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**PETROGENESIS OF THE TERTIARY LAVAS OF THE ISLE OF SKYE,
N.W. SCOTLAND**

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ABSTRACT

The Tertiary lavas of Northern Skye, N.W. Scotland comprise a pile of flat-lying, predominantly basaltic, volcanic flows. The lavas are the earliest products of the igneous activity on Skye, later manifestations including the gabbroic Cuillin complex and the Red Hills granites. The activity occurred from approximately 65 Ma to 50 Ma (Palaeocene to Eocene) within a continental environment.

The lava pile can be divided compositionally into three magma-types, the Skye Main Lava Series (SMLS), lavas of which constitute the majority of the pile, and the less abundant Preshal Mhor (PM) and Fairy Bridge (FB). This study concerns the petrogenesis of the three magma-types.

The three magma-types have a normal basaltic mineralogy; phenocrysts include olivine, plagioclase and sparse clinopyroxene; groundmasses comprise varying proportions of olivine, plagioclase, clinopyroxene, and titanomagnetite.

A typical flow comprises four zones: a basal amygdaloidal layer, a massive central portion possibly showing columnar jointing, a purple rotted amygdaloidal layer, and a capping red or brown bole.

The fractional crystallisation of the SMLS was a two-stage process initially involving the precipitation of olivine ($\pm$ minor Cr-spinel), and later fractionation of olivine and plagioclase $\pm$ clinopyroxene.

The majority of the lavas assimilated some lower crustal Lewisian granulite en route to the surface. The most basic lavas are the most contaminated.

Major and trace element modelling suggests that the SMLS magmas were generated by 15 % melting, at an above-average mantle potential temperature, within the spinel-garnet transition zone at a depth of $\sim$ 100 km. The magmas subsequently last equilibrated with mantle host rocks at 15 kb ($\sim$ 45 km).

LONG ABSTRACT

The igneous rocks of the Isle of Skye, which lies off the north west coast of Scotland between 57° and 57°45' N, are part of the British Tertiary Igneous Province. The plateau lavas are the earliest products of igneous activity on Skye, later manifestations including the gabbroic Cuillin complex and the Red Hills granites. The activity occurred from approximately 65 Ma to 50 Ma (Palaeocene to Eocene) within a continental environment. The present study is concerned with the area north of 57°18' N, throughout which the Tertiary plateau lavas crop out, covering an area of approximately 1500 km². The lavas are preserved in a shallow, faulted, oval basin with a long axis running north-west/south-east parallel to a dyke swarm. The lava field is inferred to have a maximum thickness of 760m, though the maximum exposed in any one section is 335m at the Storr. The Tertiary basaltic lavas occur at the top of the stratigraphic succession in Skye. The Skye lava pile has previously been divided into five stratigraphic units, based on field identification of inter-basaltic sediments. These sediments were taken to indicate a cessation in volcanic activity, thus enabling division of the lava pile into time units. The present study has found no compositional or petrographic evidence to support the previous stratigraphic division of the lavas.

The Skye Main Lava Series (SMLS) lavas range in composition from picritic-basalt to trachyte but the majority are basaltic. The principal basaltic phenocryst phase is olivine, which often contains microphenocryst inclusions of Cr-spinel. A large proportion of the lavas also contain plagioclase phenocrysts. Clinopyroxene and titanomagnetite occur in minor amounts, principally in the more evolved lavas. One example of a lava with a high modal proportion of large (up to 1.5 cm) plagioclase phenocrysts was analysed in the present study. The trachybasalts are texturally and mineralogically similar to the basalts, but their equivalent phases are generally more evolved. The trachytes have phenocrysts of augite and

sub-calcic augite, ilmenite, plagioclase, alkali feldspar, and biotite; and groundmasses comprise plagioclase, alkali feldspar, biotite, Fe oxides, and secondary minerals. The Preshal Mhor (PM) lavas are basaltic and are petrographically similar to the SMLS basalts. The Fairy Bridge (FB) lavas are basaltic, and are petrographically analogous to the SMLS basalts and the Preshal Mhor lavas which have phenocrysts of olivine (with Cr-spinel inclusions) $\pm$ plagioclase $\pm$ clinopyroxene.

The olivines are primarily subhedral and occur within the groundmasses and as individual phenocrysts, as monomineralic glomerocrysts, and less frequently, bi or trimineralic glomerocrysts with plagioclase, clinopyroxene, or titanomagnetite. The phenocrysts vary in composition from Fo₈₈ to Fo₆₂. The groundmass crystals range in composition from Fo₈₂ to Fo₄₀ with the majority falling into two groups between Fo₆₂₋₅₄ and Fo₈₂₋₇₂. The plagioclase laths occur within the groundmasses and as individual phenocrysts, as monomineralic glomerocrysts, and occasionally associated with olivine or augite in biminerale glomerocrysts. The phenocrysts vary in composition from anorthite (An₉₀) in the picritic basalts to alkali feldspar (An₂₀) and orthoclase (Or₂₅) in the trachytes. The groundmass laths vary in composition from An₇₉ to Or₄₀. Clinopyroxene phenocrysts are sparse in the Skye lavas. They are usually subhedral to anhedral, and occur both individually, and as monomineralic and biminerale glomerocrysts with olivine or plagioclase. The phenocrysts and groundmass crystals are predominantly salite, but there are occasional crystals of augite and, in the trachytes, sub-calcic augite. Octahedral Fe oxides are common in the groundmasses of the basalts and occur as phenocrysts in the trachytes.

There is evidence for alteration of most SMLS, PM and FB lavas by one or more of the following processes: iddingsitization of olivine, chloritization of augite, and zeolitization of groundmass minerals. Amygdaloidal lavas are common and have vesicles infilled by zeolites, quartz, or calcite.

Olivine is the most abundant phenocryst phase, having modal proportions varying from 0 to 23.38%. Plagioclase phenocryst proportions range from 0 to 20.90% (with the exception

of a big-feldspar basalt, 30.50%), and proportions of clinopyroxene phenocrysts are between 0 and 3.45%.

The Skye lavas can be divided into three magma-types on the basis of compositional differences: Skye Main Lava Series (SMLS) lavas, Preshal Mhor lavas (PM) and Fairy Bridge lavas (FB).

The SMLS is the predominant magma-type in the Skye pile. PM lavas have been identified in the Ramascaig, Beinn Totaig, and Bracadale stratigraphic units. Previously PM lavas had only been found in the highest stratigraphic unit, the Osdale group. FB lavas, previously only found in the Ramascaig stratigraphic unit, have been identified in the higher Beinn Totaig and Osdale units.

The SMLS lavas comprise hy-normative and ne-normative samples, and are thus termed transitional basalts. Distinct compositional variations exist between the most hy-normative and the most ne-normative SMLS lavas, between which there is a continuum of compositions. The continuum is represented by inter-element correlations in samples which are at a similar stage of evolution, and by planar arrays in the data-set as a whole. PM lavas are tholeiitic basalts. They have high CaO and low total alkalis (K_2O+Na_2O) relative to the SMLS. FB lavas are tholeiitic basalts. They have subtle major and trace element differences from SMLS and PM basalts.

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The SMLS, PM, and FB magma-types all have characteristic REE profiles: LREE-enriched relative to chondrite, LREE-depleted relative to chondrite, and flat, respectively.

The SMLS lavas have a wide range of initial $^{87}Sr/^{86}Sr$ (0.70312-0.70532). The PM and FB lavas are more restricted compositionally, with $^{87}Sr/^{86}Sr$ - 0.70300-0.70336 and $^{87}Sr/^{86}Sr$ - 0.70355-0.70375 respectively. A pseudochron is not detectable from the Sr isotope data of the Skye lavas. The SMLS lavas have a wide range of initial $^{143}Nd/^{144}Nd$ (0.513012-0.512106). The initial $^{143}Nd/^{144}Nd$ ratios of the PM lavas range from 0.512981-0.512976 and

those of the FB lavas from 0.512715-0.512945. A pseudoisochron is not detectable from the Nd isotope data of the Skye lavas.

