

The cumulus and post-cumulus evolution of chrome-spinels in ultrabasic layered intrusions: evidence from the Cuillin Igneous Complex, Isle of Skye, Scotland

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Abstract. Chrome-spinels from the layered Peridotite Series of the unmetamorphosed, anorogenic 60 Ma Cuillin Igneous Complex, Isle of Skye, display a wide variety of compositions. Cumulus (within seams) chrome-spinels from the lowest exposed portion of the Peridotite Series exhibit features indicative of textural equilibrium, are rich in Al and Mg, and have low values of the ratio $Cr/(Cr+Al)$. Cumulus chrome-spinels from higher up in the series are different from these: particularly, textural disequilibrium is evident, intercumulus plagioclase and olivine are present, and the chrome-spinels are rich in Cr, Fe and Ti, with high values of the ratio $Cr/(Cr+Al)$. Intercumulus (dispersed) chrome-spinels tend towards anhedral forms and define enrichment trends towards Fe (both Fe^{2+} and Fe^{3+}) with decreasing Mg, Cr and Al, and towards Al, with decreasing Fe^{2+} and Cr (and increasing Mg). Individual crystals are completely homogeneous and are devoid of reaction rims. The observed textural characteristics and compositional data of the chrome-spinels documented here suggest that the semi-quantitative peritectic reaction: aluminous chrome-spinel + melt \rightarrow plagioclase + olivine + chromian chrome-spinel, is responsible for the observed parageneses, and that both the environment of crystallization (cumulus or intercumulus) and the role of plagioclase \pm olivine crystallization are critical parameters for this geochemical trend in spinels within upper crustal magmatic systems. The effects of pyroxene crystallization on the development of this geochemical trend are also considered. This investigation highlights the need to consider the role of post-cumulus mineral-melt reactions and their influences upon the final compositions of major oxide and silicate phases within layered intrusions.

Introduction

Minerals of the Spinel Group are important components of layered ultrabasic intrusions in a variety of geologic

environments (for example, Jackson 1963; Irvine 1965, 1967; Evans and Moore 1968; Wager and Brown 1968; Irvine and Smith 1969; Cameron 1969, 1975; Haggerty 1976; Hamlyn and Keays 1979; Fisk and Bence 1980; Dick and Bullen 1984; Parsons 1987; Agata 1988; Jan and Windley 1990). Typically, they occur as early precipitated cumulus phases. Spinels are simple oxides containing various trivalent and divalent cations (and, rarely, quadrivalent cations), with the general formula $M^{2+}(Al, Fe, Cr)_2^+O_4$, and may be subdivided into three series (Deer et al. 1966; Haggerty 1976). Importantly, significant solid-solution compositional variation occurs naturally within and between these three spinel series. In addition, the distribution of cations between members of the Chromite Series and co-existing olivines in ultrabasic rocks permits the determination of equilibration temperatures (Roeder et al. 1979; Fabries 1979; Ozawa 1983). Although such geothermometric calculations are thermodynamically valid, attention must be paid to the effects of sub-solidus re-equilibration processes during protracted cooling from magmatic temperatures down to the temperature of the local geotherm. The kinetic factors which control these re-equilibration processes have not been investigated in detail. Critically, although such processes may be detrimental to geothermometric determinations, they do provide an insight into the importance of post-cumulus changes in mineral compositions at near-solidus and sub-solidus temperatures within basic and ultrabasic intrusions and, as such, permit understanding of mineral-melt and mineral-mineral reactions involving Spinel Group minerals and co-existing silicate minerals at elevated temperatures.

The cooling and crystallization of basic and ultrabasic magmas within volcanic and subvolcanic (intrusive) environments will involve all or certain of the following:

1. initial crystallization and accumulation of early precipitated phases
2. reaction between crystallized phases and (trapped) interstitial liquids
3. reaction between crystallized phases at sub-solidus temperatures during cooling

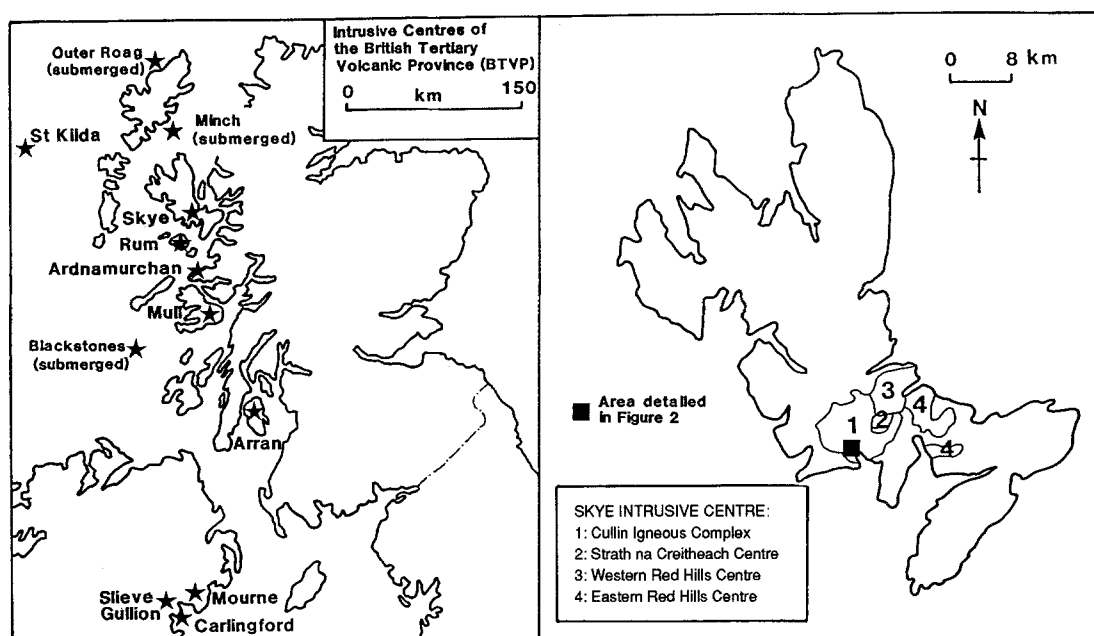


Fig. 1. Location map of Skye Intrusive Centre and Peridotite Series within the Cuillin Igneous Complex

Primary crystallization controls (i.e. stage (1), here) on spinel compositions have been investigated from a variety of magmatic systems. In addition to the initial composition of the magma, other important factors which influence the composition(s) of Spinel Group minerals are: temperature, pressure (i.e. depth of emplacement of the magma), and the oxygen fugacity of the magma as it cools and crystallizes. Also of importance will be the rate of crystallization: slow cooling will permit spinel-melt reactions to continue with decreasing temperature and thus maintain or approach compositional equilibrium. In consequence, rapidly quenched rocks may not contain spinels with true equilibrium compositions. Additionally, spinels in rapidly crystallized rocks may not exhibit the same amount of solid-solution compositional range as spinels from intrusive rocks, which cooled at much slower rates.

