be inconsistent with the interpretations placed on them by Kushiro (1969). However, there still remains a possibility that a very narrow pigeonite—diopside solvus could exist at 20 kbar and a temperature lower than 1600°C. This possibility is discussed in the next section.

The present state of knowledge is that the pigeonite—diopside solvus is definitely stable only at 1 atmosphere (Yang, 1973; Yang and Foster 1972, and Kushiro 1972), and the maximum pressure for the stability of the solvus remains unknown.
Iron-bearing pigeonite has been observed at 15 kbar and 980°C (Lindsley et al. 1974b), coexisting with more calcium-rich pyroxene and hypersthene. If pigeonite is unstable in the iron-free system at this pressure, then the pigeonite-enstatite-hypersthene three-phase triangle must converge to a diopside-enstatite-hypersthene tie-line with decreasing FeSiO$_3$ content (associated with increasing temperature) within the magnesian part of the pyroxene quadrilateral.

The enstatite-diopside solvus in the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ system

Four runs (Y2, Y3, 2A3 and 2A4 in Table 1) at temperatures above 1500°C are relevant to determination of the enstatite-diopside solvus. These are complementary to our previous results at and below 1500°C (Mori and Green, 1975). Again in this study, we experienced sluggishness of chemical reaction, even at temperatures as high as 1700°C. In the runs Y2 (30 kbar and 1700°C) and Y3 (30 kbar and 1600°C), although compositions of enstatite were rather well clustered, those of diopside showed extensive hysteresis in the change in chemistry from the pure diopside (CaMgSi$_2$O$_6$) of the starting mixes. The run at 30 kbar and 1600°C was repeated with prolonged run duration (10 hours). More closely clustered compositions of diopside resulted. The chemical compositions of pyroxenes in those runs including enstatite of Y2 (30 kbar and 1700°C) are listed in Table 3, and are compared with the data by Howells and O’Hara (1975) in Figure 4. Our data are in good agreement with theirs and further confirm the large pressure effect on the enstatite–diopside solvus at high temperatures.

At the solidus between 20–30 kbar, the enstatite and diopside show almost complete solid solution, but melting occurs just below the temperatures at which the enstatite and diopside (with their different crystal structures) limbs would intersect.

A peculiar feature observed in Figure 4 is that the diopside limbs at both 20 and 30 kbar show a slight inflection between 1500 and 1600°C. Although we prefer to regard the figure as an equilibrium phase diagram, there still remains a possibility, as suggested by the presence of the inflection, that the pigeonite–diopside solvus exists around the inflection point at 20 and 30 kbar. In this regard, it is interesting to note that Eggler (1974) suggested a coexistence of two clinopyroxenes at 20 kbar and around 1540°C based on synthesis data in the system CaO–MgO–SiO$_2$–CO$_2$. However, the pigeonite–diopside solvus, should it exist at temperatures lower than 1600°C at 20 kbar, must be much narrower than indicated by Kushiro (1969).

The data in Figure 4 were used together with those of Mori and Green (1975) in construction of the pressure-composition section (Fig. 5) which shows enstatite and diopside limbs as a function of temperature and pressure.

Application to temperature and pressure estimates of garnet lherzolite nodules from Lesotho kimberlites, and constraints on the pyroxene-solvus geothermometry

Garnet lherzolite nodules from Lesotho kimberlites have been extensively studied (e.g. Boyd, 1973) Physical conditions of equilibration for these nodules can be estimated by solving two independent geothermo-barometers. For this purpose, the MacGregor (1974) and Davis and Boyd's (1966) grids or modifications of them have been commonly used (Boyd, 1973 and Mercier and Carter, 1975).

In this section, we will also try to estimate pressures and temperatures of these nodules using Boyd’s extensive chemical data for the minerals of the garnet lherzolite nodules (Boyd, in Nixon, 1973). Although the principle of the method is the same, we will em...
employ the enstatite-diopside solvus presented in the previous section rather than that of Davis and Boyd (1966). Ca/(Mg + Ca) ratio of diopside from the nodules gives one temperature-pressure equation. Al$_2$O$_3$ contents of enstatite coexisting with diopside and garnet and with or without olivine were compiled from the experimental data by Akella and Boyd (1972, 1973, and 1974), Hensen (1973), Mysen and Boettcher (1975), Green (1973), and Mori and Green (unpublished data on the pyrolite system). All the chemical systems include at least SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, MgO, and CaO. Their temperatures and pressures vary from 900 to 1410°C and from 15 to 45 kbar. Consistency among the data is, however, not fully satisfactory. In addition, both geothermo-baometers have to be greatly extrapolated towards higher pressures and temperatures in order to be applied to the garnet lherzolite nodules. These two features greatly limit reliability of this method of temperature-pressure estimates.

Figure 6 shows a graphic method of solving the two equations. Diopside-component isopleths cross the Al$_2$O$_3$ (enstatite) isopleths giving unique solutions of temperature and pressure. Boyd's analytical data (Boyd, in Nixon 1973) show that Al$_2$O$_3$ content in enstatite is rather constant through the nodules (Al$_2$O$_3 = 1.1 \pm 0.3$ wt.%), while the Ca/(Mg + Ca) ratio varies extensively from 0.481 to 0.287. This means that the temperature-pressure trend is dependent on the Al$_2$O$_3$ isopleths and is linear within ± 3 kbar, which roughly corresponds to the variation of ± 0.3 percent Al$_2$O$_3$. If the nodules are classified into granular and sheared types (Boyd, 1973), we can find that the sheared type is more aluminous than the granular type by 0.3 weight percent. The diopside-component isopleths only limit the extent of the temperature-pressure trend determined by the Al$_2$O$_3$ isopleths.

A few data points from Boyd (in Nixon, 1973) are plotted in Figure 6. The highest temperature-pressure rock (1597, not plotted in Fig. 6) is estimated at about 85 kbar and 1950°C, and other sheared nodules approach these conditions (Fig. 6). The granular nodules yield temperatures up to 170°C. Many granular type nodules plot at lower temperatures than 900°C, but the diopside-component isopleths become temperature-insensitive. Thus, the lowest temperature-pressure values cannot be reasonably estimated.

Our estimates are very different from those by Boyd (1973) and Mercier and Carter (1975). The rather narrow range of pressure (up to 70 kbar) and temperature (up to 1430°C) by Boyd (1973) is mainly due to his use of the enstatite-diopside solvus of Davis and Boyd (1966) at 30 kbar, which shows a more calcic diopside limb below 1000°C and less calcic limb above it compared to our solvus. Mercier and Carter's (1975) revision shows temperature and pressure values up to 80 kbar and 1600°C. Again, the difference from the trend in Figure 6 is mainly due to their scheme for the enstatite-diopside solvus, which has less pressure effect on the solvus than ours.

It might be considered that the temperature-pressure trend in Figure 6 is too steep to repre-
The recommended values for the standard rocks are from Ando et al. (1974). Both sets of data are recalculated to total of 100. The numbers in parentheses represent estimated standard errors (1 sigma) of the probe analysis, and refer to the last decimal place(s).

The principal difficulty in temperature estimates on the basis of the pyroxene solvus is, as shown in the example above, the fact that we have to know pressure values by an independent method. In addition, the solvus is almost useless at temperatures below 900°C. We emphasize that the pressure-temperature estimates of Figure 6 are an illustration of the effect that the new solvus data have on the methods of pressure-temperature estimation used by Boyd (1973). We consider that the estimates of pressure-temperature in Figure 6 have very large uncertainties indeed.

Appendix: Accuracy of TPD-microprobe analysis

Standard rocks (JG-1 and JB-1) of Geological Survey of Japan were melted on an iridium strip heater following the melting procedure of Nicholls (1974). The glasses were analyzed by TPD-microprobe using the energy-dispersive analytical system with the routine analytical procedure in our laboratory (Reed and Ware, 1973) but with defocussed beam (about 10 microns). The raw data and the recommended values for the standard rocks (Ando et al. 1974) were recalculated to total of 100. This was necessary in order to compare the two sets of data since H$_2$O$^+$ and H$_2$O, etc. evaporate during the melting process.

The results are listed in Table 4. The probe data are satisfactory except for MnO. Concentrations of MnO in these rocks are nearly the same or just above the detection limit of MnO by TPD-probe (about 0.001 wt.%). For those elements with very low concentrations, the conventional wavelength-dispersive microprobe system must be used instead of the energy-dispersive TPD-microprobe. It should be noted that the standard deviations in Table 4 are due almost entirely to heterogeneities of the glasses.

**Takashi Mori and David H. Green**

**Table 4. Accuracy of TPD-probe analysis**

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<th>JG-1 recommended value</th>
<th>JG-1 TPD-probe</th>
<th>JB-1 recommended value</th>
<th>JB-1 TPD-probe</th>
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<td>1.47</td>
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</table>

The glasses were analyzed by TPD-microprobe using the energy-dispersive analytical system with the routine analytical procedure in our laboratory (Reed and Ware, 1973) but with defocussed beam (about 10 microns). The raw data and the recommended values for the standard rocks (Ando et al. 1974) were recalculated to total of 100. This was necessary in order to compare the two sets of data since H$_2$O$^+$ and H$_2$O, etc. evaporate during the melting process.

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**Acknowledgments**

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Wearing and E.H. Pedersen was particularly helpful. D.H. Eggler (Geophys. Lab.) and A.L. Boettcher (Penn. State Univ.) reviewed the manuscript with constructive criticism. These contributions are gratefully acknowledged.

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LABORATORY DUPLICATION OF PHASE EQUILIBRIA OBSERVED IN NATURAL GARNET LHERZOLITES

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Research School of Earth Sciences, Australian National University, Canberra, Australia

ABSTRACT

High pressure experiments have been carried out on two synthetic ultramafic compositions and also on natural mineral mixes at 30-40 kbar and 950-1,500°C. Olivine, orthopyroxene, clinopyroxene, and garnet coexist in the majority of runs. Because of the close similarity in chemical systems, the experimental results can be directly applied to natural garnet lherzolites. The natural garnet lherzolites show wider variety in mineral chemistry than the run products, indicating very wide ranges of pressure-temperature for their equilibration. However, mineral compositions found in some runs closely reproduce the compositions of corresponding minerals in some natural garnet lherzolites from Lesotho and Montana kimberlites and from Alpe Arami lherzolite. Thus, the phase equilibria observed in some natural lherzolites can be successfully duplicated in laboratory at appropriate P-T conditions. As a consequence, pressure and temperature estimates for these rocks would be most accurate. Though the equilibria among the four minerals are not inconsistent with general features found in simplistic chemical systems, the estimates often differ significantly from those based on geothermometers and barometers obtained in the simple systems; the Lesotho pyroxene geotherm should be located, at least in part, at lower temperatures and pressures than the previous proposal. It was also found that Fe—Mg partition coefficient among the four minerals is most sensitive between garnet and clinopyroxene and least between olivine and orthopyroxene.

INTRODUCTION

The first full analyses of coexisting olivine, orthopyroxene, clinopyroxene, and garnet experimentally produced in a natural lherzolite system under known pressure and temperature were published in 1972 (Kushiro et al. 1972). Previous studies of compositional variations among these phases were studied in simple systems such as SiO2—MgO—CaO, SiO2—Al2O3—MgO, and SiO2—Al2O3—MgO—CaO (e.g., Davis and Boyd 1966; Boyd 1970) or had yielded partial analyses of minerals in multicomponent systems (e.g., Al2O3 content in orthopyroxene, Green and Ringwood 1970). The knowledge of the simple system has now substantially increased, while accumulation of data for natural rock and synthetic multicomponent systems has been rather slow in spite of the high demands for such data. A detailed understanding of natural ultramafic rocks, especially of garnet lherzolite which is believed to be a major rock type in the mantle, requires experimentally determined phase relations among orthopyroxene, clinopyroxene, and garnet, and preferably olivine as well in natural rock systems and/or in synthetic systems containing at least SiO2, Al2O3, FeO, MgO, and CaO. Such data available at present are from Kushiro et al. (1972), Akella and Boyd (1972, 1973), and Akella (1976). The first authors present a set of chemical compositions of the four phases at 30 kbar and 1,450°C, and the second and third authors present 11 sets but without olivine in a P-T range of 25–45 kbar and 1,050–1,300°C.

Experiments in the simple systems may not be directly comparable to natural rocks but reveal essential features of phase relations among the relevant minerals.
They are much easier to perform compared to those in the multicomponent systems. By contrast, experiments in complex systems are directly comparable to the natural counterparts, but are technically difficult to carry out. Therefore, these two lines of experiments are complementary and could be best understood together.

This paper is an extension of the previous experimental study on Ca—Mg—Fe pyroxenes (Mori 1977), and probes into phase relations among coexisting olivine, orthopyroxene, clinopyroxene, and garnet both in natural rock and synthetic multicomponent systems. Most experiments used the composition of pyrolite III minus 40% olivine with variable water content. Phase boundaries, but not mineral chemistry, for this series of experiments, were reported by Green (1973). For the purpose of this paper, appropriate run products were selected from among the earlier experiments and their minerals were analyzed by TPD-microprobe. Additional high pressure experiments and probe analyses of their run products were carried out on another synthetic composition and also on natural mineral mixes.

The data obtained are compared with those in the literature. Some of the experimental runs closely duplicate the phase relations observed in some natural garnet lherzolites occurring both as inclusions in Kimberlites and as intrusives. Mineral chemistries of the majority of garnet lherzolites are, however, not matched with those in any run, indicating they were in equilibrium outside the experimental ranges of 30-40 kbar and 950-1,500°C.

EXPERIMENTAL METHODS AND RESULTS

Starting materials used in the high pressure experiments are as follows: (A) The pyrolite-40% olivine composition used by Green (1973) and prepared from sintered AR grade chemicals. The mineralogy includes olivine, orthopyroxene, clinopyroxene, plagioclase, ilmenite and chromite (Green and Ringwood 1970) at less than 1 micron grain size. (B) A synthetic glass rich in pyroxene components, or its crystalline equivalent (sintered at 950°C for 24 hours in an evacuated silica tube). (C) A mechanical mixture of olivine, orthopyroxene, clinopyroxene, and garnet separated from Norwegian garnet lherzolites (A.N.U. No. 2506, 2501) in an equal weight proportion. (D) A mechanical mixture of the same orthopyroxene and clinopyroxene in an equal weight proportion. Chemical compositions of these materials are listed in table 1.

Temperature measurement in all the experiments was by Pt/Pt90Rh10 thermocouples without correction of pressure effect on the thermocouple emf. The other details of the methods of high pressure experiments, identification of the run products, and TPD-probe analysis are the same as those described by Green (1973).

Run details are summarized in table 2. Space limitations do not allow listing of bulky probe analyses of olivine, orthopyroxene, clinopyroxene, garnet, ilmenite, and spinel obtained with TPD-probe. Representative 112 analyses are obtainable from Research School of Earth Sciences, A.N.U. For this purpose, readers may request the Librarian of R.S.E.S. for a copy of Appendix 3 (p. 197-205) of Mori’s (1976) Ph.D. thesis.

COMPARISON OF THE DATA WITH THOSE IN THE LITERATURE

Our data in this paper are most easily compared with those in the literature by plotting them in the ACF-diagram. It should be noted, however, that although olivine - orthopyroxene - clinopyroxene - garnet is an invariant assemblage in the SiO2 — Al2O3 — MgO — CaO system at fixed temperature and pressure, this does not hold true in more complex systems including TiO2, FeO, Na2O, Cr2O3, etc. Among these elements, the most influential is FeO, and it is therefore preferable to compare the data within a range of limited Mg/(Mg + Fe) ratio of, for example, orthopyroxene. The range chosen is from 0.8-0.95 which encompasses the majority
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<td>98.5</td>
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**Note:** * Added proportion of chemicals and corrected for FeO and Fe₂O₃ analyses by E. Kiss in the final product.
** Calculated composition.
*** Total Fe as FeO.
**** The other analyses are by TPD-probe or ARL-probe (marked ****).
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<td>X11</td>
<td>A 0.3</td>
<td>30</td>
<td>1,000</td>
<td>7.5</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, ilm, phlog</td>
</tr>
<tr>
<td>FF8</td>
<td>A 2</td>
<td>30</td>
<td>1,250</td>
<td>2</td>
<td>Ag₈₀Pd₅₀</td>
<td>oliv, opx, cpx, gar, gl</td>
</tr>
<tr>
<td>T10</td>
<td>A 2</td>
<td>30</td>
<td>1,200</td>
<td>1</td>
<td>Ag₈₀Pd₅₀</td>
<td>oliv, opx, cpx, gar, gl</td>
</tr>
<tr>
<td>T11</td>
<td>A 2</td>
<td>30</td>
<td>1,150</td>
<td>1</td>
<td>Ag₈₀Pd₅₀</td>
<td>oliv, opx, cpx, gar, ilm, gl</td>
</tr>
<tr>
<td>T12</td>
<td>A 2</td>
<td>30</td>
<td>1,100</td>
<td>1.5</td>
<td>Ag₇₅Pd₂₅</td>
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<tr>
<td>FF7</td>
<td>A 2</td>
<td>30</td>
<td>1,050</td>
<td>4.75</td>
<td>Ag₇₅Pd₂₅</td>
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</tr>
<tr>
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<td>A 2</td>
<td>30</td>
<td>1,000</td>
<td>29</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, ilm, phlog (?)</td>
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<tr>
<td>T6</td>
<td>A 10</td>
<td>30</td>
<td>1,050</td>
<td>4.75</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, sp (Cr₂O₃ ~ 48 wt%), gl</td>
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<tr>
<td>T7</td>
<td>A 10</td>
<td>30</td>
<td>1,020</td>
<td>4</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, ilm</td>
</tr>
<tr>
<td>T8</td>
<td>A 10</td>
<td>30</td>
<td>1,000</td>
<td>4</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, ilm, sp (Cr₂O₃ ~ 46 wt%)</td>
</tr>
<tr>
<td>T9</td>
<td>A 10</td>
<td>30</td>
<td>950</td>
<td>6</td>
<td>Ag₇₅Pd₂₅</td>
<td>oliv, opx, cpx, gar, ilm</td>
</tr>
<tr>
<td>A2</td>
<td>B (Xtal)</td>
<td>0</td>
<td>1,500</td>
<td>0.33</td>
<td>Pt</td>
<td>opx, cpx, gar, oliv (?)</td>
</tr>
<tr>
<td>A7</td>
<td>B (glass)</td>
<td>0</td>
<td>1,450</td>
<td>0.5</td>
<td>Pt</td>
<td>oliv(tr), opx, cpx, gar</td>
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<tr>
<td>A4</td>
<td>B (Xtal)</td>
<td>0</td>
<td>1,400</td>
<td>0.75</td>
<td>Pt</td>
<td>opx, cpx, gar, oliv (?)</td>
</tr>
<tr>
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<td>B (Xtal)</td>
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<td>1,350</td>
<td>1</td>
<td>Pt</td>
<td>opx, cpx, gar, oliv (?)</td>
</tr>
<tr>
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<td>C tr</td>
<td>30</td>
<td>1,200</td>
<td>2.5</td>
<td>Pt</td>
<td>oliv, opx, cpx, gar</td>
</tr>
<tr>
<td>C4</td>
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<td>30</td>
<td>1,450</td>
<td>1</td>
<td>Pt</td>
<td>opx, cpx</td>
</tr>
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</table>

**Note.**—Abbreviations: oliv—olivine, opx—orthopyroxene, cpx—clinopyroxene, gar—garnet, ilm—ilmenite, sp—spinel, phlog—phlogopite, gl—glass.
of orthopyroxenes in natural ultramafic rocks. Our data are compared with such data available from the literature in four small $T$-$P$ ranges (fig. 1). Orthopyroxenes show compositional convergence in any $T$-$P$ field, indicating relatively quick approach to equilibrium for this mineral, and also higher reliability of probe analysis due to its relatively larger grain sizes obtainable in the high pressure experiments. Clinopyroxenes at 30–31 kbar and 1,100°C also show good convergence and this may be related to the small range of Mg/(Mg + Fe) (0.88–0.93) for these data. By contrast, clinopyroxenes in the other three $T$-$P$ ranges show wide divergence. It should be noted that $A$-component of Hensen’s (1973) clinopyroxenes might be overestimated due to the lack of Na$_2$O analyses. Among the three ranges, the divergence of clinopyroxene compositions at 27–30 kbar and 1,410–1,450°C appears discouraging. The difference between Hensen’s (1973) data set and ours may be partly due to the difference in the Mg/(Mg + Fe) ratio of clinopyroxene which are 0.85 and 0.91 respectively. Akella’s (1976) data in a FeO-free system indicate, by interpolation, a clinopyroxene composition of $A_{11}C_{30}F_{59}$ at 31 kbar and 1,450°C. Thus, these three data sets are reasonably consistent. The deviated clinopyroxene composition of Kushiro et al. (1972) would represent, as was suggested by them, imperfect approach to equilibrium from the starting composition of $A_{11}C_{43}F_{56}$.

Garnets also show compositional spread in all the $P$-$T$ ranges, possibly because garnet is most sluggish in reaction to a new equilibrium composition. Our data at 30 kbar and 1,450°C and all the data of Akella and Boyd (1973) and Akella (1976) plotted in figure 1 show garnet compositions which deviate considerably from the stoichiometric join ($A = 25$). Unless garnet has solid solution towards pyroxenes in those $T$-$P$ ranges, they possibly imply either inferior analyses or presence of Fe$_2$O$_3$ (all the iron was assumed to be in the ferrous state in constructing figure 1).

Olivine can be compared only at 30 kbar and 1,450°C between Kushiro et al.’s (1972) and our data. The Fe—Mg partition coefficient between olivine and orthopyroxene is the same between these two sets of data. Consistency is observed in this regard, but our analysis shows a CaO

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**Fig. 1.** — $ACF$-plots (in mol%) to compare our analyses of garnet, orthopyroxene, and clinopyroxene with experimental data from the literature. Data sources: square—Akella and Boyd (1973), and Akella (1976), filled triangle—Hensen (1973), open triangle—Kushiro et al. (1972), and circle—this paper. $A = (Al, Cr)_2O_3$, $C = CaSiO_3$, $F = (Mg, Fe, Mn)SiO_3$. All the analyses are by microprobe, thus Fe is treated as entirely in the ferrous state. Note that Kushiro et al. reported their clinopyroxene composition as doubtful.
content of 0.75 wt% compared with Kushiro et al.'s 0.10. High CaO and also high Na$_2$O may possibly be due to contamination of clinopyroxene in our probe analysis of this particular olivine.

In summary, consistency within the published data and between our new data and the published data is not very good except for orthopyroxene analyses. However, because of the effects of such elements as TiO$_2$, FeO, Na$_2$O, Cr$_2$O$_3$, etc., the consistency is not so bad as figure 1 may suggest. The following sections should be read with cautionary allowance for the inconsistency among all the data discussed above.

OLIVINE, ORTHOPYROXENE, CLINOPYROXENE, GARNET EQUILIBRIA

**Pyroxene miscibility gap.**—Chemical compositions of coexisting orthopyroxene and clinopyroxene at known temperatures and pressures have been eagerly sought after. Our data are comprehensive in the $P$-$T$ ranges of 950–1,500°C and 30–40 kbar. Figure 2 shows compositions of the alumina-saturated pyroxenes plotted in a temperature vs. wollastonite content diagram. The spread of data, especially of clinopyroxene, is due to experimental errors, to the pressure range (30–40 kbar) of the data and to the arbitrary projection of compositions in the multicomponent system to the plane. The shaded boundaries of the miscibility gap are directly comparable with pyroxene compositions for natural garnet-orthopyroxene-clinopyroxene rocks with the Mg/(Mg + Fe) ratio of orthopyroxene between about 0.87 and 0.96.

The data are consistent with those of Akella (1976) at 1,100–1,300°C and 31–44 kbar in a natural rock system with a similar Mg/(Mg + Fe) ratio.

The pressure effect on the miscibility gap (Mori and Green 1975, 1976; Lindsley and Dixon 1976) is not seen in the figure probably because the uncertainty of the data is large enough to conceal the effect. If the analogy to the Al, Fe-free system is valid, this effect would be only 0.8 mol% wollastonite from 30–40 kbar at 1,200°C but would be 5% at 1,500°C (Mori and Green 1976).

Another method of expressing the pyroxene miscibility gap in a more sophisticated way has been developed by Wood and Banno (1973). Activity ratio of Mg$_2$Si$_2$O$_6$ in clinopyroxene and orthopyroxene ($K$) is plotted against temperature. This has been done for the new data (fig. 3) but with one difference from Wood and Banno's (1973) method of activity calculation. For this paper, Fe and Mg are assigned to M1 and M2 sites in accordance with the experimental determination of Fe—Mg intracrystalline partitions in pyroxenes (Virgo and Hafner 1969; Smyth 1973; McCallister et al. 1976) rather than
This paper

Banno, 1974

Wood & Banno, 1973

In 

Mg2Si2O6

by assuming equal Fe/Mg ratio in the two sites. Their data above 500°C give, by linear regression:

\[
\ln K_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}} - \ln K_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} = 3.080/T^\circ K - 1.181
\]

\[
\ln K_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} = 2.410/T^\circ K - 0.139
\]

where \( K_{ij} = (\text{Fe}/\text{Mg})^i/(\text{Fe}/\text{Mg})^j \), and \( i \) and \( j \) are sites in these cases, but later may also represent whole minerals.

The recent determinations of pyroxene miscibility gap in the

\[
\text{Mg}_2\text{Si}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6
\]

system (Nehru and Wyllie 1974; Mori and Green 1975; Lindsley and Dixon 1976) show that the \( \ln K \) vs. \( 1/T^\circ K \) relation is not approximated by a straight line. The spread of the data in figure 3, however, does not allow us to judge whether the relation is linear in the complex systems. Though linear relationship is less likely, it would give an equation by regression analysis:

\[
\ln K = -6.860/T^\circ K + 3.03
\]

FIG. 3.—Activity ratio of \( \text{Mg}_2\text{Si}_2\text{O}_6 \) in clinopyroxene and orthopyroxene plotted against temperature. Wood and Banno’s (1973) equation was obtained by assuming the \( \text{Fe}/(\text{Mg} + \text{Fe}) \) ratio in orthopyroxene is 0.1. Triangle-40 kbar, circle-30 kbar.

The error associated with the temperature is about ±100°C within the \( P-T \) ranges of 950–1,500°C and 30–40 kbar. The equation should not be used outside these ranges. In addition, the oversimplified nature of the solid solution models employed is illustrated since \( \ln K \) also strongly depends on the \( \text{Mg}/(\text{Mg} + \text{Fe}) \) ratio of pyroxenes. This is apparent when our data are compared with those of Akella and Boyd (1973) which show higher \( \ln K \) in more Fe-rich systems.

Figure 3 also shows the relationships obtained by Wood and Banno (1973) and Banno (1974). Our data are on the slightly higher temperature side of Banno’s equation. Wood and Banno’s equation considerably deviates from either of the others. This is because it was obtained mainly on
the basis of Davis and Boyd's (1966) experiments of pyroxenes in the

\[
\text{Mg}_2\text{Si}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6
\]

at 30 kbar, which have been revised by later works (e.g., Mori and Green 1975). Thus, the Wood and Banno geothermometer yields considerable overestimation in temperature for the rocks equilibrated below 1,000°C and underestimation of temperature for rocks equilibrated above 1,300°C.

**Alumina contents in pyroxenes.**—Compositions of orthopyroxene and clinopyroxene coexisting with garnet are plotted in the ACF-diagram (fig. 4). Both pyroxenes define compositional trends at 30 and 40 kbar. It is well known that the pyroxene miscibility gap narrows and both pyroxenes become enriched in $A$-component with increasing temperature (e.g., O'Hara 1967; Akella 1976). Our data in the multicomponent systems generally follow these sequences but with some local reversals.

$\text{Al}_2\text{O}_3$ content and $A$-component (i.e., $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 - \text{Na}_2\text{O}$) should now be clearly distinguished, particularly for clinopyroxene. In fact, $\text{Al}_2\text{O}_3$ content of clinopyroxene would show less correlation with temperature and pressure than $A$-component. For example, $\text{Al}_2\text{O}_3$ content changes irregularly from 1.300-1.100°C at 40 kbar (3.9-3.6-4.5-4.5 wt%, showing rather high $\text{Al}_2\text{O}_3$ content at lower temperature), while $A$-component monotonously decreases from 1.7-0.2%. More examples are seen at 1,200°C and 1,000°C at 30 kbar where the three sets of clinopyroxene compositions show spreads in $\text{Al}_2\text{O}_3$ content but rather convergent values of $A$-component. These effects are, of course, mainly due to the different content of $\text{Na}_2\text{O}$ in clinopyroxenes.

By contrast, the distinction between $A$-component and $\text{Al}_2\text{O}_3$ content is less important for orthopyroxene since $\text{Na}_2\text{O}$ and $\text{Cr}_2\text{O}_3$ contents are much less than in coexisting clinopyroxene. Therefore, $\text{Al}_2\text{O}_3$ content in orthopyroxene should be a better indicator of physical conditions of equilibration than that in clinopyroxene.
Figure 5 shows the $P-T$ effects on $\text{Al}_2\text{O}_3$ content of orthopyroxene coexisting with clinopyroxene and garnet. The scattered nature of $\text{Al}_2\text{O}_3$ data for orthopyroxene is a general problem in experiments and further documented by Howells (1975).

**Garnet compositions.**—All the garnets in our runs coexist with at least orthopyroxene and clinopyroxene. Compositions of garnet show $A$-component ($\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 - \text{Na}_2\text{O}$) of 24.5 ± 0.7% which is consistent with stoichiometry of garnet ($A = 25\%$) within the error. This suggests that $\text{Fe}_2\text{O}_3$ content in the garnet is insignificant.

Grossular contents are shown in figure 6. In spite of the spread of data, it is apparent that compositions in all the four runs at 40 kbar are poorer in grossular content than in any composition at 30 kbar. That is, when garnet is coexisting with orthopyroxene and clinopyroxene, grossular content decreases with increasing pressure. The same tendency has been already shown experimentally and theoretically in the system $\text{MgSiO}_3 - \text{CaSiO}_3 - \text{Al}_2\text{O}_3$ by Kushiro et al. (1967). The pressure effect on grossular content probably explains the distinction between the lower grossular content of garnets of sheared lherzolites in kimberlites and the higher grossular content of garnets of the granular lherzolites (data from Boyd 1973a). Temperature effect, which is the opposite to the pressure effect in Kushiro et al.’s experiments, cannot be assessed from the data in figure 6.

The contents of $\text{TiO}_2$ and $\text{Cr}_2\text{O}_3$ in minerals of the garnet lherzolite assemblage decrease in the order garnet-clinoptyroxene-orthopyroxene. Both $\text{TiO}_2$ and $\text{Cr}_2\text{O}_3$ in olivine are at the limit of detection for our analytical methods. $\text{Ti}$ concentration ratio on the six oxygen basis is roughly 0.7 for clinopyroxene/garnet and 0.2 for orthopyroxene/garnet. Corresponding $\text{Cr}$ ratios are roughly 0.5 and 0.2, respectively. These ratios do not show any systematic change with temperature or pressure.

**Ilmenite compositions.**—Ilmenite, when present in our runs, always coexists with at least olivine, orthopyroxene, clinopyrox-
ene, and garnet. Because of the tiny grain size of this mineral, probe analyses are not as good as those of the silicate minerals. The composition does not vary widely within the experimental T-P conditions. The Mg/(Mg + Fe) ratio slightly increases above the solidus temperature within a single series of runs at 40 kbar, and at 30 kbar varies with different H$_2$O contents. MgO content is characteristically high (12-14 wt %). Al$_2$O$_3$ and Cr$_2$O$_3$ contents are respectively within ranges of 0.3-0.8 and 1.5-3.0 wt %. All these features are remarkably similar to those of the ilmenites associated with some garnet lherzolite nodules in southern African and Siberian kimberlites (Boyd 1973a; Green and Sobolev 1975).

Fe—Mg partition between olivine, orthopyroxene, clinopyroxene, and garnet.—Among the four silicate phases olivine, orthopyroxene, clinopyroxene, and garnet, there are six different mineral pairs. However, only three pairs among them are independent. We have chosen garnet clinopyroxene, orthopyroxene clinopyroxene and garnet olivine as such pairs (fig. 7). All the iron was assumed to be in the ferrous state. The chemical formulae of the minerals, calculated on this assumption, do not show much deviation from the ideal stoichiometry of these minerals.

Again the data spread does not allow discrimination of 40 kbar data from 30 kbar data, and linear regression analysis was carried out including all the data at 40 and 30 kbar. The equations obtained are valid for this pressure range:

\[
\ln K^{\text{gari}/\text{cpx}} = 2.800/T^\circ K - 1.19
\]

\[
\ln K^{\text{opt}/\text{cpx}} = 1.500/T^\circ K - 1.07
\]

\[
\ln K^{\text{gari}/\text{oliv}} = 900/T^\circ K + 0.09
\]

Similar equations for the other pairs can be calculated from the equations above:

\[
\ln K^{\text{gari}/\text{opt}} = 1.300/T^\circ K - 0.12
\]

\[
\ln K^{\text{oliv}/\text{cpx}} = 1.900/T^\circ K - 1.28
\]

\[
\ln K^{\text{oliv}/\text{opt}} = 400/T^\circ K - 0.21
\]

This paper is, to our knowledge, the first to present simultaneous temperature calibrations of these six Fe—Mg distribution coefficients from a single series of experiments. The six equations show that temperature sensitivity varies from pair to pair. Geothermometry is best for the garnet clinopyroxene pair, and becomes less sensitive in the order olivine clinopyroxene, orthopyroxene clinopyroxene, garnet orthopyroxene, garnet olivine, olivine orthopyroxene. The last pair would be practically meaningless as a geothermometer. This conclusion on the last pair is the same as that of Matsui and Nishizawa (1974) who summarized studies on Fe—Mg partition between this pair of minerals in a Ca-free system.

The individual $K^{\text{gari}/\text{cpx}}$ values for bulk composition Mg/(Mg + Fe) = 0.85 of Raheim and Green (1974) fall within the spread of our data but those for Mg/(Mg + Fe) = 0.93 fall at lower $K^{\text{gari}/\text{cpx}}$ values. Our linear regression curve differs from that of Raheim and Green for their data in bulk compositions 0.06 < Mg/(Mg + Fe) < 0.85 and from that for Mg/(Mg + Fe) = 0.93. These differences may possibly result from the different chemical compositions of minerals (e.g., Al$_2$O$_3$ and Na$_2$O in clinopyroxene) reflecting the difference in bulk chemistry.

**Duplication of phase equilibria observed in natural garnet lherzolites**

Chemical compositions of minerals presented in this paper can be directly compared with those in natural garnet lherzolites. Our experimental compositions were not however designed to investigate differences in such minor elements as Na$_2$O, TiO$_2$, Cr$_2$O$_3$ in pyroxenes nor NiO in olivine between natural rocks and the experimental charges. At this stage of investigation, we are concerned with the major solid solution components of the four phases and we therefore use ACF-diagrams as well as Fe—Mg partition coefficients for comparison of the data. If Fe$_2$O$_3$ analyses are available for the natural minerals, they are included in A-component. Otherwise, all Fe is assumed...
LABORATORY PHASE EQUILIBRIA IN GARNET LHERZOLITES

Fig. 7.—Fe—Mg partition coefficients between garnet and clinopyroxene, orthopyroxene, and clino-
pyroxene, and garnet and olivine. Triangle-40 kbar, circle-30 kbar.

to be in the ferrous state. It should be noted that the Mg/(Mg + Fe) ratio in experimental run products is comparable to or only slightly lower than in the natural rocks. Therefore, the direct comparison in the ACF-diagram should be valid.

Nodules in Lesotho and Montana kimberlites.—All the chemical analyses of minerals from nodules in Lesotho kimberlites used in this subsection are of Boyd (1973a). The detailed chemical aspects of minerals have been discussed by Boyd (e.g., 1973b), and our unpublished probe analyses of minerals from garnet lherzolites in Lesotho kimberlites have confirmed his observations.

We have compared characteristics of our experimental assemblages at known $P$ and $T$ with the individual nodules analyzed by Boyd. Among his samples, PHN2273 and PHN1591 are very closely matched by the run products DD1 (40 kbar and 1,100°C) and DD2 (40 kbar and 1,200°C), respectively (table 3). $A$, $C$, $F$ components of the natural pyroxenes and garnet are very similar to those of the experimental counterparts. In addition, Fe—Mg partition coefficients are almost the same in the two
sets of data. To our knowledge, no experimental phase relations have ever achieved this degree of resemblance with those in natural garnet lherzolites.

Boyd (1973b) classifies garnet lherzolite nodules into granular and sheared types on the basis of texture, and he has clearly established that the sheared-type nodules show equilibration at higher temperature and pressure than those of the granular type. Both PHN2273 and PHN1591 are relatively low temperature rocks from within the group of sheared lherzolite nodules. It was previously shown that use of the Ca/(Ca + Mg) ratio of clinopyroxene and Al$_2$O$_3$ content of orthopyroxene to estimate T-P conditions of PHN2273 gave an estimate of about 1,180°C and 56 kbar (Boyd 1973a,b). A shortcoming of this method of T-P estimates is the lack of a firm basis for the direct comparison of the Ca/(Ca + Mg) ratio between natural complex clinopyroxene and the clinopyroxene solvus in the system Mg$_2$Si$_2$O$_6$–CaMgSi$_2$O$_6$. Therefore we considered that large uncertainties might be associated with both Boyd’s (1973b) and Mori and Green’s (1976) estimates. This pessimism is strikingly confirmed by the data obtained for the complex system. The present estimate of about 40 kbar and 1,100°C for PHN2273 was obtained by directly comparing compositions of olivine, orthopyroxene, clinopyroxene, and garnet, and consequently the estimate should be quite accurate.

The highest T-P nodule among Boyd's samples is PHN1597. The relationship between temperature and activity ratio of Mg$_2$Si$_2$O$_6$ (fig. 3) gives an apparent temperature of about 1,450°C for this rock at an assumed pressure between 30 and 40 kbar. Similarly the relationship between $K_{CaSiO_3}$ temperature and activity ratio indicates a temperature of about 1,400°C for an assumed pressure between 30 and 40 kbar. Thus, the run A7 (30 kbar and 1,450°C) was chosen to compare with PHN1597 (table 3). A-component of orthopyroxene and clinopyroxene and C-component of garnet are distinctively lower in PHN1597 than in A7, suggesting the pressure of this rock would be much higher than 30 kbar. If the pressure effect on Al$_2$O$_3$ solubility in the complex pyroxene is similar in magnitude to that in the Al$_2$O$_3$–MgSi$_3$O$_6$ system (MacGregor 1974) then the estimated pressure for PHN1597 would be higher than for A7 by about 30 kbar. This high pressure, in turn, causes a shift of the temperature-activity ratio equation (fig. 3) and of the
LABORATORY PHASE EQUILIBRIA IN GARNET LHERZOLITES

The lowest $T$-$P$ nodule (PHN1595) is compared with the lowest $T$-$P$ run (T9, 30 kbar and 950°C) in Table 3. The difference of C-component in both orthopyroxene and clinopyroxene is small, but indicates a temperature for this nodule substantially lower than 950°C since both the orthopyroxene and clinopyroxene solvi at the low temperature region are very steep (Mori and Green 1975). The systematic difference in Fe—Mg partition coefficients also supports temperature substantially lower than 950°C.

The Lesotho pyroxene geotherm should now be located at lower temperatures and pressures than that originally proposed by Boyd (1973b). It is with regret, however, that we can't propose an alternative position of the geotherm since the present experimental data do not cover the whole range of the mineral chemistry of the nodules.

In summary, among the garnet lherzolite nodules with wide $P$-$T$ ranges, some have very similar phase relations with those produced in our experiments, but many of them show equilibration conditions outside the experimental $P$-$T$ ranges of 30–40 kbar and 950–1,500°C. The inferred range of $T$, $P$ conditions extends to both higher and lower pressures and temperatures than the experimental range.

Intrusive garnet lherzolites.—Equilibrium temperatures of intrusive garnet lherzolites are generally so low that it is difficult to find close similarities of mineral chemistry between natural rocks and experimental products. The most comparable examples are the Alpe Arami garnet lherzolite (A2, O'Hara and Mercy 1963) and FF6 (30 kbar and 1,000°C). The slight difference in $A$- and $C$-components in pyroxenes and also in Fe—Mg partition coefficients (Table 3) suggest that the real temperature and pressure for the Alpe Arami rock were slightly lower than 1,000°C and 30 kbar. This particular rock shows the highest pressure and temperature among the intrusive garnet lherzolites we have examined so far.

The lowest $T$-$P$ rock is probably G103 from Mt. Higasi-Akaisi (Mori and Banno 1973). This is an orthopyroxene, garnet bearing wehrlite occurring as lenses within a dunite-weenrtite mass. Table 3 also compares G103 with the lowest $T$-$P$ run (T9, 30 kbar and 950°C). The low temperature nature of G103 is clearly seen in its very low C-component in orthopyroxene, high C-component in clinopyroxene and high Fe—Mg partition coefficients.

CONCLUDING REMARKS

It is a common assumption that deep-seated rocks attain equilibrium in mineral assemblages at high temperature, high pressure conditions and that this equilibrium can in some cases be preserved and brought to the surface. Likewise, experimental petrologists lean to the assumption that equilibrium in polymineralic assemblages can be easily achieved in the laboratory at high pressures and temperatures. Both these assumptions must be treated with caution but it is nevertheless encouraging that in our experiments on complex peridotite compositions we have been able to closely duplicate the compositions of four coexisting phases, olivine, orthopyroxene, clinopyroxene, and garnet, of some natural lherzolites.

The practical results of our study are figures 1–7 themselves, providing empirical calibrations applicable to garnet lherzolite mineralogy within a limited $T$-$P$ range. The application of these calibration relationships to natural garnet lherzolite inclusions in kimberlites shows that some
sheared lherzolites crystallized at 1,100–1,200°C and ca. 40 kbar but others (sheared varieties) crystallized at much higher temperatures and higher pressures while granular lherzolites crystallized at lower temperatures and pressures. We particularly draw attention to the large differences between estimates of T, P conditions based on complex systems and on simplistic deductions from the

\[ \text{MgO} - \text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 \]

system. Much of our data was obtained on experiments designed primarily to determine the solidus and major aspects of phase relationships for the pyrolite composition. The extent to which systematic relationships amongst minerals can be observed in these experiments encourages us to the view that further experiments in which there is more rigorous evaluation of Fe-loss, use of longer run times, reversal of equilibria, etc., will greatly reduce the scatter in figures 1–7 and provide high quality calibration data for natural garnet lherzolites. These experiments should proceed in parallel with studies in which the data of the simple \( \text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 \) system are extended into increasingly more complex compositions.

ACKNOWLEDGMENTS. — We thank A. J. Irving for his constructive review of an earlier version of this paper.

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Determination of liquid compositions in high-pressure melting of peridotite

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Abstract

Experimental problems in the determination of liquid compositions from the partial melting of peridotite are examined in the light of data obtained in an experimental study of the anhydrous melting of peridotite. A scanning electron microscope coupled with an energy-dispersive microprobe has been employed to examine the nature of quench phases and their effect on the melt composition, and to examine the effect of iron loss on crystal-melt equilibria. In most cases the problems of iron loss, non-equilibrium, and quench modification of the melt composition preclude direct determination of the composition of partial melts, even under anhydrous conditions. Provided the modal proportions and compositions of residual phases are known, and due allowance made for preferential adjustment of residual phases to iron loss, the compositions of equilibrium partial melts may be obtained by mass-balance calculations.

Introduction

It is now generally recognized that basaltic magmas arise by partial melting of upper mantle peridotite, dominated by magnesian olivine and orthopyroxene. Accurate determination of the liquid compositions formed by partial melting of peridotite under known conditions (melt proportion, temperature, pressure, residual phase compositions and proportions, and volatile content) is therefore an important goal in experimental petrology. A number of studies towards this end have been attempted on a variety of natural peridotite compositions under different P-T conditions and volatile contents.

In the earliest studies, phase relations only were determined and liquid compositions broadly inferred (e.g. Ito and Kennedy, 1967). In later experiments the compositions of the residual crystals and the quenched glass were determined by electron microprobe and the percentage of melt estimated visually (e.g. Kushiro et al., 1972; Mysen and Boettcher, 1975; Nehru and Wyllie, 1975). More recently Mysen and Kushiro (1977) have used beta-track counting of charges spiked with radioactive tracers to more accurately determine the percentage of melting and have relied on microprobe analysis of quenched glasses to yield compositions of the melt phase.

Implicit in this experimental approach is the assumption that the directly determined quenched glass composition is that of the equilibrium melt for those particular conditions. This assumption can be criticized on two grounds. Firstly, iron loss from the sample to the noble-metal capsules used in partial melting experiments is well documented (e.g., Nehru and Wyllie, 1975; Green, 1976; and others). The extent of iron loss is dependent on temperature and run duration, and since iron is not lost uniformly from the charge, Fe/Mg partitioning between crystal and liquid varies as a function of run duration (Stern and Wyllie, 1975; see below). Apart from changing the MgO/FeO ratio of the silicate charge, iron loss also increases the silica saturation of the bulk composition and probably of any melt component (O'Hara and Humphreys, 1977). Secondly, the growth of metastable quench crystals during the quenching of the glass can significantly modify the composition of the glass from that of the equilibrium melt (Green, 1973, 1976; Cawthorn et al., 1973; Nicholls, 1974). These problems in the direct determination of the equilibrium partial melt composition have been the focus of debate in the past concerning the hydrous melting of peridotite (e.g. Mysen et al., 1974; Green, 1973, 1976). Green showed that these problems could be
overcome and a reliable estimate of the equilibrium melt could be calculated from a knowledge of the composition of the residual phases and the bulk charge using crystal/liquid partition data.

Mysen and Kushiro (1977) considered that these problems did not greatly effect the results of their study on the anhydrous melting of peridotite, and presented a suite of glass compositions ranging from 'alkali picrite' to 'olivine tholeiite' to 'peridotitic komatiite' as the equilibrium melts from peridotite. While the compositional range of liquids is consistent with earlier interpretations of melting at this pressure (Green and Ringwood, 1967) and is broadly that anticipated over such a melting interval, discrepancies among the data cast doubt on the validity of these directly determined glass compositions as the true unmodified equilibrium melts for the stated percentage of melting. As part of a similar melting study we have evaluated the problems involved in conducting such experiments, and find that the problems can be severe enough in many cases to preclude direct determination of equilibrium melt compositions. Here we present an alternative approach for calculation of equilibrium liquid compositions.

### Experimental methods

#### Technique

Two peridotite compositions derived from pyrolite (Ringwood, 1966; Green, 1973, 1976) and Tinaquillo peridotite (Green, 1963) have been studied. In each case the composition used in the experiments is that of the peridotite minus 40 percent olivine to facilitate identification of minor phases and increase the relative proportion of melt and minor phases without eliminating olivine. Compositions (Table 1) were prepared from AR grade chemicals and sintered at 1000°C. Experiments were carried out in a solid-media (piston cylinder) high-pressure apparatus, using piston-in technique and a pressure correction of minus 10 percent nominal piston pressure. Temperatures were measured by a Pt-Pt90Rh10 thermocouple with no correction for the effect of pressure on the thermocouple emf. Pyrex-glass sleeves with graphite inserts were used in 0.5-inch diameter furnace assemblies to minimize hydrogen diffusion from the dehydrating outer talc sleeve. Samples (15–20 mg) were sealed in Pt capsules and preheated at 900°–1000°C for 8–12 hours, packed in metallic iron powder in an attempt to presaturate the capsule in iron. All runs were anhydrous and the powdered starting mix was dried overnight at 110°C. Spec-pure iron capsules were used in some short-duration runs. These experiments produced a fO₂ lower than that in the Pt capsules, resulting in elimination of chrome spinel, and in some cases the charge dissolved iron from the capsule.

#### Microprobe analysis

The charge was recovered as a coherent cylinder of crystals and glass. A portion of one split was examined in refractive-index oils. The polished mount containing the other split was examined optically in reflected light and by scanning electron microscope using a JEOL JX 50A electron microprobe-scanning electron microscope (SEM) fitted with an energy-dispersive (EDAX) analytical system. Simultaneous quantitative analysis for 10 elements (Na to Fe) of residual phases, quench phases, glass, and bulk charge was obtained by the method of Reed and Ware (1973, 1975). Optimization of the backscattered and secondary electron images enabled clear resolution and discrimination of all phases including melt and quench crystals at up to 2000 times magnification (Fig. 1). Discrimination of phases was based on both form and contrast from the back-scattered electron image, which is dependent on the mean atomic number of the target. In this way Fe-rich rims on primary phases and quench phases, e.g. quench clinopyroxene, can be distinguished by the higher Fe, Al, and Ti contents compared to the primary equilibrium phases. Glass analyses and analyses of the bulk charge were made with rapid reduced-area scans to

### Table 1. Compositions of starting material

<table>
<thead>
<tr>
<th></th>
<th>Pyrolite - 40% olivine</th>
<th>Tinaquillo peridotite - 40% olivine</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.9</td>
<td>47.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.10</td>
<td>0.15</td>
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<tr>
<td>Al₂O₃</td>
<td>5.91</td>
<td>5.35</td>
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<td>Fe₂O₃</td>
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<td>MgO</td>
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<tr>
<td>MnO</td>
<td>0.13</td>
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<td>FeO</td>
<td>28.8</td>
<td>32.0</td>
</tr>
<tr>
<td>CaO</td>
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<td>4.99</td>
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<td>Na₂O</td>
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<td>CaO</td>
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<tr>
<td>MgO</td>
<td>0.47</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.72</td>
<td>0.75</td>
</tr>
<tr>
<td>FeO</td>
<td>0.18</td>
<td>0.63</td>
</tr>
<tr>
<td>100CaO/MgO+FeO</td>
<td>0.65</td>
<td>0.68</td>
</tr>
<tr>
<td>100CaO/MgO+FeO</td>
<td>0.65</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Run time

0.17 1 2 4 7.5 hrs

Fig. 1. Scanning electron microscope photographs of partial melting runs of pyrolite — 40 percent olivine and spinel lherzolite — 40 percent olivine, showing metastable quench phases. Scale bar is 20μ long. Quench outgrowths of clinopyroxene appear bright, as do thin quench rings of more Fe-rich olivine on primary olivine (note Figs. 1E, F particularly). (A) Pyrolite, 15 kbar, 1350°C. A low percentage melting run. Residual phases are olivine (small dark euhedra), orthopyroxene (large tabular crystals), clinopyroxene (small lighter euhedra), and chrome spinel (tiny bright euhedra). Melt is light interstitial material. Quench clinopyroxene forms light-colored rims on residual phases. Note the drastic reduction of the liquid volume by the quench phases. Compositions of phases are given in Table 4. (B) Pyrolite, 15 kbar, 1400°C. Quench clinopyroxene forms rims on residual olivine and orthopyroxene. Note the presence of some discrete quench clinopyroxene in the glass (crosses, lower right) and the larger percentage of melt. (C) Pyrolite, 10 kbar, 1300°C. Quench clinopyroxene rims residual olivine and orthopyroxene, and forms discrete crystals in the glass (small crosses, lower center). Compositions given in Table 3. (D) Pyrolite, 10 kbar, 1350°C. Like C but note the higher percentage of melt. Quench clinopyroxene is less abundant, and modification of the glass composition is less severe than for A, B, and C. (E) Pyrolite, 10 kbar, 1450°C. Skeletal and dendritic quench low-calcium pyroxene forming conical spirals in glass, and dendritic rims on residual olivine. Note the similarity in the quench forms to those found in some komatiites. (F) Spinel lherzolite, 10 kbar, 1450°C. Quench low-calcium pyroxene and olivine on residual olivine. Compositions given in Table 5.

Fig. 2. $100\text{Mg}/(\text{Mg+Fe})$ ratios of the residual phase (excluding Cr spinel) and glass with varying run times. $S =$ starting composition. Olivine and glass compositions become increasingly Mg-rich as iron is lost from the charge with increasing run time. The capsules used in the 2-, 4-, and 7½-hour runs were packed in metallic iron powder for 8–12 hours at 900–1000°C in an attempt to pre-saturate the capsule in iron. Compositional data from Table 3.

compositional differences (quench rims) within phases is demonstrated in Figure 1 and confirmed by quantitative analyses of the visually discriminated areas. This technique thus permits modal analysis of these fine-grained experimental charges.

Modal analysis

Modal analysis, including the percentage of melt, was made by point counting of the SEM photographs using a 10 cm × 9 cm transparent grid; all quench phases were counted as glass. A minimum of 1200 points were counted in replicate and averaged.

Calculation of equilibrium liquid compositions

The compositions of the equilibrium liquids were calculated by mass balance after conversion of the volume percent modes to weight percent modes from appropriate mineral densities. The liquid density was calculated by the method of Bottinga and Weill.
Table 2. Experimental run data

<table>
<thead>
<tr>
<th>Run No.</th>
<th>P (kbars)</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>Capsule</th>
<th>Phases present</th>
<th>100 kg/kg Fe charge</th>
<th>ol</th>
<th>opx</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-168</td>
<td>10</td>
<td>1500</td>
<td>0.17</td>
<td>Pt</td>
<td>ol + opx + quench cpx + gl</td>
<td>84.5</td>
<td>89.1</td>
<td>89.8</td>
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<td>T-89</td>
<td>10</td>
<td>1300</td>
<td>2</td>
<td>Pt</td>
<td>ol + opx + Cr + quench cpx + gl</td>
<td>86.9</td>
<td>91.0</td>
<td>89.8</td>
</tr>
<tr>
<td>T-144</td>
<td>10</td>
<td>1300</td>
<td>4</td>
<td>Pt</td>
<td></td>
<td>87.2</td>
<td>91.3</td>
<td>90.4</td>
</tr>
<tr>
<td>T-178</td>
<td>10</td>
<td>1500</td>
<td>7.5</td>
<td>Pt</td>
<td>ol + opx + Cr + quench cpx + gl</td>
<td>88.4</td>
<td>93.0</td>
<td>90.5</td>
</tr>
<tr>
<td>T-118</td>
<td>10</td>
<td>1300</td>
<td>2</td>
<td>Pt</td>
<td>ol + opx + Cr + quench cpx + gl</td>
<td>87.0</td>
<td>92.8</td>
<td>91.3</td>
</tr>
<tr>
<td>T-159</td>
<td>10</td>
<td>1350</td>
<td>0.5</td>
<td>Fe</td>
<td>ol + opx + quench cpx + gl</td>
<td>85.1</td>
<td>90.1</td>
<td>91.0</td>
</tr>
<tr>
<td>T-101</td>
<td>10</td>
<td>1450</td>
<td>2</td>
<td>Pt</td>
<td>ol + Cr + quench px + gl</td>
<td>89.7</td>
<td>95.8</td>
<td>91.0</td>
</tr>
<tr>
<td>T-138</td>
<td>10</td>
<td>1450</td>
<td>0.25</td>
<td>Fe</td>
<td>ol + quench px + gl</td>
<td>83.5</td>
<td>91.6</td>
<td>92.9</td>
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<td>T-148</td>
<td>15</td>
<td>1500</td>
<td>2.5</td>
<td>Pt</td>
<td>ol + opx + Cr + quench cpx + gl</td>
<td>87.7</td>
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<td>89.8</td>
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<tr>
<td>T-142</td>
<td>15</td>
<td>1600</td>
<td>1</td>
<td>Pt</td>
<td>ol + opx + Cr + quench cpx + gl</td>
<td>86.2</td>
<td>92.0</td>
<td>90.5</td>
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<td>T-155</td>
<td>10</td>
<td>1450</td>
<td>0.5</td>
<td>Pt</td>
<td>ol + Cr + quench px + gl</td>
<td>90.7</td>
<td>95.6</td>
<td>92.0</td>
</tr>
</tbody>
</table>

Pyrólite - 40% olivine

<table>
<thead>
<tr>
<th>Capsule</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-168</td>
<td>ol + opx + quench cpx + gl</td>
</tr>
<tr>
<td>T-89</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-144</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-178</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-118</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-159</td>
<td>ol + opx + quench cpx + gl</td>
</tr>
<tr>
<td>T-101</td>
<td>ol + Cr + quench px + gl</td>
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<td>T-138</td>
<td>ol + quench px + gl</td>
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<tr>
<td>T-148</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-142</td>
<td>ol + opx + Cr + quench cpx + gl</td>
</tr>
<tr>
<td>T-155</td>
<td>ol + Cr + quench px + gl</td>
</tr>
</tbody>
</table>

Tinaquillo iherzolite - 40% olivine

ol = olivine; opx = orthopyroxene; cpx = clinopyroxene; Cr = chrome spinel; gl = glass

(1970) using the least modified, most magnesian glass composition (obtained by reduced area rapid scans) with adjustment for the effect of pressure on the density (Kushiro et al., 1976). Iteration of the mass-balance calculations to overcome the density difference between the equilibrium liquid and the analyzed glass made negligible difference to the resultant liquid composition. Two examples of liquids determined in this way are shown in Table 3, Figures 2 and 3, and Table 4, Figure 4. The SEM photographs of these runs are illustrated in Figure 1.

Point counting of phases was not possible for the high-degree melting runs where olivine alone or olivine and chrome spinel were residual phases, because of strong crystal settling within the charge even in runs of short duration. For these experiments (e.g., Fig. 5, Table 5) the liquid composition was calculated assuming a K_{ol}/liquid of 0.3 (Roeder and Emslie, 1970; Green and Ringwood, 1967) after allowance for iron loss from the charge (Green, 1973).

Experimental results

In the three examples presented in detail in Figures 1-5 and Tables 1-5, the calculated equilibrium
liquid composition differs from the analyzed glass compositions. The nature of the calculated equilibrium melt at 10 kbar, 1300°C, produced by approximately 25 percent melting of pyrolite, is olivine tholeiite with 16 percent normative olivine; all analyzed glasses are higher in SiO$_2$ and lower in normative olivine than the calculated melts, with both the 0.17-hour and 7.5-hour runs containing normative quartz. At 15 kbar, 1350°C the degree of melting of pyrolite is about 18 percent and the equilibrium melt is alkali olivine basalt. All glass analyses are hypersthene normative and have considerably less MgO and more SiO$_2$, Al$_2$O$_3$, and CaO than the calculated melt. At 10 kbar, 1450°C the Tinaquillo lherzolite composition is about 40 percent molten, and the composition of the calculated melt, with very high MgO and SiO$_2$, is strongly hypersthene- and olivine-normative, resembling pyroxene-rich komatiitic liquids. In the follow-

Table 3. Compositions of phase for melting of pyrolite - 40 percent olivine at 10 kbar, 1300°C

<table>
<thead>
<tr>
<th></th>
<th>0.17 hours</th>
<th>1 hour</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>ol</td>
<td>opx</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>40.5</td>
<td>54.8</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.47</td>
<td>2.87</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.93</td>
<td>13.2</td>
</tr>
<tr>
<td>FeO$_3$</td>
<td>10.5</td>
<td>6.39</td>
</tr>
<tr>
<td>MnO</td>
<td>0.20</td>
<td>0.34</td>
</tr>
<tr>
<td>MgO</td>
<td>48.1</td>
<td>31.7</td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>2.35</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>1.97</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.47</td>
<td>-</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.38</td>
<td>1.50</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>1.771</td>
</tr>
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<td></td>
<td>0.007</td>
</tr>
<tr>
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<td>3.000</td>
</tr>
</tbody>
</table>

|                | 89.1 | 89.8 | 64.3 | 89.1 | 89.4 | 89.4 | 89.8 | 89.9 | 70.4 |
|----------------|      |      |      |      |      |      |      |      |      |
|                | 4.6  | 33.1 | 4.7  | 5.1  |
|                | 85.8 | 45.9 | 85.6 | 85.3 |
|                | 9.7  | 21.0 | 9.7  | 9.6  |

1. large olivine = cl 10, %
2. small olivine = cl 5, %
3. rim compositions were obtained avoiding quench rims of pyroxene and olivine.
4. calculated equilibrium melt composition, using modal analysis, analysed crystalline phase from 1-hr run and original bulk composition.
Table 3. (continued)

<table>
<thead>
<tr>
<th></th>
<th>2 hours</th>
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<th>7.5 hours</th>
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<tbody>
<tr>
<td></td>
<td>large olivine</td>
<td>small opx</td>
<td>gl</td>
</tr>
<tr>
<td></td>
<td>core</td>
<td>rim</td>
<td>core</td>
</tr>
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<td>41.0</td>
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<td>54.8</td>
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<td>49.0</td>
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<tr>
<td>0.995</td>
<td>0.999</td>
<td>0.995</td>
<td>1.912</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td>0.178</td>
<td>0.170</td>
<td>0.167</td>
<td>0.187</td>
</tr>
<tr>
<td>0.007</td>
<td>0.007</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>1.814</td>
<td>1.810</td>
<td>1.825</td>
<td>1.668</td>
</tr>
<tr>
<td>0.011</td>
<td>0.016</td>
<td>0.010</td>
<td>0.092</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.005</td>
<td>5.001</td>
<td>5.005</td>
<td>4.001</td>
</tr>
<tr>
<td>91.1</td>
<td>91.4</td>
<td>91.6</td>
<td>89.8</td>
</tr>
<tr>
<td>4.8</td>
<td>4.8</td>
<td>35.5</td>
<td>85.9</td>
</tr>
</tbody>
</table>

Fig. 4. Ca-Mg-Fe diagram illustrating the effect of quench growth of Ca pyroxene on the determined liquid compositions. The equilibrium liquid is calculated (see text). Compositions given in Table 4.
Iron loss in experimental runs

Although Stern and Wyllie (1975) showed in an andesite melting study that iron is not lost uniformly from the charge, there appears to be a belief that equilibrium, once achieved, is maintained throughout the experiment in spite of iron loss. For example, Mysen and Kushiro (1977) claim that a 20 percent iron loss results in only a minor change in the Fe content of the olivine and disregard any greater effect on the liquid composition.

Other data obtained from runs of varying duration at the same pressure and temperature, 10 kbar and 1300°C, are presented in Table 3 to illustrate the problem. Despite attempts to presaturate the Pt capsules, all experienced iron loss [shown by the 100Mg/(Mg+Fe) ratio of the charge; Table 2]; runs in spec-pure iron resulted in iron gain. The effect of iron loss can be very significant; for example, in the 7.5-hour run the iron loss was sufficient to stabilize calcic pyroxene in the residue, whereas only olivine, orthopyroxene, and chrome spinel were present in the residue of other runs. Figure 2 and the data of Table 3 show that as iron is lost from the system, demonstrated by increasing 100Mg/(Mg+Fe) ratio of the bulk charge, orthopyroxene compositions change little, whereas olivine and glass compositions readjust more rapidly to the loss. The different rates of adjustment of the crystalline phases to iron loss are also shown by the greater compositional difference between core and rim compositions of pyroxene relative to olivine. Stern and Wyllie (1975) found that apparent garnet and clinopyroxene Fe/Mg partitioning was dependent on run duration, because garnet adjusted more slowly to Fe loss than clinopyroxene, causing (Fe/Mg)$_{olivine}$/(Fe/Mg)$_{total}$ to increase with run duration. Similar differences in the rate of adjustment of garnet and pyroxene to iron loss have been observed in eclogite melting studies (K. L. Harris, personal communication, 1978). The effect of iron loss from the system is shown in Figure 3, where all phases and the bulk composition are displaced from the equilibrium value to more Fe-poor compositions.

The effect of change of the bulk composition is most marked on liquid compositions: the 10-minute run in spec-pure Fe resulted in iron gain by both the charge and the glass, but had little effect on the compositions of residual crystals.

It is apparent that Fe diffusion rates are different for various phases and that iron is lost preferentially in the order liquid > olivine (orthosilicate) > pyroxene (chain silicate). Significant iron loss can result in the formation of olivine considerably more magnesian than the original equilibrium olivine because of attempted re-equilibration of the olivine with the increasingly iron-deficient liquid.

Equilibrium melting requires that equilibrium exists between melt and residue, and between residual phases. However, the difference in rates of adjustment of the various phases to iron loss produces non-equilibrium assemblages. Because of the different diffusion
rates in liquid and different residual crystals, measured Fe/Mg partition coefficients are dependent on run time. For example, the $K_{ol/opp} = (Fe/Mg)_{ol}/(Fe/Mg)_{opp}$ has been shown to be insensitive to temperature and pressure, and has been determined experimentally as equal to 1.1±0.1 (e.g. Mori and Green, 1978, and others). Equilibrated olivine-orthopyroxene pairs from natural peridotites have $K_{ol}$ values in this range (e.g. Nixon and Boyd, 1973; Himmelberg and Loney, 1973; Frey and Green, 1974), as do olivine-orthopyroxene pairs in experimental runs in capsule materials other than platinum-group metals (e.g. Kushiro et al., 1972). Our data in Tables 2 and 3 commonly exhibit non-equilibrium Fe/Mg partitioning between olivine and orthopyroxene. This is also evident in some previous partial melting studies where iron loss has occurred; for example, the data of Mysen and Kushiro (1977) show $K_{ol/opp}$ ranging from 0.72 to 0.85, and these values can be attributed to Fe loss and preferential readjustment of olivine to more magnesian compositions. The extent of iron loss from their experiments can also be gauged by the fact that in some of their runs the starting composition lies outside the field defined by the analyzed phases.

Several methods of alloying Pt capsules with iron have been suggested to reduce iron loss (e.g. Nichols, 1974; Ford, 1978). In order to avoid net exchange of Fe, the activity of Fe in the capsule must exactly match that in the silicate charge, i.e. this must be determined for each bulk composition, $T$, $P$, and run duration. Moreover Fe-alloyed Pt becomes brittle, difficult to seal, and may result in capsule fracture during the experiment. Methods such as those proposed by Ford (1978) and Johannes and Bode (1978) may considerably reduce iron loss, but do not remove the necessity for the investigator to thoroughly evaluate the nature and extent of compositional interchange between sample and container.

### Quench modification of equilibrium melts

Scanning electron microscope photographs (Fig. 1) reveal the presence of some quench material in all our experiments, even where none was discernible.

#### Table 4. Compositions of phase and calculated melt for pyrolite — 40 percent olivine at 15 kbar, 1350°C

<table>
<thead>
<tr>
<th></th>
<th>ol</th>
<th>opp</th>
<th>opx</th>
<th>sp</th>
<th>glass</th>
<th>melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.1</td>
<td>54.7</td>
<td>52.4</td>
<td>-</td>
<td>49.9</td>
<td>49.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.03</td>
<td>0.80</td>
<td>1.25</td>
<td>3.4</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.93</td>
<td>5.03</td>
<td>25.3</td>
<td>14.4</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>7.53</td>
<td>6.25</td>
<td>20.1</td>
<td>8.7</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>50.6</td>
<td>50.8</td>
<td>20.5</td>
<td>16.3</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.35</td>
<td>2.76</td>
<td>14.3</td>
<td>0.27</td>
<td>10.9</td>
<td>9.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>0.55</td>
<td>3.3</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.15</td>
<td>1.42</td>
<td>35.2</td>
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<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>92.3</strong></td>
<td><strong>89.8</strong></td>
<td><strong>87.8</strong></td>
<td><strong>57</strong></td>
<td><strong>65</strong></td>
<td><strong>67</strong></td>
</tr>
<tr>
<td><strong>Ca</strong></td>
<td>5.5</td>
<td>30.6</td>
<td>37.4</td>
<td>27.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
<td>84.9</td>
<td>60.9</td>
<td>39.2</td>
<td>40.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
<td>9.6</td>
<td>8.5</td>
<td>23.3</td>
<td>23.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Equilibrium olivine used in liquid calculation was calculated assuming $K_{ol/opp} = 1.1$ i.e. 100 Mg/Mg+Fe = 88.9
2. Total iron as FeO
3. Least modified glass
4. Melt calculated by mass balance; using modal analysis, analyzed crystalline phases (olivine corrected for Fe loss) and original bulk composition

#### Table 5. Compositions of phases and calculated melt for lherzolite — 40 percent olivine at 10 kbar, 1450°C

<table>
<thead>
<tr>
<th></th>
<th>ol</th>
<th>quench</th>
<th>quench</th>
<th>spinel</th>
<th>glass</th>
<th>melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.6</td>
<td>44.5</td>
<td>50.9</td>
<td>-</td>
<td>54.8</td>
<td>51.6</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.12</td>
<td>0.52</td>
<td>0.13</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>1.34</td>
<td>6.46</td>
<td>11.5</td>
<td>8.9</td>
<td>7.8</td>
</tr>
<tr>
<td>FeO</td>
<td>4.57</td>
<td>5.36</td>
<td>6.14</td>
<td>11.2</td>
<td>7.5</td>
<td>8.6</td>
</tr>
<tr>
<td>MnO</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>55.5</td>
<td>47.2</td>
<td>29.6</td>
<td>18.0</td>
<td>10.5</td>
<td>25.9</td>
</tr>
<tr>
<td>CaO</td>
<td>0.27</td>
<td>0.95</td>
<td>5.74</td>
<td>0.27</td>
<td>9.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>0.56</td>
<td>0.70</td>
<td>56.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>95.6</strong></td>
<td><strong>94</strong></td>
<td><strong>89.6</strong></td>
<td><strong>74.9</strong></td>
<td><strong>81.4</strong></td>
<td><strong>85.8</strong></td>
</tr>
<tr>
<td><strong>Ca</strong></td>
<td>11.1</td>
<td></td>
<td>22.6</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mg</strong></td>
<td>79.7</td>
<td>63.0</td>
<td>70.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
<td>9.3</td>
<td>14.4</td>
<td>13.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Total iron as FeO
2. Least modified glass composition
3. Equilibrium melt calculated from $K_{ol/opp} = 1.0$ after correction for iron loss (Green, 1973).
optically. The extent of quenched material varies from narrow (0.5–1 micron) rims of pyroxene or olivine on primary phases to broader (2–5 microns) blades of quenched pyroxene both as rims and as discrete dendrites in the glass. The dominant quench phase in these anhydrous runs is clinopyroxene with varying Ca content. Quench clinopyroxene is not surprising, since this phase most closely approaches the liquid composition over most of the melting range. Quench clinopyroxene commonly contains 6 to 12 percent Al₂O₃ and 6 to 16 percent CaO and has a high TiO₂ content (2–3 percent). These features, together with the generally lower 100Mg/(Mg+Fe) ratio and skeletal or dendritic form, serve to distinguish quench pyroxene from stable primary calcic pyroxene. In addition, quench pyroxene analyses generally are not stoichiometric. In most cases the 100Mg/(Mg+Fe) ratios of the quench and primary phases are distinct, but in some experiments a continuum was found. Because abundant quench material drastically reduces the liquid volume and results in increased concentration of highly incompatible elements in the residual melt fraction, the presence of quench rims and crystals will cause errors in any method of estimation of degree of melting or melt composition based on analyses of the glass in experimental runs.

Quench crystallization has been shown to significantly modify equilibrium melt compositions in hydrous melting of peridotite (Green, 1973, 1976), and we have therefore examined the effect of quenching on liquids in anhydrous melting experiments. Data from two experiments, one at low to moderate degrees of melting (15 kbar, 1350°C) and the other at a high degree of melting (10 kbar, 1450°C), are presented in Tables 4 and 5 and plotted on Ca–Mg–Fe (atomic) diagrams (Figs. 4 and 5). Diffusion studies (e.g., Hofmann and Magaritz, 1977) have shown a high efficiency of diffusion over short distances (e.g., D = 10⁻⁴ cm² at 1400°C), but the quenching rate in solid–media apparatus is such as to produce large compositional differences within the glass where quench phases and outgrowths occur. Moreover, the glass compositions bear little relationship to the composition of the equilibrium liquid calculated by mass balance from the proportions and compositions of the residual phases (Table 4, Fig. 4) or using published partition coefficients (Roeder and Emslie, 1970) after correction for iron loss for simple residues (Table 5, Fig. 5). Glass analyses made adjacent to quench crystals show a marked compositional difference to those obtained in larger “quench-free” pools. In neither case can these be considered as equilibrium melts.

The new data reaffirm earlier studies of the quenching problem (Green, 1973, 1976; Cawthorn et al., 1973) and show that marked changes in the liquid composition may result in partial-melting experiments where quench phases occur, even in anhydrous melting. This problem is especially severe at low degrees of melting, and previous studies have shown that the problem increases at higher pressure and in the presence of volatiles (Green, 1973, 1976; Nicholls, 1974; Mysen and Kushiro, 1977).

Conclusions

We believe that the problems of iron loss and quench crystallization in anhydrous partial melting studies employing piston-cylinder apparatus are severe enough in most cases to preclude direct determination of the equilibrium melt composition. At high degrees of partial melting quench modification is far from trivial, and at low degrees of partial melting modification of the melt may be as severe under anhydrous as under hydrous conditions. In all cases, iron loss problems in anhydrous melting are greater than under hydrous melting conditions because of the higher melting temperatures. Therefore we are forced to conclude that most, perhaps all, previously published partial melt compositions obtained by direct analysis of quenched glasses from piston-cylinder runs are in error. At the very least, all such compositions should be regarded with suspicion.

We have attempted to show that, provided run times are not unduly long (this must be determined empirically by repeated experiments of varying duration), it is possible to calculate the equilibrium liquid composition by mass balance from the compositions of the residual phases which adjust more slowly to iron loss (and using known Kp's for those phases which do adjust rapidly), provided the modal proportions of the phases (including the percentage of melt + quench) can be determined. This is possible by point counting of reflected light and SEM photographs of the polished mount where all phases, including quench phases and overgrowths, can be discriminated. Replicates are generally required to overcome inhomogeneous distribution and crystal settling. However, no liquid determined by partial-melting experiments can be regarded as safely estab-
lished in the absence of reversal studies (i.e. crystallization of the liquid composition under the same experimental conditions).

Acknowledgments

We thank W. O. Hibberson and W. C. Doran for technical assistance and advice, and Dr. A. McKee and B. J. Griffin for instruction in the use of the SEM microscope. Comments on the draft manuscript by K. L. Harris and D. J. Ellis and reviews by W. C. Luth, P. L. Roeder, and R. F. Fudali are gratefully acknowledged.

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THE OXIDATION STATE OF CARBON IN THE REDUCED-VELOCITY ZONE

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Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR, Moscow, University of Tasmania, Hobart, Australia, Monash University, Clayton, Australia, and Max Planck Institute, Mainz, Federal German Republic

Thermodynamic calculations and surveys of experimental data define the equilibrium relations between the phases representing elemental carbon (graphite and diamond), carbonates, and magnesium silicates with oxygen fugacity and the total pressure as coordinates for 1300 K. The composition has also been calculated for fluid in the C-H-O system in equilibrium with diamond at 50 kbar and 1300 K. Various characteristics of the magma and of the crystalline minerals of mantle origin show that the oxygen fugacity varies within the upper mantle from values close to those for the QFM buffer to values lower by 3-4 orders of magnitude. This range overlaps the stability range of carbon (graphite or diamond) and enters the stability range of carbonates only at the highest $f_{O_2}$. The conditions for melting of peridotite in the upper mantle are determined very probably by the II,0 potential rather than eutectic relationships between the silicates and carbonates, since this is controlled by the presence of hydrated silicates (amphibole and phlogopite) or by the presence of a water-rich fluid containing a minor quantity of CO$_2$ and having low values of $f_{O_2}$, and which interacts with the elemental carbon (graphite or diamond). The melts arising under these conditions may contain a certain proportion of CO$_2$, but on cooling and crystallization at depth they will deposit carbon (graphite or diamond).—Authors' Abstract.

INTRODUCTION

A study of the compounds of carbon present in the Earth's mantle is of interest from the viewpoint of petrology and as regards the theory of formation of mineral deposits. Diamond occurs in peridotites and eclogites of mantle origin, as well as in the kimberlites, which shows that reduced forms of carbon occur in the upper mantle. On the other hand, it has been shown that oxidized carbon in the form of CO$_2$ has a fairly high solubility in unsaturated natural magmas such as olivine melilitite [1-3] and biotite mafurite [4], as well as in the related simple silicate melts [5-7]. These studies have shown that the CO$_2$ dissolved in the melt has an appreciable effect on the character of the liquidus phases, which indicates that CO$_2$ is important in the petrogenesis of very unsaturated basalt magmas [1,5]. Another line of evidence for oxidized carbon in mantle processes is the formation of carbonates during the differentiation of alkaline ultrabasic mantle magmas, although there are uncertainties in the relationship of carbonatite magmas to silicate ones, and there has been no proof that the primary carbonatite magmas are formed by direct melting from the mantle (nevertheless, some [8] take the view that mantle carbonatite formation does occur).

Various views have also been expressed on the forms of CO$_2$ in the upper mantle. For example, H.W. Green [9] has supposed that bubbles of CO$_2$ gas occur in the peridotites in the reduced-velocity zone, and these determine the seismic characteristics of this zone. Objections have been made to this hypothesis, and it has been shown by laboratory experiment that gaseous CO$_2$ should react with rock-forming silicates in the mantle to form calcium and magnesium carbonates at pressures above about 20 kbar and temperatures close to those of the stationary geotherms [2, 8, 10, 11]. These conclusions were drawn from experiments performed at oxygen fugacities close to those given by the hematite-magnetite buffer, although it is unrealistic to expect such high oxygen fugacities in the upper mantle.

We have used the available experimental and thermochemical information on the stabilities of phase associations at high temperatures and pressures that include the rock-forming mantle silicates together with diamond and graphite in order to establish the state of oxidation of carbon in the upper mantle.

**EFFECTS OF PRESSURE AND OXYGEN FUGACITY ON THE PHASE ASSOCIATIONS OF MANTLE LHERZOLITE**

Figure 1 shows an isothermal diagram for 1300 K that demonstrates the stability of a CO$_2$-rich gas, graphite, diamond, and carbonates (dolomite and magnesite), which can be in equilibrium with a simplified mineral association as in mantle lherzolite in the system CaO-MgO-SiO$_2$-forsterite + enstatite + diopside. The horizontal lines in this diagram show the (1)-(3) equilibria, which are virtually independent of the oxygen fugacity:

1. $\frac{1}{2} \text{CaMg} (\text{CO}_3)_2 + 2 \text{MgSiO}_3 = \text{Mg}_2 \text{SiO}_4 + \frac{1}{2} \text{CaMgSi}_2 \text{O}_6 + \text{CO}_2$ (gas),
2. $\text{CaMg} (\text{CO}_3)_2 + 2 \text{MgSiO}_3 = \text{CaMgSi}_2 \text{O}_6 + 2 \text{MgCO}_3$,
3. C (graphite) $\rightarrow$ C (diamond).

The equilibrium parameters of these reactions are taken from various published sources [11-14]. The position of the equilibrium line for the oxidation of graphite with the formation of CO$_2$ + CO gas has been determined reliably from data on the free energies of formation of CO$_2$ and CO [15], the molar volume of graphite, and the compressibility and thermal expansion of the latter [16], together with the fugacities of CO$_2$ and CO (from 17) up to 15 kbar and from 18) above 15 kbar. The position of the boundary between the fields of Fo + En + Di + dolomite has been found from the reaction

$\frac{1}{2} \text{CaMg} (\text{CO}_3)_2 + 2 \text{MgSiO}_3 = \frac{1}{2} \text{CaMgSi}_2 \text{O}_6 + \text{Mg}_2 \text{SiO}_4 + \text{C} + \text{CO}_2$.

These calculations were based on thermochemical and volumetric data from 19) and 16).

The intersection of the equilibrium lines for reactions (1) and (4) gives the position of the ultrathermally invariant point at which dolomite, forsterite, enstatite, diopside, graphite, and a gas rich in CO$_2$ can coexist. This point should also lie on the curve representing the oxidation of graphite to a gas; and Fig. 1 shows that the calculated curve for this reaction does pass practically through the point of intersection of the lines for (1) and (4), which demonstrates internal consistency in the experimental and thermodynamic data.

*The reliability of these calculations is confirmed by the close agreement between the calculated monovariant line for 2Fe$_2$SiO$_4$ + CO$_2$ = 2Fe$_3$O$_4$ + 3SiO$_2$ + C and the experimental data of 50 (Fig. 2).
Fig. 1. Calculated isothermal phase boundaries for a model mantle mineral association composed of forsterite + enstatite + diopside with small amounts of carbon compounds (excess of the silica components) with the coordinates total pressure and oxygen fugacity at 1300 K. Fo forsterite, En enstatite, Di diopside, Dol dolomite, Mg magnesite, C(g) graphite, C(d) diamond. QFM curve for the quartz-fayalite magnetite buffer (corresponds to metastable equilibrium above about 14 kbar), BM curve for the hematite-magnetite oxygen buffer.

Fig. 2. P-T curves for the monovariant equilibrium $3\text{Fe}_2\text{Si}_3\text{O}_9 + \text{CO}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 + \text{C}$: 1) curve calculated by the methods described in this paper, 2) experimental results of [50], 3) curve calculated in [50] by the use of the modified Redlich-Kwong equation [51].

The intersection between the curves for (4) and (2) gives a second isothermally invariant point, at which graphite, dolomite, magnetite, forsterite, enstatite, and diopside may coexist (Fig. 1). At higher pressures, the oxidation of graphite (or of diamond at sufficiently high pressures) in the presence of mantle silicates leads to the formation of magnesite:

$$\text{Mg}_2\text{SiO}_4 + \text{C}_{\text{graphite}} + \text{O}_2 = \text{MgCO}_3 + \text{MgSiO}_4 \quad (5)$$

$$\text{Mg}_2\text{SiO}_4 + \text{C}_{\text{diamond}} + \text{O}_2 = \text{MgCO}_3 + \text{MgSiO}_4 \quad (6)$$

The slopes of the equilibrium lines for these reactions have been estimated from data on the volumes, compressibilities, and thermal-expansion coefficients for the solid phases [15, 16].

**OXYGEN FUGACITY IN MAGMAS AND XENOLITHS OF MANTLE ORIGIN**

Only restricted data are available for estimating the $f_{O_2}$ in the mantle at present. The oxygen fugacities have been determined for basalt magmas varying in composition from tholeiites to alkali olivine basalts by one of the following methods: a) measurement of $\text{Fe}^{3+}/\text{Fe}^{2+}$ for basalt melts in relation to $f_{O_2}$ in comparison with compositions of natural basalts [20-22], b) use of the Buddington-Lindsley method [23-25] with data on the compositions of coexisting iron-titanium oxides, c) measurement of the crystallization conditions for near-liquidus magnetite or chrome spinellide at controlled $f_{O_2}$ and comparison with petrographic data [22-26], and d) direct measurement of $f_{O_2}$ on active volcanoes and the use of special electrodes with volcanic products [27].
This broad range of methods gives consistent results, and they indicate oxygen fugacities close to those for the QFM buffer. This conclusion cannot be transferred directly to the redox conditions in the areas of mantle magma generation. The interaction with crustal rocks and early crystallization of olivine at low pressures causes $Fe^{3+}/Fe^{2+}$ in the melt to rise. Therefore, the oxygen fugacity corresponding to the QFM buffer should be considered as the upper limit for the mantle.

Green and Sobolev [28] have determined the compositions of garnet and ilmenite, including the $Fe_2O_3$ content of ilmenite, when these minerals crystallize at high pressures and temperatures in an apparatus of cylinder-piston type and oxygen fugacities less than those corresponding to the nickel-bunsenite buffer [29, 31]. Brey and Green [11] have observed the presence of titanomagnetite and andradite-bearing garnet at similar temperatures and pressures but higher oxygen fugacities (with an external hematite-magnetite buffer). There is a similarity in composition on the one hand between natural ilmenite and garnet from xenoliths of garnet lherzolites in kimberlites or inclusions in diamonds and on the other hand those minerals synthesized at $fO_2$ below the nickel-bunsenite value, which shows that the oxygen fugacity in the mantle is also below the value for that buffer and does not exceed $fO_2$ for the QFM buffer.

Another way of estimating the oxygen fugacity for mantle parageneses is to consider the activities of the ferroan components of olivine, orthopyroxene, and the spinel phase in relation to the equilibrium constant of the following reaction [32]:

$$6FeSiO_3 + 2Fe_2O_3 = 12FeSiO_4 + O_2 \quad (7)$$

The activities were replaced by the molar proportions of the corresponding minerals as a first approximation, which introduces some uncertainty into the results. This method of estimating $fO_2$ will become more reliable as our knowledge...

---

Fig. 3. Range of $fO_2$ (hatched area) estimated for mantle parageneses of olivine + orthopyroxene + chrome spinel phase by the use of the equilibrium constants of (7) in comparison with the monovariant lines for the following oxygen buffers: $3FeSiO_3 + O_2 \rightarrow 3Fe_2O_3 + 2O_2 = QFM$ (metastable continuation), $3FeSiO_3 + O_2 = 2Fe_2O_4 + 3SiO_2 = QFM$ and the bounds to this stability range of elemental carbon and carbonates in the presence of forsterite and two pyroxenes C-Carb (Fig. 1). Calculated for $1300^\circ$K.

Fig. 4. Chromium contents of olivines coexisting with chrome and orthopyroxene in relation to oxygen fugacity and $1140^\circ$C: 1) lunar basalts (0.2-0.4%) equivalent Cr$_2$O$_3$; 2) inclusions in diamonds (0.08-0.15% equivalent Cr$_2$O$_3$); 3) Alpine peridotites (0.01-0.022% equivalent Cr$_2$O$_3$); 4) slope for (8).
on the thermodynamic characteristics of the chrome spinelliaos improve. Analyses of existing mantle minerals from various published sources give calculated fugacities from values close to the QFM buffer down to ones lower by 2-3 orders of magnitude (Fig. 3).

One can estimate $f_{O_2}$ for the upper mantle also from the chromium content of olivine. The chromite level of olivine deposited at the same time as chromite in lunar basalts is equivalent to 0.2-0.4 mass % Cr$_2$O$_3$ and is considerably higher than that in olivine coexisting with chromite in terrestrial basalts (0.01-0.2 mass % Cr$_2$O$_3$) [31]. The temperatures and pressures of the mineral equilibria in these objects are fairly similar, so the differences are due to the very much lower $f_{O_2}$ for the lunar magmas and the entry of chromite into olivine mainly as Cr$_2$O$_3$ [34]. If we assume that all the chromium in the olivine is Cr$^{3+}$, we can relate the concentration in the mineral in equilibrium with chromite and enstatite by considering the reaction

$$2\text{MgCr}_2\text{O}_4 + 6\text{MgSiO}_3 = 8\text{Mg}_2\text{SiO}_4 + 4\text{Cr}_2\text{O}_3 + \text{O}_2.$$  \(8\)

The equation implies that the chromium concentration in the olivine should be proportional to $f_{O_2}$. Laboratory studies and analytical data for rocks show that olivine ($f_{O_2}$), crystallized from the magmas in lunar maria at about 1140°C and log $f_{O_2}$ of 13.5-13.8 (133-37) and also unpublished analytical data of D.H. Green for the lunar basalt 70215, and the olivine contains about 0.20 mass % equivalent Cr$_2$O$_3$. In contrast, terrestrial basalts deposit olivine with $0.01-0.02$ mass % equivalent of Cr$_2$O$_3$ under conditions of oxygen fugacity close to those of the QFM buffer, i.e., log $f_{O_2} = -9$ at 1140°C.

The plot of these two groups of data in coordinates of log(CrO)$_{eq}$ against log $f_{O_2}$ shows that a single straight line applies with a slope corresponding to the equation of (8) (Fig. 4).

Olivine from lherzolite xenoliths in kimberlites and basalts as a rule has low chromium content, while olivine in diamond crystals contain 0.08-0.15 mass % Cr$_2$O$_3$ [38,39]. If we assume that the temperature of formation of such olivine was close to 1140°C (i.e., somewhat above the solidus for mantle lherzolite containing MgO and CaO at 35-40 kbar) and assume that the effects of pressure on the equilibrium in (8) are approximately as for the QFM buffer, we get from Fig. 4 that the range in Cr$_2$O$_3$ in mantle olivines from about 0.2 to 0.15 mass % corresponds to $f_{O_2}$ from the QFM buffer down to values lower by 3-4 orders of magnitude.

It is clear that these estimates are based on a very simplified approach, since no account has been taken of the variations in the state of the iron in the phases in (8), nor the entry of aluminum into the chromite and various other factors. Nevertheless, the semiquantitative conclusion from (Fig. 4) remains that the oxygen potential characterizing diamond formation corresponds to the middle of the range bounded by the $f_{O_2}$ for lunar and terrestrial basalts.

Very low $f_{O_2}$ followed by measurements on the emf in cells with solid electrolytes of anionic conduction made from minerals extracted from rocks of mantle origin: olivine from tholeiite basalts and titanium garnets from alkali rocks. The result: values of the oxygen fugacity were close to the iron-wustite buffer, i.e., lower than those for the QFM buffer by about three orders of magnitude [41, 42].

**FLUIDS IN THE REDUCED-VELOCITY ZONE**

Kimberlites are undoubtedly amongst the most plutonic geological objects. Various features indicate that they are injected from depths in excess of 100 km in a catastrophic fashion, evidently as a result of fluidization of the material by low-viscosity phases. These data and various other kinds of evidence such as the gas inclusions in diamonds [43] indicate that fluids may exist in the mantle at depths in excess of 100-150 km.
Table 1

Fugacity Coefficients for Gases in the C-H-O System at 50 kbar and 1300 K and Data Required in the Calculation

<table>
<thead>
<tr>
<th>Components</th>
<th>V_{15 kbar}, cm^3</th>
<th>a_{15 kbar}</th>
<th>log \gamma_{15 kbar}</th>
<th>\log \gamma_{50 kbar}</th>
<th>*</th>
<th>\log \gamma_{50 kbar}</th>
<th>log \gamma_{50 kbar}</th>
<th>***</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2</td>
<td>27.56</td>
<td>20.15</td>
<td>1.66</td>
<td>4.99</td>
<td>4.50</td>
<td>5.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>31.73</td>
<td>24.52</td>
<td>1.65</td>
<td>5.59</td>
<td>5.10</td>
<td>4.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2</td>
<td>32.70</td>
<td>25.58</td>
<td>1.60</td>
<td>5.78</td>
<td>5.29</td>
<td>4.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2O</td>
<td>15.57</td>
<td>11.36</td>
<td>0.77</td>
<td>2.86</td>
<td>2.37</td>
<td>2.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2O</td>
<td>19.31</td>
<td>12.10</td>
<td>0.49</td>
<td>2.69</td>
<td>2.19</td>
<td>2.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The values of 15 kbar are from [17].

*Fugacity coefficients calculated on assuming constancy of the molar volumes in the pressure range 15-50 kbar.

**Fugacity coefficients calculated on assuming constancy in a in the range 15-50 kbar.

***Observed values of the fugacity coefficients for 50 kbar and 1300 K: for CO_2 from [18], for H_2 from [17], for H_2O the results of integrating the P-T relations on the basis of the P-V-T diagrams of [44].

To establish the form of carbon in such a fluid we calculated the composition of the gas phase in the C-H-O system in equilibrium with diamond at 50 kbar and 1300 K. These values are close to a certain estimates of the temperature and pressure for mineral equilibria in lherzolite nodules from kimberlites.

It was assumed that the fluid is an ideal solution of the following molecular particles: CO_2, CO, H_2, H_2O, and CH_4. Laboratory data indicating the fugacity at 50 kbar exists only for water and CO_2. In particular, estimates of the fugacity of CO_2 from data for monovariant decarbonitization reactions [18] give nearly linear isothermal curves against pressure. This means that the pressure dependence of the volume of CO_2 can be neglected within the errors of the methods for the pressure range 10-50 kbar. On the other hand, Mel'nik [17] has shown that there are approximately linear relationships between the logarithms of the fugacity coefficients and the pressure in many cases at high pressures, which corresponds to constancy of a = \frac{V}{RT/P}. Correspondingly, Table 1 gives results from extrapolating the fugacity coefficients (\gamma) of these gases from 15 to 50 kbar at 1300 K and the assumption of constant molar volume and constant a on the basis of the V, a, and \gamma taken from Mel'nik's monograph [17].

The model problem with V = constant gives elevated values for the fugacities, since the volume in fact decreases on isothermal compression, while calculations based on constancy of a may give values somewhat too low at high pressures, since the isotherms for a for most gases begin to flatten out at pressures of the order of 10 kbar, and it may be that there are minima at higher pressures.

The extrapolated \gamma can be compared with calculations from measurements at pressures over 10 kbar (Table 1): the data for CO_2 derived from decarbonitization [18] are very close to those obtained by extrapolating on the assumption V = constant, while the calculations for water on the basis of data for shock compression [44] give a result intermediate between the cases V = constant and a = constant, but approximating to the second of these models.

Figure 5 gives the dependence on log f_{CO_2} for the composition of the fluid in the C-H-O system in equilibrium with diamond for the models V = constant (Fig. 5a) and a = constant (Fig. 5b)*. The discrepancies between the two cases do not exceed an order of magnitude.

*The calculations were performed by solving a system of equations derived from the expressions for the constants of the following equilibria: C + CO_2 = CO_2, C + H_2O = CO + H_2, 2H_2 + CH_4, H_2 + H_2O = H_2O, in which we substituted for the molar proportions of the components and the fugacities of the corresponding pure gases, together with the condition X = 1 (X is the molar fraction).
Fig. 6. Atomic H/(H+O) ratios for fluid in the C-H-O system in equilibrium with diamond at 50 kbar and 1300 K in relation to log f0. The upper curve has been calculated on the assumption of constancy of the molar volume of the individual gases in the range 15-50 kbar, while the lower curve corresponds to constancy of a=V-RT/P in the same range.

Figure 5 shows that the main component of the fluid is water over a large range in oxygen fugacity. At the boundary of the diamond and magnetite fields (log f0 = -8.5) the gas phase contains CO2 to the extent of several molar %, while an f0 lower by 1-2 orders of magnitude there are appreciable amounts of CH4, which then becomes the predominant component (Fig. 5).

These calculated fluid compositions can be compared with analyses of gases extracted from natural diamonds, where one must bear in mind that the amount of carbon in a gas inclusion in this mineral may vary after trapping on account of reactions with the walls, but that the H/O ratio should remain constant. The data of Fig. 5 were therefore used to calculate H/(H+O) for the fluid, and Fig. 6 shows the dependence of this on log f0. The mean composition of the gases extracted from natural diamonds is characterised by H/(H+O) = 0.65, but individual crystals from African deposits give H/(H+O) up to 0.82 (43). In general these data indicate that the fluids in equilibrium with diamonds have oxygen fugacities ranging from the values close to the stability limit for carbonates down to values lower by three orders of magnitude. This conclusion agrees well with the estimates of f02 for mantle objects given in the previous section.

We have given data above that show that the oxygen fugacities vary from the QFM value down to values lower by about three orders of magnitude in parts where basalt magmas, lherzolite xenoliths, and diamonds from kimberlites are produced. This range in f02 may be compared with the positions of the phase fields in Fig. 1; this shows that the thermodynamic parameters of the reduced-velocity zone correspond to stability in elemental carbon or lie near to the boundary between the elemental carbon and carbonate fields. It is therefore very likely that diamond and graphite are the main carbon minerals under these P and T conditions, not carbonates.

We have shown in the previous section that the main forms of carbon in the fluid under these conditions may be either CO2 or CH4, in accordance with the exact f02 within the acceptable range. The calculations show, however, that the predominant volatile in such a fluid in a diamond-production region is water.
while the carbon compounds are present at the level of a few molar %. However, even a small amount of CO₂ in the aqueous phase may provide for appreciable amounts of carbonate associations coexisting with the silicate melt. Therefore, the compositions of the primary magmas produced from the mantle peridotite under these conditions will differ appreciably from those produced in the absence of volatiles, with enrichment in calcium and an increase in the silica deficit [1, 2, 3, 8, 11, 13]. The effects of this factor may be quite appreciable down to fO₂ lower by about an order of magnitude than those corresponding to the boundary between the fields of elemental carbon and the carbonates. This conclusion is confirmed by preliminary experiments described below. D.H. Green has performed experiments on the melting of basanite in the presence of excess water, where the reacting materials were placed in graphite capsules and kept at 27 kbar and 1250°C [46]. Semiquantitative microprobe analysis of the glass showed the presence of 3-5 mass % carbon [46], and subsequent examination by infrared spectroscopy showed that the glass contained CO₃²⁻ [11]. Although we do not know the water content of the melt or the composition of the gas phase (the quenched glass contained bubbles filled with gas), the experiments do confirm the high solubility of carbon in the form of CO₃²⁻ in a melt of olivine nepheline in equilibrium with graphite, olivine, and enstatite.

We have also performed preliminary experiments on the reaction between diamond and kimberlite magma. Small diamond crystals (0.12-0.24 mg, weight to ±0.0005 mg) have placed in a sealed internal platinum capsule together with a mixture of kimberlite composition, as well as a mixture of citric acid and oxalic acid dihydrate (this composition should give water, CO₂, and carbon after decomposition at high temperatures and pressures). The two compositions used may be defined as mixtures with the following percent of components: 43.7 kimberlite + 32 CO₂ + 22.5 H₂O + 18.8 C and 39.4 kimberlite + 32.2 CO₂ + 24 H₂O + 4.4 C. The specimens contained each 10 mg of the mixture of kimberlite with volatiles and diamond grains. The internal capsule was placed in an outer gold capsule filled with the iron-wustite buffer together with the 2% H₂O. Experiments were performed at 50 kbar and 1200°C for 0.5 and 6 hr and at 50 kbar and 1150°C for 4 hr. The pressure of 50 kbar corresponds to the nominal load in the cylinder-piston system in which the piston is driven in after attaining a given temperature and by the use of an outer shell of potassium chloride. We preferred to produce high pressures by this method instead of the use of an assembly with an external shell of tale, for which there is usually a friction correction of 10% [47]. Calibration on the basis of the quartz-sericite transformation showed that the friction correction was very much reduced with the use of a shell of KCl and was close to zero.

The results of two experiments at 50 kbar and 1200°C showed that these parameters lie above the liquidus for this composition, and the quenched products were represented by carbonate, mica, and amphibole (?) and also contained finely divided graphite. The diamond crystals lost about 1% in weight, (0.0012 mg in a 6-hr experiment). At 50 kbar and 1150°C, the point was below the liquidus and the products were represented by large idiomorphic crystals of olivine and a quenched aggregate consisting of carbonate, mica, and amphibole (?) together with finely divided graphite. The mass of the diamond crystal increased by about 1.4% (0.0034 mg). Although nonequilibrium conditions are indicated by the simultaneous presence of graphite and diamond, the change in weight of the diamond was minor by comparison with the total amount of elemental carbon deposited, being close to the error of weighing, while there were quenched carbonate minerals, all of which indicates that the solubility of CO₃²⁻ in a kimberlite melt remains high even at the low fO₂ corresponding to the iron-wustite buffer in the presence of elemental carbon (either diamond or graphite).

CONCLUSIONS

Various sources of information indicate that the oxygen fugacity in the upper mantle usually lies in the range from the QFM buffer down to values lower by 3-4 orders of magnitude. The equilibria between carbon, carbonates, and magnesian silicates are dependent on P and fO₂, and they show that this range
of oxygen fugacities largely overlaps the stability field of elemental carbon (graphite or diamond) and only near the upper limit does it lie beyond the boundary between the fields of carbon and carbonates.

From these results we conclude that carbon is present in the upper mantle probably mainly in the form of graphite or diamond and that the solidus of mantle peridotite is primarily determined not by melting involving carbonates and silicates but by equilibria involving either hydrated phases (amphibole and phlogopite) or a fluid rich in H2O at pressures above the stability limit of pargasite amphibole (48-49).

Although carbonates mostly appear to be absent near the solidus boundary for mantle lherzolite and do not influence the temperatures and pressures of melting for the primary magmas, the melts arising in the presence of aqueous fluid and elemental carbon may contain appreciable amounts of CO3^2- even at oxygen fugacities lower than those for the QFM buffer. The cooling of such a melt at high pressures may lead to the deposition of carbon as graphite or diamond, but the oxygen fugacity increases as the Earth's surface is approached, which is reflected in the mineralogy of the xenocrystals and leads to deposition of carbonates or the occurrence of fluids rich in carbonate components.

REFERENCES


Pyroxene-carbonate reactions in the upper mantle

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The $P-T$ location of the reaction diopside + magnesite $\rightarrow$ enstatite + dolomite has been determined by experimental reversals from 800 to 1300°C, 20-50 kbar. Up to $\sim$1150°C this reaction has a slope of $\sim$ 52 bar/deg, and above this temperature a slope of $\sim$ 80 bar/deg. The change in slope is attributed to the presence of disordered dolomite at high temperature.

It had previously been suggested that dolomite would be the stable carbonate mineral at the mantle solidus to depths of $\sim$150-200 km and magnesite only at greater depths, whereas our data indicate that magnesite will occur at the solidus at depths of $\sim$100-120 km for a $H_2O + CO_2$-bearing mantle. Dolomite will only occur at the solidus between $\sim$ 80 and 110 km depth. The intersection of a shield geotherm with the solidus within the stability field of magnesite produces liquids low in CaO and $Al_2O_3$—inferred to be kimberlitic magmas. Oceanic geotherms intersect the solidus in the dolomite stability field, producing liquids more enriched in CaO and of olivine melilitite composition.

1. Introduction

In investigating the nature of magmatic processes it has been demonstrated that $H_2O$ and $CO_2$ are the most abundant of the volcanic gases and are important in the magma source regions of the upper mantle. However, the possible roles in the upper mantle of reduced carbon, of gaseous $CO_2$ and of carbonate minerals such as dolomite and magnesite, are by no means clear [1-5]. Provided that $fO_2$ is, at least locally, high enough to stabilize oxidized carbon then dolomite and magnesite may occur in a peridotitic mantle at pressures above the following carbonation reactions:

$$ (1) \quad Mg_2SiO_4 + CO_2 \leftrightarrow MgSiO_3 + MgCO_3 \quad [6-9] $$

$$ (2) \quad 2 Mg_2SiO_4 + CaMgSi_2O_6 + 2 CO_2 \leftrightarrow CaMg(CO_3)_2 + 4 MgSiO_3 \quad [10,11] $$

A further important reaction, lying within the pyroxene-carbonate plane, which limits the possible occurrence of dolomite or magnesite in upper mantle lherzolitic compositions is:

$$ (3) \quad 2 MgSiO_3 + CaMg(CO_3)_2 \rightarrow CaMgSi_2O_6 + 2 MgCO_3 $$

In a reconnaissance experimental study, Kushiro et al. [12] obtained data on reaction (3), but state that its location was not accurately determined and could be shifted by $\pm 3$ kbar at temperatures between 1000 and 1200°C. Considering likely mantle geothermal gradients, these authors inferred that dolomite could be stable in the upper mantle to depths of $\sim$ 150 km ($\sim$ 50 kbar) but
that magnesite would occur at deeper levels. In investigating melting in peridotite-CO₂, the intersection of reaction (3) with the solidus for a model mantle with small CO₂ contents led to the conclusion [10,11] that dolomite would occur in the solidus from ~25 to ~50 kbar and magnesite at higher pressures. However, reconnaissance experiments on the melting of pyrolite-40% olivine composition [13] in the presence of CO₂ and H₂O yielded enstatite + dolomite + diopside near the solidus (950°C) at 20 and 25 kbar but enstatite + diopside + magnesite at 30 kbar, 950°C, and higher pressures. The latter data imply that dolomite has a role at the peridotite solidus (i.e. peridotite-C-O-H system) only at comparatively shallow depths in the upper mantle. The need for accurate determination of reaction (3) led to the present investigation.

2. Experimental method

The composition chosen for experimental study has the stoichiometry of equation (3), i.e. it lies at the intersection of the diopside-magnesite and enstatite-dolomite joins. Starting materials were prepared from: (a) synthetic diopside glass (analyzed as \( \text{Ca}_{1.008}\text{Mg}_{0.992}\text{Si}_2\text{O}_6 \)); (b) synthetic Tem-Pres clinopyroxene (analyzed as \( \text{Mg}_{1.00}\text{SiO}_3 \)); (c) natural magnesite (analyzed as \( \text{Mg}_{0.996}\text{Ca}_{0.004}\text{CO}_3 \), i.e. containing 0.30 wt.% CaO and <0.02% FeO); and (d) natural dolomite (B.S. 88) (analyzed as \( \text{Ca}_{0.505}\text{Mg}_{0.495}\text{CO}_3 \), FeO = 0.08%)—X-ray diffractometer data show that this is a highly ordered dolomite [14].

To establish relative stabilities of the two assemblages, mixtures of both reactants and products were prepared (mix A and B were used in piston cylinder experiments, mix B and C were used in belt apparatus experiments):

- **mix A** (mol. proportions)—Enst: Dol: Di: Mag = 8:4:1:2
  - (low-pressure assemblage dominant)
- **mix B** Enst: Dol: Di: Mag = 2:1:4:8
  - (high-pressure assemblage dominant)
- **mix C** (equal proportions)—Enst: Dol: Di: Mag = 2:1:1:2

(In mix C, enstatite was a mixture of orthoenstatite and clinoenstatite synthesized at 1380°C, 1 atm from gel in 3 days; diopside was crystallized from glass in 3 days at 1 atm and 1250°C.) It was known from previous studies [15] that diopside glass devitrifies to diopside pyroxene within 2–3 minutes at 1000°C and that clinoenstatite inverts to orthopyroxene equally rapidly at pressure of >10 kbar. A sample of dolomite held at 20 kbar, 850°C for 1 hour remained highly ordered, indistinguishable from the starting material. Dolomite held at 27.5 kbar, 975°C for 1 hour showed slight broadening of the (021) and (015) reflections.

2.1. Piston-cylinder experiments (Hobart)

The samples were enclosed in unsealed Ag₅₀Pd₅₀ inner capsules within a larger sealed Au capsule containing magnetite-haematite (1:9) + 5% H₂O. The purpose of the double capsule method, buffering the internal capsule at low hydrogen and high oxygen fugacities, was to prevent reduction of the carbonates to graphite during long run times. In all cases the buffer, although converted entirely to magnetite in a few cases, prevented reduction to graphite within the carbonate-silicate assemblage.

The piston-cylinder apparatus is of Boyd-England design using a talc + boron nitride high-pressure assemblage to 30 kbar and an NaCl + boron nitride high-pressure assemblage at higher pressures. Piston-in technique was used in all cases and a −10% pressure correction applied to nominal pressures using the talc pressure cells, while no pressure correction was applied to the NaCl pressure cells. These procedures were based on calibration of pressure measurement on the quartz-coesite and albite ⇔ jadeite + quartz reactions, yielding accuracy of pressure measurement of ±3% [16]. Temperatures were measured with a Pt/Pt₀₉₇₃Rh₁₀ thermocouple.

The samples were examined optically, by X-ray diffractometer and by scanning-electron microscope and electron microprobe (JEOL JXA-50A). Direction of reaction was unequivocal in all experiments above 800°C in terms of clear growth of one assemblage at the expense of the other; reversals of the equilibrium were obtained at 850°, 900°, 970°, 1020°, 1050° and 1100°C. Confirma-
tion of the X-ray diffractometry determinations of unstable and stable phases was obtained by micro-
probe analyses identifying change in composition of the stable reactants and absence of either relict 
or variable composition of unstable phases. It was 
not possible to determine the ordered/disordered 
character of the dolomite on the basis of X-ray 
diffractometry as the critical reflections of low 
intensity were overprinted by orthopyroxene re-
fections. The experiments on dolomite noted 
above, coupled with earlier work [14], establish 
that to at least 1000°C, the reaction involves highly 
ordered dolomite.

Goldsmith and Heard [14] observed the onset 
of cation disordering in dolomite at approximately 
1000°C and at 1150°C the remaining order reflec-
tions were very weak. They estimated that disorder 
was probably complete at about 1200°C. Gold-
smith [19] notes that some cation reordering by 
back reaction during quench may occur. More 
recently Reeder and Nakajima [23] conclude that 
the critical disordering temperature is between 1100 
and 1150°C—that is, just beyond the experi-
mental range studied at Hobart. They also note that 
reordering occurs during even rapid quench.

2.2. Belt apparatus (Mainz)

The belt apparatus was calibrated at room tem-
perature with the phase transitions of Bi, Tl and 
Ba and at high temperatures with the Ag-melting 
curve [18] from 20 to 40 kbar and 1050–1200°C 
and the quartz-coesite transition [17] from 30 to 36 
kbar and 800–1500°C. The latter two give excel-
 lent agreement (max. 0.2 kbar between 20 and 60 
kbar) with each other whereas the room tempera-
ture calibration would overestimate the pressure 
dramatically (e.g. by about 20 kbar at 50 kbar). 
Pressure is controlled automatically to within 300 
bar and is estimated to be accurate to 1 kbar over 
the whole range of temperatures. The temperature 
is measured with an EL 18 thermocouple 
(Pt\textsubscript{70}Rh\textsubscript{30}/Pt\textsubscript{90}Rh\textsubscript{10}) with no correction for 
the effect of pressure on the emf of the thermocouple. 
It is controlled to within 2°C; its estimated accu-

racy is ±7°C. The furnace assemblage consists of 
pyrophyllite, boron nitride, graphite heater and 
boron nitride inserts at temperatures at or below 
1300°C and soft-fired pyrophyllite inserts above 
1300°C.

Samples were studied by petrographic micro-
scope, X-ray diffractometry and by electron mi-
croprobe (ARL-SEMQ with energy-dispersive 
analysis system (Kevex)). The analyses of phases 
in Table 2 are of the most calcic enstatite and 
magnesites and least calcic dolomites and di-
opsides encountered in the experiments. Data are 
only reported from runs in which essentially com-
plete conversion to one assemblage or the other 
occurred (i.e. at \(T > 1000°C\)). Even in these cases 
relict seed compositions of enstatite or diopside 
could be found with the microprobe.

3. Experimental results

3.1. Piston-cylinder apparatus

The results of the experimental study are given 
in Table 1 and illustrated in Fig. 1. The univariant 
reaction [3] is linear over the temperature range of 
800–1100°C within experimental error and has a 
slope of 52 bar/°C. At 1000°C, the reaction oc-
curs at 29.5 kbar, i.e. 10 kbar below the value 
given by Kushiro et al. [12]. The data are con-
sistent with the results of Brey and Green [13] in a 
more complex iron-bearing composition.

![Fig. 1. Experimental data on the reaction enstatite + dolomite 
≠ diopside + magnesite. Data obtained using piston-cylinder 
apparatus, University of Tasmania.](image-url)
### TABLE 1
Results of experiments in piston-cylinder apparatus

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time (hr)</th>
<th>Capsules inner/outer</th>
<th>Starting mix a</th>
<th>Products b</th>
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<tbody>
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<td>309</td>
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<td>34</td>
<td>2.5</td>
<td>Pt/Au</td>
<td>B</td>
<td>EN + DOL + (Di) + (Mag)</td>
</tr>
<tr>
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<td>1100</td>
<td>35</td>
<td>2.5</td>
<td>Pt/Au</td>
<td>A</td>
<td>- - DI + MAG</td>
</tr>
<tr>
<td>306</td>
<td>1100</td>
<td>38</td>
<td>2.5</td>
<td>Pt/Au</td>
<td>A</td>
<td>- - DI + MAG</td>
</tr>
<tr>
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<td>Pt/Au</td>
<td>B</td>
<td>- - DI + MAG</td>
</tr>
<tr>
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<tr>
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<td>(En) + - + DI + MAG</td>
</tr>
<tr>
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<td>B</td>
<td>- - DI + MAG</td>
</tr>
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<td>A</td>
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</tr>
<tr>
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<tr>
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<td>25</td>
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<td>B</td>
<td>EN + DOL - -</td>
</tr>
<tr>
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<td>26</td>
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<tr>
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<tr>
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<tr>
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<td>EN + DOL + (Di) -</td>
</tr>
<tr>
<td>201</td>
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<tr>
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<td>A</td>
<td>(En) + (Dol) + DI + MAG</td>
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<tr>
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<td>6.5</td>
<td>A\textsubscript{85}Pd\textsubscript{50}/Au</td>
<td>A</td>
<td>(En) + (Dol) + DI + MAG</td>
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<tr>
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<td>750</td>
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<td>12.0</td>
<td>A\textsubscript{85}Pd\textsubscript{50}/Au</td>
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<tr>
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<td>750</td>
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<td>15.0</td>
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<td>(En) + (Dol) + DI + MAG</td>
</tr>
<tr>
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<td>18</td>
<td>24.0</td>
<td>A\textsubscript{85}Pd\textsubscript{50}/Au</td>
<td>B + 2%</td>
<td>(En) + (Dol) + DI + MAG + AMPH</td>
</tr>
</tbody>
</table>

a Mix A: \textsubscript{En}\textsubscript{33.3}Dol\textsubscript{26.7}Di\textsubscript{6.7}Mag\textsubscript{13.3}; mix B: \textsubscript{En}\textsubscript{13.3}Dol\textsubscript{6.7}Di\textsubscript{26.3}Mag\textsubscript{53.3}.

b DI = major phase, (Di) = minor phase.

Consideration of reaction (3) shows that at the equilibrium boundary all phases should be fixed in composition and the compositions should define the solvus gap between dolomite and magnesite and the composition gap between diopside and enstatite. Although the experiments were not designed for this purpose and run times were insufficient to eliminate all relict seed compositions, yielding a spread in pyroxene compositions in some runs, the data nevertheless show consistent patterns, viz.: (a) \textsubscript{Ca}:Mg of enstatite increases with increasing temperature, (b) \textsubscript{Ca}:Mg of diopside decreases with increasing temperature, (c) \textsubscript{Ca}:Mg of magnesite increases with increasing temperature, (d) \textsubscript{Ca}:Mg of magnesite in the diopside + magnesite field decreases with increasing pressure at constant temperature (shown by the 1100°C data), (e) dolomite, unlike magnesite, remains constant in composition between 750°C, 18 kbar and 1100°C, 34 kbar.

In relation to (a) and (b) the experimental data are consistent with recent work on the pyroxene solvus at high pressures [20–22] and point (c) is consistent with work on the dolomite-magnesite solvus in the system CaO-MgO-CO\textsubscript{2} [1].
## Phase compositions (atomic proportions)

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<tr>
<th>enstatite</th>
<th>dolomite</th>
<th>diopside</th>
<th>magnesite</th>
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### 3.2. Belt apparatus

Results are tabulated in Table 2 and illustrated in Fig. 2. The reaction was bracketed within 1 kbar over the temperature range 850–1300°C. Agreement with the piston-cylinder data at 850–1100°C is within the estimates of accuracy of pressure and temperature measurement of both apparatuses but the difference in pressure of 1–1.5 kbar is surprisingly consistent and may indicate an over- or under-estimate of pressure correction in either laboratory (both were calibrated on quartz-coesite; a transition pressure of 31.6 kbar at 1100°C is accepted in Hobart whereas Mirwald and Masonne [17] place it at 31 kbar; this value is used in the diagram).
### TABLE 2

Results of experiments in belt apparatus

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time (hr)</th>
<th>Starting mix</th>
<th>Products b</th>
<th>Phase compositions (atomic proportions)</th>
<th>Ca</th>
<th>Mg</th>
<th>Ca</th>
<th>Mg</th>
<th>Ca</th>
<th>Mg</th>
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<td>C</td>
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<td>96.8</td>
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<td>1</td>
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<td>–</td>
<td>DI + MAG</td>
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<td>–</td>
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<td>C</td>
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<tr>
<td>92</td>
<td>850</td>
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<td>2</td>
<td>C</td>
<td>EN + DOL + (Di) + (Mag)</td>
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<td>C</td>
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</table>

a Mix C: En\textsubscript{33.3} Dol\textsubscript{16.7} Di\textsubscript{16.7} Mag\textsubscript{33.3}.
b DI = major phase, (Di) = minor phase.
Fig. 3. Approximate contours of compositions of magnesite coexisting with diopside, and, at the reaction (3) boundary, with dolomite and enstatite (see Tables 1 and 2). The effect of temperature is to increase the calcium content of magnesite and the effect of pressure is to decrease the calcium content.

At temperatures below ~1150°C the slope of the reaction is 55 bar/°C, i.e. consistent with the piston-cylinder determination. However, the 1300°C data do not fit this gradient but, with the 1200°C data, yield a slope of ~80 bar/°C above ~1150°C. The additional high-pressure, high-temperature data confirm that the magnesite-dolomite solvus is asymmetric, with magnesite containing considerable Ca in solid solution. An approximate P-T dependence of the solubility of Ca in magnesite can be obtained by combining our total data set with that of Irving and Wyllie [1], as shown in Fig. 3.

4. Discussion

The experimentally determined slope of reaction (3) up to 1150°C of ~52 bar/deg is very much higher than the ~21 bar/deg calculated by Eggler et al. [30] using the high-temperature entropies tabulated by Robie and Waldbaum [29]. Calculations using the 1-bar, 298-K molar volume and entropy data of Robie et al. [31] for this reaction and the Helgeson et al. [26] data for orthoenstatite molar volume and both ordered and disordered dolomite entropies, give ~32 and ~57 bar/deg for the slope of reaction (3) for ordered and disordered dolomite, respectively. Although the slope using disordered dolomite is very similar to our experimental value of ~52 bar/deg up to 1150°C, we believe this to be coincidental. The calculated values of ΔS₁,₇ for reaction (3) are of the same order as the error bars given for the entropies and heat capacities of these minerals. In view of our own information and previous work on dolomite ordering [14,19,23] we consider that up to ~1150°C the dolomites in our experiments remains ordered.

The increase in slope of reaction (3) evident from the Mainz belt apparatus data (~55 to ~80 bar/deg) could reflect the onset of disordering in dolomite above ~1150°C. The increase in entropy due to order-disorder of ~2.75 cal/mole K (data of Helgeson et al. [26]) compares well with a value of ~3.1 cal/mole K calculated from our experimental data. This agreement may be coincidental inasmuch as only part of the entropy change may be due to cation disordering, and other contributions may arise from anion rotation [19].

The position of univariant reaction (3) is consistent with the wide brackets (1200–1400°C) at 50 kbar given by Kushiro et al. [12], but there is a 10-kbar difference at 1000°C. This discrepancy is attributed to an uncertainty in pressures measured in the tetrahedral pressure apparatus at low pressures and possible metastable run products (enstatite and dolomite) produced from enstatite and calcite starting mixes used by Kushiro et al. [12]. We consider that our reversed experimental results establish the position of this important f₃CO₂-independent silicate-carbonate reaction.

The location of the carbonation reaction (2) has not been well determined experimentally [24,25]. Our data for reaction (3) can be combined with the well-bracketed experimental data for reaction (1) of Newton and Sharp [6] and Eggler et al. [8] to
calculate the position of reaction (2). The above experimental data for the pure phases involved in reaction (1) at high $P$ and $T$ can be related to a 1-bar reference state by the relation:

$$\Delta G_{P,T} = \Delta G^\circ_{1,T} + (P - 1) \Delta V_s + RT \ln f^\circ_{CO_2},$$

where $\Delta V_s$ is the volume change of solids and $f^\circ_{CO_2}$ is the fugacity of pure CO$_2$. Molar volumes of solid phases are taken from Robie et al. [31] except that of orthoenstatite which is from Helgeson et al. [26]. The fugacity of pure CO$_2$ ($f^\circ_{CO_2}$) at the $P$ and $T$ of interest was obtained from the tabulations of Bottinga and Richet [27] instead of the MRK values of Holloway [32] which were used in similar calculations by Eggler et al. [8] for reaction (1). The resultant least squares fit to these data gave:

$$\Delta G_{P,T}\text{cal} = 19526 - 39.72 \ T(K)$$

$$-0.3705(P - 1)\text{bar} + RT \ln f^\circ_{CO_2} \quad (A)$$

Our experimental data for reaction (3) in the temperature range 850–1100°C can be described by the equations:

$$\Delta G_{P,T} = 4203 - 5.923T(K)$$

$$+ 0.11391(P - 1)\text{bar} \quad \text{(Hobart)}$$

$$\Delta G_{P,T} = 4586 - 6.355T(K)$$

$$+ 0.11391(P - 1)\text{bar} \quad \text{(Mainz)} \quad (B)$$

assuming pure phases up to 1100°C and the location of the reaction boundary to be defined by a straight line between the mid points of the 850 and 1100°C experimental brackets.

The above data can be combined to give the following equations to define the $P_{CO_2,T}$ location of reaction (2):

$$\Delta G_{P,T} = 34849 - 73.517T(K) - 0.85491(P - 1)\text{bar}$$

$$+ 2RT \ln f^\circ_{CO_2} \quad \text{(Hobart)}$$

$$\Delta G_{P,T} = 34466 - 73.085T(K) - 0.85491(P - 1)\text{bar}$$

$$+ 2RT \ln f^\circ_{CO_2} \quad \text{(Mainz)} \quad (C)$$

These data give $\Delta S_{P,T}$ of 73.517 cal/mol K for reaction (2), which lies within the range of $\Delta S_{1,1000}$ values of 71.96 and 75.75 cal/mole K calculated using ordered and disordered dolomite, respectively. These differences are within the errors associated with the calculations of the high-temperature entropies of these minerals. We are not optimistic that experimental reversals of sufficient accuracy could therefore be obtained on reaction (2) to discriminate the influence of order/disorder in dolomite at ~1100–1200°C.

Bottinga and Richet [27] showed that in thermodynamic calculations compressibility and thermal expansion should not be neglected. In addition we have considered compositional effects. The compositions of coexisting clinopyroxenes and orthopyroxenes as well as thermodynamic values for the estimation of $a_{CaMgSi_2O_6}$ were taken from Lindsey et al. [22]. The parameter for the calculation of $a_{MgSi_2O_6}$ for a regular solution model ($W = 34$ kJ) was taken from Holland et al. [18] and the same parameter was used to calculate $a_{MgCO_3}$ for magnesite inasmuch as in this phase (like in orthopyroxene) mixing properties are controlled mainly by the interaction of a small number of Ca atoms with surrounding Mg atoms. Furthermore, because olivine and gas phase are practically pure Mg$_2$SiO$_4$ and CO$_2$, respectively, and dolomites from our and Goldsmith’s [19] experiments are very close to
stoichiometric compounds we set:

\[ a_{\text{CO}_2} = 1; \quad a_{\text{Mg}_2\text{SiO}_4} = 1 \]

and:

\[ a_{\text{CaMg(CO}_3)^2}(P_2)/a_{\text{CaMg(CO}_3)^2}(P_3) = 1 \]

The compositions of magnesites coexisting with dolomites as function of temperature and pressure were derived from the experiments described in this paper and those of Irving and Wyllie [1] with the pressure correction suggested by Huang and Wyllie [39]. Interpolation between these two sets of data permitted to estimate a series of isobars plotted in Fig. 3. The volumes of solid phases were taken from Helgeson et al. [26] while compressibilities and thermal expansion are from Clark [40]. The thermal expansions for magnesite and dolomite were assumed to be the same as for calcite and the compressibility of magnesite was supposed to be the same as for dolomite. The position of reaction (2) was again calculated from the combination of reactions (1) and (3) with an iterative procedure. With this approach reaction (2) is found to occur at a higher temperature at any pressure (e.g. at 10 kbar by 10°C higher, 20 kbar by 15°C and 25 kbar by 20°C).

4.1. Stability of magnesite and dolomite along mantle geotherms

The calculated \( P_{\text{CO}_2}, T \) location of carbonation reaction (2), together with the experimentally determined location of reaction (3) are shown in Figs. 4 and 5. The positions of reactions (2) and (3) define the stability fields of carbonates in a mantle of lherzolite mineralogy (olivine + orthopyroxene + clinopyroxene ± spinel/garnet) containing a small amount of \( \text{CO}_2 \) (say < 5 wt.%) and \( \text{H}_2\text{O} \) (present only in hydrous phases). Cations like Fe, Al and Na do not seem to have a substantial influence on these reactions in lherzolitic compositions because of the basic agreement of this study with the results of Brey and Green [13].

In Fig. 5, reactions (2) and (3) are shown in relation to estimates of the earth's geothermal gradient. Estimates of the latter vary [33,34] but in areas not currently volcanically active, the ocean basin geotherm is steeper at shallower depths than the geotherm for old stable continental shield or craton areas [33,34]. The geotherm for continental crust which has experienced Palaeozoic or Mesozoic orogeny lies between these two estimates. Referring to Fig. 5, the shield geotherm lies entirely within the magnesite stability field but that for the “old” oceanic crust (i.e. > ~ 100 m.y. [33,34]) is within the magnesite stability field to depths of ~ 40 km and within the dolomite stability field at greater depths extending down to the
low-velocity zone (90–100 km, ~ 30 kbar). In regions close to mid-oceanic ridges, temperature distributions are related to mantle diapirism and magmatic emplacement, and very steep geothermal gradients enter the gaseous CO₂-stability field at shallow depths.

4.2. Stability of magnesite and dolomite on the mantle solidus

The nature of minerals stable at the solidus of the mantle at a particular pressure determines the character of the initial melt since compositions of melts are determined by cotectic or incongruent melting and solid-solution behaviour of the relevant mixtures of minerals, and by element partition coefficient between liquids and residual minerals. As noted in the introduction previous work had indicated that dolomite would be the stable carbonate mineral at the mantle solidus to depths of ~ 150–200 km. Referring to Fig. 5, the new data show that magnesite will occur at the solidus of a H₂O + CO₂-bearing mantle lherzolite at depths > 100–120 km. Dolomite may occur at the solidus only between ~ 80 and ~ 110 km. The solidus in this depth range is not well determined, the curves 2 and 3 in Fig. 5 reflecting uncertainty whether dolomite + amphibole coexist on the solidus (curve 2, D.H. Green, unpublished data) or dehydration of amphibole and decarbonation of dolomite occur below the solidus (curve 3 [10]).

In any particular crust-mantle section, the specific geothermal gradient as well as the mantle composition will determine whether or not the solidus is intersected. Estimates of the shield geotherm either do not intersect the solidus or intersect the solidus within the magnesite stability field at depths > 120 km. In our opinion, the near-solidus liquids at these depths (field K in Fig. 5) will be highly magnesian and enriched in incompatible elements but relatively low in CaO, Al₂O₃—it is inferred that these liquids will be kimberlitic, in equilibrium with olivine, pyroxenes, garnet, phlogopite and possibly ilmenite. The inference that these near-solidus liquids are highly magnesian is indicated by the liquidus relationships in the system calcite-magnesite at high pressures [1] (e.g. Fig. 4). The MgO/CaO ratio is about 1.3 of the first (carbonate-) liquid coexisting with a dolomite-rich magnesite. With increasing temperature magnesite and the coexisting liquid become drastically poorer in CaO. Thus for a composition of magnesite (Mg/Mg + Ca = 94–96) as it appears near the solidus of carbonated peridotite [13, table 4] the coexisting liquid has a MgO/CaO ratio of around 25, very much higher than the average MgO/CaO of 4–5 of kimberlites (e.g. [36,37]). The MgO/CaO of the (carbonate-) liquid varies only between 1 and 1.3 (very similar to that of primitive olivine melilitites—see e.g. [36], where dolomite is the liquidus phase in Irving and Wyllie’s [1] fig. 4.

Along the oceanic geotherm the solidus is crossed in the dolomite stability field and liquids are enriched in CaO (field OM in Fig. 5). We infer that this is the source region for olivine melilitites [13,28] and note the consistency of these P, T conditions with those deduced from experimental studies of olivine melilitite + H₂O + CO₂ [13,28] and related simple systems [10,11].

If any section through the mantle is anhydrous but contains CO₂ as a volatile species then the near parallel slopes of reaction (3) and the peridotite-CO₂ solidus (Fig. 5) may mean that magnesite will occur at greater depth on the solidus or that magnesite does not occur at the solidus at all and dolomite would remain the solidus carbonate at all pressures > ~ 25 kbar. The possible intersection of the solidus and reaction (3) is point I₀ in Wyllie’s [10] terminology. The weight of evidence favouring the presence of water in the source region of basaltic magmas (e.g. the presence of hydrous minerals in mantle xenoliths), and the difficulty in this model of producing a partial melt region at ~ 90–100 km unless geotherms are very steep, all argue against a peridotite-CO₂ model for the upper mantle.

The solidus shown for the pyrolite-CO₂-H₂O (peridotite C-O-H at f₀₂ sufficient to stabilize carbonate ± graphite) is presented as the appropriate solidus for the upper mantle and defines the fields of various mineral assemblages at the solidus. Along pyrolite solidus 1 the mineral assemblages are

1) olivine + orthopyroxene + clinopyroxene + amphibole ± plagioclase ± chrome-spinel to 10 kbar
Bearing in mind the composition of pyrolite, the abundance of the minor phases and the solubility of components such as OH\(^{-}\), CO\(_3\)^{-}, K, Na, Ti in basaltic (s.l.) melts, it is clear that phases such as amphibole, dolomite, phlogopite, ilmenite and magnesite must disappear at temperatures very close to the solidus.

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Garnet–orthopyroxene barometry for granulites and peridotites

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An experimentally calibrated geobarometer based on the solubility of alumina in orthopyroxene coexisting with garnet is presented. This geobarometer is based on experiments in the FeO-MgO-Al2O3-SiO2 and CaO-FeO-MgO-Al2O3-SiO2 systems performed at high temperatures and pressures (800–1200 °C and 5–20 kbar). Applying the geobarometer to a variety of natural garnet–orthopyroxene assemblages from granulate facies terrains and other occurrences, yields reliable and consistent pressure estimates for these samples.

Petrologists concerned with garnet peridotite xenoliths in kimberlitic diatremes have long recognized the importance of the solubility of alumina in orthopyroxene coexisting with garnet as a pressure (P)–temperature (T) indicator. More recently, petrologists have applied the garnet–orthopyroxene geobarometer to estimate the physical conditions of equilibration of crustal granulites. Earlier experimental calibrations of the variation in the alumina content of equilibrated orthopyroxene coexisting with pyrope as a function of P and T in the system MgO-Al2O3-SiO2 (MAS) have been used widely, in conjunction with other geothermometers, to construct 'palaeogeotherms' for mantle-derived garnet peridotites. More recent experimental data in the system MgO-Al2O3-SiO2 (FMAS) and CaO-FeO-MgO-Al2O3-SiO2 (CFMAS) systems, over a wide range in XMg (Mg/Mg+Fe) and XAl(Ca/Ca+Mg+Fe) bulk compositions at any one P–T condition, and at P–T conditions appropriate to the formation of crustal granulites (800–1150 °C and 5–20 kbar).

