

The Crystallisation Trends of Spinel in Tertiary Basalts from Rhum and Muck and Their Petrogenetic Significance

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Abstract. Spinel is commonly observed in alkali olivine basalts and olivine basalts that form the "Plateau Magma Series" of the British Tertiary Province. The spinels are either partly or wholly enclosed within olivine or may have adhered to olivine surfaces, and have undergone cation exchange and reaction with the cooling basaltic melt. Detailed microprobe traverses indicate complex exchange reactions involving Fe–Mg, Cr–Al, Fe^{3+} – R^{3+} and Fe^{2+}Ti – R^{3+} substitutions. Some of these changes are due to a reaction with liquid that produced plagioclase and resulted in Al depletion in the spinel. A complex series of solid solutions between hercynite–magnesioferrite–chromite and Al–Cr–titomagnetite, is indicated in a combination that precludes the disappearance of spinel by a simple peritectic reaction with the melt. The initial spinels are compositionally distinct from the chromites found in the Rhum layered series and underline the great compositional variability of liquidus spinels that can crystallise from basaltic liquid. Some of this variability may relate to the changing solubility of Cr, which behaves as a trace element, in basaltic liquids in response to slight changes in the structure of the melt.

Introduction

Phase relations in the pertinent parts of the systems $\text{CaO}–\text{MgO}–\text{Al}_2\text{O}_3–\text{SiO}_2$ and $\text{SiO}_2–\text{MgO}–\text{Cr}_2\text{O}_3$ suggest that a spinel phase should crystallise at or near the liquidus in melts of basaltic composition. Basalts and basic layered intrusions commonly contain a few percent of spinel, but the disappearance of this phase as crystallisation proceeds indicates a reaction relationship may operate between spinel and liquid. Peritectic reactions involving spinel may be predicted from phase relations in the above synthetic systems and have been inferred from studies of layered intrusions (Irvine, 1967; Henderson, 1975). However, spinels in layered intrusions frequently show post-cumulus reactions that modify the initial spinel composition (Henderson and Suddaby, 1971; Hen-

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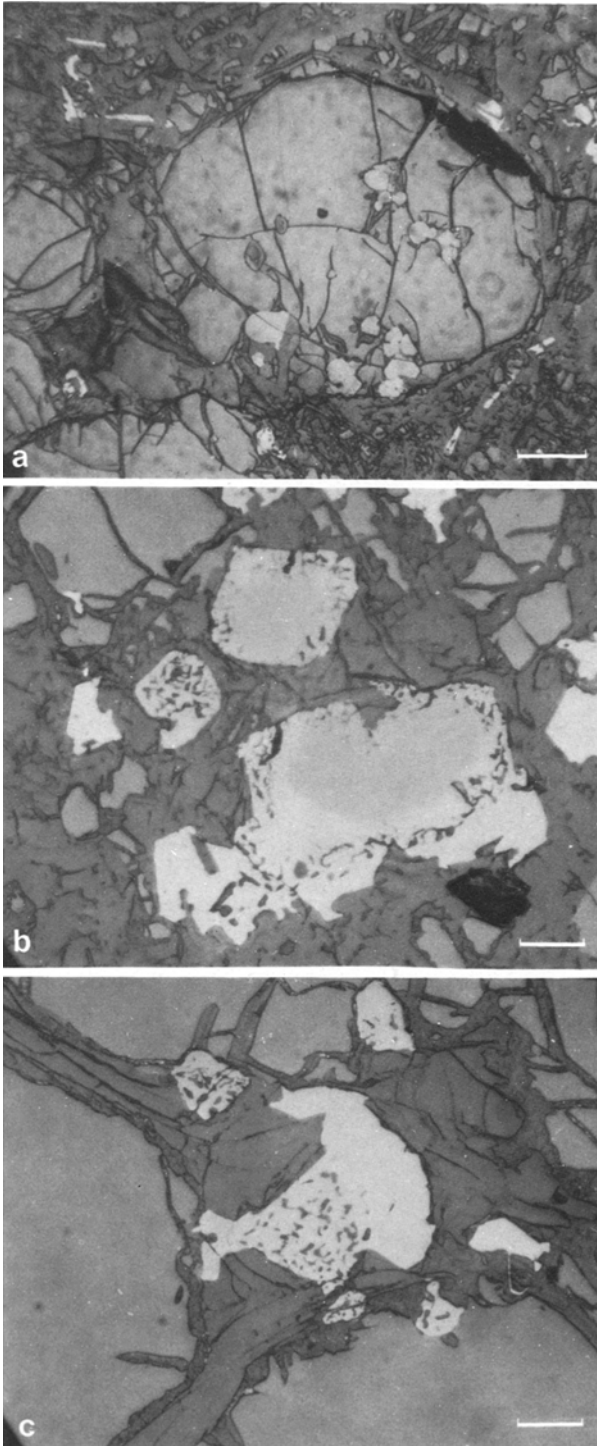