The purpose of this paper is to report the compositions of spinels from different environments within ultrabasic rocks of an unmetamorphosed anorogenic layered intrusion and to explain these data in terms of cumulus mineral phase equilibria, post-cumulus mineral-melt reactions, and/or, post-solidification processes, as deduced from mineral textures and compositions. In addition, we examine the validity of spinel-olivine geothermometry in the light of such deduced reactions. We have selected for our case study the 60 Ma Cuillin Igneous Complex, Isle of Skye, Scotland, which contains spinels in two distinct associations: in cumulate seams; and, as an interstitial phase associated with silicate minerals. Critical to this study, there is clear textural and compositional evidence for the combined roles of various cumulus and post-cumulus processes in the evolution of the spinels preserved (Hunter 1987; Irvine 1987).

Geologic setting

The 60 Ma Cuillin Igneous Complex (Fig. 1) is a composite layered intrusion of tholeiitic affinity and is dominated by cumulates consisting of various proportions of olivine, clinopyroxene, orthopyroxene, plagioclase, and spinel *sensu lato* (*s.l.*) (Bell and Harris 1986). The Complex constitutes the oldest part of the Skye Intrusive Centre, the younger units of which consist of various granites and mixed-magma intrusions. The Skye Intrusive Centre is hosted by an extensive lava field which pre-dates the intrusive activity and is one of a number of intrusive centres of the British Tertiary Volcanic Province, which extends from Skye, south, along the west coast of Scotland, into Ireland (Fig. 1). The Province may be correlated with volcanic rocks (lavas and fragmental volcanic rocks) and intrusive centres which crop out along the eastern margin of Greenland and which are of similar age (Brooks 1980). Both the British Tertiary Volcanic Province and the volcanic and intrusive rocks of east Greenland occur within continental crust and are related to ocean floor spreading processes during the formation of the North Atlantic.

The Cuillin Igneous Complex has an average diameter of 8 km and is composite, consisting of a number of ring intrusions of ultrabasic to basic composition (Fig. 1). The oldest units of the Complex are poorly layered and unlayered gabbros and form the outermost exposures, typically against intensively altered and metamorphosed basalt lava flows. Interior to these gabbros are the main layered rocks of the Complex, which consist of an Outer Layered Series and an Inner Layered Series, which are separated by a coarse-grained ring intrusion, the Druim nan Ramh Eucrite. The Outer Layered Series consists of the Peridotite Series (PS) and a younger Allivalite (i.e. bytownite troctolite) Series. Interior to, and cross-cutting these two series of layered ultrabasic rocks is a series of layered eucrites (i.e. basic gabbros, with bytownite), the Layered Eucrite Series. The inner margin of the Layered Eucrite Series is truncated by the steep-sided Druim nan Ramh Eucrite, interior to which is a younger sequence of layered rocks, the Inner Layered Series, consisting of allivalites, eucrites, and gabbros (Bell and Harris 1986).

The present study is concerned with the presence of spinel (*s.l.*) within the various lithologies of the Peridotite Series (PS) (Harker 1904; Weedon 1965; Claydon and Bell 1992). Figure 2 illustrates the six identified units of the lower portion of the PS (Claydon

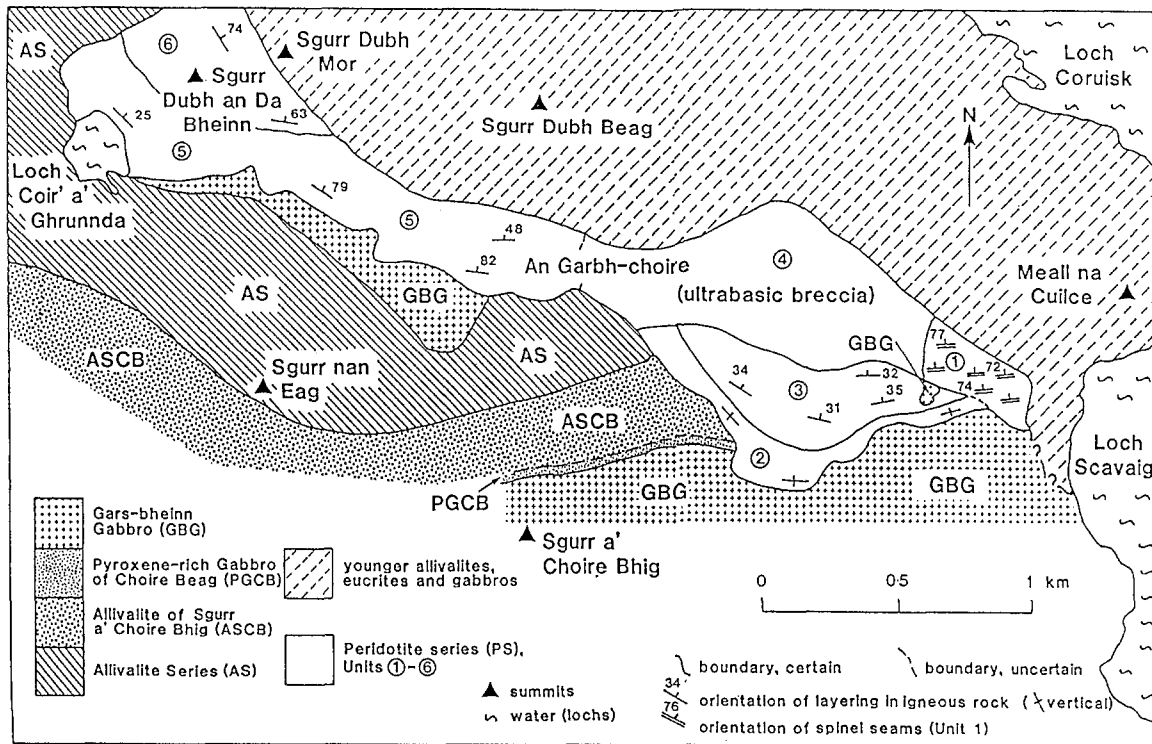


Fig. 2. Map of the Peridotite Series of the Cuillin Igneous Complex, showing general geology and structure



Fig. 3. Field photograph of steeply inclined (towards north) chrome-spinel seams within unit 1 rocks [Ordnance Survey Grid Reference (NG 4787 1967)]. Scale bar on notebook is in centimetres

and Bell 1992), which consist of cumulates dominated by olivine and spinel, with minor cumulus plagioclase, and intercumulus plagioclase and clinopyroxene. The lowest exposed portion of the PS crops out west of Loch Scavaig, in the southern part of the Cuillin Igneous Complex, and constitutes unit 1. Typically, rocks of unit

1 weather to a smooth reddish brown surface and consist of cumulus olivine (85–90% of mode) ± spinel (8–10% of the mode) and may be regarded as a series of dunites interlayered with concordant seams (up to 2 cm thick) of spinel (Fig. 2). In certain parts of unit 1 several parallel seams of spinel occur, separated by thin layers of olivine cumulate (dunite) (Fig. 3). The olivine (up to 2 mm) exhibits a small degree of normal cryptic variation, ranging from Fo_{92-94} in the lowest exposures, to Fo_{88} towards the top of the unit.

The spinel crystals within the seams towards the base of unit 1 are reddish brown in transmitted light, whilst those towards the top of the unit are opaque. Within these seams, small amounts of intercumulus olivine and plagioclase are preserved. Spinel seams may be traced along strike for several tens of metres, exceptionally up to 100 m, have sharp lower surfaces and permit the overall structure of the unit 1 rocks to be elucidated (Fig. 2) (Claydon and Bell 1992). Typically, the igneous layering, defined by the spinel seams and rare examples of model and phase layering where plagioclase occurs as a cumulus mineral, dips at a steep angle (70–80°) towards the north (Fig. 2). Spinel (0.5–1 mm) more rarely occurs disseminated throughout unit 1 rocks, either within cumulus crystals or within intercumulus crystals. Sulphide minerals constitute <1 vol.% of any examined specimen.

