# Mineral chemistry of the Mull-Morvern Tertiary lava succession, western Scotland

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# ABSTRACT

The 1800 m thick preserved remnant of the Tertiary lava succession of Mull and Morvern consists of three basic mantle-derived magma types, with compositions varying from tholeiitic to mildly alkalic, and from picritic basalts to trachytes. This results in a similarly wide range in mineral compositions. Contrary to the suggestions of previous workers the mineral chemistry of the lava succession (in conjunction with published major and trace element chemistry) is strongly supportive of a fractional crystallisation origin for the more evolved lavas.

Resorped and regrown (with more basic material) plagioclase phenocrysts found in the more-evolved are indicative of magma mixing processes involving replenishment of an evolving magma chamber with more-basic magma. Lavas containing 15-20 vol.% plagioclase phenocrysts probably represent eruptions from the top of a magma chamber where flotation cumulates of plagioclase had developed. Fragmental phenocrysts found in some highly plagioclase phyric lavas (from near the top of the preserved lava succession) suggest that the eruption of lavas may have been explosive.

KEYWORDS: Tertiary lavas, fractional crystallization, plagioclase, Mull-Morvern, Scotland.

## Introduction

THE Tertiary volcanic rocks of western Britain have been extensively studied virtually from the inception of geology as a science. Indeed, in the latter years of the 19th century and early years of this century the memoirs of the Geological Survey of Scotland on these areas, helped to shape the way we understand igneous rocks (e.g. Harker, 1904; Bailey et al., 1924). In more recent years as our knowledge of mantle dynamics, melting processes and magmatic plumbing has improved, many studies have focused on the whole-rock geochemistry and petrogenesis of the lavas of the British Tertiary Igneous Province (e.g. Thompson et al., 1972; 1982; Esson et al., 1975; Morrison et al., 1980; Thompson and Morrison 1988; Wallace et al., 1994; Kerr et al., 1995; Kerr, 1995a,b). Despite this plethora of papers there are very few published mineralogical data on any of the lava successions within the British Tertiary Igneous Province (BTIP). This paper seeks to fill that void by focusing on the mineral chemistry and petrography of lavas from the Mull-Morvern succession.

## Background

The Mull-Morvern lava succession covers an area of 840 km<sup>2</sup>, and today reaches a maximum thickness, in any one section, of 1000 m on Ben More (Fig. 1). Most of the succession is composed of transitional (tholeiitic-alkali) basalts which vary from picritic basalts (>14 wt.% MgO) near the base of the succession, to basaltic-hawaiites nearer the top of the succession. More-evolved lavas (hawaiites, mugearites, and trachytes) are found mostly near the top of Ben More (Kerr, 1995b). However, the proportion of more-evolved lavas found within the Mull succession (Kerr, 1993a) is much less than in the Skye lava sequence (Thompson et al., 1972). In the centre of Mull, the lava succession is cut by an intrusive complex composed of numerous cone sheets, ring dykes and larger intrusive bodies, with a wide range of compositions from ultramafic to rhyolitic (Skelhorn et al., 1969). This central complex was formed in the later stages of the evolution of the Mull igneous centre and its emplacement led to the circulation of hot hydrothermal fluids within the lava



FIG. 1. Map of the Mull-Morvern Tertiary lava succession showing the locations, of sampled lava sections (X) and of the samples mentioned in the text and Table 2. (Numbers along the side of the map indicate Ordnance Survey 10 km grid squares).

succession, with the result that the lavas closest to the central complex are the most altered, while those on the western fringes of the island are generally the freshest (Bailey *et al.*, 1924; Walker, 1970).

Kerr (1995*a*) has divided the Mull lava succession into three successive main magma types. Most of the lavas belong to the Mull Plateau Group (MPG); this group lies below the Coire Gorm (CG) magma type, which is only found at the top of Ben More; finally the youngest lava type exposed on Mull is the Central Mull Tholeiite (CMT) type. These CMT lavas occur within the central calderas and in the southwest of Mull. This study is based on a representative set of the 500 samples from the Mull lava succession (Fig. 2), which have all been analysed for major and trace elements. A limited selection of this whole rock data is published in (Kerr *et al.*, 1995; Kerr 1995*a*,*b*) or is available from the author on request.

During this study no formal attempt has been made to petrographically subdivide the basalts of the Mull Tertiary succession. Rather the three magma types, outlined above, have been grouped into chemically distinctive magma sub-types (see Kerr, 1995a,b), and each of these sub-types possesses a variety of textural features.



FIG. 2. Representative plots of major elements (and Cr) against MgO for the MPG lavas. Data from Kerr (1993a).

A summary of the main petrographic features of the Mull-Morvern lavas is shown in Table 1. For a more extensive appraisal of the petrography of the Mull-Morvern lava succession the reader is referred to Kerr (1993*a*).

# **Analytical methods**

Mineral analyses on a representative subset of lavas have been carried out using two machines; Cambridge Instruments Geoscan Mark 2 (University of Durham), using energy dispersive spectrometry, with an electron beam diameter of  $5-10 \mu$ m, and a beam current of 5 nA at 15 kV; and a JEOL 733 Superprobe (University of St. Andrews), using wavelength dispersive spectrometry, with a beam diameter of 1  $\mu$ m, and a beam current of 20 nA at 15 kV.

The calibration of both these machines was checked daily by analysing minerals of known composition. Minerals from several of the samples were analysed on both machines and very similar results have been obtained in all cases. Representative mineral analyses are presented in Table 2.

## Olivine

Since the most evolved rocks lie within the central zone of intense alteration (where no fresh olivine