The SMLS and FB basalts show greatest compositional affinities to within plate basalts, whereas the PM basalts are most like ocean floor basalts. Comparison with other British Tertiary Igneous Province, North Atlantic Tertiary Province and Continental Flood Basalt Province lavas has shown that the SMLS hy-normative lavas have the greatest compositional affinities with Antrim lower basalts, Icelandic, Kirwan (Antarctica), Kenyan and Siberian basalts. Whereas the ne-normative lavas are compositionally most similar to Canna plateau basalts, Icelandic, Snake River Plain (USA) and Hawaiian basalts. The Skye PM lavas are compositionally most similar to Mull PM lavas and plume, enriched (E type) MORB. The Skye FB lavas show some affinities with a sample from the Rockall trough but no direct analogies have been found in the literature.

A typical Skye lava flow comprises four zones: a basal amygdaloidal layer, a massive, possibly columnar jointed central portion, a purple amygdaloidal upper layer, and a capping red or brown bole (fossil soil horizon). The Skye boles are assumed to be sub-aerially weathered basaltic flow tops. The presence of secondary minerals indicates most of the lavas have undergone some post-consolidation alteration. Alteration of the lavas is attributed to their burial in a rapidly accumulating lava pile throughout which hot fluids were circulating. The amount of alteration to which the lavas have been subjected was measured in two ways: H_2O^+ of the sample and modal proportion of groundmass secondary minerals. There is a good positive correlation between the two measures of alteration. In a study of a lava flow-bole profiles the elements were ordered from most enriched (least soluble) to most depleted (most soluble). The sequence is Pb, Th, Nb, Zr, TiO_2 , Zn, Y, Fe_2O_3 , Cu, Al_2O_3 , Rb, Ga, Cr, Ni, Co, SiO_2 , Sr, V, Ba, Na_2O , MgO, and CaO. The relative solubility rankings of the elements for the Skye boles are comparable to those determined for Deccan laterites, although the former are obviously much less altered than the latter. Secondary mineralogies show that olivine is pseudomorphed by

iddingsite, bowlingite, chlorite, Fe oxides, and occasionally serpentine, talc, and carbonates; calcic plagioclase is replaced by zeolites, and pyroxene is occasionally replaced by chlorite and hematite. The boles show almost complete replacement of their primary basaltic mineralogy by clay minerals, but relict phenocryst textures are observed occasionally. Elements which are soluble during alteration form the main constituents of the amygdaloidal zeolites.

Two-element variation diagrams show that there is an inflection in the SMLS data-set at approximately 7 wt% MgO, thus necessitating consideration of the compositional evolution as a two stage process. From inspection of two-element variation diagrams and mixing calculations the first stage of SMLS crystallisation is consistent with the removal of 14% olivine ($\pm$ Cr-spinel), or olivine ($\pm$ Cr-spinel) and clinopyroxene in the proportions 90:10 from a parental magma with 13 wt% MgO. The second stage of crystallisation appears to have involved removal of 39 % olivine and plagioclase in the proportions 25:75, or 45% olivine, plagioclase and clinopyroxene in the proportions 23:50:27 from a magma with 7 wt% MgO. The PM data are consistent with evolution of PM lavas by removal of 15% olivine, or 21% olivine and plagioclase in approximately cotectic proportions (30:70) from a magma with 9.5 wt% MgO. The FB lavas are too restricted in composition to perform mixing calculations which would give meaningful results. Two-element variation diagrams and the similarity to the major element compositions of the SMLS suggests that they evolved by the removal of 10% olivine from a magma with 13.5 wt% MgO. The SMLS and FB basalts lie across the ol-cpx-plag plane (which approximates to the position of a low pressure thermal divide) in the normative basalt tetrahedron, PM basalts only plot on the Si-rich side of the ol-cpx-plag plane. In the normative basalt tetrahedron SMLS primitive basalts are scattered parallel to the ol-cpx join suggesting that the compositional scatter could be primary. Allowing for solid solution effects the primitive-evolved compositional trends of SMLS in the basalt tetrahedron are consistent with the crystallisation of olivine alone. At one-atmosphere pressure the SMLS and

FB basalts plot predominantly in the olivine field with some samples on or near the ol-plag cotectic, whereas the PM basalts plot at the ol-plag-cpx ternary eutectic. From consideration of changes in phase-field relations with increasing pressure it was concluded that, at high pressure, SMLS and FB whole rock and groundmass/liquid compositions could have been in equilibrium with clinopyroxene. SMLS whole rock-groundmass tie lines do not parallel the bulk compositional evolutionary trend, thus demonstrating that the phenocrysts present in the samples, i.e. olivine and plagioclase, were not responsible for the compositional evolution. In the absence of suitable mineral-liquid density contrasts the deviation of the olivine-plagioclase modal ratio from cotectic proportions was attributed to initial fractionation of olivine, followed by crystallisation of olivine and plagioclase without fractionation, either because of magmatic turbulence or compensated crystal settling. This is consistent with ideas regarding the magmatic plumbing system of the Skye lavas, i.e. many dykes cutting the continental crust.

Assuming that SMLS magmas were fractionating olivine and may have just begun to fractionate plagioclase at the time of their eruption their temperature at one-atmosphere would have been $\sim 1215^{\circ}\text{C}$. Assuming that PM lavas were fractionating olivine, plagioclase, and possibly clinopyroxene at the time of their eruption their temperature at one-atmosphere pressure would have been $\sim 1200^{\circ}\text{C}$. If, as suggested, FB lavas were precipitating olivine ($\pm$ Cr-spinel), they would have had an eruptive temperature of $\sim 1250^{\circ}\text{C}$.

On a plot of $^{86}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ some of the SMLS plot within the array of values which can be derived from the mantle, others plot outside it because they have $^{143}\text{Nd}/^{144}\text{Nd}$ ratios which are too low. From this it is concluded that the asthenospheric mantle was an important source in the generation of the Skye lavas. The Ba/TiO_2 ratio of samples was found to be a good indicator of the amount of lithospheric material contaminating the asthenospheric magmas. Samples with $\text{Ba}/\text{TiO}_2 > 90$ were taken to be contaminated by lithospheric material whereas samples with $\text{Ba}/\text{TiO}_2 < 90$ were taken to be uncontaminated by lithospheric material.

SMLS lavas under olivine control, i.e. > 7 wt% MgO, were calculated back to a potentially primary MgO content of 15 wt%, by the addition of olivine. It was found that the correlation coefficient patterns of the contaminated and uncontaminated samples were similar to each other, and to the whole 15 wt% data-set, indicating that the contamination had not had a major effect upon the compositional characteristics of the SMLS data-set.

Mixing calculations were performed using an average uncontaminated lava, an average contaminated lava, an average olivine composition (to compensate for the difference in the MgO content of the two data-sets), and a range of crustal compositions. All assemblages had solutions with sum of squares of residuals of less than one. For a set amount of contamination, here 5%, the percentage contributions of lithospheric material are perceived to be quite variable because they are dependent on the relative concentrations of the element in the magma and the contaminant. Thus, it is not necessary to invoke separate movement of elements to explain the presence of apparently large contributions from lithospheric components, when individual elements are considered. Consideration of the results of major, trace, and RE element mixing calculations in conjunction with isotopic data led to the conclusion that Lewisian granulite facies crust was the most likely contaminant of the SMLS lavas.

The stack of lava flows on Skye and an associated dyke swarm (presumed to feed to the lava flows) indicates that the magmatism was episodic through a tectonically stressed crust - ideal conditions for the assimilation of crustal material by basaltic magma.

The broad positive correlation between Ba/TiO_2 and MgO has led to the conclusion that for lavas with >7 wt% MgO the amount of contamination is related inversely to the degree of evolution.

Most of the SMLS magnesian (> 9 wt% MgO) lavas do not have geochemical or petrographic primary magma characteristics. Assuming that the most magnesian olivine phenocrysts were first formed from the parental SMLS melt, a parental composition of 14 wt% MgO was identified.

Inter-element correlations in the artificial 15 wt% MgO data-set were found to result from variation in degree of mantle melting; this led to the conclusion that scatter in the SMLS data-set resulted from secondary processes such as fractional crystallisation and crustal contamination acting upon a primary melting trend in which the high Si, low-incompatible element lavas were generated by 1.6 times the percentage melting of the low-Si, high-incompatible element lavas.