Mineral textures and mineral chemistry data

Mineral textures

Two distinct paragenetic relationships have been identified for spinel crystals of unit 1 of the PS.

1. *Seams*. These are up to 2 cm thick, are continuous along strike for distances typically of the order of 10 m, but exceptionally up to 100 m, with sharp lower boundaries against underlying olivine cumulates, and more

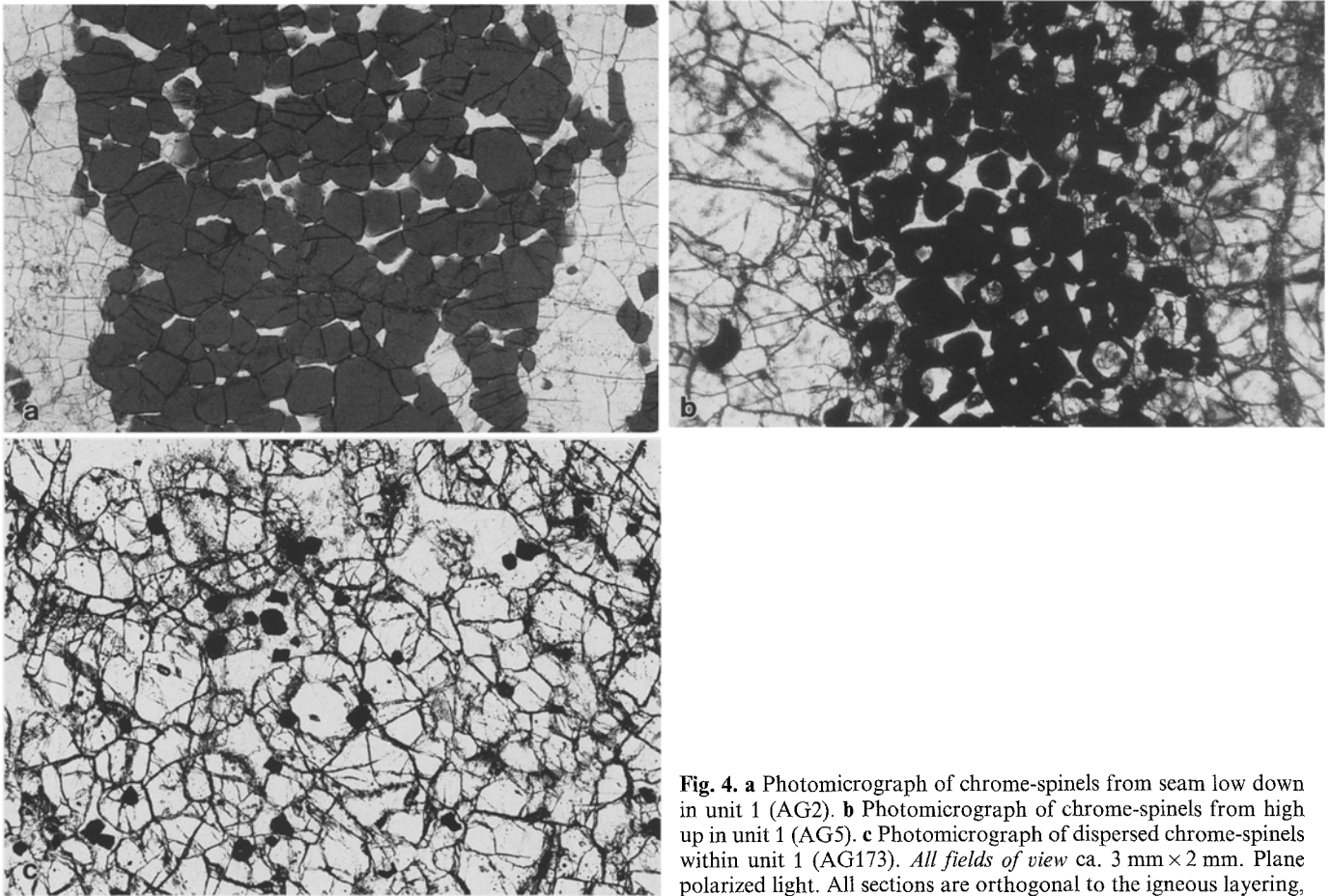


Fig. 4. **a** Photomicrograph of chrome-spinels from seam low down in unit 1 (AG2). **b** Photomicrograph of chrome-spinels from high up in unit 1 (AG5). **c** Photomicrograph of dispersed chrome-spinels within unit 1 (AG173). All fields of view ca. 3 mm × 2 mm. Plane polarized light. All sections are orthogonal to the igneous layering, with the upper surface on the right-hand-side

gradational upper boundaries (Fig. 3). Figure 4a illustrates textural features typical of a spinel seam from low down in unit 1. The spinel crystals constitute up to 95 vol.% of the seam, are generally equant (about 0.2–0.4 mm), and are reddish-brown. The most common intercumulus phase is plagioclase, often interconnected over areas covering a few spinel crystal widths, as deduced from their optical continuity and compositional homogeneity. Occasionally, olivine occurs as an intercumulus phase.

Where spinel crystals are in mutual contact, either at spinel-spinel-spinel or spinel-spinel-plagioclase triple junctions, almost planar or slightly curved boundaries are dominant. Dihedral angles (Hunter 1987) involving spinel-spinel-spinel trip junctions are typically about 120°, indicative of textural equilibrium, whereas spinel-spinel-plagioclase triple junction angles are much more variable and spinel-plagioclase boundaries have more marked curvatures. Where spinels appear to have grown freely into pore space (now represented by intercumulus plagioclase) they have idiomorphic forms, whilst allotriomorphic forms resulted where spinel-spinel mutual interference occurred. On the scale of a thin-section, these spinel seams exhibit inhomogeneous porosities, which may be attributed to their formation by settling of agglomerated grains and individual crystals to form a cumulus framework (Hunter 1987; Irvine 1987). The

low residual porosities of the spinel seams, as deduced from the small amounts of intercumulus material preserved, may be attributed to the combined effects of crystal accumulation, compaction and post-cumulus crystal growth (Hunter 1987), with the concomitant removal of the intercumulus liquid. Olivine crystals within the cumulates underlying and overlying the spinel seams frequently preserve deformation lamellae which may be attributed to the stresses set up during compaction and to melt expulsion from the original cumulate pile.