lavas
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1. Summary
TABLE

Rock type	Phenocrysts (phen.)	Groundmass (Gm) minerals and textures
Mull Plateau Group Basalts (>7 wt.% MgO; <4 wt.% To- tal alkalis)	Olivine phen. euhedral, subhedral, anhedral, skeletal $\leq 3 \text{ mm}$ altered along cracks & margins to serpentine, chlorite, oxides, iddingsite. zoned to more Fe rich margins. Enclose deep brown Crspinels (<0.3 mm). At lower whole rock MgO, labradorite phens. are found (2–3 mm).	Texture varies from fine grained (<0.3 mm) to doleritic ( $\geq$ 1 mm). Unaltered pale brown augite never form phens, but varies from ophitic, to sub-ophitic & granular. It also forms oikiocrysts (ophimottled texture). Variably altered olivines & anhedral-subhedral labradorite; sub-ophitic-to-granular Fe-Ti oxides, with rare apatite
Mull Plateau Group Basaltic-Hawaiites (5-7 wt.% MgO; 4-5 wt.% Total al- kalis)	Labradorite lath shaped microphens ( $\leq 2.5$ mm), oscillatory (normal) zoned. Occasionally these are partially resorbed & regrown, with the crystal cores being less Ca-rich than the regrown margins => implies magma mixing (see discussion section).	Mostly fine grained (<0.25 mm; occasionally up to 0.5 mm), both gm and phenocryst plagioclases can be aligned (fluxion texture). Gm consists of andesine-labradorite laths; poikilitic, to sub ophitic & granular, pale brown–lilac augite; altered olivine; anhedral Fe-Ti oxides & apatite needles being more common than in the MPG basalts
Mull Plateau Group Hawaiites (4–5 wt.% MgO; 5–6 wt.% Total alkalis)	Sparse rounded, resorbed & zoned and esine-labradorite phens. ( $\leq 3$ mm; occasionally up to 10 mm). Several flows contain ~15 vol.% of these phens. and they may represent flotation cumulates (see discussion section).	Fine to medium grained ( $\leq 0.4-0.75$ mm). Gm consists of andesine with fluxion texture; euhedral to subhedral Fe-Ti oxide (more abundant than basaltic-hawaiite); pale brown-to-lilac, ophitic-to-granular augite; abundant apatite needles & minor biotite.
Mull Plateau Group Mugearites (3-4 wt.% MgO; 6-8 wt.% Total alkalis)	Andesine-oligoclase phens. $4-5$ mm. Several flows contain $15-20$ vol. % plagioclase, which show evidence of resorption, occasional macrophens. of plag up to $15$ mm long. Euhedral microphens. of Fe-Ti oxides.	Fine grained gm (mostly <0.15 mm) with interstitial Fe-Ti oxide and some alkali feldspar (anorthoclase); granular altered olivine; apatite needles; pale brown-lilac, sub-ophitic cpx, & small amounts of biotite; all set in a mass of sub-aligned plagioclase laths.
Mull Plateau Group Benmoreites-Tra- chytes (<3 wt.% MgO; >8 wt.% To- tal alkalis)	Essentially aphyric with occasional albite and sodic alkali-feldspar phenocrysts.	Occur in the central greenschist alteration zone, thus the small grain size makes petrographic descriptions difficult. The gm consists of subaligned albite laths; interstitial sodic alkali feldspar; pale green cpx; apatite needles; abundant Fe-Ti oxide octahedra & probable biotite.
Staffa Magma sub- Type - tholeiitic member at the base of the MPG	Sparsely porphyritic ( $\leq 1 \text{ mm}$ ) with bytownite being the main phase and occurring as laths or angular fragments; occasional augite microphens displaying sector zoning; as well as olivine phens. in more primitive lavas.	Fine grained ( $<0.3$ mm) gm composed of labradorite laths; sub-ophitic to granular, pale brown cpx; interstitial Fe-Ti oxides; serpentine, chlorite or iddingsite pseudomorphs after granular olivines.
Coire Gorm type (all basaltic 7–12 wt.% MgO)	Once contained $(2-3 \text{ mm})$ euhedral olivine phens. but now they are pseudomorphed by sepentine, chlorite and oxides, some contain Cr-spinels. In more evolved lavas labradorite laths $(1-2 \text{ mm})$ predominate.	Textures are similar to MPG basalts. Grain size varies from <0.2-1 mm, and gm consists of granular, sub-ophitic or occasionally oikiocrystic cpx; plagioclse laths & anhedral oxides All lavas lie in the greenschist facies alteration zone, therefore secondary minerals like epidote, chlorite oxides & clays are common.
Central Mull Tho- leiites (4-8 wt.% MgO)	Two types of lavas based on phens.: 1) Labradorite-bytownite phyric $(4-10 \text{ mm})$ , occasionally in the form of glomeroporphyritic clusters and sometimes broken angular fragments. These phens. can comprise up to $30-40$ vol.% of the lava (cf. Donaldson, $1977$ - Skye dykes) (see discussion section); 2) Andesine-labradorite phyric (up to 5 mm), show some evidence of resorbtion and regrowth.	All lavas lie in the greenschist-facies alteration zone. The grain size of the groundmass varies from <0.2–1 mm and consists of labradorite-andesine laths; granular to sub-ophitic, pale brown cpx; interstitial to sub-ophitic Fe-Ti oxides.



FIG. 3. Plots of forsterite content against minor element variation for olivines from the MPG. The error on NiO is approximately 10% at 0.3 wt.%, and the detection limit is 0.05 wt.%.

has been found), all of the olivines analysed during the present study are from basaltic and hawaiitic lavas. Fig. 3 shows that the Mg/(Mg+Fe<sup>2+</sup>) ratio (forsterite content - Fo) of the analysed samples ranges from Fo<sub>89</sub>, in the most Mg-rich basalt, to Fo<sub>59</sub> in the evolved basaltic-hawaiite. The MPG olivines are similar to those from the Skye Main Lava Series (SMLS), where Williamson (1979), reported basalts with olivines up to Fo<sub>90</sub> and hawaiites with olivines of Fo<sub>60</sub>. Williamson (1979) was also able to analyse fresh olivines from the trachytes of the SMLS, with compositions of ~Fo<sub>20</sub>.

Where the margins of the olivines are not altered, zoning to lower Fo contents can often be observed. This usually only spans a few %Fo. However, olivines with quite marked compositional zoning can sometimes be found, e.g. sample BM10 which has a composition of  $Fo_{85}$  at the core and  $Fo_{78}$  at its rim.

In Fig. 3*a*-*d*, Fo content has been used as a differentiation index, to assess how minor elements in olivines from the MPG vary as the host magma becomes more evolved. MnO shows a reasonable scattered negative correlation with

Fo content, varying from ~0.1 wt.% in the most Mg-rich olivines, to 0.7 wt% in the more Fe-rich olivines (Fig. 3a). Williamson (1979), in his study of the SMLS, noted a similar range in values and a negative correlation between MnO and Fo content. Simkin and Smith (1970) examined the minor element variations shown by olivines which had crystallised in different environments. They suggested that the distribution of Mn in olivine was dependent on the bulk composition of the magma, and whether or not Fe-Ti oxide was a co-precipitating phase. Mn<sup>2+</sup> substitutes for Fe<sup>2+</sup> and, since the contents of both these elements in the host magma increase with differentiation (Fig. 2), this substitution becomes more feasible with increasing differentiation.

 $Cr_2O_3$  (Fig. 3b) exhibits quite a scattered pattern when plotted against Fo content. However a scattered positive correlation is still discernible. The highest  $Cr_2O_3$  contents (0.25 wt.%) occur in some of the most forsteritic olivines, while the lowest values (<0.1 wt.%) can be found in olivines from the basaltic-hawaiites. Deer *et al.* (1992) have pointed out  $Cr^{3+}$  in olivines normally resides in minute plates of