Thermodynamic treatment of garnet–orthopyroxene equilibria

The reaction buffering the alumina content of orthopyroxene coexisting with garnet may be written as

\[ \text{Enstatite (Mg,Tschermak's) + Pyrope = Orthopyroxene} \]

Enstatite

MgSi2O6 + MgAl2SiO4 = Mg3Al2Si3O12

Pyrope

Mg3Al2Si3O12

Orthopyroxene

Reaction (1) above is useful for geobarometry because of the large volume change involved (≈ 200 cal kbar⁻¹ mol⁻¹).

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The equilibrium condition for reaction (1) at a given pressure, P, and temperature, T, is:

\[ \Delta H^° - T \Delta S^° = RT \ln \left( \frac{x_{\text{Mg}}}{x_{\text{Mg}} + x_{\text{Fe}}} \right) - P \Delta V^° \]  (2)

where \( \Delta H^° \) and \( \Delta S^° \) are, respectively, the enthalpy and entropy changes of reaction (1); \( \Delta V^° \) is the standard molar volume change of reaction (1) at 298K; and the \( x \)s represent the activities of the components in orthopyroxene and garnet.

The aim of our experimental approach is to extract values of \( \Delta H^°_T \) and \( \Delta S^°_T \) from compositional data obtained over a P–T–X (composition) range. To do this we require an expression or value for \( \Delta V^° \), and a knowledge or model of the activity–composition relationships of the phases involved. While we recognize that full, explicit, thermodynamic models of the garnet and orthopyroxene solid solutions are desirable, and that site distribution data exist for orthopyroxene in some chemical systems, the nature of the data obtainable from the experiments presented here precludes the use of complicated multi-parameter solution models. A simpler approach which allows direct application to natural rock data has been pursued. Simple solution models applicable in the MAS and CMAS systems have been adopted, and essentially empirical curve-fitting parameters which describe the compositional dependences of Al-solubility in orthopyroxene in the Fe-bearing systems have been added. By taking the solid solution properties of the phases into account, the empirical terms have a similar form to terms describing non-ideal solid solution behaviour in more rigorous formulations.

In the MAS system, the activity of garnet is unity. Using the two-site model of Wood for orthopyroxene, and assuming that no Al enters the M2 site:

\[ a_{\text{Mg}}^{\text{Mg}} a_{\text{Mg}}^{\text{Fe}} = X_{\text{Mg}}^M (1 - X_{\text{Mg}}^M) Y_{\text{Mg}}^M Y_{\text{Al}}^M \]

Recent work indicates that some Al may enter the M2 site, however, the simpler model above is adopted to allow development of a practical geobarometer.

Following Wood and Banno, Mg-Al orthopyroxenes have been assumed to mix ideally at 1 bar, and non-ideal interactions at higher pressure have been arbitrarily ascribed to an excess volume of mixing term \( \Delta V_{BM} \). Substitution of this term, derived from available molar volume data, for the standard molar volume change of reaction (\( \Delta V^° \)), results in a P–T–dependent volume change of reaction, \( \Delta V^°_T \):

\[ \Delta V^°_T = -[183.3 + 178.98(X_{\text{Mg}}^M (1 - X_{\text{Mg}}^M)) \text{ cal kbar}^{-1}] \]  (3)

Thermodynamic models of the garnet–orthopyroxene equilibria in the FeO–MgO–Al2O3–SiO2 system have been used widely, in conjunction with other geothermometers, to construct 'palaeogeotherms' for mantle-derived garnet peridotites. More recent experimental data in the system MgO-Al2O3-SiO2 (FMAS) and CaO-FeO-MgO-Al2O3-SiO2 (CFMAS) systems, over a wide range in XMg (Mg/Mg+Fe) and XAl(Ca/Ca+Mg+Fe) bulk compositions at any one P–T condition, and at P–T conditions appropriate to the formation of crustal granulites (800–1150 °C and 5–20 kbar).
(reciprocal terms). While recognizing these complexities and that garnet is no longer a pure component, the effects of adding Fe to the MAS system have been ascribed to one, empirical, curve-fitting term which accounts for the variation of Al-solubility in orthopyroxene and is of the form:

\[ \Delta H_{ex} = W_{FeAl}(1 - X_{AI}^{M1})(1 - 2X_{AI}^{M1})X_{Fe}^{M1} \]

with

\[ X_{Fe}^{M1} = Fe/Mg + Fe \text{ in orthopyroxene and} \]

\[ X_{AI}^{M1} = Al/2 \text{ in 6 oxygen unit orthopyroxene} \]

Note that the \( W_{FeAl} \) parameter derived here is an empirical term only, and its magnitude is the net result of a number of effects in the orthopyroxene solid solution. Nevertheless, the \( \Delta H_{ex} \) term adequately describes the deviation of Al-contents of Fe-Mg orthopyroxenes coexisting with garnet from those of an Mg-orthopyroxene at the same \( P-T \) condition.

In the CFMAS system, further terms must be introduced to account for the decrease in alumina contents of orthopyroxenes with increasing Ca-contents of coexisting garnet. In comparison with the FMAS equation used above, where \( X_{Fe}^{M1} \) is left as unity, in CFMAS the equation is adjusted using two terms:

(1) A dilution term incorporated into the expression for \( lnK \)

\[ X_{Fe}^{M1} = (1 - X_{Fe}^{M1})^{3} \]

(2) An additional term derived from a ternary regular-symmetric solid solution model for Ca-Mg-Fe garnets, with the constraints obtained from other phase equilibrium experiments that Ca-Fe and Fe-Mg interactions in garnet are near-ideal in the \( P-T \) range of interest:

\[ RT \ln \gamma'_{Fe} = W_{CaFe}^{M1}[X_{Fe}^{M1}X_{Fe}^{M1} + (X_{Ca}^{M1})^{2}] \]

where

\[ X_{Fe}^{M1} = Ca/Ca + Mg + Fe, \text{ and } X_{Fe}^{M1} = Fe/Ca + Mg + Fe. \]

Note that this second term results in a derived \( W_{CaFe}^{M1} \) which is a curve-fitting parameter only, as the term \( (1 - X_{Fe}^{M1})^{3} \) rather than \( X_{Fe}^{M1} \), has been used for the mole fraction of garnet. Even though the derived \( W_{CaFe}^{M1} \) is an empirical parameter, the equations used here should give the correct form of Ca-Mg interaction in garnet.

Thus, in CFMAS an equation is derived which expresses the development of this equation has essentially relied on the application of compositional correction factors, derived from either the orthopyroxene (in FMAS) or the garnet (in CFMAS).

### Table 1: \( P-T \) estimates for garnet-orthopyroxene assemblages

<table>
<thead>
<tr>
<th>Locality</th>
<th>Description</th>
<th>Ref.</th>
<th>( T(\text{C}) )</th>
<th>( P ) (equation (5))</th>
<th>( P ) (other)</th>
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<td>Early Archaean coronites</td>
<td>47</td>
<td>625–700*</td>
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<td>Granulites around anorthosite</td>
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<td>Charnockites, mafic granulite</td>
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<td></td>
<td></td>
<td>67</td>
<td>3.5</td>
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</tbody>
</table>

* Garnet-clinopyroxene thermometer. † Garnet-orthopyroxene thermometer. ‡ Two-pyroxene thermometer. § Phase petrology constraints.
solid solutions, to a simple equilibrium relation applicable in MAS, and thus the derived parameters are partly empirical and may incorporate a greater number of more subtle effects in the solid solutions considered.

Experimental data on garnet–orthopyroxene equilibria

Equation (4) may be used in the reduction of experimental data obtained over a range of P-T-X mg(bulk) conditions, given that values of $X^\text{Al}_{\text{Mi}}$, $X^\text{Ca}_{\text{Mi}}$, $X^\text{Fe}_{\text{Mi}}$, and $X^\text{Fe}_{\text{Fe}}$ can be obtained experimentally. In this experimental study, two sets of experiments designed to obtain data sets for these compositional parameters have been undertaken:

1. Experiments in the system FMAS at a range of $X_{\text{mg}}$ values (=0.15, 0.30, 0.45, 0.50, 0.60, 0.70, 1.0), with bulk compositions appropriate to form garnet-orthopyroxene-quartz at a given $P$-$T$ condition. These have been performed with both almandine and Al-free enstatite mineral mixes ($X_{\text{mg}}$=0.33), and glass mixes seeded with 5% almandine or pyrope to promote garnet growth. It is considered that mineral-mix type starting materials constitute reverse mixes to glass starting materials, an assumption confirmed by analyses of orthopyroxenes grown from glass ($X^\text{Mi}_{\text{Ca}}$ decreases rimwards) and from enstatite seeds ($X^\text{Mi}_{\text{Al}}$ increases rimwards).

2. Experiments in CFMAS at $X_{\text{mg}}$=0.50 and over a range of $X_{\text{mg}}$ values (=0.02, 0.04, 0.08) so as to produce garnets of differing $X^\text{Ca}_{\text{Mi}}$ at essentially one $P$-$T$-$X^\text{mg}$ condition. In these experiments, glass starting materials with 5% almandine seeds have been used exclusively, and the effect of $X^\text{Ca}_{\text{Mi}}$ on $X^\text{Mi}_{\text{Ca}}$ has been evaluated by comparison of compositional data in this set of experiments with data previously obtained and reversed in FMAS.

All experiments have been performed in a Boyd-type, 1/2-inch, solid-medium, piston-cylinder apparatus. Temperatures were monitored by Pt/Pt90Rh10 thermocouples to within ±10°C of the set point during the prolonged run durations involved in ensuring subsolidus equilibration (4 days to 1 month, depending on the temperature). Pressures, monitored by Heise gauge, are believed to be accurate to within 0.5 kbar. All runs were of piston-in type, and a 10% friction correction has been applied to all nominal gauge pressures as tac outer sleeves were used. All samples were loaded into 3- or 4-bore Fe-metal or graphite capsules which were then sealed in noble metal outer capsules. Thus three or four mixes of differing bulk composition could be simultaneously run at one P-T condition.

Examples of the effects of $X_{\text{mg}}$ and $X^\text{Ca}_{\text{Mi}}$ on $X^\text{Mi}_{\text{Ca}}$, at various pressures for a given temperature, are illustrated in Fig. 1. The principal effects to be noted are:

$X^\text{Mi}_{\text{Ca}}$ decreases with increasing $P$ at constant $T$, $X^\text{Ca}_{\text{Mi}}$ and $X^\text{Fe}_{\text{Ca}}$

$X^\text{Mi}_{\text{Ca}}$ increases with increasing $T$ at constant $P$, $X^\text{Ca}_{\text{Mi}}$, and $X^\text{Fe}_{\text{Ca}}$

$X^\text{Mi}_{\text{Ca}}$ increases with increasing $X^\text{Ca}_{\text{mg}}$ at constant $P$, $T$, and $X^\text{Ca}_{\text{Mi}}$

$X^\text{Mi}_{\text{Ca}}$ decreases with increasing $X^\text{Ca}_{\text{mg}}$ at constant $P$, $T$, and $X^\text{Ca}_{\text{Mi}}$

The experimental data in FMAS, a total of 75 data points, have been fitted to equation (4), with $X^\text{Ca}_{\text{Mi}}$=0.0, yielding best-fit multiple and stepwise regression parameters as follows:

$$\Delta H^\text{f,T}_{\text{g}} = -5,650 \pm (250) \text{ cal mol}^{-1}$$

$$\Delta S^\text{f} = -2.93 \pm (0.30) \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$W^\text{f,T}_{\text{Fe}} = 5,157 \pm (200) \text{ cal mol}^{-1}$$

(= figures in brackets are standard errors at the 1σ level).

Compositional data in CFMAS at $X^\text{Ca}_{\text{mg}}$=0.60 have then been fitted to equation (4) using the parameter values above, to obtain a least-square fit value of $W^\text{f,Fe}_{\text{Ca}}$

$$W^\text{f,Fe}_{\text{Ca}} = 2,100 \pm (200) \text{ cal mol}^{-1}$$

Correction of equation (4) for excess molar volume terms in CaMg garnet\(^{22}\), leads to a value of 2,530±200 cal mol\(^{-1}\) for this empirical parameter, in reasonable accord with values of $W^\text{f,Fe}_{\text{Ca}}$ obtained in other studies\(^{24,25,27}\).

Equation (4) may now be rearranged into an equation expressing $P$ (kbar) in terms of $T$, $X^\text{Ca}_{\text{mg}}$, $X^\text{Mi}_{\text{Ca}}$, $X^\text{Ca}_{\text{Fe}}$, and $X^\text{Ca}_{\text{Fe}}$.

This equation is useful as a geobarometer in granulite facies garnet-orthopyroxene assemblages and in garnet peridotites:

$$X^\text{Mi}_{\text{Ca}} = 2,530 \pm 200 \text{ cal mol}^{-1}$$

$$W^\text{f,Fe}_{\text{Ca}} = 2,100 \pm (200) \text{ cal mol}^{-1}$$
Applications of garnet-orthopyroxene geobarometry

The garnet-orthopyroxene geobarometer developed here (equation (5)) has been applied to several well-documented examples of granulate facies metamorphics, and to low-Cr garnet peridotite xenoliths in kimberlites from South Africa. The results of these calculations are presented in Fig. 3 and Table 1, together with the $P-T$ conditions suggested by other workers for these samples on the basis of other geothermobarometric techniques or phase stability constraints.

Silimanite- or sapphire-bearing garnet-orthopyroxene assemblages reported from the USSR\(^{30,34}\) and Uganda\(^{36}\) yield $P$ estimates which are consistent with the stability of silimanite and with the stability of the assemblage orthopyroxene-sillimanite-quartz at 1,000°C (ref. 34). Granulites from the Enderby Land, Antarctica\(^{13}\), yield pressures of 7–9 kbar, consistent with the stability of silimanite in interlayered metapelites and with phase assemblages in associated aluminous granulites\(^{36}\).

Retrograde garnet-bearing coronas in meta-igneous granulites from several areas (Table 1) yield pressure estimates in the range 7–12 kbar, which is consistent with the reported incoming of kyanite in metapelites associated with these coronites in some areas\(^{37}\). Unrealistic or highly uncertain $P$ estimates are obtained, however, for some of these corona textures (for example, Adirondacks, Scourie). This may result from inadequacies in the experimental calibration at low Ca- and Fe-rich compositions, from the large errors inherent in the barometry at low $X_{Al}^R$ values, or from failure to obtain adjacent analyses of minerals in local equilibrium in otherwise zoned coronas. The Nain\(^{38}\), Labrador, granulites, which occur in a thermal aureole around an anorthosite pluton, yield an average pressure estimate consistent with pressures of 3.2 kbar recently obtained for these rocks from olivine-orthopyroxene-quartz equilibria\(^{39,40}\).

Granulitic and websteritic nodules from diatremes in southeastern Australia and the USA\(^{41–45}\) yield pressures of 12.5–16 kbar, which are in good agreement with pressures inferred by Irving\(^{46}\) for the equilibration of scapolite granulites from the Delegates, New South Wales. Spinel-garnet herzolite xenoliths from southeastern Australia\(^{52}\), estimated to have equilibrated at 25 kbar by O’Neill\(^{53}\) using the spinel to garnet peridotite transition as a barometer, yield pressures of 22–24 kbar using equation (5).

Comparison with most alternative pressure estimates considered here indicates that the experimentally derived geobarometer presented in equation (5) can be used successfully to estimate the pressures of formation and equilibration of garnet-orthopyroxene assemblages, provided a reliable temperature estimate can be obtained from other equilibria. Calculated pressures will, however, be heavily dependent on the deduced temperature. As in all geothermometry/geobarometry using several equilibria, it is also necessary to assume that closure temperatures are the same for the equilibria used.

We thank D. J. Ellis and C. Hatton for useful comments and K. L. Harris for his aid with the piston-cylinder apparatus. This work formed part of S. H.’s PhD research project at the University of Tasmania, and was supported by a Commonwealth of Australian Postgraduate Research Scholarship to S.H. and an ARGC grant to D.H.G.

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Equilibria in the Mg-rich part of the pyroxene quadrilateral

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ABSTRACT. Pyroxene phase relations in the Mg-rich corner of the pyroxene quadrilateral, at 1 atmosphere, have been reinvestigated. Experimental studies on sixteen selected compositions in the systems CMS and CFMS were undertaken in the temperature range 1100-1400°C. The results of this study clarify our understanding of the pyroxene stability relations at low pressure. In particular, the demonstration that there is a high-temperature stability field of orthoenstatite denies the existence of a stable (or real) invariant point defined by the reactions OE = PE + DI, PE + DI = PI, and OE + DI = PI, in the system CaMgSi$_2$O$_6$-Mg$_2$Si$_2$O$_6$. New phase relations, consistent with the experimental findings of this and other studies, for the Mg-rich corner of the pyroxene quadrilateral are presented. These new phase relations may be of use in interpreting the origin of volcanic rocks containing magnesian pigeonite.

A thorough understanding of the phase relationships of pyroxenes is essential to the interpretation of many igneous (and other) rocks. Establishing the equilibrium phase relations for pyroxenes involves not only experimental work but careful observation of the natural phase assemblages (Huebner, 1980). The occurrence of clinoenstatite (CE) in some high-Mg andesites (Jenner, 1981, 1982) is an excellent example of the interplay necessary between experimental and natural pyroxene studies. The crystallization of protoenstatite (PE) (clinoenstatite precursor: Tilley et al., 1964; Dallwitz et al., 1966; Nakamura, 1971; Huebner, 1980) over a limited compositional range and its replacement by orthopyroxene at a particular composition (cf. Dallwitz et al., 1966; Komatsu, 1980; Jenner, 1982) suggested that it may be possible to constrain the extrusion temperatures and to limit the conditions of parental magmas to the high-Mg andesites using knowledge of the stability relations of protoenstatite and orthopyroxene. Conversely, observed relations in high-Mg andesites have been important in deducing possible equilibrium phase relations in the pyroxene quadrilateral (Nakamura, 1971).

Recent uncertainty concerning the nature of the phase relations in the Mg-rich portion of the pyroxene quadrilateral (Huebner, 1980; Longhi and Boudreau, 1980) and the limited amount of data available on protoenstatite stability has necessitated a re-examination of phase relations on the enstatite-diopside join and in the system CaO-FeO-MgO-SiO$_2$ (CFMS).

Previous work and the nature of the controversy

Atlas (1952) studied phase equilibria in the system MgSiO$_3$-CaMgSi$_2$O$_6$ and also the polymorphism of MgSiO$_3$. Much of his work in the system MgSiO$_3$-CaMgSi$_2$O$_6$ was redone as part of a more comprehensive study by Boyd and Schairer (1964); however his determination of the orthopyroxene-protopyroxene transition temperature (985° ± 10°C) in the pure MgSiO$_3$ system has been confirmed by Anastasiou and Siefert (1972) and Smyth (1974).

The stability fields of Ca-poor pyroxenes in the system Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ are limited by the reactions schematically presented in fig. 1 (Warner, 1975; Mori and Green, 1975) and are related to the stability fields of orthoenstatite (OE), protoenstatite, and Ca-free high-temperature clinopyroxene (‘pigeonite’) in the system Mg$_2$Si$_2$O$_6$. The position of the invariant point A in CaMgSi$_2$O$_6$-Mg$_2$Si$_2$O$_6$ is estimated as 1.6 kbar and 1280°C (Warner, 1975; Mori and Green, 1975). This P-T location is subject to considerable uncertainty arising chiefly from inadequacies in conventional experimental techniques at low pressures and high temperatures. The location of invariant point A’ is not well constrained. The univariant reaction OE = PE (Mg$_2$Si$_2$O$_6$) passes through 1 bar, 985°C (see above) and the reaction PE = PI (pigeonite) may pass through 1 bar, 1400°C if the experiments in the Mg$_2$Si$_2$O$_6$-LiScSi$_2$O$_6$ system can be extrapolated to pure Mg$_2$Si$_2$O$_6$ (Takeuchi, 1978).
Phase relations in the pyroxene quadrilateral presented by Nakamura (1971) (see fig. 2) are consistent with the phase relations depicted in fig. 1, assuming the 1 atm. P-axis passes below invariant point A. That the 1 atm. P-axis would pass below A is inherent in the interpretation of experimental results by Warner (1975) and is consistent with the relations on the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ join as depicted by Boyd and Schairer (1964), Kushiro (1972), and Warner (1975; for P < 1.5 kbar).

Longhi and Boudreau (1980) re-investigated the system forsterite (Fo)-diopside (Di)-silica (SiO$_2$) at one atmosphere and suggested that there is an orthoenstatite liquidus field in this system. Foster and Lin (1975) had also noted the existence of an OE liquidus field in the same system. Longhi and Boudreau (1980) and Huebner (1980) presented reviews of the work by Yang and Foster (1972), Yang (1973), and Kushiro (1972), and concluded that these authors had also found evidence for the existence of an OE liquidus field; however misidentification of some of the low-Ca pyroxene phases had led to this field being overlooked.

Based on the interpretation of results from the liquidus studies Longhi and Boudreau (1980) and Huebner (1980) have suggested that the topology of the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ join at 1 atm. should be that shown in fig. 3. Longhi and Boudreau (1980) interpreted the OE field to extend from the liquidus to 1375°C (see fig. 3A), and to account for the existence of a high- and low-temperature OE field proposed that there was a bow-like shape for the PE+OE two-phase fields. Huebner (1980) proposed that two lines of evidence suggested that at low pressure OE is continuously stable from low temperature (< 1000°C) to the solidus (see fig. 3B). These are: (i) PE does not appear to be stable in the presence of augite at pressures > 2 kbar; and (ii) when natural magnesian orthopyroxenes are heated in the presence of augite, no protopyroxene was detected.

The topology of the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ join at 1 atm. as depicted in fig. 3A is inconsistent with a Schreinemaker's analysis of the pyroxene relations presented in fig. 1. The topology depicted in fig. 3B is inconsistent with a Schreinemaker's analysis of the pyroxene relations presented in fig. 1, if the invariant point A is real. However, if the invariant point A is metastable or unreal the phase relations at pressure > A and < A' are consistent with the topology of the Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ join as depicted in fig. 3B (cf. Warner, 1975; for P > 1.5 kbar).

**Present study**

**Experimental techniques.** Sixteen mixes were prepared by mechanical mixing of clinoenstatite (CE), enstatite (OE), diopside (Di), and hypersthene (HY) Mg$_2$Si$_2$O$_6$. Proportions of the end members were selected to produce (i) mixes of Mg-numbers 85,90,95 with 0.1,4 wt. % CaO; (ii) mixes of Mg-number 98 with 1,2,6 wt. % CaO; and (iii) mixes of Mg$_{80}$ with 4,6,8,15 wt. % CaO. Note that 1 wt. % CaO is equivalent to approximately 4 wt. % Di. During all stages of preparation mixes were ground to dryness under acetone a minimum of three times, in an agate mortar. Particle size in the resulting mixes was generally less than 10 microns, with 10-20 µm particles forming less than 5-20% of the mix.

Prior to the preparation of the mixes the pure phases were prepared from oxides, carbonate, or metal AR grade reagents. Details of the synthesis of the pure phases are given below.

Clinoenstatite was prepared by sintering a 1 g pellet of MgSiO$_3$ at 1300°C/1 atm. in a Pt crucible, for 48 hours. Minor amounts of quartz and olivine were present, as indicated by a routine X-ray diffractometer tracing. 300 mg of pure orthoenstatite was made by running CE at 15 kbar/1150°C for 6 hours in large capacity Ag$_{50}$Pd$_{50}$ capsules (3 mm diameter).

Diopside was prepared by sintering a pellet at 1300°C/1 atm. in a Pt crucible for 48 hours. The mix was well crystallized and no other phases were observed in the X-ray diffraction pattern. 300 mg of this Di was run at 10 kbar/1150°C for 5 hours in a large capacity Ag$_{50}$Pd$_{50}$
capsule to provide material for seeds, chemical analysis, and as a check on the 1 atm. product.

Hypersthene was prepared using a three-stage procedure. First, MgO, Fe$_2$O$_3$, and SiO$_2$ were dried for 3 hours at 600°C. Fe metal was then mixed in, and a pellet made. The resultant mix was run in an evacuated SiO$_2$ tube for 3 days at 1000°C, along with a pellet of 1.5 g of Fe metal to ensure no oxidation took place. The resulting product was poorly crystalline and very fine grained. 300 mg of well crystallized hypersthene was made at 20 kbar/1050°C by running the 1 atm. HY for 4.5 hours in Ag$_{85}$Pd$_{15}$ capsules.

Seeds of high-pressure OE and HY were added to the Mg$_{85-95}$ mixes in amounts such that the seeds were 10% OE and 30% HY contents respectively of the mixes. In the Mg$_{85-92}$ runs all the DI was from the high-pressure synthesis. The remainder of the components in the Mg$_{85-95}$ compositions and all components in other compositions were from 1 atm. sintered oxide mixes.

Run conditions. Fe-bearing runs were performed in
Fig. 3. Temperature-composition diagram for the system Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ at 1 bar. (a) Phase topology depicted by Longhi and Boudreau (1980). (b) Phase topology suggested by Huebner (1980). (Reprinted from fig. 7 (p. 235) of Huebner (1980), by permission of the Mineralogical Society of America.)

spec-pure Fe capsules sealed in evacuated SiO$_2$ tubes. OE-DI mixes were run in Pt capsules, which had been sealed by welding at the base and crimping at the top, in open SiO$_2$ tubes. Runs were made in either a 1 inch or ¾ inch 1 atm. furnace. A harness of Pt wire capable of holding three SiO$_2$ tubes, each containing up to three capsules, made it possible to run up to nine mixes at a time. The position of the hot 'spot' was checked before each run and temperature variation due to thermal gradients in the assembly and calibration is within ±5°C. The runs were drop quenched into a beaker of water.

Examination of run products. Each run was examined using three techniques: the optical microscope, SEM-microprobe, and X-ray powder camera. Optical mounts were made of crushed run products placed in refractive index oil. Emphasis in the optical work was on the detection of twinning, cracking, crystal morphology, and overall texture. The size and/or morphology of some phases, usually orthopyroxene, made it possible, in some runs, to positively associate chemical composition (from the probe) with optical properties.

X-ray camera patterns were obtained on needles made up of finely ground run products and gum tragacanth. An 11.54 cm Straumanis camera and Fe-tube were used. Identification of the phases was achieved in large part by comparison with films on standards of known composition. Standards used were: (a) natural CE separated from a high-Mg andesite from Cape Vogel, PNG; (b) synthetic OE and DI (conditions of origin described above); and (c) natural OE and DI (Mg$_{92}$) from a spinel lherzolite xenolith from Mt. Porndon, Victoria (N. Ortez, pers. comm., 1980). CE and Mg-rich pigeonite (PI) have indistinguishable X-ray powder patterns. PE was identified on the basis of the pattern given in Atlas (1952).

Probe mounts of run products were made either of small fragments or, in the case of some Ca-poor runs, a slurry of powder in resin had to be prepared first. A JEOL 50X-A SEM-microprobe with an EDAX energy dispersive system was used. Calibration of the system is described by Griffin (1979). High-pressure DI, OE, and HY were used to double check the calibration. PE is recognized by either the presence of its distinctive X-ray pattern or in the more general case by the presence of its lower temperature multiply-twinned inversion product CE. As noted, CE and PI have identical powder X-ray patterns (at least in the lines observable with our concentrations and techniques), therefore a combination of microprobe and XRD techniques is required. Thus observations and interpretations are related as follows:
Results

Attainment of equilibrium. One of the major difficulties hampering interpretation of the pyroxene phase relations in the Mg-rich portion of the pyroxene quadrilateral is that of knowing when equilibrium has been attained (Huebner, 1980). Subsolidus runs are particularly notorious for their slow reaction rates (Huebner and Turnock, 1980; Boyd and Schairer, 1964). Internal consistency, phase homogeneity, and results consistent with our knowledge of crystal chemistry are the major criteria which we have adopted in this study in recognizing or presuming the attainment of equilibrium (see also Huebner and Turnock, 1980). Run times for experiments were selected on the basis of previous experience in subsolidus (metamorphic) phase equilibrium studies (S. Harley, pers. comm., 1980). Experiments at 1300°C were run for 4 and 7 days with identical results being obtained.

Two series of Fe-bearing runs failed to meet the equilibrium requirements noted above. One series at 1100°C was run for 4 weeks; however original mix heterogeneities were present and these led to the development of quartz and olivine. These products were larger than anything in the original mix and presumably grew at the expense of the poorly crystalline hypersthene. Pure diopside and enstatite seeds were also noted.

A series of runs at 1200°C (2 weeks run time) showed phase homogeneity; however the results were inconsistent with those from higher temperature experiments in this study (see below) and also with the experiments of Longhi and Boudreau (1980), and the interpretation of Huebner (1980) (see above). In particular the three-phase assemblage PI-PE-OE was suggested to be present, based on X-ray, optical, and probe examination of the run products. This association would mark the CFMS univariant reaction OE + DI = PE + PI, which implies (fig. 2c, d) that the stability field of OE contracts to more Fe-rich Ca-poor bulk compositions. This conclusion is inconsistent with the presence of OE in Mg-rich bulk compositions in experiments at higher temperatures (see below).

Interpretation of the 1370°C and 1400°C runs in the Fe-free experiments was hampered by the presence of disequilibrium assemblages in some runs. For example, the 4% and 6% Di runs at 1400°C contain the assemblage CE (inverted PE) + OE, which with the increasing Di content would be expected to give way to OE and/or OE + PI. The 8% Di (1400°C) run however contains OE + CE + PI. A possible interpretation of this observation is that CE persists metastably in the presence of a high Ca-bearing phase, i.e. PI. This is consistent with the observation that OE increases in abundance from the 4% to 6% run and then decreases abruptly in the 8% Di run.

An attempt was made to reverse the reaction PI = DI + OE. Some of the run product from the 1370°C/15% Di run, which was homogeneous PI, was loaded in another capsule and run at 1280°C for 4 days along with an equivalent composition made up from 1 atm. sintered oxide mixes. Conditions for the run were estimated from our work and that of Warner (1975). The PI from the 1370°C run remained 'stable' at the lower temperature, while the sintered oxide mix showed signs of obvious disequilibrium, i.e. unreacted diopside seeds remained, and olivine and quartz appeared. According to Huebner (1980) (see also fig. 3a) the reaction PI = DI + OE occurs at about 1270°C and that of Warner (1975). The PI from the 1370°C run was loaded in another capsule and run at 1280°C and then decreases abruptly in the 8% Di run.

Table 1. Results of "equilibrium" subsolidus pyroxene experiments

<table>
<thead>
<tr>
<th>T(C)</th>
<th>Mix (wt.%)</th>
<th>Products</th>
<th>Composition'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>96En-40Di</td>
<td>CE</td>
<td>0.42 ((0.48-0.82) 27</td>
</tr>
<tr>
<td></td>
<td>(96 hours)</td>
<td>96En-10Di</td>
<td>0.21 (1.20-1.22) 5</td>
</tr>
<tr>
<td></td>
<td>96En-20Di</td>
<td>0.64 (0.34-0.81) 17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-30Di</td>
<td>0.14 (1.27-1.68) 17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-40Di</td>
<td>0.66 (0.36-0.77) 16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-50Di</td>
<td>0.14 (0.33-1.18) 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-60Di</td>
<td>2.30 (2.9-2.9) 14</td>
<td></td>
</tr>
<tr>
<td>1370</td>
<td>96En-10Di</td>
<td>OE</td>
<td>0.10 (0.82-1.17) 12</td>
</tr>
<tr>
<td></td>
<td>(96 hours)</td>
<td>96En-10Di</td>
<td>2.91 (2.98-3.24) 21</td>
</tr>
<tr>
<td></td>
<td>96En-20Di</td>
<td>0.94 (0.73-1.28) 9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-30Di</td>
<td>2.06 (2.06-2.35) 21</td>
<td></td>
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<tr>
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<td>96En-40Di</td>
<td>4.00 (2.74-3.38) 10</td>
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<td></td>
<td>96En-50Di</td>
<td>1.25 (0.68-0.90) 5</td>
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<td>96En-60Di</td>
<td>1.10 (1.38-1.48) 12</td>
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<td>96En-70Di</td>
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<td>96En-80Di</td>
<td>2.73 (2.18-2.30) 11</td>
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<tr>
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<td>96En-90Di</td>
<td>5.11 (4.68-5.61) 17</td>
<td></td>
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<tr>
<td>1300</td>
<td>96En-90Ca</td>
<td>CE</td>
<td>0.73 (0.68-0.80) 5</td>
</tr>
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<td>(148 hours)</td>
<td>96En-20Ca</td>
<td>1.10 (0.96-1.15) 14</td>
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<tr>
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<td>96En-30Ca</td>
<td>3.66 (3.32-4.18) 30</td>
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<td></td>
<td>96En-40Ca</td>
<td>0.9 (0.74-1.13) 16</td>
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<tr>
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<td>96En-50Ca</td>
<td>5.57 (3.4-5.3) 19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-60Ca</td>
<td>0.46 (0.74-1.22) 11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96En-70Ca</td>
<td>3.66 (3.34-3.77) 8</td>
<td></td>
</tr>
</tbody>
</table>

1 Identification based on X-ray, probe and optical examination.
2 Average CaO in wt. %.
3 n = number of analyses.
**Bulk composition.** It was difficult to check the bulk composition of an individual run because of the disaggregated texture of most of the runs. Fe loss to Pt capsules was a minor problem as indicated in Table I. Ca content of the mix was dependent on the thorough mixing and reaction of the diopside component to the mix. In general Ca contents appear to be slightly lower than expected in almost all runs, an observation attributed to persistence of diopside seeds. The difficulties in knowing the reacting composition of the mix would be a problem if we were dependent on only X-ray and optical analysis. However, with use of the microprobe we can determine the phase compositions and use these results to plot in the quadrilateral, rather than having to rely on an assumed bulk composition.

Results from experiments which met the criteria for having attained equilibrium are given in Table I and selected analysis of products are given in Table II. Details for specific run compositions or temperatures are given below.

\[ \text{Mg}_{600} = 1400^\circ \text{C}. \] The 4% and 8% Di runs were characterized by 20–30 \( \mu \text{m} \) sized crystals. Orthopyroxenes in the 6% Di run however ranged from 60–120 \( \mu \text{m} \) and may enclose low-Ca (PE or CE) crystals. The orthopyroxene is the low Ca-bearing phase, as determined by the X-ray pattern and lack of twinning.

The orthopyroxene is a stable phase in this temperature range and that its stability field extends from the \( \text{Mg}_2\text{Si}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6 \) join (CMS) into the CFMS pyroxene quadrilateral. The phase relations schematically given in fig. 4 are consistent with the experimental results and with the interpretation that the \( P = 1 \text{ atm.} \) axis passes above the invariant.

**Discussion**

The results of the 1300–1400\(^\circ\)C experiments of this study in the systems CMS and CFMS indicate that orthopyroxene is a stable phase in this temperature range and that its stability field extends from the \( \text{Mg}_5\text{Si}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6 \) join (CMS) into the CFMS pyroxene quadrilateral. The phase relations schematically given in fig. 4 are consistent with the experimental results and with the interpretation that the \( P = 1 \text{ atm.} \) axis passes above the invariant.

**Table II. Representative analyses of pyroxenes from 1 atmosphere CMS and CFMS experiments**

<table>
<thead>
<tr>
<th>T. °C</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO (mix)</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Mg no.</td>
<td>85</td>
<td>85</td>
<td>90</td>
<td>90</td>
<td>95</td>
<td>95</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>55.58</td>
<td>56.03</td>
<td>57.07</td>
<td>56.49</td>
<td>58.21</td>
<td>57.37</td>
<td>59.25</td>
<td>59.25</td>
</tr>
<tr>
<td>FeO</td>
<td>10.65</td>
<td>10.21</td>
<td>8.51</td>
<td>8.19</td>
<td>5.38</td>
<td>5.29</td>
<td>5.51</td>
<td>3.72</td>
</tr>
<tr>
<td>MgO</td>
<td>31.82</td>
<td>29.68</td>
<td>35.15</td>
<td>31.21</td>
<td>34.83</td>
<td>35.21</td>
<td>36.57</td>
<td>35.57</td>
</tr>
<tr>
<td>CaO</td>
<td>0.84</td>
<td>3.46</td>
<td>0.89</td>
<td>3.59</td>
<td>1.14</td>
<td>3.57</td>
<td>0.68</td>
<td>1.46</td>
</tr>
<tr>
<td>Mg no.</td>
<td>84.19</td>
<td>83.83</td>
<td>87.4</td>
<td>87.19</td>
<td>92</td>
<td>91.81</td>
<td>94.87</td>
<td>94.46</td>
</tr>
<tr>
<td>Ca:Mg:Fe</td>
<td>1.3/82.9/15.6</td>
<td>6.6/78.3/15.1</td>
<td>1.7/86.1/15.4</td>
<td>6.7/81.4/15.2</td>
<td>2.1/90.3/17.4</td>
<td>6.6/85.7/7.7</td>
<td>1.3/93.7/5.1</td>
<td>2.7/91.5/4.4</td>
</tr>
</tbody>
</table>

In general grain size increases from 10–20 \( \mu \text{m} \) in Ca-free runs to 30–50 \( \mu \text{m} \) in 4% CaO runs. Protoenstatite is the low Ca-bearing phase, as determined by the X-ray pattern and lack of twinning. The orthopyroxene is equigranular and has a well-defined X-ray pattern. Orthopyroxene is not obvious in the optical mounts having no distinctive morphology. Pigeonites have well-developed twinning.
point A in fig. 1. Referring to fig. 4, the temperature for the change from T1 to T2, i.e. the intersection of the PI stability field with the CMS boundary, is not fixed in this study since the three-phase assemblage OE + DI + PI was not encountered. Results from the study of Huebner and Turnock (1980) indicate that the change from phase relations in T1 to those in T2 may take place at temperatures of 1230–1300 °C and a temperature of 1275 °C is indicated in fig. 3b. The reaction OE = PE + PI (fig. 1) will not be reached before melting takes place in either CMS of CFMS, and this reaction cannot therefore be used to construct possible phase relations beyond T2 (Huebner and Turnock, 1980; Longhi and Boudreau, 1980).

The experimental results and interpretation offered here are in agreement with those suggested by Huebner (1980) both for the CaMgSi$_2$O$_6$–Mg$_2$Si$_2$O$_6$ join (fig. 3b) and the solidus phase topology in the Mg-rich portion of the pyroxene quadrilateral (see his fig. 21a). This interpretation implies that invariant point A in fig. 1 is imaginary and hence also the reactions, among others, PE + DI = PI (Nakamura, 1971; Mori and Green, 1975) and OE = PE + DI (Atlas, 1952), do not occur in real P,T space.

Experimental evidence for the existence of the reaction OE = PE + DI comes from three studies, those of Atlas (1952), Boyd and Schairer (1964), and Warner (1975). Warner (1975) investigated the position of the invariant line OE = PE + DI at 1 kbar and 1240 °C; however he noted that the results are difficult to interpret since the assemblages he obtained in different runs are incompatible. Boyd and Schairer (1964) failed to locate the solvus boundary in the OE-rich side of the system OE + DI at temperatures of 1000–1250 °C because of reaction rates. Hydrothermal runs in the lower part of this temperature range were unsuccessful and they noticed that the presence of a flux in dry runs created problems. Atlas (1952) did a number of runs using LiF flux and glasses on the OE-rich side of the OE + DI join. His results are equivocal in many respects, for instance, he reported CE + DI + OE at 12.5% Di and 1135 °C in an experiment for 12 days; however, a run at 15% Di/1130 °C for 7 days gave CE + PE + DI and at 20% Di/1140 °C for 12 days only CE + DI are reported. Atlas (1952) noted a slight inflection in the OE-DI solvus at 1050–1100 °C and he suggested that along with his experimental results this implied the presence of the reaction OE = PE + DI. Note that Boyd and Schairer also choose to interpret their runs in this manner.

The experimental evidence for the existence of the reaction OE = PE + DI is certainly equivocal and the phase relations on the Mg-rich side of the OE–DI join are subject to interpretation. It is interesting to note that if the above reaction is accepted then the PE and/or CE phase would need to contain 5–12% Di (~1.2–3% CaO). This is difficult to reconcile with the chemistry of naturally occurring clinopyroxene in high-Mg andesites and the demonstration that the occurrence of clinopyroxene is sensitive to the Ca content (normative Di/Di + Hy) of the magma (Jenner, 1982). Based on the experimental results from this study it would seem that the lack of evidence for OE in the temperature range 1000–1235 °C is probably due to the persistence of metastable CE, in a manner similar to that observed in the 1400 °C experiments noted earlier.

**Conclusions**

Experimental studies in the systems CMS and CFMS have indicated that orthopyroxene is a stable phase at least up to 1400 °C. These results...
are consistent with the results from liquidus experiments in the forsterite-diopside-silica and andorthite-diopside-enstatite-silica systems at 1 atm. (Yang, 1973; Kushiro, 1972; Longhi and Boudreau, 1980; Huebner, 1980). The results can be interpreted to imply that orthoenstatite is a stable phase from \(< 1000 ^\circ C\) to \(> 1400 ^\circ C\) in the system CMS. This is consistent with the suggestion of Huebner (1980) and suggests that the explanation offered by Longhi and Boudreau (1980) for the existence of two separate temperature stability fields of orthopyroxene is unnecessary.

The experiments also demonstrate the existence of protopyroxene along the \(\text{MgSiO}_3-\text{FeSiO}_3\) join.

The experimental results were unfortunately not of great value in ascertaining the temperature of eruption of high-Mg andesites. The assemblage present in these rocks is not sufficient to pinpoint a point at which the liquidus of high-Mg andesites intersects the pyroxene solidus. Compositional rather than temperature control determines the appearance of clinoenstatite in high-Mg andesites (Jenner, 1982). However, the phase relations depicted in fig. 3 and their extensions to CFMS (fig. 4) may be of use in interpreting the origin of volcanic rocks which are richer in CaO, and either lack or contain magnesian pigeonite. These relations would then help in deciding on the water content/liquidus temperature for second-stage lavas found in some ophiolite complexes (cf. Duncan and Green, 1980a, b; Cameron, 1980).

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Empirical geothermobarometry for garnet peridotites and implications for the nature of the lithosphere, kimberlites and diamonds

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As a result of a study on the influence of Cr on geothermometry and geobarometry empirical garnet-orthopyroxene geobarometry has been refined. The applicability to simple and complex systems is demonstrated and the modelling procedure briefly outlined. The suitability of some geothermometers for application to garnet lherzolite xenoliths and their limits of precision are discussed. Fields of pressure-temperature estimates for garnet lherzolites from various provinces are shown. Low-temperature xenoliths (< 1050°C) give estimates in accord with a conductive geotherm for the continental lithosphere. African xenoliths (both South African and "off-craton" Namibian) record a distinctive pattern, exhibiting a "temperature discontinuity", where high-temperature xenoliths (> 1050°C) give near-isobaric estimates for a range of temperatures. The depth of this "temperature discontinuity" is shallower for off-craton than for on-craton suites. Similar patterns are indicated for suites from U.S.A. and the U.S.S.R.

The temperature discontinuity is interpreted as a geologically short-lived transient state, where the deepest parts of the lithosphere are in the process of adjustment to higher heat flux from below. At the highest temperatures recorded by those suites "wet" peridotitic solidi are intersected and thus the xenoliths record events, were P,T conditions may have allowed the formation of kimberlitic or strongly undersaturated magmas at about the depths of this discontinuity. This process is inferred to lead to thermal erosion of the base of the lithosphere.

The generation and subsequent crystallization of magmas at the base of the lithosphere is inferred to be the source for diamond formation. The distinctive pattern of high- and low-temperature xenoliths in relation to the diamond stability field shows the existence of a rather small "diamond window" between about 900 and 1300°C at 40–55 kb. This window exists only underneath old, stable continents with a thick lithosphere. If recent age determinations on diamonds are correct, this implies the existence of thick continental lithosphere with similar characteristics to present-day lithosphere in the Archean.

A model is presented arguing for hot, upwelling convection streams as a possible source of heat. The model implies differences in lithospheric development according to the speed of plates, carrying a continent: Continuous lithospheric thinning by thermal erosion for steady or very slow moving plates with the break-up of a continent and the formation of an ocean as one extreme, the continuous repetition of thermal erosion and growth on cooling (underplating) of the continental lithosphere as the other extreme for fast moving plates. The latter may be the cause of a number of complexities and heterogeneities both within the deep continental lithosphere as well as in the convecting mantle.

1. Introduction

Previous studies (e.g. [1–7]) have obtained experimental data and deduced thermodynamic or empirical models for garnet-orthopyroxene and orthopyroxene-clinopyroxene equilibria. These combinations of empirical and thermodynamic results have produced expressions which allow the use of the alumina content of orthopyroxene coexisting with garnet as a geobarometer and the relative Fe/Mg partitioning between garnet and orthopyroxene [8] or the width of the miscibility gap between ortho- and clinopyroxene (e.g. [9,3]) as a geothermometer. It is thus possible to use mineral
assemblages containing garnet and orthopyroxene (± clinopyroxene) to deduce P,T conditions of crystallisation. The P,T estimation equations are applicable to rocks in which MgO, FeO, CaO, Al₂O₃ and SiO₂ are significant components. One of the most interesting garnet-orthopyroxene associations is in garnet peridotite (olivine-orthopyroxene-garnet-clinopyroxene ± phlogopite ± Cr-spinel) a rock type occurring at moderate depths in the upper mantle and characteristic of mantle xenolith suites in kimberlites and of relatively rare, tectonically emplaced peridotite (± eclogite) terrains. Cr₂O₃ is a significant component in garnets from these peridotites, typical contents vary between 2 and 8 wt.% Cr₂O₃ replacing Al₂O₃ (Fig. 1).

Cr³⁺ also competes with Al³⁺ in substitution in coexisting pyroxenes. Experiments were performed in the systems CaO-MgO-Al₂O₃-SiO₂ (CMAS) and SiO₂-MgO-Al₂O₃-CaO-Cr₂O₃ (SMACCR) and in “natural” peridotite compositions in the pressure range 20–40 kbar and temperature range 1000–1400°C to evaluate the influence of Cr₂O₃ on relevant reactions. In this paper we focus on the implications from the application of the derived geothermobarometric expressions. Experimental data, methods and modelling procedure are outlined briefly, but are presented elsewhere in more detail ([10] and Nickel et al., in preparation).

2. Experimental approach and modelling procedure

The experimental method consisted of synthesizing garnet + orthopyroxene + clinopyroxene ± olivine ± spinel assemblages at known pressures and temperatures from sintered oxide mixes and crystalline material, followed by electron microprobe analysis of coexisting phases. Fig. 2 illustrates some of the data for the system SiO₂-MgO-Al₂O₃-CaO-Cr₂O₃ (SMACCR) in which assemblages at any one P,T condition demonstrate a correlation between Al content of orthopyroxene and Cr content of coexisting garnet.

By building on prior studies in CMAS, FMAS and CFMAS [4,6,11,12] and using thermodynamic/empirical models of the minerals involved, it is possible to deduce geobarometric relationships. Thermodynamic formalisms are useful in modelling those relationships, because they help in finding the compositional parameters and mathematical expressions required for successful reproduction of experimental data. The similarity of our modelling approach to previous studies enables us to use numerical values for parameters from the literature (e.g. W⁰CaMg [13], W⁰FeAl [6]). However, these models as well as ours involve a number of simplifications and many parameters (in particular non-ideality terms) represent a summing up of physically more complex relationships. The numerical coefficients thus are largely model-dependent and empirical and should not be confused with thermodynamic properties of minerals.

![Fig. 1. Histogram of the Cr content in gt (in wt.%) from garnet peridotite nodules. A total of 133 analyses from the literature is plotted [25–34, 36–40].](image1.png)

![Fig. 2. Plot of the mole fraction of Al in the M1 site of orthopyroxene ([Al-Cr]/2) vs. the Cr/Cr+Al ratio of garnet for some sets of experimental data at three P,T conditions in the system SiO₂-MgO-Al₂O₃-CaO-Cr₂O₃ [10].](image2.png)
These will have to be determined by other means (for a discussion of the problem see Wood and Holloway [14]).

The detailed experimental results and methods of the modelling procedures are shown elsewhere ([10] and Nickel et al., in preparation), but a brief summary is given here:

The reaction used for barometry is:

\[
\text{Mg}_2\text{Si}_2\text{O}_6 + \text{MgAl}_2\text{SiO}_6 \rightarrow \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}
\]

in orthopyroxene solid solution

\(= \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\) pyrope

in garnet solid solution

Using thermodynamic approaches similar to Wood and Banno [3] we derived for the system CMAS the geobarometric relation:

\[
P = (1/AV_A) \left\{ RT \ln K_A + 3(X^{gi}_{Ca})^2 W^{gi}_{CaMg} \right\}
- \Delta H_A + T \Delta S_A
\]

(1)

Unless stated otherwise the symbols have their usual meaning in thermodynamic formalisms [15], capital letter indices refer to the name of the reaction concerned, the indices “M1” and “M2” refer to the M1 or M2 position of orthopyroxene.

We have extracted values of \(\Delta H_A = -6047\) cal and \(\Delta S_A = -3.23\) e.u. from CMAS experimental data. A value of \(W^{gi}_{CaMg} = 3000\) cal is adopted from Wood and Nicholls [13], the expression \(\Delta V = -(183.3 + 178.98 X_{Al} (1 - X_{Al})/2)\) and \(\Delta S_{rec} = 52.1\) e.u. (“rec” refers to reciprocal reactions in garnet, applying the model of Wood and Nicholls [13]).

For natural rocks, \(\text{Fe}^{2+}\) has to be considered in barometric expressions. Using parameters derived by Harley and Green [6] (i.e. \(W^{gi}_{FeAl} = 5157\) cal, \(W^{gi}_{CaMg} = 2530\) cal and \(\Delta V = -(183.3 + 178.98 X_{Al} (1 - X_{Al})/2)\)) and eliminating the compositionally very small terms \(X_{Al}^M X_{Mg}^M\) and \((X_{Cr}^M)^2\) equation (2) becomes:

\[
P = \left(1/AV_A\right) \left\{ RT \ln K_D(A) - 3(X^{gi}_{Ca})^2 W^{gi}_{CaMg} \right\}
- \left[ 2(X^{gi}_{Cr})^2 - X_{Mg}^M X_{Cr}^M \right] W^{gi}_{CrAl}
- X_{Cr}^M X_{Cr}^M \left( \Delta H_{rec} - T \Delta S_{rec} \right)
- 3X_{Fe}^{gi} X_{Fe}^{gi} W^{gi}_{FeAl} W^{gi}_{FeCa}
+ X_{Mg}^M X_{Fe}^M W^{gi}_{FeAl} - \Delta H_A + T \Delta S_A
\]

(3)

The \(K_D\) for reaction (A) is defined as:

\[
K_D(A) = \left[\left(1 - X_{Cr}^{gi}\right)^3 \left(X_{Al}^{gi}\right)^2\right] 
\times \left[ X_{Mg,Fe}^{M2} \left( X_{Mg,Fe}^{M1} \right)^2 X_{Al}^{M1} \right]^{-1}
\]

(4)

and thus the experimentally calibrated barometric equation becomes \((P\ in\ kbar, T\ in\ K):\)

\[
P = \left\{ 1/ - \left[ 183.3 + 178.98 X_{Al}^M (1 - X_{Al}^M) \right] \right\}
\times \left\{ RT \ln \left[ \left[ \left(1 - X_{Cr}^{gi}\right)^3 \left(X_{Al}^{gi}\right)^2\right] \right] \right\}
\times \left[ X_{Mg,Fe}^{M2} \left( X_{Mg,Fe}^{M1} \right)^2 X_{Al}^{M1} \right]^{-1}
- 9000 \left( X_{Ca}^{gi} \right)^2 - 3400 \left[2 \left(X_{Fe}^{gi}\right)^2 - X_{Mg}^M X_{Cr}^M\right]
- X_{Fe}^{gi} X_{Ca}^{gi} (90853 - 52.17 T)
- 7590 X_{Fe}^{gi} X_{Ca}^{gi} + 5157X_{Mg}^M X_{Fe}^M + 6047 - 3.23 T \}
\]

(5)

The site distributions are calculated in the following manner:

\[
X_{Al}^{M1} = (Al - Cr - 2Ti + Na)/2
\]

Al occupancy of M1 in opx

\[
X_{Mg,Fe}^{M1} = 1 - X_{Al}^{M1} - Cr - Ti
\]
161

M1 sites occupied by Mg and Fe

\[ X_{\text{Mg,Fe}}^{\text{M1}} = 1 - \text{Ca - Na - Mn} \]

M2 sites occupied by Mg and Fe

\[ X_{\text{Mg}}^{\text{M2}} = [\text{Mg}/(\text{Mg + Fe})] \]

M1 sites occupied by Mg only

(according expressions for \( X_{\text{Fe}}^{\text{M1}} \), \( X_{\text{Mg}}^{\text{M2}} \))

\[ X_{\text{Ca}}^{\text{M1}} = [\text{Ca}/(\text{Ca + Mg + Fe + Mn})] \]

(according expression for \( X_{\text{Fe}}^{\text{M1}} \))

\[ X_{\text{Al}}^{\text{M1}} = [\text{Al}/(\text{Al + Cr})] \]

\[ X_{\text{Cr}}^{\text{M1}} = [\text{Cr}/(\text{Al + Cr})] \]

3. Evaluation of geobarometers and geothermometers

There is no independent experimental set against which to evaluate our geobarometric expression in the Cr-bearing system, but the applicability of the barometer in the system CMAS is demonstrated in Fig. 3, where the good agreement between estimated pressure from equation (5) and the reversed experimental data of Perkins and Newton [12] and Yamada and Takahashi [16] is shown. It should, however, be noted that detailed phase relationships in the system CMAS are very complex and the results of a further study in CMAS will be presented elsewhere (Nickel et al., in preparation).

The applicability of the barometer to the natural system has been investigated by two means: Firstly we have crystallised two natural peridotite compositions (Table 1) at 35 kbar over a temperature range from 1000 to 1400°C and analysed all phases present. Thus we obtained a set of 10 run products. The pressures estimated from equation (5) yielded a mean estimate of 35.5 kbar (1.6 kbar standard deviation). Further studies in the natural system at pressures up to 50 kbar (Nickel and Brey [17], and in preparation) indicate that the barometer gives good results even at those conditions, which are outside the experimentally calibrated range.

As a second method of evaluating the barometer we selected five garnet lherzolites from South African kimberlites, all of which yielded temperature estimates of 930–960°C (using Wells’ [9] equation), but had Cr₂O₃ contents of garnet ranging from 2 to 8 wt.%. Using a previous barometric expression (Wood [4], eq. 12 including the \((X_{\text{Cr}}^{\text{M1}})^2\) term as recommended for high Cr contents) these

TABLE 1

<table>
<thead>
<tr>
<th>Starting materials for experiments in the complex system</th>
<th>TP</th>
<th>TP+Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.51</td>
<td>46.76</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.35</td>
<td>5.27</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.75</td>
<td>2.31</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>FeO</td>
<td>7.38</td>
<td>7.26</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>CaO</td>
<td>4.97</td>
<td>4.89</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>NiO</td>
<td>0.43</td>
<td>0.42</td>
</tr>
<tr>
<td>Mg/(Mg + Fe²⁺)</td>
<td>88.8</td>
<td>88.8</td>
</tr>
<tr>
<td>Cr/(Cr + Al)</td>
<td>8.6</td>
<td>22.7</td>
</tr>
</tbody>
</table>
inclusions gave systematically different pressure estimates varying with Cr$_2$O$_3$ content from 33 kbar (low Cr$_2$O$_3$) to 27 kbar (high Cr$_2$O$_3$). A dependence of the pressure estimate from a chemical parameter of one phase suggests a systematic error. Equation (5) of this work gives consistent estimates of 37 ± 2 kbar for all nodules (Fig. 4).

Application of the Harley and Green [6] or Harley [18,19] barometer gives systematically lower pressure estimates than equation (5) of this work (in the order of 3–5 kbar). This effect is mainly due to the calculation of X$_{Al}^{M1}$ in opx. The quantity used by Harley [11,18] is defined as Al/2, whereas we prefer to use the expression corrected for other elements such as Ti, Cr, and Na (see above).

The accurate determination of the quantity of Al in the M1 site of orthopyroxene requires precise analyses of Al, Cr, Ti as well as Na. For very small amounts (< 0.5 wt.%) analytical uncertainties may distort the estimate and thus the estimated error of ±3 kbar may be somewhat higher at very high pressures.

Garnet-orthopyroxene barometry is very sensitive to temperature estimation; an overestimation of temperature will cause a P overestimation and vice versa. Differences in pressure estimates using different equations (Wood [4], Harley and Green [6], Harley [18], this work) are often much smaller compared to the differences in pressure estimates obtained using differing thermometers. In particular P, T estimates at high-P, high-T conditions then become very uncertain. This has been demonstrated most recently by Finnerty and Boyd [20], where the estimates for a suite of xenoliths from Thaba Putsa [21] differ at the extreme high-T, high-P end by as much as 400°C and 50 km depths.

The widely used orthopyroxene-clinopyroxene thermometer of Wells [9] is known to deviate systematically at low (< 900°C) and high temperatures (> 1400°C) from the experimental data in the system CMS [22,23]. This has been confirmed and the lack of a necessary pressure correction been shown in a recent study in CMS [7]. Further confirmation of this result comes from the experiments in the system SMACCR and the complex system (Fig. 5). Nevertheless, the application of the Wells [9] geothermometer to garnet lherzolite xenoliths shows that most of these crystallized at

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**Fig. 4.** Pressure estimates of five South African nodules (RVD-155, PTH 405, PTH 407, PHN 2767/1 and 1570 [21,27,28,30]) by the methods of Wood [4, eq. 12 including (X$_{Al}^{M1}$)$^2$ term] and equation (5) of this work vs. the Cr content of the coexisting garnet. All nodules have equilibration temperatures between 930 and 960°C [9].

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**Fig. 5.** Comparison of estimated temperature (by the method of Wells [9]) and experimental condition in simple and complex system [10].
conditions within the $P,T$ range where the estimates are accurate to within $\pm 100^\circ$C (cf. Figs. 6 and 7).

We have also applied the thermometer of Harley [8] to a large number of garnet lherzolite xenoliths from kimberlites. This has been done by an iteration procedure, where the temperature estimate (the Harley [8] thermometer is pressure dependent) has been refined until both pressure estimate via equation (5) of this work and temperature estimate were in agreement. The estimates obtained by this method have been compared to the estimates by the Wells [9] thermometer (Fig. 6). For the great majority of estimates there is an agreement within $\pm 100^\circ$C. There is an indication that the estimates by the method of Wells are systematically higher at $T_{\text{est}}$ (Wells) > 1300°C. This was expected in the light of the systematic errors of this thermometer discussed before. However, there is also an indication that Harley’s [8] formulation yields higher estimates at low temperatures ($T$ (Wells) < 900°C), which contradicts the findings in the simple and complex systems ([7] and Fig. 5). This is not understood, but may have an explanation in the strong non-ideality of Fe behaviour in pyroxenes at low temperatures [24].

Future improvements in geothermobarometry are thus possible and necessary and will allow some further refinement. This work is in progress using a new experimental approach in the natural system in order to obtain reversible results for the most important chemical parameters ([17] and Nickel and Brey, in preparation). These refinements are likely to change the picture of $P,T$ distributions within the lithosphere somewhat at the low- and high-temperature ends of the presently estimated $P,T$ range, but are unlikely to change the overall picture of $P,T$ distributions as recorded by xenoliths from kimberlites and similar rock types using the Wells [9] thermometer in combination with the barometer described above.

4. Application of geothermobarometry and implications for the nature of the lithosphere

In Fig. 7 we illustrate the range of $P,T$ conditions calculated for xenolithic occurrences of garnet lherzolites and a few garnet pyroxenites from South
Africa, Namibia, U.S.S.R. (Siberia), U.S.A. (Thumb locality), Solomon Islands (Malaita), and Australia (N.S.W, Tasmania) [21,23,25-40]. Out of more than 160 xenoliths data we have excluded 5 samples from the representation of P,T regions. These are samples 1924 and 1925 of Nixon and Boyd [21], 6 and 16 of Mitchell [35] and XM 46 of Shee et al. [38]. The chemical data of these xenoliths (> 0.4 wt.% Na₂O in opx for samples 1924 and 1925 of Nixon and Boyd [21]) or other features (occurrence of ilmenite with large chemical grain-to-grain inhomogeneities in sample 16 of Mitchell [35]) suggest that they do not represent equilibrium assemblages or contain analytical errors. Accordingly these xenoliths give estimates not consistent with all other data points and usually give large discrepancies when applying different thermometers (Wells [9], Harley [8]). Sample XM46 of Shee et al. [38] is most probably a case where analytical uncertainties and uncertainties of the barometer play the most important role: This sample is very similar to XM48 of these authors (which is included in the P,T field for South African xenoliths), but the minute differences in element contents (< 0.06 wt.% for all oxides relevant for calculation of X^M of opx) combine in this particular case of a low-Al orthopyroxene (Al₂O₃ = 0.43 wt.%) to give a very high estimate (57 kbar compared to 52 kbar for XM48).

In Fig. 7 the fields of P,T distributions for the different geographic regions are shown in relation to various experimentally determined and extrapolated peridotite solidi [42-44]. In addition Fig. 7 shows the graphite-diamond boundary [41].

Xenoliths from South Africa and Namibia can be grouped into low- (<1050°C) and high-T (>1050°C) types. This grouping is not identical to a textural classification (sheared, granular). It has been shown in a number of localities that low-temperature xenoliths consist of both textural types [27,35,48,49]. In some African suites granular, coarse types seem to be restricted to the low-temperature group [21,25,30], but suites of xenoliths from U.S.A. [23,32] and Namibia [35] contain granular and sheared types, both of which cover the same P,T space. Thus there is no direct genetic correlation between textural type and equilibration condition.

Low-temperature xenoliths from South Africa lie close to the “Precambrian shield geotherm” of Clark and Ringwood [45] and extend into the diamond stability field at the high-pressure end. This geotherm is essentially one out of a large range of geotherms that may be calculated, assuming a conductive behaviour of the lithosphere and estimating values for conductivity and content of radiogenic elements in the lithosphere [50,51]. The near coincidence of the geotherm outlined by South African, Russian and Namibian low-temperature xenoliths argues for a very similar conductive behaviour of the lithosphere at least for old, stable cratons. Proterozoic lithosphere may, however, show similar characteristics as exemplified by the Namibian trend.

The remarkable feature of the new P,T determinations is that the high-temperature group of xenoliths sampled by kimberlites on the South African craton indicates essentially a single pressure (48–52 kbar, equivalent to 150–160 km depth) but covers a temperature range from 900° to 1400°C. The incorporation of corrections for Cr₂O₃ contents for garnet and pyroxene and the experimental confirmation of the suitability of the Wells [9] geothermometer for temperature estimation establishes a distinctive P,T distribution which implies a temperature “discontinuity” at 48–52 kbar at the time of sampling or crystallization.

Such a temperature discontinuity is also developed in garnet lherzolite xenoliths from “off-craton” olivine mellite and kimberlitic diatremes in Namibia [35]. Low-temperature xenoliths lie again close to the Clark and Ringwood [45] geotherm and are accompanied by high-temperature near-isobaric (ca. 35–40 kbar) xenoliths covering a range of temperatures. Similar to these high-T xenoliths the suite of xenoliths from off-craton minette in western U.S.A. [23,32] gives near isobaric estimates at the same level. Thus these xenoliths may be interpreted to reflect a “temperature discontinuity” coinciding with the Namibian samples but lacking the low-temperature limb.

It may be inferred that it is a characteristic of garnet lherzolite suites from old, stable cratons to have a “temperature discontinuity”—if any—at deep levels, while younger continental lithosphere may show this at shallower levels. A P,T distribu-
tion similar to South African samples is also indicated by garnet lherzolites from the Siberian craton [26,39], however, the distinctive isobaric high-temperature group is lacking or only weakly developed at somewhat higher pressures (approximately 55 kbar).

Further suites of garnet lherzolite xenoliths from southeast Australia, Malaita (Solomon Islands) and Canada (Ile Bizard) [33,36,37,40] lie on “oceanic geotherms” inferred for oceanic lithosphere [46,50,52].

Our new expression for geobarometry confirms previous conclusions (e.g. [21,35,48,53]) on the distinctive characteristics of different mantle xenoliths suites and yield, we believe, a more accurate (+3 kbar) estimate of their conditions of crystallization. The “temperature discontinuity” fills the gap between stable-continent and oceanic geotherms. This may represent a link between convective (“oceanic”) and conductive (“continental”) geotherms. Such a transient link or discontinuity can be envisaged within the framework of continental drift, plate tectonics and convecting mantle models in the following way.

A “cool”, purely conductive shield geotherm as outlined by the low-temperature South African, Namibian and Siberian data defines a $P,T$ distribution which either does not intersect the lherzolite-$H_2O$ solidus or marginally intersects it at depths > 150 km. If the earth’s LVZ is correctly attributed to very small degrees of partial melting and the mantle solidus is that defined by lherzolite-C-H-O [42,43,54–56] then a cool shield geotherm produces a thick lithosphere (> 150 km) and a very deep LVZ beneath old shield regions (e.g. parts of pre-Mesozoic Gondwana). If the continent overrides a heat source, the lithosphere will have to adjust to the new conditions. This adjustment will cause a transient discontinuity at the base of the thick “shield” lithosphere. Heat transfer from the underlying hot mantle will raise temperatures in the deep continental lithosphere so that progressively regions of this overlying lithosphere will be raised above the solidus and the lithosphere thinned by “thermal erosion”. In a very early stage tension within the overlying lithosphere may encourage fracturing to tap the melts present and the mantle xenoliths suites sampled will record both a geologically short-lived “boundary layer” of “adjusting” high-temperature xenoliths and the previous history by sampling “unadjusted” low-temperature xenoliths at shallower levels.

The heat source is debatable and may be attributed to different processes. A simple diapir model with xenoliths coming from a thermal aureole [35] could be put forward, but lacks a genetic interpretation. A continent overriding a hot-spot is also a likely situation. However, it is also possible to envisage a scenario where continents override convection cells. If a continent moves over a convecting system and moves over a “hot” upwelling stream, characteristic for “oceanic” conditions (as an example the geotherm $PJ$ [47] in Fig. 7), the process described above may also be initiated. As a consequence of this model we would expect that the initial magmatism may be of kimberlitic type, but the magmatism during the following stages may reflect distinctive continental (K-rich, Ti-depleted, Na-depleted) characteristics and progressively the imprint of “normal” oceanic (both MORB and oceanic island or “Hawaiian” geochemistry) via the establishment of an oceanic LVZ will be seen as the thinning of continental lithosphere continues.

Depending on speed and direction of the continent relative to the “upwelling stream” the continental lithosphere may move over colder regions and begin to thicken again (underplating). If the speed is too slow and the continent is more or less stable over the upwelling stream the continent may break up, and an ocean may develop. For continents which fail to break and are subject to continuous drifting we thus envisage a history of repeated “thermal erosion” and “underplating” periods which will induce a number of complexities and heterogeneities in the deep continental lithosphere (Fig. 8). For example, a period of thermal erosion will give rise to a differentiation process, where melts generated within the deep lithosphere are either placed into higher levels of the lithosphere, erupt at the surface or are lost to the convecting mantle. Melts may also come from the convecting (primitive?) mantle, which will yield different chemical/isotopic imprints. If such magmas generated in the convection stream are lost to
the continental lithosphere, then parts of the mantle material continuing to convect become “depleted”. Magmas generated either within the deep lithosphere or the convecting mantle, which fail to reach crustal levels and crystallize at depth may cause metasomatic events due to processes similar to those described in spinel lherzolites [57]. Igneous rocks or precipitates thereof, at one time welded to the deepest parts of the lithosphere may be reactivated at another time and either be brought into the lithosphere (again having a very different chemical/isotopic imprint) or may even be lost from the lithosphere and transported along with the convection stream. This way another chemical/isotopical heterogeneity (“enriched mantle”) could be introduced into the convecting mantle. Thus a process like repeated lithospheric thinning and underplating could be responsible for the creation of a large number of chemically/isotopically distinct reservoirs.

The new estimates of \( P,T \) distributions in the continental lithosphere give clues to the location of the base of the lithosphere. The base of the lithosphere was at one stage located at about 150 km beneath the South African craton as indicated by the temperature discontinuity. The maximum possible thickness of the continental lithosphere may, however, not be inferred from this discontinuity but will be defined by the intersection of the conductive “cold” geotherm defined by low-temperature xenoliths and the peridotite solidus. As may be seen from Fig. 7 the location of the solidus
at great depths (> 120 km) is experimentally controversial, will depend on the amount and composition of vapor species and has very large uncertainties in the lack of high-pressure data (the lines for small amounts of water + C-species in Fig. 7 are mere extrapolations from comparatively low-P data). Within these uncertainties it is entirely possible to equate the maximum depths of the lithosphere with the inferred base of the LVZ in oceanic regions [52], the maximum thickness thus may never have exceeded 200 km by a large margin, but was subject to frequent changes.

5. Implications for the genesis of kimberlites and diamonds

Models for the genesis of kimberlite may be seen in the light of the model outlined above. Independent of the geodynamical explanation for the source of heat the P,T determinations show that at least temporary conditions existed beneath South Africa, where a peridotitic source would melt in the presence of enough H$_2$O + other volatiles. The volatile-rich character of kimberlites argues for the availability of volatiles in the source region of kimberlites.

The liquidus of an average kimberlite composition from South Africa at about 160 km is in the vicinity of 1500°C, depending on $X_{\text{CO}_2}$ and the amount of volatiles present [58]. The near-liquidus phases of kimberlite are those of a peridotite (olivine, orthopyroxene, clinopyroxene and garnet for $X_{\text{CO}_2} = 0.5$ at approximately 1500°C, 55 kbar [58]). These conditions are consistent with experimental studies on peridotite in the presence of small amounts of water [42,52] and the assumption that kimberlite is formed as small amount (in the order of 1%) of partial melt of such a source rock [59]. Thus these conditions may be inferred for the generation of the South African kimberlites from a peridotitic source. Alternatively Brey [60] argues for a peridotitic source inside the magnesite stability field as a source region for kimberlites. In the light of the experimental data obtained recently by Brey et al. [61] on the dolomite/magnesite boundary this would imply that the temperatures required to form kimberlite are not as high, but are within the range of temperatures actually recorded by the garnet lherzolites from South Africa, i.e. 1250–1300°C at about 50 kbar.

The inferred conditions put constraints on the genesis of diamonds. Most of the high-temperature xenoliths from South Africa indicate conditions outside the diamond stability field. Any form of carbon would be concentrated into the melt in the form of a CO$_2^+$-ion because of the high solubility of CO$_2$ in undersaturated magmas [62,63]. If a kimberlitic magma is, however, injected into the adjacent wallrock or crystallizes at the base of the lithosphere ("magmatic underplating") under sufficiently low $f_{\text{O}_2}$, C would crystallize as diamond. Inclusions in diamond may reflect early crystallizing phases of the diamond precipitating magma [64]. Low $f_{\text{O}_2}$ conditions are necessary for the crystallization of diamond rather than carbonates and may be responsible for the high Cr content of olivines from diamond inclusions, which most probably contain some Cr$^{2+}$ [65,66]. Inclusions in diamond are sheltered from re-equilibration with the further crystallizing magma, retaining the refractory character of the initial precipitates. In rare cases a diamond precipitating magma may crystallize after injection into the wallrock, equilibrating completely with the wallrock under sub-solidus conditions. This could account for the rare occurrences of diamonds within a garnet lherzolite matrix [31,38,67]. In general diamond should more frequently be associated with megacrysts and other precipitates such as igneous eclogites, which is the case [67].

This model together with the constraints that the wallrock at levels shallower than about 145 km has ambient temperatures in accord with a conductive geotherm comparable to Clark and Ringwood's [45] and the data on the graphite-diamond inversion [41] predicts P,T conditions at which diamond may crystallize. These conditions are equated with the conditions of crystallization of lherzolite and eclogite xenoliths, some of which are diamond-bearing. Although the parent magmas to those crystallizing diamond may be initially at $T = 1500°C$, 55–60 kbar, diamond cannot begin to crystallize until about 1300°C, 55 kbar (see Fig. 7 for the relationship between diamond stability and
conditions of crystallization of xenoliths). Obviously the diamond precipitating magmas cannot cool below ambient conditions, i.e. 900–970°C at 40 kbar. Thus considering the range of \( P,T \) conditions defined by South African (and Russian) lherzolite xenoliths, there is a “diamond-window” of 900–1300°C and 40–55 kbar. These conditions are close to the diamond-graphite boundary.

Temperature and pressure estimates for inclusions in diamond are problematic because a full set of minerals required to give an estimate via the method outlined above is rarely present in one diamond. However, temperature estimates by methods other than two-pyroxene thermometry do show the expected range [38,66,68] and the presence of both graphite and diamond within single eclogites of inferred igneous origin [69] suggests conditions close to the graphite-diamond inversion.

It should be noted that the diamond formation is in the context of this model envisaged to be part of a rather slow crystallization process and thus implies that diamonds brought to the surface should be xenocrystic to the host magma, because the primitive character of the sampling kimberlites found at the surface makes it unlikely that these magmas have undergone fractionation to a large degree. The xenocrystic origin is supported also by differences between apparent ages of diamonds and host rocks [70].

This diamond window also places limits on the geographical distribution of diamond-bearing igneous rocks. The relatively low temperatures required for the formation of diamond at these depths exist only in areas with a thick lithosphere and these are in general areas of very old cratons. Younger parts of continents have generally a thinner lithosphere with higher ambient temperatures at equal depths, prohibiting the crystallisation of diamond. An interesting aspect of this model is that it implies a rather cold, thick continental lithosphere even in the Archean, if age data obtained from diamonds [71] are correct. In order to preserve the diamonds beneath the locations where these old diamonds are found, the continental lithosphere there may have been thicker, but should never have been thinner than 120–150 km since the Archean.

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THE LIQUIDUS SURFACE OF THE SYSTEM FORSTERITE–NEPHELINE–SILICA AT 28 kb

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ABSTRACT. The system forsterite–nepheline–quartz is a simple system analogue to natural basalts in that it includes liquid compositions that range from quartz-normative to nepheline-normative and includes the major mantle mineral phases forsterite and enstatite as refractory phases. The liquidus surface at 28 kb, vapor-absent conditions, contains three invariant points:

\[ \begin{align*}
& \sim 1365^\circ C: 'O' \text{ at } \text{Fo}_{77}\text{Ne}_{77}\text{Qz}_{16}: \text{Sp} + \text{Liq} + \text{Fo} + \text{Ne}_{ss} + \text{Liq}_2 \\
& \sim 1325^\circ C: 'K' \text{ at } \text{Fo}_{11}\text{Ne}_{67}\text{Qz}_{22}: \text{En}_{ss} + \text{Liq}_3 + \text{Fo} + \text{Jd}_{ss} + \text{Liq}_4 \\
& \sim 1290^\circ C: 'J' \text{ at } \text{Fo}_{6}\text{Ne}_{74}\text{Qz}_{20}: \text{Fo} + \text{Jd}_{ss} + \text{Ne}_{ss} + \text{Liq}_5
\end{align*} \]

J is a eutectic point marking the minimum temperature goal of liquids of "basaltic" or "peridotitic" parentage and is a strongly silica undersaturated liquid. Similarly, melts formed at "K" from a crystalline assemblage of olivine, enstatite, and jadeite (model mantle composition) are strongly nepheline-normative ("basanitic") and will only cross the olivine-albite join to enstatite normative compositions at high degrees of melting.

INTRODUCTION

Magnesian olivine, orthopyroxene, and clinopyroxene containing jadeite in solid solution are the major minerals of upper mantle peridotites. At pressures of 25 to 30 kb the three component system forsterite–nepheline–quartz contains liquidus fields of forsterite, enstatite, and jadeite and has been studied as a model for upper mantle melting behavior (Kushiro, 1968; Eggler, 1978; Windom and Boettcher, 1981). The join forsterite–nepheline–quartz is also one of the bounding joins of the simplified basalt tetrahedron (forsterite–nepheline–quartz–diopside) of Yoder and Tilley (1962). The earlier studies noted above (particularly the study of jadeite-enstatite and jadeite-forsterite joins at 28 kb by Windom and Boettcher, 1981) provided a basis for close examination of the solubilities of fluids in the C–H–O system at high pressures in liquids in this system and of the effect of dissolved volatile species on phase boundaries. However, in the course of this study (Taylor and Green, 1987), it became apparent that the inferred phase relations for the nepheline-rich part of the system (Windom and Boettcher, 1981) required confirmation. In this note we report new experimental data for this system at 28 kb and establish the liquidus phase boundaries for phases forsterite, enstatite, spinel, jadeite, and nepheline. The pressure of 28 kb is not *Department of Geology and Geophysics, Allahabad University, Allahabad, U.P. 211002, India
chosen randomly, it enables direct comparison with earlier work and is also the pressure for the top of the asthenosphere (29 ± 1 kb) based on intersections of geothermal gradients with the mantle peridotite-H$_2$O solidus (Green and Liebermann, 1976). As such it is a particularly appropriate pressure for studies of liquid compositions at small degrees of melting.

**EXPERIMENTAL METHODS**

Based on the studies of Windom and Boettcher (1981) and Taylor and Green (1987) it was possible to select four compositions lying in the area of the anticipated phase boundaries. The compositions prepared were (see fig. 1):

- FNQ-1: Fo$_{16}$Ne$_{70}$Qz$_{14}$ (wt percent proportions)
- FNQ-2: Fo$_{29}$Ne$_{19}$Qz$_{14}$
- FNQ-3: Fo$_{27}$Ne$_{71}$Qz$_{12}$
- FNQ-4: Fo$_{28}$Ne$_{55}$Qz$_{12}$

AR grade MgO, Al$_2$O$_3$, SiO$_2$, and a crushed Na$_2$Si$_2$O$_5$ glass or dried Na$_2$CO$_3$ were used to make starting materials. Na$_2$Si$_2$O$_5$ glass was prepared

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**Fig. 1.** Phase relations in the silica-undersaturated portion of the system forsterite-nepheline-SiO$_2$ at variable temperatures under 28 kb. Inset shows the position of the Fo–Ne–Qz plane in the Na$_2$O–MgO–Al$_2$O$_3$–SiO$_2$ system.

- Invariant points O, K, J.
- • Starting compositions; □ analyzed liquid (glass ± quench) compositions; ○ compositions from Windom and Boettcher (1981); ▽ composition used by Kushiro (1968), NFA-1.
by the method of Schairer and Bowen (1955). FNQ-2 and FNQ-3 mixtures were fused to glasses (checked for homogeneity by R.I. measurement) and crystallized at 900°C for 7 and 14 days respectively. FNQ-1 was prepared by sintering at 1100°C, crushing, and further sintering at 1100°C for 2 hrs. In the case of FNQ-4, Na$_2$CO$_3$ was used instead of Na$_2$Si$_2$O$_5$ glass. This mixture was heated gradually from low to high temperature and finally sintered at 1000°C for 12 hrs followed by further crushing and heating.

X-ray diffraction patterns for all mixes established the presence of forsterite, nepheline, albite, and no other identifiable phases. For experiments with FNQ-3 composition, 1 percent of seed crystals of jadeite (synthesized at 30 kb, 1000°C, 20 hrs) was used to promote nucleation of jadeite.

Experiments (table 1) were conducted in a piston-cylinder apparatus (Boyd and England, 1960) using piston-in technique and applying a pressure correction of —10 percent to the nominal load pressure.

Charges were examined optically and by electron microprobe analyses. The latter enabled us to determine the compositions of liquid in equilibrium with various phases. Microprobe analyses thus helped precise location of the phase boundaries and invariant points of figure 1.

**EXPERIMENTAL RESULTS**

Data are summarized in tables 1 and 2 and combined with previous data in the construction of the liquidus surface of figure 1. Kushiro (1968)

**Table 1**

Experimental runs in forsterite—nepheline—quartz

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T(°C)$</th>
<th>$P(kh)$</th>
<th>Run Duration (Mins)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fo$_7$Ne$<em>7$Q$</em>{14}$ (1)</td>
<td>1410</td>
<td>28</td>
<td>30</td>
<td>Fo + GI</td>
</tr>
<tr>
<td>Fo$_7$Ne$<em>7$Q$</em>{14}$ (1)</td>
<td>1380</td>
<td>28</td>
<td>40</td>
<td>Fo + Sp + GI</td>
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<tr>
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<td>1360</td>
<td>28</td>
<td>90</td>
<td>Fo + Sp + Ne$^2$ + GI</td>
</tr>
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<td>1360</td>
<td>28</td>
<td>35</td>
<td>Sp + Ne$^2$ + Fo + G1</td>
</tr>
<tr>
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<td>1340</td>
<td>28</td>
<td>25</td>
<td>Ne + ?Fo + G1</td>
</tr>
<tr>
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<td>1320</td>
<td>28</td>
<td>30</td>
<td>Ne + Fo + G1</td>
</tr>
<tr>
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<td>28</td>
<td>30</td>
<td>G1</td>
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<td>28</td>
<td>50</td>
<td>G1</td>
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<td>1330</td>
<td>28</td>
<td>60</td>
<td>Fo + Ne + Jd + G1</td>
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<td>28</td>
<td>40</td>
<td>Fo + Ne + Jd + G1</td>
</tr>
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<td>28</td>
<td>10</td>
<td>Fo + Ne + Jd + G1</td>
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<td>1500</td>
<td>28</td>
<td>10</td>
<td>G1 + Qn</td>
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<td>28</td>
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<td>Fo + G1 + Qn</td>
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<tr>
<td>Fo$_7$Ne$<em>7$Q$</em>{22}$ (3)</td>
<td>1440</td>
<td>28</td>
<td>15</td>
<td>Fo + En + G1 + Qn</td>
</tr>
</tbody>
</table>

Fo: forsterite; Sp: spinel; Ne: nepheline; En: enstatite; Jd: jadeite; Qn: quench crystals; GI: glass.

*present in minor amounts.
studied a mixture (Ne$_{62}$Fo$_{18}$Qz$_{20}$, fig. 1) under variable pressures at different temperatures in the absence of volatiles. According to his findings at 28 kb, forsterite appears as a liquidus phase at 1465°C followed by enstatite$_{ss}$, WB-1 to WB-11 (fig. 1) are the starting compositions studied by Windom and Boettcher (1981). They found that jadeite$_{ss}$ appears as a primary phase only in the composition WB-7, whereas enstatite$_{ss}$ is the liquidus phase in the compositions WB-1 to WB-6, WB-8 and WB-9. Forsterite and enstatite$_{ss}$ coexist with liquid in their runs at 1540°C in the mixes WB-10 and WB-11. We find forsterite as the liquidus phase at ~1495°C in FNQ-4 composition, and this, together with Kushiro’s composition, constrains the olivine-orthopyroxene cotectic to pass between WB-9 and FNQ-4, NFA-1 (see fig. 1). The boundary is further defined at lower temperature by glass or glass + quench analyses at 1490° to 1440°C (see fig. 1 and table 1). With the crystallization of jadeite as liquidus phases in WB-7 (Windom and Boettcher, 1981) and FNQ-3 (table 1) the peritectic point K is quite well located at 1325 ± 10°C (Windom and Boettcher, 1981) and composition Fo$_{11}$Ne$_{67}$Qz$_{22}$ (fig. 1).

With the crystallization of spinel in FNQ-1 and FNQ-2 the composition of liquid leaves the Fo–Ne–Qz plane and enters the system MgO–Al$_2$O$_3$–Na$_2$O–SiO$_2$ as ‘peralkaline’ liquid enriched in Na$_2$O, SiO$_2$ relative
to the plane. At 1365° ± 10°C when the liquid composition reaches the univariant line containing spinel, forsterite, and nepheline, spinel reacts with the liquid, and composition of the melt approaches the Fo–Ne–Qz plane. Spinel disappears as the liquid reaches the plane at the piercing point 'O' at 1365° ± 10°C. FNQ-2 contains nepheline, forsterite, and liquid at 1340° and 1320°C suggesting that the invariant point J must be <1320°C. The more siliceous composition FNQ-3 has a liquidus temperature at 1325° ± 10°C, at 1320°C contains forsterite, jadeite, and glass, and at 1280°C contains Fo, Jd, Ne, and minor glass. Analyses of glass establish the composition of the eutectic J at the inferred temperature of 1285°C in agreement with the observations of Windom and Boettcher (1981).

In table 2 we list microprobe analyses of jadeite and of enstatite. Jadeite is remarkably pure with only a very small MgO content equivalent to 2 mole percent enstatite solid solution. On the other hand enstatite contains 1.6 weight percent Na₂O equivalent to 10 mole percent jadeite solid solution and extensive (17 mole percent) Mg-Tschermak's solid solution. The latter solid solution means that enstatite lies off the Fo–Ne–Qz plane, and liquids coexisting with enstatite will move off the plane to the Na₂O, SiO₂-rich side in the Na₂O–MgO–Al₂O₃–SiO₂ system, that is “peralkaline” liquids. However, at the invariant point K, these liquids will react with enstatite to return to the plane and remain on the plane along the forsterite-jadeite cotectic (KJ).

CONCLUSIONS

Our experimental study closely defines the liquidus phase fields and invariant or piercing points in the Fo–Ne–Qz system at 28 kb. The forsterite-nepheline-jadeite eutectic (1285° ± 10°C) lies at an extremely silica-undersaturated composition Fo₅Ne₅Qz. This contrasts with the low pressure equivalent eutectic forsterite-nepheline-albite (1058° ± 5° at 1 bar) at Fo₃Ne₂Qz, and illustrates the effect of pressure in moving the silica undersaturated eutectic in the system to more undersaturated compositions.

The peritectic (piercing point) K marking the reaction

\[\text{enstatite + liquid} \rightleftharpoons \text{forsterite + jadeite} + \text{liquid}\]

at 1325° ± 10°C may be taken as a model for minimum melt compositions in peridotite containing olivine, orthopyroxene, and jadeite-bearing clinopyroxene. At 28 kb, this point lies at Fo₁₁Ne₆₇Qz₂₂, a composition that lies on the nepheline side of the Fo–Jd join and, in CIPW normative terms, is ‘basanitic’ with similar nepheline and albite contents. The dramatic shift from 1 bar melting relationships is illustrated by the composition of first liquid formed from forsterite, enstatite, and albite at 1 bar, that is, Fo₃Ne₁₂Qz₆₀ (1095° ± 5°C, Schairer and Yoder, 1961), a “quartz tholeiite” composition with normative quartz, albite and enstatite.

Because of the role of MgAl₂SiO₆ (Mg-Tschermaks silicate) solid solution in orthopyroxene, liquids derived from compositions on the Fo–Ne–
Qz plane will, at temperatures above 1325°C along the forsterite–enstatite cotectic, lie on the peralkaline (Na$_2$SiO$_3$-enriched) side of the plane.

Our experimental data are consistent with those of Windom and Boettcher (1981) and Kushiro (1968) and the choice of compositions together with microprobe analysis of quenched liquids allows the invariant points in the system to be much more closely constrained —

<table>
<thead>
<tr>
<th>Windom and Boettcher</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>K [Fo, En, Jd]</td>
<td>Fo$<em>{33}$Ne$</em>{53}$Q$_{14}$</td>
</tr>
<tr>
<td>J [Fo, Ne, Jd]</td>
<td>Fo$<em>{19}$Ne$</em>{65}$Q$_{12}$</td>
</tr>
<tr>
<td>O [Fo, Sp, Ne]</td>
<td>Fo$<em>{17}$Ne$</em>{74}$Q$_{6}$</td>
</tr>
</tbody>
</table>

The discussion of basalt petrogenesis and mantle melting by Windom and Boettcher (1981) remains relevant in the light of our new study, but the closer definition of phase boundaries will enhance the usefulness of this system for studies of the effects of volatiles on model mantle compositions at high pressures (Windom and Boettcher, 1981; Taylor and Green, 1987).

ACKNOWLEDGMENTS

We acknowledge the support for this research provided by Australian Research Grants Scheme support to D. H. Green, A. K. Gupta thanks the Australian Department of Science for support under the India-Australia Science Exchange Agreement. W. R. Taylor was supported by a Commonwealth Post-graduate Research Award. We are grateful for the assistance of K. L. Harris, W. Jablonski, J. Pongratz, and J. Beattie in maintenance of the high pressure laboratory, and of the electron microprobe, and preparation of the manuscript.

REFERENCES


but it nevertheless generates hot rising plume structures (seen as dark areas in Fig. 3a) that are not present in the \( \mu = 1 \) case (Fig. 2). The array of cold axial structures present in the initial temperature distribution persists for a short time (Fig. 3a), although their horizontal mobility appears greatly reduced by the newly formed hot plumes. This planform, consisting entirely of axial structures (both hot and cold) is, however, unstable for this heating mode. The number of cold sinking structures is soon reduced as neighbouring axial sinkers join together to form elongated cold sheet structures (Fig. 3b). This behaviour differs from the coalescence of blobs characteristic of the \( \mu = 1 \) experiment, in that the resulting sheets appear relatively stable and do not contract back into axial structures.

Although the flow velocity is greater, the evolution of this planform is generally slower than in the previous experiment, probably because the cold sinkers are kept apart by the hot plumes present here. Cold axial structures continue to coexist with elongated sheets for some time (Fig. 3b) but the general trend is for the cold sheets to continue to increase in length by the joining up of neighbouring structures. In some cases these joins are unstable and the structures thus formed break up, only to be replaced by an alternative arrangement (Fig. 3c, d).

Throughout this experiment the hot plumes form a stable class of structures, and their distribution and number evolve in a manner analogous to that of the cold blobs of the preceding experiment. The average horizontal separation between the hot plumes is, however, only about 1 of a plume per unit area (d²).

Towards the end of the experiment there are essentially four elongated cold sheets, three of which run along segments of the boundary (x = 0, x = 4 and y = 4, Fig. 3d). The structure is occasionally modified by the formation of a cold blob that appends itself to one of the cold sheets. Although there might be further evolution of the planform if the experiment were continued further it would probably be limited to a rearrangement of the structures present at the end of the experiment. Relative to the \( \mu = 1 \) experiment there has been a significant increase in the horizontal wavelength of the convection planform (the average horizontal separation between neighbouring structures of the same type), and it is possible that the side walls of the container prevent attainment of an even longer wavelength.

In summary, the two experiments described above have demonstrated a strong dependence of convection planform on the mode of heat input, for a constant viscosity layer with stress-free upper and lower boundaries. The steady-state planform of the internally heated experiment (\( \mu = 1 \)) is characterized almost entirely in terms of time-dependent cold columnar structures. With half of the heating from below (\( \mu = 0.5 \)) the cold structures appear primarily as elongated sheets, with hot axial plumes also present. In both cases the planforms are time-dependent and have evolved through several stages, to a point where the nature of the planform has stabilized, although individual features continue to change. Under these circumstances, it is unlikely that the choice of initial conditions has determined the nature of the final planform. The successive growth of different types of instabilities has eventually permitted selection of the most energetically favourable planform.

There is a clear need for further work, not only to consider the obvious cases of \( \mu = 0 \) and a larger container (for example a = 8), but also for a systematic survey to show the type of planform expected for different types of boundary conditions (for example, stationary or rigidly moving, instead of stress-free, upper boundary) and the influence of properties such as temperature or depth-dependent viscosity, less-than-infinite Prandtl number, or spherical rather than Cartesian geometry.

With respect to convection in the Earth's mantle, the \( \mu = \frac{1}{2} \) experiment is probably a closer approximation to reality than the \( \mu = 1 \) experiment; it is very likely that at least some of the heat input to the convecting layer comes from beneath. The resulting planform is also closer to what is inferred for the mantle circulation. In a simple parallel, the cold sheet structures of the experiment are the subduction zones of the Earth and the hot plumes are the cause of the hot spot traces found on the Earth's surface. Hot sheet structures rising from the base of the layer beneath ocean ridges are neither required nor expected. These parallels are perhaps coincidental in view of the many simplifications made in setting up the model (particularly the assumption of constant viscosity), but they suggest that the highly variable, possibly nonlinear viscosity of the Earth's mantle is perhaps not the major determinant of the mantle convection planform.

Finally, the timescale for the evolution of the planform in these experiments (the time unit \( d²/\kappa = 1.6 \times 10^{16} \) years even for \( d = 700 \) km) suggests that, for at least the first 10\(^8\) years, the planform of convection in the mantle was similarly evolving away from an initial state that was the outcome of the processes of planetary accretion and core formation. The convection planform of the Archaean may thus have had very little in common with the one evident at present.

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Measurement of reduced peridote-C-O-H solidus and implications for redox melting of the mantle

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Methane-bearing C-O-H fluids may be important carriers of carbon and hydrogen in the Earth's deeper mantle. It has been proposed that such fluids have a key function in the genesis of kimberlite magmas and diamond in the subcontinental mantle. Because the melting behaviour of mantle peridotite in the presence of C-O-H fluids has not been accurately located as a function of pressure, temperature and oxygen fugacity, it has not been possible to assess the validity of reduced fluid 'infiltration' models of this kind. We report here advances in high-pressure fluid buffering techniques that have allowed the C-O-H fluid-saturated solidus of a fertile peridotite to be determined to 35 kbar. The results show that initial melting of peridotite saturated with H₂O.C₂H₄ dominated fluids occurs at temperatures well above stable continental geotherms, even under quite H₂O-rich conditions. This implies that C-O-H fluid-induced melting beneath continents will be restricted to regions where CH₄ can be largely eliminated from...
the fluid by oxidation (redox melting) or where the geotherm is abnormally high (hot-spot melting), or where there is some combination of these processes.

The construction of realistic models for magma genesis in the upper mantle requires constraints on the mantle's compositional, thermal, and redox structure, combined with knowledge of the melting relations of upper mantle materials (peridotite). Geochemical studies constrain the physical properties of the upper mantle and geothermal studies provide constraints on the mantle's chemical and mineralogical composition, but these two aspects can only be linked by direct experiments at high pressure and temperature. The current debate over the oxidation state of the Earth's mantle has led to the recognition that oxygen fugacity (\(f_{O_2}\)) will be an important variable in magma genesis. Although the redox structure of the mantle is poorly known, a range of \(f_{O_2}\)s from above fayalite-magnetite-quartz to a lower limit near iron-wustite (IW) are probably appropriate. The nature of peridotite melting at the low \(f_{O_2}\)-end of this range, where \(H_2\) and \(H_2O\) are the dominant C-O-H volatiles and \(H_2\), \(C_2H_6\), \(CO_2\) are minor components depending on the temperature (\(T\)), has been the subject of some speculation.

In this paper we accurately locate the position of the peridotite-C-O-H solidus using a high-pressure fluid buffering technique that allows simultaneous control of \(f_{O_2}\) and water activity (\(a(H_2O)\)) on the graphite saturation surface at \(f_{O_2}\) near IW + 1 log unit.

The fluid buffer consists of a mixture of \(\alpha\)-WC, \(WO_3\), and graphite (WCWO) generated by reaction in situ of \(W\) metal, \(WO_3\) and C (mole ratio 29:1:60). C-O-H components are generated by pyrolysis of stearic acid (\(C_{28}H_{50}O_2\)). Peridotite of Hawaiian pyrolite composition minus 40% olivine \(^{11}\) with a bulk Mg/Mg + Fe\(^{2+}\) ratio of 0.87 was prepared as a sintered oxide mix. Samples were loaded into inner graphite capsules of 12 mg capacity and then sealed into \(Al_2O_3\) outer capsules of outer diameter 3.5 mm, together with ~170 mg of WCWO buffer mixture intimately mixed with sufficient stearic acid to generate ~3.5 mg C-O-H fluid. Talc outer sleeves were used in the high-pressure cell to contain the external \(f_{H_2}\) environment. The internal capsule design is such that fluids freely permeate both the sample and buffer.

Experiments to define the peridotite-C-O-H solidus were performed in 0.5-inch piston-cylinder apparatus using techniques described previously. Run times varied between 50 h for experiments at 1,050°C and ~10 h for 1,200°C and higher. After each run the quenched fluid phase was analysed by mass spectrometry/capsule-piercing technique, allowing \(CH_2/H_2O\) ratios to be determined. In all cases fluids were dominated by \(CH_4\) and \(H_2O\) components. The capsule-piercing device and method of analysis has been previously described. Analyses obtained by this procedure are dependent on machine-related variables (principal ionization cross-section and secondary electron yield), making spectrometer calibration necessary to obtain quantitative \(CH_4/H_2O\) ratios. Because such ratios may also have been subject to modification during quenching from high \(T\), calibration experiments were performed at 20 kbar, 1,100-1,200°C, using furnace assemblies and techniques as close as possible to those used in experiments with peridotite. \(CH_4\) - \(H_2O\) fluids over the range 0.8-0.1 \(CH_4/(CH_4+H_2O)\) were generated under pressure by thermal decomposition of \(n\)-hexacosane \((C_{28}H_{50})\) and \(Al(OH)_3\) mixtures. Additional calibration experiments were performed at \(f_{O_2} = 1W\) (ref. 6). Results show that measured \(CH_4/(H_2O)\) ratios are too low by a factor of 2.0 ± 0.4 for \(CH_4/(CH_4+H_2O)\) between 0.1 and 0.7. For \(CH_4/(CH_4+H_2O) > 0.7\), the correction factor approaches unity.

In Fig. 1, fluid analyses from experiments with pyrolite at pressures from 9 to 35 kbar are plotted as a function of temperature and corrected \(CH_4/(CH_4+H_2O)\) ratio. Water activities and reference buffer curves at 25 kbar were calculated from a modified Redlich-Kwong equation of state, calibrated for C-O-H fluid mixtures under upper mantle conditions of pressure and temperature. With the exception of four points that lie at very low water-rich compositions, analyses buffered by WCWO define a strongly temperature-dependent but pressure-insensitive line of best fit (\(R = 0.94\)) having the equation

\[ \log f_{O_2} (\pm 0.2) = 11.82 \pm 33.780/T + 0.066 \]

where \(T\) is in Kelvin and \(P\) is pressure in bar. The equation incorporates a pressure term calculated from molar volume data. Relative to IW, WCWO lies ~0.5 log units above at 1,000°C and ~1.3 log units above at 1,250°C.

Experimental results for the system Hawaiian pyrolite-C-O-H are presented in Fig. 2. The subsolidus region is dominated by a large amphibole stability field that is truncated by the solidus at pressures less than 20 kbar. At \(P<20\) kbar amphibole persists to 15-20°C above the solidus. Compositionally, amphiboles are \(Mg\)-enriched peridotite-C-O-H solidus.

Fig. 1 Fluid compositions analysed by mass spectrometry plotted in terms of \(CH_4/(CH_4+H_2O)\) ratio (calibrated) versus run temperature for pressures of 9-35 kbar. \(CH_4/(CH_4+H_2O)\) ratios are independent of pressure within the limits of experimental uncertainty. Dashed line is the curve of best fit to the data points (•); open circles are data points excluded from the regression. Also shown are the 25-kbar reference buffer curves for 1W + 0.5, 1W + 1.0 and 1W + 1.5 log \(f_{O_2}\) units and calculated water activities for \(P = 25\) kbar. The WCWO buffer is reproducible to within ±0.2 log \(f_{O_2}\) units. There are no alloying problems that limit the usefulness of WCWO as encountered with buffers such as iron-wustite-graphite.17 All fluid analyses were performed with a VG-micromass 7070F double-focusing mass spectrometer and out using a capsule-piercing device pre-baked at 150°C and evacuated to 10⁻⁷ torr.
temperatures than those in ref. 13 due to dilution of the fluid.
The graphite-present peridotite-C-O-H solidus surface may then be mapped out in P-T space. In buffered experiments this path may be quantitatively described if fluid compositions are known; in unbuffered experiments this path may be related in that both follow paths in a H2O-rich, their effect in depressing the peridotite solidus is not as marked as at lower pressures in that both CH4 and H2O appear to be important in determining melting temperature.

The shape of the peridotite-C-O-H solidus differs from that found under water-undersaturated conditions where the solidus 'back-bends' near 30 kbar as a result of a large change in a H2O over a small pressure interval due to amphibole breakdown. Because volatile activities are controlled and vary gradually and continuously, no back-bend of the peridotite-C-O-H solidus is observed. The solidi determined in both types of experiment are, however, related in that both follow paths in P-T-aH2O space. In buffered experiments this path may be quantitatively described if fluid compositions are known; in unbuffered experiments a H2O is undefined at pressures less than amphibole breakdown.

Using the regressed equation for WCWO and calculated activity coefficients for C-O-H fluid species, water activities may be determined along the experimental solidus (see Fig. 2). The graphite-present peridotite-C-O-H solidus surface may then be mapped out in P-T-aH2O space, given the bounds provided by the water-saturated solidus (a H2O < 1) (ref. 13) and volatile-absent solidus (a H2O ~ 0) of pyrolite (T. J. Falloon, unpublished results). The water-saturated solidus with graphite or diamond present (namely the water-maximum solidus) will lie at higher temperatures than those in ref. 13 due to dilution of the fluid phase with both CH4 and CO2 (ref. 11). The decrease in a H2O is most pronounced at P < 10 kbar; at P > 15 kbar, a H2O exceeds 0.95 along the water maximum solidus.

Based on the above analysis, in Fig. 3 we present a projection of the C-O-H saturated solidus surface showing solidus curves for several water activities. We make the assumption that the solubility of solid components in the dominantly CH4-H2O fluids is not large enough to affect significantly the calculated activities. This is an acceptable approximation in the system peridotite-H2O-CO2 (ref. 14) and analogous behaviour is predicted for the reduced system.

At pressures less than 13 kbar the solidi in Figs 2 and 3 show large temperature depressions relative to the volatile-absent solidus, even though the fluid is CH4-rich. Similar behaviour is observed in the system peridotite-H2O-CO2 at pressures where CO2 is only weakly soluble in silicate melts. Between 13 and 20 kbar the peridotite-C-O-H solid have an unusually shallow dP/dT slope that marks a change in the topology of the solidus surface between low and high pressures. It is in this region where a H2O is controlled by WCWO that fluid compositions change rapidly from CH4-dominated at low pressures to H2O-dominated at high pressures (see Figs 1 and 2). Although fluids become H2O-rich, their effect in depressing the peridotite solidus is not as marked as at lower pressures in that both CH4 and H2O appear to be important in determining melting temperatures. This behaviour could reflect a pressure-dependent increase in the solubility of reduced components in the melt phase.

At P > 25 kbar, the peridotite-C-O-H solidi show large temperature shifts away from the water-maximum solidus for only small dilutions of the fluid with CH4. This shift is the opposite to that found at P < 13 kbar and is significant in that only solidi close to the water-maximum will be crossed by stable continental geotherms (CG in Fig. 3). For more CH4-rich fluids (a H2O < 0.9), C-O-H solidi lie at temperatures well above CG. Thus these results clarify proposals for the generation of kimberlitic magmas by access of reduced C-O-H fluids from the deep mantle. It is inappropriate to use peridotite-H2O-CO2 phase relationships in evaluating models calling on reduced C-O-H fluids because of the rapid changes in solidus temperature moving from oxidized, through a H2O-tending to unity, to reduced CH4.
H₂O fluids. Kimberlitic magmas will not be produced at low temperatures in the presence of CH₃H₂O fluids. The caution that must be exercised in extrapolating from oxidized to reduced systems, is therefore emphasized.

We may conclude from Fig. 3 that the involvement of reduced C-O-H fluids in kimberlite magmatism must be restricted to regions of the subcontinental mantle where there is significant thermal perturbation, such that temperatures lie on or above the kinked geotherm PG in Fig. 3. Alternatively, if a CH₃ thermal perturbation, such that temperatures lie on or above C-O-H fluids in kimberlite magmatism must be restricted to be lowered and a CH₃ is raised such that the solidus and geotherm intersec. We term these two processes 'hot-spot' style melting and 'redox' melting respectively.

Although not all petrologists favour open system fluid infiltration models to explain the origin of kimberlites, all would recognize the need for a source of volatile components. If this source is a fluid phase then reduced CH₃ fluids can be stable in the subsolidus mantle at fO₂ below the water maximum (that is, <1W + 2 log units, see ref. 2). The infection in peridote-C-O-H solids at 80–100 km depth, however, will exclude reduced fluids from the shallow mantle by melting (for example intersection with high heat flow geotherms such as SEAG) and by amphibole crystallization (see Fig. 3). Thus evidence for the migration of reduced fluids is unlikely to be preserved in spinel herzolites as has been suggested by the results of recent fO₂ sensing studies.

We acknowledge the technical assistance of N. Davies and K. Harris. This project was supported by a National Research Fellowship (W.R.T.) and the Australian Research Grants Scheme (D.H.G.).

---

**Table 1 Isotopic compositions of O, C and Sr in calcite and chert from the Elephant Moraine, Antarctica**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>⁸⁷Sr/⁸⁶Sr</th>
<th>⁸⁸Sr/⁸⁶Sr</th>
<th>¹⁸O (SMOW)</th>
<th>¹³C (PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>582</td>
<td>Calcite</td>
<td>0.71417 ± 2</td>
<td>-21.1*</td>
<td>-22.9*</td>
<td>-21.5*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.75± 7.5</td>
<td></td>
<td>22.410± 2</td>
<td>22.0± 1</td>
</tr>
<tr>
<td>583</td>
<td>Calcite</td>
<td>0.71402 ± 4</td>
<td>-14.2*</td>
<td>-23.1*</td>
<td>-14.2*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.0</td>
<td></td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>584</td>
<td>Calcite</td>
<td>0.71383 ± 3</td>
<td>-12.91*</td>
<td>-22.563</td>
<td></td>
</tr>
<tr>
<td>585</td>
<td>Calcite</td>
<td>0.71488 ± 3</td>
<td>-13.7*</td>
<td>-22.0</td>
<td></td>
</tr>
<tr>
<td>586</td>
<td>Chert</td>
<td>ND</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>587</td>
<td>Calcite</td>
<td>0.71484 ± 1</td>
<td>-13.7*</td>
<td>-22.0</td>
<td></td>
</tr>
<tr>
<td>588</td>
<td>Calcite</td>
<td>0.71417 ± 2</td>
<td>-21.1*</td>
<td>-22.9*</td>
<td>-21.5*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.75± 7.5</td>
<td></td>
<td>22.410± 2</td>
<td>22.0± 1</td>
</tr>
</tbody>
</table>

All ⁸⁷Sr/⁸⁶Sr ratios were corrected for isotopic fractionation to ⁸⁶Sr/⁸⁶Sr = 0.11940.

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**Extreme ¹⁸O depletion in calcite and chert clasts from the Elephant Moraine on the East Antarctic ice sheet**

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Two large moraines are presently forming near the margin of the East Antarctic ice sheet west of Victoria Land where the flow of the ice sheet is disturbed by subglacial bedrock ridges of the Transantarctic Mountains (Fig. 1). During the 1983–84 search for meteorites in this area several clasts, composed of black acicular calcite crystals, were collected from the Elephant Moraine (76°17′35″S and 157°20′05″E) where they are abutting out of the ice°. Additional samples of this calcite were later collected from the Elephant Moraine during the 1984–85 and 1986–87 field seasons, but none were found at the Reckling Moraine at 76°15′S and 157°20′05″E. The calcite clasts are strongly depleted in ¹⁸O (δ¹⁸O = -20.5 ± 0.4%) with reference to standard mean ocean water, SMOW and in ¹³C (δ¹³C = -22.6 ± 0.1%), with reference to the PDB standard) in addition to being enriched in radiogenic ⁸⁷Sr/⁸⁶Sr (⁸⁷Sr/⁸⁶Sr = 0.71417 ± 0.00002) relative to sea water. These results suggest that the calcite precipitated from aqueous solutions discharged by hot springs under the East Antarctic ice sheet.

The specimen shown in Fig. 2 (sample 582 in Table 1) was collected during the 1983–84 field season. It consists of black acicular calcite crystals aligned approximately at right angles to undulating layers. It resembles certain kinds of algal stromatolites that may be difficult to distinguish from calcite clasts. The black calcite also occurs as crusts on sedimentary material and is less frequently associated with coarsely banded opaline chert ranging in colour from white to yellowish green.
EXPERIMENTAL INVESTIGATIONS
BEARING ON THE NATURE OF THE
MOHOROVIČIĆ DISCONTINUITY

By PROF. A. E. RINGWOOD and DR. D. H. GREEN

Department of Geophysics, Australian National University,
Canberra

The hypothesis that the MohorovičiĆ Discontinuity
(Moho) might be caused by a phase change from
basalt to eclogite has been widely discussed during recent
years1-8. Evaluation of this hypothesis has been impeded
by the paucity of experimental data on the nature of
the transition. We have recently carried out a detailed
investigation of the basalt-eclogite transformation at
high pressures and temperatures. Experiments were
performed on two basaltic glasses which were prepared
under controlled oxidation conditions. The chemical
and normative compositions of these glasses are given in
Table 1. The analyses are those of typical tholeiitic
basalts and representative of the most abundant magma
type occurring in continental areas.

Samples of these glasses were subjected to various

| Chemical analyses* and norms of basalt glasses used in experiment |
|-------------------------|---------------------|
| Glass A | Glass B |
| SiO₂ | 49.23 | 51.58 |
| TiO₂ | 2.12 | 1.84 |
| Al₂O₃ | 13.70 | 14.45 |
| Fe₂O₃ | 2.84 | 3.36 |
| FeO | 9.65 | 8.30 |
| MnO | 0.16 | 0.14 |
| MgO | 8.37 | 7.28 |
| CaO | 18.88 | 14.83 |
| Na₂O | 1.82 | 2.00 |
| K₂O | 0.08 | 0.72 |
| P₂O₅ | 0.21 | 0.18 |
| H₂O | 0.79 | 0.09 |
| Ilmenite | 4.2 | 3.6 |
| Magnetite | 4.2 | 3.6 |
| Apatite | 0.4 | 0.4 |
| Orthoclase | 0.5 | 4.8 |
| Albite | 15.4 | 22.1 |
| Anorthite | 29.3 | 25.5 |
| Diopside | 10.6 | 17.1 |
| Hypersthene | 23.7 | 20.6 |
| Olivine | — | — |
| Quartz | 2.8 | 2.4 |

* Chemical analyses by A. J. Easton, Australian National University.
desired pressures between 0 and 30 kilobars at a temperature of 1,100° ± 15° C in an apparatus similar to that described by Boyd and England. The temperature of 1,100° C was chosen because experience showed that it permitted the attainment of equilibrium in sub-solidus runs of reasonable duration—mostly 4–6 h. Pressure on the sample is believed to be known within ± 5 per cent. Relative pressures over limited pressure intervals are much more precise than this since the principal errors are systematic. The reader is referred to the original papers for details concerning experimental precision and procedure. After completion of a run, the charge was quenched, and then examined by optical, X-ray and electron microprobe techniques. More than 40 runs have been carried out so far and more are planned.

The results of runs on glass A will be discussed first. At pressures less than 15 kb (1,100° C) the glass crystallizes to pyroxene + plagioclase. The amount of plagioclase compared to pyroxene decreases with increasing pressure. This is evidently caused by solid solution of plagioclase components (principally calcium and aluminium) in pyroxene. At 15·5 kb, pyroxene and plagioclase are joined by pyrope–almandine garnet. As pressure is increased above 15·5 kb the proportion of garnet steadily increases while plagioclase steadily decreases, finally disappearing at a pressure between 22 and 25 kb. At 20 kb quartz appears, and increases in abundance as pressure changes from 20 to 22-25 kb. Quartz is evidently liberated by the breakdown of residual sodic plagioclase into jadeite which enters into solid solution in pyroxene. A further change observed between 20 and 25 kb is an increase in the garnet/pyroxene ratio with increasing pressure. Garnet is apparently formed by breakdown of aluminous pyroxene rich in CaAl₂SiO₆ and MgAl₂SiO₆ components. Above 25 kb, no further changes are observed; the assemblage consists of pyrope-rich garnet, pyroxene (probably poor in tetrahedrally co-ordinated aluminium) and quartz. Such an assemblage is a true eclogite. The minimum pressure required for stability of this assemblage at 1,100° C is between 22 and 25 kb and probably close to 23 kb.

The experimental results on glass B are generally similar to those discussed here. Garnet first appears close to 15 kb, while between 18 and 22·5 kb, plagioclase is distinctly more abundant than in glass A. This would be expected from the relative abundances of plagioclase in the norms of A and B. Final conversion to a true eclogite is accomplished close to 23 kb.

Two aspects of the experimental results deserve emphasis. First, a minimum pressure of 23 kb at 1,100° C is required for the stability of an eclogite of tholeiitic composition. Secondly, the transformation from basalt to eclogite involves a complex series of solid solution
Fig. 1. Stability fields of basalt, garnet granulite and eclogite of tholeiitic composition as defined by (I) direct experimental data at 1,100° C, (II) the assumptions that the Moho is caused by a basalt-eclogite transformation, with eclogite stable beneath the Moho and that the temperature at the Moho is 600° C, and (III) the assumption that the width of the garnet granulite field is proportional to absolute temperature equilibria which occur over a pressure interval of 8 kb, which is equivalent to a depth range in the Earth of 24 km. The transformation proceeds via a transitional mineral assemblage characterized by the coexistence of pyrope-almandine garnet, aluminous pyroxene and sodic plagioclase. This assemblage corresponds closely with the assemblage observed in Nature when dry basaltic rocks are metamorphosed in the garnet granulite facies. To a first approximation the transformation from basalt (or pyroxene granulite) to eclogite involves a regular increase in the proportion of garnet and a regular decrease in plagioclase. We would therefore expect the increase in seismic velocity associated with the transformation to occur more or less uniformly over the entire transition pressure interval of 8 kb.

We will discuss these results in detail in a forthcoming paper and show that they are unfavourable to the hypothesis that the continental Moho is caused by an isochemical phase transformation from basalt to eclogite. The principal arguments leading to this conclusion follow those already stated in more general terms by Bullard and Griggs and may be summarized as follows.
A considerable number of heat flux determinations in Australia have shown that the early Precambrian shield of Western Australia is characterized by a mean heat flux of 1.0 μcal/cm²/sec, whereas large areas in east Australia yield a mean heat flux of 1.9 μcal/cm²/sec. These large regional differences imply the existence of corresponding regional differences in temperature at the Moho. It is very difficult to construct an acceptable chemical and physical model of the crust in which these differences are smaller than 200°C (refs. 7-9). Depths to the Moho in regions of Western and East Australia covered by adequate heat flux measurements have been determined using explosions as seismic sources. There is no systematic difference in crustal thickness between the two regions. Doyle (personal communication) considers that the crustal thicknesses do not differ by more than 5 km (1.4 kb). If the continental Moho is a phase transition from basalt to eclogite then the equilibrium curve for this transition must be defined by the temperatures and pressures occurring at the Moho beneath Western and East Australia. The geophysical evidence quoted here implies that a temperature change of 200°C alters the transition pressure (approximately...
10 kb) by less than 1.4 kb. Making generous allowances for the various sources of uncertainty, it can be shown from these results that eclogite should be stable at a pressure as low as 16 kb at 1,100° C. This consequence of the phase change hypothesis is in serious conflict with the experimental results quoted here, which show that a pressure of 23 kb is required for the stability of eclogite at 1,100° C.

(2) It is highly probable that the temperature at the continental Moho exceeds 550° C in regions where the heat flux is $1.5 \mu$cal/cm²/sec or greater. Many such regions are known. This raises a further difficulty for the phase change hypothesis, as seen in Fig. 1. If the Moho is assumed to be a phase change from basalt to eclogite, the line $BM$ on Fig. 1 must define the stability field of eclogite. The width of the garnet granulite transition zone given by the line $AB$ is known from experiments at 1,100° C. At lower temperatures the width will probably be smaller. As a first approximation we will assume that this width is proportional to absolute temperature. The line $AC$ then defines the stability field of basalt or pyroxene granulite. With the temperature at the Moho specified, it can be shown that the positions of geotherms which are consistent with continental heat-flux and with permissible distributions of radioactivity are very restricted and fall between curves 1 and 2 on Fig. 1. For this family of geotherms we see immediately that it is not possible to pass from the basalt field into the eclogite field with increasing depth. Accordingly the Moho cannot be explained as a basalt–eclogite transition if this diagram is applicable. If the temperature at the Moho should be higher than 600° C the difficulties become even more extreme.

(3) The foregoing difficulty is not so serious when the temperature at the Moho is less than 500° C (Fig. 2). However, in this case we see that the geotherm is constrained to intersect the transition zone over a wide depth range between points $D$ and $M$. This would necessitate a crustal model in which an increase in seismic $P$ velocity from 7 and 8 km/sec was spread uniformly throughout the lower 20 km of the crust. The actual nature of the seismic depth-velocity profile in this region is not well known, nevertheless, few seismologists would regard such a velocity distribution as probable.

We have discussed the bearing of our results on the nature of the continental Moho to which our results are more directly applicable. It is also possible to construct analogous arguments bearing adversely on the possibility that the oceanic Moho represents a phase change from basalt to eclogite.

We thank Dr. F. R. Boyd and Mr. O. R. McClunin of the Geophysical Laboratory, Washington, D.C., for advice and assistance in setting up the high-pressure apparatus.


An experimental investigation of the gabbro to eclogite
transformation and its petrological applications
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mineral assemblages of a variety of basaltic compositions have been studied
experimentally in the pressure range from 1 bar to 30 kb at temperatures above 1000°C and
below the basalt solidus. At low pressures, less than 10 kb at 1100°C, the mineral assemblages
match those of gabbros and pyroxene granulites but at pressures above 21 kb at 1100°C the
major phases are pyrope–almandine garnet and clinopyroxene and the mineral assemblages
match those of eclogites. At intermediate pressures the mineral assemblages are characterized by
co-existence of garnet, clinopyroxene, plagioclase and, commonly, quartz. The transition interval
between the gabbroic and eclogitic assemblages is a broad one characterized by gradual increase
in garnet and in the pyrope content of the garnet, and decrease in plagioclase and in the anorthite
content of the plagioclase. The roles of variable Si0 2 -saturation, Na 20 content, albite: anorthite
ratio of plagioclase, oxidation state, and of variations in the Mg/(Mg Fe 2+) (atomic) ratio have
been studied to determine the influence of particular chemical parameters on the pressure at
which a given phase (e.g. garnet) appears or disappears.
Low values of the Mg/(Mg Fe 2+) ratio cause garnet to appear at lower pressures. In
undersaturated compositions (olivine-normative), garnet appears at lower pressures than in
quartz-normative compositions and in addition there is an intermediate assemblage of alurninous
pyroxenes ± plagioclase ± spinel present, particularly in magnesian basalts, between the low
pressure olivine-bearing and higher pressure garnet-bearing assemblages. The pressure required
for elimination of plagioclase varies from 15 to 20 kb at 1100°C in the spectrum of basaltic
compositions studied.
The pressure required for the appearance of garnet and disappearance of plagioclase in a given
composition is strongly dependent on temperature. P–T gradients for these boundary reactions
in a quartz tholeiite composition have been established in the 1000-1250°C temperature range.
When extrapolated to lower temperatures, these gradients suggest that eclogite mineralogy is
stable in dry basaltic rocks along normal geothermal gradients throughout the entire crust. The
observed mineral assemblages at various pressures and the effects of chemical parameters on
mineralogy in a given P–T field are closely matched with natural pyroxene granulite and eclogite
occurrences and with experimental work in simple systems. The experimental work provides
some quantitative data on dry solid–solid reactions which are strongly pressure and temperature
dependent and which, in natural rocks, provide criteria for subdivision of granulite facies
metamorphic rocks into high pressure, intermediate pressure and low pressure types. By
comparison of the experimental data with estimates of the P 20, T conditions of other metamorphic facies, based in part on dehydration reactions, it is argued that eclogite mineralogy may
be stable in dry basaltic rocks within the almandine amphibolite facies, the glaucophane schist
facies and part of the greenschist facies of regional metamorphism.

Abstract The
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Acknowledgements

References
INTRODUCTION

Modern high pressure techniques, particularly the use of solid-media, internally heated pressure apparatus, reproduce in the laboratory the pressures and temperatures which are present in the lower crust and upper mantle. Within the limits imposed by reaction rates, deep-seated processes such as metamorphic recrystallization and magma generation by partial melting can be closely matched in the laboratory. In this paper we report the results of experimental crystallization of basaltic rocks at high pressures and temperatures and relate these studies to the observed mineral assemblages of gabbros, pyroxene granulites and eclogites. The choice of basalt compositions for experimental study was determined by several factors. Firstly, basaltic rocks are constituents of almost all metamorphic terranes. Secondly, the experimental study provides data necessary to evaluate a current hypothesis that the Mohorovičić Discontinuity (i.e. the rapid change of seismic velocity at the base of the crust) is due to a change from gabbroic mineralogy (density 2.9–3.1) to eclogite mineralogy (density 3.4–3.6) over a relatively narrow depth interval. Thirdly, there is strong evidence that basaltic magmas originate in the upper mantle and experimental study of basalts under these conditions yields information which is directly relevant to the origin and behaviour of basalt magma at depth.

(a) Previous investigations

The first experimental synthesis of eclogite was carried out by Boyd and England (1959) who crystallized a natural basalt glass at 33 and 40 kb at a temperature of 1200°C. The glass contained 1–5% free quartz in the C.I.P.W. norm but the mineral assemblage observed was garnet, clinopyroxene and 5–10% quartz or coesite. It is clear that the mineral assemblage matches those of natural eclogites [the preliminary report of minor calcic plagioclase in the high pressure assemblage was not confirmed (Boyd, personal communication)].

Kennedy (1956) had previously reported crystallization of a basaltic glass to feldspar-rich assemblages at temperatures of 800 and 1000°C and pressures of 10–15 kb. At higher pressures plagioclase was not observed but the nature of the minerals present was not established. Kennedy (1959) crystallized a basaltic glass at high pressures in a uniaxial piston–anvil apparatus. At low temperatures he obtained an assemblage of “jadeitic” pyroxene above 10 kb and a plagioclase bearing assemblage below 10 kb. In the absence of garnet with the “jadeitic” pyroxene, there is no certainty that the experimental conditions were within the eclogite stability field. A further difficulty with the piston–anvil apparatus is the large uncertainty in pressure measurement at pressures around 10 kb (Kitahara and Kennedy, 1964, pp. 5395–5396; Myers et al., 1963).

Yoder and Tilley (1962) reported the results of experiments on natural basalts and eclogites in a gas apparatus at 10 kb and a piston-cylinder solid media apparatus above 20 kb. At 1 bar and 10 kb, three natural eclogites were recrystallized to gabbroic assemblages dominated by plagioclase and clinopyroxene. In contrast to these experiments, the Glenelg eclogite (Ga + Cpx + Qz) remained stable at pressures of 20, 30 and 31.4 kb. Garnet + pyroxene assemblages were obtained from a series of natural basalts at pressures of 30 kb and a temperature of 1200°C. In one
run at 20 kb, 1200°C the olivine tholeiite (1921 Kilauea flow) yielded garnet + clinopyroxene.

Yoder and Tilley's results show that at pressures of 30 kb and higher and possibly as low as 20 kb, basaltic rocks at 1200°C are in the field of eclogite stability. We have previously reported some preliminary results (Ringwood and Green, 1964) of the present study and applied the data to the hypothesis that the Mohorovicic Discontinuity represents the gabbro → eclogite transition zone.

(b) Present investigation

The present investigation was begun with the aim of establishing the minimum pressures at which eclogite is stable and particularly of investigating the breadth and nature of the transition between the low pressure gabbro or pyroxene granulite assemblages and the high pressure eclogite assemblages. The latter part of the project was suggested by the apparent disagreement between the suggested "pyroxenite" transitional assemblage based on experimental work (Yoder and Tilley) and the transitional mineral assemblage of Ga + Cpx + Plag ± Qz defined by the natural rocks (e.g. Gjelsvik, 1952, p. 128). A study of the breadth and gradient of the transition zone and the dependence of the pressure and temperature of this transition zone on bulk composition is of first importance to the hypothesis that the Mohorovicic Discontinuity is caused by the gabbro to eclogite transition since the intersection of the transition zone and geothermal gradients will define the depth range over which changes in density and seismic velocity would occur.

Several selected basaltic compositions have been crystallized at closely spaced pressure intervals defining the first appearance, the changes in relative proportions and the disappearance of various mineral constituents. We have then prepared basaltic compositions differing from the previous in only one chemical parameter [e.g. Mg/(Mg + Fe²⁺) ratio, oxidation state etc.] in order to investigate the effects of the chosen chemical parameter on the reactions observed in the initial composition. In this way the study has been extended from particular examples to generalities of the behaviour of basalts at high pressure. The mineral assemblages observed and the sequence of appearance of phases closely match those found in natural high grade metamorphic rocks. Thus a detailed comparison of the experimental and natural assemblages can be made and the experimental data used to evaluate the P–T conditions which must have operated in producing observed metamorphic assemblages and gradients.

Our data demonstrate a wide P–T field of eclogite stability in the normal continental crust given that conditions are anhydrous or $P_{H_2O} \ll P_{\text{load}}$. This has far-reaching consequences on

(a) the chemical nature and evolution of the continental crust
(b) processes of orogeny and epeirogeny
(c) the nature of the Mohorovicic Discontinuity and its apparent absence in certain crust–mantle profiles
(d) Convective-type movements and vertical movements of gravitationally unstable masses in active orogenic and volcanic areas.

The geophysical applications of our experimental data are discussed in an accompanying paper (Ringwood and Green, 1966). In this paper we present our
An experimental investigation of the gabbro to eclogite transformation

Experimental Procedure

(a) Preparation and description of basalt compositions studied

The chemical compositions of the basalt glasses studied experimentally are listed in Table 1. These compositions were obtained by utilizing a natural, analyzed basalt (e.g. the alkali-poor quartz tholeiite from the Pololu Series of Hawaii) and adding to this composition known weights of oxides, analyzed minerals or metallic iron to produce a composition of the required oxidation state, alkali content or degree of undersaturation. Compositions were intimately mixed and constituents ground together, then fused at 1400-1500°C, quenched to a glass, reground and checked for homogeneity by immersion of the powdered glass in R.I. liquids. The glasses were found to be homogeneous in the sense that there were no observable variations in refractive index and crystalline phases were absent.

The alkali-poor olivine tholeiite was prepared by mixing weighed proportions of analyzed clinopyroxene and garnets from Norwegian eclogites (Green and Easton, unpublished data). The mixture was then ground, fused, quenched to a glass and checked for homogeneity.

The oxidized alkali basalt composition (Table 1) was prepared by holding the alkali olivine basalt glass in an open crucible at 800°C for 6 hr. The glass devitrified either wholly or in part to a very fine intergrowth of plagioclase, clinopyroxene, orthopyroxene and magnetite. Chemical analysis showed that there had been extensive oxidation (from 1.87% Fe₂O₃ to 9.82% Fe₂O₃). The calculated composition after oxidation is given in Table 1, column 6. The extremely magnesian [100Mg/(Mg + Fe²⁺) ~ 90] and extremely iron rich [100Mg/(Mg + Fe²⁺) ~ 10] “basalt” compositions were prepared from A.R. chemicals, fused under controlled oxidation conditions, and quenched to a glass.

In melting the basalt compositions to glass using platinum tubes or crucibles, loss of Fe to solid solution in the platinum may be appreciable. After several control experiments, calculated amounts of Fe powder were added to compensate for this effect. Since our melting was carried out in some cases in sealed platinum tubes and in other cases in an open crucible in an argon atmosphere in contact with graphite at 1400-1500°C, we have made duplicate analyses of our final glasses for FeO and Fe₂O₃. The glass compositions were then recalculated to 100% using the figures for FeO and Fe₂O₃ determined by analysis. The compositions obtained in this way are listed in Table 1.

(b) Apparatus and experimental method

Experimental crystallization of the basalt glasses was carried out using a single-stage piston-cylinder apparatus similar to that described by Boyd and England (1960a, b, 1963). The apparatus was operated in the range 5-40 kb and at temperatures between 1000 and 1300°C. In determining the pressure on the sample the pressure on the 3-in. piston was measured with a Heise gauge and the pressure on the half-in. piston (sample chamber pressure) calculated from the known areas of the pistons. Experiments on the quartz—coesite transition using the furnace
Table 1. Chemical compositions of basaltic glasses used in experimental work

<table>
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<tr>
<th></th>
<th>Quartz tholeiite (A) (glass)</th>
<th>Over-saturated basalts Quartz tholeiite (B) (glass)</th>
<th>Magnesian quartz tholeiite (glass)</th>
<th>Iron-rich quartz tholeiite (glass)</th>
<th>Alkali olivine basalt</th>
<th>Under-saturated compositions Oxidized alkali olivine tholeiite (A)</th>
<th>Olivine tholeiite (B)</th>
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<td>36.9</td>
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<td>23.7</td>
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<tr>
<td>Ol</td>
<td>—</td>
<td>—</td>
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<td>8.4</td>
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<tr>
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<td>4.2</td>
<td>3.8</td>
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<td>4.2</td>
<td>3.6</td>
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<td>Ap</td>
<td>0.5</td>
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<td></td>
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<tr>
<td>Haem</td>
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<td></td>
<td>—</td>
<td>—</td>
<td>0.2</td>
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<tr>
<td>Chrom</td>
<td>—</td>
<td>—</td>
<td></td>
<td>—</td>
<td>—</td>
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<td>0.3</td>
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<td>Normative olivine</td>
<td>—</td>
<td>—</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Normative plagioclase</td>
<td>An₄₄</td>
<td>An₅₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Analyst: A. J. EASTON, Department of Geophysics and Geochemistry, Australian National University, Canberra.
assemblies described later and furnace assemblies in which the talc sleeve was replaced by silver chloride have shown that a pressure correction of 10% should be made because of friction and imperfect pressure transmission particularly by the talc sleeve (Green et al., 1966). Our experimental runs were brought almost to pressure, the temperature was then raised to the required value and the pressure finally raised to the set value. The sample pressure was calculated from this nominal value by applying the pressure correction of —10%. The absolute accuracy of the pressure determinations is probably about ±3% (Green et al., 1966) but the precision of closely spaced runs following the same experimental procedure is much better than this and pressure differences between runs are considered accurate to better than 0.5 kb.

The pressure vessel has an internal furnace consisting of a graphite cylinder and the sample capsule is located at the hot spot by fired pyrophyllite and ceramic spacers (Boyd and England 1960a 1963). For the runs on the quartz tholeiite glasses at 1000 and 1100°C, we used a simple talc cylinder as the pressure medium (Fig. 1(a)). In the runs above 1100°C on the quartz tholeiite glasses and in all runs on the undersaturated, olivine-normative glasses, it was found necessary to use an inner cylinder of boron nitride between the talc and graphite cylinders (as in Fig. 1(b)) in order to prevent access of water to the sample capsule. For the latter furnace assemblies the boron nitride sleeve and all inserts were dried for 1 hr at 1000–1100°C in an argon atmosphere and stored in a desiccator until used.

