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THE DISTRIBUTION OF TRACE ELEMENTS DURING DIFFERENTIATION OF THE MT. WELLINGTON DOLERITE SILL

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INTRODUCTION

During a study of the geochemistry of some trace elements in soils developed on dolerite in Tasmania, considerable variation was found in the trace element composition of the parent materials. In order to gain a fuller understanding of the amount and manner of this variation a detailed study was made of the Mt. Wellington sill.

Edwards (1942), in a broad chemical and mineralogical study of dolerites in Tasmania, found variations in composition within the sills and dykes examined. He attributed these changes to fractional crystallization and gravitative differentiation in the cooling magma of the sills, similar to that which is postulated to have occurred in the Skaergaard intrusion of East Greenland and the Palisade sill of New Jersey. The comprehensive study of the distribution of trace elements in the Skaergaard intrusive by Wager and Mitchell (1951) has been a notable contribution to the geochemistry of these elements. Wilson (1950) studied the distribution of some trace elements in the Mt. Wellington sill using a semi-quantitative spectographic method and found some broad trends in composition with depth in the sill which he attributed to differentiation.

As the distribution of trace elements in the dolerite sill was of interest to the general study of differentiation and, in this particular case, a necessary background for a fuller understanding of the variations occurring in the parent material of the soils, it was decided to repeat some of the work previously done and to study additional elements in a greater number of samples.

METHODS

Twenty samples were collected at fairly regular intervals up the Mt. Wellington sill from the Pinnacle Road at sites corresponding to bench marks established by the Geology Department, University of Tasmania.

These samples were broken into small pieces, sub-sampled, and crushed in a steel mortar, which, from experience, has proved to be free of contaminating trace elements. Each sub-sample was finely ground in a mechanical grinder (mullite mortar and pestle) and then mixed with an equal weight of graphite. Co, Zr, Ni, Cu, V, Mo, Ga, and Mn were determined quantitatively using the standard emission spectrographic methods developed by the Spectrographic Group of the Division of Soils. All samples were volatilized in triplicate in a 15 ampere D.C. arc using anode excitation and standards were prepared by the method of successive additions. This method has a precision of ± 10 per cent. It is believed that for some elements this is also a reliable measure of accuracy and this is supported by results obtained by McKenzie, Oertel and Tiller (1958) for the standard rocks Gl and Wl (Fairbairn, *et al*, 1951).

Zn was determined by X-ray fluorescent spectrography while P and K were determined by chemical methods.

Mineral fractions were separated from some samples by centrifuging the very finely ground rock in bromoform. This procedure was repeated to get a satisfactory separation and the iron ore fraction was removed with a bar magnet. Examination under the petrological microscope showed that there was negligible contamination of the separates analysed.

RESULTS AND DISCUSSION

Table 1 shows the height of each sample above the base of the sill, the height above sea level and the trace element content of the 20 samples collected from the Mt. Wellington sill. Table 2 gives the analyses of the separated mineral fractions.

Distribution of Trace Elements

Cobalt

Cobalt increased gradually with depth for the whole sill, from 35-40 p.p.m. in the upper more differentiated part to 50-55 p.p.m. in the lower basic part. Most of the Co occurred in the pyroxene fraction and was highest in the more iron-rich pyroxenes of the upper part of the sill. Although the iron ore fraction contributed little to the total Co of the rock it had a higher Co content than the pyroxenes and again, the highest values are from the upper part of the sill. Co, presumably, mainly replaced Fe^{2+} iron in these minerals. The plagioclase fraction had a uniformly low Co content throughout the sill at about 15 p.p.m. Although the Co content of the pyroxenes and iron ore was higher in the upper part of the sill, it was more than compensated for by the larger amounts of plagioclase there.

TABLE 1.

