Chapter 4
THE ROSEBERY OREBODY: FORM, METAL ZONING AND MINERALOGY

4.1 FORM

Massive sulphide ore at Rosebery forms a tabular sheet dipping 45°E with an overall strike length of 1500 m and a depth interval of at least 800 m (Figs 4.1 and 4.2). In longitudinal projection (Fig. 4.3) a zone of barren host rock broadening at depth divides the massive sulphide orebody into a northern section comprising the A and B lenses, and a southern section comprising from the north the D, E and F lenses. The G lens represents a major parasitic fold (Fig. 4.1). In the southern zone, a lower horizon of massive sulphide ore comprising the D, E and F lenses is generally separated from a stratigraphically higher number of barite-sulphide lenses (the H lens, Fig. 4.3) by weakly mineralized, schistose sericitic host rock (Figs 4.1 and 4.2). The lower massive sulphide horizon is generally a continuous sheet of ore in the central part of the mine, but commonly splits into a number of lenses separated by carbonate- or sericite-rich host rocks towards the southern and northern ends of the mine.

This complex distribution of ore is at least partly, and possibly entirely, the result of deformation that is believed to have occurred during the Devonian Tabberabberan Orogeny (Section 3.3). Brathwaite (1972) showed that folds within the orebody had variable pitches in the mean cleavage direction of the surrounding rocks, tended to display irregular morphology and had a limited axial extent, features he ascribed to relative tectonic mobility of the ore with respect to the country rocks. A major anticlinal parasitic fold in the orebody (Figs 4.1 and 4.2) which pitches north at between 55° and 85° is the most important structural element in the mine.
Fig. 4.1  East-west cross section of the Rosebery ore zone at 500N. Note that mine co-ordinates, drill hole footages, and reduced levels are all in feet. The altitude zero = 10,000 feet for altitudes below sea level. Drawn from mine plans prepared by mine staff.
ROSEBERY MINE
Cross Section 500 N

10 LEVEL
11 LEVEL
12 LEVEL
SEA LEVEL
13 LEVEL
14 LEVEL
15 LEVEL

GLACIAL SEDIMENTS
MASSIVE PYROCLASTICS
BLACK SLATE
HOST ROCK
FOOTWALL SCHIST AND CHERT
DOMINANTLY BARITE
DOMINANTLY SPHALERITE / GALENA
SPHALERITE / GALENA / PYRITE / CHALCOPYRITE
DOMINANTLY PYRITE / CHALCOPYRITE

SCALE 1000:1

0 50 100 150 200 250 300 350 400 FEET
0 50 100 METERS

SUCCESSORS
Fig. 4.2 Geological plan, 15 level, Rosebery mine, showing ore lenses and sections samples through orebody (sections 2 and 3 projected). Drawn from mine plans.
Fig. 4.3 Longitudinal projection of the Rosebery ore zone showing relative positions of ore lenses (see insert). The H lens is the barite orebody, lenses A to G comprise the massive sulphide orebody. Drawn from mine plans. Recent drilling has shown the barren zone between the A and B lenses and the southern ore zone to be narrower than indicated in the diagram (M.J. McDonald, pers. comm. in Green et al., 1981). Drawn from a plan prepared by mine staff.
Some minor folds in the orebody may be of synsedimentary origin. Adams et al. (1976) believed that the parasitic fold forming the G lens was the result of gravitational slumping soon after ore deposition. Their principal arguments were the lack of continuity of barite-rich ore around the fold structure (Figs 4.1 and 4.2) and the asymmetrical mineralogical zooning in the G lens between about 100 and 500 N (Fig. 4.2). The form of the contact between the host rock and the black slate (Fig. 4.1) and cleavage-bedding relations in the black slate are in accord with the tectonic fold model (Brathwaite, 1972), although it is difficult to disprove a synsedimentary origin for the fold.

4.2 GROSS MINERALOGY AND TEXTURE

The sulphide ore consists essentially of pyrite, sphalerite, galena, and chalcopyrite. Minor minerals include tetrahedrite, tennantite, arsenopyrite, magnetite, electrum, a bismuthian sulphosalt with a composition close to Fe-bearing aikenite (J.F. Stephens, pers. comm.), enargite (?), gold, electrum, pyrrhotite, meneghinite, jordanite, bourronite, hematite, and rutile. Major gangue minerals include chlorite, muscovite, barite, and a wide range of carbonate minerals (Section 4.4 (viii)). Minor gangue minerals include albite and spessartine (Stillwell, 1934; Williams, 1960; Brathwaite, 1974; Smith, 1975; this study), and coarse-grained barite.

The barite orebody (H lens) consists of banded barite-sulphide mineralization. Major sulphides are sphalerite and galena with minor pyrite, tetrahedrite, tennantite, chalcopyrite, and hematite. Arsenopyrite has not been recorded in this ore. Apart from barite, Mn-rich carbonate is the major gangue mineral. Accessory quartz, albite, and sericite are present (Brathwaite, 1974), and chlorite is rare (105182, 105183 of Table 4.1, this study).
Carbonates occur mainly at the strike limits of the sulphide ore-body, as lenses within the sulphide and as local concentrations in the host rock (Brathwaite, 1974), particularly below the F lens and, to a lesser extent, the H lens (Dixon, 1980).

The most striking primary textural feature of the massive ore is the presence of a fine compositional banding on a scale of 0.1 to 10 cm thick (Brathwaite, 1974) which is present in all ore types except for compact Pb-Zn rich ore at the southern end of the mine (Table 4.1). Brathwaite (1972) showed that this layering was structurally concordant with ore-host rock contacts and with bedding in the host rock and black slate, strongly suggesting a primary origin. Although the sulphide lenses have been interpreted as an originally continuous sheet (Brathwaite, 1972, 1974), this has yet to be established and it is possible that the ore is diachronous. Textures indicative of open-cast reworking of ore such as scours and clastic textures are absent.

Colloform banding is present in some samples (Table 4.1), and manganoan carbonates in the massive ore commonly occur as colloform growths inside sulphides, probably indicating growth in cavities after sulphide deposition.

Metamorphic textures predominate at the microscopic scale. Sphalerite, galena, chalcopyrite, barite, and quartz form a fine-grained polygonal matrix with pyrite and arsenopyrite occurring as porphyroblasts (Brathwaite, 1970, 1974) and grain boundaries approach a minimum interfacial free energy state (Stanton, 1964). These textures indicate static annealing and post-deformational recrystallization of the sulphides (Stanton, 1972), although remnant deformational textures, such as cataclastic brecciation
### Table 4.1

**MINERALOGY AND TEXTURE OF SAMPLES FROM SELECTED SECTIONS.**

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| 193           | 400S 1271E 9554 | 4.09                  | B  | B  | E  | C  |     |     |     |       | c  |
| 194           | 400S 1261E 9552 | 2.74                  | B  | B  | E  | C  |     |     |     |       | c  |
| 195           | 400S 1260E 9551 | 1.98                  | C  | A  | E  | C  |     |     |     |       | c  |
| 196           | 400S 1259E 9550 | 1.98                  | E  | B  | E  | C  |     |     |     |       | c  |

| 100.955       | 800S 2080E 8807 | 2                     | B  | B  | E  | C  |     |     |     |       | c  |
| 192           | 800S 2085E 8804 | 1.03                  | C  | A  | E  | B  |     |     |     |       | c  |
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Approximate mineral abundances: A, 50%; B, 20-50%; C, 5-20%; D, 1-5%; E, 1%. Abbreviations: Py, pyrite; S1, sphalerite; Cp, chalcocpyrite; Gn, galena; Thd, tetrahedrite; Apy, arsenopyrite; Mt, magnetite; Q, quartz; Mu, white mica; Cl, chlorite; Cb, carbonate; Ab, albite; Ba, barite; Au, gold; Bi, bismuthian sulphosalt similar to aikenite. Numbers after Apy abundance refer to morphological type (see text). Textural terms: b, banded; c, compact; coll, colloform. Because of structural complexity, stratigraphic sequence of samples in the G lens is uncertain; elsewhere the structural and stratigraphic footwalls coincide.
of pyrite and arsenopyrite, and kinked twin lamellae in sphalerite persist in some samples (Brathwaite, 1974). The predominance of annealing textures makes it difficult to establish which of the minor minerals formed prior to deformation; criteria for distinguishing pre-metamorphic minerals important from the viewpoint of ore genesis will be discussed in Section 4.4.

4.3 METAL ZONING

Mineralogic and metal zonation perpendicular to the strike of the orebody at Rosebery are typical of volcanic-hosted massive sulphide deposits and have been well documented by Brathwaite (1974). Within the D, E and northern part of F lenses pyrite and chalcopyrite are enriched at the base, and sphalerite and galena become more abundant upward. G lens is atypical in that the normal across-layer mineralogical zonation is inverted (Adams et al., 1976), with its eastern limb missing or extremely attenuated. The basal Cu-rich zone does not extend throughout the ore zone (Brathwaite, 1974). In the southern part of the orebody there is a lateral zonation from Cu-rich to Pb-Zn-rich ore southward. The northern section of the orebody (A and B lenses) is richer in Pb and Zn and poorer in Cu compared with the D and G lenses to the south (Brathwaite, 1970). Contacts between basal chalcopyrite-rich and overlying sphalerite-galena-rich ore are generally sharp (e.g. Brathwaite, 1974, Table 1). In the southern part of the mine stratiform lenses of disseminated to semi-massive pyrite-chalcopyrite mineralization in a chloritic gangue occur a few tens of metres below the main massive ore zone. One of these lenses becomes richer in galena and sphalerite southward (Fig. 4.2).

To illustrate the lateral metal zonation for the southern-central ore zone it was necessary to attempt a pre-folding reconstruction of the orebody. As shown in Fig. 4.4, this has been done by rotation of the
G lens through 180° about an axis pitching vertically in the plane of the orebody and placing G lens between E and F lenses. This, admittedly crude, reconstruction is consistent with the inverted across-layer metal zonation of G lens and also with the structural interpretation of Brathwaite (1972). It should be noted that no allowance can be made for local tectonic thickening which should be most extreme near the fold hinge marked by the intersection of E, F and G lenses. However, the relative pre-folding positions between any two sections through the orebody should be approximately correct. Company assay data were used for the metal zoning study and mean metal abundances for complete sections through the orebody on an approximate grid spacing of 30 m were calculated (Fig. 4.5). The distributions of Pb, Zn, Cu, Ag, Au, Fe, and the mass ratios of Zn/Fe and Zn/Pb were investigated using trend surface analysis. The distributions are shown in Fig. 4.6a-g which are third-order trend surface contours of the southern section of the mine (the C, D, E, F, and G lenses) plotted on a north-south longitudinal projection.

All third-order surfaces, with the exception of Zn/Pb, were statistically significant at the 99% level of confidence or better (Table 4.2), and the pattern for Zn did not change when the data were split into halves using random number tables, and contoured separately. As the trend surface programme produces a normal distribution of residuals, the distribution of values for the elements were plotted on histograms. Fe, Zn, Pb, and Zn/Fe data have normal distributions, and the mass percentages (mass ratio in the case of Zn/Fe) were used as input data for the computer programme. Cu, Ag and Au have lognormal distributions and the logarithms for these elements were used.
Method of unfolding ore body

(a) Present configuration. Arrows indicate stratigraphic facing.

(b) Pre-folding reconstruction

Fig. 4.4 Sketch to illustrate method of unfolding of the orebody structure.
Fig. 4.5  Distribution of data points for metal zoning study plotted on an unfolded longitudinal projection. The major structural perturbation, the G lens, is indicated by dashed line.
Table 4.2

FIT OF TREND SURFACES

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<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;75</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

* Third-order trend surfaces shown are based on regression of the logarithms of the element concentrations.

† Statistical data shown are from an earlier regression of Cu input as wt.%. As the distribution of Cu values is clearly lognormal the values of F will clearly be minima, i.e. the confidence levels, expressed as percentages for all regressions, would have been higher if the statistics for the distribution of log Cu had been output.
The patterns of Pb and Zn distribution (Figs 4.6a,b) are approximately concordant. They are asymmetric with maxima occurring near the northern upper and southern lower parts of the southern ore zone and a minimum somewhat north of the centre. The pattern for Ag shows a minimum in a similar position to those of Pb and Zn (Fig. 4.6c). The more limited data for Cu (Fig. 4.6d) show a maximum in the lower central area, whereas Fe has a maximum further north. The pattern for Au is broadly similar to that for Ag, but a ridge of higher values occurs near the copper maximum (Fig. 4.6f), consistent with the observation of free gold in the pyrite-chalcopyrite ore (Brathwaite, 1974; this study). The complex Au distribution is a function of mineralogy. Up to 2 ppm Au is present in Rosebery pyrite (Henley & Stephenson, 1978), and free gold is present in pyrite-chalcopyrite ore (Brathwaite, 1974; this study) and in tetrahedrite-rich ore (Stillwell, 1934). Smith (1975) noted a high gold content of 50.3 ppm in the copper concentrate which consists predominantly of chalcopyrite and tetrahedrite-tennantite. Brathwaite (1970) noted a high correlation of Au and Ag contents in mine assays. Silver occurs almost exclusively in tetrahedrite, tennantite, and galena. Significantly, the third-order trend surface is similar to the pattern that might have been inferred from the above discussion.

Perhaps the best index of the metal zonation is the Zn/Fe ratio (Fig. 4.6g) which reveals the metal distribution corrected for such factors as variable proportion of gangue minerals. The Zn/Fe ratio distribution is similar to those for Pb and Zn.

Chayes (1970) stated that the criterion of accepting a trend surface of order \((k+1)\) was that terms of this order alone significantly improved the fit at order \(k\). He arbitrarily chose the 99% confidence level to define "significant improvement". If the regression failed this criterion at order \((k+1)\) Chayes believed the regression should not proceed to higher order terms. As shown in Table 4.2 the quadratic
Fig. 4.6  Third-order trend surfaces of weighted average assay data for the entire thickness of the sulphide orebody determined at each point shown in Fig. 4.5. The zero co-ordinate is shown as a guide to location.

(a) Pb%
(b) Zn%
(c) Ag g/t
(d) Au g/t
(e) Cu %
(f) Fe %
(g) Zn/Fe mass ratio
terms for the metal distributions meet this requirement for Fe and the Zn/Fe ratio alone. Nevertheless, display of third-order surfaces is justified because:

(a) The third-order surfaces for all elements and the Zn/Fe ratio are significant at the 99% confidence level.

(b) Geochemically similar elements such as Zn, Pb and Ag show similar metal distributions. The more complicated Au distribution is consistent with the mineralogical evidence and the fact that a Au/Cu correlation has been noted in other massive sulphide deposits, for example Mount Chalmers, Queensland (Large & Both, 1980).

(c) Third-order surfaces are the least complicated mathematically to adequately display the metal distributions and visually are in accord with colour-coded diagrams showing different ranges of element ratios constructed before the trend surface analysis was carried out.

(d) The pattern for Zn was maintained when the data were halved.

The distribution of the Zn/Pb ratio did not meet the Chayes criterion at any level (Table 4.2) and was not different from random using the method of Howarth (1967).

The lateral metal zonation revealed by the trend surface analysis is considered to be a pre-metamorphic feature of the orebody, essentially unaffected by deformation and metamorphism, as no evidence of effects of metamorphic remobilization of metals on the large scale has been seen.
4.4 MINERALOGICAL ZONATION

A number of sections through the orebody corresponding to the Fe maximum (section 1, Fig. 4.2), the Pb and Zn minimum (section 3) and a section just north of the Cu maximum (section 2) were sampled. In addition samples were taken from the barite orebody. The sample locations are indicated in Fig. 4.2 and Table 4.1, and the mineralogy and texture of the samples are listed in Table 4.1. Rather than repeat a textural description of all minerals which may be found in Brathwaite (1974), only the salient features involving minerals of genetic importance will be stressed here.

4.4 (i) Arsenopyrite

As shown in Table 4.1, and as noted by Brathwaite (1974), arsenopyrite is widely distributed in small amounts in the sulphide orebody, but is absent in the barite orebody. Two distinct morphologies of arsenopyrite have been observed in the sulphide ore. The first type is restricted to certain laminae, and occurs as relatively coarse euhedra averaging about 0.5 mm in diameter, and is commonly associated with pyrite, in some cases as overgrowths on pyrite (Stillwell, 1934), in pyrite-rich bands (Fig. 4.7). Type 1 arsenopyrite, because of its distribution, the presence of fractured grains in massive ore, and the occurrence of coarse arsenopyrite (0.8 mm diameter) euhedra, with adjacent fibrous pressure shadows of quartz, in one specimen of sericitic host rock towards the top of the massive sulphide lens (105163, Table 4.1, Fig. 4.8) is regarded as a primary component of the ore. Type 2 arsenopyrite is in the form of minute euhedra (<0.1 mm diameter), which are commonly corroded, in tetrahedrite-tennantite pools in sphalerite (Figs 4.9 and 4.10). Common associates of type 2 arsenopyrite are chalcopyrite, galena and very fine-grained pyrite euhedra. This type of arsenopyrite was first described by Stillwell (1934).
Fig. 4.7  Intergrown pre-cleavage arsenopyrite euhedra with pressure shadows of quartz in sericitic host rock intercalation in the D lens (105163). Pre-cleavage quartz vein on the right. Plane polarized light, width of field is 4 mm.

Fig. 4.8  Band of type 1 arsenopyrite (apy) intergrown with pyrite (white, higher relief than apy) in sphalerite (dark grey) with associated galena (light grey, low relief). Specimen 100011. (Brathwaite, 1970, photo of section loaned by Dr P.B. Barton, Jr. held at the U.S. Geological Survey). Reflected light, width of field is 1.1 mm.
Fig. 4.9  Corroded arsenopyrite (apy), pyrite (py), tennantite (tnt), chalcopyrite (cpy) and galena (gn) in matrix of darker grey sphalerite (sl). Reflected light, width of field is 1.1 mm. Part of area of complex intergrowth near centre of photograph shown in Fig. 4.10 below. Specimen 100011.

Fig. 4.10  Sphalerite (mid grey) enclosing embayed pyrite (py) and gangue (dark grey). Strongly corroded arsenopyrite (apy) is surrounded by tennantite (pale grey), chalcopyrite (cp) and minor galena (gn) (very light grey). Reflected light, width of field is 0.27 mm. Specimen 100011.
Two grains of euhedral to subhedral type 1 arsenopyrite in contact with pyrite were analysed on the electron microprobe by W. Jablonski using the standard asp 200 (Kretschmar & Scott, 1976; Table 4.3). The grains were up to 0.5 mm across, showed no significant zoning and ranged in composition from 31.02 to 32.42 atom % As (Green et al., 1981). Seven grains not visibly in contact with pyrite ranged from 30.38 to 32.04 atom % As (Table 4.3). Assuming the pyrites and arsenopyrites of the first group were in equilibrium, the experimental data of Kretschmar & Scott (1976) indicate temperatures between 370 and 455°C and log \(a_{S_2}\) values of -5 to -8 (Fig. 7.2).

4.4 (ii) Sphalerite

Sphalerite compositions are shown in Fig. 4.11 and listed in Table 4.4. In the few cases where copper was detected in an analysis an equivalent molar amount of Fe was subtracted from the FeS content of sphalerite as recommended by Urabe (1974), although the ravages of Barton's (1978) "chalcopyrite disease" are not as severe as those found by Barton (op. cit.) in sphalerites from the Furutoke mine, Japan. This may be due to nucleation of any chalcopyrite impurities and migration to grain boundaries during metamorphism. In transmitted light, sphalerite grains are homogeneous.

Sphalerite from the sulphide ore, excluding that in pyrrhotite-bearing assemblages, has a range in FeS content from 0.94 to 5.10 mole %, with a marked enrichment in the pyrite-rich D and G lenses compared with the Zn-Pb-rich F lens. There is a good correlation between sphalerite composition and the layer-parallel metal zoning, with sphalerites from the Fe- and Cu-rich sections of the mine (D and G lenses) having higher FeS contents than those from the Zn-Pb-rich ore of the F lens; both being higher than those in the barite lode (H lens). Individual grains and some polished sections show little variation, but other sections (e.g. 105174)
### Table 4.3

**COMPOSITION OF ARSENOPYRITE.**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Location</th>
<th>As, at.%</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Arsenopyrite with pyrite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100942</td>
<td>A lens</td>
<td>31.02-31.87 (3)</td>
<td>31.51</td>
<td></td>
</tr>
<tr>
<td>105166</td>
<td>D lens</td>
<td>31.25-32.42 (4)</td>
<td>32.08</td>
<td></td>
</tr>
<tr>
<td><strong>Arsenopyrite without visible pyrite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100942a</td>
<td>A lens</td>
<td>30.38-31.94 (4)</td>
<td>31.17</td>
<td></td>
</tr>
<tr>
<td>100942b</td>
<td>A lens</td>
<td>29.83-32.32 (4)</td>
<td>31.63</td>
<td></td>
</tr>
<tr>
<td>100942c</td>
<td>A lens</td>
<td>29.91-30.95 (3)</td>
<td>30.49</td>
<td></td>
</tr>
<tr>
<td>100942d</td>
<td>A lens</td>
<td>30.99-31.52 (2)</td>
<td>31.26</td>
<td></td>
</tr>
<tr>
<td>105163a</td>
<td>D lens</td>
<td>31.03-31.81 (2)</td>
<td>31.42</td>
<td></td>
</tr>
<tr>
<td>105163b</td>
<td>D lens</td>
<td>31.12-31.31 (4)</td>
<td>31.24</td>
<td></td>
</tr>
<tr>
<td>105163c</td>
<td>D lens</td>
<td>31.60-32.04 (2)</td>
<td>31.82</td>
<td></td>
</tr>
</tbody>
</table>

Numbers in parentheses give number of analyses of one crystal; analyses by W. Jablonski using the University of Tasmania electron microprobe and standard arsenopyrite asp 200 (Kretschmar & Scott, 1976).
Fig. 4.11 Mole percent FeS in sphalerites in the Rosebery sulphide and barite (H lens) orebody (see Table 4.4). Sample numbers for the H lens are prefixed by 100, the remainder by 1051.
Table 4.4

COMPOSITION OF SPHALERITE IN THE SULPHIDE OREBODY.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Metres above footwall</th>
<th>FeS, mole %</th>
<th>Cds, mole %</th>
<th>MnS, mole %</th>
<th>Number of grains</th>
<th>Number of analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>D LENS:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105161</td>
<td>2.38</td>
<td>1.31-1.89</td>
<td>1.60</td>
<td>nd</td>
<td>nd</td>
<td>1</td>
</tr>
<tr>
<td>105162</td>
<td>2.19</td>
<td>2.85-4.26</td>
<td>3.41</td>
<td>0.23 (7)</td>
<td>0.30 (3)</td>
<td>5</td>
</tr>
<tr>
<td>105170</td>
<td>3.7</td>
<td>3.47-3.93</td>
<td>3.74</td>
<td>nd</td>
<td>nd</td>
<td>2</td>
</tr>
<tr>
<td>105171</td>
<td>1.8</td>
<td>4.92</td>
<td>4.92</td>
<td>nd</td>
<td>nd</td>
<td>1</td>
</tr>
<tr>
<td>G LENS:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105176</td>
<td>10.0</td>
<td>1.52-3.21</td>
<td>2.16</td>
<td>0.38 (1)</td>
<td>0.59 (8)</td>
<td>11</td>
</tr>
<tr>
<td>105174</td>
<td>0</td>
<td>1.33-5.22</td>
<td>3.39</td>
<td>0.35 (1)</td>
<td>0.43 (1)</td>
<td>8</td>
</tr>
<tr>
<td>F LENS:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105178</td>
<td>4.6</td>
<td>0.94-1.10</td>
<td>1.03</td>
<td>0.20 (2)</td>
<td>0.13 (1)</td>
<td>2</td>
</tr>
<tr>
<td>105179</td>
<td>1.8</td>
<td>1.01-2.18</td>
<td>1.60</td>
<td>0.20 (2)</td>
<td>0.10 (1)</td>
<td>6</td>
</tr>
<tr>
<td>H LENS:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100902</td>
<td>?</td>
<td>0.65</td>
<td>nd</td>
<td>nd</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>100903</td>
<td>?</td>
<td>0.65</td>
<td>nd</td>
<td>nd</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

* Figures for Cds and MnS represent the means of those analyses in which the metal was detected. The figures in parentheses are the number of analyses in which the element was detected.

Analyses of electron microprobe, University of Tasmania.
Locations of samples given in Appendix 1.
Stratigraphic relationships of samples from the G lens uncertain (see Appendix 1).

nd = not detected.

Analyses by author, except for 100902 and 100903 by W. Jablonski.
show considerable inhomogeneity. This inhomogeneity also extends to the MnS content of sphalerites; in specimen 105176, for example, Mn was detected in 8 of the 23 analyses and in those eight showed a range of 0.34 to 1.43 mole % MnS.

McLeod (1978) analysed sphalerites and gangue minerals from two sections on 15 level. In one section, 30 m north of section 1 in the D lens (Fig. 4.2) a range of 3.84 to 7.34 mole % FeS in sphalerite was found with a general increase in FeS content up the section. In the other section 90 m north of section 3 in the F lens, the FeS content of sphalerite varied from 1.74 to 2.75 mole % and showed no general trend. In both sections, seven samples were analysed with one analysis from each. Another sample from the same section in F lens had a sphalerite with 16.38 mole % FeS but this was associated with lath- and rhomb-shaped magnetite of probable metamorphic origin (McLeod, 1978). These results support the general relationship between FeS content of sphalerite and the lateral metal zoning noted above, but it is clear there is no consistent vertical zoning.

The composition of sphalerite from the pyrrhotite assemblages is discussed under metamorphism (Section 7.2 (ii)).