In the runs at 1000 and 1100°C on the quartz tholeiite glasses, the sample was enclosed in an unsealed platinum tube of 0.003 in. wall thickness. This arrangement, used with the furnace assembly of Fig. 1(a), allowed access of water (from dehydration of the talc adjacent to the graphite cylinder) to the charge during long runs. While the access of water did not cause crystallization of a hydrous phase such as amphibole in the oversaturated quartz tholeiite compositions and may have appreciably increased reaction rates, it caused a small and random amount of partial melting in some of the 1100°C runs. This procedure was unsuitable for the undersaturated, olivine-normative compositions because access of water caused the formation of amphibole as a major phase and thus obscured the roles of olivine, garnet and plagioclase in the assemblages. In the runs on undersaturated basalt compositions, a platinum tube of 0.006 in. wall thickness was used and both ends of the capsule were sealed by welding. This procedure, coupled with the drying of the furnace components (Fig. 1(b)) described previously, effectively decreased entry of water in runs shorter than 4 hr.

Temperatures were measured by a Pt/Pt10% Rh thermocouple directly in contact with the platinum capsule. The recorded temperature was controlled within ±5°C of the set point and the precision of temperature measurement when allowance is made for temperature gradients in the sample is about ±15°C. The temperatures recorded have not been corrected for any pressure effect on the e.m.f. of the thermocouple. The duration of runs varied with the temperature. In general, runs at 1200°C or higher temperatures were for one hour, runs at 1100°C were for 2–4 hr and runs at 1000°C from 4–6 hr. The runs were quenched from temperature to 200°C in less than 30 sec by turning off the power to the furnace.

(c) Examination of sample

The sample capsules were carefully opened and a small fraction crushed and examined optically in immersion oils of various refractive indices. X-ray powder
photographs or diffractometer traces or both were obtained and in some examples polished surfaces and thin sections were prepared to investigate the distribution of phases in the experimental charges.

Relative changes from run to run in the proportions of phases were best studied by comparison of diffractometer charts. The approximate proportions of garnet and pyroxene were also estimated by comparison of the powder photographs with those of a series of finely ground standard mixtures of natural minerals. The refractive indices of garnets were measured using immersion liquids calibrated against a Leitz-Jelley refractometer. Garnet cell sizes were calculated from the X-ray powder photographs.

(d) Oxidation state of samples after high pressure runs

At high temperatures, iron is appreciably soluble in platinum. The basaltic compositions contain appreciable iron and are enclosed in platinum tubes during the experimental runs so that loss of Fe to solid solution in the platinum and resulting
oxidation of remaining FeO may be a significant factor

\[ 3\text{FeO} \rightarrow \text{Fe} + \text{Fe}_2\text{O}_3 \]

(in platinum)

To evaluate this effect semi-micro chemical analyses for FeO and Fe$_2$O$_3$ were carried out on 2-8 mg samples from our experimental runs. The results are given in Table 2.

The data demonstrate that loss of Fe from our samples does occur and, as would be expected for a diffusion process, is strongly temperature and time dependent. Thus the run on the quartz tholeiite B at 1200°C for 1 hr resulted in slightly greater Fe loss than the 4 hr run at 1100°C and the latter resulted in greater iron loss than the 4 hr run at 1000°C.

Although loss of Fe to the platinum capsule does occur, this does not result in oxidation of the samples, since in all cases the Fe$_2$O$_3$ content of the final charge is less than the original Fe$_2$O$_3$ content. The presence of the graphite furnace at high temperature in contact with water released from dehydration of the talc, presumably causes the environment of the sample to be a reducing one as hydrogen may readily diffuse through the platinum capsule.

The effects of loss of iron and of reduction do not change the basaltic compositions to an appreciable degree. Thus, recalculation of the norm for run 285 shows that the reduction of the Fe$_2$O$_3$ and slight decrease in total Fe content, changes the quartz tholeiite (B) composition from having 2-5% normative quartz to 0-2% normative quartz. In the alkali basalt composition, run 134, the decrease of almost 2% in FeO changes the normative nepheline content from 2-2 to 1-4% Ne. These two examples are the extremes of those analyzed and in the other runs analyzed the changes in normative composition are less than these examples.

It is clear from these results that compositional uncertainties introduced by loss of iron and changes in redox states during runs are minor and will not significantly affect the interpretation of experiments discussed in subsequent sections.

**Experimental Results**

(a) *Quartz tholeiite (Quartz tholeiites (A) and (B))*

The details of the experimental conditions and phases identified in the runs on the two quartz tholeiite compositions are given in Tables 3 and 4. The presence of minor amounts of glass in many runs at 1100°C is attributed to lowering of the minimum melting temperature of the composition to below 1100°C due to entry of small amounts of water. No hydrous phases were identified in any of the runs. The glass, ore-mineral and rutile were identified optically whilst garnet, pyroxene, plagioclase and quartz were identified by optics and X-ray diffraction (powder photographs and diffractometer charts).

Pyroxene occurs as a fine-grained anhedral aggregate showing moderate birefringence. Quartz and plagioclase form amoeboid interstitial or included patches, usually disconnected, with refractive index much lower than pyroxene or garnet and appearing isotropic. Glass occurs in similar form but where melting has occurred to a greater degree the glass forms an intergranular continuum, occasionally expanding into distinct segregations. Garnet is very distinctive optically because of its high
Table 2. Analyses for FeO and Fe$_2$O$_3$ contents of the basalt glasses before and after experimental crystallization at high temperature and pressure

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Composition</th>
<th>$P$(kb)</th>
<th>$T$ (°C)</th>
<th>Time (hr)</th>
<th>FeO</th>
<th></th>
<th>Fe$_2$O$_3$</th>
<th></th>
<th>Total Fe as FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>7</td>
<td>Qz tholeiite (A)</td>
<td>9-0</td>
<td>1100</td>
<td>2</td>
<td>9-58</td>
<td>9-65</td>
<td>0-81</td>
<td>2-84</td>
<td>10-31</td>
</tr>
<tr>
<td>37</td>
<td>Qz tholeiite (A)</td>
<td>27-0</td>
<td>1100</td>
<td>4</td>
<td>6-84</td>
<td>9-65</td>
<td>2-14</td>
<td>2-94</td>
<td>8-78</td>
</tr>
<tr>
<td>285</td>
<td>Qz tholeiite (B)</td>
<td>13-5</td>
<td>1000</td>
<td>4</td>
<td>9-81</td>
<td>8-39</td>
<td>0-37</td>
<td>2-46</td>
<td>10-14</td>
</tr>
<tr>
<td>57</td>
<td>Qz tholeiite (B)</td>
<td>18-0</td>
<td>1100</td>
<td>4</td>
<td>9-31</td>
<td>8-39</td>
<td>0-28</td>
<td>2-46</td>
<td>9-56</td>
</tr>
<tr>
<td>336</td>
<td>Qz tholeiite (B)</td>
<td>15-8</td>
<td>1200</td>
<td>1</td>
<td>8-53</td>
<td>8-39</td>
<td>0-96</td>
<td>2-46</td>
<td>9-39</td>
</tr>
<tr>
<td>85</td>
<td>Alkali basalt</td>
<td>11-3</td>
<td>1100</td>
<td>4</td>
<td>11-64</td>
<td>12-42</td>
<td>0-92</td>
<td>1-87</td>
<td>12-47</td>
</tr>
<tr>
<td>97</td>
<td>Alkali basalt</td>
<td>13-5</td>
<td>1100</td>
<td>4</td>
<td>11-50</td>
<td>12-42</td>
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</tr>
<tr>
<td>134</td>
<td>Alkali basalt</td>
<td>18-0</td>
<td>1100</td>
<td>4</td>
<td>10-69</td>
<td>12-42</td>
<td>1-78</td>
<td>1-87</td>
<td>12-29</td>
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<tr>
<td>516</td>
<td>Oxidized alkali</td>
<td>13-5</td>
<td>1100</td>
<td>3</td>
<td>5-85</td>
<td>4-15</td>
<td>7-31</td>
<td>9-82</td>
<td>11-85</td>
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</tr>
<tr>
<td>520</td>
<td>Oxidized alkali</td>
<td>20-2</td>
<td>1100</td>
<td>3</td>
<td>7-82</td>
<td>4-15</td>
<td>5-79</td>
<td>9-82</td>
<td>13-03</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>359</td>
<td>Qz tholeiite Mg$_{10}$</td>
<td>6-8</td>
<td>1000</td>
<td>1</td>
<td>19-19</td>
<td>20-74</td>
<td>2-67</td>
<td>3-63</td>
<td>21-60</td>
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<tr>
<td>358</td>
<td>Qz tholeiite Mg$_{10}$</td>
<td>9-0</td>
<td>1000</td>
<td>2</td>
<td>19-93</td>
<td>20-74</td>
<td>2-37</td>
<td>3-63</td>
<td>22-07</td>
</tr>
<tr>
<td>354</td>
<td>Qz tholeiite Mg$_{10}$</td>
<td>11-3</td>
<td>1000</td>
<td>2</td>
<td>20-79</td>
<td>20-74</td>
<td>1-65</td>
<td>3-63</td>
<td>22-28</td>
</tr>
</tbody>
</table>

Analyst: E. Kiss; Department of Geophysics and Geochemistry, Australian National University, Canberra.
refractive index. It is commonly subhedral or with well-developed crystal faces and almost invariably it contains small inclusions (plagioclase, rutile, pyroxene) particularly near the garnet centre. Rutile appears as needles or prisms, appearing colourless with very high refractive index, very high birefringence and straight extinction. In contrast the ore-mineral (probably a magnetite-ulvospinel solid solution) is opaque to translucent (brown or green-brown in colour and isotropic). The ore mineral is generally anhedral but equant in form.

The main features of the results in Tables 3 and 4 may be summarized as follows. At 1100°C, mineral assemblages at pressures up to and including 13.5 kb are dominantly of pyroxene and plagioclase. Quartz may be present (cf. normative composition of Table 1) but if so is below the limit of detection. Between 13.5 and 14.6 kb garnet becomes a stable phase and from this pressure to 18-20 kb, the mineral assemblage is characterized by the co-existence of garnet, pyroxene and plagioclase as major phases. Within this pressure range the amount of plagioclase decreases and the amount of garnet increases at the higher pressures. The garnet also shows a distinct decrease in refractive index as it becomes more abundant at the higher pressures. The role of TiO₂ in the assemblage also apparently changes around 13.5 kb at 1100°C. Below this pressure, TiO₂ is probably present in the ore-mineral described previously but this phase decreases and then disappears whereas rutile becomes more common at pressures above 13.5 kb.

Plagioclase decreases in abundance relative to pyroxene between 5 and 13.5 kb. This is well shown by the alkali-poor quartz tholeiite (A) runs at 1000, 1050 and 1100°C (see Fig. 2). At 1100°C and greater than 13.5 kb, plagioclase decreases more rapidly with increasing pressure and is not detectable on X-ray powder photographs or diffractometer traces above 20.2 kb. In contrast quartz reflections are identifiable above approximately 20 kb. At pressures greater than 21 kb, 1100°C, the quartz tholeiite compositions have typical eclogite mineralogy of pyroxene + garnet (pyrope-almandine) + quartz + rutile.

The most important difference between the two tholeiite compositions is in the stability field of the plagioclase. In the quartz tholeiite B composition, plagioclase reflections are clearly identifiable at 18 kb, 1100°C whereas in the alkali-poor quartz tholeiite A the presence of plagioclase at 18 kb, 1100°C or at higher pressures could not be established from X-ray data. At 19.1 kb, 1100°C, both plagioclase and quartz reflections are identifiable in quartz tholeiite B but at 20.2 kb the plagioclase reflections are no longer identifiable and the quartz reflections are much stronger.

From the measurements of cell-size and refractive index of the garnets, an estimate of their composition can be obtained. A further limitation on garnet composition is provided by the measurement of the FeO and Fe₂O₃ contents of the quartz tholeiite composition after the high pressure runs (see page 774). These results imply a very low Fe₂O₃ content in the mix as a whole so that we may deduce that the andradite content of the garnets is very low. Accordingly, the garnet compositions in Table 11 are calculated in terms of pyrope, almandine and grossular end-members. The X-ray diffraction patterns are not sufficiently diagnostic to yield much information on the nature of the pyroxene phases although there is evidence for the presence of orthopyroxene in the 1 atm, 4-5, 9 and 13.5 kb runs.

Further series of runs on the normal quartz tholeiite (B) composition were carried
Table 3. Alkali-poor quartz tholeiite (quartz tholeiite (A))

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Press. (kb)</th>
<th>Time (hr)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
<th>Phases identified</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>1100</td>
<td>1050°C</td>
<td>26-0</td>
<td>4</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Ore-mineral (brown, translucent) uncommon; Glass rare</td>
<td></td>
</tr>
<tr>
<td>94</td>
<td>1100</td>
<td>4-5</td>
<td>4</td>
<td>Px</td>
<td>Pl</td>
<td>Pl</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Ore-mineral uncommon; Glass common (&lt;20%)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1100</td>
<td>9-0</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Orea-mineral very rare; No definite glass; Pl/Px ratio less than 4-5 kb, 1100°C run</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1100</td>
<td>13-5</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Orea-mineral very rare; No definite glass; Pl/Px ratio less than 9 kb, 1100°C run</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1100</td>
<td>14-6</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet as rare euhedral porphyroblasts; Rare glass; N_a = 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1100</td>
<td>15-8</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet more abundant than in 14-6 kb run; Rare glass; N_a = 1-770 ± 0-01, o_a = 11-50 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1100</td>
<td>16-9</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet more abundant than in 15-8 kb; Uncommon glass; N_a = 1-755 ± 0-01, o_a = 11-50 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1100</td>
<td>18-0</td>
<td>4</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>TiQz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet more abundant than in 16-9 kb run; Rare glass, N_a = 30-35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1100</td>
<td>20-2</td>
<td>4</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Quartz more abundant than in 18 kb run; Uncommon glass; N_a = 1-750 ± 0-01</td>
<td></td>
<td></td>
<td></td>
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<td>22-5</td>
<td>4 ½</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Rare glass; N_a = 1-760 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>1100</td>
<td>24-9</td>
<td>4</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>No definite glass; N_a = 1-745 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1100</td>
<td>26-0</td>
<td>4</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Rare glass; N_a = 1-745 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1050</td>
<td>9-0</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>No identifiable garnet; Pl/Px ratio less than 9 kb, 1050°C run</td>
<td></td>
<td></td>
<td></td>
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<td>6</td>
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<td>13-5</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Orea-mineral (brown, translucent) uncommon; Glass rare</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>1000</td>
<td>11-3</td>
<td>2 ½</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Orea-mineral (brown, translucent) uncommon; Glass rare</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1000</td>
<td>13-5</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet rare; N_a = 1-765 ± 0-01</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>1000</td>
<td>15-8</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet euhedra more common N_a = 1-75 ± 0-01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1000</td>
<td>18-0</td>
<td>2</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Very fine, poorly crystallized aggregate; scattered, small garnets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>1100</td>
<td>18-0</td>
<td>½</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Fine-grained, garnet more common than 1hr run, still poorly crystallized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>1100</td>
<td>18-0</td>
<td>1</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>No definite glass. Euhedral garnet, fine pyroxene, interstitial low R.I. phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1100</td>
<td>18-0</td>
<td>2</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Rare glass. Euhedral, poikilitio garnet, pyroxene granular, interstitial and included low R.I. phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1100</td>
<td>18-0</td>
<td>4</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>TiQz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Rare glass. Euhedral, poikilitio garnet, pyroxene granular, interstitial and included low R.I. phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1100</td>
<td>18-0</td>
<td>6</td>
<td>Px</td>
<td>Pl</td>
<td>Ga</td>
<td>TiQz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Uncommon glass. Well crystallized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1100</td>
<td>18-0</td>
<td>12</td>
<td>Px</td>
<td>Ga</td>
<td>Rutile</td>
<td>Glass</td>
<td>Uncommon glass. Well crystallized</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1100</td>
<td>22-5</td>
<td>1 ½</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Garnet as small euhedra in pyroxene aggregate with low R.I. interstitial phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1100</td>
<td>22-5</td>
<td>1 ½</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Rare glass—local patches. Well crystallized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1100</td>
<td>22-5</td>
<td>6</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Uncommon glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>1100</td>
<td>22-5</td>
<td>6</td>
<td>Px</td>
<td>Ga</td>
<td>Qz</td>
<td>Rutile</td>
<td>Glass</td>
<td>Uncommon glass</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Phases identified optically only are italicized, those identified by optics and X-ray are not italicized.
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Press. (kb)</th>
<th>Time (hr)</th>
<th>Phases identified</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>1000</td>
<td>12</td>
<td>6</td>
<td>Rutile Ore</td>
<td>No garnet. Rutile less common than semi-opaque ore-mineral</td>
</tr>
<tr>
<td>285</td>
<td>1000</td>
<td>13.5</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Very rare garnet porphyroblasts.</td>
</tr>
<tr>
<td>313</td>
<td>1000</td>
<td>13.5</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Rare garnet porphyroblasts. Less ore mineral than in 12-4 kb run</td>
</tr>
<tr>
<td>315</td>
<td>1000</td>
<td>14.0</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Rare garnet porphyroblasts. Ore mineral rare</td>
</tr>
<tr>
<td>314</td>
<td>1000</td>
<td>15.5</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Rare garnet porphyroblasts. Not well crystallized</td>
</tr>
<tr>
<td>321</td>
<td>1000</td>
<td>16.0</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Well-crystallized. Common garnet euhedra in pyroxene + plagioclase</td>
</tr>
<tr>
<td>305</td>
<td>1000</td>
<td>18.0</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Well-crystallized. Very common garnet euhedra</td>
</tr>
<tr>
<td>320</td>
<td>1000</td>
<td>19.1</td>
<td>6</td>
<td>Rutile Ore</td>
<td>Abundant garnet. Minor interstitial low R.I. phase</td>
</tr>
<tr>
<td>65</td>
<td>1100</td>
<td>13.5</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Abundant garnet. Minor interstitial low R.I. phase</td>
</tr>
<tr>
<td>57</td>
<td>1100</td>
<td>18.0</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Rutile rare</td>
</tr>
<tr>
<td>61</td>
<td>1100</td>
<td>19.1</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Rutile rare</td>
</tr>
<tr>
<td>60</td>
<td>1100</td>
<td>20.2</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Rutile rare</td>
</tr>
<tr>
<td>67</td>
<td>1100</td>
<td>22.5</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims but centres with inclusions</td>
</tr>
<tr>
<td>68</td>
<td>1100</td>
<td>27.0</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>330</td>
<td>1200</td>
<td>15.8</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>338</td>
<td>1200</td>
<td>16.9</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>340</td>
<td>1200</td>
<td>18.0</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>327</td>
<td>1200</td>
<td>20.2</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>339</td>
<td>1200</td>
<td>21.4</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>340</td>
<td>1200</td>
<td>21.4</td>
<td>3</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>344</td>
<td>1200</td>
<td>22.5</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>347</td>
<td>1200</td>
<td>23.6</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>298</td>
<td>1250</td>
<td>18.0</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>289</td>
<td>1250</td>
<td>20.2</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>300</td>
<td>1250</td>
<td>20.2</td>
<td>4</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>301</td>
<td>1250</td>
<td>27.0</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
<tr>
<td>306</td>
<td>1250</td>
<td>29.3</td>
<td>1</td>
<td>Rutile Ore</td>
<td>Glass rare. Euhedral garnet, clear rims + pyroxene + low R.I. phase</td>
</tr>
</tbody>
</table>

* "W" signifies "wet" run using talc furnace sleeve, "D" signifies "dry" run using talc + boron nitride sleeve.
Fig. 2. Diffractometer traces from high pressure runs on the two quartz tholeiite compositions. Patterns of poor intensity resulted from use of extremely small samples. Comparison of runs at 14.6 kb in both compositions demonstrates the first appearance of garnet reflections. Between 18 kb and 20.2 kb the traces demonstrate the persistence of plagioclase to higher pressures in quartz tholeiite (B) than in quartz tholeiite (A).
out at 1000°C, wet conditions, and 1200 and 1250°C, dry conditions, in an attempt to establish temperature gradients for the observed reactions. At both 1000 and 1200°C, closely parallel mineralogical changes were observed with a broad field of garnet + pyroxene + plagioclase assemblages between the gabbroic (pyroxene + plagioclase) assemblage and the eclogitic (garnet + pyroxene + quartz) assemblage, (Fig. 7 and Table 4). At 1000°C garnet, absent at 12.4 kb, first appears at 13.5 kb and increases in amount present up to about 20 kb. At 1200°C, garnet is absent at 15.8 kb but appears in the 16-9 kb and 18 kb runs.

At 1000°C, plagioclase reflections disappear and quartz reflections appear between 16.9 and 18 kb. At 1200°C, plagioclase reflections disappear between 22.5 and 23.6 kb and at 1250°C between 23.6 and 24.8 kb.

The relative intensities of garnet and pyroxene reflections (at pressures above that required to eliminate plagioclase) in the 1000 and 1100°C runs compared with the 1200 and 1250°C runs indicate lower garnet contents in the higher temperature runs. This may be due to a higher Al₂O₃ solubility in the higher temperature pyroxenes as an alternative to garnet.

(b) Alkali olivine basalt

The glass of alkali olivine basalt composition has a high normative olivine and normative plagioclase content and a low normative diopside content (Table 1). The runs crystallized at lower pressures (1 atm, 4.5, 6.8 and 9 kb, Table 5) have mineralogies similar to that expressed by the norm giving strong plagioclase and olivine reflections and weak pyroxene reflections (Fig. 3). Small equant, anhedral grains of a brown, apparently isotropic phase with very high refractive index are evenly distributed through the runs and are most probably spinels of magnetite, ulvo-spinel and herecnite solid solution. Comparison of the 9 kb run with the 1 atm and 4.5 kb runs shows a slight increase in the intensity of the pyroxene reflections relative to olivine and plagioclase.

The runs at 10.1 kb and particularly 11.3 kb, show increased intensity of pyroxene reflections and decreased intensity of olivine and plagioclase (Fig. 3). Very weak reflections corresponding to those of spinel are observed and optically, the small, high R.I., isotropic grains are more abundant and green to pale green in colour. In the 12.4 run, rare, but very distinctive euhedral, porphyroblastic garnet is present in association with common small green to green-brown spinel. Pyroxene and plagioclase are present as major phases and there is a small amount of amphibole present.

In the 13.5 kb run there are uncommon large porphyroblasts of garnet with euhedral form and in some cases containing small included green-brown, semi-opaque grains similar to that of the 4.5-9 kb runs. Spinel reflections cannot be identified in the X-ray diffraction pattern, plagioclase reflections are weaker than in the lower pressure runs and pyroxene reflections are stronger. In the 14.6, 15.8, 16.9 and 18 kb runs, garnet porphyroblasts become more common and garnet reflections increase in intensity at the expense particularly of plagioclase. In the 18 kb run, the small amount of interstitial low R.I. phase is identified as plagioclase from extremely weak X-ray reflections. In these runs there is consistently a small amount of high R.I. phase (R.I. > garnet) of green to brown colour and apparently isotropic. This is
Table 5. Alkali olivine basalt

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Pressure (kb)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>155</td>
<td>1100</td>
<td>1 Atm.</td>
<td>6</td>
<td>Ol Px Pl Ore</td>
<td></td>
</tr>
<tr>
<td>153</td>
<td>1100</td>
<td>6-8</td>
<td>4</td>
<td>Ol Px Pl Ore</td>
<td></td>
</tr>
<tr>
<td>88</td>
<td>1100</td>
<td>9-0</td>
<td>2</td>
<td>Ol Px Pl Ore</td>
<td></td>
</tr>
<tr>
<td>92</td>
<td>1100</td>
<td>10-1</td>
<td>2</td>
<td>Ol Px Pl Ore (Spinel)</td>
<td>Amph Plagioclase and olivine less abundant. More common small pale green spinel. Trace of amphibole</td>
</tr>
<tr>
<td>167</td>
<td>1100</td>
<td>11-3</td>
<td>4</td>
<td>Px Pl Ore (Spinel)</td>
<td>Amph Plagioclase less than 10-1 kb run. No definite olivine. Common small green spinel. Trace of amphibole</td>
</tr>
<tr>
<td>483</td>
<td>1100</td>
<td>12-4</td>
<td>3</td>
<td>Px Pl Ga Ore (Spinel)</td>
<td>Amph Garnet rare but very distinctive. Spinel (green-brown translucent) very common</td>
</tr>
<tr>
<td>165</td>
<td>1100</td>
<td>13-5</td>
<td>4</td>
<td>Px Pl Ga Ore (Spinel)</td>
<td>Amph Plagioclase less than 11-3 kb run. Uncommon large garnet porphyroblasts. Trace of amphibole</td>
</tr>
<tr>
<td>484</td>
<td>1100</td>
<td>14-6</td>
<td>3</td>
<td>Px Pl Ga Ore</td>
<td>Amph Garnet well-crystallized, commonly poikilitic to semi-opaque mineral</td>
</tr>
<tr>
<td>90</td>
<td>1100</td>
<td>16-9</td>
<td>2</td>
<td>Px Pl Ga Ore</td>
<td>Amph Garnet more common than 15-8 kb run. Plagioclase reflections weak. Uncommon small semi-opaque ore. Trace amphibole</td>
</tr>
<tr>
<td>95</td>
<td>1100</td>
<td>20-2</td>
<td>4</td>
<td>Px Ga Ore Rutil</td>
<td>Not well-crystallized. Anhedral, poikilitic garnet, less abundant than in 18 kb run</td>
</tr>
<tr>
<td>96</td>
<td>1100</td>
<td>22-5</td>
<td>4</td>
<td>Px Ga Rutil</td>
<td>Well-crystallized. Abundant garnet. Common rutile. Semi-opaque absent or very rare</td>
</tr>
<tr>
<td>100</td>
<td>1100</td>
<td>24-8</td>
<td>4</td>
<td>Px Ga Rutil</td>
<td>Abundant garnet, pyroxene. Common rutile</td>
</tr>
<tr>
<td>100</td>
<td>1100</td>
<td>27-0</td>
<td>4</td>
<td>Px Ga Rutil</td>
<td>Less garnet than 24-8 kb run and not as well-crystallized as 24-8 or 38 kb runs</td>
</tr>
<tr>
<td>163</td>
<td>1100</td>
<td>36-0</td>
<td>4</td>
<td>Px Ga Rutil</td>
<td>Greenish sieve garnet with high R.I. inclusions (1 rutile). Pyroxene has distinct red-brown colour.</td>
</tr>
</tbody>
</table>
probably a spinel dominantly of magnetite–ulvospinel composition. At 18 kb this is joined by uncommon small needles of highly birefringent rutile and above 20.2 kb, rutile is common and the semi-opaque, green brown(?) spinel is absent.

Neither plagioclase nor quartz can be identified in the runs at pressures greater than 18 kb. The run at 36 kb, 1100°C differs from those at 27 kb and lower pressures in that the garnet tends to be anhedral and poikilitically includes many (?) rutile grains. The pyroxene is also distinctive in being a red-brown colour.

(c) Oxidized alkali olivine basalt

To determine the pressures of appearance and disappearance of phases in a highly oxidized, undersaturated composition, the oxidized alkali basalt composition was prepared as described previously. The calculated composition after oxidation is given in Table 1 column 6 and is no longer nepheline-normative but contains 7% normative hypersthene. The effect of oxidation is also to increase the \((100\text{Mg})/(\text{Mg} + \text{Fe}^{2+})\) ratio from 60 to 82 and increase the normative magnesium/iron ratio of the silicate minerals, e.g. normative olivine changes from \(\text{Fo}_{66}\) to \(\text{Fo}_{100}\).

The results of the experimental runs on this composition are given in Table 6.

### Table 6. Oxidized alkali olivine basalt

<table>
<thead>
<tr>
<th>Pressure (kb)</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Opx + (Sp–Mt) + ?Ol</td>
<td>Opaque (Sp–Mt) is abundant and is deep brown, translucent to almost opaque. Olivine possibly present in minor amount</td>
</tr>
<tr>
<td>13.5</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Opx + (Sp–Mt)</td>
<td>(Sp–Mt) is abundant and is translucent with green brown colour. Plagioclase abundant</td>
</tr>
<tr>
<td>14.6</td>
<td>1100</td>
<td>2 W</td>
<td>Pl + Cpx + Opx + (Sp–Mt) + Amph.</td>
<td>Similar to 13.5 kb run but amphibole also present in minor amount</td>
</tr>
<tr>
<td>15.8</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Opx + Ga + (Sp–Mt)</td>
<td>Garnet very uncommon but provides excellent comparison with spinellid (small, green-brown translucent). Plagioclase very common</td>
</tr>
<tr>
<td>18</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Opx + Ga + (Sp–Mt)</td>
<td>Plag and Opx both decreased from 15.8 kb run. Garnet well crystalized and moderately common</td>
</tr>
<tr>
<td>20.2</td>
<td>1100</td>
<td>3 D</td>
<td>Cpx + Opx + Ga + (Sp–Mt) + Rt</td>
<td>No definite plagioclase (or quartz) Opx decreased, Ga increased from 18 kb run. Rutile present. Spinellid is red-brown translucent to opaque.</td>
</tr>
<tr>
<td>22.5</td>
<td>1100</td>
<td>4 D</td>
<td>Cpx + Opx + Ga + (Sp–Mt) + Rt</td>
<td>Similar to 20.2 kb run</td>
</tr>
<tr>
<td>31.5</td>
<td>1100</td>
<td>4 D</td>
<td>Cpx ± Opx + Ga + Rt</td>
<td>Ga/Px greater than 22.5 kb run (Sp–Mt) apparently absent. Opx minor, less than 22.5 kb</td>
</tr>
</tbody>
</table>
The low pressure (9 kb) assemblage shows common deep brown, translucent to opaque grains considered to be a spinellid rich in magnetite. At 13.5 kb olivine is absent, orthopyroxene and the spinellid are more common and the spinellid is translucent with green-brown colour. It is considered that between 9 and 13.5 kb there has been reaction of olivine and plagioclase to yield increased (MgAl$_2$O$_4$) component in the spinel solid solution and increased orthopyroxene. Garnet first appears as very minor grains at 15.8 kb and at this pressure plagioclase and the green-brown translucent spinellid are still major phases.

Between 15.8 and 18 kb both orthopyroxene and plagioclase decrease at the expense of garnet but plagioclase is still identifiable by X-ray means at 18 kb. Plagioclase could not be identified at 20.2 and 22.5 kb and the spinellid is opaque or translucent, red-brown and accompanied by rutile. A run at 31.5 kb differs from those at 20.2 and 22.5 kb in having a greater garnet/pyroxene ratio, a much lower orthopyroxene content and the spinellid phase is absent or very rare.

(d) Olivine tholeiite (olivine tholeiite (A))

This composition (Table 1) has been mainly used in experimental partial melting work at high pressure but there are several sub-solidus runs aimed at defining the pressure required for the appearance of garnet (Table 7). At 9 kb, 1100°C the assemblage contains common olivine, plagioclase, pyroxene and minor green-brown translucent spinel. At 10.1 kb, 1100°C olivine is also present but much less common than at 9 kb, plagioclase has also decreased but spinel is more common. A large number of runs were carried out on this composition at 11.3 kb, 1100°C, in efforts to find experimental techniques for keeping the sample dry and preventing or decreasing the formation of amphibole. Apart from one unexplained run which contained minor euhedral garnet, these runs at 11.3 kb contain the assemblage pyroxene (clinopyroxene or orthopyroxene) ± plagioclase ± spinel ± amphibole. One run at 12.4 kb, 1100°C, also contains no garnet and minor amphibole but runs at 13.5 kb, 1100°C, contain minor euhedral garnet with pyroxene, plagioclase and minor amphibole.

The pressure required for appearance of garnet in this composition is thus less than 13.5 kb and probably around 12 kb. There is some ambiguity in the experimental results and this may in part be caused by the variable water and amphibole content of the runs. As in the alkali olivine basalt, olivine is present in moderate amount at 9 kb but rapidly decreases in favour of spinel and pyroxene at pressures above 9 kb. A small field of pyroxene + plagioclase ± spinel assemblage, again lies between the olivine-bearing and garnet-bearing assemblages.

(e) Alkali-poor olivine tholeiite (olivine tholeiite B)

The glass composition listed in Table 1 as olivine tholeiite B was prepared specifically to examine the pressure required for appearance of garnet and disappearance of plagioclase in a sodium-poor, anorthite-rich undersaturated composition, cf. Loch Duich eclogite (Yoder and Tilley).

The experimental runs were carried out at 1100°C, with dried samples and furnace assemblies and runs of 3 hr length. The results are tabulated in Table 8. There is a slight decrease in the amount of olivine present between 4.5 and 6.8 kb but a marked decrease between 6.8 and 9 kb. At 10.1 kb olivine could not be identified. There was
Table 7. Olivine tholeiite (A)

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Pressure (kb)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>485</td>
<td>1100</td>
<td>1 atm</td>
<td>6 D</td>
<td>Ox, Px, Pl</td>
<td></td>
</tr>
<tr>
<td>84</td>
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<td>9</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
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<tr>
<td>489</td>
<td>1100</td>
<td>10-1</td>
<td>2 D</td>
<td>Ox, Px, Pl</td>
<td></td>
</tr>
<tr>
<td>487</td>
<td>12-4</td>
<td>12</td>
<td>Ox, Px, Pl</td>
<td>Spinel</td>
<td>Further decrease in plagioclase. No definite garnet porphyroblasts. Spinel moderately common</td>
</tr>
<tr>
<td>469</td>
<td>13-5</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Ga</td>
<td>Weak plagioclase, weak garnet reflections but distinctive garnet porphyroblasts. Spinel minor or absent</td>
</tr>
<tr>
<td>459</td>
<td>1210</td>
<td>9</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Glass</td>
</tr>
<tr>
<td>453</td>
<td>1230</td>
<td>9</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Glass</td>
</tr>
<tr>
<td>452</td>
<td>1180</td>
<td>13-5</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Spinel</td>
</tr>
<tr>
<td>456</td>
<td>1220</td>
<td>13-5</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Spinel</td>
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<td>441</td>
<td>1220</td>
<td>13-5</td>
<td>3 D</td>
<td>Ox, Px, Pl</td>
<td>Spinel</td>
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<tr>
<td>113</td>
<td>1300</td>
<td>18</td>
<td>1 D</td>
<td>Ox, Px, Pl</td>
<td>Glass</td>
</tr>
</tbody>
</table>

Table 8. Alkali-poor olivine tholeiite (olivine tholeiite (B))

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Pressure (kb)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
<th>Estimated garnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>4-5</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ox + Ol</td>
<td>Olivine common</td>
<td>—</td>
</tr>
<tr>
<td>543</td>
<td>6-8</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ox + Ol + Sp</td>
<td>Olivine common (&gt;9 kb). Rare spinel</td>
<td>—</td>
</tr>
<tr>
<td>507</td>
<td>9</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ox + Ol + Sp</td>
<td>Minor spinellid. Olivine uncommon (&lt;5%). Opx more common</td>
<td>—</td>
</tr>
<tr>
<td>508</td>
<td>10-1</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ox + Ga + Sp</td>
<td>Rare garnet. Olivine absent. Sp. less than in 9 kb run</td>
<td>1-2%</td>
</tr>
<tr>
<td>506</td>
<td>11-3</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ox + Ga</td>
<td>Plagioclase much less than 10-1 kb. Opx also decreased. Garnet markedly increased</td>
<td>20%</td>
</tr>
<tr>
<td>515</td>
<td>12-4</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ga</td>
<td>Low R.I. phase probably plagioclase</td>
<td>30%</td>
</tr>
<tr>
<td>509</td>
<td>13-5</td>
<td>1100</td>
<td>3 D</td>
<td>Pl + Cpx + Ga</td>
<td>Minor low R.I. phase may be plagioclase. Ga/Px greater than in 11-3 kb run</td>
<td>40%</td>
</tr>
<tr>
<td>510</td>
<td>16-8</td>
<td>1100</td>
<td>3 D</td>
<td>Cpx + Ga</td>
<td>No evidence for plagioclase. Ga/Px greater than in 13-5 kb run</td>
<td>45%</td>
</tr>
<tr>
<td>511</td>
<td>18-0</td>
<td>1100</td>
<td>3 D</td>
<td>Cpx + Ga</td>
<td>Ga/Px greater than in 15-8 kb run</td>
<td>50%</td>
</tr>
<tr>
<td>535</td>
<td>22-5</td>
<td>1100</td>
<td>3 D</td>
<td>Cpx + Ga</td>
<td>Ga/Px greater than 18 kb run. Ga &gt; Px</td>
<td>56%</td>
</tr>
</tbody>
</table>
less olivine in this composition at 9 kb than in either the alkali basalt or olivine tholeiite A runs at the same pressure and temperature. The decrease in olivine is accompanied by the appearance of spinel and an increase in the amount of orthopyroxene present (Fig. 3).

Garnet appears as very rare euhedral crystals at 10·1 kb but increases sharply at 11·3 kb (Fig. 3). Plagioclase, spinel and orthopyroxene also show a marked decrease between 10·1 and 11·3 kb, but plagioclase remains detectable by X-ray means at this pressure, i.e. about 15–20% plagioclase. At 12·4 kb and 13·5 kb the amount of garnet increases and plagioclase cannot be identified with certainty by X-ray means. Interstitial low R.I. material present in the 12·4 kb run and in lesser amount in the 13·5 kb run is probably plagioclase.

In the 13·5, 15·8, 18 and 22·5 kb runs only garnet and pyroxene can be identified by X-ray means. However, there is a very clear increase in the Ga/Px ratio between 13·5 and 22·5 kb implying that garnet is forming at the expense of pyroxene at the higher pressures (Fig. 3).

(f) Iron-rich compositions

Two “rock” compositions were prepared which are normatively very similar to quartz tholeiite B and the alkali basalt but differed in having 100Mg/(Mg Fe	extsuperscript{2+}) (molecular ratio) = 2·10 instead of 100Mg/(Mg + Fe	extsuperscript{2+}) = 60 as in the initial compositions. The final compositions are given in Table 1 and the results of high pressure runs on the compositions are given in Table 9.

In the iron-rich quartz tholeiite compositions, melting occurs at a much lower temperature than in the initial quartz tholeiite composition. Thus at 1100°C, 13·5 kb the iron-rich quartz tholeiite contained common garnet and lesser pyroxene in abundant pale brown glass. At the same P–T conditions the initial quartz tholeiite contained no garnet and only very minor glass. A run at 1000°C, 11·3 kb gave an assemblage with minor, well crystallized porphyroblasts of garnet with major pyroxene and plagioclase. In two runs at 6·8 and 9 kb, large amounts of magnetic, semi-opaque spinellid and quartz (with plagioclase and minor pyroxene) contrast with the minor amount or absence of these phases at 11·3 kb, 1000°C. Analysis of the sample after the runs showed no significant change in oxidation state.

Two runs at 1000°C on the iron-rich alkali basalt composition were carried out at 6·8 and 9 kb. Both runs contain abundant fayalitic olivine, common plagioclase and minor opaque mineral. There is less olivine and more pyroxene in the 9 kb run than the 6·8 kb run and the higher pressure run also contains garnet as a minor phase.

(g) Magnesium-rich compositions

The experimental results on two highly magnesian glasses are given in Table 9. These glasses are normatively similar to the alkali basalt and quartz tholeiite B compositions but have 100 Mg/(Mg + Fe	extsuperscript{2+}) ratios of about 90.

In the magnesian quartz tholeiite composition the first appearance of minor garnet is at 16·9 kb, 1100°C. At 15·8 kb, pyroxenes and plagioclase are major phases but at 18 kb, porphyroblastic garnet is common and plagioclase is much less abundant. There is no evidence for the occurrence of spinel at pressures below those required to form pyrope garnet. The plagioclase content in the oversaturated composition at
Fig. 3. Diffractometer traces from high pressure runs on olivine tholeiite (B) (alkali-poor) and alkali olivine basalt. The traces demonstrate the reaction of olivine at lower pressures in the olivine tholeiite (B) composition (cf. runs at 9 and 10.1 kb). The relatively abrupt increase of garnet at 11.3 kb in olivine tholeiite (B) contrasts with the alkali olivine basalt composition and the gradual increase in garnet between 11 and 20 kb is well shown. The occurrence of amphibole in the alkali basalt compositions results in uncertainty in the roles of garnet and orthopyroxene. The limit of detection of plagioclase in olivine tholeiite (B) is 11.3 but plagioclase is clearly identifiable at 15.8 and 16.9 (not shown) in the alkali olivine basalt composition.
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Press. (kb)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Quartz tholeiite (normatively similar to quartz tholeiite (B)) with Mg/Mg + Fe&lt;sup&gt;2+&lt;/sup&gt; (mol. ratio) ≈ 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>359</td>
<td>1000</td>
<td>6-8</td>
<td>1 W</td>
<td>Px Pl Qz</td>
<td>Magnetite</td>
</tr>
<tr>
<td>358</td>
<td>1000</td>
<td>9-0</td>
<td>2 W</td>
<td>Px Pl Qz</td>
<td>Magnetite</td>
</tr>
<tr>
<td>364</td>
<td>1000</td>
<td>11-3</td>
<td>2 W</td>
<td>Px Pl Qz Ga</td>
<td>Ore-mineral</td>
</tr>
<tr>
<td>353</td>
<td>1100</td>
<td>13-5</td>
<td>2 W</td>
<td>Px</td>
<td></td>
</tr>
<tr>
<td>364</td>
<td>1000</td>
<td>6-8</td>
<td>1 D</td>
<td>Ol Px Pl</td>
<td>Ore-mineral</td>
</tr>
<tr>
<td>365</td>
<td>1000</td>
<td>9-0</td>
<td>1 D</td>
<td>Ol Px Pl</td>
<td>Ore-mineral</td>
</tr>
<tr>
<td>(B) Alkali basalt (normatively similar to alkali basalt of Table 1) with Mg/Mg + Fe&lt;sup&gt;2+&lt;/sup&gt; (mol. ratio) ≈ 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>351</td>
<td>1100</td>
<td>10-1</td>
<td>2 D</td>
<td>Px Pl</td>
<td>Amph Spinel</td>
</tr>
<tr>
<td>349</td>
<td>1100</td>
<td>11-3</td>
<td>4 D</td>
<td>Px Pl</td>
<td>Minor Spinel</td>
</tr>
<tr>
<td>350</td>
<td>1100</td>
<td>13-5</td>
<td>2 D</td>
<td>Px Pl</td>
<td>Minor Spinel</td>
</tr>
<tr>
<td>362</td>
<td>1100</td>
<td>18-0</td>
<td>4 D</td>
<td>Px Pl Ga</td>
<td>Minor Spinel</td>
</tr>
<tr>
<td>360</td>
<td>1200</td>
<td>9-0</td>
<td>1 D</td>
<td>Ol Px Pl</td>
<td>Minor Spinel</td>
</tr>
<tr>
<td>363</td>
<td>1200</td>
<td>11-3</td>
<td>1 D</td>
<td>Ol Px Pl</td>
<td>Amph Spinel</td>
</tr>
<tr>
<td>355</td>
<td>1200</td>
<td>13-5</td>
<td>1 D</td>
<td>Px Pl</td>
<td>Amph Spinel</td>
</tr>
<tr>
<td>357</td>
<td>1200</td>
<td>15-8</td>
<td>1 D</td>
<td>Px Pl</td>
<td>Amph Spinel</td>
</tr>
<tr>
<td>362</td>
<td>1200</td>
<td>18-0</td>
<td>2 D</td>
<td>Px Ga</td>
<td>Minor Spinel</td>
</tr>
<tr>
<td>360</td>
<td>1200</td>
<td>20-2</td>
<td>2 D</td>
<td>Px Ga</td>
<td>Minor Spinel</td>
</tr>
</tbody>
</table>

(D) Quartz tholeiite with Mg/Mg + Fe<sup>2+</sup> (mol. ratio) ≈ 90

(D) Quartz tholeiite with Mg/Mg + Fe<sup>2+</sup> (mol. ratio) ≈ 90

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Press. (kb)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>491</td>
<td>1100</td>
<td>15-8</td>
<td>3 W</td>
<td>Px Pl</td>
<td>Rutile</td>
</tr>
<tr>
<td>493</td>
<td>1100</td>
<td>16-9</td>
<td>3 W</td>
<td>Px Pl Ga</td>
<td>Rutile</td>
</tr>
<tr>
<td>500</td>
<td>1100</td>
<td>18-0</td>
<td>4 W</td>
<td>Px Pl Ga</td>
<td>Rutile</td>
</tr>
</tbody>
</table>
15.8 and 16.9 kb is much greater than the plagioclase content between 13.5 and 18 kb at 1200°C in the undersaturated magnesian composition.

In the experiments on the undersaturated magnesian alkali olivine basalt glass, the runs at 1100°C contained common amphibole. Garnet was present at 18 kb, 1100°C, but absent at 13.5 kb, 1100°C. The runs at 1200°C contained only traces of amphibole. Olivine is very common at 9 kb and coexists with common plagioclase and pyroxene. However, at 11.3 kb, olivine is very rare and plagioclase is much less abundant. Spinel is detectable both optically and by X-ray reflections and increases in amount present in the 13.5 and 15.8 kb. In both these latter runs, plagioclase reflections are only weakly present but the presence of this phase is consistent with the optical observation of an interstitial low R.I. phase with the pyroxene and spinel.

At 18 kb, large colourless, poikilitic garnets are present but not common. Spinel and definite plagioclase reflections are absent but the small amount of low R.I. phase visible optically may be plagioclase. At 20.2 kb, garnet is common and is pyrope-rich with a refractive index close to 1.71.

InVESTIGATION OF ATTAINMENT OF EQUILIBRIUM AND REVERSIBILITY OF REACTIONS

The choice of starting materials is an important factor in evaluating the significance of high pressure experimental runs. If natural rocks are used there is considerable difficulty in grinding the sample sufficiently fine for reaction to occur and to obtain homogeneity (e.g. Yoder and Tilley note the persistence of metastable kyanite, garnet and pyroxene in many of their low pressure runs using natural eclogite starting materials). Fine-grinding of natural rocks or minerals may also change the bulk composition of the sample to an appreciable extent. In our experimental study we have used basaltic glasses as starting materials. Whilst this eliminates the problems mentioned previously, the use of glass as starting material means that there is a possibility for nucleation of metastable phases during devitrification of the glass and such metastable phases may persist for the length of the experimental run. In contrast, other phases may be slow to nucleate (e.g. pyrope garnet, Boyd and England, 1962) and their absence may reflect non-equilibrium rather than their instability.

(a) Sequence of crystallization during devitrification of basaltic glass at high pressure

To investigate the sequence of crystallization of the initial glasses and any time-dependence of the mineral assemblages produced we have carried out a series of runs on the alkali-poor quartz tholeiite (A) at 18 kb, 1100°C. The length of runs was varied from ½ to 12 hr and the results are given in Table 3 and Fig. 4. Garnet was present, but near the limit of detectability by X-ray means in the ½ hr run and plagioclase was present in sufficient amount to be identifiable by X-ray means. The charge consisted of about 80% pyroxene. In the 1 and 2 hr runs garnet increased at the expense of pyroxene but in the runs of 4 hr or longer there was no apparent change in the garnet and pyroxene proportions. Runs of 2 hr or longer gave well-crystallized charges with subhedral or euhedral garnet, finely granular pyroxene and interstitial
Fig. 4. Sequence of crystallization from basaltic glass at 18 and 22.5 kb. The runs at 18 kb for varying times are on quartz tholeiite (A) composition and illustrate the gradual increase in garnet at the expense of pyroxene in runs up to 2-4 hr (see fig. 2). At 18 kb there is a decrease in plagioclase content with longer runs but at 22.5 kb plagioclase does not appear and the growth of garnet from metastable pyroxene over ½-2 hr is again demonstrated.
low R.I. phase. In the 4 hr run there was slight partial melting with segregation of small glass patches and the degree of partial melting increased in the 6 and 12 hr runs. The intensity of the plagioclase reflections is greater in the ½ and 1 hr runs than in the 2–12 hr runs.

Two runs at 18 kb, were carried out on the quartz tholeiite (B) composition for ½ and 3 hr under “dry” conditions, i.e. using the inner boron nitride furnace sleeve. The ½ hr run and 3 hr run contain similar amounts of plagioclase but garnet is not detectable by X-ray means in the ½ hr run—optical examination reveals uncommon, very small garnets. The amount of garnet and garnet/pyroxene ratio is not as great in the 3-hr “dry” run as in the 4 hr “wet” run and implies metastable persistence of some pyroxene in the “dry” run. The comparison is an indication of the catalytic effect of water in increasing reaction rates.

A sequence of runs at 22.5 kb, 1100°C, on the alkali poor quartz tholeiite shows a similar sequence of crystallization (Table 3) with short runs consisting dominantly of pyroxene and the Ga/Px ratio increasing in longer runs (Fig. 4). Plagioclase was not observed in any of the 22.5 kb runs.

From these experiments we infer that in the P–T fields where garnet, pyroxene and plagioclase or garnet, pyroxene and quartz are the major phases, the initial devitrification of the glass is mainly to a complex metastable pyroxene. Garnet is relatively slow to nucleate and grows at the expense of the pyroxene over a period up to 2 hr. After 2–4 hr under our experimental conditions the sample shows no further changes in the garnet:pyroxene ratio. Runs for longer times only increase the degree of partial melting.

(b) Low-pressure stability limit of garnet

The previous experiments demonstrate that garnet is stable at 18 kb, 1100°C in the quartz tholeiite compositions but that it is much slower than pyroxene to nucleate and grow. It is thus necessary to establish that the first appearance of garnet and the decreasing proportion of garnet in runs below 18 kb are equilibrium effects and not effects of slower nucleation of garnet at low pressures.

A mixture of the same chemical composition as quartz tholeiite (B) was prepared using analyzed garnets and pyroxenes from Norwegian eclogites (Green and Easton, unpublished data). This was finely ground and optical examination showed that although much of the material was less than 1–2 μ grain size, some garnet and pyroxene fragments remained greater than 20–30 μ. An experimental run at 11·3 kb, 1100°C, gave common pyroxene + plagioclase + minor garnet but a run at 13·5 kb, 1100°C (outside the stability limit for garnet defined by the runs using glass starting material) contained pyroxene + plagioclase + garnet (Table 10). The experiments were inconclusive as the garnet present in both runs was anhedral, smaller in grain size than much of the original garnet and probably metastable relics. The runs illustrate the difficulty of attaining equilibrium using starting material of natural rocks or natural minerals.

An alternative approach was made using glass of quartz tholeiite B composition to which 2% of extremely finely ground garnet was added (1–3 μ grain size). The results of runs on this seeded mixture are given in Table 10. These experiments demonstrate that garnet is stable at 14·6 kb, unstable at 12·4 kb and most probably...
Table 10. Reversibility of reactions on quartz tholeiite (B) composition

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Press. (kb)</th>
<th>Time (hr)</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eclogite of quartz tholeiite (B) composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Coarse-grained</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>1100</td>
<td>11.3</td>
<td>4 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>332</td>
<td>1100</td>
<td>13.5</td>
<td>6 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>333</td>
<td>1100</td>
<td>18-0</td>
<td>6 W</td>
<td>Px</td>
<td>Ga</td>
</tr>
<tr>
<td>(b) Fine-grained (Al₂O₃ admixture)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1200</td>
<td>9-0</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
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<tr>
<td>331</td>
<td>1200</td>
<td>11.3</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>327</td>
<td>1200</td>
<td>12.4</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>328</td>
<td>1200</td>
<td>13.5</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>330</td>
<td>1200</td>
<td>16.9</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>334</td>
<td>1200</td>
<td>20.2</td>
<td>1 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>(c) Garnet seeded (2%) quartz tholeiite (B) glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>505</td>
<td>1100</td>
<td>12.4</td>
<td>4 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>503</td>
<td>1100</td>
<td>13.5</td>
<td>3 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>504</td>
<td>1100</td>
<td>14.8</td>
<td>3 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>(d) Quartz tholeiite (B) crystallized at 900°C, 27 Kb–Px + Ga + Qz assemblage, in part metastable pyroxene as Px/Ga greater than 27 kb, 1100 °C runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>609</td>
<td>1100</td>
<td>16.9</td>
<td>2 W</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>611</td>
<td>1100</td>
<td>18.0</td>
<td>4 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
<tr>
<td>613</td>
<td>1100</td>
<td>19.1</td>
<td>4 D</td>
<td>Px</td>
<td>Pl</td>
</tr>
</tbody>
</table>

Note: These three runs show very similar plagioclase, garnet and pyroxene contents to the original runs at the same conditions, using glass starting material.
unstable at 13.5 kb. These results are in agreement with the first appearance of garnet at 14.6 kb from the unseeded glass.

(c) Possible metastable persistence of plagioclase to high pressures

In the quartz tholeiite compositions, the presence of plagioclase with garnet and pyroxene up to pressures around 20 kb could result from metastable growth of plagioclase during devitrification of the glass and persistence of the metastable phase throughout the length of the run. The presence of plagioclase in the ½ hr, 18 kb, 1100°C run, previously described and its apparent decrease in longer runs would be consistent with such a process.*

We attempted to crystallize plagioclase at 17–20 kb from initial mixes of the same chemistry as quartz tholeiite (B) but prepared from analyzed garnets and pyroxenes from eclogites. The results were inconclusive—samples were either too coarse for complete reaction or extremely fine grinding introduced gross contamination. However it was demonstrated that an initial mix composed of garnet + omphacite + quartz (+Al₂O₃ introduced during grinding in an alundum mortar) crystallizes to assemblages of pyroxene + garnet + plagioclase between 12.4 and 20.2 kb at 1200°C and assemblages of pyroxene + spinel + plagioclase + glass at 9 kb, 1200°C and 11.1 kb, 1200°C (Table 10). The Al₂O₃ contamination changed the bulk chemistry from quartz normative with about 14% Al₂O₃ to corundum-normative with 25–30% Al₂O₃.

Greater success was obtained in preparing a fine-grained eclogite mineralogy by holding a large sample of quartz tholeiite (B) glass at 27 kb, 900°C, for 2 hr. The glass crystallized to a fine-grained pyroxene + garnet + quartz assemblage and plagioclase was completely absent. The Ga/Px ratio was smaller than those in previous 27 kb runs indicating that some of the pyroxene was metastable. Portions of this sample were then re-run at 16.9, 18, and 19.1 kb, 1100°C (Table 10). In all cases the assemblage consisted of pyroxene + garnet + plagioclase in closely similar proportions to those observed in the initial runs on the quartz tholeiite glass at the same pressures. Plagioclase decreased in amount with increasing pressure. The experiments demonstrate the growth of plagioclase from crystalline pyroxene + garnet + quartz assemblages at pressures near 20 kb. We conclude that plagioclase is in equilibrium with pyroxene + garnet at pressures up to 20 kb, 1100°C in quartz tholeiite B composition.

(d) Conclusion

The above investigation of crystallization and equilibrium in the quartz tholeiite composition shows that there is no evidence that the use of glassy starting material causes growth of long-persisting metastable phases or non-nucleation of other phases, at least for the compositions and experimental procedures used in this study. Conversely the use of glasses rather than natural mineral mixes avoids difficulties of fine grinding, contamination and lack of reaction. We have not made similarly detailed

* This observation could also result from increased partial melting in longer runs or from growth of plagioclase during the first few minutes of the run when the temperature is at 1100°C but the pressure in the furnace has not reached equilibrium and is less than 18 kb. If plagioclase formed at this stage it may take a little time to react away.
studies of the crystallization of glasses other than the quartz tholeiite but the consistency of our results does not suggest any greater difficulties in attaining equilibrium.

**Discussion of Experimental Results**

(a) **Main features of the mineral assemblages**

In the preceding sections we have described the mineral assemblages experimentally obtained under high pressure, high temperature conditions from a variety of basalt compositions. In all cases we found that at temperatures between 1000°C and the solidus the mineralogy of the chosen compositions at low pressures is closely comparable with the mineralogy of gabbros and dolerites of similar chemistry. In contrast, at high pressures all the compositions have mineralogies dominated by garnet and pyroxene, all are without plagioclase and many contain quartz and rutile. The high pressure mineralogy is closely comparable to the mineralogy of natural eclogites.

The transitional mineral assemblages between the low-pressure granulite and high pressure eclogite assemblages in a broad spectrum of basalts from quartz-normative to picritic compositions are characterized by the association of garnet ± clinopyroxene ± plagioclase ± quartz ± orthopyroxene. Within the transition interval the mineralogical changes are gradual with increase in garnet and decrease in plagioclase as the pressure is increased. The pressure at which a given phase appears or disappears in the experimental runs is dependent on bulk chemistry. The strong chemical control of mineralogy means that clarity in usage of rock names is necessary, particularly in the use of the term “eclogite”. In this paper we use “eclogite” for a rock of basaltic chemistry consisting mineralogically of garnet (almandine–pyrope solid solution) ± clinopyroxene with or without quartz, kyanite, hypersthene or olivine as minor minerals. Plagioclase is absent as a primary phase from rocks strictly classifiable as eclogites and in addition the clinopyroxene of eclogites contains jadeite solid solution and a high jadeite/Tschermak’s silicate ratio (White, 1964). The reasons for choosing this definition will become apparent in later sections. The definition is in harmony with much modern usage of the rock name.

(b) **Mineral reactions and equilibria of the gabbro to eclogite transition**

While the mineral assemblages observed at 1100°C at pressures below 7 kb may be classed as gabbroic and those observed above 21 kb may be classed as eclogitic, there is a sequence of mineralogical changes within this interval which illustrate the gradual nature of the gabbro to eclogite transition. In Figs. 5 and 6 the variations in mineralogy at 1100°C for the pressure range up to 27 kb are shown for the quartz tholeiite (B) composition and the alkali olivine basalt composition. These diagrams illustrate the approximate mineralogical compositions of the transitional assemblages at any particular pressure and comparison of the two diagrams shows the important role of undersaturation, i.e. olivine-normative character, in bringing in spinel + plagioclase + pyroxenes as a transitional mineralogy and in causing reactions involving anorthite to begin at lower pressures.

In Fig. 7 the temperature and compositional dependence of the pressure for incoming of garnet and disappearance of plagioclase is illustrated for the oversaturated quartz tholeiite compositions in the temperature range 1000–1250°C.
An experimental investigation of the gabbro to eclogite transformation

Fig. 5. Diagrammatic representation of the change of mineralogy with change of pressure at 1100°C in the quartz tholeiite (B) composition.

Fig. 6. Diagrammatic representation of the change in mineralogy with pressure at 1100°C in the alkali olivine basalt composition. The role of nepheline is uncertain and it is probable that some reactions involving olivine cause hypersthen to appear at lower pressures (4-5 kb) than shown in the diagram (cf. Fig. 3). Further work on reactions involving iron-bearing olivine, nepheline, plagioclase and spinel at pressures less than 10 kb is necessary.
Fig. 7. Pressure-temperature dependence of the appearance of garnet and disappearance of plagioclase in the quartz tholeiite compositions. The first appearance of garnet in quartz tholeiites with 100 Mg/Mg + Fe\(^{2+}\) = 61 is on the high pressure side of “AB”. The line “G” marks the first appearance of garnet in quartz tholeiite with 100 Mg/(Mg + Fe\(^{2+}\)) = 10 and the line “F” marks the first appearance of garnet in quartz tholeiite with 100 Mg/(Mg + Fe\(^{2+}\)) = 90. Plagioclase is absent on the high pressure side of the line CD in quartz tholeiite (B) composition but is absent on the high pressure side of the line “E” in quartz tholeiite (A) composition.

The line BD is the approximate solidus of the dry quartz tholeiite (B) composition.

At pressures lower than those of curve AB, Fig. 7, the quartz tholeiite compositions [with 100 Mg/(Mg + Fe\(^{2+}\)) = 60] crystallized to the typically gabbroic or pyroxene granulite assemblage of pyroxene(s) + plagioclase + accessory opaque mineral + accessory rutile. A small amount of quartz was probably present. Comparisons of intensities of X-ray reflections for runs between 4.5 and 13.5 kb at 1000, 1050 and 1100°C in both A and B compositions show that plagioclase decreases relative to pyroxene abundance with increasing pressure. Density of the charges increases with pressure over the same pressure range. It is inferred that this is a result of increasing
solubility of Al₂O₃ in pyroxene with increasing pressure according to the idealized reactions

(a) \( \text{CaAl}_2\text{Si}_2\text{O}_8 + m\text{MgSiO}_3 \rightleftharpoons \text{CaMgSi}_3\text{O}_6 + (m - 2)\text{MgSiO}_3\cdot\text{MgAl}_2\text{SiO}_6 + \text{SiO}_2 \)

(b) \( \text{CaAl}_2\text{Si}_2\text{O}_8 + m\text{CaMgSi}_2\text{O}_6 \rightleftharpoons m\text{CaMgSi}_3\text{O}_6\cdot\text{CaAl}_2\text{SiO}_6 + \text{SiO}_2 \)

These reactions imply that the pyroxenes of the transitional mineral assemblage are characteristically rich in Al₂O₃ as Tschermak's molecule substitution. On the other hand the jadeite content of the clinopyroxene is low up to pressures around 18–20 kb, marking the final disappearance of plagioclase.

Between curves AB and CD in Fig. 7 garnet increases in amount and becomes more pyrope-rich with increasing pressure (Table 11). The growth of garnet may be represented by a combination of the equations

(c) \( 4(\text{Mg,Fe})\text{SiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{orthopyroxene} \rightarrow (\text{Mg,Fe})_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Ca(Fe, Mg)Si}_2\text{O}_6 + \text{SiO}_2 \)

(d) \( 2(\text{Mg,Fe})\text{SiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{Ca(Fe, Mg)Al}_2\text{Si}_3\text{O}_{12} + \text{SiO}_2 \)

Table 11. Compositions of garnets in the quartz tholeiite compositions at high pressure

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (kb)</th>
<th>R.I.</th>
<th>( a_0 ) (Å)</th>
<th>Estimated composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz tholeiite (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>14.6</td>
<td>1.770–1.775</td>
<td>—</td>
<td>\text{Pyr}<em>{26} \text{Alm}</em>{46} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>15.8</td>
<td>1.765 ± 0.01</td>
<td>11.59 ± 0.01</td>
<td>\text{Pyr}<em>{24} \text{Alm}</em>{48} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>16.9</td>
<td>1.755 ± 0.01</td>
<td>11.59 ± 0.01</td>
<td>\text{Pyr}<em>{41} \text{Alm}</em>{26} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>18.0</td>
<td>1.750 ± 0.01</td>
<td>—</td>
<td>\text{Pyr}<em>{46} \text{Alm}</em>{26} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>20.2</td>
<td>1.750 ± 0.01</td>
<td>—</td>
<td>\text{Pyr}<em>{46} \text{Alm}</em>{26} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>22.5</td>
<td>1.750 ± 0.01</td>
<td>11.59 ± 0.01</td>
<td>\text{Pyr}<em>{49} \text{Alm}</em>{23} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>24.8</td>
<td>1.745 ± 0.01</td>
<td>—</td>
<td>\text{Pyr}<em>{49} \text{Alm}</em>{23} \text{Gross}_{28}</td>
</tr>
<tr>
<td>1100</td>
<td>27.0</td>
<td>1.745 ± 0.01</td>
<td>—</td>
<td>\text{Pyr}<em>{49} \text{Alm}</em>{23} \text{Gross}_{28}</td>
</tr>
</tbody>
</table>

Quartz tholeiite (B)

| 1100 | 14.6 | 1.775 ± 0.01 | — | \text{Pyr}_{24} \text{Alm}_{48} \text{Gross}_{28} |
| 1100 | 27.0 | 1.745 ± 0.01 | — | \text{Pyr}_{49} \text{Alm}_{23} \text{Gross}_{28} |

These reactions involve members of solid solution series and are spread over a broad \( P-T \) interval. Garnet may also form from break-down of the aluminous pyroxenes according to the equations

(e) \( m\text{MgSiO}_3 \cdot \text{MgAl}_2\text{SiO}_6 \rightleftharpoons \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + (m - 2)\text{MgSiO}_3 \)

(f) \( m\text{CaMgSi}_3\text{O}_6\cdot\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{MgSiO}_3 \rightleftharpoons \text{CaMg}_2\text{Al}_2\text{Si}_3\text{O}_{12} + m\text{CaMgSi}_2\text{O}_6 \)
The evidence from our experimental results is that these reactions do not proceed to the right until pressures of 16–20 kb.

Since the reactions at lower pressures within the transitional mineral assemblages involve anorthite molecule but the assemblages are characterized by the persistence of plagioclase, we infer that this plagioclase becomes more sodic with increasing pressure in the transitional mineral assemblages. This will continue until the coupled reaction of albite to yield jadeite solid solution in the clinopyroxene keeps pace with reaction of the anorthite molecule

\[
\text{albite} + \text{diopside} \rightarrow \text{"omphacite"}
\]

In Figs. 5 and 6 attention has been drawn to the observation that garnets first appearing at lower pressures are almandine-rich (Table 11). Since the garnet increases in amount and becomes more pyrope-rich at higher pressure, the partition of iron and magnesium between garnet and pyroxene will vary with increasing pressure, i.e. at constant temperature the Ga:Cpx and Ga:Opx distribution coefficients for Fe/Mg will vary with pressure and in addition the “garnet to rock tie line” in a Ca–Mg–Fe plot will change with increasing pressure (cf. Coleman et al., 1965; Subramaniam, 1956).

The role of TiO\(_2\) in our assemblages is of interest. At low pressures the deep-brown translucent to opaque mineral present in minor amounts is assumed to be a magnetite–ulvospinel solid solution. Minor rutile is also present. However, above 13.5 kb in the quartz tholeiite compositions the semi-opaque mineral rapidly decreases and rutile increases in abundance. It is possible that the instability of the ulvospinel is related to the increased activity of SiO\(_2\)

\[
\text{Fe}_2\text{TiO}_4 + 2\text{SiO}_2 \rightleftharpoons 2\text{FeSiO}_3 + \text{TiO}_2
\]

In the undersaturated alkali-olivine basalt composition, rutile does not replace the spinel as the main Ti-bearing phase until pressures above 18 kb. In this composition, free quartz does not occur and the reactions involved in the breakdown of the ulvospinel are presumably more complex. In this context it is worth noting that while rutile is a common phase in eclogites, magnesian ilmenite is stable in the more undersaturated garnet peridotites—this implies instability of the pair magnesian olivine + rutile under high pressure conditions

\[
(\text{Fe,Mg})_2\text{SiO}_4 + \text{TiO}_2 \rightleftharpoons (\text{Fe,Mg})\text{TiO}_3 + (\text{Fe,Mg})\text{SiO}_3
\]

The experimental data on the quartz tholeiite compositions thus lead to the conclusion that the transitional mineral assemblages between gabbro and eclogite are characterized by

(a) pyroxenes rich in Al\(_2\)O\(_3\) as Tschermak’s silicate substitution and relatively poor in jadeite

(b) persistence of plagioclase but of composition commonly more sodic than normative calculations would suggest

(c) by the association of garnet + clinopyroxene + plagioclase ± quartz.
(c) Control of mineral assemblages by variations in chemistry of basalts

(i) Degree of silica saturation. The discussion in the previous section referred mainly to mineralogical changes observed in the oversaturated quartz-normative tholeiite compositions. In the undersaturated alkali olivine basalt and olivine tholeiite compositions reaction between olivine and plagioclase becomes important at about 7 kb at 1100°C. This is at a considerably lower pressure than similar reactions (in this case between orthopyroxene and plagioclase) occur in the oversaturated compositions. In the compositions with 100Mg/(Mg + Fe²⁺) ≈ 60–70 the reactions at around 7–9 kb yield spinel and pyroxene at the expense of olivine and plagioclase. The following idealized reactions are considered to be important

\[
2\text{Mg}_2\text{Si}_2\text{O}_6 + 2\text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{CaMgSi}_2\text{O}_6 \cdot \text{CaAl}_2\text{Si}_2\text{O}_6 + 2\text{MgSiO}_3 \cdot \text{MgAl}_2\text{Si}_2\text{O}_6
\]

olivine \hspace{1cm} anorthite \hspace{1cm} aluminous diopside \hspace{1cm} aluminous enstatite

\[
2\text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{CaMgSi}_2\text{O}_6 + 2\text{MgSiO}_3 + \text{MgAl}_2\text{O}_4
\]

olivine \hspace{1cm} anorthite \hspace{1cm} diopside \hspace{1cm} enstatite \hspace{1cm} spinel

In more iron-rich compositions, there may be no intermediate spinel-bearing assemblage and olivine and plagioclase may react to yield garnet

\[
2(\text{Fe},\text{Mg})_2\text{Si}_2\text{O}_6 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons (\text{Fe},\text{Mg})_2\text{Al}_2\text{Si}_3\text{O}_{12}
\]

olivine \hspace{1cm} anorthite \hspace{1cm} garnet

In compositions of similar Mg/(Mg + Fe²⁺) ratio, garnet appears at lower pressures in undersaturated compositions than in oversaturated compositions, e.g. at 12.4 kb in the alkali olivine basalt but at 14.6 kb in the quartz tholeites (A) and (B). The appearance and increase of garnet at higher pressures in the undersaturated compositions is coupled to a decrease in plagioclase and a decrease in spinel. The reactions involved are probably approximated by the reaction

\[
(\text{Fe},\text{Mg})_4\text{Al}_2\text{O}_4 + \text{CaAl}_2\text{Si}_2\text{O}_8 + 4(\text{Fe},\text{Mg})\text{SiO}_3 \rightleftharpoons 2\text{Ca}_{0.5}(\text{Fe},\text{Mg})_{2.5}\text{Al}_2\text{Si}_3\text{O}_{12}
\]

spinel \hspace{1cm} anorthite \hspace{1cm} orthopyroxene \hspace{1cm} garnet

We infer from our data that olivine and anorthite-rich plagioclase could not co-exist in a basaltic composition at 1100°C at pressures greater than 11 kb.

In the undersaturated compositions, plagioclase disappears at lower pressures than in the quartz tholeites of similar normative plagioclase composition and abundance, e.g. compare alkali olivine basalt with quartz tholeiite (B), or olivine tholeiite (A) with the alkali-poor quartz tholeite (A). In these undersaturated compositions the albite breakdown may be coupled to reactions involving spinel and free quartz may not appear as a new phase.

\[
\text{NaAlSi}_3\text{O}_8 + 2(\text{Mg},\text{Fe})\text{SiO}_3 + (\text{Mg},\text{Fe})\text{Al}_2\text{O}_4 \rightleftharpoons \text{NaAlSi}_2\text{O}_6 + (\text{Mg},\text{Fe})_3\text{Al}_2\text{Si}_3\text{O}_{12}
\]

albite \hspace{1cm} orthopyroxene \hspace{1cm} spinel \hspace{1cm} jadeite \hspace{1cm} garnet

Coupled reactions such as that above could lead to elimination of plagioclase at lower pressures than reactions involving release of quartz, cf. albite + nepheline → jadeite and albite → jadeite + quartz reactions (Fig. 8).

The compositions of basalts used in this study provide little evidence on the effects of more extreme undersaturation and the presence of normative nepheline. In the alkali-olivine basalt compositions the run at 1 atm contains olivine and there is no
evidence for the presence of orthopyroxene. This is in agreement with the normative composition but contrasts with the presence of probable orthopyroxene at 4-5 kb and higher pressures (Fig. 3). The decrease in olivine and plagioclase and increase in pyroxene between 1 atm and 4-5 kb suggests that the olivine + plagioclase reaction in this composition is spread over a broad pressure interval and at lower pressures may be coupled to reactions involving nepheline.

(ii) Albite content and albite:anorthite ratio. The effects on the gabbro–eclogite transition of varying the albite content of the composition and thus the normative plagioclase composition can be gauged by comparing results on quartz tholeiites (A) and (B) and by comparing olivine tholeiite (B) (Na₂O-poor) with the alkali olivine basalt and with olivine tholeiite (A). The quartz tholeiite (B) composition was prepared from the alkali-poor quartz tholeiite composition by addition of analyzed albite and orthoclase, mixing and remelting. The higher albite content has the effect of extending the stability field of plagioclase to higher pressures and increasing the proportion of plagioclase present in lower pressure runs. Plagioclase decreases below the limit of detection by X-ray means at 18–19 kb in quartz tholeiite (A) but at 20–21 kb in quartz tholeiite (B). This trend is expected to continue and the pressure required for elimination of plagioclase in andesites and dacites should be considerably higher. This is in agreement with the experimental work of Green and Lambert (1965) on an adamellite composition where at 950°C plagioclase remained stable up to 21 kb* and at 1100°C, the albite content of the feldspar solid solution remained large up to 24-5 kb.*

Although in the quartz tholeiites examined it is an increase in albite content which extends the stability field of plagioclase to higher pressures, an increase in anorthite may have a similar effect. In the compositions examined the disappearance of anorthite molecule is due to reaction with olivine or orthopyroxene as described in the previous section. However in some basaltic compositions, particularly high-alumina basalts, the content of enstatite and olivine is too low to account for removal of anorthite. Anorthite molecule may to some degree go into pyroxene solid solution but may also remain in a stable plagioclase phase to higher pressures, close to the pressure required for breakdown of anorthite according to the reaction—

\[ \text{anorthite} \rightarrow \text{grossular} + \text{kyanite} + \text{quartz} \]

T. H. Green (personal communication) has made a detailed study of subsolidus relations in a high-alumina basalt composition and a kyanite–eclogite composition and finds plagioclase stable to slightly higher pressures than we observed in the quartz tholeiite compositions.

In the undersaturated compositions, plagioclase decreases below the limit of X-ray detection between 17 and 18 kb in the alkali olivine basalt (Fig. 3). In the alkali-poor olivine tholeiite (B), the Na₂O content is only 0.8% and the normative plagioclase is An₈₃. In this composition plagioclase decreases below the limit of X-ray detection at the very much lower pressure of 12–13 kb and plagioclase is apparently completely absent at and above 15.8 kb (Fig. 3).

* These values are corrected for a 10% friction correction, not applied by Green and Lambert.
The comparison of olivine-rich undersaturated basalts demonstrates the strong control by the \( \text{Na}_2\text{O} \) content and albite/anorthite ratio of the pressure at which plagioclase disappears. A more indirect effect of the plagioclase composition involves reaction with the olivine. The alkali olivine basalt and olivine tholeiite (A) both have normative plagioclase compositions of about \( \text{An}_{80} \) and in both cases olivine shows a marked decrease between 9 and 10 kb. However, in olivine tholeiite (B) with plagioclase composition \( \text{An}_{83} \), olivine decreases sharply in abundance between 6·8 and 9 kb. In addition, garnet first appears at 10·1 kb in this composition whereas it does not appear till 12·4 kb in the alkali olivine basalt and olivine tholeiite (A) compositions. Since the \( \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) \) ratios of all three rocks are closely similar the reason for the appearance of garnet at lower pressure in the alkali-poor olivine tholeiite is presumably complex, perhaps involving differences in spinel, aluminous pyroxene or modal plagioclase compositions.

Thus, in general, it is apparent that the composition and relative abundance of plagioclase in basaltic compositions exercises important control over the pressure at which an assemblage of garnet + pyroxene ± quartz is produced. In rocks with the molecular ratio (of normative minerals) \((\text{Opx} + 2\text{O}l)/\text{An} > 2\), the plagioclase will be stable to higher pressures in the rocks of higher albite content. Plagioclase will disappear at particularly low pressures in a composition rich in olivine and with very anorthite-rich normative plagioclase. The plagioclase composition also influences reactions involving the ferromagnesian phases. Reaction between olivine and plagioclase occurs at lower pressures in a composition rich in olivine and with very anorthite-rich normative plagioclase.

(iii) Oxidation. It has been suggested by CHURCH (in press, and personal communication) that in rocks with high \( \text{Fe}^{3+}/\text{Na} \) or magnetite/albite ratios, the plagioclase could disappear at relatively low pressure yielding acmite aluminous pyroxenes or acmite pyroxenes with garnet. Possible idealized reactions are as follows:

\[
\begin{align*}
\text{(p)} \quad & 2\text{NaAlSi}_3\text{O}_8 + \text{Fe}_3\text{O}_4 + \text{CaMgSi}_2\text{O}_6 \rightleftharpoons \\
& \text{albite} \quad \text{magnetite} \quad \text{diopside} \\
& 2\text{NaFe}^{3+}\text{Si}_2\text{O}_6 + \text{Ca}(\text{MgFe})_2\text{Al}_2\text{Si}_3\text{O}_{12} + \text{SiO}_2 \\
& \text{acmite} \quad \text{garnet} \quad \text{quartz} \\
\text{(q)} \quad & 2\text{NaAlSi}_3\text{O}_8 + \text{Fe}_3\text{O}_4 + m\text{CaMgSi}_2\text{O}_6 \rightleftharpoons \\
& \text{albite} \quad \text{magnetite} \quad \text{diopside} \\
& m\text{CaMgSi}_2\text{O}_6+\text{FeAl}_2\text{Si}_3\text{O}_6·2\text{NaFe}^{3+}\text{Si}_2\text{O}_6 + \text{SiO}_2 \\
& \text{Pyroxene with acmite + Tschermak's silicate solid solution} \quad \text{quartz}
\end{align*}
\]

The experiments on the oxidized basalt, when compared with the runs on the original alkali olivine basalt and runs on the olivine tholeiite compositions with low \( \text{Fe}^{3+} \) contents, show that oxidation delayed the appearance of garnet to a higher pressure, comparable with that at which garnet first appeared in the "magnesian alkali olivine basalt". Oxidation and the increase in the \( \text{Fe}^{3+}/\text{Na} \) ratio does not cause reactions such as (p) and (q) above to run at lower pressures. On the contrary, plagioclase persists to higher pressures in the oxidized composition than in the original alkali olivine basalt composition. At higher pressures, above those required to eliminate plagioclase, magnetite and orthopyroxene decrease in favour of
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804 garnet—this observation implies a possible reaction as follows—

\[
2\text{NaAlSi}_2\text{O}_6 + \text{Fe}_2\text{O}_4 + 2\text{MgSiO}_3 + \text{SiO}_2 \rightleftharpoons 2\text{NaFe}^{3+}\text{Si}_2\text{O}_6 + \text{Mg}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}
\]

jadeite magnetite orthopyroxene quartz acmite garnet

(iv) Iron to magnesium ratio. A reconnaissance study of the effects of Fe/Mg ratio on the \(P-T\) stability fields in the gabbro–eclogite transition was suggested by the observation that the garnets which formed at low pressure in the quartz tholeiite compositions were almandine-rich and garnet became more pyrope-rich with increasing pressure. In the experiments on the “iron-rich” and “magnesium-rich” compositions we are able to compare compositions with closely matched normative mineralogy but with values of the 100Mg/(Mg + Fe\(^{2+}\)) atomic ratio at the extremely magnesian end (90) and extremely iron-rich end (10). The range of this ratio in common basalt types is from around 40 to 70.

In the iron-rich quartz tholeiite the appearance of garnet at 11.3 kb, 1000°C is at a considerably lower pressure than in the original quartz tholeiite (13.5 kb, 1000°C) (Fig. 7). In the alkali olivine basalt compositions, garnet first appears at about 8 kb, 1000°C, in a composition with 100Mg/(Mg + Fe\(^{2+}\)) \simeq 10 but first appears at 12.4 kb, 1100°C, or about 11 kb, 1000°C in a composition with 100Mg/(Mg + Fe\(^{2+}\)) \simeq 60. In addition, the appearance of garnet at low pressure in the iron-rich alkali basalt composition, eliminates the spinel + pyroxenes + plagioclase assemblage. In the run at 10 kb, 1000°C, on the iron-rich composition fayalitic olivine and garnet co-exist but in the original alkali olivine basalt composition olivine and garnet did not occur together in the same assemblage.

The experiments on the magnesium-rich compositions confirm the trends noted above. Thus garnet does not appear until about 16.9 kb at 1100°C in the extremely magnesian quartz tholeiite (Fig. 7). In the magnesian alkali olivine basalt composition there is a broad field of the pyroxenes + spinel + plagioclase assemblage between the low pressure olivine bearing and high pressure garnet-bearing assemblages with garnet appearing at about 16.5 kb, 1100°C.

Although the experiments are of a reconnaissance nature, they demonstrate clearly that the pressure required for appearance of garnet in any basaltic assemblage is strongly controlled by the iron/magnesian ratio of the rock. Thus in the quartz tholeiite compositions, variation of the 100Mg/(Mg + Fe\(^{2+}\)) ratio from 10 to 90 causes a difference of about 4 kb at 1000°C or a difference of about 250°C at 15 kb in the conditions necessary for the appearance of garnet. Considering the variation of the 100Mg/(Mg + Fe\(^{2+}\)) ratio in common basalts, differences in conditions of about half the range indicated are probably applicable in natural rocks.

(v) Water content. Our experimental procedures do not allow a controlled study of the effects of variation in water content and \(P_{\text{H}_2\text{O}}\) on the behaviour of our high pressure mineral assemblages. However, the early difficulties in preventing access of large amounts of water from dehydration of the talc furnace sleeve have yielded some useful information on the role of amphibole at high pressure.

Even with the precautions detailed previously, it is apparent that water (or hydrogen) migrates into the capsule and in long runs, hydrous phases may form, particularly in the undersaturated compositions. It was found that in unsuccessful runs in which amphibole formed to a large extent, the phases which were reduced in
abundance or eliminated from the assemblage were olivine, plagioclase or garnet, depending on the particular \( P-T \) conditions. When examined optically, charges with amphibole present are patchy with pools of pale-brown and pleochroic amphibole of coarse grain-size which contrast with the fine grained two-phase aggregate of pyroxene and low R.I. plagioclase. The greatest difficulty in eliminating amphibole from the assemblages was experienced in the 10–20 kb range. It appears that at pressures of 10 kb and less, a temperature of 1100°C was sufficient to dissociate the amphibole under the \( P_{H_2O} \) conditions prevailing \( (P_{H_2O} < P_{Load}) \) in both oversaturated and undersaturated compositions.

At pressures between 10 and 20 kb, runs at 1100°C on the undersaturated glasses contain amphibole in major or minor amounts depending upon the nature of the drying procedure and the length of the run. The data suggests that amphibole (probably of small compositional range) is stable at 1100°C over this pressure range under conditions of quite low \( P_{H_2O} \).

This behaviour contrasts with that of the quartz tholeiites in which under conditions of ready access of water, amphibole did not form at the same \( P-T \) conditions or even in runs at 1000°C. At pressures above 20 kb, amphibole did not form at 1100°C in the undersaturated compositions, either because there was no access of water to the charge or because the amphibole was unstable relative to the assemblage pyroxene + garnet + water under our experimental conditions. The breakdown products of amphibole in the high pressure field are quite different from those at low pressure, e.g. the breakdown of common hornblende may be represented by the following equations:

\[
\begin{align*}
\text{(s)} \quad & \text{NaAlSi}_3\text{O}_8 + \text{NaAlSi}_4\text{O}_4 + 4\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{CaMgSi}_2\text{O}_6 \\
& \text{albite} \quad \text{nepheline} \quad \text{anorthite} \quad \text{diopside} \\
& + 6\text{Mg}_2\text{SiO}_4 + 4\text{H}_2\text{O} \\
& \text{olivine} \quad \text{water} \\
\text{Low Pressure} \\
& 4(\text{Na}_{0.5}\text{Ca}_{2}\text{Mg}_{4}\text{Al}_{2.5}\text{Si}_{6.5}\text{O}_{22}(\text{OH})_2) \\
& \text{Common hornblende (DEER et al., 1963, p. 272)} \\
& \text{High Pressure} \\
& 2\text{NaAlSi}_2\text{O}_6 + 4\text{CaMg}_2\text{Al}_2\text{Si}_3\text{O}_{12} + 4\text{CaMgSi}_2\text{O}_6 \\
& \text{jadeite} \quad \text{garnet} \quad \text{diopside} \\
& + 2\text{Mg}_2\text{SiO}_4 + 4\text{H}_2\text{O} \\
& \text{olivine} \quad \text{water}
\end{align*}
\]

The \( \Delta V \) terms in these reactions will be dependent on the nature of the solid reaction products but particularly on the specific volume of water at the conditions of reaction. If we consider the simplest breakdown reaction for an amphibole end member, i.e. 

\[
\begin{align*}
\text{(t)} \quad & \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightleftharpoons 2\text{CaMgSi}_3\text{O}_6 + 3\text{MgSi}_3\text{O}_3 + \text{Si}_2\text{O}_5 + \text{H}_2\text{O} \\
& \text{tremolite} \quad \text{diopside} \quad \text{enstatite} \quad \text{quartz} \quad \text{water} \\
& 277 \text{ cm}^3 \quad 133 \text{ cm}^3 \quad 94 \text{ cm}^3 \quad 23 \text{ cm}^3
\end{align*}
\]

(at room \( T \) and \( P \))
then it is apparent that the $\Delta V$ term will change sign according to whether the volume of water (18 g) is greater or less than 27 cm$^3$, i.e. whether the specific volume of water is greater or less than 1.5 cm$^3$. At 1 bar, 1000°C, the specific volume of water is 5875 cm$^3$, at 1 kb, 1000°C, the specific volume is 5.7 cm$^3$ but at 10 kb, 1000°C, the specific volume is 1.2 cm$^3$ (Sharp, 1962). Although thermal expansions of the solid phases have not been considered it is apparent that at sufficiently high pressure at 1000°C, probably about 10 kb, the $\Delta V$ term for the reaction will change sign. This implies that the gradient of the $P$–$T$ curve for the above reaction will change sign. From experimental work we know that the gradient is positive at low pressures and high temperatures and thus must become negative at sufficiently high pressures and high temperatures.

This conclusion may be applied to the breakdown of other amphibole end members. Thus we conclude that, in general, at sufficiently high pressures the temperature required for breakdown of amphibole will decrease with increasing water or load pressure. This explanation may account for the common appearance of amphibole in the 10–20 kb range at 1100°C and its absence in our experimental runs carried out at higher pressures but otherwise identical experimental conditions. The conclusion also implies considerable limitations in the stability of amphibole within the upper mantle (cf. Oxburgh, 1964).

(d) Effect of temperature variation

The effect of temperature in changing the pressure required for appearance or disappearance of a phase is clearly shown in Fig. 7. However, an increase in temperature may also cause changes in the mineral assemblage observed by changing the limits of solid solution between components. For example, at temperatures above 1100°C in the olivine tholeiite (A) composition the aluminous pyroxenes + spinel + plagioclase assemblage occupies a wider pressure field. Thus at 9 kb the runs at 1210 and 1230°C have lower olivine contents than the run at 1100°C and also lower plagioclase contents. The mineral assemblage is dominated by clinopyroxene and porphyroblastic orthopyroxene with minor plagioclase. At 13.5 kb, in contrast to the 1100°C run, garnet is absent at 1180 and 1220°C; plagioclase is less abundant than in the 1100°C run and the mineral assemblage is again Cpx + Opx + Spinel + plag. The increase in pyroxene content and decrease in olivine and plagioclase content with increasing temperature at 9 kb and the similar effect at 13.5 kb are attributed to increased solid solution of Al$_2$O$_3$ in pyroxene. It is to be noted that in the quartz tholeiite compositions at 9 and 13.5 kb there is no observable decrease in plagioclase content with increase in temperature in the 1000–1200°C range. It is inferred that this difference in behaviour is a result of the presence of free SiO$_2$ in the quartz tholeiite rather than olivine or spinel—thus SiO$_2$ released by the breakdown of anorthite molecule to calcium Tschermak’s silicate (CaAl$_2$SiO$_6$) in pyroxene, reacts with olivine or spinel in the undersaturated compositions. The maximum solubility of Al$_2$O$_3$ in co-existing pyroxenes, particularly in the clinopyroxene, in this pressure range is only attained in quartz-free assemblages.

(e) Comparison with experimental data on simple systems

We have in Fig. 8 compared the experimentally derived transition interval with some experimentally determined equilibria in simple systems. It may be noted that
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Fig. 8. Comparison of the experimentally determined boundaries AB and CD (as in Fig. 7) with reactions in simple systems. The stippled zone about "CD" represents the probable range of P-T over which the boundary "CD" (marking the disappearance of plagioclase in quartz tholeiite compositions) could occur due to variations in chemistry in rocks classifiable as basalts of quartz tholeiite type. Similarly the stippled zone about "AB" represents the range in P-T conditions for the first appearance of garnet in quartz tholeiites with variable 100 Mg/(Mg + Fe²⁺) from 40 to 70 approximately. The P-T fields for "eclogite", "high-pressure granulite" etc., as used in the text, are shown. The boundary shown between the low-pressure and intermediate-pressure granulites is given by the high pressure limit of stability of the pair olivine + plagioclase in the basaltic compositions with 100Mg/(Mg + Fe²⁺) ≈ 60. N₁ Position of kyanite = sillimanite boundary at 750°C (Newton, 1966).

* N₂ Position of Ky-Sill-And triple point calculated by Newton.
* B Position of Ky-Sill-And triple point found by Bell (1963).

the curve for plagioclase disappearance in the quartz-tholeiite compositions is nearly parallel to and lies on the low pressure side of the albite ⇔ jadeite + quartz curve. The position of the latter curve is well established at high temperatures (Birch and Lecomte, 1960) but its extension to low temperatures is based on thermochemical and uniaxial piston–anvil data and cannot be considered firmly established. The field relationships in the glaucophane schist terranes of California demonstrate that the jadeite + quartz stability field must lie on the high pressure side of the calcite–aragonite equilibrium—this provides a limit to the possible shifting of the albite ⇔ jadeite + quartz boundary to lower pressures as the calcite–aragonite equilibrium is probably well established at low pressures.
The stability relationships of the garnet end members, almandine and pyrope, are shown. At temperatures up to 1200°C pyrope requires a much higher pressure for stability than almandine. The first garnet to appear in all our compositions is more almandine-rich than the garnets stable at higher pressure, and in all the quartz tholeiite compositions the first appearance of garnet lies within the stability field of pure almandine as reported by Yoder (1955). This is also true for the alkali olivine basalt and olivine tholeiite (A) compositions but in the iron-rich alkali olivine basalt and particularly the olivine tholeiite (B) composition the first appearance of garnet lies just outside the almandine stability field (garnet stable at 10 kb, 1100°C whereas almandine breaks down at 10 kb, 1070°C). The discrepancy is not a gross one and might be explained by stabilization of the garnet by spessartine or grossular solid solution or possibly by errors in temperature or pressure measurement.

In Fig. 8 we have compared the experimental data for reactions in basaltic compositions with the experimentally determined kyanite sillimanite polymorphic transformation. In plotting this curve we have used the reversed reactions obtained by Clark (1961) in the 1300-1500°C range using a solid media pressure apparatus of the same design as we have used. Clark applied a friction correction of —8% which is sufficiently close to our value of —10%, considering Clark's higher experimental temperatures. To fix the curve at low pressure we have used the point (marked N2 in Fig. 8) determined at 750°C, 8.1 ± 0.3 kb by Newton (1966) using mixtures of kyanite + sillimanite and determining which phase grows at the expense of the other. Newton also used a solid-media piston-cylinder apparatus and applied a friction correction of about 15% (Newton 1965). The approximate position of the kyanite, sillimanite, andalusite triple point calculated by Newton is shown as N1.

The slope of the kyanite—sillimanite curve as plotted is 21.5 bars/°C. Clark et al. (1961) calculated a gradient of 21.2 bars/°C using low pressure and low temperature thermochemical data. Newton (1966) prefers a value of 17.7 bars/°C for the slope, utilizing more recent high temperature heat capacities. These alternative values for the slope of the curve would not greatly change its position with respect to our boundary reactions provided either the data of Clark or Newton (1966) is accepted as accurately fixing the boundary in a restricted range of P and T. However, we have also plotted the triple point (marked B in Fig. 8) determined by Bell (1963) using a rotating piston–anvil apparatus at temperatures down to 3-400°C. These data are clearly incompatible with that of Newton and, when coupled with the reversal and synthesis data of Clark (1961) define a kyanite ⇌ sillimanite boundary slope of only 13 bars/°C, in disagreement with the thermochemical calculations. The experimental determinations using the rotating piston–anvil device are also subject to very large uncertainties of pressure distribution in the sample and to large uncertainties in pressure calibration (Kitahara and Kennedy; Myers et al., 1963). A final reason for selecting the experimental data of Newton in preference to that of Bell, is the large body of geological evidence and opinion that kyanite is stable at much lower pressures than the minimum of 8 kb suggested by Bell's data.

The relative positions of the kyanite–sillimanite curve and the curves AB and CD show that at temperatures above 900°C (i.e. where there is experimental data on both systems) eclogite facies rocks should contain kyanite and never sillimanite. In contrast rocks associated with the assemblage Opx + Cpx + Plag + Qz, unless
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the latter assemblage is of extremely magnesian composition, should contain sillimanite if their chemistry is appropriate. Basic rocks with the Cpx + Ga + Plag + Qz assemblage could co-exist with sillimanite-bearing rocks in the lower pressure part of their stability field but could co-exist with kyanite-bearing rocks in the high-pressure part of their stability field. In Fig. 8 the line AB and the kyanite–sillimanite boundary are seen to converge slightly and, in the temperature range at which many natural granulites possibly form (500–650°C), the kyanite–sillimanite curve lies very close to and on the high pressure side of the extrapolation of AB marking the first appearance of garnet in an oversaturated basalt of Mg/(Mg + Fe²⁺) = 60. It will be shown in later sections that this conclusion is in harmony with the observed mineralogy of natural granulites and pelites. In Fig. 8 we have estimated a zone about AB representing the range of pressures at a given temperature at which garnet should first appear in a range of quartz tholeiites varying in 100Mg/(Mg + Fe²⁺) ratio from about 40 to 80. The intersection of this zone with the kyanite–sillimanite line illustrates how an Opx + Cpx + Plag + Qz assemblage in a very magnesian basaltic composition and a Ga + Cpx + Plag + Qz assemblage in an iron-rich composition may both co-exist stably with kyanite-bearing rocks.

It is apparent from Fig. 8 and the above discussion that the accurate determination of the kyanite–sillimanite boundary is extremely desirable and will provide an excellent guide, when considered with the natural assemblages, to the extrapolation of the granulite and eclogite facies boundaries to lower pressures.

(f) Reactions in natural rocks—coronas and coronites

Unambiguous examples of reactions between certain mineral pairs are provided by the coronas or reaction rims which may occur in basaltic rocks. Olivine is very commonly mantled by coronas, particularly when in contact with plagioclase and the sequence of mantling minerals is commonly olivine core, hypersthene rim, diopside, garnet, plagioclase. GJELSVIK has described excellent examples of reactions between both olivine and plagioclase and hypersthene and plagioclase to yield garnet + clinopyroxene + orthopyroxene assemblages. GJELSVIK (pp. 43, 51, 55, 58) notes that the recrystallized plagioclase becomes more sodic as the reaction with olivine or orthopyroxene proceeds. BUDDINGTON (1952, pp. 49–50) also makes the same observation in discussing garnet formation in metamorphosed olivine-normative basalts of the Adirondacks. In the dolerites described by GJELSVIK the normative plagioclase is fairly constant at about An₆₀ and the olivine compositions range from 30 to 45% fayalite; orthopyroxene in the olivine-free dolerites is about 30% ferrosilite and the 100Mg/(Mg + Fe²⁺) values for eight analysed dolerites (p. 79) are 56, 57, 60, 70, 52, 65, 55, 56 (I–VIII respectively). The compositions are mostly more iron-rich than our experimental compositions. GJELSVIK notes that the range of refractive index of the garnets ranges from 1.765 to 1.800—these values are slightly higher than the garnets we have observed experimentally.

In comparing GJELSVIK’s rocks with our experimental data it appears that these rocks show arrested stages of metamorphism in the high pressure granulite field (p. 819) i.e. on the high pressure side of the curve for the incoming of garnet in oversaturated compositions. In this context it is worth noting that GJELSVIK does not record spinel-bearing coronas—the reason for this is probably in part the relatively Fe-rich
composition of the dolerites and also because the corona formation was under too high pressure conditions (in our experimental work the role of spinel was most important at pressures below those required to form garnet in the oversaturated compositions).

Gjelsvik (pp. 106, 128) argues that the conditions of metamorphism of the dolerites indicate conditions intermediate between the granulite and eclogite facies within the relatively anhydrous inner parts of the dolerites but amphibolite facies in the border zone where greater water contents were available. These conclusions are in harmony with the facies relations between granulites, eclogites and amphibolites of Fig. 10.

Oosterom (1963) has described a layered sequence of ultramafic to gabbroic rocks from Stjernoy, Norway, in which olivine in plagioclase-bearing rocks is surrounded by coronas. The coronas again consist of an inner zone of orthopyroxene, sometimes apparently entirely replacing the olivine core, surrounded by a symplectitic intergrowth of orthopyroxene + spinel + clinopyroxene. Garnet does not occur in these coronas. Similar though less vermicular spinel + orthopyroxene intergrowths occur in lesser abundance in gabbro gneiss (pyroxene granulite); these rocks are olivine-free (chemically they are olivine normative), and the spinel–orthopyroxene intergrowths may reflect exsolution of $\text{Al}_2\text{O}_3$ from the pyroxene rather than the olivine + plagioclase reaction. There are no unequivocal examples of the hypersthene + plagioclase reaction to yield garnet or spinel bearing assemblages. Garnet occurs in rocks interbanded with the gabbro gneiss but in association with hypersthene and plagioclase, and not with diopside. Thus the Stjernoy area of Norway shows granulite facies metamorphism in which olivine and plagioclase are incompatible and are replaced by the spinel + aluminous pyroxenes assemblage. Orthopyroxene and plagioclase remain a stable association. Comparison with Gjelsvik’s data from Sunnmøre and our experimental work indicates that the Stjernoy rocks have been metamorphosed in the intermediate pressure part of the granulite field (p. 816), i.e. at pressures below those necessary for formation of garnet in oversaturated basalts but above those causing reaction between olivine and plagioclase and probably above the pressures required for breakdown of cordierite. It is to be noted that sillimanite is a common constituent of rocks interbanded with the gabbro gneiss (pyroxene granulite). Kyanite apparently does not occur on Stjernoy although one locality is reported on neighbouring Seiland (Oosterom, p. 279).

The occurrence of spinel + pyroxene rather than garnet + pyroxene as coronas about olivine is attributable to two factors:

(a) The reactions occurred at relatively low pressure in the field where olivine + plagioclase are in reaction relation but hypersthene and plagioclase are stable together.

(b) The reaction products from olivine + plagioclase were spinel + pyroxene rather than garnet + pyroxene because of the extremely magnesian character of the Stjernoy rocks.

Thus the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ values are as follows:

(i) Olivine metagabbros $82–83.5$
(ii) Olivine gabbros $70–86$
(iii) Gabbro gneiss $66–86$
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These rocks are thus much more magnesian than the metamorphosed dolerites described by GJELSVIK and are comparable with compositions intermediate between the alkali olivine basalt and its extremely magnesian equivalent used in the experimental work.

There are many other descriptions of coronites in the literature but the two examples selected above show excellent compatibility with the experimentally observed sequence and illustrate how the experimental data can be applied in the understanding of two apparently contrasting corona types.

PETROLOGICAL APPLICATION OF EXPERIMENTAL RESULTS

(a) The definition of "eclogite"

In a previous section (p. 802) we defined our usage of the term "eclogite" stressing the absence of plagioclase as a stable phase in eclogites, the high jadeite/Tschermak's silicate ratio of the clinopyroxene and the restriction to basaltic chemistry. This definition is in harmony with much modern usage utilizing the garnet + clinopyroxene association and the omphacitic character of the clinopyroxene. However, it is not in agreement with a wider usage of "eclogite" as a rock which contains pyrope-almandine garnet and clinopyroxene as major phases but may also contain plagioclase and specifies only that the pyroxene be jadeite-bearing (cf. WHITE, p. 884).

In selecting the $P$–$T$ conditions marking the boundary for eclogite stability (with our usage of the term eclogite) we must select a pressure above which plagioclase is absent in all compositions and above which the content of Tschermak's silicate in the pyroxenes is also low. We have shown that the pressure required to eliminate plagioclase from the mineral assemblage is very different for different basaltic compositions—the extreme cases studied are olivine tholeiite (B) with plagioclase eliminated at 13.5 ± 1.1 kb at 1100°C and quartz tholeiite (B) with plagioclase eliminated at 20.5 ± 0.5 kb. In basalts of higher calcic plagioclase content relative to olivine + enstatite, and particularly if the normative molecular ratio (Opx + 2O)/An < 2, then the pressure required to eliminate plagioclase in compositions resembling kyanite eclogites is slightly higher than for quartz tholeiite (B) (T. H. GREEN, personal communication).

It is obvious that the mineral assemblage of olivine tholeiite (B) between 13.5–21 kb conforms with the first part of our eclogite definition, i.e. Ga + Cpx assemblage without plagioclase. However, we have shown that in the 13.5–18 kb range at 1100°C the ratio garnet/clinopyroxene increases with increasing pressure. In a two phase garnet + pyroxene assemblage this implies that at the lower pressure the pyroxene contains $Al_2O_3$ solid solution as Tschermak's silicate substitution and that with increasing pressure this exsolves to form garnet. In the absence of plagioclase, the normative albite of olivine tholeiite (B) is in jadeite solid solution in the pyroxene and the increasing garnet/pyroxene ratio of the assemblage implies also an increasing Jd/Ts ratio for the clinopyroxene. The observation that the garnet/pyroxene ratio remains approximately constant above 18 or 20 kb also argues that the Jd/Ts ratio of the pyroxene remains constant and at a high value.

According to our present usage, the term eclogite would not be applicable to the mineral assemblages formed below 20 kb at 1100°C in any of the compositions
examined. The mineral assemblages at lower pressures fall outside the eclogite definition either in containing plagioclase or having a low Jd/Ts ratio.

The classification of clinopyroxene as typical of eclogite or of granulite is on the same basis that White uses for the natural assemblages. The experimental observation that elimination of high Tschermak's silicate in pyroxene in favour of garnet occurs at similar pressures to the disappearance of sodic plagioclase in quartz tholeiite compositions is in harmony with the natural eclogites, i.e. we do not find quartz normative basalt compositions with garnet + clinopyroxene + quartz mineralogy, lacking plagioclase, in which the clinopyroxene is rich in Tschermak's silicate. Conversely we do not find olivine normative basaltic rocks with the assemblage garnet + clinopyroxene + plagioclase in which the clinopyroxene has a high jadeite and low Tschermak's silicate content.

We consider that the present definition of eclogite is practical in providing a basis for classification of natural rocks. In addition the experimental work shows that "eclogite" used in this manner has petrogenetic significance in defining very high pressure mineral assemblages. It must be stressed however that the granulite—eclogite boundary, even when defined as above, is a transitional boundary (Figs. 8 and 10) in which there is a field of indifference in which the criteria for classification may give conflicting answers and the arbitrary nature of petrographic classification becomes evident. Thus it is clear from the experimental work of Green and Lambert that plagioclase may be stable in rocks not of basaltic chemistry under conditions where plagioclase is unstable in basaltic rocks. Such rocks, if observed naturally, should not be called eclogites although they may belong to the eclogite metamorphic facies. The rocks described by Kozlowski (1958) appear to belong to the eclogite facies and the "plagioclase-eclogite" described by Kozlowski is an excellent example of a rock of andesitic composition in which the pyroxene has a very high jadeite/Tschermak's silicate ratio, i.e. is clearly eclogitic, yet the rock contains stable sodic plagioclase. For rocks such as these we would prefer new rock names, recognizing that the assemblages belong to the eclogite facies and not to the granulite facies. In contrast, "plagioclase-eclogites" (Cpx + Ga + Flag assemblages) described by Church (in press) from Donegal contain pyroxenes low in jadeite but rich in acmite + Tschermak's silicate and of the type we consider typical of granulites. Our definition would classify these rocks as granulite facies and differentiate them from the assemblages described by Kozlowski.

(b) Stability of eclogite within the crust

In Figs. 7, 8, 10 we have shown the $P-T$ gradients determined experimentally in the quartz tholeiite compositions for the incoming of garnet and disappearance of plagioclase. When extrapolated to lower temperatures these boundaries converge slightly and would intersect the temperature axis at atmospheric pressure at about 200°C. In projecting the boundaries to lower temperatures, we have no data below 1000°C and the uncertainties in temperature and pressure measurement in the apparatus could alter the gradient shown if any error is systematic (e.g. pressure effect on e.m.f. of the thermocouples) rather than random. Secondly the boundaries may be curved rather than straight, particularly if reactions other than those considered, become important at low temperatures, e.g. reaction of magnetite and albite.
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The gradients determined for the reactions in the quartz tholeiites are very similar to gradients determined for other solid-solid reactions in silicates (Fig. 8) and in particular the comparison with breakdown curves for albite and albite + nepheline are very relevant. The gradient for the appearance of garnet lies between the stability curves of almandine and pyrope. These comparisons provide support for the extrapolation of our experimental data. It will be shown in a later section that the natural occurrences of granulites and eclogites provide evidence that the kyanite–sillimanite boundary lies close to but on the high pressure side of the boundary for incoming of garnet in oversaturated compositions. This is also consistent with the relationships of Fig. 8 and suggests similar gradients for both boundaries.

If we consider the range of probable geothermal gradients in stable continental crust and pre-Cambrian shield areas then the estimates of temperature at the base of a 35 km crust range from around 300°C in areas of low heat flow to around 700°C in areas of higher heat flow (Birch, 1955; Clark, 1962; Clark and Ringwood, 1964; Howard and Säss, 1964). Our data indicate that eclogite or high pressure granulite would be the stable mineral assemblage in dry basaltic rocks throughout the entire crust along normal geothermal gradients. This conclusion differs from that of Yoder and Tilley (p. 504), i.e. “it appears that eclogite (without plagioclase) is not stable within either the oceanic or continental crust at any temperature”. The reason for the contradiction lies in Yoder and Tilley’s use of the “transition” interval defined experimentally by Kennedy (1959) at 500°C. Reasons for not accepting these data as defining the gabbro to eclogite transition have been given previously and were recognized by Yoder and Tilley (p. 504).

The geophysical applications of our conclusions on eclogite stability will be fully treated in a separate paper (Ringwood and Green, 1966). Our data imply that any basic igneous rock, cooling from igneous temperatures within the earth’s crust will enter first the field of incompatibility of olivine and plagioclase, then of orthopyroxene and plagioclase and finally enter the eclogite stability field. Whether or not such reactions occur in basaltic rocks will be determined by a number of factors, e.g.

(i) The temperature at which the reaction boundaries are intersected. Reactions are much more likely in a body cooling at 30 km depth (where the orthopyroxene + plagioclase reactions would occur at about 800°C) than in a body cooling at 5 km depth where the same reaction should occur at about 300°C.
(ii) The rate of cooling in relation to the kinetics of the reactions.
(iii) The access of water leading to hydrous mineral assemblages.

The relationship of the experimentally determined and predicted stability field for eclogites to the $P-T$ conditions for other metamorphic facies is considered in a later section.

(c) Natural eclogites

Several authors, in examining natural eclogite occurrences, have considered that these represent wide variations in the temperature at which they have crystallized (Coleman et al., 1965; Den Tex, 1965, p. 121). This is in harmony with the prediction of Figs. 8, 10 and leads to the possibility of distinction between eclogites of low temperature of crystallization and those of high temperature of crystallization.
Differences in partition co-efficients between garnet and pyroxene offer one possible means of making such a distinction (Banno and Matsui, 1965). Another possibility lies in the role of magnetite and acmite. Church (in press and pers. comm.) has studied plagioclase + garnet + clinopyroxene rocks occurring as deformed rims to garnet coronite metagabbro in Donegal, Eire. Church reports increasing garnet contents matched by decreasing feldspar and magnetite and suggests the reaction albite + magnetite + diopside ⇌ acmite + garnet + quartz (cf. pp. 806–807) in which the right hand side would be favoured by high pressure. Many pyroxenes of natural eclogites contain high acmite contents. This is particularly true of eclogites from glaucophane schists and these eclogites do not seem to contain magnetite as a separate phase. On the other hand magnetite is a common accessory mineral of eclogites apparently associated with amphibolite and granulite terranes (Eskola; Yoder and Tilley, 1962) and the pyroxenes of these eclogites contain variable acmite content. For these assemblages the left-hand side of the following equation appears to be favoured under the eclogite facies conditions

\[
2\text{NaAlSi}_2\text{O}_6 + \text{Fe}_3\text{O}_4 + \text{Ca(MgFe)}\text{Si}_2\text{O}_6 + \text{SiO}_2 \Leftrightarrow \\
\text{jadeite} + \text{magnetite} + \text{diopside} \Rightarrow \text{acmite} + \text{garnet} + \text{quartz}
\]

In our experiments on the oxidized alkali basalt at 1100°C, the left-hand side of this equation, or its equivalent involving orthopyroxene instead of diopside (p. 806) was favoured up to between 22.5 and 32.5 kb.

The comparison of experimental and natural assemblages suggests that the role of acmite and magnetite in eclogite assemblages may be of importance in identifying low and high temperature eclogite assemblages. A schematic diagram of the possible relationships between the reactions involving magnetite and the stability field of eclogite is shown in Fig. 9.

In descriptions of natural eclogites, alteration of garnet and omphacite is commonly reported. If eclogites are stable in dry rocks to very low pressures at low temperatures, then the interpretation of such alteration is of significance. If the alteration is to hydrous assemblages containing amphibole, chlorite, mica, zoisite etc., then there is little we can deduce about relative changes in load pressure or in temperature. However, a number of authors (Eskola, 1921; Alderman, 1936) have described omphacite altering to fine symplectites of plagioclase and clinopyroxene. These eclogites must be regarded as having left the eclogite stability field and entered the granulite stability field. In terranes showing polymetamorphism (as in both examples described above, cf. McDougal and Green, 1964) such a sequence would not be unexpected and there are many examples of metamorphic terranes showing superimposed high-temperature and low pressure metamorphism on earlier high pressure metamorphism (e.g. the Saxon granulites described by Scheumann, 1954, and Scheumann and Huckenholz, 1961). In contrast there are many eclogites of metamorphic terranes which do not show any evidence for retrogressive alteration in the plagioclase + pyroxene stability field and which are consistent with a post-crustalization history entirely within the eclogite stability field.
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(d) The "pyroxenite" facies

From their experimental study of the stability fields for gabbro and eclogite YODER and TILLEY suggested that the transition from basalt to eclogite proceeds via an intermediate pyroxenite assemblage (p. 505). This conclusion was based on general grounds on the possibility that pyroxenes at high pressure could accept increasingly large amounts of jadeite, acmite, Tschermak's silicate and calcium-titanium pyroxene molecule in solid solution. In addition, YODER and TILLEY considered that the results of several experimental runs gave support to this concept. Because of the apparent conflict in the nature of the transitional mineral assemblages and the absence or rarity of pyroxenites of basaltic chemistry, the evidence for this conclusion will be examined in relation to our own experimental data.

YODER and TILLEY considered that experimental evidence supporting the pyroxenite assemblage or "pyroxenite facies" came from one run on the Loch Duich eclogite at 10 kb, 1150°C, and runs on a natural olivine nephelinite at 31.4 and 40 kb. The Loch Duich eclogite at 10 kb, 1150°C yielded a charge entirely of clinopyroxene; at higher temperatures glass was present and at lower temperatures magnetite and residual garnet were present. No repeat runs or tests of stability of the monomineralic pyroxene run were made and metastability is a possible explanation for the unusual mineralogy. However, the Loch Duich eclogite is olivine normative (11%), very iron rich (100Mg/(Mg + Fe²⁺) = 35) and with low Na₂O content (1.09% Na₂O, Ab = 9.4%, An = 28.5%). Our experiments have shown that these factors in a
basalt-like chemistry will tend to favour reaction to eliminate olivine and plagioclase in favour of garnet and pyroxene at lower pressures relative to more normal basalts.

The clinopyroxene + spinel assemblage was obtained at 31.4 kb and 40 kb from the olivine nephelinite, i.e. at pressures where the eclogite mineralogy is stable in the other basaltic compositions. The olivine nephelinite composition is an extremely undersaturated one and allotment of Al₂O₃ and SiO₂ to Na₂O to form jadeite and of SiO₂ to CaO + (Mg,Fe)O to form diopside shows that there remains insufficient SiO₂ to form garnet with the remaining Al₂O₃ and (Mg,Fe)O. Thus an eclogite (pyrope-almandine garnet + clinopyroxene) would not be expected from this composition at high pressures.

KUSHIRO and YODER (1964, pp. 108–114) find support for the transitional pyroxenite assemblage from their studies on 1:1 anorthite:enstatite and 1:2 anorthite:enstatite mixes. In the enstatite + anorthite mix, KUSHIRO and YODER find that anorthite disappears around 15 kb at 1300°C to yield an assemblage of pyroxene solid solutions + quartz. Garnet appears at about 19 kb at 1300°C. KUSHIRO and YODER extrapolate from these simple systems to conclude that (p. 111) “it may be suggested that olivine gabbro transforms to plagioclase and spinel-bearing pyroxenite or olivine and spinel-bearing pyroxenite in the lower part of the continental crust.” They also suggest (p. 113) that quartz-bearing pyroxenites (derived from silica saturated basalts) would be stable over a smaller depth range in the continental crust. It is clear that the “pyroxenite” concept of KUSHIRO and YODER differs from the earlier concept of YODER and TILLEY in that olivine, plagioclase, spinel or quartz are essential components of the mineral assemblages. YODER and KUSHTO have inadequately considered the role of albite, fayalite or ferrosilite solid solution on the nature and P–T conditions of the reactions studied. Our previously published (1964) and present results on complex basalt compositions demonstrate that these components eliminate the role of possible pyroxenites as the transition assemblage in typical saturated and undersaturated basaltic compositions, at temperatures below 1100°C. The pyroxene-rich assemblages observed in olivine tholeiite (A) between 9 and 13.5 kb above 1100°C are a near approach to “pyroxenite” as used by the above authors. However, their restriction to undersaturated compositions at temperatures very close to the solidus and the essential role of plagioclase and spinel are noteworthy.

The data of KUSHIRO and YODER are compatible with and provide insight into the important role of pyroxene in the studies on natural basalt compositions in the 10–20 kb range. In the quartz tholeiite compositions, the molecular ratio of normative hypersthene to anorthite is slightly greater than 2:1 and these compositions thus provide an excellent comparison for the (anorthite + 2 enstatite) mix of YODER and KUSHIRO. As described previously there is a distinct increase in the pyroxene to plagioclase ratio in the quartz tholeiite compositions between 9 and 13.5 kb. This was attributed to reaction of anorthite molecule to yield aluminous clinopyroxene solid solution. The residual plagioclase (still a major component over this pressure interval) would become more sodic. KUSHIRO and YODER show that at 1100°C anorthite disappears by reaction with enstatite at about 12½ kb to yield clinopyroxene ss + orthopyroxene ss + quartz. In the complex composition anorthite molecule is partly stabilized by the albite and Ca²⁺ becomes distributed principally between aluminous diopside solid solution and plagioclase. It is likely that the presence of hypersthene rather
than enstatite causes reaction with anorthite to begin at lower pressures (10 kb rather than 12.5 kb).

In the quartz tholeiite compositions [with $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 61$] garnet appears at about 14 kb at 1100°C, and increases in amount and becomes more pyrope-rich as pressure increases. In the simple anorthite + enstatite system, garnet appears at about 17.5 kb at 1100°C and is a pyrope–grossular solid solution. The garnet in this case is derived from the breakdown of the aluminous pyroxene and increases in amount at the expense of pyroxene at higher pressures. These results are closely comparable with our results on the magnesian quartz tholeiite [100Mg/(Mg + Fe$^{2+}$) $\approx$ 90]. In this composition garnet (pyrope-rich) first appears between 16 and 17 kb but in contrast to the anorthite–enstatite mix, plagioclase remains a major phase at this pressure although it is presumably much more sodic than the normative plagioclase. A greater contrast in the incoming of garnet is provided by the Fe-enriched quartz tholeiite (also with an anorthite:orthopyroxene ratio of about 1:2) where garnet appears at about 11 kb at 1000°C.

The comparison between the results on the simple system enstatite + anorthite and on the natural oversaturated basalt compositions has been made in detail to illustrate the difficulties in extrapolating from simple systems to natural basalts. To summarize, the results from the anorthite + enstatite mix give information on only one possible reaction within the transition zone and neglect the stabilizing or more reactive effects of other solid solution components of the natural minerals. The “pyroxenite” assemblage of Yoder and Tilley and Kushiro and Yoder (1964) is not the normal transitional assemblage in quartz tholeiites because:

(a) The presence of albite as a major component stabilizes plagioclase as a major phase up to pressures at which albite begins to form jadeite solid solution in diopside (about 16–18 kb at 1100°C). This effectively limits the complete reaction of anorthite molecule.

(b) The presence of iron as a major component enables garnet to appear at a lower pressure.

(c) The transition zone in quartz tholeiite compositions is characterized by stability of pyroxenes with high (Fe,Mg)Al$_2$SiO$_6$ and (CaAl$_2$SiO$_6$) substitution but these coexist with garnet, plagioclase and minor quartz. The mineral assemblages do not conform to the petrographic use of the term pyroxenite and the latter rock type could only be of significance as a transitional assemblage in non-basaltic, extremely magnesian, anorthite-bearing rocks.

In the forsterite + anorthite mix, Kushiro and Yoder find that olivine disappears at a comparatively low pressure (9 kb at 1300°C, 8 kb at 1000°C) to yield assemblages of aluminous pyroxenes + spinel + anorthite. Garnet does not appear until near 18 kb at 1300°C and the transition field between olivine and garnet bearing assemblages consists of aluminous pyroxenes + anorthite + spinel, the two latter phases decreasing with increasing pressure over the transition interval.

From a similar detailed comparison of our results on olivine normative under-saturated basalts with Kushiro and Yoder’s study of the forsterite + anorthite mix, we may conclude:

(a) Olivine and anorthite molecule are in reaction relationship at lower pressures than enstatite and anorthite. While in magnesian compositions the reaction
products are aluminous pyroxenes and spinel, increasing iron content in basalts suppresses this intermediate assemblage in favour of garnet + pyroxene + plagioclase.

(b) Anorthite molecule is again partly stabilized to higher pressures in the presence of olivine or enstatite by the presence of albite as a major component. Thus transitional assemblages between olivine gabbro and eclogite, although rich in aluminous pyroxenes, also contain spinel + plagioclase, or garnet + plagioclase as essential phases.

(e) The most favourable compositions for producing transitional assemblages of pyroxenes + minor spinel have a very high Mg/(Mg + Fe) ratio, normative olivine and a very low albite content. Such compositions are not typically basaltic. The Loch Duich eclogite conforms to the latter two criteria but is very iron rich. In comparison with the experiments on the iron-enriched alkali basalt, garnet would be expected at low pressures in this composition and a monomineralic clinopyroxene assemblage is unlikely. It is considered most probable that the "pyroxenite" obtained by Yoder and Tilley from this composition is a metastable assemblage either entirely of quench clinopyroxene (implying possible access of water to their charge) or of quench + primary clinopyroxene.

(e) \textit{Discussion of natural basic granulites in the light of the experimental study of the gabbro to eclogite transition}

De Waard (1965a,b) has advocated that the appearance of garnet in quartz bearing granulites, from reaction between hypersthene and plagioclase, be used to subdivide granulite facies into high and low pressure subfacies. On the other hand the appearance of garnet in pyroxene granulite has also been attributed to differences in bulk chemistry, garnet appearing in undersaturated compositions where two pyroxenes + plagioclase are stable in oversaturated compositions, cf. Fyffe et al. (1958, p. 234); Yoder and Tilley (1962, pp. 512–513). The experimental results indicate that there is a lower pressure part of the granulite facies field where the latter conclusion is valid, i.e. the association Ga + Cpx + Opx + Plag is characteristic of undersaturated rocks whereas Cpx + Opx + Plag is characteristic of oversaturated rocks. On the other hand, the experimental data provide excellent support for the suggestion that Ga + Cpx in oversaturated rocks is a diagnostic assemblage of a higher pressure subfacies of the granulites. Earlier recognition of the role of this reaction in facies classification is apparent in the diopside almandine subfacies of Turner (1948) and in Gjelsvik (1952, p. 128).

In this section various granulite facies areas, described in the literature, are reviewed specifically for the presence or absence of garnet in oversaturated and undersaturated rocks, the nature of the pyroxenes and the relationship with kyanite or sillimanite in associated rocks. It is convenient to group the granulite facies into:

(a) \textit{Low-pressure granulites}. Characterized by the association olivine + plagioclase and by the occurrence of cordierite.

(b) \textit{Intermediate-pressure granulites}. Characterized by the association orthopyroxene + plagioclase but incompatibility of olivine + plagioclase.
(c) **High-pressure granulites.** Characterized by the association garnet + clino-
pyroxene + quartz and incompatibility of hypersthene and plagioclase.
Such a division is shown in Fig. 8 and because of solid solution effects it is apparent
that the boundaries between the assemblages must be diffuse and the \( P-T \) conditions
for a given boundary reaction will depend in part on the rock composition.

(i) **High-pressure granulites**

The high grade metamorphic areas of S.E. Germany, southern Poland and western
Czechoslovakia include some of the classical areas of granulite facies. In reviewing
these granulites ESKOLA (1939) notes that sillimanite and kyanite both occur and
that it is not possible to decide which polymorph is typical for the granulite facies.
PIETZSCH (1963) summarizes the geology of the Saxon granulites and notes the
association in the “randgranulite” of basic rocks with the assemblage Ga + Opx +
Cpx + Plag (labradorite) + Ilm and more acid gneiss with kyanite + garnet. It is
not possible to ascertain whether Ga + Cpx occurs in oversaturated basaltic rocks
or not. Eclogites are reported locally and at Lengefeld, Erzgebirge “eclogites” with
garnet + omphacite + hornblende + albitic plagioclase + quartz have accessory
kyanite. Locally albitic plagioclase becomes dominant in schlieren and is associated
with biotite + garnet, minor omphacite, minor hornblende. If these rocks are of
basaltic chemistry then they would fall in the high pressure granulite facies \( P-T \)
field but if they are of dioritic or more acid composition then they could be of eclogite
facies (cf. GREEN and LAMBERT). It is of importance in this context to determine
the pyroxene composition. PIETZSCH (p. 685) notes that sillimanite granulites occur
in the Saxon granulite terranes but the sillimanite is regarded as secondary after
kyanite and notes that garnet is also altering to biotite (SCHUEMANN and HUCKENHOLZ).

An excellently documented occurrence of eclogite facies rocks (as here defined) of
non-basaltic chemistry has been described from the Eastern Sudetes by KOZLOWSKI
(1958). An interbanded sequence consists of dark coloured eclogites (garnet +
clinopyroxene + quartz) and leucocratic rocks of sodic plagioclase, microcline, quartz,
garnet, mica, minor aggregate amphibole (after pyroxene probably) and local rutile
and kyanite. There is continuous gradation between the contrasting rock types.
KOZLOWSKI has analyzed the pyroxene from an “eclogite” and this falls well within
the eclogite field of WHITE with a Jd/Ts ratio of about 4. On the other hand the rock
contains 17\% modal plagioclase (oligoclase \( \text{An}_{41} \)). The total-rock analysis shows that
chemically the rock is andesitic rather than basaltic. Its normative composition is
compared with quartz tholeiites (A) and (B) in Table 12.

The differences from quartz tholeiite (A) and (B) are such that we would expect
plagioclase to disappear at slightly higher pressures in KOZLOWSKI’s “eclogite” than
in quartz tholeiite (B). Comparison of the “eclogite” and the associated acid granulite
(73\% SiO\(_2\)) with the present experimental work on basaltic compositions and the
previously reported work on acid adamellite (GREEN and LAMBERT) shows excellent
agreement between observation and experimental predictions. These rocks appar-
ently crystallized close to the curve CD of Figs. 8, 10. The associated aluminosilicate
mineral is kyanite, not sillimanite.

SMULIKOWSKI (1960a) also describes eclogites from the Eastern Sudetes; these
do not contain plagioclase and are of basaltic chemistry. Kyanite is a minor mineral
<table>
<thead>
<tr>
<th>Material</th>
<th>Qz thol (A)</th>
<th>Qz thol (B)</th>
<th>Eclogite (Kozlowski, 1958)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qz</td>
<td>2.8</td>
<td>2.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Or</td>
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<td>4.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Ab</td>
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<td>22.1</td>
<td>22.6</td>
</tr>
<tr>
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<td>29.3</td>
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<td>22.3</td>
</tr>
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<td>20.6</td>
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<td>4.2</td>
<td>3.6</td>
<td>1.9</td>
</tr>
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</tr>
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</tr>
<tr>
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<td>61</td>
<td>61</td>
<td>48.5</td>
</tr>
</tbody>
</table>

Table 12

in some examples. Smulikowski (1960b) notes that these eclogites occur in an amphibolite facies terrane and considers that they are not exotic or relict to that terrane. The descriptions of these Saxon and Eastern Sudetes rocks indicate that these areas are of high pressure crystallization embracing conditions both of the high-pressure granulite and eclogite facies. The Eastern Sudetes area is one in which eclogite facies metamorphic assemblages are present in basaltic, andesitic and acid compositions.

Den Tex (1961) and Den Tex and Vogel (1962) have described high grade pyroxene granulites and hornblende granulites from NW Spain. The assemblage Ga + Cpx + Plag + Qz ± Hyp and eclogite-like rocks of Ga + Cpx + Qz + Rut (the Cpx is not regarded as omphacite) occur in a terrane largely of hornblende–clinozoisite granulites. Eclogites with omphacitic pyroxene, garnet, quartz, rutile and sometimes kyanite, occur in the eastern part of the area. Kyanite is also reported from gneisses apparently overlying the granulites. Although data are incomplete this region appears to contain garnet + clinopyroxene + plagioclase + quartz assemblages grading to eclogites and kyanite appears to be the stable Al₂SiO₅ polymorph.

Von Knorring and Kennedy (1958) have described basic gneisses from Ghana with the mineral assemblage Cpx + Ga + Plag + Qz + Scap + Rut. The rocks are olivine normative but the absence of orthopyroxene and presence of quartz in the metamorphic assemblages show that the rocks have crystallized in the high-pressure granulate field. The clinopyroxenes of these granulites are rich in Tschermak’s silicate and aecmite.

Lovering (1959, 1964), Lovering and White (1964) and Joplin (1963) have described granulitic inclusions of Ga + Cpx, Ga + Cpx + Plag, Opx + Cpx + Plag assemblages occurring locally in breccia pipes in eastern Australia. The Ga + Cpx assemblages have been described as eclogites (Lovering, 1959, 1964). Comparison of the rock analyses of “eclogites” and “granulites” listed by Joplin and of the rock and mineral analyses published by Lovering (1964) and Lovering and White suggests that the different mineralologies may simply reflect different bulk chemistries crystallized under granulate facies conditions. Thus the Opx + Cpx + Plag ± Scap
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assemblages without garnet, and the Ga + Plag + Scap assemblages compared by Lovering and White both contain pyroxenes rich in Al$_2$O$_3$ (6-12% Al$_2$O$_3$ in clinopyroxene, 3-5% in orthopyroxene) but the Al$_2$O$_3$ is present as Tschermak's silicate with very low jadeite solid solution (Lovering and White, p. 204). It may be noted that the maximum Al$_2$O$_3$ content (which involves an Al for Si substitution of 12.5-15%) in clinopyroxene occurs in the garnet-bearing granulites. The appearance of garnet in two rocks and its absence in others described may be attributed to the differing pyroxene contents relative to potential garnet or Tschermak's silicate from the olivine + anorthite reaction. Thus in the Opx + Cpx + Plag granulites, olivine + anorthite reacted to yield Tschermak's silicate solid solution in the pyroxenes. In the Cpx + Ga + Plag granulites, the maximum solubility of Tschermak's silicate in the pyroxenes for the $P-T$ conditions operating is exceeded resulting in appearance of garnet. The greater Mg/(Mg + Fe$^{2+}$) ratio, allowing for oxidation (Lovering and White, p. 201-202), of the Opx + Cpx + Plag assemblages also is unfavourable to the appearance of garnet. The additional analyses of inclusions from the Delegate basaltic breccia pipe listed by JoplIn are also strongly suggestive of chemical control of mineralogy of rocks of essentially the same $P-T$ environment. Thus the Opx + Cpx + Plag granulites (JoplIn, pp. 303, 304) are distinctly higher in SiO$_2$ and have low normative olivine contents. In these assemblages neither olivine, garnet nor spinel is present but the pyroxenes are rich in Tschermak's silicate (Lovering and White, 1964). The Ga + Px + Plag granulites have lower SiO$_2$ contents, high Na$_2$O contents, high normative olivine contents and have normative nepheline. The olivine + plagioclase reaction has gone to completion but the pyroxene present is insufficient to accommodate all the Al$_2$O$_3$ (Tschermak's silicate) released, resulting in appearance of garnet. The high Na$_2$O content cannot be accommodated, at the pressures operating, in jadeite solid solution, resulting in persistence of plagioclase. The "eclogites" or Ga + Cpx assemblages consistently show very low SiO$_2$, and high normative olivine contents. They have lower anorthite contents and lower Na$_2$O contents than the garnet granulites. The olivine + anorthite reaction yielding garnet + aluminous pyroxenes has gone to completion and the lower Na$_2$O content can be accommodated in solid solution in the calcic clinopyroxene.

One example, with the extremely high 100 Mg/(Mg + Fe$^{2+}$) ratio of 94, has the spinel + pyroxene + garnet assemblage as might be anticipated from our experiments on the magnesian alkali basalt. It has been suggested by Lovering (1959, 1964) that the granulitic materials probably represent material from the lower crust while the eclogitic and ultra-basic fragments represent material from the upper mantle. However, the data which have been published to date, when examined in the light of our experimental studies demonstrating the variety of mineral assemblages stable at a given $P-T$ in a variety of bulk chemical compositions, strongly suggest that the Delegate basic inclusions represent mineral assemblages stable in a restricted $P-T$ environment. The rocks probably represent stable assemblages of rather high temperature granulites, having crystallized either in the intermediate pressure granulite field or near the boundary between intermediate and high pressure granulite fields. The latter conclusion is based on the absence of quartz-bearing assemblages, the appearance of garnet in the Sp + Ga + Px pyroxenite, and the
absence of garnet in compositions low in normative olivine. Because of this alter-
native explanation for the mineral assemblages of these granulites and "eclogites"
it is unfortunate that recent specialized studies of these rocks (e.g. LOVERING and
Morgan, 1963; FORBES, 1965) have reported them as "Australian eclogites" and
made comparison with the South African eclogites in kimberlite pipes.