The SMLS magmas last equilibrated at a pressure of 15 kb and a temperature of 1380°C. This corresponds to a mantle potential temperature of 1430°C (considerably higher than the average mantle potential temperature of 1280°C proposed by McKenzie and Bickle, 1988). The above geophysical data predict a melt thickness of 2 km, a melt fraction of 15 %, and a depth where melt generation began of ~ 100 km (just within the garnet zone). Inversion of the Skye lavas REE data, using a new technique of McKenzie and co-workers, calculated that SMLS lavas represented the smallest melt thickness and degree of melt at the greatest depth (1.9 km, 10%, 110-80 km), FB lavas represented a larger melt thickness with a slightly higher degree of melt at a shallower depth (2.8 km, 11%, 105-70 km) and PM lavas resulted from the greatest amount and degree of melt at the shallowest depth (5.49 km, 15%, 65-95 km).

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Dedicated to my parents

John Scarrow (1914-1981) and Kay Scarrow (1928-1990)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter outlines the main characteristics of continental flood basalts (CFBs) and the ideas relating to their genesis. Having considered CFB provinces generally, a synopsis of the characteristics of the British Tertiary Igneous Province and specifically Skye is given, and the history of research in the area is summarised. A detailed assessment of the work on the petrogenesis of the lavas is given in Chapter 2, History of Petrogenetic Research.

1.2 Continental flood basalt magmatism

1.2.1 Introduction

With the exception of mid-ocean ridge basalts, continental flood basalt provinces (CFBs), account for the largest volume of terrestrial magmatism (Figure 1.1). Such provinces were originally referred to as plateau basalts (Geikie, 1897), or traps (e.g. Woodworth, 1912). CFBs are characteristically tholeiitic, fissure-fed, laterally-extensive, sheet-like, sub-horizontal, sub-aerial lava flows, which cover large regions of the continents. There is often associated intrusive igneous activity, which takes the form of plutons, extensive sills and dyke swarms. Table 1.1 presents the ages and dimensions of the major CFB provinces. It can be seen that in many provinces vast quantities of magma were erupted within only a few million years. Work on the Columbia River and Snake River provinces has indicated average magma-production rates similar to equivalent-length sections of mid-ocean ridge systems with spreading rates of 10 and 0.3-3 cm p.a. respectively (Thompson, 1977). Considerably faster extrusion rates have been suggested for individual flows, for example up to 1 km³/day along each 1 km length of a vent system (Swanson *et al.*, 1975).

1.2.2 Geochemistry

CFB tholeiites are Fe-rich and Mg-poor compared with mid-ocean ridge tholeiites (Dupuy and Dostal, 1984; MacDougall, 1988). The large volume of material produced in CFB provinces has resulted in much debate as to whether CFBs are primary mantle melts or the products of fractional crystallisation from a picritic parent. If primary the lavas could give important information about the state of the mantle region from which they were produced. Cox (1980) and Thompson *et al.* (1983) reviewed the subject, and both favoured the picritic parent hypothesis. Cox (1980) noted that most CFBs have Fe/Mg ratios which are too high to have been in equilibrium with upper mantle olivine. Using the results of experimental petrology on CFBs, and peridotites, Thompson *et al.* (1983) concluded that most CFBs are also too silica saturated, or Mg-poor, or both, to be primary melts of anhydrous lherzolitic mantle. Picrites suitable to be parental to CFBs are observed in several CFB provinces, for example the Karoo, the Deccan and the North Atlantic Tertiary Province (NATP). The relatively uniform major element composition of many CFBs has been interpreted as giving further support to the concept of a picritic parent since low pressure fractional crystallisation of a gabbroic assemblage of olivine + clinopyroxene + plagioclase from a picrite would buffer major element concentrations. The Fe-rich character of CFBs has, therefore, been attributed to their fractional crystallisation history rather than the composition of their source regions (Cox, 1980).

1.2.3 Mantle Source

A fundamental problem in the study of CFBs is the character and location of the mantle source region of the basaltic magmas. It has been shown that basaltic magmatism in an oceanic environment, i.e. mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), is the result of melting in the convecting upper mantle, that is, the asthenosphere (e.g. Wilson, 1989). However, for CFBs there are two potential source regions within the upper mantle, the lithosphere and the asthenosphere. Whether CFBs are derived from the sub-continental

lithospheric mantle, or the convecting asthenosphere, has been the topic of much discussion. The physical properties which distinguish the two potential mantle source regions are important geochemically. Since if convection is taken to be the major process which homogenises the mantle, then in the convecting asthenosphere even large (10-100 km) compositionally distinct areas of mantle can be reduced to a scale smaller than that sampled by basaltic melting in a relatively short time period (ca. 200 Ma, Hoffman and McKenzie, 1985). Therefore, it is often assumed that, the only region in which trace element enrichments (produced by metasomatizing fluids or silicate melts) can be preserved long enough to be reflected in isotopic systems is the colder rigid lithosphere.

CFBs typically have isotopic signatures which are "enriched" relative to bulk earth, MORB, and OIB i.e. they have lower $^{143}\text{Nd}/^{144}\text{Nd}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$. Such signatures indicate the presence of a component which has been enriched in incompatible trace elements and has, as a consequence, had low Sm/Nd and high Rb/Sr, over a long period of time. Such trace element and isotopic characteristics occur in continental crustal material (Carlson *et al.*, 1981; Thompson *et al.*, 1983; Mahoney *et al.*, 1982), and in the sub-continental lithospheric mantle (Hawkesworth *et al.*, 1984a). Both contamination of asthenospheric melts within the continental crust and direct lithospheric mantle melting are possible geologically, although the latter has been the subject of some debate because it is cold and depleted in basaltic components relative to the underlying asthenosphere, so it is perhaps unlikely to yield large volumes of magma. A complication in the asthenospheric magmas versus lithospheric magmas debate is that there is much more variation in CFB compositions, than there is in MORB, and OIB compositions. Basalts within a single CFB province often show as much major and trace element, and isotopic compositional variation as is observed in CFBs worldwide.

Peate (1989) presented an excellent summary of the recent asthenospheric magma versus lithospheric magma discussions, the main points of which are given below.

The crux of the whole matter would appear to be the nature of the lithospheric mantle.

If this can be characterised then its presence can be detected, and the influence of it upon CFB magmatism quantified, thus leaving the crustal, and asthenospheric mantle components (upon which there are often more compositional constraints) to be distinguished separately, typified, and quantified. Recent studies of the textures and geochemistry of mantle xenoliths brought up to the surface during the eruption of basalts and kimberlites have given information about lithospheric trace element enrichment processes. A review by Hawkesworth *et al.* (1984a) concluded that there were two main types of mantle enrichment processes affecting the lithospheric mantle, those which resulted in the mantle xenoliths containing phlogopite, and those which did not. The first type of mantle enrichment process, which produced low Ti/K and high Rb/Sr ratios, was attributed to the movement of H₂O-rich fluids. The second, which produced high Ti/K and low Rb/Sr ratios, was thought to be the result of the movement of small volume (basanitic) silicate melts. Both processes enrich light rare earth elements relative to heavy rare earth elements by approximately the same amount. So, with time, the mantle affected by the enrichments would evolve to high ⁸⁷Sr/⁸⁶Sr, low ¹⁴³Nd/¹⁴⁴Nd, and low ⁸⁷Sr/⁸⁷Sr, low ¹⁴³Nd/¹⁴⁴Nd respectively. The trace element and isotopic characteristics outlined above have been detected in lamproites and kimberlites (Fraser *et al.*, 1985), and in some CFBs (Hawkesworth *et al.*, 1983).

On a plot of εNd (ε being a ratio that represents the deviation of the isotopic composition of a sample from bulk earth) versus εSr, CFB data depart from the asthenospheric mantle array of values defined by MORB and OIB samples, by having either a shallow high-εSr, high-εNd trend, or a steep low-εSr, low-εNd trend. Such variations could result from either assimilation of high-Rb/Sr upper crustal material and low-Rb/Sr lower crustal material into asthenospheric magmas (e.g. Carter *et al.*, 1978), or from the melting of sub-continental lithospheric mantle which had previously been enriched in trace elements (e.g. Hawkesworth *et al.*, 1984a). Therefore, it is obvious that it may not be clear whether the lithospheric component which is detectable in many CFBs is of crustal or mantle origin.