4.4 (iii) Pyrrhotite

Brathwaite (1972, 1974) reported pyrrhotite occurring as massive bodies discordantly replacing massive folded sulphides towards the southern extremity of the Pb-Zn massive sulphide orebody. Although no mine exposures of pyrrhotite were accessible to the writer, drill core specimens show that as massive pyrrhotite mineralization is approached the grain size of the ore increases sharply over a few centimetres. For example, pyrite porphyroblasts vary from 0.1 to 0.2 mm in diameter in massive sphalerite-galena to 2 mm euhedra at the margins of the pyrrhotite bodies. Typical mineral assemblages from galena-sphalerite ore
to pyrrhotite-rich mineralization include: sphalerite-galena-tetrahedrite-pyrite, coarse grained pyrite-sphalerite-galena (76-748), pyrrhotite-pyrite-arsenopyrite-chalcopyrite-sphalerite-galena (76-747), pyrrhotite-pyrite-chalcopyrite-sphalerite (76-745), and sphalerite-magnetite-pyrrhotite-chalcopyrite-galena (76-746). Hematite occurs as inclusions in pyrrhotite in 76-745. Brathwaite (1974) reported that the pyrrhotite was a mixture of the hexagonal and monoclinic varieties. Because of its cross-cutting, replacement relationship with the folded galena-sphalerite ore and its coarse grain size the pyrrhotite is almost certainly of metasomatic origin. The pyrrhotite contains fractured tourmaline grains and thus be related to late Devonian hydrothermal activity (M. Solomon, pers. comm.).

4.4 (iv) Magnetite and hematite

Magnetite has been recorded in a few specimens of pyrite- or chalcopyrite-rich ore (e.g. 76-751, 105162, 105168, 105177) commonly as rounded grains in sphalerite-rich laminae. Brathwaite (1974) also noted magnetite porphyroblasts in pyrite-rich samples. These occurrences are considered to be of primary origin. In addition, magnetite-hematite-pyrite lenses occur within and above the massive sulphide orebody. In one sample from the top of the F lens (105194) pyrite euhedra with pressure shadows of chalcopyrite occur in an iron oxide-rich matrix consisting of laths of hematite, largely replaced by magnetite, and magnetite octahedra. Pyrite-magnetite-hematite-barite zones occur within and at the strike limits of individual lenses of the barite orebody. The hematite laths are essentially undeformed, and have been partially replaced by magnetite. The occurrence of hematite peripheral to lenses of sulphide mineralization, with or without barite, suggests that it may be original and has undergone static recrystallization after deformation. On the 16 level at 900N, hematite-pyrite replaces barite-sulphide mineralization at the top of the H lens.
4.4 (v) Barite

Barite is generally absent in the Fe- and Cu-rich sections of the orebody, though in specimen 105176, barite occurs as clots passing laterally into discontinuous streaks parallel to the banding in the ore. As this specimen is from an area of structural complexity in which tectonic interfingering occurs between units of the sulphide and barite orebodies, it is uncertain at which stage the barite formed. Barite occurs in coarse-grained irregular blebs in the A lens, and in the footwall of the F lens as wispy veins (105180, 105181) presumably of late-stage hydrothermal origin (Green et al., 1981). The barite in the A lens has a similar sulphur isotopic composition to that in the barite orebody and may therefore have formed later than the sulphide ore (Section 6.2(i)).

There is no doubt that barite was an original constituent of the barite orebody, because it occurs as laminae interspersed with barite-sulphide or barite-carbonate bands.

4.4 (vi) Albite

Albite is the sole feldspar found in the vicinity of the orebody, and it is present in a few samples, widely scattered geographically, in either sulphide-poor or in sphalerite-rich bands poor in pyrite (105167, 105168, 105175, 105181). Brathwaite (1974) noted that albite was a common accessory mineral in the barite orebody.

4.4 (vii) Chlorite

Chlorite is common throughout the iron-rich ore of the D, E and G lenses but is relatively rare in the Pb-Zn-rich ore of the southern part of the F lens. The presence of chlorite in the samples from the barite lode (105182, 105183) represent the first reported occurrences of chlorite from this orebody. Indeed, these samples taken from a deep drill hole below the level of mining are more pyrite-rich that those examined from
operating levels in the mine by Brathwaite (1970). Chlorite occurs in pyritic ore either as irregular lenses a few centimetres long lying parallel to ore layering, or as elongate grains either irregularly scattered to arranged parallel to banding (Fig. 4.12). The chlorite may represent a diagenetic or metamorphic alteration product of exhalative montmorillonite (McLeod, 1978).

The chlorites analysed in this study (Table 4.5) fall into the fields of the aluminous chlorites, thuringite and ripidolite, using the classification of Foster (1962). The mole ratio of Fe/Fe+Mg+Mn varies from 0.25 to 0.86, and the silicon and aluminium occupancy of the octahedral site varies from Si$_{2.49}$Al$_{1.51}$ to Si$_{2.74}$Al$_{1.26}$. Chlorites from the massive ore fall into two groups: a high Fe group, including the samples from the D and G lenses which has Fe/Fe+Mg+Mn ratios greater than 0.65, and a low Fe Group, from sphalerite-rich ore in the F lens and barite orebody, which has Fe/Fe+Mg+Mn ratios of less than 0.32.

McLeod (1978) defined two groups of chlorite on mineralogical association. The first group, associated with sphalerite ore, has Fe/Fe+Mg+Mn ratios of 0.32 to 0.86 and silicon-aluminium substitution on the tetrahedral site ranging from Si$_{2.42}$Al$_{1.58}$ to Si$_{2.58}$Al$_{1.42}$.

The second group, associated with chalcopyrite mineralization, has Fe/Fe+Mg+Mn ratios of 0.22 to 0.58 and tetrahedral substitution varying from Si$_{2.53}$Al$_{1.47}$ to Si$_{2.75}$Al$_{1.25}$, although many samples in this latter group are from disseminated chalcopyrite mineralization in the footwall of the F lens.

Chlorite compositions are shown in Fig. 4.13, in which both the data of McLeod (1978) and those of the present study are plotted. The data fall into three groups based on Fe/Fe+Mg+Mn ratios:
Fig. 4.12  Composition of chlorites from Rosebery from McLeod (1978) and this study. The composition of chlorites from Prince Lyell (Walshe & Solomon, 1981; Hendry, 1981), Mattagami Lake (Roberts & Reardon, 1978) and Woodlawn (Ayres, 1979) are shown for comparison. Fields for chlorite types from Foster (1962).
Table 4.5
COMPOSITION OF GANQUE MINERALS

<table>
<thead>
<tr>
<th>Sample number</th>
<th>m above football</th>
<th>MgO</th>
<th>FeO</th>
<th>MnO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. CHLORITE, wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D lens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>105164/la</td>
<td>18.3</td>
<td>7.76</td>
<td>32.1</td>
<td>0.85</td>
<td>0.07</td>
<td>23.32</td>
<td>23.52</td>
<td>0.37</td>
<td>87.99</td>
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<tr>
<td>105167/1a</td>
<td>11.0</td>
<td>3.88</td>
<td>36.29</td>
<td>0.92</td>
<td>0.07</td>
<td>20.69</td>
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<td>82.06</td>
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</tr>
<tr>
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<td>0.79</td>
<td>0.13</td>
<td>20.00</td>
<td>19.95</td>
<td>0.15</td>
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<tr>
<td>105167/3a</td>
<td>11.0</td>
<td>4.69</td>
<td>35.31</td>
<td>0.94</td>
<td>0.08</td>
<td>23.45</td>
<td>23.17</td>
<td>0.12</td>
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</tr>
<tr>
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<td>1.8</td>
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<td>0.11</td>
<td>23.17</td>
<td>22.92</td>
<td>0.15</td>
<td>90.58</td>
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<td>5.52</td>
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<td>89.00</td>
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<tr>
<td>G lens</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>105174/1</td>
<td>16.1</td>
<td>3.74</td>
<td>42.21</td>
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<tr>
<td>105174/2a</td>
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<td>9.09</td>
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Analyses by electron microprobe, University of Tasmania.
nd = not determined.
Fig. 4.13  Banded sulphide ore (100011) consisting of sphalerite (dark grey), pyrite (white, high relief), galena (grey, low relief) and coarse recrystallized flakes of chlorite (black, lower left) orientated parallel to banding. Reflected light, width of field is 1.1 mm.

Fig. 4.14  Sphalerite (black) and carbonate (white to grey) from specimen 105167. Recrystallized carbonate surrounds vugh-filling colloform carbonate (centre). Transmitted light. Scale bar 1 mm.
(i) Fe/Fe+Mg+Mn > 0.6

This group includes most of the chlorites from the D and G lenses associated with both sphalerite- and chlorite-rich mineralization (cf. McLeod, 1978).

(ii) Fe/Fe+Mg+Mn < 0.35

This group includes chlorites from the barite lode, most chlorites from sphalerite-rich mineralization of the F lens, and some chlorites from the chalcopyrite-rich disseminated mineralization stratigraphically below the F lens.

(iii) Fe/Fe+Mg+Mn between 0.4 and 0.6

This is an overlapping field comprising most of the chlorites from the footwall of F lens, the single chlorite analysed from the footwall schist, and chlorites from the D and F massive sulphide lenses.

Thus, as with the sphalerite and sulphur isotopic compositions (Chapter 6), the composition of chlorite appears to be more closely controlled by the lateral, rather than the vertical, metal zoning of the sulphide orebody.

The chlorites from groups (i) and (iii) partly overlap the field of chlorites from Prince Lyell (Hendry, 1981; Walshe & Solomon, 1981) but are markedly richer in Fe and Al than chlorites from the massive ore at Woodlawn (Ayres, 1979) and chlorites from Mattagami Lake (Roberts & Reardon, 1978; Fig. 4.13).

Most of the chlorites analysed have less than the maximum number of cations (10) in their structural formulae. Of those that do have 10 cations in their formula, the minimum number of Fe$^{3+}$ ions in the structure required to balance the trivalent charge on the octahedral and tetrahedral sites varies from 0.067 (analysis 2, Table 7.1) to 0.384 (analysis 5, Table 7.1), the latter chlorite being from the barite lode. For the remainder of the analyses the vacancy in the octahedral site
varies from 0.08 to 0.194 (analyses 3 and 4, Table 7.1). The chlorites without vacancies in their structure are found less than a centimetre from chlorites with significant vacancies in their structures (e.g. 105174, Table 7.1).

4.4 (viii) **Sericite**

Sericite is an ubiquitous, but generally rare, gangue mineral throughout the orebody (Table 4.1). The sericites at Rosebery are phengitic and contain 0.18 to 0.35 atoms of Mg+Fe in the 2 octahedral positions. Gee (1970) noted that the Rosebery sericite was enriched in Ba and his analyses showed a range of 2.5 to 3.5 mass % BaO. The present analyses (Table 4.5) show a range in BaO content from 1.1 to 4.2 % BaO with no noticeable variation except that the samples from the footwall schist and the barite orebody fell at the low end of the range.

4.4 (ix) **Carbonate**

The few carbonate analyses reported in Table 4.1 show a wide variation in composition from manganoan siderite, through magnesian and ferroan kutnahorite to manganoan calcite. This range has been extended by Dixon (1980) to include manganoan dolomite, dolomite and ankerite. According to Dixon (1980) most of the carbonate appears to be of replacement origin, including at least some of the oolitic carbonate of Brathwaite (1974). Some of the carbonate may also have precipitated in cavities, notably some of the colloform carbonate such as that in specimen 105167.
Chapter 5

HYDROTHERMAL ALTERATION

5.1 GEOLOGICAL AND TEXTURAL RELATIONSHIPS

Extensive zones of quartz-sericite alteration are present within the footwall pyroclastics beneath the Rosebery and Hercules orebodies. Other smaller zones of alteration occur around the minor deposits of Knoyna, Grand Centre, Jupiter and Ring P.A. (Fig. 3.1). That the alteration preceded cleavage development is shown by a number of features including fracturing of pyrite euhedra, the presence of pressure shadows of quartz, chlorite, carbonate or chalcopyrite adjacent to pyrite grains and the development of more intense cleavage in the more strongly sericitized rocks. Such alteration within the Mount Read Volcanics has long been recognised as associated with ore (Edwards, 1939; Solomon, 1964). Loftus-Hills et al. (1967) first advanced the hypothesis that their presence indicated that mineralisation was probably related to Cambrian hydrothermal activity, thus advancing the case for exhalative ore formation which had been proposed tentatively earlier (Hall & Solomon, 1962).

In the footwall pyroclastics there is a general lateral passage towards ore from weakly cleaved rocks with relatively fresh albite phenocrysts in which vitroclastic textures are well preserved (77-2, 77-3, 75-771), through semischists in which strongly sericitized feldspar phenocrysts are elongate flecks with a near vertical pitch in the cleavage plane (e.g. 77-370, 75-755, 75-754) to schists in which sericite flecks after feldspar and chlorite streaks, representing relict fiamme, present the only evidence of the original nature of the rock. In a number of samples (e.g. 75-368, 75-661, -755), plagioclase phenocrysts are replaced by K-feldspar in the zone of partial sericitization (Fig. 5.1), a feature also noted in the
Fig. 5.1 Photomicrograph of blotchy texture of K-feldspar replacement of albite phenocrysts from vitric-crystal tuff from footwall pyroclastics (75-661). The groundmass is strongly sericitized. Crossed nicols, width of field is 4 mm.

Fig. 5.2 Photomicrograph of cleaved pyritic quartz-sericite schist with quartz pressure shadows adjacent to pyrite (105129). Cleavage from top left to bottom right. Relict vitroclastic texture can be seen in the bottom left hand corner of photograph. Transmitted light, width of field is 4 mm.
fringes of the sericitic alteration zone at Mount Lyell (Cox, 1981).

Alteration is not restricted to the footwall pyroclastics. Strong to moderate sericitization of plagioclase is common in the massive pyroclastics within a few hundred metres above the black slate in the Rosebery mine area (77-701; 105190), although plagioclase in some intrusive quartz-feldspar porphyry bodies is virtually unaltered (75-388). Sericitic alteration of plagioclase predominates over carbonate alteration in ten of the eleven thin sections of the massive pyroclastics examined from drill hole 71R, collared some 1.7 km north of the Rosebery mine area (Fig. 3.1). Carbonate alteration of feldspar phenocrysts is common in rocks fringing the sericitic alteration zones, and occurs in both the footwall pyroclastics (75-771; 75-765) and in the massive pyroclastics (75-384, 75-384A, 75-773, H955-310). It is, therefore, difficult to ascribe different alteration assemblages to either the footwall or massive pyroclastics away from areas strongly affected by footwall alteration.

For a few hundred metres stratigraphically below the massive sulphide orebody, there is virtually complete obliteration of primary textures, although relict vitroclastic textures occur in specimen 105129 (Fig. 5.2). An important rock type in the altered footwall rocks is a strongly silicified schist, in some places chert-like, which is well-developed in the upper part of the footwall pyroclastics below the Fe- and Cu- part of the orebody, but also occurs at lower stratigraphic levels (Brathwaite, 1974). This rock is termed the quartz schist by the mine geologists (Hall et al., 1953). Rectangular aggregates of medium grained quartz betray the former existence of feldspar in a few specimens (105134; 105145). Prominent rock types include quartz-sericite-pyrite schists (105115, 105119, 105121, 105132, 105134, 105137, 105140, 105142a, 105148, 105153) and quartz-chlorite-sericite-pyrite schist (105145, 105147). Chlorite is present in varying but minor amounts in most specimens of quartz-sericite schist, and
carbonate occurs in a number of specimens (105119; 105153) and is a major mineral in 105145. Chlorite and chalcopyrite are common in rocks underlying the Fe- and Cu-rich sections of the orebody (between 100N and 500S), although there is no evidence of a chlorite-rich alteration pipe similar to those found beneath some of the Canadian Archaean deposits (Sangster & Scott, 1976). However, Brathwaite (1970, 1975) has described subconformable lenses of pyrite- and chalcopyrite-rich mineralisation occurring as veinlets, bands and disseminations in zones of quartz-rich schist up to 90 m long and 12 m thick beneath the southern and central sections of the orebody. A bismuthian sulphosalt with a composition similar to aikenite (J.P. Stephens, pers. comm.) occurs as inclusions in chalcopyrite in a few specimens (105137, 105152b, 105151) and minor arsenopyrite occurs in the latter sample. Minor to trace galena and/or sphalerite are present in specimens 105142a and b, 105145, 105147, 105149 and 105151 as inclusions in pyrite or in pressure shadows. Hematite and rutile occur in phyllosilicate-rich bands in a number of the samples and in 105147 hematite is partly replaced by magnetite.

Tourmaline is present in specimens 105131, 105142a and b, 105148, 105160 and 105151, and in the majority of cases occurs as veinlets with quartz and/or carbonate crosscutting the cleavage. Where euhedral tourmaline crystals are intergrown with pyrite, evidence exists for thermal annealing of the surrounding rock, for example, recrystallisation of fibrous quartz in pressure shadows adjacent to pyrite to form a polygonal texture (105142b). In the same specimen chlorite and minor green biotite with a decussate texture are associated with the tourmaline. It thus appears that the bulk of the tourmaline post-dates cleavage development. In one specimen (105151) much of the tourmaline is intergrown with, and orientated parallel to, fibrous quartz in pressure shadows and some of the tourmaline may be of Cambrian age.
In one specimen from the footwall schist (105129), quartz-sericite-pyrite schist (Fig. 5.2) is cut by a vein of chalcopyrite-carbonate-albite-barite-pyrite (Fig. 5.4). The albite is clear, and unlike virtually all phenocryst albite from the Mount Read Volcanics, lacks microinclusions of sericite, carbonate or other minerals. It occurs both within the vein and as a vein selvage. Similar secondary albite occurs in a few specimens of the footwall schist (e.g. specimen 31784A, Solomon, 1964) and locally in the massive sulphide and barite orebodies. It may be a product of boiling hydrothermal solutions (see Section 8.2).

In addition to the products of Cambrian hydrothermal alteration, post-cleavage alteration is locally prominent. As well as the tourmaline veins in the footwall schist, late-stage cross-cutting veinlets of tourmaline-quartz occur in the Rosebery lodes and Koonya areas. Within the western correlates of the massive pyroclastics in the Black P.A. – Jupiter mine area, extensive zones of sericitization and silicification of pyroclastic rocks occur. Within this area are a small number of small vein-type deposits with various combinations of Sn-Bi-Cu-Pb-Zn mineralisation in gangue assemblages of quartz+tourmaline+fluorite+calcite (e.g. Black, P.A., Salisbury, Chamberlain; Hills, 1915). The textures of these assemblages are in sharp contrast with those of the footwall schist in that sericitization, although it has locally resulted in complete destruction of feldspar phenocrysts, forms a poorly defined very fine-grained mesh texture in rocks in which post-cleavage veins of unstrained quartz+carbonate abound (Fig. 5.3). In outcrop, these rocks are distinguished by their massive nature, pale green colour, waxy lustre and profusion of quartz veins.

5.2 CHEMICAL CHANGES

Chemical analyses of fresh and altered rocks from the Primrose Pyroclastics in the Rosebery and Hercules areas are presented in Table 5.1.
Fig. 5.3 Silicified tuff from massive pyroclastics (75-603) with quartz phenocrysts and vein of unstrained quartz. Groundmass consists of granular quartz and a mesh of very fine-grained sericite. Compare textures in Figs 5.2 and 4.7. Crossed nicols, width of field is 4 mm.

Fig. 5.4 Vein assemblage of chalcopyrite (black), twinned albite, quartz (white, just above largest albite grain), carbonate (dark grey, bottom left) and barite (white grain to left of large albite) in quartz-sericite schist (105129). Crossed nicols, width of field is 4 mm.
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Sample description; locality; coordinates:
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2. Vitric crystal tuff, footwall pyroclastics (77/3); 4.3 km S of Rosebery mine; 7803E 7023N.
3. Vitric crystal tuff, footwall pyroclastics (31789A); 500 m N of Hercules mine.
4. Vitric lithic tuff, massive pyroclastics (83-7); 2 km S of Rosebery mine; 7908E 7240N.
5. Andesite tuff, massive pyroclastics (83-8); Mount Read road; 7770E 6689N.
6. Rhyolite lava, Mt Black Volcanics (83-9); Farrell tramway; 8000E 8019N.
7. Vitric crystal tuff, footwall pyroclastics (83-10); 900 m N of Hercules mine; 7652E 6757N.
8. Pyritic quartz-sericite schist (105157); drill hole R1751, 2216-2231 ft; 20M 2530C, RL8125.
9. Pyritic sericite-chlorite-quartz schist (105158); drill hole R1714, 830-870 ft; 475N 1120E, RL9076.
10. Sericite-quartz schist, trace pyrite (105159); drill hole R1715, 2216-2231 ft.
11. Pyritic quartz-chlorite-sericite schist (105160); drill hole 69R, 138-153 ft.
12. Sericite-chlorite schist at top of footwall pyroclastics (31784A); 0.8 level main adit, Rosebery mine.
13. Sericite-quartz schist with albite, footwall pyroclastics (31786A); 0.8 level main adit, Rosebery mine.
14. Quartz schist; drill hole R1163, 468 ft.

Analyses 3, 12 and 13 from Solomon (1964).
Analysis 14 from Smith (1975).
Remainder of analyses by J. Furst and L.M. Hay, Department of Mines, Tasmania, by XRF and other techniques.
nd = not determined.
All specimens analysed were taken from drill core or blasted from fresh outcrop. The uniform primary lithology of the footwall pyroclastics suggests that comparisons of element concentrations between altered and unaltered rocks may represent chemical changes due to alteration (analyses 1 to 3 versus analyses 7 to 14, Table 5.1).

Finlow-Bates & Stumpfl (1981), using chemical analyses of rocks from alteration zones around Canadian and Tasmanian massive sulphide deposits, suggest that TiO$_2$ and Zr remain immobile during hydrothermal alteration and become passively concentrated during net leaching of other components from the rock, or become depleted during net addition of other elements.

They therefore concluded that processes of alteration and magmatic differentiation could be distinguished on a TiO$_2$-Zr plot (Finlow-Bates & Stumpfl, 1981, Fig. 8; inset Fig. 5.5, this thesis). Alteration of volcanic rocks with two different original compositions (inset Fig. 5.5) will result either in passive concentration of Zr and TiO$_2$ (trend Y) or depletion (trend X) with the loci of the various lines XY passing through the origin. From the limited data of this study it appears that felsic units of the Primrose Pyroclastics, including both altered and unaltered rocks, form a coherent population on a TiO$_2$-Zr plot (Fig. 5.5).

It is, therefore, valid to use the approach of comparing oxide ratios to TiO$_2$ in altered and unaltered samples to compute gains and losses of various elements (Iijima, 1974). Iijima used the index

$$\left(\frac{[RO/\text{TiO}_2]_A}{[RO/\text{TiO}_2]_p} - 1\right) \times 100\%$$

where $[RO/\text{TiO}_2]_A$ and $[RO/\text{TiO}_2]_p$ are the mass ratios of any oxide RO to TiO$_2$ in the altered and parent rocks respectively. This gives a measure of percentage gains and losses of various components. The results of this
Fig. 5.5  Plot of TiO₂ versus Zr content of different rock types from the Mount Read Volcanics (this study). All but one rock fall close to a line passing through the origin. Inset shows different effects of magmatic differentiation and relative depletion or concentration due to hydrothermal alteration (after Finlow-Bates & Stumpfl, 1981; see text).

Fig. 5.6  Plot of TiO₂ versus Al₂O₃ content of different rock types from the Mount Read Volcanics in the Rosebery area (from Smith, 1975 and this study). Note how all rocks analyzed, with the exception of two specimens from the massive pyroclastics, fall on a line passing through the origin.
DIFFERENTIATION

Zr (ppm.)

Zr (ppm.)

MOUNT BLACK VOLCANICS
MASSIVE PYROCLASTICS
FOOTWALL PYROCLASTICS
FOOTWALL SCHIST

MOUNT BLACK VOLCANICS
MASSIVE PYROCLASTICS
FOOTWALL PYROCLASTICS
FOOTWALL SCHIST

AL₂O₃ (MASS %)

0 5 10 15
The following general conclusions emerged:

1. Al, Nb and Zr appear to neither have been enriched nor depleted. Al and Zr in particular show coherent behaviour.
2. Mg, Mn, Rb, K, H$_2$O and nonsulphide Fe are generally enriched.
3. Na and Sr are strongly depleted and so is Ca where there is a low carbonate content.
4. Ba shows more erratic behaviour, but is generally enriched.
5. Variation in P and V is not considered significant because the concentrations of these elements were close to their detection limits.

Exceptions to the above trends occur in the 'quartz schist' where depletions in Mn and Mg as well as Na, Ca and Sr occur in rocks with more than 78% SiO$_2$ (Smith, 1975). In these rocks (Table 5.1, analysis 14) SiO$_2$, K, Rb and H$_2$O are the only components enriched.

Because of the parallel effects alteration has on Zr and Al$_2$O$_3$ (Table 5.2) a plot of TiO$_2$ against Al$_2$O$_3$ is shown in Fig. 5.6, enabling the more extensive data of Smith (1975), who did not analyse rocks for Zr, to be compared with the data of the present study. The diagram shows a straight line trend passing through the origin, further suggesting that the footwall pyroclastics and at least some units in the massive pyroclastics had a similar original composition.

5.3 COMPARISON WITH OTHER DEPOSITS

A review of alteration around volcanic-hosted massive sulphide deposits (Franklin et al., 1981) has revealed that the only chemical change common to all deposits is a decrease in Na in footwall rocks near ore. Many Canadian Archaean Cu-Zn deposits are underlain by
Table 5.2

PERCENTAGE CHANGE IN CHEMICAL COMPONENTS IN ALTERED FOOTWALL PYROCLASTICS EXPRESSED RELATIVE TO TiO₂.