Analyses of Samples from the Mt. Wellington Sill

Sample No.	Height above Sea Level	Height above Base Feet	Co ppm	Zr ppm	Ni ppm	Cu ppm	V ppm	Mo ppm	Mn ppm	Ga ppm	Zn ppm	P %	K %
D1	4,166	1,209	37	220	14	140	290	9.0	1,250	25	72	.077	1.26
D2	4,124	1,167	40	200	16	140	350	8.5	1,300	25	89	.070	1.12
D3	4,012	1,055	39	210	18	130	320	9.0	1,250	23	....	....	....
D4	3,925	968	34	190	17	140	320	9.1	1,350	30	....	....	....
D5	3,841	884	36	210	16	130	350	8.4	1,300	26	....	....	....
D6	3,784	827	34	180	18	140	270	8.9	1,250	26	....	....	....
D7	3,666	709	40	170	40	120	340	9.4	1,300	25	....	....	....
D8	3,436	479	44	170	37	150	370	9.1	1,400	25	72	.056	.92
D9	3,377	420	41	130	45	110	370	8.7	1,350	25	....	....	....
D10	3,306	349	53	140	83	100	360	8.3	1,400	20	....	....	....
D11	3,263	306	45	110	98	73	320	7.5	1,300	17	....	....	....
D12	3,240	283	47	110	110	79	340	6.8	1,200	16	64	.035	.56
D13	3,152	195	51	120	120	73	390	9.3	1,300	19	....	....	....
D14	3,130	173	53	130	120	79	430	8.2	1,500	22	....	....	....
D15	3,089	132	53	140	98	86	420	8.1	1,450	22	....	....	....
D16	3,066	109	50	130	90	87	380	8.8	1,250	18	....	....	....
D17	3,000	43	44	130	81	89	360	8.4	1,350	18	....	....	....
D18	2,978	21	51	150	93	97	370	9.8	1,350	20	61	.047	.69
D19	2,957½	½	48	150	88	110	380	9.3	1,650	23	....	....	....
D20	2,957	....	53	150	87	100	380	8.2	1,600	21	57	.047	.64

.... = No data—Analyses based on samples ignited at 500° C.

TABLE 2.

Trace Element Content of Mineral Fractions Separated from Dolerite

Sample No.	Height above Base Feet	Mineral Fraction	Co	Zr	Ni	Cu	V	Mo	Mn	Ga
D2	1,167	Feldspars	17	170	7.4	100	150	6.1	730	26
		Pyroxenes	83	180	36	130	580	11	3,900	11
		Iron Ore	130	570	120	170	2,600	47	4,900	39
D8	479	Feldspars	18	140	17	100	140	6.8	590	24
		Pyroxenes	92	180	86	170	580	12	3,700	12
		Iron Ore	96	470	210	250	2,200	41	5,700	34
D12	283	Pyroxenes	66	96	140	49	460	7.3	2,500	7.4
D18	21	Feldspars	15	93	26	65	160	5.3	450	22
		Pyroxenes	57	99	110	75	410	6.9	2,300	9.1
		Iron Ore	82	330	210	240	960	32	2,000	27

All results expressed as p.p.m.

Nickel

This element has been much more influenced by the processes of differentiation than the other elements studied. The Ni content of the sill was fairly constant at about 15 p.p.m. for the upper 400 feet, increased sharply to about 40 p.p.m. for the 400 feet below this and increased further to a maximum of 120 p.p.m. between 200 feet and 300 feet above the base. This maximum corresponded to the zone of magnesian pyroxenes described by Edwards (1942).

Analysis of the composite mineral fractions showed that, in contrast to Co, Ni readily entered the earlier-formed pyroxenes and iron ore minerals. The data suggested that, in the later stages of crystallization in an iron-enriched magma, the Ni was incorporated a little more readily into the iron ore minerals than the pyroxenes. The Ni content of the plagioclase fraction was low in each fraction studied but increased with depth. Although the Ni distribution in the sill was strongly correlated with the Mg profile shown by Edwards (1942), there must also be significant replacement of Fe^{2+} iron at least in the magnetite.