Spinel seams from high up in unit 1 are much less continuous along strike, are darker, and contain much greater amounts of intercumulus material. Typically, individual spinel crystals tend towards euhedral forms where they are separated from neighbouring crystals by thin films of intercumulus plagioclase (An₈₈) (Fig. 4b). Where spinel crystals are touching, they have almost planar contacts. Dihedral angles are highly variable, indicating a significant departure from textural equilibrium (Hunter 1987). A small proportion of the spinel crystals have highly embayed margins where they are in contact with plagioclase. Where the intercumulus phase is olivine, often taking the form of large poikilitic plates, the majority of the spinel crystals are highly embayed, suggesting that some form of dissolution process involving removal or redistribution of the spinel phase has occurred. Occasionally these large poikilitic olivines ap-

Table 1. Representative analyses of spinels from unit 1 of the Peridotite Series

Sample No. Lithology Type	AG2(1) Dunite Cum(S)	AG2(2) Dunite Cum(S)	AG2(3) Dunite Cum(S)	AG157(1) Dunite Cum(S)	AG157(2) Dunite Cum(S)
SiO ₂	—	—	—	0.06	0.03
TiO ₂	0.20	0.24	0.21	0.25	0.21
Al ₂ O ₃	50.78	50.84	51.64	49.68	49.34
Cr ₂ O ₃	14.74	15.32	14.80	15.61	16.35
Fe ₂ O ₃	4.05	3.49	3.72	4.85	4.65
MgO	21.92	21.49	22.03	20.53	20.37
FeO	5.87	6.73	6.11	8.30	8.48
Total	97.60	98.16	98.57	99.28	99.43
FeO*	9.45	9.93	9.44	12.64	12.66
Formula (on the basis of 32 oxygens)					
Si	—	—	—	0.012	0.006
Ti	0.032	0.038	0.033	0.041	0.034
Al	12.929	12.889	12.991	12.638	12.558
Cr	2.516	2.604	2.496	2.664	2.791
Fe ³⁺	0.648	0.560	0.592	0.776	0.744
Mg	7.054	6.888	7.006	6.603	6.553
Fe ²⁺	1.048	1.200	1.080	1.480	1.512
Mn	0.007	0.009	0.011	0.036	0.040
Total	24.234	24.188	24.209	24.250	24.238
Sample No. Lithology Type	AG157(3) Dunite Cum(S)	AG5(1) Dunite Cum(S)	AG5(2) Dunite Cum(S)	AG5(3) Dunite Cum(S)	AG173(1) Troctolite Intercum(I)
SiO ₂	0.02	—	—	—	0.02
TiO ₂	0.23	0.95	0.92	1.46	1.36
Al ₂ O ₃	52.13	28.76	28.37	16.37	17.94
Cr ₂ O ₃	14.26	29.99	30.00	36.78	39.80
Fe ₂ O ₃	4.37	10.46	10.47	13.55	10.48
MgO	21.58	12.77	12.62	8.11	9.53
FeO	7.21	17.19	17.15	22.21	20.64
Total	99.80	100.12	99.53	98.48	99.77
FeO*	11.16	26.62	26.58	34.35	30.11
Formula (on the basis of 32 oxygens)					
Si	0.004	—	—	—	0.004
Ti	0.037	0.176	0.172	0.302	0.269
Al	13.011	8.355	8.297	5.304	5.584
Cr	2.386	5.841	5.885	7.991	8.307
Fe ³⁺	0.688	1.880	1.896	2.680	4.416
Mg	6.809	4.688	4.667	3.323	3.749
Fe ²⁺	1.264	3.440	3.456	4.888	2.016
Mn	0.029	0.089	0.093	0.131	0.125
Total	24.228	24.469	24.466	24.619	24.470

pear to have textural features which suggest that they have cumulus status (Irvine 1982; Hunter 1987). However, based upon their obvious poikilitic form in certain parts of the spinel seams, it is more likely that they have formed by coalescence and recrystallization of smaller intercumulus crystals (see Hunter 1987). Within the cores of a significant proportion of the spinel crystals are anhedral crystals of plagioclase feldspar, more rarely

of olivine, or olivine and plagioclase. Boundaries between the inclusion phase(s) and the surrounding spinel crystal are typically irregular, suggesting that some form of dissolution reaction has been preserved in an arrested state. The olivine cumulates (dunite) which are associated with the spinel seams from high up in unit 1 are uniform in composition, with olivine typically Fo₈₈, associated with rare intercumulus plagioclase (An₈₈).

Table 1. (continued)

Sample No. Lithology Type	AG244(1) Peridotite Intercum(I)	AG244(2) Peridotite Intercum(I)	AG244(3) Peridotite Intercum(I)	AG249(1) Feld. per. Intercum(I)	AG249(2) Feld. per. Intercum(I)
SiO ₂	0.04	0.04	0.24	0.03	0.08
TiO ₂	1.46	0.99	1.05	3.95	4.12
Al ₂ O ₃	16.55	20.96	20.33	6.66	6.93
Cr ₂ O ₃	39.65	37.06	37.85	20.47	22.11
Fe ₂ O ₃	10.83	10.60	10.28	34.99	32.39
MgO	7.80	11.60	11.46	3.86	3.89
FeO	23.09	17.47	17.84	29.70	29.95
Total	99.42	98.72	99.05	99.66	99.47
FeO*	32.86	27.03	27.11	61.14	59.11
Formula (on the basis of 32 oxygens)					
Si	0.012	0.011	0.062	0.011	0.027
Ti	0.297	0.193	0.204	0.956	0.986
Al	5.267	6.416	6.213	2.525	2.600
Cr	8.462	7.607	7.757	5.208	5.562
Fe ³⁺	5.040	2.008	1.944	7.064	6.920
Mg	3.140	4.487	4.426	1.849	1.846
Fe ²⁺	2.128	3.672	3.752	7.488	7.112
Mn	0.136	0.101	0.107	0.120	0.118
Total	24.482	24.495	24.465	25.221	25.171

Lithology: feld. per.: feldspathic peridotite (all lithologies according to Irvine 1982). Type: cum: cumulus (S: seam); intercum: intercumulus (I: inclusion). Total iron was determined as FeO* and

subsequently partitioned between ferrous (Fe²⁺) and ferric (Fe³⁺) iron by the method of Finger (1972)

2. *Dispersed crystals.* These occur as isolated crystals (in three-dimensions) throughout the PS, but are particularly characteristic of the unit 1 rocks. They range up to 1 mm and are always opaque, except where adjacent to seams low down in unit 1. They occur either as inclusions within silicate cumulus phases, or within intercumulus minerals, with significant compositional characteristics accompanying each association. Figure 4c illustrates a typical paragenetic association of the dispersed spinels. Typically, the dispersed spinels have allotropic forms (Fig. 4c). Where in contact with olivine, their mutual interface is sharp and without any apparent reaction, but where in contact with plagioclase (typically intercumulus), the interface is more diffuse.

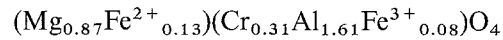
Mineral chemistry data

All mineral analyses were determined on a Cambridge Instruments Geoscan V electron probe micro-analyzer at the Grant Institute of Geology, University of Edinburgh, using wavelength-dispersive techniques. Standard operating conditions were 20 kV accelerating voltage, 30 nA beam current, and an integrated counting time of 40 s. The beam diameter was in the region of 2.5 µm. Standards comprised well-characterized natural silicates and pure metals. ZAF and dead-time corrections were applied. Total iron was determined as FeO*, and for spinel analyses was subsequently partitioned between ferrous (Fe²⁺) and ferric (Fe³⁺) by the method of Finger (1972).

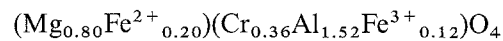
No significant or systematic compositional zoning is present within any of the spinels analyzed and alteration

to the secondary phase "ferritchromit" (Haggerty 1976) was not detected.