<table>
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<th>10</th>
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<td>+8</td>
<td>+2</td>
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</tbody>
</table>

* Includes all Fe expressed as FeO.
** Includes all non-sulphide Fe expressed as FeO.
' Parent rock is taken as the average of analyses 1-3 (Table 5.1) for major elements and analyses 1 and 2 for trace elements.
chlorite-rich alteration pipes surrounded by sericitic haloes, although pipe-like alteration is lacking in the Takiyuak deposits, North West Territories. The chloritic alteration pipes are characterized by Na, K and, in some cases, Ca depletion and by Mg, Fe and, generally, Mn enrichment. In Phanerozoic deposits hosted by felsic and intermediate volcanics, chloritic alteration pipes are generally less prominent. Possible exceptions are Woodlawn, N.S.W. and Buchans, Newfoundland. At Woodlawn a zone of chlorite schist and chert immediately underlies ore. This zone is semi-conformable with the stratigraphy, but may, in part, represent a transposed pipe-like structure. The chlorite schist and the orebody are surrounded by an extensive zone of pyritic quartz-sericite-chlorite rocks in which feldspars have been destroyed. The latter zone extends some 200 m into post-ore rocks and is marked by depletion in Na, Ca, and Sr and enrichment in Mg, Ba and, generally, Fe and Si (Petersen and Lambert, 1979). At Buchans chloritization and silicification of footwall rocks is accompanied by $\text{H}_2\text{O}$, Mg, Fe, Mn, Si and base metal enrichment and Ca, Na, Sr and K depletion (Thurlow et al., 1975).

In contrast to Rosebery, rocks associated with other Tasmanian Cambrian volcanic-hosted deposits do not display Mg enrichment. At Que River alteration related to mineralization is associated with variable depletion of Na, Ca and Mg and enrichment in Si, K and, sporadically, Mn (Whitford et al., 1983). At Mt. Lyell, the major changes noted were loss of Na, Ca, Rb and Sr and addition of Ba and $\text{H}_2\text{O}$ (Walshe and Solomon, 1981). The chemical changes documented at Rosebery are most similar to those associated with the Kuroko deposits of Japan. For example, at Fukazawa footwall alteration involved depletion in Na, Ca and Sr; enrichment in K, Mg and S and highly variable, but generally enhanced Cu, Pb and Zn values (e.g. Green et al., in press; Date et al., in press).
In summary, a depleted Na content of footwall volcanic sequences appears to be the most reliable guide to ore and is used in exploration for Kuroko deposits (e.g. Date et al., 1979).

5.4 TRACE ELEMENTS IN FOOTWALL PYRITE

Loftus-Hills & Solomon (1967), Loftus-Hills (1968) and Price (1972, cited by Willan & Hall, 1980) found that in volcanic-hosted deposits pyrites associated with copper mineralisation tended to have higher trace Co contents and Co/Ni ratios than pyrites associated with lead and zinc mineralisation.

The Co content of pyrites from the footwall schist (for separation method see Appendix 3) ranges from 7 to 1010 ppm (including nine samples from Loftus-Hills, 1968) with a mean of 240 ppm. The range and mean for Ni are < 1 to 94 ppm and 36 ppm respectively. Apart from two samples, the pyrites with more than 300 ppm Co lie in a zone on the longitudinal projection of the orebody that includes the areas of highest Cu and Fe in the overlying massive orebody (Fig. 5.7). This zone coincides with that found by Loftus-Hills (1968) to include nearly all the highest Co and Co/Ni values of pyrite in the massive ore. Values of the Co/Ni ratio in footwall schist pyrite in excess of 10 occur in an area encompassing the high Co zone and a tail pitching steeply to the south roughly parallel to the margin of the overlying massive ore (Fig. 5.7). The Ni content of pyrite shows no systematic distribution. The samples from the massive orebody analysed by Loftus-Hills (1968) were somewhat lower in both Co (range 0 to 167 ppm, mean 67 ppm) and Ni (range 1 to 83 ppm, mean 14 ppm) compared with the samples from the footwall schist. This may be a reflection of a higher degree of supersaturation of solutions which precipitated pyrite in the massive ore (e.g. McIntire, 1963).
The product of acid leaching of roasted pyrite was analysed by AAS using a nitrous oxide-acetylene flame. This method was found to give comparable results to that of Loftus-Hills (1968) involving removal of iron by di-isopropyl ether and an acetylene/air flame.

### Table 5.3

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Coordinates (feet)</th>
<th>R.L. (mine) (feet)</th>
<th>Drill hole number and footage</th>
<th>Co</th>
<th>Ni</th>
<th>Co/Ni</th>
<th>Mn</th>
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<td>R1840, 1767</td>
<td>60</td>
<td>8</td>
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<td>785</td>
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<td>R1920, 1939</td>
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<td>9346</td>
<td>R1971, 210</td>
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<td>9146</td>
<td>R1982, 245</td>
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<td>3</td>
<td>35</td>
<td>69</td>
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<td>9132</td>
<td>R2037, 443</td>
<td>392</td>
<td>&lt;1</td>
<td>105</td>
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</tr>
</tbody>
</table>
Fig. 5.7 Distribution of the Co content of pyrite in the footwall schist, plotted on an unfolded longitudinal projection. The Fe and Cu maxima are close together because the projection has not been unfolded. The lighter dashed line encloses the area of pyrites with Co contents of more than 300 ppm, and the dot-dash line encloses the area of pyrites with a Co/Ni mass ratio in excess of 10.
Though it is not yet possible to quantify the significance of the high Co zone, it is suspected that it loosely defines a hydrothermal conduit. High Co values in pyrite coincide with the zone of highest Cu values at the Prince Lyell deposit (Walshe & Solomon, 1981). It should be restated that although the high Co zone coincides approximately with zones of high Fe- and Cu- in the massive sulphide ore, because of structural complexity the relative positions of the Fe-, Cu- and Co-rich zones are not well constrained.
6.1 INTRODUCTION

Previous sulphur isotopic analyses have been published by Stanton & Rafter (1966) and Solomon et al. (1969). Stanton & Rafter (op. cit.) analysed mixed sulphides from the massive orebody at Rosebery and recorded a range in $\delta^{34}\text{S}$ values from +8.8 to +15.5\%o. Solomon et al. (op. cit.) analysed individual sulphides from the footwall schist, sulphide and barite orebodies, black slate and veins in the massive pyroclastics. They also reported $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of barites from the barite orebody and $\delta^{18}\text{O}$ values from the barite orebody. $\delta^{34}\text{S}$ values of sulphide minerals from the sulphide orebody ranged from +9.0 to +13.8\%o (excluding galena), and barites had $\delta^{34}\text{S}$ values between +38.5 and +40.1\%o. $\delta^{34}\text{S}$ values of sulphides from the barite orebody ranged from +17.4 to +19.2\%o (sphalerite or sphalerite-galena mixtures) and barites had $\delta^{34}\text{S}$ values between +34.6 and +41.2\%o. Pyrites from the black slate, inferred to be of biogenic origin on the basis of the Co and Ni trace element study of Loftus-Hills (1968), showed a wide range of $\delta^{34}\text{S}$ values between +2.3 and +25.3\%o.

Data from co-existing sulphides, generally handpicked from relatively coarse grained ore specimens, yielded no consistent isotopic temperatures.

The present work was designed to complement and extend the previous studies. Sampling was made in some detail of the three sections through the sulphide orebody (Fig. 4.2) near the Fe, Cu and Pb-Zn maxima found in the metal zoning study. In addition, samples were analysed from:
1. Sulphides from the F lens studied by Brathwaite (1970, 1974);
2. Pyrites from the footwall schist;
3. Pyrite and pyrrhotite from the extreme southern edge of the sulphide orebody;
4. Sulphides from the barite lode;
5. Oxide-rich mineralization overlying both ore horizons.

Most of the isotope analyses were done at the C.S.I.R.O. Minerals Research Laboratory, Sydney, under the direction of J.W. Smith. To ensure, as well as possible, that contemporaneously precipitated sulphides were analysed, 200 mg specimens were drilled from individual laminae within the fine-grained ore, and sulphur from individual sulphides was separated by the technique developed by J.W. Smith (Smith & Croxford, 1973). Briefly, this method involves reacting a sulphide sample sequentially with 10% acetic acid for 24 hours to remove carbonates, cold 1N HCl, boiling 1N HCl and boiling 2N HCl under a stream of nitrogen. The $\text{H}_2\text{S}$ released is bubbled through an AgNO$_3$ solution and the Ag$_2$S precipitated was heated with Cu$_2$O at 900°C to produce SO$_2$ for isotopic analysis. The leachate was analysed for Cu, Pb, Zn and Fe. Generally S from galena is released before S from sphalerite in the sequential leaching process. Pyrrhotite is also readily attacked by 1N HCl, and the technique was used to separate sulphur from pyrrhotite from pyrite sulphur in sample 105193.

Checks on the leaching process include comparison of the molar ratios of S in the Ag$_2$S produced and Pb and Zn in the leachate. Samples which originally contained only sphalerite and pyrite, and consequently leached S only from sphalerite at each stage of the process, gave $\delta^{34}\text{S}$ values for sphalerite precise to $\pm 0.1\%$, which is about the accuracy of the mass spectrometer. Consequently, it is regarded that the leaching technique is currently the most convenient for sulphur isotope studies of co-existing minerals from fine-grained massive ores.
Pyrite and chalcopyrite remain in the residue after acid treatment. Samples were selected with negligible chalcopyrite to eliminate the problem of separating these minerals.

In the pyrite-barite sample pyrite was dissolved with HNO₃ and the released H₂S collected as Ag₂S. The residual barite was treated by the method of Rafter (1957) to yield SO₂ for isotopic analysis.

All chemical separations and combustion of Ag₂S and FeS₂ specimens to SO₂ was done by the writer. M.S. Burns analysed the leachates from the chemical separation and M.S. Burns and J.W. Smith of C.S.I.R.O. performed the mass spectrometric analyses.

A few of the samples were analysed by the writer at the University of Tasmania. These samples were drilled from polished sections.

The precision of analyses from the CSIRO was ±0.1‰, whereas those done at the University of Tasmania were precise to at least ±0.1‰ and in most cases ±0.05‰. Because of problems with standards, values from the CSIRO and the University of Tasmania may vary by 0.3‰. Such variation in no way affects the conclusions of this study.

6.2 RESULTS OF THE SULPHUR ISOTOPE STUDY

6.2 (i) Sulphide orebody

The three main sections sampled showed little variation and no obvious trend in δ³⁴S within each section (Table 6.1). The section sampled through the D lens, near the pyrite-rich focus of mineralization (Section 1, Fig. 4.2) showed a small range in δ³⁴S of +8.9 to +9.4‰ with a high value of +13.4‰ at the top of the section. This sample, however, occurs above a thin interval of weakly mineralized sericitic slate and probably reflects a different, presumably later, phase of ore deposition. The values of the G lens are higher than those of the D lens and those for the upper part of the F lens are higher again. The values of the samples from the lowest (in a vertical and not necessarily a stratigraphic sense) are lower than other samples from the F lens (100958, 100960, 100961, Table 6.1) and are similar to samples from the D lens.

All available isotopic data for the sulphide orebody are plotted on an unfolded longitudinal projection (Fig. 6.1). Where separated
### Table 6.1: Sulfur Isotope Results

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Coordinates (mine)</th>
<th>R.L. (m)</th>
<th>ε²⁹S CDT(‰)</th>
<th>T (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>py</td>
<td>s1</td>
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</table>

#### A. SULPHIDE OREBODY

1. Sampled sections**

**D lens:

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Coordinates (mine)</th>
<th>R.L. (m)</th>
<th>ε²⁹S CDT(‰)</th>
<th>T (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>105161</td>
<td>700N 1000E 9664</td>
<td>13.4</td>
<td>11.1</td>
<td>10.8</td>
</tr>
<tr>
<td>164</td>
<td>700N 990E 9664</td>
<td>8.9</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>165</td>
<td>700N 904E 9664</td>
<td>9.8</td>
<td>9.6</td>
<td>9.6</td>
</tr>
<tr>
<td>170</td>
<td>700N 942E 9664</td>
<td>9.3</td>
<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
<td>173</td>
<td>700N 912E 9664</td>
<td>9.4</td>
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</table>

**G lens:

<table>
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<tr>
<th>Sample Number</th>
<th>Coordinates (mine)</th>
<th>R.L. (m)</th>
<th>ε²⁹S CDT(‰)</th>
<th>T (°C)*</th>
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<tbody>
<tr>
<td>105175</td>
<td>700N 1140E 9512</td>
<td>11.6</td>
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<tr>
<td>177</td>
<td>700N 9512</td>
<td>11.0</td>
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<tr>
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<td>700N 1300E 9512</td>
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<tr>
<td>174</td>
<td>700N 9512</td>
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</table>

**F lens:

<table>
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<th>T (°C)*</th>
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<td>100926</td>
<td>400S 1281E 9557</td>
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<td>928</td>
<td>400S 1274E 9555</td>
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<td>930</td>
<td>400S 1271E 9554</td>
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<td>933</td>
<td>400S 1261E 9552</td>
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<td>934</td>
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<td>400S 1260E 9551</td>
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<td>937</td>
<td>400S 1253E 9550</td>
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<td>958</td>
<td>800S 2060E 8807</td>
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<td>960</td>
<td>800S 2058E 8804</td>
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<td>961</td>
<td>800S 2056E 8801</td>
<td>7.1</td>
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</table>

2. Previous data (summarized)

- **Solomon et al. (1969), 22 samples**
  - 8.6 - 9.0 - 7.6 - 38.5 - 250 - >500
  - One sample (33446) of coexisting barite (39.6, 39.7) and pyrite (10.8, 10.9), gives T = 170°C

- **Stanton & Rafter (1966), 26 samples mixed sulphides, 15.5 to 8.8**

3. Pyrite-pyrhotite, south end of F lens

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Coordinates (mine)</th>
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<td>130N 1250E 9664</td>
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<td>196</td>
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#### B. FOOTWALL SCHIST: PYRITE

1. This study

<table>
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<tr>
<th>Sample Number</th>
<th>Coordinates (mine)</th>
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<th>T (°C)*</th>
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<td>139</td>
<td>13N 1124E 9506</td>
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<td>132</td>
<td>238S 1445E 9348</td>
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<td></td>
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<tr>
<td>115</td>
<td>476N 1104E 9350</td>
<td>10.6</td>
<td></td>
<td></td>
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<td>141</td>
<td>1490N 1946E 9138</td>
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<td>143</td>
<td>567S 1805E 8950</td>
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<td>135</td>
<td>932S 1260E 9548</td>
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<td>148</td>
<td>800S 3266E 8480</td>
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2. Solomon et al. (1969)

<table>
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#### C. BARITE OREBODY

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2. Pyrite-hematite-barite above barite orebody

<table>
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3. Previous data, Solomon et al. (1969)

<table>
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<tr>
<td>23949</td>
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Analyses for this study carried out at CSIRO Institute of Earth Resources, Sydney; mass spectrometry by J.W. Smith and M.S. [lurns, except samples 100926-100961, which were analyzed by the writer at the University of Tasmania.

* From Ohlloto & Rye (1979).

** See Table 4.1.
Fig. 6.1 The distribution of $\delta^{34}$S values of sulphide minerals (Solomon et al., 1969; this study) and ore samples (Stanton & Rafter, 1966) from Rosebery plotted on an unfolded longitudinal projection. The method of unfolding is shown in Fig. 4.4. The northings of samples from the D and G lenses have been shifted north at the levels of the mine where the G lens exists. See Table 6.1 for sample locations. The relative positions of footwall schist pyrite and samples from the massive orebody may have been affected by the unfolding, because no attempt has been made to unfold the footwall schist.
Table 6.2

<table>
<thead>
<tr>
<th></th>
<th>ROSEBERRY¹</th>
<th>HEATH STEELE BI²</th>
<th>WOODLAWN³</th>
<th>SHAKANAI NO.1⁴</th>
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</thead>
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<tr>
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<td>1.14</td>
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<tr>
<td>T</td>
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<td>231</td>
<td>283</td>
</tr>
<tr>
<td>σ</td>
<td>0.84</td>
<td>0.32</td>
<td>0.38</td>
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<tr>
<td>n</td>
<td>15</td>
<td>23</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Mean Δ py-gn</td>
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<td>2.70</td>
<td>3.57</td>
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<td>σ</td>
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<td>n</td>
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<tr>
<td>Mean Δ sl-gn</td>
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<td>0.31</td>
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<tr>
<td>n</td>
<td>11</td>
<td>12</td>
<td>12</td>
<td>4</td>
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</tbody>
</table>

T = temperature (°C)
σ = standard deviation of fractionation factors (Δ)
n = number of samples.

¹ This study, Solomon et al., (1969)
² Lusk & Crockett (1969)
³ Ayres et al. (1979)
⁴ Kajiwara (1971).
minerals were analysed, galena is not plotted. The date on mixed sulphides (Stanton & Rafter, 1966) is included. This is justifiable since the average ΔS₁-gn fractionation in the sulphide orebody is 1.3% (this study, Solomon et al., op. cit.) and the maximum 2.0%, the average Zn/Pb weight ratio in the deposit is 3, corresponding to a molar S ratio in sphalerite: galena of 9.5. Therefore, the $\delta^{34}$S value of a sphalerite-galena mixed sample would be at most only 0.2% lower in $\delta^{34}$S than a hypothetical pure sphalerite.

The data (Fig. 6.1) show an increase in $\delta^{34}$S of sulphides from the northern to the southern section of the mine, assuming the reconstruction is correct. It is noteworthy that this increase parallels an increase in the Pb+Zn/Fe ratio in the massive ore, this trend being the reverse of that noted at the Shakanai No. 1 deposit (Kajiwara, 1971), and at the Heath Steele Bl deposit (Lusk, 1972). This pattern is perturbed by an anomalously high $\delta^{34}$S value of a mixed sulphide sample from the northern end of the C lens of +14.5%.

The value of +16.1% for pyrite from coarsely crystalline pyrite-pyrrhotite mineralization at the southern end of the massive sulphide ore is similar to those from Pb-Zn-rich fine-grained ore nearby. This is consistent with the interpretation of Brathwaite (1974) that the pyrrhotite is a replacement product of pre-existing sulphide ore.

The $\delta^{34}$S values of pyrite samples from the top of the D lens from pyrite-magnetite mineralization were +11.5 and +18.9%, higher values than those of the underlying massive ore. The barite from the sulphide ore of the A lens yielded values of 39.6 to 40.1% (Solomon et al., 1969) and barite-pyrite fractionation factors give temperatures of the order of 200 to 220°C for these samples. To achieve 90% isotopic equilibrium at pH 4-7 for a solution with a total sulphur concentration of 0.01 m requires coexistence of sulphide and sulphate species for 90 years prior
to coprecipitation of pyrite and barite (Ohmoto & Lasaga, 1982), a condition unlikely to have been met in the exhalative environment. The barite in these samples is coarse grained and textural evidence indicates that it probably post-dates deposition of the sulphide orebody. The $\delta^{34}S$ values of the barite fall within the range of values of barite from the barite orebody, with which the barite from the A lens may be associated.

6.2 (ii) Footwall schist

$\delta^{34}S$ values of pyrite from the footwall schist are generally similar to those in the overlying massive ore. Pyrite from near the northern margin of strong pyrite dissemination in the footwall rocks (105143, 14.5%) has a higher $\delta^{34}S$ value than most sulphides from the D and C lenses, but one mixed sulphide sample analysed by Stanton & Rafter (op. cit.) from this zone has an identical $\delta^{34}S$ value (Fig. 6.1). A general correlation may be seen from the few samples analysed (Table 8) in the main southern zone of mineralization between higher Co/Ni ratios, lower Mn contents and lower $\delta^{34}S$ values of footwall schist pyrites and higher Fe/Pb+Zn ratios and lower $\delta^{34}S$ values in the overlying massive sulphide orebody.

6.2 (iii) Barite orebody

Sulphide minerals from the barite lode have higher $\delta^{34}S$ values than those of the underlying sulphide orebody, with the results for pyrite and sphalerite ranging from 14.5 to 19.8%. Barite shows a range of 34.6 to 41.2%, which compares with a variation in Cambrian anhydrites of 27 to 35% (Kaplan, 1975). For most of the Cambrian the $\delta^{34}S$ of seawater sulphate was about 30%. Consequently, the precipitated barite has $\delta^{34}S$ values which are probably in excess of the coeval seawater by several permil. The $\delta^{34}S$ values of pyrite from
pyrite-barite-hematite mineralization above the barite lode are higher (+20.7 %o and +27.6 %o) and barite co-existing with the pyrite with the higher $\delta^{34}\text{S}$ value has a value of +33.1 %o.

These results show another marked difference with those of Kajiwara (op. cit.) from the Shakanai mine where pyrite from hematite-quartz-pyrite mineralization has distinctly lower $\delta^{34}\text{S}$ values (-6.0 to +4.6 %o) compared with the underlying black ore (+3.0 to +5.2 %o).

6.3 ISOTOPIC FRACTIONATION BETWEEN COEXISTING MINERALS

Sulphur isotopic temperatures determined in the studies of Solomon et al. (1969) and in this study are shown in Fig. 6.2 and listed in Table 6.1. The range of isotopic temperatures is wide, from less than 100°C to greater than 500°C, and no difference can be detected between the isotopic temperature ranges of the two investigations. In some cases, pairs of minerals from co-existing pyrite-sphalerite-galena triplets yield internally consistent isotopic temperatures, but in only two samples, 105176 (330 - 340°C) and 105179 (275 - 345°C) are these temperatures within the range believed feasible for the formation of the Rosebery deposit.

Despite the wide range in isotopic temperatures, the sulphides from Rosebery show the equilibrium order of fractionation of $\delta^{34}\text{S}$ values (pyrite-sphalerite-chalcopyrite-galena) with the exception of one sphalerite-chalcopyrite pair analysed by Solomon et al. (1969). Gross isotopic disequilibrium between chalcopyrite and other sulphide minerals is common in massive and disseminated ore deposits of volcanic association being noted also at Heath Steele, New Brunswick (Lusk & Crockett, 1969), Mt Lyell (Walshe & Solomon, 1981), Raul, Peru (Ripley & Ohmoto, 1977), Woodlawn (Ayres et al., 1979), and the deposits at Notre Dame Bay, Newfoundland (Bachinski, 1977).
Fig. 6.2 (a) Histogram showing sulphur isotope temperatures derived from coexisting minerals from the sulphide orebody.
(b) Sulphur isotope temperatures derived from barite-sulphide and sulphide pairs from the barite orebody.
Comparison with data from other massive sulphide deposits in regionally metamorphosed terrains, namely the Heath Steele B zone (Lusk and Crocket, op. cit.) and Woodlawn (Ayres et al., op cit.) shows that the wide spread of Δ values between coexisting sulphide pairs is typical of these deposits (Table 6.2). Similar data for an unmetamorphosed deposit (Shakanai No. 1, Kajiwara, 1971) are included for comparison. For all cases, isotopic temperatures are calculated from the equations listed in Ohmoto & Rye (1979). The regional metamorphic grade at Woodlawn is chlorite-grade greenschist facies (Gilligan et al., 1979); biotite is developed sporadically in the deeper levels of the Rosebery mine and biotite-grade greenschist facies metamorphism occurs at Heath Steele (Goodfellow, 1975).

A particularly vexing question facing investigators of metamorphosed ore deposits is whether sulphur isotope fractionation data give information on original temperatures of deposition or represent partial, or complete, metamorphic equilibration. It is generally accepted that the isotopic temperatures from the Shakanai mine are depositional (Kajiwara, 1971), and this may be due to the fact that Eldridge (1981)*, found that over 90% of Kuroko sulphides occur as coarse, euhedral crystals formed by hydrothermal recrystallization of primary fine grained ores. This process takes place either by continued passage of solution through the growing sulphide mound during deposition on the seafloor (Eldridge, op. cit.)* or by convective circulation of solutions through the mound (Barton, 1978). Solomon and Walshe (1979) referred to, but did not specify the mechanism of this process which they termed "isotopic annealing". They suggested that finely banded ores such as Rosebery, Captains Flat and Heath Steele, deposited as thin sheets away from the immediate area of a hydrothermal vent, might escape such a process. Certainly, the preservation of the sub-millimetre scale banding exhibited by these ores is difficult to explain by the large scale migration of
metals and sulphur implicit in the Barton and Eldridge models.

Ohmoto and Rye (1979) suggest that isotopic re-equilibration may occur during metamorphism at upper amphibolite facies grades, as indicated, for example, by the 620°C isotopic temperature of Broken Hill ore (Both and Smith, 1975), but suggested it is not attained at lower grades.

The only definite conclusions that can be reached with respect to Rosebery at this stage are:

1. Reheating of the massive sulphide ore during greenschist facies metamorphism does not generally appear to have imprinted sulphur isotopic equilibrium.

2. It is uncertain whether the equilibrium order of $\delta^{34}S$ values (i.e. $\delta^{34}S_{py} > \delta^{34}S_{sl} > \delta^{34}S_{gn}$) observed at Rosebery, was attained during original deposition or diagenesis, or whether it reflects partial equilibration during regional metamorphism. Some insight into this question might be gained by examining sulphur isotope values from currently active submarine hydrothermal systems.

6.4 SOURCE OF SULPHUR

Determination of the source of sulphur in ore deposits is important in the erection of a genetic model, but is not obtainable by examining sulphur isotopic evidence alone. The situation is well summarised by Trudinger (1976), * p. 159:

"Clearly then isotopic evidence per se cannot provide a basis for definitive conclusions regarding the origin of sulphide deposits but must be viewed in the light of all attendant geological, geochemical and mineralogical information".