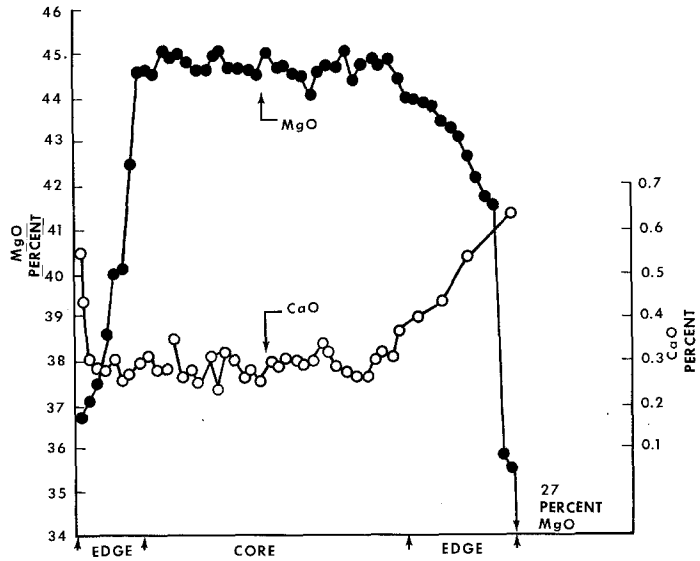
Fig. 1a-c. Textures of spinels in basalt M12

a Fragmented olivine phenocryst wholly and partly enclosing zoned spinels. Note some of the spinels have broken out completely into the matrix. Scale bar is 300 microns

b Zoned spinels partly reacted with basaltic melt. The aluminous spinel in the cores are less reflective and zone outward to Al-Ti chromite. Reaction with the melt to produce plagioclase at the expense of spinel (s.s) is represented by a "wormy" texture. Scale bar is 100 microns

c Extensive reaction between spinel and melt to form a symplectic intergrowth of Al-poor spinel and plagioclase in an embayment within olivine. Similar textures develop within discrete spinels totally removed from olivine, suggesting that olivine is not involved in the reaction. Note the rim of more highly reflective titanomagnetite. Scale bar is 100 microns

Fig. 2. Traverse across a phenocrystic olivine containing spinel. Note the overall homogeneity with respect to Mg, Ca and strong zoning within a thin marginal zone



derson, 1975) and the large difference in sinking velocity between spinel and ferromagnesian minerals (Jackson, 1971) can lead to ambiguity regarding the crystallisation relationships between intimately associated spinels and silicate phases. Variations in the compositions of spinel within the Rhum layered series have been documented by Henderson and Suddaby (1971), Henderson (1975) and Donaldson (1975) in which two distinct trends were recognised. One trend involved a gradual increase in Al/Cr ratio at relatively constant Fe^{3+} , the other involved an enrichment in Fe^{3+} at the expense of both Al and Cr. However, Donaldson (1975) has observed the opposite trend to the latter. In the present study, spinels occurring in transitional olivine basalts from the Islands of Rhum and Muck in the British Tertiary Province, have been studied in detail with regard to their overall chemical variability and relationship to silicate phases. The chemical variability in the spinels is related to the extent to which they have been exposed to the cooling basalt magma, hence it is possible to document the changes that take place during reaction of spinels with silicate liquid.

A series of cation substitutions takes place involving $\text{Fe}^{2+} - \text{Mg}^{2+}$; $\text{Cr} - \text{Al}$; $\text{Fe}^{3+} - \text{Cr}$, Al ; and Fe , $\text{Ti} - \text{Al}$, Cr , exchanges. These substitutions are more complex and extensive than those observed in spinels from basic layered intrusions, possibly due to the limited proportion of intercumulus liquid in the latter, limited temperature range over which cumulus spinel was in contact with intercumulus liquid, or the major element buffering effect of surrounding cumulus silicate phases.

Petrochemistry of Zoned Spinels in Basalts

Spinels have been analysed in two basalts, an alkali olivine basalt (M12) from Muck and a transitional alkali olivine basalt (SR 157) from Rhum. In both