The Co/Ni ratio is known to change considerably in sequences of rock formed by differentiation processes. This ratio varied sixfold in this sill, from a minimum of 0.43 in the magnesian-rich zone, to a maximum of 2.6 in the uppermost part of the sill. The Co/Ni ratios of the chilled margin, taken to indicate the original magma, and the uppermost part of the sill are similar to the ratios quoted by Rankama and Sahama (1949) for gabbros and granites respectively, although the actual Co and Ni values for the top of this sill are much higher than for granites.

Zirconium

Zirconium decreased gradually with depth from a maximum of 220 p.p.m. in the most acidic differentiates to a minimum of 110 p.p.m. at about 300 feet above the base and then increased to 150 p.p.m. in the "chilled" margin. This agreed with the well-known fact that Zr is highest in the acid igneous rocks. Zr was most abundant in the iron ore fractions and the Zr content of all fractions was highest in the upper parts of the sill because of the increased amount of Zr in the residual magma. Although it is known that Zr^{4+} may replace Fe^{2+} and Ca^{2+} in some minerals, it is possible that the "pyroxene" fraction, as separated, contained some zircons.

Copper

The Mt. Wellington sill had a constant Cu content of about 130 p.p.m. in the upper 600 feet. There was a small peak of concentration 500 feet above the base and this was thought to correspond to the slight accumulation of iron which Edwards (1942) had described. The Cu content was lowest 200-300 feet above the base, corresponding to the zone of maximum magnesium and nickel content.

Cu had entered the later pyroxenes, presumably by replacement of Fe^{2+} iron, with much greater ease than the earlier magnesian pyroxenes. The higher Cu content of the later-formed feldspars could be due to the greater ease of replacement of Na in the more sodic plagioclase, combined with a higher concentration of Cu in the residual magma. The Cu contents of the plagioclase and pyroxene fractions were of the same magnitude in each rock sample; copper was, however, more abundant in the iron ore fraction. Although this is further evidence that Cu is readily replacing Fe^{2+} iron, there is the possibility, as has been discussed by Wager and Mitchell (1951) and Cornwall and Rose (1957) that some may have occurred as the sulphide or metal.

Manganese

Although the Mn content of the rock samples did not vary significantly with depth, there was a small increase from the top to 500 feet above the base. Below this the values were usually lower except for a peak at about 150 feet above the base. Analyses of the mineral fractions showed that Mn was most abundant in the iron ore minerals, and to a slightly less extent in the pyroxenes with the highest values in the upper parts of the sill. The Mn content of the plagioclase fraction was much lower but still increased in the upper parts of the sill.

Molybdenum

This element was fairly constant at about 9 p.p.m. throughout the whole sill except for significantly lower values about 300 feet above the base, corresponding again to the zone of early formed magnesian pyroxenes. Whereas molybdenum was fairly constant at about 6 p.p.m. in all the plagioclase fractions, its abundance in the later formed pyroxenes was much greater than in the earlier ones. Mo was highly conctenrated in the iron ore fractions, particularly in the upper parts of the sill.

Vanadium

Although the changes were small there was a definite tendency to increase towards the bottom of the sill. The vanadium contents of the plagioclase and pyroxene fractions were each fairly constant throughout the sill with much higher values for the latter fraction. Vanadium was most abundant in the iron ore fraction in which V^{4+} could readily replace Fe^{3+} and Ti^{4+}.

Gallium

The uniformly high content of about 25 p.p.m. in the upper 800 feet of the sill corresponds closely with the higher plagioclase content found by Joplin and Jaeger (1957). The lowest values found, 16 p.p.m. 300 feet above the base, occur in the zone of magnesium enrichment. Apparently Ga replaces the larger Fe^{3+} ion of magnetite more readily than the smaller Al^{3+} ion of the feldspars for the mineral separations showed that Ga was most concentrated in the iron ore minerals and, to a less extent, in the plagioclase. Because of the large amounts of plagioclase present in the rock, compared to the minor amounts of iron ore, this has determined the Ga distribution. Although the Ga content of the plagioclase fraction was fairly constant in each case, that of the pyroxenes and iron ore minerals increased in the upper part of the sill suggesting that Ga entered these minerals more readily in the later stages of crystallization.