Sample BNI0 BM10 BR5BR5BM1BM5MR9MR9BM2MR2MR2MR2MR2MR2MR2MR3BM4BCH3BCH3BCH3Lithology BBBBBBBBBBBBBBBBHLithology BBBBBBBBBBBBBBBBHLithology BBBBBBBBBBBBBBHLithology BBBBBBBBBBBBBHS102395539513176736533876351336263703362637193626Cr4010.350.060.080.020.030.010.010.030.010.000.030.000.00Cr4010.350.390.300.330.300.160.140.140.130.010.000.02Cr4010.350.390.330.330.330.330.330.330.330.340.340.340.340.340.34Cr4010.350.450.450.450.450.450.450.450.490.49Cr4010.350.330.330.330.330.330.330.330.340.340.340.34																					
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Sample	BM10	BM10	BR5	BR5	BM1	BM5	MR9	MR9	BM2	MR2	MR2	MR2	MR2	MR2	AM5	BM4	BCH2	BCH2	BR19	BR19
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Litholo£	y B	В	B	B	в	В	B	B	В	в	В	В	B	B	В	B	В	B	Η	Н
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	SiO,	39.65	39.51	40.57	40.07	40.46	37.70	39.21	37.85	39.65	39.75	37.89	39.21	37.67	36.63	38.76	36.31	38.86	37.03	36.26	37.07
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Al_2\tilde{O}_3$	0.15	0.28	0.00	0.09	0.20	0.08	0.42	0.15	0.30	0.10	0.22	0.12	0.00	0.00	0.11	0.07	0.03	0.01	0.00	0.66
FeC $14.63$ $14.48$ $11.54$ $13.31$ $12.62$ $24.69$ $21.13$ $19.20$ $14.12$ $16.38$ $24.14$ $16.80$ $25.76$ $31.33$ $18.93$ $29.77$ $19.51$ $28.60$ $22.19$ $31.75$ $0.49$ $0.49$ $0.49$ $0.11$ $0.11$ $0.11$ $0.11$ $0.12$ $0.20$ $0.33$ $0.33$ $0.33$ $0.33$ $0.34$ $0.28$ $0.34$ $0.28$ $0.34$ $0.38$ $0.33$ $0.34$ $0.29$ $0.36$ $0.26$ $0$	$Cr_2O_3$	0.06	0.00	0.53	0.00	0.08	0.02	0.07	0.08	0.16	0.16	0.11	0.13	0.10	0.00	0.03	0.00	0.06	0.02	0.00	0.00
	FeO	14.63	14.48	11.54	13.31	12.62	24.69	21.13	19.20	14.12	16.38	24.14	16.80	25.76	31.33	18.93	29.97	19.51	28.60	32.19	30.87
NiO         0.26         0.39         0.32         0.16         0.12         0.20         n.d.         0.17         0.04         0.19         0.18         0.21         0.12         0.11         0.11         0.11         0.11         0.11         0.11         0.11         0.11         0.11         0.11         0.12         0.11         0.12         0.11         0.12         0.11         0.12         0.11         0.12         0.11         0.14         0.25         0.33 <th< td=""><td>MnO</td><td>0.37</td><td>0.42</td><td>0.18</td><td>0.36</td><td>0.29</td><td>0.30</td><td>0.33</td><td>0.30</td><td>0.12</td><td>0.20</td><td>0.55</td><td>0.20</td><td>0.33</td><td>0.53</td><td>0.21</td><td>0.50</td><td>0.28</td><td>0.45</td><td>0.49</td><td>0.59</td></th<>	MnO	0.37	0.42	0.18	0.36	0.29	0.30	0.33	0.30	0.12	0.20	0.55	0.20	0.33	0.53	0.21	0.50	0.28	0.45	0.49	0.59
	NiO	0.26	0.39	0.32	0.16	0.12	0.20	n.d.	0.14	0.28	0.33	n.d.	n.d.	0.17	0.04	0.19	0.18	0.21	0.12	0.11	0.00
Ca0 $0.29$ $0.28$ $0.30$ $0.37$ $0.29$ $0.37$ $0.29$ $0.37$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ $0.30$ <td>MgO</td> <td>44.29</td> <td>44.45</td> <td>46.98</td> <td>45.30</td> <td>45.83</td> <td>36.43</td> <td>38.73</td> <td>41.05</td> <td>44.73</td> <td>42.73</td> <td>36.06</td> <td>43.02</td> <td>35.27</td> <td>30.93</td> <td>41.77</td> <td>31.78</td> <td>40.41</td> <td>33.46</td> <td>29.48</td> <td>29.75</td>	MgO	44.29	44.45	46.98	45.30	45.83	36.43	38.73	41.05	44.73	42.73	36.06	43.02	35.27	30.93	41.77	31.78	40.41	33.46	29.48	29.75
Sum $99.71$ $99.71$ $99.70$ $100.74$ $99.70$ $100.32$ $99.80$ $100.10.32$ $99.80$ $100.10.32$ $99.80$ $100.10.32$ $99.70$ $99.87$ $100.31$ $99.45$ $99.67$ $100.16$ $99.25$ CationsperfouroxygensSi $1.00$ $0.99$ $1.00$ $1.00$ $1.00$ $1.00$ $1.00$ $1.00$ $0.09$ $0.00$	CaO	0.29	0.28	0.30	0.33	0.37	0.29	0.62	0.32	0.29	0.32	0.47	0.29	0.35	0.33	0.25	0.38	0.30	0.42	0.50	0.63
Cationsper fourxygensfourxygensSi1.000.991.001.001.001.001.000.991.000.991.000.991.000.991.000.991.000.991.000.991.000.00<	Sum	77.66	76.66	100.74	99.70	100.32	99.80	100.58	99.10	<b>99</b> .66	99.98	99.70	99.87	<b>86</b> .66	99.83 1	00.31	99.45	1 79.66	100.16	99.25	99.94
Si [100 0.99 1.00 1.00 1.00 1.00 1.00 1.01 0.99 1.00 1.00	Cations	per	fouroxy£	cus																	
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Si	1.00	0.99	1.00	1.00	1.00	1.00	1.01	0.99	1.00	1.00	1.00	1.00	1.00	1.00	0.99	0.99	1.00	0.99	1.00	10.1
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Al	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Fe <sup>2+</sup> 0.31         0.31         0.24         0.28         0.26         0.55         0.45         0.42         0.30         0.36         0.57         0.72         0.40         0.68         0.42         0.64         0.74         0           Mn         0.01	C L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Fe <sup>2+</sup>	0.31	0.31	0.24	0.28	0.26	0.55	0.45	0.42	0.30	0.36	0.53	0.36	0.57	0.72	0.40	0.68	0.42	0.64	0.74	0.69
Ni 0.01 0.01 0.01 0.01 0.00 0.00 0.00 0.0	Mn	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01
Mg       1.66       1.67       1.73       1.69       1.43       1.48       1.57       1.68       1.60       1.42       1.53       1.39       1.26       1.59       1.25       1.34       1.21         Ca       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.02       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01	ïz	0.01	0.01	0.01	0.00	0.00	0.00	I	0.00	0.01	0.01	I	I	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	Mg	1.66	1.67	1.73	1.69	1.69	1.43	1.48	1.57	1.68	1.60	1.42	1.63	1.39	1.26	1.59	1.29	1.55	1.34	1.21	1.23
Total 3.00 3.00 2.99 2.99 2.99 3.00 2.99 3.01 3.00 2.99 2.99 3.00 2.99 3.00 3.01 3.00 3.00 3.00 2.97 Fo% 84.4 84.5 87.9 85.8 86.6 72.4 76.6 79.1 84.9 81.7 72.7 82.0 70.9 63.8 79.7 65.4 78.7 67.6 62.0 6	Ca	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
Fo% 84.4 84.5 87.9 85.8 86.6 72.4 76.6 79.1 84.9 81.7 72.7 82.0 70.9 63.8 79.7 65.4 78.7 67.6 62.0 6	Total	3.00	3.00	2.99	2.99	2.99	3.00	2.99	3.01	3.00	2.99	2.99	3.00	2.99	3.00	3.01	3.00	3.00	3.00	2.97	2.99
	Fo%	84.4	84.5	87.9	85.8	86.6	72.4	76.6	79.1	84.9	81.7	72.7	82.0	70.9	63.8	7.97	65.4	78.7	67.6	62.0	63.9