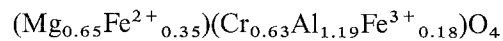
Spinel forming the structurally lower seams have a restricted range of compositions which lie close to the solid-solution join MgAl₂O₄–MgCr₂O₄–FeAl₂O₄–FeCr₂O₄ [i.e. spinel sensu stricto (*s.s.*)–picrochromite–hercynite–chromite, (compare Haggerty 1976)]. Fe₂O₃ contents are typically <5 wt%, TiO₂ contents are <0.25 wt%, and SiO₂ is present in only trace amounts. Compositions are in the range:



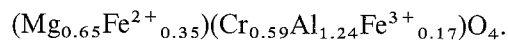
to



Spinel forming the seams in the upper part of unit 1 have compositions which extend above the base of the spinel composition prism (Haggerty 1976), to include significant Fe₂O₃ contents, often >5 wt%, and TiO₂ contents, often >0.25 wt%, towards the solid-solution end-members Mg₂TiO₄–Fe₃O₄–Fe₂TiO₄ [i.e. magnetoferrite–magnetite–ulvospinel, (see Haggerty 1976)]. Compositions are in the range:



to



Spinel dispersed throughout unit 1 have compositions in the ranges:

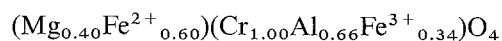


Table 2. Representative analyses of olivines from unit 1 of the Peridotite Series

Sample No. Lithology Type	AG1(1) Dunite Cum	AG1(2) Dunite Cum	AG2(3) Dunite Cum	AG2(4) Dunite Cum	AG2(5) Dunite Cum	AG5(3) Dunite Cum	AG5(4) Dunite Cum
SiO ₂	41.23	41.58	41.05	41.02	41.07	40.44	40.53
Al ₂ O ₃	0.02	0.02	0.10	0.03	0.02	0.05	0.01
CaO	0.10	0.07	0.05	0.08	0.07	0.09	0.06
MgO	50.01	50.07	52.04	52.19	52.07	48.27	47.43
FeO*	7.60	7.65	6.07	6.17	5.99	10.27	11.19
MnO	0.18	0.24	0.14	0.13	0.13	0.18	0.19
NiO	0.33	0.34	0.33	0.33	0.33	0.42	0.39
Total	99.57	99.97	99.80	99.95	99.97	99.72	99.80
Atomic %							
Fo	92.16	92.12	93.85	93.77	93.93	89.72	88.29
Fa	7.84	7.88	6.15	6.23	6.07	10.28	11.71
Formula (on the basis of 4 oxygens)							
Si	1.005	1.009	0.993	0.991	0.998	0.998	1.003
Al	0.001	—	0.003	—	0.001	0.001	—
Ca	0.003	0.002	0.001	0.002	0.002	0.002	0.002
Mg	1.821	1.812	1.876	1.880	1.872	1.775	1.749
Fe	0.155	0.155	0.123	0.125	0.121	0.212	0.232
Mn	0.004	0.005	0.003	0.003	0.003	0.004	0.004
Ni	0.006	0.007	0.006	0.006	0.006	0.008	0.008
Total	2.995	2.990	3.005	3.007	3.003	3.000	2.998

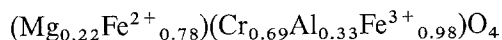
Lithology according to Irvine (1982). Type: cum = cumulus

Table 3. Representative analyses of plagioclases from unit 1 of the Peridotite Series

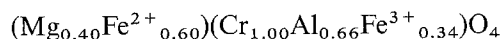
Sample No. Lithology Type	AG1(1) Dunite Intercum	AG1(3) Dunite Intercum	AG2(1) Dunite Intercum	AG2(2) Dunite Intercum	AG5(1) Dunite Intercum	AG5(8) Dunite Intercum
SiO ₂	46.71	46.58	45.84	46.33	47.65	46.42
Al ₂ O ₃	33.92	33.57	33.66	33.86	33.00	33.78
CaO	17.66	18.20	18.09	18.15	16.74	18.00
MgO	0.03	0.02	0.03	0.05	0.04	0.03
FeO*	0.16	0.18	0.10	0.18	0.19	0.30
BaO	0.01	0.01	0.01	—	—	0.02
Na ₂ O	1.43	1.39	1.45	1.26	2.16	1.21
K ₂ O	0.01	0.02	0.02	0.02	0.04	0.01
Total	99.93	99.97	99.20	99.85	99.82	99.77
Atomic %						
An	87.16	87.81	87.24	88.72	80.92	89.43
Ab	12.79	12.08	12.64	11.15	18.86	10.49
Or	0.05	0.10	0.02	0.13	0.22	0.07
Formula (on the basis of 32 oxygens)						
Si	8.595	8.588	8.552	8.547	8.767	8.530
Al	7.358	7.296	7.377	7.364	7.157	7.317
Ca	3.481	3.597	3.603	3.588	3.299	3.690
Mg	0.009	0.007	0.008	0.015	0.012	0.008
Fe	0.025	0.028	0.016	0.028	0.030	0.045
Ba	—	—	—	—	—	0.002
Na	0.511	0.495	0.522	0.451	0.769	0.433
K	0.002	0.004	0.005	0.005	0.009	0.003
Total	19.981	20.015	20.083	19.998	20.043	19.981

Lithology according to Irvine (1982). Type: cum = cumulus; intercum = intercumulus

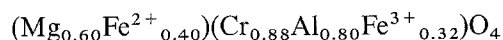
to



defining a compositional trend toward enrichment in iron (both Fe^{2+} and Fe^{3+}), and:



to



defining a compositional trend towards enrichment in aluminium.

There is no systematic relationship between the composition of dispersed spinels and structural location (i.e. height) within unit 1.