Zinc

The six rock samples analysed for this element showed a gradual decrease in content with depth and suggested that the residual magma had been enriched with respect to Zn.

Phosphorus and Potassium

Although these elements were not studied to the same extent as the trace elements, it was considered that the few results obtained warranted inclusion in this discussion. Values for potassium agree very well with the corresponding values of Edwards (1942). Results for both P and K support the evidence of others that these elements are concentrated in the residual magma and are, therefore, most abundant in the later differentiates.

General Discussion

Although significant changes with depth have been shown for some trace elements in this sill, they do not compare, with the possible exception of Ni, with the great variations found between the various differentiates of the very much larger Skaergaard intrusive. However, the changes which have been noted generally agree with the conclusions drawn from other studies on the effect of differentiation of basic magma on the geochemistry of the trace elements.

These changes within the Mt. Wellington sill can be summarized as follows: Of the elements studied only Ni is strongly concentrated in the early differentiates. Co, Mn, Mo, Zn, V and Ga did not show such marked variations throughout the sill but, of these, Co and V were more abundant in the early differentiates, Ga and Zn were higher in the later differentiates and Mo was impoverished in the zone of magnesian pyroxene accumulation. Cu and Zr were more strongly concenterated in the residual magma and therefore were most abundant in the upper part of the sill. Wilson (1950) found similar trends for Ni and Cu and also showed that Cr was strongly concentrated near the base of the sill.

Some Comments on Differentiation of the Mt. Wellington Sill

The results show no significant difference in composition between the samples collected at the contact (D20) and six inches above it (D19) and the average composition of these samples has been considered as the composition of the original magma. This makes the usual assumptions that the magma being intruded was homogeneous throughout, that no alteration of the margin or incorporation of country rock had occurred and that solidification occurred too quickly in this narrow margin to be affected by the differentiation processes which occurred in the cooling magma above. Sample D18, collected 20 feet above the contact, does not differ significantly from the analysis of the "chilled" margin, except for Mn, and supports the idea that there had been no significant differentiation, at least with respect to these trace elements, in the lower 20 feet of the sill. Results have shown that above this level the processes of differentiation have had a real significance on the trace element composition of the sill.

The average composition of the sill was calculated assuming that the analysis of each sample represented the dolerite of its part of the sill (weighting each analysis according to the amount represented) and that the small variations in rock

TABLE 3.—*The Average Composition of the Mt. Wellington Sill*

Composition of Sill	Co	Zr	Ni	Cu	V	Mo	Mn	Ga
Calculated Weighted Average....	39	150	47	105	320	8.4	1,400	21
*Assumed Composition of Magma	51	150	88	105	380	8.8	1,600	22

* Average of the analyses of samples D19 and D20. Results expressed as p.p.m.