TABLE 2a. Representative olivine compositions from the Mull lava succession

A.C. KERR

300

B - basalt; H - hawaiite

A3B	TM	$\begin{array}{c} 52.10\\ 0.45\\ 0.45\\ 7.25\\ 7.25\\ 0.07\\ 0.01\\ 0.03\\ 9.34\\ 0.01\\ 0.02\\ 0.01$	>
W4 C	MT (	1.78 0.67 0.67 0.228 0.019 0.019 0.021 0.021 0.010 0.010 0.010 0.021 0.010 0.021 0.021 0.021 0.021 0.022	2
191	T S	14         2 <th2< th="">         2         <th2< th=""> <th2< th=""></th2<></th2<></th2<>	
) BN		49 17 17 17 10 10 10 10 10 10 10 10 10 10 10 10 10	
MR29	Σ	50.36 1.85 1.85 9.16 9.16 9.16 9.24 1.27 9.24 1.29 0.00 0.01 0.02 0.02 0.02 0.02 0.02 0.02	• > .
BR19	Н	48.09 3.19 4.70 8.52 8.52 9.23 1.51 1.82 1.53 1.82 0.09 0.01 0.00 0.00 0.09 0.09 0.09 0.09	
BR27	B-H	$\begin{array}{c} 47.38\\ 3.60\\ 0.00\\ 0.35\\ 0.35\\ 0.02\\ 0.92\\ 0.92\\ 0.92\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.02\\ 0.00\\ 0.02\\ 0.01\\ 0.01\\ 0.01\\ 0.02$	222
BR27	B-H	$\begin{array}{c} 48.97\\ 2.51\\ 3.32\\ 0.00\\ 10.41\\ 10.88\\ 0.07\\ 0.07\\ 0.08\\ 0.07\\ 0.$	
BM8	в	$\begin{array}{c} 50.03\\ 1.41\\ 1.41\\ 0.12\\ 0.16\\ 0.17\\ 0.34\\ 0.17\\ 0.34\\ 0.04\\ 0.18\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.03\\ 0.01\\ 0.01\\ 0.01\\ 0.03\\ 0.01$	
BM8	В	49.86 1.25 1.25 0.01 0.18 0.18 0.13 0.18 0.04 0.01 0.01 0.01 0.02 0.02 0.02 0.02 0.02	
BM8	В	$\begin{array}{c} 50.09\\ 1.26\\ 1.26\\ 0.00\\ 0.09\\ 0.76\\ 0.76\\ 0.76\\ 0.76\\ 0.76\\ 0.76\\ 0.09\\ 0.00$	-
MR2	В	50.54 1.28 3.23 0.77 0.77 0.17 0.17 0.17 0.17 0.17 0.17	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
MR2	В	50.47 1.23 7.22 7.22 7.22 7.22 0.31 99.66 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.23 0.23 0.23 0.23 0.23 0.23 0.23	
BM51	В	$\begin{array}{c} 47.48\\ 2.97\\ 2.97\\ 2.97\\ 11.18\\ 11.57\\ 11.57\\ 0.65\\ 99.97\\ 0.09\\ 0.00\\ 0.00\\ 0.00\\ 0.00\\ 0.04\\ $	2
BM2	В	$\begin{array}{c} 48.83\\ 1.94\\ 1.94\\ 1.94\\ 0.73\\ 0.73\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.25\\ 0.02$	
BM5	В	$\begin{array}{c} 51.12\\ 0.97\\ 0.97\\ 2.29\\ 0.49\\ 0.34\\ 0.34\\ 0.16\\ 0.16\\ 0.16\\ 0.16\\ 0.16\\ 0.10\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.01\\ 0.02\\ 0.01\\ 0.02\\ 0.01\\ 0.02\\ 0.02\\ 0.02\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.01\\ 0.02$	2
BM5 rim	в	50.55 1.31 2.95 0.31 8.46 0.22 0.33 99.61 1.89 0.04 0.01 0.01 0.01 0.02 0.02 0.02 0.03 0.02 0.01 0.02 0.03 0.02 0.01 0.02 0.02 0.23 0.24 0.27 0.27 0.27 0.27 0.27 0.27 0.27 0.27	
BM5 core	В	52.36 0.88 0.88 7.57 7.57 7.57 0.14 15.65 1.55 21.21 0.22 0.22 0.22 0.02 0.02 0.02 0.0	;
BR5	y B	50.14 1.56 3.93 9.07 8.33 0.31 14.50 0.31 14.50 1.86 0.70 0.70 0.70 0.70 0.70 0.70 0.70 0.7	2
Sample	Litholog	SiO <sub>2</sub> TiO <sub>2</sub> Cr <sub>2</sub> O <sub>3</sub> FeO MnO MnO MnO Mn Mn Mn Mn Mn Mn Mn Mn Mn Mn Mn Wn Wn Wn Wn Wn Wn Wn Wn Wn Wn Wn Wn Wn	

TABLE 2b. Representative clinopyroxene compositions from the Mull lava succession

B - basalt; H - hawaiite; M - mugearite; T - trachyte; CMT - Central Mull tholeiite