Table 1. Selected Microprobe analyses of zoned spinels in sample M12

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Al ₂ O ₃	33.39	30.63	28.85	29.00	28.56	25.86	17.25	7.61	28.93	24.78	5.34	4.15	2.33	27.76	28.50	9.28	4.62	1.93
Cr ₂ O ₃	21.58	21.83	21.51	23.03	22.91	22.00	20.23	13.54	20.46	18.89	9.41	3.24	1.20	19.46	25.40	21.03	14.48	1.51
Fe ₂ O ₃	15.51	15.29	16.92	14.74	13.59	13.10	10.14	18.72	17.00	1.36	16.19	12.47	13.19	14.56	11.15	16.66	17.22	13.63
FeO	9.40	15.08	16.25	18.42	21.15	24.84	35.21	37.89	18.86	37.37	42.62	48.74	52.62	24.10	22.80	35.38	40.60	51.85
MnO	0.46	0.61	0.50	0.53	0.56	0.60	0.74	0.75	0.58	0.74	0.75	0.93	2.53	0.60	0.58	0.74	0.79	2.36
MgO	18.36	14.45	13.74	12.22	10.59	9.09	5.94	5.40	11.92	5.77	4.92	4.85	0.68	9.56	9.19	5.25	4.67	1.31
TiO ₂	0.92	1.40	1.74	1.52	1.93	3.92	11.27	15.62	1.63	11.90	20.07	24.71	27.04	3.61	1.48	11.96	17.65	26.75
Total	99.62	99.29	99.51	99.46	99.46	99.29	99.33	100.78	99.53	99.38	100.81	99.31	99.09	99.59	99.65	99.10	100.30	99.34
Al	9.12	8.64	8.16	8.32	8.32	7.68	5.36	2.48	8.32	7.44	1.76	1.28	0.72	8.16	8.32	3.04	1.60	0.64
Cr ₃	3.92	4.16	4.08	4.40	4.48	4.40	4.24	2.96	3.92	3.76	2.08	0.72	0.24	3.84	4.96	4.56	3.28	0.32
Fe ₂	2.64	2.72	3.04	2.72	2.48	2.48	2.00	3.92	3.12	0.24	3.44	2.64	2.96	2.72	2.08	3.44	3.68	3.04
Fe	1.76	3.04	3.28	3.76	4.40	5.20	7.76	8.88	3.84	7.92	10.16	11.92	13.12	5.04	4.72	8.16	5.92	12.80
Mn	0.08	0.08	0.08	0.08	0.08	0.16	0.16	0.16	0.16	0.16	0.16	0.24	0.64	0.16	0.16	0.16	0.16	0.56
Mg	6.32	5.12	4.96	4.40	3.84	3.36	2.32	2.24	4.32	2.16	2.08	2.00	0.32	3.52	3.44	2.16	2.00	0.56
Ti	0.16	0.24	0.32	0.24	0.32	0.72	2.24	3.28	0.32	2.24	4.32	5.36	6.08	0.64	0.24	2.48	3.76	5.92
Total cations	24.00	24.00	23.92	23.92	24.00	24.00	24.08	23.92	24.00	23.92	24.00	24.16	24.08	24.08	23.92	24.00	24.00	24.00
Cr/Cr + Al	0.30	0.32	0.33	0.35	0.35	0.36	0.44	0.54	0.32	0.34	0.54	0.34	0.24	0.32	0.38	0.60	0.67	0.34
Mg/Mg + Fe ²	0.78	0.63	0.60	0.54	0.47	0.39	0.23	0.20	0.53	0.21	0.17	0.14	0.02	0.41	0.41	0.21	0.17	0.04
Fe ³ /Fe ³ + Al + Cr	0.17	0.18	0.20	0.17	0.16	0.17	0.17	0.42	0.20	0.02	0.47	0.57	0.75	0.18	0.13	0.31	0.43	0.75
Ti/Ti + Al + Cr	0.01	0.02	0.03	0.02	0.03	0.06	0.19	0.37	0.02	0.17	0.52	0.73	0.86	0.05	0.02	0.24	0.43	0.85
Fe ³ /Fe ³ + Fe ²	0.60	0.47	0.48	0.42	0.36	0.32	0.20	0.30	0.44	0.17	0.25	0.18	0.18	0.35	0.31	0.29	0.28	0.19

Notes to Table 1: M12 is an alkali olivine basalt (2% normative nepheline) from Isle of Muck, Inner Hebrides. Analyses 1-8 represent a traverse across a spinel partly enclosed in olivine (analysis 1) and partly reacted with melt (analysis 8). Analyses 9-13 are a core to rim traverse of a spinel strongly reacted with melt. Analyses 14-18 are partly reacted spinel. Fe₂O₃ values computed assuming stoichiometry, structural formulae on basis of 32 oxygens