As a consequence of this uncertainty, two schools of thought have to some extent arisen, with research workers being divided into those who advocate asthenospheric magmas contaminated by crustal material and those who favour lithospheric magmas. An important point regarding the debate was made by Hawkesworth *et al.*, (1983) who stated that the controversy should not be over whether the processes took place, but over how the two processes could be detected and distinguished. Complicating factors, e.g. that lithospheric magmas could assimilate crustal material, and asthenospheric magmas could assimilate lithospheric mantle, led to the view that the interpretation of CFBs by isotopic signatures alone could be ambiguous; and should therefore, be considered in conjunction with other compositional characteristics. Combined major and trace element, and isotopic studies have been used to distinguish processes occurring in the source region from those acting on the magmas during their passage to the surface. Such an approach depends upon the different behaviour of certain elements between the crust and the mantle, which would enable the region that had the largest affect upon the composition of the CFB magmas to be detected.

The asthenospheric magma hypothesis was supported by Thompson *et al.* (1983). They concluded, on the basis of trace element concentrations, that most CFBs had sub-lithospheric, OIB-type, asthenospheric mantle source compositional characteristics. The possibility that such a source could exist under the continents was demonstrated by Fitton and Dunlop (1985). From their work on the Cameroon line, West Africa, they found that the products of the volcanism, which had an OIB-type composition, extended from off-shore onto the continent with no compositional difference between the two settings, thus demonstrating that the volcanism in the two settings must have originated in the same mantle source region. Thompson *et al.* (1983) invoked crustal contamination of the OIB-type magma to explain the enrichment of elements such as K, Rb, and Ba, and the depletion of Nb, and Ta observed in some CFBs. Nevertheless, they did not rule out the possibility that the variation in trace element

concentrations outlined above could have been produced by a component of subducted sediment in the mantle source region of the magmas.

Some support for the lithospheric magmas hypothesis has come from the CFBs which are thought to be related to the breakup of Gondwanaland during the Mesozoic (i.e. Paraná, Karoo, Antarctica, Tasmania). Basalts from these provinces have enriched isotopic signatures (high ϵSr and low ϵNd) even in some samples which are thought to be unaffected by crustal contamination (e.g. Hawkesworth *et al.*, 1984b; Erlank *et al.*, 1984). It has been suggested that, because the late-stage lavas with asthenospheric isotopic characteristics found in some provinces could not be modelled as uncontaminated versions of isotopically-enriched magma types, they must be from a different source region than the main volume of the magmatism. So they could only be produced once a considerable amount of stretching had taken place (e.g. Erlank *et al.*, 1984). So, CFBs associated with the breakup of Gondwanaland may have a sizable magmatic component from the lithospheric mantle.

Nevertheless, the debate continues since recent work by Ellam and Cox (1991) has shown that the trace and major element, and isotopic characteristics of some of the Karoo basalts can be explained by the mixing of magmas derived from asthenospheric MORB-like mantle (thought to be plume related) and lamproitic material derived from the lithosphere.

A feature of some CFB provinces which has fuelled the asthenosphere-versus-lithosphere debate is the coexistence of two magma-types with distinct geochemical and isotopic characteristics (i.e. the High-Ti lavas and the Low-Ti lavas e.g. Bellieni *et al.*, 1984; Erlank *et al.*, 1984). The contrast between sub-provinces showing markedly different incompatible element concentrations was first noted by Cox *et al.* (1967) and has resulted in much discussion about the source regions of the two groups. Since neither group has OIB-type compositional characteristics, a heterogeneous lithospheric mantle source, in which the heterogeneities resulted

in the compositional differences between the two magma types, has been proposed by several authors (e.g. Hawkesworth *et al.*, 1984b; Erlank *et al.*, 1987). On the one hand, the High-Ti basalts have high concentrations of high field strength elements (HFS) and low large ion lithophile element (LIL)/HFS ratios which suggest that their source region was enriched by small degrees of partial melt. On the other hand, the Low-Ti basalts are relatively depleted in HFS elements and have high LIL/HFS ratios which has been taken to suggest that there is a subduction component, i.e. subducted sediment or fluid from the slab in their mantle source (Hawkesworth *et al.*, 1991). The mantle source of these magma-types is still the subject of much debate.

From the preceding literature it can be seen that many CFBs possibly contain a significant component derived from the sub-continental lithospheric mantle (Hawkesworth *et al.*, 1984b, 1988; Duncan *et al.*, 1984; Marsh, 1987; Allegre *et al.*, 1987; Thompson and Morrison, 1988). So, it is the process by which the material becomes involved in the CFB magmatism that has now become the focus of attention. The two main alternatives are, that lithospheric material is assimilated by asthenospheric material during its passage to the surface, or that the lithospheric mantle is itself completely melted. Some opposition exists to the concept of complete remelting of the lithosphere because it is cold, and depleted in basaltic components. However, it has been suggested that there was a major change in the mechanism of lithospheric stabilization at the time of the Archaean/Proterozoic boundary, and consequently in the composition of lithospheric material. Hawkesworth *et al.*, (in prep) have suggested that during the Archaean the lithosphere produced was the depleted Fe-poor residue of komatiite extraction, sampled at the present day in cratonic regions, as xenoliths of garnet peridotite brought to the surface in kimberlites (e.g. see Boyd, 1987). The residue, being less dense than the asthenosphere surrounding it, rose and plated onto the base of the continental lithosphere. In contrast Hawkesworth *et al.* (in prep.) proposed that the post-Archaean lithosphere stabilised by

conductive cooling of the asthenosphere at the base of the continental lithosphere, thus producing a lithosphere which would be compositionally similar to the asthenosphere, sampled at the present day as spinel peridotite xenoliths in alkali basalt regions. Peate (1989) suggested that the post-Archaeon lithosphere is a suitable source for CFB magmas, whereas Archaeon lithosphere would be too depleted in basaltic components. He supported the hypothesis with the observation that no CFBs have been found that are older than Proterozoic.

The debate as to whether asthenospheric or lithospheric material is the dominant component in CFB magmatism continues for individual provinces, and remains one of the fundamental questions in igneous petrology at the present day.

1.2.4 Tectonic Setting

CFB provinces generally occur in extensional tectonic settings. They are often associated with the development of continental margins by thinning and rifting of the continental lithosphere during continental break-up; for example the Mesozoic activity of the Karoo and Paraná provinces is associated with the break up of the Gondwanaland super-continent (e.g. see Peate 1989), and the North Atlantic Tertiary Province (comprising the British Tertiary Igneous province, the Greenland province, the Faeroes and Jan Mayen) is related to the opening of the North Atlantic (e.g. see Dickin, 1988).

1.2.5 Ultimate cause of the Volcanism

Many theories have been devised to account for the production of CFB magmatism. Models of production vary somewhat gradationally from one in which the Pangean super-continent is suggested to have acted like an insulating lid, causing the temperature of the underlying lithospheric mantle to rise, and eventually to melt, through models which invoke subduction-induced asthenospheric convective overturn, to the pure plume models which invoke

the interaction of narrow, semi-cylindrical upwellings of hot mantle material which may thermally erode the lithosphere en route to the surface. Originally thought to be the driving force for plate tectonics (Morgan, 1981), recent work has shown that at least some plumes are the upwelling limbs of small-scale convection cells, which appear to be unrelated to, and detached from, the motion of the plates (Watson and McKenzie, 1991). It is still unclear how and where plumes originate.

Several models which do not specifically invoke a mantle plume have been proposed to explain the CFB volcanism associated with the breakup of Gondwanaland.

A non-plume theory was proposed by Briden and Gass (1974) and elaborated by Anderson (1982). Briden and Gass (1974) suggested the Pangea super-continent would have had an insulating effect upon the underlying mantle, causing a rise in the temperature of the sub-continental lithosphere in the absence of mid-ocean ridges to disperse the heat. The consequent temperature increase would result in extensive melting of the lithospheric mantle. Continental rifting would ensue, and eventually sea-floor spreading would be established, so that magmatism in continental interiors would decline as the asthenospheric mantle convected heat away through the mid-ocean ridges.