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# THE MULL TERTIARY LAVAS

Sample	BR5	MR9	MR9	BM51 p core	BM51 g mass	MR2	BR22	BR27	BR19	MR37 p rim	MR37 ] p core g	MR29 2 mass	BM61	BM61	W4 p core	W4 g mass	CA3B p core	CA3B p rim	CA3B g mass
Lithology	В	в	В	В	В	в	В	B-H	Н	Н	H	M	Т	Т	SMT	SMT	CMT	CMT	CMT
SiO <sub>2</sub>	50.17	52.50	56.97	51.13	55.10	51.47	52.03	54.52	55.36	55.99	55.50	63.61	64.55	65.36	46.10	50.41	45.69	49.03	49.89
$TiO_2$	0.05	0.13	0.25	0.00	0.23	0.08	0.23	0.22	0.26	0.27	0.08	0.12	0.05	0.05	0.05	0.08	0.00	0.04	0.09
$Al_2 \tilde{O}_3$	30.49	28.47	25.86	30.21	26.16	30.27	29.51	27.53	27.02	25.84	27.13	23.55	19.45	19.64	34.40	31.18	35.54	31.06	31.32
FeO	0.81	0.62	0.68	0.45	1.33	0.55	0.72	0.58	0.53	1.02	0.50	0.52	0.43	0.29	0.09	0.51	0.52	0.56	0.80
MnO	0.02	0.06	0.00	0.13	0.00	0.00	0.00	0.00	0.01	0.06	0.00	0.06	0.00	0.01	0.07	0.00	0.00	0.00	0.05
MgO	0.39	0.30	0.17	0.39	0.63	0.03	0.18	0.34	0.15	0.34	0.29	0.00	0.00	0.00	0.09	0.21	0.20	0.21	0.11
CaO	13.90	12.98	9.22	14.25	11.23	13.04	13.55	11.04	9.58	9.55	10.55	4.13	0.17	0.25	17.60	14.26	17.90	15.52	14.75
$Na_2O$	3.66	4.40	6.20	3.38	5.02	4.00	3.76	5.28	5.81	5.88	5.55	7.09	2.64	5.56	1.29	3.29	1.42	2.74	3.18
$K_2O$	0.10	0.09	0.31	0.00	0.24	0.19	0.16	0.15	0.31	0.37	0.32	1.61	12.70	8.92	0.05	0.18	0.04	0.05	0.05
Sum	99.59	99.64	99.67	99.94	99.94	99.63	100.14	99.66	99.02	99.31	99.92	00.78	66.66	100.08	99.74	100.12	101.31	99.21	100.24
Cations no	r oiaht	UPDUVO																	
Si	2.30	2.40	2.57	2.33	2.51	2.35	2.37	2.48	2.52	2.54	2.51	2.80	2.95	2.95	2.13	2.29	2.08	2.27	2.27
Li	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Al	1.64	1.54	1.38	1.63	1.40	1.63	1.58	1.47	1.45	1.39	1.45	1.23	1.05	1.05	1.87	1.67	1.90	1.69	1.69
$Fe^{2+}$	0.03	0.02	0.03	0.02	0.05	0.02	0.03	0.02	0.02	0.04	0.02	0.02	0.02	0.01	0.00	0.02	0.02	0.02	0.03
Mn	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.03	0.02	0.01	0.03	0.04	0.00	0.01	0.02	0.01	0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01
Ca	0.68	0.64	0.45	0.70	0.55	0.64	0.66	0.54	0.47	0.47	0.51	0.21	0.01	0.01	0.87	0.69	0.87	0.77	0.72
Na	0.32	0.39	0.54	0.30	0.44	0.35	0.33	0.46	0.51	0.52	0.47	0.62	0.23	0.49	0.12	0.29	0.13	0.25	0.28
К	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.10	0.74	0.51	0.00	0.01	0.00	0.00	0.00
Total	5.01	5.01	5.00	5.00	5.01	5.00	5.00	5.00	5.01	5.00	5.00	4.98	5.01	5.02	5.00	4.99	5.01	5.01	5.00
An	67.4	61.7	44.3	70.0	54.5	63.6	66.0	53.2	46.8	46.3	51.2	21.9	0.8	1.2	88.0	8.69	87.2	75.6	71.7
Ab	32.0	37.8	53.9	30.0	44.1	35.3	33.1	45.9	51.4	51.6	46.9	68.0	23.8	48.1	11.7	29.1	12.5	24.1	28.0
Or	0.6	0.5	1.8	0.0	1.4	1.1	0.9	0.9	1.8	2.1	1.9	10.2	75.3	50.7	0.3	1.0	0.2	0.3	0.3
Abreviatic	ns as T	able 2b	except;	- TMS ;	- Staffa	Magma	sub-Ty]	pe; p co	re – ph	enocryst	core; p	rim – p	henocry	st rim;	g mass	- ground	lmass felo	lspar	

TABLE 2c. Representative feldspar compositions from the Mull lava succession

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exsolved Cr-spinels rather than within the crystal lattice. Since the olivines from the most primitive basalts contain more Cr-spinel inclusions (Table 1), the higher  $Cr_2O_3$  of the more forsteritic olivines may be due to the electron beam striking a small exsolved plate of Cr-spinel. Although Cr normally exists in the  $Cr^{3+}$  state, it can, under reducing conditions, also exist as  $Cr^{2+}$ . In this 2+ state it could conceivably substitute for Fe<sup>2+</sup> which has a similar atomic radius. Henderson (1982) reported an average partition coefficient for Cr in olivine of 2.1.

The chief control on the Cr content of olivine (in the form of exsolved chromite), seems to be the abundance of Cr in the magma from which the olivine crystallises. As the MPG lavas evolved further their Cr content falls substantially (Fig. 2) thus explaining why olivines from MPG hawaiites contain less  $Cr_2O_3$ . This fall in whole rock  $Cr_2O_3$ is because Cr is compatible, not only in Cr-spinel, but also in clinopyroxene.

NiO shows a reasonable positive correlation with Fo content (Fig. 3*c*), and varies from ~0.45 wt.% in high MgO basalts, to <0.1 wt.% in the hawaiites. The distribution of Ni, like Mn, is dependent upon the bulk composition of the melt (Simkin and Smith, 1970). Ni is highly compatible in forsteritic olivine (*K*d - 14; Henderson, 1982) substituting readily for the similarly sized Mg<sup>2+</sup> cation.

On Fig. 3d it can be seen that the lowest CaO values (~0.2 wt.%) are generally found in the more forsteritic olivines, with higher values (~0.6 wt.%) in the Fe-rich olivines. Simkin and Smith (1970) proposed that the crystallisation environment played a major role in determining the Ca content of olivines, with deep crystallising plutonic rocks having lower CaO (<0.1 wt.%) in their olivines, than extrusive and shallow intrusive rocks (>0.1%). This therefore implied a pressure control on the CaO content of olivines, with the larger Ca cation finding it more difficult to substitute for the smaller Mg, Ni and Mn cations at higher pressures. However, experimental studies by Jurewicz and Watson (1988) have determined Ca partition coefficients of olivine in a melt at varying temperatures, pressures and  $f_{O_2}$ . They proposed that the Ca content of an equilibrated olivine is chiefly dependent on both the CaO and the FeO content of the melt. High FeO values result in olivines with higher CaO contents. It was also observed that  $f_{O_2}$  has no direct effect on CaO content, and although temperature does not greatly effect Ca

partitioning, it does influence the CaO/MgO distribution.

The general increase in CaO in the less forsteritic olivines from the MPG, may reflect increasing CaO in the melt, up to the onset of plagioclase fractionation at  $\sim 7-8$  wt.% MgO (Fig. 2). However, modelling of fractional crystallisation (Kerr, 1993*a*) suggests that the higher CaO contents of the more fayalitic MPG olivines, are more likely to be the result of the higher Fe contents of the host magmas, as proposed by Jurewicz and Watson (1988).

# Clinopyroxene

The pyroxene quadrilateral diagram (after Morimoto, 1988) summarises the compositional ranges for the various types of Mull lavas outlined in Table 2 (Fig. 4). The MPG pyroxenes range in composition from diopside and diopsitic augite  $(Ca_{46}Mg_{45}Fe_9)$  in the most basic lavas, to hedenbergite  $(Ca_{46}Mg_{22}Fe_{32})$  in the trachytes. Fig. 4 also shows a field for the pyroxene compositions from the Skye lava succession (Thompson, 1974; Williamson, 1979). The compositions of MPG pyroxenes are similar to the SMLS, however, the pyroxenes from the MPG trachytes are more calcic than those from the SMLS trachytes.