The importance of these approaches is summarised below:

1. Geological evidence places important constraints on the
possible sources of sulphur in an ore deposit. Clearly the rhyolitic footwall rocks and Cambrian seawater are possible sources for Rosebery sulphur (Chapter 3) but their proportions and possible other sources are open to debate. Further, any successful model must also account for the distribution of isotopes in the orebody.

2. Geochemical data provide a framework for the interpretation of sulphur isotopic data. For example, theoretical calculations and experimental studies are the basis of isotopic geothermometry. Also, fractionation of sulphur isotopes from their source to their depositional site is dependent on such environmental factors such as the temperature, pH and redox state of sulphur in hydrothermal solutions as first pointed out by Sakai (1968).

3. If isotopic and mineralogic equilibrium is attained during ore deposition, then the mineral assemblage can provide a sensitive indicator of the above parameters. Ohmoto (1972) developed Sakai's approach by quantifying the relationships among temperature, pH, total sulphur content, redox state of sulphur and fractionation of sulphur isotopes and demonstrated the relationship between these variables and deposit mineralogy.

Notwithstanding the above, various kinetic factors can prevent the application of this thermodynamic approach. One of the most important of these effects occurs during microbial reduction of sulphate to sulphide (e.g. Schwarcz and Burnie, 1973). In addition, reservoir effects such as the Rayleigh Fractionation process (as discussed for the Kuroko deposits by Kajiwara, 1971) can also result in considerable isotopic fractionation.

Given this complexity, it is hardly surprising that a multiplicity of sources has been suggested for the sulphur in massive sulphide deposits.
Early investigators (e.g. Tupper, 1960)*, influenced to a large extent by the small range of \( \delta^{34}S \) values in deposits they studied, favoured a predominantly magmatic source for the sulphur. This belief has persisted mainly in Russian and European studies (e.g. Chukhrov, 1974; Gehrisch et al., 1975; Buadze and Kaviladze, 1979)*. Chukhrov (op. cit.) reviewed Russian and western literature, and concluded:

"The sulfur-isotope composition of the sulphides of deposits included in the volcanogenic sequences indicates its origin entirely or in the main from deep-seated sources". A similar conclusion was reached for the ores of Sulitjelma, Norway by Gehrisch et al. (1975).*

In the Japanese, North American, and Australian literature, numerous investigators have favoured a seawater sulphur source, but two diametrically opposed mechanisms have been invoked. Sangster (1968, 1971, 1976, *) has emphasised that the sulphur isotopic compositions of Phanerozoic sulphide deposits display a parallelism with that of the contemporaneous seawater sulphate, the ore sulphur being lower in \( \delta^{34}S \) by 17.4\%/oo for volcanic-hosted deposits and 13.0\%/oo for sediment-hosted deposits, provided \( \delta^{34}S \) values for sulphides falling outside two standard deviations from the mean for a deposit are excluded. Because this fractionation is close to that attending biogenic sulphate reduction in open systems, Sangster argued for a biogenic origin for ore sulphide. However, in a recent review, Gustafson and Williams (1981)*, have pointed out that Sangster's relationship is spurious for sediment-hosted deposits. For volcanic-hosted deposits, numerous investigators have followed the lead of Ohmoto et al. (1970)*, Kajiwara (1971) and Ohmoto (1972) who suggested partial inorganic reduction of seawater sulphate at elevated temperatures was compatible with the mineralogic and sulphur isotopic data. However in some of the
deposits for which this mechanism has been invoked, for example, Woodlawn (Ayres et al. 1979) and the deposits of Notre Dame Bay (Bachinski, 1977) the presence of pyrrhotite and/or arsenopyrite (see section 8.2 this thesis) suggest that the sulphur which formed these deposits was totally reduced and thus $\delta^{34}$S values lying between that of magmatic sulphide and seawater sulphate may suggest a dual sulphur source. The total or partial reductions of seawater sulphate is generally believed to occur during convective circulation of seawater through the underlying rocks (e.g. Ohmoto et al. 1970; Ohmoto and Rye, 1974) and in such a setting mixing of sulphur from a number of sources is not unexpected.

Such models have been suggested by Solomon (1976), Ripley and Ohmoto (1977) and Green (1979). An interesting variant on this theme was discussed at length by Arnold et al. (1977*), who noted a variation of sulphur isotope ratios among the Iberian pyrite deposits. Pyrites from deposits situated close to volcanic centres (e.g. La Zarza, San Miguel, Rio Tinto) displayed $\delta^{34}$S values closest to that of meteoritic sulphur and showed a tight clustering of $\delta^{34}$S values (e.g. San Miguel, $\delta^{34}$S $\text{py} = 2.80 \pm 4.40$ $\text{‰}$), whereas deposits such as Noveau Sotiel, which is hosted by distal tuffs and sedimentary rocks, had $\delta^{34}$S $\text{py}$ values of $-30.88 \pm 4.06$ $\text{‰}$. Deposits in intermediate settings, overlying proximal tuffs (e.g. San Platon, massive sulphides with $\delta^{34}$S $= 19.44 \pm 4.07$ $\text{‰}$) showed intermediate values. Deposits such as Noveau Sotiel were regarded as being formed by metal fixation from sulphide-depleted hydrothermal solutions far from their exhalative source by sulphide generated from the biological reduction of seawater sulphate. For deposits of the Rio Tinto type, because Arnold (1976*) firmly believed that sulphate reduction under reasonable geological conditions was impossible
between 70 and 350°C, Arnold et al. (1977) favoured a model in which sulphur was leached from carbonaceous Devonian phyllites underlying the volcanic substrate to the deposits. By considering an appropriate mix of biogenic pyrites from Upper and Lower Devonian formations, and by making assumptions regarding their sulphur isotopic compositions, these workers considered that the pyrite leaching model could explain the $\delta^{34}S$ values of the Rio Tinto-type deposits and at the same time satisfy Sangster's statistical relationship. This model, although perhaps unnecessarily complex serves to emphasize the multiplicity of sulphur sources which may be invoked.

Lydon (in Franklin et al., 1981) has pointed out that within a given mining district the $\delta^{34}S$ values of massive sulphide deposits tend to fall into local groupings. Examples include the Bathurst district, New Brunswick (Lydon, op. cit.), the Hokuroku district, N.E. Japan (Kajiwara and Date, 1971) and the deposits of the Mount Read Volcanic belt (Solomon et al., 1969). Lydon (op. cit.) stated that "this suggests that the source of the sulfur is localized and spatially variable, consistent with the hypothesis that the sulfur was derived from the underlying rock column". He further showed that there was a tendency for Phanerozoic Pb-Zn-Cu deposits, associated generally with mixed sedimentary - or metasedimentary-felsic volcanic terrains to have higher $\delta^{34}S$ values than Cu-Zn deposits associated with mafic volcanic rocks. A possible cause of this relationship will be offered later in this section.

Limits on the possible mechanisms of sulphur and metal generation in hydrothermal solutions and their bearing on sulphur isotope fractionation are provided by recent geochemical studies. Firstly, experimental studies of seawater-rock interaction at elevated temperatures (e.g. Bischoff and Dickson, 1975; Dickson, 1977; Mottl...
and Holland, 1978; Mottl et al., 1979) have done much to promote understanding of natural processes of hydrothermal circulation, but, because of the complicated nature of the systems involved and the short duration of some experiments compared with natural processes, it may be difficult to extrapolate these results to the real world. Secondly study of the kinetics of sulphate reduction and of sulphide-sulphate isotopic exchange (Robinson, 1973; Igumnov, 1976; Sakai and Dickson, 1978; Ohmoto and Lasaga, 1982; Shanks et al., 1981) have placed useful constraints on the interpretation of isotopic data. Thirdly, modelling of the hydrology of hydrothermal circulation (e.g. Solomon, 1976; Norton and Cathles, 1979; Cathles, 1981), particularly if allied with kinetic data, offer a powerful tool in the understanding of processes of ore formation, but at present it would appear that many crucial parameters such as rock permeabilities are insufficiently well known to provide a quantitative understanding of processes. Finally the discovery of a natural laboratory of massive sulphide ore formation at 21°N on the East Pacific Rise, and attendant detailed geochemical studies (e.g. Von Damm and Edmond, 1981; 1982; Edmond et al., 1982; Styrt et al., 1981; Haymon and Kastner, 1982; Arnold and Sheppard, 1981; Kerridge et al., 1983) have provided much detailed information of ore formation mechanism. Results from all of these avenues will be used in an interpretation of the Rosebery data.

The increase in δ34S through the inferred depositional sequence at Rosebery is consistent with the increase in δ34S of H2S produced by progressive reduction of seawater sulphate in an euxinic basin (e.g. Ohmoto & Rye, 1979). However, a biogenic origin of the sulphur is discounted because of two factors:

1. The similarity in the range of δ34S and Co values of the footwall schist pyrites and those from the overlying massive ore
suggests that $H_2S$ and metals were transported together from depth to
the site of ore deposition.

2. The $\delta^{34}S$ values of sulphides in any vertical section through
the ore (5 m to about 30 m thick) show a small range (< 5.6%),
which is not the case either in pyrite from ancient and modern
sediments (Schwarz and Burnie, 1973) or in ore deposits in
which biogenic reduction at the site of deposition is believed
to have contributed to the $H_2S$ fixed in sulphides (e.g. Anger
et al., 1966; Smith & Croxford, 1973).

Hence it is necessary to consider other modes of ore formation.
Provided the $\delta^{34}S_{ES}$ value of a melt lies in the range 0 ± 3‰, $H_2S$ of
magmatic hydrothermal origin may have a value between -13 and +7‰ depending on the $a_{O_2}$ of the melt and the redox reactions taking place
between the aqueous phase and the wall rocks after fluid separation
(Ohmoto and Rye, 1979). Pyrites precipitated in equilibrium from a
magmatic hydrothermal fluid between 200 and 300°C can therefore have
$\delta^{34}S$ values as high as 8.2 to 9.8‰, assuming a maximum $\delta^{34}S_{ES}$ of
3‰ in the original melt.

Because most Rosebery sulphides have higher $\delta^{34}S$ values either
a component relatively enriched in $\delta^{34}S$ or a reservoir effect is
required to explain the isotope data. The latter process will be
considered first. If crystallization proceeds from a limited reservoir
of sulphur in solution and if the crystals do not requilibrate with
the solution the $\delta^{34}S$ values of sulphides precipitated will obey the
Rayleigh fractionation equation:

$$
\delta^{34}S = \left[ (\delta^{34}S)_0 + 1000 \right] f^{-1} - 1000 \ 0/oo
$$

Where $\delta^{34}S$ is the $\delta^{34}S$ value of solution sulphide where a fraction, $f$, of the original reservoir remains, $(\delta^{34}S)_0$ is the original $\delta^{34}S$ value of solution sulphide and $\alpha$ is the fractionation factor where
\[ \Delta = \delta^{34}_{S_A} - \delta^{34}_{S_B} = 1000 \ln \alpha \]  

and \[ \alpha = \frac{(^{34}/^{32})_A}{(^{34}/^{32})_B} \]

In terms of sulphide minerals, the composition of the Rosebery orebody translates into 47% pyrite, 44% sphalerite, 5% galena and 4% chalcopyrite (assuming for argument that all Cu resides in chalcopyrite). In terms of sulphur content of the ore this translates into 62.2% pyrite sulphur, 5.5% chalcopyrite sulphur, 29.1% sphalerite sulphur and 3.2% galena sulphur. For purposes of illustration it is therefore sufficiently accurate to consider the orebody sulphur as a mixture of 68% pyrite sulphur and 32% sphalerite sulphur. Assuming a depositional temperature of 300°C and isotopic equilibrium between precipitating numerals and \( H_2S \) in solution yields a bulk fractionation factor of:

\[ \alpha_{\text{ore}} = 1.0021 \times 0.68 + 1.0003 \times 0.32 = 1.0015 \]  

Thus equilibrium precipitation of ore depletes the residual \( H_2S \) in solution in \( ^{34}S \). Assuming all \( H_2S \) in solution is incorporated into sulphide numerals, a situation that would cause the most extreme Rayleigh fractionation, results in a decrease in \( \delta^{34}_{H_2S} \) from an initial value of \( 8^0/oo \) to \( 6.9^0/oo \) after 50% precipitation to \( 3.5^0/oo \) after 95% precipitation (Fig. 6.3.9). This is the opposite trend to that needed to explain the trend of \( \delta^{34}S \) increase from the D to the F lens in the orebody.

Yaroshevich and Tvalchreidze (1981) have considered the isotopic effects of non-equilibrium crystallization of sulphides. They presented the following equation:

\[ \Delta^{34}S_i = 10^3 \left( \frac{K_{\text{eq}}}{(K_{\text{eq}} - 1)} \right) + \]
Fig. 6.3

(a) Effect of Rayleigh Fractionation on the $\delta^{34}$S values of $H_2S$ (lower curve) and pyrite (upper curve) during equilibrium and disequilibrium crystallization respectively of a mixture of pyrite and sphalerite in the proportions present in the Rosebery orebody.

Lower curve: equilibrium crystallization at 300°C.
Upper curve: disequilibrium crystallization. Fractionation factors for this case are based on those at 21°N, East Pacific Rise (Kerridge et al., 1983).

(b, inset) Effect of crystallization rate ($V$ crystallization) on the $\delta^{34}$S value of a sulphide mineral. $\Delta$ ads is the fractionation due to formation of an adsorption layer on the crystal surface. $\Delta$ eq is the equilibrium fractionation between the mineral and solution component. (After Yaroshevich and Tvalchrelidze, 1981).
\[
(K_i - 1) \exp \left\{ \frac{\Phi \cdot V_{cr}}{V_c} \right\} 
\]

where \(K_i\) and \(K_A\) are the constants of isotopic and adsorption equilibria between phase \(A\) and solution component \(i\) respectively, \(V_{cr}\) and \(V_{ads}\) are the rate of crystallization of \(A\) and the rate of formation of the adsorption layer between crystal \(A\) and liquid component \(i\) respectively, \(\gamma\) is the thickness of the adsorption layer, and \(D_i\) is the rate of diffusion of component \(i\) through the solution.

As \(V_{cr} \to \infty\), \(\Delta^{34}S_i \to 0\) \(\ldots (6.7)\)

As \(V_{cr} \to 0\), \(\Delta^{34}S_i \to 10^3 \cdot (\frac{K_A}{K_{eq}} - 1) \cdot \Delta^{34}S_{eq} A_i\) \(\ldots (6.8)\)

At intermediate values of \(V_{cr}\) the adsorption term becomes important and Yaroshevich and Tvalchrelidze (op.cit*) predicted this could lead to a reversal in the equilibrium distribution of \(\delta^{34}\)S values between a crystallizing mineral and the sulphur species in solution (Fig. 6.3b).

An actualistic example of this phenomenon may be seen in the sulphur isotope distribution between \(H_2S\) discharged from the hydrothermal vents and precipitating sulphide minerals on the East Pacific Rise at 21°N. Fluids, discharging at 350°C, precipitate sulphide minerals on contact with seawater forming a black, smoke-like plume of turbulently mixing hydrothermal solution and seawater (Spiess et al., 1980*). The exhalative sites consist of basal sulphide mounds on which rest constructional hollow chimneys which form the locus of fluid venting. The chimneys display a cross-sectional mineralogical zonation with an internal zone of Cu-Fe sulphides (chalcopyrite-cubanite-pyrrhotite)
passing outward in some cases through a bornite-chalcocite zone to a zone of euhedral sphalerite and/or wurtzite plus pyrite and/or marcasite intergrown with anhydrite to an outer spin of fine grained pyrrhotite, sphalerite and pyrite in a matrix of anhydrite. The outer skin material is essentially identical in mineralogy and texture to material filtered from the exhalative sulphide "smoke" (Haymon and Kastner, 1981; Haymon, 1983). Sulphur isotope analysis of HgS precipitated from vent fluid before it had the opportunity to mix with seawater yielded a $\delta^{34}S$ value of $3.70^\circ/oo$ (Kerridge et al., 1983). As the precipitation of HgS would have been virtually instantaneous it appears valid to consider this value as that of the $H_2S$ in the discharging fluid. Fine grained sediment scooped from the mound surface near a black smoker and considered to represent fallout of fine particulate sulphide from the ascending plume yielded the following $\delta^{34}S$ values: pyrrhotite, $0.73^\circ/oo$; sphalerite, $1.38^\circ/oo$; pyrite, $1.27^\circ/oo$ (Kerridge et al., op.cit). Kerridge et al. suggested that the isotopic composition of the discharging vent fluid might have been the same during formation of the sulphide sediment. If so, this represents an actualistic example of the kinetic fractionation process discussed by Yaroshevich and Tvalchrelidze (1981). If the fractionation factors from the East Pacific Rise sediment ($\Delta_{py}^{H_2S} = -2.43^\circ/oo$; $\Delta_{sl}^{H_2S} = 2.32^\circ/oo$) are then applied to the Rosebery model a bulk $\omega_{H_2S}$ value of 0.9976 can be calculated. Assuming total precipitation of sulphide and an initial $\delta^{34}H_2S$ value of $10.43^\circ/oo$, it can be seen that the disequilibrium Rayleigh fractionation model can lead to substantial increases in the $\delta^{34}S$ values of pyrite during precipitation. Thus after 50% sulphur fixation, $\delta^{34}Spy$ has increased to $9.68^\circ/oo$ and after 95% precipitation the value is $15.29^\circ/oo$ (Figure 6.3a). This is in reasonable agreement with the range of $\delta^{34}S$ values of pyrite in the sulphide orebody (7.1 to $17.2^\circ/oo$; Table 6.1).
The face that Rosebery sulphide ore shows an equilibrium order of fractionation with $\delta^{34}\text{S}$ values of coexisting triplets increasing in the order galena < sphalerite < pyrite might seem inconsistent with the Rayleigh model. However approach to isotopic equilibrium on a very local (sub-hand specimen) scale might have been achieved during regional metamorphism or during annealing shortly after primary deposition. In this context it is interesting to note that sulphides from an active black smoker in the 21$^\circ$N hydrothermal area are grossly out of isotopic equilibrium ($\delta^{34}\text{S}_{\text{py}} = -0.08 \pm 0.10\%/oo$) whereas sulphides in the basal mound, largely composed of collapsed chimney material, exhibit an equilibrium order of fractionation ($\delta^{34}\text{S}_{\text{py}} > \delta^{34}\text{S}_{\text{sl}} > \delta^{34}\text{S}_{\text{cp}}$) and isotopic temperatures in the range 425 to 465$^\circ$C using the geothermometer of Kajiwara and Krouse (1971) (Kerridge et al., op. cit. *). These temperatures are about 100$^\circ$C higher than that of the venting fluid and Kerridge et al. suggested that the approach to equilibrium might be due to a secondary reheating episode. Thus the equilibrium order of fractionation amongst sulphide triplets at Rosebery need not pose a serious problem to the application of the disequilibrium Rayleigh Model.

However, it is considered that a number of factors mitigate against the disequilibrium model at Rosebery. Firstly, the conditions necessary for the model to work satisfactorily ($m \Sigma S \leq m (\Sigma \text{Pb} + \Sigma \text{Zn}) + 2 m \Sigma \text{Fe}$) and extrapolation of the disequilibrium fractionation factors from the East Pacific Rise case to the Rosebery situation) may not be applicable (Section 8.2 this thesis). Secondly, the model requires a vent site located beneath the D lens and southward flow of solutions crystallizing sulphides throughout ore deposition. Such a configuration is difficult to reconcile with the apparent zonation of $\delta^{34}\text{S}_{\text{py}}$ values.
in the footwall schist and is not in accord with a pattern allowing
shifts in the site of fluid venting with time (Section 8.3, this
thesis). For these reasons, a model involving change in the \( \delta^{34}\text{S}_{\text{LS}} \)
value of the ore solution with time will now be considered. It
should be kept in mind, however, that open system crystallization might
be responsible for the fluctuations in \( \delta^{34}\text{S} \) values in the vertical
sections sampled through the orebody and, in particular, might in part
account for the anomalously high \( \delta^{34}\text{S} \) values of pyrite in oxide facies
mineralization at the top of the sulphide and barite orebodies.

If the \( \delta^{34}\text{S}_{\text{H}_{2}\text{S}} \) value of the Rosebery ore solution exceeded 90/oo, it is necessary to invoke the participation of a source of sulphur
with a high \( \delta^{34}\text{S} \) value in the ore forming process. The most obvious
sources, consistent with the geological evidence, are Cambrian seawater
sulphate or sulphate leached from evaporites. Because no evaporites
are preserved in the Cambrian of Tasmania, it is necessary to infer
their \( \delta^{34}\text{S} \) values from those preserved elsewhere. In the Early and
Middle Cambrian the \( \delta^{34}\text{S} \) values of evaporitic anhydrite ranged from
+26.4 to +35.5/oo (Kaplan, 1975; Claypool et al., 1980*) and since
the equilibrium fractionation between anhydrite and SO\(_4^{2-}\) ion is small
\( (\Delta^{34}\text{S}_{\text{SO}_4^{2-}} = 1.65^0/oo \text{ at } 25^0\text{C}; \text{Thode and Monster, } 1965^* ) \) a \( \delta^{34}\text{S} \) value
for seawater or leached evaporitic sulphate of 300/oo may be assumed.

In the convective circulation of seawater, during its evolution
into an oreforming hydrothermal solution, a number of disequilibrium
reactions involving sulphur species can occur. For example, Krouse
et al. (1977)* found a \( \delta^{34}\text{S} \) range of secondary pyrites in oxidised
basalts near the Mid Atlantic Ridge of -33.4 to -4.8/oo. These
rocks consisted of the assemblage hematite or goethite \( \pm \) celadonite \( \pm \)
saponite \( \pm \) pyrite and were formed by seawater-basalt interaction at
temperatures less than 150°C and possibly as low as 5°C. The sulphur
content of the rocks was extremely variable (60 to 1090 ppm) but a net sulphur loss of 50 to 60% was computed by Andrews (1979). * Because $SO_4^{2-}$ is unlikely to be an effective oxidising agent at these temperatures, Andrews (op.cit) suggested that dissolved oxygen in seawater might have been the active oxidising agent. He envisaged reactions of the form:

$$4FeS + 7O_2 + 6H_2O = 4FeO(OH) + 8H^+ + 4SO_4^{2-}$$  \hspace{1cm} (6.9)

$$4FeS + 5O_2 + 4H_2O = 4FeO(OH) + 4H^+ + 2S_2O_3^{2-}$$  \hspace{1cm} (6.10)

with subsequent hydrolysis of the thio sulphate and sulphide to $HS^-$ and $SO_4^{2-}$ as the mechanism of producing both the depletion of rock sulphur and the low $^{34}S$ values of the secondary pyrite.

Another possible cause of isotopic disequilibrium might be kinetic fractionation during inorganic reduction of seawater sulphate at higher temperatures. Grinenko et al. (1969) * investigated this effect by passing a stream of atomic hydrogen (138-230°C) or molecular hydrogen (290°C) through boiling $H_2SO_4$. The product of reduction, $SO_2^-$, was oxidized to $SO_4^{2-}$, precipitated as $BaSO_4$, and analysed. Theoretical considerations indicated that the kinetic isotope effect, which ranged from 16°/oo at 138°C to 8.6°/oo at 290°C, was due to the breaking of the S-O bond (Grinenko et al., op.cit).

Reservations exist concerning the applicability of these results to seawater sulphate reduction under geological conditions, and more pertinent experiments have been carried out. Mottl et al. (1979) reacted samples of basalt and andesite with seawater at water:rock ratios of 1-3 and temperatures of 300-500°C for periods of 4 to 19 months in sealed capsules. In virtually all experiments except those with a holocrystalline starting material a sulphide mineral was formed, dominantly pyrite at 300 and 400°C (in one 300°C run pyrrhotite formed) and pyrite, and/or pyrrhotite formed at 500°C.
Ohmoto et al. (1976) analysed the \( \delta^{34}\text{S} \) values of sulphides from four runs (particular runs not specified) and found a \( \delta^{34}\text{S} \) range of 8.0 to 20.7\(^0/00\). These data suggest that at least some seawater sulphate was reduced in the experiments because of the isotopic composition of the starting materials (\( \delta^{34}\text{S} = 1^0/00 \) for basalt, 21\(^0/00 \) for seawater sulphate). Runs with basalt and sulphate-free Na-K-Ca-Cl solutions showed similar \( \text{H}_2\text{S} \) concentrations at conclusion to similar experiments in the basalt-seawater system (Mottl et al., 1979), thus suggesting an approach to equilibrium saturation with iron sulphide was achieved. However, quench solutions in all experiments in which pyrrhotite formed revealed non-zero concentrations of sulphate, a situation not thermodynamically compatible with pyrrhotite stability at the final molalities of \( \text{S} \) found in the solutions at the conclusion of the experiments. It should be noted that it took between 1 and 3.5 hours to quench the runs. Thus any anhydrite, which has decreasing solubility with increasing temperature (Holland and Malinin, 1979\(*\)), which formed during heating or water:rock interaction at temperature might have partly redissolved during the quench, as pointed out by Mottl et al. (1979). Hence the sulphate concentrations recorded at the termination of these runs probably did not reflect those at experimental temperatures. It is instructive to note that an experiment of much shorter duration (10 days) between rhyolite and seawater at 300\(^\circ\)C, in which the solution could be sampled at conditions, showed a decrease in sulphate concentration from an initial 2649 mg/kg to 0.16 mg/kg, with traces of \( \text{H}_2\text{S} \) formed (Dickson, 1977). Anhydrite was present in the solid run products. Therefore, Mottl et al. (1979) and Ohmoto et al. (1976) showed that seawater sulphate could be reduced under reasonable geological conditions at temperatures of 300\(^\circ\)C and higher, but they did not determine the extent of this reduction, nor did they clarify whether kinetic or equilibrium isotopic effects occurred. In
order to answer some of these questions Shanks et al (1981*) reacted fayalite ± SiO₂ with seawater in experiments at 200, 250 and 350°C for between 35 and 239 days. The choice of starting materials precluded sulphide generation from any but a seawater sulphate source and, in addition, their apparatus enabled solution sampling at conditions. At 200°C no dissolved H₂S was detected, but mass balance calculations indicate that a small amount of pyrite might have formed in two of the runs. At 250°C, H₂S was produced and the presence of pyrite was again inferred by mass balance calculations. At 350°C and water:

"rock" mass ratios of 40 to 130, solid phase assemblages of pyrite + hematite + magnetite + talc ± quartz ± anhydrite were produced. Assuming Rayleigh fractionation, Shanks et al. (op.cit.) calculated that isotopic equilibrium was achieved between solution SO₄²⁻ and H₂S at 350°C over a period of 67 days and at 250°C after 126 days. For the 350°C experiments, with fayalite as starting material, the extent of SO₄²⁻ removal from solution depended on the water/"rock" ratio. At a w/r of 40, the total SO₄ concentration had declined from 27 to about 0.4 mmolal after 40 days, but after 67 days at w/r of 130 the total SO₄ content was higher about 10 mmolal. In natural systems, however, SO₄²⁻ removal is far more efficient because Ca leached from the rock promotes anhydrite precipitation at temperatures of 150°C and higher, based on the results of numerous experiments summarised by Janecky and Seyfried (1983*).