TABLE 4.—*Analyses of Jurassic Dolerite from Different Localities in Tasmania*

Sample No.	Locality.	Co ppm	Zr ppm	Ni ppm	Cu ppm	Mo ppm	Mn ppm	Zn ppm	P %	K %
H166/16	10 m. W. of Geeveston	42	110	86	75	7.9	1,300	42	.041	.65
H165/12	2 m. S. of Henrietta	58	91	140	60	8.4	1,650	51	.034	.44
H164/11	1½ m. S.W. of Devonport	44	99	110	62	8.1	1,300	57	.035	.55
H159/12	7 m. S.E. of Tarraleah	44	150	52	110	8.8	1,400	72	.051	.82
H167/12	3 m. S.W. of Kempton	48	140	69	89	9.3	1,400	70	.044	.73
H131a/8	1 m. S. of Western Lagoon	46	140	65	110	7.9	1,350	70	.050	.82
H129a/6	2 m. W. of Ross	46	170	63	99	8.5	1,150	63	.051	.98
H160/12	1½ m. E. of Hamilton	48	160	58	110	8.3	1,350	76	.050	.84
H127a/10 .	2½ m. S.W. of Nugent	34	180	23	140	7.6	1,100	73	.062	1.07
H86a/11	4 m. E. of Forcett	48	150	79	100	8.6	1,350	72	.047	.71
H163/11	1 m. S. of Hadspen	37	140	58	80	7.9	1,250	80	.046	.76
H128a/11 ..	3 m. N.E. of Gretna	37	130	66	81	8.1	1,150	57	.028	.84
H161a/10 ..	Near top of Mt. Nelson	46	200	26	140	8.0	1,300	84	.061	1.09
H162/10	Near bottom of Mt. Nelson	58	87	140	58	7.6	1,350	57	.029	.35
H126a/9	3 m. N. of Sorell	28	195	8	110	8.3	1,250	....	....	....
H174/10	5 m. N.W. of Richmond	32	138	44	97	7.6	1,380	....	....	....
H173/12	1 m. S.W. of Brighton	30	94	67	65	7.9	1,190	....	....	....

.... = No data—Analyses based on samples ignited at 500° C.

density (Joplin and Jaeger, 1957) would not be sufficient to affect any conclusions made. This calculated average composition of the sill is compared with the assumed composition of the magma in Table 3.

It may be seen that the average composition of the sill is lower than the magma for Mn, V, Co, and, in particular, Ni. It happens that Ni is also the element most influenced by the processes of differentiation. Providing that the assumptions concerning the composition of magma are correct, it follows that a large proportion of the Ni of the introduced magma has been lost from the column during differentiation. Although there is evidence (Edwards, 1942) that approximately 200 feet of the sill has been eroded away this could not account for the noted discrepancy. Ni has been shown by Wager and Mitchell (1951), Storm and Holland (1957) and others, to have its lowest content in the uppermost part of differentiated intrusives, whereas the average Ni and Co contents of this eroded portion of the sill would have to be approximately 300 p.p.m. and 100 p.p.m. respectively to account for the discrepancy noted.

The analytical data of Edwards (1942) suggest that the average Mg content of the sill is also much lower than would be expected if the "chilled" margin truly represents the composition of the magma. Furthermore, it is noted that the Mg contents of all "chilled" margins analysed, including both lower and *upper* contacts, show very little variation. This supports the basic assumption concerning the composition of the magma, as the upper contact is not likely to have received any elements such as Mg and Ni during differentiation even if it did remain fluid enough for a sufficient period. Wilson (1950) noted that the Ni and Cr composition of the base was higher than the average for the sill but he claimed he had evidence for differentiation in the "chilled" base and suggested that this base was not indicative of the magma but that it had received additions during differentiation.

There is, therefore, reasonable doubt whether the dolerite "column", as sampled,, represents a simple case of vertical differentiation in a closed chamber. There has possibly been some lateral movement of early-formed magnesian pyroxenes, the main host of the Ni, to an adjacent part of the sill or through a possible vent in the floor of the sill which sealed on partial cooling of the magma. Actually, the dolerite "column", as sampled from the Pinnacle Road, represented only a very oblique section of the sill, and sampling would be necessary in horizontal as well as vertical planes to check any lateral movement of materials. Detailed studies on vertical bore cores available for some dolerite sills in other parts of Tasmania would be very worth-while.

Dolerite in Other Parts of Tasmania

Many samples of dolerite were analysed from several parts of Tasmania in connection with the basic study of the soils formed on dolerite. These results, together with the general locality of each sample, are shown in Table 4. The range in composition found and the relation between the content of the different trace elements show that differentiation processes, similar in effect to those described in this paper, are very widespread in Tasmania. For example, it may be seen that, in general, samples with the high Ni contents have low Cu and Zr contents and vice versa. By noting this type of relationship a good approximation can often be made to the relative position of the sample in its original intrusive body.

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