Table 2. Selected microprobe analyses of zoned spinels in SR157

	1	2	3	4	5	6	7	8	9
Al ₂ O ₃	46.08	45.91	37.00	32.42	25.88	21.91	14.24	6.56	4.56
Cr ₂ O ₃	8.35	10.11	10.94	12.75	13.53	13.80	12.68	5.53	0.88
Fe ₂ O ₃	16.18	13.60	20.54	21.26	24.38	26.35	31.69	32.01	26.67
FeO	9.36	11.65	12.40	15.92	19.39	22.70	25.86	37.29	44.37
MnO	0.05	0.07	0.09	0.17	0.20	0.21	0.23	0.33	0.48
MgO	20.01	18.61	17.36	15.22	12.92	10.71	8.68	5.28	3.88
TiO ₂	0.83	0.91	1.97	2.66	3.90	4.55	6.34	12.91	18.27
Total	100.86	100.86	100.60	100.40	100.20	100.23	99.72	99.91	99.11
Al	11.68	11.76	9.84	8.96	7.44	6.48	4.48	2.16	1.60
Cr ₃	1.44	1.76	2.00	2.40	2.64	2.72	2.64	1.20	0.24
Fe ₂	2.64	2.24	3.52	3.76	4.48	5.04	6.40	6.80	5.84
Fe	1.68	2.08	2.40	3.12	4.00	4.80	5.76	8.80	10.80
Mn	—	—	—	—	0.08	0.08	0.08	0.08	0.08
Mg	6.40	6.00	5.92	5.28	4.72	4.00	3.44	2.24	1.68
Ti	0.16	0.16	0.32	0.48	0.72	0.88	1.28	2.72	4.00
Total cations	24.00	24.00	24.00	24.00	24.08	24.00	24.08	24.00	24.24
Cr/Cr + Al ₂	0.11	0.13	0.17	0.21	0.26	0.30	0.37	0.36	0.11
Mg/Mg + Fe	0.79	0.74	0.71	0.63	0.54	0.46	0.37	0.20	0.13
Fe ³ /Fe ³ + Al + Cr	0.17	0.14	0.23	0.25	0.31	0.35	0.47	0.67	0.77
Ti/Ti + Al + Cr	0.01	0.01	0.03	0.04	0.07	0.09	0.15	0.45	0.69
Fe ³ /Fe ³ + Fe ²	0.61	0.52	0.59	0.55	0.53	0.52	0.53	0.44	0.35

Notes to Table 2. SR157 is an olivine basalt (3% normative hypersthene) from Rhum, Inner Hebrides. Analyses 1–9 represent a traverse from pristine spinel (analysis 1) enclosed within olivine to reacted spinel (analysis 9) in contact with melt. Fe₂O₃ values and structural formulae computed as in Table 1

samples some spinels are enclosed by olivine which prevented subsequent reaction between spinel and the silicate melt (Figure 1a). Microprobe traverses across olivines enclosing spinel (Figure 2) indicate they are largely unzoned except for thin marginal region where zoning is pronounced. The Fe/Mg ratio of the olivine also remains unaffected by the enclosing spinel. Probably spinel began to crystallise prior to eruption, closely followed by olivine which may have nucleated on the spinels, and grew in an isothermal environment prior to eruption. The zoned margins represent more rapid olivine growth following eruption and cooling. The spinels enclosed within olivine do not appear to have undergone cation exchange with the olivine. However, turbulent flow following eruption resulted in fragmentation of some of the olivines and the spinels were partly exposed to the cooling silicate melt. As a result of these conditions the spinels underwent degrees of reaction and cation exchange with the melt (Figure 1b, c).

Microprobe traverses across selected spinel grains are shown in Tables 1 and 2 and the main cation variations are shown in Figures 3 and 4. The variations in composition represent the spectrum of cationic substitutions

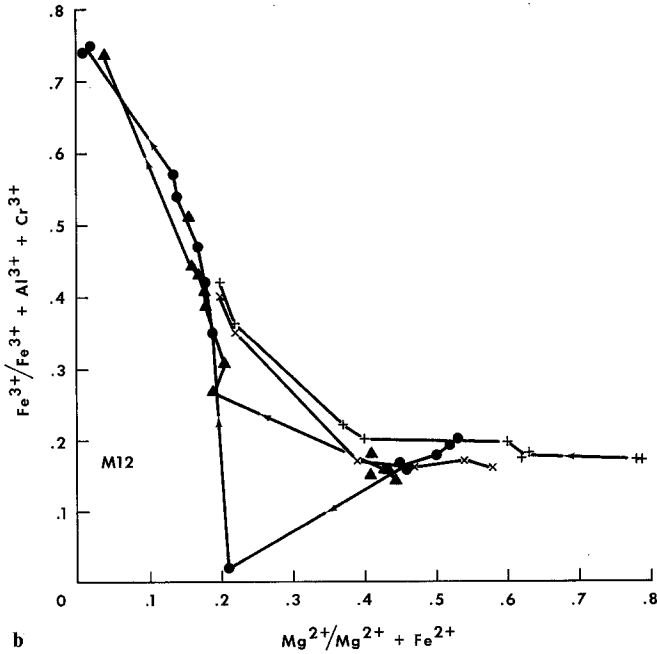
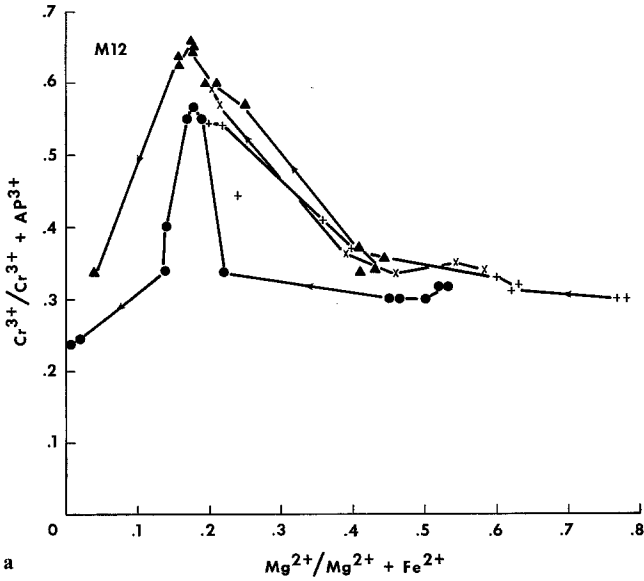
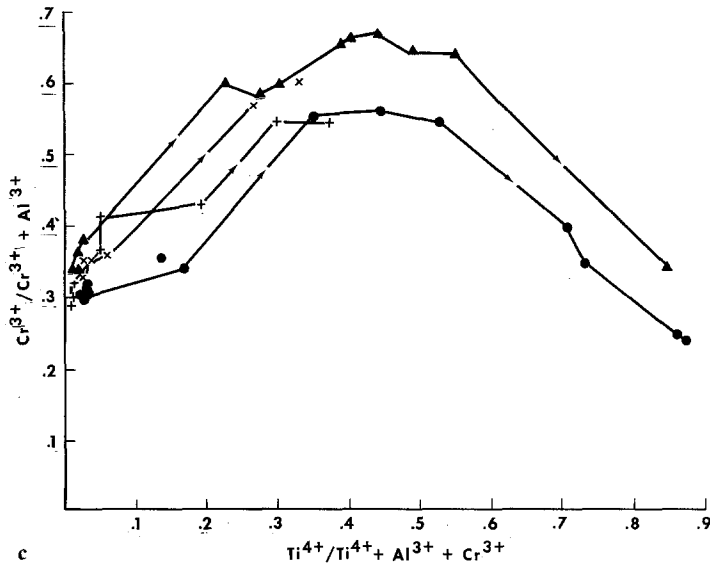