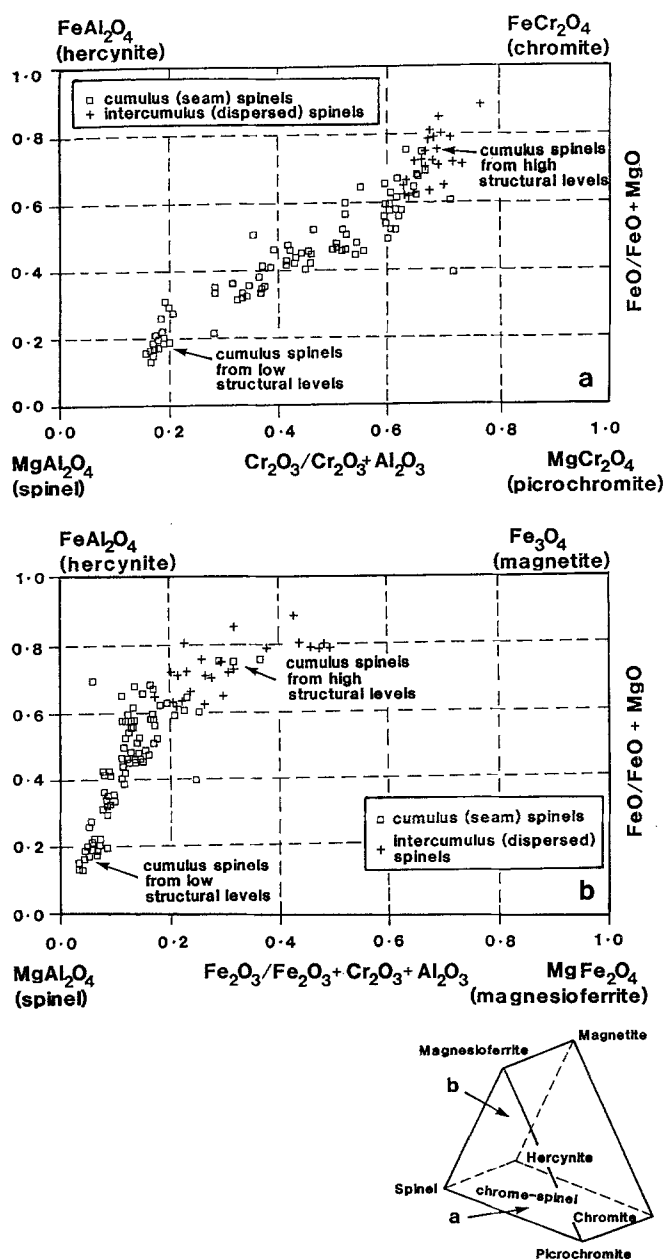


Fig. 5. Plots of $\text{FeO}/(\text{FeO} + \text{MgO})$ vs. $\text{Cr}_2\text{O}_3/(\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ and $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ for unit 1 chrome-spinels

Thus, the spinel (*s.l.*) of the PS may precisely be referred to as chrome-spinels (*s.s.*) according to the classification scheme set out by Haggerty (1976). Representative analyses of chrome-spinels from the various recognised mineral environments are presented in Table 1.

Representative cumulus olivine compositions from unit 1 are presented in Table 2, whilst Table 3 lists compositions of cumulus and intercumulus plagioclases. Both phases are of relatively constant composition within individual specimens at any one structural level within unit 1 of the PS; however, olivine does exhibit a small but significant amount of normal cryptic variation, from Fo_{92-94} to Fo_{88} . Olivines are invariably fractured, with the development of small amounts of associated secondary Mg-rich hydrous phases.

The chrome-spinels from the structurally higher seams, relative to those forming the structurally lower seams, are richer in Cr, Fe and Ti, and poorer in Mg and Al. In particular, MgO varies inversely with respect to TiO_2 . These compositional variations are reflected in the different colorations of the chrome-spinels: reddish-brown and black, respectively. In addition, the hollow cores and embayments of the spinels from the structurally higher seams are considered to be related to this compositional variation.

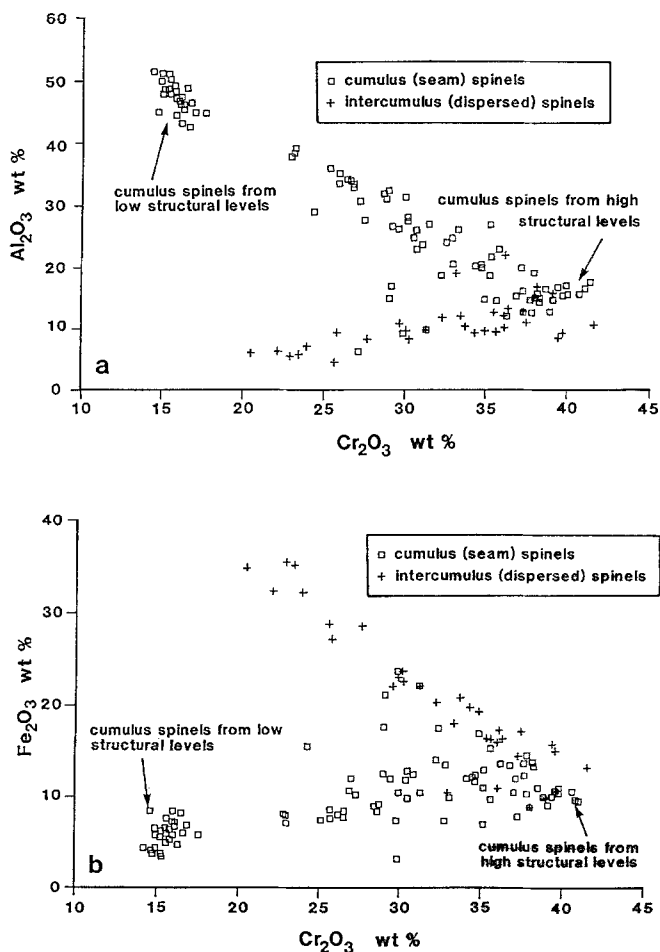


Fig. 6. Plots of Cr_2O_3 vs. Al_2O_3 and Fe_2O_3 for unit 1 chrome-spinels.

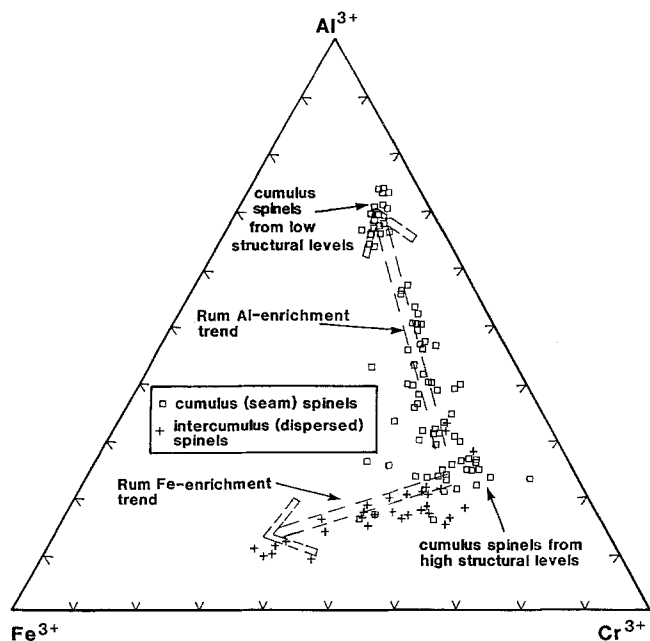


Fig. 7. Ternary plot of $\text{Al}^{3+} - \text{Fe}^{3+} - \text{Cr}^{3+}$ for unit 1 chrome-spinels. The Rum Al- and Fe-enrichment trends are from Henderson (1975)

Due to the extensive solid-solution compositional variation exhibited by minerals of the Spinel Group (Haggerty 1976), it is useful to plot mineral chemistry data on variation diagrams which involve ratios of up to four of the dominant cations. For the Skye chrome-spinels the most useful ratios are: $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$; $\text{Cr}/(\text{Cr} + \text{Al})$; and, $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$, which reflect the two cation sites within the spinel structure. Data are presented in plots of $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ against $\text{Cr}/(\text{Cr} + \text{Al})$ and $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$, respectively, in Fig. 5.