Elliot (1975), and Cox (1978) suggested that mantle convection might be important in the generation of CFB magmas. Both authors observed the alignment of the Paraná, Karoo, Antarctica and Tasmania provinces parallel to and approximately 2,000-4,000 km behind the Pacific margin of reconstructed Gondwanaland along which there had been subduction since the Devonian. Froidevaux and Nataf (1981) suggested that the magmatism could be the product of the upwelling limb of convective rolls which would develop on the continental side of a subduction zone. Such magmatism would occur 3,000-4,000 km inland of the subduction zone, and its timing would be consistent with the 200 to 300 Ma time delay of the onset of the volcanism after subduction was active. However, Duncan *et al.*, (1984) preferred the idea that

the upwelling limb would result in the heating and melting of the sub-continental lithosphere.

In contrast to the ideas outlined above, a plume theory for the generation of CFBs based on plate reconstructions of CFB provinces and extrapolation of present day hotspots (the surface expression of mantle plumes) to their palaeopositions was proposed by Morgan (1981). He showed that most CFB provinces had a hotspot at, or near, the site of volcanism, and proposed that a plume beneath the continental interior caused gradual heating and thermal erosion of the sub-continental lithosphere over a period of 10 to 30 Ma, resulting in CFB magmatism. White and McKenzie (1989) further examined the effect of causing the continental lithosphere to rift above a mantle plume. They suggested that a plume had an elevated potential temperature (i.e. the temperature the asthenosphere would have if it were brought to the surface adiabatically without melting) of approximately 150-200°C relative to normal asthenosphere ($1280 \pm 30^\circ\text{C}$) in a region of 1000 km radius. So, rifting of the continental lithosphere resulted in the production of magma by decompression melting in upwelling asthenospheric material. McKenzie and Bickle (1988) had showed that the volume of melt generated was dependent on the mantle potential temperature, and on the amount of lithospheric stretching, with extension over a plume generating up to twice the amount of melt produced during the same amount of stretching over a mantle of normal temperature. The plume model of McKenzie and co-workers accounted for the large volume and rapid extrusion rate of CFBs, the relation to rifting, and the subsidence and uplift history of the continental margin. It was noted by Peate (1989) that there are no satisfactory examples of the geochemical signature of the plume (i.e. asthenospheric OIB material) being detected in CFB magmatism. Yet the plume concept is essentially physical. Consideration of the relative speed of thermal and compositional diffusivity in a plume reveals that it may not always be possible to detect a plume compositionally (Watson S., 1992 pers. comm.).

In the light of the recent geophysical research the lack of CFB magmatism at many rifts and continental margins has been attributed to the absence of deep mantle thermal plumes in most of such settings (e.g. Peate 1989).

1.3 The British Tertiary Igneous Province

1.3.1 Introduction

The British Tertiary Igneous Province (BTIP) is part of the larger North Atlantic Tertiary Province (NATP) (Figure 1.2). The igneous activity in the BTIP includes gabbroic and granitic central complexes, plateau lavas, and a regional dyke swarm (Figure 1.3). It formed between 65 Ma and 50 Ma (e.g. Wilson, 1989, Dickin, 1988).

The accessibility of the BTIP and in particular Skye, and the diversity of igneous rock types present within it, which include extrusive (basaltic lavas and tuffs), and subsurface (gabbroic and granitic complexes, dykes, and sills) products of the igneous activity in the region, has led to it being a focus of geological research for over 200 years. Study of the region has followed a pattern which is typical for classic geological areas, i.e. one generation of geologists work on the area and concludes all that they can from the knowledge and analytical techniques available at the time, then attention is turned to other, less well known, regions: New theories are formed and geological knowledge increases from the study of the new regions, and analytical techniques improve because of advances in technology: A new generation of research workers readdress the classic area in an attempt to apply new knowledge and techniques to the problems raised by the earlier studies. So, the cycle continues, with the theories and results produced by each generation being, not necessarily the right answer, but instead, the one which best fits the data available at that time.

The previous research in the BTIP can be divided into three stages. The first stage involved geological mapping, the aim of which was to identify and classify the igneous rocks

in the region. The geological mapping was continued during the second stage of research in the area. In addition petrographic and mineralogical studies were undertaken to try to unravel the structure, origins, relationships between, and mineralogical evolution of, the various igneous centres (little attention was paid to the chemical composition of the rocks at this stage since limited laboratory resources made analytical work impractical). The third stage of research involved petrogenetic geochemical and isotopic studies that focused on the large amount of data produced when analytical work became simpler (as a result of technological advances in X-ray fluorescence, mass spectrometry and experimental studies). The geochemical and isotopic studies addressed the questions posed by early workers. They also considered more general petrogenetic problems such as the identification of primary magmas, the properties and origins of more evolved lavas, the state of the source region, melting processes, cooling and fractionation processes, mechanisms of magma-transport and emplacement, contamination of magma with crustal material, and sub-solidus processes.

Igneous rocks from the BTIP have been used to test numerous petrological, and geochemical, models, and theories. Consequently, any study of the region is potentially overwhelmed by the volume of previous literature available. A summary and critical assessment of previous work is essential before the unresolved problems can be recognized, and the resulting aims of the proposed study identified.

In reviewing the previous BTIP literature a unique opportunity presents itself. The historical development of petrogenetic thinking can be outlined; and the influences upon it of, popular opinion and advances in analytical techniques, assessed.

The following sections are by no means a comprehensive review of the previous work on the BTIP, or the igneous rocks of Skye (for which the reader is referred to Harker, 1904; Anderson and Dunham, 1966; Sutherland, 1981; Thompson, 1982a; Thompson, 1982b; Dickin,

1988), but discuss the work relevant to the present study.

1.3.2 Age and Duration

Age determinations for the rocks of the BTIP can be split into two categories. The early studies obtained dates for the igneous activity based on the classification and the dating of plant remains found in inter-basaltic sediments. More recent works have dated the igneous rocks using various radiogenic isotopic systems, the methodology for which was originally devised by Hahn and Walling (1938). Such dating methods were made possible by the discovery of radioactivity by Becquerel in around 1880. In 1890 Soddy and Rutherford proposed that the rate of spontaneous disintegration of atoms of radioactive elements to form atoms of another element could be expressed as a function of a decay constant and the number of radioactive elements present.

The discovery of radioactivity had a profound effect upon the study of geology because it resulted in the study of heat production in rocks (it also provided an explanation for the presence of pleochroic halos, found around radioactive minerals). In 1905 Rutherford and Boltwood realised the potential of radioactivity to provide a means of measuring the age of rocks and minerals. Early work in this field concentrated on trying to determine the age of the earth. A review of the early geological work using radioactivity and the potential of the technique, as seen at the time, is given in a classic work by Holmes "The Age of the Earth" (1913). More recently several different methods of radiometrically dating rocks have been developed. In 1943 the first ages of Rb-rich minerals, determined from the decay of naturally occurring ^{87}Rb to ^{87}Sr , were published (Hahn, *et al.*, 1943). Nevertheless it was not until the 1950s, when mass spectrometers, based on a design by Nier, became available, that the Rb-Sr method of dating became widespread. The mass spectrometers enabled the isotopic analysis of solids, and the concentration of Rb and Sr could be measured by isotope dilution (which was less laborious than the previous method of chromatography). Other isotopic systems used for

dating of igneous rocks were based on the same principles as the Rb/Sr method. The K/Ar method was developed by Nier (1935) and Von Weizsacker (1937), because of the discovery of radioactive K (Aston, 1921), and the knowledge that K occurs in many common geological minerals. Nevertheless, the $^{40}\text{K}/^{40}\text{Ar}$ method did not become established until about 1950. In an attempt to overcome some of the limitations of the original K/Ar system, such as potential Ar loss, and sample inhomogeneity, Merrilue and Turner (1966) developed the $^{40}\text{Ar}/^{39}\text{Ar}$ method. The U/Pb, and Th/Pb isotopic dating methods were developed by Rutherford because they were radioactive elements which occurred commonly in igneous minerals. More recently the Sm/Nd system has been employed in radiometric dating. The advantage of it over the other systems already listed was that the elements were rare earth elements (REE), and thus immobile during hydrous alteration, so their concentrations were unlikely to be affected by sub-solidus processes. Various other less well-known isotopic systems could be used as geochronometers, they include K/Ca and Re/Os, Lu/Hf, La/Ce and La/Ba the last four of which have so far been of limited use because the elements have very low concentrations in igneous rocks. It was not until the 1950s when there was greatly improved knowledge of decay mechanisms, and mass-spectrometers had been considerably improved (resulting from war-time atomic bomb and atomic energy projects) that the use of isotopic systems in the dating of rocks became widespread.