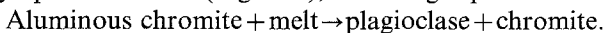
Fig. 3a-c. Cation variations in zoned spinels from alkali olivine basalt M12
a Variations in $Mg/(Mg + Fe^{2+})$ relative to $Cr/(Cr + Al)$. Individual grain traverses are represented by different symbols. Arrows represent directions of core to rim zoning
b Variations in $Mg/(Mg + Fe^{2+})$ relative to $Fe^{3+}/(Fe^{3+} + Cr + Al)$. Symbols as in Figure 3a
c Variations in $Ti/(Ti + Al + Cr)$ relative to $Cr/(Cr + Al)$. Symbols as in Figure 3a



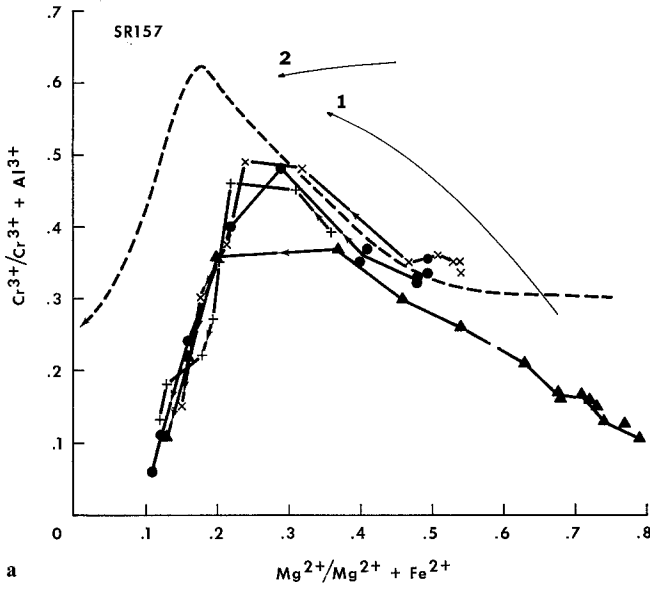
produced by spinels which have reacted with the silicate melt to varying degrees. The original spinels crystallised from the two basalts are not compositionally equivalent. Spinels from the olivine basalt SR157 are noticeably more enriched in Al_2O_3 relative to Cr_2O_3 but have similar Mg/Fe ratios to spinels in the alkali olivine basalt M12 (Figures 2a, 3a).

Reaction with the silicate melt results in a series of cation exchanges. These involve single-cation substitution of Fe^{2+} for Mg^{2+} , Cr^{3+} for Al^{3+} , Fe^{3+} for Cr^{3+} and Al^{3+} . Extensive reaction with the liquid resulted in enrichment in Ti in the spinels probably by a coupled substitution of $Fe^{2+}Ti^{4+}$ for $Al^{3+}Cr^{3+}$.