DAVIDSON (1943) gives an excellent descriptive account of the high grade
metamorphic rocks of South Harris. In basic rocks the following mineral assemblages
occur:

\[
\begin{align*}
\text{Cpx + Opx + Plag + Hbl} & \quad \text{basaltic and picritic compositions} \\
\text{Cpx + Plag + Ga} & \\
\text{Cpx + Opx + Plag + Ga + Qz} & \\
\text{Cpx + Ga ("eclogites")} & \\
\text{Plag + Cpx + Ga—anorthosites} & \\
\text{Ol + Opx + Cpx + Sp + Hbl—peridotites} &
\end{align*}
\]

DAVIDSON stresses that there are no quartz-bearing "eclogites" (i.e. Ga + Cpx + Qz
assemblages) and most, if not all, of the Ga + Cpx bearing rocks appear to be
olivine normative. On the other hand the association Ga + Opx + Cpx + Plag +
Qz does occur, and there is evidence in some rocks for the reaction Hyp + Plag →
Ga + Qz, and for the reverse reaction (garnet surrounded by coronas of hypersthene
and plagioclase). DAVIDSON demonstrates that picroites (with 100Mg/(Mg + Fe^{2+}) ≈
90 and over 20% normative plagioclase) yield Ol + Sp + Px. The pyroxenes present
in the basic rocks, particularly the Ga + Cpx assemblages, are rich in (Ca, Mg)
Al₂SiO₆.

DAVIDSON notes the presence of kyanite in paragneisses associated with or enclos-
ing the basic rocks. DEARNLEY (1963, p. 292, 296) describes the paragneisses (Lever-
burgh paragneisses) as containing both kyanite and sillimanite. The assemblage
Ga + Cpx + Plag + Hbl occurs in basic rocks but in adjacent tonalites, the Cpx +
Opx + Plag + Qz assemblage occurs. (DEARNLEY, p. 294). Elsewhere, DEARNLEY
(p. 262) notes the common presence of minor quartz in the metabasaltic assemblages
and records the Ga + Cpx + Plag + Qz assemblage also from paragneiss (p. 246)
and from tonalite (p. 268).

From the descriptions summarized above we interpret the South Harris granulites
as products of metamorphism within the Cpx + Ga + Plag + Qz granulite field
but rather near to the low pressure boundary. It also appears that the conditions
were very close to the kyanite–sillimanite boundary.

(ii) **Intermediate pressure granulites**

The Lewisian metamorphic rocks at Scourie, Sutherland, described by O'HARA
(1961) provide an excellent demonstration of the stability of the Ga + Opx + Cpx +
plag assemblage in undersaturated basic rocks. Examination of O'HARA's data
shows that the rock with least normative olivine also has least modal garnet. Two
ultrabasic rocks with normative plagioclase contain the assemblage Ol + Hy +
Sp + Hbl ± Aug; both plagioclase and garnet are absent. Quartz normative basic
rocks have the Opx + Cpx + Plag + Qz mineral assemblage and the mineral
assemblages have apparently crystallized in the intermediate pressure granulite field (i.e. the Opx + Cpx + Plag + Qz and Cpx + Plag + Ga ± Opx) field for oversaturated and undersaturated compositions respectively). The relative roles of spinel and garnet in this and the South Harris examples are in harmony with the experimental data on effects of Mg/Fe ratio.

The regional metamorphic terrane of the Adirondacks contains rocks of both amphibolite and granulite facies. ENGEL and ENGEL (1962), DE WAARD (1964, 1965) and BUDDINGTON (1963) discuss the role of local variations in $P_{H_2O}$ or availability of water in causing apparent intermixing of amphibolite, hornblende granulite and pyroxene granulite facies mineral assemblages, particularly in basic or intermediate orthogneisses. However, BUDDINGTON recognizes the possibility of mapping garnet isograds and an orthopyroxene isograd denoting the first appearance as major minerals of these minerals in rocks of restricted and specified chemistry. In order of increasing temperature and load pressure, BUDDINGTON has mapped the following isograds:

1. Appearance of garnet in biotite + quartz + plagioclase gneiss.
2. Appearance of orthopyroxene (with amphibole and clinopyroxene) in amphibolite layers in gneiss.
3. Appearance of garnet in metagabbro gneiss, amphibolite and diorite gneiss—this may be interpreted as the first appearance of garnet in sufficiently anhydrous, undersaturated basic compositions.
4. Appearance of garnet in syenite and quartz-syenite gneisses. Garnet is also present in metagabbro, amphibolite, diorite gneiss and anorthositic gneisses. This may be interpreted as the first appearance of garnet in oversaturated compositions, i.e. the reaction Opx + Plag $\Rightarrow$ Ga + Cpx + Qz (cf. DE WAARD, 1964, pp. 359–360; 1965, p. 460).

DE WAARD (1964) has described an area of the Adirondacks in which there are intermingled assemblages of amphibolite, hornblende granulite and pyroxene granulite facies. DE WAARD attributes the variation in part to variation in water content and $P_{H_2O}$ over the area, but also draws attention to apparent intermixing of the Cpx + Opx + Plag + Qz ± Hbl assemblage with the Cpx + Ga + Plag + Qz ± Hbl assemblage. DE WAARD (1964, pp. 359–360) considers that this intermingling within a relatively small area, and involving assemblages on both sides of the boundary reaction (Opx + Plag $\Leftarrow$ Cpx + Ga + Qz), is caused by variations in cation ratios in the rocks. No data substantiating this conclusion for the area under discussion are given but our experimental work suggests that variations in Mg/(Mg + Fe$^{2+}$) ratio could produce the observed relationships.

DE WAARD (p. 348) records sillimanite as a phase in assemblages classifiable as both amphibolite and granulite facies. Kyanite is not reported. It is clear that the area described by DE WAARD lies close to the boundary between intermediate and high pressure granulite assemblages (cf. DE WAARD, 1964). The assemblages may denote conditions on either the high or low pressure side of the boundary for the appearance of garnet in our quartz tholeiite compositions, dependant on whether assemblages of contrasted type are of consistently different Mg/(Mg + Fe$^{2+}$) ratio and the relationship of this ratio to that of our experimental compositions. It is most significant that
sillimanite rather than kyanite is the stable aluminosilicate and kyanite is apparently unknown from the Adirondacks (BUDDINGTON, 1966, pers. comm.). Comparing this area with the South Harris locality discussed previously, the basic rocks indicate similar $P-T$ conditions of metamorphism in the two areas and suggest that the $\text{Opx} + \text{Plag} \Leftrightarrow \text{Ga} + \text{Cpx} + \text{Qz}$ boundary zone lies very close to but on the low pressure side of the kyanite $\Leftrightarrow$ sillimanite boundary.

The granulite and charnockite terranes of India include the Sittampundi Complex described by SUBRAMANIAM. In this complex, SUBRAMANIAM described “eclogites” of $\text{Ga} + \text{Cpx} + \text{Opx} \pm \text{Plag} \pm \text{Hbl}$. One such example, called a “bronzitic pyropite”, contains 1% Pl, 2% Hbl, 6% Cpx, 7% Opx, 72% Ga and 10% secondary symplectite but the analysis shows 3% normative albite, 47% anorthite, 5% diopside, 18% olivine and 21% hypersthene. Such a composition is rather similar to olivine tholeiite (B) and plagioclase would be expected to disappear at comparatively low pressure in the granulite facies. A second “plagioclase eclogite” with 1-5% Qz, 19% Pl, 12% Hbl, 7% Cpx, 7% Opx, 32% Ga, 19% symplectite contains 14% normative albite, 45% anorthite, 13% diopside, 7% hypersthene and 19% olivine. The presence of quartz in the metamorphic assemblage may indicate partial reaction of $\text{Opx} + \text{Plag} \Leftrightarrow \text{Ga} + \text{Qz}$, but is more probable due to the presence of appreciable hornblende. A xenolith of pelitic material in the complex contains sillimanite, not kyanite. It is considered that the Sittampundi Complex reflects metamorphism in the intermediate pressure field of the granulite facies and on the sillimanite side of the sillimanite–kyanite inversion.

The granulites and charnockites described by HOWIE (1955) from Madras clearly demonstrate stability of the $\text{Opx} + \text{Cpx} + \text{Plag} + \text{Qz}$ assemblage. Even in several olivine normative compositions, garnet does not appear, in part because of the presence of hornblende and in part because of $\text{Al}_2\text{O}_3$ solid solution in the pyroxenes. Two examples of pyroxenite from Pammal Hill contain modal spinel (0-5 and 4-2%) and highly aluminous orthopyroxenes (4-6 and 4-4% $\text{Al}_2\text{O}_3$) and clinopyroxenes (5-0 and 5-9% $\text{Al}_2\text{O}_3$) but normatively contain 12% and 23% normative anorthite, and 8 and 18% normative olivine. Both rocks are very low in $\text{Na}_2\text{O}$ and have high $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios and the mineral assemblages are in harmony with the experimental data on Mg-rich and Na-poor compositions. The contrasting mineralogies of the pyroxenites and granulites provide a natural demonstration of the restricted compositions from which pyroxenites may crystallize as the transitional mineral assemblage between gabbro and eclogite, cf. page 816. Like the granulites of Madras, those of Uganda (GROVES, 1935), Varberg, Sweden (QUENSEL, 1951; HOWIE and SUBRAMANIAM, 1957), Broken Hill, New South Wales (BINNS, 1962, 1964), Musgrave Ranges, central Australia (WILSON, 1959) and Dronning Maud Land, Antarctica (Banno, Tatsuma, Ogura and Katsura, 1963) are characterized by the $\text{Cpx} + \text{Opx} + \text{Plag} + \text{Qz} \pm \text{hornblende}$ assemblage in oversaturated rocks. In undersaturated rocks the presence of hornblende obscures the possible role of garnet or olivine in many examples. Groves describes a garnetiferous norite (undersaturated) from Uganda and also one example of a quartz diorite composition (Mt. Wati, W. Nile district) which contains $\text{Ga} + \text{Opx} + \text{Cpx} + \text{Plag} + \text{Qz}$. The rock has an $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio of 33. In the Varberg granulites a similar undersaturated basic rock with $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) \approx 60$
An experimental investigation of the gabbro to eclogite transformation contains Ga + Cpx without quartz but the Ga + Opx + Cpx + Plag + Qz assemblage occurs in an oversaturated rock with the very low 100Mg/(Mg + Fe2+) = 23. Banno et al. clearly distinguish the absence of garnet in oversaturated pyroxene granulites and its presence in the Ga + Opx + Cpx + Plag ± Hbl assemblages of undersaturated rocks. These authors also point out the low Al2O3 (<2%) contents of the pyroxenes in these Antarctic granulites and in this respect they are similar to the pyroxenes of the granulites of Broken Hill (Binns, 1962). In the Broken Hill area Binns (1964, pp. 327–8, 300) describes the Ga + Cpx + Hbl + Plag assemblage in an apparently undersaturated rock but also (p. 327, pp. 299–300) describes Ga + Cpx + Plag(An78) + Qz + Hbl from an oversaturated granulite. It is to be noted that the latter rock is the most Fe-rich of those collected in the vicinity (Pinnacles locality, pp. 289–290) with 100Mg/(Mg + Fe2+) ratio of 30. The Broken Hill area is important in that the aluminosilicate in the associated pelites in the granulite facies is sillimanite but it is associated in many rocks with both almandine-rich garnet and cordierite (presumably Mg-rich). The association of cordierite and hypersthene is not recorded. The elimination of this mineral pair (cordierite + hypersthene) is considered by De Waard (1965) to mark the boundary between pyroxene hornfels and pyroxene granulite facies. The presence of cordierite rather than its higher pressure breakdown products (pyrope–almandine + sillimanite + quartz) is used by De Waard to characterize the lowest pressure subfacies of the granulite facies, while the association Ga + Cpx + Plag + Qz, marks the highest pressure subfacies of the granulite facies. In the Broken Hill area both assemblages occur but the Ga + Cpx + Plag + Qz assemblage may be regarded as anomalous in the sense that it occurs in an iron-rich composition, and garnet thus appears at a lower pressure than in more typical basic compositions. It is considered that metamorphic conditions in the granulite facies at Broken Hill are in the intermediate pressure field of the granulite facies but transitional towards the low pressure (cordierite granulite) field. Unfortunately, because of the abundance of hornblende, it is unknown whether, in basaltic chemistry of “normal” Mg/(Mg + Fe2+) ratio, the assemblage olivine + plagioclase would be stable—the relationship of this assemblage to the presence or absence of cordierite is of considerable interest.

The granulites of central Australia (Musgrave Ranges) are of the intermediate pressure type—cordierite is apparently absent, the Opx + Plag association is stable in oversaturated rocks but the Ga + Cpx + Opx + Plag assemblage occurs in an olivine normative composition. (Wilson, 1959, Rock No. 30543). Ramberrg (1949) lists granulite parageneses from West Greenland and notes that associated paragneisses include assemblages with garnet + sillimanite and also assemblages with cordierite. It appears that the assemblages discussed may have derived from a terrane with rather variable metamorphic conditions. Thus Ramberrg lists two “enderbites” (hornblende free) with the assemblage Opx + Cpx + Plag + Quartz, and one with the assemblage Opx + Cpx + Ga + Plag + Quartz. The latter rock has a more calcic plagioclase (An48 compared to An25 for the non-garnetiferous rocks) and is slightly more magnesian. There is no obvious chemical factor responsible for the appearance of garnet in this rock and not in the other enderbites. Hornblende is abundant in the undersaturated, quartz-free gneisses and the assemblage Opx + Cpx + Plag + Hbl is the most common one. Ramberrg lists one example of
an Opx + Cpx + Ga + Plag + Hbl assemblage and in this rock the orthopyroxene is about Ens_{55}. In contrast two more magnesian rocks with orthopyroxene of Ens_{83} and Ens_{78} have the assemblages olivine (Fo_{95}) + Cpx + Opx + Plag(An_{45}) + Hbl and olivine (Fo_{82}) + Cpx + Opx + Sp + Hbl. It appears that the rocks described represent a metamorphic gradient which locally includes the low pressure granulite field (the presence of olivine + plagioclase, the presence of cordierite) and locally extends into the high-pressure granulite field (the Ga + Cpx + Plag + Qz assemblage). Such variations in mineralogy could arise from temperature fluctuations rather than implying local variations in pressure.

(iii) Low-pressure granulites

The granulites of Lapland (Eskola, 1952), south-west Finland (Parras, 1958), Dangin, Western Australia (Pride, 1945) and Ontario, Canada (Wynne-Edwards and Hay, 1963) are examples of the low pressure granulite facies as proposed by De Waard (1965) or the cordierite-granulite sub-facies of Eskola (1952). The West Australian granulites with the association of cordierite + hypersthene + almandine appear to mark a particularly low pressure assemblage, the pair cordierite + hypersthene commonly being considered typical of the pyroxene hornfels facies (Turner and Verhoogen, 1960, pp. 521–2; and De Waard, 1965). No olivine + plagioclase assemblages are reported but this may be attributed to the common hornblende present rather than incompatibility of the pair under dry conditions. Sillimanite, not andalusite (cf. De Waard, 1965, p. 458) is the stable aluminosilicate.

In the granulites of Lapland, Eskola (1952) describes the Cpx + Opx + Plag ± Qz assemblage in basic rocks and notes the co-existence of olivine + plagioclase in more ultrabasic granulites. There is no record of spinel or garnet in these rocks. Almandine-rich garnet occurs in the assemblages Ga + Hy + Hbl + Plag implying incompatibility of the hypersthene + cordierite assemblage. One example, apparently too magnesian to yield garnet, instead contains the assemblage hypersthene + sillimanite implying breakdown of magnesium–iron cordierite. However, cordierite is a common phase in associated gneisses. The Lapland granulites appear to demonstrate that the Ol + Plag assemblage which we find under low pressure experimental conditions, is stable within the field of the cordierite–almandine granulites. On the other hand the Broken Hill and W. Greenland granulites, previously discussed, appear to show that the stability field of cordierite may extend into the higher pressure field where the plagioclase and olivine reaction to yield garnet + pyroxene has at least partly occurred. The pyroxenes of the granulites described by Eskola are extremely low in Al_{2}O_{3} in rocks where both clinopyroxene and orthopyroxene co-exist. In contrast, hypersthenes co-existing with garnet but not clinopyroxene contain very high Al_{2}O_{3} contents. The role of Al_{2}O_{3} substitution in granulate pyroxenes is clearly a complex one and comparisons of closely matched mineral parageneses are necessary. The experimental study suggests that Al_{2}O_{3} contents of co-existing pyroxenes should be low in the low pressure granulite field and distinctly higher in the intermediate pressure field. Effects of temperature differences may mark the pressure effects but a qualitative comparison of various granulite terranes is in agreement with this prediction.
(iv) Conclusions

The data on natural granulite facies rocks summarized in this section demonstrate that a sub-classification of granulite facies rocks into low pressure, intermediate pressure and high pressure assemblages on the basis of the assemblages observed experimentally is relevant and applicable to natural rocks. The observations on natural rocks confirm and illustrate the conclusion from the experimental work that variations in cation ratios, particularly Mg/Fe and Ca/Na, may strongly affect the P—T conditions at which particular mineral pairs will react, thus giving rise to apparent mixing of characteristic facies assemblages. It is also clear that the kyanite—sillimanite reaction is one of the most important in metamorphic petrology, not only in the lower grades of metamorphism but also in the amphibolite and granulite facies.

(f) Comparison of experimental data with estimates of the P—T environments for various metamorphic facies

In Fig. 10 the data and estimated gradient for the gabbro to eclogite transition is compared with estimates of the $P_{H_2O}$, $T$, conditions appropriate to various metamorphic facies. The latter estimates are those of FYFE, TURNER and VERHOOGEN (1958). The estimates by ENGEL and ENGEL (1962) and DEN TEX (1965) of the P—T conditions for the amphibolite—granulite facies boundary are similar although at a slightly lower temperature ($600^\circ$C). The P—T estimates for metamorphic facies of FYFE, TURNER and VERHOOGEN are presented on the model that $P_{H_2O} \approx P_{Load}$ during metamorphism. This simplifying assumption is certainly not valid for many terranes, particularly high-grade amphibolite and granulite terranes. This is convincingly argued by BUDDINGTON (1963) for the intermingled amphibolites, hornblende granulites and pyroxene granulites of the Adirondacks. BUDDINGTON draws attention to the different behaviour of paragneisses, i.e. rocks which initially as sediments, contained high water contents, and orthogneisses, i.e. rocks which initially were nearly dry magmas. Arguments that $P_{H_2O}$ is very commonly much less than load pressure and variable in a metamorphic terrane, have also been presented by YODER (1952, 1955) and GREENWOOD (1960, 1962).

Our experiments are made in dry or near-dry conditions with $P_{H_2O} < P_{Load}$. Thus in comparing the experimental data with the facies diagram of FYFE, TURNER and VERHOOGEN we are attempting to correlate the stable mineral assemblage in a dry basaltic rock, e.g. a dyke, sill or flow, under regional metamorphic conditions when the country rocks in general have higher water pressures and yield hydrous mineral assemblages.

Figure 10 suggests that eclogites could be stable under the higher pressure parts of the almandine amphibolite facies and greenschist facies and throughout the glaucophane schist facies. This presupposes that the basaltic compositions remain dry and that the kinetics of reaction are sufficiently rapid or catalyzed by shearing and deformation to allow the higher temperature gabbroic mineralogies to react. We consider that the field occurrences of eclogites are quite compatible in many cases with these stability relations. Thus many of the classic eclogite localities of Europe occur in medium grade metamorphic terranes, commonly of amphibolite facies, and such eclogites typically have borders of amphibolite and show gradual
Fig. 10. Comparison of experimentally determined boundaries with estimates of boundaries of metamorphic facies by FYFE, TURNER and VERHOOGEN (1958). “AB” and “CD” are the same as in Figs. 7 and 8 and the curve XY marks the first appearance of garnet in the iron-rich alkali olivine basalt composition. The vertical shading indicates the zone over which “AB” may occur due to variations in 100 Mg/(Mg Fe²⁺) from 10 to 90, and the horizontal shading indicates the zone over which plagioclase is absent in one or more, but not all, of the compositions studied.

The “Pressure” axis denotes load pressure for the experimental data but water pressure = load pressure for the estimates of the metamorphic facies boundaries. The basalt solidus for $P_{H_2O} = P_{load}$ and the upper limit of amphibole stability are from YODER and TILLEY (1962).

Gl. S.—Glaucophane Schist facies
Z.—Zeolite facies
G.S.—Greenschist facies
Alm. Amph.—Almandine amphibolite facies
G.—Granulite facies

E.H.—Epidote hornfels facies
H.H.—Hornblende hornfels facies
P.H.—Pyroxene hornfels facies
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replacement of the eclogite assemblage by amphibolite. These eclogites have commonly been interpreted as exotic to the metamorphic environment in which they occur, but the relationships expressed in Fig. 10 favour a simpler alternative, i.e. that the eclogites and amphibolite facies rocks were stable together under the same $P_{\text{Load}}$ and $T$ conditions but locally very different $P_{\text{H}_2\text{O}}$ conditions.

The eclogites of the glaucophane schist terranes of California may provide a further example of "wet" assemblages (glaucophane-rich) co-existing with dry eclogite assemblages. In considering the eclogites associated with glaucophane schists it is also quite possible that at sufficiently high pressure the assemblage garnet + pyroxene + water is stable at low temperature with respect to amphibole even with $P_{\text{H}_2\text{O}} = P_{\text{Load}}$, i.e. the dehydration temperature for glaucophane in the eclogite stability field may decrease with increasing pressure, cf. page 808.

There are a number of descriptions of eclogite or amphibole-bearing eclogitic rocks which are closely associated with rocks of the greenschist facies. Examples include the eclogite from the Lyell Highway, Tasmania (SPRY, 1963), the "eclogitic amphibolites" from near Caracas, Venezuela (DENG, 1959), eclogite boulders in conglomerate derived from a greenschist terrane in Guajira Peninsula, Colombia (J. P. LOCKWOOD, 1965, pers. comm.) and eclogites and glaucophane-bearing eclogites derived from pillow lavas and other basic igneous rocks in the "Ophiolite Series" of the western Alps, Switzerland (BEARTH, 1959). In the latter example, BEARTH recognizes a sequence of alteration of dolerite and basalt (including pillow lava) to anhydrous eclogite (garnet + omphacite + rutile ± zoisite). The eclogite shows various stages of alteration to glaucophane schist and finally to greenschist assemblages (prasinite facies) of albite + actinolitic hornblende + epidote + chlorite. This example is suggestive of alteration of dry basalt to a stable eclogite assemblage at low temperature, and partial or complete replacement of this by hydrous assemblages as access of water continues. The replacement of the glaucophane schist assemblages by greenschist possibly implies a rise in temperature later in the metamorphic history of the rocks. The rocks described by BEARTH do not appear to be exotic to their environment and the complex intermingling of gabbroic, eclogitic and hydrous assemblages may reflect simply access of water to metastable high temperature igneous or stable low temperature, dry eclogite assemblages.

It may be noted that, in general, the low temperature of the greenschist facies compared with the amphibolite and granulite facies would make reactions sluggish, particularly in dry rocks. Conditions may be slightly more favourable in the glaucophane schist facies with higher shearing stress and with $P-T$ conditions probably well within the eclogite stability field.

The conclusion that eclogites are stable over a wide range of $P_{\text{Load}}-T$ conditions parallels that recently expressed by COLEMAN et al. (1965). We differ, however, from many previous authors in suggesting that at low temperature, eclogite may be stable under shallow crustal conditions of metamorphism. Because of this probable wide $P-T$ field for eclogite stability, COLEMAN et al. query the use of the term "eclogite facies". Our data possibly clarify the position by accenting the different roles that $P_{\text{Load}}$ and $P_{\text{H}_2\text{O}}$ may play in the metamorphic facies concept. Thus the relatively pressure independent (above 1-2 kb $P_{\text{H}_2\text{O}}$) dehydration reactions are intersected at high angles in a $P_{\text{Load}}-T$ diagram by solid–solid reactions such as the
cordierite breakdown or the plagioclase-orthopyroxene reaction and provide the basis for a 3-dimensional \((T, P_{\text{Load}}, P_{\text{H}_2\text{O}})\) metamorphic facies grid. Subdivisions of the hornblende and pyroxene granulite sub-facies based on intersections of the hornblende breakdown curve with solid-solid reactions have been summarized and in part proposed by De Waard (1965).

The existence of highly temperature and pressure dependent reactions such as we have outlined experimentally is the underlying basis for the recognition of metamorphic "lineages", "regimes", or "types" as in the recent papers of Miyashiro (1961), den Tex (1965), and Coleman et al. (1965).

We suggest that future work on natural eclogites may establish criteria for subdivision of the eclogite facies on a predominantly temperature controlled basis, cf. page 49 and Coleman et al., 1965. However, even if natural eclogites have crystallized under conditions embracing a wide temperature field, this conclusion may also apply to the pyroxene granulite and pyroxene hornfels facies. These two facies, like the eclogite facies, are based on anhydrous mineral assemblages, and under conditions of low \(P_{\text{H}_2\text{O}}\) may be stable to low temperatures. The low temperature boundaries to these facies, like the eclogite facies, are determined by dehydration reactions, and thus the extent of the \(P_{\text{Load}}, T\) field occupied by these facies will depend on \(P_{\text{Load}}, P_{\text{H}_2\text{O}}\) inter-relationships. Criteria for separating comparatively low-temperature pyroxene granulite facies rocks from high-temperature pyroxene granulites have received little attention but are as important in this facies as in the eclogite facies.

Difficulties arise in application of the metamorphic facies concept in uncritical acceptance of the hypothesis that \(P_{\text{H}_2\text{O}} \approx P_{\text{Load}}\) and if an attempt is not made to disentangle the effects of these two independent variables. There is a need for identification and use of solid–solid reactions involving anhydrous phases as a basis for a \(P_{\text{Load}}-T\) petrogenetic grid. The study of basaltic rocks at high pressure reported in this paper goes some way towards this goal.

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AN EXPERIMENTAL INVESTIGATION OF THE GABBRO—ECLOGITE TRANSFORMATION AND SOME GEOPHYSICAL IMPLICATIONS

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SUMMARY

A detailed experimental investigation of the gabbro—eclogite transformation in several basalts has been carried out. More than 200 runs at temperatures between 900 and 1,250°C and pressures up to 30 kbar were made, and the resultant phase assemblages studied by optical and X-ray techniques. In all the basalts studied, the transformation from the low-pressure gabbroic assemblage (pyroxene + plagioclase) into the high-pressure eclogite assemblage (garnet + pyroxene) was found to proceed via a transitional mineral assemblage characterised by co-existing garnet, pyroxene and plagioclase. This mineral assemblage closely resembles that displayed in nature by basic rocks in the garnet—clinopyroxene—granulite sub-facies. The width of the transitional assemblage (garnet granulite) varies from 3.4 to 12 kbar at 1,100°C in different basalts and the pressures required for incoming of garnet and elimination of plagioclase likewise vary widely according to the particular basaltic composition studied. These variations are caused by small differences in chemical composition, and are interpreted in terms of the principal mineral equilibria which are involved in the transformation. In passing from gabbro to eclogite via the garnet granulite assemblage, the proportion of garnet is observed to increase regularly with pressure, whilst the proportion of plagioclase decreases regularly. Thus the increase in density and seismic velocity from gabbro ($p \sim 3.0$ g/cm³, $V_p \sim 6.9$ km/sec) to eclogite ($p \sim 3.5$ g/cm³, $V_p \sim 8.3$ km/sec) is uniformly smeared out over the entire garnet granulite transition interval.

The effect of temperature upon the pressures required for the gabbro—eclogite transformation is investigated. Our experimental results, together with the results of other workers on simple systems closely related to the gabbro—eclogite transformation, strongly indicate that eclogite would be stable relative to gabbro and garnet granulite throughout large regions of the normal continental crust. This conclusion has important tectonic implications.

The bearing of the experimental results upon the hypothesis that the continental Mohorovičić discontinuity is caused by an isochronal transformation from gabbro to eclogite is examined. It is concluded that this hypothesis must be rejected on the following grounds:

1. Eclogite, not gabbro, appears to be stable throughout the continental crust.
(2) The experimental temperature gradient of the transformation is incompatible with inferred geophysical relationships between the temperature at the base of the crust and thickness of the crust.
(3) The transformation cannot explain the seismic velocity distribution in the crust.
(4) Minor changes in chemical composition strongly affect the pressure required for eclogite stability. This makes it difficult to understand the uniformity of crustal thickness in stable continental regions.
(5) The density of eclogite (3.5 g/cm$^3$) is higher than the density of the upper mantle inferred from gravity observations.
(6) An upper mantle of eclogitic composition would be gravitationally unstable.

The chemical composition of the continental crust is discussed in the light of the widely accepted geophysical model that it consists of a layer of granitic material overlying or passing gradually downwards into a gabbroic layer. Our experimental results are in conflict with the view that the lower crust is generally of gabbroic composition. It is more likely that the lower crust consists on the average of intermediate rocks in the eclogite facies.

Although the gabbro-eclogite transformation is not believed to play a significant role in the structure of stable continental regions, it may be of major importance in tectonically active areas where the Mohorovičić discontinuity cannot be clearly recognized, e.g., regions of recent orogenesis, continental margins, island arcs and mid-oceanic ridges. It is shown that the basalt-eclogite transformation may provide a tectonic engine of great orogenic significance. Large volumes of basalt, when extruded and intruded at and near the earth's surface may become transformed to eclogite under suitable circumstances on cooling. Because of the high density of eclogite, such large scale transformations would generate gravitational instability. Large blocks of eclogite would sink through the crust, dragging it down initially into a geosyncline, and later causing extensive deformation (folding). Because the density of eclogite (3.5 g/cm$^3$) is greater than that of the ultramafic rocks which make up most of the mantle (3.3 g/cm$^3$) blocks of eclogite will sink deep into the mantle, and may undergo partial fusion, leading to generation of andesitic and granodioritic magmas which rise upwards and intrude the folded geosyncline.

**INTRODUCTION**

It is well-known that rocks of basaltic chemical composition may exhibit several distinct mineral assemblages. Two such assemblages are those of gabbro (plagioclase + pyroxene) and eclogite (garnet + pyroxene). One of the first workers to appreciate the relationships between these rock types was Fermor (1913, p.41, 1914) who pointed out that eclogite ($\rho \approx 3.5$ g/cm$^3$) must be a high pressure form of gabbro or basalt ($\rho \approx 3.0$ g/cm$^3$). This led him to propose that the earth's outer mantle was composed of eclogite and that the transformation between basaltic crustal rocks and the eclogitic mantle (infra-crust) would have some important tectonic implications. Similar views were strongly advocated in the 1920's by Holmes (1926a, b, 1927) and Goldschmidt (1922). Holmes showed that the seismic velocity of eclogite was similar to that observed in the upper mantle and argued that...
the crust–mantle boundary, now defined as the Mohorovičić (M) discontinuity was caused by a transformation from gabbro to eclogite. Holmes also emphasized the tectonic consequences of this model — changes in temperature at the crust–mantle boundary would cause transformation of gabbro to eclogite or vice versa, resulting in crustal uplift or depression.

In the period 1930–1950, the concept of an eclogitic mantle lost ground to the long-standing rival hypothesis that the upper mantle was generally of peridotitic composition, and that accordingly the crust–mantle boundary represented a change in chemical composition. However, an important paper by Birch (1952) re-opened the whole question. Basing his arguments on geochemical grounds and upon the elastic properties of minerals, Birch was led to favour an eclogitic rather than a peridotitic mantle. Although the principal argument against peridotite subsequently proved to be unfounded, owing to inaccuracies in some of the early experimental data on elastic properties of minerals, this paper resulted in a revival of interest in the subject. This was stimulated by the first syntheses by Coes (reported by Roy and Tuttle, 1956) of several eclogitic mineral components in a high pressure–temperature apparatus. Apparatus of this type was also developed by Birch and his students, and by Kennedy, with the objective of determining the important equilibria involved in the basalt–eclogite transformation by direct experiment. Pioneering results in this field were published by Robertson et al. (1957) and Kennedy (1956, 1959). These authors concluded that their preliminary experimental results were generally favourable to the hypothesis that the M-discontinuity is a phase change.

A novel argument was introduced by Lovering (1958) on the basis of an achondritic earth model. According to this model the earth's mantle is dominantly (~ 60%) composed of material similar to basaltic achondrites, which under the p, t conditions obtaining, would crystallize as eclogite. Since this material occurred mainly in the outer part of the mantle, it was argued that the crust–mantle boundary was probably caused by a phase change from basalt to eclogite. However this model was based upon an assumed relationship between chondritic and achondritic meteorites which its author has since abandoned (Lovering, 1962) and accordingly its status is questionable.

The geochemical, geothermal and tectonic consequences of the gabbro-eclogite transformation were briefly explored during this period by Sumner (1954) and more thoroughly by Lovering (1958) and Kennedy (1959). Interest in this subject has cascaded in recent years and a large number of papers dealing either directly or indirectly with the properties and consequences of the transformation have appeared, e.g., Harris and Rowell (1960), MacDonald and Ness (1960), Bullard and Griggs (1961), Wetherill (1961), Yoder and Tilley (1962), Broecker (1952), Wylie (1963), Stishov (1963). Some of these authors favour the phase change hypothesis; others oppose it. We will review specific arguments in later sections.

The prime cause of the wide divergences of opinion on this important subject is lack of detailed experimental data on the nature of the transformation and on the variations in physical properties accompanying the transformation. The objective of the present investigation, which has been in progress for 3 years, has been to fill this gap. We have chosen several representative basalts, subjected them to a wide range of closely spaced p, t conditions, and then investigated the chemical and physical nature of the
mineral phases produced and their stability fields. Over 200 runs at high pressures and temperatures have been carried out. These have led to a detailed understanding of many important aspects of the gabbro-eclogite transformation, particularly relating to the transitional mineral assemblages which intervene between the gabbro and eclogite stability fields. The present paper deals with the geophysical implications of these results. An accompanying paper, dealing with the geochemistry, petrology and mineralogy of the transformation is being published elsewhere (Green and Ringwood, 1966). A preliminary account of our early results has already been published (Ringwood and Green, 1964).

Before proceeding, a brief discussion of our usage of the term "eclogite" is desirable. In this paper we regard "eclogite" as a rock of basaltic chemical composition characterised by the mineral assemblage, garnet + pyroxene ± quartz. Plagioclase is not present. The density of such a rock is > 3.3 g/cm³ and its P-wave velocity is > 8 km/sec. This definition is somewhat loose from the petrologic point of view but is convenient and adequate for the discussion of many geophysical problems covered herein. In the accompanying paper dealing with the petrology of the transformation, a more rigid definition based upon detailed mineralogic criteria is used. We emphasize that our present usage of "eclogite", "garnet granulite" and "pyroxene granulite" is in the form of descriptive rock terms, without implications as to the metamorphic classification of these rocks.

EXPERIMENTAL

Previous experimental investigations

The transformation of gabbro to eclogite is a complex equilibrium between mineral solid solutions involving many components. One approach is to study related equilibria in simple systems between individual components which participate in the gabbro-eclogite transformation. This approach is exemplified in the pioneering work by Robertson et al. (1957) who investigated the equilibrium:

\[ \text{Na Al Si}_3 \text{O}_8 + \text{Na Al Si}_2 \text{O}_4 = 2 \text{Na Al Si}_2 \text{O}_6 \]

albite  nepheline  jadeite

Such investigations have yielded much important information which will be referred to in later sections. However, they are not capable in themselves of solving many of the major geophysical problems which are associated with the gabbro-eclogite transformation. These require direct experiments upon complex chemical systems of basaltic compositions.

Such experiments were first undertaken by Kennedy (1956) who crystallized basaltic glasses at high temperatures (800–1,000°C) and pressures. At pressures below 10–15 kbar, depending upon temperature, he found that basaltic glass crystallized to a felspar-bearing assemblage. Above these pressures, felspars were not found and Kennedy suggested that the mineral assemblages might be eclogitic. However no positive identification of the mineralogy of the high-pressure assemblage was reported. Subsequently, Kennedy (1959) described the crystallization of basaltic glass at 500°C.
Below 10 kbar, felspar was observed. At pressures above 10 kbar, the amount of felspar decreased and finally a "rock made up dominantly of jadeitic pyroxene" was observed. The suggestion that this assemblage was "eclogitic" cannot be accepted in the absence of garnet as a major phase. Furthermore, from our experiments on the kinetics of crystallization of basaltic glasses at high pressure (Green and Ringwood, 1966) we strongly suspect that Kennedy's pyroxene was metastable and not relevant to the gabbro-eclogite transformation.

The first definite conversion of basalt to eclogite was obtained by Boyd and England (1959) at 1,200°C in the pressure range 33-40 kbar. This was followed by the well-known work of Yoder and Tilley (1962) who crystallized a number of basalts and eclogites at pressures of 10 kbar, 20 kbar and 30 kbar in the temperature range 1,200-1,400°C. This work showed clearly that basalt was stable relative to eclogite at 10 kbar, whereas eclogite appeared to be stable above about 20 kbar. At 30 kbar, eclogite was definitely stable relative to liquid.

![Fig.1. Stability fields for basalt and eclogite as proposed by Yoder and Tilley (1962, p.498). (Symbols used are explained in their paper.)](image-url)

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stable. The work at 20 kbar was not completely definite since only one run was made in which a basalt was converted into an eclogite assemblage at that pressure. The remaining runs were conducted with eclogite as a starting material, and in view of our subsequent experience with this starting material, it is difficult to be confident that equilibrium was attained.

Yoder and Tilley (1962) constructed a diagram for the gabbro-eclogite transformation based upon their results around 1,200°C and Kennedy's results at 500°C (Fig.1). On the basis of this diagram they discussed the continental M-discontinuity and concluded that it might be caused by a gabbro-eclogite transformation. This diagram has frequently been reproduced by other workers and cited as the experimental background for their theoretical discussions. Unfortunately this diagram is misleading and does not permit valid conclusions to be drawn concerning the nature of the M-discontinuity. Any discussion of the latter depends critically upon a knowledge of the \( p, I \) gradient of the transition and the transition interval. The gradient and transition zone in Fig.1 are seen to be dependent upon Kennedy's results at 500°C which are unacceptable for reasons discussed earlier.

A detailed study of the transformation at 1,100°C on two basalts was reported by Ringwood and Green (1964) who concluded that the continental M-discontinuity was not caused by an isochemical gabbro-eclogite transformation. Their arguments are developed in greater detail in the present paper.

The present investigation

Although basalts constitute an easily recognisable and distinct petrologic class of rocks, their chemical compositions vary over a substantial range, necessitating further classification into various sub-classes. One of the principal objectives of the present investigation was to study the effects of varying chemical compositions (if any) upon the gabbro-eclogite transformation. Typical representatives of the principal types of basalt were accordingly chosen for investigation (Table I). These were as follows: typical quartz tholeiite (2), a quartz tholeiite rather poorer than usual in alkalis (3), a typical alkali olivine basalt (4), and an alkali-poor olivine tholeiite (6). In addition, a typical oceanic high-alumina olivine basalt (7) has been studied by Mr. Trevor Green who has kindly permitted us to refer to his results. An investigation was also made of the effects of certain other chemical parameters on the transformation. The alkali olivine basalt (4) was oxidised to an \( \text{Fe}_2\text{O}_3/\text{FeO} \) ratio of 2 : 1, to elucidate the effects of a high oxidation state (5). The effects of changes in \( \text{FeO}/\text{MgO} \) ratios on the transformation were also studied in a separate series of experiments. The chemical and normative compositions of the principal basaltic compositions which were investigated are given in Table I.

Our experimental procedure is described in detail in the accompanying paper (Green and Ringwood, 1966), and accordingly a brief summary will suffice in the present case. The basalt compositions in Table I were obtained either from natural analyzed basalts and/or minerals or from synthetic starting materials. After fine grinding and intimate mixing, the components were melted in a controlled atmosphere and quenched to a homogeneous
### TABLE I

Chemical compositions of basaltic glasses used in experimental work

<table>
<thead>
<tr>
<th></th>
<th>(1) High-alumina basalt</th>
<th>(2) Quartz tholeiite</th>
<th>(3) Alkali-poor quartz tholeiite</th>
<th>(4) Alkali-olivine basalt</th>
<th>(5) Oxidised alkali olivine basalt</th>
<th>(6) Alkali-poor olivine tholeiite</th>
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| 100 x Mg (mol) | 68                       | 61.0                 | 61.0                             | 60                        | 82                                | 66                               |

\[\text{Mg + Fe}^{2+}\]

Norms

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<tr>
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<td>-</td>
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</table>

1 Analyst: A.J. Easton, Department of Geophysics and Geochemistry, Australian National University, Canberra.
glass. The contents of FeO and Fe$_2$O$_3$ in the glass were then determined by chemical analysis and are given in Table I.

Glass samples so prepared were sealed into platinum capsules and subjected to various desired temperatures and pressures between 900°C and 1,250°C and pressures between 5 kbar and 40 kbar in an internally heated, high-pressure apparatus. The apparatus used was a replica of that described by Boyd and England (1960). The reader is referred to their paper for details of experimental techniques and operation. Temperatures were measured by a Pt–Pt 10% Rh thermocouple in contact with the charge, and are accurate to ± 15°C. No correction for the effect of pressure on thermocouple EMF was applied. The thermocouple was also used in conjunction with a suitable controller to regulate power input into the graphite furnace so that recorded temperature was kept steady within ± 5°C of the desired setting. Total pressure delivered by the high-pressure piston is given within 0.5% by a Heise gauge in the hydraulic circuit. A correction of - 10% was applied to the total pressure so obtained in order to determine the pressure actually operating on the sample. This correction is required because of friction and imperfect pressure transmission in the apparatus and talc pressure medium. The magnitude of the pressure correction was evaluated in a separate series of experiments (Green et al., 1966). Absolute pressures so obtained are probably correct to ± 3%, whilst relative pressures over limited pressure intervals are undoubtedly much more precise than this.

Runs lasted between 1-6 h, the majority being of 4 h duration. After completion of a run, the charge was quenched in a few seconds by terminating the power to the furnace. After removal from the apparatus it was investigated by optical and X-ray methods. Relative proportions of phases present in runs were determined by comparison of X-ray diffractometer records and powder films of samples with those of specially prepared standards.

One of the problems in experimental work of this nature is whether or not chemical equilibrium was reached in the runs. This problem was investigated in considerable detail. The sequence of crystallization of basalt glass at 1,100°C was followed in a series of runs ranging in length from 1/4 to 12 h. Runs of short period were dominated by the appearance of metastable complex pyroxenes, which broke down on longer runs to form stable pyroxene plus garnet. At 1,100°C, runs of 2 h sufficed to achieve equilibrium in most cases. Most of our runs were nevertheless carried out for 4 h. The question of reversibility was studied in detail in one of the quartz tholeiites (2). The maximum pressure at which plagioclase could be identified in runs initially of glass was the same as that at which plagioclase was grown from starting material consisting of garnet + pyroxene but of identical chemical composition. Similar reversibility was demonstrated for the incoming of garnet.

Changes in oxidation state of the charge and loss of iron to the platinum container during runs were also investigated by chemically analyzing for FeO and Fe$_2$O$_3$ after completion of runs. It was demonstrated that under the conditions employed, loss of iron and changes in oxidation state were of minor proportions.

RESULTS

A detailed chemical and mineralogical discussion of the experimental runs

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is given in the accompanying paper (Green and Ringwood, 1966). Our aim in this section is to outline the major generalizations which can be drawn from the experiments. In Fig. 2 we have compared in a simplified form, the phase assemblages which were found in the typical basalts studied at 1,100°C, as a function of pressure. Although the pressures required for appearance and disappearance of phases vary between individual basalts, there is an important qualitative resemblance between the sequence of phase assemblages displayed by all rocks with increasing pressure. For each basalt, there are clearly three principal mineral stability fields, corresponding closely with naturally observed mineral assemblages. The low-pressure assemblage is that of gabbro or pyroxene granulite. It is characterised by the presence of pyroxene and plagioclase ± olivine ± quartz ± spinel, according to the particular bulk chemistry. Garnet is not present. Within the stability field of this mineral assemblage it is observed that the ratio of plagioclase to pyroxene decreases with increasing pressure. This is caused in part by solid solution of plagioclase components (principally anorthite) in pyroxene as Tschermak's molecule, which increases with pressure. It is also caused by reaction of plagioclase with olivine to form aluminous pyroxenes ± spinel.

Fig. 2. Principal mineral assemblages displayed by several basaltic compositions (Table I) as a function of pressure at 1,100°C. Solid circles denote experimental runs.

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In each basaltic composition, as pressure increases, a point is reached at which garnet appears in the mineral assemblage. With further increase in pressure, the proportion of garnet steadily increases, whilst the proportion of plagioclase correspondingly decreases. Thus, we have here a field of co-existing garnet, pyroxene and plagioclase. The pyroxenes in the garnet granulite field are rich in Al$_2$O$_3$ in the form of Mg and Ca Tschermak’s molecules. With further increase of pressure, these components are rejected and crystallize as garnet and accordingly the garnet/pyroxene ratio rises. Plagioclase becomes more sodic as it decreases in abundance. At the highest pressures, sodic plagioclase breaks down to form jadeite which enters into solid solution in the pyroxene. Free quartz may or may not be formed, depending upon the silica saturation of the rock. A further increase in garnet/pyroxene ratio occurs as the Tschermak’s molecule component of the pyroxene is reduced to low levels. These transformations mark the beginning of the eclogite mineral assemblage, characterized by the co-existence of pyrope-rich garnet, omphacite ± quartz.

Thus we see that in all the basalt compositions studied, the transformation from gabbro or pyroxene granulite to eclogite proceeds through an intermediate mineral assemblage characterised by co-existing garnet, pyroxene(s) and plagioclase. This possesses an extensive stability field varying from 3.5 to 12 kbar in width, and is identical with the natural garnet-clinopyroxene granulite subfacies recognizable in some metamorphic terranes (De Waard, 1965; Green and Ringwood, 1966).

The results plotted in Fig. 2 show that rather modest changes in chemical composition cause large changes in the pressures and width of the gabbro-eclogite transformation. Thus, the pressures at which garnet first appears vary between 9.6 and 15.2 kbar, whilst the pressure required to cause the final disappearance of plagioclase varies between 13.0 and 23.3 kbar. These variations are of considerable geophysical significance and will be further discussed in the section on the nature of the M-discontinuity. The reasons for the variation are readily explicable in terms of the chemical and mineralogical equilibria involved in the transformation, and are discussed in detail in the accompanying paper (Green and Ringwood, 1966). The pressures required for the incoming of garnet are smaller in undersaturated rocks (Fig. 2, Table I, 1, 4, 6) than in oversaturated rocks (Fig. 2, Table I, 2, 3, 5) whilst the pressure required for the final disappearance of plagioclase is decreased in basaltic compositions which are poorer than usual in soda (Fig. 2, Table I, 3, 6). Changes in FeO/MgO ratio have an important influence over the pressure required for the incoming of garnet, these pressures being smaller the higher the FeO/MgO ratio of the rock. Such changes do not appear to markedly affect the pressure required for the disappearance of plagioclase, although our data relating to this point are rather scanty. Neither do changes in oxidation state affect the pressure at which plagioclase disappears (Table I, 5). However, the entrance of garnet requires higher pressures in highly oxidised rocks (Table I, 5).

Finally, in Fig. 3, the results of experiments on a quartz tholeiite (2) over a range of temperatures are given. These results establish a temperature gradient for the transformation which permits extrapolation to lower temperatures. The slopes of the boundaries for the incoming of garnet and disappearance of plagioclase tend to converge at lower temperatures. This appears to be a real phenomenon, although it may not be as marked as it
Fig. 3. Mineral assemblages observed in quartz tholeiites (Table I, 2 and 3) over a range of temperature and pressure conditions. The eclogite field lies above $CD$ and the pyroxene granulite field lies below $AB$. Area between $AB$ and $CD$ represents the garnet granulite stability field. Boundary $BD$ is the solidus. $Px =$ pyroxene, $Pl =$ plagioclase, $Gd =$ garnet, $Qz =$ quartz. Plagioclase is absent on the high-pressure side of $CD$ in quartz tholeiite 2, but is absent on the high-pressure side of the line $E$ in quartz tholeiite 3 composition. The line $G$ marks the appearance of garnet in highly iron-enriched quartz tholeiite; $F$ marks the first appearance of garnet in magnesium quartz tholeiite.

CHANGES IN PHYSICAL PROPERTIES ASSOCIATED WITH THE TRANSFORMATION

A considerable amount of information is available on the densities and
seismic velocities of basalts and gabbroic rocks (Birch, 1960, 1961). The densities of most fresh rocks of this type are close to 3.00 g/cm$^3$, whilst the corresponding P-wave velocities (corrected for the effect of initial porosity) mostly range from 6.8 to 7.1 km/sec. On the other hand, less is known about the seismic velocities and densities of eclogites. Birch (1960) attempted to determine these quantities but his samples had clearly been subjected to considerable secondary alteration and his results ($\rho = 3.33 - 3.44$ g/cm$^3$, $V_p = 7.3 - 7.8$ km/sec) cannot be held to be characteristic of fresh eclogites. Indeed most whole-rock samples of eclogite which have been measured for density by other workers appear to have suffered secondary alteration, resulting in systematic underestimates of the densities of eclogite. Thus, Kennedy (1959) states that the mean density of eclogite is 3.3 g/cm$^3$, whilst according to Lovering (1958) the mean density is 3.4 g/cm$^3$. We shall see below that these densities are too low and that the geophysical consequences of a substantially higher mean density ($\sim 3.5$ g/cm$^3$) for eclogite are far-reaching.

Some of the best determinations of the densities of eclogite were obtained by Eskola (1921). The rock descriptions indicate a small amount of secondary alteration so that the densities which he obtained are probably slightly low (Table II). The average density of this group is 3.54 g/cm$^3$. Alternatively the densities of eclogites can be calculated directly from their chemical compositions, which are cast into “eclogite norms”, the compositions of garnets and pyroxenes being made similar to those in natural eclogites. The densities of individual minerals can either be measured directly on unaltered, separated samples, or else they can be calculated with adequate precision from knowledge of densities of their end-member components and mineral compositions. The density of the whole rock is then obtained by combining the densities of individual minerals. Results of such calculations for some of the basaltic compositions which we have investigated and also for some natural eclogites are given in Table II and III. Finally, the density of a sample of alkali olivine basalt (1) which had been subjected to a pressure of 30 kbar at 1,100°C was measured directly and found to be 3.54 g/cm$^3$. From these results we see that the densities of undersaturated rocks of basaltic composition are usually between 3.5 and 3.6 g/cm$^3$, whereas the densities of quartz tholeites in eclogitic facies are somewhat lower. Quartz tholeite (2) with 13% free quartz ($\rho = 2.65$ g/cm$^3$) has a density of 3.43 g/cm$^3$. It is possible that some quartz-rich tholeites may have somewhat lower densities than this. However, enrichment in quartz is usually accompanied by increase in the FeO/MgO ratio of the rock. This leads to an increase in density which compensates for the higher amount of quartz. Indeed, the quartz tholeite (2) has an abnormally low FeO/MgO ratio for its degree of silica saturation and its density is therefore probably minimal for this type of rock.

Considering all the available data, the average density of eclogites of quartz tholeite composition is probably close to 3.45 g/cm$^3$, whilst that of eclogites of olivine tholeite composition is probably around 3.55 g/cm$^3$. The average for eclogites generally may be taken as 3.50 g/cm$^3$.

Seismic velocities of eclogites may be obtained from the velocity-density relationship of Birch (1961). These are also given in Table II and III. An alternative method is to calculate the seismic velocities from the elastic properties of end-member mineral components (Ringwood, 1966a).
TABLE II
Compositions, densities and seismic velocities of some eclogites

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rodhaugen Duen</td>
<td>Lyngenes</td>
<td>Silden Glenelg</td>
<td>Loch Duich</td>
<td>Hawaiian magma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>48.7</td>
<td>41.5</td>
<td>45.33</td>
<td>52.4</td>
<td>50.05</td>
<td>42.60</td>
<td>46.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.7</td>
<td>15.9</td>
<td>13.06</td>
<td>11.0</td>
<td>13.37</td>
<td>12.41</td>
<td>12.9</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.2</td>
<td>0.0</td>
<td>tr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.4</td>
<td>3.4</td>
<td>1.58</td>
<td>2.4</td>
<td>3.71</td>
<td>3.50</td>
<td>2.1</td>
</tr>
<tr>
<td>FeO</td>
<td>6.8</td>
<td>16.2</td>
<td>12.73</td>
<td>8.0</td>
<td>10.39</td>
<td>16.94</td>
<td>9.6</td>
</tr>
<tr>
<td>MnO</td>
<td>0.2</td>
<td>0.4</td>
<td>0.22</td>
<td>0.2</td>
<td>0.25</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>16.7</td>
<td>4.2</td>
<td>17.28</td>
<td>10.6</td>
<td>6.49</td>
<td>7.23</td>
<td>14.6</td>
</tr>
<tr>
<td>CaO</td>
<td>13.9</td>
<td>12.4</td>
<td>7.57</td>
<td>11.5</td>
<td>11.00</td>
<td>11.18</td>
<td>9.9</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.4</td>
<td>2.6</td>
<td>0.79</td>
<td>2.3</td>
<td>2.38</td>
<td>1.09</td>
<td>1.5</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.2</td>
<td>0.1</td>
<td>0.16</td>
<td>0.5</td>
<td>0.36</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.2</td>
<td>1.35</td>
<td>0.4</td>
<td>1.55</td>
<td>3.64</td>
<td>3.84</td>
<td>2.3</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>2.4</td>
<td>0.19</td>
<td>0.12</td>
<td>0.08</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.2</td>
<td>0.22</td>
<td>0.1</td>
<td>0.45</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(S, CO$_2$)</td>
<td>100.3</td>
<td>100.7</td>
<td>100.5</td>
<td>100.3</td>
<td>100.34</td>
<td>100.43</td>
<td>100.2</td>
</tr>
<tr>
<td>Accessories and secondary minerals</td>
<td>-</td>
<td>6.5</td>
<td>3.6</td>
<td>-</td>
<td>6.6</td>
<td>5.6</td>
<td>-</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.51</td>
<td>3.61</td>
<td>3.57</td>
<td>3.42</td>
<td>3.44</td>
<td>3.66</td>
<td>3.55</td>
</tr>
<tr>
<td>V$_P$ (km/sec)</td>
<td>8.4</td>
<td>8.3</td>
<td>8.5</td>
<td>8.1</td>
<td>8.2</td>
<td>8.4</td>
<td>8.5</td>
</tr>
</tbody>
</table>

1No.1, 2, 3, 4 were measured directly on relatively fresh rocks (Eskola, 1921). Nevertheless these rocks contained a few percent of secondary minerals. No.5 and 6: Densities were calculated from known compositions and proportions of minerals. Analyses from Yoder and Tilley (1962). No.7: Composition of parental Hawaiian magma type (MacDonald and Katsura, 1961) Composition was calculated into an eclogite norm and the rock density obtained from densities of individual minerals. P velocities for no.1, 3, 4, 5, 7 were calculated from densities according to method given by Birch (1961), solution 7. Velocities of no.2 and 6 are lower than are given by this solution, because of their high iron content.

For the Kilauea Iki "eclogite", V$_P$ obtained by this method is 8.41 km/sec (Table II). This compares with 8.48 km/sec obtained from the Birch relationship. As would be anticipated, the seismic velocities of eclogites decrease markedly with an increasing amount of free quartz.

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TABLE III
Mineralogical compositions, densities and seismic velocities of eclogitic facies of some of the basaltic compositions given in Table I*

<table>
<thead>
<tr>
<th></th>
<th>(1) High Al.</th>
<th>(2) Quartz tholeiite</th>
<th>(4) Alkali olivine basalt</th>
<th>(6) Alkali-poor olivine basalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>51.8</td>
<td>43</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>38.0</td>
<td>43</td>
<td>48</td>
<td>45</td>
</tr>
<tr>
<td>Quartz</td>
<td>8.5</td>
<td>13</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Rutile</td>
<td>1.7</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Olivine</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.49</td>
<td>3.43</td>
<td>3.54</td>
<td>3.61</td>
</tr>
<tr>
<td>Vp (km/sec)</td>
<td>8.3</td>
<td>8.2</td>
<td>8.4</td>
<td>8.6</td>
</tr>
</tbody>
</table>

(Birch, 1961)

*No.1, 2, 6: Compositions were cast into eclogite norms and densities were calculated from these. No.4: Density was measured directly upon a synthetic eclogite made by holding glass of this composition at 30 kbar and 1,100°C for 2 h.

Having discussed the densities and seismic velocities of gabbros and eclogites, we can now consider the manner in which these vary as gabbro is transformed to eclogite with increasing pressure. To investigate these questions, a series of closely spaced runs was made on the basalt compositions (Fig.2). The proportions of phases present were estimated by comparison of powder patterns and diffractometer records of runs with specially prepared standards. Although the precision of this method is not high, the principal conclusions which follow are beyond reasonable doubt.

In all cases, as the pressure increases from zero up to the point at which garnet first appears, there is an increase in the pyroxene/plagioclase ratio caused by solid solution of plagioclase components in pyroxenes which become notably aluminous. The rocks in the higher pressure range are perhaps better regarded as pyroxene granulites rather than gabbro. The change in the pyroxene/plagioclase ratio would necessarily cause a slight increase in densities with pressure. The density of the pyroxene granulites just before entry of garnet are probably about 3.05-3.10 g/cm³. The incoming

TABLE IV
Results of runs at 1,100°C on alkali-poor olivine tholeiite

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>Phases present</th>
<th>( \rho ) (g/cm³)</th>
<th>( V_p ) (km/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>pyroxenes, plagioclase, olivine spinel</td>
<td>3.1</td>
<td>7.3</td>
</tr>
<tr>
<td>10.1</td>
<td>pyroxenes, plagioclase, rare garnet</td>
<td>3.1</td>
<td>7.3</td>
</tr>
<tr>
<td>11.3</td>
<td>pyroxenes, plagioclase, 20% garnet</td>
<td>3.38</td>
<td>8.0</td>
</tr>
<tr>
<td>12.4</td>
<td>pyroxene 60, plagioclase 10, garnet 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.5</td>
<td>pyroxene 60, garnet 40, trace plagioclase?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.8</td>
<td>garnet 45, pyroxene 55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>garnet 50, pyroxene 50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>garnet 55, pyroxene 45</td>
<td>3.61</td>
<td>8.6</td>
</tr>
</tbody>
</table>

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THE GABBRO–ECLOGITE TRANSFORMATION

Fig. 4. Approximate proportions of mineral phases present in quartz tholeiite (2) in the pressure range 0–30 kbar at 1,100°C.

Fig. 5. Approximate proportions of mineral phases present in the alkali basalt (4) in the pressure range 0–30 kbar at 1,100°C.

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of garnet marks the beginning of the garnet granulite field which is transitional between pyroxene granulite and eclogite. As pressure increases throughout this field, the proportion of garnet steadily increases, whilst the proportion of plagioclase steadily decreases. To a first approximation the changes in mineralogy across the garnet granulite zone occur at a uniform rate (Fig. 4, 5) and accordingly the corresponding changes in seismic velocity and density will also change regularly throughout the garnet granulite zone. With the exception of the alkali-poor olivine tholeiite which is discussed below, there is no suggestion of the presence of a narrow pressure interval within the garnet granulite field, characterised by an abnormal increase of garnet and/or decrease of plagioclase.

Yoder and Tilley (1962) previously discussed the question of whether a wide transitional field (which we have now established) would be an objection to the hypothesis that the M-discontinuity is a phase change. They argue that although the total width of the transition zone may be large, the "effective change in seismic velocity will be realized over a much smaller pressure range" because of the large contribution to the seismic velocity change caused by the incoming of garnet. Accordingly, they believe that the "Mohorovičić discontinuity under the continents may be the result of the transformation of basalt to eclogite."

With one partial exception, the results which we have described on a variety of basalts effectively contradict this interpretation. The results on the alkali-poor olivine tholeiite (6) are in contrast to the others. Here, the incoming of garnet and the disappearance of plagioclase occur within a pressure interval of only 3.4 kbar. Much of this change occurs within 2.3 kbar. Results are given in Table IV. The chemical and mineralogical reasons for this behaviour are discussed in the accompanying paper (Green and Ringwood, 1966). Although the transformation of this basalt into a garnet–pyroxene rock free of felspar is nearly complete at 12.4 kbar, the rock contains only 30% of garnet, and the pyroxene is highly aluminous. With increasing pressure between 12.4 and 22.5 kbar, there is a large increase in garnet/pyroxene ratio and a corresponding large increase in seismic velocity and density (Table IV).

The transitional interval in the oxidised alkali-olivine basalt (5) is smaller than in the unoxidised basalt, owing to a higher pressure required for the appearance of garnet. However, there is an extensive field of spinel present in this basalt between 5 kbar and 25 kbar, and in fact the change in density and seismic velocity between the gabbroic and eclogite facies of this basalt are more "smeared out" than in any of the basalts which we have studied.

STABILITY OF ECLOGITE WITHIN THE CRUST

The accompanying paper (Green and Ringwood, 1966) contains a detailed comparison of our experimental results on the gabbro–eclogite transformation, with petrological observations of basaltic rocks which have been metamorphosed in the granulite facies in the earth's crust. Under such conditions, basaltic rocks are transformed successively with increasing pressure into aluminous pyroxene–plagioclase assemblages (pyroxene granulites), then into garnet–aluminous pyroxene–plagioclase assemblages and finally into eclogites. The mineralogy of the transformations observed in our experiments
in the range 1,000–1,250°C corresponds extremely closely to the sequence of mineralogical changes observed in the granulite facies, which were probably established at temperatures in the vicinity of 500–800°C. The correspondence between experimental and natural mineral equilibria justifies extrapolation of experimental results to lower temperatures in order to interpret the conditions of formation of natural granulites and eclogites.

The pyroxene granulite, garnet granulite and eclogite stability fields have been delineated between 1,000 and 1,250°C for the quartz tholeiite (2) composition. These experiments, including reversal of the boundaries shown, have provided a reliable value for the width of the transition zone in this temperature interval. Because of the small experimental temperature interval, the gradients of the two boundaries of the garnet granulite field have an appreciable uncertainty. Accordingly, we have used the average of these two gradients, which are based upon twice the number of experiments as were available for either single boundary, as the gradient for downward extrapolation of the transition zone (Fig.6). The mean gradient thus obtained is 21 bar/°C.

Fig.6. Extrapolated stability fields of eclogite, garnet granulite and pyroxene granulite–gabbro for the quartz tholeiite (2) composition. The broken lines AB and CD are the experimental boundaries from Fig.3. Extrapolation is based upon the average of the gradient AB and CD together with the assumption that the width of the garnet granulite zone is proportional to absolute temperature. (See text.)

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The simplest procedure for extrapolation to lower temperatures would be to use this mean gradient, together with the mean transition interval as obtained from Fig.3. The use of this procedure would not alter any of the conclusions reached in subsequent sections. In Fig.3 and 6 it is seen that although the experimental boundaries are approximately parallel, they nevertheless converge toward lower temperatures. This is probably a real feature but the small temperature range covered by experiments makes the degree of convergence difficult to estimate with any confidence. It would perhaps be more realistic to use an extrapolation which allows for a modest decrease in transition width with falling temperature. Accordingly, in Fig.6, we have set the width of the transition zone to be proportional to absolute temperature, using a mean gradient of 21 bar/°C as discussed above. This procedure is somewhat arbitrary, but probably represents a slight improvement upon the assumption of parallel boundaries. When experimental uncertainties are taken into account, it is consistent with the experimental boundaries established between 1,000 and 1,250°C (Fig.6).

With these assumptions, the granulite field boundaries have been extrapolated to low pressures and temperatures (Fig.6). It is seen that the temperature on the garnet granulite/eclogite boundary at a pressure corresponding to the base of the normal continental crust (10 kbar) is 670°C. If the temperature at the base of the crust is lower than 670°C, then eclogite would be the stable form of a basalt of this composition throughout the crust. The temperature distribution in the crust is determined principally by the surface heat flux and the depth distribution of radioactivity. Numerous models have been investigated by Birch (1955), Clark (1961, 1962), Clark and Ringwood (1964) and others. Their results show that in stable continental regions of normal crustal thickness, and characterised by heat flows between 0.8 and 1.5 μcal/cm²sec the temperature at the base of the crust is usually less than 670°C for most reasonable assumptions concerning radioactivity distribution. This conclusion is practically certain for Precambrian shields characterised by heat flows between 0.8 and 1.5 μcal/cm²sec. The temperature at the base of the crust of these regions is probably less than 450°C. Such temperature distributions, taken in conjunction with the experimental results discussed above, indeed imply that eclogite is the stable modification of quartz tholeiite throughout very large regions of normal continental crust. This conclusion was unexpected by us when this project was commenced, and if correct, would have profound tectonic consequences. For this reason it deserves careful scrutiny. One is tempted to ask whether uncertainties in experimental data and in the extrapolation to lower temperatures are sufficiently large to invalidate this conclusion. We have examined our data with this in mind. If the maximum reasonable allowance for possible experimental errors is made the temperature of the eclogite/garnet granulite boundary for quartz tholeiite at 10 kbar could be brought down to 500°C. However, this is almost certainly higher than the temperature at the M-discontinuity beneath Precambrian shields, and consequently eclogite would be stable in the crust in such regions. The only escape from this conclusion would be to introduce a much larger curvature into the extrapolated phase boundaries than appears plausible.

Quartz tholeiite is the most common type of continental basaltic rock. However, there are also other important classes of continental basalts which have been investigated in our experiments. Of the six basalts which we
investigated, four required smaller pressures to reach the eclogite stability field than the quartz tholeiite (2) discussed above. If the gradient of the transformation in these basalts is similar to the one which we investigated, then our conclusion regarding eclogite stability in the crust is generalized and reinforced. In the case of the alkali-poor olivine tholeiite (Table IV) this conclusion may be considered practically certain. The only basalt which required a higher pressure to reach the eclogite stability field than quartz tholeiite (2) is the high-alumina olivine basalt, a typical oceanic tholeiite. If the transformation in this basalt has the same slope, the eclogite/garnet granulite boundary (Fig 6) would intersect the continental M-discontinuity at a temperature of 540°C, which is probably higher than the temperature at this depth in many continental regions. In such regions eclogite would be the stable form of this basalt also.

An alternative method of establishing the gradient of the transition zone is by comparison with the known gradients in simple systems which are closely related to the gabbro-eclogite transformation. It is reasonable to assume that the gradients in these simple systems will be generally similar to that of the gabbro-eclogite transformation. As was discussed briefly in the section "Results" and more fully by Green and Ringwood (1966), the principal equilibria occurring near the garnet granulite/eclogite boundary are the breakdown of sodic plagioclase to form jadeite + quartz (jadeite enters into solution in pyroxene) and the breakdown of aluminous pyroxenes form garnet and low-alumina pyroxenes. The gradients of several of these equilibria (Table V, no.1,2,3, and 5) have been established experimentally and are plotted on Fig.6. It is seen that they are generally parallel to the

### Table V

Gradients of simple equilibria related to the garnet granulite-eclogite transition

<table>
<thead>
<tr>
<th>No.</th>
<th>Equilibrium</th>
<th>dp/dt (bar/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>albite = jadeite + quartz</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>albite + diopside = omphacite (40% Jd) + quartz</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>aluminous enstatite (&lt; 6% Al₂O₃) = enstatite</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>albite + nepheline = 2 jadeite</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>clino.pyroxene + orthopyroxene + anorthite + spinel = garnet + clinopyroxene</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>clino.pyroxene + orthopyroxene + forsterite + spinel = garnet + forsterite + clinopyroxene</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>clino.pyroxene + orthopyroxene + quartz = garnet + quartz + pyroxene</td>
<td>107*</td>
</tr>
<tr>
<td>8</td>
<td>4 enstatite + spinel = forsterite + pyrope</td>
<td>17</td>
</tr>
</tbody>
</table>

*References: (1) Birch and Le Compte (1960); (2) Kushiro (1965); (3) Boyd and England (1964); (4) Robertson, Birch and MacDonald (1957); (5), (6) Kushiro and Yoder (1965); (7) Kushiro and Yoder (1964); (8) MacGregor (1964).

*This gradient is based upon very limited experimental data and has a large uncertainty.

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experimentally determined slope of the basalt–eclogite transformation. The slopes of several other simple equilibria which are related to the basalt–eclogite transformation are also given in Table V, no. 4, 6, 7, and 8. The average slope of the eight equilibria in Table V is 20 bar/°C compared to our mean slope for the basalt–eclogite transformation of 21 bar/°C. (Fig. 3, 6). Thus we see that if the slopes of the simple equilibria are used as the basis for extrapolation, the conclusion regarding stability of eclogite in the normal continental crust is reinforced.

The experimental observations discussed above, when considered as a whole, strongly suggest that eclogite is the stable modification of most rocks of basaltic composition under dry conditions within large regions of continental crust. In the case of undersaturated, alkali-poor basaltic rocks occurring in continental regions with a heat flow ≤ 1.0 μcal/cm²·sec, this conclusion is practically certain. Such compositions are in fact, characteristic of many natural eclogites (Table II).

It is important to consider the bearing of geological field evidence upon the above conclusion. Eclogites occurring in the crust clearly have more than one mode of origin. Those occurring in diamond pipes and perhaps those occurring as inclusions or segregations in ultramafic bodies appear to have been originally derived from the mantle. However, there is another important class of eclogite occurrences as small lenses, inclusions and sometimes as conformable bodies in regional metamorphic rocks of amphibolite, green-schist and glaucophane schist facies. The origin of these eclogites is not settled, but many competent geologists consider that they have been formed in situ in the crust, by metamorphism of basaltic rocks under conditions of relatively low water vapour pressure, and in some cases, of localized shear stress (Backlund, 1936; Korzhinsky, 1937; Kozlowski, 1958; Smulikowski, 1960; Bearth, 1959; Coleman et al., 1965). This conclusion is in complete harmony with the experimental evidence. A detailed review of geological and petrological evidence relating to the occurrence of granulitic and eclogitic rocks in the crust is given by Green and Ringwood (1966).

Although there is strong observational evidence that basalt may be transformed into eclogite in the crust under appropriate conditions, it is well known that in the exposed crust, eclogites are extremely rare rocks compared to gabbros, dolerites and basalts. It might be held that this fact argues against the conclusion advanced above. There are, however, additional factors which may be responsible for the rarity of eclogite:

(a) The vast majority of rocks of basaltic composition have been emplaced in the crust originally as magmas, which complete their crystallization above 1,000°C. At these temperatures, most basaltic rocks would crystallise dominantly to plagioclase and pyroxene at all levels within the crust. On cooling in a normal crustal environment, the basalts would pass through the garnet granulite stability field into the eclogite stability field, as previously discussed. Whether a given basaltic rock will actually undergo these transformations depends upon kinetic factors. The transformations are apparently extremely sluggish at low temperatures and under dry conditions, so that if a gabbroic assemblage can be brought to a temperature below about 200–300°C under conditions of low water vapour pressure and shear stress, it may be preserved indefinitely. The common occurrence of unaltered basalts, dolerites and gabbros in the crust is thus ascribed to their kinetic stability and not to their thermodynamic stability.

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Similar arguments apply to the survival of basic granulites in the crust. Such rocks are often produced by the intense regional metamorphism of basic rocks under fairly dry conditions. Regional metamorphism is usually a consequence of an abnormal rise in temperature in large areas of the crust due to processes which are poorly understood. Basaltic rocks are then converted to pyroxene and/or garnet granulites under equilibrium conditions in the abnormal geothermal field. Whether they will then revert to eclogite when crustal temperatures cool to the normal state depends again upon kinetic factors.

(b) When subjected to regional metamorphism at low to moderate temperatures and high water vapour pressures, basaltic rocks are usually converted into various hydrated mineral assemblages, e.g., amphibolites, greenschists, glaucophane schists. These assemblages are stable for basaltic rocks in such environments. Neither eclogite nor gabbro is stable in the crust under conditions of high water vapour pressure. (The previous conclusion that eclogite is the stable form of basalt specifically referred only to relatively dry conditions.)

(c) A third factor contributing to the rarity of crustal eclogite is the high density of this type of rock (section "Changes in physical properties associated with the transformation"). If a large volume of basaltic rock should be transformed into eclogite within the crust, an acute gravitational instability would be caused. The contrast in density between eclogite (~3.5 g/cm³) and crustal rocks (~2.85 g/cm³) would probably result in the body of eclogite sinking physically through the crust into the mantle. The situation would be strictly analogous but opposite in sense to the diapiric intrusion of salt domes and gneiss domes in the crust. This topic is reopened in the section "Possible tectonic consequences of the gabbro-eclogite transformation".

NATURE OF THE MOHOROVIČIĆ DISCONTINUITY

The hypothesis that the Mohorovičić discontinuity is caused by a phase change from basalt to eclogite is currently receiving a great deal of attention. In its most general form, this hypothesis has been applied as an explanation both of the continental and oceanic M-discontinuities. There are, however, some serious objections to this general statement of the hypothesis.

Harris and Rowell (1960), Bullard and Griggs (1961) and Wetherill (1961) have shown that temperature and pressure distributions beneath oceans and continents are fundamentally inconsistent with the postulate that oceanic and continental M-discontinuities are caused by the same phase change. The inconsistency is a consequence of the crossing of oceanic and continental geotherms at shallow depth owing to the different distributions of radioactivity beneath these contrasting areas. A second objection raised by Bullard and Griggs and Wetherill (and noted also by MacDonald and Ness, 1960) concerned the wide variation of heat flux observed at the earth's surface. This in turn implied the presence of substantial temperature variations at similar depths in the crust and upper mantle, which, according to the phase change hypothesis should be closely correlated with depth to the M-discontinuity. The required correlation is not observed.

To survive these objections, a more restricted form of the phase change...
change hypothesis must be introduced. Thus, it might be assumed (1) that a gabbro-eclogite transformation is responsible for the M-discontinuity beneath continents, but not beneath oceans, or vice versa, and (2) that the pressure at which the gabbro-eclogite transformation occurs is almost independent of temperature.

Stishov (1963) has reviewed the relevant evidence and has accepted the above limitations. He prefers to adopt a restricted form of hypothesis which maintains that the continental M-discontinuity is caused by the gabbro-eclogite transformation, whereas the oceanic M-discontinuity is caused by a chemical change to ultramafic material. This view has also been taken by Yoder and Tilley (1962), Wyllie (1963) and Van Bemmelen (1964). It is probable that most of those (e.g., Kennedy, 1959) who wish to retain the phase-change hypothesis would accept this choice since the objections to a gabbro-eclogite transformation at the oceanic M-discontinuity are generally regarded as being stronger than for the same transition at the base of the continental crust. Our experimental results are directly applicable to this restricted version of the phase-change hypothesis. Indeed, they appear to confront the hypothesis with several insuperable difficulties which are discussed below.

**Stability of eclogite within the crust**

In the previous section strong evidence was presented supporting the conclusion that eclogite is thermodynamically stable under the p, l conditions existing in very large regions of normal continental crust. Conversely, gabbro and basalt are thermodynamically unstable under these conditions. This conclusion, if accepted, absolutely invalidates the hypothesis that the M-discontinuity in such regions is caused by a reversible phase change from gabbro to eclogite.

**Relationship between temperature at M-discontinuity and thickness of crust**

Numerous measurements of surface heat flux have disclosed that this quantity varies by a factor of two or more in stable continental regions (Lee and Uyeda, 1965). The geothermal models of Birch (1955), Clark (1961, 1962) and Clark and Ringwood (1964) have shown that these variations imply the existence of temperature differences of 200°C or more at a depth of 37 km. If the M-discontinuity is caused by a phase change, such temperature differences might be expected to result in large variations in crustal thickness. (Bullard and Griggs, 1961). Geophysical data on the Australian continent are particularly well suited for evaluation of this effect. There is a large systematic difference in the heat flux between the oldest areas of the west Australian Precambrian shield (mean value 1.0 μcal/cm²/sec) and the off-shield areas (mean value 2.0 μcal/cm²/sec). Geothermal calculations (Howard and Sass, 1964) imply that the minimum temperature difference at 37 km beneath the two regions is 200°C. Seismic measurements of crustal thickness have been made in both provinces, in regions adequately covered by heat-flow data. The latest results (Everingham, 1965) give a crustal thickness beneath the west Australian Shield of 42 km which is the same as the thickness of the
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crust in the Snowy Mountains of eastern Australia (Doyle et al., 1966). There is a substantial margin of error in these determinations and the close agreement is partly coincidental. Nevertheless the evidence for similarity of crustal structures in both regions is very strong. Most of the possible errors in these determinations are systematic and it is highly probable that the average crustal thicknesses within these areas are similar within 7 km (J.R. Cleary, H.A. Doyle and R. Underwood, personal communication, 1966). Accordingly if the M-discontinuity is caused by a phase change, the pressure at which this occurs must be relatively insensitive to temperature (dp/dt < 9 bar/degree).

In the diagram (Fig. 1) of the basalt—eclogite transformation constructed by Yoder and Tilley (1962) the gradient was placed at 7 bar/degree. If this value is correct, then observations on crustal thickness and surface heat flow would not be in conflict with the phase-change hypothesis. However, we have already pointed out that this diagram is almost certainly incorrect. In the previous section we have detailed the direct and indirect experimental evidence for the gradient of the transition and obtained a value of 21 bar/degree (also: section "Results"; Fig. 3 and 6). This value, even allowing for a generous uncertainty on the basis of possible experimental error, cannot be reconciled with the requirements of the phase-change hypothesis. It would result in large variations in crustal thickness with surface heat flow. For example the crustal thickness in eastern Australia would be at least 16 km greater than on the west Australian Shield.

Seismic velocity distribution in the crust

A critical requirement of the phase change hypothesis is its ability to explain the seismic velocity distribution in the crust. Determination of the velocity profile in the crust is a difficult and incompletely solved problem. Generalisations are dangerous owing to wide variations in crustal structure in different areas. Nevertheless, if we restrict our attention to stable continental regions, where indeed the M-discontinuity appears to be defined most clearly, some valid general statements which are highly relevant to the present investigation can be made.

It is widely agreed in such areas that seismic velocity increases significantly with depth. In some areas there may be a rapid increase in velocity around 20 km (Conrad discontinuity) caused by crustal layering, whereas in other areas this may be absent. The lower crust is commonly characterised by velocities between 6.5 and 7.0 km/sec (Tuve et al., 1954; Tatel and Tuve, 1955; Gutenberg, 1955, 1959; Steinhart et al., 1961). The nature of the transition from the lower crust to the mantle ($V_p \approx 8.2$ km/sec) is not well understood, and may well vary widely from place to place. In some regions there is evidence for reflections from the M-discontinuity (Dix, 1965). In such regions the transition would be sharp (< 0.25 km wide). There is still some doubt about the reality of these reflections (Steinhart et al., 1961). However, it is widely believed that a large part of the increase in velocity from about 7.0 km/sec to 8.2 km/sec occurs in a limited depth range which is probably smaller than 5 km thick (Tuve et al., 1954; Tatel and Tuve, 1955; Nakamura and Howell, 1964; Phinney, 1964). The former authors have published a range of permissible velocity distributions for the...
crust in Maryland (Fig. 7). It appears probable that similar limits would apply to crustal velocity profiles in many other stable continental areas.

Accordingly it is important to see whether the experimental observations on the transformation are consistent with the probable form of the crustal velocity profile. The experimental results at 1,100°C (Fig. 2) indicated that in most basaltic compositions the transformation between gabbro and eclogite proceeded via a transition zone of garnet granulite varying in width between 4 and 12 kbar. Furthermore it was shown (section "Changes in physical properties associated with the transformation") that the change in seismic velocity associated with the transformation was approximately linear across the entire width of the transition zone. The width of the transition zones would be smaller at lower temperatures. In the previous section it was suggested that the width might be approximately proportional to absolute temperature. To place the phase-change hypothesis in its most favourable light, we will ignore all of the experimental data relating to the gradient of the transition, and will assume that the M-discontinuity is in fact caused by the basalt-eclogite transformation, and that therefore the eclogite field is entered at a depth of approximately 37 km. This assumption is unrealistic; however, our principal aim at this point is to test the internal consistency of the phase-change hypothesis. We will assume that the temperature at the M-discontinuity is 550°C. This is a median value in relation to many geothermal calculations (Birch, 1955; Clark, 1961, 1962; Clark and Ringwood, 1964). The particular value is based upon a continental geothermal model of the latter authors corresponding to a surface heat flow of 1.2 μcal/cm²/sec. Substantial changes in the assumed temperature at the M-discontinuity would not alter the arguments which follow.

The combination of our experimental results at 1,100°C with the above assumptions suffice to define the stability fields of gabbro, garnet granulite and eclogite for each of the basalt compositions experimentally investigated (Fig. 8). We have constructed diagrams for four of the six basalts studied.
Fig. 8. Hypothetical eclogite, garnet granulite and pyroxene granulite–gabbro stability fields for several basalts based upon experimental observations at 1,100°C and upon the assumption that the continental Mohorovičić discontinuity is caused by a "phase change" and that eclogite is therefore stable below Moho. A typical temperature–depth distribution, corresponding to a surface heat flow of 1.2 μcal/cm²-sec, as given by Clark and Ringwood (1964) is also represented. The corresponding diagrams for quartz tholeiite and oxidised alkali-olivine basalt would closely resemble the diagram for quartz tholeiite (2).


The diagram for the alkali-poor quartz tholeiite would be almost identical to that of the normal quartz tholeiite, as would the oxidised alkali-olivine
basalt. (The garnet granulite field of the latter is slightly smaller, but the physical transition zone is effectively widened by the presence of abundant spinel, both on the high- and low-pressure sides of the garnet granulite field. This has the effect of "smearing" out the transformation.)

Turning to Fig. 8A which applies to the high-alumina olivine basalt, we see that the average geotherm lies in the eclogite field throughout the crust, except for a grazing entry into the garnet-granulite field around 5 kbar. Since the geotherm does not even enter the gabbro field, there is no possible way in which the rapid velocity increase around 37 km which is responsible for the M-discontinuity, can be caused along this geotherm. With the alkali-olivine basalt (Fig. 8B) the geotherm commences near the boundary of the gabbro-garnet granulite fields (V_p ~ 7.0 km/sec) and gradually penetrates deeper into the garnet granulite field with increasing depth, until the eclogite field is reached at the M-discontinuity. The velocity change is thus smeared out through the entire depth of the crust for rocks of this composition. The velocity distribution in the case of the quartz tholeiite is intermediate between those of the high-alumina basalt and alkali basalt (Fig. 8C).

Thus we see that for five out of the six rocks investigated, velocity distributions resembling those in Fig. 7 cannot be explained in terms of a gabbro-eclogite transformation. The difficulty is of a general nature, and is caused jointly by the occurrence of a substantial transition interval at constant temperature and by the fact that geotherms tend to cross the stability field boundaries at low angles, resulting in a great enlargement of the effective transition intervals.

The only basaltic composition which is not subject to the above objection is the alkali-poor olivine tholeiite (6). The transformation interval of this rock is small and the geotherm intersects it at a high angle, resulting in the velocity increase at the M-discontinuity being confined to an interval of 9 km. This is somewhat high, but perhaps not impossible.

Although an explanation of the M-discontinuity in terms of a phase change in this particular rock is not subject to the difficulties noted in this section for other basalts, it is even more open to other objections. The assumptions employed in the construction of Fig. 8D lead to a gradient for the transformation of 4.5 bar/°C. This cannot be reconciled with the experimental data quoted in the previous section. Of all the rocks which were investigated, the eclogitic assemblage of this rock is the most certain to be stable throughout the continental crust. Further difficulties in explaining the M-discontinuity in terms of the transformation of this particular rock will be discussed later in this section.

Effect of changes of chemical composition upon transition parameters

One of the principal objectives of the experimental investigations was to investigate the effect of changes in chemical composition upon the pressures and temperatures required for the basalt-eclogite transformation. The relevant information is given in Fig. 2. We see that the pressures required to stabilise eclogite vary by about 11 kbar at 1,100°C for the basaltic compositions studied. Although the corresponding pressure range at the average temperature at the M-discontinuity (550°C) might be somewhat smaller than this, a major reduction is not likely since the gradients of the transformations in individual basalts are probably rather similar.
If the lower crust and upper mantle is generally of basic composition, it is reasonable to expect that all of the common classes of basaltic compositions would be represented. The large effect on transition pressures caused by rather minor changes in chemical compositions would lead to wide fluctuations in depth to the M-discontinuity, or to further "smearing-out" of the velocity distribution in the transformation zone, depending upon the scale of occurrence of particular basaltic compositions. This would make it difficult to interpret the comparative uniformity of crustal thicknesses in stable continental regions and the nature of the seismic velocity distribution in the crust (Fig. 7).

Density of the upper mantle

Limitations on the density of the upper mantle arise from the interpretation of gravity observations and from the theory of isostasy. Most interpretations of gravity data are made on the assumption of a mantle density close to 3.3 g/cm³, although Talwani et al. (1959) found that a density of 3.4 g/cm³ yielded a satisfactory solution for the gravity profile over the Puerto Rico Trench. (However, their interpretation is not unique - Morgan, 1965). Worzel and Shurbet (1955) reviewed available data on continental and oceanic crustal structures and densities and concluded that isostatic balancing of standard oceanic and continental sections required a mantle density of 3.27 g/cm³ if the crustal density was 2.84 g/cm³. Actually, it is the density contrast between crust and mantle which is determined by gravity observations. Drake et al. (1959) concluded that the average density difference between crust and mantle was close to 0.43 g/cm³. Limitations on the density of the crust are obtained from direct observation of the occurrence and densities of crustal rocks combined with geologic inferences concerning their abundances. Another method of obtaining the near crustal density is from the seismic velocity distribution in the crust, combined with knowledge of the relationship between seismic velocity and density for common rock types (Birch, 1961). Arguments based upon the above methods have led to the widely accepted view that the mean density of the normal continental crust is between 2.8 and 2.9 g/cm³. From these values, together with the density contrast between crust and mantle as given by gravity data, we may conclude that the density of the upper mantle is usually between 3.3 and 3.4 g/cm³. This is further supported by an independent method of density determination based upon inversion of surface wave data. (Dorman and Ewing, 1962).

The densities of eclogites were reviewed in the section "Changes in physical properties associated with the transformation". They ranged between 3.42 and 3.66 g/cm³. The average density is about 3.5 g/cm³. Densities in the lower part of the range are usually caused by the presence of quartz in the eclogite. Eclogites which are believed on strong evidence to be derived from the mantle (e.g., inclusions in diamond pipes and peridotites) do not contain quartz, and their mean density is substantially higher than 3.5. Accordingly, if the upper mantle beneath the M-discontinuity is of eclogitic composition, it is unlikely that the density of this region would be smaller than 3.5 g/cm³. This is substantially higher than the probable density of the upper mantle which was concluded above to lie between 3.3 and 3.4 g/cm³. On these grounds the hypothesis of an eclogitic upper mantle
does not appear probable. Woollard (1962) has reached a similar conclusion on analogous grounds.

**Gravitational instability of an eclogitic upper mantle**

Most of those who have advocated the presence of an eclogitic layer beneath the crust have also maintained that this passed downwards into a zone of ultramafic or perioditic composition (Goldschmidt, 1922; Holmes, 1926a,b, 1927; Birch, 1952; Lovering, 1958; MacDonald, 1959; Wyllie, 1963; Stishov, 1963). Opinions regarding the thickness of the eclogite layer have varied widely, however, recent advocates, e.g. Wyllie (1963), have inclined to the view that the eclogite zone is only of the order of a few tens of kilometers thick. This seems required if the much greater abundance of peridotite inclusions compared to eclogite inclusions in diamond pipes is to be explained.

Thus, according to these authors, the upper mantle consists of a layer of eclogite, with a density of 3.5 g/cm³ or greater, overlying a zone of peridotite (mean density 3.32 g/cm³). The extreme gravitational instability of this model should be remarked. It appears highly improbable that such an unstable configuration could have been established and maintained in the earth's gravitational field for 4.5 billion years. We will return to this aspect in the section on possible tectonic consequences of the gabbro-eclogite transformation.

**Conclusion**

In this section we have discussed a number of objections to the hypothesis that the Mohorovičić discontinuity in normal continental regions is caused by an isochemical phase transformation from gabbro (or basalt) to eclogite. These were as follows:

1. Our experimental evidence strongly suggests that eclogite is thermodynamically stable under dry conditions throughout the normal continental crust and that basalt is thermodynamically unstable. The M-discontinuity cannot then be caused by an equilibrium basalt-eclogite transformation.

2. Experimental evidence on the effect of temperature on the pressure required for the gabbro-eclogite transformation cannot be reconciled with the rather small differences in crustal thickness in normal continental areas characterised by widely differing surface heat flows, and by inference, widely different temperatures at the base of the crust.

3. In most rocks of basaltic composition, the transformation from gabbro to eclogite occurs over a broad pressure interval, and the rate of change of seismic velocity is approximately uniform across this interval. Furthermore the effective breadth of the transformation in the earth would be greatly expanded owing to the tendency of geotherms to cross phase boundaries at low angles. The large effective width of the transformation in the earth makes it impossible to explain the M-discontinuity which requires a substantial velocity increase within a depth of approximately 5 km.

4. Small changes in basaltic chemical composition have a large effect upon the pressure required for a gabbro-eclogite transformation. On a small scale, this would cause further smearing of the transformation zone.
if the M-discontinuity was caused by a phase change. On a large scale it would lead to improbably large fluctuations in the thickness of the crust.

(5) The average density of eclogites is 3.5 g/cm$^3$, whereas the density of the upper mantle is generally believed to lie between 3.3 and 3.4 g/cm$^3$.

(6) Most current advocates of the phase change model argue that the eclogite layer (density 3.5 g/cm$^3$) immediately below the continental crust passes downwards into peridotite (density 3.3 g/cm$^3$). Such a configuration would possess a high degree of gravitational instability and is inherently improbable.

The above arguments, when considered together, can lead to only one conclusion: The Mohorovičić discontinuity beneath normal continental areas is not caused by an isochemical phase change between gabbro (basalt) and eclogite. Conversely, this implies that the only alternative explanation of the M-discontinuity, i.e., that it is caused by a change in chemical composition, must be accepted. The most probable explanation of the M-discontinuity is the widely accepted view that it is caused by a change from intermediate or basic rocks which characterise the lower crust, into ultrabasic peridotite, which is the predominant rock type of the upper mantle.

It is possible to postulate other types of chemical discontinuity. For example it might be suggested that the M-discontinuity is caused by a change from lower crustal rocks of intermediate composition into an upper mantle of eclogite. Such a model would forfeit most of the advantages which were previously believed to be inherent in the phase change hypothesis, e.g., changes in temperature at the M-discontinuity causing large vertical movement of the earth's crust. This model is also in conflict with points 5 and 6 above.

Finally, some comments on the nature of sub-oceanic Mohorovičić discontinuity may be appropriate. Because of the smaller temperature extrapolation and the knowledge that the basic chemical equilibria were identical, our experimental results are more applicable to a direct discussion of the nature of the sub-continental M-discontinuity than to its oceanic counterpart. Nevertheless, many of the arguments previously used are of a general nature and may be applied in the oceanic case.

Most advocates of the hypothesis that the M-discontinuity is caused by a gabbro-eclogite transformation have believed that this hypothesis is more applicable to the sub-continental than to the sub-oceanic M-discontinuity. When it was shown by Harris and Rowell (1960) and Bullard and Griggs (1961) that the M-discontinuity in both regions could not be caused by the same phase transformation, it was argued that the phase change hypothesis applied to the continental crust, whereas the sub-oceanic M-discontinuity was probably caused by a change in chemical composition (Yoder and Tilley, 1962; Wyllie, 1963; Stishov, 1963; Van Bemmelen, 1964). We have previously concluded that the continental M-discontinuity cannot be explained in terms of a phase change. If these arguments are accepted, the proposition that the oceanic discontinuity is nevertheless caused by a phase change does not appear enticing.

The specific objections to the phase-change hypothesis for the oceanic M-discontinuity are similar to those made in the sub-continental case. The problem of a transition interval is even more severe since the increase in seismic velocity from 6.7 to 8.2 km/sec must occur within about 2 km, equivalent to a pressure interval of 0.5 kbar. Although the width
of the transitional field between basalt and eclogite is probably much smaller at 150°C than at 550°C, it is almost certainly substantial. Because of the approximate parallelism of geotherms and mineral stability field boundaries, the effective width of the transition is greatly expanded, and thus it becomes extremely difficult to explain the observed seismic profile. There is also the fact that large variations of surface heat flow observed in oceanic regions (Von Herzen and Uyeda, 1963) imply the existence of temperature differences at the base of the oceanic crust of the order of 100°C. Such temperature differences, in conjunction with the experimentally inferred gradients for the gabbro-eclogite transformation, would lead to large variations in crustal thickness in oceanic regions, which should be closely correlated with heat flow. The uniform crustal thicknesses in deep oceanic basins are not consistent with these inferences. Finally there are the difficulties connected with the large density of eclogite, previously noted.

An alternative suggestion regarding the nature of the sub-oceanic upper mantle has recently been made by Kennedy (discussion by Engel et al., 1965). According to this suggestion, the oceanic M-discontinuity is caused by a non-equilibrium transition from an oceanic tholeiite crust into a low-grade, hydrous metamorphic equivalent in the glaucophane schist or greenschist facies. The suggestion possesses some merit, in that it emphasizes the probability that at the low temperatures occurring at the base of the oceanic crust, rocks of basaltic composition are likely to display hydrated mineral assemblages (see also, Ringwood, 1962b). This has always been an objection to proposals that anhydrous eclogite is the predominant rock type immediately beneath the oceanic M-discontinuity. However, it does not appear probable that the proposed low-grade metamorphic equivalents of basalt would possess the required seismic P-wave velocities of around 8.2 km/sec. The densities of rocks of basaltic composition in glaucophane schist and greenschist facies rarely if ever, exceed 3.3 g/cm³. According to Birch's (1961) velocity-density relationship, such rocks would possess seismic velocities in the vicinity of 7.8 km/sec, which are substantially smaller than the observed mantle velocities. The densest low-grade metamorphic rock of basaltic composition known to the authors is an epidote amphibolite (Christensen, 1965). This has a density of 3.26 g/cm³ and a seismic P-velocity (corrected for initial porosity) of 7.45 km/sec. It is just possible that rocks of basaltic composition consisting dominantly of minerals such as lawsonite, jadeite, epidote and amphibole may have higher velocities and densities than the above rock. Further data on low grade metamorphic rocks are clearly required. In the light of present evidence, Kennedy's suggestion does not appear promising.

COMPOSITION OF THE CONTINENTAL CRUST.

Seismic velocity distributions in stable continental crusts vary substantially from place to place. Nevertheless some generalizations can be made. Strong evidence exists that seismic velocity shows a net increase with depth. Velocities in the upper crust are commonly in the range 6.0–6.3 km/sec whilst in the deeper crust, velocities between 6.6 and 7.0 km/sec are often inferred. The smaller velocities correspond to those of acidic igneous and metamorphic rocks and suggest that the upper crust is dominantly of "granitic"
composition. The interpretation is reinforced by direct geological observation upon exposed basement complexes. The seismic velocities of the lower crust are similar to those of basalts, dolerites, diabases and gabbros (Birch, 1961) and accordingly it has become widely accepted among geophysicists that the lower crust is composed of these rocks (e.g., Birch, 1958; Gutenberg, 1955, 1959). Thus there has arisen the concept of a two-layer crust, the upper layer being granitic, and the lower layer of gabbroic composition. The transition between these layers may be gradual or relatively sharp. In the latter case, a seismic discontinuity, the Conrad, may result.

Sufficient information now exists to show that this model is seriously wrong. In the section on stability of eclogite within the crust, strong evidence was presented that gabbro was not thermodynamically stable under P, T conditions existing in the normal continental crust. It is also most improbable that gabbro could be present as a metastable assemblage in the lower crust. Temperatures of 400-600°C are probably characteristic of this region and with long periods of time available, thermodynamic equilibrium would almost certainly be reached. Under dry conditions, as was shown in the section above, basic rocks in the crust would then probably occur in the form of eclogite. Taking the most conservative possible view, and making the maximum allowance for possible experimental errors, it might be concluded that some basaltic rocks would occur in the higher pressure grades of the garnet granulite mineral assemblage rather than in the eclogite assemblage.

If the lower crust is composed of dry basic rocks occurring as eclogites or high-grade garnet granulites, the density of this region would lie between 3.3 and 3.6 g/cm$^3$ and it would possess a seismic P velocity of between 7.5 and 8.5 km/sec. These physical properties cannot be reconciled with the observed and inferred properties of the lower crust in most regions and accordingly we must reject the crustal model. This appears to leave two alternatives:

(a) The lower crust is composed of rocks of intermediate chemical composition occurring in the eclogite facies. Such rocks would contain quartz and alkali felspars together with garnet and jadeitic pyroxene and would yield seismic velocities and densities which are acceptable for the lower crust (Green and Lambert, 1965).

(b) The lower crust cannot be considered dry and a substantial water vapour pressure exists. Under such conditions neither eclogite nor gabbro would be stable. Rocks of basaltic composition might then crystallise dominantly as amphibolites which might possess acceptable seismic velocities and densities (Christensen, 1965).

In our opinion, alternative (a) is much more probable as a general explanation than (b) although the latter may be applicable under certain restrictive conditions. A lower crust of amphibolite might be formed where vast thicknesses of basaltic lavas had accumulated upon an oceanic crust during the early stages of subsidence of a geosyncline. In a water-rich environment of this nature, if the basalts were sufficiently permeable, they would probably be converted to hydrated mineral assemblages (zeolite, glaucohane schist and greenschist facies). As temperatures at the base of the geosyncline rose to about 400°C, reconstitution to amphibolites would occur.

The response of amphibolites (once formed) to further metamorphism
depends upon the particular combination of pressure, temperature and water vapour pressure to which they are subjected. Field observations in metamorphic terrains provide direct evidence upon this point. With increasing grade, amphibolites are observed to be transformed into pyroxene granulites. It appears that this transformation may occur at temperatures between 500°C and 700°C and at rather moderate pressures. An excellent example of the gradual transformation of amphibolite into pyroxene granulite is described by Engel and Engel (1962). They estimate that the temperature required for this transformation was about 625°C and the depth was of 10 km or greater.

In most regions in the stable continental crust, the temperatures now existing at the M-discontinuity may be in the vicinity of 450-650°C, as previously discussed. Under these conditions, basic rocks in the amphibolite facies at the base of the crust may be marginally stable. However, we must consider the earlier history of the normal continental crust. In most regions, at shallow depth crystalline basement rocks are found. Formation of the assemblage of granitic and metamorphic rocks referred to as "basement" implies that at an earlier stage of crustal evolution, the temperatures within the present upper 15 km of the crust were much higher than normal, perhaps 400-500°C, and locally even higher. At the time when these temperatures were generated, the temperatures in the lower crust must have been much higher, probably in the vicinity of 600-1,000°C. Under such conditions, amphibolites would have been converted into granulites and it is probable that the lower crust would have become rather thoroughly dehydrated. Subsequently, after its period of active evolution had proceeded to completion (next section) the crust slowly cooled to its present state. However, amphibolites have not been reformed in the lower crust simply because of lack of water. The possibility that large volumes of the lower crust consisting of impermeable granulites may become rehydrated on cooling by downward access of water from the upper crust appears remote, although it may occur on a local and restricted scale. Accordingly, we conclude that the lower regions of the normal continental crust are probably essentially "dry". Similar views have been expressed by Heier and Adams (1965) on geochemical grounds and by Den Tex (1965) on petrological grounds.

If this conclusion is accepted then, for reasons previously given, the dominant rock type cannot be of overall basic composition. It is more likely that the lower crust consists of rocks of intermediate composition occurring in the eclogite facies. The stable mineral assemblage would be quartz, K-Na felspar(s), garnet and clinopyroxene. Kozlowski (1958) has described natural examples of such rocks, whilst Green and Lambert (1965) have experimentally demonstrated the stability of a similar mineral assemblage in a more acidic composition. A stimulating discussion of the petrology of the lower crust has been provided by Den Tex (1965), who reaches a conclusion parallel to that expressed above. He regards the lower crust as consisting of a heterogeneous mixture of anhydrous acid granulites, charnockites and eclogites, with a mean composition approaching that of intermediate rocks.

POSSIBLE TECTONIC CONSEQUENCES OF THE GABBRO-ECLOGITE TRANSFORMATION

Our previous discussion of the nature of the Mohorovičić discontinuity has
been restricted to regions where the latter is well-defined, for example in stable continental regions and in deep oceanic basins. There are, however, many regions on the earth where the M-discontinuity is poorly defined, and where the crust is separated from the "mantle" by layers of rock possessing P-wave velocities between 7 and 8 km/sec. Whether these intermediate velocity layers are to be regarded as crust or mantle is to some extent subjective. In fact, the very existence of an M-discontinuity in such regions is in doubt. Frequently, the seismic data are consistent with a continuous transition of velocities between crust and mantle with no evidence of a discontinuity. The existence and position of the latter is often inferred from gravity data which do not permit unique solutions.

Regions characterised by intermediate crust-mantle seismic velocities or by abnormally low upper-mantle velocities are of great tectonic importance. They include mid-oceanic ridges, some oceanic rises, island arc regions, some continental margins, continental rifts and continental regions which have undergone comparatively recent mountain building. A review of these regions is given by Cook (1962). Several explanations of the nature of the intermediate-velocity material have been proposed. Cook (1962) suggests that it is a physical mixture of mantle and crustal material. Ringwood (1962a, b) and Thompson and Tagawa (1964a, b) suggest that it is undifferentiated ultramafic mantle material consisting of the mineral assemblage olivine, pyroxene and plagioclase (plagioclase pyrolite) whilst R.P. von Herzen (personal communication, 1962) attributes the lower velocities to abnormally high mantle temperatures as are indicated by the high heat flows often observed over mid-oceanic ridges. Finally Pakiser (1965) suggests that the intermediate velocity regions are caused by the gabbro-eclogite transformation.

On critical examination, none of the above hypotheses appears capable of supplying the sole explanation of the nature of the intermediate velocity material in tectonically active regions. Rather, it appears that all of the explanations may be applicable to different regions to different extents. In this section, we will discuss the possible role of the gabbro-eclogite transformation in such regions.

Previously, we have argued that the gabbro-eclogite transformation is not responsible for the M-discontinuity in stable continental regions or in deep oceanic basins. However, most of these arguments are not directly applicable in the cases of many tectonically active regions possessing intermediate crust-mantle velocities. Since these are often characterised by high heat flows and consequent high sub-surface temperatures, it is possible for gabbroic and garnet granulite assemblages to be stable in the crust, and to transform downwards to eclogite. This transformation would give rise to a wide zone of intermediate seismic velocities (section "Nature of the Mohorovičić discontinuity"). Furthermore, as we shall see, the high density of eclogite may not be an objection to its presence in active orogenic zones, as is the case in stable continental regions.

In the following discussion, we will adopt the hypothesis (Ringwood 1962a, b; 1966a, b) that the primitive composition of the upper mantle lies between basalt and peridotite, and closer to peridotite. This hypothetical parental upper-mantle rock has been called pyrolite. Fractional melting of pyrolite yields basalt magma and leaves behind a refractory residue of dunite or peridotite. There are strong reasons for believing that
the continental crust has evolved by fractional melting and differentiation processes from the upper mantle over geologic time (Rubey, 1951, 1955; Bullard, 1952; Wilson, 1954; Engel, 1963). This implies that the mantle immediately beneath continents is depleted in low-melting components and easily fractionated elements, and is probably similar in composition to dunites and Alpine peridotites. Beneath oceanic areas it appears that the upper mantle has not been subjected to substantial fractionation, and accordingly the more primitive pyrolite may extend upwards to the M-discontinuity.

The mean density of the upper mantle according to the pyrolite model is 3.30 g/cm$^3$ (Clark and Ringwood, 1964). According to this model, the low-melting point fraction is basalt. Accordingly, in regions undergoing differentiation, large volumes of basaltic magma may be extruded at the surface of the solid earth. On cooling, this magma will crystallise initially as plagioclase and pyroxene, with a mean density of 3.0 g/cm$^3$. However, we have seen that in normal continental regions, the thermodynamically stable assemblage is eclogite, not gabbro. Accordingly, on further cooling under dry conditions, piles of basalt extruded at the earth's surface would pass through the garnet granulite field into the eclogite stability field. If the kinetic conditions should be favourable to transformation, basalt will be converted to eclogite with a mean density of 3.5 g/cm$^3$. If this should occur throughout a large volume (i.e., of the order of tens of km$^3$) of basalt resting on the earth's surface, an acute gravitational instability would be caused, and it is improbable that the crust would be able to withstand the accompanying stresses indefinitely. The block of eclogite would eventually sink diapirically through the crust into the mantle. Since its density is greater than that of the mantle, it would continue to sink until it reached a zone of similar density. This may well be very deep in the mantle.

The sinking of a large block of eclogite in such a manner would cause severe crustal deformation (Ramberg, 1963; Morgan, 1965). Initially the crust might be dragged down into a deep depression (trench or geosyncline) and finally, when the block became detached and sank into the mantle, the crust would be dragged together in compression (folding). Furthermore, depending upon the $p$, $t$ conditions in the mantle, and the rate of sinking, the eclogite might suffer partial fusion on its downward journey. Magmas thus formed (andesites, granodiorites) would rise and penetrate the deformed crust.

According to the above speculations, the basalt–eclogite transformation may generate the driving force for a tectonic engine, which might in turn be responsible for the major crustal orogenic cycle. The conditions under which this engine might operate are varied and flexible. There are, however, certain essential prerequisites. Two of the most fundamental of these are: (1) that eclogite is thermodynamically stable relative to basalt in the normal geothermal gradient in the crust; (2) that kinetic factors will permit the transformation of large volumes of basalt into eclogite within the crust.

The validity of (1) has been extensively discussed in the section on stability of eclogite within the crust. It was concluded that this prerequisite was highly probable. The second is more doubtful since the direct evidence bearing upon the subject is limited. However, there is strong geological observational evidence that under appropriate conditions, basalt may become converted to eclogite (section above; Green and Ringwood, 1966).
ditions required are apparently (a) temperatures of 300°C and greater, (b) low, but not zero, partial pressure of water, (c) sufficient time, (d) (perhaps) shear stress. The only condition which appears somewhat difficult to fulfil is (b). However, it might be realized in basaltic lavas which were extruded rapidly on the sea floor, forming a thick, impermeable pile. Ramberg (1963) has shown by a series of model experiments that the structural conditions which result in the extrusion of basic lavas are likely to be accompanied by the intrusion of much greater total volumes as sills and dykes within the crust. Large volumes of intruded basaltic magma are likely to crystallise to dense impermeable gabbros and dolerites which would be particularly resistant to hydration, and if subjected to the correct time-temperature conditions, susceptible to transformation to eclogite.

We will not argue this question of transformation kinetics any further. Clearly it needs detailed consideration and intensive studies of cases where eclogites are believed by geologists to have formed in situ by transformation of basalt. In the subsequent discussion we will assume that the transformation is possible under appropriate conditions, and use this assumption as the keystone of an hypothesis of orogenesis.

Proposed model of an orogenic cycle

The following speculative and simplified model (Fig.9) illustrates the development of a geosyncline near a continental margin, in the absence of an offshore island arc. A possible example is the eugeosyncline now believed to be forming off the east coast of the U.S.A. (Drake et al., 1959). This model is chosen to demonstrate the possibilities of the basalt-eclogite transformation engine. It is not unique, and numerous variants could be devised. With some relatively minor changes the model could be applied to the evolution of island arcs and trenches.

Stage 1 (Fig.9A)

Hypothetical initial state with normal continental section directly adjacent to deep oceanic section. The temperature distribution beneath deep oceanic basins probably results in a decrease of density with depth in the first 100 km (Clark and Ringwood, 1964). The oceanic upper mantle is therefore potentially gravitationally unstable. For the instability to become manifest, a triggering effect is necessary, e.g., a horizontal temperature gradient, such as is found near the continental-oceanic borders. The combination of these effects may localise orogenic activity near some continental margins (Ringwood, 1962a; MacDonald, 1963).

Stage 2 (Fig.9B)

Erosion on the continent with consequent deposition of sediments on the neighbouring oceanic crust (assumed to be of basaltic composition) leads to the accumulation of a thick wedge of sediments. Gravitational instability in the sub-oceanic mantle leads to the upward rise of masses of primary mantle material (pyrolite) from the low velocity-low density zone. (This process is better termed advection - Elsasser, 1963 - rather than convection.) Rising masses of pyrolite undergo fractional melting, yielding basaltic
magma. Magma becomes separated from residual dunite-peridotite and rises into crust, becoming interlayered with sediments. A much larger volume of basaltic magma does not reach the surface, and intrudes the oceanic crust (Ramberg, 1963) causing a large thickening of the crust. The generation of crustal thickening by magmatic activity was discussed in some detail by Drake et al. (1959) in connection with the geosyncline off the east coast of the U.S.A. In this example, there was little evidence for the present existence of volcanic activity. However, the occurrence of earlier activity was inferred from the presence of seamounts and from the pattern of magnetic anomalies. The lack of obvious volcanism near continental margins cannot be used to infer the absence of deep-seated magmatic activity. Because of high density, basaltic magmas may not readily penetrate a thick

Fig. 9A–D (Legend see p. 419).

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Fig. 9. Model for an orogenic cycle near a continental margin (e.g., east coast of U.S.A., Drake et al., 1959) in the absence of an off-shore island arc, based upon the gabbro–eclogite transformation as a tectonic engine.

A. Hypothetical initial state. B. Mantle advection and crustal thickening.
C. Transformation of thick basaltic crust to eclogite. D. Gradual sinking of eclogite lower crust leading to formation of geosyncline or trench.
E. Catastrophic sinking of eclogite into mantle, folding of geosyncline, intrusion of Alpine ultramafics into folded geosyncline.
F. Fractional melting of sinking eclogite to yield intermediate-acid magmas which rise and intrude geosyncline.
G. Isostatic rise of folded geosyncline to form Alpine mountain chain, widespread regional metamorphism.
H. Erosion of mountains, major diapirc differentiation under gravity leading to re-establishment of M-discontinuity, further cooling at depth resulting finally in a stable shield. (Not to scale.)

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wedge of unconsolidated sediments. Such magmas would be more likely to spread out and accumulate at the base of the sediments (Ramberg, 1963).

Stage 3 (Fig. 9C)

Intruded and extruded basalts cool to the temperature of their surroundings. They are subjected to increased load pressure from the sediments which overlie them. Basaltic rocks are accordingly in the eclogite stability field. Under suitable kinetic conditions, transformation of basalt to eclogite occurs throughout much of the thickened basaltic crust.

Stage 4 (Fig. 9D)

The wedge of dense eclogite begins to drag the crust downwards forming a downbuckle. Vast thicknesses of sediments may accumulate in this downbuckle forming a geosyncline. If access of sediments is prevented by other geologic factors an oceanic trench may form instead. Morgan (1965) and Elsasser (1966) have also developed the concept of oceanic trenches being caused by the falling of a dense sinker in the mantle and have shown that this model leads to a satisfactory solution of gravity and seismic data. Slumping of sediments within the geosyncline occurs as it deepens. The weight of the sediment causes increased pressure, thus pushing basaltic rocks further into the eclogite field. During geosynclinal sedimentation the temperatures throughout the crust are abnormally low. There is a long time lag before thermal blanketing by sediments causes temperatures in the crust to rise beyond the normal geothermal distribution.

Stage 5 (Fig. 9E)

Downward sinking of the eclogitic lower crust becomes catastrophic. Large blocks of eclogite become detached and sink deep into the mantle. Downward sinking of eclogite causes major crustal deformation dragging the crust into compression (Morgan, 1965) and folding the sediments in the geosyncline. The folding is accompanied by net crustal shortening and thickening in the deformed zone. Foundering of lower crust causes a major disturbance in the underlying mantle, which leads to large scale intrusion of Alpine peridotites into the folded geosyncline.

Stage 6 (Fig. 9F)

Eclogite bodies sink into the low-velocity zone of the mantle and undergo partial fusion. Andesitic and dacitic magmas are generated, and rise upwards, intruding the folded geosyncline as bodies of quartz diorites and granodiorite, and causing extensive andesitic and dacitic volcanic activity. (The generation of the calc-alkaline suite of igneous rocks by partial fusion of basaltic material under eclogitic conditions is at present being studied experimentally by Mr. Trevor Green and one of the authors - A.E. Ringwood. Preliminary results indicate that this mechanism is extremely promising).

Stage 7 (Fig. 9G)

Crustal compression relaxes as eclogitic bodies sink through low-velocity
zone. The folded geosynclinal wedge rises isostatically to form an Alpine mountain chain. Temperatures in the thick crust become abnormally high due to the combined effects of radioactive heat generation in situ and conduction from large intrusions of primary calc-alkaline magmas from the mantle as discussed in stage 6. This leads to regional metamorphism in the base of the fold-mountain belt and generation of secondary granitic magmas by partial fusion of crustal rocks. The lower crust at this stage, is a heterogeneous mixture of metamorphic rocks, andesitic and dacitic material, primary unFractionated plagioclase pyrolite from the upper mantle, residual Alpine peridotites and dunites from the mantle, and rocks of basaltic composition. However, because of the abnormally high crustal temperatures, basaltic rocks would now occur in the stability fields of pyroxene granulite and garnet granulite rather than eclogite. The physical heterogeneity of the rocks of the lower crust and upper mantle cause the seismic velocity distribution between crust and mantle to be approximately continuous. The Mohorovičić discontinuity cannot be recognized at this stage.

Stage 8 (Fig.9H)

During this, the final and longest stage of crustal evolution, the mountains gradually become eroded, and the crust develops a relatively stable gravitational and rheological configuration. Large bodies of ultramafic rocks previously intruded into the crust, sink diapirically back into the mantle and large volumes of lighter acidic rocks in the mantle rise diapirically into the crust. The result of this separation of large volumes of rocks in the gravitational field according to their densities, is the re-establishment of a distinct and recognizable boundary between generally intermediate but heterogeneous lower crustal rocks in the granulite and eclogite facies and the ultramafic rocks of the upper mantle. Thus, the Mohorovičić discontinuity which was present beneath the oceanic crust at the beginning of the cycle, but which was obliterated during the active phase of orogenesis, becomes re-established in the stable continental crust.

The major cycle lead ultimately to strong upward concentration of radioactive elements in the upper part of the crust. Further erosion of the upper crust causes the heat producing elements to be dispersed into new geosynclines which are being formed at the continental margins. The strong upward concentration of radioactivity, combined with its net depletion by erosion in highly evolved continental crusts, ultimately results in lower subcrustal temperatures. These cause the crust and mantle beneath it to assume the state of relative gravitational stability and tectonic rigidity which is characteristic of Precambrian shields (Ringwood, 1962a,b; Clark and Ringwood, 1964). Thus the major geologic cycle completes its course.

Further applications of model

The model proposed in the previous paragraph is an illustration of the manner in which the basalt-eclogite transformation might provide an engine for driving the orogenic cycle. Numerous variations of the model are conceivable. For example the hypothesis of ocean floor renewal proposed by Hess (1962) can be restated using the basalt-eclogite transformation as the
principal driving force, as in Fig. 10. According to this model, gravitational instability develops in the mantle beneath mid-oceanic ridges. Primary mantle material (pyrolite) from the low-velocity zone advects inwards towards the ridge and then upwards. Fractional melting of pyrolite occurs during upward motion leading to generation of basaltic magma, together with residual unmelted peridotite. The axes of the ridges are characterised by high heat flow and the sub-surface temperatures are high enough to maintain stability of the basaltic mineral assemblage. The mid-oceanic ridges thus develop as tensional features composed of heterogeneous mixtures of gabbro, peridotite and pyrolite. The oceanic crust moves outwards from these axial structures as in the Hess model. Conversion of basalt to eclogite occurs near continental margins and/or island arcs, as discussed in the previous model, providing a major source of gravitational instability. It is not necessary that the eclogite should sink vertically. The paths of sinking blocks of eclogite will be determined partly by the "viscosity" distribution within the surrounding mantle, which in turn is determined by the temperature distribution. If the active orogenic belts near continental margins are characterised by abnormally high sub-crustal temperatures, it is possible that the sinking blocks of eclogite might move downwards and inwards towards the continent, thus providing an explanation for the occurrence of deep-focus earthquakes. The overall flow patterns in the upper mantle shown in Fig. 10 are not to be compared with the regular cells contemplated in most of the conventional theories of convection. They are probably highly complex, as in the "advection" configurations of Elsasser (1963). Furthermore they are irreversible since they involve chemical differentiation. In

Fig. 10. Modification of ocean-floor spreading hypothesis (Hess, 1962) using basalt–eclogite transformation as tectonic engine. (Not to scale.)

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In this sense they have affinities with the "mass—circuits" advocated by Van Bemmelen (1964).

Finally, we should consider the possible future of present geologic structures which are characterised by great thicknesses of basaltic lavas resting upon the crust, e.g., Hawaii, Iceland and mid-oceanic ridges, rises and seamounts in general. These vast structures will be stable as long as their internal temperature distributions are high enough to maintain them in the gabbro stability field or in the medium grades of the garnet granulite stability field. In fact, these structures are all young, and characterised by high heat flows. We can look forward to the time when volcanic activity subsides, and the mantle is no longer a source of advective heat. When this stage is reached, there will be a general cooling of the entire structures, and transformation into eclogite will probably occur in the deeper levels. The islands and ridges will then subside into the mantle, causing complex crustal deformation. Since the minimum melting point of common basalts in the eclogite facies is much smaller than the minimum melting point of pyrolite (unpublished data) the subsiding eclogites may undergo fractional melting during sinking, resulting in production of large volumes of intermediate and acidic magmas. The magmas will rise to the surface and it is possible that they may form the nucleus of new continental blocks. In such a manner a continental nucleus could be formed directly in the midst of an ocean, without requiring a supply of sedimentary material from a nearby continent. This process may indeed be presently operating in some island arc areas far removed from continents, e.g., the Aleutian Islands. It is interesting to speculate that "continental" islands such as Fiji and New Zealand may have originated from basalt piles.

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Experimental Crystallization of Anhydrous Granite at High Pressures and Temperatures

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Abstract. Pressures up to 40 kb at temperatures of 950°C and 1100°C have been applied to a glass of granitic composition (adamellite). The experiments at 950°C demonstrate that the adamellite crystallizes to quartz + plagioclase + alkali feldspar + orthopyroxene ± clinopyroxene at pressures less than 13% kb, but at higher pressures garnet and clinopyroxene form at the expense of orthopyroxene and plagioclase. However, even at pressures sufficiently high (above 20 kb at 950°C) to eliminate plagioclase and produce an eclogite mineralogy in basaltic rocks, the adamellite contains plagioclase as a major phase. At higher pressures a quartz + sanidine + jadeite + garnet assemblage is formed. The incoming of garnet at moderate pressures could cause increasing seismic velocity with depth in the continental crust. The data indicate the probable mineralogy of acid gneisses or granulites under conditions of eclogite facies metamorphism.

INTRODUCTION

Experimental studies of simple compositions and deductions from observations of natural rocks have provided some knowledge of the behavior of acid rocks under conditions of high pressure, such as exist in the deep crust and upper mantle. The present investigation is aimed, in particular, at establishing the mineral assemblages present in granitic rocks under anhydrous conditions where eclogite is stable in basaltic rocks [Yoder and Tilley, 1962; Ringwood and Green, 1964]. Ramberg [1952] suggested that 'a rock consisting of potash feldspar, acidic plagioclase and quartz (and some biotite) is, in all likelihood, a stable one under the physical conditions of the eclogite facies' (p. 166). He also suggested (p. 168) that the quartz-feldspathic gneiss, commonly of amphibolite facies mineralogy, enclosing the eclogite lenses of western Norway [Eskola, 1921] could originally have crystallized in the same metamorphic assemblage, enclosing the eclogite lenses of western Norway [Eskola, 1921] could originally have crystallized in the same metamorphic facies as the eclogites but later recrystallized much more readily than the partly amphibolitized eclogites.

Fyfe et al. [1958, p. 236] also noted that the only mineral assemblages definitely assignable to the eclogite facies occur in rocks of basaltic composition. They suggested that rocks of other chemistry may be represented by mineral assemblages identical with those in other metamorphic facies, e.g. granulites. Another possibility is that eclogite facies conditions may only be reached at a crust or mantle level where basic rocks are developed to the exclusion of other material. A third possibility [Ramberg, 1952, p. 164; Fyfe et al., 1958, p. 155] is that granitic rocks might invariably begin to melt under conditions allowing metamorphism of basic rocks to eclogites.

EXPERIMENTAL METHOD

The granitic composition selected for experimental study is that of the average adamellite of Nockolds [1954]. This composition was prepared from analytical reagent chemicals which were ground together, fused and quenched to a glass, and reground. Control of total Fe content and oxidation state of the mixture is difficult because of entry of Fe into the platinum tube during fusion. The glass was thus analyzed for FeO and total Fe as Fe₂O₃ by A. J. Easton. The final mixture (Table 1) is slightly richer in Fe₂O₃ and poorer in FeO than Nockold's average adamellite. In the norm calculation and in our experiments this results in low orthopyroxene content.

Fyfe et al. [1958, p. 236] also noted that the only mineral assemblages definitely assignable to the eclogite facies occur in rocks of basaltic composition. They suggested that rocks of other chemistry may be represented by mineral assemblages identical with those in other metamorphic facies, e.g. granulites. Another possibility is that eclogite facies conditions may only be reached at a crust or mantle level where basic rocks are developed to the exclusion of other material. A third possibility [Ramberg, 1952, p. 164; Fyfe et al., 1958, p. 155] is that granitic rocks might invariably begin to melt under conditions allowing metamorphism of basic rocks to eclogites.
TABLE 1. Chemical Composition and Norms of Nockold's Average Adamellite and of the Adamellite Used in This Experimental Study

<table>
<thead>
<tr>
<th>Composition, wt. %</th>
<th>Nockold's Average</th>
<th>Adamellite</th>
<th>CIPW Norms</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(anhydrous)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>69.50</td>
<td>69.56</td>
<td>Quartz</td>
<td>24.9</td>
<td>25.7</td>
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<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.56</td>
<td>0.56</td>
<td>Corundum</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>14.72</td>
<td>14.72</td>
<td>Orthoclase</td>
<td>27.2</td>
<td>27.2</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.23</td>
<td>1.73</td>
<td>Albite</td>
<td>28.6</td>
<td>28.5</td>
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<td>FeO</td>
<td>2.28</td>
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<td>Anorthite</td>
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<tr>
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<td>Diopside</td>
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<td>3.4</td>
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<tr>
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<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>4.61</td>
<td>Apatite</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

(Plagioclase Ab<sub>72</sub>An<sub>28</sub>)

Table 1 ably accurate to ±10°C (there may be a small, unknown pressure effect on the emf of the Pt/ Pt-10Rh thermocouple).

The powdered adamellite glass was dried at 110°C and loaded into a Pt capsule with welded base. The open end was crimped but not sealed by welding. The furnace assembly used is essentially the same as that described by Boyd and England [1963], and all furnace parts except the outer talc cylinder were dried in an argon atmosphere at 1100°C for 1 hour and stored in a desiccator until use. The methods were adequate to ensure that no detectable hydrous phases formed in our experimental runs and that significant partial melting due to random access of water did not occur, except possibly in the 2½ kb, 950°C run. In one run at 35 kb, 950°C, in which a simple talc furnace with no inner boron nitride sleeve was used, a mica (?) was found in the mineral assemblage.

Our experimental conditions thus resemble those conditions presumed to operate during high-grade regional metamorphism when rocks lacking hydrous phases are produced or during crystallization of anhydrous acid magmas such as give rise to intrusive charnockites [Turner and Verhoogen, 1960, pp. 346–348].

One series of 4-hour runs at 950°C in the pressure range 2½ to 35 kb yielded well-crystallized charges having grains from 1 to 10 μ in size. A second series of runs at 1100°C for 1 hour gave well-crystallized, slightly coarser-grained charges. Several runs were done in duplicate. One 12-hour run was done at 950°C, 27½ kb to investigate the possible operation of Ostwald's step rule. The charges were examined optically and by X-ray techniques (powder photographs and diffractometer charts).

**EXPERIMENTAL RESULTS**

*Runs at 950°C (Table 2).* At 12½ kb, quartz, alkali feldspar, and plagioclase are present as major phases as shown by X-ray diffraction data. Pyroxene and rutile could be identified optically. The pyroxene crystals are lath-shaped, with very low birefringence and straight extinction; they are considered to be dominantly or entirely orthopyroxene. The alkali feldspar is a member of the high sanidine–high albite solid solution series with composition determined as 1. The lime content of the plagioclase could not be determined [cf. Smith, 1956].

The amount of pyroxene in the lower pressure runs is insufficient for determination by X rays. Orthopyroxene was identified optically in the 1½- and 15-kb runs but could not be identified in the 17½-kb run. Clinopyroxene (moderate birefringence, oblique extinction) is present in the 15-kb run and particularly in the 17½-kb run. At 22½ and 25 kb the clinopyroxene con-

1 Alkali feldspar compositions are given in weight per cent [Tuttle and Bowen, 1958]. The anorthite content of the alkali feldspar solid solution could not be determined. This may affect the estimated albite and sanidine proportions.
TABLE 2. Results of Experimental Runs at High Pressures at 950°C for Four Hours

<table>
<thead>
<tr>
<th>Pressure, kb</th>
<th>Phases Present*</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2½</td>
<td>Pl Alk Qz Px (?) Liq</td>
<td>Common glass.</td>
</tr>
<tr>
<td>12½</td>
<td>Pl Alk Qz Px</td>
<td>Alk = San₄Ab₂; garnet rare.</td>
</tr>
<tr>
<td>13½</td>
<td>Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; garnet rare.</td>
</tr>
<tr>
<td>15</td>
<td>Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; garnet increasing.</td>
</tr>
<tr>
<td>17½</td>
<td>Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; garnet increasing.</td>
</tr>
<tr>
<td>20</td>
<td>Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; Px distinctly increasing and jadeite-rich.</td>
</tr>
<tr>
<td>22½</td>
<td>Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; Px (jadeite-rich) increasing.</td>
</tr>
<tr>
<td>25</td>
<td>Pl (?) Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; Px absent.</td>
</tr>
<tr>
<td>25 (12 hr)</td>
<td>Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; Pl (?) uncertain and very minor; Px (jadeite) a major phase.</td>
</tr>
<tr>
<td>27½</td>
<td>(?) Pl Alk Qz Px Garnet</td>
<td>Alk = San₄Ab₂; Pl absent; jadeite a major phase.</td>
</tr>
<tr>
<td>30</td>
<td>Alk Qz Px Garnet</td>
<td>Alk &gt; San₄; minor coesite; minor mica (?) phase—access of water to charge.</td>
</tr>
<tr>
<td>35</td>
<td>Alk, Qz + Coes., Px Garnet</td>
<td></td>
</tr>
</tbody>
</table>

* Minor rutile present in all runs.

Abbreviations:
Pl, plagioclase; Alk, alkali feldspar of high albite-sanidine series; Qz, quartz; Px, pyroxene; Coes, coesite; San, sanidine; Ab, albite; Liq, liquid.

The composition of the alkali feldspar remains approximately constant in the range San₄₄Ab₂₀ up to 25 kb. It is also to be noted that the compositions of the alkali feldspar in both the 4- and 12-hour runs at 25 kb are identical within the accuracy of the method (Table 4). Between 25 and 27½ kb and between 27½ and 30 kb, there are marked decreases in the albite content. However, even at 30 kb, where plagioclase is absent as a separate phase, there is some albite solid solution in the alkali feldspar (San₄₄Ab₂₀).

Rare crystals of garnet, distinguished optically by its very high refractive index (> 1.7), equant form, and isotropic character, are present in the 13½- and 15-kb runs. Garnet is more abundant in the 17½-kb run but is still barely detectable by X rays. Garnet continues to increase in the 20- and 22½-kb runs but remains fairly constant in the amount present in higher-pressure runs.

In the run at 35 kb, the presence of minor coesite with a greater amount of quartz implies metastability in the observed mineral assemblage.

Runs at 1100°C (Table 3). These runs show an important difference from those at 950°C in that only one feldspar phase, a member of the sanidine-high albite solid solution series, is identifiable. No reflections unambiguously attributable to plagioclase were observed. Some feldspar reflections observed in several runs at 950 and 1100°C are compared in Table 5. In the 950°C runs the small but distinct peak at 2θ = 21.85° is considered to be due to plagioclase and the neighboring peak at 2θ = 21.45° to be due to the alkali feldspar solid solutions. In the 1100°C
TABLE 3. Results of Experimental Runs at High Pressures at 1100°C for One Hour

<table>
<thead>
<tr>
<th>Pressure, kb</th>
<th>Phases Present*</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Alk Qz Px</td>
<td>Alk = San_{14}Ab_{81}; Px mainly orthopyroxene</td>
</tr>
<tr>
<td>16\frac{1}{2}</td>
<td>Alk Qz Px Garnet</td>
<td>garnet very rare; Alk = San_{21}Ab_{74}; garnet increasing.</td>
</tr>
<tr>
<td>17\frac{1}{2}</td>
<td>Alk Qz Px Garnet</td>
<td>garnet increasing; Px is clinopyroxene.</td>
</tr>
<tr>
<td>20</td>
<td>Alk Qz Px Garnet</td>
<td>Alk = San_{25}Ab_{71}</td>
</tr>
<tr>
<td>22\frac{1}{2}</td>
<td>Alk Qz Px Garnet</td>
<td>garnet increasing; Px is clinopyroxene.</td>
</tr>
<tr>
<td>25</td>
<td>Alk Qz Px Garnet</td>
<td>Alk = San_{49}Ab_{53}</td>
</tr>
<tr>
<td>27\frac{1}{2}</td>
<td>Alk Qz Px Garnet</td>
<td>Alk = San_{41}Ab_{69}; Px increasing and distinctly jadeitic.</td>
</tr>
<tr>
<td>30</td>
<td>Alk Qz Px Garnet</td>
<td>Alk = San_{46}Ab_{74}; Px increasing and dominantly jadeitic.</td>
</tr>
<tr>
<td>40</td>
<td>Alk Coes Px Garnet</td>
<td>Alk = San_{106}Ab_{8}</td>
</tr>
</tbody>
</table>

* Minor rutile present in all runs; abbreviations as in Table 2.

runs there is only a single peak in this region, and it shows a shift in position with increasing pressure consistent with decreasing albite content of a high-temperature alkali feldspar solid solution.