In terms of the trivalent cations, Fe^{3+} , Cr^{3+} , and Al^{3+} , the chrome-spinels within the seams, including those which occur as an included mineral in cumulus silicate phases, define a compositional trend of increasing Cr/Al with relatively little change in Fe^{3+} concentration, with increasing structural level in unit 1, whilst the dispersed (*i.e.* intercumulus) chrome-spinels from throughout unit 1 show relatively little variation in the ratio Cr/Al, but significant variation in the Fe^{3+} content. The high $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$, $\text{Cr}/(\text{Cr} + \text{Al})$ and $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})$ ratios of the intercumulus chrome-spinels are clearly illustrated in Fig. 5. These compositional distinctions are also evident in X-Y variation diagrams involving Al_2O_3 , Fe_2O_3 , and Cr_2O_3 (Fig. 6). Finally, variations in the amounts and relative variations of ratios of the trivalent cations may be discriminated in the ternary plot presented in Fig. 7. Also plotted on Fig. 7 are the Al- and Fe-trends exhibited by chrome-spinels from the layered ultrabasic rocks of Rum (see later).

Interpretation and conclusions

Current theories pertinent to the compositions exhibited by spinels (*s.l.*) in basic and ultrabasic rocks fall within two main categories. The first of these includes the spinel

whose composition is determined at the time of crystallization, and any compositional changes are caused either by variations in the chemistry of the parent magma, or by intensive thermodynamic parameters which influence the crystallization process (for example, pressure). The second category includes those spinels which crystallize with one (or, possibly, more than one) relatively uniform composition from a magma, and are modified, either by post-cumulus mineral-melt reactions (prior to complete crystallization of the parent magma), or by sub-solidus mineral-mineral reactions.

The sharp lower contacts of the chrome-spinel seams within unit 1 of the PS, lead to the conclusion that they formed by crystal settling and accumulation processes, during periods when olivine crystallization and/or fractionation (settling) were not significant (Irvine 1987). This interpretation is supported both by the mineral textures preserved within the seams (see earlier), as well as by the compositional evidence that the most aluminous chrome-spinels, both within the seams and dispersed as inclusions within cumulus minerals immediately above and below the seams, are associated with the most primitive olivine compositions (Fo_{92-94}), which presumably crystallized at the highest temperature. These chrome-spinels also have the highest MgO and lowest TiO_2 concentrations, consistent with a high temperature, magmatic origin (Fisk and Bence 1980) (Fig. 8; Table 1).

It may be argued that the Al-rich chrome-spinels are the result of reaction with intercumulus melt, but the available textural evidence strongly suggests that this reaction was prevented by their rapid isolation during the accumulation process (Fig. 4a). A more likely origin for the aluminous chrome-spinels is crystallization at a somewhat higher pressure, during ascent of the parent magma from its source region (Fisk and Bence 1980). Bell and Claydon (1992) concluded that the parental magma to the PS was ultrabasic in composition, especially enriched in magnesium and calcium, and that prior to the formation of the magma chamber associated with the development of the PS, the magma had precipitated, or at least was carrying, a significant quantity of olivine (and presumably spinel) primocrysts. The early

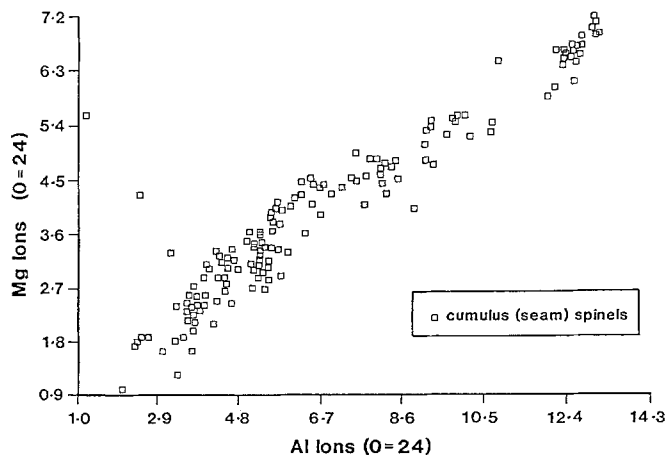


Fig. 8. Variation of Mg and Al for unit 1 chrome-spinels

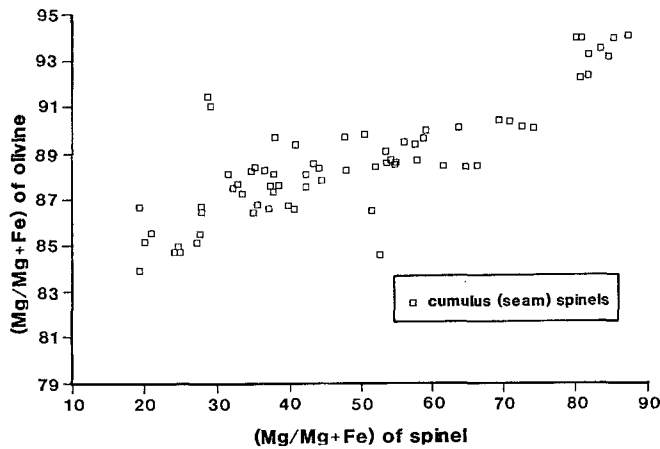


Fig. 9. Variation of magnesium content in co-existing olivines and chrome-spinels from unit 1

saturation of the magma with an Mg- and Al-rich spinel may indicate that the Al-content of the magma was also relatively high (see Donaldson et al. 1973).

In complete contrast, chrome-spinels within the structurally higher seams of unit 1 of the PS exhibit obvious reaction features (Fig. 4b) and their compositions are notably enriched in chromium, relative to aluminium. These loosely packed seams, associated with significant intercumulus material (plagioclase and/or olivine), permitted reaction between the chrome-spinels and intercumulus melts. Initially, such reactions will have taken the form of one or more cation-exchange reactions of the type: $\text{Fe}^{2+} \rightleftharpoons \text{Mg}^{2+}$; $\text{Cr}^{3+} \rightleftharpoons \text{Al}^{3+}$; and, $\text{Fe}^{3+} \rightleftharpoons \text{Cr}^{3+} + \text{Al}^{3+}$ (Haggerty 1976). Subsequent late-stage exchange reactions are also possible, resulting in changes in the concentration of titanium: $(\text{Ti}^{4+} + \text{Fe}^{2+}) \rightleftharpoons (\text{Cr}^{3+} + \text{Al}^{3+})$ (Haggerty 1976).

Figure 9 illustrates the sympathetic variation in magnesium number ($\text{Mg}\# = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$) of the chrome-spinels with that of the associated olivines. Significantly, chrome-spinels having the highest $\text{Mg}\#$ (= approx. 85) (and the lowest Cr-content, typically <15 wt%) are associated with the most magnesian olivine (Fo_{90-94}), whilst rocks which consist of olivine which is less forsteritic (Fo_{88}) contain chrome-spinels with values of $\text{Mg}\#$ between 10 and 40, and with the highest Cr-contents (up to 40 wt%). From the data presented in Fig. 9, it is clear that there is significant variation in $\text{Mg}\#$ of the chrome-spinels within rocks containing olivine in the limited composition range Fo_{88-90} . This inflection in the plot correlates with the appearance of cumulus plagioclase in the unit 1 rocks (Claydon and Bell 1992).

Clinopyroxene and orthopyroxene are the only other common major phases which are capable of extracting significant amounts of chromium from basic and ultrabasic magmas (K_d^{Cr} mineral/melt $\gg 1$). Both phases are virtually absent from the unit 1 rocks and, indeed, do not constitute major components of any part of the PS (Claydon and Bell 1992): as previously noted, the three dominant phases are olivine, chrome-spinel and plagioclase.