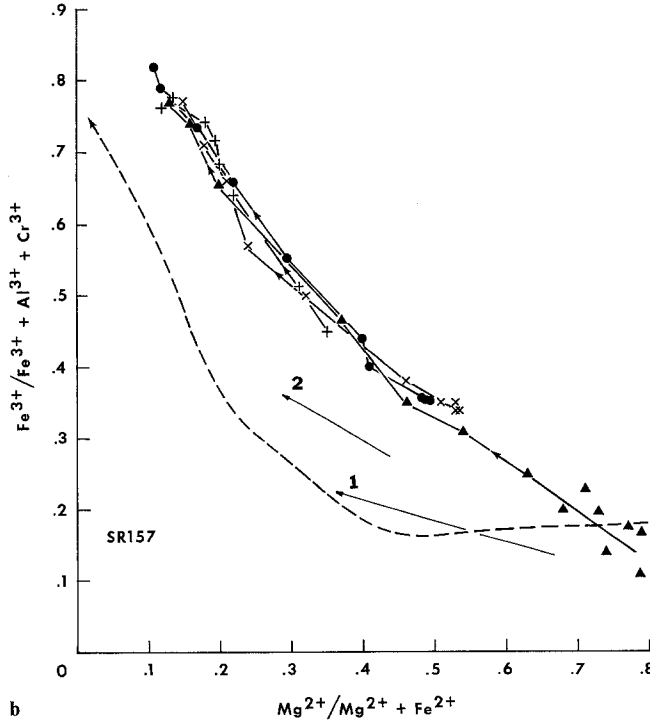
Although the reaction trends are similar for spinels in both basalts, in detail they show some differences. For instance, spinels from the olivine basalt show a continuous increase in the $Fe^{3+}/(Fe^{3+} + Cr + Al)$ ratio as the Mg/Fe ratio decreases, whereas the former ratio remains either constant or decreases slightly during the initial stages of reaction in the alkali olivine basalt. This difference may be due to initial differences in the Fe^{3+}/Fe^{2+} ratio in the two melts, since the alkali olivine basalt has a lower Fe^{3+}/Fe^{2+} ratio (Ridley, 1971). Apart from this initial difference, the subsequent zoning trends are similar, and initially involve a substantial increase in the Cr/Al ratio. This increase coincides with a textural change in which the spinel becomes intergrown with plagioclase in a symplectic texture (Figure 4), reflecting a peritectic reaction:



These changes are accompanied by gradual increases in the Fe^{3+} and Ti^{4+} content of the spinels, but the Fe^{3+}/Fe^{2+} ratio remains constant and only decreases markedly once titaniferous magnetite precipitates. Because of the large octahedral site preference energy of Cr^{3+} and none for either Al^{3+} or Fe^{3+} , the increase in ferric ion reflects the substitution of $Fe^{3+} \rightarrow Al^{3+}$ rather than



a



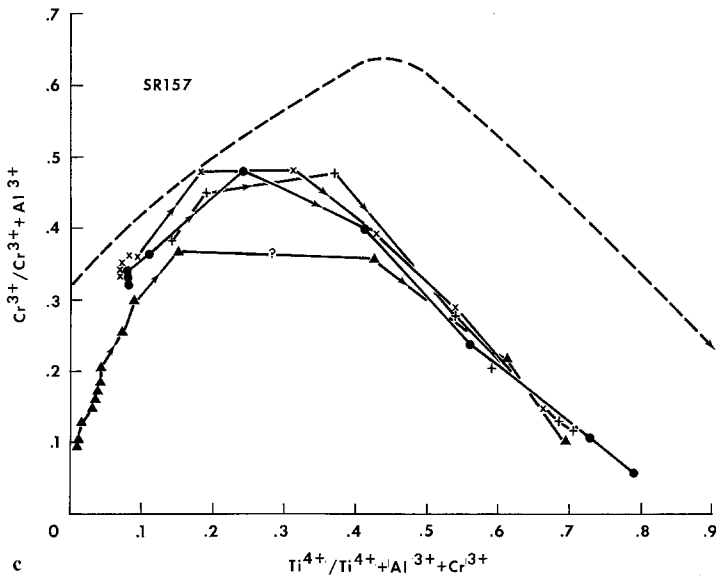
b

Fig. 4a-c. Cation variations in zoned spinels from olivine basalt SR157

a Variations in $Mg/(Mg + Fe^{2+})$ relative to $Cr/(Cr + Al)$. The dashed line is the average trend for zoned spinels in alkali olivine basalt M12. Curves 1, 2 indicate the extent of cation variation in spinels from a spinel seam (curve 1) and discrete spinels with allvalite (curve 2) from the Rhum Layered Series (Henderson, 1975)

b Variations in $Mg/(Mg + Fe^{2+})$ relative to $Fe^{3+}/(Fe^{3+} + Cr + Al)$. Dashed line and curves 1, 2 as in Figure 4a

c Variations in $Ti/(Ti + Al + Cr)$ relative to $Cr/(Cr + Al)$. Dashed line as in Figure 4a



$\text{Fe}^{3+} \rightarrow \text{Cr}^{3+}$ as is evident from the gradually decreasing spinel (s.s) component in Table 2.

The zoned spinels are finally rimmed by titanomagnetite compositionally identical to the discrete grains in the basaltic groundmass. These rims were precipitated directly from the cooling melt upon the surface of previously reacted spinel, essentially protecting the spinels from further cation exchange and reaction with the silicate melt.