It is apparent from the foregoing discussion, that in geologically reasonable times isotopic equilibrium might be achieved between aqueous SO₄²⁻ and H₂S during convective seawater circulation. The experiments leave it unclear whether the processes of anhydrite precipitation and sulphate reduction can lead to quantitative SO₄²⁻ removal, but analyses of the 350°C hydrothermal fluid at the East Pacific Rise at 21°N which show 6.5 mmolal H₂S and zero sulphate concentration (Von Damm and
Edmond, 1981) suggests that they can. As mentioned earlier, the fluid \( H_2S \) has a \( \delta^{34}S \) value of 3.70\(^{\circ}/oo\) (Kerridge et al., 1983\(^*\)), consistent with a mixture of about 86\(^{\circ}/oo\) basalt-derived \( H_2S \) (\( \delta^{34}S = 1^{\circ}/oo \)) with 14\(^{\circ}/oo\) \( H_2S \) derived by total reduction of seawater sulphate. Styrt et al. (1981\(^*\)) suggested that such a simple mixing calculation might not be appropriate to a situation in which \( H_2S \) derived from partial reduction of seawater sulphate might have \( \delta^{34}S \) values up to 15\(^{\circ}/oo\) less than the parent sulphate. Kerridge et al. (op.cit.) pointed out that this effect depended on whether partial sulphate reduction proceeded some anhydrite precipitation. Thus, partial sulphate reduction would produce \( H_2S \) with \( \delta^{34}S \) values less than that of seawater. Subsequent precipitation of \( ^{34}S \)-enriched anhydrite would reduce the bulk \( \delta^{34}S \) value of the convecting solution and hence seawater-derived \( H_2S \) could be substantially lower than that of the parent seawater sulphate.

It should be noted here that input of modified \( \delta^{34}S \)-enriched seawater into the higher temperature regimes of anhydrite precipitation (\( \geq 150^\circ \)C) and sulphate reduction (\( \geq 250^\circ \)C) would act against this effect. Such heavy sulphate could be produced at lower temperatures either by Andrews' (1979) mechanism of formation of low \( \delta^{34}S \) secondary pyrite discussed above or by microbial reduction of seawater sulphate near the seafloor.

Fortunately, independent evidence exists that sheds light on this problem. Strontium isotopic analyses suggest that about 90% of the strontium in the existing fluid is of basaltic origin (Albarede et al., 1981) as do As/S ratios, if it is assumed that As acts as a tracer for the S mobilized from the basalt (Von Damm and Edmond, 1981). Hence it seems reasonable, at least for the early stages of water/rock interaction, to assume that anhydrite precipitation is a process occurring at lower temperatures than, and essentially independently from, reduction of seawater sulphate.
A model for sulphur isotope exchange during basalt-seawater interaction predicted on the above assumptions has been developed by Shanks et al. (1981). In their model, anhydrite precipitation was complete at the onset of reduction when the sulphate concentration was taken to be 1 mmolal. It was assumed that basalt contained 31.2 mmol/kg reduced sulphur (1000 ppm), that seawater sulphate was totally reduced and that total sulphur concentrations in solution were buffered at 1 mmolal by iron sulphide solubility. Further it was taken that basalt and H₂S produced from reduced seawater sulphate were homogeneously mixed at any stage of the reaction, and the tacit assumption was made that the system was closed. Sulphate reduction was governed by the reaction:

\[ 8\text{Fe}^{2+} + 5\text{SO}_4^{2-} + 10\text{H}^+ \rightarrow \text{H}_2\text{S} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \]  \hspace{1cm} (6.11)

where the 10% FeO in the basalt was only reduced to magnetite, that is only \(\frac{2}{3}\) of the original FeO was available for reaction. Thus at any stage of reaction the \(\delta^{34}\text{S H}_2\text{S}\) value is given by

\[ \delta^{34}\text{S H}_2\text{S} = \frac{m\text{SO}_4 w/r \cdot \delta\text{SO}_4 + m\text{S} \cdot \delta S}{m\text{SO}_4 w/r + m\text{S}} \left(\frac{0}{100}\right) \]  \hspace{1cm} (6.12)

where \(m\text{SO}_4\), \(m\text{S}\) are sulphate concentration of evolved seawater before reduction and reduced sulphur content of basalt (m/kg)

\(\delta\text{SO}_4\), \(\delta S\) are the \(\delta^{34}\text{S}\) values of seawater sulphate and basalt respectively

\(w/r\) is the water/rock mass ratio.

In the case under review, given the assumptions \(\delta\text{SO}_4 = 20^{0/100}\), \(\delta S = 0^{0/100}\).

\[ \delta^{34}\text{S H}_2\text{S} = \frac{0.02 w/r}{10^{-3} w/r + 31.2 \times 10^{-3}} \left(\frac{0}{100}\right) \]  \hspace{1cm} (6.13)
The results of this analysis indicate that the proportion of H₂S produced by seawater sulphide increases steadily and at a water:rock ratio of 31.8 the concentrations of seawater and basalt-derived H₂S become equal and δ³²S H₂S = 10⁰/oo. At a water:rock ratio of 116 all "FeO" in basalt has been converted to magnetite. This value represents a threshold in solution behaviour. At water:rock ratios less than 116, the solution generated by water:rock interaction is H₂S- dominant; at higher ratios a mixed H₂S:SO₄²⁻ solution is produced.

The situation for rhyolite: Cambrian seawater interaction differs from that outlined above in a number of important respects:

1. Cambrian seawater had a δ³⁴S value of about 30⁰/oo compared with 20⁰/oo for modern seawater.

2. Basalt is higher in FeO content than rhyolite. A value of 1.2% for the FeO content of rhyolite will be assumed for discussion purposes (Table 5.1 analyses 1 and 2).

3. The total sulphur content of rhyolite is less than that of basalt. Schneider (1978) lists an average value of 284 ppm for rhyolite and 423 for dacite, trachyte, latite and andesite. A value of 10 mmole/kg (321 ppm) will be assumed for purposes of discussion. It was again assumed that 1 mmolal seawater sulphate entered the zone of reduction, 1 mmolal H₂S was sufficient to cause pyrite saturation and that the δ³⁴S value of igneous sulphide was 0⁰/oo. In terms of applicability of the reduction model to the Rosebery case, it is clear that at least part of the H₂S in solution derived by seawater : rock interaction would be lost from the system (i.e. fixed in massive ore and probably partly dispersed in seawater after exhalation). In the extreme open system case the δ³⁴S H₂S value is given by:
\[
\text{w/r} = \frac{mS}{mSO_4} \ln \frac{\delta SO_4 - \delta S}{\delta SO_4 - \delta ^{34}S_{H_2S}} \quad (6.14)
\]

In practice, values of \(\delta ^{34}S_{H_2S}\) were selected and progressively refined to calculate \(\delta ^{34}S_{H_2S}\) at unit increments of w/r.

In the closed system case Equation 6.12 reduces to:

\[
\delta ^{34}S_{H_2S} = \frac{0.03 \text{ w/r}^0}{0.001 \text{ w/r} + 0.01} /oo \quad (6.15)
\]

The results of this calculation are summarised in Figure 6.4, and a number of important conclusions may be drawn. Firstly, the point at which seawater derived \(H_2S\) becomes of equal importance to leached volcanic \(H_2S\) occurs at a lower water/rock ratio (10 for the closed system case). Secondly, the threshold at which all "FeO" in the rock is converted to \(Fe_2O_4\) occurs at a much lower water/rock ratio (about 13.9). At this stage the \(\delta ^{34}S_{H_2S}\) value is 17.46/oo for the closed system case and 22.54/oo for the open system case (Fig. 6.5). The real value would lie somewhere between these limits.

The numerical values of water/rock ratio are dependent on the choices of \(mSO_4\) entering the reduction zone and \(mH_2S\) in equilibrium with pyrite. These values are constrained in the natural system by parameters such as temperature, pH, redox state and in the case of \(mZnSO_4\), also by \(Ca^{2+}\). For example, doubling of both \(mZnSO_4\) and \(mH_2S\) to \(2 \times 10^{-3}\) would have the effect of halving the water/rock ratio at each stage of the process, but would not affect the \(\delta ^{34}S_{H_2S}\) values.
Relative abundance of $\text{H}_2\text{S}$ from rhyolite and seawater sources for rhyolite-seawater interaction at temperatures above 260°C. Original sulphur concentrations are assumed to be 10 mmol/kg in rhyolite and 1 mmol/kg in evolved seawater. Approximate pyrite saturation boundary from Shanks et al. (1981).
Fig. 6.5

Change in $\delta^{34}S$ values of $H_2S$ during rhyolite-seawater interaction. Conditions as for Fig. 6.5. Range of $\delta^{34}S$ values for pyrite, sphalerite and barite from the Rosebery sulphide and barite orebodies are shown at right. $\delta^{34}S$ values of +27.6 and +33.1% are for co-existing pyrite and barite in oxide facies mineralization at top of barite orebody.
The model predicts a steady increase in $\delta^{34}\text{S}$ values throughout ore deposition in an H$_2\text{S}$- dominated solution. The redox state of the solutions which formed the Rosebery sulphide orebody will be discussed in Section 8.2 of this thesis. It should be noted that there are minor occurrences of barite in the A and F lenses and in the footwall schist, but as discussed in Section 6.2(i), the textural and sulphur isotope evidences suggest that much of this barite post-dates formation of the sulphide orebody.

However, assuming for the moment that the solutions which formed the sulphide ore were H$_2\text{S}$- dominant, it is apparent that the transition from H$_2\text{S}$- dominant to mixed SO$_4$- H$_2\text{S}$ solutions may occur at geologically reasonable water-rock ratios in felsic terrains but whether this would occur in sequences underlain by basaltic rocks is doubtful.

For the barite orebody, the ubiquitous occurrence of barite and the wide range of barite $\delta^{34}\text{S}$ values, of up to 41.2‰ (Solomon et al., 1969), indicate that partially reduced Cambrian seawater sulphate is a significant component of the sulphate in this ore. However, the finely layered nature of the barite ore suggests deposition in a marine environment, and thus barite $\delta^{34}\text{S}$ values might not reflect those of the ascending ore solution. In a mixing situation the $\delta^{34}\text{S}$ value of barite would be governed by three sources (a) SO$_4$ in the discharging solution (b) the ambient seawater sulphate and (c) sulphate formed from disequilibrium oxidation of H$_2\text{S}$. Because of the sluggish nature of isotopic equilibration between reduced and oxidised sulphur species and the essentially instantaneous rates likely for barite precipitation, it is highly probable that there would be no isotopic equilibration during precipitation. Because present day seawater contains 0.027 mESO$_4$ and only a maximum of $2 \times 10^{-4}$ m dissolved O$_2$ (Holland 1978), the effect of the third source (up to $10^{-4}$ m SO$_4$ produced) will be swamped by the other two. A very good approximation of the $\delta^{34}\text{S}$ value of precipitated barite is thus given by:
\[
\delta S_{i f} = \frac{(\delta S_{04}/\delta S_i)_{i.mE_{i}} \cdot \delta S_{04} \cdot F + (1-F) \cdot mE_{04} \cdot \delta S_{04} \cdot \delta S_{sw}}{F(\delta S_{04}/\delta S_i)_{i.mE_{i}} + (1-F) \cdot mE_{04} \cdot \delta S_{sw}}
\]

where: \(\delta S_{04}\) is the \(\delta^{34}S\) value of sulphate; the subscripts \(f, i, sw\) refer to the hydrothermal fluid-seawater mixture, ascending hydrothermal fluid and seawater respectively; \(mE_{i}\) is the total molality of sulphur in the ascending solution; \(mE_{04}\) is the total molality of sulphate in seawater; \((\delta S_{04}/\delta S_i)\) is the molal ratio of total sulphate to total sulphur in solution; and \(F\) is the fraction of hydrothermal fluid in the mixed solution.

If hydrothermal solution-seawater mixing is the dominant cause of cooling of the ore-forming fluid, then the cooling effect can be closely approximated by:

\[
T_f = T_i - (1 - F)(T_i - T_{sw})
\]

where \(T\) is temperature (Sato, 1972).

For the case where \(\delta E_{i}\) varies between 0 and 30\%, \(\delta S_{04} = 30\%\), a series of values of \(\delta S_{i f}\) is illustrated in Fig. 6.6 assuming sulphur isotopic equilibrium in the venting solution and \(T_i = 300^\circ C\) \((\delta S_{04}-H_2S = 20.0^\circ/oo)\), for a range of values of \((\delta S_{04}/\delta S_i)_{i}\) and \(mE_{i}\). The curves show that where the total concentration of sulphur in solution is low (0.001 m) only a limited amount of mixing will give rise to a rapid convergence of the \(\delta^{34}S\) value of sulphate towards that of seawater. This is consistent with the observations at the Shakanai No. 1 deposit where the \(\delta^{34}S\) values of barite (Kajiwara, 1971) are close
Fig. 6.6 Curves showing the effects of mixing of seawater and hydrothermal sulphate on the $\delta^{34}S$ values of sulphate assuming $m_{\text{SO}_4}$ in seawater = 0.02 and a $\delta^{34}S$ value of seawater sulphate of 30%. Curves are constructed for $\delta^{34}S_{\text{VS}}$ values of the venting solution of 0 to 30% and for $m_{\text{VS}}$ of the venting solution of 0.02 (left hand curves) and 0.001 (right hand curves). Discharge temperature of the venting solution is 300°C and isotopic equilibrium ($\Delta_{\text{SO}_4-\text{H}_2\text{S}}$) as assumed for the discharging solution. Curves are drawn for various ($m_{\text{SO}_4}/m_{\text{VS}}$) ratios of the venting solution of 0.9 (a), 0.5 (b), and 0.1 (c).
EFFECT OF HYDROTHERMAL SOLUTION : SEA WATER MIXING ON $\delta^{34}S_{\text{SO}_4}$

Left hand curves: $m_{\Sigma \text{Si}} = m_{\Sigma \text{SO}_4 \text{SW}} = 0.02$

Right hand curves: $m_{\Sigma \text{Si}} = 0.001 = 0.05 \times m_{\Sigma \text{SO}_4 \text{SW}}$

(a) $(m_{\Sigma \text{SO}_4} / m_{\Sigma \text{S}}) = 0.9$

(b) $(m_{\Sigma \text{SO}_4} / m_{\Sigma \text{S}}) = 0.5$

(c) $(m_{\Sigma \text{SO}_4} / m_{\Sigma \text{S}}) = 0.1$

% Seawater incorporation
to that of the coeval miocene seawater value of 21 to 23°/oo (Kaplan, 1975, Claypool et al., 1980*), but is not consistent with the situation at Rosebery where the δ³⁴S values of barites appear to be all higher than that of the contemporary seawater, the maximum departure being about 11°/oo. For example, if δ³⁴S = 30°/oo, (m²SO₄/m²S) = 0.5, the initial values of hydrothermal H₂S and SO₄ would be 18.4 and 41.6°/oo respectively, assuming a temperature of 250°C. 10% sea-water mixing would drop the temperature to around 225°C, but apparent isotopic temperatures of H₂S-SO₄ pairs would be 280°C and 480°C at values of m²S of 0.027 and 0.001 respectively.

In such an environment of rapid fluid mixing, coprecipitated sphalerite and galena would probably exhibit isotopic disequilibrium. Sulphur isotope compositions of barite-sulphide pairs will yield maximum temperatures of ore deposition only; it is perhaps noteworthy that the lowest sulphur isotope temperature for a sulphate-sulphide pair at Rosebery (255°C) is derived from the barite with the highest δ³⁴S value of +41.2°/oo.

Hence 290°C (the highest barite-sulphide isotopic temperature) should be regarded as an upper limit for deposition of the barite orebody, but temperatures in the order of 250°C seem more reasonable. This agrees with the generally low pyrite and chalcopyrite content of this ore. Further, a high δ³⁴S value of total sulphur in the system (220°/oo) is indicated and a Cambrian sea-water source (δ³⁴S ≈ 30°/oo) is possible.

However, after deposition of the sulphide orebody, the water: rock interaction model predicts that disseminated sulphides with δ³⁴S values in the range of 17.5 to 22.5°/oo would exist in the Fe₃O₄- bearing wall rocks. In this situation the fluid would become undersaturated with respect to pyrite and leaching might take place according to the reaction:

\[ 4 \text{FeS}_2 + 4\text{H}_2\text{O} + 6\text{H}^+ = 4\text{Fe}^{2+} + 7\text{H}_2\text{S} + \text{SO}_4^{2-} \]  \hspace{1cm} (6.18)
Assuming that equilibrium is established between incoming seawater sulphate and $\text{H}_2\text{S}$ leached from disseminated sulphides such that:

$$7 \text{m} \text{H}_2\text{S}_f + \text{m} \sum \text{SO}_4^2_f = \text{m} \sum \text{S} \approx 10^{-3}$$

(6.19)

and:

$$\delta \text{ES} = \frac{7 \delta \text{DS} + \delta \text{SO}_4}{8}$$

(6.20)

and assuming isotopic equilibrium at 250°C:

$$\delta^{34}\text{SISO}_4^2_f - \delta^{34}\text{SH}_2\text{S}_f = 23.2$$

(6.21)

where $\delta^{34}\text{SISO}_4^2_f$, $\delta^{34}\text{SH}_2\text{S}_f$ are the final $\delta^{34}\text{S}$ values and molalities of sulphate and $\text{H}_2\text{S}$ respectively after the leaching process and isotopic equilibration, $\delta \text{ES}$ is the $\delta^{34}\text{S}$ value of total sulphur in the system, $\delta \text{DS}$ is the $\delta^{34}\text{S}$ value of disseminated sulphide in the rock, and $\delta \text{SO}_4$ is the $\delta^{34}\text{S}$ value of the evolved seawater sulphate entering the system.

For the closed system case

$$\delta^{34}\text{S}_{\text{H}_2\text{S}_f} = 16.12^0/00$$

$$\delta^{34}\text{SISO}_4^2_f = 39.32^0/00$$

In the open system case

$$\delta^{34}\text{S}_{\text{H}_2\text{S}_f} = 20.57^0/00$$

$$\delta^{34}\text{SISO}_4^2_f = 43.77^0/00$$

However other reactions are possible, for example, oxidation of pyrite to hematite or magnetite, thus,

$$6\text{FeS}_2 + 12\text{H}_2\text{O} + 2\text{Fe}_3\text{O}_4 + 11\text{H}_2\text{S} + \text{SO}_4^2^- + 2\text{H}^+$$

(6.22)

$$8\text{FeS}_2 + 16\text{H}_2\text{O} + 4\text{Fe}_2\text{O}_3 + 15\text{H}_2\text{S} + \text{SO}_4^2^- + 2\text{H}^+$$

(6.23)

In the latter case, $\delta^{34}\text{S}_{\text{H}_2\text{S}_f}$ values would be 16.79°/oo for the closed system and 2.56°/oo for the open system (Fig. 6.5). For both cases, there is an overlap between the $\delta^{34}\text{S}$ values predicted for $\text{H}_2\text{S}$ formed by total reduction of sulphate plus leaching of igneous sulphide and $\delta^{34}\text{S}$.
values of $H_2S$ formed by sulphide in a system in which both $SO_4^{2-}$ and $H_2S$ are present. Thus the water : rock interaction model can explain the overlap in the $\delta^{34}S$ values of sulphides in the sulphide and barite orebodies. Clearly, in a natural system the change from total sulphate reduction to pyrite leaching to produce $SO_4 + H_2S$ would not be as sharply defined as in the model and there might be some degree of transition between the processes. Oxidation of "FeO" to $Fe_3O_4$ is also a simplistic view of a complex process, and some phases in equilibrium with a system involving partial reduction of seawater sulphate and pyrite leaching might well have $Fe^{2+}/Fe^{3+}$ mole ratios greater than the value of 0.5 for magnetite. In this context it is interesting to note that a chlorite which appears to have equilibrated with the barite ore at temperatures of about 250°C during retrogressive metamorphism (Section 7.6; Chlorite 3, Table 7.1) has an $Fe^{2+}/Fe^{3+}$ mole ratio of 3. Hence the 1.2% FeO assigned to Rosebery rhyolite is an effective minimum value. In fact, the least altered footwall pyroclastics samples (Analyses 1 and 2, Table 5.1) contain an average of 2.03% total iron expressed as FeO. The FeO content of the totally unaltered rhyolite was probably in the range 1.6 to 1.7%.

Another potential problem with the interpretation concerns the kinetics of isotopic equilibration between $SO_4^{2-}$ species and $H_2S$ at temperatures of about 250°C. For a solution with a pH of 5 and a total sulphur content of $10^{-2}$ m the time required to achieve 90% isotopic equilibrium would be about 1.7 years according to the model of Sakai and Dickson (1978*), and 4.4 years according to Ohmoto and Lasaga (1982). For a solution with a ES content of $10^{-3}$ m these time estimates would be greater by an order of magnitude. At 300°C, pH = 5, $mES = 10^{-2}$, 90% equilibrium is achieved in 24 days (Sakai and Dickson) or 140 days (Ohmoto and Lasaga). Fluid flow rates of $10^{-4}$ to $10^{-2}$ km/yr are typical for porosity-controlled hydrothermal flow, whereas for
fracture-controlled flow the rate is 0.1 to 10 km/yr (Cathles, 1981*; Cathles pers. comm. in Ohmoto and Lasaga, 1982). Hence for a flow path length of 5 km in a zone in the subsurface at 250°C, consistent with the dimensions of a convective cell necessary to form a deposit the size of Rosebery (e.g. Solomon, 1976), a close approach to isotopic equilibrium would be achieved by a fluid with a S content of 10^-3 m in porosity-controlled flow or at the lower limit of the stated range of fracture-controlled flow rates. This interaction would probably take place in the downgoing limb of a hydrothermal convection cell because fractures probably control the sites of hydrothermal discharge (e.g. Solomon, 1976; Scott, 1978), which would be a relatively fast process with $\delta^{34}S_{H_2S}$ values controlled by the temperature of the reservoir.

Despite these uncertainties the seawater circulation model does account for both the trend in isotope values of increasing $\delta^{34}S$ of sulphide minerals with inferred depositional sequence at Rosebery, their approximate $\delta^{34}S$ values and the reason for the transition from sulphide-rich to barite-rich ore. The model can also explain the relationship pointed out by Lydon (in Franklin et al., 1981), where Pb-Zn-Cu deposits hosted in felsic volcanic sequences have higher $\delta^{34}S$ values than Cu-Zn deposits in basaltic sequences. This is because the sulphur isotopic effect of the seawater-derived $H_2S$ component is felt in more pronounced a fashion at lower water/rock ratios than in relatively sulphur-rich basaltic systems. Similarly, the onset of exhalation of mixed $SO_4^{2-}/H_2S$ solutions may occur at water/rock ratios an order of magnitude lower in rhyolitic compared with basaltic terrains. In the latter case, water : rock ratios of about 116, the threshold at which mixed $SO_4^{2-}/H_2S$ solutions appear, are probably achieved rarely, if ever. However the redox state of sulphur in solution is a function of temperature as well as water/rock ratio. Despite this caveat, the frequent occurrence of Cu-rich deposits and scarcity of Cu-poor, Zn-rich and barite containing deposits in basalt sequences might suggest that temperatures sufficiently
high for Cu transport (>300°C) and hence total reduction of seawater sulphate may be commonly achieved during generation of hydrothermal fluids in mafic volcanic terrains. This may not always be the case in felsic volcanic terrains. For example, the Kuroko deposits of Japan, while generally having a higher Cu/Pb+Zn ratio than Rosebery (Table 8.1), formed mainly at temperatures of less than 300°C, with chalcopyrite formation during a brief higher-temperature episode (Pisutha-Arnond et al., 1981). Hence for the bulk of the interval of mineralisation sulphur with a mixed redox state was responsible for ore formation (e.g. Kajiwara, 1971) and δ34S values for sulphides are lower than at Rosebery (mostly +4 to +8‰). A similar situation might apply to the ores of Buchans, Newfoundland which are underlain by some 4 km of basalt (Thurlow and Swanson, 1981) and have δ34S values of 4.7 to 8.7‰ (py, sl, cp; Kowalik et al., 1981).