The more Fe-rich pyroxenes found in the MPG basalts probably crystallised at a late stage from residual, more evolved magma. In order to test this proposal, the cores and rims of several pyroxene crystals have been analysed (e.g. BM5; Table 2*b*). The rims contain more FeO,  $TiO_2$ ,  $Al_2O_3$ , MnO and  $Na_2O$  than the cores, along with less  $SiO_2$ , MgO, CaO and  $Cr_2O_3$ . These intra-lava chemical trends reflect crystallisation from an increasingly evolved magma. Similar inter-lava trends have also been found (see below)

In addition to the MPG analyses, pyroxenes from the Staffa Magma sub-Type (SMT), and the Central Mull Tholeiites (CMT) have also been analysed. Fig. 4 shows that the SMT and CMT pyroxenes (in common with other tholeiites) generally contain lower Ca than the more alkaline MPG basalts. The pyroxenes in the SMT sample (W4) range from  $Ca_{42}Mg_{47}Fe_{11}$  to  $Ca_{42}Mg_{41}Fe_{17}$ , while in the CMT (sample CA3A) the two analysed pyroxenes have an average composition of  $Ca_{43}Mg_{45}Fe_{12}$ .

 $Al_2O_3$  and  $TiO_2$  (Fig. 5*a*,*b*) behave in a similar fashion to each other with increasing differentia-





FIG. 4. Clinopyroxene compositions from the Mull lava succession plotted on a quadrilateral diagram, along with the range of compositions for pyroxenes from the SMLS (Williamson, 1979). The compositional fields are taken from Morimoto (1988).

tion [lower Mg/(Mg+Fe+Mn+Ca)], and Fig. 5f reinforces this point. This covariance of Al and Ti in a suite of pyroxenes from genetically related rock types, is due to the coupled substitution;

$$(Mg, Fe)^{VI} + 2Si^{IV} \rightarrow Ti^{VI} + 2Al^{IV}$$

Other Hebridean Tertiary lavas (e.g. the SMLS, Williamson, 1979) and intrusive bodies (e.g. the Shiant Isles Sill, Gibb, 1973 and the Trotternish Sill, Skye, Gibson, 1988) also display a similar positive correlations between AI and Ti. Fig. 5f however, also reveals that there is excess AI available for other substitutions, and these probably include;

 $(Mg, Fe)^{VI} + Si^{IV} \rightarrow AI^{VI} + AI^{IV} \text{ and,}$  $(Mg, Fe)^{VI} + Si^{IV} \rightarrow (Fe^{3+}, Cr)^{VI} + AI^{IV}$ Larsen*et al.*(1989)

The products of these coupled substitutions are known as the 'Tschermaks' pyroxene components, and can account for the large scatter in Al content, when compared to Ti (Figs. 5b and a respectively). Herzberg and Chapman (1976) showed that the 'tschermakite' component in clinopyroxene from a spinel lherzolite increased with increasing temperature. The pyroxenes from the lower temperature evolved lavas of the MPG generally plot closer to the Ti:2Al line (Fig. 5f) than the higher temperature basalts. This observation supports the conclusions of Herzberg and Chapman (1976). Similarly, Larsen *et al.* (1989) in their study of the Tertiary basalts from the Scoresby Sund region, East Greenland, noted that the groundmass pyroxenes (which would have crystallised at lower temperatures) generally contained less of the tschermaks component than the pyroxene phenocrysts.

Pyroxenes from one of the trachytic lava flows of the MPG contain significantly lower levels of Ti and Al than are observed in the hawaiites and mugearites. Plagioclase begins to fractionate from the MPG magmas at ~8-9 wt.% MgO, while Fe-Ti oxide will fractionate below ~5-6 wt.% MgO (Kerr, 1993a). Significant quantities of Al will therefore be removed from the magma before Ti is extracted. However, the basaltic pyroxenes have 2Al>Ti and, as has already been demonstrated, this excess Al which contributes to the tschermaks component of the pyroxenes will be removed before the Al involved in the couple substitution with Ti. Therefore, the coupled substitution (Mg, Fe)<sup>VI</sup> +  $2Si^{IV} = Ti^{VI} + 2Al^{IV}$ is dependent upon the quantity of Ti available. Fractional crystallisation of Fe-Ti oxides from the MPG trachytes will lower the concentration of Ti in the melt, and so will impair the coupled substitution of Ti and Al.

Sample C4 (analyses connected by a line on Fig. 5a and b) contains pyroxenes with more Ti and Al than the rest of the MPG pyroxenes. Kerr, 1993b has shown that this lava belongs to a sub-type of the MPG, which may have been



FIG. 5a-e. Minor element variations in pyroxenes plotted against 100Mg/(Mg+Fe+Mn+Ca). The line connecting two of the analyses on figures a and b. is explained in the text; **f.** plot of atomic Ti vs. Al.

contaminated with a small-fraction-melt from the lithospheric mantle. As a result they are enriched in the incompatible trace elements (including  $TiO_2$ ). Therefore the higher concentrations of Ti and Al in the pyroxenes of this lava, simply reflects the more Ti rich nature of the original melt.

 $Cr_2O_3$  varies from over 1 wt.% in the pyroxenes of some of the least evolved samples, to virtually zero in the hawaiites, mugearites, and trachytes, although the pyroxenes from the basalts themselves also span a similar range of  $Cr_2O_3$ contents (Fig. 5c). Cr probably exists as a 3+ cation in these magmas and so it can, along with Al, substitute for Si and Fe (or Mg) to form a tschermaks molecule (see above). The Cr content of the pyroxenes falls rapidly at <40% En (Fig. 5c), suggesting that the Cr content of the liquid has been rapidly depleted by the fractionation of Cr-spinel and clinopyroxene. A similar feature was noted by Gibson (1988) in the pyroxenes of the Tertiary Trotternish sills from Skye.

MnO (Fig. 5d), displays quite a wide scatter, with values varying from 0.6 wt.% in the trachytes to <0.1 wt.% in some of the basalts. As in olivine, Mn readily substitutes for Fe<sup>2+</sup> within the pyroxene structure and, as a result, a negative correlation between Mn and Mg/(Mg+Fe+Mn+Ca) can be observed with increasing Mn and Fe in the melt. The scatter on this diagram may be due to the fact that Mn can substitute for Fe<sup>2+</sup>, not only in pyroxene, but also in olivine and Fe-Ti oxides. The Na<sub>2</sub>O content of pyroxene (Fig. 5e) shows a broad tendency to increase with progressive differentiation of the host rock, from <0.3 wt.% in the most basaltic lavas, to 1.2 wt.% in the more evolved magmas. This may well reflect the coupled substitution,

$$(Mg^{2+})^{VI} + (Ca^{2+})^{M2} = (Al^{3+}, Fe^{3+})^{VI} + (Na^{+})^{M2}$$

since  $Fe^{3+}$  and Na increase within the melt as differentiation proceeds.

The minor element variation in the pyroxenes from the Staffa Magma sub-Type and the CMT span the same compositional range as the more magnesian pyroxenes of the MPG. An exception to this seems to be Na, with the pyroxenes from the SMT and the CMT containing quite low levels (<0.3 wt.%) in comparison with the MPG. This fact reflects the more tholeiitic character of the magmas from which the pyroxenes crystallised.

# Feldspar

Fig. 6*a* summarises the compositional range exhibited by the feldspars of the Mull lava succession, in terms of the An, Ab and Or components. The MPG feldspars vary from  $An_{74}$  Ab<sub>25</sub> Or<sub><1</sub> (bytownite) in the most magnesian basalts (MR2 and BM8) to  $An_{<1}$  Ab<sub>24</sub> Or<sub>75</sub> (sanidine) in the groundmass of the trachytes (BM61). Williamson (1979) reported that the plagioclases from the SMLS ranged in composition from  $An_{73}$  Ab<sub>26</sub> Or<sub><1</sub> in the basalts, to  $An_2$  Ab<sub>67</sub> Or<sub>31</sub> in the trachytes.

and rims of several plagioclase phenocrysts reveals that, except where the crystals have suffered resorption and regrowth of fresh material, they seem to show normal zoning.