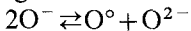
Summarily, the initial spinels to crystallise from these basaltic liquids were Al-chromites differing somewhat in the extent of spinel (s.s)-hercynite solid solution. Exposure to the cooling silicate melt resulted in a complex series of cation exchanges in which the spinel became enriched in the magnesian-ferrite, chromite and ulvospinel (minor) components compared to the original spinel (s.s)-magnesiochromite-hercynite solid solution. The gradual increase in Fe/Mg ratio, enrichment in Ti, but constancy of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio reflect the changing chemistry of the cooling silicate melt in that the internal, closed-system fraction involves initial Fe—Ti enrichment under relatively constant $f\text{O}_2$ conditions (Ridley, 1973). The spectacular increase in the Cr/Al ratio in the spinels resulted from a peritectic reaction in which the spinel lost Al_2O_3 during the crystallisation of plagioclase.

Crystallisation of Spinels from Basaltic Liquids

These detailed studies indicate that the composition of spinels in equilibrium with basaltic melt changes dramatically in response to decreasing temperature

and oxygen fugacity. The changes involve several cation exchanges but generally suggest that an extensive solid solution series exists between Cr—Al spinels and Fe—Ti spinels, comparable to the chromite-magnetite solution series documented by Hill (1970). These solid solutions preclude the possibility that complex spinels will disappear from a cooling basalt system by a simple peritectic reaction of the type olivine + spinel + liquid \rightarrow plagioclase + olivine, as would be predicted in simple synthetic systems, and as also suggested by Thayer (1946) and Irvine (1967). Rather the spinel exchanges cations with liquid along a cotectic reaction line that may involve spinel, olivine and plagioclase, resulting in a gradually less aluminous spinel as plagioclase precipitates. Other reactions are possible, depending upon the bulk composition of the system, the composition of the initial spinel and the activities of various cations (Cr, Al, Ti, Fe²⁺, Fe³⁺) in the liquid as it fractionates. Total reaction of Cr—Al spinel may only occur once pyroxene crystallises, although as observed here this was precluded by precipitation of ulvospinel-magnetite which effectively shielded the spinels from further reaction with the liquid.

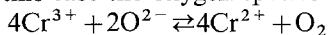
Basaltic liquids are capable of crystallising liquidus spinels of widely varying composition including Al-poor chromites and Cr-rich hercynite-spinel solid solutions. Generally there is a poor correlation between the bulk composition of the basalt and the composition of the liquidus spinel, particularly in Cr/Al ratio. Basalts with only a few hundred ppm Cr will precipitate a Cr-bearing spinel (Hill, 1970) suggesting a limited solubility of Cr in basaltic liquids. In this respect, Cr is an interesting element to study further since, unlike the other major cations in the spinel structure, it acts as a trace element in the silicate liquid. Its crystallochemical behaviour must therefore be affected by the structure of the liquid, and changes in the structure may have important consequences for the solubility of chromite in the melt as well as the precipitation of chromite from the melt. This can be illustrated in two ways, firstly with reference to the observation that the solubility of Cr in basaltic liquids increases with increasing pO₂ (Hill and Roeder, 1974). This is indicated by the precipitation of chromite from basaltic liquids containing more than 400 ppm Cr at fO₂ values less than 10⁻⁶–10⁻⁷ atm. (Hill and Roeder, 1974). This behaviour can readily be understood by relating changes in oxygen fugacity to changes in liquid structure. The polymerisation of silicate liquids results in an equilibrium being established in terms of oxygen species (Toop and Sammis, 1962).



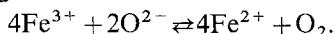
in which O⁻ are singly bonded oxygen ions, O[°] are doubly bonded oxygens and O²⁻ are free oxygen ions. A shift of the equilibrium to the left results in a lower degree of polymerisation, and hence more octahedral sites, a shift to the right results in a higher degree of polymerisation and less octahedral sites. Under high oxygen fugacities the melt contains more free oxygen ions, and equilibrium shifts to the left as the melt depolymerises. Cr³⁺ has a high octahedral site preference energy (37.6 Kcal mole⁻¹, Burns, 1970) and since it is a trace constituent in basaltic melts its solubility will be sensitive to the availability of octahedral sites. Hence depolymerisation with increasing fO₂ should increase the solubility of chromite in the liquid and hence the fO₂ condi-

tions at the site of partial melting will have important consequences for the Cr content of the erupted liquid.