However, the model in at least a semi-quantitative way supports the earlier contention of the writer (Green, 1979) that the mineral zonation and sulphur isotopic evolution of the Rosebery deposit could result from progressive seawater : rhyolite interaction and depletion of the footwall rocks in ferrous iron and reduced sulphur. Such a process might explain why, within a given cluster of massive sulphide orebodies, the major deposits tend to occur relatively low in the volcanic sequence and that deposits at a higher stratigraphic level are generally rarer. This process therefore can answer the criticism stated by Franklin et al. (1981, p. 610):

"... the convection cell hypothesis does not satisfactorily explain the observation that in many mining areas, a majority of massive sulphide deposits are confined to a relatively narrow stratigraphic interval compared to the time span occupied by volcanic activity...".

The thermodynamic validity of some of the conclusions reached in this discussion will be examined in Chapter 8.
7.1 INTRODUCTION

Textural evidence suggests that the metasomatism which produced the massive pyrrhotite at the southern end of the mine [Section 4.4(iii)] and spessartine (Section 7.4) post-dated cleavage development of Devonian age. However, neither folding nor metamorphism has destroyed the fine banding in the ore. Lack of large scale metamorphic re-equilibration is borne out by variation of sphalerite and chlorite compositions throughout the orebody and on the single polished section scale (e.g. 105174; Table 4.4), and by lack of consistent sulphur isotope fractionation factors between sulphide minerals (Table 6.1).

The purpose of this chapter is to employ geological and mineralogical criteria to place some constraints on the conditions of metamorphism and on the degree of attainment of local metamorphic and metasomatic equilibrium.

7.2 PRESSURE ESTIMATES

7.2 (i) Geological Estimate

The thickness of Cambrian volcanic rocks overlying the Rosebery ore horizon is perhaps 2500 m, to which can be added 1800 to 3300 m of Late Cambrian to Early Devonian sedimentary rocks (Blissett, 1962; Campana & King, 1963). An assumed average dip of 45° for these rocks yields a total overburden of 6000 to 8000 m and an assumed average rock density of 2.65 gm cm⁻³ gives a lithostatic pressure of about 1.6 to 2.1 kbar.
7.2 (ii) Sphalerite Geobarometry

Sphalerite in the pyrrhotite-bearing mineralization was examined in an attempt to determine the pressure. Sphalerite from a specimen (76-746) with the assemblage sphalerite-magnetite-pyrrhotite-chlorite-galena contains 11.4 to 15.1 mole % sphalerite. Sphalerite from the assemblage pyrrhotite-pyrite-arsenopyrite-chalcopyrite-galena-sphalerite (76-747) contains 14.3 to 16.6 mole % FeS, the point analysed falling near pyrite-pyrrhotite-sphalerite triple points and, in one case, from sphalerite partly enclosed by pyrite. The range in FeS content in the latter specimen corresponds to a pressure of 3.1 to 5.2 kbar using the sphalerite geobarometer of Hutchinson & Scott (1981). These pressures are high compared with the geological estimate and it appears probable that the sphalerite compositions have re-equilibrated below 248°C, the upper stability limit of monoclinic pyrrhotite (Scott & Kissin, 1973), rendering the use of the sphalerite geobarometer invalid. Treatment of pyrrhotite grains with magnetic colloid (Craig and Scott, 1974, p. S18) reveals a granular aggregate of subhedral grains with monoclinic pyrrhotite predominating over the hexagonal (non-magnetic) phase.

7.3 Pyrite-Pyrrhotite Sulphur Isotope Fractionation

The coarse grainsize of pyrite-pyrrhotite intergrowths, their clear replacement relationship to earlier folded sphalerite-galena rich ore indicates a pyrrhotite origin by post-folding metasomatic replacement of pre-existing sulphide ore (p. 4.26, this thesis). Thus, thermal breakdown of pyrite which leads to marked 34S enrichment in residual pyrrhotite (Puchelt, 1968; Gehrisch et al., 1975* Yaroshevich and Tvalchrelidze, 1981*) is not applicable in this case. The fractionation factor, $\Delta_{\text{py-po}} = 0.9\%$, yields an isotopic temperature of 304°C (Kajiwara and Krouse, 1971), but allowing for experimental error of $\pm 0.2\%$ in the $\Delta$ value plus 10% uncertainty in the experimental calibration, gives a possible temperature range of 222 to 413°C. Although hydrothermal transport and redeposition of pyrite and pyrrhotite in a temperature gradient can yield isotopic disequilibrium effects at 300°C (Yaroshevich and Tvalchrelidze (op. cit.), the temperature gradient in their experiments was extreme (50°C/m), and it is more likely that under the condition of pyrrhotite formation at Rosebery that isotopic equilibrium was achieved (c.f. Eldridge and Ohmoto, 1980; Kajiwara, 1971, Section 6.4 this thesis). Samples 105175 and 105179 yield near concordant py-sl-gn isotopic temperatures in the range 275-345°C (Table 6.1) which are consistent with the pyrite-pyrrhotite temperature. More analysis of pyrite-pyrrhotite pairs and precise isotopic measurements by ion microprobe are required to settle the question of conditions of isotopic equilibrium in the Rosebery orebody.
7.4 BIOTITE AND GARNET

Spessartine was reported in one sample by Stillwell (1934) and in this study was found in a drillcore sample (105150) of altered host rock (?) about 500 m below the present level of mining. The mineral assemblage in this rock is quartz-chlorite-garnet-carbonate-biotite-tourmaline-muscovite-pyrite-sphalerite-chalcopyrite. Textural evidence suggests that chlorite, pyrite, quartz, sphalerite, and muscovite are pre-cleavage, but garnet mimetically overgrows the cleavage (Fig. 7.1) and unlike pyrite from the same specimen is not fringed by pressure shadows of chlorite. Hence the garnet was formed in a post-deformational metamorphic event. It is partly altered to chlorite, quartz and carbonate.

The average compositions of garnet and co-existing chlorite from electron microprobe analyses are garnet (Mg0.02Ca0.27Mn2.66Fe0.17)(Fe0.21Al1.79)(Al0.12Si2.88)O11.99 and chlorite (Mg1.41Fe2.99Mn0.31Al1.33)(Al1.33Si2.61)O9.99(OR)8. The chlorite is the richest in Mn of those analysed from Rosebery.

Little definitive information as to temperature conditions can be gained from this assemblage. Hsu (1968) investigated the thermal stability of spessartine in the system FeO-MnO-Al₂O₃-SiO₂-H₂O under a wide range of aO₂ conditions. He found that pure spessartine formed from quartz + Fe-Mn chlorite + spinel at temperatures greater than 420°C at 2 kbar P_H₂O. The lack of spinel in the Rosebery assemblage described above and the presence of Mg in the chlorite casts some doubt on the validity of using the presence of spessartine as a geothermometer at Rosebery.

Winkler (1979) stated that the reaction: stilpnomelane + phengite = biotite + chlorite + quartz + H₂O corresponds very closely to the boundary between the classic chlorite and biotite zones (i.e. the first appearance of biotite in assemblages lacking stilpnomelane). Winkler (op. cit.) quoted the experimental work of Nitsch (1970) who determined the temperature of the reaction above as less than 430°C at 1 kbar and 445 ± 10°C at 4 kbar.
Fig. 7.1 Photomicrograph of garnet-bearing rock (105150) from footwall of orebody. Partly retrograded garnet euhedra (white, high relief) in a matrix of chlorite and quartz (white to light grey). Pyrite grains (black) have adjacent pressure shadows of quartz and chlorite (note large grain at lower right). Width of field 4 mm, plane polarized light.
However, biotite is known to form at lower temperatures in other environments and iron-rich biotite first appears at about 320°C in the arkosic sand reservoir of the Salton Sea geothermal field (Helgeson, 1967).

7.5 ARSENOPYRITE-TENNANTITE

The compositions of arsenopyrite coexisting with pyrite indicates a temperature range of 370 to 455°C (Section 4.4 (i)). The commonly observed reaction relationship between arsenopyrite and tetrahedrite-tennantite also has potential as a geothermometer. Type 2 arsenopyrite occurs in fahlore as euhedra which are commonly embayed (Figs 4.9 and 4.10). This textural relationship is common in eastern Australian massive sulphide deposits, having been previously noted at Rosebery by Stillwell (1934) and at Woodlawn by Ayres (1978). This section discusses this relationship from a thermodynamic viewpoint.

The mineral association in type 2 arsenopyrite suggests that the following equation might be representative of the arsenopyrite-tennantite reaction:

\[ 4\text{FeAsS} + 10\text{CuFeS}_2 + \text{ZnS} + 7\text{S}_2(g) = \text{Cu}_{10}\text{FeZnAs}_4\text{S}_{13} + 13\text{FeS}_2 \]  

(7.1)

for which

\[ K_s = \frac{a_{\text{tnt}}}{a_{\text{S}_2}^7} \]

(7.2)

assuming the activity for sulphides other than tennantite to be unity. This assumption should introduce an uncertainty of less than ± 0.04 in \( \log a_{\text{S}_2} \) over the range of conditions considered.

The free energy of formation of tennantite has not been determined experimentally, but may be estimated by the method of Craig & Barton (1973) who determined that the free energy of formation of a sulphosalt could be approximated by the expression
\[ \Delta G^O = \sum_{i=1}^{n_i} \Delta G^O_i + k \sum_{i=1}^{n_i} N_i RT \]  

(7.3)

where \( \Delta G^O \) is the free energy of formation of the sulphosalts,
\( N_i \) is the mole fraction of the \( i^{\text{th}} \) simple sulphide component normalized to one sulphur atom in its formula,
\( \Delta G^O_i \) is the free energy of formation of the \( i^{\text{th}} \) simple sulphide,
\( R \) is the gas constant (1.9872 cal deg \(^{-1}\) mol \(^{-1}\)),
\( T \) is temperature in degrees kelvin,
\( k \) has a value of 1.2 ± 0.8.

There is considerable scatter in the value of \( k \) according to the composition of the sulphosalts (Craig & Barton, 1973, Fig. 1). The following points are relevant:

(i) \( k \) is greater for Sb-bearing sulphosalts than those of Bi;
(ii) \( k \) for Cu- and Ag-bearing sulphosalts is greater than those of Pb;
(iii) there are no free energy data for As-bearing sulphosalts.

Because tetrahedrite (\( \text{Cu}_{1.2} \text{SbS}_{1.3} \)) and tennantite (\( \text{Cu}_{1.2} \text{As}_{4} \text{S}_{1.3} \)) form a complete solid solution series in nature it is considered appropriate to model the value of \( k \) for tennantite by that of \( \text{CuSbS} \) which is the closest antimonian analogue of tennantite for which an independent value of free energy exists. A value of \( k \) equal to 2.154 has therefore been adopted.

Ideal solid solution has been assumed for tetrahedrite and tennantite. The activity of tennantite is assumed to be related to its mole fraction by:

\[ a_{\text{tnt}} = X_{\text{tnt}}^k \]  

(7.4)

Fahlore minerals from Rosebery have a wide range of composition of As/Sb+As ratios varying from 0.005 to 0.91 (Smith, 1975). The same 18 analyses show an average content of Zn+Fe atoms in the formula, normalized to 13 S atoms of 1.92 and a Zn/Fe ratio ranging from 0.21 to 1.52, with an average value of 1.44. The formula for tennantite of \( \text{Cu}_{10} \text{FeZnAs}_{4} \text{S}_{13} \)
(Eqn. 7.1) is therefore applicable to Rosebery tennantite, with the mole fraction of tennantite, \(X_{\text{tnt}}\), referring to the mole ratio \(\text{As/}\text{Sb+As}\).

Fig. 7.2 is a log \(a_{\text{S}_2}\)-temperature diagram showing values of \(X_{\text{tnt}}\) satisfying equation 7.1. Pure tennantite can co-exist with pyrite + arsenopyrite over the temperature range 415 to 465°C. This is in good agreement with the experimental work of Sugaki (1957), who heated a natural sample of tennantite (no analysis given) and noted no reaction at 350°C, but corrosion of arsenopyrite at 450°C. It is clear from Fig. 7.2 that the reaction relationship observed between arsenopyrite and fahlore can occur over a wide range of temperatures depending on the value of \(X_{\text{tnt}}\), and that even a single fahlore composition is stable with the assemblage pyrite + arsenopyrite over a wide range of temperatures.

For example, fahlore with \(X_{\text{tnt}}\) of 0.1 can coexist with the assemblage sphalerite-pyrite-chalcopyrite-arsenopyrite over a temperature range of about 310 to 385°C. Precise application of the arsenopyrite-fahlore reaction relationship would require the following:

(i) experimental verification, including evaluation of the activity composition relationships of fahlore; and

(ii) independent evaluation of \(a_{\text{S}_2}\), for example by analysis of the FeS content of coexisting sphalerite.

Despite these qualifications the embayment of arsenopyrite by fahlore at Rosebery where 15 of the 18 fahlore analyses of Smith (1975) indicate an \(\text{As/}\text{Sb+As}\) ratio in excess of 0.1, indicates peak metamorphic temperatures above 300°C and probably above 350°C. As "tetrahedrite" is an important Ag-bearing mineral at Rosebery (Smith, 1975; Henley & Stephenson, 1978) the arsenopyrite-fahlore reaction relationship also has implications regarding the redistribution of precious metals during metamorphism.
Fig. 7.2  log \( a_{S_2} \) versus \( 1/T \) diagram showing stability boundaries of minerals in the Fe-As-S system, contours of mole \% FeS in sphalerite, mole \% As in arsenopyrite, and estimated position of reaction boundary between fahlore and arsenopyrite for various values of tennantite activity assuming \( a_{\text{tnt}} = K_{\text{tnt}} \).
7.6 **CHLORITE**

Walshe & Solomon (1981) developed a six-component solid solution model for chlorite which assumed ideal mixing for cations on energetically equivalent sites. This model was applied by Walshe (in Green et al., 1981) in an attempt to define the chemical environment of ore formation at Rosebery, assuming that the chlorites did not re-equilibrate during subsequent hydrothermal activity or metamorphism.

Unfortunately, Walshe (pers. comm., 1981) has recognized a number of errors and deficiencies in his model. Walshe & Solomon (1981) defined the following thermodynamic components in the chlorite solid solution:

- **C1**: \( \text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \)
- **C2**: \( \text{Mg}_5\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_8 \)
- **C3**: \( \text{Fe}^{2+}_5\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_8 \)
- **C4**: \( \text{Fe}^{2+}_5\text{Fe}^{3+}\text{Si}_3\text{Fe}^{3+}\text{O}_{10}(\text{OH})_8 \)
- **C5**: \( \square_2\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \)
- **C6**: \( \text{Fe}^{2+}\text{Fe}^{3+}\text{Al}_4\text{Si}_4\text{AlO}_{11}(\text{OH})_7 \)

where the \( \square \) denotes a vacancy in the structure.

The deficiencies in the model of Walshe & Solomon (1981) include errors in the representation of the third law entropy and heat capacity data for the end member \( \text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \) (C1) and that the activity of C4 is best represented by its mole fraction (Walshe, pers. comm.). On the basis of modelling the behaviour of the Creede chlorite (Barton et al., 1977), Walshe now favours a non-ideal mixing situation for C6 where its mole fraction \( (X_6) \) is related to its activity \( (a_6) \) by:

\[
\log a_6 = \log X_6 + \frac{1352(1-X_6)^5}{RT}
\]  

(7.5)

An electron microprobe analysis of chlorite provides information on the total Fe, Mg, Mn, Si, Al, Ti and Cr content which can be related to the content of the components C1 to C5 above and the following
minor components

C7 : Mn$_5$Al$_3$Si$_3$AlO$_{16}$(OH)$_8$
C8 : Fe$^{2+}$$_{5}$CrSi$_3$CrO$_{16}$(OH)$_8$
C9 : \( \Box_{0.5}Ti_{0.5}Fe^{2+}_4AlSi_3AlO_{16}(OH)_8 \)

C7, C8 and C9 can be eliminated by the following relations:

\[ A = \Sigma Mg \] (7.6)
\[ B = \Sigma Fe - 5X_8 - 4X_9 \] (7.7)
\[ C = \Sigma Al - 2X_7 - 2X_9 \] (7.8)
\[ D = \Sigma Si - 3X_7 - 3X_8 - 3X_9 \] (7.9)
\[ E = 1 - X_7 - X_8 - X_9 \] (7.10)

The following equations can be set up:

\[ 6X_1 + 5X_2 = A \] (7.11)
\[ 5X_3 + 7X_4 = B \] (7.12)
\[ 2X_2 + 2X_3 + 4X_5 = C \] (7.13)
\[ 4X_1 + 3X_1 + 3X_3 + 3X_4 + 4X_5 = D \] (7.14)
\[ X_1 + X_2 + X_3 + X_4 + X_5 = E \] (7.15)

Solving these equations for \( X_1 \) to \( X_5 \) yields:

\[ X_1 = \frac{A + B + C + 3D - 16E}{2} \] (7.16)
\[ X_2 = \frac{-2A - 3B - 3C - 9D + 48E}{5} \] (7.17)
\[ X_3 = \frac{14A + 16B + 21C + 28D - 196E}{10} \] (7.18)
\[ X_4 = \frac{-2A - 2B - 3C - 4D + 28E}{2} \] (7.19)
\[ X_5 = \frac{-A - B - C - D + 10E}{2} \] (7.20)

Valid solutions require that the mole fractions of each species (i.e. \( \Sigma Mg \), \( Fe^{3+} \), etc.) be positive. In fact it was found that only \( Ti^{3+} \) or \( Fe^{3+} \) was ever negative.

Where \( Fe^{3+} \) (i.e. \( X_4 \)) < 0, eliminating \( X_4 \) from 7.12, 7.14 and 7.15:
\[
X_1 = \frac{A + B + 5D - 20E}{6} \\
X_2 = \frac{-B - 5D + 20E}{5} \\
X_3 = \frac{B}{5} \\
X_4 = \frac{-A - B + D + 2E}{6}
\]

Where \( \Box \) (i.e. \( X_5 \)) \( < 0 \), eliminating \( X_5 \) from 7.13, 7.14 and 7.15:

\[
X_1 = D - 3E \\
X_2 = \frac{A - 6D + 18E}{5} \\
X_3 = \frac{-2A + 5C + 12D - 36E}{10} \\
X_4 = \frac{-C - 2D + 8E}{2}
\]

These equations satisfy charge and mass balance constraints for the five components considered, but independent determination of water content is necessary to fix \( X_6 \). Following Walshe & Solomon (1981), \( X_6 \) can be incremented at the expense of \( X_3 \) and at a given \( P \) and \( T \) the equilibrium values of \( X_6 \) and \( a_{O_2} \) solved by simultaneous satisfaction of 7.30 and 7.32 which are based on reactions 7.29 and 7.31.

\[
\begin{align*}
\text{Mg}_5\text{Al}_2\text{Si}_3\text{AlO}_10(\text{OH})_8 + \frac{5}{7} \text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_3\text{Fe}^{3+}\text{O}_10(\text{OH})_8 + \frac{35}{21}\text{SiO}_2 + \frac{10}{21}\text{H}_2\text{O} & = \\
\text{Fe}^{2+}_5\text{AlSi}_3\text{AlO}_10(\text{OH})_8 + \frac{5}{6} \text{Mg}_6\text{Si}_8\text{O}_10(\text{OH})_8 + \frac{5}{6}\text{O}_2(g)
\end{align*}
\]

for which

\[
\log a_{O_2} = 2.8K_1 + 2.8 \log a_2 + 2 \log a_4 - \frac{7}{4} \log a_1 - 2.8 \log a_3
\]

assuming the activity of water to be unity.

\[
\begin{align*}
\text{Fe}^{2+}_5\text{AlSi}_3\text{AlO}_10(\text{OH})_8 + \frac{4}{5}\text{O}_2(g) & = \\
\text{Fe}^{2+}_4\text{Fe}^{3+}\text{AlSi}_3\text{AlO}_11(\text{OH})_7 + \frac{4}{5}\text{H}_2\text{O} & (1)
\end{align*}
\]

for which

\[
\log a_{O_2} = -4 \log K_3 - 4 \log a_3 + 4 \log a_6
\]

In practice, values of \( \log a_{O_2} \) were calculated at temperatures of 250, 300 and 350°C and pressures of 1 kbar, 2 kbar and the saturation
pressure of pure water, for increments of $X_6$ of 0.1 or 0.01 and the values of $X_6$ and $\log a_{O_2}$ satisfying both 7.30 and 7.32 were solved graphically.

A check of the internal consistency of the calculations was provided by calculating the reaction quotient, $Q_3$, for:

$$
\begin{align*}
&Mg_5AlSi_3AlO_{10}(OH)_8 + \frac{5}{7}Fe_5^{2+}Fe^{3+}Si_3Fe^{3+}O_{10}(OH)_8 + \frac{3}{7}Fe_5^{2+}AlSi_3AlO_{10}(OH)_8 \\
&+ \frac{25}{21}SiO_2 = 10\frac{1}{7}Fe_4^{2+}Fe^{3+}AlSi_3AlO_{11}(OH)_7 + \frac{5}{6}Mg_6Si_4O_{10}(OH)_8 \\
&+ \frac{5}{21}H_2O(l)
\end{align*}
$$

(7.33)

where 7.33 = 7.29 + $10^{7/3} \times 7.31$

and for which

$$
\log Q_3 = \frac{10}{7} \log a_6 + \frac{5}{7} \log a_1 - \log a_2 - \frac{5}{7} \log a_3 - \frac{3}{7} \log a_3
$$

(7.34)

The value of $Q_3$ was compared with the equilibrium constant for the reaction, $K_3$.

Assuming the assemblage pyrite-chlorite-arsenopyrite-quartz is in equilibrium (Green et al., 1981), the lower limit of $a_{O_2}$ is defined by the reaction

$$
Fe_5^{2+}Fe^{3+}Si_3Fe^{3+}O_{10}(OH)_8 + 7FeS_2 = 14FeS + 4H_2O(l) + 3SiO_2 + 4O_2(g)
$$

(7.35)

for which

$$
\log a_{C_2} = \frac{1}{4}(\log K_4 + \log a_4)
$$

(7.36)

The upper limit of $a_{O_2}$ for a given chlorite composition is defined by the reaction

$$
Fe_5^{2+}Fe^{3+}Si_3Fe^{3+}O_{10}(OH)_9 + 7FeS_2 + 14As

= 14FeAsS + 4H_2O(l) + 3SiO_2 + 4O_2(g)
$$

(7.37)

for which

$$
\log a_{O_2} + \frac{1}{4}(\log K_5 + \log a_4)
$$

(7.38)

since the activity of FeAsS does not depart significantly from unity in sulphur-rich assemblages (Kretschmar & Scott, 1976).
The conditions of equilibration of ten chlorites from Rosebery lacking octahedral site vacancies have been examined. These include the three chlorites previously studied by Walshe (in Green et al., 1981) and another seven chlorites from the D and F lenses analysed by McLeod (1978). Structural analyses and mole fractions of thermodynamic components are shown in Table 7.1.

The results of the calculations are listed in Table 7.2 and shown in Figs 7.3, 7.4 and 7.5. There was good internal consistency in the calculations. At the values of $X_6$ simultaneously satisfying equations 7.30 and 7.32, $Q_3$ and $K_3$ usually agreed within $\pm 0.01$ log units. For example, for chlorite 1 (Table 7.1) at the saturation pressure of water and 300°C, the equilibrium value of $X_6$ was estimated graphically as 0.36 and the log $a_{O_2}$ as -33.54 after calculations carried out at $X_6 = 0, 0.01, 0.1, 0.2, 0.3$ and 0.4. This procedure was checked by recalculation at $X_6 = 0.35, 0.36$ and 0.37. The results are tabulated below:

<table>
<thead>
<tr>
<th>$X_6$</th>
<th>$\log a_{O_2}$ from equation 7.26</th>
<th>$\log a_{O_2}$ from equation 7.28</th>
<th>$\log Q_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>-33.593</td>
<td>-33.634</td>
<td>-0.3134</td>
</tr>
<tr>
<td>0.36</td>
<td>-33.558</td>
<td>-33.572</td>
<td>-0.3039</td>
</tr>
<tr>
<td>0.37</td>
<td>-33.552</td>
<td>-0.2942</td>
<td>-0.2942</td>
</tr>
</tbody>
</table>

The calculation indicates an equilibrium value of $X_6$ between 0.36 and 0.37 and a log $a_{O_2}$ value between -33.522 and -33.558, which is in excellent agreement with the graphical solution. Moreover, the equilibrium value of $\log K_3$ of -0.299 lies between the calculated values of $\log Q$ of -0.3039 and -0.2942 at $X_6 = 0.36$ and 0.37 respectively.