An excellent review of the radiometric dates, and palaeomagnetic data, used to determine the age and duration of the igneous activity in the BTIP, including the Skye lavas, was given by Mussett *et al.*, (1988). From dates for the currently-exposed parts of the province they concluded that the activity occurred between 63 Ma and 50 Ma i.e. Palaeocene to Eocene on the time scale of Palmer (1983) (used throughout the present work). They concluded that the most prolific activity had occurred at 59 Ma (Palaeocene). Although the magmatism of the area was predominantly basic, acidic products are present late in the igneous succession. Mussett *et al.* (1988) noted that there was no common pattern in the type and duration of magmatism

in the different centres of the BTIP, but the geologically more complex igneous areas generally took longer to form. Their results are summarised in Figure 1.4.

1.4 Skye

1.4.1 Introduction

The igneous rocks of the Isle of Skye, which lies off the N. W. coast of Scotland between 57° and 57°45' N, are part of the BTIP. The plateau lavas are the earliest products of the igneous activity on Skye, later manifestations including the gabbroic Cuillin complex and the Red Hills granites (Figure 1.5). This activity occurred from approximately 65 Ma to 50 Ma (Palaeocene to Eocene) within a continental environment (Figure 1.5).

On the basis of both geological and topographic features the island can be divided into three distinct parts (Figure 1.5).

- i. The Sleat peninsula (Figure 1.6) in the south east is composed of Lewisian gneiss, Torridonian sedimentary rocks, Moine Schists, and Cambro-Ordovician sedimentary rocks. These rocks form rounded hills of up to 700 m O.D.
- ii. The mountainous central part of the island formed of Tertiary intrusive gabbro and granites which reach heights of 1000 m O.D and 775 m O.D respectively.
- iii. North Skye, which consists of a plateau-type topography indented by large sea-lochs. Jurassic sedimentary rocks crop out along the east coast and are capped by up to 700 m of Lower Tertiary plateau lavas and occasional pyroclastic rocks.

The present study is concerned with the area north of 57°18' N (Figure 1.7), throughout which the Tertiary plateau lavas crop out, covering an area of approximately 1500 km². The lavas are preserved in a shallow, faulted, oval basin with a long axis trending north-west/south-

east parallel to a dyke swarm (Figure 1.8). The lava field is inferred to have a maximum thickness of 760 m (Anderson and Dunham, 1966), though the maximum exposed in any one section is 335 m at the Storr (Figure 1.6).

On the eastern side of the Trotternish peninsula (Figure 1.6) the lavas form an escarpment which rises from sea-level at Portree, culminates at 787 m at the Storr then descends to sea level in the north. In contrast the western slopes of the Trotternish ridge are gentle and mostly follow the low westward dip of the lavas.

The Watnish peninsula has a central ridge of lavas which rarely reaches more than 330m above sea-level. In Duirinish the lavas are almost flat-lying or dip shallowly to the east.

The Tertiary basaltic lavas occur at the top of the stratigraphic succession in Skye (Figure 1.5).

1.4.2 Previous work

1.4.2.1 Introduction - the early research

The early work on the Skye lavas (the first stage of research in the area, Chapter 2, History of Petrogenetic Research, section 2.2) concentrated on descriptive studies of the structure of the lava field (Macculloch, 1816; 1817; 1819). It was not until the 1870s that the second stage of research began with the use of the modern techniques of microscopical petrography on the Skye basalts (Judd and Cole, 1883; Geikie, 1879). The flat-lying basalts were found to include thick massive sheets and columnar sheets, structure-less amygdaloidal flows, and banded or stratiform flows (Geikie, 1888). They were described as containing phenocrysts of olivine, plagioclase, and clinopyroxene (Judd, 1886). Some consideration was given to their time relationships (Geikie, 1867b). Judd (1886) proposed the lavas were emitted from a central vent, but Geikie (1888; 1897) having observed there was no obvious thickening towards a centre suggested eruption of the lavas through fissures.

The first detailed petrographic and mineralogical descriptions of the Skye lavas was given by Harker in the "Tertiary Igneous Rocks of Skye" (1904). This classic work formed the basis of many later studies. In it Harker combined field observations, petrological, mineralogical, and geochemical data to try to resolve the problems which remained unanswered by previous studies of the region. He concentrated on the association of the igneous rocks, rather than their petrogenesis, and produced an overall synthesis of the igneous rocks on Skye (a feat which has yet to be attempted by later workers). Nevertheless, one of his main conclusions, that the prismatic jointed layers previously described as flow-centres, were sills, has not been supported by later workers (Wilson, 1937; Anderson and Dunham, 1966) who could find no evidence for sills within the lava field; also, detailed field work by Kennedy (1933) showed that the composite sills in the south of the area described by Harker were composite lava flows.

After the detailed studies outlined above the attention of the British petrologists turned to other igneous provinces, e.g. East Greenland (Wager and Deer, 1939). Apart from a description of the plateau lavas by Richey (1948), and a mention of the basalts, some feldspar-phyric mugearites, and trachytes in an excursion guide by Wager *et al.* (1948) there was little research interest in the BTIP until the late 1950s and early 1960s. New ideas arising from the study of other provinces, and advances in experimental studies led to further work in the BTIP to test various concepts in a region in which the relationships between the igneous rocks, and the mineralogy and petrology were well established.

1.4.2.2 Structure of the lava field

1.4.2.2.a Introduction

The Tertiary basaltic lavas generally lie either directly on Jurassic strata, or on the earliest products of igneous activity on Skye, the basal palagonitic tuffs (Figure 1.9), although basal pillow lavas have been identified in the Portree area (Anderson and Dunham, 1966).

1.4.2.2.b Palagonite tuffs

The basal tuffaceous horizon comprises volcanic ash, lapilli, and bombs. It includes some pillow lavas and globe breccias, and has associated shale and plant debris. The tuffs are considered to have been deposited in shallow lakes on a peneplained surface of Jurassic rocks (Anderson and Dunham, 1966).

1.4.2.2.c Inter-basaltic sediments

Many of the Skye lava flows have distinctive red tops formed by the decomposition of basalt by weathering to give lateritic clays or boles (King, 1976). The red material between the lava flows was first noted by Geikie in 1897. The presence of the red boles was used by Wilson (1937) to support his theory of an extrusive origin for the Skye basalts.

Anderson and Dunham (1966) proposed that the lavas were erupted from fissures, and divided them by the presence of palaeosoils, and sometimes fossil plant material, which they suggested developed during periods of volcanic quiescence (Figure 1.10). King (1976) noted that the lava field is now so extensively faulted that it is very difficult to relate the sedimentary beds to each other, and to the episode to which they belong. He gave a detailed description of the occurrence and character of the inter-basaltic sediments within the lava pile (Figure 1.6).