Secondly, during the crystallisation of a spinel phase, other things being constant i.e., the concentration of Cr in the liquid, it is well established that increasing fO_2 will promote the precipitation of spinel from basic magmas. In this case the oxygen-species equilibrium can be written as:



and



In both these cases increasing fO_2 results in increases in Cr^{3+}/Cr^{2+} and Fe^{3+}/Fe^{2+} ratios. However, the redox potentials of these reactions are such that within the range of Fe^{3+}/Fe^{2+} expected for basaltic magma the Cr^{2+} content of the magma will be negligible. Hence the antipathetic relationship between chromite solid solution in the spinel phase and fO_2 must largely be determined by the availability of Fe^{3+} -bearing "components" (magnesioferrite, magnetite) in the melt. The fact that chromite is a substantial component of liquidus spinels, when we consider its dilute concentration in basaltic melts, must be largely due to the availability of abundant octahedral sites once the spinel begins crystallising.

Irvine (1975) has also considered the behaviour of Cr with reference to the structure of silicate melts at the Muscox intrusion, concluding that the occasional precipitation of abundant chromite was the result of periodic contamination of basaltic melt with granitic melt. There are however, many controls on silicate melt structure, one of which has been discussed above; another would be the concentration of dissolved water (Kushiro, 1975). It is emphasized that quite small changes in the availability of octahedral sites in the liquid may have a dramatic effect on the behaviour of transitional series trace elements whilst having little or no effect on cations present in major proportions or elements without octahedral site preference energies. There are probably many other factors, which determine the composition of liquidus spinels in basaltic liquids, especially the initial concentration of Cr in the liquid which itself would be a function of temperature and pressure conditions in the zone of partial melting and the mineralogy of the source material.

It is interesting to note that the liquidus spinels examined in this study are quite distinct from the more chromite-rich spinels found in the Rhum Layered Series (Henderson and Suddaby, 1971; Henderson, 1975; Donaldson, 1975) and yet the basalts are not distinctly different from the proposed parental liquid to the Rhum layered rocks (Brown, 1956)¹. Additionally, well-defined accumulations of spinel are observed in only two units out of about 19 rhythmic units of olivine, plagioclase and clinopyroxene. This suggests extensive crystallisation of spinel in the Rhum magma chamber only took place under *abnormal conditions of crystallisation*, yet these conditions were not reflected in any composition changes in the silicate phases (Wager and Brown, 1967). Thus large-scale contamination of the basaltic magma, of the kind envisaged by Irvine (1975),

¹ However, Donaldson (1975) suggests the parental liquid was closer in composition to a eucrite which conceivably may have been quite rich in Cr_2O_3

is precluded². Periodic influx of magma having a slightly lower oxygen partial pressure or lower water content, may be sufficient to promote the precipitation of chromite prior to the appearance of olivine. The residual liquid would hence be strongly depleted in Cr to the extent where crystallisation of chromite was slowed and ceased once clinopyroxene began to crystallise.

The cation exchanges documented here from individual basalt samples are complex and extensive as a result of incomplete reaction and melt fractionation and in general sense are comparable to the changes in spinel composition observed with upward progression in basic layered intrusions. In the latter cases, compositional variations are ascribed to subsolidus re-equilibration and reaction between cumulus minerals and intercumulus liquid. In the Rhum intrusion the pattern of Al enrichment at the expense of Cr (Henderson and Suddaby, 1971) and Cr+Al substitution for Fe³⁺ (Donaldson, 1975) are opposite to those described here, and imply an *increase* in temperature during reaction, as noted by the above authors. Such a situation might arise if the heat from hotter magma converging along the chamber floor conducted downwards through the cumulus material.

The comparatively limited extent of post-cumulus reaction in most cumulus spinel suggests a combination of limited volume of intercumulus liquid, limited contact between spinel and liquid (possibly as a result of filter-pressing loss of liquid), and a closer approach to true equilibrium exchange between the spinel and liquid compared to the reactions described here.

Conclusions

The cores of spinels that spilled into the basaltic liquid have diffuse boundaries and are chemically gradational with the rimming spinel. These features suggest that the chemical zoning has resulted from a reaction between spinel and liquid whereby the spinel was made over to more Fe- and Ti-rich spinel in response to the changing composition of the basaltic liquid. Superimposed upon this was a peritectic-type reaction in which aluminous spinel was made over to chrome-spinel with the precipitation of plagioclase. The changing composition of the spinel in terms of Fe²⁺, Mg, Ti, Fe³⁺ and Cr must therefore reflect similar changes in the liquid as the major silicate phases olivine, plagioclase and clinopyroxene precipitated and the oxygen fugacity and structure of the liquid changed.

² The Rhum pluton is intimately associated with large volumes of granophyre that probably developed by melting of Precambrian rocks that roofed the magma chamber (Wager and Brown, 1967). Irvine (1975) has noted that this is also common association in many layered intrusions, proposing that basaltgranite mixing may consequently take place. There is clear evidence for basalt-granite hybridisation on Rhum with a dramatic increase in the precipitation of spinel (Dunham, 1964) and minor mixing of basalt with granophyre within the Rhum magma chamber cannot be precluded. Periodic influx of new magma (Wager and Brown, 1967) would provide a suitable mixing mechanism. Hybridisation may also be important in the formation of the enigmatic "mugearites" of Rhum and Canna which have precipitated highly magnesian proxenes (Ridley, 1973)

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