Using the TRACE 3 program (Nielsen, 1988), Kerr, 1993*a* has calculated the composition of the first plagioclase to crystallise from the bulk rock composition. For the most part these values agree well with the measured plagioclase phenocryst compositions in the flow, however in some of the flows it has been observed that the plagioclase phenocrysts have maximum An values 2-3%more than their calculated composition, and so might be xenocrystic in origin. Since these crystals are only slightly more basic than the calculated equilibrium plagioclase, their disequilibrium compositions will have a negligible effect on the whole-rock composition.

The plagioclase phenocrysts in the SMT and the CMT are generally more calcic than those of the MPG (Fig. 6a). The SMT can contain up to  $An_{88}$ , while the plagioclase phenocrysts of the CMT range up to  $An_{87}$ , and are zoned to less calcic compositions at their margins. The groundmass plagioclase found in these lavas falls within the compositional range of plagioclases from the MPG. Highly calcic plagioclase phenocrysts and cognate xenoliths, largely composed of calcic plagioclase, have been found in dykes from NW Skye (Donaldson, 1977), and more recently from inclined sheets from the Loch Scridain area of Mull (Preston and Bell, 1997).

Figs. 6b and c shows the variation of MgO and  $TiO_2$  with An content. Within the feldspar structure, Mg can substitute for Ca, and Ti for Al (Deer *et al.*, 1992). The abundance of each of these elements in the feldspars of the Mull lava succession seems to be broadly dependent on the  $TiO_2$  and MgO content of the melt from which they crystallised. The CMT and the SMT lavas contain lower whole-rock MgO contents, despite their high An plagioclase, and so the Mg content of the plagioclases is also low.

The highest Ti contents found in the MPG feldspars is 0.3 wt.% in the hawaiites. However, with increasing fractionation of Fe-Ti oxides, the Ti content of the melt starts to fall, and this is reflected in the lower Ti contents of feldspars from the mugearites and trachytes. The  $K_2O$  content of the feldspars (Fig. 6*a*) similarly displays a marked tendency to increase with increasing fractionation, and this parallels the increasing K content of the melt.



FIG. 6a. Feldspar compositions of the different rock types from the Mull lava succession. b and c MgO and TiO<sub>2</sub> variation in the feldspars from the Mull lava succession plotted against percentage Anorthite content.

## **Oxide** minerals

It is convenient to divide the oxide minerals into two groups; (1) octahedral Cr spinel crystals which are enclosed, or partially enclosed by euhedral to subhedral olivines; and (2) irregular crystals of Fe-Ti oxide within the groundmass of the basalts, which can also occur as subhedral to euhedral crystals in the more evolved lavas.

## Cr-spinels enclosed in olivines

Cr-spinel is only found enclosed, or partially enclosed, within olivine crystals in the most basic lavas (Table 1). It is therefore highly likely that Cr-spinel was the first phase to crystallise from many of the more picritic, Cr-rich basalts and, it is probable that these Cr-spinels provided sites at which olivine nucleation could occur (Kerr, 1993*a*). However, if these spinels were only partially enclosed within olivines, reaction with more differentiated melts in the later stages of crystallisation could have led to the formation of more Cr- and, in some cases, more Fe<sup>3+</sup>-rich spinels (Fig. 7*a*). i.e.

## Al-rich chrome-spinel + melt $\rightarrow$

Cr-rich chrome spinel + plagioclase (Ridley, 1977; Bell and Claydon, 1992)

Thus the three MPG Cr-spinels which contain the most Al, may well represent the composition of the primary unaltered Cr-spinel, while those with more Cr than Al, have perhaps undergone reaction with more residual melts.

Bell and Claydon (1992) in a study of Crspinels in from the Tertiary Cuillin intrusive complex, Skye, observed that the cumulus (seam) spinels were more enriched in Al than those dispersed throughout the rest of the intrusion. They, like Ridley (1977), proposed that the primary character of the spinels had been Alrich, and they attributed the lower Al contents of the dispersed spinels, to a similar reaction with the residual melt. Fig. 7b shows the fields for cumulus and dispersed spinels from Bell and Claydon (1992) in terms of FeO/(FeO+MgO) and  $Cr_2O_3/(Cr_2O_3+Al_2O_3)$ , along with Cr-spinels from the present study, and also suggests that the spinels in the MPG basalts which contain lower-Al values, may well have reacted with the residual melt.

Pressure also exerts a strong control on the relative distribution of Cr and Al in early



FIG. 7. Plots showing compositional data from the Cr-spinels found in the MPG basalts; a variation of Fe<sup>3+</sup>, Al and Cr. The shaded area represents the compositional range of Cr-spinels from the SMLS (Williamson, 1979). b FeO/(FeO+MgO) against Cr<sub>2</sub>O<sub>3</sub>/(Cr<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>). Also shown are the fields for cumulus and dispersed spinels from the Cullin intrusion (Bell & Claydon, 1992). c. Cr+Al vs. Ti (O = 32) for Cr-spinels from the basalts of the MPG and SMLS (Williamson, 1979).

crystallising spinels (Fisk and Bence, 1980; Dick and Bullen, 1984), with higher pressures favouring the formation of more Al-rich spinels. Dick and Bullen (1984) suggested that this may well be due to the pressure-dependence of the partition coefficient of Cr, which varies from 1, at depths appropriate to melt segregation, to the generally accepted higher values at lower pressures. Thus the Al-rich chrome-spinels, which have been found in the basalts of the Small Isles, the SMLS, the Cuillin intrusion, and now also in the basalts of the MPG, may have crystallised at quite considerable depths. This conclusion is entirely consistent with the major element data, which suggest that these basalts last equilibrated at pressures around 9 kbar (Thompson, 1974; Kerr, 1993a).

Figs. 7*a,b* also suggest that during the reaction, Al-rich chrome-spinel + melt  $\rightarrow$ \_Cr-rich chrome spinel + plagioclase, other substitutions involving both Fe<sup>2+</sup> and Fe<sup>3+</sup> are important. A negative correlation between Cr+Al and Ti in the MPG spinels (Fig. 7*c*) suggests that late stage exchange processes (possibly Cr<sup>3+</sup> + Al<sup>3+</sup>  $\rightarrow$  Ti<sup>4+</sup> + Fe<sup>2+</sup>; Haggerty, 1976), with melts enriched in Ti, have also played a role in modifying the composition of the primary spinels. Corroded relics of Cr-spinel, showing progressive replacement by itaniferous magnetite, have been found in the least fractionated lava flows of the Lower Fionchra Formation, Isle of Rum (Emeleus, 1985).