In the 950°C runs at 12\frac{1}{2} to 20 kb, the reflection at 2θ = 27.75° has greater intensity than at 2θ = 27.45°. This is the reverse of the relationship found in the high albite-sanidine solid solution series [Donnay and Donnay, 1952] and is considered to be due to the superposition of the most intense albite peak (at 2θ = 27.77°) on the lower-intensity high albite-sanidine peak at 2θ = 27.75°. In the 1100°C runs the intensity relationships for this pair of lines are compatible with a single feldspar phase of the high albite-sanidine solid solution series.

The feldspar at 1100°C is distinctly richer in albite than the corresponding alkali feldspar in the 950°C runs at the same pressure. The feldspar becomes steadily more potassic with increasing pressure up to 27\frac{1}{2} kb. Between 27\frac{1}{2} and 30 kb there is a much larger decrease in albite content, from Ab_9 to Ab_8, and by 40 kb the alkali feldspar is pure sanidine.

Garnet is absent at 15 kb and 1100°C but is present at 16\frac{1}{4} kb and increases in amount present in the 17\frac{1}{2}- and 20-kb runs. Above 20

TABLE 4. Variation in Composition of Alkali Feldspar with Change in Pressure

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Pressure, kb</th>
<th>Δ2θ</th>
<th>Feldspar Composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>12\frac{1}{2}</td>
<td>0.62</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>13\frac{1}{2}</td>
<td>0.62</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.62</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>17\frac{1}{2}</td>
<td>0.60</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.58</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>22\frac{1}{2}</td>
<td>0.63</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>25 (4 hr)</td>
<td>0.61</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>25 (12 hr)</td>
<td>0.63</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>27\frac{1}{2}</td>
<td>0.51</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.29</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>&lt;0.2</td>
<td>&gt; San_{14}Ab_{81}</td>
</tr>
<tr>
<td>1100</td>
<td>15</td>
<td>0.93</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>17\frac{1}{2}</td>
<td>0.92</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>22\frac{1}{2}</td>
<td>0.83</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.77</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>27\frac{1}{2}</td>
<td>0.70</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.40</td>
<td>San_{14}Ab_{81}</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>&lt;0.10</td>
<td>San_{14}Ab_{81}</td>
</tr>
</tbody>
</table>

* In weight per cent, from data of Tuttle and Bowen [1958, p. 12].
GRANITE AT HIGH PRESSURES

TABLE 5. Comparison of Major Feldspar Reflections in Selected Runs at 950°C and 1100°C

<table>
<thead>
<tr>
<th>Pressure, kb</th>
<th>950°C Runs</th>
<th>1100°C Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2θ* deg</td>
<td>Relative Intensity*</td>
</tr>
<tr>
<td>21.45</td>
<td>10</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>21.83</td>
<td>15</td>
<td>2θ01 Pi</td>
</tr>
<tr>
<td>27.45</td>
<td>40</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>27.80</td>
<td>60</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>21.45</td>
<td>8</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>21.85</td>
<td>11</td>
<td>2θ01 Pi</td>
</tr>
<tr>
<td>27.75</td>
<td>42</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>22.40</td>
<td>10</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>21.85</td>
<td>7</td>
<td>2θ01 Pi</td>
</tr>
<tr>
<td>27.45</td>
<td>42</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>27.75</td>
<td>37</td>
<td>2θ01 Pi</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>27.45</td>
<td>40</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>27.70</td>
<td>17</td>
<td>2θ01 San-Ab</td>
</tr>
<tr>
<td>27.0-27.25</td>
<td>19</td>
<td>2θ01 San-Ab</td>
</tr>
</tbody>
</table>

* Determined relative to the quartz 1011 peak at 2θ = 26.65°.
† Cf. Donnay and Donnay [1952].

There is apparently no further increase in the intensity of the garnet reflections.

The pyroxene laths at 15 and 16\% kb include both orthopyroxene and clinopyroxene (identified by optical examination). There is a large increase in clinopyroxene content, and the pyroxene becomes dominantly jadeitic between 25 and 7\% kb.

**INTERPRETATION OF RESULTS**

The incoming of garnet at 13\% kb, 950°C, and 16\% kb, 1100°C, is attributed to the reaction

\[
\text{(Fe, Mg)SiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{CaFe, Mg}_2\text{Al}_2\text{Si}_2\text{O}_8 + \text{SiO}_2
\]

hyperssthene anorthite

⇌ (Fe, Mg)_2Al_2Si_2O_12

amlandine-rich garnet

+ Ca(Fe, Mg)_2Si_2O_6 + SiO_2
diopside quartz

Hence hyperssthene, anorthite, garnet and diopside are members of solid solution series, the above reaction will be spread over a P-T interval. Between 16\% 20 kb at 1100°C and 13\% and about 20 kb at 950°C, the observed increase in garnet is thought to be due to the progressive elimination of hyperssthene or hyperssthene solid solution in clinopyroxene. As pressure increases the degree of Tschermak's silicate (Ca, Mg) AlSiO_3 substitution in the pyroxene probably also decreases in favor of garnet [Ringwood and Green, 1964; Boyd and England, 1964]. Because of the appreciable FeO content of our composition and the apparent absence of magnetite, it is probable that there is a small amount of acmite molecule present in our runs—possibly as a separate acmitic clinopyroxene below 15 kb and in clinopyroxene solid solution at higher pressure.

The normative composition of the plagioclase in the mixture is oligoclase (Ab_2An_30). The degree of solid solution of albite in the alkali feldspar will cause the modal plagioclase at 950°C to be more calcic than this. However, the reac-
tion of anorthite molecule with pyroxene to yield garnet would enrich the plagioclase in albite. The disappearance of plagioclase as a separate phase at 950°C is due to the above reaction involving anorthite and to the breakdown of albite to yield jadeite and quartz ($\text{NaAlSi}_3\text{O}_8 \Rightarrow \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$). Between 20 and 25 kb at 950°C this reaction becomes important, as shown by the increasing amount of pyroxene and its increasingly jadeitic composition and by the decrease in the amount of plagioclase. The jadeite so formed enters into solid solution with the diopside present, but at pressures greater than 25 kb at 950°C and 27 1/2 kb at 1100°C the jadeite component is dominant, as shown by the X-ray diffraction pattern. In the 1100°C runs the breakdown of albite molecule to yield jadeite + quartz is responsible for the changing composition of the alkali feldspar phase. Above 27 1/2 kb the more rapid decrease in albite content is consistent with the data from the simple albite system [Birch and Le Comte, 1960], establishing the limit of albite stability at 1100°C at about 28 kb. However, between 27 1/2 and 30 kb and between 30 and 40 kb at 1100°C, albite component stabilized by solid solution in the alkali feldspar continues to yield further jadeite and quartz as the alkali feldspar approaches pure sanidine.

This effect is more noticeable at 950°C, where, at 30 kb, with plagioclase finally eliminated as a stable phase, the alkali feldspar still contains about 23 wt.% albite. However, at 950°C the trace of plagioclase present in the 4-hour run at 27 1/2 kb is outside the stability field of albite (Figure 1), and it is probable that equilibrium was not attained in this run. A similar conclusion may be drawn from the presence of a trace of plagioclase at 25 kb in the 4-hour run and its absence in the 12-hour run. The presence of plagioclase in these two runs may be an example of the operation of Ostwald's step rule [Fyfe et al., 1958, p. 73]; i.e., a phase of higher entropy has nucleated first from the glass and in the time of the experiment has not been completely crystallized to the equilibrium assemblage. A similar explanation is invoked for the presence of X-ray diffraction pattern of anorthite molecule with pyroxene to yield garnet would enrich the plagioclase in albite. The disappearance of plagioclase as a separate phase at 950°C is due to the above reaction involving anorthite and to the breakdown of albite to yield jadeite and quartz ($\text{NaAlSi}_3\text{O}_8 \Rightarrow \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$). Between 20 and 25 kb at 950°C this reaction becomes important, as shown by the increasing amount of pyroxene and its increasingly jadeitic composition and by the decrease in the amount of plagioclase. The jadeite so formed enters into solid solution with the diopside present, but at pressures greater than 25 kb at 950°C and 27 1/2 kb at 1100°C the jadeite component is dominant, as shown by the X-ray diffraction pattern. In the 1100°C runs the breakdown of albite molecule to yield jadeite + quartz is responsible for the changing composition of the alkali feldspar phase. Above 27 1/2 kb the more rapid decrease in albite content is consistent with the data from the simple albite system [Birch and Le Comte, 1960], establishing the limit of albite stability at 1100°C at about 28 kb. However, between 27 1/2 and 30 kb and between 30 and 40 kb at 1100°C, albite component stabilized by solid solution in the alkali feldspar continues to yield further jadeite and quartz as the alkali feldspar approaches pure sanidine.

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...of quartz and coesite within the coesite stability field at 950°C and 35 kb.

The results on the adammellite composition are consistent with the few results published in similar compositions. Thus Yoder and Tilley [1962, p. 516] report that the standard granite crystalized to a sanidine solid solution + quartz at 20 kb, 1100°C. They do not comment on the presence or absence of minor pyroxene or garnet. Luth et al. [1964] report studies at water pressures of 4 to 10 kb in the system KAlSi₃O₈ - NaAlSi₃O₈ - SiO₂ - H₂O. The high water pressure suppresses the beginning of melting to around 650°C and the liquidus surface intersects the high albite-sanidine immiscibility gap. The data presented here show that in the presence of a moderate Ca content, two feldspars coexist at 950°C over the pressure range 12½ to 25 kb, but in the same bulk composition there is only one feldspar of the high albite-sanidine solid solution present at 1100°C over the same pressure range.

GEOLOGICAL APPLICATIONS

Mineral assemblages of acid rocks under eclogite facies conditions. Yoder and Tilley [1962] and Ringwood and Green [1964 and unpublished] have experimentally crystallized basaltic compositions to eclogite mineralogy. The latter authors found that the pressure at which plagioclase disappeared to yield garnet + pyroxene + quartz mineral assemblages depended on the bulk composition of the basalt but that in normal basaltic compositions plagioclase was unstable at 1100°C at pressures greater than 23 kb. Extrapolation of data for 1000 and 1200°C (Ringwood and Green, unpublished) indicates that plagioclase is unstable at pressures greater than 20 kb at 950°C in basaltic compositions.

At 20 kb and 950°C, the adammellite consists of quartz, sanidine solid solution, plagioclase, pyroxene, garnet, and rutile. This assemblage is stable to between 25 and 27½ kb and is also typical of the lower pressure range, 13½ to 20 kb, although the proportion of phases varies. Basaltic rocks, particularly of quartz tholeiite composition, crystallize in this lower pressure range to granulite facies mineral assemblages of pyroxene + plagioclase + garnet + quartz [Ringwood and Green, 1964]. Thus the experimentally defined boundary between mineral assemblages matching those of basaltic rocks in the granulite facies and basaltic rocks in the eclogite facies does not correspond to a major change of mineralogy in an anhydrous adammellite composition. It has been noted, however, that the pyroxene in the adammellite at 22½ and 25 kb, 950°C, is distinctly rich in jadeite. Thus in a granitic composition, recognition of a clinopyroxene of high jadeite (and probably low Tschermak's silicate) substitution coexisting with pyrope-almandine garnet would establish the assemblage as eclogite facies. This hypothetical rock, with a mineralogy dominated by quartz, sanidine (or orthoclase), and plagioclase could in no sense be called an 'eclogite' but would have the megascopic and microscopic character of an acid, garnetiferous pyroxene granulite. Under higher pressures the granite (broadly defined) will crystallize as a quartz-jadeite-sanidine-garnet rock. To our knowledge, acid rocks of eclogite facies, as defined above, have not been identified in any natural occurrence. There is a possibility that careful identification of the pyroxene and garnet compositions from acid 'granulites' and gneisses, particularly terranes containing eclogite lenses, could establish the existence of natural acid rocks of eclogite metamorphic facies.

In the experimental runs, the appearance of garnet is a direct consequence of increasing pressure at crystallization and is attributed to reaction between hypersthene and plagioclase. It is stressed that the garnet formed coexists with calcic clinopyroxene (with or without hypersthene). In some naturally occurring gneisses and granulites, the Al₂O₃ content may be higher and the assemblages hypersthene + plagioclase + garnet + alkali feldspar + quartz, and plagioclase + garnet + sillimanite + alkali feldspar + quartz may occur. These assemblages do not indicate crystallization within the garnet field of Figure 1.

An examination of literature on granulite and charnockite terranes establishes a direct comparison with crystallization in the garnet-free and garnet-bearing fields of Figure 1. Thus the charnockite series of Madras [Howie, 1955; Howie and Subramaniam, 1957] and the charnockites of central and western Australia [Wilson, 1959] characteristically have the lower pressure assemblage of plagioclase ± alkali feldspar + quartz + hypersthene + augite in rocks of acid or intermediate composition. A similar
generalization applies to the granulites of Lapp-
land [Eskola, 1952], Broken Hill [Binns, 1964],
and in general to the charnockites of Uganda
[Groves, 1935] and Varberg, Sweden [Quensel,
1951]. In the latter two areas there are oc-
casional examples in which the hypersthene +
plagioclase reaction to yield garnet and clino-
pyroxene has been recognized [Groves, 1935, p.
183; Howie and Subramaniam, 1957, p. 572].
Excellent examples of the association of garnet
+ clino.pyroxene ± hypersthene with two feld-
spars and quartz in acid and intermediate rocks
from the Adirondacks have been described by
Buddington [1963] and De Waard [1964]. Both
authors recognize the possibility of mapping a
garnet isograd in quartz-rich rocks subdividing
the pyroxene granulite facies into a lower pres-
sure assemblage with hypersthene + clino-
pyroxene + plagioclase and a higher pressure
assemblage of garnet + clino.pyroxene + plagi-
oclase ± hypersthene. The present work pro-
vides experimental confirmation of the signifi-
cance of these assemblages in deducing relative
T and P conditions of various granulite terrains.

Nature of the lower continental crust. In
seismic velocity profiles through the crust an in-
crease in compressional seismic velocity, \( V_p \),
with depth is usually postulated [Birch, 1958;
Steinhart and Meyer, 1961]. At shallower depths
within the crust, values of \( V_p = 5.8 \) to 6.3 km/
sec are indicated, increasing to 6.7 to 7.0 at the
base of the crust. In some studies a relatively
sharp increase in seismic velocity within the crust
(the 'Conrad discontinuity') has been sug-
gested, but later workers have favored a gradual
increase in velocity [cf. Gutenberg, 1955, p. 20;
Tatel and Tuve, 1955].

In Figure 1 the boundary curve marking the
incoming of garnet in the experimental runs on
the adamellite composition is projected to lower
pressures and temperatures. It is emphasized
that this extrapolation can be only qualitative in
the absence of experimental data in the 500-
600°C range. In Figure 1, the probable range of
\( T \) and \( P \) [Clark, 1962; Clark and Ringwood,
1964; Birch, 1955] at the Mohorovicic disconti-
nuity for an average continental crust (35 km
thick) is also illustrated. Provided that condi-
tions are anhydrous, the stable mineral assem-
blage of the adamellite in the lower crust will
contain garnet and the amount of garnet will
increase with depth. If the partial pressure of
water is not sufficiently low, biotite and/or hornb]
blend may be stable at the rather low tempera-
tures and prevent the appearance of garnet.

Ringwood and Green [1964] have shown that
in a quartz tholeite composition, garnet appears
at approximately the same \( P-T \) conditions as
are now found for the adamellite composition.
It is probable that the spectrum of igneous
rock compositions between quartz tholeite and
adamellite, i.e., the calc-alkaline series of dori-
monzonite, quartz diorite, and granodiorite
undergo similar reactions with garnet and
pyroxene increasing with depth. There are na-
tural occurrences of garnetiferous acid and in-
termediate charnockites, and also basic garnet-
granulites, which may be consistent with this
conclusion. Rocks departing from the common
igneous compositions (pelitic sediments, marbles
and quartzites) cannot be incorporated into the
above generalization.

Because seismic wave velocity is pro-
to the density of the rock traversed, it is obvious
that the presence of the dense-phase garnet in
rocks of the lower continental crust would cause
a velocity increase. Birch [1961, p. 2218] has
found an equation, \( V_p = -0.30 + 2.54 \rho \), from
which approximate seismic compressional ve-
locities at 10 kb confining pressure can be cal-
culated for granitic rocks, if the density of the
rocks is known.

The density of the rock before the incoming
of garnet can be approximately calculated from
the normative mineralogy, assuming that ilmen-
ite is replaced by rutile, and magnetite and
some albite by acmite, in conformity with the
observations on the experimental runs. The
density thus calculated is 2.68 to 2.69 g/cm³
and, from Birch's equation, would give \( V_p = 6.51 \) km/sec at 10 kb confining pressure. The
reaction between hypersthene and plagioclase
to yield garnet and clino.pyroxene should yield
about 6 to 7% garnet. The density of the high-
pressure assemblage formed by this reaction was
calculated as 2.72 g/cm³, giving \( V_p = 6.61 \) km/
sec at 10 kb confining pressure. Thus the in-
crease in seismic velocity caused by the incom-
ing of garnet in the average adamellite composi-
tion studied should be about 0.1 km/sec. Some
confirmation of this is provided by values of
density of 2.73 g/cm³ and 2.79 g/cm³ obtained
with the Berman balance for the runs at 17½
kb, 950°C, and 22½ kb, 950°C, respectively.
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Ringwood and Green [1964] have given the approximate seismic velocity of a quartz tholeiite before the incoming of garnet as 7.0 km/sec, and this rises with increasing pressure until an eclogite velocity of approximately 8.0 km/sec is reached.

Some generalized conclusions can be made from the above data. If there are essentially anhydrous conditions throughout much of the lower continental crust, the incoming of garnet in any of acid, intermediate, or basic igneous compositions will cause appreciable velocity increases. Comparison of the calculated velocity values for acid and basic compositions with the observed values suggests that the incoming of garnet in a composition as acid as the average adamellite will not give an increase in $V_p$ sufficiently large to match the observed values. On the other hand, in a basaltic composition, the incoming of garnet in the lower crust will probably give values of $V_p$ too high in comparison with the observed values. It seems that, if the appearance of garnet as a stable phase in the igneous rock compositions described is a real process under lower crustal conditions, an overall intermediate composition best fits the available data. The above arguments are not relevant if the ferromagnesian phases in this spectrum of rock compositions within the real lower crust are dominantly hydrous (hornblende, biotite, muscovite). Nevertheless, our data suggest a possible explanation of increased densities in the continental crust.

**Conclusions**

At 950°C the mineral assemblage in a dry granite composition under pressure high enough to produce eclogite mineralogy in basaltic rocks is quartz, plagioclase, alkali feldspar, pyroxene, garnet, and rutile. At higher temperatures only one feldspar is present (an albite-rich member of the sanidine-high albite solid solution series). At higher pressures the plagioclase breaks down to yield jadeite and the alkali feldspar gradually approaches pure sanidine. The resulting assemblage, at pressures equivalent to those at 100 to 150 km depth is quartz + sanidine + jadeitic pyroxene + garnet.

In the anhydrous adamellite composition, and probably in the series of igneous compositions between adamellite and quartz tholeiite, garnet is stable under conditions equivalent to high-pressure granulate facies. If conditions in the lower crust are anhydrous, this may be a significant factor in producing increasing seismic velocity with depth, without the necessity for any major change in chemical composition.

**Acknowledgment.** Thanks are due to Knut S. Heier who critically read the manuscript.

**References**


(Manuscript received June 1, 1965; revised July 20, 1965.)
The chemistry and petrography of garnet pyroxenite ("eclogite") inclusions in olivine nephelinite tuff at Salt Lake Crater, Hawaii, are examined in relation to recent experimental studies of melting and subsolidus relations in basaltic rocks at high pressure. It is concluded that the rocks originated as accumulates of liquidus or near-liquidus sub-calcic clinopyroxene derived from alkali olivine basalt or basanite at a pressure of approximately 13-18 kb. The original accumulate cooled from temperatures of 1350-1400°C to about 1000°C at constant pressure causing exsolution of garnet from the original highly aluminous pyroxene and reaction of spinel and pyroxenes to yield garnet and olivine. The P, T conditions of initial accumulation and later recrystallization of the garnet pyroxenites diverge widely from the P, T conditions responsible for the formation of natural eclogites occurring in metamorphic terranes or as inclusions in kimberlite pipes.

1. INTRODUCTION

An olivine nephelinite tuff at Salt Lake Crater, Oahu, contains ejected blocks of dunite, peridotite, pyroxenite and "eclogite" (garnet pyroxenite of this paper) [1-4]. The presence of rocks containing pyrope-almandine garnet and described as eclogites, has assumed considerable importance in recent literature, particularly in discussions of the hypothesis that the earth's upper mantle may be of eclogitic rather than peridotitic composition. Specimens of the Salt Lake Crater "eclogites" have been examined for U and Th content and the implications of the results to mantle heat production have been discussed by Tilton and Reed [5] and Lovering and Morgan [6]. These investigations involve the hypothesis that rocks such as the Salt Lake Crater "eclogites" are volumetrically significant in the upper mantle and may indeed represent the nearest approach to primary upper mantle material brought to the earth's surface in oceanic regions [5,7-9].

On the other hand Kuno [10,11,20] reported a complete gradation between olivine eclogite, olivine-free eclogite and pyroxenite and interpreted the rocks as direct crystallization products of basaltic magma, possibly tholeiitic, at high pressures. Kuno suggested derivation of the material from a local lens or pocket within the dominantly peridotitic upper mantle.

Recent experimental work [12,13] on the nature and compositions of phases crystallizing from basaltic magmas at high pressure strongly suggests that the Salt Lake Crater garnet pyroxenites were primarily local crystal accumulates at high pressure from olivine-rich basaltic magmas.

2. PETROGRAPHY AND MINERALOGY

Yoder and Tilley [2] and White [14] have described examples of the Salt Lake Crater garnet pyroxenites and given analytical data on the minerals present. Specimens [A.N.U. Nos. 2817, 2818, 2819] supplied to the author by Dr. G.A. MacDonald are closely similar to those previously described. Pyroxenites are the dominant phases with uncommon and unevenly distributed garnet, olivine, spinel and biotite occurring as minor phases in some examples. The grain size is highly variable, but large, anhedral clinopyroxene crystals are typical and, in some examples, a few orthopyroxene crystals or spinel crystals of similar large size occur. Garnet is anhedral with three rather distinctive modes of occurrence:

(a) As small blebs and plates within large pyroxene crystals and interpreted as direct exsolution of garnet from the pyroxenes.

(b) As small or medium-sized anhedral crystals marginal to pyroxene crystals and in some cases forming partial rims around the pyroxenes.

(c) As coronas entirely surrounding relict spinel grains. There is a gradation from rela-
Table 1

Compositions of natural "eclogites" or garnet pyroxenites occurring as ejected blocks in tuff at Salt Lake Crater, Oahu, Hawaii. The compositions are calculated to pyroxene formulae.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.41</td>
<td>49.26</td>
<td>48.46</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.41</td>
<td>8.63</td>
<td>7.96</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.62</td>
<td>0.62</td>
<td>0.43</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.43</td>
<td>0.31</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.58</td>
<td>3.24</td>
<td>3.55</td>
</tr>
<tr>
<td>FeO</td>
<td>5.61</td>
<td>5.09</td>
<td>4.32</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>17.72</td>
<td>19.40</td>
<td>19.96</td>
</tr>
<tr>
<td>CaO</td>
<td>12.17</td>
<td>12.44</td>
<td>12.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.24</td>
<td>0.88</td>
<td>1.90</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.11</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>Other constituents</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H₂O, CO₂, P₂O₅)</td>
<td>0.75</td>
<td>0.42</td>
<td>0.54</td>
</tr>
<tr>
<td>100Mg (atomic ratio)</td>
<td>85</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>Mg-Fe²⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Compositions of pyroxenes obtained in experimental partial melting runs at high pressure [13].

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Olivine basalt</th>
<th>Alkali olivine basalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (kb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coexisting phases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquidus phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relation to liquidus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.3</td>
<td>50.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.9</td>
<td>9.9</td>
</tr>
<tr>
<td>FeO</td>
<td>6.4</td>
<td>5.5</td>
</tr>
<tr>
<td>MgO</td>
<td>30.8</td>
<td>23.1</td>
</tr>
<tr>
<td>CaO</td>
<td>2.6</td>
<td>10.8</td>
</tr>
<tr>
<td>100Mg (Mg-Fe²⁺)</td>
<td>90</td>
<td>88</td>
</tr>
</tbody>
</table>


Tightly large spinel grains of deep green colour with proportionately narrow garnet coronas to very small, opaque "spinel" grains with proportionately thick garnet coronas.

Olivine occurs in some specimens as anhedral grains in a partial corona outside the garnet coronas described above. More rarely, euhedral or subhedral olivine grains occur within the larger pyroxene crystals.

Large clinopyroxene crystals show extensive exsolution of orthopyroxene forming plates, irregular patches or mantling overgrowths. Larger orthopyroxene crystals exsolve relatively minor amounts of clinopyroxene as thin lamellae. The abundance and habit of the orthopyroxene is consistent in at least some of the specimens with an origin entirely by exsolution from the clinopyroxene.

In some specimens there is retrogressive alteration of garnet to an inner rim of brown, turbid material and an outer rim of pyroxene and spinel kelyphitic intergrowth.

Chemical analyses of pyroxenes from garnet pyroxenite and pyroxenite [2,14] show high Tschermak’s silicate ((Ca, Mg)Al₂SiO₆) substitution in both orthopyroxene and clinopyroxene. Although the clinopyroxene contains jadeite and acmite solid solution, White [15] has shown that the proportion of jadeite to Tschermak’s silicate in the Salt Lake Crater "eclogite" is much lower than in typical eclogites of metamorphic terranes [16,17] or occurring as inclusions in kim-
berlites [18] or garnet peridotites [19]. White [15] observes that the compositions of the Salt Lake Crater pyroxenes are closer to those observed in granulite facies metamorphic rocks.

3. CHEMICAL COMPOSITIONS

The chemical compositions of three garnet pyroxenite nodules have been published [2, 3, 20] and are reproduced in table 1. The compositions are very similar and are distinctive in their high MgO content and Mg/(Mg+Fe$^{2+}$) ratio, low Al$_2$O$_3$ content and high SiO$_2$ content. The components, showing the widest variations among the three compositions are Na$_2$O and K$_2$O. The compositions are quite unlike picritic or basaltic magmas in their chemistry but, as shown in table 1, two of the examples [2, 3] calculate almost ideally as pyroxene compositions. The third example [20] shows an excess of cations in the WXY sites suggesting that this composition would be better calculated as an admixture of a small amount of olivine or of spinel with the major pyroxene. The pyroxene structural formulae calculated in table 1 have high Tschermak’S silicate substitution, all have moderate, acmite or acmite and jadeite contents and, if regarded as originally a single phase pyroxene, exhibit low calcium contents and thus a very high degree of solid solution of (Mg, Fe)$_2$SiO$_4$ in clinopyroxene.

Recent experimental study [12, 13] of basalt melting relations at high pressure has demonstrated the important roles of aluminous orthopyroxene and aluminous, sub-calcic clinopyroxene as liquidus and near-liquidus phases in olivine-rich tholeitic and alkaline basalts in the 9-18 kb pressure range. The compositions of clinopyroxenes [13] crystallized experimentally from an olivine basalt (1% normative hypersthene, 27% normative olivine, 100Mg/(Mg+Fe$^{2+}$) = 68) and an alkali olivine basalt (2% normative nepheline, 26% normative olivine, 100Mg/(Mg+Fe$^{2+}$) = 60) are given in table 2. These compositions were determined by electron microprobe analysis for Fe, Ca, Al and calculation of Mg and Si assuming ideal pyroxene composition. Na and Ti have not been determined but T.H. Green (personal communication) has shown that liquidus and near-liquidus clinopyroxenes of basaltic compositions between 9 and 20 kb contain from 0.5 to 1.5% Na$_2$O and have about 1% TiO$_2$.

The pyroxene compositions in table 2 are very similar to the bulk chemical composition of the analyzed Salt Lake Crater garnet pyroxenites. The similarity is greatest in the case of the liquidus clinopyroxene from the alkali olivine basalt at 18 kb, 1320°C. Comparing the analyzed pyroxenites with the minerals of table 2 it is apparent that an admixture of orthopyroxene and clinopyroxene would produce an accumulate with lower CaO content than the Salt Lake Crater rocks of table 1, but such accumulates would retain similar SiO$_2$ and Al$_2$O$_3$ contents. An accumulate of minor olivine with major clinopyroxene (e.g. table 2, column 2) could produce similar bulk compositions, although the CaO content of clinopyroxene coexisting with olivine at 9 kb is high in comparison with the analyzed "eclogites". It may be noted that an accumulate of minor olivine with sub-calcic clinopyroxene could be derived at 18 kb from a more olivine-rich parent magma than the alkali olivine basalt of Green and Ringwood [13] i.e. a nepheline-normative picrite. The data of table 2 and of Green and Ringwood [13] also demonstrate that a liquid with 100Mg/(Mg+Fe$^{2+}$) = 65-70 would precipitate liquidus pyroxenes at high pressure with 100Mg/(Mg+Fe$^{2+}$) ratios of 85-88.

4. ORIGIN OF THE SALT LAKE CRATER GARNET PYROXENITES

The chemical compositions and the petrography of the Salt Lake Crater garnet pyroxenites both provide evidence for their origin as monomineralic accumulates of aluminous clinopyroxene from olivine-rich nepheline-normative basaltic magma at a pressure near 13-18 kb, i.e. at depths of about 60 km. In some examples variable amounts of olivine may have accumulated with the clinopyroxene implying a parent magma with around 30% normative olivine [13]. In other examples, minor quantities of spinel may have precipitated with the clinopyroxene - this would be consistent with experimental data on olivine-rich basalts at 13.5 kb [13] showing that spinel joins clinopyroxene at temperatures below the liquidus. On the other hand, at 18 kb, garnet appears at near-solidus temperatures in the partial melting interval of the basalts studied experimentally [13].

In natural accumulative rocks, derived by gravitative settling of crystals from basaltic magmas at low pressure, the accumulate commonly contains at least some entrapped basaltic liquid [21]. In the case of accumulative rocks at high pressure, a similar relationship might occur but the interprecipitate liquid at high pressure would crystallize as aluminous-pyroxene ± olivine, spinel or garnet.
5. POST-ACCUMULATION HISTORY OF SALT LAKE CRATER GARNET PYROXENITES

Fig. 1 illustrates the experimentally determined [22, 23] stability fields for pyroxene granulite, garnet-clinopyroxene granulite and eclogite mineral assemblages in an oversaturated quartz tholeiite composition. The data of Green and Ringwood [22] is also sufficient to define boundaries marking the incoming of garnet from spinel-bearing assemblages and the reaction of olivine and plagioclase to yield spinel + pyroxene assemblages in the undersaturated olivine-normative composition of the Salt Lake Crater garnet pyroxenites. A further boundary defined by the exsolution of garnet from the aluminous clinopyroxene can only be approximately located at present [24] but will have higher dP/dT than the reactions deriving garnet from the spinel, pyroxene and plagioclase assemblage.

The position of the liquidus of an alkali olivine basalt with $100\text{Mg}/(\text{Mg}+\text{Fe}^2+) \approx 65$ and the pressure at which subcalcic clinopyroxene (of composition close to the analyzed Salt Lake Cra-
ter rocks) occurs on the basalt liquidus is also shown in fig. 1. On cooling at constant pressure, a crystal accumulate of liquids clinopyroxene would enter the garnet + aluminous pyroxene stability field and garnet would exsolve from the pyroxene, decreasing the Tschermak's silicate content of the latter. The amount of solid solution of orthopyroxene in clinopyroxene decreases rapidly on the 1400°C to 1200°C temperature interval [13, 25, 26] so that cooling of the pyroxene accumulate would also be accompanied by extensive exsolution of orthopyroxene from clinopyroxene.

If cooling proceeded to sufficiently low temperatures (about 1000°C at 18 kb) an accumulate would enter the eclogite stability field on the high pressure side of the eclogite, fig. 1. This field is characterized for the particular chemistry of the Salt Lake Crater rocks by an assemblage of major garnet (30-35%) and pyroxenes with very low Tschermak's silicate content. The analytical data on pyroxenes given by Yoder and Tilley [2] and White [14] show that the Salt Lake Crater pyroxenes do not have this character, but retain a high degree of Tschermak's silicate solid solution. On the other hand, the presence of olivine coexisting with garnet, and, in some examples, the apparent reaction of spinel and pyroxene to yield olivine and garnet, yields one of the assemblages considered by O'Hara [27] to be diagnostic of the eclogite facies. The experimentally determined curve [28] for the reaction

\[ \text{MgAl}_2\text{O}_4 + 4\text{MgSi}_3\text{O}_8 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Mg}_2\text{Si}_4\text{O}_9 \]

spinel enstatite pyrope olivine

lies on the high pressure side of curve CD whereas the experimentally determined curve [32] for the reaction

\[ \text{orthopyroxene}_{\text{ss}} + \text{clinopyroxene}_{\text{ss}} + \text{spinel} = \text{garnet}_{\text{ss}} + \text{forsterite (grossular-pyrope)} \]

(as determined in the system 1 anorthite + 2 forsterite [32]) lies on the low pressure side of curve CD. The data currently available on the relative stability fields of olivine + garnet relative to pyroxene + spinel indicates that chemical composition exerts a major control. Co-existing olivine + garnet could occur in some chemical compositions while other, less mafic chemical compositions contained garnet + aluminous clinopyroxene + plagioclase + quartz under the same \(P, T\) conditions [22, 31; fig. 1].

In fig. 1, the probable \(P_{\text{load}}, T\) fields of eclogites occurring in three different environments [22, 29, 17] have been plotted in relation to the \(P, T\) environments of the Salt Lake Crater garnet pyroxenites. The deduced conditions of crystallization of the three types of eclogite and the Salt Lake Crater garnet pyroxenites are very different and the Salt Lake Crater rocks did not crystallize in the eclogite \(P, T\) field as delimited experimentally [22]. The garnet pyroxenites would not be classified as eclogites utilizing the criteria of clinopyroxene composition advocated by White [15] nor on the restricted definition of eclogite adopted for petrological classification by Green and Ringwood [22]. However, the Salt Lake Crater garnet pyroxenites conform to a wider definition of "eclogite" embracing rocks of pyrope-almandine garnet and calcic clinopyroxene [29, 23]. The classification and nomenclature of the Salt Lake, Crater rocks clearly depend on the particular criteria adopted. The nomenclature adopted for these rocks is of secondary importance to the recognition that the mineral assemblage denotes \(P, T\) conditions of crystallization different from those of the classical eclogites of metamorphic terrane such as those of Norway or of the eclogites occurring as inclusions in kimberlite pipes.

The cooling and recrystallization of the garnet pyroxenites was not accompanied by appreciable deformation, but does imply a time break before the fragments of accumulative material were included in an eruption of olivine nepheline magma. Although the inclusions cannot be regarded as cognate in relation to the magma which brought them to the surface it is possible that their parent magma was an earlier magma batch of similar or less undersaturated type. The abundant lherzolite fragments [14] in the Salt Lake Crater nepheline tuff may be more representative of the oceanic upper mantle and include examples of the wall-rock associated with local accumulative pyroxenite.

6. CONCLUSIONS

The pyroxene + garnet + olivine + spinel mineralogy of ejected blocks in olivine nepheline tuff at Salt Lake Crater indicates conditions of crystallization of about 1000°C and load pressures of 13-18 kb. Under these conditions other quartz-normative basaltic rocks consist of plagioclase + garnet + clinopyroxene + quartz [22] i.e. high pressure granulite facies assemblages. The garnet + pyroxene assemblages may be regarded as high temperature, high pressure granulites and were derived from depths of 40-60 km, i.e. well within the upper mantle beneath the Hawaiian Islands.
The chemical compositions of the garnet pyroxenites and the distinctive petrographic features indicate major exsolution of both garnet and orthopyroxene from a host clinopyroxene provide compelling evidence for initial formation of the rocks as crystal accumulates at 13-18 kb of liquidus sub-calcic clinopyroxene from basaltic magma. The nature of the parent magma was most probably an olivine-rich alkali basalt or basanite. Exsolution, and reaction between pyroxene and spinel, developed during cooling of the accumulate from the liquidus temperature of 1350°C-1400°C to about 1000°C. A later eruption of olivine nephelinite magma carried fragments of the garnet pyroxenite along with common lherzolite fragments [14] to the surface.

The garnet pyroxenites do not represent "parental" or "primitive" upper mantle material and are not examples of a primitive magma entrapped and crystallized within the upper mantle.

In discussions and hypotheses on the nature of the oceanic upper mantle, limited significance should be attached to the Salt Lake Crater garnet pyroxenites. These are best regarded as a local segregation of precipitated material in a former magma chamber within an ultramafic upper mantle.

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REFERENCES


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ABSTRACT

Large boulders of eclogite in Tertiary conglomerate in the Guajira Peninsula, Colombia, are considered to be derived from a metamorphic sequence (Etpana Formation) of albite-epidote-amphibolite and greenschist facies and containing local serpentinite lenses. Two examples of the eclogitic rocks and their constituent garnet and pyroxene have been chemically analysed. One rock, with a bulk chemical composition approaching that of sodic trachyte, consists of almandine, jadeite (Jd 68Ac 4) and quartz as major phases, and minor primary scapolite, calcite, clinozoisite+paragonite, apatite, rutile and hematite. The association of very jadeite-rich pyroxene with almandine garnet is unique among eclogitic rocks. The second rock has a bulk chemical composition of alkali olivine basalt or hawaiite and contains primary almandine-omphacite (Jd sAc s)-rutile. The eclogitic rocks are similar to those described from glaucophane schist terranes of California and elsewhere. The mineral parageneses and element partition relationships are used to estimate conditions of crystallization of the eclogitic rocks as \( p_{\text{total}} = 7-12 \) kbars, \( p_{\text{H}_2\text{O}} \ll p_{\text{total}} \) and \( T = 200-400^\circ\text{C} \). The almandine+omphacite+rutile eclogite shows partial alteration to an albite-epidote-amphibolite assemblage.

INTRODUCTION

During mapping in the Guajira Peninsula of Colombia, one of the authors (J. P. L.) discovered large boulders of eclogite in middle Tertiary conglomerate bordering the Cerros de Parashi. The distribution of the conglomerate and demonstration of very local provenance for coarse detritus within it (Lockwood, 1965), indicated that the source for the eclogite boulders lay within the Etpana Formation, a group of phyllites of albite-epidote-amphibolite and greenschist facies of regional metamorphism which also contains local serpentinite lenses. The mineral parageneses and element partition relationships are used to estimate conditions of crystallization of the eclogitic rocks as \( p_{\text{total}} = 7-12 \) kbars, \( p_{\text{H}_2\text{O}} \ll p_{\text{total}} \) and \( T = 200-400^\circ\text{C} \). The almandine+omphacite+rutile eclogite shows partial alteration to an albite-epidote-amphibolite assemblage.

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been inferred (Green and Ringwood, 1967) that eclogites could form stably in dry ($p_{\text{H}_2\text{O}} \ll p_{\text{load}}$) basaltic rocks in metamorphic terranes classifiable as within the amphibolite, albite-epidote-amphibolite, green-schist and lawsonite-glaucophane schist facies, assuming that the latter hydrous assemblages formed in country rocks in which $p_{\text{H}_2\text{O}} \approx p_{\text{load}}$. The examination of natural eclogites associated with rocks of different metamorphic facies may establish criteria by which eclogites formed under very different $p_{\text{load}}, T$ conditions can be recognized. For this purpose we have chemically analyzed the Guajira eclogites and their constituent minerals.

**Geological Setting**

The eclogite specimens are from a middle Tertiary conglomerate 6.3 km north of the village of Parashi and near the northwestern margin of the Guajira Peninsula (Fig. 1). In this area the eclogites are abundant constituents of the conglomerate and are associated with boulders of quartzite, calcareous meta-argillite and serpentinite which are identical to rock types of the Etpana Formation outcropping nearby. Also associated are boulders of quartz diorite and dacite porphyry from the Parashi quartz

![Fig. 1. Geologic sketch map of the Parashi area, Guajira Peninsula, showing the location of eclogite-bearing conglomerate.](image-url)
diorite, a mid-Eocene (48±4 m.y.) stock which intrudes the Etpana Formation. The conglomerate is very coarse, and some eclogite boulders reach 50 cm in diameter. It is believed that the eclogites are derived from within the Etpana Formation, possibly from a higher level, since eroded away (Lockwood, 1965). Efforts to locate in situ sources for the eclogite boulders were unsuccessful.

The Etpana Formation originally consisted of a thick series of finely bedded shales and quartz sandstones with local tuffaceous beds. Its age is believed to be Mesozoic, and possibly Cretaceous, but no fossils have been found. This series has been regionally metamorphosed in Late Cretaceous or earliest Tertiary time to yield phyllites including the following mineral assemblages:

1. quartz-albite-biotite-muscovite-(sericite)-(chlorite)
2. albite-epidote-chlorite-(biotite)-(actinolite)-(calcite)
3. quartz-albite-epidote-biotite-almandine
4. quartz-biotite-muscovite-almandine
5. albite-epidote-biotite-hornblende (blue green)

These assemblages are indicative of a range of metamorphic conditions from the greenschist facies (1, 2) to the albite-epidote-amphibolite facies (5) using the nomenclature of Fyfe and Turner (1966). Regional metamorphism of serpentinites within the Etpana Formation is most obvious within the area of albite-epidote-amphibolite facies and emplacement of these bodies predates the regional metamorphic effects. Glaucophane schist has not been reported in the Guajira Peninsula but it may be relevant that Dengo (1950) described garnet amphibolites containing glaucophane and sodic-pyroxene from near Caracas, Venezuela. Although this area lies about 500 km east of Guajira Peninsula, the Mesozoic reconstruction of the northern Andean and Caribbean orogenic regions by Carey (1958) would place the two eclogite areas about 50 km or less apart.

**Petrography**

The eclogites consist of deep red garnets set in fine-grained, grey-green aggregates mainly of pyroxene. The garnets are euhedral, and in some examples are large, well-formed crystals showing near perfect rhombododecahedral form. Some eclogites contain coarse crystals (to 3 cm) of a yellow-green epidote-group mineral. There is a strong preferred orientation of pyroxene crystals and a tendency to lenticular or streaky inhomogeneity in abundance of the main phases.

A.N.U. 2832 (JPL J-291A)

This rock consists of about 15 percent of euhedral, very large (to 1.5 cm) garnets set in very fine grained (0.01 to 0.05 mm) pyroxene and quartz. The pyroxene and quartz are inhomogeneously distributed and there are lenticular patches (1–3 mm) in which calcite is
ECLOGITE FROM COLOMBIA

locally an important phase. The garnet has a deep red core and paler margin. The outer one-fourth to one-third is virtually free of inclusions but the inner zone has abundant quartz and rutile and minor apatite and pyroxene. Refractive index and the unit cell dimension of the garnet also vary from rim to core (Table 2). Some pyroxene crystals, particularly the larger ones, have concentric or patchy zoning—the nature of this zoning has not been determined.

The rock is remarkably fresh and shows no kelyphitic or grain-boundary alteration of either pyroxene or garnet.

The following minor or accessory minerals are present:

**Scapolite** is a very widely distributed accessory constituent as very small, anhedral grains associated with the quartz and pyroxene. Textural relations indicate that it is in equilibrium with pyroxene and quartz. Scapolite is more abundant near calcite patches.

**Clinozoisite** is very rare but forms moderately large (≈1 mm) poikiloblastic crystals with euhedral outer margins and common inclusions of quartz and pyroxene. It is intimately intergrown with colorless *paragonite* crystals. The identification of paragonite is based on quantitative electron microprobe analysis: Na$_2$O = 5.2±0.3%, K$_2$O = 0.2±0.1%, Fe$_2$O$_3$ = 0.2±0.1%. Paragonite only occurs in close proximity or intergrowth with clinzoisite. The intimate and local association of clinzoisite and paragonite is suggestive of replacement of pre-existing *lawsonite* porphyroblasts according to the reaction

$$4 \text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 2\text{H}_2\text{O} + \text{NaAlSi}_2\text{O}_6 \rightarrow 2\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12} (\text{OH}) + \text{NaAl}_2\text{Si}_3\text{O}_{10} (\text{OH})_2$$

**Calcite** was identified by X-ray powder diffraction and aragonite was not observed.

**Rutile** is a common minor constituent occurring randomly throughout garnet or pyroxene-rich areas and also in small stringers or lenses in the pyroxene-rich areas.

**Hematite** occurs rarely as single or clusters of grains. The grains are polycrystalline and formed from 6–10 crystals in radial growth. In several cases the radial growth of hematite is centered on relict cores of pyrite.

A *petite* is a minor accessory mineral, locally (in quartz patches) forming quite large subhedral crystals.

It is inferred that the assemblage garnet, pyroxene, quartz, scapolite, clinozoisite+paragonite (or lawsonite) rutile, hematite, apatite was a primary mineral assemblage representing equilibrium or a close approach thereto. Calcite may have inverted from aragonite.

A.N.U. 2833 (JPL J-291)

This eclogite contains much more garnet than the previous example and quartz is absent. Garnet is euhedral and medium-grained (0.5–3 mm) and the pyroxene is finer grained (0.05–0.3 mm) subhedral, and shows a strong preferred orientation. Garnet has a deeper pink color in the cores of crystals than at the margins and some pyroxene crystals are also distinctly zoned. Optical properties of both minerals vary from rim to core (Table 1). Rutile and apatite are common accessory minerals and there are very rare laths of glaucophane, either in association with pyroxene or included in the garnet crystals.
### Table 1. Chemical Compositions, CIPW Norms and Approximate Modes of Guajira "Eclogites"

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#### Analyses

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#### Norms

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### Chemical Compositions of Rocks and Minerals

The whole-rock compositions of the two specimens (2832 and 2833) are given in Table 1, together with their CIPW norms and approximate...
modes calculated from the rock and mineral analyses. Specimen 2832 is virtually unaltered and the Fe$_2$O$_3$ and FeO contents calculated from the mineral analyses are in good agreement with the analyzed FeO and Fe$_2$O$_3$ contents. The observed secondary alteration in specimen 2833 is apparently accompanied by oxidation of the FeO since the measured Fe$_2$O$_3$ content is considerably greater than that calculated from the mode and mineral analyses.

The composition of specimen 2832 is unique in comparison with other garnet+pyroxene or garnet+pyroxene+quartz assemblages. The high SiO$_2$ content coupled with very high Na$_2$O and low CaO and MgO contents denote a composition which cannot be classified, even loosely, as basaltic. This is further reinforced by the calculation of the CIPW. norm. On the other hand, apart from the K$_2$O content, the composition and CIPW. norm of 2832 are comparable with compositions of sodic trachytes or possibly benmoreite. There are no relict textures preserved but the observed tendency for calcite to occur in lenticular patches suggests that calcite amygdules may originally have been present.

Eclogitic rocks showing similarity in some components with 2832 include a banded pyroxene-bearing glaucophane schist from California (Coleman, Lee, Beatty and Brannock, 1965, p. 490-56-CZ-59), an oligoclase-omphacite-garnet-quartz "eclogite" from East Sudetes (Kozlowski, 1958, p. 726) and an eclogite inclusion in a basaltic diatreme from Utah (O'Hara and Mercy, 1966a, p. 342). None of these examples share with 2832 the combination of high Na$_2$O and high SiO$_2$ content and all differ in mineralogical detail from 2832.

The chemical composition of specimen 2833 is similar to many other eclogites in the literature, and, except for its very low K$_2$O content is typically "basaltic." More specifically the chemical composition and CIPW. norm of 2833 are closely comparable with hawaiite. Low K$_2$O content is a common characteristic of many eclogitic rocks and may be due to mobility of this component during garnet+pyroxene crystallization.

**Garnet compositions.** It was possible in both specimens to obtain garnets of very high purity, the only observed contaminant being minor, very small needles of rutile. The two garnets are of remarkably similar composition (Table 2), despite differences in bulk chemical composition of the host rocks. Both are characterized by very high FeO, moderate MnO and low MgO contents. Calculation of structural formulae gives a satisfactory check on the analyses, but requires that some Fe$^{2+}$ enter the divalent ion positions. This is commonly found in almandine garnet analyses (cf. Deer, Howie and Zussman, 1961, p. 86) but may be due to
the difficulty of getting garnet completely into solution under inert atmosphere conditions.

Both analyzed garnets are almandines with low to moderate grossular + andradite contents, low pyrope and very low spessartine contents. Almandine contents are higher, grossular contents are lower and pyrope contents are similar to those in garnets reported by Coleman et al., (1965) from eclogites associated with glaucophane schists (Fig. 2). On the other hand, the garnets analyzed by O'Hara and Mercy (1966) from inclusions in basaltic diatremes have lower grossular contents than the Colombian garnets, lower almandine contents and higher pyrope contents (fig. 2).

Samples were hand-picked from the core and rim of the coarse garnet in 2832 to determine the nature of the strong color zoning. Comparison of the measured values of refractive index and unit-cell dimension from rim and core (Table 2) with the diagrams of Sriramadas (1957) indicates that the cores are enriched in almandine and depleted in pyrope relative to the rims. The compositional zoning in garnet 2832 is probably similar.

![Fig. 2. Ca-Mg-(Fe+Mn) diagram (atomic proportions) illustrating the compositions of coexisting garnet (X), clinopyroxene (O) and host-rock (+) in eclogites of "low temperature type"
A. Colombia specimen 2832 (A'-replot without Ca as CaCO₃)
B. Colombia specimen 2833
**Table 2. Chemical Compositions, Structural Formulae and Proportions of Garnet End-Members in Garnets from Guajira “Eclogites”**

<table>
<thead>
<tr>
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<th>2833 Ga</th>
<th>2832 Ga</th>
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<tr>
<td>SiO₂</td>
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<td>TiO₂</td>
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<td>—</td>
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<tr>
<td>Al₂O₃</td>
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<td>99.96</td>
<td>99.69</td>
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**Molecular Proportions**

- Almandine: 69% 64%
- Andradite: 2% 2%
- Grossular: 18% 16.5%
- Pyrope: 10% 16%
- Spessartine: 1% 1.5%

**Physical Properties**

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<th>Mg/Fe²⁺</th>
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<td>(atomic)</td>
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<td>20</td>
<td>0.16</td>
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<tr>
<td></td>
<td>20</td>
<td>0.25</td>
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**Pyroxene compositions.** The extremely fine grain-size of specimen 2832 prevented complete purification of the clinopyroxene. Optical and X-ray powder examination showed the presence of quartz and rare apatite and rutile. Plagioclase was not detected. The analyzed concentrate (>90% pyroxene) was corrected by subtracting 0.2% apatite (indicated by the P₂O₅ content of 0.11% in the analyses) and 7.8% quartz (determined by calculation of the analysis to an ideal pyroxene composition + excess quartz). A pure pyroxene concentrate was obtained from specimen 2833.

Although both pyroxenes are rich in jadeite + acmite and both have very high Mg/Mg + Fe²⁺ ratios (Table 3), they are very different chemically and reflect the different total rock compositions. The pyroxene from specimen 2833 is an omphacite, closely comparable with pyroxenes in eclogites associated with glaucophane schists of California and New
### Table 3. Chemical Compositions, Structural Formulae and Proportions of Pyroxene End-Members in Pyroxenes from Guajira “Eclogites”

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<td>Acmite</td>
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<td>8</td>
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<tr>
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<td>38</td>
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<tr>
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<td>2</td>
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<tr>
<td>Diopside</td>
<td>13</td>
<td>46</td>
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<tr>
<td>Hedenbergite</td>
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<td>6</td>
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**Optical Properties**

<table>
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<tr>
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<th>2832 Px</th>
<th>2833 Px</th>
<th>2832 Px</th>
<th>2833 Px</th>
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<tr>
<td>a (minimum)</td>
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<td>1.672±0.002</td>
<td>9.494±0.002</td>
<td>9.596±0.002</td>
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<tr>
<td>b (average)</td>
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<td>1.679±0.003</td>
<td>8.623±0.001</td>
<td>8.783±0.002</td>
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<tr>
<td>c (maximum)</td>
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<td>1.697±0.002</td>
<td>5.223±0.001</td>
<td>5.266±0.002</td>
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<td>68-70°C</td>
<td>107°26’±1’</td>
<td>106°54’±1’</td>
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<tr>
<td>Z(\perp c)</td>
<td>49±1°</td>
<td>48-60°C</td>
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</table>

|Molecular Proportions|
| Acmite | 14 | 8 |
| Jadeite | 68 | 38 |
| Tschermak’s silicate | 3 | 2 |
| Diopside | 13 | 46 |
| Hedenbergite | 2 | 6 |

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*a The analyzed pyroxene concentrate (column 1) has been corrected for an admixture of 7.8% Quartz, 0.2% Apatite to yield the composition of column 2. b Unit cell values determined using USGS computer program No. 9214 (Least Squares Unit Cell Refinement) and an IBM 7090 computer at the Stanford University Computation Center. c In zoned crystals, 2V_2>c>2V_2rim and Z\(\perp c\)>Z\(\perp c\)rim.*
Caledonia (Coleman et al. 1965). The pyroxene falls near the maximum jadeite content of the eclogitic pyroxenes described by Coleman et al. The pyroxene from specimen 2832 is a jadeite (68 mole % jadeite) which has minor acmite (14%) and diopside-hedenbergite (15%) solid solution. We know of no previous report of such jaditic pyroxene coexisting with garnet and quartz, but in its chemical composition, the jadeite is similar to the Clear Creek, New Idria, jadeite (Coleman 1961) and to other jadeite described by Coleman (1965) and Coleman et al. (1965). These examples of jadeite are not associated with garnet but commonly occur with glaucophane, albite, and crossite in tectonic inclusions in serpentinite. The most sodic pyroxenes coexisting with almandine-pyrope garnet previously described are those containing 9.01% Na₂O (50% Jd, 12% Ac) and 8.80% Na₂O (50% Jd, 10% Ac) from basaltic diatremes in Arizona and Utah (O'Hara and Mercy, 1966a). The latter two pyroxene compositions lie between the two Colombian examples—this is well illustrated on a triangular Jd–Ac–(Di+He+Tsch) plot (Coleman et al. 1965). The Guajira rocks thus greatly extend the compositional range of jadeite-bearing pyroxenes occurring in eclogitic rocks, i.e. in equilibrium with almandine-pyrope garnet and in the absence of plagioclase. It is emphasized that the high jadeite content of pyroxene 2832 is attributed directly to the particular bulk chemical composition of the rock 2832 and does not necessarily imply p–T conditions of crystallization different from those of the eclogites and pyroxenes described by Coleman et al. (1965).

**Material Parageneses and Element Partition**

_Mg, Fe partition_: The values of the partition coefficient K'_{Mg,Fe} for the Guajira eclogites are 43 (2832) and 30 (2833) and are similar to those of the glaucophane schist terrane eclogites (range 11–38, average 21, Banno and Matsui 1965; Banno, unpublished).

The eclogites described by O'Hara and Mercy (1966a) have K'_{Mg,Fe} values of 13 (GR6) and 21 (GR1) i.e., within the range of the eclogites of glaucophane schist terranes or transitional towards those of amphibolite facies terranes. The presence of lawsonite (Watson, 1960) in eclogites from this locality is further evidence for a relatively low temperature of crystallization of the Arizona-Utah eclogites.

_Ca, Mg, Fe distribution between garnet and pyroxene, and the role of zoisite_: Coleman et al. have argued that eclogites from glaucophane schist terranes (Group C eclogites) contain garnets of characteristically high

\[ K'_{Mg,Fe} = \frac{\left(\frac{Mg^{2+}/Fe^{3+}}{Mg^{2+}/Fe^{3+}}_{ox}\right)_{Gp}}{\left(\frac{Mg^{2+}/Fe^{3+}}{Mg^{2+}/Fe^{3+}}\right)_{Gg}}. \]
almandine and high grossular-andradite contents. The Guajira eclogites contrast with those described by Coleman et al. in having garnets with much lower contents of grossular-andradite and the eclogites described by O'Hara and Mercy (1966a) appear to continue this trend with garnets of even lower Ca-content. The use of a Ca-Mg-(Fe+Mn) (atomic proportions) plot (Fig. 2) illustrates the relative compositions of coexisting garnet and pyroxene and the control that total rock chemistry plays in determining the Ca-content of garnet. The differences in Ca, Mg, Fe distribution between the Group C eclogites (Coleman et al. 1965), the Guajira eclogites and the Arizona eclogites are attributed to differences in bulk chemical composition rather than to different conditions of crystallization.

The latter point is more clearly illustrated in an ACF plot (A = Al$_2$O$_3$ + Fe$_2$O$_3$ - (Na$_2$O + K$_2$O); C = CaO; F = FeO + MgO + MnO (Fig. 3). The presence of clinozoisite\(^1\) as a separate phase in some eclogites implies that the rock composition lies in field A of Figure 3 and the coexisting garnet should contain the maximum grossular content for the particular \(p-T\) conditions. In the three clinozoisite or epidote bearing eclogites plotted in Figure 3 (A, 1, 2) the rock compositions lie well on the Ca-Al side of the garnet-clinopyroxene join, consistent with the interpretation of the clinozoisite or epidote as a stable, essential phase. These three clinozoisite-bearing eclogites should contain garnets with maximum grossular content, but, as shown in Figure 3, the grossular-andradite content varies from 20 mole % (A or 2832) to 29% (No. 2) or 39% (No. 1). Either the three assemblages represent very different \(p-T\) conditions of equilibrium or other chemical factors, not evident in Figure 3, determine the Ca-content of garnet. The analysis by Banno (1967) of factors determining the Ca-content of garnet in the analogous assemblages of kyanite eclogite favors the latter interpretation. In the case of kyanite eclogites, the maximum grossular content of garnet may be greater in quartz-free eclogite than in quartz-bearing kyanite eclogite (O'Hara and Mercy, 1966b). In the clinozoisite eclogites plotted in Figure 3, assemblage 1 (113-RGC-58) does not contain quartz and has the highest grossular content while both assemblages 2 and A contain free quartz. Banno has also shown, following Sobolev, Zyuzin and Kuznetzova (1965), that the grossular content of garnet is strongly dependent on the Na$_2$O content of the coexisting pyroxene, and for garnets with greater than 60 percent pyrope-almandine the grossular content of garnet decreases with increasing Na$_2$O content of pyroxenes. Assemblages 1 and 2 contain similar Na$_2$O contents in their respective pyroxenes (5.9% and 6.5%) but as-

\(^1\) Lawsonite may be expected to play a similar role to clinozoisite.
Fig. 3. ACF diagram (mol. proportions) for zoisite eclogites (1, 2, A) and simple garnet + pyroxene eclogites from Colombia (B) and Arizona (3, 4). Symbols and numbers as in Fig. 2. A' is a replot of whole rock composition 2832(a) corrected for CO₂ content, assuming the presence of CaCO₃. B' and 3' are whole rock compositions derived by correcting the analyzed FeO, Fe₂O₃ contents to values derived from the mineral analyses and the approximate mode.

Figs. 3a, 3b, 3c illustrate the deduced variation in maximum solid solution of grossular in garnet and the position of the ga-px-cz field in quartz-free eclogite (3a) in quartz-bearing eclogite (3b) and in a garnet+jadeite+quartz (3c) assemblage.

Assemblage A with 12.1 percent Na₂O in the pyroxene, in accord with Ban- no's arguments, has a lower grossular content. Thus we consider that the positions of the two-phase garnet+pyroxene and three-phase garnet + pyroxene+clinozoisite fields in ACF diagrams of the eclogite facies are sensitively dependent on the presence or absence of quartz and on the jadeite+acmite content of the coexisting pyroxene (Figs. 3a–c). The two-phase garnet+pyroxene assemblages of 2833 (B in Fig. 3) and GK6, GR1 (O'Hara and Mercy, 1966a) lie within the appropriate two-phase
field and on the (Fe+Mg)-rich side of the garnet-pyroxene join of specimen 2832.

The data presented show that the mineral compositions and parageneses of the Guajira rocks are generally similar to those of the Group C eclogites of Coleman et al. (1965) i.e., eclogites associated with glauco-phonite schists. The observed differences in mineral compositions are attributed to differences in total rock chemical composition and to mineral partition relationships. The presence of traces of glauco-phonite in specimen 2833, the absence of kelyphitic alteration of garnet and pyroxene, and the distinctive textures of these rocks (sharply euhedral, zoned garnets enclosed in much finer grained lepidoblastic pyroxene±quartz) are further points of similarity to the Group C eclogites.

The Guajira eclogites also have similar mineralogical characteristics to the Arizona-Utah eclogites (Watson, 1960; O'Hara and Mercy, 1966a) but the latter eclogites occur as xenoliths in a volcanic diatreme. They are associated with xenoliths of crustal sedimentary and metamorphic rocks, and ultramafic rocks ranging from harzburgite to talc schists. Their mode of occurrence has invited comparison of these eclogites with those occurring in diamond-bearing kimberlite pipes but their mineralogy, element partition relationships and bulk chemical compositions are unlike the rather restricted group of eclogites occurring in kimberlites. It is suggested that the Arizona-Utah eclogites are accidental xenoliths of low-temperature eclogites similar to those of California.

**Conditions of Metamorphism**

From the mineralogical data presented it is possible to place some limits on the \( p, T \) conditions of the Guajira eclogites by comparison with various experimental studies (Fig. 4). The clinopyroxene 2832 contains 15 percent diopside and 15 percent acmite solid solution and the pressure required for its stability in the presence of quartz is below that required for its stability in the presence of quartz is below that required for the albite=rayeite+quartz reaction (Birch and Le Comte, 1960; Kushiro, 1965; Coleman, 1965). The field association in California of similar jadeitic pyroxene+quartz assemblages with aragonite rather than calcite (Coleman, 1965) suggests conditions of crystallization between 7 and 11 kbars for an assumed temperature of 300°C.

The association of clinozoisite+quartz and the presence of paragonite place some limits on the temperature of crystallization (Holdaway 1966, Eugster and Yoder 1955) but the suggestion that the intimately associated clinozoisite and paragonite have replaced lawsonite places a more severe restriction on the initial conditions of crystallization of specimen
ECLOGITE FROM COLOMBIA

2832 (Newton and Kennedy, 1963). The coupled reaction of lawsonite with jadeite and the probability that $p_{\text{H}_2\text{O}} \ll p_{\text{total}}$ (as indicated by the absence of amphibole and chlorite from 2832) would effectively lower the breakdown temperature of lawsonite (Fig. 4).

Fig. 4. Diagram illustrating the estimated $p_{\text{total}}$, T field of crystallization (heavily shaded area) of the almandine-jadeite-quartz-clinozoisite assemblage of specimen 2832. The lines AB and CD are from Green and Ringwood (1967) and represent the appearance of garnet and disappearance of plagioclase respectively in a dry quartz tholeiite composition with 100 Mg/Mg+Fe$^{++}$ = 60. The P, T field on the high pressure side of CD is regarded as the field of stability of eclogite under dry conditions. The positions of the albite $\Rightarrow$ jadeite+quartz, calcite$\Rightarrow$aragonite and the stability relations of lawsonite are taken from the literature (see text). The fields X, Y, Z are estimated P, T fields for formation of eclogites in glaucophane schist terranes (X), in amphibolite or high grade metamorphic terranes such as Norway, Germany, France (Y) or as xenolithic inclusions in diamond-bearing kimberlite pipes (Z) (cf. Green, 1966). The positions of estimated geothermal gradients in oceanic and continental regions are also shown.
The available data on mineral stability fields and the rather distinctive mineral paragenesis of specimen 2832 yield an estimate of the conditions of crystallization of this assemblage as $T = 200 - 400^\circ$C, $p_{\text{total}} = 7 - 12$ kbars and $0 < p_{\text{H}_2\text{O}} < p_{\text{total}}$ (Fig. 4). The accompanying specimen (2833) may have crystallized in the same $p$, $T$ environment or under somewhat lower pressure conditions. The stability of these assemblages relative to hydrated assemblages such as glaucophane schists or amphibolites is attributed to local water pressures being very much less than total pressure.

Acknowledgments

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On the Occurrence of Eclogite in Western Norway

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On the Occurrence of Eclogite in Western Norway*

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Abstract. Recent experimental data show that eclogites may form in the crust under conditions where total pressure exceeds water pressure. The regional distribution of eclogites in Western Norway and their association with crustal rocks makes their formation in the crust the most attractive hypothesis. Before a mantle origin should be assigned to any rock within this eclogite and garnet peridotite area it should be demonstrated that their country rocks are in a metamorphic state incompatible with the load pressures required for eclogite stability. Criteria for ascertaining eclogite formation in the crust are discussed.

Introduction

At the present time there is intense interest in the nature of the upper mantle. Goldschmidt (1922) suggested that eclogites could be possible upper mantle constituents. The feasibility of this suggestion has been amply verified by experimental studies of the basalt-eclogite transition. It has also been shown (e.g. Bearth, 1959) that basaltic rocks of surface or near-surface origin can be depressed in the crust and become eclogites. Thus when an eclogite is encountered in a metamorphic terrain the question must arise: “Is this rock formed in the crust or has it been introduced from the mantle?” Because the upper mantle is in fashion, there is perhaps a tendency to mantle-ize, if possible. Today, there is an increasing body of evidence suggesting that convective and gravitative forces may drag crustal materials deep into the mantle. Similarly, there have long been suggestions of tectonic emplacement of upper mantle materials in orogenic regions (de Roever, 1957).

Recently, we visited a number of eclogite and garnet peridotite occurrences in Romsdal, Sunnmøre and Nordfjord, Western Norway. Some of these were included in Eskola’s (1921) classical studies on eclogites. Most recent studies of these eclogites have interpreted them as metamorphosed dolerites, gabbros and other crustal rocks (Gjelsvik, 1952; Hernes, 1954; Kolderup, 1955, 1960; Schmitt, 1963, 1964; Bryhni, 1966) but others have argued for tectonic emplacement of upper mantle eclogite and garnet peridotite into crustal gneisses (O’Hara and Mercy, 1963; Lappin, 1966; Carswell, 1968a, b). Our attention was focussed on the immense difficulty of proving that these eclogites were indeed upper mantle or tectonically emplaced.

This problem has partly arisen from lack of clear data concerning the conditions of formation of eclogites and particularly from an erroneous conviction that the

* Publication no. 8 in “the Norwegian geotraverse project”. 
pressures required for eclogite stability are only attained within the upper mantle. Recent data clarify these points. First, we know that eclogites do form from crustal materials and the metamorphosed pillow lavas described by Bearth (1959) are a striking example. Second, experimental studies have shown that at moderate temperature, eclogites can form from rocks of appropriate composition, at pressures well within the crustal range (Green and Ringwood, 1967). If we consider that crustal thicknesses of 45 km are not uncommon and may reach 60 km in active orogenic regions, then metamorphic assemblages formed at load pressures of 15—17 kb may be expected in crustal materials. Eclogites could be stable in dry basaltic rocks at such pressures at temperatures below 900°C. On the other hand partial melting of crustal materials could occur at these conditions if hydrous minerals are present.

**Eclogite and Amphibolite Relationships**

It is of considerable importance to understand the stability of eclogite mineralogy relative to amphibolite. Green and Ringwood (1967) and Essene and Fyfe (1967) predicted that at sufficiently high $P_{H_2O}$ the assemblage garnet + omphacite + water (eclogite) would be stable relative to amphibole. Preliminary experiments by Essene et al. (1969) show that at a temperature of 700°C, a pressure ($P_{H_2O} = P_S$)\(^1\) of $21 \pm 3$ kb is required for the breakdown of amphibolite to yield eclogite. Fyfe and Fry (1969) also considered the stability of eclogite in wet rocks where $P_{H_2O} = P_S$. Their analysis was based on data concerning the stability of amphiboles and the gabbro-eclogite transition. If these data are treated thermodynamically it is possible to construct a phase diagram for the amphibolite → eclogite transition which shows that if $P_{H_2O} = P_S$, eclogites cannot form in any normal crust but would be replaced by amphibolite or amphibole-rich assemblages.

From both the experimental and thermodynamic data, it can be said with some certainty that if eclogites are to form in the crust we must have conditions of relatively dry rocks or $P_{H_2O} < P_S$ and a total pressure in accord with the gabbro-eclogite transition (Fig. 1). How and when the transition occurs will depend on all the factors involved in a solid state reaction requiring diffusion over distances related to the grain-size and fabric of the original basaltic materials. Studies of Fe/Mg distribution coefficients between garnet and clinopyroxene (Banno and Matusi, 1965; Lovering and White, 1969) suggest that eclogite formation occurs over a wide temperature range and thus probably over a range in pressure. On the basis of these Fe/Mg distribution coefficients, absence of glaucophane and lawsonite and presence of kyanite and calcic hornblende, the Norwegian eclogites are inferred to have crystallized at higher temperatures than for example, the Californian eclogites.

**Country Rocks**

Before an eclogite found in the crust is given a mantle origin, it is necessary to first consider whether or not the host crustal rocks exhibit a mineralogy which would indicate pressures significantly lower than those required for the basalt-\(^1\) $P_S = \text{pressure on solid phases. } P_f = \text{pressure on fluid phase if this is present. } P_{H_2O} = \text{water pressure.}$
eclogite transition, taking into account that the enclosing rocks may represent a much wetter metamorphism. In this connection it is of considerable interest to compare the kyanite-sillimanite curve with that of gabbro-eclogite (Fig. 1). It will be noted that these are similar in slope and position. It would be surprising to find eclogites in sillimanite-zone metamorphic rocks, but eclogite or high pressure granulite ($gs + cp\pm plag \pm quartz$) assemblages should be typical of dry basic rocks in kyanite-zone metamorphic rocks.

In Western Norway kyanite has occasionally been reported in rocks associated with eclogites (Schmitt, 1963; Lappin, 1966; Bryhni, 1966; Green; unpublished). Sillimanite occurs in some of the gneisses but Schmitt (1963) demonstrated that, in Hareid, it postdates eclogite formation and locally replaces kyanite. Kyanite-bearing gneisses and eclogite are associated in Eastern Sudetes, Poland (Kozlowski, 1958) and apparently also in the Alps. In California, the association of eclogites with metasediments which have crossed the albite–jadeite–quartz boundary
(Fig. 1) demonstrates that in this area also the country rocks have been well within the eclogite stability field.

In Western Norway we were impressed by the frequency of occurrence of eclogite or garnet-bearing coronites. In fact, over a very wide area, it seems that almost every basic rock contains a pyroxene-garnet assemblage, often partially destroyed by later amphibole formation. There may be more than one period of basaltic intrusion in this area (bodies range from syn-tectonic or pre-tectonic lenses and boudins to clearly intrusive late-tectonic or post-tectonic sheets). It is also as yet uncertain whether the coronites represent cooling of an igneous body into the high pressure granulite field or through this field into the eclogite stability field (Fig. 1). However, it is apparent that reactions have occurred on a regional scale appropriate to load pressures in excess of 10 kb. In this environment, it is unnecessary to ascribe other eclogite and garnet peridotite lenses to a mantle origin, their mineral assemblages may be in no way incompatible with their country rock environment. In an excellent, detailed study of the Eiksundsdal Eclogite Complex and its associated country rocks, Schmitt (1963, 1964) demonstrated a common origin for interlayered eclogites and garnet peridotite and provided evidence for their initial crystallization as olivine, pyroxene and plagioclase-bearing basaltic accumulates, later metamorphosed along with their country rock environment, under high pressure conditions.

Advocates of an upper mantle origin for the eclogites and garnet peridotites have emphasized the “tectonic contacts” against the enclosing gneiss. However, if dry basic rocks are enclosed in wetter metasediments their mechanical or deformational properties will not be similar. This will make description of tectonic features indicating tectonic emplacement a matter of extreme difficulty. For instance, do shear zones on serpentinite margins always imply large scale tectonic movements or do they reflect large differences in the mechanical properties of the rocks being deformed? There are excellent examples showing that such differences are highly significant in deformation and in Western Norway it should be emphasized that boudin structure and lenticular form of contrasted rock types are common within the gneiss and are not a characteristic of eclogite or peridotite alone.

The Role of Partial Melting in Eclogite-Bearing Terrains

Having recognised that crustal eclogites would require the involvement of dry basaltic materials one might well ask what would be the ideal situation for the production of eclogites? Clearly deep burial of a massive pile of dry basaltic material would be appropriate. Free movement of water vapour, i.e. a permeable rock column, would likewise provide a mechanism by which $P_{\text{H}_2\text{O}} < P_\text{S}$ (Yoder, 1955), but it is improbable that such permeability exists during a deep metamorphism or could cause a sufficient difference in the variables. With respect to Norwegian rocks one can suggest another model. It is possible that here one is working with a very old basement which has been through a cycle of partial melting and hence dessication. After such a cycle or during the late stage of such a cycle, water will be present only in minerals such as biotite and hornblende. If such a basement were intruded by basic dykes, conditions could be unfavourable
Fig. 2. Diagram illustrating the possible effects of partial melting in a mixed amphibolite + feldspathic gneiss terrain under conditions of $P_{H_2O} < P_s$. Solid lines refer to feldspathic gneiss, dashed lines refer to basic compositions. Lightly stippled area: gabbro→eclogite transformation in "dry" basaltic compositions ($P_{H_2O} = 0$). A solidus for feldspathic gneiss (plagioclase + K-feldspar + quartz + biotite ± amphibole) for $P_{H_2O} = P_s$. A' solidus for $P_{H_2O} = 6$ kb. B solidus for amphibolite (hornblende + quartz ± plagioclase ± garnet ± biotite) for $P_{H_2O} = P_s$. B' solidus for $P_{H_2O} = 2$ kb. X maximum stability limit of amphibole from amphibolite B for $P_{H_2O} = P_s$. X' stability limit for $P_{H_2O} = 2$ kb. O→O' Postulated path of metamorphic terrain during prograde, metamorphism in deeply buried "basement". N→N' Variation in $P_{H_2O}$ in a low melting liquid from gneiss A during prograde metamorphism O→O'. The positions of solidi, amphibole breakdown etc. are estimated from data by Yoder and Tilley (1962), Essene et al. (1969), Lambert and Wyllie (1968), and Green (unpublished data). Lines of equal water pressure (A', B' etc.) have been drawn as straight lines but in real systems will be slightly curved

to amphibolite formation, but given sufficient burial, could be favourable for eclogite formation ($P_{H_2O} < P_s$; Figs. 1, 2). These conditions would particularly apply to an older basement involved in a second orogenic and metamorphic episode. The possibility of partial melting under these high pressure conditions, water being supplied by destruction of hornblende and biotite, would also strongly influence the $P_{H_2O}$ conditions. In Fig. 2 we consider metamorphism and partial melting of a basement including feldspathic gneiss and amphibolite in which water is present in hornblende and biotite. Point O represents a condition along a geothermal gradient which the metamorphic terrain attains during deep burial. At O, $P_s = 15$ kb, $T = 750^\circ$ C and $P_{H_2O}$ is some value determined by the phase assem-
blages, particularly the hornblende and biotite. $O$ lies at a temperature higher than the solidus for $P_{H_2O} = P_s$ so that any breakdown of biotite or hornblende solid solutions to anhydrous phases and water will immediately cause melting. The condition for the reaction biotite + hornblende + etc. $\rightarrow$ melt + etc. may be exceeded in the feldspathic, but not for the different phase composition and assemblage of the amphibolite.

The melt formed at $T = 750^\circ$ C, $P_s = 15$ kb, $P_{H_2O} \approx 6$ kb will contain approximately 10% water (Burnham, 1967, p. 65) and, if the gneiss originally contained 1% water, then the degree of melting accompanying the destruction of the hydrous phases is $\approx 10\%$. At this point the magma may segregate and migrate, becoming essentially an independent chemical system open to reaction with surrounding rocks, or it may remain as a dispersed fluid phase ($P_s = P_F > P_{H_2O}$) within the chemical system defined by the feldspathic gneiss bulk composition. In either case, temperature increases ($0 \rightarrow 0'$) will lead to an increase in the amount of partial melting of anhydrous silicates, residual from the reaction: biotite + hornblende + etc. $\rightarrow$ melt + etc. If the volume of the melt increases from 10 to 20% of the initial gneiss, or doubles in volume by reaction with enclosing rocks, then the water content will drop to 5%, giving, at $T = 850^\circ$ C, $P_s = 15$ kb a value of $P_{H_2O} \approx 1 - 2$ kb (Burnham, 1967, p. 37). Such estimates are rough. For instance, if there is no segregation of magma from its initial source rock, then $P_{H_2O}$ cannot decrease below 2.5 kb at 850$^\circ$ C or the melt will crystallize (Fig. 2). Similarly, any breakdown of hydrous phases in neighbouring rock types may increase the water content and partially counteract the effect of increased partial melting. Nevertheless, it is clear that partial melting of crystalline rocks containing small amounts of water may lead to low values of $P_{H_2O}$, yielding a "buffered" condition of $P_s = P_F > P_{H_2O}$ (see also Burnham, 1967, pp. 64-72.) The approximate variation in $P_{H_2O}$ in the feldspathic gneiss as temperature increases from 750 to 850$^\circ$ C is shown in Fig. 2 by the shaded area N-N'. The resultant decrease in $P_{H_2O}$ during the partial melting may make amphibole unstable in neighbouring amphibolite leading to breakdown to eclogite + a small fraction of water-rich melt.

This point can be put in another way with respect to Fig. 2. Consider a region of mixed granitic-basaltic materials at a pressure such as 15 kb and 900$^\circ$ C where $P_{H_2O}$ is controlled by the vapour pressure of minerals such as hornblende and biotite. Let us assume that $P_{H_2O}$ in the environment has some value (say 5 kb) set by the hydrates. From Fig. 2 it is obvious that both granite and basalt could melt. Granitic fractions will progressively melt until $P_{H_2O}$ reaches about 2 kb causing hydrated minerals to decompose. But as this $P_{H_2O}$ is lower than can be reached by the more basic melt this will lose water to more acid fractions and solidify. The net result is a transfer of water from basic to acid regions.

We consider that partial melting in a metamorphic terrain of low water content and mixed gneisses can effectively lower the partial pressure of water and buffer it at a low value, leading to dehydration of mineral assemblages, particularly in more refractory mafic rock types. This situation is very different from that occurring where dehydration occurs without partial melting.

In Western Norway migmatization occurs within the gneisses throughout the eclogite-bearing region. Age relations of this migmatization to the eclogite crystallization remain unknown. In particular we have observed small irregular patches
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of plagioclase + hornblende + quartz (+ biotite + garnet) pegmatite closely associated with many eclogite lenses. They commonly occur in the necks of eclogite boudins or as irregular schlieren in the country rock gneiss. Such patches may have been liquids at the time of eclogite crystallization and have been undersaturated in water ($P_{H_2O} < P_p$). If during a later temperature drop in the area, these bodies of liquid began to crystallize, then their $P_{H_2O}$ would rise, causing crystallization of hornblende and minor biotite from the liquid and local hydration with growth of amphibole in neighbouring eclogite. This explanation may account for the presence in some eclogites of large poikiloblastic hornblende whose form suggests replacement of garnet and pyroxene at an early stage, differing markedly from the kelyphitic and patchy amphiboles of later alteration stages.

Concluding Statement
Before a mantle origin is assigned to eclogite and garnet peridotites associated with crustal rocks, it is quite necessary to show that the crustal rocks are in a metamorphic state incompatible with the load pressures required for eclogite stability. In this respect it is of paramount importance to distinguish mineralogical differences due to differences in $P_{H_2O}$ or other chemical characteristics from differences in $P_s$ and $T$. Examination of the Western Norway eclogites on this basis has not yet been carried out but there is fragmentary evidence strongly suggesting the regional extent of high pressure metamorphism characterized by $P_{H_2O} < P_s$ and pressures appropriate to eclogite and garnet peridotite metamorphism of pre-tectonic, syntectonic and late tectonic gabbroic and ultramafic rocks.

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EXPERIMENTAL STUDY OF AMPHIBOLITE AND ECLOGITE STABILITY

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EXPERIMENTAL STUDY OF AMPHIBOLITE AND ECLOGITE STABILITY

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The amphibolite-eclogite transition is often observed in metamorphic rocks and may be expected to occur in the lower crust or upper mantle if \( P_{H_2O} \approx P_s \). Many simple amphiboles become unstable at high water pressures due to backbending of dehydration reactions or to solid–solid transitions involving sheet silicates. Contrary to YODER and TILLEY (1962), eclogite is expected to be stable relative to amphibolite at sufficiently high water pressures because of the formation of dense garnet and the high compressibility of water vapor. Experiments in progress on several basaltic compositions have produced eclogite at the expense of amphibolite at high water pressures. Seeding has been found to be important as hornblende crystallizing from glass will persist at least 4 kb above its stability field defined by reversals with garnet-pyroxene-amphibole mixtures. In reconnaissance experiments on a quartz tholeiite and an alkali olivine basalt, hornblende appears at high water pressures between 15–25 kb and 700–900 °C. Biotite appears to be stable in the alkali olivine basalt to at least 40 kb at these temperatures. Basaltic amphibolites do not appear to be stable very far into the low-velocity zone even at \( P_{H_2O} = P_s \) confirming LAMBERT and WYLLIE's (1968) earlier experiments. Biotite however seems to be stable deeper in the mantle (at least for potassic basalts) than previously considered possible if \( P_{H_2O} \approx P_s \) and may be a source of water for magmas when partially melted.

1. Introduction

Eclogite and amphibolite relationships have long been of interest to the petrologist as both rocks are closely associated in metamorphic terranes. The classical petrological studies of HEZNER (1903), BRIERE (1920), ESKOLA (1921) and TILLEY (1936, 1937) showed that early-formed eclogites have often become partially hydrated to amphibolites. ESKOLA (1939) originally placed the eclogite facies at the highest pressures and temperatures, but it is now recognized that eclogites may form at relatively low pressures as well. If eclogites form at relatively low temperature and low \( P_{H_2O}/P_T \), then increase of water pressure could hydrate the eclogites to amphibolites (or glaucophane schists) as suggested by SAHLSTEIN (1936), BEARTH (1959), GREEN and RINGWOOD (1967) and others. For \( P_{H_2O} \leq P_T \), other gases must be very abundant to keep \( P_F \approx P_T \), or there can be no vapour phase as in the water-deficient region (YODER, 1955). A third possibility is that the thermodynamic properties of intergranular films of impure water are markedly different from those of pure water. Most eclogites (except for rare scapolite-bearing varieties) show little evidence of abundant gas other than water, though of course they need not be evident in the preserved solid phases. One may again question the possibility of crystallizing a coarse-grained eclogite from an initial olivine-pyroxene-feldspar rock in the absence of a vapour phase without leaving traces of the original basaltic minerals, though BEARTH (1965) has observed all steps of the basalt–eclogite transition for some unusual eclogites. The possibility that the partial pressure of impure water is considerably lower “in solution” along grain boundaries than pure water vapour at the same \( P-T \) cannot be properly evaluated at present. To avoid the apparent difficulty in these explanations ESSENE and FYFE (1967) postulated that eclogites are stabilized relative to amphibolites at high water pressures and showed that density data alone confirm this prediction. Similarly, GREEN and RINGWOOD (1967, p. 805-6) showed that amphibolites including the simple end member tremolite, will break down to anhydrous products and water vapour at sufficiently high \( P_{H_2O} \) and argued that this would considerably restrict the stability of amphibole in the upper mantle. Experiments are clearly needed to resolve the role of water pressures in the formation of eclogites.
Previous experiments

Yoder and Tilley (1962) showed that the stable solidus assemblage for many basaltic rocks is amphibolite for $P_T = P_{H_2O} > 2$ kb, $< 10$ kb, $T > 600 ^{\circ}C$, concluded that eclogite is unstable in the presence of water for all water pressures. However the beginning of melting could develop a positive slope and the disappearance of amphibole a negative slope at high water pressures due to the formation of garnet and the high compressibility of water. The combination of these two aspects leads to the stabilization of eclogite relative to amphibolite at sufficiently high water pressures (fig. 1).

![Figure 1](image.png)

**Fig. 1.** A possible geometry for the beginning of melting and stability of amphibole in basaltic rocks. The solid-solid transformation of feldspar to garnet and the high compressibility of water combine to stabilize eclogite at high water pressures.

$Fs = $ Feldspars, $Px = $ Pyroxenes, $gn = $ garnet.

This geometry has been confirmed in preliminary synthesis experiments on hornblende stability under its natural composition and in a gabbro by Lambert and Willie (1968). Hensen and Green (unpublished) established the synthesis limit of hornblende in an alkali olivine basalt* with similar results also for $P_{H_2O} \approx P_T$ (fig. 2). These experiments show that eclogite is stable at high water pressures but represent syntheses mostly in the supersolidus region.

Thermodynamic calculations

Many simple amphiboles can be shown to be unstable at high water pressures by thermodynamic calculations which permit extension of experimental data to higher water pressures (see Appendix I for thermodynamic data and procedures)*. The simple dehydration of tremolite (Boyd, 1959) will develop a negative slope at high water pressures due only to the rapid compressibility of water vapor, as predicted by Green and Ringwood (1967). At high enough water pressures the curve $tremolite = diopside + enstatite + quartz + water$ will cross the $talc = enstatite + quartz + water$ curve and a solid-solid decomposition of tremolite $= talc + diopside$ is found instead (fig. 3). A similar solid-solid transformation predicted for anthophyllite by Greenwood (1963) is also shown in fig. 3, though calculations using Robie et al.'s (1967) volume data would move this curve to at least 50 kbar. Glaucophane might similarly be expected to break down to talc + jadeite at high pressures (shown schematically in fig. 3), and the curve could be located more exactly if dependable experiments were available for the stability of glaucophane. Amphiboles may also break down at high water pressures.

![Figure 2](image.png)

**Fig. 2.** Stability of amphibole for an alkali olivine basalt as determined by syntheses in cold-sealed gold capsules. The restriction of garnet to relatively high pressures is probably a reflection of the lack of initial garnet nuclei. This stability of amphibole compares well with the hot-sealed synthesis runs of fig. 3, showing that water pressures were not significantly lowered by chance leaks during the run. Am = Amphibole, Bi = Biotite, Px = Pyroxenes.

* These calculations ignore the possibility of partial melting at high water pressures.
high water pressures because the products themselves react to form denser phases, as shown in fig. 3 for a "hornblende" $= \text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$. The initial point for the curve “hornblende” $= \text{anorthite} + \text{diopside} + \text{enstatite} + \text{water}$ is taken at 900°C and 1 kb* and when the feldspar reacts with pyroxenes to yield garnet the stability of this amphibole is sharply backbent (fig. 3). While the true stability of this “hornblende” may be represented instead by some reaction as

$$\text{hornblende}_A = \text{hornblende}_B + \text{pyroxenes} + \text{feldspars} + \text{quartz} + \text{water vapor},$$

the effect of high water pressures when garnet is produced may be qualitatively represented as in fig. 3**.

The instability of these amphiboles at high water pressures disagrees markedly with similar estimates by O’Hara (1967), who extended the stability of amphiboles vertically regardless of reactions among the products giving garnet at the expense of feldspars. O’Hara’s schematic amphibole stability curves are unrealistic and should be disregarded. Extrapolation of simple amphibole stabilities to high water pressures demonstrates that they may decompose by increasing water pressure but bear little on the stability of complex amphiboles which may first react with other phases in natural basaltic compositions.

4. Present experiments

The writers attempted to establish the upper stability limit of amphibole in an alkali olivine basalt and quartz tholeiite for $P_{\text{H}_2\text{O}} = P_S$ by sealing glassy crystalline samples with water and holding them in a piston cylinder apparatus at $P$ and $T$ for $>24$ hours (see appendix II for details of experimental procedure). Amphibole disappeared rather sharply within a 2-kb interval (figs. 4, 5) and in the case of the alkali olivine basalt, compared rather well with earlier experiments with cold-sealed capsules (fig. 3). When the crystalline mixtures of the earlier runs (amphibolite and eclogite) were rerun, amphibole was found to be unstable in a region where it had previously been synthesized, and did not perceptibly grow at the expense of the garnet and pyroxene until the pressure had been lowered 5–10 kb below the original synthesis limit. While the reversal limits are rather wide in these preliminary experiments, they illustrate the danger of accepting short time synthesis experiments as representing equilibrium at these relatively low temperatures, even if the synthesis experiments are well controlled.

![Fig. 3. Stability of various amphiboles estimated at high water pressures. Trem = Tremolite, Di = Diopside, En = Enstatite, Q = Quartz, Hnbde = “Hornblende”, Gn = Garnet, Opx = Orthopyroxene, Cpx = Clinopyroxene, An = Anorthite, Anth = Anthophyllite, Tc = Talc, Jd = Jadeite, Gl = Glauconphane.](image)

![Fig. 4. Stability limit of amphibole in an alkali olivine basalt comparing synthesis runs with reversals. Am = Amphibole, Ec = Eclogite.](image)
5. Stability limit of amphibole in an albite-rich quartz tholeiite, comparing synthesis runs with reversals.

The boundary appears to be rather sharp and reproducible.

The solidus was difficult to locate for these basaltic compositions due to the formation of quench amphibolite and the formation of only a small amount of glass on the solidus. It was estimated from the runs plotted in Figs. 4 and 5 and by comparison with YODER and Tilley's (1962) and LAMBERT and Wyllie's (1968) data.

The solidus for the alkali olivine basalt with 26% normative olivine is thought to be 50-75° higher than that for the quartz-normative tholeiite.

The upper stability of amphibole in supersolidus will involve reaction with melt as well as vapor, and these data have been included to place gross limits on the possible slopes for the supersolidus curves. GREEN and Ringwood (1967) found amphibole between 10.1 and 16.8 kbar at 1100°C with $P_{H_2O} < P_T$ in the alkali olivine basalt and this is used in Fig. 6 to diagnostically fix the amphibole stability. Yoder and Tilley's data on the stability of amphibole in various basalts have been consulted to estimate the amphibole stability in the quartz tholeiite (Fig. 7).

The subsolidus reaction of amphibolite to eclogite is likely to be a sharp transition but a gradual reaction among amphibole, garnet and pyroxenes (and feldspars?). It is best thought of as a sliding reaction with a number of substitutions in each phase and may be generalized as:

$$\text{hornblende}_A + \text{garnet}_B + \text{pyroxene}_C = \text{hornblende}_D + \text{garnet}_E + \text{pyroxene}_F + \text{quartz} \pm \text{olivine} + \text{water}.$$
large number of end members. The area over which this sliding reaction will occur has not been determined experimentally and much longer run times (≈ 1 month) may be needed to establish this zone.

5. Interpretation

The present data suggest that eclogite will form at the expense of amphibolite when pressures are somewhere in the region of 10–30 kb at medium temperatures for basaltic rocks at high water pressures. This generally confirms Lambert and Wyllie’s (1968) experiments, but the difference between syntheses and reversals found here suggests that their synthesis experiments may be in error and should not be used for any specific argument as to magma generation in the upper mantle. Stability of one amphibole in a basaltic rock or under its own composition is no guide to the behavior of another amphibole in an ultramafic rock. Certainly their incoming of garnet at \( P > 18 \text{ kb} \) (Lambert and Wyllie, 1970) is open to doubt as no garnet nuclei were available in the starting mix. Tighter reversals are needed before evaluating the possibility that crustal eclogites form at high water pressures.

Garnet amphibolites lacking feldspar are expected to have higher densities (3.2–3.4 g/cm\(^3\)) and higher estimated seismic velocities (\( V_p = 7.6–8.0 \text{ km/s} \)) than previously thought possible for hydrated basic rocks, and may be important in the lower crust or upper mantle (< 70 km), if water pressures are high. Garnet amphibolites lacking feldspar have been found in high-pressure crustal rocks (Essene, 1967) and may be widespread in the lower crust.

The apparent stability of biotite in the potassic alkali olivine basalt suggests that trioctahedral mica may be an important hydrous phase in the upper mantle. The decomposition of several amphiboles at high water pressures (fig. 3) apparently involves formation of another sheet silicate (talc) at high water pressures. Sclar (1970) has synthesized a 10 Å micaceous phase in the system MgO–SiO\(_2–\)H\(_2\)O at \( P > 30 \text{ kb} \) and \( T < 500 \text{ °C} \) but has not yet shown whether this phase is stable by reversals nor reported its relation to other phases of \( \approx 10 \text{ Å} \) as attapulgite. Kushiro et al. (1967) have examined phlogopite at high pressures and claim it is stable to at least 100 kb, but they have located a solidus in the system outside their stability field for phlogopite, whereas Luth (1967) has shown that phlogopite breakdown curve intersects the solidus at only 2 kb water pressure. This suggests that Kushiro et al. may have had \( P_{\text{H}_2\text{O}} < P_T \) in their runs; they may have also had trouble with quench phlogopite. In a later series of experiments, Yoder and Kushiro (1969) confirmed Luth's data and showed that phlogopite remains stable up to 1200 °C and 40 kb.

Appendix I

The thermodynamic calculations in fig. 3 were based on experimental data, and extended to high pressures and temperatures with the well-known relations

\[ \frac{\delta G}{\delta T} = -\Delta S, \quad \frac{\delta G}{\delta P} = \Delta V. \]

The free energy data for water were taken from Bingham et al. (1968) below 10 kb, and above 10 kb from Sharp (1962). Measured high-temperature entropies (\( S_T - S_{298} \)) are not available for talc, tremolite, and "hornblende" and were estimated by summing the high-temperature entropies of other silicates:

\[ \text{talc} = 2 \text{ serpentine} - 3 \text{ brucite*}, \]
\[ \text{tremolite} = \text{talc} + 2 \text{ diopside**}, \]

and the entropy of "hornblende" was assumed equal to tremolite. From these estimates, the high-temperature entropies of talc and tremolite were fitted to a quadratic equation of the form

\[ S_T - S_{298} = a \ln T + b10^{-3}T + c10^{5}T^{-2} + d, \]

where the values of \( a, b, c, d \) are given in table 1.

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<thead>
<tr>
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<tr>
<td>Talc</td>
<td>+126.26</td>
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<td>+24.89</td>
<td>−74.02</td>
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<tr>
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<td>+10.02</td>
<td>+38.63</td>
<td>−136.6</td>
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The molar volumes (\( V^0 \)) of the silicates were taken from Robie et al. (1967) and the standard entropy (\( S^0_{298} \)) from Luth (1966); these data are not available for "hornblende" and were estimated: \( V^0 = 270.5 \text{ e.u.} \) and \( S^0_{298} = 131.6 \text{ e.u.} \) In making the calculations the charging of the

* Entropy data for serpentine and brucite are from King (1967).
** High-temperature entropy data for diopside are from King (1960).
Table 2

<table>
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<tr>
<th></th>
<th>amphibole</th>
<th>garnet</th>
<th>pyroxene</th>
<th>biotite</th>
<th>rutile</th>
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= major component; x = minor component; tr = trace.

Possibility of the solids was neglected, i.e. $\Delta V_{\text{solids}} = $ constant.

Because of the approximations involved in the estimation of volumes and entropies at high pressures and temperatures, the slopes and locations of the solid-solid reactions can only be regarded as approximate. Negative slopes for these curves cannot be ruled out at present.

Appendix II: Details of experimental procedure

The starting material for the synthesis runs were mixes of the appropriate composition prepared as described by Green and Ringwood (1967). Weighed amounts of glass (10–40 mg) were sealed in Au, Pt or Pt-Pd capsules with 5–10 wt% water added with a microburette. The capsules were sealed with a carbon-finder and reweighed to ensure against loss of the water. For reversals, products of earlier runs containing amphibolite and eclogite were mixed, weighed with additional water and rerun. The capsules were closed with a talc assembly which fitted into the standard graphite furnace and external talc sheath of the Boyd piston-cylinder apparatus. Pt-(Pt+10% Rh) chromel–alumel thermocouples were used to measure control temperatures to ±10 °C. Pressure (10–40 kbar) was first applied then the cell was brought to temperature (600–900 °C) with the piston remaining on the compression stroke; a –10% pressure correction is applied to all runs. Synthesis run times were generally 12–24 hours, but successful reversals required at least 2–3 days. At temperatures >800 °C large pressure and/or temperature drops often occurred due to talc hydration, and boron nitride was substituted for the K-feldspar component to give biotite. The decrease in $d$-spacing (see 221 $d$-spacings (see Eocene and Fyfe, 1967).
References

YODER, H. S. and C. E. TILLEY (1962) J. Petrol. 3 (2), 342–
EXPERIMENTAL DUPLICATION OF MINERAL ASSEMBLAGES IN BASIC INCLUSIONS OF THE DELEGATE BRECCIA PIPES

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subsidius phase relationships have been determined with a piston-cylinder apparatus for compositions representing a garnet clinopyroxenite, a garnet-plagioclase clinopyroxenite and a spinel-garnet websterite from the Delegate basic breccia pipes. Modes of experimentally produced and natural assemblages have been compared to deduce conditions of final equilibration for these inclusions of 14–16 kb, 1050–1100 °C. Some important features of the genesis of the inclusions have been clarified, particularly the role of solid state exsolution phenomena. A relatively high-temperature origin (possibly as basaltic accumulates) is likely for all garnet pyroxenite inclusions in nephelinitic basalts and breccias.

1. Introduction

The garnet-bearing basic inclusions of the Delegate pipes in southeast Australia (LOVERING and WHITE, 1969) are intensively studied examples of a small class of inclusions (rich in pyroxenes, garnet and, in some cases, plagioclase) which have been also described from nephelinitic breccias and basalts of Hawaii (YODER and TILLEY, 1962; WHITE, 1966; JACKSON, 1966), New Zealand (DICKEY, 1968), Algeria (GIROD, 1967), Kenya (SAGGERSON, 1968) and elsewhere in eastern Australia (LOVERING and WHITE, 1964).

This paper is a report of an experimental study undertaken with a view to (a) delimiting conditions of equilibration of the Delegate inclusions and (b) elucidating some features of their genesis.

2. Procedure

Examples of three different inclusion types were selected for study from the material analysed by LOVERING and WHITE (1969):

Garnet clinopyroxenite R392: homogeneous aggregate of clinopyroxene (56%), garnet (35%) with narrow rims of fine clinopyroxene-spinel-“clay” aggregate (8.5%), and a trace of pyrite. Assignment of secondary phases to garnet implies primary weight percent proportions of approximately clinopyroxene 53, garnet 47.

Garnet-plagioclase clinopyroxenite R130: nonhomogeneous aggregate of clinopyroxene, garnet (rimmed by turbid, fibrous material and fine clinopyroxene, orthopyroxene, plagioclase and opaque) and plagioclase (Ab61An39Or3) with accessory rutile, apatite and scapolite. The primary weight percent proportions of phases computed from total rock and mineral data are approximately clinopyroxene 45, garnet 31, plagioclase 22, accessories 2.

Spinel-garnet websterite R394: aggregate of very coarse clinopyroxene with finer interstitial orthopyroxene, scattered large spinel grains (rimmed by garnet) and a trace of olivine and sulphides. The clinopyroxene contains abundant oriented orthopyroxene lamellae, garnet blebs and minor spinel. The computed weight percent proportions are approximately clinopyroxene 68, orthopyroxene 10, garnet 12, spinel 10.

It is important to note that a mineralogical gradation exists between the Delegate garnet and garnet-plagioclase clinopyroxenites; the clinopyroxenes and garnets have very similar compositions in all these inclusions (LOVERING and WHITE, 1969), and certain finely-banded examples display both mineral assemblages in adjacent bands.

The experimental runs were carried out on homogeneous glasses prepared by fusing the natural rock.
powders in an argon atmosphere. The glasses were seeded with 10% of clinopyroxene + garnet of the appropriate composition. Chemical analyses of the starting materials (recalculated volatile-free from rock analyses incorporating redetermined Fe data) are presented in table 1. R392 and R394 are quite similar except for the Mg/Fe$^{2+}$ ratio and both show affinities with an alkali-poor olivine tholeiite composition studied by GREEN and RINGWOOD (1967a); R130 resembles an alkali olivine basalt composition but has high-alumina character.

### TABLE 1

<table>
<thead>
<tr>
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<th>Garnet-plagioclase clinopyroxenite (R130)</th>
<th>Garnet clinopyroxenite (R392)</th>
<th>Spinel-garnet websterite (R394)</th>
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* Redetermined by wet chemical analysis of glass (E. Kiss, analyst). Other values recalculated from analyses of LOVERING and WHITE (1969).

** Calculated from mineral analyses and mode (since the value given by LOVERING and WHITE (1969) is inconsistent with mineral data).

Subsolidus phase relationships were determined for each composition with piston-cylinder apparatus (piston-in technique) using a dry furnace assembly with boron nitride sleeve (cf. GREEN and RINGWOOD, 1967a). In general, graphite sample capsules were employed for runs below 1100 °C and sealed platinum capsules used to establish the solidi (although the latter were used exclusively for runs on R394). Run times of 1 hour (1400 °C, 1300 °C), 2.5 hours (1200 °C), 6 hours (1100 °C) and 18 hours (1000 °C) were used.

Relative proportions of garnet and clinopyroxene were estimated (especially for the garnet clinopyroxene runs) by visual comparison of X-ray powder photographs with those of accurate garnet–clinopyroxene mixtures. Proportions of garnet, clinopyroxene and plagioclase in runs on the garnet-plagioclase clinopyroxene composition proved more difficult to determine and were estimated from powder mounts and, in some cases, from thin-sections of charges. Electron microprobe analysis of selected run products is in progress.

### 3. Results

The three phase diagrams determined experimentally are described briefly below and essential features are shown on a composite diagram (fig. 1). Reported pressures include a −10% correction to the nominal load pressure calculated for the ½-inch piston (GREEN et al. 1966).

#### 3.1. Garnet clinopyroxenite R392

In order of increasing pressure, the subsolidus mineral assemblages observed for this composition are clinopyroxene + plagioclase + olivine (below a), clinopyroxene + plagioclase + spinel (below b), clinopyroxene + plagioclase + garnet + spinel (below c), and clinopyroxene + garnet (above c, 13 kb at 1100 °C). Minor amounts of amphibole occur in runs below 1100 °C and 18 kb. Within the field of clinopyroxene + garnet, subparallel lines of equal garnet percentages are oblique to the solidus; the minimum proportion of garnet is about 20% on the solidus at the low pressure boundary of the clinopyroxene + garnet field.

#### 3.2. Garnet-plagioclase clinopyroxenite R130

At the investigated pressures (above 12 kb) this composition shows a broad field of clinopyroxene + garnet + plagioclase in varying proportions bounded above by a "closed field" (20.5 kb at 1100 °C) by a field of clinopyroxene + garnet (+ quartz?). Minor amphibole is again present in lower temperature and pressure runs.

#### 3.3. Spinel-garnet websterite R394

Although the websterite composition closely resembles the garnet clinopyroxenite (except for a higher Mg/Fe$^{2+}$ ratio), the phase diagram for R394 is quite different in having a subsolidus field of clinopyroxene + spinel + orthopyroxene bounded on the low temper
**GARNET CLINOPYROXENITE**
- GARNET-PLAGIOCLASE CLINOPYROXENITE
- SPINEL-GARNET WEBSTERITE

Temperature °C

1000 1100 1200 1300

**EXPERIMENTAL DUPLICATION OF DELEGATE BASIC INCLUSIONS**

**Discussion**

1. **Genesis of the Delegate inclusions**

Despite several isotope studies (e.g. Lovering and Atsumoto, 1968), the relationships of the Delegate inclusions to associated basaltic materials has not been unambiguously ascertained. From the present study no deductions can be made concerning the original status of the inclusions, but some insight can be gained to the processes of development of the present mineral assemblages.

1.1. **Garnet clinopyroxenites and garnet-plagioclase clinopyroxenites.** As an alternative to formation by direct crystallisation of clinopyroxene and garnet, Lovering and White (1969) suggested that the Delegate garnet clinopyroxenites may be the end products of exsolution of garnet at high pressure from an original complex pyroxene aggregate, a hypothesis also proposed (Green, 1966) for garnet websterite inclusions in olivine nepheline tuff at Salt Lake Crater, Hawaii. The fact that there is a minimum of 20% garnet 80% clinopyroxene on the solidus of R392 precludes an origin wholly by exsolution processes for the garnet of these rocks. It is possible that 20% of the observed garnet of R392 is primary and a further 27% has exsolved from pyroxene, however there is no textural evidence of exsolution in this or any other of the Delegate garnet clinopyroxenites examined.

For reasons outlined above, it seems likely that the garnet-plagioclase clinopyroxenites have had a similar type of origin to the garnet clinopyroxenites, and the occurrence of banded examples of both types (particularly composite examples) is at least consistent with their origin as accumulates from a magma. It should be noted however that the banded rocks do not show cumulus textures.

4.1.2. **Spinel-garnet websterite.** In the spinel-garnet websterite R394 there is excellent textural evidence for the exsolution of garnet, most orthopyroxene and minor spinel from original clinopyroxene as well as for the reaction of spinel with clinopyroxene to yield garnet. From the experimentally determined phase diagram, it is apparent that these changes could take place in an initial high-temperature pyroxene(s)—spinel(—olivine) assemblage as it cooled approximately isobarically to enter the clinopyroxene + garnet + spinel field (cf. Green, 1966). Entirely analogous textures have been figured for garnet websterites from Hawaii (100 Mg/(Mg + Fe2+) = 85; Yoder and Tilley, 1962), Algeria (100 Mg/(Mg + Fe2+) = 87; Girod, 1967) and Kenya (100 Mg/(Mg + Fe2+) = 84; Saggerson, 1968), and have been observed in some inclusions from Kakanui, New Zealand (J. F. Lovering, personal communication).

4.2. **Conditions of equilibration of the Delegate inclusions**

Possible P–T fields of formation for each of the three rocks studied could be delimited using knowledge of the modes of both experimentally produced and natural
assemblages (see fig. 1). Although each of the assemblages could have crystallised over quite a wide range of physical conditions, there is a restricted $P$-$T$ field (14–16 kb, 1050–1100 °C) within which all three could have equilibrated. Textural and mineral chemical evidence strongly suggests that the garnet and garnet-plagioclase clinopyroxenites formed under similar conditions (near 15 kb, 1100 °C), and it is possible for the spinel-garnet websterite to have also finally equilibrated under very similar conditions (near the boundary of the garnet- and orthopyroxene-bearing fields of fig. 1), although this assemblage requires a history involving higher temperatures (perhaps up to 1200 °C).

The suggested range of conditions of final equilibration 14–16 kb, 1050–1100 °C implies an origin for these inclusions in the uppermost part of the Earth’s mantle at a depth of about 50 km. It is notable that the deduced temperature is considerably above that anticipated along an average continental geothermal gradient (Clark and Ringwood, 1964). Available data for garnet pyroxenites from Delegate, Hawaii, Kakanui and Algeria show that for this group partition coefficients of Fe$^{2+}$/Mg between coexisting garnet and clinopyroxene (cf. Banno and Matsui, 1965) are consistently low with a small range (1.9–2.8). By comparison with data for eclogites from glaucophanitic terranes, amphibolite–granulite terranes and inclusions in kimberlite (Lovering and White, 1969; Banno and Matsui, 1965), these data can be used to deduce a similar high-temperature origin for all garnet pyroxenites in nephelinitic basalts and breccias.

From available experimental data (Green and Ringwood, 1967b) it appears possible to obtain garnet clinopyroxenites and/or garnet-plagioclase clinopyroxenites as near-solidus accumulates from an alkali olivine basalt magma at about 15 kb. However, the inferred conditions of final equilibration of these inclusions are ca. 100 °C below the dry alkali olivine basalt solidus. Thus, if these inclusions do indeed represent local precipitates and the mineralogical banding is of accumulative origin, then a subsequent recrystallisation on cooling to ca. 1100 °C (15 kb) is required (explaining the absence of cumulus textures). The layering may alternatively represent flow banding made up of schlieren of early crystallised phases in a residual liquid finally crystallising as pockets of relatively Fe-rich garnet-plagioclase clinopyroxenite.

The rare spinel-garnet websterite with its high Mg/Fe$^{2+}$ ratio could represent an original near-liquid pyroxene(s)–spinel (–olivine) precipitate from an olivine basalt magma. However, precipitation from a clinopyroxene magma would require conditions at least 70 °C above the websterite solidus, and it seems necessary in this scheme to invoke depression of the dry basalt liquid (most likely by the presence of water). Such liquid depression could also have occurred in magma postulated as precipitating the garnet and garnet-plagioclase clinopyroxenites, particularly since hornblende occurs in many Delegate examples.

5. Conclusions

5.1. The inferred conditions of final equilibration of the Delegate garnet-bearing basic inclusions are in the $P$-$T$ range 14–16 kb, 1050–1100 °C. Very similar high-temperature conditions of formation are indicated for other garnet pyroxenites from nephelinitic basalts and breccias.

5.2. Certain features of these Delegate inclusions are consistent with an origin as local high pressure precipitates from a basaltic magma. In order to reconcile experimental basalt data it is necessary to propose a hydrous parent magma and/or post-accumulation solid state changes.

5.3. The Delegate garnet and garnet-plagioclase clinopyroxenites may be products of direct crystallisation of clinopyroxene, garnet and plagioclase. The garnet of these rocks cannot have originated entirely by exsolution from clinopyroxene. If solid state exsolution processes played a role in the development of these assemblages, evidence of their operation has been obliterated by recrystallisation.

5.4. The Delegate spinel-garnet websterite is inferred to be the end product of approximately isobaric cooling of a high temperature pyroxene(s)–spinel (–olivine) aggregate involving exsolution of garnet, orthopyroxene (and spinel) and the reaction of spinel with clinopyroxene. To judge from documented occurrences of similar rocks, such an origin (suggested by textural evidence) is indicated for those garnet pyroxenites characterised chiefly by 100 Mg/(Mg + Fe$^{2+}$) ≥ ca. 85.

Acknowledgements

The authors wish to thank Drs. J. F. Lovering and A. J. R. White for the samples of analysed Delegate.
EXPERIMENTAL DUPLICATION OF DELEGATE BASIC INCLUSIONS

[Text continues with acknowledgments and references]

References

Genetic relationship between eclogite and hornblende + plagioclase pegmatite in western Norway*

DAVID H. GREEN & BJØRN O. MYSEN


The role of water during metamorphism of eclogites and surrounding quartzofeldspathic gneisses in western Norway has been studied. The appearance of small patches and veinlets of hornblende + plagioclase + quartz (+ biotite + garnet) is attributed to partial melting of gneisses adjacent to eclogite in a high pressure metamorphic terrain (P > 8 kb, T > 600 °C, approx.). This melting is responsible for the lowering of $P_{H_2O}$ during metamorphism whereby the interlayered mafic bands are stabilized as eclogite. Other large eclogite bodies in western Norway were pre- or synmetamorphic mafic intrusions and accumulates which retained an essentially anhydrous character during metamorphism.

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Several recent studies of eclogites have presented evidence that natural eclogites have crystallized over a wide range of temperatures. Experimental studies of eclogite stability in relation to pyroxene granulites and amphibolites have similarly shown that eclogites may be stable over a wide range of conditions existing at crustal to upper mantle depths in the earth. These studies have also emphasized the critical role of water pressure in determining eclogite stability relative to amphibolite or garnet amphibolite. Thus for eclogite stability at other than very high pressure and high temperature conditions, the fugacity or activity of water in the metamorphic environment must be very low (Green & Ringwood 1967, D. H. Green & Ringwood 1971).

The presence of essentially anhydrous eclogite bodies as lenses or bands within leucocratic gneisses containing biotite, amphibole and epidote as major phases and the common presence of amphibolite margins near the eclogite bodies, have led many authors to conclude that the eclogite mineral assemblage is exotic to its metamorphic environment in the leucocratic gneiss. The eclogites have been inferred to be tectonically emplaced from deeper, higher grade metamorphic conditions (e.g. the upper mantle) into shallower, crustal metamorphic conditions. This interpretation has been

* Contribution No. 46 to the Norwegian Geotraverse Project.
particularity applied to the eclogite lenses in gneiss occurring in western Norway (O'Hara & Mercy 1963, Lappin 1966), yet definitive evidence to establish incompatibility in the $P_{\text{load}}$, $T$ conditions of metamorphism of the gneiss and eclogite has not been published. It has thus become important to examine eclogite occurrences, particularly those occurring apparently as an integral part of a regional metamorphic terrain, to ascertain relationships between eclogites and surrounding gneisses, and to designate processes acting locally or regionally which produced the $P_{\text{load}}$, $P_{H_2O}$, $T$ conditions appropriate to eclogite stability.

The present paper arises from a reconnaissance study by one of us (DHG) in the field and by petrographic examination of several eclogite bodies in the Nordfjord and Sunnmøre districts of western Norway. This has been followed by a more detailed study of the Ulsteinvik eclogite by the co-author (BOM). The localities are given in Fig. 1. The investigation is primarily aimed at determining whether the gneiss mineral assemblages, at least in some local areas, reflect a pressure and temperature compatible with eclogite stability in rocks with low $P_{H_2O}$. An hypothesis suggesting the possible role of partial melting at high pressures in creating conditions favourable for eclogite stability (Bryhni et al. 1970) led us to make a detailed ex-
amination of several examples of garnetiferous pegmatite patches or veinlets associated with eclogite bodies. The aim of this was to seek mineralogical characteristics which might be diagnostic for a high pressure origin for these pegmatites, rather than ascribing them to later activity associated with instability of the eclogites.

Field and petrographical characteristics of several eclogites

(a) Eclogite at Ulsteinvik, Hareidland

Near Ulsteinvik, an extremely large body of eclogite (garnet + clinopyroxene + quartz + rutile + biotite) has clearly transgressive contacts against metasedimentary gneisses (Mysen & Heier 1971). The contact is locally ‘welded’ passing from medium-grained eclogite to garnet-rich quartz-feldspathic gneiss. There is an absence of shearing in the gneiss and amphibolitization along the eclogite borders is uncommon. Immediately at the contact in a few areas: there is a 15-30 cm band of garnet quartzite – this appears to be a contact phenomenon rather than a horizon in the banded gneiss. The eclogite has developed mineralogical banding manifested by variation in modal garnet/groundmass ratio. The attitude of the banding is variable and not always parallel to the contacts with enclosing gneiss (see also Mysen & Heier 1971). The enclosing gneisses are remarkably garnet-rich and a common rock type is a coarse gneiss containing garnet + quartz + K-feldspar + (plagioclase + pyroxene symplectite) + biotite + rutile. The plagioclase + pyroxene symplectite in the gneiss has plagioclase as the major phase whereas the symplectite (in some cases mantling residual omphacitic clinopyroxene) in the eclogite has clinopyroxene as the major component. At Ulsteinvik there are bands of marble and impure marble within the gneiss which serve to define the transgressive nature of some of the eclogite contacts. The impure marble locally contains the assemblage calcite + quartz + plagioclase + garnet + pyroxene and also contains several small included pods of coarse kyanite + zoisite + K-feldspar + biotite + garnet.

Our initial field examination suggests emplacement of a large mafic igneous dyke in a folded metasedimentary sequence. The mafic igneous rock then recrystallized to eclogite under essentially dry conditions during a regional metamorphism in the area. The completeness of the transformation to eclogite and the absence of corona textures suggests an emplacement during or prior to the regional metamorphism. We did not observe evidence of igneous or cumulate textures in the banding expressed by the eclogite minerals, garnet, pyroxene, rutile and quartz and thus consider that these phases are not primary phases crystallized from the melt. This conclusion is supported by a more detailed investigation of the eclogite (Mysen 1971). It should also be noted that the presence of marble horizons in the gneiss would have determined that, at least locally, conditions would be those of high P CO2 and low P H2O. The general absence of amphibolite at the contact of eclogite with the garnet-rich and calcareous gneisses is further evidence for
low $P_{H_2O}$ in the gneiss. Mysen (1971) has shown that the primary mineralogy of the gneiss reflects compatibility with the crystallization of the mafic rock as eclogite.

(b) Olivine pyroxenite and eclogite on Kvamsøy

On the north coast of the island of Kvamsøy a large lenticular body of pyroxenite occurs within biotite, amphibole and garnet-bearing leucocratic gneisses. The body is largely websterite with minor and variable proportions of olivine and garnet. Some specimens show primary, very turbid, clinopyroxene and orthopyroxene with complex exsolution indicating cooling of an initial high-temperature pyroxene assemblage. Garnet occupies an intergranular position and is probably pseudomorphous after plagioclase; in some rocks, fine-grained saussuritic alteration products appear interstitially to the pyroxenes and may represent breakdown of relict plagioclase. Pyroxene is partly recrystallized and some olivine may be secondary from the reaction: pyroxenes, + spinel $\rightarrow$ garnet + olivine + pyroxenes$_2$.

Locally within the pyroxenite there are dykes and irregular patches of eclogite and at least one example of a gabbro showing garnet + clinopyroxene corona textures from reaction between pyroxene + olivine and plagioclase. The pyroxenite shows variable degrees of alteration to amphibolite and the eclogite is also locally retrogressively altered to plagioclase amphibolite. Similar but smaller bodies of olivine + garnet pyroxenite, enstatite eclogite and eclogite occur on the southern coast of Kvamsøy. The field and petrographic study suggests that these rocks are portions of olivine pyroxenite and pyroxenite igneous accumulates with some gabbroic patches, layers or dykes which show partial reaction of higher temperature (and/or lower pressure) mineral assemblages to eclogite facies mineralogy.

The main pyroxenite is veined by quartz and becomes increasingly amphibolitized towards the eastern edge. One of these veins of 7–12 cm width, contains quartz + feldspar + tourmaline as major phases with minor mica and garnet. The pyroxenite is altered to hornblende for a short distance (10–45 cm) on either side of the vein and it appears that the vein has acted as a source of water for hydration of the wallrock. Along the vein/amphibolite contact there is a zone (<1 mm wide) with rather common pink garnet. Rarer, small garnets also occur within the vein. It is suggested that a small vein of hydrous silica-rich fluid was emplaced into the pyroxenite causing local hydration particularly as the vein material crystallized. The crystallization of garnet as a phase in such a silica and water rich environment appeared unusual and an indication of the presence of very high pressure during emplacement of the vein – the latter suggestion derives from the experimental studies by T. H. Green & Ringwood (1968, 1971) on the role of garnet as a phase in the crystallization of quartz-rich dacitic or rhyodacitic rocks at high pressure. For this reason the composition and mineralogy of the vein has been studied in greater detail (see below).
The general characteristics of the lenticular, often boudinaged, eclogite lenses occurring in gneiss in the Nordfjord—Sunnmøre districts of western Norway have been described by Eskola (1921), Gjelsvik (1952), Lappin (1966), Bryn (1966) and Bryhni et al. (1969). In the present study, we wanted to compare garnet compositions in the gneiss with those in the eclogite, and particularly to examine the mineralogy of hornblende pegmatite patches or schlieren which commonly occur in close association with the eclogite lenses. The reason for this approach stems from the suggestion by Bryhni et al. (1970) that partial melting in the gneiss may occur at high load pressures and moderately high temperature, leading to a lowering of water pressure ($P_{\text{H}_2\text{O}}$) and stability of eclogite mineralogy in the more refractory mafic rocks. The mineralogy of several pegmatite patches was examined, seeking evidence for their crystallization at high load pressures.

(i) Eclogite at Sandvik, southern shore of Gursken, Gúrsköy. At this locality a lens of garnet dunite, in part with mylonitic foliation, occurs within leucocratic gneiss. Shoreline exposures show small lenses of eclogite in gneiss to the west of the body and immediately to the north-east of the dunite there is a distinctive lens of eclogite containing interlayered garnet-rich gneiss. The neighbouring banded gneiss is also garnetiferous and contains an irregular, inhomogeneous (particularly in grain size) patch of hornblende + biotite pegmatite with minor garnet.

(ii) Eclogite at Ånes, near Maurstad, east of Bryggja, Nordfjord. At this locality a very distinctive, finely interbanded quartz eclogite and garnet quartzite occurs and is traceable, as a discontinuous, boudinaged horizon in the leucocratic gneiss, for several hundred metres. It is probably the same horizon described by Bryhni et al. (1969) from Kvalneset, west of Totlandsvåg, and the general features of the gneiss in this area have been described by these authors. At Ånes the rocks are mainly hornblende-biotite-plagioclase-microcline-quartz gneiss with variable proportions of garnet and/or epidote (clinozoisite). Small boudins of epidote + biotite + garnet + magnetite + plagioclase rock and much larger boudins of eclogite (garnet + clinopyroxene + clinozoisite + quartz + phengite) with interbanded garnet + clinozoisite quartzite (garnet + clinozoisite + quartz + phengite ± pyroxene ± hornblende) are occasionally observed within the gneiss.

The gneiss suite also includes irregular schlieren and cross-cutting patches of hornblende + plagioclase + K-feldspar + quartz + biotite pegmatite. These are particularly evident at the terminii of the eclogite boudins or within the folded gneiss between boudins. In eclogite near the pegmatite there is commonly a growth of poikilitic hornblende of deep, blue-green colour, resembling that of the pegmatite, but aligned parallel to the eclogite foliation and with textural relationships suggesting partial replacement and equilibration with the garnet + pyroxene of the eclogite. Bryhni et al. (1970) suggested
that such amphibole could result from local hydration of eclogite due to rise of $P_{H_2O}$ associated with crystallization of a melt-phase to yield the hornblende pegmatite.

Mineralogy and chemical composition of veins and surrounding rocks and their relation to eclogite stability and partial melting

Bryhni et al. (1970) have suggested that the association of eclogite boudins in gneiss with hornblende pegmatite, as described in the Sandvik and Åsnes localities, is not accidental but rather that the presence of a small melt fraction, undersaturated with water, plays an essential part in depressing $P_{H_2O}$ to values low enough for eclogite to be stable relative to amphibolite. In the following sections we present chemical and mineralogical data on the hornblende pegmatite patches as a step towards establishing whether or not these hornblende pegmatite patches could be high pressure crystallization products of a low melting phase. The quartz and feldspar-rich vein within garnet pyroxenite from Kvamsøy was similarly examined as a possible example of a melt phase at similar pressure conditions.

(a) **Kvamsøy pegmatite vein**

Megascopically the vein consists of similar proportions of quartz and dull-white feldspar with minor, large, black prisms of tourmaline. In thin section quartz, andesine ($An_{38}$) and tourmaline form large, subhedral crystals. They are primary phases in the vein. Small euhedral garnet crystals are rare but occur included in quartz, tourmaline and plagioclase and are also of primary origin. Approximately 15–20% of the rock consists of distinctive areas of very fine-grained mosaic dominated by plagioclase, in part antiperthite, with white mica (phengitic muscovite, see Table 1), kyanite, and accessory microcline and green biotite (in part as rims around the white mica, or intergrown with it). The kyanite occurs as subhedral, randomly oriented prisms and it is apparent that the assemblage of plagioclase, muscovite, kyanite results from the breakdown of a former single phase, of similar grain size to the quartz, plagioclase and tourmaline. In some areas of the plagioclase mosaic, kyanite is absent and sericitic mica is more common. The nature of the breakdown products suggests that the pre-existing phase was paragonite, possibly with muscovite solid solution. It is inferred that a paragonite-rich mica reacted as follows:

$$2SiO_2 + Na_2Al_2Si_6O_{20}(OH)_4 \rightarrow 2NaAlSi_3O_8 + 2AlSiO_3 + 2H_2O$$

Quartz Paragonite Albite Kyanite Vapour

The reaction presumably results from a drop in $P_{H_2O}$ after the initial crystallization of the vein.

At the margin of the vein against the amphibolite, garnet is more common
and rare garnet also occurs within the amphibolite. The amphibolite consists of blue-green hornblende and quartz, with small amounts of sphene,apatite and garnet. Further from the vein the rock becomes a partly amphibolitized pyroxenite in which olivine, very turbid orthopyroxene and clinopyroxene are probably primary phases and in which anhedral garnet and some clearer orthopyroxene adjacent to olivine are probably products of reaction between olivine and plagioclase resulting in elimination of the latter. Later growth of hornblende has been at the expense of olivine, pyroxenes and garnet.

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*dite: E. Kiss, Australian National University.
*Fe determined: FeO, Fe2O3 calculated from structural formulae.
The garnets (Table 1) within the pegmatite vein are almandine with rather high grossular and variable spessartine contents. The very low pyrope contents contrast with the garnet within the amphibolite and garnets at the contact between the vein and amphibolite. It appears that the latter garnets reflect equilibrium or approach to equilibrium with the magnesian amphibolite composition whereas the garnet within the vein reflects the high degree of iron-enrichment relative to magnesium anticipated in a low temperature melt fraction. The amphibole within the amphibolite may be classed as common hornblende — it differs from the other amphiboles analysed in this study in higher SiO₂ content, lower alkalis, lower Al₂O₃ content and higher Mg/Mg+Fe ratio (Table 1).

The muscovite differs from the white mica within eclogite at Åsnes in higher Al₂O₃, lower SiO₂ and lower alkali content. The tourmaline is blue to blue-green in thin section and partial microprobe analyses yielded a composition appropriate to rather magnesian schorl (SiO₂=33.5%, Al₂O₃=35.0%, Fe as FeO=5.7%, MgO=6.6%, CaO=1.3%).

(b) Hornblende pegmatite at Sandvik, Gurskøy

The pegmatite body consists of inhomogeneously distributed hornblende, plagioclase and quartz as major phases with accessory microcline, biotite, garnet, ilmenite and sphene, and apatite. Grain size is variable. The absence of foliation and orientation of hornblende and biotite is in marked contrast with the enclosing gneiss. The small garnet grains are included within both amphibole and feldspar-rich areas, and show no evidence for instability or breakdown reactions. The plagioclase is near Ab₉₂An₁₈ composition, some crystals contain a few blebs of exsolved K-feldspar. Microcline is common in the thin sections examined although the chemical analyses (Table 2) indicate a comparatively low K-content – the apparent difference may reflect the common problem of sampling the pegmatitic body. Thin rims of contrasted composition on some feldspar margins and the presence of myrmekite on grain boundaries indicates local, late-stage reactions involving the feldspars.

Electron microprobe analysis of garnet from within the pegmatite shows that there is very large variation in spessartine content with manganese enrichment at the rims. The cores of the garnets are grossular-almandines with very low pyrope content. The high grossular content (10.7–10.8% CaO) in the garnet is in marked contrast with the low CaO content (1–2% CaO) of almandine garnet ‘xenocrysts’ occurring in andesitic or dacitic magmas (Green & Ringwood 1968).

The amphibole is relatively homogeneous in composition and the analysis given in Table 2 is the average of several grains, including both edge and core areas. The amphibole is a ferrohastingsite with rather high K₂O content – the occupancy of the vacant site in the amphibole structure being approximately equally shared by potassium and sodium.
### Table 2. Analyses of total rock and minerals of the hornblende pegmatite from Gursken, Gursköy.

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<th>Garnets from pegmatite</th>
<th>Amphibole from pegmatite</th>
<th>Garnet from neighbouring gneiss dd</th>
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</table>

|                | 100.01                | 99.5                   | 100.2                    | 98.5                             |

|                | aa                    | bb                     | cc                       | dd                               |
| Si             | 3.03                  | 3.02                   | 6.15                     | Si                               |
| Al             | 1.89                  | 1.87                   | 1.85                     | Al                               |
| Fe+++          | 0.11                  | 0.13                   | 0.54                     | Fe+++                            |
| Fe++           | 1.69                  | 1.54                   | 0.18                     | Fe++                             |
| Mn             | 0.15                  | 0.43                   | 0.51                     | Mn                               |
| Mg             | 0.18                  | 0.12                   | 3.01                     | Mg                               |
| Ca             | 0.92                  | 0.93                   | 0.08                     | Ca                               |

|                | Andradite             | Grossular              | Almandine                | Spessartine                      | Pyrope                            |
|                | 5.7                   | 25.5                   | 57.5                     | 5.1                              | 6.1                               |
|                | 6.5                   | 24.2                   | 51.0                     | 14.2                             | 4.0                               |
|                | Z                     | Y                      | X                        | W                                | A                                 |
|                | 8.00                  | 1.23                   | 3.94                     | 2.00                             | 0.76                              |
|                | Andradite             | Grossular              | Almandine                | Spessartine                      | Pyrope                            |

|                | 5.7                   | 25.4                   | 58.6                     | 4.6                              | 5.7                               |

|                | a Analyst: B. Bruun, Mineralogisk-Geologisk Museum, Oslo. |
|                | b Total Fe determined; FeO, Fe₂O₃ calculated from structural formulae. |

The gneiss adjacent to the pegmatite contains quartz (~ 35%), feldspars (~ 40%), garnet (~ 20%), biotite (~ 5%) and amphibole (~ 3%) and minor amounts of sphene, apatite and opaque minerals. Biotite and amphibole are strongly aligned and also tend to be concentrated in thin bands. The feldspars show complex unmixing features similar to those in the pegmatite. Plagioclase (Ab₇₂An₂₈) contains varying amounts of exsolved microcline (antiperthite) and microcline also occurs as separate grains, some with string perthite intergrowth. Amphibole is strongly pleochroic from very dark blue-green to deep olive green and yellow-green. It is similar in colour and optical properties to the amphibole in the pegmatite and is probably also ferrohastingsite. Biotite is strongly pleochroic from colourless to very dark brown.
The garnet is subhedral, pale pink in thin section, and commonly contains inclusions of quartz, plagioclase, antiperthite, sphene, or opaque minerals. Microprobe analysis (Table 2) shows that the garnet composition is the same, within analytical limits, as the garnet of the pegmatite. The high calcium content, giving a grossular (+ andradite) solid solution of over 30%, is again notable, particularly in a rock with no calcium-rich zoisite and with plagioclase of only An28 composition.