It can be seen from Figs 7.3, 7.4 and 7.5 that most of the chlorites are in equilibrium with the assemblage quartz-pyrite-arsenopyrite at temperatures of about 250°C but fall in the pyrrhotite field at temperatures of around 300 to 350°C. The curves do not permit any estimate of pressure.
### Table 7.1

**Structural Formulae of Chlorites**

<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>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.504</td>
<td>0.643</td>
<td>1.238</td>
<td>1.930</td>
<td>2.899</td>
<td>1.881</td>
<td>0.900</td>
<td>0.747</td>
<td>0.598</td>
<td>0.883</td>
<td>2.348</td>
<td>0.569</td>
</tr>
<tr>
<td>Mn</td>
<td>0.159</td>
<td></td>
<td>0.138</td>
<td>0.124</td>
<td>0.199</td>
<td>0.225</td>
<td>0.194</td>
<td>0.251</td>
<td>0.178</td>
<td>0.110</td>
<td>0.158</td>
<td>0.114</td>
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<tr>
<td>Fe$^{2+}$</td>
<td>2.834</td>
<td>4.004</td>
<td>1.177</td>
<td>2.509</td>
<td>1.489</td>
<td>2.665</td>
<td>3.422</td>
<td>3.663</td>
<td>3.762</td>
<td>3.608</td>
<td>2.115</td>
<td>3.299</td>
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<tr>
<td>Fe$^{3+}$</td>
<td>0.246</td>
<td>0.067</td>
<td>0.304</td>
<td>0.05</td>
<td>0.008</td>
<td>0.063</td>
<td>0.107</td>
<td>0.13</td>
<td>0.147</td>
<td>0.207</td>
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<td>Ca$^{3+}$</td>
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<td>0.006</td>
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<td>1.538</td>
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<td>0.326</td>
<td>0.020</td>
<td>0.005</td>
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<td>0.038</td>
<td>0.039</td>
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**Components**

- Mg$_2$Si$_2$O$_5$(OH)$_4$ (C1) -0.508 -0.354 -0.447 -0.461 -0.417 -0.456 -0.538 -0.58 -0.533 -0.484 -0.359 -0.533
- Mg$_3$Al$_2$Si$_2$O$_10$(OH)$_6$ (C2) 0.904 -0.553 1.184 0.5392 1.0802 0.9234 0.8256 0.8454 0.7572 0.7572 0.901 0.753
- Fe$_2$Al$_2$Si$_2$O$_10$(OH)$_6$ (C3) 0.479 0.767 0.044 0.472 0.293 0.4561 0.6201 0.5954 0.6457 0.5831 0.423 0.653
- Fe$_2$Fe$^3+$Si$_2$O$_10$(OH)$_6$ (C4) 0.123 0.034 0.192 0.025 0.004 0.0315 0.0535 0.065 0.0735 0.1035
- Fe$_2$Fe$^3+$Al$_2$Si$_2$O$_10$(OH)$_6$ (C5) - - - - - - - - - - 0.004 0.097
- Fe$_2$Fe$^3+$Al$_2$Si$_2$O$_11$(OH)$_7$ (C6) - - - - - - - - - - 0.005
- Fe$_2$Fe$^3+$Al$_2$Si$_2$O$_10$(OH)$_6$ (C7) 0.032 - 0.028 0.0248 0.0398 0.045 0.0388 0.0502 0.0356 0.022 0.032 0.023
- Fe$_2$Fe$^3+$Si$_2$O$_10$(OH)$_6$ (C8) 0.005 - - - - - - - - - - 0.006
- D$_2$Al$_4$Si$_4$O$_10$(OH)$_8$ (C9) - - - - - - - - - - 0.024 0.012 0.018

Sample numbers and localities:

1. Sample 105174/2a, Table 4.5
2. Sample 105174/1, Table 4.5
3. Sample 105183/1, Table 4.5
4. 41483 DDH 91925, 133', 1 lens, 15 level, 3755 1167E, 96631,3L
5. 41484 DDH 91925, 140', 1 lens, 15 level, 3755 1174E, 96631,3L
6. 41464 DDH 92066, 50', 1 lens, 15 level, 801N 952E, 96661,3L
7. 41460 DDH 92066, 70', 1 lens, 15 level, 801N 972E, 96661,3L
8. 41447 DDH 92066, 64', 1 lens, 15 level, 801N 966E, 96661,3L
9. 41449 DDH 92066, 60', 1 lens, 15 level, 801N 966E, 96661,3L
10. 40451 DDH 92066, 74', 1 lens, 15 level, 801N 972E, 96661,3L
11. Sample 105147/1, Table 4.3
12. Sample 105174/4, Table 4.3

Samples 4 to 10 from McLeod (1978), Fe$^3+$ content obtained by solution of equations 7.21 through 7.28.
Table 7.2
VALUES OF LOG aO₂ AND X₆ FOR ROSEBERY CHLORITES.

<table>
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<tr>
<th>Chlorite Number (from Table 7.1)</th>
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<th>2</th>
<th>3</th>
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<td></td>
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<td></td>
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<tr>
<td>P&lt;sub&gt;sat&lt;/sub&gt;</td>
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<td>0.34</td>
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<td>0.014</td>
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<td>0.017</td>
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<td>0.09</td>
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<td>0.027</td>
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<td>0.01</td>
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<td>0.017</td>
<td>0.08</td>
<td>0.06</td>
<td>0.16</td>
<td>0.14</td>
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</table>

* For each T, P condition, the value of log aO₂ is the upper number. The lower number is X₆.
Fig. 7.3  Log $aO_2$ versus $1/T$ diagram showing equilibration conditions for chlorites from Rosebery (nos. 1 to 10; Table 7.1) compared with the positions of the oxygen activity buffers hematite-magnetite (hem-mt), pyrite-arsenopyrite-arsenic-chlorite (py-apy-As-chl), pyrite-pyrrhotite-chlorite (py-po-chl) at a pressure equivalent to that of the liquid-vapour curve for pure water. The curves for py-apy-As-chl and py-po-chl are drawn for the average conditions for chlorites 4 through 10 and chlorite 1.
Fig. 7.4  As for Fig. 7.3, but at a total pressure of 1 kilobar.
Fig. 7.5  As for Fig. 7.3, but at a total pressure of 2 kilobars.
Chlorite 2 is clearly anomalous and intersects the pyrite-pyrrhotite-
chlorite curve at about 170°C at the saturation pressure of water and at
about 100°C and 2 kbar $P_{H2O}$. This anomaly may be the result of analytical
error. Chlorite 3 has equilibrated at substantially higher oxygen activi-
ties than the other chlorites. This sample is from the barite lode and
the higher oxidation state is consistent with the mineralogy of that ore-
body, namely abundant barite, no arsenopyrite or magnetite, and hematite
present at the top of the orebody (Brathwaite, 1974; this study).

The mineralogy of the sulphide orebody and the chlorite chemistry
is consistent with a temperature of chlorite-sulphide equilibration of
around 250°C. A pressure estimate could be arrived at by analysis of the
water content of some of the chlorites. For example, chlorite 7 (Table 7.2)
would be a suitable candidate with calculated values of $X_6$ at 250°C of 0.47
at saturation pressure, 0.34 at 1 kbar, and 0.09 at 2 kbar. Other chlorites
(e.g. chlorite 6) show little variation of $X_6$ with changing pressure and
would be of little use. Unfortunately most chlorite in the sulphide ore-
body is too fine-grained and too sparse for physical separation for the
analysis of water content. Another approach would be to use the
following reaction involving chlorites with a vacancy in their structure:

\[
2\text{Mg}_6\text{Al}_3\text{Si}_4\text{Al}_2\text{O}_{16}(\text{OH})_2 + \frac{10}{3} \text{SiO}_2 + \frac{8}{3} \text{H}_2\text{O}(\ell) \]
\[
= \square_{2}\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 + \frac{10}{6} \text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \quad (7.39)
\]

for which

\[
\log Q_6 = \log a_6 + \frac{10}{6} \log a_1 - 2 \log a_2 \quad (7.40)
\]

Unfortunately, neither of the chlorites containing component 5
(numbers 11 and 12, Table 7.1) give realistic solutions, assuming either a
random mixing solid solution model, or activity equal to mole fraction.
In both cases unrealistically high temperatures ($> 350°C$) and/or pressures
($> 2$ kbar) would be required for equality of $Q_6$ and $K_6$. Chlorites with an
 octahedral site vacancy are probably stable at temperatures below about 280 to 300°C (Walshe, 1982) and therefore are compatible with the temperatures of equilibration of chlorites from Rosebery with full occupancy of the octahedral site.

7.7 DISCUSSION

The chlorite solid-solution model has the potential to yield useful information on low grade metamorphic or hydrothermal events. In the case of the Rosebery sulphide orebody, equilibrium appears to have been established between pyrite, arsenopyrite and chlorite at temperatures of about 250°C. This temperature of equilibration is fairly uniform among chlorites from the D, F and G lenses and this factor, together with the prevalence of annealed textures in the chlorite, suggests that the chlorite compositions have been reset during metamorphism and therefore do not provide information on conditions of ore formation (cf. Green et al., 1981). Further evidence for local equilibrium being established between chlorite, sulphides and sulphates is provided by the very much higher values of $a_{\text{O}_2}$ indicated for the chlorite in the barite orebody.

There is considerable doubt as to whether the temperatures recorded by the chlorites reflect peak metamorphic conditions. The localized occurrence of spessartine and biotite, the sulphur isotope fractionation between pyrite and pyrrhotite, the compositions of arsenopyrite and the arsenopyrite-fahlore relationship all indicate that temperatures in excess of 350°C and possibly up to 400°C were achieved in the Devonian. It seems unlikely, however, that a temperature of 450°C, the maximum temperature indicated by the arsenopyrite geothermometer, was reached.

It is suggested that chlorite compositions continued to change during retrograde metamorphism and maintained equilibrium with the sulphide mineral assemblage down to temperatures of 250°C or less.
However the fact that the iron-rich silicate assemblages at Rosebery co-exist with a similar sulphide suite to that at Woodlawn where magnesium-rich silicates occur (McLeod, 1978) suggests that residual information regarding the conditions of ore formation might be obtained from the chlorite, but the means are not yet available to quantify this.
8.1 INTRODUCTION

In the study of unmetamorphosed ore deposits it is possible to employ fluid inclusion, mineralogic and isotopic data to derive a precise estimation of the temperature, salinity and isotopic composition of the ore fluid and from these to proceed to a sophisticated discussion of the physical environment of mineralization, sources of metals and fluids and mechanisms of ore deposition. The papers of Barton et al. (1977) and Casadevall & Ohmoto (1977) are two of the many outstanding examples of this approach.

In metamorphosed massive sulphide deposits many avenues of this type of approach are closed. For example the lack of primary fluid inclusions prevents accurate estimation of original fluid composition and salinity and the history of temperature changes. Also use of mineralogical criteria is fraught with difficulty due to changes in mineral composition and assemblages during metamorphism. A number of causes of these problems are as follows:

1. Formation of mineral assemblages initially in disequilibrium due to the steep thermal and chemical gradients at the site of ore deposition. A good example is the coexistence of pyrrhotite and anhydrite in the sulphide chimneys in the hydrothermal vents of the East Pacific Rise 21°N latitude (Styrt et al., 1981).

2. Preservation of disequilibrium assemblages during diagenesis and prograde metamorphism. An example of the former is the complex multistage diagenetic replacement relationship between fine-grained exhalative sulphides and later coarse-grained sulphides in the Kuroko ores of north-eastern Honshu (Eldridge & Ohmoto, 1980). An example of the latter is the preservation of hematite in massive metasomatic pyrrhotite at Rosebery (specimen 76-745). In this case, this is confirmatory evidence of the later formation of pyrrhotite.
3. Partial re-equilibration during retrograde metamorphism. An example is the contrast between the lower temperatures suggested by the compositions of chlorite at Rosebery and the occurrence of residual biotite and spessartine of an earlier higher temperature phase of the metamorphism or metasomatism.

These features can yield useful information on the thermal and chemical history of the orebody, but if unrecognized or misinterpreted they may lead to false interpretations on the environment of ore formation. For example, Green et al. (1981) attempted to employ the composition of chlorite towards the elucidation of the chemical conditions of ore formation at Rosebery. However, as discussed in the previous chapter, the chlorite probably only retains information of retrograde metamorphic conditions.

The only constraints that can be applied relate to the pre-metamorphic mineralogy of the deposit, sulphur isotopes, metal zoning and the form and geology of the deposit. Hence, of necessity, much of the discussion in this chapter is speculative and treads the time-worn path of argument by analogy with other ore deposits and active geothermal systems.

8.2 CHEMICAL ENVIRONMENT OF ORE FORMATION

The single most useful constraint on the redox condition of the discharging Rosebery ore solutions is the widespread occurrence of pre-metamorphic arsenopyrite+pyrite in the sulphide orebody. This effectively restricts the $aS_2$ of the ore-forming fluid within a narrow range (Fig. 7.1). A range of total sulphur concentration in the ore fluid of between $10^{-2}$ and $10^{-3}$ m is assumed. This is in accord with that of most ore deposits forming at temperatures between 200 and 350°C (e.g. Barnes, 1979, Table 8.2) and with the concentration of sulphur in the fluids currently precipitating base metal sulphides on the seafloor on the East Pacific Rise at 21°N latitude ($m_{Ls} \approx m_{H_2S} = 6.5 \times 10^{-3}$; Edmond et al., 1982).

A further assumption of the control of $aS_2$ by major sulphur species in solution allows the estimation of $m_{Ls}$ by the following equilibria:
\[ 2\text{H}_2\text{S}(\text{aq}) + \text{O}_2(g) = 2\text{H}_2\text{O}(l) + \text{S}_2(g) \]  

(8.1)

for which

\[ \log K_{17} = 2 \log a_{\text{H}_2\text{O}} + \log a_{\text{S}_2} - 2 \log a_{\text{H}_2\text{S}} - \log a_{\text{O}_2} \]  

(8.2)

\[ \text{H}_2\text{S}(\text{aq}) + 2\text{O}_2(g) = 2\text{H}^+ + \text{SO}_4^{2-} \]  

(8.3)

for which

\[ \log K_{11} = 2 \log a_{\text{H}^+} + \log a_{\text{SO}_4^{2-}} - \log a_{\text{H}_2\text{S}} - 2 \log a_{\text{O}_2} \]  

(8.4)

If values for the concentrations of alkali and alkaline earth metals in solution are known, the total sulphur content of the fluid 

\( mL_S = m\text{H}_2\text{S} + m\text{HS}^- + m\text{S}^{2-} + m\text{NaSO}_4^- + m\text{KSO}_4^- + m\text{MgSO}_4^0 + m\text{CaSO}_4^0 \)

determined using the expressions of Ripley & Ohmoto (1977) for the log K values for reactions 8.1 and 8.3 and the dissociation constants for the metal sulphate ion pairs and the expressions for activity coefficients of Helgeson (1969, equation 43). The thermodynamic data used are listed in Appendix 4. The use of \( \log (\text{ESO}_4/\text{EH}_2\text{S}) \) diagrams is only valid where equilibrium exists between reduced and oxidized sulphur species, a condition clearly unlikely to prevail where sulphide precipitation is occurring in an exhalative situation. However these diagrams should provide useful constraints on the most reduced, pre-discharge nature of the fluids.

Rather than assuming values for cation concentrations and ratios in solution, a 3.5 m NaCl solution has been used to model the hydrothermal solution. The choice of the salinity was governed by the nature of the orebody (see later). The mean ion activity coefficient expressions of Silvester and Pitzer (1976) were used and the assumption that 

\[ \gamma \pm \text{NaCl} = \gamma_{\text{Na}^+} \neq \gamma_{\text{Cl}^-} \]  

(8.5)

was also used. Ignoring other cations probably introduces little additional uncertainty into the calculations because:
(a) The presence of K-mica, sporadic occurrence of albite and absence of K-feldspar in the footwall schist suggests that molal K/Na ratios in the fluid were low, ranging from maximum values of about 0.06 at 150°C to 0.13 at 350°C (White, 1968).

(b) The strong depletion of Ca in the footwall rocks suggests that the Ca content of the fluid was relatively low. The occurrence of carbonate minerals in the footwall would permit estimation of Ca molality if the CO₂ content of the fluid could be estimated independently.

(c) The Mg content of hydrothermal fluids is typically low. For example, the Kuroko ore forming fluid contains 0.01 ± 0.05 m Mg (Pisutha-Arkond and Ohmoto, 1980) and the East Pacific Rise 21°N hydrothermal fluid contains negligible Mg (Von Damm and Edmond, 1982).

The mean ion activity coefficient takes into account both ion-solvent interaction and ion pairing whereas specification of the molality of free cations as was done by Ripley and Ohmoto (1977), Walshe and Solomon (1981) and Green et al. (1981) only takes the former effect into account and ignores ion pairing between chloride and the major cations. Therefore the present approach can consider an isocompositional fluid over a range of temperatures (because the stability constant of the NaCl⁰ ion pair increases sharply with increasing temperature) and thus permits a more realistic estimation of such factors as metal contents of the fluid.

Figure 8.1a is a log (ΣSO₄/ΣH₂S) versus T diagram showing the salient features of the mineralogy of the deposit. The presence of arsenopyrite + pyrite restricts the solution composition to one in which H₂S is the dominant sulphur species at a pH within one unit of neutrality and temperatures less than 360°C. The fact that arsenopyrite is widespread throughout the sulphide orebody therefore suggests that the δ³⁴S values of sulphides in this orebody closely reflect the bulk δ³⁴S value of the ore-forming fluid. Slight fluctuations from these
Fig. 8.1  Log $\frac{ES}{\Sigma H_2S}$ diagram displaying the possible fields of formation of the massive sulphide and barite ore bodies. Cross-hatched pattern: sulphide orebody, stipple: barite orebody. Diagram conditions: $m_{NaCl} = 0.002$, $m_{NaCl} = 3.5$, pH = 1 unit acid.

(a) Light solid lines: contours of mole % FeS in sphalerite. Dashed lines: values of $\delta^{34}S_{H_2S}$ for a $\delta^{34}S_{LS}$ value of 30‰. The curves A, B, C, represent hydrothermal solution-seawater mixing paths (see text).

(b) Light solid lines: iron solubility in parts per million. Dashed lines: zinc solubility in parts per million.
conditions can account for minor variations in the mineralogy of the deposit. For example, decrease in m\(\text{FeS}\) to \(10^{-3}\), as probably would occur during sulphide deposition, allows for the formation of magnetite under conditions shown by the wire mesh pattern in Fig. 8.1a (see Appendix 5). The presence of magnetite therefore does not indicate conditions of high \(\text{SO}_4/\text{H}_2\text{S}\).

Discharge of a 300°C solution, initially saturated with pyrite and arsenopyrite, is considered in terms of three different mixing paths in Figs. 8.1a and 8.1b. Path A assumes continuous equilibration of the hydrothermal solution and seawater with 0.5 m chloride and 0.027 m \(\text{SO}_4\). Because of the sluggish kinetics of \(\text{SO}_4/\text{H}_2\text{S}\) equilibration (Ohmoto and Lasaga, 1982) this condition will not adequately describe redox reactions in the fluid but provides an indication of the approach to saturation with respect to sulphate minerals, provided allowance is made for the increase in \(m \text{SO}_4^{2-}\) during mixing. Either path B (seawater mixing occurring at constant \(a\text{S}_2\)) or path C (the seawater sulphate added during mixing acting as an inert component) probably provide a more realistic description of the redox path of the solution during mixing.

The minimum FeS content of sphalerite in equilibrium with arsenopyrite should be about 8 to 10 mole % between 250 and 350°C. In fact, with the exception of a few analyses by McLeod (1978), Rosebery sphalerites have lower FeS contents. This may be due to adjustment of sphalerite compositions during post-peak metamorphic annealing. Alternatively, these minerals may have been deposited in disequilibrium and the composition of sphalerite are the remaining evidence of that disequilibrium. The latter interpretation is supported by the inhomogeneity of sphalerite compositions on the polished section scale (Table 4.4) and the progressive decrease in the FeS content of sphalerite from the D and G lenses to the F lens. Textural evidence of attempts by the assemblage to reach an equilibrium state is provided by the adjacent embayed pyrite.
crystals in sphalerite, and arsenopyrite partly replaced by tennantite-
tetrahedrite (Fig. 4.10).

The discrepancy between the presence of arsenopyrite and the FeS contents of sphalerite could be accounted for by the discharge of solutions initially saturated with pyrite and arsenopyrite but undersaturated with respect to sphalerite. A solution following path B or C (Fig. 8.1a) would continue to precipitate pyrite as it passed out of the arsenopyrite field and reached saturation with sphalerite. The iron contents of sphalerite might then yield information on the minimum degree of undersaturation of sphalerite in the pre-discharge fluid. Such an explanation could also account for the common interspersion of pyrite- and sphalerite-rich laminae on the millimetre scale in the sulphide orebody.

Fig. 8.1b shows contours of Fe and Zn solubility. Cooling along path A would not result in the precipitation of significant quantities of sphalerite. However cooling of a solution initially saturated with pyrite and arsenopyrite along path B or C and first achieving saturation with respect to sphalerite between the 1 and 5 mole % FeS contours could precipitate pyrite and sphalerite in roughly the proportions observed in the orebody. A similar mechanism could be involved in formation of the Zn-Pb-rich ore at the southern end of the F lens, but because the solubility of pyrite is more strongly temperature dependent than that of sphalerite in the temperature range 200-280°C, a slightly lower discharge temperature can explain the higher Zn/Fe ratio of this ore.

The presence of rare secondary albite in the ore lenses and in the footwall schist provides some evidence that the ore solutions may have been boiling at some stage. The vein assemblage albite-quartz-carbonate-barite-chalcopryte-pyrite from specimen 105129 (Fig. 5.3) cuts altered tuff containing the mineral assemblage sericitie-quartz-pyrite. Iso-
enthalpic boiling of a solution under conditions in which the vapour and liquid phases maintain equilibrium favours saturation of pyrite, anhydrite, calcite, quartz (Drummond, 1981), and chalcopyrite (Bush, 1980a,b) under initial temperature conditions of 250 to 350°C, initial pH of 5, mEC of 0.5, mES of 10^{-2} (or probably less), and a wide range of redox conditions between the SO_4^{2-}/H_2S and CH_4/CO_2 buffers. Occurrence of barite in the vein would not necessarily require oxidizing conditions, provided the barium concentration was sufficiently high initially. The amount of boiling required to increase the pH to the albite stability field would be less than 10% under these conditions and a temperature decrease of not more than 20°C would be involved (Drummond, 1981). The relative scarcity of sulphides and albite in the footwall schist indicates that boiling was localized and/or short-lived and may have only involved some of the higher temperature copper-bearing solutions which were close to saturation with pyrite. The minimum water depth required to prevent a 3.0 m NaCl solution from boiling at 300°C is about 765 m (Haas, 1977). This figure becomes dramatically higher as other volatiles are added to the system. For example, the addition of 0.5 m CO_2 raises the depth to around 2200 m (Drummond, 1981).

A remaining problem is that the copper contents in the fluid predicted by the thermodynamic data of Walshe and Solomon (1981) are less than 0.1 ppm throughout Fig. 8.1b. Further experimental studies on the solubility of copper-iron sulphides under hydrothermal conditions are apparently required.

Incorporation of the stability constant for the BaCl^+ ion pair (Drummond, 1981) gives a more realistic picture of the temperature dependence of barite solubility than that of previous diagrams (e.g. Green et al., 1981) which only considered Ba concentration in terms of the Ba^{2+} ion. A predischarge condition of the fluids responsible for the formation of the barite orebody within the stippled regions of
Figs. 8.1a and 8.1b can explain the high Zn/Fe ratios of this ore and the relatively low FeS contents of the sphalerite. Also the wide range of $\delta^{34}\text{S}$ values of barite, most well in excess of the value inferred for the contemporary seawater sulphate, are explicable provided barite was close to saturation at the point of discharge (about $4 \times 10^{-3}$ $\text{m} \Sigma\text{Ba}$), Fig. 8.1a. Such a model suggests that the bulk $\delta^{34}\text{S}$ value of this hydrothermal solution was close to 30%, a value markedly higher than those suggested for the sulphide orebody. The total sulphur content of the solution is limited by the absence of bornite in the barite orebody. For example, under the redox conditions favoured for deposition of this ore, a solution with $10^{-2}$ $\text{m} \Sigma\text{S}$, pH one unit acid and a temperature less than about 260°C would precipitate bornite rather than chalcopyrite (Appendix 5). For a solution with a total sulphur content of 0.002 $\text{m}$ chalcopyrite would be stable down to 230°C or lower.
The initial $\delta^{34}\text{S}_{\text{LS}}$ value for the Fe-rich ore was about 8.5%, considerably less than the value for totally reduced Cambrian seawater sulphate. Incorporation of a component of sulphur derived from the leaching of igneous rocks by hydrothermal solution is therefore indicated (Green, 1979) as had earlier been suggested for other massive sulphide deposits by Solomon (1976) and Ripley & Ohmoto (1977) and as has been demonstrated in the East Pacific Rise 21°N hydrothermal solutions (Styrt et al., 1981; Von Damm and Edmond, 1981). As the contribution of rock sulphur declined, presumably because of its progressive extraction from the rocks, the relative amount of seawater-derived sulphur would increase and this mechanism satisfactorily explains the increase in $\delta^{34}\text{S}$ values with time.

8.3 DEPOSITION ON THE SEAFLOOR

A reconstruction of the Rosebery orebody prior to deposition of the barite orebody (after Green et al., 1981) is shown in Fig. 8.2. Although interpretation of pre-folding thickness of various parts of the orebody is made difficult by tectonic thickening in fold hinges, it appears that on 15 level the ore is thickest in the southern part of D lens, E lens and G lens, and thins to the north and south (see also Brathwaite, 1974, fig. 4). In the distal sections of the orebody the massive sulphide tends to splay and interfingers with massive carbonate or the host rock (Brathwaite, 1974). The orebody appears to occupy what were topographic depressions but the fine banding in the ore and the lack of fragmental features, graded bedding, channelling and cross lamination as seen in some Canadian (MacGeehan et al., 1981) and Japanese deposits (Ito et al., 1974) indicates that this feature is not a result of processes of post-depositional downslope movement of ore.

Two processes have been invoked to explain this distribution. Solomon & Walshe (1979) suggested that because of a shallow depth of seawater (Brathwaite, 1974; Green, 1975b) a discharging buoyant plume of hydrothermal fluid would stagnate at the water/air interface and spread...
Fig. 8.2 Reconstruction of the Rosebery sulphide orebody prior to formation of the barite lode. The pipe-like feature in the southern section of the orebody is loosely defined by the zone of high Co content in footwall schist pyrite, but in reality zones of sulphide dissemination are subconformable with the massive orebody (see text). The vent-like feature is based on recent mine drilling which intersected a zone of Cu-rich ore in the northern section of the mine (M.J. McDonald in Solomon et al., 1981) (from Green et al., 1981).
laterally, raining fine-grained particulate sulphides to form the thin sheet-like orebody. Pyrite and chalcopyrite were assumed to have quench precipitated to form a mound over the vent, whereas galena and sphalerite were precipitated at lower temperatures when the plume had attained a sufficiently high vertical velocity to transport particulate sulphides away from the vent area. The model thus predicted contemporaneous formation of proximal pyrite-chalcopyrite and distal sphalerite-galena.