#### Magnetite and ilmenite within the groundmass

The compositional variation of these oxide minerals within the MPG is summarised in Fig. 8, along with some oxide compositions from SMLS basalts (Williamson, 1979). Illmenites, which sometimes occur as exsolution lamellae in magnetite, as expected contain abundant Ti and  $Fe^{2+}$  along with variable (0-10 wt.%) amounts of Fe<sup>3+</sup>. Opaque minerals of the magnetite series make up the rest of the groundmass oxides. In Fig. 8a,b it can be seen that these magnetites span quite a wide compositional range, and this range seems to be dependent on the bulk composition of the melt from which they crystallised. The highest Cr contents occur in magnetites from the MPG basalts (Fig. 8b > 0.1 wt.% Cr<sub>2</sub>O<sub>3</sub>), while magnetites from the more evolved lavas contain virtually no Cr at all. These two observations tally with the whole-rock chemistry of the lavas, i.e. basalts frequently contain >500



FIG. 8a, b. Plots of Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> against TiO<sub>2</sub> for the groundmass oxide minerals of both the MPG and the SMLS (from Williamson, 1979). All the symbols except filled diamonds (ilmenites) represent magnetite or titano-magnetite. (Magnetites from hawaiites are denoted by an 'h' beside the sample point).

ppm Cr, and more evolved lavas usually have <100 ppm.

The more basaltic MPG lavas contain magnetite with >20 wt.% TiO<sub>2</sub>, while the one analysed magnetite from an hawaiite contains ~30 wt.% TiO<sub>2</sub>. As a result these oxides can be called 'titano-magnetites'. However, as Fig. 8a reveals, the magnetites from more evolved lavas (mugearites and trachytes) show a steadily declining Ti content with increasing differentiation. This fall in the Ti content of the magnetites, is explained by the fractionation of Fe-Ti oxides at lower whole rock MgO contents. It is interesting to note that this decrease in Ti in magnetite is matched by a concomitant increase in Fe<sup>3+</sup>, leading to an excellent negative correlation between the two variables. This increase in Fe<sup>3+</sup> with increasing differentiation, is presumably a reflection of the more oxidised state of the last melts to crystallise from these more evolved magmas.

# **Concluding discussion**

The petrographic observations and the mineral chemistry discussed in this paper, strongly suggest that the processes of fractional crystallisation have played a fundamental role in the development of the Mull Plateau Group, the Coire Gorm magma type and the Central Mull Tholeiites. This particular line of evidence for fractional crystallisation is commensurate with the substantial evidence from whole rock geochemistry (Fig. 2 and Kerr, 1993a) for fractional crystallisation. This may seem like rather an obvious statement, however, it needs to be viewed in its historical context. Previous to this study (Kerr, 1993a,b, 1995a,b; Kerr et al., 1995) the only significant published work on the Mull Plateau group lavas was that of Beckinsale et al. (1978), in which they state; "fractional crystallisation ...... has not been a major factor in the production of evolved magma compositions [on Mull]". It is therefore imperative that the clear evidence for fractional crystallisation observable in the mineral chemistry is stressed.

Nevertheless, the results presented in this paper show that other magma chamber processes have also been important during the evolution of the Mull lava succession; not least among these is the evidence for magma mixing processes (e.g. Sparks and Huppert, 1984). Magma mixing is quite difficult to observe in the chemistry of a suite of lavas unless mixing occurs between acidic and basic end magmas. However, petrographic indications of magma mixing between basaltic and slightly more evolved (basaltic hawaiites and hawaiites) magmas is observable. One of the chief lines of evidence for this magma mixing is the partial resorption of plagioclase phenocrysts (in some of the more evolved lavas) probably as a result of the influx into the chamber of a more basic (hotter) magma. This resorption produced partially rounded plagioclase, on which morebasic plagioclase subsequently regrew from the mixed (more basic) magma, leading to reversely zoned crystals. Sometimes, the plagioclase phenocrysts are resorped but little regrowth is observed, possibly because the magma was erupted (and so cooled quickly) very shortly after resorption, so allowing little time for regrowth to occur. This magma mixing cannot be readily detected in the major or trace element chemistry, as it can in some British Tertiary suites (e.g. Marshall, 1984). This is probably because mixing was not between magmas of widely

varying compositions, e.g. rhyolite and Fe-Tirich basalt, but was between magmas which were closer in composition.

Another important magma chamber process which can be inferred from the petrography of the more-evolved hawaiites and mugearites is highlighted by the occurrence of some flows which contain 15 to 20 vol.% plagioclase phenocrysts. It seems likely that these represent flotation cumulates at the top of a magma chamber. The origin of highly plagioclase phyric mid-ocean ridge basalts has also been explained in terms of flotation cumulates (Bryan, 1983), as have plagioclase phyric basalts found with in the Deccan Traps continental flood basalt province (Cox and Mitchell, 1988).

As was noted above, the more basic plagioclase phenocrysts found in the Central Mull Tholeiite lavas are generally more calcic than their Mull Plateau Group counterparts (Fig. 6a). These phenocrysts can comprise up to 30–40% of the lava, form euhedral to subhedral lath-shaped crystals, and often form glomeroporphyritic crystal clusters. Several of these lavas appear to be partially composed of more angular fragments of calcic plagioclase, sometimes with strained and kinked twinning.

Donaldson (1977) studied a suite of tholeiitic gabbroic dykes from Skye, which are compositionally akin to these Central Mull Tholeiite lavas (known as the Preshal More type on Skye). These dykes contain abundant megacrysts and xenoliths of anorthite/bytownite plagioclase. He proposed that the phenocrysts concentrated in shallow chambers, through which fresh magma, containing calcic plagioclase phenocrysts was pulsing. These low-alkali, high-CaO magma batches may have left their plagioclase phenocrysts in the chamber, before erupting as the sparsely porphyritic Preshal More magma type. Donaldson (1977) showed that although these phenocrysts had crystallised from low-alkali, high CaO magmas, the phenocrysts and the matrix in each dyke were therefore not strictly cognate. In a recent study of gabbroic xenoliths from the Loch Scridain tholeiitic sills on Mull (which are of the Central Mull Tholeiite type) Preston and Bell (1997) reached a similar conclusion.

The high abundance of plagioclase phenocrysts in some the Central Mull Tholeiite lavas, also suggests that they similarly did not crystallise from the groundmass in which they now reside. It is probable that these phenocrysts formed by concentration in a magma chamber, but unlike Skye where feldspar-phyric tholeiitic (Preshal More) lavas did not reach the surface, on Mull they obviously did. One of the reasons for this may be that the Mull lavas were erupted with explosive force. Evidence for such explosive activity comes from the fragmental nature of some of the plagioclase crystals. This extra pressure would have enabled more viscous plagioclase phyric magmas to be expelled from the chamber, with some forming lava flows and perhaps the more explosive eruptions forming ash-crystal tuffs. Similar explosive tuffs have recently been described from the inter-lava red bole horizons with the SMLS and the MPG (Emeleus *et al.*, 1996).

The lavas of the Staffa Magma-sub type which occur at, or near, the base of the Mull lava succession (Kerr, 1995b) also contain microphenocrysts of highly calcic plagioclase ( $An_{84-88}$ ). These commonly occur as angular fragments which may be grouped together to form glomerocrysts, occasionally along with pyroxene phenocrysts. The fragmental nature of some of these plagioclase phenocrysts suggests that they may have been torn off the walls of a magma chamber, or conduit, during eruption.

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