1.4.3 Age and Duration

There has been considerable disagreement as to the age of the Skye lavas. Early studies concentrated on determining the age of the lavas by the classification, and the dating, of plant remains found in inter-basaltic sediments. Dates ascertained in this way ranged from Maastrichtian to Oligocene, corresponding to 70 Ma to 24.6 Ma on the time scale of Palmer (1983). The first research into the plant remains was done by Simpson (1951, 1952, and 1961). He dated material found in the basal palagonite tuffs and intra-basaltic sediments of Skye, Mull,

and Ardnamurchan as Oligocene (38 Ma to 24.6 Ma). To try to constrain the age of the lavas better King (1976) collected plant remains from inter-basaltic sedimentary horizons in Glen Osdale west-south-west of Healabhal Mhor, Sgurr a' Ghobhainn, and south of Loch Eynort (Figure 1.6). The specimens, which were generally poorly preserved, were a mixed micro-fossil assemblage, comprising in situ angiosperm pollen grains, miospores, and reworked miospores, and phytoplankton (acritarchs and dinoflagellate cysts). King (1976) noted that although the overall angiosperm pollen assemblage lacked diversity it was consistent with an Upper Cretaceous (70 Ma), or Tertiary (<65 Ma) age. He went on to suggest however that the absence of Aquilapollentites and representatives of the Normapolles group ruled out a Late Cretaceous age thus indicating deposition in the Early Tertiary (Palaeocene (66.4 Ma to 57.8 Ma) or Eocene (57.8 Ma to 36.6 Ma). The assemblages contained a lot of reworked material. The Osdale samples showed evidence of reworking from a Rhaetian (215 Ma to 208 Ma) source (Ovallipollis ovalis, Ricciisporites tuberculatus, and Rhaetipollis germanicus); whereas the Sgurr a' Ghobhainn assemblages contained evidence of reworking of sediment of a similar age, Rhaetian - basal Hettangian (215 Ma to 206 Ma), Liassic (208 Ma to 187 Ma) and Middle Jurassic (176 Ma) rocks. The presence of a Dinoflagellate cyst, possibly "Astrocysta" cretacea, was taken to be indicative of a Mid-Cretaceous source (King, 1976).

Work on the remnant magnetism by Khan (1960) gave a Lower Miocene age for the lavas, and showed them all to have reverse magnetism. The reverse magnetism was suggested to indicate production in one magnetic epoch, so limiting the activity to 1 Ma (e.g. see Mussett *et al.*, 1988).

Mussett *et al.* (1988) concluded that there was considerable disagreement in radiometric dates obtained for the Skye lavas. The differences were attributed to such problems as technical precision, argon loss (when the K/Ar system was used), and the effect of hydrothermal

alteration. Consequently, the lavas have not been radiometrically dated reliably yet (Mussett *et al.*, 1988). A general observation can be made as to the age of the lavas relative to other igneous rocks on Skye. The Palaeocene age obtained for plant remains found in inter-lava sediments (King, 1976) is consistent with Rb-Sr ages for the Skye intrusives (Moorbath and Bell, 1965; Dickin 1981), in that it is older than them. The igneous sequence proposed for Skye is extrusive lavas ca. 63 Ma (e.g. Mussett *et al.*, 1988), intrusive gabbros - the Cuillins, and intrusive granite - the Red Hills ca. 57 Ma (Moorbath and Bell, 1965).

1.4.4 Stratigraphy

1.4.4.1 Introduction

Division of CFB provinces into stratigraphic units is a priority of any study of such provinces. This is because igneous sequences may be expected to have more coherent petrographies and compositions on short time-scales (i.e. within a single stratigraphic unit) than over the province as a whole. Therefore, identification of the petrogenetic processes affecting the lavas may ideally be made simpler by the consideration of individual units.

The proximity of compositionally different lava types, i.e. olivine basalt and mugearite, in Skye led Anderson and Dunham (1966) to propose that they had been extruded from different fissures related to a central volcano. They noted that if the observed sequence had been built up by the vertical emplacement of flows the thickness of the lava field would have exceeded 2200m. Therefore, they concluded that faults of that magnitude would be required to explain the observed examples of juxtaposition of the olivine basalts and mugearites (which were considered to be the early, and the late extrusive products of the same magmatic evolutionary series) if the lava pile had been extruded as a single vertical stack. Anderson and Dunham (1966) commented that there was abundant evidence to suggest that the Jurassic rocks which underlie the lavas were not far below sea level anywhere, and so the existence of faults with

more than 300m vertical displacement was improbable. Field evidence suggested that several units which thinned away from a centre (potentially the site of the fissure from which they were erupted) could be distinguished. Therefore, Anderson and Dunham proposed that the lava pile was composed of flows erupted from several fissures operating at different times and in different places, with some meeting, and overlap of the products of the different fissures occurring at their margins.

In the North Skye Memoir (1966) which accompanies the one-inch Portree (80) and Rubha Hunish (90) sheets, Anderson and Dunham divided the Skye lavas into five stratigraphic units. The division was based on the field identification of inter-basaltic sediments, which were taken to indicate a cessation in volcanic activity, thus enabling the division of the lava pile into time units.

The composition and thickness of the stratigraphic units, and the composition of the dykes cutting them, are summarised below.

Osdale Group (500m).

TOP

Alternating basalt and mugearite flows.

Dykes: tholeiitic.

Bracadale Group (120m).

Alternating mugearite and trachyte flows.

Dykes: trachytic.

Beinn Totaig Group (600m).

Alternating basalt and mugearite flows.

A porphyritic basalt at the top of the group.

Dykes: mugearitic.

Ramascaig Group (800m).

Alternating porphyritic and non porphyritic basalts.

A mugearite flow at the top of the group.

Dykes: gabbroic.

Beinn Edra (300m).

Non-porphyritic basalts with a few porphyritic flows

and a mugearite at the top of the Group.

Dykes: picritic.

BASE

Figure 1.11 summarises the present day and suggested former extent of the stratigraphic units proposed by Anderson and Dunham (1966).

1.4.4.2 The Stratigraphic Groups

1.4.4.2.a The Beinn Edra Group

This group was considered to have been extruded from a north-north-west trending fissure located in Trotternish, possibly now occupied by the picrite dykes at Beinn Tuath (Figure 1.6). The base of the unit is seen in Uig Bay, and in the north and east of Trotternish. Its top is exposed as a thick mugearitic capping from the Storr to Beinn Edra on the Trotternish peninsula. Anderson and Dunham (1966) suggested that a mugearite flow (lying 30m above the base of the unit) south of Tianavaig Bay, in the Ollach District, could be correlated with a mugearite capping the unit from the Storr to Beinn Edra (lying 335m above the base of the unit). They thus inferred the southerly thinning of the Beinn Edra group.

1.4.4.2.b The Ramascaig Group

It has been proposed that this group is penecontemporaneous with the Beinn Edra Group.

Yet, the only evidence to support this proposal is that lavas of both groups are in contact with the underlying Jurassic sediments, and are overlain by the lavas of the other groups. There is no field evidence available to enable determination of their relative ages. The fissure from which this group erupted could have been either in the Loch Bracadale area or offshore, west-north-west of Idrigil point. At its centre it is at least 760 m thick. The group and, where their tops and bases are exposed, the individual flows, appear to thin to the north and north-east. In the west the flows could be faulted below sea level. In the south and east the flows of this group are covered by more recent flows.

1.4.4.2.c The Beinn Totaig Group

This group lies between the Beinn Edra Group to the east and the Ramascaig Group to the west. Anderson and Dunham proposed that the group was extruded from a fissure in the Mugeary area, 6.5 km south west of Portree. It comprises basalts, several thick mugearite flows (some of which are composite porphyritic and non-porphyritic (Kennedy, 1931)), and a capping-porphyritic basalt. A break in volcanic activity at the top of the group is marked, in the Glen Osdale region, by the presence of ashy and shaley plant-bearing sediments.

1.4.4.2.d The Bracadale Group

The centre of extrusion for this group may have been a fissure aligned from Ben Skudaig to Ben Aketil (Figure 1.5). The group varies from basic to acid in composition. It is the thinnest, 120m, and least extensive (Figure 1.11).

1.4.4.2.e The Osdale Group

The remnants of this group are similar in composition to the Beinn Totaig Group. Anderson and Dunham (1966) proposed that the lavas of this group were extruded from a centre further west than the Bracadale Group.

The stratigraphy, established by the presence of inter-basaltic sediments, is still referenced (Thompson *et al.*, 1972; Dickin, 1988). Nevertheless, the lack of clear systematic petrographic or compositional change in the characteristics of the lavas of the different stratigraphic groups with time has inevitably led to petrogenetic interpretation of the pile as a whole (Thompson, 1982b).

The previous work on the petrogenesis of the Skye lavas is summarised and assessed in Chapter 2, History of Petrogenetic Research.

Figure 1.1 Location of the major continental flood basalt provinces (solid), their related hotspots (●), (dashed lines show the approximate position of ridges and seamounts), and voluminous extrusive rocks on rifted continental margins (hatched).