There is no evidence of incompatibility or arrested reactions between the phases plagioclase, quartz, microcline, ferropargasite, biotite, garnet, sphene and apatite in either the pegmatite or the gneiss. However, in both rocks the complex perthitic and antiperthitic relations of the feldspars imply a complex history. The microcline may not be a primary phase but may result from unmixing of higher temperature alkali feldspar.

(c) Eclogite, garnet-hornblende gneiss and hornblende pegmatite from Ånes, near Brygga, Nordfjord

The eclogite is banded and compositionally variable quartz eclogite. The specimen analysed is a quartz eclogite with minor zoisite and accessory mica, rutile and apatite. The eclogite has pronounced foliation with the pyroxene and zoisite crystals showing a high degree of dimensional and crystallographic orientation. The white mica is concentrated along foliation planes and in such thin bands may become a major phase. The pyroxene is partially altered to a fine intergrowth of pyroxene + plagioclase; garnet has thin kelyphitic borders and the white mica typically has a kelyphitic reaction rim in which brown biotite is a major phase, usually in parallel growth with the white mica which it replaces. Amphibole is absent as a primary phase in the eclogite examined in detail but is locally present as a fine-grained alteration product of garnet and pyroxene. In other parts of the eclogite horizon, amphibole is a minor phase, either crystallizing with or slightly post-dating the garnet and pyroxene. This amphibole resembles that in the gneiss in its pleochroic scheme but is less strongly coloured — it is probably hastingsite rather than ferrohastingsite.

Mineral analyses from the eclogite are presented in Table 3. The garnet contains almandine, grossular and pyrope as major components. The grossular content is similar to that in garnet from the hornblende pegmatite and garnetiferous gneiss but the garnet in eclogite has a higher pyrope content and higher pyrope/almandine ratio than other garnets analysed. The coexisting pyroxene is an omphacite with 43% jadeite + acmite — it resembles omphacites from other Norwegian eclogites, particularly those from Duen (Eskola 1921), Naustdal (Binns 1967), Selje (Green 1969) and Kvalneset (Bryhni et al. 1969). The coexisting zoisite (Table 3) has a very low ferric iron content, consistent with its absence of pleochroism and weak birefringence. The white mica is phengite with low sodium content and a deficiency of potassium. The (Mg, Fe) content of the phengite is consistent with the
Chemical composition of eclogite, hornblende pegmatite and minerals from eclogite and neighboring gneiss, Åsnes, Bryggja, Nordfjord. The garnet and amphibole of the hornblende gneiss vary in composition: the thin section – the analyses illustrate this variation.

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yst: E. Kiss, Australian National University (wet-chemical analysis).
yst: N. J. Ware, Australian National University (microprobe analysis).
yst: B. Bruun, Mineralogisk-Geologisk Museum, Oslo.

Fe determined; FeO, Fe2O3 calculated from structural formulae.
observation that biotite is a breakdown product within the kelyphitic border
to the white mica. The kelyphitic border, if it is synchronous with that
developed from the omphacite (pyroxene + plagioclase intergrowth) is a con-
sequence of a decrease in pressure at high temperature or an increase in
temperature at high pressure.

The composition of the specimen of the hornblende biotite pegmatite
analysed resembles that from Gursken in its SiO$_2$, Al$_2$O$_3$, FeO, and CaO
contents and in normative quartz + total feldspar. However, both the
Na$_2$O/K$_2$O and Mg/Mg + Fe$^{++}$ ratios are considerably higher in the Gursken
example. The analysed pegmatite sample from Åsnes did not contain garnet
and was not examined further mineralogically. The specimen (14) of mig-
matitic gneiss contains garnet and hornblende of rather variable mineral
chemistry. The garnet contains 33–35 mol % grossular + andradite but is
more pyrope-rich (10–16%) than the garnet from the Sandvik pegmatite
or the Kvamsøy vein. The amphibole is hastingsite rather than ferrohasting-
site as in the Sandvik pegmatite. The amphiboles have similar calcium con-
tents but there is lower alkali content in those from the Åsnes banded gneiss.
The clinozoisite within the gneiss was not analysed but its zoning and stronger
birefringence indicate higher Fe$^{+++}$ content than that in the pegmatite.

Petrogenetic significance of garnet in pegmatite and gneiss

The garnet occurring in these pegmatite patches and the surrounding gneiss
is typically almandine-rich but contains 30–32% grossular + andradite solid
solution. Almandine-rich garnet may form at low pressures in quartz-
bearing assemblages as exemplified by its presence in thermal aureoles and
accompanying cordierite in regional metamorphic rocks. This is confirmed
by experimental studies on the stability of almandine and almandine + quartz
(Hsu 1968, Hensen 1970) and on the stability of almandine-pyrope garnets
However, it is characteristic that these almandine-rich garnets, forming at
P < 8 kb, are low in CaO-content (1–2% CaO) and in grossular + andradite
solid solution. Hence knowledge of their stability relationships cannot be
directly applied to natural garnets with > 30% grossular + andradite solid
solution.

Garnet with 33% grossular solid solution is compositionally equivalent
to the lower pressure assemblage fayalite + anorthite or, when accompanied
by quartz, to ferrosilite + anorthite. Grossular (33%) – almandine (67%) is
stable relative to fayalite + anorthite at P > 7 kb at 900 °C (Green & Hib-
berson 1970) and the equilibrium boundary for grossular-almandine +
+ quartz = anorthite + ferrosilite must lie on the high pressure side of the
garnet breakdown curve. The experiments on natural basaltic compositions
(Green & Ringwood 1967) yielded garnets with 28% grossular, 46–48%
almandine, at pressure 14.5 kb, 1100 °C. Extrapolated to 800 °C, a pressure
of 9 kb for stability of garnet (>30% grossular) + quartz is indicated. If the garnet in the pegmatite patch at Sandvik and that in the vein on Kvamsøy formed by crystallization from a melt phase, as suggested by the form and textures of the bodies, then the experimental studies of the crystallization of garnet from andesitic and rhyodacitic melts (Green & Ringwood 1968, T. H. Green & Ringwood 1971, Green 1971) are relevant. Garnet was observed in equilibrium with liquid at small degrees of melting in the presence of water at pressures ≤ 9 kb. In a rhyodacite composition, experiments were carried out with 2%, 5% and 10% H₂O and the lowest pressure and temperature at which garnet was analyzed was 111.5 kb, 900 °C, 5% H₂O. This garnet contained 6.6% CaO (i.e. 17% grossular + andradite) and was in equilibrium with quartz + plagioclase + amphibole + pyroxene. At 13.5 kb, 870 °C with 5% water in the rhyodacite, garnet contained 8.4% CaO (23% grossular, 59% almandine + spessartine). Garnets with 12.6% CaO and 11% CaO were obtained at 13.5 kb, 800 °C, 10% H₂O and at 13.5 kb, 900 °C, 5% H₂O, respectively, in an andesite composition. Co-existing phases were amphibole, clinopyroxene and glass (Green 1971).

We conclude that the weight of evidence from experimental and natural rocks shows that the association of quartz and almandine-rich garnets with approximately 30 mol % grossular solid solution, particularly in rocks with sodic plagioclase or with kyanite, or white mica, is formed at high pressures, in excess of those pressures required for the common garnet-sillimanite gneiss terrains. The pressure at crystallization of the hornblende plagioclase pegmatite and hornblende gneiss is probably adequate for eclogite stability in dry basaltic rocks (>8 kb at 600 °C to >15 kb at 900 °C, Green & Ringwood 1967, D. H. Green & Ringwood 1971).

Conclusions

We have examined the mineralogy of several pegmatite patches and veinlets and associated gneiss and eclogite in an attempt to ascertain whether the apparent mineralogical contrast between eclogite and country rock necessarily implies a difference in load pressure or in temperature at crystallization. The compositions of the major phases plagioclase, microcline, amphibole and quartz are not definitive of high pressure conditions although the low SiO₂ contents (in the presence of free quartz) and high K/Na ratios of the amphiboles (ferrohastingsite) may in the future prove to have petrogenetic significance. On the other hand the presence of kyanite, phengite and zoisite + quartz are all consistent with or indicative of high pressure (cf. Velde et al. 1970). We consider that probably the best evidence for high pressure crystallization of the gneisses and pegmatite patches lies in the grossular-rich compositions of the almandine garnets in the gneiss and pegmatites, and their similarity in this respect to the garnet occurring in the eclogites. We conclude that there is no convincing evidence for any dif-
ference in load pressure and temperature at crystallization between the eclogite lenses and their country rock and thus that the eclogites are not exotic bodies or tectonically emplaced in their present environment. The differences in mineralogy between eclogite and country-rock gneisses are attributed to chemical parameters and differences in activity of water.

There is evidence for local melting during the main metamorphism in the form of migmatic hornblende + garnet gneisses, hornblende pegmatites and small pegmatitic veinlets. We conclude that the presence of a melt phase during deep crustal, high pressure metamorphism may locally be an essential factor in stabilizing eclogite relative to amphibolite. In a rock with limited water content, melting may initially occur with breakdown of one or more of the hydrous phases but if the temperature continues to rise the melt acts as a 'sponge' withdrawing water from and lowering $P_{H_2O}$ in the country rocks (Burnham 1967, Bryhni et al. 1970). This may lead to breakdown of amphibolite to eclogite. This mechanism may be of prime significance in the genesis of the finely-banded quartz eclogite and garnet quartzite, apparently of metasedimentary origin occurring as boudinaged horizons within the hornblende gneiss (e.g. Åsnes locality). The character of the low melting fraction under these high pressure conditions is not a micaceous granite but appears to be hornblende granodiorite or hornblende adamellite. This is consistent with results from experimental studies (Green 1971) suggesting derivation of dacitic to rhyodacitic liquids by partial melting at higher pressures in the presence of water.

We wish to stress, however, that we do not regard local partial melting as a necessary prerequisite for eclogite stabilization or even that this is the major process responsible for the eclogites in western Norway. Provided the $P_{\text{Load}}$, $T$ conditions for eclogite stability are operative (Green & Ringwood 1967, D. H. Green & Ringwood 1971), other factors may cause low $P_{H_2O}$. In western Norway we conclude that the pre-metamorphic or syn-metamorphic emplacement of large bodies of basic igneous rock produced rocks which largely remained anhydrous during metamorphism. Similarly, the local or regional $P_{CO_2}$ may be very high. Both the latter factors were probably important in the crystallization of the large eclogite around Ulsteinvik. The Kvamsøy pyroxenite and eclogite probably also resulted from in situ recrystallization of a basic igneous complex.

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REFERENCES


A COMPARISON OF RECENT EXPERIMENTAL DATA ON THE GABBRO-GARNET GRANULITE-ECLOGITE TRANSITION

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ABSTRACT

Recent experimental data presented by Ito and Kennedy on the mineralogical variations in the gabbro to eclogite transformation are shown to be consistent with earlier experiments on a variety of basaltic compositions. The new results support, for a specific composition, two of the major conclusions of our previous work: (1) the gabbro to eclogite transformation takes place through a rather broad transition interval in which mineralogies appropriate to high-pressure granulite assemblages are formed, and (2) the slope of the gabbro to eclogite transition interval is such that eclogite is the stable mineralogy for dry basaltic rocks along normal geothermal gradients in the continental crust (stable or shield regions).

INTRODUCTION

The crystallization of a variety of basaltic rocks at subsolidus conditions at temperatures of 1,100°-1,250° C and at pressures up to 40 kbar was reported by Ringwood and Green (1964, 1966), Green and Ringwood (1967a), and T. H. Green (1967). Similar experiments on a rhyodacite composition (Green and Lambert 1965) and on andesite and gabbroic anorthosite compositions (T. H. Green 1970) have also been published. These experiments established a general pattern of mineralogical variation with increasing pressure from low-pressure pyroxene + plagioclase + olivine assemblages through pyroxene + plagioclase + garnet ± quartz assemblages to plagioclase-free assemblages dominated by garnet + clino-pyroxene. It was shown that the width of the mineralogical transition zone is strongly controlled by the chemical composition of the rock, parameters of importance including the degree of silica saturation, the Ab/(Ab + An) ratio of the plagioclase, and the Mg/(Mg + Fe++) ratio of the rock.

Cohen et al. (1967) published data on the mineralogy of an olivine tholeiite (NM5) at pressures up to 40 kbar and at temperatures thought to be subsolidus. Their results gave a much narrower pressure interval for the pyroxene + garnet + plagioclase field (garnet granulite) than predicted for the NM5 composition from a comparison with the spectrum of compositions studied in the Canberra laboratory. Ito and Kennedy (1968, p. 179) contrasted their narrow pressure interval for the gabbro eclogite transition with the broader interval in the Canberra results and noted (p. 179), "It seems barely possible that the continental Mohorovicic discontinuity can be a phase change if the transition takes place over an interval of 4kb but it seems quite impossible if the transition takes place over an interval of 9kb." Subsequently, Ito and Kennedy (1970, 1971) have reinvestigated the subsolidus mineralogy of NM5 at high pressures and obtained results differing drastically from their previous data. The pressure interval between appearance of garnet and disappearance of plagioclase is now reported as ~7 kbar on the solidus or ~15 kbar at 1,100° C. In presentation of their more recent data, Ito and Kennedy (1971) also state that their new data are "remarkably in contrast to those published by Green and Ringwood (1967a)." The authors do not detail where the supposed conflict in experimental data occurs, but make the unjustified inference that the problem of melting, which in part invalidated their own earlier results, also invalidates the work of Ringwood and Green (1966), Green and Ringwood (1967a) and T. H. Green (1967, 1970). Ito and Kennedy there-
fore state that our conclusions on eclogite stability in the crust and upper mantle cannot be justified. It will be shown in the following discussion that the latest Ito and Kennedy work is in excellent agreement with our earlier work and conclusions, and, indeed, adds little information to that already presented in our work. Furthermore, the conclusions of Ito and Kennedy (1971) on the role of garnet granulite and eclogite in orogenic regions where the M-discontinuity cannot be clearly identified, closely follow those of our 1966 paper.

In discussing the application of their later experimental results, Ito and Kennedy (1970, p. 81, fig. 3) state, “In areas where the intermediate layer is absent, typically in stable shield areas, the Mohorovicic discontinuity may be a chemical change from acidic or intermediate rocks to eclogite.” In oceanic regions, Ito and Kennedy (1970, p. 81, fig. 3) suggest that the oceanic crust is generated as “the intermediate layer of garnet granulite [considered to be present at the ridges] disappears forming a crust of schist by progressive hydration near the surface and forming the normal mantle layer of eclogite by isochemical transition [emphasis added] at greater depths.” Eclogite is thus regarded as the major rock type of the uppermost mantle.

**Experimental Determination of the Solidus in Basaltic Compositions**

Figure 1 shows the solidus for NM5 as determined by Ito and Kennedy (1971) compared with that of Cohen et al. (1967) and Ito and Kennedy (1970). The drastic lowering of the solidus in the latest results is due to their recognition that the absence of quartz in the eclogite field is due to melting and not to SiO2 solid solution in the omphacitic pyroxene (Cohen et al. 1967, p. 509–510). It can be seen from figure 1 that the solidus of NM5 is now almost identical with that deduced by Green and Ringwood (Ringwood and Green 1966; Green and Ringwood 1967a) for their quartz tholeiite. Since in both NM5 and the quartz tholeiite compositions the solidus at high pressure is for mineral assemblages with pyroxene (omphacitic) + garnet ± plagioclase (sodic) + quartz, a close similarity is predictable and the new data remove the anomaly present in the earlier results of Cohen et al. (1967) and Ito and Kennedy (1970). However, although Ito and Kennedy (1971) recognize the mineralogical similarity between eclogitic assemblages in NM5 and the quartz tholeiite compositions, they do not compare the nearly identical solidi illustrated in figure 1. The solidus for an olivine tholeiite composition (20% normative olivine) is plotted in figure 1 also and differs considerably from the quartz eclogite solidi (Green and Ringwood 1967b). This olivine tholeiite theoretically contains a small amount of olivine in eclogite mineralogy if TiO2 is calculated as rutile or a small amount of quartz if TiO2 is calculated as ilmenite—thus the real high-pressure assemblage is predicted to be garnet + pyroxene + very minor ilmenite + very minor rutile. The higher solidus temperature of this olivine tholeiite (quartz-free eclogite) does not conflict with the data from the quartz tholeiites and indeed provides support for the concept that the garnet + pyroxene join acts as a thermal divide between lower-temperature solidi in either olivine eclogite or quartz eclogite compositions (O'Hara 1963). Confirmatory evidence for the difference in slope between solidi of quartz-free eclogite and quartz eclogite may be found in Irving and Green (1970). It should be noted, however, that the solidi of all quartz eclogites or of all quartz-free eclogites will not be identical but will depend on Fe/Mg ratio of the pyroxene and garnet, on jadeite + acmite solid solution in the clinopyroxene, and on the presence or absence of minor phases such as kyanite, apatite, K-feldspar, etc. The experimental problem of detecting small amounts of melting may also prevent detection of small differences in solidus temperatures.

**Width of the Gabbro to Eclogite Transition Interval**

The NM5 composition at low pressures has an olivine gabbro mineralogy (olivine + pyroxene + plagioclase), but at higher pres-
sure passes through a transitional garnet granulite assemblage (garnet + pyroxenes + plagioclase ± quartz) to an eclogite assemblage (garnet + pyroxene [omphacite] + quartz). In figure 1, the width of the garnet granulite transition interval as re-

determined by Ito and Kennedy (1971) is compared with that of quartz tholeiite B of Green and Ringwood (1967a). Figure 2 illustrates a comparison of the width at 1,100°C of the garnet granulite transition interval of NM5 with those determined for

![Graph showing comparison of experimentally determined solidi and subsolidus boundaries.](image)

**Fig. 1.**—Comparison of experimentally determined solidi and subsolidus boundaries. Dashed lines refer to the solidus, garnet appearance, and plagioclase disappearance of Ito and Kennedy (1971) and the previous data for the same olivine tholeiite by Cohen et al. (1967). The short lines labeled with question marks are the approximate boundaries for garnet appearance and plagioclase disappearance as determined in 1967. The solid lines refer to the experimentally determined boundaries for quartz tholeiite B of Green and Ringwood (1967a). The dotted lines for plagioclase disappearance and garnet appearance illustrate the slopes for those boundaries actually used for extrapolation to lower temperatures; these lie well within experimental error in relation to the solid lines which were drawn from the experimental points. The line labeled *Ol. Tholeiite* is the solidus for a composition yielding quartz-free eclogite (garnet + clinopyroxene + rutile + ilmenite) and contrasts with the solidi for the two quartz eclogite compositions.
a variety of basaltic and more siliceous compositions in the Canberra laboratory. In table 2, we have listed some of the chemical parameters important in determining reactions in the gabbro to eclogite transition for a variety of basalts studied experimentally. Comparison of simple oxide contents or of CIPW norms of the compositions can be made by referring to the original papers and to table 1.

The incoming of garnet in NM5 composition results from the olivine + plagioclase reaction. The pressure (fig. 2) required for the first appearance of garnet in NM5 at 1,100°C is 10.5 kbar, which is lower than that for garnet appearance in the high-alumina basalt (12 ± 0.5 kbar), but marginally higher than that in the alkali-poor olivine tholeiite. The differences are caused by the lower Mg/(Mg + Fe⁴⁺) ratio of NM5 compared with the high-alumina basalt (Green and Ringwood 1967a, p. 787; Green and Hibberson 1970) and the higher anorthite content of the plagioclase of the alkali-poor olivine tholeiite (An₇₈ compared with An₆₈ [NM5] and An₆₇ [high alumina basalt]) (Green and Hibberson 1970). The data on appearance of garnet in NM5 are thus in excellent agreement with the previous Canberra data on olivine tholeiite compositions. The appearance of garnet in hypersthene + quartz normative (low pressure) compositions occurs at higher pressures and reflects the higher pressure required for the hypersthene + plagioclase reaction to yield garnet + quartz (see Kushiro and Yoder 1966).

The disappearance of plagioclase in basaltic compositions involves elimination of the albite component by solid solution as jadeite in the clinopyroxene and elimination of the anorthite component either by reaction with olivine or enstatite, or (in rocks with high An/[Ol + Hy/2] ratios) by anorthite breakdown to yield higher grossular solid solution in garnet + kyanite + quartz. In table 2 the compositions of pyroxene and garnet in the various basalts at pressures sufficient to eliminate plagioclase are tabulated and the mineralogical character of
TABLE 1


<table>
<thead>
<tr>
<th></th>
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<td>SiO2</td>
<td>49.93</td>
<td>48.47</td>
<td>52.16</td>
<td>50.3</td>
<td>49.94</td>
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<td>TiO2</td>
<td>1.34</td>
<td>1.48</td>
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<td>16.17</td>
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<td>1.5</td>
<td>1.5</td>
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<td>FeO2</td>
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<td>12.60</td>
<td>8.39</td>
<td>7.6</td>
<td>6.90</td>
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<td>MnO</td>
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<td>0.20</td>
<td>0.14</td>
<td>0.16</td>
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<td>7.59</td>
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<td>7.36</td>
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<td>7.28</td>
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<td>CaO</td>
<td>9.33</td>
<td>9.91</td>
<td>9.44</td>
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<td>11.86</td>
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<td>Na2O</td>
<td>2.92</td>
<td>2.20</td>
<td>2.68</td>
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<td>2.76</td>
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<td>K2O</td>
<td>0.37</td>
<td>0.41</td>
<td>0.73</td>
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<tr>
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<td>0.19</td>
<td>0.21</td>
<td>0.18</td>
<td>0.16</td>
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<td>CIPW norms:</td>
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<td></td>
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<tr>
<td>Qz</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Or</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ab</td>
<td>22.1</td>
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<tr>
<td>An</td>
<td>33.5</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di</td>
<td>17.1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Hy</td>
<td>11.9</td>
<td></td>
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<tr>
<td>Ol</td>
<td>6.2</td>
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<td>Ilm</td>
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<td>Ap</td>
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<tr>
<td>Mt</td>
<td>2.2</td>
<td></td>
<td></td>
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</table>

Note.—Attention is directed to the exceptionally low normative diopside content of NM5 and the high normative olivine content in these respects this composition is very unlike the average oceanic tholeiite of Engel et al. (1965). The calculated composition of the "eclogite component" (garnet + pyroxene + quartz) of NM5 at 20.5 kbar, 1,100 °C is also listed.

The final eclogite assemblage is noted. The molecular ratio (An + Ab)/(Di + Ol + Hy/2 + Mt + Ilm) also is significant as the lower this ratio (for value < 1), the lower the pressure required for disappearance of plagioclase. Note that, unlike the high-alumina basalt (modeled on the average oceanic tholeiite of Engel et al. [1965], see table 1) or the andesite composition, the basalt NM5 does not yield quartz + kyanite eclogite. In this composition, the high anorthite content is compensated for by the high olivine + hypersthene content. The disappearance of plagioclase in NM5 composition is thus determined by the pyroxene + plagioclase → pyroxene + quartz reaction, where pyroxene has higher jadeite content than pyroxene. From table 1, it can be seen that the jadeite content of the eclogite pyroxene decreases in the sequence NM5, quartz tholeiite B, quartz tholeiite A, to alkali-poor olivine tholeiite. The pressure required for plagioclase disappearance decreases consistently in the same sequence.

The fact that the Ito and Kennedy (1971) data closely confirm the previous data of Green and Ringwood (1967a) on quartz tholeiite B can be demonstrated in another way. Ito and Kennedy (1971) note that above 20 kbar at 1,100 °C the pyroxene in the NM5 composition is omphacitic and, although minor plagioclase is present, the mineral assemblage is called plagioclase eclogite. This usage of the terms "eclogite" and "plagioclase eclogite" agrees with the discussion in Green and Ringwood (1967a, p. 811–812). Ito and Kennedy (1971, fig. 4) give the density difference for NM5 mineralogy between the lower-pressure boundaries of the eclogite field and the plagioclase
<table>
<thead>
<tr>
<th>Composition of eclogitic pyroxene</th>
<th>Andesite (Green 1970)</th>
<th>NMS (Ito 1971)</th>
<th>Average Oceanic Tholeiite (Calculated)</th>
<th>High Alumina Basalt (Green and Ringwood 1966)</th>
<th>Quartz Tholeiite B (Green and Ringwood 1967a)</th>
<th>NMS-9.3% Plagioclase (Eclorite Component of Plagioclase Eclogite)</th>
<th>Quartz Tholeiite A (Green and Ringwood 1967a)</th>
<th>Alkali-poor Olivine Tholeiite (Green and Ringwood 1967a)</th>
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</thead>
<tbody>
<tr>
<td><strong>Grossular content of eclogite garnet</strong></td>
<td>JD72, Dih2</td>
<td>JD02, Dih5.5</td>
<td>JD2, Dih65</td>
<td>JD2, Dih65</td>
<td>JD4, Dih66</td>
<td>JD4, Dih66</td>
<td>JD4, Dih66</td>
<td>JD4, Dih66</td>
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<tr>
<td>Molecular ratio: (An+Ab)/Di+Ol+Hy/2+Itn+Mt</td>
<td>1.95</td>
<td>1.00</td>
<td>1.03</td>
<td>1.01</td>
<td>0.85</td>
<td>0.83</td>
<td>0.70</td>
<td>0.53</td>
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<td>Normative olivine (wt. %)</td>
<td>9</td>
<td>14</td>
<td>4.0</td>
<td>6</td>
<td>2.5</td>
<td>15.1</td>
<td>3</td>
<td>23</td>
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<td>100 Mg/(Mg+Fe++) Basalt type</td>
<td>49</td>
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<td>65</td>
<td>61</td>
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<td>Eclogite type</td>
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<td>Qz</td>
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<tr>
<td>Pressure (kbar) for plagioclase disappearance at 1,100°F</td>
<td>26 ± 1</td>
<td>26</td>
<td>23.5 ± 1</td>
<td>20 ± 1</td>
<td>20.5</td>
<td>18 ± 1</td>
<td>13 ± 1</td>
<td>13 ± 1</td>
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<tr>
<td>Pressure (kbar) for garnet appearance 1,100°F</td>
<td>13.5 ± 1</td>
<td>10.5</td>
<td>12 ± 0.5</td>
<td>14 ± 0.5</td>
<td>10.5</td>
<td>14 ± 0.5</td>
<td>9.5 ± 0.5</td>
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</table>

* Calculated.
† Measured.
eclogite field as $3.45 - 3.36 = 0.09$ g/cubic centimeter. Their actual measurements at $1,200^\circ$C give $3.44 - 3.33 = 0.11$ g/cubic centimeter. If we take $0.10$ g/cubic centimeter as the difference in density between the eclogite and plagioclase eclogite (20 kbar, $1,100^\circ$C) mineralogies, then we may calculate, from the nature of the reactions eliminating plagioclase, that the plagioclase eclogite at 20 kbar, $1,100^\circ$C contains $9.3\%$ plagioclase (assuming composition $\text{An}_{11}$). The chemical composition of the eclogite component of NM5 at 20.5 kbar, $1,100^\circ$C (i.e., after removal of the $9.3\%$ plagioclase) is given in table 1. The pyroxene in the plagioclase eclogite at 20.5 kbar, $1,100^\circ$C is calculated as $\text{Jd}_{41} \text{Di}_{59}$, which is almost identical in $\text{Jd}/(\text{Jd} + \text{Di})$ ratio with that of quartz tholeiite B ($\text{Jd}/[\text{Jd} + \text{Di}] = 43$), although quartz tholeiite B also contains 19% acmite solid solution. It is apparent from the chemical parameters in table 2 that the disappearance of plagioclase in quartz tholeiite B which we determined at $20 \pm 1$ kbar at $1,100^\circ$C is entirely consistent with Ito and Kennedy's data producing a quartz + plagioclase eclogite from NM5 composition at 20.5 kbar, $1,100^\circ$C in which the pyroxene is $\text{Jd}_{41} \text{Di}_{59}$ and the garnet has 21 mol% grossular.

"FINE STRUCTURE" OF THE GABBRO TO ECLOGITE TRANSFORMATION

Green (1967) published a density versus pressure curve for experimental runs on an alkali basalt composition. The garnet granulite transitional mineralogy correlated with a more rapid rate of density increase in the 10–20 kbar pressure interval. Ito and Kennedy (1970) published similar data through which they drew a curve with two regions of very rapid increase in density which they correlated with the incoming of garnet and outgoing of plagioclase, respectively. Ito and Kennedy (1971) showed that their previous data were obtained on runs quenched from above the solidus and gave a revised and slightly "smoothed" curve for densities determined at $1,200^\circ$C but continued to maintain that their data justified recognition of two sharp density increases. Their experimental data are shown in figure 3 with symbol size indicating uncertainty of $\pm 0.01$ g/cubic centimeter in $\rho$ for the determinations; this estimate is conservative. We contend that there is no experimental justification for the stepped density versus pressure curve drawn by Ito and Kennedy, although we agree that the slope of the density versus pressure curve for this composition is probably slightly steeper in the 11–16 kbar pressure interval (where the olivine + hypersthene + plagioclase $\rightarrow$ garnet + quartz reaction is of major importance) than in the 16–25 kbar interval (where the reaction is dominantly pyroxene$_1$ + plagioclase $\rightarrow$ pyroxene$_2$ + quartz). The NM5 composition, with exceptionally low normative diopside and high anorthite and olivine + hypersthene contents (table 1), is one in which the reaction forming garnet at the expense of anorthite is accentuated and the low diopside content inhibits the rate of take-up of jadeite solid solution. Ringwood and Green (1966) and Green and Ringwood (1967a) had previously called attention to the effect of chemical composition in determining the relative importance of component reactions in the gabbro-eclogite transformation. Theoretical consideration of these component reactions, all involving solid solutions with end-members having very different stability fields, shows that the incoming of garnet or disappearance of plagioclase must occur gradually over a $PT$ interval with compositions of solid solutions changing until one of the phases involved in the reaction disappears. The failure of Ito and Kennedy to observe change in the Mg/($\text{Mg} + \text{Fe}$) ratio of garnet through the garnet granulite stability field is inconsistent with theoretical analysis of the reactions involved or with the published garnet compositions of Green and Ringwood (1967a), and T. H. Green (1967) and may be due to problems in iron contamination of their charge. Although Ito and Kennedy (1971), quoting Banno (1970), argue that pressure effect on the Fe/Mg distribution coefficient between garnet and pyroxene may cause
garnet to become more Fe-rich with increasing pressure, this effect is minor (Banno 1970). Furthermore, this effect is irrelevant to the reaction being considered—the production of garnet (± clinopyroxene, ± quartz) at the expense of olivine, orthopyroxene, and plagioclase. This is not simply an exchange reaction between garnet and clinopyroxene solid solution. Ito and Kennedy (1970, 1971) attach considerable geophysical significance to the presence of "steps" in the density versus pressure curve, correlating these with seismic velocity "discontinuities" in the deep crust or crust-mantle boundary. In attempting this application of their data, Ito and Kennedy argue for a major significance for the results of NM5 composition on the basis of similarity of NM5 composition to the average composition of oceanic tholeiites (tables 1 and 2). However, the comparisons of tables 1 and 2 demonstrate important differences.
in both chemical composition and eclogite mineralogy between NM5 and average oceanic tholeiite. In addition, more recent data on deep-sea basalts shows very clearly that there is large variation in chemical composition between individual samples. Thus, even if it could be convincingly demonstrated that there are sharp mineralogical boundaries for a specific basalt composition, these discontinuities would be diffuse or smeared out if present in a sequence of chemically diverse individual lava flows or intrusions.

**EXTRAPOLATION OF PHASE BOUNDARIES TO LOW TEMPERATURE**

Ito and Kennedy (1971) state, "Our results on the stability field of eclogite are remarkably in contrast to those published by Green and Ringwood (1967a)." This statement is untrue. In figures 1 and 2 and the preceding sections, we have shown that the experimental results obtained at 1,100°C and on the solidus by Ito and Kennedy are in excellent agreement with our own experimental data. In figure 4, we compare the extrapolation to lower temperatures which we have previously made with that now advocated by Ito and Kennedy (1971). They note the difference in slope of our line of best fit (27.5 bars/degree centigrade between 1,000°C and 1,250°C) for the outgoing of plagioclase in quartz tholeiite B composition relative to their chosen line of best fit (20 bars/degree centigrade between 800°C and 1,200°C) for NM5 composition. However, we recognized the limitations of our data in defining accurate slopes for the phase boundaries; application of our estimates of precision in PT measurement would allow slopes of 18–36 bars/degree centigrade between 1,000°C and 1,250°C for the boundary marking the outgoing of plagioclase. Thus we did not take 27.5 bars/degree centigrade as the slope of the plagioclase-out boundary and in fact devoted considerable discussion (Ringwood and Green 1966, p. 399–402) to the extrapolation of our experimental boundaries to lower temperatures. We noted that both the incoming of garnet and outgoing of plagioclase are complex reactions involving solid solutions of plagioclase, pyroxenes, olivine, and garnet. The net result of this discussion was the extrapolation of the plagioclase-out boundary at 24 bars/degree centigrade; this is illustrated in figures 1 and 4. Ito and Kennedy (1971) argue that the slope for the simple system reaction albite → jadeite + quartz is now well determined at 20 bars/degree centigrade and that this slope is consistent with their data on the outgoing of plagioclase in NM5. Accordingly, the outgoing of plagioclase boundary for NM5 is extrapolated at 20 bars/degree centigrade in figure 4. Ito and Kennedy's argument that, where the outgoing of plagioclase is due to the pyroxene + plagioclase → pyroxene + quartz reaction, then the 20 bar/degree centigrade slope should be applied, is only an approximation. Thus the plagioclase present is not pure albite, and its disappearance involves coupled reactions. The anorthite component either reacts with enstatite solid solution in the clinopyroxene to yield garnet + quartz or alternatively breaks down to yield grossular solid solution + kyanite + quartz (as in the compositions studied by T. H. Green 1967; see also table 2).

The approximation suggested by Ito and Kennedy for extrapolation of the gabbro to eclogite boundaries has been applied in figure 4, as it is based on arguments at least as good as the 24 bars/degree centigrade slope used in our earlier work. Thus the garnet-granulite → plagioclase eclogite boundary for NM5, which is equivalent to the disappearance of plagioclase in the rock composition of table 1, second column, has been extrapolated and intersects the temperature axis at 100°C. Extrapolation of the plagioclase-out boundary for quartz tholeiite B (figs. 4, 2) at 20 bars/degree centigrade would give an identical lower boundary to the eclogite field. A similar exercise could be carried out for plagioclase disappearance in compositions 1–10 (figs. 2 and 4). It is seen from figure 4 that the temperature on the garnet granulite to eclogite (or plagi-
Fig. 4.—Comparison of extrapolation to lower temperatures of phase boundaries between eclogite, garnet granulite, and gabbroic mineral assemblages as advocated by Ringwood and Green (1966), Green and Ringwood (1967a) (dashed lines and vertically and horizontally shaded fields labeled “G&R”) with the extrapolations advocated by Ito and Kennedy (1971) (stippled fields, lines labeled “I&K”). The numbered crosses at 1,100°C mark the disappearance of plagioclase in the compositions 1–10 of figure 2. According to the arguments of Ito and Kennedy (1971), lines at 20 bars/degree centigrade could be drawn through each of these points to extrapolate the disappearance of plagioclase to lower temperatures; such a line for quartz tholeiite B (composition 2) would be coincident with the garnet granulite → plagioclase eclogite boundary of Ito and Kennedy (1971) (or garnet granulite → eclogite boundary for composition of table 1, second col.) if these are also extrapolated at 20 bars/degree centigrade. The dashed line labeled “I&K 18 bars/°C” is the line taken from Ito and Kennedy’s figure 4 marking the low-pressure boundary of their plagioclase eclogite field. Ito and Kennedy (1971) drew this line at 18 bars/degree centigrade without justifying this by either experiment or argument. If indeed it is argued that this boundary is more complex than the plagioclase-out boundary for NM5 (and thus Ito and Kennedy’s arguments for a 20 bar/degree centigrade slope are not acceptable), then it must be admitted that the only evidence on the slope of this boundary is that it lies within the experimental limits of our quartz tholeiite B data, that is, between 18 and 36 bars/degree centigrade.
class eclogite for NM5) boundary at a pressure corresponding to the base of the normal continental crust (10 kbar) is 600°C if the extrapolation at 20 bars/degree centigrade from Ito and Kennedy's experimental data is followed (compared with 670°C from the Ringwood and Green [1966] extrapolation). The temperature for the garnet granulite to plagioclase eclogite boundary is 530°C at 10 kbar if the 18 bars/degree centigrade slope of Ito and Kennedy (1971, fig. 4) is used. However, this slope is arbitrary, whereas Ito and Kennedy have presented a reasoned argument for the 20 bars/degree centigrade slope. If this reasoned argument is not accepted, then the only relevant experimental data are those on quartz tholeiite B (Green and Ringwood 1967), that is, 27 ± 9 bars/degree centigrade. If the temperature at the base of the stable continental crust is <600°C, then eclogite would be the stable mineralogy of quartz tholeiite B composition throughout the continental crust. Similarly, quartz + plagioclase eclogite or quartz eclogite (± kyanite) would be the stable form of NM5 basalt, the high alumina basalt (1) or andesite (9) throughout the continental crust. The discussion and argument of Ringwood and Green (1966, p. 398-423) will apply to the gabbro-garnet granulite-eclogite transformation and its geophysical significance whether the Ito and Kennedy 20 bars/degree centigrade or the Green and Ringwood 24 bars/degree centigrade slopes are used for extrapolation. This particularly applies to the argument that, since the geothermal gradient and garnet granulite boundary are subparallel in the 0-10 kbar interval, no large mineralogical change (without chemical change) can occur over a small depth interval along the geothermal gradient. It may be noted that the boundary advocated by Ito and Kennedy (1971) for the upper pressure limit of the gabbro field is identical to that shown by Green and Ringwood (1967a, fig. 8) for the upper pressure limit of their low-pressure granulite field, that is, the reaction of olivine + plagioclase to yield garnet or spinel + pyroxenes (see fig. 4).

CONCLUSIONS

The recent experimental studies by Ito and Kennedy (1971) provide improved data on the position of phase boundaries of the gabbro, garnet granulite, and eclogite assemblages for a specific olivine tholeiite composition. Ito and Kennedy's conclusion that their new data are inconsistent with earlier data obtained in our own laboratory is shown to be incorrect and apparently based on an inadequate understanding of the role of chemical differences between the various basalts. We have shown that the curves for the solidus, the incoming of garnet, and the outgoing of plagioclase determined by Ito and Kennedy (1971) are consistent, within experimental uncertainty, in both position and slope with boundaries determined in our laboratory on relevant basaltic compositions. Ito and Kennedy (1970, 1971) have failed to demonstrate unequivocally their assertion that there are two "sharp" increases in density within the gabbro to eclogite transition marking the appearance of garnet and rapid decrease in plagioclase, respectively. Thus we consider that Ito and Kennedy's attempt to relate these sharp density increases to "Conrad" and Mohorovicic discontinuities is without foundation, even for the specific basalt composition which they studied.

The experimental work by Ito and Kennedy supports, for their olivine tholeiite composition, two of the major conclusions from our earlier studies:

1. The transition between gabbroic and eclogitic mineral assemblages occupies a broad pressure interval between the incoming of garnet and disappearance of plagioclase. The positions of the boundaries and the width of the field for the transitional garnet granulite mineral assemblage are sensitive to variations in the chemical compositions of basalts.

2. The extrapolation of experimentally determined boundaries to lower temperatures suggests that eclogite mineralogy is stable in dry basaltic rocks along normal geothermal gradients throughout the con-
continental crust in stable or shield regions. This aspect of the experimental study has been treated fully previously (Ringwood and Green 1966; Green and Ringwood 1967a).

These two conclusions, using arguments developed previously (Ringwood and Green 1966), effectively eliminate the gabbro-eclogite transition as an explanation for the existence of the M-discontinuity in oceanic or stable continental crustal environments and render it highly improbable that eclogite is the major constituent rock type of the upper mantle.

REFERENCES CITED


Experimental Study of the Stability of Cordierite and Garnet in Pelitic Compositions at High Pressures and Temperatures

I. Compositions with Excess Alumino-Silicate

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Department of Geophysics and Geochemistry, Australian National University

Received October 28, 1971

Abstract. The stability of cordierite and garnet relative to their anhydrous breakdown products, i.e. hypersthene, sapphireine, olivine, spinel, sillimanite and quartz, has been studied experimentally in model pelitic compositions (system MgO-FeO-Al2O3-CaO-K2O-SiO2). Below 1000° C cordierite breaks down according to the divariant reaction cordierite + garnet + sillimanite + quartz (1) for most values of the MgO/MgO+FeO ratio (X). At very high values of X (ca. X > 0.9) garnet in reaction (1) is replaced by hypersthene. The position and width of the divariant field (in terms of pressure and temperature) in which cordierite and garnet coexist, is a function of the Al2O3/MgO FeO ratio. If this ratio is increased then the stability field of garnet is reduced and that of cordierite extended towards higher pressure. Compositions of coexisting cordierite and garnet in divariant equilibrium have been analysed by electron probe micro-analyser. These compositions are unique functions of pressure and temperature. Above ca. 1000° C the breakdown of cordierite involves the phases sapphireine and herecynite-rich spinel in Mg-rich and Fe-rich compositions respectively.

A. Introduction

The occurrence of cordierite in rocks from granulite facies terranes has aroused a great deal of interest among petrologists. Cordierite has been regarded as a low pressure mineral, and therefore as atypical of deep-seated regional metamorphism. Similarly the occurrence of almandine in contact aureoles has led to controversy, as almandine-rich garnets were thought to be stable only at relatively high pressure. Coexisting cordierite and garnet are known both from high grade amphibolite and granulite facies terranes and from high level, low pressure, contact aureoles. In the latter, however, garnet occurs in addition to cordierite only in very iron-rich rocks. This has led some authors (e.g. Chinner, 1962) to stress the importance of the effect of rock-chemistry as well as that of physical parameters on the stability of cordierite and garnet. A knowledge of the phase equilibria controlling the stability of cordierite and garnet (relative to their anhydrous breakdown products) as a function of pressure, temperature and bulk composition, will therefore be of considerable value for the understanding of the conditions of formation of metamorphic rocks.

Most previous work has concentrated on the determination of the stability of the magnesian and iron end-members of the minerals cordierite and garnet.
(under their own compositions), e.g. the stability of pyrope (Boyd and England, 1959) the stability of almanine (Hsu, 1968), the stability of Mg-cordierite (Schreyer and Yoder, 1960, 1964) and Fe-cordierite (Richardson, 1968). These studies provide essential information about the stability of the end-member phases, but are of limited value to quantitatively or even qualitatively explain and unravel the more complex equilibria that occur in natural rocks.

A study of the pyrope-almandine join at 2 kb pressure by Hsu and Burnham (1969) has shown some of the complexities in the phase relationships of intermediate garnets and comes much closer to simulating the actual equilibria of natural rocks.

Hirschberg and Winkler (1968) have studied the stability of garnet and cordierite in two natural Ca-poor, metapelitic compositions. Their work shows the effect of the Mg/Mg+Fe\(^{2+}\) ratio on the stability of garnet and demonstrates the existence of a field in which cordierite and garnet coexist in the presence of biotite, sillimanite and quartz, thereby reproducing a natural rock assemblage.

The present investigation (also Hensen and Green, 1969, 1970) differs from the previous studies mentioned above in that it has endeavoured to make a systematic study of the effect of Mg/Mg+Fe\(^{2+}\) ratio on the relative stability of the ferromagnesian minerals in a chemical environment similar to that existing in natural metapelitic rocks. This has been made possible by the use of the electron microprobe for analysis of the extremely fine-grained, experimentally-produced, phases. As the chemical composition of coexisting ferromagnesian phases can be accurately measured, a detailed consideration of the pressure-temperature-composition relationships is possible. The present experimental investigation using bulk compositions modelled on natural metapelites should elucidate the equilibria occurring in metamorphic rocks and provide quantitative information about the physical conditions required for the formation of various cordierite and garnet bearing assemblages.

A theoretical treatment of divariant and univariant reactions in the system MgO-FeO-Al\(_2\)O\(_3\)-SiO\(_2\), which can be used as a model for the more complex compositions studied experimentally, has been given by Hensen (1971, in press).

**B. Compositions Studied**

In order to closely reproduce the mineral assemblages formed in natural rocks during high grade metamorphism, the compositions used in the present study have been modelled on natural pelitic compositions (see Table 1).

The most important chemical variable that affects the relative stability of ferromagnesian phases is the Mg/Mg+Fe\(^{2+}\) ratio. Therefore the compositions studied have been chosen to bring out the effect of this ratio on the phase relationships. For practical reasons the synthetic compositions have been enriched in the major elements that constitute the phases of interest (i.e. cordierite, garnet and hypersthene) relative to natural pelites. Minor and trace elements have not been included.

Silica-saturated cordierite-garnet bearing rocks can be divided into three groups on the basis of their Al\(_2\)O\(_3\)/FeO+MgO ratio (A/F+M). This is most aptly demon-
Table 1. Compositions of synthetic mixes used in experimental study

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<th>B₈₀</th>
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100 Mg/Mg + Fe²⁺ 0 30 50 70 100 30 70 70

Normative plagioclase composition (% An)

51.0 51.9 52.4 53.2 54.0 43.4 44.4 55.5

Fig. 1. Position of synthetic compositions A, B and C in various compositional diagrams. 

AEC: A Al₂O₃-(K₂O + Na₂O), C CaO, F FeO + MgO. AEFM: A Al₂O₃-(CaO + K₂O + Na₂O), F FeO, M MgO, SiO₂-(MgO + FeO)-Al₂O₃: SiO₂ = SiO₂-6(K₂O + Na₂O)-2CaO, Al₂O₃ = Al₂O₃-(K₂O + Na₂O + CaO), MgO + FeO

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100 Mg/Mg + Fe²⁺ 0 30 50 70 100 30 70 70

Normative plagioclase composition (% An)

51.0 51.9 52.4 53.2 54.0 43.4 44.4 55.5

strated graphically (Fig. 1)

Three series of compositions, representing the three groups, have been chosen for experiment. The A- and B-series have A/F + M < 1 and the C-series has A/F + M > 1.

2 Abbreviations used in the text and figures are: Cordierite (OI), Garnet (Ga), Hypersthene (Hy), Olivine (Ol), Sapphirine (Ss), Spinel (Sp), Sillimanite (Ss), Kyanite (Ky), Quartz (Qz), Feldspars (Fsp).
Each series consists of a number of compositions with varying Mg:Mg$^+$-Fe$^{2+}$ ratios. Five compositions (Table I, Fig. 1) in the B-series ($B_0$, $B_{20}$, $B_{30}$, $B_{50}$, $B_{100}$), two in the C-series ($C_{10}$, $C_{20}$), and one in the A-series ($A_{50}$) have been studied experimentally. In this paper we are concerned with the experimental results on the C-series. Experiments on the A- and B-series will be reported in a forthcoming paper (Hensen and Green, II. in prep.).

C. Apparatus and Techniques

The experiments have been carried out in a single-stage, solid media, piston-cylinder apparatus of Boyd and England (1960, 1963) design. All experimental runs have been carried out in graphite capsules to minimize the possibility of Fe-loss to platinum containers and to retain conditions of low oxygen fugacity. Above 800$^\circ$ C, dried furnace assemblies with inner boron nitride sleeves, identical to those described by Green and Ringwood (1967), have been used. By this method essentially dry conditions are maintained during the runs, preventing hydration or partial melting. At 800$^\circ$ C assemblies with talc oxides only have been used.

Temperatures were controlled by Pt-Pt 10% Rh thermocouples at 100$^\circ$ C and above. A Chromel-Nichrome, Nippon Steel $1000^\circ$ C and below, inserted in temperature control is assumed to be $\pm 10^\circ$ C. The maximum difference between the Chromel-Nichrome thermocouples and Pt-Pt 10% Rh couples, at 1111$^\circ$ C, has been believed to be $\pm 10^\circ$ C. Unfortunately no data for the variation of the pressure with temperature are not available as yet. However, if improved production of piston-cylinder apparatus up to 15,000 bars will be available, it may be possible to verify these.

Fig. 1

Data of the type:

Each glass showed the following minerals during recrystallization: 1. Na$_2$O, K$_2$O, Plagioclase, and K-feldspar. The analysis of the starting material showed that the glass contained no detectable free alkali elements (Na and K) during experimentation.

At the use of glass as starting material initially proved unreliable owing to the appearance and persistence of metastable low pressure phases (e.g., cordierite) and extremely low nucleation rates of high pressure phases (e.g., garnet). A seeding technique was used. Finely ground crystalline material, containing both the high and low pressure assemblages, obtained from large capacity runs on glass, is mixed with glass in the 1:1 ratio. It has been found that the glass shards crystallize in a short time (5-60 min) to the low pressure assemblage up to pressures well beyond its stability limit. Therefore an increase in the high pressure assemblage takes place at the cost of the low pressure assemblage (and vice versa).

Three seeded starting material, listed below, was prepared by slow heating of the high pressure assemblage. Starting material (I) was used for most experiments. Starting material (II) was used to investigate the relative stability of garnet and cordierite, while (II) and (III) were used to investigate the relative stability of garnet and sillimanite and sapphire.

1. 10% low pressure assemblage, containing cordierite, minor sillimanite, quartz, and feldspar.
2. 10% high pressure assemblage, containing garnet, sillimanite and minor feldspar.
3. 90% glass.
The starting material used for experiments on the C2 composition contained 20% high pressure assemblage (crystallized from glass at 950°C-8.1 kbar, containing major garnet, sillimanite, quartz and minor spinel) and 80% glassy phryite.

The best indication that equilibrium has been closely approached is provided by the microprobe analyses of the experimental phases. These analyses show the garnets and cordierites within each experimental run are remarkably uniform in composition. Agreement between experiments using different starting materials is also good and distribution coefficients between coexisting garnet and cordierite agree within experimental error in different compositions, for example, in the B2 and C2 compositions.

On the other hand, the persistence of garnet seeds with virtually unchanged composition as cores in more iron-rich garnet at 900°C, and sometimes also at 1000°C, indicates that diffusion rates in the solid phases are low and that complete chemical equilibrium has not always been reached. The effect of low reaction rates on adjacent, in comparison to existing, boundaries, and most of such cases, however, has been possible, to determine the direction in which reaction is proceeding.

Because reaction rates are strongly temperature dependent, run times vary from around 15 hours at 1100°C to 96 hours at 800°C. These times have proved to be adequate for the purpose of this investigation.

Evidence of low oxygen fugacity under the present experimental conditions is obtained from the work on iron endmember compositions (Hensen and Green, in prep.), given below.

1. The coexistence of fayalite and quartz with minor hercynite, P/100 = 1000 and 1000°C = 1.8, and 3.6 kbar.

2. The stability of almandine + quartz (Figure, pentlandite,) at 1000°C - 1050°C = 0.6 kbar.

The very low ferrie-iron content of the hercynite, coexisting with quartz at 1050°C = 3.6 kbar, it contains only 8% more magnetite.

The coexistence of fayalite and quartz and the fact that spinel has only 8% more magnetite solid solution show that conditions are more reducing than those of quartz-fayalite-magnetite buffer (Staufer and Eugster, 1962).
determined principally by the X-ray powder method. In the case of the incoming of garnet, where only a small change in the abundance of that phase occurs, the interpretation of the X-ray data has been confirmed by the examination of polished sections of the runs in question. When a decrease of garnet had been interpreted from the X-ray data, irregular, resorbed grains (seeds) of garnet were observed optically. Rounded grains with increased size were found in the runs in which garnet grew (Fig. 2).

D. Procedure for Quantitative Electron Probe Analysis of Experimental Phases

An electron probe X-ray microanalyser (Applied Research Laboratories, EMX model) has been used for the quantitative analysis of the experimentally produced phases. Partial analyses for the elements Fe, Ca, and Mg, which can be measured simultaneously, were made in most cases. Grains larger than 5–8 microns can be accurately analysed with a beam size of 1–2 microns.

Garnet Analysis

Garnet forms porphyroblasts which range up to 30 microns in size. However, garnet is commonly finer-grained (3–15 microns) and has small inclusions of other phases.

To obtain the garnet analyses the electron beam was moved over the grain by electronic controls, allowing detection of zoning of the crystal or the presence of inclusions, even in very small grains. For each experimental run, a large number (15–30) of grains were measured. All garnet analyses were made with a single garnet standard. The analytical precision is ±1.5% of the amount present for the elements Fe and Mg and ±4% for Ca.

Because the unknown garnets were analysed only for three elements, it was not possible to use a normal (direct) correction procedure. After corrections were made for beam current drift, background and dead time, the equivalent weights of almandine, grossular and pyrope were calculated from the Fe, Ca and Mg values. The calculated (3-component) garnet analysis has been used to obtain corrected values for Fe, Ca and Mg. The following corrections have been made: absorption correction (Philibert, 1963; Duncumb and Shields, 1966); fluorescence correction (Reed, 1965). A constant of 11.6 was used for the J-values: atomic number correction (Duncumb and Reed, 1968). Corrected endmembers were computed and automatically printed out on triangular garnet diagrams.

Cordierite Analysis

Cordierite could not be recognized in polished sections. It can only be found by moving the sample under the electron beam, while watching the X-ray intensities of the three elements (Fe, Ca, Mg). Analyses of small areas of only a few microns in size, which are very low in Ca and have intermediate amounts of Fe and Mg and which were thought to represent cordierite, do give calculated cordierite totals of close to 100 per cent. The Mg/Mg+Fe\(^{3+}\) ratios of these analyses generally fall in a restricted range for each run, as do the garnet analyses.

3 It is assumed that the garnet contains no ferric iron. The totals obtained suggest this assumption is valid within the limits of error.
Cordierite and Garnet in Pelites. 1

They are therefore believed to represent the actual range in cordierite compositions. Uncorrected values for Fe and Mg were used for the calculation of the Mg/Mg+Fe²⁺ ratio of the cordierite since it was found empirically that the omission of the correction procedure did not significantly affect the results.

Settings Used for Analyses

Accelerating voltage 10-12 kilovolts
Emission current 80-100 milliamps
Sample current 0.035-0.045 microamps
Counting time 20 seconds.

E. Experimental Results for C₇₀ Composition

The experimental data and the deduced phase relations are represented in Figs. 3 and 4. At low pressure the assemblage cordierite-sillimanite-quartz-feldspars (a) is found over the temperature range covered by the experiments, i.e. 800-1150°C.

At temperatures below 1100°C this assemblage is replaced towards higher pressure by garnet-cordierite-sillimanite-quartz-feldspar (b). The boundary for the incoming of garnet has a negative slope. Its position has been determined using the following criteria:

1. On the high pressure side of the boundary the amount of garnet has markedly increased (Fig. 2). Electron probe microanalysis showed that the composition of the garnet differs considerably from that of the seeded garnet which has 100 X\textsubscript{Mg}=70 (i.e. the Mg/Mg+Fe²⁺ ratio of the bulk composition; see next section for chemical data).

2. On the low pressure side of the boundary garnet either disappears, or its amount decreases or remains unchanged. The garnets are small and have irregular shapes (see Fig. 2). Analyses of the small grains indicate that these garnets invariably have the same Mg/Mg+Fe²⁺ ratio as the bulk composition (i.e. of the garnet seeds), and therefore they are regarded as non-equilibrated relics which failed to disappear due to the low reaction rates close to the equilibrium boundary for the incoming of garnet.

At 900 and 1000°C cordierite and garnet are found to coexist over a restricted pressure interval. The high pressure boundary of this interval, which also has a negative slope, marks the disappearance of cordierite. Since no experiments have been carried out in which cordierite grew from a garnet-sillimanite-quartz assemblage on the low pressure side of the boundary, this boundary can be regarded only as a high pressure limit for the stability of cordierite. It is believed, however, that it represents the equilibrium boundary for the stability of cordierite because the results are in close agreement with those on the B₇₀ composition (Hensen and Green, II, in prep.) in which a reversal was carried out at 900°C showing the phase boundary inferred on the basis of seeded glass experiments to be correct.

On request detailed tables with experimental results can be obtained from the authors.

5 Fig. 4 shows the interactions of divariant reactions with univariant phase boundaries. The univariant boundaries have been derived by a synthesis of experimental evidence on all compositions in the C- and B-series (Hensen and Green, III, in prep.).
Fig. 2 A–D. Microphotographs of polished surfaces of experimental runs (C12 composition). Groundmass consists of cordierite-sillimanite-quartz-feldspar in all cases. A) 1000°C, 7.2 kb (run 1747). Garnet (high relief) decreased. B) 1000°C, 8.1 kb (run 1884). Garnet increased. C) 900°C, 8.1 kb (run 1898). Garnet slightly decreased; note angular shapes. D) 900°C, 9 kb (run 1459). Garnet increased.
At 900° C–10.8 kb the assemblage garnet-sillimanite-quartz-feldspar (c) is found. However, at 1000° C hypersthene appears as an additional phase at pressures above the breakdown of cordierite.

Because work on Bₐ raised doubts regarding the stability of hypersthene under these conditions, an attempt has been made to verify the observed field of coexistence of garnet-hypersthene-sillimanite-quartz-feldspars (d).

In a run, using starting material (I) containing seeds of both hypersthene and sapphirine, in addition to garnet and cordierite, hypersthene disappeared and the assemblage garnet-minor sapphirine-sillimanite-feldspars-trace of quartz (h) was obtained. This results indicates that assemblage (d) is metastable with respect to (h) at 1050° C, 10.35 kb, and probably also with respect to (c) at 1000° C. The resulting phase relationships shown in Fig. 3 are consistent with those found in the Bₐ composition.

At 1100° C the sequence of assemblages is relatively complicated. On the basis of experiments using starting materials (I) and (II) the following sequence of assemblages has been deduced to be stable with increasing pressure.

- cordierite-sillimanite-quartz-feldspars (a)
- cordierite-spinel-sillimanite-quartz-feldspars (e)
- cordierite-sapphirine-sillimanite-quartz-feldspars (g)
- sapphirine-sillimanite-quartz-feldspars (f)
- sapphirine-garnet-sillimanite-quartz-feldspars (h)
- garnet-sillimanite-quartz-feldspars (c)

The assemblage garnet-hypersthene-sillimanite-quartz-feldspars (d) is believed to be metastable.

At 800° the stability relations of garnet and cordierite are obscured by the appearance of biotite giving rise to the assemblages cordierite-garnet-biotite-sillimanite-quartz-feldspars (i) and garnet-biotite-sillimanite-quartz-feldspars (j) at 10.8 and 11.7 kb respectively. Biotite does not appear at pressures below 9–10 kb at this temperature. Both runs at 10.8 and 11.7 kb are outside the sillimanite stability field as determined by Richardson et al. (1968), and the persistence
Fig. 4. P-T diagram showing the relation of divariant bands (shaded), determined for the C<sub>30</sub> and C<sub>30</sub> compositions, with univariant phase boundaries. These univariant curves are based on a synthesis of all experimental evidence on the C- and B-series of compositions. Points (Sp), (Hy), (Si) and (A) are invariant points of sillimanite in these runs is therefore regarded as a metastable feature. The K<sub>2</sub>Si boundary in Figs. 3 and 4 differs slightly from that proposed by the above authors (Hensel and Essene, 1971).

**Chemical Analyses of Experimentally Produced Phases**

Microprobe analyses of garnet and cordierite are given in Table 2a. Attention should be drawn to the remarkably uniform composition of the garnets formed within each experimental run. This uniformity of composition indicates that equilibrium has been closely approached in these experiments and justifies the use of the analytical data for the deduction of the P, T, X relationships for this series.

The analyses show that the Mg/(Mg+Fe)<sup>2+</sup> ratio of the garnet varies as a function of pressure and temperature. Garnet is most iron-rich at low pressures and becomes progressively more magnesian with increasing pressure. The Mg/(Mg+Fe)<sup>2+</sup> ratio decreases with decreasing temperature, at constant pressure, indicating that contours for constant garnet composition will have negative slopes on a P-T diagram. The garnet contains a small amount of grossular, i.e. 6±1 mole %. There is no detectable change in this amount as a function of either pressure or temperature.

In runs at 900° C and in one case at 1000° C (run 2395) Fe-rich garnet have Mg-rich cores. The difference between core and rim in these garnets can be considerable, as shown in Fig. 6 (run 2459). The Mg-rich cores are believed to be the result of the persistence of nonequilibrated garnet seeds. The disequilibrium between core and rim will not significantly affect the overall chemistry.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (°C)</th>
<th>Press (Kb)</th>
<th>Garnet analyses</th>
<th>No. of analyses</th>
<th>Percentage of total falling within these limits</th>
<th>Corderite analyses</th>
<th>Spinel analyses</th>
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</thead>
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<td>Mole % gross</td>
<td>100 Mg/Mg+Fe²⁺</td>
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Table 2. Microprobe analyses of experimentally produced phases

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<th>Run No.</th>
<th>Temp. (°C)</th>
<th>Press (Kb)</th>
<th>Garnet analyses</th>
<th>No. of analyses</th>
<th>Percentage of total falling within these limits</th>
<th>Corderite analyses</th>
<th>Spinel analyses</th>
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<td>100 Mg/Mg+Fe²⁺</td>
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b) C30 composition

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<th>Garnet analyses</th>
<th>No. of analyses</th>
<th>Percentage of total falling within these limits</th>
<th>Corderite analyses</th>
<th>Spinel analyses</th>
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<td>100 Mg/Mg+Fe²⁺</td>
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<td>20</td>
<td></td>
<td></td>
<td>26-34</td>
<td>4-6</td>
</tr>
</tbody>
</table>
of the run since the seeds only constitute a very small weight fraction of each run. In addition to zoned garnets, homogeneous grains also occur in run 2459. These have a distinctly lower Mg/Mg+$Fe^{2+}$ ratio than the rims of zoned garnets suggesting that the garnets are too small (3-15 μ) for the complete resolution of the core and rim by the present technique.

The cordierite analyses, given in Table 3, are few in number, but allow an evaluation of the distribution coefficient of Fe and Mg between cordierite and garnet. The calculated values for the distribution coefficients are given below.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (°C)</th>
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<th>$X_{Cd}$</th>
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<tr>
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<tr>
<td>2459</td>
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<td>9</td>
<td>81 ± 1</td>
<td>4.5 ± 0.6</td>
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There is no detectable change in the value of $K_D$ between 900 and 1000°C. Sapphirine has been analysed in one run. The analysis is given below.

<table>
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<th>SiO$_2$</th>
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<td>Al$_2$O$_3$</td>
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<tr>
<td>FeO</td>
<td>8.57</td>
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<tr>
<td>MgO</td>
<td>17.27</td>
</tr>
<tr>
<td>99.71</td>
<td>100 Mg/Mg+$Fe^{2+}$ = 78</td>
</tr>
</tbody>
</table>

Sapphirine is the only ferromagnesian mineral present in run 1899. The change in Mg/Mg+$Fe^{2+}$ ratio relative to the bulk composition (with 100 $X_M$=70) is attributed to partial melting which has the effect of enriching the residual crystalline material in magnesium.

Discussion of Results

The reactions which have been inferred from the changes in mineralogy, are listed in Table 3. The most important feature of the phase diagram (Fig. 3) is the stability field for the assemblage: cordierite-garnet-sillimanite-quartz-feldspar.
This assemblage corresponds to the following divariant reaction in the system MgO–FeO–Al₂O₃–SiO₂:

\[ \text{Cd} \leftrightarrow \text{Ga} + \text{Si} + \text{Qz} \] (1)

The garnet contains 5–7 mole % grossular component, and therefore this assemblage is not strictly divariant. The composition of the coexisting plagioclase could have an effect on the grossular content of the garnet and therefore on its stability. The total change in composition of the plagioclase from low pressure, where no garnet is present, to high pressure, where garnet is the only ferromagnesian phase, can be calculated for a known garnet composition. It is found that the normative plagioclase composition must change from An₄₄.2 to An₉₉.₂ across the divariant band in Fig. 3. This constitutes a change of ca. 34% in anorthite content over the pressure interval of the divariant band, while the grossular content of the garnet remains constant (within analytical error).

Similarly in B₇₀, the garnet contains the same amount of grossular, over roughly the same pressure interval, although the plagioclase composition is different (An₄₃ to An₉₆). This also shows that within these admittedly restricted limits the grossular content of the garnet is not measurably influenced by the composition of the plagioclase. Therefore, although the equilibria involving garnet are not strictly univariant or divariant because of solid solution of grossular component in the garnet, these reactions can be treated as simple univariant and divariant reactions and will be referred to as such in the remainder of the paper. It should be noted that the foregoing does not imply that the presently determined phase relations (in terms of \( P, T \) and \( X \)) would also hold for the Ca-free system MgO–FeO–Al₂O₃–SiO₂. A comparison of a Ca-free with a Ca-bearing composition, both with the same Mg/Mg+Fe²⁺ ratio, shows important differences in \( P, T, X \) relations, although the reactions remain unchanged (Hensen and Green, II, in prep.).

At 1000°C hypersthene appears at pressures higher than the breakdown of cordierite. In terms of phase relations the appearance of hypersthene could mean that we have crossed the univariant curve marking the breakdown of the pair Cd-Ga to Hy-Si-Qz [reaction (Sa, Sp); Hensen, 1971, in press]. This interpretation showing the experimental results to be consistent with the theoretical model was adopted (Hensen and Green, 1970) until it appeared from the data on the B₇₀ and B₉₀ compositions that the occurrence of hypersthene is a metastable feature. Assemblage (d) is deduced to be a stable assemblage in more magnesian compositions (see Fig. 9).

At 1100 and 1150°C the appearance of spinel instead of garnet at 8.2 kb indicates that the reaction Cd=Sp+Qz (2) is stable with respect to reaction Cd=Ga+Si+Qz (1) because the garnet seeds that were present in the starting material disappeared. The stability fields of the divariant assemblages Cd-Ga-Si-Qz and Cd-Sp-Qz are separated by the univariant reaction (Fig. 4) Sp+Qz=Cd+Ga+Si (1). The experimental evidence obtained from the C₁₀₀ composition (next section) suggests that this reaction has a positive slope, which requires the volume change of this reaction to be negative.

At higher pressure, above the field for Cd-Sp-Qz (e) we find the assemblage Cd-Sa-Qz (g) which corresponds to the divariant reaction Cd=Sa+Qz (3). Assemblages (e) and (g) are separated by the univariant boundary (Fig. 4) for

7 See Hensen (1971, in press).
the reaction \( \text{Cd} + \text{Sp} \rightarrow \text{Sa} + \text{Qz} \) (II). This is a degenerate univariant reaction, involving only four phases, owing to the fact that cordierite, sapphire, spinel and quartz are co-planar in compositional space.

Reaction (II) has not been reversed, i.e. sapphire has not been broken down to cordierite and spinel. The boundary, required between the stability fields of the assemblages \( \text{Cd-Ga-Si-Qz} \) (b) and \( \text{Cd-Su-Qz} \) (g) (Figs. 3 and 4) must be \( \text{Cd} + \text{Ga} + \text{Si} \rightarrow \text{Sa} + \text{Qz} \) \( \Delta V = -\text{ve} \; \text{III} \).

At 1100°C-9 kb no sapphire was formed in the runs using the normal starting material. With a mix seeded with sapphire, however, only sapphire was found after the run. This result, together with the occurrence at 1050°C, 10.35 kb of the assemblage garnet-sapphire-sillimanite-trace quartz-feldspars (k) indicate the existence of the divariant reaction \( \text{Sa} + \text{Qz} \rightarrow \text{Ga} + \text{Si} \) (4). As shown in Fig. 4 this reaction intersects on the univariant curve (III) and has a positive slope (i.e. \( \Delta V = -\text{ve} \)).

At low temperature, around 800°C, reaction (1) must intersect the kyanite-sillimanite phase boundary. As a result the stability field of cordierite is reduced towards lower temperature, but the reaction \( \text{Cd} \rightarrow \text{Ga} + \text{Ky} + \text{Qz} \) probably still has a negative slope.

F. Experimental Results in \( C_{30} \) Composition

The experimental data and deduced phase relations are shown in Figs. 7 and 4. At low temperature, below 950°C, the following three assemblages are found

---

8 Assuming sapphire has the molecular ratio of \( \text{MgO} + \text{FeO} \): \( \text{Al}_2\text{O}_3 : \text{SiO}_2 = 2:2:1 \). If sapphire is more aluminous, sillimanite must appear in addition on the left-hand side of reaction (II).

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with increasing pressure: cordierite-sillimanite-quartz-feldspar (a), cordierite-garnet-sillimanite-quartz-feldspar (b), and garnet-sillimanite-quartz-feldspar (c). The boundary for the appearance of garnet (a) has not been accurately fixed. A hydrothermal experiment at 750°C, 3.8 kb indicates that garnet is not stable under these conditions.

The phase boundary for the disappearance of cordierite has a negative slope. Two runs at 1000°C, 7.2 kb, of 13 and 65 hours' duration demonstrate the effect of run duration on the amount of reaction. In the former run, a moderate amount of cordierite is still present while in the longer run only a trace of cordierite remains. In the longer run the garnet has the same Mg/Mg+Fe²⁺ ratio as the bulk composition (100 X₁₀ = 30 ± 2). These two runs also show that metastable cordierite crystallizes from the glass initially before reaction to the high pressure assemblages takes place. In a run at 800°C, 9 kb the reaction rate appears to have been too low to eliminate cordierite in three days.

At 1050 and 1100°C the intermediate pressure assemblage cordierite-garnet-sillimanite-quartz-feldspar (b) is replaced by cordierite-spinel-sillimanite-quartz-feldspars (d).

At 1100°C, 6.3 kb, above the breakdown of cordierite, the assemblage is spinel-sillimanite-quartz-feldspars (e) and is replaced at 9.9 kb by garnet-sillimanite-quartz-feldspars (e). These two assemblages are separated by a boundary with a positive slope. Microphotographs of two runs at 1100°C, 9 and 9.9 kb, with assemblages (e) and (c) respectively are shown in Fig. 5.

Composition of Experimentally Produced Phases
The results of microprobe analyses of garnet, cordierite and spinel are given in Table 2. Only one run provided the analysis of a garnet-cordierite pair. The garnet analyses from the high temperature runs, the 1100°C run (no. 1960) in

\[ fO_2 \]

9 The iron wüstite buffer that was added had oxidized to magnetite at the completion of the run. It seems likely that the \( fO_2 \) was close to that of the quartz, fayalite, magnetite buffer.
particular, show the effect of partial melting on the Mg/Mg + Fe\(^{2+}\) ratio of the solids. These analyses clearly indicate that Fe distributes in favour of the melt with the result that the Mg/Mg + Fe\(^{2+}\) ratio of the garnet, being the only ferromagnesian phase present, increases. The large range of composition found in each of these runs, supports the observation that melting occurs locally and indicates that an overall equilibration of solids and liquid has not taken place.

### Table 3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta V)</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Univariant reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sp + Qz = Cd + Ga + Si</td>
<td>- ve</td>
<td>(1)</td>
</tr>
<tr>
<td>Sp + Cd = Sa + Qz</td>
<td>- ve</td>
<td>(11)</td>
</tr>
<tr>
<td>Cd + Ga = Hy + Ky + Qz</td>
<td>- ve</td>
<td>(3)</td>
</tr>
<tr>
<td>Cd + Ga = Hy + Si + Qz</td>
<td>- ve</td>
<td>(4)</td>
</tr>
<tr>
<td>b) Divariant reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd = Ga + Si + Qz</td>
<td>- ve</td>
<td>(2)</td>
</tr>
<tr>
<td>Cd = Sp + Qz</td>
<td>- ve</td>
<td>(3)</td>
</tr>
<tr>
<td>Sp + Qz = Ga + Si</td>
<td>- ve</td>
<td>(4)</td>
</tr>
<tr>
<td>Cd = Ga + Ky + Qz</td>
<td>- ve</td>
<td>(5)</td>
</tr>
<tr>
<td>Cd = Hy + Si + Qz</td>
<td>- ve</td>
<td>(6)</td>
</tr>
<tr>
<td>Cd = Hy + Ky + Qz</td>
<td>- ve</td>
<td>(7)</td>
</tr>
<tr>
<td>Hy + Si = Ga + Qz</td>
<td>- ve</td>
<td>(8)</td>
</tr>
<tr>
<td>Hy + Ky = Ga + Qz</td>
<td>- ve</td>
<td>(9)</td>
</tr>
<tr>
<td>Sa + Qz = Hy + Si</td>
<td>- ve</td>
<td>(10)</td>
</tr>
<tr>
<td>Sp + Qz = Sa</td>
<td>- ve</td>
<td>(11)</td>
</tr>
</tbody>
</table>

a. Reactions marked (x) have not been observed experimentally but have been deduced from a combination of experimental and theoretical evidence.

### Discussion of the Results

Cordierite is restricted to lower pressure in this composition compared to \(C_{28}\). The divariant band for the assemblage cordierite-garnet-sillimanite-quartz-feldspar \(b\) lies at the low pressure side of the band for the same assemblage in the \(C_{28}\) composition, and there is no overlap between the two bands for the temperature range studied (i.e. 800–1050° C; Fig. 4). Note that limiting boundaries of the divariant bands are interpreted to diverge slightly with decreasing temperature. As a result an overlap between the bands will occur at low temperature. This is an expression of the fact that the distribution coefficient \((K_m)\) increases with decreasing temperature, thus allowing the same garnet and cordierite to coexist in both bulk compositions (compare Hensen, 1971, in press).

The garnet contains 5 mole % grossular, and this amount is apparently independent of pressure and temperature (for the \(P-T\) range covered by the experiments). As the proportion of garnet increases, the normative plagioclase composition changes from Ab\(_{43.3}\) to Ab\(_{32.7}\) across the divariant band.

The stability field of the divariant assemblage \(b\) is limited towards high temperature by the univariant reaction \((Cd + Ga + Si = Sp + Qz)\). Consideration
of experimental data from both the B- and C-series and of constraints on possible intersections of reactions, show that reaction (1) should have a positive slope. On the high temperature side of this boundary we find the assemblage cordierite-spinel-sillimanite-quartz-feldspars (d) representing the divariant reaction Cgd±Sp±Qz (2). On the high pressure side of the breakdown of cordierite, the fields of stability of assemblages (c) and (e) are believed to be separated by the divariant reaction Cσ±Sσ±Sp±Qz (3). This reaction has to occur on the high temperature side of reaction (1) since it can only occur inside the stability field of Sp—Qz.

Since the stability field of spinel will be sensitive to oxygen fugacity the field of spinel should enlarge at the expense of that of garnet with increasing fO₂. The present results are probably close to the minimum stability limit for aluminous spinel in this composition.

The results on the C30 composition can be combined with those on C70 to construct P-X diagrams for the C-series of compositions. In this manner, additional restrictions on the data are introduced by the geometry of the diagram relating the two sets of experimental results.

6. P-T-X Relationships in the C-Series of Compositions

The experimental and analytical results on the C50 and C30 compositions have been combined and extrapolated to obtain the general P-T-X relationships for the entire compositional range of the C-series (100 Mg/Mg+Fe²⁺=0 to 100). P-X diagrams have been used for the graphical representation of the phase relations. The Mg/Mg+Fe²⁺ ratio is regarded as the only significant chemical variable influencing the relative stability of the ferromagnesian phases. The deduced phase relationships are relevant only to assemblages formed under conditions of low fO₂, containing excess plagioclase, sillimanite and quartz. The presence of alkali feldspar is not required and, as discussed earlier, the composition of the plagioclase can be disregarded, at least for intermediate plagioclase compositions (oligoclase-byanwtonite).

The P-X diagrams (Figs. 8 and 9) have been constructed using the following information:

1. The phase boundaries deduced from the experimental results on the C70 and C30 compositions (Figs. 3 and 7). The phase boundaries limiting divariant fields in the P-T diagrams are represented by points on the P-X diagram, while univariant boundaries appear as isobaric lines on the P-X plane. Experimental uncertainty has not been shown for these points in order to obtain a clearer representation of the phase relationships.

2. The Mg/Mg+Fe²⁺ ratios of coexisting phases in the experimental runs obtained by microprobe analyses (Table 2).

3. The distribution coefficients derived from the above microanalyses. Given the position of one compositional curve (e.g. X₁₅₀), the position of the other one (e.g. X₁₀₀) is determined for a given Kᵣ.

4. The reactions for the end members in the systems FeO-Al₂O₃-SiO₂ and MgO-Al₂O₃-SiO₂. The breakdown curve of Fe-cordierite (Richardson, 1968) has been extrapolated to higher temperature. In the presence of plagioclase, Fe-
Cordierite and Garnet in Pelites. I

Fig. 8. a P-X diagram for C-series at 1100° C showing divariant loops and isobaric univariant boundaries. Solid squares are points transferred from the P-T diagrams based on experimental data. b P-X diagram at 1035° C. The positions of the phase boundaries in both diagrams (a) and (b) are approximate.

cordierite will probably break down at slightly lower pressure than in the simple ternary system. For the Mg-endmember reactions, the data obtained on the B<sub>100</sub> composition have been used.

5. The results of analyses of coexisting phases in the B-series. The value of K<sub>p</sub> determined at a certain temperature in the B-series may be applied to the same mineral pair in the C-series at the same temperature provided K<sub>p</sub> is independent of pressure.

The P-X diagrams in Figs. 8 and 9 illustrate the stability relationships of the various mineral assemblages as a function of pressure and composition for each chosen temperature. The curves marking the boundaries of the divariant fields also fix the compositions of the coexisting phases in divariant equilibrium. The univariant and divariant reactions that occur in the P-X diagrams are given in Table 3.

**P-X Diagrams**

1100° C (Fig. 8a)

The phase relationships as shown on the diagram are partly hypothetical. The divariant field for the assemblage Sn-Sp-Qz has not been found experimentally, but its existence and its position relative to the other assemblages is theoretically...
predicted. For the construction of the reaction $Ga + Si = Sp + Qz$ (5) the experimental results on the $B_{3b}$ composition have also been used.

$1035^\circ C$ (Fig. 8b)
The $P-X$ diagram at this temperature is most easily understood by reference to the $P-T$ diagram representing the univariant phase boundaries (Fig. 4). At $1100^\circ C$ a vertical line (constant $T$) passes on the high temperature side of the invariant point (Hy). At $1035^\circ C$ such a line passes in between the invariant points (Hy) and (Sp), whereas at $1000^\circ C$ it passes on the low temperature side of the invariant point (Sp).

$1000^\circ C$ (Fig. 9a)
At this temperature, the stability field of $Sp-Qz$ is restricted to iron-rich compositions. In intermediate compositions the divariant reaction (1) is encountered. At high pressure and on the Mg-rich side of the diagram, the univariant boundary $Cd+Ga = Hy+Si+Qz$ is inferred to occur. Above the isobaric boundary for this univariant reaction we have the divariant assemblage $Cd-Hy-Si-Qz$ and $Ga-Hy-Si-Qz$ or the trivariant assemblage $Hy-Si-Qz$.

$900^\circ C$ (Fig. 9b)
The assemblage $Sp-Qz$ is no longer stable and the $Ga-Hy-Si$ assemblages are further restricted to Mg-rich compositions. At high pressure the $Ky-Si$ phase boundary intersects with the reaction $Ga+Qz = Hy+Si$ changing it to $Ga+Qz = Hy+Ky$. The latter reaction has a negative slope (Hensel and Essene,
Cordierite and Garnet in Pelites.

Fig. 9a–c. P-X diagrams for C-series at 1000, 900 and 800°C. • phase boundaries transferred from the P-T diagrams based on experimental data; • X_Cd and X_Ga (compositional range and pressure uncertainty shown). Dashed boundaries are approximate. (a) 1000°C; (b) 900°C; (c) 800°C

1971), which should produce the sharp kink in the X_Cd and X_Hy curves on the diagram.

800°C (Fig. 9c)
The extrapolated upper and lower boundaries of the divariant fields have been used for the construction of an approximate P-X diagram. The Ky\(\pm\)Si boundary occurs at considerably lower pressure and intersects the reaction Cd\(\Rightarrow\)Ga+Si+Qz \(\Delta V = -\text{ve}\) (1). At pressures above the intersection we find Cd\(\Rightarrow\)Ga+Ky+Qz \(\Delta V = -\text{ve}\) until the univariant curve limiting the coexistence of cordierite and garnet Cd+Ga\(\Rightarrow\)Hy+Ky+Qz \(\Delta V = -\text{ve}\) is reached. Above this isobaric boundary, we have the reactions Ga+Qz\(\Rightarrow\)Hy+Ky \(\Delta V = -\text{ve}\) and Cd\(\Rightarrow\)Hy+Ky+Qz \(\Delta V = -\text{ve}\).

II. Conclusions

We have obtained experimental data on the relative stability of a variety of phase assemblages in anhydrous model pelitic compositions. In particular we have established experimental conditions for the replacement of the low pressure cordierite-sillimanite-quartz assemblage by garnet-cordierite-sillimanite-quartz and then by garnet-sillimanite-quartz with increasing pressure.

The positions of phase boundaries are very sensitive to the Mg/Mg\(\text{++}\)Fe\(\text{++}\) ratio and the compositions of coexisting ferromagnesian minerals in divariant equilibrium are unique functions of temperature and pressure. This last aspect is of particular interest because of its petrological application and will be further developed in a later paper (Hinsen and Green, 111, in prep.).
Acknowledgements. We wish to thank Professors C. Wayne Burnham, E. J. Essene and A. E. Ringwood for comments and discussions during the course of the work. We are grateful to Professor W. Schreyer, Dr. A. L. Graham and A. J. Irving for initial reading of the manuscript and to W. Hibbersen, A. Major, E. Kiss and E. Pedersen for their invaluable technical help.

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Experimental Study of the Stability of Cordierite and Garnet in Pelitic Compositions at High Pressures and Temperatures
II. Compositions without Excess Alumino-Silicate

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Abstract. The stability of cordierite and garnet has been studied experimentally in complex, silica oversaturated compositions (in the systems MgO—FeO—Al₂O₃—CaO—Na₂O—K₂O—SiO₂) in which the molecular ratio Al₂O₃/FeO MgO < 1. Compositions with 100 Mg/Mg + Fe²⁺ ratios (X) of 0, 30, 50, 70 and 100 have been used to investigate the role of this ratio in determining phase assemblages and P, T coordinates of reactions. The minimum pressure for appearance of garnet at a given temperature is strongly dependent on Xtotal rock.

The X-values of co-existing phases (chiefly garnet, cordierite, hypersthene) in divariant equilibrium are a function of temperature and pressure and have been experimentally determined at 900°C, 1000°C and 1100°C. At high temperature (> 1050°C) the phases sapphirine and spinel are stable with quartz in Mg-rich and Fe-rich compositions respectively. Experiments in the system MgO-FeO-Al₂O₃-SiO₂ show that for a given X-value and temperature the pressure required to produce Ca-free garnet from hypersthene—cordierite assemblages is 1-2 kb greater than that required to produce garnet containing 6 ± 2 mol percent grossular solid solution in the more complex Ca-bearing system.

Introduction

This paper is the second in a series of three papers dealing with an experimental study of the stability of cordierite and garnet. A general introduction and discussion of experimental and analytical techniques has been given previously (Hensen and Green, 1971).

The present paper deals with pelitic compositions without excess alumino-silicate (Al₂O₃/FeO MgO < 1). The study provides new data on the upper stability of the assemblage cordierite-hypersthene-quartz and the extent of the P-T field for the divariant assemblage cordierite-hypersthene-garnet-quartz as a function of the Mg/Mg + Fe²⁺ ratio.

In the interpretation of the experimental data extensive use has been made of the theoretically derived phase relations for the system MgO—FeO—Al₂O₃—SiO₂ (Hensen, 1971) as a model for the observed relations in the complex system under study (i.e. MgO—FeO—Al₂O₃—SiO₂—CaO—K₂O—Na₂O).

Compositions Studied

The major part of this study deals with the B-series of compositions. This series is modelled on a relatively alumina-poor metapelitic (Table 1). It differs from the

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C-series in having a lower $\text{Al}_2\text{O}_3/\text{FeO} + \text{MgO}$ ratio $(1/3 < (A/F + M) < 1)$; sillimanite is therefore absent in low pressure assemblages.

Three intermediate members of the series, $B_{70}$, $B_{50}$ and $B_{30}$ and the two end members $B_{100}$ and $B_0$ have been investigated. The results have been combined to deduce the $P$-$T$-$X$ relations for this series involving the phases cordierite (Cd), hypersthene (Hy), garnet (Ga), sapphirine (Sa), olivine (Ol), spinel (Sp) and sillimanite (Si), in the presence of excess plagioclase (Pl), alkali feldspar and quartz (Qz).

To evaluate the stability of grossular-free garnet, a simple 4-component composition $B_{70}$S has been studied. This composition lacks CaO, Na$_2$O and K$_2$O, but is otherwise equivalent to the $B_{70}$ composition (Table 1).

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>$B_0$</th>
<th>$B_{50}$</th>
<th>$B_{30}$</th>
<th>$B_{70}$</th>
<th>$B_{100}$</th>
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<td>SiO$_2$</td>
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<tr>
<td>K$_2$O</td>
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<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>—</td>
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<tr>
<td>$100 \text{Mg/Mg} + \text{Fe}^{2+}$</td>
<td>0</td>
<td>30</td>
<td>50</td>
<td>70</td>
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<td>Normative plagioclase composition</td>
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<td>51.9</td>
<td>52.4</td>
<td>53.2</td>
<td>54.1</td>
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</table>

### Phase Relations in the $B_{70}$ Composition

The starting material used in the experiments consisted of:

- 10% low pressure assemblage, crystallised from glass at 1000°C, 7.2 kb, containing cordierite, hypersthene, minor spinel, quartz and feldspars.
- 10% high pressure assemblage, crystallised at 1100°C, 18 kb, consisting of garnet, quartz, minor feldspars, minor metastable corundum and minor glass.
- 80% glass (for preparation methods see Hensen and Green, 1971).

### Experimental Results

The experimental data are given in Fig. 1. At temperatures from 800–1050°C, the following assemblages have been observed with increasing pressure:

(a) cordierite-hypersthene-quartz
(b) cordierite-garnet-hypersthene-quartz
(c) cordierite-garnet-quartz
(h) garnet-hypersthene-sillimanite-quartz

1 Experimental data on this composition have been reported previously (Hensen and Green, 1970), but the present paper includes new analytical data and resulting changes in interpretation. On request tables with experimental and analytical results can be obtained from the authors.
Fig. 1. a $P$-$T$ diagram for B$_{70}$ composition. The observed mineral assemblages are indicated by letters also used in the text. b $P$-$T$ diagram showing the relative position of the derived phase relations (Fig. 1a) to the univariant boundaries constructed by a synthesis of all experimental evidence of B- and C-series of compositions. Divariant fields are shaded.
(d) garnet-sillimanite-quartz

The boundary (a—b) marking the incoming of garnet has been determined as follows. Garnet seeds break down on the low pressure side of this curve and grow at higher pressure at the expense of the low pressure assemblage (which crystallised from the glass initially). This is shown in a series of three photographs for the incoming of garnet at 1000° C (Fig. 2). At the lower pressure (5.4 kb), only a few skeletal garnet relics remain after the run. At 6.3 kb there is no detectable change in the amount of garnet, but the garnets have irregular outlines. At 7.2 kb garnet has clearly increased and has taken on a round subhedral shape.

At temperatures above 1050° C two more assemblages were encountered

(e) garnet-sapphirine-hypersthene-quartz

(f) sapphirine-hypersthene-quartz

At 750° C the following assemblage occurs:

(g) cordierite-biotite-quartz

All assemblages also contain feldspars. The observation that feldspars are less abundant in runs at 1100° C than at lower temperatures suggests that a small amount of partial melting takes place in the highest temperature runs. Several runs contain two of the above assemblages simultaneously and one run even three (see Fig. 1). These runs always occur close to the boundaries between two (or three) assemblages and are believed to reflect disequilibrium due to low reaction rates under such conditions.

In the interval in which garnet and cordierite coexist the amount of garnet increases while that of cordierite decreases with increasing pressure. The amount of hypersthene shows a distinct decrease at the incoming of garnet and further decreases while garnet increases. Runs using entirely crystalline starting materials have been carried out to establish reversals for the disappearance of cordierite at 900° C and 1000° C and for the appearance of sapphirine above 1050° C (Hensen and Green, 1970).

Microprobe Analysis of Experimentally Produced Phases

Analyses of garnet, cordierite and hypersthene have been obtained following the procedure described in Hensen and Green (1971). The composition of the garnets is uniform in most runs, indicating that equilibrium was closely approached in the experiments.

Garnet becomes more magnesian with increasing pressure, at constant temperature, and more iron-rich with decreasing temperature, at constant pressure. The grossular content of the garnet (6±2 mole % grossular) does not change significantly and is similar to that of the garnets in the C40 composition (Hensen and Green, 1971).

Owing to the fine grain size of the corclierite and contamination by other phases the number of reliable cordierite analyses is small. From a large number of

Fig. 2a—c. Polished mount showing incoming of garnet (high relief) at 1000° C. a: corroded garnet relics at 5.4 kb. b: irregular partly corroded seeds at 6.3 kb. c: garnet grown at 7.2 kb
analyses on each run, those with the best calculated totals were selected—these generally have Mg/Mg + Fe²⁺ ratios within a restricted range.

The Mg/Mg + Fe²⁺ ratio of the hypersthene is intermediate between those of garnet and cordierite. The hypersthene is aluminous probably containing about 10–12% Al₂O₃ (Hensen and Essene, 1971). The distribution coefficients² (Kᵦ) for the analysed mineral pairs are given in Table 2a. An increase in Kᵦ with decreasing temperature is shown by these data. At 1000°C an aberrant value (run 1560) may be due to the highly magnesium character of the cordierite and suggests mixing in cordierite may be non ideal.

Interpretation of Results

The experimentally determined boundaries have been interpreted in terms of reactions. As discussed previously, (Hensen and Green, 1971) the stability of the garnet is probably not significantly influenced by the composition of the plagioclase, and, as a result, the reactions can be treated univariant and divariant. The divariant reactions are represented by bands on a P-T diagram (Fig. 1). Within these bands, reactants and products of the reactions coexist. With increasing pressure, the phases on the high volume side of each of the reactions decrease in amount while the others increase. At the same time, the Mg/Mg + Fe²⁺ ratio of

$$2 \ K_D = \frac{X_{\text{Cd}} (1-X_{\text{Ga}})}{X_{\text{Ga}} (1-X_{\text{Cd}})} .$$

Table 2. Measured Kᵦ values for the B-series

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (° C)</th>
<th>Press (Kb)</th>
<th>100 (X₀Ga)</th>
<th>Kᵦ(Cd-Ga)</th>
<th>Kᵦ(Cd-Hy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) B₇₀</td>
<td>1694</td>
<td>1100</td>
<td>7.2</td>
<td>79-80</td>
<td>2.7±0.3</td>
</tr>
<tr>
<td></td>
<td>1573</td>
<td>1000</td>
<td>7.2</td>
<td>78-81</td>
<td>3±0.6</td>
</tr>
<tr>
<td></td>
<td>1560</td>
<td>1000</td>
<td>9.0</td>
<td>90-91</td>
<td>5.5±0.5</td>
</tr>
<tr>
<td></td>
<td>1586</td>
<td>900</td>
<td>6.3</td>
<td>77-78</td>
<td>3.6±0.6</td>
</tr>
<tr>
<td></td>
<td>1570</td>
<td>900</td>
<td>7.2</td>
<td>78-80</td>
<td>3.8±0.5</td>
</tr>
<tr>
<td>b) B₆₀</td>
<td>1781</td>
<td>1100</td>
<td>6.3</td>
<td>66-69</td>
<td>2.9±0.4</td>
</tr>
<tr>
<td></td>
<td>2731</td>
<td>1000</td>
<td>6.3</td>
<td>68-70</td>
<td>3.7±0.5</td>
</tr>
<tr>
<td></td>
<td>2722</td>
<td>1000</td>
<td>7.2</td>
<td>~70</td>
<td>~3.7</td>
</tr>
<tr>
<td></td>
<td>2685</td>
<td>900</td>
<td>6.3</td>
<td>66-67</td>
<td>3.9±0.4</td>
</tr>
<tr>
<td></td>
<td>2665</td>
<td>900</td>
<td>6.3</td>
<td>74-76</td>
<td>4±0.5</td>
</tr>
<tr>
<td></td>
<td>2668</td>
<td>900</td>
<td>5.4</td>
<td>75-76</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>c) B₅₀</td>
<td>2039</td>
<td>1100</td>
<td>5.4</td>
<td>51-54</td>
<td>2.9±0.2</td>
</tr>
<tr>
<td></td>
<td>1711</td>
<td>1050</td>
<td>4.5</td>
<td>45-49</td>
<td>2.8±0.2</td>
</tr>
<tr>
<td></td>
<td>1689</td>
<td>1000</td>
<td>3.6</td>
<td>34-38</td>
<td>2.6±0.2</td>
</tr>
<tr>
<td></td>
<td>1726</td>
<td>1000</td>
<td>4.5</td>
<td>44-50</td>
<td>3.0±0.4</td>
</tr>
</tbody>
</table>
the ferromagnesian phases increases. The necessity for all phases to become more magnesian is clear if one considers that the compositions of the coexisting phases are related by a distribution coefficient \( K_B \) (see Hensen, 1971).

The divariant band for the assemblage cordierite-hypersthene-garnet-quartz-feldspars \((b)\) represents the reaction \( \text{Cd} + \text{Hy} \rightleftharpoons \text{Ga} + \text{Qz} \) \((6)\). At the high pressure side of this reaction we have the assemblage garnet-cordierite-quartz-feldspars \((c)\) which is trivariant. At still higher pressure cordierite should break down according to reaction \( \text{Cd} \rightleftharpoons \text{Ga} + \text{Si} + \text{Qz} \) \((1)\). However, the assemblage \( \text{Ga-Cd-Si-Qz} \) has not been encountered experimentally in the present composition. Its occurrence can be predicted, because cordierite and hypersthene do not occur in the appropriate molar proportions to form garnet according to reaction \((6)\).

Previously (Hensen and Green, 1970), before analytical data were obtained, the divariant band for the assemblage \( \text{Cd-Ga-Hy-Qz} \) was deduced to be considerably wider, hypersthene being present up to and beyond the boundary marking the breakdown of cordierite. This interpretation of the results required the existence of the reaction \( \text{Cd} + \text{Ga} \rightleftharpoons \text{Hy} + \text{Si} + \text{Qz} \), thereby explaining the occurrence of the assemblage \( \text{Ga-Hy-Si-Qz} \) at 1000° C—9.9 and 10.8 kb (compare Fig. 1 b). However, the analytical data indicate that the hypersthene which was tentatively determined by X-ray in the runs just below the breakdown of cordierite, is very small in amount and likely to be metastable. This can be deduced by comparing the cordierite and garnet compositions \( X_{\text{Cd}} \) and \( X_{\text{Ga}} \); determined by microprobe analysis), with the \( \text{Mg/Mg}^+ + \text{Fe}^{2+} \) ratio of the bulk composition \( X_b \). The procedure is most easily demonstrated by an AFM diagram (Fig. 3). As cordierite and garnet become more magnesian, a point is reached at which the \( \text{Cd-Ga} \) join passes through the point representing the bulk composition. At the pressure corresponding to this situation, hypersthene will disappear from the mineral assemblage. Using this graphical check, it has been found that in all runs where previously a trace of hypersthene was found, the \( \text{Cd-Ga} \) join passes through the point representing the bulk composition (Fig. 3). It is therefore concluded that the stability field of \( \text{Cd-Hy-Ga-Qz} \) is smaller than was previously believed. The upper boundary of the divariant band containing this assemblage probably has a small negative slope (dashed boundary in Fig. 1).

In accordance with the present interpretation, hypersthene in the assemblage garnet-hypersthene-sillimanite-quartz-feldspars \((c)\) is also interpreted to be metastable. This is supported by the experimental results on the \( C_{70} \) composition (Hensen and Green, 1971).

The boundary marking the high pressure limit of sapphirine, previously interpreted to represent the univariant boundary \( \text{Ga} + \text{Sa} + \text{Qz} \rightleftharpoons \text{Hy} + \text{Si} \) is believed to be a divariant band representing the reaction \( \text{Sa} + \text{Qz} \rightleftharpoons \text{Ga} + \text{Si} \) \((4)\). This interpretation is in better agreement with the experimental data. The divariant band \( \text{Ga-Sa-Si-Qz} \) has a moderate positive slope and is consistent, within experimental error, with that deduced from the \( C_{70} \) results.

The breakdown of garnet at high temperature is interpreted to take place over a divariant interval according to the reaction \( \text{Hy} + \text{Sa} + \text{Qz} \rightleftharpoons \text{Ga} \) \((7)\).
Fig. 3. AFM diagram showing the Mg/Mg + Fe²⁺ ratios of coexisting cordierite, garnet and hypersthene (determined by microprobe analysis) in runs on the B₇₀, B₅₀ and B₃₀ compositions. Note that in runs where hypersthene is interpreted to be present as a trace, the Cd-Ga join passes through the point representing the bulk composition. The hypersthene is probably aluminous but this has not been shown in the diagram. Temperature (°C) and pressure (kb) conditions shown.

The divariant field (e) in Fig. 1) for this reaction is separated from the divariant assemblages Cd-Hy-Ga-Qz (b) and Cd-Ga-Sa-Qz (not observed experimentally) by the univariant reaction Cd + Ga ⇄ Hy + Sa + Qz (IV).

At high temperature, the trivariant assemblage Hy-Sa-Qz (f) is probably bounded on the low pressure side by the degenerate divariant reaction Cd ⇄ Sa + Qz (3) which is indicated by assemblage (a/j) in Fig. 1, and bounded also by the degenerate univariant reaction Cd + Sp ⇄ Sa + Qz (II). The existence of a stability field for the assemblage Cd-Hy-Sp in this composition has not been verified experimentally. However, the relationships as shown in Fig. 1 are dictated by the geometry because the lower boundary of the divariant field Cd-Hy-Ga-Qz intersects the univariant curve Cd + Ga ⇄ Hy + Sp + Qz (V) rather than the curve Cd + Ga ⇄ Hy + Sa + Qz (IV).
Cordierite and Garnet in Pelitic Compositions. II

Phase Relations in the B\textsubscript{50} Composition

The starting material used in the experiments consisted of:

- 10\% low pressure assemblage, crystallised from the glass at 1000° C-5.4 kb, consisting of cordierite, hypersthene, spinel, feldspars and quartz.

- 10\% high pressure assemblage, crystallised from glass at 1100° C—18 kb, consisting of garnet, quartz, minor kyanite, minor feldspars and a trace of corundum.

- 80\% glass

Experimental Results

The experimental data are given in Fig. 4. The phase assemblages found at 1000° C with increasing pressure are:

(a) cordierite-hypersthene-quartz-feldspars
(b) garnet-cordierite-hypersthene-quartz-feldspars
(c) garnet-cordierite-quartz-feldspars
(d) garnet-sillimanite-quartz-feldspars

and at 1100° C

(a) cordierite-hypersthene-feldspars-quartz
(b) garnet-cordierite-hypersthene-feldspars-quartz
(c) garnet-spinel-feldspars-quartz

At 1150° C two additional assemblages occur:

(f) cordierite-hypersthene (trace)-spinel-quartz (trace)
(g) hypersthene-spinel-feldspars-quartz-cordierite (trace)

At 1000 and 1100° C and low pressure, the garnet seeds have disappeared and assemblage (a) occurs. At 900 and 1000° C and pressures close to the inferred boundary for the incoming of garnet, garnet is present but no detectable change in the amount of garnet is observed. Analyses show it has a high calcium content (7-14 mole % Gr\textsubscript{e}) and a 100 Mg/Mg + Fe\textsuperscript{2+} ratio that is close to 50 (i.e. the composition of the seed garnets).

Above the boundary between assemblages (a) and (b) (Fig. 4) garnet increases in amount. Chemical analyses show these garnets to have a much lower Mg/Mg + Fe\textsuperscript{2+} ratio than that of the seed material.

The amount of hypersthene sharply decreases with increasing pressure after the incoming of garnet. The problem of hypersthene detectability has been overcome indirectly by making use of the analytical data on garnet and cordierite as discussed previously (Fig. 3).

Cordierite persists to pressures above those at which hypersthene disappears. It finally breaks down, and the assemblage garnet-sillimanite-quartz-feldspars (d) is found at 1000° C, 9.9 kb and 1050° C, 9 kb.

At 1100° C, 8.1 and 9 kb, the assemblage garnet-spinel-quartz-feldspars-trace of hypersthene (e) occurs. The spinel is fine grained and is present throughout the run. At 10.8 kb spinel has completely disappeared and the high pressure assemblage (d) is found.

\textsuperscript{4} These runs contain a trace of cordierite.
The feldspar reflections on the powder photographs do not show any detectable changes with pressure. At low pressure and high temperature, both quartz and feldspars decrease in amount due to partial melting.
Compositions of Experimentally Produced Phases

Analyses of garnet, cordierite and hypersthene provide the same general picture as encountered in the B$_{70}$ composition.

Runs 2665 and 2668, containing added water, show a high degree of partial melting. As a result, Fe is concentrated in the melt and the residual solids are enriched in Mg (for discussion see Hensen and Green, III, in press).

The distribution coefficients derived from the analyses of coexisting minerals are given in Table 2b. The $K_D$ values are not significantly different from those obtained from more magnesian pairs in the B$_{70}$ composition (Table 2).

Discussion of the Results

Garnet appears at lower pressure in this composition than in the more magnesian B$_{70}$ composition (compare Figs. 1 and 4). Garnet is produced by the same divariant reaction as in B$_{70}$ i.e. Cd + Hy $\rightleftharpoons$ Ga + Qz (6).

The garnet is considerably more iron-rich in this case, demonstrating that the stability field of garnet increases with decreasing Mg/Mg + Fe$^{2+}$ ratio.

When hypersthene disappears, we should find the trivariant assemblage cordierite-garnet-quartz-feldspars (c). The composition of cordierite and garnet will not change with increasing pressure until the divariant band for the breakdown of the particular cordierite is reached. (Hensen, 1971). At that point, sillimanite should appear. This expected sequence has not been found in the experiments. No difference has been observed in the pressure at which cordierite disappears compared with B$_{70}$. The occurrence of cordierite at 1000$^\circ$C, 9 kb is inconsistent with both the results of the C-series (Hensen and Green, 1971), those of the B$_{70}$ and B$_{30}$ compositions, and must be attributed to the metastable persistence of cordierite under these conditions. The upper boundary of the divariant region, as derived from the above data, should occur at approximately 1000$^\circ$C, 8 kb, i.e. at a pressure one kilobar less than that indicated by the present experiments.

The occurrence of spinel at 1100$^\circ$C, 8 kb and 9 kb is consistent with the results on the C$_{30}$ and B$_{30}$ compositions.

The trivariant fields of assemblages Ga-Si-Qz-Fsp (d) and Ga-Sp-Qz-Fsp (e) are separated by the divariant reaction Sp + Qz $\rightleftharpoons$ Ga + Si (5). At low pressure, this reaction intersects, and is terminated by the univariant reaction Sp + Qz $\rightleftharpoons$ Cd + Ga + Si (1). On this univariant boundary, the theoretically required divariant bands for the reactions Cd $\rightleftharpoons$ Ga + Si + Qz (1) and Cd $\rightleftharpoons$ Sp + Qz (2) intersect also, as shown in Fig. 4b. A schematic representation of the $P$-$T$ relations, showing the intersecting bands more clearly is given in Fig. 5.

Garnet breaks down at high temperature according to the divariant reaction Hy + Sp + Qz $\rightleftharpoons$ Ga (8). The trivariant field for H$_{y}$-Sp-Qz is limited on the low pressure side by the reaction Cd $\rightleftharpoons$ Sp + Qz (2).

Reactions (8) and (2) and (6) intersect the univariant curve limiting the coexistence of garnet and cordierite: Hy + Sp + Qz $\rightleftharpoons$ Cd + Ga (V). This reaction is interpreted to have a positive slope (Fig. 4b and 5). The volume change of reaction (V) should change sign near invariant point (Si). This is required because theoretically, the metastable extensions of reactions Cd + Ga $\rightleftharpoons$ H$_{y}$ + Si + Qz, Sp + Qz $\rightleftharpoons$ Cd + Ga + Si (I) and reaction (V) should go through one metastable invariant point (Hensen, 1971).
Fig. 5. Schematic phase relations at high temperature in B₅₀ and B₃₀ compositions, showing the relative position of divariant bands and univariant boundaries (compare Figs. 4 and 6) Numbers in brackets refer to reactions, compare Table 3

The position of all reactions involving spinel is probably very sensitive to oxygen fugacity, with increasing O₂ enlarging the stability field of assemblages containing this phase.

Phase Relationships in the B₃₀ Composition
The starting material used in the experiments consisted of:
20% of intermediate pressure assemblage crystallized from glass at 1000°C, 5.4 kb, containing cordierite, garnet, hypersthene, spinel, quartz and feldspars. ± 80% glass.

Experimental Data
The experimental results are given in Fig. 6.
At 1000°C and 1050°C the following sequence of assemblages is found with increasing pressure:
(a) cordierite-olivine (Fe-rich)-feldspars-quartz
(b) cordierite-hypersthene-feldspars-quartz
(c) garnet-cordierite-hypersthene-feldspars-quartz
(d) garnet-spinel-feldspars-quartz
(e) garnet-spinel-feldspars-quartz
At 1100°C the sequence is:
(a/h) cordierite-hypersthene-spinel-feldspars-quartz
Cordierite and Garnet in Pelitic Compositions. II

Fig. 6. a P-T diagram for B$_{90}$ composition. Observed phase assemblages are indicated by letters also used in the text. b P-T diagram showing relation of divariant (shaded) and univariant boundaries. Compare a

(e) garnet-spinel-feldspars-quartz
(e/d) garnet-sillimanite-feldspars-quartz-trace of spinel

At 1000 and 1050°C, the divariant assemblage cordierite-hypersthene-garnet-quartz-feldspars (b) occurs over a restricted Pressure interval. As in the case of the B$_{90}$ and B$_{96}$ experiments, the disappearance of hypersthene has been determined indirectly (see Fig. 3).

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At 1000° C spinel appears at 6.3 kb and persists up to 10.8 kb, sillimanite being absent, and the high pressure assemblage consists of: garnet-spinel-quartz-feldspars (e).

At 1050° C and 1100° C, partial melting presents a major problem in this iron-rich composition. The analytical data provide evidence of the effect of partial melting on the Mg/Mg + Fe²⁺ ratio of the residual solids. It is estimated from the analytical data, that at most a 15–20% increase in the Mg/Mg + Fe²⁺ ratio of the solids, compared to the bulk composition, may have taken place.

At 1100° C spinel appears on the low pressure side of the boundary marking the appearance of garnet. It is quite abundant at 5.3 kb where garnet has increased, and remains a major phase up to 9 kb. At 10.8 kb the presence of sillimanite, although below the X-ray detection limit, could be verified optically.

Composition of Experimentally Produced Phases

The grossular content of the garnets is lower than for the B₇₀ and B₅₀ compositions (i.e. 4 mole % compared to 6 mole % grossular). The measured distribution coefficients of Mg and Fe between cordierite and garnet are given in Table 2c. The $K_D$ values are slightly lower than those in the more magnesian compositions (Table 2a, b) suggesting mixing may be non ideal in the phases concerned.

Discussion of the Results

Compared to the B₇₀ and B₅₀ compositions, the appearance of garnet occurs at lower pressure. Garnet is formed by the same divariant reaction $Cd + Hy = Ga + Qz$ (6). On the high pressure side of this band, the assemblage cordierite-garnet-quartz would be expected to occur followed at still higher pressure by the disappearance of cordierite by the reaction $Cd = Ga + Si + Qz$ (1). Reaction (1) has not been encountered experimentally in the B₅₀ composition. The dashed phase boundaries in Fig. 6 show the phase relations as required by the theoretical restrictions (see B₇₀ and B₅₀ compositions). The results on the C₅₀ composition (Hensen and Green, 1971), showing the relative stabilities of garnet and spinel, indicate that the occurrence of spinel-quartz instead of garnet-sillimanite in the 1000° C runs must be metastable. At 1100° C, the occurrence of garnet-spinel-quartz-feldspars between 5.4 and 10.8 kb is consistent with the C₅₀ results and with the theoretical model (Hensen, 1971). This assemblage should be followed towards higher temperature by garnet-hypersthene-spinel-quartz representing the breakdown of garnet according to the divariant reaction $Hy + Sp + Qz = Ga$ (8). Between the assemblage Ga-Hy-Sp-Qz and the assemblage Cd-Ga-Hy-Qz, the univariant reaction $Hy + Sp + Qz = Cd + Ga$ (V) should occur. The geometry of the phase relationships in the high temperature part of the diagram is identical to that in the B₅₀ composition (Fig. 5).

At low pressure, olivine rather than hypersthene coexists with cordierite. This suggests we have crossed the divariant reaction (represented by a single line in Fig. 6), $Ol + Qz = Hy$ (Smith, 1970). As indicated by experiments on the present composition and also by those on composition B₀, olivine instead of hypersthene will participate in the reactions limiting the stability of garnet and cordierite in compositions with $100 \text{Mg/Mg+Fe}^{2+} < 30$. 
The position of the resulting in variant point has been estimated (Fig. 6 b). One of the univariant curves radiating from the invariant point is the reaction $\text{Hy} + \text{Sp} + \text{Qz} \rightleftharpoons \text{Cd} + \text{Ga}$ (V). This reaction is replaced below the invariant point (for low values of $\frac{\text{Mg}}{\text{Mg} + \text{Fe}^2+}$ ratio) by $\text{Ol} + \text{Sp} + \text{Qz} \rightleftharpoons \text{Cd} + \text{Ga}$. The stability field of $\text{Cd} \cdot \text{Ol}$ should be limited towards high temperature by $\text{Ol} + \text{Cd} \rightleftharpoons \text{Hy} + \text{Sp} + \text{Qz}$ (VI). Two more quartz bearing reactions going through the invariant point are $\text{Cd} + \text{Ol} \rightleftharpoons \text{Hy} + \text{Ga} + \text{Qz}$ and $\text{Ol} + \text{Sp} + \text{Qz} \rightleftharpoons \text{Ga} + \text{Hy}$ (Hensen, 1971, Fig. 10).

Phase Relations in the $B_{100}$ Composition

The starting materials used for the experiments consisted of:

(I) a (4:1) mixture of glass and high pressure assemblage consisting of garnet + kyanite + quartz + trace of aluminous enstatite. This high pressure assemblage was synthesized from glass at 1200° C and 27 kb. The grossular content of the garnet is $11 \pm 1$ mole %.

(II) a (4:1) mixture of a fired oxide-mix, consisting of cordierite, pyroxene, feldspars and quartz (?), with the same high pressure assemblage.

Experimental Data

The results of the experiments and their interpretation in Fig. 7. At low pressures the charge consists of cordierite-aluminous enstatite-quartz (?)-feldspars (a).

At intermediate pressure two different assemblages are found depending on the temperature.

At 1100° C and 1200° C the phases sapphirine-aluminous enstatite-quartz-feldspars (c) are found.

At 1000° C, 12.6 kb, the assemblage aluminous enstatite-sillimanite-quartz-feldspars-minor corundum—relict garnet (b) occurs (note that kyanite and garnet were seeded).

![Fig. 7. P-T diagram for $B_{100}$ composition. Observed mineral assemblages are indicated by letters also used in the text](image-url)
At 900° C, 12.6 kb the assemblage enstatite-kyanite-feldspars-trace of quartz-trace of corundum-relict garnet is encountered. At 1100° C, 14.4 kb and 1200° C, 16.2 kb, the assemblage garnet-sillimanite-feldspars-quartz occurs. The grossular content of garnet is 5 ± 2 mole % at 1100° C and 7 ± 2 mole % at 1200° C (note that the garnet seeds have 11 ± 2 mole % grossular).

Discussion of the Results
The disappearance of cordierite with increasing pressure (Fig. 7) is due to the following reactions: cordierite ⇌ sapphirine + quartz (1) at 1100° C and 1200° C, and cordierite ⇌ aluminous enstatite + sillimanite + quartz (2) at 1000° C.

Below 900° C, sillimanite in reaction (2) is replaced by kyanite due to intersection with the kyanite-sillimanite phase boundary giving rise to the reaction: cordierite ⇌ aluminous enstatite + kyanite + quartz (2'). At intermediate pressure we have the reaction: aluminous enstatite + sillimanite ⇌ sapphirine + quartz (3).

The position of the phase boundaries for the reactions (1), (2) and (3) and of the invariant point at their intersection, has been taken from the proposed phase diagram for the system MgO—Al2O3—SiO2 (Hensen and Essene, 1971). This is justified because the relative stabilities of the phases cordierite, aluminous enstatite and sapphire are probably not significantly affected by the presence of Ca.

The reactions for the incoming of garnet can be expressed as follows: At \( T > 1100° C \): sapphirine + aluminous enstatite + calcic plagioclase + quartz ⇌ grossular-pyrope + less calcic plagioclase + quartz (5).

At a temperature of approximately 950° C, reaction (5) intersects the kyanite-sillimanite phase boundary (Fig. 7). The run at 900° C, 12.6 kb in which garnet shows no sign of growth, suggests that the reaction: aluminous enstatite + calcic plagioclase + kyanite ⇌ grossular-pyrope + less calcic plagioclase + quartz (5') may have a negative slope. A negative slope is also deduced for the similar reaction without plagioclase and grossular (5') (in the system MgO—Al2O3—SiO2 (Hensen and Essene, 1971).

The present data show that a relatively small amount of grossular (4–8 mole %) has a considerable effect on the stability of pyrope-rich garnet. At temperatures above 1050° C, the stability limit of garnet (+ quartz) is lowered by ca. 2 kb compared to pure pyrope + quartz (compare Hensen and Essene, 1971, Fig. 1).

As shown in Fig. 7, the stable coexistence of cordierite and garnet is precluded in this composition. This is a necessary result of the interpretation that reactions (2') and (5'), involving kyanite instead of sillimanite, diverge with decreasing temperature.

Phase Relations in the Bc Composition
The starting material used in the experiments consists of high pressure assemblage and glass in a 1:4 ratio. The high pressure assemblage was crystallised from the

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5 Corundum is associated with partial melting which occurs locally in the charge due to access of water through the capsule walls.

6 The numbering of reactions in this section is not related to that used in the intermediate compositions.
glass at 950° C—4.5 kb and contains the minerals garnet, hercynite, quartz and feldspars.

**Experimental Data and Interpretation**

At 1000° C, 1.8 kb, the assemblage consists of: fayalite-hercynite-quartz-feldspars. At 1050° C and 3.6 kb only hercynite and minor quartz occur accompanied by major glass. The disappearance of fayalite is probably caused by melting rather than by oxidation. At both 1000° C and 1050° C the assemblage garnet-hercynite-quartz-feldspar is found at 2.7 and 4.5 kb respectively. At 900° C this assemblage forms at 1.8 kb. The amount of grossular in the garnet is low (ca. 4 ± 2 mole %, determined by X-ray diffraction).

The composition of the spinel (8 ± 2 mole % magnetite) does not measurably change with temperature.

The growth of garnet in the runs on the B-series compositions at high temperature (900–1100° C) is due to the reaction: fayalite + hercynite + quartz ⇌ almandine. Because of the solid solution of magnetite this equilibrium should be very sensitive to oxygen fugacity.

**P-T-X Relations for B-Series of Compositions**

The experimental and analytical evidence obtained for the B-series of compositions have been combined for the construction of a number of isothermal P-X diagrams (Fig. 8). Extrapolation between the different members of the B-series allows the prediction of P-T-X relations for the entire compositional range of this series. The type of information used for the construction of the diagrams is the same as that discussed previously (Hensen and Green, 1971). In the B-series, however, divariant reactions that involve three ferromagnesian minerals are encountered (Table 3) and this introduces some additional complications. In the P-X diagrams for this type of divariant equilibria, the curves representing the change in com-

<table>
<thead>
<tr>
<th>Divariant reactions a</th>
<th>Univariant reactions a</th>
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<tr>
<td>Reaction No.</td>
<td>Reaction No.</td>
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<tr>
<td>Cd± Ga + Si + Qz</td>
<td>Sp ± Qz ± Cd + Ga + Si</td>
</tr>
<tr>
<td>Cd± Sp + Qz</td>
<td>Cd ± Sp = Sa + Qz</td>
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<td>Cd± Sa + Qz</td>
<td>Cd + Ga + Si = Sa + Qz</td>
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<tr>
<td>Sa ± Qz ± Ga + Si</td>
<td>Cd + Ga = Hy + Sa + Qz</td>
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<tr>
<td>Sp ± Qz ± Ga + Si</td>
<td>Hy + Sp + Qz = Cd + Ga</td>
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<tr>
<td>Cd + Hy ± Ga + Qz</td>
<td>Cd + Ol = Hy + Sp + Qz</td>
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<td>Hy + Sa + Qz ± Ga</td>
<td>Cd + Ga = Hy + Si + Qz</td>
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<td>Hy + Sp + Qz ± Ga</td>
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<td>Ol + Sp ± Qz ± Ga</td>
<td>Ol + Sp + Qz ± Ga + Hy</td>
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a The reactions have been written such that the right hand side always has the lower volume.

b Reactions marked (x) have not been observed experimentally but have been deduced from a combination of experimental and theoretical evidence.
Fig. 8a–c. P-X diagrams for B-series at 1100° C, 1000 and 900° C. The heavy curves in these diagrams represent the compositions of coexisting phases. They do not delineate divariant stability fields (compare Fig. 9). Heavy lines: compositional contours applicable only to the B-series. Light dashed lines: Phase boundaries taken from the C-series (Hensen and Green, 1971). These are applicable to the B-series above the disappearance of hypersthene. Olivine-hypersthene equilibrium estimated (see text). Solid circles: appearance of garnet and disappearance of hypersthene. Solid rectangles: $X_{Cd}$ and $X_{Ga}$ (compositional range and pressure uncertainty shown).
position of the coexisting phase do not, as a rule, also define the boundaries of a divariant stability field, as they do in divariant equilibria with only two ferro-magnesian solid solutions (Hensen, 1971).

In the B-series cordierite and hypersthene are not in the proper proportions to yield garnet and quartz, cordierite being in excess. As a result, the reactions described for the C-series (Hensen and Green, 1971) occur in addition to the reactions involving hypersthene, which are characteristic for this series. This would also be the case for any bulk composition with \( \frac{1}{3} \frac{A}{F} + \frac{1}{3} M < 1 \). In the following \( P-X \) diagrams, the phase relations unique to this series have been indicated in heavy lines, whereas the remaining boundaries, discussed previously, are shown as thin dashed lines. For clarity of representation, only compositional contours are shown whereas boundaries limiting the stability fields of the divariant assemblages with three solid solutions (Table 3) have been omitted from the \( P-X \) diagrams. The relation of compositional contours and stability fields is shown schematically in Fig. 9. This diagram represents the situation for a bulk composition with \( \frac{1}{3} \frac{A}{F} + \frac{1}{3} M < 1 \).

**P-X Diagrams**

**1100° C (Fig. 8a).** Cordierite persists on the high pressure side of the divariant field containing the assemblage \( Cd-Hy-Ga-Qz \). It breaks down eventually to either spinel plus quartz or, for a small range of very magnesian bulk compositions, to sapphire plus quartz (reactions (2) and (3) respectively). \( Ga-Sa-Qz \) will persist at the high pressure side of the field \( Ga-Hy-2a-Qz \) and sapphirine will eventually break down by reaction \( Sa + Qz \rightarrow Ga + Si \) (4).

Both the incoming of garnet and the disappearance of hypersthene for any composition in the B-series will fall inside the \( X_{Cd} \) and \( X_{Ga} \) curves (heavy lines in Fig. 8). The points representing the incoming of garnet in the \( B_{70} \) and \( B_{90} \) composition (from the \( P-T \) diagrams; Figs. 1 and 4) are shown by solid circles on the diagram (compare Fig. 9).

The position of the compositional contours for the reaction \( 01 + Qz \Rightarrow Hy \) (9) have been roughly estimated from the work of Smith (1970) and Lindsley (1965). Recent calculations by Wood and Strens (1971) suggest the estimate is not grossly in error.

**1000° C (Fig. 8b).** At 1000° C, the most salient feature of the \( P-X \) diagram is the divariant reaction \( Cd + Hy \Rightarrow Ga + Qz \) which occurs over most of the compositional range of the B-series. Reaction (6) is terminated by the univariant curve \( Cd + Ga \Rightarrow Hy + Si + Qz \) on the high pressure, magnesian-rich side of the diagram and by the curves \( Cd + Ol \Rightarrow Hy + Ga + Qz \) and \( Ol + Sp + Qz \Rightarrow Cd + Ga \) on the low pressure, iron-rich side of the diagram. The resulting divariant reactions are shown in Figs. 8b and 9.

**900° C (Fig. 8c).** At 900° C, the phase relations are similar to those at 1000° C. The loop formed by the \( X_{Ga} \) and \( X_{Cd} \) curves has widened. This is an expression of the increase of \( K_y \) with decreasing temperature.

At high pressure, for very magnesian compositions, the reaction \( Hy + Si \Rightarrow Ga + Qz \) is intersected by the \( Ky \Rightarrow Si \) boundary, and as a result we have \( Hy + Ky \Rightarrow Ga + Qz \).
Fig. 9. Schematic P-X diagram at 1100° C showing relation of stability fields (shaded) of
divariant assemblages and compositional curves ($X_{Cd}$, $X_{Ga}$ etc.) for a bulk composition with
$\frac{1}{3} < Al_2O_3/FeO + MgO < 1$ (Cd): cordierite present but not involved in the reaction. $X_{Cd}$: curve for cordierite not involved in divariant equilibrium. Composition is fixed by distribution
coefficient. $X_{Cd}$: curve for "second reaction" involving cordierite (reactions involving spinel,
sapphire and sillimanite). Horizontal lines are univariant boundaries. Compare Fig. 8

Note that the compositions of the phases in the univariant equilibrium Cd +
Ga $\Rightarrow$ Hy + Si + Qz are more magnesian than at 1000° C. This is required because
the Mg/Mg + Fe$^{2+}$ ratio of the phases on the univariant boundary increase with
decreasing temperature and increasing pressure.

At 900° C, cordierite and garnet are stable together down to the pure Fe-side
of the diagram, where we have the reaction cordierite + fayalite $\Rightarrow$ almandine +
quartz.

Phase Relations in the System MgO—FeO—Al$_2$O$_3$—SiO$_2$ (B$_{30}$S Composition)
The B$_{30}$S composition does not contain CaO, Na$_2$O and K$_2$O, but is otherwise
equivalent to the B$_{30}$ composition. The study of this composition was undertaken
to evaluate the stability of grossular free garnet.
Starting Materials

The two starting materials used in this investigation are made up of crystalline materials only.

I. 10 weight % high pressure assemblage, crystallised from glass at 1100°C—18 kb, consisting of garnet, sillimanite and quartz.
+ 90 weight % low pressure assemblage, crystallised from glass at 850°C—6.3 kb, consisting of cordierite, hypersthene and quartz.

II. 40 weight % high pressure assemblage (as above).
+ 60 weight % low pressure assemblage (as above).

Experimental Data

At 1000°C, the following assemblages have been encountered with increasing pressure.

\[ \text{Cd-Hy-Qz} \]  
\[ \text{Ga-Cd-Hy-Qz} \]  (a) Garnet appears at 8.1 kb.  
\[ \text{Ga-Cd-Oz and Cd-Ga-Si-Qz} \]  (c) Hypersthene breaks down between 8.1 and 9.9 kb.  
\[ \text{Ga-Si-Qz} \]  (d) Cordierite disappears between 9.9 and 10.8 kb.

Using starting material I, a run at 1000°C, 9.9 kb yielded \[ \text{Ga-Hy-Si-Cd-Qz} \]. For this 5-phase assemblage to be in stable equilibrium, the run conditions must lie on a univariant phase boundary. It is more probable that one of the phases is metastable. To test this, a different starting material (II) was run under the same conditions. This run, initially with less Cd-Hy-Qz, yielded Cd-Ga-Si-Qz-trace of Hy. Cordierite and garnet increased relative to the starting material, whereas sillimanite decreased and hypersthene disappeared. The run demonstrates that hypersthene is not stable relative to garnet and cordierite in the presence of sillimanite and quartz, and the assemblage \[ \text{Ga-Cd-Si-Qz} \] is considered to be stable at 1000°C, 9.9 kb. Similarly, a run at 1000°C, 10.8 kb using starting material (II), yielded the assemblage \[ \text{Ga-Si-Qz-trace of Cd} \]. This demonstrates that \[ \text{Ga-Qz-(Si)} \] is stable relative to \[ \text{Hy-Si-(Qz)} \] under these conditions.

At 1100°C, garnet is appears at 9 kb, and cordierite disappears between 9 and 10.8 kb. Sapphirine has not been observed in this composition. At 900°C, 7.2 kb and 800°C, 7.2 kb reaction rates are very low, and the garnet seeds persist below the deduced boundary for the appearance of garnet.

Chemical Analyses of Experimental Phases

The \[ \text{100 Mg/Mg + Fe}^{2+} \] ratio determined by microprobe analysis of the garnets in a run at 1100°C, 10.8 kb is exactly 70. Since garnet is the only ferromagnesian phase present in this run and thus should have the 100 Mg/Mg + Fe\(^{2+}\) ratio of the bulk composition, i.e. 70, this result confirms the accuracy of the analytical method. The garnet close to the interpreted low pressure boundary of the divariant band for the phases \[ \text{Ga-Cd-Hy-Qz} \] is considerably enriched in Fe compared to the bulk composition (100X\( _{Ga} = 53 \pm 2 \) at 1000°C, 8.1 kb and 100X\( _{Ga} = 60 \pm 2 \) at 1100°C, 9 kb). The distribution coefficient between hypersthene and garnet at 1100°C (K\( _{D(Hy, Ga)} = 2 \pm 0.3 \)) is not significantly different from that obtained in the B\( _{0} \) composition.
No cordierite analyses have been obtained so that the distribution coefficients for \( Cd-Ga \) and \( Cd-Hy \) have not been determined.

**Discussion of the Results**

The observed changes in mineral assemblages can be explained by the divariant reactions \( Cd + Hy \leftrightarrow Ga + Qz \) (6) for the appearance of garnet, and \( Cd \leftrightarrow Ga + Si + Qz \) (1) for the disappearance of cordierite.

A comparison with the results on the complex \( B" \) composition brings out the following important differences. Firstly, at 1000 and 1100°C, garnet appears at a pressure ca. 1 kb higher than in the \( B" \) composition. Secondly, cordierite persists stably up to a pressure ca. 1 kb higher than in \( B" \), as demonstrated by a reversal experiment at 1000°C, 9.9 kb. Lastly, sapphirine does not appear in this composition.

The occurrence of garnet at a lower pressure in \( B" \) must be attributed to the stabilizing effect of grossular. This demonstrates that the incorporation of a relatively small amount of grossular has an important effect on the stability of garnet, as was also shown by the comparison of the \( B_{100} \) and \( Py + Qz \) compositions.

The observation that at 1000°C cordierite persists to higher pressure indicates that, in the presence of Si and Qz, a higher pressure is required to stabilize a pure almandine-pyrope garnet with the same 100 Mg/Mg + Fe²⁺ ratio.

The total absence of sapphirine at 1100°C may be due to the fact that no sapphirine seeds were available in the starting material.

In conclusion, it should be emphasized that the present results show the important effect of the presence of plagioclase on the stability of garnet relative to cordierite, and underline the difficulty of predicting phase relationships in complex systems from simple system data.

**Conclusions**

The important role of the Mg/Mg + Fe²⁺ ratio in determining the relative stability of cordierite and garnet has been demonstrated. It has also been shown that a small (4-8 mole %) of grossular solid solution stabilizes an almandine-pyrope garnet to lower pressure by as much as two kilobars. Therefore, the presence of calcium (in the form of plagioclase) can be a deciding factor for the occurrence of garnet. The experimental results indicate, however, that the composition of the plagioclase (\( An_{30-80} \)) coexisting with cordierite and garnet will have a negligible effect on garnet composition and thus on garnet stability. This is also supported by observations on natural rocks (Reinhardt, 1968; see also Hensen and Green, 1970). The grossular contents of the experimental garnets (3-8 mole %) compares well with that of natural garnets suggesting that this variable is not very temperature dependent.

The distribution coefficients for Fe²⁺ and Mg, between cordierite and garnet obtained at temperatures of 900–1100°C are lower than those generally reported from natural rocks (3-5 compared to 5-10 for natural rocks: Reinhardt, 1968; Saxena and Hollander, 1969; Gorbatshev, 1968). This indicates that \( K_D \) decreases
with increasing temperature. The experiments suggest that $K_D$ may also depend on composition and increases at high values of $X^7$.

Appendix

The Problem of the Relative Composition of Coexisting Garnet and Hercynite-Spinel

Hsu and Burnham (1969) concluded from their experimental evidence that spinel has a lower Mg/Mg + Fe$^{2+}$ ratio than coexisting pyrope-almandine. However, microprobe analyses of (Hensen, unpublished) coexisting, intimately intergrown garnet (94% pyrope-almandine) and hercynite-spinel from a natural rock from Antarctica show that in this natural rock example the Mg/Mg + Fe$^{2+}$ ratio is higher in the spinel phase ($X_{Ga} = 36$ and $X_{Sp} = 41$ i.e. $K_D(Sp-Ga) = 1.2$). Another example in which $X_{Ga} < X_{Sp}$ is provided by coexisting minerals in the Cortlandt (N.Y.) hornfelses, Barker (1964).

It cannot be deduced with certainty from the present experimental evidence whether $X_{Sp} > X_{Ga}$.

It appears possible that the distribution of Fe$^{2+}$ and Mg in very Fe-rich bulk compositions is significantly influenced by oxygen fugacity. Since the experiments by Hsu and Burnham (1969) were carried out under more oxidizing conditions (QFM buffer) than the present experiments, their conclusions are not necessarily inconsistent with the assumption of $X_{Sp} > X_{Ga}$ made here.

References


Hensen, B. J., Green, D. H.: Experimental study of cordierite and garnet in pelitic compositions at high pressures and temperatures. II. Synthesis of experimental data and geological applications. In prep.


Richardson, S. W., Bell, P. M., Gilbert, M. C.: Kyanite-sillimanite equilibrium between 700° C and 1500° C. Am. J. Sci. 266, 513–551 (1968).

Recently Currie (1971) concluded on the basis of experiments using gels as starting materials, that $K_D$ increases threefold from 600 to 900° C. Currie’s results are inconsistent with those presented here.