Recognition that the massive pyroclastics at Rosebery were emplaced by cold subaqueous mass flows, that limited boiling had occurred in the footwall rocks, and the fact that the sulphur isotope distribution indicated that the orebody was laterally diachronous, forced modification of the model. Further, sulphides produced by a rain of sulphide particles from a plume stagnated at the seawater-air interface, would produce a massive, rather than laminated, deposit (M. Solomon, pers. comm.).

Solomon (in Green et al., 1981) suggested that the pattern of ore distribution could be accounted for by invoking the discharge of solutions of higher salinity (around 3.5 m NaCl). This type of solution was previously not favoured (Solomon & Walshe, 1979) because of the lack of evidence for evaporites in the Rosebery area. The presence of chert of possible prior evaporite origin in detritus in the Rosebery Group and the low palaeolatitude make it possible that circulating hydrothermal fluids encountered evaporites (Section 3.7). Indeed, the palaeogeographic model for the evolution of the Dundas Trough (Section 3.8) suggests that the Mount Read Volcanics in the Rosebery area might be underlain by evaporite-bearing sequences.

The density of 3.5 and 5.0 m NaCl solutions (from Haas, 1976) is shown in Fig. 8.3. Curves of mixing of these solutions with seawater calculated from equation 6.2 are also shown. The density of the mixed solutions was obtained by interpolation of values listed in Haas (1976).
Fig. 8.3 Curves showing density of 3.5 and 5 m NaCl solutions as a function of temperature and the density of various hydrothermal fluid-seawater mixtures assuming the temperature of the entrained seawater in 0°C and the density is 1.028 gm cm⁻³. Different assumptions regarding the temperature of the ambient seawater affects the condition of the point of neutral buoyancy of the mixed solution (see Green et al., 1981).
As shown in Fig. 8.3, a solution discharged into seawater with a temperature of 300°C and a salinity of 3.5 m or less will never achieve neutral buoyancy, whereas a 3.5 m NaCl solution discharged at 250°C will achieve negative buoyancy at a temperature of about 80°C and a 5 m NaCl solution will reach a point of neutral buoyancy at a temperature of about 130°C. The latter two solutions are examples of the Type II solutions of Sato (1972), which, after initial behaviour as buoyant plumes, become denser than seawater, sink and flow laterally downslope. This situation is somewhat complicated by the fact that non-linear mixing phenomena may permit a hydrothermal fluid with a salinity sufficiently different from that of seawater to split into a more saline, dense phase and a less saline buoyant phase (e.g. Turner and Gustafson, 1978; Russell et al., 1981). This process could lead to the onset of reversing buoyancy behaviour at higher temperatures and lower salinities than indicated by Fig. 8.4. Sato (1976) suggested that Rosebery might be a product of a Type II solution, but he favoured a process in which the sinking hydrothermal solution deposited particulate sulphides in the immediate vicinity of the hydrothermal vent whereas Solomon (in Green et al., 1981) allowed the possibility of transport of particulate material in the bottom-hugging dense solution over considerable distances. Solomon's model permits a multistage history of the behaviour of the ore fluid. He proposed that the initial formation of pyrite-chalcopyrite ore was from a buoyant plume with pyrite and chalcopyrite precipitating before the plume had attained sufficient upward velocity to carry particulate material. These minerals formed a mound around the vent, overlain, and surrounded by, fine-grained sphalerite, pyrite and galena which settled from the margins of the plume (Fig. 8.4a). This part of the model is essentially identical to that of Solomon & Walshe (1979). Subsequently exhaled, slightly cooler solutions (3.5 m NaCl, 250°C), which were incapable of transporting sufficient quantities of copper to precipitate significant amounts of chalcopyrite, behaved as reversing buoyancy plumes (Fig. 8.4b). The resulting currents denser than seawater were supposed to deposit particulate sphalerite, galena and pyrite in a moat formed between the early pyrite-chalcopyrite mound and the relatively elevated margins of the basin.
Fig. 8.4 Sketch to illustrate possible modes of ore deposition at Rosebery from buoyant and reversing buoyancy plumes, respectively, representing the situation during deposition of (a) the Fe- and Cu-rich phases, and (b) the Pb-Zn-rich phases (from Green et al., 1981).
(Fig. 8.4b). The reversing buoyancy plume could interrupt the upward flow producing pulsatory behaviour. The fine-scale banding in much of the Rosebery ore could be produced by the pulses of fluid combined with precipitation of different minerals at different stages of the mixing process, as discussed in the previous section.

Solomon recognized that the model faced the difficulty of accounting for the fact that continued passage of solutions through a hydrothermal vent, defined by the pyrite with higher cobalt contents, appeared to be inconsistent with the fact that pre-deformational cross-cutting veins were rare in the orebody. He suggested that lateral spreading of solutions beneath the mound and venting at its margins might resolve the apparent discrepancy.

The fine banding and paucity of brecciation in the Rosebery ore suggests a relatively quiescent mode of formation from a low-power discharge system as defined by Henley & Thornley (1979). The footwall rocks at Rosebery are an ignimbrite sequence, composed initially of inter-stratified impermeable welded and permeable non-welded zones. This would result in a considerable component of horizontal flow along the permeable horizons, particularly after the solutions commenced to boil, a situation similar to that currently operating in the El Tatio geothermal field, Chile (Ellis & Mahon, 1977). Also the formation of an impermeable cap rock, the quartz schist, by precipitation of silica forming a near surface, subhorizontal seal would aid subhorizontal sub-surface flow. These effects may have been more important than a massive sulphide mound in diverting solution flow and could also explain the concordant, disseminated pyrite-chalcopyrite mineralization and lack of major quartz-sulphide vein mineralization in the footwall schist. The relative paucity of footwall mineralization might suggest that either the solutions were generally undersaturated at the onset of boiling or that boiling was a relatively unimportant process. Hydraulic fracturing appears to have played only a minor role, the albite-chalcopyrite-bearing veinlet in specimen 105129
being a possible example of deposition of sulphides from a boiling hydrothermal solution in a small hydraulic fracture. If the zone of pyrites with Co/Ni ratios greater than 10 (Fig. 5.8) is considered to represent a zone of relatively high temperature outflow it is conceivable that the locus of fluid venting is controlled by a fracture system plunging southward (in terms of present orebody orientation) roughly parallel to the margins of the orebody. This zone would include the zone of sulphides with low $\delta^{34}\text{S}$ values at depth in the F lens.

It is apparent that the pattern of subsurface flow of hydrothermal solutions might be of considerable importance in controlling the distribution of mineralization types in the massive ore. Shifts in the site of solution outflow would help explain other features of the orebody such as the larger scale (up to 3 m) layering of banded pyrite- and sphalerite-rich ore described by Brathwaite (1974), as well as the broader sulphur isotope and metal zonation and the fluctuations in the $\delta^{34}\text{S}$ values of sulphides in the vertical sections sampled through the orebody. Such a process could act in concert with the behaviour of hydrothermal solutions following discharge in causing the complex ore distribution at Rosebery.

8.4 GENERATION OF THE ORE SOLUTION

The sulphur isotope data and mineralogy have been interpreted as indicating formation of the sulphide orebody by a hydrothermal solution with a low $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$ ratio with the sulphur having a mixed seawater volcanic parentage. As reduction of sulphate by volcanic rocks requires temperatures of 250°C or higher (Mottl et al., 1979; Ohmoto & Rye, 1979) convective circulation of seawater through the pre-ore rocks is required, and a subvolcanic pluton, such as those known from the Mount Read Volcanics, seems a likely mechanism (Solomon, 1976).

Polya (1981) has described the mineralogy of the Murchison Granite, an elongate pluton some 8 km east of Rosebery (Fig. 2.2), and of the
overlying three kilometres of volcanic rocks. The zonation of hydrothermal assemblages upward from the granite is:

2. Epidote + chlorite + calcite + magnetite ± biotite ± allanite.
3. Chlorite + sericite ± albite ± hematite ± magnetite.

There is a parallel zonation of $\delta^{34}$S values of sulphides from about +9‰ in the granite to +17‰ in sulphides in the Farrell Slate. Although the latter sulphides occur in Devonian fissure veins a Cambrian origin for the sulphur has previously been suggested (Solomon et al., 1969). The mineralogic and sulphur isotope distributions suggest a higher rock/water ratio and a greater contribution of igneous sulphur in the pluton (Polya, 1981). This situation might be relevant to that at Rosebery where the earlier-formed sulphides are relatively enriched in pyrite and chalcopyrite and have comparable $\delta^{34}$S values to those within, and adjacent to, the Murchison Granite. The later Pb-Zn-rich mineralization with its higher $\delta^{34}$S values reflects a greater contribution from seawater sulphur, lower temperatures and, possibly, a source region higher in the volcanic pile. The barite orebody was formed from more oxidized solutions, in which the sulphur was possibly entirely of seawater origin. Again, lower temperatures, probably combined with a depletion of disseminated volcanic sulphides in the source region of the fluid appear responsible (Green, 1979). The Pb isotope studies of Gulson & Porritt (1982) and Whitford et al. (1983) do not suggest a major component of Pb from other than a volcanic source. The Cambrian massive sulphides (Rosebery, Hercules, Que River, Mount Lyell) display a tight clustering of lead isotope ratios ($^{207}$Pb/$^{204}$Pb ~ 15.6; $^{206}$Pb/$^{204}$Pb ~ 18.3). Moreover both the host volcanics and ore from Que River plot on a common isochron of 540 ± 30 Ma, an age which is consistent with the geological evidence.
If, as suggested by Solomon (1981), the relatively reduced solutions that formed the Rosebery deposit derived their characteristics by interaction with a substantial thickness of sedimentary rocks underlying the deposit, then these rocks must have had similar lead isotope ratios to the Mount Read Volcanics. Gee's (1970) geochemical study of the black slate at Rosebery and other slates in the Mount Read Volcanics did indeed suggest a volcanic source for these rocks, but the slates he analysed are of post-ore age, and the exposed thickness of the pre-ore sequence at Rosebery is insufficient to provide confirmatory or negating evidence for Solomon's proposal. However, the interaction of the ore-forming solution with evaporites is suggested as a mechanism for generating the high salinities required by the reversing buoyancy plume model, it being difficult to generate the required salinities by any other means.

Recent experimental investigations of the interactions of seawater with volcanic rocks (e.g. Dickson, 1977; Mottl et al., 1979) and geochemical studies of submarine hot springs (McDuff & Edmond, 1982; Edmond et al., 1982) have provided an insight into the possible processes involved in the generation of an ore-forming fluid from seawater. The sulphate content of seawater is reduced by heating due to the precipitation of anhydrite and magnesium hydroxy-sulphate (Bischoff & Seyfried, 1978; McDuff & Edmond, 1982). The precipitation of the latter phase and extraction of Mg(OH)$_2$ to clay minerals (Dickson, 1977) results in a decrease in the pH of the solution. At temperatures above 250$^\circ$C the residual sulphate is reduced by the oxidation of ferrous to ferric iron in the rocks (Ohmoto & Rye, 1979; Mottl et al., 1979) and at this stage sulphur may be leached from the country rocks. An increase of pH due to boiling of the ascending solution near the rock-water interface may have been responsible for deposition of some or all of the chalcopyrite in the footwall rocks and the minor occurrences of albite.
8.5 FEATURES OF ROSEBERY-TYPE DEPOSITS

Solomon (1981) considered that Rosebery was the type example of a class of massive sulphide deposits which includes Woodlawn and Captains Flat, New South Wales and the deposits of the Bathurst area, New Brunswick.

All of these deposits are associated with footwall sequences dominated by felsic tuffs and/or sedimentary rocks in contrast to the massive lavas and phreatic breccias which occur, for example, near many of the Kuroko deposits of Japan (e.g. Ishihara et al., 1974) and at Buchans, Newfoundland (Thurlow et al., 1975; Thurlow and Swanson, 1981).

In contrast to the well defined alteration pipes containing stringer mineralization that typify the Canadian Archaean deposits and are common in the Hokuroku district, Japan, ore bodies of the Rosebery type generally display discordant sericitic and/or chloritic alteration zones, with sub-concordant sections rich in disseminated sulphides. The alteration associated with 30 deposits of the Bathurst district has recently been reviewed by Jambor (1979). Jambor concluded that although stringer-type footwall mineralization is rare in the district, the majority of massive ore deposits overlie their hydrothermal conduits directly. Where footwall disseminated mineralization exists, it has a higher Cu/Pb+Zn ratio than overlying massive ore, which also displays an upward decrease in this ratio. Similarly at Woodlawn, pyrite and chalcopyrite occur in sub-concordant zones of chlorite schist stratigraphically below the orebody, although this could be due, in part, to the effects of deformation or an originally more discordant feature (Ayres, 1979; Petersen and Lambert, 1979). The nature of footwall alteration at the abandoned Captains Flat orebody is poorly known. Pyrite occurs in sericitized rhyolitic crystal tuff up to 100 m below the orebody. Much of the pyrite
occurs in "tiny irregular quartz veins", and local concentrations of chalcopyrite occur in a stratiform massive pyrite lens stratigraphically below the main massive sulphide orebody (Davis, 1976).

Massive ores of the class are typically finely laminated and commonly have a thin sheet-like aspect. This is generally believed to be due to ore accumulation in topographic depressions on the sea floor (e.g. Petersen and Lambert, 1979; Davis, 1976; Jambor, 1979) but, except in the case of a few of the New Brunswick deposits (Jambor, op. cit.), there is no evidence that resedimentation of previously formed sulphides was involved.

All examples of the class contain arsenopyrite ± stannite ± pyrrhotite (Ayres, 1979; Davies, 1976; Hall, 1967; Brathwaite, 1974) reflecting deposition from relatively reduced solutions in which \( \text{H}_2\text{S} \) was the dominant sulphur species. Further, sulphur isotope studies of a number of these orebodies show that the mixed volcanic-seawater source deduced for the bulk of the Rosebery orebody may also be a common factor. \( \delta^{34}\text{S} \) values of sulphides range from 6.0 to 10.2\% at Captains Flat (mixed sulphides, Stanton and Rafter, 1966) from 6.7 to 9.2\% at Woodlawn (galena excluded, Ayres et al., 1979), from 11.1 to 16.3\% at the Heath Steele Bl orebody, Bathurst (excluding galena, Lusk and Crockett, 1969) and four samples of pyrite from Hercules ranged from 11.2 to 13.2\% (Solomon et al., 1969). Another feature of these ores, is that although there is generally an equilibrium order of fractionation between sulphide minerals with \( \delta^{34}\text{S} \) values increasing in the order galena < sphalerite < pyrite, sulphur isotope temperatures show a wide scatter presumably reflecting a failure to achieve complete isotopic equilibrium during ore deposition (Chapter 6, this thesis). In contrast sulphur isotope fractionation temperatures from the Shakanai No.1 deposit, Hokuroku district, Japan (Kajiwara, 1971) and from the footwall stockwork zone of the Lucky Strike orebody,
Buchans (Kowalik et al., 1981) probably reflect temperatures of deposition or of recrystallization of sulphides. Eldridge and Ohmoto (1980) have shown that much of the Kuroko massive ore consists of coarse grained euhedral sphalerite, galena and pyrite formed by sub-surface recrystallization of fine grained "primitive" ore. This coarser material is probably similar to that analysed by Kajiwara and this mechanism, proposed by Solomon and Walshe (1979), explains the reasonable isotopic temperatures of the Kuroko ores. In Rosebery-type ores, if the fine banding reflects deposition from a plume with reversing buoyancy, sphalerite and galena precipitated after discharge, either in a reversing plume and subsequently settling in a topographic depression or crystallizing in a trapped brine pool, are removed from the immediate vent area. These minerals would thus have less opportunity for subsequent recrystallization and isotopic exchange, as argued in a slightly different fashion by Solomon and Walshe (op. cit.).

Solomon (1981) has pointed out that many of the features of Rosebery-type deposits are analogous to those of sediment-hosted massive sulphide ores, including the fine banding, high tonnages, high Pb+Zn/Cu ratios, poorly developed footwall alteration zones and formation from relatively reduced solutions as inferred from the presence of arsenopyrite. He suggested that these features might be due to the occurrence of a significant proportion of sediments in the footwall sequences. This is indeed supported by the geology of the Bathurst district, Woodlawn and Captains Flat, but because of limited exposure of pre-ore rocks at Rosebery and Hercules remains an open question in the latter cases. In this context, it is of interest to note that Fehn (1979) suggested that slight variations in the lead isotope ratios of the black ore deposits of the Hokuroku district, Japan, were probably a reflection of a variable contribution to the
ore leads from Mesozoic metasedimentary rocks underlying the Miocene volcanic units. These metamorphic rocks, which include a high proportion of carbonaceous phyllites, occur only a few hundred metres below the Kosaka mine which displays none of the features listed above, so it is clear that carbonaceous rocks alone are not a sufficient factor to produce the reduced Rosebery-type ore solutions.

Similarly, the extent to which reversing plume behaviour as opposed to the nature of the footwall rocks controlled the distribution patterns of the massive ore is debatable. For example, the metal zoning study of Lusk (1969) of the Heath Steele B-1 orebody, Bathurst showed a copper-rich centre of mineralization, probably representing a hydrothermal vent (Solomon and Walshe, 1979), flanked by lead-zinc-rich zones. In this orebody there is no discernable lateral zonation of sulphur isotope values of the ore minerals (Lusk and Crockett, 1969). Such a pattern is consistent with a single static hydrothermal vent area existing throughout the episode of ore deposition and the distribution of the lead-zinc-rich zones being controlled by the palaeotopography and the behaviour of reversing plumes. The more complicated situation at Rosebery with lateral sulphur isotope zonation in the sulphide orebody, as argued earlier, suggests a shift in the locus of hydrothermal discharge during ore deposition. The apparent association of Rosebery-type deposits with footwall sequences in which horizontal variations in permeability were likely factors controlling the pattern of sub-surface solution flow, as suggested by the presence of ignimbrite in the footwall at Rosebery and well-bedded sedimentary-volcanic sequences in the other Rosebery-type deposits, may promote the "multi-channel", "defocussed", "quiescent" mode of solution discharge envisaged by Jambor (1979) for the deposits of the Bathurst area. In contrast, footwall sequences composed principally of massive, impermeable volcanic rocks might be expected to result in
well developed stockworks formed by hydraulic fracturing due either to fluid boiling (e.g. Henley and Thornley, 1979) or by a crack-seal mechanism (Solomon, pers. comm) and focussed high power solution discharge. The latter mechanism, originally involved to explain quartz veining and development of zones of high permeability in regional metamorphic terrains (Etheridge, 1983*, Etheridge et al., 1983*; Cox and Etheridge, 1983*), involves sealing of the sub-surface rocks in the upper parts of the upwelling zone of a hydrothermal system by mineral precipitation followed by an increase in pressure to values exceeding hydrostatic pressure plus the tensile strength of the rocks (a few tens of bars). Pressure decrease on consequent fracturing, plus the enhanced possibility of seawater mixing, would lead to the deposition of silica and also perhaps carbonates and sulphides. In the above cases, the hydrothermal vents, and also the rhyolite domes associated with a number of Kuroko-type deposits, might be a reflection of regional basement fracture patterns (e.g. Scott, 1978).

It is apparent that Rosebery and Kuroko-type polymetallic volcanic-hosted deposits are end members of a possible continuum. Some features of the two ore types are summarized below (Table 8.1). It should be realized that no unmetamorphosed or undeformed example of a Rosebery-type deposit is known and that features of these deposits are inferred from field evidence. For example, is the lack of associated anhydrite and gypsum associated with these ores merely a reflection of their inability to survive metamorphism? Can the inferred high salinities of the ore forming solutions of Rosebery-type deposits be corroborated by independent evidence? Future research is clearly required to settle these questions.
<table>
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<th>ROSEBERY-TYPE DEPOSITS</th>
<th>KUROKO-TYPE DEPOSITS</th>
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<tr>
<td><strong>Footwall Rocks</strong></td>
<td>Either ignimbrite (Rosebery and Hercules) or more commonly mixed clastic and pyroclastic sequences.</td>
<td>Generally massive lavas, overlain by phreatic breccias. Rhyolite domes common near ore, but are not universally developed (Exception: Undu, Fiji).</td>
</tr>
<tr>
<td><strong>Footwall Alteration and Mineralization</strong></td>
<td>Varies from broad zone of sericitization, discordant on a regional scale (Rosebery) to negligible recognizable alteration (some deposits of Bathurst area). Subconformable zones of chlorite ± sericite alteration with disseminated pyrite (pyrrhotite) ± chalcopyrite may occur.</td>
<td>Generally discordant sericitized zone with stockwork quartz-sulphide mineralization.</td>
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<tr>
<td><strong>Form and Texture of Massive Ore</strong></td>
<td>Commonly single, or a few sheet-like ore-bodies. Laminated sulphides common. Clastic transported ore uncommon.</td>
<td>Commonly clusters of squat unit orebodies. Clastic or compact texture, with replacement textures common on microscopic scale. Where ore is topographically controlled it has accumulated by transport of clastic sulphides by mass flow processes.</td>
</tr>
<tr>
<td><strong>Metal Ratios</strong></td>
<td>Pb + Zn/Cu generally &gt; 7. Exceptions: Wedge, McMaster, Captain (Bathurst district).</td>
<td>Pb+Zn/Cu generally ≤ 3 Exception: Buchans, Pb + Zn/Cu = 17.</td>
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<tr>
<td><strong>Characteristic Minerals</strong></td>
<td>Primary arsenopyrite ± pyrrhotite. Bornite generally absent. No anhydrite or gypsum. Carbonate minerals common in or near ore.</td>
<td>No arsenopyrite or pyrrhotite. Bornite may be present. Anhydrite ± gypsum bodies common near ore (except at Buchans).</td>
</tr>
<tr>
<td><strong>Examples</strong></td>
<td>Rosebery, Hercules, Woodlawn, Captains Flat, deposits of Bathurst district.</td>
<td>Kuroko deposits of Japan, Buchans (Newfoundland), Undu (Fiji).</td>
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The eruption of subaerial ignimbrite in the Rosebery area was followed by cauldron collapse and generation of marine conditions which persisted during deposition of the host rock and the Rosebery orebody, the black shale and the lower several hundred metres of the massive pyroclastics. The Rosebery Group was deposited in a marine forearc basin to the west and was probably coeval in part with the massive pyroclastics. The fault contact between the Rosebery Group and the Primrose Pyroclastics and the faulting within the Rosebery Group is of a syntectonic compressional origin and there is little evidence to suggest that the contact was an early rift margin to the central sequence of the Mount Read Volcanics as suggested by Corbett (1981).

The stratiform, finely banded nature of the Rosebery orebody suggests an exhalative origin as suggested by Brathwaite (1974). The widespread presence of arsenopyrite in the sulphide orebody implies ore deposition from solutions in which H₂S was the dominant sulphur species. This in turn suggests that the δ³⁴S values of the sulphide minerals are approximately equivalent to those of the ore-forming H₂S, and permits their use as stratigraphic markers. The sulphur isotope values suggest that the ore is diachronous and that the δ³⁴S value of the ore fluid changed from about +8.5 to +12‰ during deposition of early Fe- and Cu-rich mineralization to about +15 to +17‰ during formation of later stage Pb-Zn ore. These data indicate derivation of the ore sulphur from a mixture of sulphur derived from igneous rocks and reduced Cambrian seawater sulphur, with the latter source becoming more important with time.

The sulphide orebody has a thin sheet-like aspect and formed largely by lateral accretion. The Fe-Cu-rich zone overlies a zone in the footwall carrying pyrite with anomalous enrichment in Co. An extension of this
zone contains pyrites with lower Co content but high Co/Ni ratios and these zones may loosely define a linear hydrothermal conduit. Temperatures may have been as high as 300°C during coprecipitation of chalcopyrite and pyrite and the presence of vein mineralization in the footwall containing albite and chalcopyrite suggests the ascending ore solution may have been boiling at this stage.

Two processes may have acted in harmony to produce the observed distribution of ore types. The first of these (suggested by Solomon in Green et al., 1981) involves deposition of the early Fe-Cu-rich ore from a buoyant plume followed by formation of the Pb-Zn-rich ore by a plume with reversing buoyancy. The second involves a shift of the locus of fluid venting with time probably due to sealing of the earlier hydrothermal vent. The former model requires solutions of high salinity (>3.5 mNaCl), but derivation of this salinity by solution of evaporites is not inconsistent with the palaeogeography of the Rosebery area in the Cambrian as deduced in this study.

The barite orebody, which overlies and is separated from the massive sulphide orebody by siltstone, may have formed from a solution with a higher oxidation state in which partly reduced seawater sulphate was the predominant source of the sulphur in the ore. The temperature of formation of this ore was probably about 250°C.

Derivation of the ore solution is believed to have been by convective circulation of seawater under the influence of high level Middle Cambrian granitoid plutons.

Metamorphism and local metasomatism of the orebody was most intense after Devonian deformation and peak temperatures of probably at least 350°C were reached. The higher temperature assemblages may be local phenomena related to Late Devonian hydrothermal activity: Information on later retrograde metamorphism is provided by the compositions of chlorite which indicate equilibration at temperatures around 250°C with the $\Delta$CO$_2$ being buffered by the mineral assemblages in adjacent rocks.
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ADDITIONAL REFERENCES