Application of the geothermometry equation of Roeder et al. (1979), based upon the mole fractions of Fe and Mg in co-existing olivines and spinels and the relative concentrations of the trivalent cations in the spinels (Tables 1 and 2), produces temperature estimates in the range 500–1500°C for the more aluminous chrome-spinels within the seams low down in unit 1. The less aluminous (and more chrome-rich) cumulus chrome-spinels from seams high up in unit 1 and the dispersed (i.e. intercumulus) chrome-spinels from the upper part of unit 1, however, record temperatures in the range 400–1400°C. The significant spread in, and relatively low values of, temperature recorded by many of the measured spinel-olivine pairs are such that they clearly reflect, at least in part, the post-magmatic cooling history of the PS. We therefore conclude that significant changes in $\text{Mg}\#$ of co-existing spinels and olivines have occurred subsequent to their precipitation at magmatic temperatures. Similar findings are reported by Henderson and Wood (1981) and Eales and Reynolds (1986) from the Rum and Bushveld intrusions, respectively.

The compositional trends noted from the chrome-spinels of the PS of the Cuillin Igneous Complex are in contrast to those deduced by Henderson and Suddaby (1971), Henderson (1975) and Henderson and Wood (1981) for chrome-spinels from the Eastern Layered Series of the Rum Igneous Complex (see Fig. 7) (Brown 1956). Two compositional trends were identified for Rum, and it was postulated that the more chromian chrome-spinels which occur as inclusions within cumulus silicate phases represent the initial spinel composition produced by crystallization from the parent magma, and that their preservation within such silicate phases prevented subsequent reaction with the magma. From this initial chrome-spinel composition the two divergent trends were produced, depending upon the local environment of the chrome-spinel. Henderson (1975) proposed that the trend of increasing Al-content resulted from reaction with olivine and plagioclase, or olivine and a melt rich in the plagioclase components, whilst chrome-spinels which were free to react with intercumulus melt over a considerable temperature interval were made over to a more Fe^{3+} -rich composition.

A detailed investigation of solid-solution mineral compositions within one of the main cyclic units (Unit 10) of the Eastern Layered Series of Rum established the presence of significant cryptic variation (Dunham and Wadsworth 1978). Each cyclic unit consists of the following cumulate sequence (from base to top): chrome-spinel, olivine \pm chrome-spinel, olivine + plagioclase, olivine + plagioclase + clinopyroxene. All of these silicate phases exhibit normal cryptic variation throughout most of the cyclic unit. However, at a small but significant distance below the top of the cyclic unit a reversal occurs within the cryptic variation and which continues up into the next (overlying) cyclic unit, before there is a return to normal cryptic variation. Consequently, the chrome-spinel seams occur within the cumulate pile occupying intervals in which there are rapid reversals of cryptic variation in the silicate phases (such as Fe-Na-rich minerals to Mg-Ca rich minerals, which

is in contrast to the more typical magmatic evolutionary trend). Dunham and Wadsworth (1978) attributed this reversal in cryptic variation to an introduction of new, more primitive magma into the chamber where the cumulates were forming, with this new primitive magma then mixing with any remaining differentiated magma.

More recently, Dunham and Wilkinson (1985) have identified compositional variations within the chrome-spinel seams of Rum, from Al-rich types at the bases of seams, through to Cr-rich types at the tops of seams. This observation led them to suggest that the more aluminous chrome-spinels were the first-formed crystals, after the influx of a new batch of magma into the chamber.

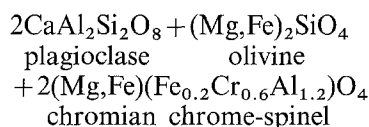
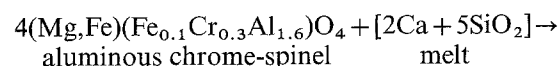
One important mineralogical difference which distinguishes the ultrabasic rocks of the Rum Igneous Complex from the unit 1 rocks of the PS on Skye is the almost ubiquitous presence of both cumulus and intercumulus crystals of clinopyroxene within the former (Dunham and Wadsworth 1978), with measured Cr₂O₃ contents of at least 0.65 wt% (Dunham and Wilkinson 1985). The presence of this phase offered an alternative site for chromium and may, at least partly, explain the fundamental difference in the Cr–Al–Fe partitioning during cumulus and post-cumulus processes with the two intrusions.

From studies of synthetic systems, predictable peritectic reactions have been inferred whereby spinel (*s.l.*) may crystallize with either olivine or plagioclase, but would cease crystallization once both minerals are on a common cotectic (Irvine 1967). Evidence from the chrome-spinels documented here, together with those studied from the Rum Igneous Complex (Henderson and Suddaby 1971; Henderson 1975; Henderson and Wood 1981; Bevan 1982; Dunham and Wilkinson 1985) clearly indicate that post-cumulus reactions have modified primary spinel compositions. Several cation-exchange reactions are involved due to the diverse solid-solution relationships which exist within the spinel group of minerals (i.e. across the three identified series; Irvine 1965, 1967; Haggerty 1976). In addition, such wide-ranging solid-solution effects will preclude the possibility of spinels ceasing to crystallize from a basic or ultrabasic magma by some form of peritectic reaction. Instead, a crystallizing spinel (*s.l.*) will exchange cations with its parent melt along some form of reaction line, possibly involving coexisting olivine and plagioclase, resulting in a gradually less aluminous spinel as plagioclase crystallizes, according to the reaction:

Al-rich chrome-spinel + melt → Cr-rich chrome-spinel + plagioclase

and where pyroxene is not an important crystallizing phase.

For the spinels documented here, the following semi-quantitative reaction shows reasonably good agreement with the compositions noted from the lower (more aluminous) and upper (more chromian) seams:



A decrease in Mg# and an increase in the TiO₂ content of the chrome-spinel accompanied the Al–Cr exchange during this peritectic reaction.

This equation is essentially the reverse of that proposed by Henderson (1975) to account for the Cr and Al trends in chrome-spinels from the Rum Igneous Complex, but is similar to that proposed by Dunham and Wilkinson (1985). Thayer (1946) proposed a similar explanation for the textural and compositional features of chromites and chrome-spinels within basic and ultrabasic rocks from La Constancia, Cuba. Ridley (1977) reported a similar reaction relationship for chrome-spinels within mildly alkaline to transitional basalts from the Early Tertiary lava field of the Inner Hebrides, Scotland.

The general equation just given explains the increased amounts of intercumulus plagioclase and the small but significant amounts of intercumulus olivine associated with the more chromian spinel seams. Essentially, the most chromian spinels are associated with rocks containing abundant intercumulus, or occasionally cumulus, plagioclase.

Figures 6 and 7 show that a few chrome-spinels exist which occur as inclusions within cumulus silicate phases (and therefore are considered to be part of the seam association) and which plot along the dispersed (i.e. intercumulus) Fe³⁺-enrichment trend. Such anomalous compositions either developed relatively late in the overall crystallization history and consequently were affected by conditions similar to those which caused the Fe³⁺-enrichment trend, but prior to being armoured by a silicate phase, or, alternatively, the spinel may not have been totally enclosed by its armouring silicate phase, and was subsequently exposed to the melt by fracturing of the silicate phase.

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