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Experimental Study of the Stability of Cordierite and Garnet in Pelitic Compositions at High Pressures and Temperatures

III. Synthesis of Experimental Data and Geological Applications

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Abstract. In pelitic rocks, under conditions of low $f_0^2$ and low $f_H^2$, the stability of the mineral pair cordierite-garnet is limited by five univariant reactions. In sequence from high pressure and low temperature to high temperature and low pressure these are: cordierite + garnet = hypersthene + sillimanite + quartz, cordierite + garnet = hypersthene + sapphirine + quartz, cordierite + garnet = hypersthene + spinel + quartz and cordierite + garnet = olivine + spinel + quartz. In this sequence of reactions the Mg/Mg ± Fe$^{2+}$ ratio of all ferro-magnesian minerals involved decreases continuously from the first reaction to the fifth. The five univariant boundaries delimit a wide $P$-$T$ range over which cordierite and garnet may coexist.

Two divariant equilibria in which the Mg/Mg ± Fe$^{2+}$ ratio of the coexisting phases are uniquely determined by pressure and temperature have been studied in detail. $P$-$T$-$X$ grids for the reactions cordierite + garnet + sillimanite + quartz and cordierite + hypersthene + garnet + quartz are used to obtain pressure-temperature estimates for several high grade metamorphic areas. The results suggest temperatures of formation of 700–850°C and load pressures of 5–10 kb. In rare occasions temperatures of 950–1000°C appear to have been reached during granulite metamorphism.

On the basis of melting experiments in pelitic compositions it is suggested that Ca-poor garnet xenocrysts found in calc-alkaline magmas derive from admixed pelitic rocks and did not equilibrate with the calc-alkaline magma.

Introduction

The results of the experimental study of cordierite and garnet stability at high pressures and temperatures, reported in two previous publications (Hensen and Green, 1971, 1972) are applied in this paper to problems concerning the occurrence of cordierite and garnet in natural rocks of metamorphic and igneous origin.

Problems included in the discussion are the absence of cordierite from most amphibolite grade metamorphic terranes, the rarity of cordierite-kyanite paragenesis and the coexistence of cordierite and garnet in rocks that have apparently formed over a wide range of metamorphic conditions.

The experimental data on pressure-temperature-composition relationships are used to obtain pressure-temperature estimates for the formation of metamorphic rocks containing divariant mineral assemblages such as cordierite-garnet-sillimanite-quartz and cordierite-garnet-hypersthene-quartz.

The experimental results are also relevant to the formation of the rare paragenes hypersthene-sillimanite (kyanite)-quartz and sapphirine-quartz. These assemblages suggest unusually high temperatures of metamorphism.

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An explanation of the genesis of cordierite and garnet xenocrysts in igneous rocks is given on the basis of results on melting relationships in pelitic compositions.

General $P$-$T$ Diagram for Silica-Saturated Pelitic Compositions

In order to relate the phase relations observed in the individual bulk compositions and to test the results for internal consistency, a general $P$-$T$ diagram has been constructed using the experimental data on the B- and C-series of compositions (Hensen and Green, 1971, 1972) and the theoretical constraints discussed in Hensen (1971). This diagram (Fig. 1) gives the univariant phase boundaries that are relevant to all model pelitic compositions studied in this investigation. The univariant phase boundaries limit the stability fields of specific mineral pairs or specific three-phase assemblages. The general topology of the $P$-$T$ diagram is similar to that of the theoretical phase diagram for the system MgO-FeO-Al$_2$O$_3$-SiO$_2$ (Hensen, 1971, Fig. 1) and the discussion given previously is applicable also to Fig. 1.

Additional constraints on the position and slope of some of the univariant boundaries are introduced by the positions of the invariant points in the end-member compositions $B_0$ and $B_{100}$. These constraints are imperfect, since the invariant points in these end-member compositions are not accurately known, but they impose another requirement for internal consistency on the data which can be used for the construction of the “best fit” $P$-$T$ diagram. Divariant reactions change to univariant reactions when all ferromagnesian phases simultaneously become pure Mg or pure Fe end-members. Similarly, the univariant reactions in Fig. 1 along which each of the coexisting ferromagnesian phases becomes increasingly more magnesian with increasing pressure, will be terminated when all phases become pure magnesian end-members. This happens at an invariant point in the end-member system at which the same phases occur as in the univariant equilibrium in the complex system. For the magnesian (high pressure) portion of the diagram, three such invariant points exist, as shown in Fig. 1. The relationships for two of these, the invariant points (Py) and (Cd) in the end-member system are self explanatory (compare Hensen and Green, 1972).

However, the third case involving the univariant curves $Cd + Ga \Rightarrow Hy + Si + Qz$ and $Cd + Ga \Rightarrow Hy + Ky + Qz$ needs some explanation. Because of the interference of the Si $\Rightarrow$ Ky phase boundary, the univariant boundaries in the simple system are deflected, and give rise to two metastable invariant points situated one on each side of the Si $\Rightarrow$ Ky boundary. The assemblages at these invariant points are $Cd-En-Py-Si-Qz$ and $Cd-En-Py-Ky-Qz$. The metastable extensions of each of the above univariant curves must pass through the corresponding metastable invariant points. The entirely metastable univariant reaction, in the Mg-end end-member system, $Cd + En \Rightarrow Py + Qz$ is required to pass through both metastable invariant points mentioned above.

1. Reactions can be treated as univariant provided plagioclase (An$_{50}$–An$_{85}$) is present in the assemblages (Hensen and Green, 1971).
2. Abbreviation used are cordierite (Cd), garnet (Ga), hypersthene (Hy), sillimanite (Si), kyanite (Ky), enstatite (En), pyrope (Py), sapphirine (Sa), spinel (Sp), hercynite (Hc), olivine (Ol), quartz (Qz), orthoclase (Or), biotite (Bi). Reactions are written such that the volume change is always negative.
Experimental Study of the Stability of Cordierite and Garnet in Pelitic Compositions

The position of the two invariant points in the low pressure, iron-rich portion of the diagram is only very approximately known. The limiting reaction for the breakdown of almandine (in the presence of plagioclase) i.e. fayalite + hercynite + quartz \(\rightleftharpoons\) almandine has been taken from the results on the B_0 composition (Hensen and Green, 1972) and allows us to estimate the invariant point involving the phases Fe-cordierite, almandine, fayalite, hercynite and quartz. The position of the invariant point involving the phases Fe-cordierite, almandine, hercynite, sillimanite and quartz has to occur on the low temperature, high pressure side of the invariant point mentioned above.

The strong curvature in the univariant phase boundary for the reaction 

\[ \text{Hy} + \text{Sp} + \text{Qz} \rightleftharpoons \text{Cd} + \text{Ga} \]  

(V) is required because theoretically it must intersect in one point with the reactions 

\[ \text{Cd} + \text{Ga} \rightleftharpoons \text{Hy} + \text{Si} + \text{Qz} \]  

and 

\[ \text{Sp} + \text{Qz} \rightleftharpoons \text{Cd} + \text{Ga} + \text{Si} \]  

The point of intersection corresponds to the metastable invariant point (Sa) in the system MgO-FeO-Al_2O_3-SiO_2 (Hensen, 1971, Table 1). In order for the curve for reaction (V) to backbend, the volume change of the reaction must change from positive to negative. The volume change of this reaction is probably very small (in the order of 2 or 3%). Calculations using linearly extrapolated volume

\[ \text{3 The possible effect of oxygen fugacity is disregarded here.} \]
data suggest that, for appropriate $K_D$ values, which determine the coefficients of the univariant reactions given the composition of one of the phases, the volume change of the reaction could be negative for relatively high values of $\text{Mg/Mg}^+\text{Fe}^{2+}$ of the coexisting phases and positive for low values of the same ratio, thus permitting the curvature of reaction (V) (shown in Fig. 1).

**P-T-X Grid for the Divariant Equilibria Cd $\Rightarrow$ Ga+ Si+ Qz (1)**

and Cd $\rightarrow$ Hy $\Rightarrow$ Ga $+$ Qz (6)

The divariant reaction (1) and (6), described in Hensen and Green (1971 and 1972, respectively) are of particular interest, since the $P-T-X$ relations determined experimentally should provide information about the temperature and pressure of formation of natural high grade meta-pelites. Ideally the $\text{Mg/Mg}^+\text{Fe}^{2+}$ ratios of a single cordierite-garnet pair from a divariant assemblage are diagnostic of the temperature and total pressure at crystallization. For the purpose of direct application to natural assemblages, the $P-T-X$ relations are shown in $P-T$ diagrams contoured for constant garnet ($X_{Ga}$) and cordierite ($X_{Cd}$) composition (Figs. 2 and 3). The $X_{Ga}$ and $X_{Cd}$ values have been taken from the $P-X$ diagrams discussed in Hensen and Green (1971, 1972). Given the $\text{Mg/Mg}^+\text{Fe}^{2+}$ ratios of coexisting garnet and cordierite, pressure and temperature are determined by the point of intersection of the appropriate $X_{Cd}$ and $X_{Ga}$ contours.
The accuracy in slope \( (\frac{dP}{dT}) \) and position of the contours are limited by uncertainties in pressure and temperature calibration and problems inherent in extrapolation from high temperature results to lower temperatures. Owing to the low angle of intersection of the \( X_{cd} \) and \( X_{Ga} \) curves the temperature derived from a Cd-Ga pair has a considerably larger uncertainty than the pressure. The following evidence supports the \( P-T-X \) relations as represented in Figs. 2 and 3:

1. A negative slope for the breakdown of cordierite in reaction (1) has been well established and is in agreement with experimental evidence from both the Fe and Mg end-member systems (Richardson, 1968; Schreyer and Yoder, 1964; Hensen and Green, 1970, 1971).

2. Hirschberg and Winkler (1968) found that a cordierite with 100 Mg/Mg+Fe\(^{2+}\) of ca. 68 coexisting with sillimanite, quartz and biotite, does not show any sign of breakdown to garnet at 700° C, 7 kb, in the presence of garnet seeds. Compared with the present results, this indicates that \( X_{cd} \) contours must at least be horizontal \( \frac{dP}{dT} = 0 \) and that a negative slope for the contours is consistent with their data. Note that Hirschberg and Winkler’s experiments were carried out in hydrothermal apparatus. If a larger pressure correction were required for the present data from solid media apparatus, the negative slope would be accentuated. Hirschberg and Winkler also found a negative slope for the appearance of garnet in a more Fe-rich composition. Their point at 700°
$-6 \text{ kb (100 } X_{\text{Cd}} = 45 \pm 10, 100 X_{\text{Ga}} = 0 \pm 10)$ is consistent within experimental error with the present results.

3. Recent reversal experiments by Hensen (1972, in press) have demonstrated that the $P$-$T$-$X$ data reported here represent equilibrium values.

In Figs. 2 and 3 the contours are shown to terminate on the kyanite-sillimanite phase boundary. In actual fact the contours should be deflected on this boundary but since no experimental data are available this is not shown in the diagrams.

The $X_{\text{Ga}}$ curves for both divariant assemblages (1) and (6) intersect on the universal curve $\text{Cd} + \text{Ga} \rightleftharpoons \text{Hy} + \text{Si} + \text{Qz}$. Most of the intersections are on the metastable extension of this univariant boundary on the high pressure side of the invariant point (Sp) (compare Fig. 1).

Influence of Factors Other than the Mg/Mg$^+$ Fe$^2+$ Ratio on the $P$-$T$-$X$ Relations

Ca-Content
The grossular content of the experimentally produced garnets ranges from $4 \pm 1$ mole-% in the $B_{30}$ composition to $6 \pm 1$ mole-% in the $B_{70}$ composition. Since most experiments on iron-rich composition $B_{30}$ were carried out at low pressure and most runs on the magnesium-rich composition $B_{70}$ at relatively higher pressure, it is not possible to separate the effects of pressure and composition on the amount of grossular$_{ss}$ in the garnet. Grossular solid solution has an important effect in extending the stability of garnet in the various assemblages (Hensen and Green, 1971; 1972).

Mn- and Ti-Content
Since Mn tends to concentrate in garnet, its presence will increase the stability field of garnet with respect to the other ferromagnesian phases. However, most garnets from cordierite-garnet bearing rocks have low Mn-contents (Mn < 1 weight %), and thus the present data should be applicable. The Ti-content is also very low in the garnets and therefore can be disregarded as an important factor.

Oxygen Fugacity
In the present experiments, carried out in graphite capsules, oxygen fugacity is low (Hensen and Green, 1971). Variations in oxygen fugacity could affect the solid-solid equilibria studied in the following ways.

If ferric iron substitutes in one or several of the ferromagnesian phases, this would alter the relative stability of these phases. Almandine appears to have negligible Fe$^{3+}$ substitution (Hsu, 1968). Analyses of experimental garnets suggest that Ca is accommodated in the form of grossular$_{ss}$ rather than as andradite$_{ss}$. In most analyzed garnets from natural cordierite-garnet, andradite substitution is low (<2 mole-%). Aluminous hypersthene could incorporate some ferric iron, and the stability of hypersthene with regard to garnet and cordierite may be extended under more oxidizing conditions than those prevailing in the present experiments, resulting in a displacement of the $\text{Ga} + \text{Cd} \rightleftharpoons \text{Hy} + \text{Si} + \text{Qz}$ to
lower pressure and temperature. The stability of hercynite-magnetite solid solutions will also be extended by increasing \( f_{O_2} \).

If an additional magnetite-rich spinel phase forms in the divariant assemblage as a result of high oxygen fugacity, then the equilibrium between the other ferromagnesian phases is not affected, provided the assumption that these phases do not incorporate Fe\(^{3+}\) is correct. This situation is analogous to the addition of a hydrous phase, e.g. biotite (Hensen, 1971). Cordierite and garnet analyses from natural rocks show low ferrie iron (Barker, 1962). Thus, provided variations in \( f_{O_2} \) do not eliminate either garnet or cordierite in favor of magnetite, the experimentally derived \( P-T-X \) relationships for reaction (1) should be applicable for variable \( f_{O_2} \) and in the presence or absence of magnetite as an additional phase.

**Structural State and Water Content of Cordierite**

The structural state of the cordierite produced in the experiments has not been determined. The effect of the structural state on the stability of cordierite is unknown and is not considered in this investigation. Although Schreyer and Yoder (1964) concluded that synthetic hydrous cordierites contain only molecular \( H_2O \), the role of water in cordierite is still subject to debate (Farrel and Newnham, 1967).

Recent experimental evidence (Newton, 1972) suggests \( P_{H_2O} \) significantly influences cordierite stability. However, the effect of \( P_{H_2O} \) on cordierite stability is probably nonlinear (Newton, personal communication) and may only be significant under extremely dry conditions (\( P_{H_2O} \rightarrow 0 \)). This is also suggested by the results obtained in this study on the magnesium end-member system, which are consistent with Newton's (1972) "wet" cordierite stability. It is concluded that even though conditions of \( P_{H_2O} < P_{\text{total}} \) prevailed in the experiments (Hensen and Green, 1971) enough water was present to stabilize the cordierites to conditions identical or very close to the maximum stability limit under "wet" conditions (\( P_{H_2O} = P_{\text{total}} \)).

**Summary and Geological Applications**

The results obtained in this study have provided a general phase diagram for metapelitic rocks (Fig. 1), which delineates the maximum stability fields of mineral associations of interest to petrologists, such as cordierite-garnet, hypersthene-sillimanite-quartz, hypersthene-kyanite-quartz, cordierite-garnet-sillimanite, and sapphirine-quartz.

Most of these assemblages were found to be stable over a wide range of \( P-T \) conditions and thus the positions of univariant phase boundaries separating the assemblages only provide rather broad limitations on their conditions of formation.

More specific temperature-pressure estimates for cordierite-garnet-bearing rocks can be derived by the use of the \( P-T-X \) relations of divariant equilibria. The contoured \( P-T \) diagrams discussed above (Figs. 2 and 3) are most appropriate for this purpose. Ideally, the load pressure and temperature of a divariant cordierite-garnet assemblage can be determined, given the Mg/Mg+Fe\(^{3+}\) ratio of a single garnet-cordierite pair. Similarly, the garnets or cordierites of two different
divariant [(1) and (6)] assemblages from neighbouring rocks can be used for the same purpose.

It must be emphasized that the present results cannot be regarded as final. Improved pressure corrections for solid media apparatus may change the absolute values and the slopes of the phase boundaries and compositional contours presented in the P-T, P-X and contoured P-T diagrams. However, the present results demonstrate the viability of the method and show where more detailed experimental work is needed to complete the picture. The results also indicate to

Table 1. Chemical data on coexisting cordierite and garnet from natural rocks

<table>
<thead>
<tr>
<th>Locality</th>
<th>(X_{Cd})</th>
<th>(X_{Ga})</th>
<th>(K_{D(Cd-Ga)})</th>
<th>Assemblage</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sierra Nevada</td>
<td>0.48</td>
<td>0.12</td>
<td>7</td>
<td>(1)</td>
<td>5 mole % Spess</td>
</tr>
<tr>
<td>(California)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td>Oberpfalz</td>
<td>0.50</td>
<td>0.11</td>
<td>8</td>
<td>(1)</td>
<td>13 mole % Spess</td>
</tr>
<tr>
<td>(Germany)</td>
<td>0.46</td>
<td>0.8</td>
<td>10</td>
<td>(1)</td>
<td>6 mole % Spess</td>
</tr>
<tr>
<td>Lochnagar</td>
<td>0.47</td>
<td>0.14</td>
<td>5</td>
<td>(6)</td>
<td>No. Hy.</td>
</tr>
<tr>
<td>(Scotland)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 mole % Sp</td>
</tr>
<tr>
<td>Bethanga</td>
<td>0.54</td>
<td>0.20</td>
<td>5</td>
<td>(1)</td>
<td>3 mole % Spess</td>
</tr>
<tr>
<td>(Victoria)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(d)</td>
</tr>
<tr>
<td>St. Catherine</td>
<td>0.54</td>
<td>0.14</td>
<td>7</td>
<td>(1)</td>
<td>3.5 mole % Spess</td>
</tr>
<tr>
<td>(Massif Central</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(e)</td>
</tr>
<tr>
<td>(France)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sturbridge</td>
<td>0.68</td>
<td>0.28</td>
<td>5.5</td>
<td>(1)</td>
<td>(f)</td>
</tr>
<tr>
<td>(Massachusetts)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gananoque area</td>
<td>0.60</td>
<td>0.24</td>
<td>5</td>
<td>(1)</td>
<td>(g)</td>
</tr>
<tr>
<td>(Ontario)</td>
<td>0.81</td>
<td>0.44</td>
<td>5</td>
<td>(6)</td>
<td>(g)</td>
</tr>
<tr>
<td>Lapland</td>
<td>0.73 (?)</td>
<td>0.35</td>
<td>5</td>
<td>(1)</td>
<td>(h)</td>
</tr>
<tr>
<td>(Finland)</td>
<td>—</td>
<td>0.46</td>
<td></td>
<td>(6)</td>
<td>No Cd.</td>
</tr>
<tr>
<td>N. MacRobertson</td>
<td>0.71</td>
<td>0.28</td>
<td>6</td>
<td>(1)</td>
<td>(i)</td>
</tr>
<tr>
<td>Land (Antarctica)</td>
<td>0.75</td>
<td>0.28</td>
<td>8</td>
<td>(1)</td>
<td>&lt;2 mole % Spess</td>
</tr>
<tr>
<td>and Kemp Land</td>
<td>0.80</td>
<td>0.36</td>
<td>7</td>
<td>(6)</td>
<td>&lt;2 mole % Spess</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>0.40</td>
<td>7</td>
<td>(1)</td>
<td>&lt;2 mole % Spess</td>
</tr>
<tr>
<td>Enderby Land</td>
<td>—</td>
<td>0.49</td>
<td></td>
<td>(1)</td>
<td>(l)</td>
</tr>
<tr>
<td>(Antarctica)</td>
<td>—</td>
<td>0.50</td>
<td></td>
<td>(1)</td>
<td>Associated with</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sa-Hy-Qz-Si and Cd</td>
</tr>
<tr>
<td>Aldan Shield</td>
<td>—</td>
<td>29–35</td>
<td></td>
<td>(1)</td>
<td>(R.I. determinations)</td>
</tr>
<tr>
<td>(U.S.S.R.)</td>
<td>—</td>
<td>32–38</td>
<td></td>
<td>(6)</td>
<td>(m)</td>
</tr>
<tr>
<td></td>
<td>0.83 (?)</td>
<td>0.50</td>
<td>5</td>
<td>(1) and (6)</td>
<td>Associated with</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hy-Si-Qz</td>
</tr>
</tbody>
</table>

References: (a) Best and Weiss (1964); (b) OKrusch (1969); (c) Chinner (1962); (d, e, i, j, k) Hensen (unpublished microprobe analyses); (f) Barker (1962); (g) Reinhardt (1968); (h) Eskola (1952); (m, n) Marakushev and Kudryavtsev (1965)

petrologists working on natural metamorphic rocks the key assemblages on which to obtain detailed chemical data for use as comparative or absolute indicators of physical conditions of metamorphism.

**Application to Natural Assemblages**

In high-grade amphibolite and granulite facies terranes, both the assemblages *cordierite-garnet-sillimanite-quartz-alkali feldspar-plagioclase±biotite* [corresponding to reaction (1)] and *cordierite-hypersthene-garnet-quartz-alkali feldspar-plagioclase±biotite* [corresponding to reaction (6)] are commonly found (Wynne-Edwards and Hay, 1963; De Waard, 1966). Pressure-temperature conditions of formation have been estimated for some selected data from the literature together with some new electron probe analyses (Table 1). The cordierite-garnet-sillimanite parageneses (Table 1) include relatively high pressure contact aureoles (examples a and b), migmatitic gneiss terranes (e, f and d) and typical granulite areas (i, k, h, g, m and l).

**Deep Level Contact Aureoles**

The *P, T* estimates for formation of the contact metamorphic rocks (Fig. 4; a, b) must be regarded as maximum limits, since in both occurrences the garnet contains considerable spessartine (5-13 mole-%). This could significantly affect the stability of garnet, allowing it to form at lower pressure than the spessartine-free garnets studied experimentally (Okrusch, 1969, 1971).

In the Lochnagar aureole (Chinner, 1962; Fig. 4; c) the assemblage *biotite-sillimanite-quartz* is absent. Biotite-sillimanite is only found in silica-undersaturated assemblages. This indicates that in the aureole, temperatures exceeded those for the “univariant” boundary, Cd+Ga+Or+H₂O ⇌ Bi+Si+Qz (Hy; Hensen, 1971). In complex pelitic rocks, this univariant reaction, which will have a positive slope, must pass below 3 kb at 700°C, according to the experimental results of Hirschberg and Winkler (1967). Because hypersthene is absent from the assemblage *garnet-cordierite-quartz* the rock must have formed on the high pressure side of the particular *XGa* contour for assemblage (6). However, the natural garnet contains 4 mole-% spessartine, which probably allows it to be stable at lower pressure.

**Migmaitic Gneisses from Amphibolite Facies, Terranes**

The rocks from St. Catherine (Massif Central, France), the Bethanga gneiss, Victoria and Sturbridge, Massachusetts (Barker, 1962) were probably formed under conditions intermediate between those of the deep-seated aureoles and granulite terranes. The garnets have a higher pyrope content than in the aureoles and are generally lower in Mn, and thus more comparable to the experimental garnets. The garnets from the Bethanga gneiss are strongly zoned, having a Mg-rich core (100 *XGa* = 20) and more Fe-rich (100 *XGa* = 10) and Mn-rich rim, possibly indicating retrograde metamorphism. The foregoing illustrates the danger of indiscriminately using wet analyses for the purpose of pressure and temperature estimation by the present method or for determining distribution
coefficients. In cordierite zoning it is less pronounced. The values given in the table are from cores of both garnets and cordierites.

Granulite Terranes

The cordierite-garnet rocks described by Rheinhardt (1968) occur in a metamorphic terrane also containing pyroxene granulites.

The chemical data for $X_{\text{Cd}}$ and $X_{\text{Ga}}$ in Table 1 have been in part recalculated from Reinhardt’s data. The interesting aspect of these data is the co-occurrence of two cordierite-garnet-bearing assemblages, i.e. Cd-Ga-Si-Qz (1) and Cd-Ga-Hy-Qz (6). The $X_{\text{Ga}}$ and $X_{\text{Cd}}$ contours for assemblage (6) and of assemblage (1) intersect approximately in one point [point (g) in Fig. 4] (Reinhardt’s samples R-114 and W-53). Assuming the chemical data to be correct, the Ontario rocks show the experimental data to be internally consistent to the extent that the $P$-$T$ estimates for two different assemblages from natural rocks are in close agreement.

4 $\text{Fe}^{3+}/\text{Fe}^{2+}$ was readjusted as required by structural formulae.
The Lapland cordierite-bearing granulites have been described by Eskola (1952) probably formed at a pressure around 8–9 kb and above 760° C. This estimate is based on a cordierite-garnet pair from a sillimanite-bearing assemblage plus the constraint of the kyanite ⇌ sillimanite boundary. The high pyrope content of garnets (100 $X_{Ga} = 44-46$) coexisting with hypersthene and quartz supports a high pressure origin. The alumina content of the hypersthene is high ($Al_2O_3 = 8.26$) suggesting high temperature. Eskola describes two-pyroxene granulites and ultrabasic rocks containing the assemblage olivine-plagioclase from the same area. The occurrence of these assemblages and the low $Al_2O_3$ content of coexisting pyroxenes in the basic granulites have led Green and Ringwood (1967) to postulate a low pressure origin for the Lapland granulites. The present estimate (Fig. 4; $h$) would put the conditions of formation of these granulites well within the intermediate granulite field as defined by Green and Ringwood. Within the latter field, olivine and plagioclase would not be compatible. The discrepancy remains unresolved, but deserves attention.

The Antarctic rocks (Fig. 4; i, j, k) were collected by I. R. McLeod in Northern MacRobertson Land and Kemp Land. Kyanite was not found in any of these rocks. The pelitic rocks are associated with two-pyroxene granulites (locally containing garnet) and high-grade amphibolites (or hornblende granulites; McLeod, personal communication).

The Aldan shield occurrence has been described by Khlestov (1964) and Marakushev and Kudryavtsev (1965). They report the assemblage hypersthene-sillimanite-quartz, and they interpret this to be indicative of the breakdown of the cordierite-garnet pair under the prevailing metamorphic conditions, e.g. $Cd + Ga ⇌ H_y + S_i + Qz$. Khlestov (1964) estimates the compositions of the phases at this boundary to be $100 X_{Cl} = 68; 100 X_{Ga} = 36; 100 X_{Hy} = 59$. On the other hand, Marakushev and Kudryavtsev (1965) give the values $100 X_{Cl} = 83; 100 X_{Ga} = 50$ and $100 X_{Hy} = 67$. In the latter paper, an analysis of hypersthene is given with $100 X_{Hy} = 67$. The hypersthene is extremely aluminous (9.35 weight % $Al_2O_3$) and contains very high ferric iron ($Fe_2O_3 = 6.05$ weight %; $Fe^{3+}/Fe^{3+} + Fe^{2+} = 0.23$). The high $Fe^{3+}$ is attributed to a $S_i + Fe^{2+} ⇌ Al + Fe^{3+}$ type substitution.

This occurrence of hypersthene-sillimanite-quartz is of particular interest because these natural assemblages are inconsistent with the experimental data. The $X_{Ga_{as}}$ (and $X_{Cd_{as}}$) curves for d variant assemblages (1) and (6) (Figs. 2 and 3) do not intersect within the garnet+cordierite stability field. At 800 and 900° C, the $X_{Ga_{as}}$ contour for reaction (1) occurs at approximately three and two kilobars respectively higher pressure than that for reaction (6). Assuming the high ferric iron content of the analyzed hypersthene to be correct, then the type of substitution advocated by Marakushev and Kudryavtsev (1965) may provide an explanation for the discrepancy between the experimental and natural data. The stability field of a hypersthene containing major ferric iron may be extended with respect to cordierite and garnet by high oxygen fugacity. Under conditions of high oxygen fugacity, $X_{Ga}$ and $X_{Cd}$ contours for reaction (6) could possibly be displaced towards higher pressure compared to their position determined in the present experiments under relatively reducing conditions. If this were the case, the intersection of $X_{Ga_{as}}$ in reactions (1) and (6) could take place at lower temperature, which implies that the univariant reaction $Cd + Ga ⇌ H_y + S_i + Qz$
(Figs. 1 to 3) will occur at considerably lower pressure. Provided the assumption that reaction (1) will remain unaffected is correct, the univariant boundary could then occur around 900 to 950°C and ca. 9 kb. These seem extreme conditions, but the temperature estimate is consistent with the very high alumina content of the hypersthene. Also the assemblage hypersthene-sillimanite-quartz is extremely rare. Only two other occurrences are known to the authors, one from Lapland (Eskola, 1952) and one from the Anabar Massif, U.S.S.R. (Luts and Kopaneva, 1968).

An interesting occurrence of a sapphirine-quartz rock from the Antarctic has been described by Dallwitz (1968). The experiments indicate that the assemblage sapphirine-quartz can only occur stably at very high temperature (around 1000°C) and pressure (above 8 kb). A high temperature-high pressure origin is also supported by the extremely high Al-content of the coexisting hypersthene (10.6 weight % Al₂O₃) and the high pyrope-content of the garnet (Py₅₀). A more detailed description of this occurrence will be given elsewhere (Hensen, in prep.). Another example of a sapphirine-quartz rock has recently been reported from a granulite terrane in central Labrador (Morse and Talley, 1971).

**Cordierite-Kyanite Paragenesis**

Cordierite and kyanite are only very rarely found together (Hietanen, 1956; Wenk, 1968; Fonteilles et al., 1964). The experimental data indicate that under relatively dry conditions and below ca. 850°C, the stability fields of Mg-rich cordierite and kyanite have a considerable overlap (Figs. 1 and 4). Under condition of \( P_{H₂O} = P_{\text{total}} \), Mg-cordierite and kyanite are compatible at 800°C and 10 kb (Schreyer, 1968). In the presence of K-feldspar the assemblage phlogopite-kyanite-quartz is probably stable at high water pressures. Therefore, the stable coexistence of cordierite and kyanite will be restricted either to rocks which formed under conditions of \( P_{H₂O} \ll P_{\text{total}} \) or to rocks without K-feldspar (i.e. \( H₂O \) or \( K₂O \) deficient environments).

**The Absence of Cordierite from Amphibolite Grade Metapelites**

Cordierite is not only absent from most kyanite-bearing rocks but also from numerous occurrences where sillimanite is the stable Al₂SiO₅ polymorph. This may be due to the fact that at pressures from 4–10 kb the univariant reaction, \( Cd + Ga + Or + H₂O \rightleftharpoons Bi + Si + Qz \) (Hess, 1969; Hensen, 1971) essentially represents the low temperature limit of cordierite stability in most pelitic rocks with excess K-feldspar and water. This follows from the observation that cordierite and biotite are both magnesian and close in composition, whereas garnet is much more Fe-rich. Therefore, the above univariant reaction will involve the breakdown of cordierite in most bulk compositions and the breakdown of garnet only in very magnesian bulk compositions. This may explain why garnet rather than cordierite is found in most low-grade (“wet”) amphibolite terranes, whereas cordierite in addition to garnet is more common in high grade amphibolite and granulite areas (cf. Chinner, 1962).

5 Recent experimental evidence (Newton, 1972) suggests the stability field of sapphireine-quartz may be extended to approximately 800°C under essentially anhydrous conditions.
The Role of Partial Melting in Relation to the Stability of Garnet and Cordierite

Under moderate to high grades of metamorphism the water content of a metamorphic rock may be entirely bound in hydrous minerals, e.g. micas and amphiboles. If the temperature is raised partial melting may occur at a $P_{H_2O}$ defined by the mineral assemblage. During partial melting the hydrous phases melt incongruently to yield a $K_2O + H_2O$ rich melt and a crystalline residuum enriched in ferromagnesian silicates, calcic plagioclase and aluminosilicate. If the melt fraction is segregated or removed the residual phases, comprising the bulk of the rock, form a mineral assemblage depleted in $K_2O$ and $H_2O$ (von Platen and Höller, 1966; Grant, 1968; Bryhni et al., 1970). Thus, partial melting under conditions of $P_{H_2O} < P_{total}$ may effectively dehydrate a metamorphic terrane containing pelitic rocks and produce granulite assemblages with garnet, cordierite, hypersthene and aluminosilicate.

The Occurrence of Garnet and Cordierite Xenocrysts in Granitic and Andesitic Magmas

Several experiments carried out in the present study illustrate the nature of melting in the presence of small amounts of water. In the model pelitic composition B' (Hensen and Green, 1972) the subsolidus assemblage at 6.3 kb, 900°C is garnet + cordierite + hypersthene + quartz + feldspars. The garnet has 100 Mg/Mg+Fe2+= 34±2 and contains 7±1 mole-% grossular and the coexisting cordierite has 100 Mg/Mg+Fe2+= 66; $K_D=5$. In another run at the same $P$ and $T$, a small amount (ca. 1%) of water was added in an attempt to increase reaction rates. This run showed major melting and consisted of garnet + cordierite + plagioclase + glass. The garnet has 100 Mg/Mg+Fe2+= 43±2, and 8.5±1.5 mole-% grossular and the coexisting cordierite has 100 Mg/Mg+Fe2+= 75; $K_D=5$.

At 1 kb lower pressure, i.e. 5.4 kb, 900°C, an anhydrous run contained garnet + hypersthene + cordierite + quartz + feldspars, but a run with water added, contained hypersthene (100 Mg/Mg+Fe2+= 57) + cordierite (100 Mg/Mg+Fe2+= 75) + plagioclase + glass. The experiments illustrate the role of melting in leaving an anhydrous residuum and particularly show the pressure-sensitive nature of the residual phases (i.e., of liquidus phases for the melt fraction). The two experiments, in which there is a similar large degree of partial melting, show that at a certain pressure Ca-poor almandine-rich garnet may exist in equilibrium with a melt, but that at 1 kb less garnet will react with the liquid to yield hypersthene and cordierite. The experiments provide laboratory simulation of the formation of inclusions of garnet-bearing restites (residua) in anatetic silica-rich magmas, showing this type of reaction of garnet (Zeck, 1968). The experiments also provide insight into the occurrence of grossular-poor, almandine-rich garnet xenocrysts in rhyolites and andesites, associated in some cases with hypersthene and/or cordierite xenocrysts. The compositions of such magmas are essentially hypersthene-diopside normative, and experimental studies (T. H. Green and A. E. Ringwood, 1968a, b) showed that garnet occurring on or near the liquidus, at pressures >10 kb, was grossular-rich (>10% grossular, usually 20-30% grossular-andradite). Garnets formed under subsolidus conditions in such bulk compositions (hypersthene-diopside normative) are similarly grossular-rich (>20 mole-% grossular, D. H. Green and A. E. Ringwood, 1967; T. H. Green, 1970) in
contrast to the garnets formed in pelitic compositions (hypersthene + corundum normative) at pressures below 10 kb (<10 mole-% grossular, Hensen and Green, 1971, 1972). The data obtained in the present study suggest that garnet xenocrysts with <2% CaO occurring in calc-alkaline magmas may never have been in equilibrium with their host magma (if this is hypersthene + diopside normative), but represent relict or refractory phases from partial melting of minor admixed pelitic rocks (hypersthene + corundum normative). The garnets probably reflect local crystal-liquid equilibrium at <10 kb in a compositionally heterogeneous "magma" and may be considered evidence for the presence of mixed "crustal" lithologies in the source region for andesitic magmas rather than a more homogeneous peridotite source composition.

Conclusions

Natural cordierite-garnet-bearing metapelites have apparently formed over a wide range of pressure-temperature conditions. Almost all estimated $P-T$ points fall in the field of intermediate pressure granulites as defined by Green and Ringwood (1967) (Fig. 4). From most areas it is as yet unclear how the mineralogy and chemistry of basic granulites is related to that in the accompanying cordierite-garnet-bearing rocks. This is a point of great interest and merits detailed investigation in field studies.

In some areas exceptional temperature conditions must have prevailed in the earth's crust during high grade metamorphic events. The assemblages sapphire-quartz and hypersthene-sillimanite-quartz indicate that temperatures of 900–1000° C may have been reached in some cases where pressures were in the order of 10 kilobars. The heat source causing such high temperatures could have been the intrusion of large volumes of essentially dry basic magmas into the lower crust. Such melts could have liquidus temperatures around 1200–1300° C and could possibly raise temperatures in adjacent metasediments to the required values. The metasedimentary rocks must have lost most of their water in previous metamorphic events or possibly were dehydrated, with extraction of partial melt, by the basic magma.

References


Experimental Study of the Stability of Cordierite and Garnet in Pelitic Compositions


Richardson, S. W., Bell, P. M., Gilbert, M. C.: Kyanite-sillimanite equilibrium between 700° C and 1500° C. Am. J. Sci. 266, 513–541 (1968).


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Talc-Garnet-Kyanite-Quartz Schist from an Eclogite-Bearing Terrane, Western Tasmania

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Abstract. Talc-garnet-kyanite-quartz schist occurs in an eclogite-bearing terrane in the Precambrian of Western Tasmania. It is argued that this rock was formed at a pressure of \(\leq 10\) kb and a temperature of \(600^\circ \pm 20^\circ\)C.

Chemical zoning in the garnet and talc preserves evidence of increasing temperature during growth of the major minerals.

Introduction

A talc+garnet+kyanite+quartz schist was discovered in a study of eclogites and surrounding schists from the Precambrian of Western Tasmania.

A rock of this chemical composition (Table 1) may crystallize in a variety of alternative mineral assemblage, each assemblage restricted to a limited P/T stability field. Possible mineral assemblages include pyrophyllite+chlorite+quartz ± albite ± sphene at low P/T conditions and kyanite+staurolite+gedrite+quartz, hypersthene + kyanite(sill) + garnet + quartz, cordierite + sillimanite + quartz at higher P/T conditions. The To + Ga + Ky + Qz mineral assembly is therefore of special interest as a P/T indicator. It is also of interest that the rock is closely

Table 1. Chemical composition of the talc-garnet-kyanite-quartz schist

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<tr>
<th></th>
<th>71–310</th>
<th>71–312</th>
<th>C.I.P.W. Norms</th>
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<td>71–310</td>
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<td>SiO₂</td>
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<td>70.1</td>
<td>q</td>
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<tr>
<td>TiO₂</td>
<td>0.4</td>
<td>0.4</td>
<td>co</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.8</td>
<td>9.0</td>
<td>or</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.1</td>
<td>0.1</td>
<td>ab</td>
</tr>
<tr>
<td>MnO</td>
<td>0.1</td>
<td>0.1</td>
<td>an</td>
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<tr>
<td>MgO</td>
<td>10.7</td>
<td>9.6</td>
<td>hy</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.4</td>
<td>mt</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1</td>
<td>0.1</td>
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<td>K₂O</td>
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<td>ap</td>
</tr>
<tr>
<td>P₂O₅</td>
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<tr>
<td>Mg value(^a)</td>
<td>65.6</td>
<td>70.9</td>
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\(^a\) Mg value = \(\frac{100 \times Mg}{Mg + Fe^{++}}\) (atomic proportions).
associated in the field with eclogite, which also places limits on the P/T conditions of the metamorphism (Green and Ringwood, 1967).

Recently, new occurrences of Tc+Ky mineral assemblages have been reported from Afghanistan (Kulke and Schreyer, 1973), Zambia (Vrana and Barr, 1972) and Switzerland (Chinner and Dixon, 1973). The experimental work of Schreyer and Seifert (1969a) in the system MgO—Al2O3—SiO2—H2O suggests that these assemblages formed at a pressure in excess of 10 kb.

However, as far as the authors are aware, almandine garnet has not previously been described in association with the talc+kyanite+quartz assemblages. According to the experimental work in the system MgO—Al2O3—SiO2—H2O by Schreyer and Seifert (1969b), the lower pressure limit for the occurrence of garnet (pyrope), probably through the breakdown of mineral assemblages involving talc+kyanite or talc+yoderite, is about 15 kb at about 750°C.

The Tc+Ga+Ky+Qz assemblages occurs in the Lyell Highway-Collingwood River area about 25 miles east of Queenstown, Western Tasmania. The rock occurs in an eclogite/garnet amphibolite bearing terrane where the dominant rock types are garnet-mica schists/mica schists, phyllites and quartzites of upper greenschist facies (high P) metamorphism.

The Tc+Ga+Ky+Qz schist was found (in February 1971) on the southern bank of Collingwood River about 150 m upstream from the mouth of Scarlet Creek (392 300 yds E, 1810500 yds N).

The detailed field relations are uncertain because of poor outcrop and very strong isoclinal folding. The sample is from 1/2-1 m band(s) interlayered with garnet+phengite-bearing quartzite.

Chemical Compositions of Rock and Minerals

Whole rock analyses (Table 1) were made in duplicate using standard X-ray fluorescence spectrography technique (Norrish and Hutton, 1969). Na2O was determined by flame photometer, FeO by spectrophotometry and H2O by weight loss at 1100°C (E. Kiss, analyst). The minerals (Table 2 and 3) were analyzed using an electron microprobe and non-dispersive X-ray analytical system, based on the TPD microprobe (Fontijn et al., 1969). Full details of the instrument and analytical procedures are described elsewhere (Reed and Ware, 1973). Some partial (zoning of Ga) and complete analyses were done on an ARL microprobe.

Petrography

The rock has the appearance of a strongly crenulated garnet+mica knotted schist, grey in colour and with pink garnet porphyroblasts. In thin section, the texture of the rock is porphyroblastic/lepidoblastic and the most important primary minerals are talc, quartz, garnet and kyanite (listed in order of abundance). Secondary minerals are different Mg-rich chlorites. Accessory minerals are rutile and rounded zircons.

Primary Minerals

Talc has a very faint yellowish-greenish colour and varies in Fe-content (probably due to zoning) with Mg-values between 90.5 (rim to quartz) and 93 (core).
Table 2. Microprobe analyses and atomic proportions of the primary minerals; garnet, talc and kyanite

<table>
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<tr>
<th></th>
<th>Garnet rim to qz</th>
<th>Garnet between core and rim</th>
<th>Garnet core</th>
<th>Garnet core</th>
<th>Talc rim</th>
<th>Talc core</th>
<th>Kyanite</th>
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<td>SiO₂</td>
<td>39.3</td>
<td>37.9</td>
<td>36.6</td>
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<tr>
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<tr>
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<td></td>
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<tr>
<td>K</td>
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<tr>
<td><strong>Σ</strong></td>
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<td>8.013</td>
<td>8.060</td>
<td>7.995</td>
<td>7.017</td>
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<td>12</td>
<td>12</td>
<td>11</td>
<td>11</td>
<td>5</td>
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</tbody>
</table>

Total Fe given as FeO.

Aluminium and sometimes sodium occurs in a small and varying amount (see Table 2), possibly in finely intergrown phyllosilicates of other species. Garnet has variable grainsize between 0.04 mm and 4 mm. The larger grains are poikiloblastic with inclusions of quartz, kyanite, talc and rutile. The garnets are mostly anhedral due to secondary alteration, however, at quartz contacts and when small garnets occur entirely within quartz, the primary euhedral shape is observed.

The larger garnets are strongly zoned (see Fig. 1 and 2, and Table 2) with the grossular component decreasing from 23 mol % in the core to 2 mol % at the rim. Whenever garnet occurs in contact with quartz there is an increase of grossular-component of up to 6% in the outer 10-20 μ. These crystals are considered to approach retention of the complete primary zoning of the garnets. The Mg-value increases continuously from 15 in the core through 45 (2 mol % grossular) towards the rim to 49 (6 mol % grossular) at the margin against quartz (see Fig. 1 and 2). When secondary alteration occurs (at the contact between talc and garnet) the Mg-value decreases in the outer 150 μ. The size of this alteration zone (5-150 μ) in the garnet varies with the amount of secondary chlorite(s) formed. Mn is
Fig. 1. The Ca—Mg—Fe diagram illustrates the varying garnet and talc compositions (arrow from core to rim). Dashed line with arrow illustrates the secondary effect (formation) of Mg rich-chlorites

Table 3. Microprobe analysis and atomic proportions of the secondary minerals: chlorites

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<td>Chl at Ga (normal type)</td>
<td>Chl at Ga (normal type)</td>
<td>Chl within Ga</td>
<td>Chl within Ky</td>
<td>Chl at Ky</td>
<td>Chl at talc</td>
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<td>11.1</td>
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<tr>
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<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
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</table>

Total Fe given as FeO.
Fig. 2. The Al—(Fe+Mn)—Mg diagram illustrates the change in Mg-value of the garnet, the varying amount of Al in the talc and the various compositions of the chlorites. Al-content of garnet has been adjusted by removal of the grossular component. The numbers in the figure refer to Table 3.

not an important constituent of this rock (see Table 1) however, Mn is seen to follow Fe in its zonation pattern within garnet, generally decreasing from core to rim. The zoning of the garnets also varies with size as small garnets show only the rim composition of the larger garnets. The grossular-component in the core increases according to size.

Kyanite mostly occurs with a rim of chlorite in talc. Larger grains (1.5 mm) are deformed with the same crenulation as talc. The size varies from (0.1-1.5 mm). Kyanite contains inclusions of rutile, quartz and talc, the latter occurring parallel to the {100}-cleavage. The kyanite contain a small amount of Fe₂O₃ (0.3%) (Table 2). Small (0.3 mm) euhedral kyanite prisms with no alteration are seen within quartz.

Quartz has undulose extinction and occurs as aggregates parallel to the general trend defined by the talc and kyanite orientation.

Secondary Minerals
The secondary minerals can all be classified as chlorites (Table 3). Four distinctly different chlorites have been recognized, one within kyanite (high Al), one marginal to talc (high Mg), one within garnet (reflecting the garnet chemistry) and chemically similar larger chlorites usually occurring as a secondary reaction
mostly involving garnet and talc. The chlorite associated with kyanite is close to the chlorite at garnet in chemical composition, however, a higher Al content (Table 3 and Fig. 2) demonstrates the involvement of kyanite in its formation.

The variation in chemistry of the chlorites is best seen in Fig. 2 clearly pointing out a greater variation in the chlorite chemistry than in that of the primary minerals, consistent with a secondary origin and either disequilibrium or equilibrium within a very local domain.

**Petrogenesis.** The chemical system of this rock differs from the simple MgO—Al₂O₃—SiO₂—H₂O of the kyanite-talc schists from Afghanistan (Kulke and Schreyer, 1973) and Zambia (Vrana and Barr, 1972) by also having FeO and a small CaO content (Table 1).

The association with quartz-rich meta-sediments, the high normative quartz content (about 40–50%) and the occurrence of rounded zircons as accessories indicates a supracrustal origin for this rock, where weathering of ultramafic/basic rocks or deposition of ultramafic/basic tuffs mixed with quartz-rich sediments may have been important. The garnet contains up to 0.15 Cr₂O₃ which also favours derivation from an igneous source rather than Mg-rich dolomitic sediments. A possibility of Mg-metasomatism by Mg-rich solutions emanating from neighbouring impure carbonates during metamorphism, as suggested by H. Kulke and W. Schreyer (1973) is in this case considered very unlikely, as Mg-rich metasediments have not been found in the locality. The CaO content of the rock is too low for an origin as an impure dolomite. Removal of Ca from a siliceous dolomite parent rock by metasomatic processes is not at all reasonable as the metasedimentary rocks of the surrounding area are characterized by low Ca-contents.

Use of the P/T diagram in the system MgO—Al₂O₃—SiO₂—H₂O (Schreyer and Seifert, 1969) or in the system MgO—Al₂O₃—SiO₂ (Hensen and Essene, 1970) is somewhat limited in discussion of the physical conditions of metamorphism in this case because of additional FeO-component and a small amount of CaO component in the system. However, analogous assemblages in the anhydrous systems contain garnet+kyanite+quartz together with hypersthene rather than talc. In the dry end member system (MgO—Al₂O₃—SiO₂) enstatite+kyanite and pyrope+quartz cannot coexist stably over a divariant P/T range. The addition of another component (FeO) to the system will enlarge the stability field of a particular phase depending on the distribution of Fe and Mg between the coexisting ferromagnesian phases (Hensen and Essene, 1970). Thus in the Fe—Mg system there exists a field of coexistence of Ga+Ky+Hy+Qz at pressure below the stability field of pyrope and quartz. In the mineral assemblage involving talc rather than enstatite, (Mg/Fe)₉ > (Mg/Fe) garnet. If talc has a similar role to hypersthene in the anhydrous reactions then with increasing FeO content the stability field of garnet moves to lower P and/or higher T with respect to talc. The addition of one more component, FeO, to the system opens up the possibility for the coexistence of talc+garnet+kyanite+quartz.

The work by Hensen and Green (1973) in the system MgO—FeO—Al₂O₃—SiO₂ can give some information about the P/T conditions of this rock, since the anhydrous phases Ga+Ky+Qz coexist stably together in preference to alternatives such as Cd±Sill+Qz, Hy+Sill(Ky)+Qz. As seen from the P/T diagram [Fig. 2, Hensen and Green (1973)] for the divariant reaction Cd⇌Ga+Si(Ky)+Qz...
a garnet with Mg-value 50 (rim) would be stable together with Ky (not sillimanite) in preference to the assemblage Ga(more Fe-rich)+Cord+Sill(Ky)+Qz at a pressure above 10 kb (T-820°). It is not known, however, how the Ga compositional contours on this P/T diagram should be deflected on the Si/Ky phase boundary, if they continue with a negative slope the pressure must be even higher as the temperature of crystallization of the rock is ≈820°C as discussed below.

Until experimental data on a suitable chemical system are available at lower temperature this rock provides little information about the temperature during metamorphism. Migmatites do not occur in the metamorphic terrane in Western Tasmania. This means that the upper temperature limit has to be below the beginning of melting, which with the chemical systems available in garnet + quartz + albite + phengitic mica schists (i.e. normative plagioclase An7 Ab93) probably would be below 650°C at the pressure conditions indicated (melting of albite+quartz, Merrill et al., 1970).

The distribution coefficient $K_D$ between coexisting garnet and clinopyroxene of eclogites decreases with increasing temperature (Banno, 1970). We have done experiments on variation of $K_D$ with varying temperature, pressure and varying Mg-value (5-95) of quartz tholeiite compositions (Råheim and Green, 1973 unpublished data), and our preliminary conclusion on the maximum temperature of the eclogite is 600°C±20°C at a pressure of 10 kb. This temperature estimate is in good agreement with that (600°C) derived from the Si4+-content of 3.3±0.1 in phengite micas from the eclogite and the surrounding schists, using the stability curves for various phengite micas of Velde (1967).

Nearly all the CaO content of this rock is concentrated in the garnet. We have not discussed the effect of CaO in the Tc + Ga + Ky + Qz schist as very little experimental data exist with relation to this chemical system. Grossular solid solution has, however, an important effect in extending the stability of garnet in the various assemblages (Hensen and Green, 1971, 1972). This has little relevance in the previous discussion of the pressure conditions of the Tc + Ga + Ky + Qz schist as this is based on the garnet rim (Mg-value 45-50) which only contains a small grossular content (2-6%). The grossular component in almandine-pyrope garnet is known to increase with increasing pressure and a relative high grossular content indicates high pressure rather than high temperature (T. H. Green, 1967; Råheim and Green 1973). This is of some interest when looking at the zoning pattern of CaO of the garnets in this rock, where the grossular component decreases from 23 mol % in the core to 2 mol % at the rim. If this zoning is due to a change in physical conditions during the growth of the garnet (Råheim and Green, 1973 unpub. data) the zoning pattern of CaO may either be due to a drop in pressure, or more likely, an increase in temperature at about the same pressure.

The Mg-value increases monotonically from core to rim. This could be explained by an increase in pressure at constant temperature, as a pressure increase would result in a shift of the tielines of the 3 phase triangle Ky—Ga—Tc towards the Mg side in a AFM diagram. This explanation, however, is incompatible with the CaO zoning of the garnet discussed above implying a pressure drop or temperature

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increase during garnet growth. As experimental data clearly demonstrate that the Mg-value of a garnet in equilibrium with a more magnesian phase such as pyroxene increases with increasing temperature (Råheim and Green, 1973 unpub. data) we conclude that the zoning of the garnet is mostly due to a temperature increase. Comparing the zoning pattern of FeO and MgO between garnet and talc (care must be taken to avoid secondary effects) it is seen that in talc the Mg-value decreases from core to rim, which is opposite to garnet. A comparison of $K_D(Ga/Tc)_{core} = 75.9$ and $K_D(Ga/Tc)_{rim} = 11.3$ also supports the inference that the zoning of these minerals is largely due to an increase of the temperature as $K_D$ values generally decrease with increasing temperature (Saxena, 1968; Banno, 1970).

The secondary minerals which involved local chemical systems (reactions at grain boundaries) have occurred as a result of one to three possible later tectonic events in the area. Rb-Sr work in progress (Råheim and Compston) on the mineral systems indicate that the freezing of the Rb—Sr isotopic system in the talc appears to be about 200 m.y. older than that in the chlorite. As seen from Fig. 2 the chlorites have been formed mostly through reactions involving Ga+Tc+H$_2$O and Ky+Tc+H$_2$O. As chlorites provide little information about more exact P/T conditions all we can say about this at present is that the secondary effect (or effects) on this rock occurred at a relative low P and T compared to the first period of metamorphism, estimated as P/T conditions at about $\geq 10$ kb and 600° ± 20°C.

Conclusion

1. This is the first report, to our knowledge, on the coexistence of Tc+Ky+Ga+Qz. When experimental data are available on a chemical system similar to this rock at the appropriate P/T conditions the Tc+Ga+Ky+Qz mineral assembly will probably prove to be an excellent P/T indicator.

2. The zoning of the garnet (and talc) together with the decrease of $K_D(Ga/Tc)$ from core to rim of talc and garnet, indicate that the rock after reaching a high pressure (high CaO content in core) was then subject to increase in temperature at high pressure.

3. The mineral assemblage Tc+Ga+Ky+Qz is restricted to high confining pressures at or above some 10 kb. The temperature condition is 600° ± 20°C, determined by $K_D(Ga/Cpx)$ value of the eclogites and the Si$^{4+}$ content in phengite micas from the same area.

4. Superimposed on this 600°C, $\geq 10$ kb, metamorphism, secondary reactions within, at, or between Ky, Ga and Tc, caused by one to three possible later tectonic events, produced chlorites of widely varying chemical compositions.

References


Talc-Garnet-Kyanite-Quartz Schist

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Experimental Determination of the Temperature and Pressure Dependence of the Fe-Mg Partition Coefficient for Coexisting Garnet and Clinopyroxene

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Abstract. An experimental study initiated to calibrate the distribution coefficient

\[ KD = \frac{\text{Fe}_0}{\text{Mg}_0} \]

in eclogites as a geothermometer has been done on (a) a mineral mix, (b) a glass of the typical tholeiite composition and (c) a series of glasses of tholeiite compositions with 6.2 < \frac{\text{Mg}^+ + \text{Fe}^{++}}{\text{Mg} + \text{Fe}^{++}} < 93.

The mineral mix was found to be unsuitable as reactant due to incomplete equilibration but the minimum \( KD_{\text{Ga,Cpx}} \) of the mineral mix and the \( KD_{\text{Ga,Cpx}} \) from glass of tholeiite composition are identical within experimental uncertainty. These data constitute a reversal of the garnet/clinopyroxene partition relationship and provide justification of the use of glass as a reactant for the project. To eliminate any uncertainty in interpretation of mineral analyses due to possible variation in Fe\(^{++/+}\) between runs, experiments were carried out in iron capsules on the nine tholeiite glasses, thus maintaining iron as Fe\(^{++}\).

Microprobe analytical techniques yielded mineral analyses of comparable accuracy to analyses of natural phases for experiments within the temperature range from 600°C to 1500°C and a pressure range from 20 kb to 40 kb.

It has been shown that for 6.2 < \frac{\text{Mg}^+ + \text{Fe}^{++}}{\text{Mg} + \text{Fe}^{++}} < 85, the bulk chemical composition does not perceptibly affect the \( KD \) value. At 30 kb the \( KD \) value ranges from 18.0 at 800°C to 1.45 at 1400°C, defining the linear relationship in a \( \ln KD \) vs \( 1/T(°K) \) plot. The pressure dependence of the \( KD \) value has been shown to be greater than previously predicted. There is a straight line relationship in \( \ln KD \) vs Pressure (kb) between 20 and 40 kb at constant temperature (1000°C). This enables us to determine \( KD = f_n(T, P) \) and \( T(°K) = \frac{3686 + 28.35 \times P(\text{kb})}{\ln KD + 2.33} \).

This expression uniquely determines the temperature of equilibration of natural eclogites of basaltic bulk composition when the \( KD_{\text{Ga,Cpx}} \) is known and a pressure estimate can be given.

Introduction

The study of natural eclogites from different lithologic and tectonic associations, including the kimberlite pipes, gneissic terranes and blueschist terranes, has in recent years led to recognition of mineralogical characteristics which typify and distinguish these eclogites. In particular Sobolev (1970), Coleman et al. (1965), Banno and Matsui (1965), Essene and Fyfe (1967) and Banno (1970) noted differences in the relative distribution of iron and magnesium between coexisting garnet and clinopyroxene and Banno (1970) classified natural eclogites principally

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on this basis, inferring that differences in the iron-magnesium distribution coefficient were caused by different P, T conditions of equilibration of the eclogites. In a theoretical treatment, Banno (1970) defined the garnet/clinoxyroxene distribution coefficient \( K^{\text{glex}} = (\text{Fe}^{3+}/\text{Mg})_{\text{garnet}}/(\text{Fe}^{2+}/\text{Mg})_{\text{clinoxyroxene}} \) and argued that \( K_D \) should decrease with increasing temperature, increase with increasing pressure and be relatively insensitive to changes in chemistry reflected in other, minor, components of the pyroxene (jadeite, enstatite) or garnet (grossular, spessartine) solid solutions. Banno predicted that \( K_D \) would be sensitively dependent on \( T \) but that the pressure dependence would be smaller. For constant pressure \( (K_D)_p = f_n(T) \) \( \Delta H_x = \frac{\Delta S_x}{RT} \), thus providing a potential geothermometer of considerable use since natural eclogites have \( K_D > 35 \) to \( K_D < 2.1 \). Mysen and Heier (1972) attempted a quantitative evaluation of the \( K_D = f_n(T) \) relationship by using published data for analyzed garnet, clinopyroxene pairs together with the published estimate of temperature of equilibration for each assemblage to plot a linear relationship of \( \ln K_D \) vs \( 1/T \). This approach depends on the validity of the \( P, T \) estimates for the different metamorphic terranes, most of which have large uncertainties. Secondly the range of pressure estimates (from 6–36 kb, Mysen and Heier, 1972)) is so large that, even if the pressure effect on \( K_D \) is as small as Banno (1970) estimated, data over so large a pressure range should define a curve (if \( T \alpha P \)) or broad scatter (if \( T \not\alpha P \)) on the \( \ln K_D \) vs \( 1/T \) plot. Thirdly, as noted by Mysen and Heier (1972), Bryhni and Griffin (1971) and Råheim (1974), the presence of zoning makes chemical analyses of separated minerals of unknown value for estimates of \( K_D \). The use of the electron microprobe for mineral analyses permits analyses of adjacent grains and evaluation of the zoning of minerals as records of changing \( P, T \) conditions during prograde or retrograde metamorphism (Råheim, 1974).

The potentially wide application of the \( K^{\text{glex}} \) in temperature and pressure calibration of metamorphic assemblages led us to attempt to experimentally determine the variation of \( K^{\text{glex}} \) as a function of pressure, temperature and one major compositional parameter, the \( \frac{100\text{Mg}}{\text{Mg} + \text{Fe}^{2+}} \) or Mg-value for the bulk rock composition. In order to enable direct application to the most common natural metamorphic eclogite type (quartz eclogite) the bulk composition chosen was that of a tholeiite (quartz tholeiite B of Green and Ringwood, 1967) for which the stability fields of granulite, garnet granulite and eclogite had previously been determined.

**Experimental Methods**

a) **Instrumental Techniques**

The high-pressure-high temperature experimental runs were carried out using a piston-cylinder apparatus of Boyd and England (1960) design. Runs were made under piston-in conditions and nominal piston pressures were corrected by a (–10%) pressure correction to yield the sample pressure. Calibration of our piston-cylinder technique has been confirmed by reversal experiments on the quartz coesite transformation at 1100°C (Green, Ringwood and Major, 1966) and on the albite jadeite + quartz reaction at 600°C (Brey, Hibberson and Green, unpublished data). Temperature variation is ± 5°C about the control point with an accuracy estimated as ± 10°C.
Experimental runs were examined optically (crushed sample) and by electron microprobe (TPD instrument, produced by Technisch Physiche Dienst, Delft Technical University, Delft, The Netherlands (Fontijn et al., 1969). Quantitative analysis of samples is based on a Li-drifted silicon detector and full details of analytical and correction procedure are given by Reed and Ware (1973). The analytical conditions employed an electron beam accelerating voltage of 15 kV, an electron beam diameter of <0.5 microns and a specimen current of 3 nano-amps. Analyses for nine elements (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe) were obtained simultaneously (analysis time 100 seconds) at each point. The energy-dispersed relative intensity spectra were recorded on a Northern Scientific (NS 710) multichannel pulse height analyzer at a count rate of around 4 400 counts per second. This electron microprobe and analytical system is ideal for the very fine grain size and multicomponent nature of the experimental charges and avoids the problems and uncertainties inherent in sequential analysis for different elements using wavelength-dispersive X-ray crystal spectrometer detection methods. The quality of data on mineral chemistry and major element partition between coexisting phases (as measured by adherence to structural formulae constraints and by reproducibility of partition data) under experimental conditions are comparable with data obtained from natural rocks. Analyses of minerals of known composition permit the estimation of accuracy of analysis as ± 2% relative at concentration levels above 10 weight percent for all elements except Na. Na analyses with a concentration of about 5 weight percent have an estimated error of ±0.2—±0.3 wt %. The limit of detection is 0.1 weight percent for K to Fe and 0.2% for Na, Mg, Al and Si.

b) Evaluation of Suitability of Glass or Mineral Mix as Reactants — Reversibility of Garnet, Pyroxene Partition Relationship

In the light of earlier studies (Green and Ringwood, 1967; Hensen and Green, 1971, 1972) using glass and seeded glass starting materials, it was necessary to evaluate whether use of glass, in which nucleation of garnet and/or pyroxene without selective partition of Fe and Mg could yield $K_{G^*_{cpx}} = 1$, and use of a natural mineral mix with $K_{G^*_{cpx}} = 10 ± 2$ would both yield identical $K_p$ values at the experimental $P, T$ conditions. The experiments should also evaluate whether one starting mix or the other was more rapid in reaching equilibrium or had other advantages for the project. The initial compositions selected for study were the quartz tholeiite B composition of Green and Ringwood (1967, 1972) and similar quartz eclogite bulk composition of 31.5% garnet + 58.5% clinopyroxene + 10% quartz prepared as a mineral mix. Glass tholeiite B composition was prepared from A.R. grade chemicals and its composition checked by electron microprobe analysis (Table 1, column 1) and spectrophotometric analysis for Fe$_2$O$_3$ and FeO. The glass was crushed in agate mortar and repeatedly elutriated (acetone) to obtain a grain size <10 microns (about 75% < 5 microns). The mineral mix was prepared from garnet and clinopyroxene separated to 99% purity from a Tasmanian eclogite (Spry, 1963; Råheim, 1974). The minerals were ground in a Spex mill using a steel cylinder and tungsten carbide balls. Iron was extracted magnetically after repeated crushing and elutriation to obtain a sufficient fraction of grain-size < 10 microns (about 75% < 5 microns). The minerals were then mixed in proportions to yield a basaltic bulk composition. Based on microprobe analyses of the minerals (Table 1, columns 3 and 4), a theoretical bulk composition was calculated (Table 1, column 2) and checked by determination of FeO, Fe$_2$O$_3$ contents by spectrophotometry (E. Kiss).

To ensure the same run conditions for both reactants, both the glass (10 mg) and mineral mix (10 mg) were sealed in the same silver-palladium capsule (Ag$_5$Pd$_{12}$ at 1100°C, Ag$_8$Pd$_{30}$ at 1200°C; Pt at >1300) but were separated by a close-fitting AgPd, or Pt disc. No mixing of the two samples occurred during the run. The electron microprobe analyses of the minerals were plotted in a Ca:Mg:Fe (molecular proportions) diagram together with the bulk chemical composition. Since all experiments were carried out within the eclogite stability field for this bulk composition (Green and Ringwood 1967, 1972) the mineral assemblage obtained is garnet + clinopyroxene + quartz + rutile. Thus, in a Ca:Mg:Fe diagram, garnet to clinopyroxene tie-lines should pass through the bulk composition point unless there is present another Ca, Mg or Fe-bearing phase such as mica, a partial melt or unless there is oxidation or reduction of iron. The Ca:Mg:Fe diagram also has the advantage that microprobe analyses of garnet
Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Quartz tholeiite (glass)</th>
<th>Quartz eclogite (mineral)</th>
<th>Ga (mineral mix)</th>
<th>Cpx (mineral mix)</th>
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<td>Average of 10 analyses</td>
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<td>22.53</td>
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<td>16.90, 17.2</td>
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</table>

* Fe total as FeO.

Mineral analyses from the mineral mixes (Fig. 1a and Table 3) demonstrate that total equilibrium was not attained in any of these runs (30 kb, T = 1300°C to 800°C). In all cases, the analyzed garnets show a scatter in composition from the original garnet (core composition) to a garnet with higher MgO content (rims). Conversely, pyroxene rim compositions are more Fe-rich than relict pyroxene cores (original composition). In the 30 kb, 1100°C run the minimum $K_D$ value is 2.7 calculated from rim compositions of garnet and clinopyroxene but the maximum $K_D$ value calculated from core compositions approaches that of the reactants, $K_D = 8.6$ (Fig. 1a). The data from the mineral mix demonstrates that reaction has occurred but has been limited by the grain size of the reactants and by the slow rate of intracrystalline diffusion. Our data demonstrate that experimental studies utilizing natural minerals as starting materials, even if a grain size of <10 μm can be achieved without bulk composition change, are suspect unless absence of relict reactants and absence of mineral zoning can be demonstrated. Our experience is that experiments using natural rocks as reactants where the rocks are ground contaminated by clinopyroxene or vice versa will plot on the tie line and accurately define the tie line trend, although not its end-points nor the $K_D$-value.
Calibration of Garnet-Clinopyroxene Fe/Mg Partition as a Geothermometer

Fig. 1a and b. Chemical analyses of garnet and clinopyroxene plotted in Ca:Mg:Fe (molecular proportions) diagrams together with the bulk chemical compositions. The experimental run conditions are 1100°C and 30 kb.

to <100 mesh (i.e. <70 microns) have negligible chance of reaching equilibrium under P, T, time conditions similar to those employed herein i.e. up to 9 days at 900°C, 4 days at 1000°C, 2 days at 1100°C etc. (Table 3). This conclusion applies even in the presence of a large amount of melt (1300°C, 30 kb, 6 hr).

In contrast to the mineral mix, the garnets and clinopyroxenes analyzed in the portion of the run using glass as reactant are tightly clustered with spreading of the analyses along the tie line connecting the two concentrations of compositions (Fig. 1b). The high quality of the analytical data and the consistent variation of $K_D$ from 1.7 at 1300°C/30 kb to 6.5 at 800°C/30kb (Table 3) which we obtained in these reconnaissance experiments revealed the desirability of eliminating several other uncertainties in the experimental techniques. Although the garnet-clinopyroxene tie-line was well-defined for the experiments using glass starting material, the tie-line in higher temperature runs (>900°C) did not pass through the bulk composition (Ca:Mg:Fe++) as defined by the analyzed FeO content of the starting glass (Fig. 1b). However the tie-line passes very close to the Ca:Mg:Fe point for the bulk composition, implying that most or all FeO in the original glass had been reduced to FeO, changing the 100 x Mg/Mg + Fe++ value from 61.7 to 55.2. The presence or absence of Fe+++ also introduces uncertainty into calculation of clinopyroxene structural formulae. (cf. Essene and Fyfe, 1967; Mysen and Griffin, 1973).

The series of experiments designed to evaluate the feasibility and attainable accuracy of the project to empirically determine $K^{cryst}$.oz led to the following conclusions:

(a) The microprobe analytical techniques yielded mineral analyses of comparable accuracy to analyses of natural phases.

(b) The use of a mineral mix as reactant results in incomplete equilibration and persistence of relict cores of original minerals, even for minerals ground to <10 microns grain size.

(c) The use of a glass and a mineral mix as reactants under the same P, T, time, conditions demonstrates that the $K^{cryst}$.oz defined by analyses of minerals crystallized from the glass is identical within experimental uncertainty with the minimum $K^{cryst}$.oz obtained from
Table 2. Compositions of tholeiitic glasses of variable Mg-value prepared for experiments and analyzed by electron microprobe after preparation. The number at the head of each column is the Mg-value for the glass listed

<table>
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<th>Tholeiite used for calculation of new bulk compositions</th>
<th>93</th>
<th>85</th>
<th>76.6</th>
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(analyses of rims of garnet and clinopyroxene. These data constitute a reversal of the garnet-clinopyroxene partition relationship and provide justification of the use of glass as a reactant for the project.

d) The reproducibility and accuracy of the data warrant the elimination of uncertainty in both the bulk composition and in the clinopyroxene in terms of Fe⁺⁺/Fe⁺⁺⁺ ratios. This can be achieved by using metallic Fe sample capsules.

c) Bulk Composition as a Chemical Variable

We wished to determine the effect on K_p,Cpx of variable Fe/Mg of the bulk composition, keeping other chemical variables, particularly Na/Ca and Ca/Al ratios, constant. From the molecular proportions of oxides in a tholeiite composition (Table 2, column 1) we calculated new bulk compositions, keeping the same molecular proportions for all components except Mg and Fe, and adjusting these to give selected values in the range 100 Mg/Mg Fe⁺⁺⁺ = 5—95. Glasses were prepared from A.R. reagents with the final step being fusion in an induction furnace with graphite susceptor and iron-impregnated platinum crucible. Fe and FeO₂ proportions in the final mix were adjusted to give only FeO⁺⁺⁺ slight excess of metallic Fe in the glass. After fusion excess metallic iron was removed by magnet and the glass, after fine crushing to (< 10 µm), was analyzed for FeO and FeO₂ (E. Kiss, analyst). In all cases metallic Fe occurred and FeO₂ content was zero or negligible (< 0.5% FeO₂). As a check on composi-
Calibration of Garnet-Clinopyroxene Fe/Mg Partition as a Geothermometer

Electron microprobe analyses using a defocussed (30 \( \mu \)m) beam and slowly moving sample, were made of both glasses and of experimental runs. The compositions obtained are presented in Table 2. In two cases (Mg\(_{55.4}\) and Mg\(_{55.6}\)) a weighing error resulted in CaO contents that were too high but since the bulk composition remained appropriate to quartz eclogite and the error only changed the Ca:Gpx ratio and the clinopyroxene composition slightly, it was decided to use these glasses for experiments. Similarly some loss of Fe to sample containers (Pt) occurred during glass preparation changing the 100 Mg/Mg+Fe ratios to those listed in Table 2.

**d) Experimental Techniques**

Experimental runs above 800°C were carried out in iron capsules with close-fitting lids and containing about 15 mg of sample. At 800°C and below, welded Ag\(_{75}\)Pd\(_{25}\) capsules were used. All runs at and above 1100°C were carried out under dry conditions using dried (110°C) sample, a boron nitride sleeve within the assembly and dried (at >1000°C) furnace components (cf. Green and Ringwood, 1967). Runs at 1000°C and 900°C, used samples which were not dried but contained a trace of adsorbed water from ambient atmospheric conditions and runs <800°C contained 1% H\(_2\)O added.

The use of iron capsules ensured that Fe\(^{+++}\) could be ignored as a component of pyroxene or garnet solid solutions and removed any ambiguity in the Ca:Mg:Fe\(^{+++}\) plotting of bulk rock and analyzed minerals. A trace amount of metallic iron is seen in some runs. In a few runs, however, particularly those for the glass with Mg-value = 55.4, there has been some reduction of the charge leading to appearance of small spheres of metallic Fe. In these cases, the garnet-pyroxene tie-line passes to the Mg-rich side of the 'original' bulk composition. The presence of a melt fraction in the runs has a similar effect since (Fe/Mg)Gna/(Fe/Mg)Lna < 1 and (Fe/Mg)Gpx/(Fe/Mg)Lpx < 1. In experiments where these problems occur, the garnet/clinopyroxene \( K_D \) values depend entirely on the quality of the mineral analysis data without the additional constraint that tie-lines pass through the original bulk composition point in a Ca:Mg:Fe diagram. The problem of reduction of the charge in some runs, only seems to occur for runs which have higher run nos. than 4587 (see Table 3). The cause of the anomalous reduction to metallic iron may have been abnormally high impurity contents (C, Si, Mn) in one batch of the iron capsules used.

Following the experimental runs, iron capsules conveniently split into discs, which could be readily mounted and polished for electron microprobe analyses. In this way proximity to the capsule wall was avoided during mineral analysis, avoiding problems (in most runs, see above) of iron loss or iron gain to the sample. The experiments below 800°C using Ag\(_{75}\)Pd\(_{25}\) capsules show no evidence for Fe-loss and the Fe\(^{+++}\) content remains insignificant (Fe\(^{+++}\) buffered by the graphite furnace to values near the nickel : nickel oxide buffer) so that for these experiments, the garnet-pyroxene tie-line passes through the bulk rock composition in the absence of phengitic mica as a stable phase or to the Fe-rich side of the bulk rock composition if phengitic mica is present.

**e) Presentation of Mineral Analytical Data**

A total of 1405 chemical analyses of minerals have been made. Initially all analyses, whether satisfactory or unsatisfactory on the basis of the structural formula criterion, were plotted in a Ca:Mg:Fe diagram as a working diagram for each experiment (e.g. Fig. 2a). These data usually defined strong clustering for both garnet and clinopyroxene with also a well-defined tie-line trend (Fig. 2a). If a given analysis was poor on the structural formula criterion and in addition did not lie on the tie-line trend, this analysis was discarded. Those garnet and clinopyroxene analyses defining a tight cluster near the tie-line extremity were then examined to select the garnet and clinopyroxene compositions yielding the best structural formula. These analyses were used to calculate \( K_D \) and are presented in Tables 4, 5 and Tables A-1.1.

Clinopyroxene was located for analysis by maximizing Ca-intensity from the detector. Clinopyroxene analyses show little scatter in the Ca-Mg-Fe diagram and good concentrations of analytical points were normally obtained with very few analyses (about 10). Garnet analyses, 1 Obtainable on request from the authors.

Table 3. Details of experimental runs and analytical data on garnets and clinopyroxenes

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Table 4. Chemical analyses of garnet and clinopyroxene for the Mg-value 69.4 composition at 30 kb

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Table 5. Chemical analyses of garnet and clinopyroxene for the Mg-value 69.4 composition at 30 kb

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SiO₂ 3.000 3.000 3.000 3.000* 1.907 1.900 1.865 1.853
Ti 0.063 0.051 0.099 0.122 0.031 0.030 0.078 0.059
Al 1.984 1.905 1.859 1.843 0.508 0.549 0.524 0.560
FeO 1.109 1.072 0.977 0.895 0.140 0.146 0.148 0.168
Mn 0.014 0.014 0.011 0.015
MgO 1.282 1.361 1.440 1.482 0.514 0.504 0.486 0.488
CaO 0.559 0.586 0.588 0.567 0.540 0.539 0.534 0.517
Na₂O 0.027 0.026 0.295 0.298 0.318 0.273
K 0.009 0.012 0.012 0.005 0.009 0.007
Σ 8.000 8.000 8.000 8.000 3.947 3.958 3.951 3.981
SiO₂ 3.000 3.000 3.000 3.000* 1.907 1.900 1.865 1.853
Ti 0.063 0.051 0.099 0.122 0.031 0.030 0.078 0.059
Al 1.984 1.905 1.859 1.843 0.508 0.549 0.524 0.560
FeO 1.109 1.072 0.977 0.895 0.140 0.146 0.148 0.168
Mn 0.014 0.014 0.011 0.015
MgO 1.282 1.361 1.440 1.482 0.514 0.504 0.486 0.488
CaO 0.559 0.586 0.588 0.567 0.540 0.539 0.534 0.517
Na₂O 0.027 0.026 0.295 0.298 0.318 0.273
K 0.009 0.012 0.012 0.005 0.009 0.007
Σ 8.000 8.000 8.000 8.000 3.947 3.958 3.951 3.981

Example 1: Mg55.4 composition at 800°C, 30 kb (Run 4462) contains garnet with Ca:Mg:Fe zoned from 17.9: 30.6: 51.5 to 21.1: 28.0: 51.0 at core and rim respectively. Example 2: Mg69.9 composition at 1000°C, 30 kb (Run 4283) contains garnet Ca; Mg: Fe zoned from 16.9: 43.9: 39.2 to 19.1: 43.0: 37.9 at core and rim respectively.

Reasons for this include the presence of quartz and rutile in the garnet and also the presence of very slight compositional zoning of the garnet with less CaO content in the core than in the rim and small variation in the Mg-value between core and rim. Since rim compositions were less variable, clearly in juxtaposition to clinopyroxene and were similar throughout the run, defining a strong Ca:Mg:Fe concentration, the rim analyses were used to define KD values (Table 3) and provide the garnet analyses of Tables 4 and 5 and A-I.

In most runs at and below 1200°C, under dry conditions, it was not possible to obtain raw garnet analyses with sufficiently low SiO₂ to yield good structural formulae because of ubiquitous quartz inclusions. The chemical analyses and structural formula given in Table 5 have therefore in most cases been normalized by making Si(“D = 3 (for 12 oxygens) in the structural formula and proportionately adjusting the other components to sum to 5.

Example 1: Mg55.4 composition at 800°C, 30 kb (Run 4462) contains garnet with Ca:Mg:Fe zoned from 17.9: 30.6: 51.5 to 21.1: 28.0: 51.0 at core and rim respectively. Example 2: Mg69.9 composition at 1000°C, 30 kb (Run 4283) contains garnet Ca; Mg: Fe zoned from 16.9: 43.9: 39.2 to 19.1: 43.0: 37.9 at core and rim respectively.

3 Tables A-I are available from the authors on request.

a Ga not corrected.
Fig. 2a and b. Examples of Ca:Mg:Fe "working" diagrams. In Fig. 2b clinopyroxene has been determined by the intersection of the lines mica-clinopyroxene and garnet-clinopyroxene

Table 5. Chemical analyses of garnet and clinopyroxene for the Mg-value 69.4 composition at 1100°C

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1002Na
2Na + Fe²⁺ + Mg + Ca
100 Mg
Mg + Fe²⁺
Garnet analyses contain up to 0.3 ± 0.1% Na₂O and it is considered that Na enters the garnet structure as either an Na-Ti or Na-Si for Ca-Al substitution (Ringwood and Major, 1971). The Na content of garnet is not attributed to interference by neighbouring or included clinopyroxene since similar Na contents are found in garnet cores even when these are zoned to lower Ca contents. In the 600°C, 30 kb, run (4549, Fig. 2b) the garnet grain size of approximately 3 microns is such that complete resolution from neighbouring clinopyroxene was not possible and the garnet analysis was corrected by subtracting clinopyroxene sufficient to decrease the Na₂O to 0.2%. In contrast to this, the run at 700°C, 30 kb, Mg₃7.4 (4517) required no correction for pyroxene admixture to the garnet analysis.

Fig. 2a, of run 4517 illustrates the data treatment and all mineral analyses for this run are given in Table 1. Following selection of the individual garnet and clinopyroxene analyses for $K_D$ calculation as above the error on the $K_D$ (Table 3) was estimated from the maximum and minimum $K_D$ obtained using the limits of clustered analyses which obey the satisfactory structural formula constraint (see Fig. 2a). We emphasize that the final $K_D$ and estimation of error is based on selection of data on qualitative grounds and does not involve any statistical treatment of the data.

Experimental Results

A. Mineralogical Changes due to Changing Temperature at Constant Pressure (30 kb), in Eclogites of Different Mg-Values

**Garnet.** As seen from Fig. 3a-f, the Mg-value of garnet increases with increasing temperature for each composition studied. Only small changes occur in the amount of grossular component of the garnet. Fig. 3a may indicate a slight increase of grossular component with increasing temperature from 900-1100°C. The 800°C — run, however, has the highest grossular component (see Fig. 3c), and this run differs from higher temperature runs in the presence of a significant amount of phengite. A similar correlation of higher grossular content of garnet and the presence of phengite is seen in Fig. 3d. We conclude that, in the simple eclogite mineralogy (garnet+clinopyroxene+quartz) increasing temperature at 30 kb has very little effect on grossular content of garnet, but that the appearance of phengite (competing with garnet and pyroxene for Fe, Mg, Al) causes an increase in grossular content of garnet.

**Clinopyroxene.** As seen from Fig. 3a and 3c the Mg-value of clinopyroxene decreases with increasing temperature. From a comparison between Fig. 3b and Fig. 3c it is seen that the effect of a change in the redox state of Fe⁺⁺⁺→Fe and the occurrence of a melt (the 1300°C-run and possible the 1200°C-run) would disturb this simple relationship and make the Mg-value higher. As not all the clinopyroxene analyses are regarded as good enough to calculate the jadeite content following a similar method to that described by Essene and Fyfe (1967) and Mysen and Griffin (1973) a complete understanding of the behaviour of the jadeite — component with increasing temperature can not be obtained from the data. However we have calculated the $2Na^++Mg^{++}+Fe^{+++}+Ca^{++}$ of the pyroxenes (see Table 3). From this it appears that the jadeite content does not decrease significantly with increasing temperature unless a change in the mineral association occurs at the same time (the presence of phengite at low temperature, the presence of melt at high temperature).

Similarly, we cannot obtain a complete understanding of the behaviour of the Ca-Tschermak's molecule, CaAl₂SiO₆ (abbr. Ca–Ts) and the Ti-Ca-Tschermak's...
molecule, CaTiAl$_2$O$_6$ (abbr. Ti-Ca-Ts) from the clinopyroxene analyses. The A:C:F (molecular proportions) diagrams, however, Fig. 4a–c give an overall picture of increasing Ca-Ts and Ca-Ti-Ts with temperature. This may occur in "steps" as there seems to be little difference between the 900–1100°C runs in Fig. 4b while the 800°C runs clearly have lower Ca-Ts (and Ca-Ti-Ts). The decrease of Ca-Ts content of pyroxene between 900°C and 800°C is matched by increase in grossular content of garnet and by the appearance of phengite as an important member of the mineral association, as noted previously.

Fig. 4a shows an increase in Ca-Ts between the 1000–1200°C runs and the 1300°C run for the Mg$_{60.4}$ composition but a similar effect cannot be seen in the 1100–1300°C runs for Mg$_{55.4}$ composition (Fig. 4c) possibly because of the bulk composition changes due to Fe-reduction in those runs.

We conclude that, in the eclogite mineral assemblage the Ca-Ts and Ca-Ti-Ts substitutions in clinopyroxene increase with increase in temperature, but note
Fig. 4a–c. A-C-F diagrams (molecular proportions) illustrate chemical changes in garnet and clinopyroxene for Mg$^{64}$ and Mg$^{56.4}$ bulk composition as a function of temperature. All runs at 30 kb.

<p>| | | |</p>
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<td>Fig. 4a-c. A-C-F diagrams (molecular proportions) illustrate chemical changes in garnet and clinopyroxene for Mg$^{64}$ and Mg$^{56.4}$ bulk composition as a function of temperature. All runs at 30 kb.</td>
<td></td>
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It can also be seen from Fig. 4a-c that the clinopyroxene becomes more sub-

...
B. Mineralogical Changes due to Changing Pressure at Constant Temperature (1100°C) in Eclogites of Different Mg-Values

Garnet. The most important change in garnet composition with pressure is, as seen from Fig. 5a, an increase in grossular component with increasing pressure. The Mg-value appears to decrease slightly between 30 and 40 kb. This increasing grossular content of the garnet with increasing pressure can also be seen between 30 and 40 kb of Fig. 5b. The interpretation of Mg55.4 data is in this case more complicated than Mg69.4 data as the 40 kb runs (Mg69.4) have been effected by a considerable reduction of Fe2+→Fe. In the 20 kb run (Mg69.4) melt is present, and as seen from Fig. 6a and Fig. 6b illustrating the runs on the Mg55.4 composition where all the runs have melt, little or no change of grossular component as a function of pressure occurs in those garnets coexisting with melt. We conclude that the grossular component in garnet in eclogite mineral assemblages increases with increasing pressure. This is the same conclusion as we reached in our study of the Lunar Highland Basalt composition (Råheim and Green, 1974). However, the increase in grossular component of garnet with increasing pressure is only true for sub-solidus reactions.

Clinopyroxene. In Fig. 5a it is seen that the Mg-value of clinopyroxene increases with increasing pressure at 1100°C; at the same time the amount of jadeite content in the clinopyroxene is also increasing \( \frac{2\text{Na}^+ + \text{Fe}^{2+} + \text{Mg}^{2+} + \text{Ca}^{2+}}{2\text{Na}^+ + \text{Fe}^{2+}} = 21.3 - \text{29.4 at 20 kb, 33.5 at 30 kb, 41.3 at 40 kb, Table 3} \) and as seen from Fig. 5b the Ca-Ts (and Ca-Ti-Ts) clearly decreases with increasing pressure. The decrease in Ca-Ts is accompanied by an increase in grossular content of garnet, as was also observed in our study of Lunar Highland Basalt (Råheim and Green, 1974). There is also an increase of the amount of garnet relative to clinopyroxene. As in the case of the garnets of the Mg55.4 bulk composition (Fig. 6a) the clinopyroxenes formed at different pressures are not suitable for comparison, because of the change in bulk composition due to \( \text{Fe}^{2+} \rightarrow \text{Fe} \) and the occurrence of melt in the 20 kb run. The jadeite content, however, increases with increasing pressure. The presence of melt in all the Mg69.4 bulk composition runs (Fig. 6b) has also made a comparison difficult. The large amount of melt has created a particular problem in the three different 20 kb runs on Mg69.4 composition, as it appears from Fig. 7a that while the garnet compositions have only minor differences between these runs, the Mg-value of clinopyroxene has clearly increased with experimental run-time. The jadeite content of the pyroxenes has decreased drastically (see Table 3) and as seen from Fig. 7b the Ca-Ts and Ca-Ti-Ts have also decreased with time.

Our explanation in this case is that we are dealing with disequilibrium situation, caused by an increase of melt with time, having large effect on the composition and amount of clinopyroxene and only minor effect on garnet. The garnet has had only a small change in composition from the initial growth, and as such is really in disequilibrium as it has not equilibrated as the conditions of the run (increasing melt) have changed with time.

Because of this disequilibrium problem these runs have not been taken into consideration when looking at the effect of changing \( K_p \) with changing pressure. A shorter run time may have solved the problem, the difficulty in such a case
Fig. 5a and b. Ca:Mg:Fe diagram and Al:Ca:(Fe + Mg) diagram illustrate chemical changes in garnet and clinopyroxene for Mg$_{9.4}$ bulk composition as a function of pressure. All runs at 1100°C

Fig. 6a and b. Ca:Mg:Fe diagram illustrating chemical changes in garnet and clinopyroxene for Mg$_{55.4}$ and Mg$_{55.5}$ bulk compositions as a function of pressure. All runs at 1100°C.
would of course be to get crystals large enough for successful probing. Only the shortest run (24 hr) gives a minimum $K_D$ value (2.3) which overlaps within the experimental error, that determined from three runs on the $\text{Mg}_{69.4}$ composition or that from $\text{Mg}_{55.4}$ composition at 20 kb, 1100°C. The $K_D$ values from the latter compositions, rather than those from the $\text{Mg}_{25.6}$ composition are considered to reliably define the $K_D$-value at 20 kb.

C. Changes in Mineral Compositions due to Changing Mg-Value of Eclogite at Constant Temperature and Pressure

Garnet. In the comparison of experiments at 30 kb, 1000°C, it is apparent (Fig. 8 a + b) that the grossular content of the garnet increases with decreasing Mg-value of the bulk chemical composition for those bulk compositions with Mg-value $<76.6$. We have shown in a preceding section that in a constant composition at constant pressure, the grossular content of garnet is insensitive to temperature increase ($T>1000^\circ$C). This conclusion can be applied to infer that the grossular contents of garnets at $1000^\circ$C, 30 kb in the $\text{Mg}_{76.6}$, $\text{Mg}_{65}$, and $\text{Mg}_{50}$ compositions would be similar to the grossular contents of analyzed garnets at $1100^\circ$C, 30 kb, $1200^\circ$C, 30 kb and $1300^\circ$C, 30 kb in the $\text{Mg}_{76.6}$, $\text{Mg}_{65}$, and $\text{Mg}_{50}$ compositions respectively. These data are therefore plotted in Fig. 8a + b yielding a smooth
increase in grossular with decreasing Mg-value and constant P and T over the whole range $Mg_{50} --> Mg_{62}$.

We have judged the analyzed garnets from $Mg_{70}$, $Mg_{65}$ at 1000°C, 30 kb and from $Mg_{65}$ at 1100°C, 30 kb as disequilibrium compositions on the basis of their compositions and textural relationship (few, patchy and anhedral garnet). The original glass apparently devitrifies to a pyroxene of composition close to that of the glass, together with a finegrained (not analyzable) Al-rich phase which is possibly spinel. Similarly, the pyroxenes of both the $Mg_{65}$, 1100°C, 30 kb and $Mg_{60}$, 1200°C, 30 kb plot very close to the bulk compositions and are inferred to be disequilibrium compositions (Figs. 9 a+b). As scattered garnet nuclei grow from the pyroxene, the latter would become more Mg-rich but $K_{D}^{\text{cpx}}$ values calculated from such disequilibrium assemblages will be low in comparison with equilibrium values obtained from more iron-rich compositions. At higher temperatures, the more sluggish nucleation and reaction rates of the magnesian compositions are not a problem and $K_{D}^{\text{cpx}}$ values approach and finally reach those of the more Fe-rich compositions as the temperature increases (Table 3). A similar problem occurs at 20 kb, 1100°C in the $Mg_{68.4}$ composition, where the analyzed pyroxene from a 48 hr run plots very close to the bulk composition and the $K_{D}^{\text{cpx}}$ value is low. In this case, we solved the problem experimentally by first crystallizing the run (4332) at 30 kb for one hour to obtain abundant
Calibration of Garnet-Clinopyroxene Fe/Mg Partition as a Geothermometer

Fig. 9. (a-c) Ca:Mg:Fe diagrams of the $Mg_{63}$-$Mg_{64.4}$ composition runs. Note that in all these cases the lower temperature runs are in disequilibrium. (d) Al:Ca:($Fe+Mg+Mn$) diagram illustrates the compositional change of garnet and clinopyroxene as a function of temperature for the $Mg_{63}$ and $Mg_{62}$ composition runs. Pressure 30 kb.

garnet nuclei but hopefully a small grain size. The pressure was then dropped to 20 kb and held for a further 55 hrs. This procedure appears to have been effective for run 4332 but the procedure carries the risk of memory effects from the 30 kb situation. Such memory effects appear to be present in run 4358 which was held for 2 hrs at 30 kb and in which the grossular content of the garnet (20%) and $K_{P}^{CaP}$ value overlap those present in the 30 kb run (same $T$, same composition).

We thus infer that at constant pressure and temperature, decreasing Mg-value of the bulk composition leads to a smooth and regular increase in grossular content of the garnet from 11.5% grossular at $Mg_{63}$ to 28% grossular at $Mg_{62}$ ($P=30$ kb, $T=1000^\circ$C).

**Clinopyroxene.** At 30 kb, 1000°C, the jadeite content $\left(\frac{100 \times 2Na^+}{2Na^++Fe^{2+}+Ca+Mg}\right)$ of clinopyroxenes increases with decreasing Mg-value for Mg-values $<69.4$. Table 3. For reasons given above, the clinopyroxenes of more magnesian bulk compositions at 30 kb, 1000°C are considered to be disequilibrium compositions. The Ca-Ts and Ca-Ti-Ts contents of clinopyroxene decrease with decreasing Mg-value in the same runs (Fig. 11 b).

At 1300°C, 30 kb (also at 1400°C, 30 kb) there is no significant difference in jadeite content between the $Mg_{63}$ and $Mg_{62}$ compositions but the jadeite content
of pyroxene in the Mg$_{56.4}$ composition is greater than that of the Mg$_{65}$ composition, in conformity with the relationship established at 1000°C, 30 kb in the more Fe-rich compositions (Table 3).

The Distribution Coefficient $K_D = \frac{(\text{Fe}_0/\text{Mg}_0)_{\text{en}}}{(\text{Fe}_0/\text{Mg}_0)_{\text{px}}}$ as a Geothermometer

A. Effect of Chemistry (Mg-Value from 6.2 to 93) on the Distribution Coefficient

Table 6 contains the mean and standard deviation of the preferred $K_D$-values at various temperatures for the compositions listed. The range of uncertainties on the individual $K_D$ values are listed in the fourth column (see Table 3 for individual run details). As discussed previously, compositions with Mg value $>76.6$ at 1000°C do not yield equilibrium assemblages and the $K_D$ of these runs are lower (3.0 for Mg$_{76.6}$ and 2.0 for Mg$_{65}$) than the $K_D$ values from more iron rich compositions (3.35). However, as seen from Table 6 the $K_D$ value for the Mg$_{76.6}$ run at 1100°C 30 kb is the same as the $K_D$ values for the more iron rich compositions. At 1100°C, compositions with Mg-value $>85$ do not give acceptable data. The $K_D$-value for the Mg$_{65}$ composition does not overlap with values from more iron-rich compositions at any temperature, suggesting that very high Mg-values of the bulk composition affect the $K_D$ value. Based on our experiments we can therefore conclude that for $6.2 < \text{Mg}^{++} < 85$ the bulk chemical composition does not perceptibly affect the $K_D$-value.

We have not made any attempt to test the effect of changing the amount of CaO, Al$_2$O$_3$ and Na$_2$O of the bulk chemical systems used. From this study, we have a limited knowledge of the effect of varying CaO as in the preparation of one glass (Mg$_{76.4}$) a weighing error gave higher CaO (Fig. 8a, Table 2) than in the other compositions. Also the Mg$_{65.4}$ composition has more CaO than intended (Table 2) due to a considerable loss of Fe to the platinum crucible during the making of the glass. In these two compositions, however, runs at the same $P$ and $T$ conditions give the same $K_D^{\text{en}}$ value (except when the disequilibrium problem occurs) and indicate that the variation of at least up to 1.5 wt% CaO of the bulk has no effect on $K_D$. Additional information on the effect on $K_D$ of variation in bulk composition comes from an experimental study of the lunar highland basalt composition (Råheim and Green, 1974) with very high Al$_2$O$_3$ and CaO and virtually no Na$_2$O. The Mg-value of this composition is 72.5, within the range studied in this work, but the lunar highland basalt composition gives higher $K_D$ values than the compositions dealt with in this paper. At 1100°C, 30 kb, $K_D=4.0$ for the lunar highland basalt composition, compared to $K_D=2.65 \pm 0.05$, for the tholeiite compositions. The clinoptyroxene and garnet compositions in the lunar highland basalt at 30 kb, 1100°C are very different in grossular content of garnet, in Ca-Tschermak silicate content of clinoptyroxene and in jadeite content of clinoptyroxene, from the phases in the tholeiite compositions. These large differences go beyond the compositional range of phases present in natural eclogites but show similarities to phase compositions in some grosspydites occurring as inclusions in kimberlite pipes. We emphasize therefore that our conclusions on $P, T$ variation of $K_D$ apply to bulk compositions of basaltic character, and do
Table 6. The mean and standard deviation of preferred $K_D$-values of different composition and the range of uncertainty on individual $K_D$'s at 30 kb and temperature ranging from 1000°C to 1300°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$K_D = \frac{(FeO/MgO)<em>{ga}}{(FeO/MgO)</em>{cpx}}$</th>
<th>Compositions (Mg-value = 100 Mg/Mg + Fe)</th>
<th>Range of uncertainty on individual $K_D$'s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td>$3.35 \pm 0.05$</td>
<td>Mg$<em>{65.4}$, Mg$</em>{66.4}$, Mg$_{67.4}$</td>
<td>$\pm 0.1$ to $\pm 0.4$</td>
</tr>
<tr>
<td>1100°C</td>
<td>$2.65 \pm 0.05$</td>
<td>Mg$<em>{55.4}$, Mg$</em>{55.4}$, Mg$_{56.4}$</td>
<td>$\pm 0.1$ to $\pm 0.2$</td>
</tr>
<tr>
<td>1200°C</td>
<td>$2.15 \pm 0.05$</td>
<td>Mg$<em>{45.4}$, Mg$</em>{45.4}$, Mg$_{46.4}$</td>
<td>$\pm 0.05$ to $\pm 0.15$</td>
</tr>
<tr>
<td>1300°C</td>
<td>$1.73 \pm 0.07$</td>
<td>Mg$<em>{35.4}$, Mg$</em>{35.4}$, Mg$_{36.4}$</td>
<td>$\pm 1$ to $\pm 0.2$</td>
</tr>
</tbody>
</table>

not necessarily extend to bulk compositions of grossly different character such as anorthosite, where the known mineralogy under eclogite facies conditions includes garnet and clinopyroxene of compositions very different from the minerals present in eclogite. We agree with Banno (1970) that in common eclogites (basaltic bulk chemistry) the dependence of $K_D$ on minor chemical variation is probably not large. In particular we have shown that variation of Mg-value of the bulk chemical system over a wide range (well beyond that of common basalts) has no detectable effect on $K_D^{cpx}$ value.

B. Effect of Temperature on Distribution Coefficient

Based on the conclusion above, it has been possible to obtain good data on $K_D$-values over a relatively wide range of temperatures (1400°C-600°C, at 30 kb, Table 3) by using bulk chemical composition with high Mg-value for the highest temperature (1400°C, 30 kb, Mg$_{66}$) and compositions with lower Mg-value for the lower temperatures (700°C, 30 kb, Mg$_{54.4}$, 600°C, 30 kb, Mg$_{56.4}$). These experimental constraints were dictated by the presence of excessive melting at high temperatures using bulk chemical systems with the lower Mg values (37.4 and below) and very sluggish reaction rates using bulk chemical system with higher Mg values (76.6 and above) at lower temperatures (see previous discussion of the disequilibrium problem). The distribution coefficient $K_D^{cpx}$ clearly decreases with increasing temperature. In a $\ln K_D = \frac{1}{\frac{1}{T} + 2.418}$ plot (Fig. 10a) a single straight line is defined by all the data on compositions $<$Mg$_{66}$ with a linear relationship of $\ln K_D = \frac{4639}{T} - 2.418$ (at $P=30$ kb) (see Fig. 10a). Similarly the runs of the Mg$_{66}$ composition also appear to plot on a single straight line, but with a more gentle slope than for the other compositions (see Fig. 10a). The relationship may also be expressed as $T = \frac{4639}{\ln K_D + 2.418}$ ($P=30$ kb) allowing calculation of temperature of equilibration for an eclogite crystallized at 30 kb.

5 We also ran experiments at 900°C, 30 kb, 240 hr., 800°C, 30 kb, 240 hr., and 700°C, 30 kb, 720 hr. using the Mg$_{45.4}$ composition. In spite of these long run times we did not produce any crystals of a size large enough for probe analysis (largest crystals 1 micron). These runs demonstrated the importance of using bulk compositions with lower Mg-values at lower temperatures.
C. Effect of Pressure on Distribution Coefficient

The application of the linear relationship of $K_D = \frac{4639}{T(\circ K)} - 2.418$ at 30 kb (Fig. 10a) is very limited unless the pressure effect on the $K_D$ value is known well enough to make extrapolations to conditions operative in the crust and upper mantle. From Fig. 10b it is seen that the distribution coefficient $K_D$ increases with increasing pressure at constant temperature. Changes in the Mg-value of bulk chemical systems appear to have little effect as no difference in $K_D$ is observed in the bulk chemical systems (Mg values: 69.4, 55.4, 25.6). The straight line relationship between the 20 kb, 30 kb and 40 kb runs on the ln $K_D$ versus P(kb) plot (Fig. 10b), enables us to use the relationship $\ln K = \frac{\Delta v}{RT} (P - P_0) + \ln K_0$ ($T$ const), (Banno, 1970), to calculate a pressure coefficient $p^* (=2.357)$ for the exchange reactions involving the Fe and Mg 'end-members of the garnet and clinopyroxene solid solutions present in the tholeiite compositions. The pressure coefficient $p^*$ corresponds to $\Delta v$ in the equation given above, derived for the simple CaO, MgO, FeO, H$_2$O$_3$, SiO$_2$ system.

The pressure effect on $K_D$ for the more complex tholeiite chemical systems is considerably larger than reported by Banno (1970), where $\Delta v =1.33$ cm$^3$
was reported for the simple chemical systems involved in the following exchange reaction: \( \text{CaMgSi}_2\text{O}_6 + \frac{1}{3}\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} \rightarrow \text{CaFeSi}_3\text{O}_6 + \frac{1}{3}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \).

If the formula volumes for diopside (66.09 cm\(^3\)), hedenbergite (68.30 cm\(^3\)), almandine (38.42 cm\(^3\)) and pyrope (37.76 cm\(^3\)) are calculated from the cell constants listed in Table 5-1 of Robie et al. (1966), \( \Delta v = 1.55 \text{ cm}^3 \) for the exchange reaction given above. This however is not enough to account for the difference between the \( \Delta v \) determined by Banno (1970) for the simple chemical exchange reaction given above and our experimentally determined \( p^* \). Furthermore, new data on the formula volumes for pyrope (37.71 cm\(^3\)), almandine (38.48 cm\(^3\)) (Takahashi and Liu, 1970) diopside (66.20 cm\(^3\)) and hedenbergite (67.88 cm\(^3\)) (Rustein and Young, 1969) give a \( \Delta v = 0.91 \) for the same exchange reaction. Therefore, based on a theoretically determined \( \Delta v \) it appears that pressure should have even less effect on \( K_{D}^{\text{Gr}+\text{Cpx}} \) than predicted by Banno 1970.

Our experimental data demonstrate that pressure has a larger effect on the relative Fe-Mg distribution between garnet and clinopyroxene in eclogite than predicted from available thermodynamic data on simple end-member phases. The study exemplifies very well the current inability to extrapolate quantitatively from simple system thermodynamic data to complex mineral equilibria in natural rock compositions.

In Fig. 10b the line showing \( K_{D} \) variation with pressure at 800°C, has been
calculated by using the experimentally determined $p^*$ in \( \ln K_D = \frac{p^*}{RT} (P-P_0) + \ln K_o \) to determine the $K_D$-value at 40 kb and 20 kb corresponding to the $K_D$-values found at a different temperature (800°C) at 30 kb (Fig. 10b). These data can then be used to define the temperature vs. $K_D$ variation for a wide range of pressure. This information is presented in Fig. 10a as a series of $\ln K_D$ vs. $\frac{1}{T(°K)}$ ($P=\text{constant}$) curves for values of $P$ from 5 kb to 40 kb. On this diagram, the curves end against a forbidden field boundary defined by the stability field of eclogite as defined by Green and Ringwood (1967, 1972).

Conclusions

From the data defining the pressure, temperature and compositional effects on $K_D$, we are in a position to express quantitatively the function $K_D=\text{f}(T,P)$ which has the general expression $\ln K_D = \frac{a}{T} + \frac{p^*}{RT} (P-P_0) + b$ where $a$ and $b$ are constants which can be determined from our experimental data. By using

\[
\frac{p^*}{R} a = -2.33 \ln K_D + 2.33
\]

the relationship $T(°K) = \frac{3686 + 28.35 \times P(\text{Kb})}{\ln K_D}$. For $P < 30$ kb and $T > 1000°C$, the relationship can be more conveniently expressed as

\[
\ln \frac{K_D}{K_D} = \frac{3686 + 28.35 \times P(\text{Kb})}{\ln K_D} - 2.33
\]

or more conveniently

\[
\ln \frac{K_D}{K_D} = \frac{3686 + 28.35 \times P(\text{Kb})}{\ln K_D} - 2.33
\]

Fig. 11, we can uniquely obtain the temperature of an eclogite when the $K_D$-value is known and a pressure estimate can be given.

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An Experimental Study of the Effect of Ca Upon Garnet-Clinopyroxene Fe—Mg Exchange Equilibria

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Abstract. A series of basaltic compositions and compositions within the simple system CaO—MgO—FeO—Al₂O₃—SiO₂ have been crystallized to garnet-clinopyroxene bearing mineral assemblages in the range 24-30 kb pressure, 750°-1,300°C temperature. Microprobe analyses of coexisting garnet and clinopyroxene show that \( K_0(\text{Fe}^{2+}/\text{Mg}^{2+}/\text{Fe}^{2+}/\text{Mg}^{2+}) \) for the Fe—Mg exchange reaction between coexisting garnet and clinopyroxene is obviously dependent upon the Ca-content and apparently independent of the Mg/(Mg+Fe) content of the clinopyroxene and garnet. The Ca-effect is believed to be due to a combination of non-ideal Ca—Mg substitutions in the garnet and clinopyroxene.

Our data and interpretation reconciles previous inconsistencies in the temperature dependence of \( K_0 \) values determined in experimental studies of simple systems, complex basalt, grospydite and garnet peridotite compositions. Previous differences between the effect of pressure upon \( K_0 \) as predicted from simple system theory (Banno, 1970), and that observed in experiments on multicomponent natural rock compositions (Råheim and Green, 1974a) can now be resolved.

We have determined \( K_0 \) as a function of \( P, T, \) and \( X_{Ca}^{Gr} \) (grossular) and derived the empirical relation

\[
T(°K) = \frac{3104 X_{Ca}^{Gr} + 3030 + 10.86 P(kb)}{\ln K_0 + 1.9034}
\]

This empirical relationship has been applied to garnet-clinopyroxene bearing rocks from a wide range of geological environments. The geothermometer yields similar estimates for garnet-clinopyroxene equilibration for neighbouring rocks of different composition and different \( K_0 \) values. In addition, temperature estimates using the above relationship are more consistent with independent temperature estimates based on other geothermometers than previous estimates which did not correct for the Ca-effect.

An alternative approach to the above empirical geothermometer was attempted using regular solution models to derive Margules parameters for various solid solutions in garnets and clinopyroxenes. The derived Margules parameters are broadly consistent with those determined from binary solution studies, but caution must be exercised in interpreting them in terms of actual thermodynamic properties of the relevant crystalline solid solutions because of the assumptions which necessarily have to be made in this approach.

Introduction

Eclogites occur in a wide variety of geological environments (e.g., Coleman et al., 1965) and the stability fields of various eclogites have been experimentally determined in several laboratories (e.g., Yoder and Tilley, 1962; Green and Ringwood, 1967; Ito and Kennedy, 1968). It is well known that eclogites from different geological environments have different \( K_0 \) values (\( K_0=(\text{Fe}/\text{Mg})^{Gr}/(\text{Fe}/\text{Mg})^{Cpx} \) where Fe=Fe²⁺ (e.g., Banno, 1970; Coleman et al., 1965; Lovering and White, 1969; Mysen and Heier, 1972) and these differences have been interpreted in terms of different \( P, T \) conditions of formation. Råheim and Green (1974a) experimentally calibrated \( K_0 \) as a function of \( P \) and \( T \) for a series of natural basaltic rocks crystallized to eclogite at 20-40 Kb, 600°-1,400°C. They stressed that their results could only be used as a practical geothermometer for rocks of basaltic composition, as the effects of large variations in concentration of other components upon \( K_0 \) was largely unknown. Empirically Råheim and Green (1974a) observed that the bulk chemical composition did not
perceptibly affect the $K_0$ for basaltic rocks in the range Mg/(Mg + Fe) = 0.062 - 0.85. Furthermore they concluded that the effect of pressure upon $K_0$ for multicomponent equilibria was greater than that estimated on thermodynamic grounds for simple system equilibria (Banno, 1970). Considerable discussion has arisen concerning the magnitude of this pressure effect (e.g. Wood, 1975; 1977). Also, experimental studies for simple systems, garnet peridotite, and highly aluminous compositions have yielded empirical $K_0$ values differing from those for basaltic systems (Kushiro et al., 1972; Räheim and Green, 1974a and b; Hensen, 1973; Akella, 1976; Mori and Green, 1978).

The present experiments were designed to test the effects of clinopyroxene and garnet compositional variations (Na, Ca) upon $K_0$. The possibility that garnet solid solutions are non-ideal has previously been suggested from natural rock data on garnet-biotite and garnet-clinopyroxene equilibria (e.g., Saxena, 1973, p. 33; Ganguly and Kennedy, 1974) and from simple system experiments and solution calorimetry studies on pyrope-grossular solid solution (Hensen et al., 1975; Newton et al., 1977; Wood, 1977). Recently Ganguly (1978) attempted to use such data to take account of the effect of Ca in garnet on $K_0$, but his analysis does not adequately describe this effect as documented by our new experimental data.

### General Thermodynamic Considerations

For the garnet-clinopyroxene Fe—Mg exchange reaction

$$\frac{1}{3} \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_8 + \text{CaFeSi}_2\text{O}_6 \rightarrow \frac{1}{3} \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_8 + \text{CaMgSi}_2\text{O}_6$$

the equilibrium constant $K$ for this reaction may be defined (Banno, 1970) as

$$K = \left( \frac{a_{Fe^{2+}}^{(4)}}{a_{Mg}^{(4)}} \right) \left( \frac{a_{Si}^{(6)}}{a_{Fe}^{(2)}} \right)$$

where $a_i$ is the activity of component $i$ in phase $j$. Taking a standard state of pure solids at the pressure and temperature of interest, then at equilibrium

$$\Delta G_{Fe^{2+}}^{(2)} = \Delta H^o - T \Delta S^o + (P - 1) \Delta V^o = -RT \ln K.$$  (3)

If the minerals are ideal solid solutions ($a = x$) then

$$K = \left( \frac{X_{Fe}^{(2)}}{X_{Mg}^{(4)}} \right) \left( \frac{X_{Si}^{(6)}}{X_{Fe}^{(2)}} \right) = K_0$$

where $K_0$ is the distribution coefficient, $X_{Fe}^{(2)}$ is the mole fraction of Fe$^{2+}$ in the three equivalent divalent sites in the garnet structure and $X_{Si}^{(6)}$ is the mole fraction of Fe$^{2+}$ in the clinopyroxene etc. If the minerals are not ideal then $a = xy$ where $y$ is defined as the activity coefficient. Thus

$$K = \frac{X_{Fe}^{(2)} X_{Mg}^{(4)} X_{Si}^{(6)} X_{Fe}^{(2)} X_{Mg}^{(4)} X_{Si}^{(6)}}{X_{Mg}^{(4)} X_{Fe}^{(2)} X_{Mg}^{(4)} X_{Fe}^{(2)}} = K_0 \cdot K_y.$$  (5)

The distribution coefficient ($K_0$) can be obtained from the mineral compositions, and in the case of ideal solid solutions can be considered a function of $P$, $T$ only.

However when deviations from ideal solid solution exist, this model is inadequate to explain the variations in the measured $K_0$ with $P$, $T$ and compositional changes, and the application of a rigorous thermodynamic treatment (e.g., Thompson, 1967) to such Fe—Mg exchange equilibria requires a knowledge of the activity coefficients $\gamma$ of the various solid solutions. There is as yet little unambiguous data available on the activity-composition relationships for many binary solid solutions (see Wood, 1977; Hensen et al., 1975; Newton et al., 1977).

In theory at least, it is possible to derive activity-composition relationships for different solid solutions from multicomponent experimental data by linear regression analysis of the non-ideal contributions in terms of regular solution model Margules or interaction parameters (see Thompson, 1967). Unfortunately our knowledge of the mixing properties of many binary solid solutions is insufficient to justify such a rigorous treatment for reaction (1) (see discussion).

A limitation of our approach is that the effects of nonideality in the garnet and clinopyroxene solid solutions are cumulative in their effects on $K_0$, and it is not possible to readily isolate nonideality in garnet from that in clinopyroxene since the equilibrium under investigation involves solid solutions in both phases. Thus the approach adopted here is the derivation of a general equation as a practical geothermometer in terms of the variation in $K_0$ with $P$, $T$, and $X_{Ca}^{(2)}$. This allocation of all the non-ideal effects on $K_0$ to the Ca-substitution in garnet is justified for this approach as the variation in $Di$ and $CaTs$ contents of clinopyroxene is in the same sense as that of Ca in the coexisting garnet with variations in $P$, $T$, and rock composition.

### Experimental Methods

A series of simple system synthetic glasses with varying Mg/(Mg + Fe) were prepared using AR grade chemicals (Table I). To these were added various amounts of either CaAl$_2$Si$_2$O$_6$ glass, NaAlSi$_2$O$_6$ glass or natural orthopyroxene (Green, 1969, OpX 2539). The orthopyroxene seeds were ground to less than 2 $\mu$m grain size. Experiments were also performed on several multicomponent lunar glass mixes (Table I).

The simple system glasses and seeds were prepared in appropriate proportions so as to produce under the $P$, $T$ conditions of the eclogite facies as defined by Green and Ringwood (1967), the following mineral assemblages with increasing Ca-contents of the garnets (Fig. I).

- $\text{Gt—Cpx—OpX ± Qtz}$
- $\text{Gt—Cpx—Qtz}$
- $\text{Gt—Cpx—Qtz—Kyanite}$

High pressure experiments were carried out using piston cylinder apparatus at the Geology Department, University of Tasmania. Experimental techniques are similar to those described by Green and Ringwood (1967). Temperature was measured using a Pt/Pt$\alpha$Rh$_{10}$ thermocouple. The recorded temperature was controlled to within $\pm 5^\circ$C of the set point, and the precision of temperature measurement when allowance is made for temperature gradients in the samples is $\pm 1^\circ$C (calibration experiments by W. Hibberson).

A variety of capsule materials were used, depending upon the run conditions and starting mixes. In order to ensure that there was no iron loss nor oxidation, experiments were initially carried...
Table 1. Simple system and natural rock compositions used in experimental study

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>53.78</td>
<td>52.23</td>
<td>50.81</td>
<td>56.39</td>
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<td>TiO₂</td>
<td>7.25</td>
<td>8.25</td>
<td>8.95</td>
<td>9.85</td>
<td>8.59</td>
<td>7.91</td>
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<tr>
<td>Al₂O₃</td>
<td>10.11</td>
<td>9.85</td>
<td>9.59</td>
<td>9.00</td>
<td>8.19</td>
<td>8.01</td>
</tr>
<tr>
<td>Cr₂O₃</td>
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<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>FeO</td>
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<td>19.96</td>
<td>21.73</td>
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<tr>
<td>MnO</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>MgO</td>
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<td>8.96</td>
<td>5.23</td>
<td>32.64</td>
<td>11.55</td>
<td>7.6</td>
</tr>
<tr>
<td>CaO</td>
<td>13.38</td>
<td>13.00</td>
<td>12.64</td>
<td>0.55</td>
<td>9.42</td>
<td>12.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>99.87</td>
<td>99.71</td>
<td>99.6</td>
</tr>
</tbody>
</table>

1: Synthetic glass Mg<sub>50</sub>  
2: Synthetic glass Mg<sub>50</sub>  
3: Synthetic glass Mg<sub>50</sub>  
4: Orthopyroxene used for addition to glasses 1-4. Opx 2539 (Green, 1969)  
5: Synthetic Lunar Glass 12009 (Green et al., 1971)  
6: Synthetic Lunar Glass 14310 (Green et al., 1972)

Fig. 1. Molecular Al—Ca—(Fe+Mg) plot of starting mix compositions and diagrammatic representation of the range in Ca-contents of garnets from the different mineral assemblages.

out in Spec Pure Fe capsules. However it was found that reduction of FeO occurred in the more iron-rich glasses, with blebs of metallic iron being produced. When this occurred the pyroxene would reequilibrate to more Mg-rich compositions much faster than the garnet, resulting in an erroneously high K<sub>d</sub> value. Similar problems were previously encountered in attainment of equilibrium using mineral mixes rather than glasses as starting materials (Räheim and Green, 1974a). These experiments were repeated in graphite capsules, which at 30 kb pressure maintain a higher oxygen fugacity than that of metallic iron, whereas at very low pressures graphite is more reducing than metallic iron (Ryabchikov et al., in preparation). At low temperatures (~750°C) the presence of an H₂O-rich fluid phase was necessary to speed reactions and experiments were carried out with water in sealed Ag₃Pd₂₅ capsules.

In order to be certain that variations in K<sub>d</sub> values between samples were due to compositional effects and not to variations in run conditions, large diameter metallic iron and graphite capsules were prepared with up to four separate sample holes in each. Thus for each run up to four different starting mixes could be studied under identical experimental conditions. Such capsules were sealed inside large diameter Ag<sub>3</sub>Pd<sub>25</sub> capsules together with a minor amount of water.

All mineral analyses have been obtained using a Si(Li) detector attached to a JEOL scanning electron microscope-microprobe at the University of Tasmania, following the methods outlined by Reed and Ware (1975).

Results

1. Attainment of Equilibrium

The experimental technique, starting materials (glass) and run times are similar to those of Räheim and Green (1974a) in their study of K<sub>d</sub> (Gt—Cpx) and hence their detailed discussion on attainment of equilibrium is also applicable to the present experiments. Räheim and Green showed that the use of a mineral mix (with high K<sub>d</sub>) as reactants resulted in incomplete equilibration and persistence of relic cores of starting minerals. The use of a glass and a mineral mix as reactants under the same P, T time conditions demonstrated that the K<sub>d</sub> defined by minerals crystallized from the glass is identical within experimental uncertainty with the minimum K<sub>d</sub> obtained from analyses of rims of garnet and clinopyroxene from the mineral mix. These observations, together with the general lack of zoning in our own run product compositions provides good evidence for equilibration in our experiments. In those cases where compositional zoning was observed in our run products, the range in K<sub>d</sub> values and mineral compositions are given in Table 2.

2. Presentation of Data

Experimental run conditions and results are given in Table 2 and summarized in Figs. 2-5. It has been found that at constant P and T, variations of up to 30 mole % jadeite in the clinopyroxene do not, within experimental error, affect the K<sub>d</sub> (Table 2). This is consistent with ideal jadeite-diopside solid solutions at high temperatures as suggested by Ganguly (1973). In contrast there is a marked dependence of K<sub>d</sub> upon the Ca content of the garnet. For practical purposes a suitable method for displaying this variation is to plot the variation of K<sub>d</sub> with X<sub>Gt</sub> (Ca/Ca+Mg+Fe of garnet). This does not necessarily imply that the observed variation of K<sub>d</sub> with changing rock composition is solely due to variations in X<sub>Gt</sub> (see Discussion).
Table 2. Run details
Run

P
(kb)

T
(°C)

Starting mix

Time
(h)

Capsule

KD

Garnet
Mg

Fe

Wo

En

Fs

CaTs

3.64
3.03
2.31
1.96
3.29
2.45
2.32
1.91
3.00
2.22
1.84
1.47
2.332.13
1.622.10
4.094.52
2.21
2.3
2.09
1.73
2.59

0.437
0.308
0.189
0.158
0.459
0.311
0.228
0.170
0.410
0.261
0.182
0.131
0.3350.341
0.1850.216
0.472

0.344
0.437
0.492
0.574
0.324
0.423
0.450
0.586
0.374
0.499
0.592
0.650
0.4210.463
0.6200.538
0.103

0.218
0.254
0.319
0.268
0.217
0.266
0.322
0.243
0.216
0.240
0.226
0.219
0.2440.197
0.1950.245
0.425

0.303
0.374
0.301
0.295
0.270
0.340
0.328
0.262
0.273
0.336
0.309
0.227
0.211
0.247
0.295
0.295

0.335
0.425
0.436
0.513
0.290
0.390
0.438
0.508
0.312
0.400
0.455
0.544
0.294
0.326
0.426
0.426

0.058
0.082
0.122
0.123
0.059
0.100
0.135
0.110
0.060
0.086
0.094
0.124
0.073
0.065
0.083
0.083

0.303
0.118
0.139
0.069
0.379
0.167
0.098
0.119
0.354
0.176
0.142
0.105
0.422
0.362
0.196
0.196

0.479
0.440
0.452
0.616
0.195

0.313
0.332
0.341
0.270
0.560

0.361
0.279
0.214
0.250
0.300

0.446
0.377
0.294
0.358
0.273

0.131
0.123
0.106
0.090
0.304

0.062
0.108
0.056
0.058
0.122

Graphite

3.43

0.207
0.227
0.207
0.113
0.245

Graphite
Graphite

3.7
2.382.43
2.67
2.01
3.02.85
4.635.07
4.485.30
5.38
4.16
4.62
5.47.55
9.5414.15
4.034.51
5.69
4.29
6.93
8.3214.67

0.454
0.1750.212
0.207
0.208
0.3010.275
0.2630.196
0.2930.252
0.297
0.306
0.231
0.3760.365
0.3240.342
0.1870.196
0.328
0.235
0.220
0.3320.293

0.176
0.4860.468
0.313
0.415
0.3500.365
0.1320.134
0.150
0.139
0.124
0.154
0.122
0.1570.123
0.1140.094
0.2480.237
0.342
0.232
0.183
0.2990.223

0.370
0.338
0.320
0.481
0.377
0.3490.360
0.6050.670
0.557
0.609
0.579
0.540
0.648
0.4670.512
0.5620.564
0.5650.567
0.330
0.533
0.597
0.3690.484

0.326
0.332
0.332
0.328
0.317
0.387
0.387
0.424
0.424
0.424
0.424

0.284
0.437
0.437
0.377
0.360
0.351
0.351
0.285
0.285
0.304
0.304

0.162
0.125
0.125
0.217
0.162
0.122
0.122
0.282
0.282
0.250
0.250

0.227
0.105
0.105
0.077
0.161
0.140
0.140
0.009
0.009
0.021
0.021

0.417
0.417
0.410
0.410
0.455
0.467
0.391
0.385
0.316
0.363
0.408
0.355
0.355

0.291
0.259
0.317
0.317
0.341
0.372
0.379
0.382
0.325
0.391
0.385
0.340
0.340

0246
0.298
0.174
0.174
0.177
0.156
0.213
0.203
0.055
0.209
0.181
0.050
0.050

0.045
0.024
0.100
0.100
0.025
0.005
0.016
0.029
0.140
0.036
0.026
0.034
0.034

Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe
Fe

T-26
1%26
1%26
1%26
1%27
1-27
1%27
1%27
1%28
1%28
1-28
1%28
1%36

30
30
30
30
30
30
30
30
24
24
24
24
24

1,200
1,200
1,200
1,200
1,300
1,300
1,300
1,300
1,200
L200
1,200
1,200
1,300

0.7 Ec Mg70 +0.3 CaTs
0.88 Ec Mg70 +0.12 CaTs
1.0 Ec Mg70
0.63 Ec Mg70 +0.37 Opx 2539
0.7 Ec Mg70 + 0.3 CaTs
0.88 Ec Mg70 +0.12 CaTs
1.0 Ec Mg70
0.63 Ec Mg70 +0.37 Opx 2539
0.7 Ec Mg70 + 0.3 CaTs
0.88 Ec Mg70 + 0.12 CaTs
1.0 Ec Mg70
0.63 Ec Mg70 +0.37 Opx 2539
0.7 Ec Mg70 + 0.3 CaTs

1-36

24

1,300

0.88 Ec Mg70 + 0.12 CaTs

T-43A

30

1,100

0.7 Ec Mg30 + 0.3 CaTs

T-47
1%47
T-47
T-52
T-52
T-52
T-52
T-53

30
30
30
30
30
30
30
30

1.200
1,200
1,200
1,200
1.200
1.200
1.200
1,200

1.0 Ec Mg70
0.945 Ec Mg70 +0.055 Jd
0.833 Ec Mg70 +0.167 Jd
0.7 Ec Mg70 + 0.3 Jd
1.0 Ec Mg30
0.88 Ec Mg30+0.12 CaTs
0.7 Ec Mg30 + 0.3 CaTs
1.0 Ec Mg70

45
45
45
6
6
6
6
26

1-53
T-53
T-53

30
30
30

1,200
1,200
1,200

1.0 Ec Mg50
0.88 Ec Mg50 + 0.12 CaTs
0.7 Ec Mg50 + 0.3 CaTs

26
26
26

1-72

30

900

1.0 Ec Mg30 + 11 2 0

1194

Graphite in Ag 75 Pd 25

1-72

30

900

0.88 Ec Mg30 + 0.12 CaTs + F1 2 0

1194

Graphite in Ag 75 Pd 25

1-72
T-77
T-77
T-77

30
15
15
15

900
900
900
900

0.7 Ec Mg30 + 0.3 CaTs + F1 2 0
0.88 Ec Mg30 +0.12 CaTs+ H 2 0
1.0 Ec Mg30 + F1 2 0
0.7 Ec Mg30 + 0.3 CaTs + H 2 0

1194
1324
1321
1324

Graphite in Ag 75 Pd 25
Graphite in Ag 75 Pd 25
Graphite in Ag 75 Pd 25
Graphite in Ag 75 Pd 25

T-8I

30

750

0.7 Ec Mg30 +0.3 CaTs + 1 1 2 0

1694

Graphite in Ag 75 Pd 25

1-88

30

900

Lunar 12009+H 2 0

150

Graphite in Ag„Pd„

1-96
T-96
T-I10
1-I26

30
30
30
30

900
900
750
750

Lunar 14310+ H 2 0
Ec Mg50 + H 2 0
Lunar 12009 + H 2 0
Lunar 14310+ F1 2 0

1684
1684
264
161

Graphite in Ag 75 Pd 25
Graphite in Ag 75 Pd 25
Ag" Pd 25
Ag 75 Pd 25

54
54
54
40
40
40
40

51.

Fe
Fe

-

Fe
Fe
Fe
Graphite
Graphite

Graphite

Graphite
Graphite

0.385

0.149

0.469

0.376

0.275

0.250

.1d

0.112
0.329
0.243

0.099

0.164

0.220
0.220

D.J . Ellisa ndD.H . G reen: Garnet-Cli nopyroxene Fe—M g Exch ange Equili bri a

Ca

•
48
48
48
48

Clinopyroxene


The variation of $K_D$ with $X_{Ca}^{Gt}$ at 30 kb, 1,200°C is shown in Fig. 2. It has been found that within experimental error the $\ln K_D - X_{Ca}^{Gt}$ variations are independent of the Mg/(Mg+Fe) content of the run products (see Table 2, Runs T-26, T-52), in agreement with the earlier work of Råheim and Green (1974a). This feature will be further discussed in a later section. The $K_D - X_{Ca}^{Gt}$ variation for the temperature range 750°-1,300°C is shown in Fig. 3. The 1,100°C experimental data of Råheim and Green (1974a and b) for terrestrial and high alumina lunar basaltic compositions is included and displays the same relationships as our own data.

At lower temperatures the variation in $K_D$ with $X_{Ca}^{Gt}$ should be more pronounced than at higher temperatures because the effects of non-ideal substitutions become larger at low temperatures (see e.g. Thompson, 1967). However our low temperature data does not cover as large a range of $X_{Ca}^{Gt}$ as at high temperatures, and hence the magnitude of this compositional dependence to $K_D$ is not as clearly demonstrated at low temperatures. This is due to a contraction in the compositional range of coexisting garnet-clinopyroxene at lower temperatures for which we can investigate $K_D - X_{Ca}^{Gt}$ relationships (Fig. 4). In contrast our data shows that the range in $X_{Ca}^{Gt}$ for the above assemblages expands with increasing pressure. It has previously been shown that $X_{Ca}^{Gt}$ decreases with increasing pressure for the assemblage garnet-clinopyroxene-orthopyroxene (Kushiro et al., 1967; Mori and Green, 1978).

It is possible to select from our own data together with that of Råheim and Green (1974a and b) and Mori and Green (1978) sufficient garnet-clinopyroxene pairs with constant $X_{Ca}^{Gt}$ (~0.2) to show that there is an approximately linear relationship for the variation of $\ln K_D$ with temperature at constant pressure (Fig. 5). Garnet peridotites with low $X_{Ca}^{Gt}$ fall on $\ln K_D - 1/T$ lines at lower $K_D$ values for a given $T$ than do basaltic eclogites with higher $X_{Ca}^{Gt}$ contents (Fig. 3). The demonstration of $K_D$ variation with $X_{Ca}^{Gt}$ reconciles most of the previous discrepancies in experiment-
3. The Variation of $K_D$ With $X_{Ca}^{Gr}$ and $T$ as a Practical Geothermometer

Experimental data on the variation of $K_D$ over a wide range of pressure, temperature and rock compositions indicate that within experimental error, $K_D$ variations under any given $P, T$ conditions can be satisfactorily accounted for by the associated change in $X_{Ca}^{Gr}$. This variation in $K_D$ can be quantified by assuming that at $X_2=0$ the exchange reaction (1) may be considered ideal. Thus

$$\Delta G^\circ_{P, T}(X_{Ca}^{Gr}=0) = \Delta H^\circ - T \Delta S^\circ + (P - 1) \Delta V^\circ$$

$$= -RT \ln K = -RT \ln K_D. \quad (4)$$

In this manner all non-ideal effects on $K_D$ at the one pressure can be accounted for by the following relationship

$$\ln K_D = a X_{Ca}^{Gr} + b. \quad (5)$$

The above constants in (4) and (5) can be determined from the experimental data. Reliable data is available for the variation of $K_D$ over a wide range of $X_{Ca}^{Gr}$ only at high temperatures (1,100°–1,300°C), because of the previously mentioned contraction in the range of $X_{Ca}^{Gr}$ for garnet-clinopyroxene pairs with decreasing temperature. Data for $X_{Ca}^{Gr}=0.2$, at 30 kb covers the widest range of temperature (Figs. 3 and 5). A least squares fit to this data (Table 3) gives

$$\ln K_D = 3983/T(°K) - 1.9034. \quad (6)$$

There is also data for a range in $X_{Ca}^{Gr}$ at 30 kb, 1,100°–1,300°C. Least squares fits of the form of (5) can be used to extrapolate the variation in $\ln K_D$ for constant values of $X_{Ca}^{Gr}$ to lower temperatures, but extrapolations from only a 200°C temperature range using few data points is inaccurate. In particular the value of $\Delta S$ derived from the 1,100°–1,300°C least squares fit to the $X_{Ca}^{Gr}=0.2$ data differs considerably from that of the 750°–1,300°C temperature range. For these reasons it is preferable to use only our best data to derive a general equation to express the variation in $\ln K_D$ with temperature and $X_{Ca}^{Gr}$. The least squares fit to the 30 kb, $X_{Ca}^{Gr}=0.2$ data [Eq. (6)] for the temperature range 750°–1,300°C can be combined with that for the variation in $\ln K_D$ with $X_{Ca}^{Gr}$ at 30 kb, 1,200°C (Table 3) to derive the following equation, applicable at 30 kb

$$\ln K_D = \frac{3104 X_{Ca}^{Gr} + 3356}{T(°K)} - 1.9034. \quad (7)$$

The derivation of this equation assumes $\Delta S$ is constant and $\Delta H^\circ = f X_{Ca}^{Gr} + 0$. In a thermodynamic sense this is consistent with a symmetric regular solution model (see Thompson, 1967) of non-ideal substitution of Ca in Mg–Fe garnets. This would be expected on crystal chemical considerations as there is apparently no ordering of atoms in this substitution. All of the eight coordinated sites in the garnet structure are symmetrically equivalent and the distribution of the divalent cations over these sites is expected to be random or nearly so (Novak and
4. The Effect of Pressure on $K_D$

Equation (7) is of limited application without knowledge of the effect of pressure on $K_D$. There has been considerable discussion about the magnitude of this pressure effect (Banno, 1970; Råheim and Green, 1974a; Wood, 1975; 1977), which may be related to the volume change of the exchange reaction (1) (Banno, 1970).

$$\frac{\partial \ln K}{\partial P} = \frac{\Delta V}{RT}. \quad (8)$$

Råheim and Green (1974a) calculated the effect of pressure on $K_D$ from their experimental data, and considered that it was much larger than that predicted by Banno (1970) from X-ray molar volume data ($\Delta V = 2.357$ and $1.33 \text{ cm}^3$ respectively). This overestimate of the pressure effect by Råheim and Green (1974a) is due to the comparison of $K_D$ data at different pressures for garnets with differing $X_{Ca}^{Gt}$, which thus also incorporates the change in $K_D$ due to non-ideal Ca-substitution - a feature also commented on recently by Wood (1977).

The molar volume data of Takahashi and Liu (1970) (pyrope, 113.12 cm$^3$; almandine, 115.45 cm$^3$) and Rutstein and Yund (1969) (diopside, 66.20 cm$^3$; hedenbergite, 67.88 cm$^3$) gives $\Delta V = -0.9033 \text{ cm}^3 (-0.0216 \text{ cal/bar})$ for reaction (1). This value, when combined with the above relationships (4, 5 in 7) enables the derivation of a general equation to express the variation of $K_D$ with $P$, $T$, and $X_{Ca}^{Gt}$

$$T(°K) = \frac{3104 X_{Ca}^{Gt} + 3030 + 10.86 P(kb)}{\ln K_D + 1.9034}. \quad (9)$$

Discussion

Although Eq. 9 is applicable as a practical geothermometer for garnet-clinopyroxene assemblages from a wide range in $P$, $T$, $X$ conditions, it must be remembered that the included constants cannot be interpreted solely in terms of the thermodynamic mixing properties of the garnet solid solutions. In particular the variation in the measured $K_D$ as a function of $X_{Ca}^{Gt}$ is simply a convenient method of representing the net effect of the influence of the different solid solutions upon $K_D$. There is an increase in Ca and Al content of the clinopyroxene (as Di and/or CaTs) with increase in Ca content of the coexisting garnet (see Fig. 4).

High pressure experimental and solution calorimetry studies (Hensen et al., 1975; Newton, 1977) have shown that there is a positive excess enthalpy of mixing ($\Delta H^{ex}$) in Ca—Mg garnet solid solutions, even though these two studies derived very different $\Delta H^{ex}$ values. Up to about $X_{Ca}^{Gt}=0.5$ this variation can be adequately described by a regular solution model, though at higher $X_{Ca}^{Gt}$ contents a subregular solution model is more appropriate (Newton, 1977). Wood (1977) suggested that Ca—Mg garnet non-ideality may be the sole factor affecting $K_D$ with changing rock compositions at constant $P$ and $T$. As noted by Wood (1977), Ca—Mg garnet non-ideality at any given $P$ and $T$ implies that an increase in $X_{Ca}^{Gt}$ results in an increase $\gamma_{Ca}^{Gt}$, which in order to keep the equilibrium constant $K$ the same, must result in a decrease in Mg and hence the measured $K_D$ increases. If this were the only non-ideal substitution, then the effect of $X_{Ca}^{Gt}$ upon $K_D$ would diminish with increasing iron content.

This would be in apparent contradiction to the experimentally determined variation of $K_D$ with $X_{Ca}^{Gt}$ and Mg/(Mg + Fe). Our data has shown that the effect of Ca upon $K_D$, as reflected by increasing $X_{Ca}^{Gt}$ does not decrease with increasing iron content. The 30 kb, 1,200°C data (Table 2), shows that within experimental error there is no measurable difference in $K_D$ for a given $X_{Ca}^{Gt}$ for garnets in the range Mg/(Mg + Fe) = 0.79 — 0.24 (see also Råheim and Green, 1974a).

We have partly confirmed this observation by analysis of the 30 kb, 1,200°C experimental data in terms of ternary (garnet) and quaternary (clinopyroxene) regular solution models. This approach demonstrates that the effect of Ca upon $K_D$ is due to a combination of non-ideal Ca—Mg substitutions in both the garnet and clinopyroxene. These substitutions would have opposite effects on $K_D$ and it is suggested that the total excess Gibbs free energy of mixing for the exchange reaction (1), as evidenced by the measured variation in $K_D$ with $X_{Ca}^{Gt}$, is independent of the Mg/(Mg + Fe$^2$) of the rock, within experimental error.

Unfortunately the assumptions which are necessary at present for the derivation of activity—composition relations of the relevant binary solid solutions from multicomponent equilibria render such parameters as having little thermodynamic significance. The various Margules parameters vary by up to a factor of five depending upon the method of calculating the clinopyroxene quaternary end-members (either CaAl$_2$SiO$_6$, Ca$_2$Si$_2$O$_6$, Mg$_2$Si$_2$O$_6$, Fe$_2$Si$_2$O$_6$ or CaAl$_2$SiO$_6$, CaMgSi$_2$O$_6$, Mg$_2$Si$_2$O$_6$, Fe$_2$Si$_2$O$_6$). The latter components, although representing ‘real’ pyroxene components, do not adequately describe iron-
rich clinopyroxene. Analysis of the same data using the two models of end member components indicates the important effect of either Wo—En or Di—CaTs together with Ca—Mg in garnet on the exchange reaction \( K_D \).

Caution must be exercised when comparing these values with those derived from specific binary solid solution studies or in attempting to include such independently derived parameters in the above calculations. Thus studies of the Ca—Mg garnet binary system by high pressure experiment (Hensen et al., 1975) and solution calorimetry (Newton et al., 1977) derived excess enthalpies of mixing for this substitution which differ by a factor of two. These different results bracket the range predicted from the analysis of our own multicomponent data, depending upon the method of pyroxene end member calculations.

Recent work has also shown that the intracrystalline partitioning of Mg and Fe\(^{2+} \) between the \( M1 \) and \( M2 \) sites in clinopyroxene \( K_D = (FeM1/MgM1) \cdot (MgM2/FeM2) \) increases with increasing temperature and decreases with increasing CaSiO\(_3\) content of the clinopyroxene (Saxena et al., 1974; McCullister et al., 1976). This implies that Ca selectively replaces Mg in the clinopyroxene \( M2 \) site, which would have the effect of decreasing the \( Gt-Cpx \) Fe—Mg \( K_D \) with increasing Ca-content of the clinopyroxene. Ca—Fe substitution in clinopyroxene should be more ideal than Ca—Mg substitution as there is an increase in miscibility between clinopyroxene and orthopyroxene with increasing iron contents.

Although the existence of a miscibility gap between coexisting clinopyroxene and orthopyroxene supports our large values calculated for the clinopyroxene interaction parameters, it is difficult to quantitatively evaluate these values by comparison with data for even the simple Ca—Mg binary pyroxene system. Phase equilibria data on the Di—En join cannot strictly be used to evaluate activity-composition relations by means of strictly regular solution models as Di and En do not obey the same equation of state, having different crystal structures (see the work of Warner and Luth, 1974; Saxena and Nehru, 1975).

Hence we believe that the effect of all of the above competing factors on reaction (1) is such that the nett excess Gibbs free energy of mixing at a given \( P \) and \( T \) remains approximately constant with changing Mg/(Mg + Fe), within the error of the experimental techniques.

The applicability of Eq. (9) can be checked by comparison with experimental data of Råheim and Green (1974a) for very iron-rich eclogites (Mg/(Mg + Fe)=0.18–0.035, 20 kb pressure) which were not used in the derivation of our geothermometer. Our Eq. (9), in which the effect of Ca upon \( K_D \) is independent of Mg/(Mg + Fe), gives deviations from the stated experimental temperature of 5°–85°C, which is within the scatter of our own experimental data.

We have also applied Eq. (9) to other experimental data not used in the derivation of this equation (Hensen, 1973; Råheim and Green, 1974a and b; Akella, 1976; Wood, 1976; Mori and Green, 1978). These data cover the range \( P=15–45 \) kb, \( T=600°–1,450°C , X_{Ca}=0.12–0.44 \). The majority of our temperature estimates lie within ±5% of the stated temperature, which is the uncertainty associated with our own data. Furthermore, our estimates do not show any bias towards overestimating or underestimating equilibration temperatures for any particular rock type using Eq. (9).

**Geological Application**

The geological application of Eq. (9) requires a knowledge of the Fe\(^{3+} \) content of the garnet and clinopyroxene. The use of probe data with total iron as FeO can cause large errors in temperature calculations if a significant proportion of the iron is Fe\(_2\)O\(_3\) (e.g., glaucohanic schist terrains). The reader is referred to the comments of Ryburn et al. (1975) on the methods of calculating Fe\(^{3+} \) and the errors which can develop if this is neglected.

Several examples may be cited where the application of our experimentally calibrated geothermometer results in a refinement of temperature estimate compared to earlier methods. Recent compilations of \( K_D \) data for eclogites (e.g., Irving, 1974) show that Ca-rich garnet varieties (grosopydites, kyanite eclogites) generally have higher \( K_D \) values than other kiberlitic eclogites and garnet peridotites. Smyth and Hatton (1977) have described a coesite-sandine grosopydite which they deduced from the structural state of the feldspar and the presence of coesite to have equilibrated above 29 kb pressure, 900°C. Application of previous geothermometers to this rock (Råheim and Green, 1974a) indicates too low an equilibration temperature (825°C at 30 kb). Our data indicate a temperature of 1,055°C, which is more consistent with thermal regimes in the mantle at that pressure.

Wood (1975) has described some garnet-clinopyroxene orthogneisses from South Harris, Scotland, for which previous \( Gt-Cpx \) \( K_D \) temperature estimates gave too low an equilibration temperature (≈730°C) compared to other methods of temperature and pressure estimation (see Wood, 1975). Application of Eq. (9) gives higher temperatures of equilib-
Table 4. Comparison of estimated temperature of equilibration (°C) of garnet peridotite, eclogite and metarodingite (rim compositions, P=25 kbar) from Cima di Gagnone, Switzerland (Evans and Trommsdorff, 1978; Evans et al., 1979)

| Sample no. | $K_D$ | $X^Gt_{Ca}$ | $T_1$ | $T_2$ | $T_3$ | $T_4$
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<tr>
<td>160-4-8</td>
<td>6.35</td>
<td>0.133</td>
<td>717</td>
<td>777</td>
<td>846</td>
<td>867</td>
</tr>
<tr>
<td>95-2-C</td>
<td>5.17</td>
<td>0.141</td>
<td>781</td>
<td>833</td>
<td>770</td>
<td>786</td>
</tr>
<tr>
<td>264-3</td>
<td>4.81</td>
<td>0.140</td>
<td>802</td>
<td>853</td>
<td>821</td>
<td>843</td>
</tr>
<tr>
<td>163-K</td>
<td>6.16</td>
<td>0.17</td>
<td>756</td>
<td>786</td>
<td></td>
<td></td>
</tr>
<tr>
<td>248-6</td>
<td>8.7</td>
<td>0.34</td>
<td>798</td>
<td>705</td>
<td></td>
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<tr>
<td>249-J</td>
<td>9.24</td>
<td>0.33</td>
<td>775</td>
<td>692</td>
<td></td>
<td></td>
</tr>
<tr>
<td>163-P</td>
<td>11.76</td>
<td>0.41</td>
<td>774</td>
<td>643</td>
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</table>

Fig. 6. $\ln K_D - X^Gt_{Ca}$ plot of the garnet peridotite, eclogite and metarodingite data from Evans and Trommsdorff (1978) and Evans et al. (1979) - see Table 4. The straight line is the predicted $\ln K_D - X^Gt_{Ca}$ dependence at 780°C, 25 kb, using Eq. (9).

The above examples of similar temperature estimates for isofacial eclogites and peridotites with such different chemistries and $K_D$ values provides good evidence for the use of application of Eq. (9) and is an apriori justification for the assumptions made in the derivation of this relationship as a practical geothermometer. It must be remembered that in a thermodynamic sense the observed variation of $K_D$ with $X^Gt_{Ca}$ represents the net effect of all competing factors (non-ideal substitutions) in both the garnet and clinopyroxene solid solutions. In this regard, further data on binary solid solutions derived from high pressure experimental, solution calorimetry and X-ray studies are awaited.

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Petrogenesis of Eclogite Inclusions in the Moses Rock Dyke, Utah, U.S.A.

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With 7 Figures

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Summary

A detailed electron microprobe study of the mineralogy of fifteen eclogites from the Moses Rock kimberlitic dyke, Utah, has demonstrated complexity in compositional zoning of minerals. Most of the eclogites examined are of the almandine-jadeite type and zonal and irregular variation in grossular content of garnet and acmite, jadeite and diopside-hedenbergite content of pyroxene produce large uncertainties in temperature estimates based on Fe/Mg partitioning between garnet and clinopyroxene. Zoning patterns of increasing $X_{Mg}$ in both clinopyroxene and garnet, and increasing $X_{Jd}$ in clinopyroxene, suggest the introduction of Mg and Na throughout the evolution of these essentially bimineralic assemblages. Averaged data yield temperatures from 340°C to 500°C at 10 kbar for compositions of rims of coexisting garnet and clinopyroxene. Two samples contain pyrope-rich garnets but coexisting pyroxenes are extremely magnesian and temperatures of equilibration of both primary omphacite-pyrope and secondary omphacite-almandine/pyrope-chlorite are only slightly higher (500–650°C at 10 kbar) than those for almandine jadeite eclogites and estimates overlap with those of some examples of the latter type. Unlike the majority of almandine-jadeite eclogites, two examples contain garnets with almandine-cores and pyrope-rich rims without accompanying variation in grossular content. The simple interpretation of these samples as evidence of garnet growth during prograde metamorphism is precluded by complex zoning in coexisting clinopyroxene. The eclogites provide evidence for the presence of a metamorphic terrane including rock types resembling those of blueschist terranes beneath the Colorado Plateau but do not permit deduction of the $P, T$ path by which such rock types reached their $P, T$-conditions (~10 kbar, 400–600°C) of metamorphism.

Zusammenfassung

Petrogenese von Eklogit-Einschlüssen im Moses Rock Dyke, Utah, U.S.A.

Eine detaillierte Studie der Mineralogie von fünfzehn Eklogiten vom Moses Rock Kimberlit-Dyke (Utah) mittels Mikrosonde zeigte komplexe Zonierung der Zusammen-

Zwei Proben enthielten pyropreichen Granat, die koexistierenden Clinopyroxene sind extrem Mg-reich und die Gleichgewichtstemperaturen sowohl von primärem Omphacit-Pyrop als auch von sekundärem Omphacit-Almandin/Pyrop-Chlorit sind nur geringfügig höher (500°C—600°C bei 10 kb) als die für Almandin-Jadeit-Eklogite; die Schätzungen überlappen mit denen von einigen Proben des letzteren Typs.

Im Gegensatz zur Mehrheit der Almandin-Jadeit-Eklogite enthalten zwei Proben Granate mit almandinreichen Kernen und pyropreichen Rändern ohne gleichzeitige Schwankungen im Grossulargehalt. Eine einfache Interpretation dieser als Beweis für Granatwachstum während prograder Metamorphose muß jedoch ausgeschlossen werden, da die koexistierenden Clinopyroxene komplex zoniert sind.

Die Eklogite können als Beweis angesehen werden für das Vorhandensein eines metamorphen Bereichs unter dem Colorado-Plateau, der Gesteinstypen enthält, die denen der Gla phanschieferfacies ähneln. Es können jedoch keine Aussagen über den P-T-Weg gemacht werden, über den diese Gesteinstypen ihre heute feststellbaren P-T-Bedingungen (400°C—600°C, 10 kb) erreicht haben.

Introduction

Recent experimental calibrations of Fe—Mg distribution between coexisting garnet and clinopyroxenes as a function of pressure and temperature have been used to estimate equilibration temperatures for eclogitic or garnet-clinopyroxene inclusions in kimberlites, and to estimate P-T paths of prograde metamorphism based on zoning relationships in the garnets and clinopyroxenes (Råheim and Green, 1974; Råheim and Green, 1975; Ryburn et al., 1976; Helmsteadt and Doig, 1975). The experimental study of Råheim and Green (1974) explored the effects of P, T and Mg:Fe variation on the Fe/Mg distribution coefficient between garnet and clinopyroxene in a quartz eclogite. A new experimental calibration of the garnet-clinopyroxene geothermometer which evaluated the effect of calcium (grossular) solid solution in garnet on Fe/Mg partitioning (Ellis and Green, 1979) is applied herein to eclogitic inclusions in kimberlite from the Moses Rock dyke, Utah, U.S.A.

The dyke, described by McGechin (1969), McGechin and Silver (1970) an McGechin et al. (1977), is one of a group of diatremes containing xenoliths (O’Hara and Mercy, 1966; Watson and Morton, 1968) which are thought to
have sampled a column of crust and mantle. Xenoliths include eclogite, granulite, amphibolite and ultramafic rocks including lherzolite, harzburgite and spinel websterite.

The similarity of the eclogite inclusions in the Colorado Plateau kimberlite diatremes to Franciscan jadeite-almandine rocks and other Group C eclogites (Coleman et al., 1965; Helmstaedt and Doig, 1975; Watson and Morton, 1968), led to the suggestion that these eclogite inclusions represent samples of subducted oceanic crustal material affected initially by blueschist metamorphism (Essene and Fyfe, 1967; Helmstaedt and Doig, 1975; Green, Lockwood and Kiss, 1966). Råheim and Green (1975) interpreted the Fe/Mg zoning in garnet and clinopyroxene from a Moses Rock eclogite as evidence for prograde metamorphism in a descending slab, with magnesian garnet rims produced at higher pressures and temperatures than the almandine rich cores.

A new experimental study (Ellis and Green, 1979) has demonstrated correlation between $K_{\text{Fe/Mg}}$ and the grossular content of garnet. As the Fe/Mg zoning in garnet and clinopyroxene is also accompanied in some cases by zoning in grossular content of garnet, it is necessary to re-evaluate the evidence for prograde metamorphism in the Moses Rock xenoliths. To this end, microprobe analyses of 15 eclogites from the Moses Rock Dyke, collected in 1970, have been carried out.

Petrography and Mineralogy

The eclogites are very similar to those from Garnet Ridge (Watson and Morton, 1968; Smith and Zientek, 1979) and are generally medium to fine grained granular or foliated rocks with subhedral to euhedral porphyroblasts and poikiloblasts of red to pale pink garnet set in a foliated groundmass of granoblastic to prismatic clinopyroxene. In a number of samples the garnet displays atoll texture (Spry, 1969; Smith and Zientek, 1979). Generally clinopyroxene is more abundant than garnet, which in some samples is absent or restricted to lenses in an otherwise monomineralic clinopyroxene rock. The essential mineralogy of the inclusions is garnet and clinopyroxene with minor rutile, phengite, pyrite, altered lawsonite, and, in one rock, quartz (Table 1).

Two samples (46398 and 46415) contain coarse pale pink garnet with coarse pale green clinopyroxene, the latter containing exsolution lamellae. Coarse colourless chlorite rims the garnet and occurs along cracks in the garnet, with fine clinopyroxene occurring in apparent equilibrium with the chlorite (cf. Helmstaedt and Schulze, 1979). These samples possess a marked foliation defined by the primary clinopyroxene and the chlorite.
In all other samples the pyroxene is either apple green and granular, or pale green to colourless and prismatic. The clinopyroxenes are often optically zoned, with extinction bands and zones (see Smith and Zientek, 1979). Garnet is commonly zoned from pink cores crowded with inclusions of clinopyroxene, rutile, quartz and phengite, to colourless inclusion-free rims. Rutile occurs as inclusions in the other primary phases and as anhedral yellow grains. Turbid areas which consist dominantly of fibrous radiating masses of zoisite are common in many of the samples. An additional phase, phengite, occurs in a number of xenoliths as subhedral grains in textural equilibrium with garnet and clinopyroxene, or together with clinopyroxene enclosed in atoll garnets. Phengite is a primary phase in these rocks, resembling that in eclogites from Oregon (Ghent and Coleman, 1973) and Arizona (Watson and Morton, 1968), and many other blueschist or eclogite-bearing gneissic terrains.

Mineral Chemistry

Simultaneous analysis for ten elements (Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe) has been obtained using a JEOL JXA-50A microanalyser and EDAX energy dispersive system under operating conditions of 15 KeV and 80 sec analysis time. Data reduction by the TAS-SUEDS programme (Griffin, 1979) is based on the methods of Reed and Ware (1975). In each sample, we have obtained spot analyses of rims, cores and intermediate zones of garnet and clinopyroxene. Additionally, detailed mapping of several clinopyroxene and garnet grains has been carried out. Small area scans (50 × 50 μm²) of phengite and larger area scans (500 × 500 μm²) of zoisite-lawsonite masses have been used to obtain average compositions.

The difficulties of estimating ferric iron from microprobe analyses have been discussed elsewhere (Essene and Fyfe, 1967; Ryburn, Råheim and Green, 1976). For pyroxenes where Na is high (5–13 wt.% in these samples) and Feₜₒₜₜ is low, the Fe³⁺ calculation is critical because the allocation of some iron to acmite produces a relatively major change in Mg number of the pyroxene. Small changes in the Mg number of mangesian pyroxene, resulting from errors in SiO₂, Al₂O₃ or Na₂O analysis which affect the Fe³⁺ calculation, will cause a marked change in KD* and hence in the estimated temperature.

Fe³⁺ for pyroxenes in these eclogites has been calculated as follows (Essene, pers. comm., 1978):

\[ KD^* = \frac{Fe^{2+}}{Mg^{2+}} ga/ \frac{Fe^{2+}}{Mg^{2+}} cpx. \]
### Petrographic Features of Eclogites from the Moses Rock Dyke

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<td>46398 45 45</td>
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Table 1. Petrographic Features of Eclogites from the Moses Rock Dyke
Using the pyroxene formula $M_4O_6$, based on 4 cations rather than 6 oxygen with $Si^{4+} < 2$ and $Si^{4+} + Al^{3+} > 2$: the pyroxene molecules are allocated in the sequence $CaTiAl_2O_6$, $CaAl_2SiO_6$, $NaAlSi_2O_6$, $NaCrSi_2O_6$ and $NaFe^{3+}Si_2O_6$, the acmite and Fe$^{4+}$ content thus being determined by

$$Na - (Al + Cr - 2(2-Si-Ti) - 2 Ti) = Na - Al - Cr + 2(2-Si).$$

Fig. 1. Garnets in eclogites from Moses Rock. Grossular + andradite — almandine + spessartine — pyrope diagram. Group $A$, $B$, $C$ boundaries after Coleman et al., 1965. Solid symbols — rim compositions: Open circles for 398 and 415 are for rims coexisting with chlorite-jadeite, otherwise all other open symbols are for cores. Tie lines join cores rims of typical samples. Numbers as in text

Garnet

Representative analyses of cores and rims of garnets from each eclogite are plotted in Figs. 1, 3, and 4.

Four groupings of garnet can be made on the bases of rim Mg numbers and core to rim zoning patterns (Fig. 1):

1. 46398 and 46415 contain garnets with $X_{Mg}^{\text{rim}} = .7$, and low grossular contents ($Gr_{10}$). These garnets coexist with omphacitic pyroxene (Na$_2$O = 3-4 wt.%), in contrast to the jadeite-acmite pyroxenes occurring in all other inclusions studied. Adjacent to chlorite, these garnets become calcic ($Gr_{30}$) and more Fe rich ($X_{Mg} = .5$) (Fig. 4).

2. 4607 and 46400: Garnets show negligible grossular zoning ($Gr_{8}-Gr_{10}$), but range from almandine cores ($X_{Mg} = .2$ to .3) to pyrope-almandine rims ($X_{Mg} = .5$ to .6).
(3) 46401 and 46413 contain garnets showing an increase in grossular from cores to rims along with an increase in Mg number (cores $Py_{21}Gr_{14}Alm_{65}$ to rims $Py_{34}Gr_{20}Alm_{46}$ in 46413).

(4) The Remaining samples contain almandine garnets with rim Mg numbers in the range .25 to .4, depending on the particular sample. In all these samples, garnet zones from almandine-grossular rich cores to more pyrope-rich and grossular poor rims (cores $Gr_{20}$ to rims $Gr_{9-14}$). These garnets coexist with omphacite-jadeite pyroxenes, like the garnets of groups (2) and (3) above ($Na_2O > 7$ wt.%).

Spessartine contents of all garnets are generally low, 1–2 mol.%, however manganese may be enriched in some cores (up to 10 mol.% spessartine). Andradite contents are 0.5 to 5 mol.%, with higher $Fe^{3+}$ contents usually calculated for garnet cores.

The garnet plot of Fig. 1 (after Coleman et al., 1965) illustrates that all garnet core compositions except 46415 and 46398 lie in the field of Group C eclogites, i.e. eclogites associated with glaucophane schist facies metamorphics. The garnets in 46415 and 46398 indicate that these two samples are of different origin to all other samples studied.
Pyroxenes

Electron microprobe analyses of clinopyroxenes from the eclogite inclusion are presented in Figs. 2, 3 and 4. The pyroxenes form a series between jadeite (up to 90 mol.% Jd) and diopside-hedenbergite (up to 73 mol.% Di—Hd) with acmite up to 18 mol.%.

Samples 415 and 398 contain the lowest Jd—Ac pyroxenes, Jd_{40-30} Ac_{5-0}. These omphacites are the only examples containing calcium Tschermak's molecule. They are highly magnesian, X_Mg = 90–95, and coexist with the most magnesian garnets studied. More sodic pyroxene compositions (X_Jd = 50, Fig. 2A) in these samples occur in contact with chlorite and garnet.

The remaining samples contain jadeite-omphacite with acmite up to 18 mol.% and pyroxenes show a wide range of jadeite contents (Fig. 2), both within any one sample and between samples. In this group of rocks, especially those with highly jadeitic pyroxenes, Fe^{2+} and Mg^{2+} are small and the calculation of Fe^{3+} produces large changes in Mg number*. Given the uncertainty in calculated Fe^{3+} contents from structural formulae, K_D^{Fe_{cpx}/Mg} values will have high uncertainty and considerable scatter even in homogeneous material.

In any one sample there is considerable scatter of pyroxene compositions along the Jd—Diop join (Fig. 2). Râheim and Green (1975) found zoning in a Moses Rock eclogite pyroxene from Jd_{45} core to Jd_{54} rim, with a small decrease in acmite. This zoning, in pyroxene, accompanied by variation in grossular content of garnet, is consistent with the thermodynamic treatment of Banno (1967), who argued that X^{cpx}_{Jd} will increase with decreasing X^{gross}_{Gross}. Preliminary data in this study (Fig. 2) demonstrate widespread zoning in the jadeites, but more detailed work established that optically zoned pyroxenes showed irregular core to rim changes in jadeite component. Some pyroxenes indicated decrease in X_{Jd} towards rims, oscillatory zoning, or anomalously high X_{Jd} zones within grains. In addition coexisting rims have been found with markedly different X_{Jd} and X_{Mg}, indicating disequilibrium persisting, at least in some domains, to grain boundaries.

To further elucidate the nature and pattern of zoning in the jadeites, grains from some samples have been selected and mapped in detail (403, 404, 405, 419, 425). This work has produced a consistent pattern for the grains analysed (Fig. 5).

(a) Contoured maps can be constructed for a number of chemical variables (Jd, Ac, Mg/Mg + Fe^{total}, X_{Mg}). For the data obtained, closed concentric contours can be drawn.

(b) Na_2O decreases from cores to rims.

* (Fe^{3+}/Fe^{total}) varies from .6 to .9.
Fig. 3. Ca—Mg—Fe\(^{2+}\) diagram of coexisting garnet-clinopyroxene rims from eclogites. Numbers as indicated in text. Note the wide field of bulk composition in terms of \(X_{Mg}\).

Fig. 4. Composite Ca—Mg—Fe\(^{2+}\) and Al—Ca—(Fe+Mg) triangular diagrams for eclogites 46415 and 46398. ga\(_1\), cpx\(_1\) refer to the primary assemblage; ga\(_2\), cpx\(_2\) refer to the ga—cpx—chl assemblage. Chlorite — filled circles; primary ga—cpx — filled triangles; secondary ga—cpx — open triangles.
(c) Jadeite decreases from cores to rims, but may increase again near garnet.
(d) Acmite generally increases from cores to rims.
(e) Mg/Mg + Fe\textsuperscript{total} increases from cores to rims.
(f) Recalculated $X_{Mg} = \frac{Mg}{Mg + Fe^{2+}}$ increases from cores to rims, reflecting both increasing Acmite and increasing Mg/Mg + Fe\textsuperscript{total}.

All these pyroxenes coexist with garnets which show an increase in $X_{Mg}$ from cores to rims, and either a decreasing or constant $X_{Ca}^{ga}$. Two samples (404, 403) contain garnets with only minor zoning, however the jadeites show marked zoning. The pyroxene zoning pattern, for the grains studied, appears to be independent of the type of garnet zoning in the same rock.
Fig. 5. Hand contoured maps of selected clinopyroxene grains, 46403C7 and 46404C9 in Fig. 5a, and 46405C, 46419C and 46426C in Fig. 5b. Three maps of each clinopyroxene are given, A, B, and C, depicting the compositional variables as follows:

A. Mg number \((\text{Mg/Mg+Fe}^{2+}) \times 100\) calculated after acmite estimation. B. Jadeite, as a mole fraction. Here \(Jd = X_{Al}\). C. Acmite, calculated as \(\text{Na-Al}\). All data are based on electron-microprobe analysis for 10 elements at each analysis point. Contour values are as follows: Fig. 5a. Pyroxene 46403C7: A. \(X_{Mg} = 60, 70, 80, 85\). B. \(X_{Jd} = 0.60, 0.70, 0.80\). C. \(X_{Ac} = 0.02, 0.12\). Pyroxene 46404C9: A. \(X_{Mg} = 60, 65, 70, 75, 80\). B. \(X_{Jd} = 0.70, 0.75, 0.80, 0.85\). C. \(X_{Ac} = 0.03, 0.08\). Fig. 5b. Pyroxene 46405 C: A. \(X_{Mg} = 78, 80, 82, 84\). B. \(X_{Jd} = 0.50, 0.55, 0.60\). Pyroxene 46419C: A. \(X_{Mg} = 77, 78, 79, 80, 81, 82\). B. \(X_{Jd} = 0.50, 0.52, 0.55, 0.58, 0.60\). C. \(X_{Ac} = 0.07, 0.08, 0.09, 0.10, 0.11\). Pyroxene 46426C: A. \(X_{Mg} = 80, 85\). B. \(X_{Jd} = 0.50, 0.55, 0.60\). C. \(X_{Ac} = 0.10, 0.12, 0.14\).

**Lawsonite**

Area scans \((500 \times 500 \mu m^2)\) of turbid, altered fibrous regions in the eclogites indicate the presence of lawsonite and its breakdown products. Zoisite and a white mica can be identified optically and rare clear relicts may be lawsonite (Watson and Morton, 1968). Minor amounts of MgO, FeO,
Na$_2$O and excess CaO over the requirements for lawsonite or zoisite appear in the analyses. These result from the presence of the mica, possibly a paragonite (Table 2). The breakdown of lawsonite has been interpreted (Watson and Morton, 1968) as a very late stage alteration, possibly occurring during entainment into the kimberlite. Under conditions of $p_{\text{H}_2\text{O}} = p_{\text{total}}$, lawsonite breaks down following the reaction: \( \text{law} = \text{zois} + \text{ky} + \text{Qz} + \text{H}_2\text{O} \) (Newton and Kennedy, 1963; Nitsch, 1972). At 10 kbar, this breakdown occurs at around 500°C with the formation of the high temperature, low pressure zoisite bearing assemblage. At lower temperature, in the system Na$_2$O–CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O, jadeitic pyroxene may participate: \( \text{law} + \text{jd cpx} = \text{zois} + \text{pa} + \text{Qz} + \text{H}_2\text{O} \) (Green, Lockwood and Kiss, 1968). This breakdown may occur due to temperature increase, a reduction in $p_{\text{total}}$ or a reduction in $p_{\text{H}_2\text{O}}$.

These breakdown reactions span the temperature interval obtained using garnet-clinopyroxene Fe–Mg partitioning (see thermometry section). The evidence that the breakdown of lawsonite to zoisite + paragonite is a late event provides support for the rim temperatures inferred by geothermometry for the garnet-clinopyroxene pairs. The earlier stability of lawsonite is evidence for high $p_{\text{H}_2\text{O}}$ during the formation of these group C eclogites.

**Phengite**

Electron microprobe analyses of phengites coexisting with garnet (± clinopyroxene) in a number of the jadeite-almandine rocks are presented in Table 2. These results are plotted on the SiO$_2$–R$^3$–R$^2$ diagram (after Velde, 1967) of Fig. 6. Important features of these phengites are:

1. All have a very high Si$^{4+}$ content (7.3 to 7.6 cations for 22 oxygens), and no Ti$^{4+}$.
2. Recalculated analyses show that no Fe$^{3+}$ is present.
3. Mg numbers vary between inclusions, but are restricted to the range Mg$^{84}$ to Mg$^{90}$.
4. All the phengites contain a minor amount of calcium (.8 to 1.7 wt.% or .11 to .23 cations per 22 oxygen). This calcium is assigned to the K$^+$ site and produces the ideal charge value of 2 for the inter-sheet site. The R$^2+$ in Fig. 6 is Mg + Fe$^{2+}$, and generally excess Si$^{4+}$ over 6 cations is close to the number of R$^2+$ cations.
5. The phengites occur as inclusions within garnet and in the equigranular groundmass, and hence are a primary phase.

The phengites lie along the muscovite-celadonite join (Fig. 6) and are higher in Si$^{4+}$ than the phengites in eclogites from Oregon (Ghent and Coleman, 1973).
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Fig. 6. Composite triangular diagrams illustrating phengites and chlorites. From left to right: (1) $R^{4+}(Si)-R^{3+}(Al)-R^{2+}(Mg+Fe)$ plot. Note this is an expanded triangle, extending only to $R^{2+}$ and $R^{3+}$. Crosses — phengites from Moses Rock eclogites. Filled circles — phengites from Oregon eclogites (Ghent and Coleman, 1973). (2) Al—Fe—Mg diagram. Crosses — phengites; filled square — chlorites in 46415, 46398. (3) Al—Ca(Fe+Mg) diagram. Crosses — phengites; filled square — chlorites

Chlorite

Colourless, coarse, platy chlorite occurs as rims on garnet and in cracks in garnet in samples 46415 and 46398, the most magnesian eclogites. The chlorite is texturally a secondary or replacement phase. Analyses of chlorite are presented in Table 2.

The essential features of these chlorites are the high magnesium numbers Mg$_{93}$, and the high Si$_{4+}$ content. These chlorites are plotted with coexisting garnets in Fig. 4.

The garnets coexisting with chlorite in 415 and 398 are more calcic ($Gr_{30}$) and less magnesian ($X_{Mg} = 50$) than rim compositions in contact with clinopyroxene only. Clinopyroxenes coexisting with chlorite also have enhanced jadeite content ($X_{jd} = .5$) (cf. Helmstaedt and Schulze, 1979). These features suggest the reaction: low Ca garnet + low Na cpx + H$_2$O = Mg chlorite + higher Ca garnet + higher Na cpx. If this is the correct interpretation of the compositional and textural observations, the temperature of formation of the chlorite can be estimated using the $K_{D_{Fe/Mg}}^{ca/cpx}$ for the newly formed garnet and clinopyroxene.
The observation that this reaction only occurs in the most magnesian eclogites with \( K_D \) values suggesting the highest \( T \), indicates that these samples have undergone a different thermal evolution to the jadeite-almandine rocks which are both mineralogically and texturally distinctive. In a later section we discuss the relationship of the conditions of crystallization of the secondary assemblage for these eclogites to the conditions of crystallization of the distinctive almandine-jadeite rocks.

**Table 2. Microprobe Analyses of Phengites, Chlorite, and Lawsonite**

<table>
<thead>
<tr>
<th></th>
<th>Phengite 402M2</th>
<th>Phengite 407M3</th>
<th>Chlorite 398</th>
<th>Lawsonite 405LI</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>58.16</td>
<td>55.32</td>
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<tr>
<td>TiO₂</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.90</td>
<td>22.02</td>
<td>20.92</td>
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</tr>
<tr>
<td>FeO</td>
<td>2.12</td>
<td>1.13</td>
<td>4.58</td>
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</tr>
<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>6.63</td>
<td>5.80</td>
<td>31.95</td>
<td>1.70</td>
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<tr>
<td>CaO</td>
<td>.80</td>
<td>.81</td>
<td></td>
<td>16.63</td>
</tr>
<tr>
<td>K₂O</td>
<td>10.39</td>
<td>10.59</td>
<td>.27</td>
<td></td>
</tr>
<tr>
<td>Normalized to</td>
<td>96</td>
<td>96</td>
<td>88</td>
<td>88.5</td>
</tr>
<tr>
<td>Si</td>
<td>7.656</td>
<td>7.276</td>
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<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>.033</td>
<td></td>
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</tr>
<tr>
<td>Al</td>
<td>2.778</td>
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<td></td>
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<tr>
<td>Fe³⁺</td>
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<td>.358</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1.302</td>
<td>1.135</td>
<td>4.459</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
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<td>.113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.744</td>
<td>1.777</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>13.827</td>
<td>13.875</td>
<td>9.986</td>
<td></td>
</tr>
<tr>
<td>( X_{Mg} )</td>
<td>84.78</td>
<td>90.09</td>
<td>92.57</td>
<td></td>
</tr>
</tbody>
</table>

Note: (1) Phengite structural formulae on the basis of 22 oxygen. Chlorite structural formula on the basis of 14 oxygen. (2) Microprobe oxide values have been adjusted to total 96 for phengites, 88 for chlorites and 88.5 for lawsonite to allow for the ideal amount of water in each mineral.

**Equilibration Pressures**

In the absence of quartz and plagioclase, reactions involving jadeite or calcium Tschermaks’ pyroxene cannot be used to estimate pressure for these eclogites. Previously (Råheim and Green, 1975; Krogh and Raheim, 1978) jadeite zoning in the pyroxenes has been used to support the concept of changing \( P, T \) conditions during growth of the eclogite assemblages.
In this study, the absence of the buffering assemblages plagioclase-quartz or nepheline-quartz in the rocks means that $a_{pl}^{px}$ is not fixed at a particular $P$ and $T$. Jadeite contents are a function of bulk rock composition and eclogites with a wide range of Na$_2$O contents in pyroxene may have formed under similar $P, T$ conditions.

*Velde* (1967) and subsequently *Råheim* (1977) have noted the pressure dependence of the Si$^{4+}$ content of phengite. According to the stability curves of *Velde* (1967), the Si$^{4+} > 3.6$ in the phengites from these eclogitic inclusions indicates minimum pressure of 10 kbar, at temperatures of 500°C under conditions of $p_{H_2O} = p_{total}$. Considering the absence of any other consistent and reliable method of pressure estimation for these rocks, a nominal pressure of 10 kbar has been used in the calculation of all temperature estimates.

**Geothermometry**

The temperature of formation of the eclogites have been calculated using a new garnet-clinopyroxene Fe—Mg exchange thermometer which accounts for the grossular ($X_Ca$) content of garnet (*Ellis and Green*, 1979):

$$T^\circ K = \frac{3104 \text{ Ca } + 3030 + 10.86 \text{ P (kbar)}}{\ln K_D + 1.9034},$$

where $Ca = X_{g}^{\text{garnet}} \text{ Ca}/\text{Ca} + \text{Mg} + \text{Fe}$

and

$$K_D = \frac{\text{Fe}^{2+} \text{ garnet}}{\text{Fe}^{2+} \text{ cpx}} \text{ Mg}.$$  

Resulting temperatures calculated from core and rim compositions of garnet and clinopyroxene are presented in Table 3 and Fig. 7.

With $X_{Ca}^{\text{g}}$ generally low in these eclogites (<.3), temperature estimates based on the Ellis-Green calibration are lower than temperatures obtained by application of the Råheim-Green thermometer. As $X_{Ca}^{\text{g}}$ is usually higher in cores than on garnet rims, the temperature difference between cores and rims is not as great using the Ellis-Green equation compared to the Råheim-Green method which did not account for the effects of calcium.

In phengite-bearing samples, the garnet-phengite Fe—Mg $K_D$ thermometer (*Krogh and Råheim*, 1978) gives temperatures higher than rim temperatures based on the Ellis-Green calibration but comparable to Raheim-Green estimates, as would be expected given that the garnet-phengite method is based on limited experimental data and comparison with the Raheim-Green thermometer (*Krogh and Råheim*, 1978).
The conspicuous zoning in some of the garnets (Fig. 1) and particularly the inhomogeneity of the clinopyroxenes (Figs. 2, 5) in any one sample, cause great difficulties in temperature estimation and in the interpretation of coexistence, equilibrium or disequilibrium. Combined with analytical uncertainty, this produces a wide scatter of temperature estimates based on rim compositions alone (Fig. 7). Several different approaches have been used in temperature calculation to evaluate the reliability of the estimates:

(a) Coexisting garnet-clinopyroxene rims have been used to give individual $K_D$ values and hence a number of independent temperature estimates for each rock. Such data gives a range of $K_D$ values and thus of rim temperature estimates, illustrated in Fig. 7.

(b) All garnet and clinopyroxene rim data for each rock have been averaged to give a mean $K_D$, $\sigma$, and a mean estimated rim temperature (Fig. 7, Table 3).

(c) To evaluate the interpretation of a prograde history with increase of temperature from cores to rims, garnet cores have been combined with both a high $X_Mg$ clinopyroxene composition and an average $X_Mg$ clinopyroxene in each sample. This method assumes a constant bulk composition throughout the evolution of the assemblage and overlooks the inhomogeneity of the pyroxenes illustrated by detailed compositional mapping of individual pyroxene grains. $K_D$ and temperature estimates based on garnet core compositions combined with averaged clinopyroxene compositions are given in Table 3.

Considering the problems of analytical errors, Fe$^{3+}$ estimation, and compositional inhomogeneity even near rims, rim temperature estimates using method (b) are considered most reliable and fall within the range of temperature estimates using method (a). The apparent “core” temperatures calculated by method (c) are, in general, within 100°C of the averaged rim temperature estimate, and are consistently lower. With a ± 50°C error in the thermometry at best, these core temperatures are not significantly different from rim temperatures at a pressure of 10 kbar for all samples except 400, 401, 413 and 407 (Fig. 7). These four samples contain garnets with marked zoning parallel to the almandine-pyrope join (Fig. 1), and could be predicted from the garnet diagram (Coleman et al., 1965) to have a prograde temperature change from cores to rims.

A further attempt at temperature estimation utilizes the data collected on the carefully mapped, well zoned, pyroxene grains (Table 3b). Assuming the selected jadeite cores to be in equilibrium with garnet cores for these particular samples, 10 kbar apparent core temperatures are higher than rim temperatures, but the latter are in good agreement with the averaged rim data (method (b)). The apparent decrease in temperature from core to rim in samples 404 and 403 occurs primarily because of the zoning in clinopyroxenes 404C9 and 403C7. Garnets in these samples exhibit only minor
Petrogenesis of Eclogite Inclusions in the Moses Rock Dyke

Table 3. Garnet-Clinopyroxene Geothermometry (°C), Moses Rock Eclogites, at 
P = 10 kbar

A. Almandine-Jadeite Eclogites
using garnet zoning and averaged clinopyroxenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rim $K_D$ average</th>
<th>Core $K_D$ average</th>
<th>Rim Temperature Ellis-Green</th>
<th>Core Temperature Ellis-Green</th>
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<tbody>
<tr>
<td>46407</td>
<td>6.86</td>
<td>56.10</td>
<td>600</td>
<td>660</td>
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<td>46401</td>
<td>22.26</td>
<td>110.77</td>
<td>477</td>
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<tr>
<td>46413</td>
<td>18.28</td>
<td>34.33</td>
<td>464</td>
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<td>46402</td>
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<td>339</td>
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<td>46403</td>
<td>24.55</td>
<td>58.17</td>
<td>427</td>
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<td>23.09</td>
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<td>46418</td>
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<td>23.69</td>
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<tr>
<td>46426</td>
<td>24.50</td>
<td>51.95</td>
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<td>445</td>
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selected zoned clinopyroxenes with zoned garnets — detailed mapping

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<tr>
<th></th>
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<tbody>
<tr>
<td>403C7</td>
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<td>4.21</td>
<td>420</td>
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<tr>
<td>404C9</td>
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<td>5.35</td>
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<td>520</td>
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<tr>
<td>426C</td>
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<td>444</td>
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B. Omphacite-Pyrope Eclogites

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<tbody>
<tr>
<td>46415</td>
<td>6.85</td>
<td>12.80</td>
<td>637</td>
<td>660</td>
</tr>
<tr>
<td>46398</td>
<td>13.39</td>
<td>21.79</td>
<td>500</td>
<td>533</td>
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</tbody>
</table>

zoning and always lie within group C (Coleman et al., 1965) and are similar in every respect to garnets from other samples where no core to rim temperature decrease has been deduced. Such inconsistencies, found when we examine the zoning patterns in greater detail than Råheim and Green (1975) or Helmstaedt and Doig (1975), caution against assuming that garnet cores were ever in equilibrium with core clinopyroxene compositions as we now find them. The changing bulk
Fig. 7. Mean temperature estimates (filled circles) and errors (horizontal bars) for Moses Rock eclogites. Temperature in °C. The error is calculated from ± 1 σ values in $X_{\text{Mg}}$ for garnet and clinopyroxene rims and hence is purely analytical and sampling error. Temperatures are calculated for $P = 10$ kbar using the Ellis-Green thermometer (Ellis and Green, 1979)

composition through time implied by clinopyroxene zoning complicates the interpretation of garnet zoning by introducing another undefined variable, i.e. $X_{\text{bulk}}, P, T, p_{\text{H}_2\text{O}}, f_{\text{O}_2}$. Equilibration temperatures indicated by garnet-clinopyroxene rim $K_D$ values for the large group of eclogites with almandine rich garnets with pronounced Ca-zoning are consistent between samples, with unusually high (418-501°C) or low (402-339°C) temperatures probably resulting from errors in acmite calculation. The omphacite-pyrope eclogites (415, 398) have formed at 600°C for an assumed pressure of 10 kbar. The samples (407, 400, 401, 413) with garnets zoning into “group B” (Fig. 1) give rim temperatures of 460°C-620°C. Three of these samples (407, 400, 401) provide the clearest indications for temperature increase during metamorphism (Table 3), although it is difficult to assume internal equilibrium for these samples if we recognize the evidence for disequilibrium presented above and the inconsistencies in thermometry produced by the assumption of equilibrium in many of the samples.
Evolution of the Assemblages

1. Omphacite-Pyrope Eclogites

The primary mineral assemblage in these rocks consists of essentially unzoned omphacite and pyropic garnet (Fig. 1). The calculated temperatures of formation at 10 kbar for these rocks are 500–640°C (Ellis-Green geothermometer), although a pressure of formation of greater than 10 kbar is likely.

In these eclogites a secondary assemblage of Mg chlorite plus sodic pyroxene ($Jd_{50}$) and a second, more calcic, garnet has formed, resulting in a higher $K_D^{Ga/Cpx}$ (Fig. 4, Table 3b). This secondary assemblage, a high pressure one as indicated by the coexistence of Mg chl + ga + cpx, also records a similar temperature (560–640°C at 10 kbar) to the primary assemblage.

Helmstaedt and Schulze (1977, 1979) have reported a similar eclogite inclusion from Moses Rock, in which they recognized the reaction to the chlorite bearing assemblage and attempted to balance the reaction based on the observed compositions of the phases. While their mineral compositions are different from compositions in the samples considered here, their conclusion that the system had to be open to $H_2O$ and $Na_2O$ applies equally to these samples.

Rim $K_D^{Ga/Cpx}$ for a number of the jadeite-almandine assemblages (group C type) are in the range 12–20, overlapping with $K_D$'s for the chlorite bearing secondary assemblage in these mangesian eclogites ($K_D = 13–20$). However $X_{Ga}^{ca}$ in the chlorite assemblage is much higher than in the group C rims ($X_{Ga}^{ca} = .3$ compared with .1). Using the Ellis-Green thermometer, this calcium content implies higher temperatures of equilibration of the chlorite bearing assemblage at similar $K_D$ and $P$ (up to 130°C higher than the group C types). Thus, only the lowest $K_D$, highest $T$ jadeite-almandine eclogites overlap or approach the calculated temperatures of equilibration of chlorite secondary assemblage in the omphacite-pyrope eclogites.

Helmstaedt and Schulze (1977, 1979) propose that these omphacite-pyrope eclogites suffered hydration and retrogression when brought into contact with subducted Na rich ocean floor rocks, now represented by the jadeite-almandine eclogites occurring as inclusions in Moses Rock and elsewhere.

According to this view, the formation of the Mg chlorite-garnet-clinopyroxene assemblage occurred under the same physical conditions as the development of the jadeite-almandine rims. This generalization is not fully supported by the data herein, however, as only some of the jadeite-almandine type eclogites (407, 400, 401) appear from the geothermometry to have been subjected, during the final stages of their formation at depth, to similar $P,T$ conditions as those inferred for the chloritic eclogite assemblage. Most of the jadeite-almandine eclogites indicate lower temperatures of crystallization.
2. Jadeite/Omphacite-Almandine Eclogites

Preliminary work on zoning in similar inclusions from Moses Rock has been used to infer a $P,T$ path for a subducted slab (Råheim and Green, 1975; Ryburn, Råheim and Green, 1976; Helmstaedt and Doig, 1975). Data reported here indicates that, using the Ellis-Green geothermometer, core to rim temperature differences for most eclogites are within the error of measurement and no pressure or temperature difference need be invoked even if we select the data to conform to the "normal" zoning patterns. Detailed chemical mapping of selected pyroxene grains from our samples (Fig. 5) further indicates that assumptions of equilibrium in other than coexisting rim compositions are probably invalid. In these circumstances, only the rim temperature estimates are considered reliable.

Helmstaedt and Schultze (1977) interpreted a simple subsolidus evolution in similar type C eclogite inclusions:

(a) formation of lawsonite eclogite,
(b) growth of atoll garnets and their rings, with the growth of jadeite rich pyroxene rims,
(c) alteration of lawsonite to zoisitic assemblages.

Detailed work herein and by others (Smith and Zientek, 1979) demonstrates much more complexity in stage (b) above.

Smith and Zientek (1977, 1979), in a detailed study of zoning in some garnets and clinopyroxenes from eclogitic inclusions at Garnet Ridge have recognized:

(a) sharp compositional zoning to Mg-rich, Ca-poor bands in garnet, with Mg sometimes decreasing adjacent to the rim
(b) Mg, Ca oscillatory zoning in garnet
(c) gradational zoning to Mg-rich Ca-poor rims in another garnet,
(d) sharp, oscillatory and gradational zoning in pyroxenes.

They describe the pyroxene zoning as being mainly variation in $Di$–$Jd$, with only minor variation in $Ac$ (compare Fig. 2). In their samples, $X_{Mg}^{Pyx}$ increases from cores to rims, in agreement with most trends observed in this study.

Smith and Zientek (1979) suggest non-equilibrium growth of the assemblage in the presence of a fluid phase to account for the zoning and other textural observations. The data herein supports this interpretation and preclude the use of $K_D$ data to infer real core to rim temperature differences. From a comparison of data obtained here and by other workers, it is apparent that there is a diversity of complex zoning patterns both in the garnets and pyroxenes, which cannot be understood as yet in any simple way.

Graphical analysis of compositions of garnets and pyroxenes in these eclogites requires a change in the bulk composition of the system since no participating third phase is now present. If the phases were reacting with a
fluid phase bearing Mg, Na and Ca ions or complexes, then they can change composition with the apparent bulk composition becoming more magnesian. Smith and Zientek (1979) describe interstitial brown Mg-silicates between prismatic pyroxenes in eclogites from Garnet Ridge, and cite this as further evidence for an important fluid phase. Such a fluid phase would be of appropriate composition to produce the hydration and reaction in the omphacite-pyrope eclogites discussed above.

3. Eclogites 407, 400, 401, 413

These samples are texturally and mineralogically similar to the other jadeite-omphacite-almandine eclogites but the garnet zoning patterns are distinctive (Fig. 1). This could imply a different chemical evolution in these rocks, involving a marked temperature increase as the garnets move into the group B field. However, clinopyroxenes in these samples also show wide compositional scatter (407 and 400, Fig. 2), so that the problems of non-equilibrium previously discussed also apply to these rocks. 407 and 400 give rim temperatures of 600°C and 620°C respectively. These temperatures are higher than temperatures of other jadeite-almandine rocks at 10 kbar and the distinctive zoning in the garnets of these samples suggests slightly different metamorphic conditions (P, T). The variations in these eclogite characteristics may reflect only the variation in physical-chemical conditions across or within a glaucophane-schist belt, and do not necessarily imply any significant pressure, temperature, change down a descending crustal slab.

Status of the Descending Slab Theory

The data presented confirm the affinity of most eclogites with the type C eclogites characteristic of glaucophane schist terranes and of low temperature, relatively high pressure origin. Two samples contain pyrope-rich garnets more characteristic of mantle eclogite types. However the $K_D^{gax/cpx}$ data for both the primary mineralogy and secondary mineralogy (chlorite, garnet, omphacite) confirm temperatures of crystallization of these assemblages as being only slightly higher than but convergent with the range of temperatures of the group C eclogites. The crustal section beneath the Moses Rock diatreme includes eclogites of unusual chemical compositions ranging from low soda types to extremely sodic varieties, as indicated by clinopyroxene compositions and modal proportions (Fig. 2, Table 1). However, a detailed understanding of the prograde metamorphic path or earlier character of these rocks cannot be inferred from a study of chemical zoning patterns in coexisting garnets and clinopyroxenes. Any $P$-$T$ evolutionary
path for these eclogites has generally been obscured by compositional zonir patterns possibly resulting from metasomatic effects within individual samples.

Acknowledgements

We thank Dr. D. J. Ellis, Professor E. J. Essene, Mr. K. L. Harris and Professor W. Schreyer for their discussion and interest in this work. Mr. B. J. Griffin instructed S.L.H. in the use of the electron microprobe, and his role in the continued functioning of this facility is gratefully acknowledged.

The paper is dedicated to the late Dr. T. McGetchin who enthusiastically introduced D.H.G. to the Moses Rock diatreme and its environs in 1970.

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Garnet-forming Reactions in Mafic Granulites from Enderby Land, Antarctica—Implications for Geothermometry and Geobarometry

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ABSTRACT

This study of mafic granulites from Enderby Land, Antarctica, demonstrates the control of rock compositions upon the reactions involved in the formation of garnet by cooling through part of the pyroxene granulite-eclogite transition. The rocks were originally a sequence of cumulates precipitated from an enclosing quartz tholeiite dyke which were then metamorphosed at granulite facies conditions. Subsequent mineral reactions and compositional zoning in minerals record an unusual period of cooling of this terrain from ~ 900-600°C. No textural nor chemical evidence for further reaction between phases below this temperature has been detected.

The formation of garnet in the metamorphosed quartz tholeiite dyke is consistent with previous descriptions of plagioclase feldspar reacting with opaque oxide or orthopyroxene to form garnet and clinopyroxene or quartz with decreasing temperature. The disappearance of plagioclase feldspar in the more mafic, quartz-free rocks involves a different series of reactions in which fassaitic clinopyroxene and garnet, with or without spinel or orthopyroxene, developed. A wide range of exsolution products is found within the different original aluminous clinopyroxenes

\[
\begin{align*}
\text{Cpx}_1 & \rightarrow \text{Cpx} + \text{Opx} \\
\text{Cpx}_2 & \rightarrow \text{Cpx} + \text{Opx} + \text{Gt} \\
\text{Cpx}_3 & \rightarrow \text{Cpx} + \text{Gt} \\
\text{Cpx}_4 & \rightarrow \text{Cpx} + \text{Gt} + \text{Plag} + \text{Mt} \\
\text{Cpx}_5 & \rightarrow \text{Cpx} + \text{Plag} + \text{Mt} + \text{Ilm} + \text{Qtz}.
\end{align*}
\]

The wide variety of primary metamorphic mineral assemblages as well as reaction coronas and exsolutions provides an opportunity to test the internal consistency of several geothermometers and geobarometers. Mineral pairs of higher temperature 'primary' metamorphic character which persist as stable assemblages to lower temperatures retain a record of cooling through compositional zoning, and 'closure temperatures' for different mineral pairs can be inferred. In contrast, rocks which contain mineral assemblages such that cooling to even lower temperature produced newly formed secondary phases, record in these newly formed mineral pairs equilibration temperatures well below these closure temperatures for cation exchange between zoned, primary phases. Although individual thermometers indicate a wide range in temperatures for the different generations of assemblages (≥ 900–600°C), there is excellent agreement in temperature estimates for each mineral assemblage using different geo-thermometers (Fe²⁺–Mg exchange in Gt–Cpx, Gt–Opx, Opx–Cpx; Ca–Mg exchange in Opx–Cpx). These features can be used to deduce a segment of the P–T-time cooling history of this granulite terrain, a distinctive feature of which is the considerable cooling interval near the base of the crust with only slight uplift following the peak metamorphism.

The mineral assemblages at this one small outcrop are similar to the garnet pyroxenite and granulite suite of xenoliths found in some basaltic diatremes (e.g. Lovering & White, 1969) which is consistent with Lovering & White's (1969) and Irving's (1974) interpretation that such apparently varied suites of xenolith types could all have formed within a very spatially restricted area.

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INTRODUCTION

A distinctive feature of the Napier Complex granulites of Enderby Land Antarctica is the 'near isobaric' cooling following the peak metamorphism (8-10 kb, 900-980 °C) which this terrain underwent (Ellis, 1980). This cooling to \( \approx 600 \) °C was not accompanied by any regional penetrative deformation and resulted in the formation and preservation of a wide range in secondary mineral assemblages as well as compositional zoning in primary minerals. Mineral assemblages and reactions in the pelitic rocks are described elsewhere (Ellis et al., 1980; Ellis, 1980) and this paper presents the petrology of the mafic granulites.

A fundamental question in metamorphic petrology is whether \( P-T \) estimates record the conditions of formation of a mineral assemblage as opposed to subsequent cation exchange down to much lower temperature. In particular, the extent to which various geothermometers reflect the temperature of formation of a mineral assemblage depends upon intercrystalline diffusion rates. Diffusion rates should vary for different mineral systems and also depend upon initial temperatures of metamorphism and the subsequent cooling rate (e.g. Lasaga, 1983). Rocks metamorphosed at temperatures above a given closure temperature (\( T_c \) for a given cooling rate) for cation exchange in a particular mineral pair may retain a record of cooling to this closure temperature, but will show no evidence of cooling below this temperature.

There now exist a number of reasonably accurate geothermometers and geobarometers which can be applied to the Antarctic granulite terrain. The successive development of at least three petrographically distinct mineral assemblages as well as compositional zoning in primary minerals during cooling can be used to examine the internal consistency of various geothermometers. The rocks also record differences in closure temperatures to cation diffusion in mafic granulites.

GEOLOGICAL SETTING

This paper describes an ultramafic pod of pyroxenite and garnet pyroxenite within a basaltic dyke metamorphosed in granulite facies from the Archaean Napier Complex of Enderby Land, Antarctica. The rocks were collected by Ellis and geologists of the Australian Bureau of Mineral Resources during a regional mapping program with the Australian National Antarctic Research Expedition in the 1976-1977 summer field season.

Enderby Land is part of the Precambrian East Antarctic Shield and consists of high-grade metamorphic rocks forming the Napier and Rayner Complexes (Ravich & Kamenev, 1972, 1975; Sheraton et al., 1980). The Napier Complex has an extensive Archaean geological history with ages ranging from 3700 Ma to 2500 Ma (Black & James, 1983) whereas the adjacent Rayner Complex includes some remetamorphosed Napier Complex rocks and appears to have formed about 1000 Ma ago.

The Napier Complex rocks are significantly higher metamorphic grade than those of the Rayner Complex (Sheraton et al., 1980) and consist of pyroxene-quartz-feldspar gneiss, with subordinate mafic granulite, pyroxenite and a variety of siliceous, aluminous and ferruginous metasediments (Sheraton et al., 1980). Osumilite, sapphirine-quartz, spinel-quartz and hypersthene-sillimanite-quartz are present in the aluminous sediments and are described elsewhere (Sheraton et al., 1980; Ellis et al., 1980; Ellis, 1980; Grew, 1980). Systematic regional variations exist in the distribution of these mineral assemblages as well as in the occurrence of garnet in the mafic rocks (see Sheraton et al., 1980). Primary garnet is generally absent from mafic granulites associated with these high temperature aluminous mineral assemblages in the centre of the Napier Complex, but occurs away from these areas such as the Amundsen Bay–Casey Bay area, described here.
At least five different generations of mafic dykes have been recognized in the Napier Complex (Sheraton et al., 1980), the youngest of which are not metamorphosed. The mafic rocks described here outcrop on the unnamed nunatak at the northern end of Wyers Ice Shelf near the western shore of Amundsen Bay (49° 50' E, 67° 07' S, Fig. 1). They comprise a 4-5 metre wide boudin in a basic gneiss, the foliation of which is parallel to that of the enclosing foliated quartz-feldspar granulites. The boudin consists largely of coarse-grained clinopyroxenite and subordinate finer grained pyroxenite and garnet clinopyroxenite. At the margins of the pod are irregular bands of similar rock types, which in addition contain some plagioclase. These plagioclase-bearing varieties consist of porphyroblasts of clinopyroxene set in a finer grained pyroxene-feldspar assemblage. The enclosing basic gneiss contains folded lenticular layers of garnet orthopyroxenite, which are up to 5 cm thick and about 30 cm in length. A thin layer of sapphirine-bearing granulite occurs at the contact between the basic gneiss and the quartz-feldspar granulites. The sapphirine-bearing assemblage is separated from the quartz-bearing rocks by a thin zone of orthopyroxene.

PETROLOGY

1. The basic gneiss

This rock consists of clinopyroxene, orthopyroxene, garnet, plagioclase feldspar, quartz, opaque minerals and minor biotite and amphibole. The opaque oxide consists of ilmenite and lesser magnetite which have exsolved haematite and hercynite respectively. Medium to coarse grained plagioclase and pyroxene have amoeboid grain boundaries and undulose
FIG. 2A. Thin section photograph of the basic gneiss (77284029) showing a corona of garnet with quartz inclusions surrounding magnetite and ilmenite (black) where originally in contact with plagioclase feldspar (light grey). Plane polarised light. Width of plate is 3·5 mm.

FIG. 2B. Thin section photograph of coexisting spinel (dark grey) and magnetite (black), together with thin exsolution lamellae of spinel in the magnetite. Garnet corona surrounds the spinels. Sample 77284028. Plane polarised light. Width of plate is 3·5 mm.
FIG. 2C. Thin section photograph of garnet exsolution lamellae in clinopyroxene, garnet clinopyroxenite sample 77284022. Cross polarised light. Width of plate is 1·5 mm.

FIG. 2D. Thin section photograph of idiomorphic garnet inclusions in clinopyroxene, together with a second generation of garnet exsolved from the clinopyroxene. Note the zones of clinopyroxene devoid of exsolutions near the idiomorphic garnet. Sample 77284022. Cross polarised light. Width of plate is 3·5 mm.
extinction. The plagioclase contains rounded inclusions of quartz. The pyroxenes have rare exsolution lamellae and recrystallized, strain free margins of fine-grained pyroxene. One large clinopyroxene porphyroblast contains lamellae of plagioclase, quartz, magnetite and ilmenite aligned along the (100) direction of the host clinopyroxene.

Garnet is present as coronas around the Fe-oxides and orthopyroxene where these minerals were originally in contact with plagioclase. The garnet coronas around orthopyroxene contain fine-grained inclusions of clinopyroxene and those around the Fe-oxides contain vermicular inclusions of quartz (Fig. 2A). The Fe-oxides do not have garnet reaction rims where they abut against clinopyroxene.

A chemical analysis of this rock is given in Table 1 (sample 77284029). The composition is similar to a quartz tholeiite, with 1-15 per cent quartz in the CIPW norm, and a low K$_2$O content. It is somewhat similar in composition to the quartz tholeiites A and B of Green & Ringwood (1967), though more iron-rich (Mg/(Mg + Fe$^{2+}$) = 0.50 compared to 0.61).

Representative mineral analyses are given in Table 2. The plagioclase is only slightly zoned (Or$_{1.7}$Ab$_{48.2}$An$_{50.8}$-Or$_{2.2}$Ab$_{50.8}$An$_{47.0}$). The orthopyroxene (En$_{56}$) has high iron and low Al$_2$O$_3$ contents (1-2-1-9 wt. per cent) (Fig. 3), and the clinopyroxene is rich in FeO, Na$_2$O and TiO$_2$, and has low Al$_2$O$_3$. Plagioclase (An$_{52}$) exsolved from clinopyroxene is similar in composition to that in the rest of the rock. Average electron microprobe beam area-scan analyses of the clinopyroxene together with the exsolved plagioclase, quartz and opaque oxides (Table 6) show that the original pyroxene had higher CaO, Al$_2$O$_3$ and Na$_2$O contents (5.8 per cent jadeite and 8.7 per cent Ca-Tschermaks molecule). Garnet is present as reaction rims around opaque oxides, and is more iron-rich (Mg/(Mg + Fe$^{2+}$) = 0.25) than that from the

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**Fig. 2E** Thin section photograph of idiomorphic garnet inclusion in clinopyroxene. The clinopyroxene has exsolved lamellae of twinned plagioclase (grey-white colour with twinning at a high angle to lamellae length) and lamellae of garnet (black). Note the zones of clinopyroxene devoid of exsolutions near the idiomorphic primary garnet. The primary garnet has rounded inclusions of plagioclase. Sample 77284027. Cross polarised light. Width of plate is 3.5 mm.
Table 1

Rock analyses

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CIPW norm

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<td>0.131</td>
<td>0.343</td>
<td>0.039</td>
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<tr>
<td>Fe²⁺</td>
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<td>0.442</td>
<td>0.405</td>
<td>0.148</td>
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<tr>
<td>Mn</td>
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<td>0.012</td>
<td>0.030</td>
<td>0.011</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.887</td>
<td>0.805</td>
<td>0.589</td>
<td>0.667</td>
<td>0.379</td>
</tr>
<tr>
<td>Ca</td>
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<td>0.785</td>
<td>0.391</td>
<td>0.618</td>
<td>0.824</td>
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</tr>
<tr>
<td>Na</td>
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<td>0.011</td>
<td>0.035</td>
<td>0.043</td>
<td>0.064</td>
<td>0.169</td>
</tr>
<tr>
<td>K</td>
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<td>—</td>
<td>0.016</td>
<td>0.012</td>
<td>0.004</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Cation sum

| 4.034| 3.999| 4.046| 4.081| 3.977| 3.869|

| 100 Mg/(Mg + Fe²⁺) | 73.5 | 81   | 63.3 | 58.6 | 81.8 | 50.2 |

1. Pyroxenite 77284023*.
2. Clinopyroxenite 77284019.
4. Garnet clinopyroxenite 77284023.
5. Plagioclase pyroxenite 77284025.
6. Sheared basic gneiss 77284029.

* Registered Bureau of Mineral Resources sample number.
n.d.—not detected.

garnet clinopyroxenite. The clinopyroxene inclusions in the garnet are more Mg-rich than the larger primary porphyroblasts in association with orthopyroxene and plagioclase (Table 2).

The ferric iron content of pyroxenes is commonly determined by charge balance considerations from probe data. A comparison between the method adopted here and
### Table 2

**Compositions of minerals in the basic gneiss**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>49.55</td>
<td>50.48</td>
<td>n.d.</td>
<td>51.29</td>
<td>55.13</td>
<td>n.d.</td>
<td>n.d.</td>
<td>37.89</td>
<td>37.60</td>
<td>51.46</td>
<td>50.88</td>
<td>51.56</td>
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<tr>
<td>TiO₂</td>
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<td>47.28</td>
<td>0.15</td>
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<td>0.85</td>
<td>48.69</td>
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<td>n.d.</td>
<td>0.23</td>
<td>0.29</td>
<td>n.d.</td>
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<tr>
<td>Al₂O₃</td>
<td>3.76</td>
<td>1.96</td>
<td>n.d.</td>
<td>2.91</td>
<td>28.41</td>
<td>n.d.</td>
<td>n.d.</td>
<td>21.63</td>
<td>21.18</td>
<td>2.28</td>
<td>1.40</td>
<td>1.37</td>
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<tr>
<td>Cr₂O₃</td>
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<td>0.11</td>
<td>n.d.</td>
<td>0.97</td>
<td>0.61</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.56</td>
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<td>10.02</td>
<td>2.63</td>
<td>n.d.</td>
<td>67.43</td>
<td>7.37</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.28</td>
<td>2.17</td>
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<tr>
<td>FeO</td>
<td>9.66</td>
<td>25.06</td>
<td>40.16</td>
<td>9.50</td>
<td>n.d.</td>
<td>32.21</td>
<td>42.09</td>
<td>26.82</td>
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<td>6.45</td>
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<tr>
<td>MnO</td>
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<td>0.14</td>
<td>n.d.</td>
<td>0.29</td>
<td>0.77</td>
<td>0.91</td>
<td>n.d.</td>
<td>0.99</td>
<td>n.d.</td>
<td>0.19</td>
<td>n.d.</td>
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<tr>
<td>MgO</td>
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<td>19.07</td>
<td>1.26</td>
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<td>n.d.</td>
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<td>4.57</td>
<td>3.75</td>
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<td>CaO</td>
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<tr>
<td>Na₂O</td>
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<td>0.42</td>
<td>5.91</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.39</td>
<td>0.27</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Total SiO₂ 100.36 100.20 99.03 100.26 99.71 101.75 100.06 100.00 100.00 100.23 100.19 100.11

- 1. Cpx core, sheared basic gneiss 77284029 (core of coexisting Plag—An₄₈).
- 2. Opx core, sheared basic gneiss 77284029.
- 3. Ilmenite, sheared basic gneiss 77284029.
- 4. Cpx which has exsolved Plag and opaque oxides + quartz 77284029.
- 5. Plag exsolved out of above Cpx 77284029.
- 6. Magnetite exsolved out of above Cpx 77284029.
- 7. Ilmenite exsolved out of above Cpx 77284029.
- 8. Gt reaction rim between Plag (An₄₈) and Opx 77284029, next to Cpx inclusion.
- 9. Above Gt next to Opx rim, 77284029.
- 10. Cpx inclusion in above Gt, 77284029.
- 11. Core of Opx rimmed by above Gt, 77284029.
- 12. Rim above Opx next to Gt, 77284029.

Fe³⁺ in pyroxenes determined from probe analyses using the formula Fe³⁺ = 4 - 2 Si - 2 Ti - Al - Cr + Na (see Appendix 1).

Fe³⁺ in opaque oxides determined by the methods of Carmichael (1967) from probe data.
direct determination of ferrous and ferric iron contents in pyroxenes is presented in Appendix 1.

2. The pyroxenite websterite

The pyroxenite, which occurs with the clinopyroxenite and garnet clinopyroxenite in the boudin, is a dense, coarse-grained, brown-black coloured rock. It consists of even grained orthopyroxene and clinopyroxene (av. 0.5 cm grain size) with triple point grain boundaries. Orthopyroxene is pleochroic (pink-pale green) and contains very fine exsolution lamellae believed to be of assumed clinopyroxene. Rare kinkbands and minor amount of recrystallization along grain boundaries are also developed. Medium and fine-grained magnetite and green spinel are present along the recrystallized grain boundaries.

A chemical analysis of one pyroxenite sample (Table 1, sample 77284023) shows that it has low Na$_2$O, TiO$_2$ and Al$_2$O$_3$ and a high MgO content (Mg/(Mg$\text{+}$Fe$^\text{2+}$) = 0.73).

Representative mineral analyses for two pyroxenite samples are given in Table 3. They differ slightly in Mg/(Mg$\text{+}$Fe) ratio. The clinopyroxene has low Al$_2$O$_3$, Na$_2$O and TiO$_2$ contents and is essentially a diopside-enstatite-hedenbergite solid solution with only a minor amount of Ca-Tschermaks component (3-7 mol. per cent CaAl$_2$SiO$_6$, using the method of Kushiro, 1962). The orthopyroxene is a bronzite (En$_{75-76}$) with low CaO and Al$_2$O$_3$ contents.

3. The clinopyroxenite

The clinopyroxenite is a coarse-grained, very dark green rock composed mainly of large clinopyroxenes with well developed cleavage traces (average grain size is 1 to 2 cm). In thin section it consists of clinopyroxene, very rare orthopyroxene with amoeboid grain boundaries, and finer grained (av. 0.1 mm) recrystallized margins of clinopyroxene, orthopyroxene and pargasitic hornblende. The large clinopyroxenes contain broad exsolution lamellae of orthopyroxene (0.05 mm wide) which usually do not extend to the recrystallized rims of the clinopyroxenes. The lamellae have numerous transverse cracks in them, a feature
which has been noted in exsolutions from clinopyroxene inclusions from the Delegate basalt pipe (Irving, 1974). A minor amount of fine-grained magnetite is present, mainly along grain boundaries.

The analysed sample of clinopyroxenite (Table 1) has low alkalies (0.16 wt. per cent Na₂O), TiO₂, Al₂O₃ and high CaO and Fe₂O₃ contents. This is reflected in its CIPW norm which has high Di and Hy and only 7 per cent An and 1 per cent Ab.

Mineral analyses for the clinopyroxenite are given in Table 3. The host clinopyroxene between the exsolved lamellae of orthopyroxene is very similar in composition to that of the pyroxenites, and contains only 5 mol. per cent Ca-Tschermak’s molecule. However the exsolved orthopyroxene lamellae (En₇₀₋₇₂) are more iron-rich than the orthopyroxene from the pyroxenites (Fig. 3). The original clinopyroxene, prior to exsolution, would have been less calcic and more iron-rich and contained less Al₂O₃ (Table 6).

4. The garnet clinopyroxenite

The nomenclature for these rocks follows that adopted by Irving (1974). Lovering & White (1969) used the term fassaite eclogite for somewhat similar rocks characterized by Na₂O-poor clinopyroxenes which are found as xenoliths within the Delegate nephelinite
pipe. The term eclogite usually has the connotation of a jadeite-rich (omphacitic) pyroxene, whereas the Antarctic clinopyroxenes are sodium-poor diopsides, salites, aluminous augites and fassaites (using the terminology of Clarke & Papike, 1968). Also, as these rocks did not equilibrate in the 'eclogite facies' as defined by Green & Ringwood (1967), but at lower pressures, the non-genetic term garnet clinopyroxenite is preferred.

In hand specimen the garnet clinopyroxenites are medium grained (1-2 mm) equigranular rocks consisting mainly of pink-red garnet and black clinopyroxene. In thin section they consist of granular pyroxene and garnet, mainly with triple point grain boundaries. Garnet is sometimes present as idiomorphic inclusions in the clinopyroxene. Patches free of garnet tend to have coarser grained clinopyroxene. A minor amount of orthopyroxene is locally present. Granular, green spinel and magnetite have coronas of garnet separating them from the clinopyroxene. Original coexisting spinel-hercynite and magnetite have coronas of garnet. The magnetite also contains later exsolved green spinel (Fig. 2B). The pale green clinopyroxenes contain a variety of exsolution products. Clinopyroxene in small grains and at contacts with garnet tends to be devoid of exsolution lamellae.

The simplest type of exsolution product consists of lamellae and blebs of garnet oriented parallel to (110) and less commonly to (110) of the host clinopyroxene (Fig. 2C). The exsolution assemblages are garnet; garnet-plagioclase-opaque oxide; garnet-orthopyroxene-opaque oxide. The exsolved garnet and plagioclase commonly alternate along the length of an individual lamella. Where coarser grained clinopyroxenes contain idiomorphic inclusions of garnet there is an exsolution-free zone around the inclusion (Fig. 2D, E). There is commonly a thin zone of fine-grained garnet along the grain boundaries of clinopyroxenes which have exsolved garnet, possibly due to migration of the exsolved phase to grain boundaries.

Chemical analyses of two samples of garnet clinopyroxenite are given in Table 1. They have lower SiO$_2$ and higher TiO$_2$, Al$_2$O$_3$, FeO and Na$_2$O contents than the pyroxenite and clinopyroxenite. One sample is olivine-hypersthene normative, while the other has normative olivine, nepheline (2.57 per cent) and leucite (1.11 per cent) which is expressed in the mode as biotite. They do not correspond in chemical composition to basaltic rocks because of the low alkalies (0.5 wt. per cent Na$_2$O) and high magnesium and iron contents. Furthermore their compositions do not recast as stoichiometric clinopyroxenes, but are deficient in SiO$_2$, suggesting that they contained spinel prior to cooling and garnet formation. The moderate Fe$_2$O$_3$ content reflects the presence of modal magnetite in this rock.

Representative analyses of the minerals from the garnet clinopyroxenite are shown in Table 4. Compared to the pyroxenite and clinopyroxenite there is a considerable range in clinopyroxene composition in this rock type. The clinopyroxene contains a high Ca-Tschermak's content (10-16 mol. per cent). Clinopyroxenes without exsolution lamellae are zoned towards contacts with garnet. Mg/(Mg + Fe) increases and Al$_2$O$_3$ decreases from core to rim near garnet. The garnet is also zoned, but in an opposite sense, for it becomes more iron-rich towards clinopyroxene (Mg/(Mg + Fe) = 0.49-0.56 from core to rim). The garnets are largely pyrope-almandine containing about 20 mol. per cent grossular and 3 mol. per cent spessartine. These Mn contents are higher than those of the garnets from the petrographically similar garnet clinopyroxenite xenoliths in basalt pipes described by Lovering & White (1969).

The clinopyroxene near the exsolutions is of similar composition to the rims of exsolution-free clinopyroxene next to the large garnets. Microprobe beam area-scan analyses of areas of exsolution and host clinopyroxene (Table 6) indicate that there was an initial range in composition of these clinopyroxenes, as evidenced, by the different types of exsolution assemblages. The original clinopyroxenes were fassaites, with high Al$_2$O$_3$ and
**Table 4**

<table>
<thead>
<tr>
<th>Composition of minerals in the garnet clinopyroxenites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Garnet core, garnet clinopyroxenite 77284028.</td>
</tr>
<tr>
<td>2. Cpx core, garnet clinopyroxenite 77284028.</td>
</tr>
<tr>
<td>5. Garnet exsolution lamellae, garnet clinopyroxenite 77294021.</td>
</tr>
<tr>
<td>6. Cpx host which has exsolved Gt + Gpx + Mt. Garnet clinopyroxenite 77294021.</td>
</tr>
<tr>
<td>7. Opx exsolution lamellae, garnet clinopyroxenite 77284021.</td>
</tr>
<tr>
<td>8. Mt exsolution lamellae, garnet clinopyroxenite 77284021.</td>
</tr>
<tr>
<td>9. Garnet exsolution lamellae, garnet clinopyroxenite 77284022.</td>
</tr>
<tr>
<td>10. Cpx host to above exsolution lamellae, garnet clinopyroxenite 77284022.</td>
</tr>
</tbody>
</table>

**Tables**

<table>
<thead>
<tr>
<th>Cations</th>
<th>Molar Ratios</th>
<th>Cations</th>
<th>Molar Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1.000</td>
<td>FeO</td>
<td>0.000</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.050</td>
<td>MnO</td>
<td>0.020</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.040</td>
<td>Fe₂⁺⁺</td>
<td>0.010</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.020</td>
<td>Fe₂⁺</td>
<td>0.000</td>
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<tr>
<td>CaO</td>
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<td>FeO⁺⁺</td>
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<tr>
<td>Na₂O</td>
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<td>MgO</td>
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<td>K₂O</td>
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<tr>
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<td>FeO</td>
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<td>TiO₂</td>
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<td>Al₂O₃</td>
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<td>Fe₂⁺⁺</td>
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<td>Cr₂O₃</td>
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<td>CaO</td>
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<tr>
<td>Na₂O</td>
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<td>MgO</td>
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<td>Cations</td>
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<td>0.000</td>
</tr>
</tbody>
</table>

**Note:**
- Cations: Si, Ti, Al, Cr, Ca, Na, K, Mg, Fe, Oxygens: Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, O
- Cations: Molar Ratios: SiO₂, TiO₂, Al₂O₃, Cr₂O₃, CaO, Na₂O, K₂O, Cation
- Oxygens: SiO₂, TiO₂, Al₂O₃, Cr₂O₃, CaO, Na₂O, K₂O, Cation
- Molar Ratios: FeO, MnO, MgO, CaCO₃, O

**References:**
low Na₂O and TiO₂ contents (up to 17.9 mol. per cent Ca-Tschermak’s and less than 5.8 mol. per cent jadeite component).

The orthopyroxene which together with garnet exsolved from the clinopyroxene is more iron-rich (Mg/(Mg + Fe) ≈ 0.71) than that of the pyroxenite and clinopyroxenite (Tables 3, 4). It has a high Al₂O₃ content (4.59 wt. per cent) and a low CaO content (1 mol. per cent CaSiO₃). Garnet present as reaction rims to spinel and magnetite is more grossular and spessartine-rich (Py₃.₄Al₃.₄Gr₂.₃Sp₄.₆) than the other garnets.

The green spinel is a hercynite (Mg/(Mg + Fe²⁺) ≈ 50) with less than 2 wt. per cent Cr₂O₃. The coexisting primary hercynite and magnetite contain appreciable magnetite (4 mol. per cent) and spinel-hercynite (17 mol. per cent) in solid solution respectively. The spinel is also zoned at the edge against magnetite, being depleted in magnetite component and higher in Mg/(Mg + Fe²⁺) ratio (Fig. 4). Green spinel exsolved out of the primary magnetite has even a lower magnetite content and higher Mg/(Mg + Fe²⁺) ratio and the host magnetite is considerably depleted in spinel solid solution. These features can be explained by widening of the solvus in the FeAl₂O₄–Fe₃O₄ system at low temperature (Turnock & Eugster, 1962) and a temperature dependence to the partitioning of Fe²⁺–Mg between coexisting spinel and magnetite. It is possible that at the highest temperature of metamorphism the coexisting hercynite–magnetite formed a single phase which recrystallized at lower temperature.

![Diagram](https://via.placeholder.com/150)

**Fig. 4.** Compositions of coexisting spinel and magnetite from garnet clinopyroxenite (Table 4) plotted on a spinel-hercynite-magnetite triangular diagram. Filled circles represent area-scan analyses of large coexisting spinel and magnetite. Open circles represent zoned rims of the above spinel and magnetite pairs against each other. Triangles represent spinel exsolved from magnetite and the host magnetite, connected by dashed lines (see Fig. 2B). The location of the solvus in the hercynite–magnetite binary system (Turnock & Eugster, 1962) is indicated by the position of temperature pairs from 600–850 °C on the diagram. Method of projection: Ti removed as Fe₂TiO₄, then molecular Fe₃O₄:FeAl₂O₄:MgAl₂O₄ plotted where Al = Al + Cr.
5. *The plagioclase clinopyroxenite*

This rock consists of medium-coarse grained clinopyroxene porphyroblasts (up to 1 cm) set in medium-grained equigranular clinopyroxene and plagioclase feldspar. The plagioclase shows slight optical zoning.

A chemical analysis of this rock is given in Table 1. The clinopyroxene porphyroblasts are of similar composition to those in the matrix (Table 5). They are richer in sodium than the other analysed pyroxenes. The plagioclase is zoned from cores of \( \text{Or}_{0.8}\text{Ab}_{27.7}\text{An}_{71} \) to rims of \( \text{Or}_{0.5}\text{Ab}_{21}\text{An}_{78} \).

### Table 5

*Compositions of minerals in the plagioclase clinopyroxenite and garnet orthopyroxenite*

<table>
<thead>
<tr>
<th></th>
<th>1 Cpx</th>
<th>2 Plag</th>
<th>3 Gt</th>
<th>4 Opx</th>
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<td>32-74</td>
<td>22-67</td>
<td>4-68</td>
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</tr>
<tr>
<td>FeO</td>
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<td>n.d.</td>
<td>21-84</td>
<td>15-68</td>
<td>22-77</td>
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<td>23-60</td>
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<td>MnO</td>
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<td>0-00</td>
<td>0-21</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>MgO</td>
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<td>12-17</td>
<td>27-33</td>
<td>11-01</td>
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<tr>
<td>CaO</td>
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<td>14-57</td>
<td>3-36</td>
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<td>0-08</td>
<td>3-77</td>
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<tr>
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<td>100-00</td>
<td>100-18</td>
<td>100-00</td>
<td>100-18</td>
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</table>

1. Cpx, plagioclase pyroxenite 77284025.
2. Plagioclase, plagioclase pyroxenite 77284025.
3. Gt core, garnet orthopyroxenite 77284030.
4. Opx core, garnet orthopyroxenite 77284030.
5. Gt rim, garnet orthopyroxenite 77284030.
6. Opx rim, garnet orthopyroxenite 77294030.
7. Gt exsolved from Opx, garnet orthopyroxenite 77284030.
8. Ilmenite, garnet orthopyroxenite 7728402030.

n.d.—not detected.

6. *The garnet plagioclase clinopyroxenite*

This rock consists of clinopyroxene, garnet, plagioclase, orthoclase, spinel, and biotite. Large porphyroblasts of clinopyroxene, medium grained garnet and orthoclase are set in fine-grained plagioclase, garnet and spinel. The orthoclase has triple point grain boundaries. Spinel is mainly present as rounded inclusions in garnet and less commonly in plagioclase. Some garnet is present as thin rims around plagioclase. The larger
clinopyroxenes have exsolved garnet and plagioclase. A minor amount of biotite is also present.

7. The garnet orthopyroxenite

This rock occurs as discontinuous folded lenses in the sheared basic gneiss, separate from the boudin. It consists of equigranular hypersthene, garnet, and ilmenite, together with very rare biotite, plagioclase, and accessory zircon. It appears to be an equilibrium assemblage, with well developed triple point grain boundaries. The hypersthene contains minute needles of rutile and very rarely has sparse exsolution lamellae of garnet.

Mineral analyses are given in Table 5. The orthopyroxene has a similar Mg/(Mg + Fe) ratio to that in the clinopyroxenites, but with a lower Ca content. It is zoned, becoming more magnesium-rich (En\textsubscript{72} to En\textsubscript{75}) and Al\textsubscript{2}O\textsubscript{3} poor (4.7 to 3.7 wt. per cent) from core to rim where in contact with garnet. The garnet is also zoned, becoming more iron-rich from core to rim (Mg/(Mg + Fe) = 0.50-0.41). The opposed trends of Mg/(Mg + Fe) zoning in orthopyroxene and garnet grains is similar to that observed in the clinopyroxene-garnet pairs from the garnet clinopyroxenite. The garnets differ in composition from that in the other rock types, with lower grossular and spessartine contents (Py\textsubscript{45.7}, Alm\textsubscript{44.8}, Gr\textsubscript{8.8}, Sp\textsubscript{0.5}), which reflects the much lower Ca content of this rock, as indicated by the absence of clinopyroxene.

8. The sapphirine-phlogopite granulite

A thin zone of sapphirine-bearing rocks occurs at the boundary between the basic gneiss and the surrounding quartz-feldspar granulites. The sapphirine-bearing rocks are separated from the quartz-bearing granulites by a thin layer of orthopyroxene. The assemblages found in this zone are

\[
\text{Sapphirine-orthopyroxene-biotite } \pm \text{ plagioclase } \pm \text{ spinel}
\]

\[
\text{Orthopyroxene-quartz-plagioclase-alkali feldspar}
\]

\[
\text{Garnet-biotite-sapphirine}
\]

The green spinel is present as rounded inclusions in the sapphirine.

DEVELOPMENT OF THE MINERAL ASSEMBLAGES

A magmatic origin for the basic gneiss and enclosed pyroxenites is based on geochemical grounds as there are no relict igneous textures preserved. Three types of metamorphic textures can be distinguished petrographically, the primary-, exsolution- and corona-mineral assemblages. The primary assemblages record the early conditions of metamorphism which can thus be calculated on the basis of porphyroblast core compositions. The secondary assemblages clearly postdate the primary metamorphic mineralogy.

In some rocks the presence of the same minerals in both primary and secondary assemblages provides an opportunity to compare the consistency of different geothermometers over a temperature range (Tables 7, 8). In particular there are three generations of garnet: primary, exsolution and corona.

The primary mineral assemblages are believed to record a high temperature metamorphic event in which homogeneous coarse grained mineral assemblages equilibrated. Subsequent exsolution and corona assemblages developed in response to decreasing temperature and do not necessarily record separate metamorphic events. There are no petrographic or field criteria which allow event correlation for exsolution or corona assemblages in differing rock compositions. It is known empirically from experiments that chemical differences, for instance in Mg/Fe ratio, will cause reaction boundaries, such as garnet appearance, to be
intersected at different \( P-T \) conditions. Also, experimental evidence demonstrates that Fe-rich compositions are more reactive at lower temperatures than Mg-rich compositions. Differing intercrystalline and intracrystalline diffusion rates will also control the appearance, retention and elimination of exsolution textures in favour of granoblastic, recrystallized assemblages. A penetrative deformation and metamorphism event at low temperatures would have resulted in complete recrystallization and obliteration of all textural evidence for an earlier high temperature history and cooling path.

These petrographic observations can be quantified in terms of the thermal history of these rocks by selecting key mineral associations from the primary, exsolution, and corona assemblages on the basis of petrographic relationships.

1. **Magmatic origin of mafic rock compositions**

The pyroxenite, clinopyroxenite and plagioclase pyroxenite compositions (Table 1) are appropriate for accumulates dominated by orthopyroxene or clinopyroxene with minor olivine or spinel. The increases in \( \text{Al}_2\text{O}_3, \text{TiO}_2, \text{Na}_2\text{O} \) and \( \text{K}_2\text{O} \) and decrease in \( \text{Mg}/(\text{Mg} + \text{Fe}) \) ratio, from these rocks through the garnet clinopyroxenites to the enclosing basic gneiss, are consistent with origins as magmatic cumulates or cumulates + entrapped liquid in the enclosing basaltic body. The garnet clinopyroxenite compositions may be recast as aluminous pyroxene + magnetite-bearing spinel or as olivine + plagioclase + pyroxenes ± spinel whereas the basic gneiss approaches an evolved tholeiitic basalt composition.

2. **Mineral reactions during granulite facies metamorphism**

(i) **The basic gneiss**

Reaction coronas of garnet around olivine, opaque oxide and orthopyroxene in metamorphosed basaltic rocks have been described from many other metamorphic terrains (e.g. Gjelsvik, 1952; de Waard, 1965; Griffin, 1971; Wood, 1975; McLelland & Whitney, 1977, 1980). Coronas of garnet around spinel in silica-undersaturated mafic rocks have been described from metamorphic terrains and from granulite xenoliths in basaltic pipes (e.g. Green, 1966; Lovering & White, 1969; Griffin, 1971; Irving, 1974; Wilkinson, 1974). Reactions rims of orthopyroxene around olivine, and garnet around opaque oxide are more common than reaction coronas of garnet around orthopyroxene in granulite terrains because of the higher pressures required for the formation of the latter (Green & Ringwood, 1967).

The development of an eclogite from a pyroxene granulite or gabbro mineral assemblage proceeds via an intermediate stage in which olivine, Fe-oxide and orthopyroxene react with plagioclase to form garnet (Green & Ringwood, 1967). The plagioclase becomes increasingly sodic as a result of these reactions. The presence of garnet–clinopyroxene and garnet–quartz intergrowths as coronas around orthopyroxene and Fe-oxide respectively suggests that the following garnet-forming reactions occurred, even though quartz intergrown with garnet may suggest it is a product rather than a reactant:

\[
\text{An} + \text{Opx} = \text{Gt} + \text{Cpx}
\]
\[
\text{An} + \text{Fe-oxide} + \text{Qtz} = \text{Gt}.
\]

If each reaction was independent then the garnets would contain 33 mol. per cent grossular, with that around the Fe-oxides being free of pyrope. This is not the case, and the garnets are the same in composition for both corona types. These observations have previously been made by McLelland & Whitney (1977) in their studies of Adirondack anorthosite–charnockite suite garnet coronas. They proposed that the above sorts of
'partial' reactions be combined as a generalized reaction for the development of garnet coronas:

\[
2 \text{An} + (6 - \alpha)(\text{Mg,Fe})\text{SiO}_3 + \alpha(\text{Fe-oxide}) + (\alpha - 2)\text{SiO}_2 \leftrightarrow \text{Ca}(\text{Mg,Fe})_5\text{Al}_4\text{Si}_2\text{O}_{24} + \text{Ca}(\text{Mg,Fe})\text{Si}_3\text{O}_6
\]

where \(\alpha\) is a function of the Mg and Fe contents of the garnets and pyroxenes. However, garnet + quartz coronas were not found in the Adirondack samples although the assemblage has been reported from the nearby Morin anorthosite complex in Quebec by Martignole & Schrijver (1971). The occurrence of quartz in the Enderby Land samples is equivocal in so far as it may be either a reactant or product of the garnet-forming reactions depending upon the relative amounts of Fe and Mg present. Calculations for the minerals listed in Table 2 imply that quartz should be considered a reactant using the calculation methods of McLelland & Whitney (1977), even though petrographic criteria would suggest that quartz intergrown with garnet in coronas around opaque oxide is a product.

The generalized reaction above treats iron oxides simply as a source of FeO, and neglects the role of TiO\(_2\) and Fe\(_2\)O\(_3\). Simplified reactions between anorthite and ulvospinel or ilmenite require the respective development of ilmenite and rutile as the products of garnet formation:

\[
\text{An} + \text{Usp} + \text{Qtz} = \text{Gt} + \text{Ilm}
\]

and

\[
\text{An} + \text{Ilm} + \text{Qtz} = \text{Gt} + \text{Rutile}.
\]

However in the presence of Fe\(_2\)O\(_3\) in the opaque oxides reactions take place as a function of \(f_0_2\):

\[
\text{An} + \text{Usp} - \text{M}t_{ss} + \text{Qtz} = \text{Gt} + \text{Usp} + \text{O}_2
\]

and

\[
\text{An} + \text{Ilm} - \text{Hm}_{ss} + \text{Qtz} = \text{Gt} + \text{Ilm} + \text{O}_2.
\]

Although we are not certain whether magnetite or ilmenite was the reactant, it appears that an initial Ilm-Hm\(_{ss}\) reacted with plagioclase and quartz to form a less haematite-rich ilmenite surrounded by newly formed garnet intergrown with relic quartz. At still lower temperature the ilmenite exsolved magnetite.

The opaque oxides did not react with clinopyroxene, which suggests that reactions did not continue to sufficiently low temperature such that the following reaction could occur (Banno & Green, 1968):

\[
2 \text{Ab} + \text{Mt} + \text{Di} = 2 \text{Acmite} + \text{Gt} + \text{Qtz}.
\]

The development of an appreciable acmite content in eclogite clinopyroxenes is restricted to temperatures below that of this reaction, as in glaucophane schist terrains (e.g. Church, 1967; Black, 1974). Clinopyroxenes from granulate facies terrains such as Enderby Land are characterized by high Ca-Tschermak and low jadeite contents (see White, 1964; Kushiro, 1969).

(ii) The metamorphosed cumulates

The metamorphosed cumulates provide an excellent example of the effects of slight differences in bulk rock compositions upon the mineral reactions and development of different mineral assemblages in mafic rocks under granulate facies metamorphism. The reactions differ from those in the basic gneiss in that quartz did not take part in garnet formation at the highest temperature \(T_1\) of metamorphism in these silica-undersaturated, Mg-rich rocks.
Table 6

*Pre-exsolution high temperature pyroxene compositions determined by area scan analyses of host clinopyroxene and exsolutions.*

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*Cations on the basis of 6 oxygens*

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1. Clinopyroxene (Cpx + Opx), clinopyroxenite 77284019.
2. Clinopyroxene (Cpx + Opx + Gt + Plag), garnet clinopyroxenite 77284021.
3. Clinopyroxene (Cpx + Gt), garnet clinopyroxenite 77284020.
4. Clinopyroxene (Cpx + Gt + Plag), garnet-plagioclase pyroxenite 77284027.
5. Clinopyroxene (Cpx + Plag + Qtz + Opaque), sheared basic gneiss 77284029.

n.d.—not detected.

At the peak of metamorphism (T₁) the igneous cumulate assemblages (Opx + Cpx + O1 + Plag + Sp) reacted to form a variety of garnet-bearing assemblages. Coexisting pyroxenes in the Mg-rich websterites readjusted by recrystallization and decrease in mutual solid solution due to expansion of the pyroxene miscibility gap with decreasing temperature. The reactions which occurred in the more Fe, Na and Al-rich, Fe-oxide and plagioclase-bearing cumulates can be explained by the following reactions:

\[
\text{Opx + (Sp-Mt)ss + Plag} \rightarrow \text{Gt + Cpx + Spinel}
\]
\[
\text{An + Olivine + Magnetite + Opx} \rightarrow \text{Gt + Cpx + Spinel.}
\]

The resultant mineral assemblages formed at T₁ are shown in Table 7. The clinopyroxenes are characterized by a high Ca-Tschermak (CaAl₂SiO₆) content. Garnet and clinopyroxene
Magmatic (inferred) and metamorphic (observed) mineral assemblages at the different stages of evolution of the mafic granulites at 8–9 kb pressure

Table 7

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<td>Opx + Cpx</td>
<td>Cpx + Gi (± Sp ± Opx)</td>
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<tr>
<td>Opx + Cpx + Plag + Mt</td>
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<th>Metamorphic texture</th>
<th>Primary porphyroblasts</th>
<th>Exsolution lamellae in primary porphyroblasts and mineral coronas in pyroxenites</th>
<th>Mineral coronas in basic gneiss and opaque oxide intergrowths</th>
</tr>
</thead>
<tbody>
<tr>
<td>(± spinel)</td>
<td>(area scans of core compositions)</td>
<td>Cpx Gi Qtz Plag (Opx, Mt, Ilm)</td>
<td></td>
</tr>
</tbody>
</table>

(± spinel) coexist with either orthopyroxene or plagioclase, but not both, depending upon the initial proportions of reactant phases.

Upon cooling from this main metamorphism the pyroxenites readjusted in mineral composition by exsolution due to continued expansion of the pyroxene miscibility gap. The garnet clinopyroxenites readjusted by Fe–Mg cation exchange and unmixing. Fe–Mg cation exchange between the rims of adjacent garnets and clinopyroxenes resulted in them becoming more Fe- and Mg-rich respectively, towards the grain contacts. This resulted in the $(K_{Gt},(Fe/Mg)_{Gt},(Mg/Fe)_{Cpx}$ increasing from core to rim.

The aluminous, fassaitic clinopyroxenes formed at $T_1$ readjusted in composition on cooling by a wide variety of unmixing processes (Table 7). This is due to the decreased solubility of aluminium in clinopyroxene in quartz-deficient assemblages with decreasing temperature (see Herzberg, 1978a, b).

Of particular interest is the development of a second generation of plagioclase feldspar in the exsolution products. At high temperatures (metamorphic $T_1$), igneous plagioclase reacted to form an aluminous clinopyroxene and garnet, but at lower temperatures there is a marked decrease in the solubility of $Al_2O_3$ in clinopyroxene, resulting in the clinopyroxenites readjusting to less aluminous compositions. Slight differences in the original pyroxene compositions have caused subtle but important differences in the exsolution product assemblages (Table 6, Fig. 5). In the CaO–MgO–$Al_2O_3$–SiO$_2$ system, reactions involving plagioclase are univariant but in systems with Na$_2$O and FeO reactions occur over a broad temperature interval, and changes in temperature are reflected by changes in mineral compositions. For example, the Ca content of garnet varies among the different assemblages.

The stability of the garnet–plagioclase tie-line shown in Fig. 5 is consistent with granulite facies conditions of metamorphism, rather than the eclogite stability field where the garnet–plagioclase tie-line (grossular poor garnet) is broken because of the stability of coexisting clinopyroxene–kyanite (O'Hara, 1960; Green & Ringwood, 1967). High temperature ($T_1$) clinopyroxene, which exsolved only orthopyroxene at lower temperature had relatively low $Al_2O_3$ content compared to those which exsolved either garnet or plagioclase (Table 6). Those which exsolved both garnet and orthopyroxene were more Mg-rich than those which exsolved only garnet. Similarly, those which exsolved both garnet and plagioclase were more Ca- and Al-rich.
Subsolidus unmixing of an aluminous clinopyroxene can also explain the development of the plagioclase clinopyroxenite. A chemical analysis of this rock (Table 1) recalculates on the basis of six oxygen atoms per formula unit to a stoichiometric clinopyroxene, somewhat similar in composition to the clinopyroxene in the garnet clinopyroxenites (with 9 mol. per cent Ca-Tschermak and 1.5 mol. per cent jadeite content). Direct and inferred evidence for such unmixing processes in clinopyroxenes has been presented for xenoliths in basalts (e.g. Green, 1966; Lovering & White, 1969; Wilkinson, 1974), and more rarely from other granulite terrains (e.g. Griffin, 1971; Battey & Davidson, 1977). The Antarctic granulite samples are more Fe-rich and contain less Na and Al than the xenolith samples however.

Lovering & White (1969) described samples in which garnet, orthopyroxene and spinel were exsolved from clinopyroxene. They inferred that other granulate xenoliths in the Delegate basalt had developed by unmixing from originally aluminous clinopyroxenes

\[ \text{Cpx}_1 \rightarrow \text{Cpx}_2 + \text{Spinel} + \text{Opx} \]

which at lower temperatures exsolved further

\[ \text{Cpx}_2 \rightarrow \text{Py} - \text{Gr} \text{Gt} + \text{An} \]

Also

\[ \text{Cpx} \rightarrow \text{Cpx} + \text{Opx} + \text{Sp} + \text{An} \]
\[ \text{Cpx} \rightarrow \text{Cpx} + \text{Gt} \]
They state (p. 41) that quartz or anorthite should be a by-product of spinel exsolution from an aluminous clinopyroxene, but observed neither. The Antarctic clinopyroxenes provide an example of such a reaction. Also, the variety of exsolutions and mineral assemblages present in the xenoliths of the Delegate basalt pipe and elsewhere, have been inferred to have all equilibrated under similar $P\cdot T$ conditions (see Lovering & White, 1969; Irving, 1974). The Antarctic granulites provide direct evidence that with small compositional differences in original mineral compositions, a wide range of mineral assemblages can develop through subsolidus unmixing under isofacial conditions.

Garnet is believed to have developed at the highest temperatures of metamorphism in the metamorphosed cumulates, but only at lower temperature in the quartz tholeiite dyke. This is consistent with experimental studies of garnet formation in both the simple system Fo–An (Kushiro & Yoder, 1966) and complex systems (Green & Ringwood, 1967). In rocks of a basaltic composition, Na-rich feldspar is stable to higher pressures than a Na-poor feldspar. Feldspar-free pyroxenites are not formed as transitional assemblages between basalt and eclogite at temperatures below 1100 °C. In contrast, silica undersaturated compositions with less Na$_2$O, such as the Antarctic cumulates, in which anorthite-rich plagioclase and spinel may be present, can develop a pyroxenite assemblage. Green & Ringwood (1967) also note that in magnesian compositions the reaction products are aluminous pyroxene–spinel, whereas increasing iron content in basalt suppresses this intermediate assemblage in favour of garnet–pyroxene–plagioclase (such as the metamorphosed quartz-tholeiite dyke). The most favourable compositions for producing transitional assemblages of pyroxenes and minor spinel have a very high Mg/(Mg + Fe) ratio, normative olivine and a very low albite content, such as the Loch Duich 'eclogite' described by Mercy & O'Hara (1968) or the metamorphosed Antarctic cumulates. Similarly the reaction of aluminous orthopyroxene and clinopyroxene with spinel to form garnet is consistent with experimental studies on the simple system 1:1 anorthite:forsterite and on a xenolith from the Delegate pipe (Kushiro & Yoder, 1966; Irving, 1974).

The development of extensive unmixing in the clinopyroxenes of the metamorphosed cumulates, and their higher Al$_2$O$_3$ contents compared to the clinopyroxenes from the basic gneiss can be explained in terms of the differing effect of temperature on the solubility of Al$_2$O$_3$ in clinopyroxene from the different assemblages. At temperatures above that of the development of garnet in the basic gneiss, the solubility of aluminium (as CaAl$_2$SiO$_6$−Ca-Tschermak's molecule) in clinopyroxene coexisting with plagioclase and quartz (and not garnet) can be described by the reaction:

$$\text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{CaAl}_2\text{Si}_2\text{O}_6 + \text{SiO}_2.$$ 

In quartz deficient assemblages such as the garnet clinopyroxenites, which contain a more fassaitic clinopyroxene, the equilibrium between garnet and clinopyroxene can be described by

$$\text{Ca}_2\text{MgAl}_2\text{Si}_3\text{O}_{12} \rightleftharpoons \text{CaMgSi}_2\text{O}_6 + \text{CaAl}_2\text{Si}_2\text{O}_6.$$ 

The anorthite reaction is considered by Ellis (1980) and the garnet reaction has been studied by Herzberg (1978a, b). At $\approx 10$ kb pressure, the solubility of CaTts defined by the anorthite reaction is largely independent of temperature whereas that defined by the garnet reaction is much more temperature dependent, and decreases with decreasing temperature (see Herzberg, 1978a, fig. 7). This explains the higher Al$_2$O$_3$ contents and widespread development of exsolutions in the clinopyroxenes from the metamorphosed cumulates compared to the metamorphosed quartz tholeiite.
TEMPERATURES AND PRESSURES OF METAMORPHISM

Initial temperatures of crystallization of the mafic cumulates and solidification of the basaltic dyke are inferred to be \( \approx 1100^\circ C \) (at 10 kb pressure) by comparison with the experimental data of Green & Ringwood (1967). Temperatures and pressures of mineral equilibration during the subsequent granulite facies metamorphism and deformation, as well as the later development of secondary metamorphic assemblages can be estimated by a number of methods. The coincidence in \( P-T \) estimates based on these independent methods for each individual mineral assemblage provides evidence for the reliability of these geothermometers and geobarometers for metamorphic terrains.

Temperatures have been calculated by using \( Fe^{2+}-Mg \) exchange reactions between garnet-clinopyroxene, garnet-orthopyroxene, orthopyroxene-clinopyroxene; \( Ca-Mg \) exchange between orthopyroxene-clinopyroxene; ulvospinel-magnetite and ilmenite-hematite equilibria. Temperature estimates based on coexisting plagioclase and alkali feldspar (Stormer, 1975) are too inaccurate for K-feldspars with low Ca contents and have not been employed (Powell & Powell, 1977).

The \( Ca-Mg \) miscibility gap between coexisting Opx and Cpx has been widely used in geothermometry. Lindsley (1983) has shown that the commonly used Wells (1977) thermometer considerably overestimates the temperatures of equilibration of \( Fe \)-rich, low temperature metamorphic pyroxenes in the light of recent experimental data. The Lindsley (1983) graphical method and that of Kretz (1982) should be employed for estimating temperatures. All three methods are reported in Table 8, as the Mg-rich composition of the Antarctic pyroxenes considerably diminishes this inconsistency. Lindsley (1983) notes that his graphical method enables the calculation of two independent temperatures based on each limb of the pyroxene solvus. Application of these two methods to the Antarctic samples confirms Lindsley's (1983) observation that for metamorphic pyroxenes the orthopyroxene gives much lower temperatures than the coexisting clinopyroxene. Lindsley (1983) states that it is unclear whether this difference reflects imprecision in the calibration of the thermometer or whether the orthopyroxenes may have undergone minor retrograde reaction that does not appear in the clinopyroxene. This problem is not apparent if temperatures are computed from the ratios of activities of \( MgSiO_3 \) in coexisting clinopyroxene and orthopyroxene. This is because the equilibrium constant \( (N_{Ca}/N_{Mg})^{Cpx} \) is changed by a trivial amount with large changes in orthopyroxene composition. For example, orthopyroxene with either 1 or 4 mol. per cent \( CaSiO_3 \) changes the temperature estimate using activity ratios (e.g. Wells's 1977 method) by only 20°C whereas the independent orthopyroxene method of Lindsley (1983) would indicate a temperature difference of 300°C, and should not be used.

Pressures were estimated using the Gt-Plag-Opx-Qtz barometer of Perkins & Newton (1981) for assemblages considered to be in equilibrium. The solubility of aluminium in orthopyroxene coexisting with garnet provides a useful means of estimating pressures. The barometer of Wood (1974) is commonly used but has recently been experimentally re-investigated by Harley & Green (1982), with particular application to granulite terrains. Pressures estimated using the Wood (1974) equation are generally 0·5 to 2 kb lower than that of the Harley & Green (1982) barometer. These barometers are based on the solubility of \( MgAl_2SiO_6 \) in orthopyroxene and erroneously low pressures are calculated if Al coupled with \( Fe^{3+} \) \((MgAlFe^{3+}SiO_6)\) is not first removed.

A similar net transfer reaction between clinopyroxene and garnet is another potential barometer:

\[
Ca_2MgAl_2Si_3O_{12} = CaMgSi_2O_6 + CaAl_2SiO_6.
\]
<table>
<thead>
<tr>
<th>Sample number</th>
<th>Assemblage</th>
<th>Temperature °C</th>
<th>Pressure kb</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>$T^1$</td>
<td>$T^2$</td>
</tr>
<tr>
<td>77284029</td>
<td>Cores of separate Cpx and Opx porphyroblasts</td>
<td>902</td>
<td>880</td>
</tr>
<tr>
<td></td>
<td>Cores of Cpx-Plag(-Qtz) porphyroblasts</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plag-Ilm-Mt-Qtz exsolves from Cpx</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gt-Cpx corona to Plag-Opx porphyroblasts.</td>
<td>614</td>
<td>616</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>77284019</td>
<td>Recrystallized Cpx and Opx porphyroblasts</td>
<td>929</td>
<td>840</td>
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<td></td>
<td>Cpx host and Opx exsolution lamellae</td>
<td>895</td>
<td>770</td>
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<tr>
<td>77284023</td>
<td>Separate Cpx and Opx grains</td>
<td>906</td>
<td>800</td>
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<tr>
<td>77284024</td>
<td>Gt reaction rim between Cpx-Plag</td>
<td>853</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separate Cpx and Opx grains</td>
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<td>790</td>
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<td>Gt with idiomorphic Cpx inclusion</td>
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<td>Gt exsolved from Cpx</td>
<td>749</td>
<td></td>
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<tr>
<td>77284021</td>
<td>Reaction rim around spinel</td>
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<td>Gt-Opx-Mt exsolved from Cpx</td>
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<td>826</td>
</tr>
<tr>
<td>77284022</td>
<td>Gt-Cpx zoned rims</td>
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<tr>
<td></td>
<td>Gt exsolved from Cpx</td>
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<td>77284027</td>
<td>Gt-Cpx cores</td>
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<td></td>
<td>Gt-Cpx zoned rims</td>
<td>750</td>
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<td>Gt exsolved from Cpx</td>
<td>776</td>
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<td>77284028</td>
<td>Gt-Cpx cores</td>
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<tr>
<td></td>
<td>Gt-Opx zoned rims</td>
<td>691</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gt exsolved from Opx</td>
<td>653</td>
<td></td>
</tr>
</tbody>
</table>

T$^1$  Gt-Cpx geothermometer of Ellis & Green (1979).
T$^3$  Opx-Cpx geothermometer of Wells (1977).
T$^4$  Op$\times$-Cpx geothermometer of Lindsley (1983); Cpx limb of solvus only used.
T$^5$  Opx-Cpx Ca-Mg geothermometer of Kretz (1982).
T$^6$  Opx-Cpx Fe-Mg geothermometer of Kretz (1982).
T$^7$  Usp-Ilm $T^f_0$, method of Spencer & Lindsley (1981).
P$^1$  Gt-Opx geobarometer of Harley & Green (1982).
P$^3$  Cpx-Plag-Qtz geobarometer of Ellis (1980).
a  Temperature of 900°C used in calculation.
b  Temperature of 646°C used in calculation.
c  Pressure based on zoned rim of Opx next to secondary garnet.
d  650-610—range in $T$ based on Fe$^{2+}$ and $\Sigma$Fe as FeO used respectively in calculation.
Herzberg (1978a, b) developed a thermodynamic model for this reaction, but application to the Antarctic garnet pyroxenites implies pressures of minus 13 kb. Pressures estimated by this equation change greatly with small changes in temperature, so that it cannot be used as an accurate barometer for crustal rocks.

Pressures can also be estimated from the concentration of Ca-Tschermak molecule in clinopyroxene coexisting with plagioclase and quartz (Wood, 1977):

$$\text{CaAl}_2\text{Si}_2\text{O}_8 = \text{CaAl}_2\text{Si}_6\text{O}_{16} + \text{SiO}_2.$$  

The equation of Ellis (1980) has been used for both primary porphyroblasts of plagioclase-clinopyroxene-quartz and also for plagioclase-quartz-opaque oxides exsolved out of clinopyroxene in the basic gneiss. This provides a good barometer as the equilibrium constant is largely insensitive to temperature at about 10 kb.

A guide to pressures can be estimated by comparison with the experimental study of garnet formation in quartz tholeiites A and B of Green & Ringwood (1967), though the Antarctic basic gneiss is slightly more Fe-rich. Comparison with these data indicates that the Antarctic granulites equilibrated at about 9-10 kb pressure (at ~ 800°C).

Pressure and temperature estimates for the initial metamorphism and subsequent retrograde reactions and exsolutions are given in Table 8. Several points can be made from these estimates. Each specific mineral assemblage which had been deduced on petrographic criteria to reflect textural equilibrium shows excellent coincidence in estimated temperature among the different geothermometers (Fe-Mg for Gt-Cpx, Gt-Opx, Opx-Cpx; Ca-Mg for Opx-Cpx; and Usp-IIm). Thus for the garnet pyroxenite (77284021) in which a high temperature clinopyroxene adjusted to a less aluminous and more Ca-rich composition by exsolving Gt-Opx-Mt, chemical equilibrium for both Fe-Mg and Ca-Mg reactions was achieved at a temperature of ~ 830°C.

Fe-Mg equilibrium was also achieved during the much lower temperature (~ 640°C) reaction of plagioclase and orthopyroxene to coronas of garnet and clinopyroxene in the quartz-bearing basic gneiss (77294029). The primary orthopyroxene porphyroblast is depleted in CaO, Al\text{2}O\text{3} and FeO at its rim to the corona. Thus although orthopyroxene was a reactant, its rim is also zoned due to exchange reaction with the new garnet and clinopyroxene.

Both the Fe-Mg and Ca-Mg Opx-Cpx temperature estimates are in excellent agreement with that of the Fe-Mg Gt-Cpx estimate (Table 8). Small changes in the En-Fs content of clinopyroxene due to Fe\text{3}+ calculations can result in large changes in temperature estimates at very low temperatures. This is due to the steepness of the limbs of the pyroxene solvus at very low temperature. However for both the Lindsley (1983) and Kretz (1982) methods, maximum calculated temperatures are only 650°C and 633°C respectively (Table 8).

The exsolved blebs of separate magnetite and ilmenite from aluminous clinopyroxene in the basic gneiss (77284029) indicate an exsolution temperature of 580°C and a \text{f}_O\text{2} of 10^{-18}, equivalent to QFM buffer. Initial metamorphic \text{f}_O\text{2} conditions could not be calculated because of the reaction of opaque oxide to form garnet in the basic gneiss. Also, the unreacted opaque oxide (within clinopyroxene or quartz) is ilmenite, though now with the minor exsolved magnetite. The coexisting ilmenite and exsolved magnetite give an exsolution temperature of ≈ 580°C but initial T, \text{f}_O\text{2} conditions could not be calculated in the absence of primary magnetite.

The petrographic evidence for the successive development of different mineral assemblages (primary metamorphic, exsolutions and coronas) is confirmed by the consistent relative temperature differences calculated for these assemblages. An overall temperature range of some 300°C is indicated. An initial metamorphism at ≈ 900°C, 9-11 kb is indicated on the
basis of pyroxene porphyroblasts in the basic gneiss and pyroxenites. Garnet pyroxenite formation overlapped this temperature down to \( \approx 850 \, ^\circ C \), with petrographic evidence being the idiomorphic garnet-pyroxene pairs. Fe-Mg exchange at the rims of the garnet-pyroxene pairs indicates chemical readjustment and zoning down to \( \approx 750 \, ^\circ C \). The various exsolution products from these aluminous clinopyroxene cores developed at 750–800 \( \, ^\circ C \). The final documented reaction, the development of garnet-clinopyroxene (–quartz) coronas in the basic gneiss occurred at even lower temperature (\( \approx 640 \, ^\circ C \)) but at slightly lower pressure than the initial metamorphism (8–9 kb). There is excellent agreement between pressures estimated by the Gt-Opx and Gt-Plag-Opx-Qtz barometers (Table 8). Pressure estimates based on the CaTs-An-Qtz barometer are 1–2 kb higher and probably indicate a small error in the formulated barometer. However, both the Gt-Opx and CaTs-An-Qtz barometers indicate a similar decrease in pressure for the secondary compared to primary assemblages (Fig. 6). The equilibrium constants for the CaTs-An-Qtz and Gt-Opx barometers have slopes of about \(-4 \text{ bars}^\circ C \) and \(47 \text{ bars}^\circ C \) respectively. If the mineral reactions involving these barometers had closed at high temperature then the pressure differences between initial

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**Fig. 6.** \( P-T \) summary of the igneous and metamorphic evolution of the basic rocks shown by the shaded band. B–B is the approximate solidus of a quartz tholeiite magma at 9–12 kb pressure (Green & Ringwood, 1967). Discontinuous shading represents the inferred cooling from magmatic to the calculated peak metamorphic conditions. Continuous shading represents the subsequent metamorphic cooling path with only minor uplift. A–A represents the minimum pressure for the appearance of garnet in a quartz tholeiite composition (Mg61) from Green & Ringwood (1967). Dots connected by line are based on CaTs-An-Qtz pressure estimates, crosses Gt-Opx pressure estimates, and open circle Gt-Opx-Plag-Qtz. Horizontal bars show the range in temperature estimates for the various geothermometers for all generations of mineral assemblages (see Table 8 for individual sample comparisons). Note the restricted low temperature range of opaque oxide temperatures compared to the other geothermometers.
metamorphism and lower temperature secondary reactions would have been considerably different than indicated. This suggests that mineral equilibrium was maintained in the different generations of assemblages in response to falling temperature.

DISCUSSION

Inconsistent temperature estimates for a metamorphic rock may be due to inaccuracies in one or more of the geothermometers which were used or to different closure temperatures for cation exchange in the different mineral pairs. The excellent agreement in temperature estimates for each generation of the Antarctic mineral assemblages (Table 8)—primary, corona, exsolution—provides evidence for the relative accuracy of the geothermometers used here. However the ≈ 300 °C range in temperatures together with the correlation of relative temperature with petrographic evidence for the successive formation of primary and secondary minerals has bearing on the closure temperatures for cation exchange geothermometers.

Simple cation exchange is related to volume diffusion and should depend on temperature and cooling rate. Recorded temperatures using different geothermometers show coincidence or divergence depending on the particular local path of cooling-uplift following peak metamorphism. Rocks initially metamorphosed above a given closure temperature for cation exchange in a mineral pair may retain a record of cooling to this temperature but will show no record of cooling below this temperature.

The question then arises as to why a particular exchange reaction can indicate chemical equilibrium at low temperature for secondary phases, yet still indicate frozen-in higher temperature equilibrium for primary phases, even in a single thin section. Thus both primary porphyroblasts and recrystallized pyroxene grains in the basic gneiss and pyroxenite retained, on cooling, compositions indicative of initial metamorphism at ≈ 900 °C. This suggests that the closure temperature for Ca–Mg and Fe–Mg exchange between these primary grains was not much less than 850–900 °C (probe traverses across primary Opx–Cpx pairs revealed no zoning). Primary garnet–clinopyroxene pairs in the garnet pyroxenites on the other hand show evidence of compositional zoning (Fe–Mg) and exsolution over a 100 °C interval down to ≈ 750 °C. This indicates a closure temperature for diffusion of ≈ 750 °C for both intercrystalline exchange (Fe–Mg zoning) and intracrystalline net transfer (exsolution) reactions. The presence of exsolutions in the cores of these pyroxenes but zoned rims at contacts with garnet provides evidence for the distances over which intercrystalline diffusion operates at these temperatures.

Intercrystalline diffusion resulted in Fe–Mg exchange and zoning at garnet–pyroxene contacts but the greater distances to cores of pyroxenes meant that they did not readjust by exchange. Instead they readjusted over smaller distances by intracrystalline diffusion and net transfer reaction to form exsolutions.

Reactions which involve a solvus such as between coexisting orthopyroxene and clinopyroxene can be described by either an exchange reaction (Di_{Cpx} + En_{Opx} = En_{Cpx} + Di_{Opx}) or a net transfer reaction (En_{Cpx} = En_{Cpx}). This distinction is trivial in a thermodynamic sense but has bearing on the mechanism of pyroxene equilibration. Homogeneity of coexisting pyroxenes at the peak metamorphism indicates that chemical equilibrium was achieved by exchange between coexisting grains on a millimetre scale. On cooling, pyroxenes in the basic gneiss and pyroxenite did not readjust by exchange because of high closure temperatures. In the garnet pyroxenites chemical readjustment at grain boundaries was achieved over small distances by exchange reaction but cores of crystals readjusted not with surrounding primary grains but on a much smaller scale by intracrystalline diffusion. In both cases the closure temperature for intercrystalline diffusion (between primary garnet–pyroxene rims as
In contrast the much lower equilibration temperature (≈ 640 °C) for Gt-Cpx-Qtz corona formation in the basic gneiss (Gt-Cpx and Opx-Cpx thermometry) is not due to intercrystalline diffusion between stable primary mineral grain boundaries. It has already been proposed that the closure temperature for intercrystalline diffusion was ≈ 850–900 °C for this rock, as evidenced by the preservation of unzoned primary pyroxenes where in contact. However, Gt-Cpx and Opx-Cpx exchange reaction thermometers indicate low equilibration temperatures for corona phases because equilibrium was achieved by growth of new phases at the contact of reacting orthopyroxene and plagioclase by net transfer reaction rather than exchange reaction between constant volume primary phases.

Intercrystalline diffusion is in part controlled by point defects within crystal lattices and has a high activation energy. In contrast, corona formation is the result of interphase boundary reactions in which relic high temperature phases, frozen in composition to intercrystalline diffusion, are consumed below their \( T_c \) to produce newly formed phases, the growth of which does not depend upon point defects within the reactant crystals. Thus mineral coronas, which formed above a particular closure temperature to cation exchange, may record, together with primary minerals, zoning down to this closure temperature. In contrast mineral coronas formed by reaction at even lower temperatures will record their temperature of formation 'anomalously' below this closure temperature but will not undergo further cation exchange.

An additional factor is that the two apparently independent corona forming reactions around orthopyroxene and ilmenite must have involved Mg-Fe\(^{2+}\) migration along grain boundaries to sites of Gt-Cpx and Gt-Qtz growth over distances equivalent to the grain size of the primary metamorphic fabric (see petrography). These distances are greater than those of intercrystalline diffusion at higher temperature and may indicate the presence and influence of an intergranular fluid phase (and minor deformation) during this low temperature stage of the rocks' \( P-T-t \) path.

The lowest temperatures are calculated for magnetite-ilmenite intergrowths (580 °C). This indicates that the opaque oxides continuously re-equilibrated to very low temperatures with a closure temperature (≈ 580 °C) much lower than that of the silicate minerals.

The above petrologic data and interpretation demonstrate that in high-grade metamorphic terrains which have not undergone penetrative deformation since the peak metamorphism, the preservation of different generations of mineral assemblages enables the \( P-T \) path of cooling to be calculated for these rocks. In particular, these observations confirm the earlier proposal of Ellis (1980) that a distinctive feature of the Napier Complex is that following peak metamorphic conditions the base of the crust essentially cooled with only a slight decrease in pressure. A temperature decrease of some 250–300 °C with only a very small uplift following metamorphism and deformation is unusual for metamorphic terrains, as many other regions show evidence of uplift rather than cooling following the main metamorphism. This is consistent with the proposal of Ellis (1980) that the heat source for this unusual granulite facies metamorphism was underplating of the crust by igneous material on a regional scale, followed by cooling of the crust back towards a more steady state geotherm, implying unusually stable tectonic conditions. A characteristic feature of the Napier Complex is the development of lower temperature secondary coronas and mineral assemblages. In contrast, the bordering Rayner Complex, which represents in parts a reworking of the Napier Complex some 1000–1500 Ma later (Sheraton et al., 1980), involved rehydration, deformation and metamorphism during uplift. In marked contrast to the reactions evident in Napier Complex rocks, secondary mineral assemblages, coronas and mineral zoning are all...
to lower pressure rather than lower temperature assemblages in this younger mobile zone (Ellis, 1983).

ACKNOWLEDGEMENTS

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REFERENCES


Stormer, J. C., Jr., 1975. A practical two feldspar geothermometer. Ibid. 60, 667-74.


### APPENDIX 1

Comparison of method of calculating Fe\(^{3+}\) content of clinopyroxene (sample 77284020) from probe data, with wet chemical determination of ferrous iron

<table>
<thead>
<tr>
<th></th>
<th>Probe analysis</th>
<th></th>
<th>Wet chemistry</th>
<th></th>
<th>Probe recalculated</th>
<th>Wet chemistry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Point A</td>
<td>Point B</td>
<td>A</td>
<td></td>
<td></td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>48.89</td>
<td>48.79</td>
<td>48.89</td>
<td>48.89</td>
<td>48.79</td>
<td>48.79</td>
<td></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.25</td>
<td>0.34</td>
<td>0.25</td>
<td>0.25</td>
<td>0.34</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>7.09</td>
<td>7.13</td>
<td>7.09</td>
<td>7.09</td>
<td>7.13</td>
<td>7.09</td>
<td></td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.12</td>
<td>n.d.</td>
<td>0.12</td>
<td>0.12</td>
<td>n.d.</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.83</td>
<td>2.49</td>
<td>3.08</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>11.54</td>
<td>11.77</td>
<td>8.99</td>
<td>9.30</td>
<td>9.00</td>
<td>9.30</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.40</td>
<td>0.44</td>
<td>0.40</td>
<td>0.40</td>
<td>0.44</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>18.04</td>
<td>17.82</td>
<td>18.04</td>
<td>18.04</td>
<td>17.82</td>
<td>17.82</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>13.26</td>
<td>13.21</td>
<td>13.26</td>
<td>13.26</td>
<td>13.21</td>
<td>13.21</td>
<td></td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.31</td>
<td>0.40</td>
<td>0.31</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.90</strong></td>
<td><strong>99.90</strong></td>
<td><strong>100.18</strong></td>
<td><strong>100.15</strong></td>
<td><strong>100.21</strong></td>
<td><strong>100.25</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Cations on basis of 6 oxygen atoms**

<table>
<thead>
<tr>
<th></th>
<th>Probe recalculated</th>
<th>Wet chemistry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.808</td>
<td>1.807</td>
<td>1.797</td>
</tr>
<tr>
<td>Ti</td>
<td>0.007</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>Al</td>
<td>0.309</td>
<td>0.311</td>
<td>0.307</td>
</tr>
<tr>
<td>Cr</td>
<td>0.004</td>
<td>—</td>
<td>0.003</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>—</td>
<td>—</td>
<td>0.078</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>0.357</td>
<td>0.365</td>
<td>0.276</td>
</tr>
<tr>
<td>Mn</td>
<td>0.013</td>
<td>0.014</td>
<td>0.012</td>
</tr>
<tr>
<td>Mg</td>
<td>0.094</td>
<td>0.098</td>
<td>0.088</td>
</tr>
<tr>
<td>Ca</td>
<td>0.526</td>
<td>0.524</td>
<td>0.522</td>
</tr>
<tr>
<td>Na</td>
<td>0.022</td>
<td>0.029</td>
<td>0.022</td>
</tr>
<tr>
<td>Cation sum</td>
<td>4.040</td>
<td>4.043</td>
<td>4.012</td>
</tr>
<tr>
<td>100 Mg/(Mg + Fe(^{2+}))</td>
<td>73.57</td>
<td>72.94</td>
<td>78.16</td>
</tr>
</tbody>
</table>

Wet chemistry (K\(_2\)Cr\(_2\)O\(_7\) titration) gave 9.13 and 9.46 wt. per cent FeO, i.e. average 9.3 wt. per cent FeO, thus 2.48-2.74 wt. per cent Fe\(_2\)O\(_3\).

The ferric iron content in clinopyroxene, in the absence of wet chemistry, was determined by Fe\(^{3+}\) = 4 - 2 Si - 2 Ti - Al - Cr + Na + K from the probe data.

As can be seen, the difference between wet chemistry and recalculation on the basis of stoichiometry is very small—100 Mg/(Mg + Fe\(^{2+}\)) differs by less than half a per cent.

n.d.—not determined.