Projection is Aitoff equal area. (After White and McKenzie, 1989; and Rampino, 1989)

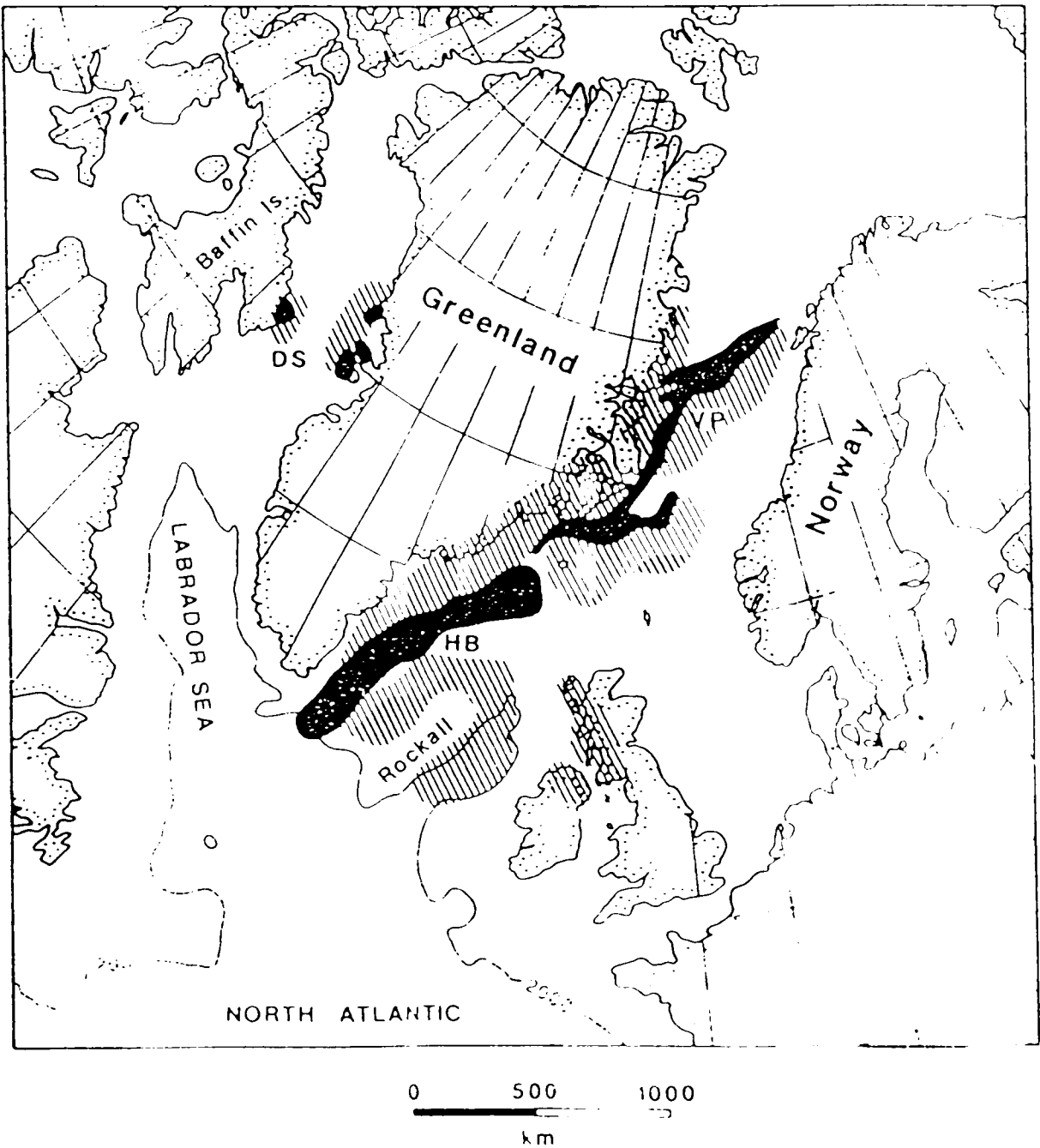
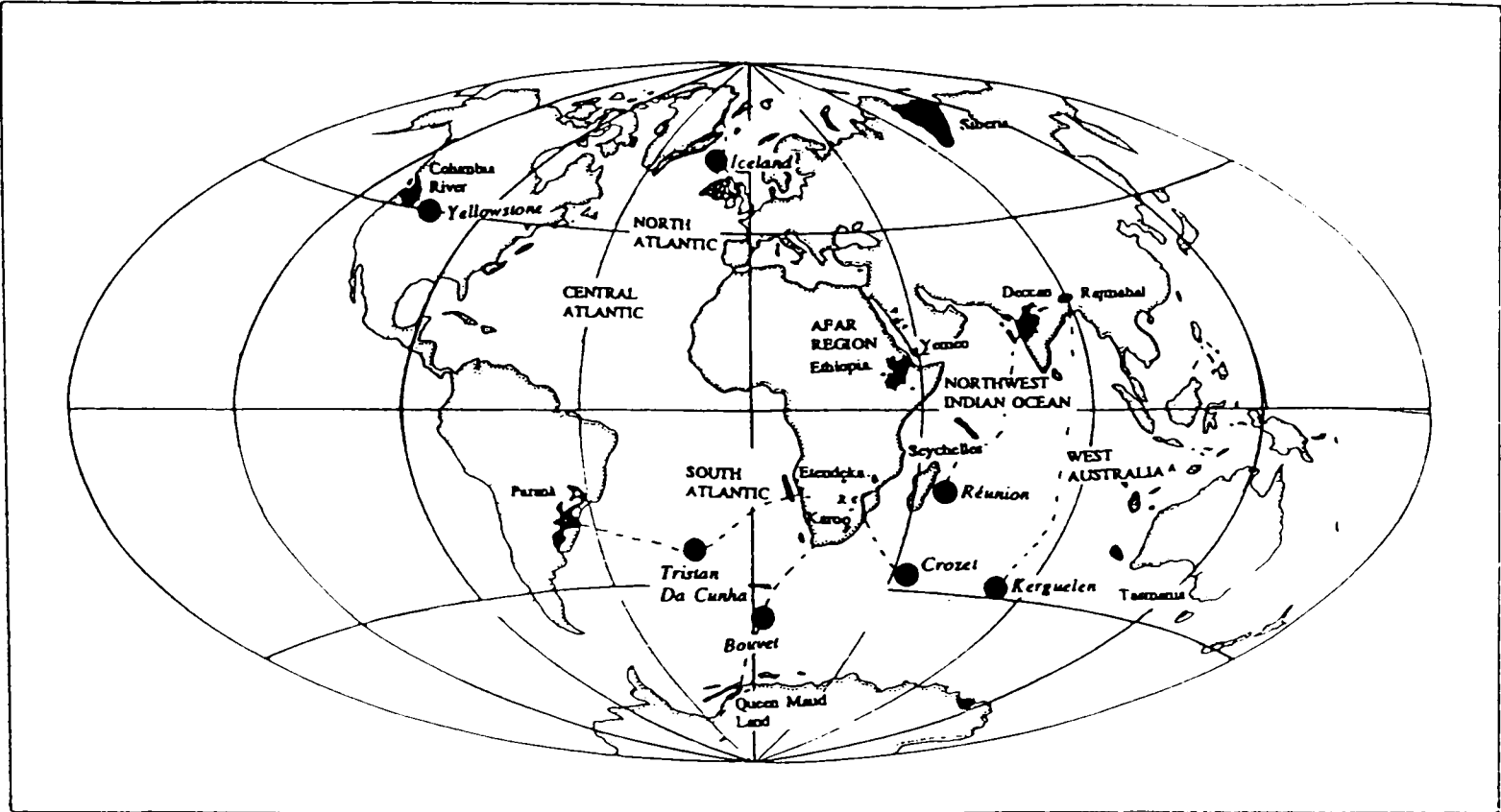


Figure 1.2 The North Atlantic Tertiary Province.

Reconstruction at magnetic anomaly time 23, just after the onset of oceanic spreading.

Sea-ward dipping reflectors - solid, extent of Tertiary igneous activity - hatched.

Projection is equal area centred on East Greenland.

(After White and McKenzie, 1989).

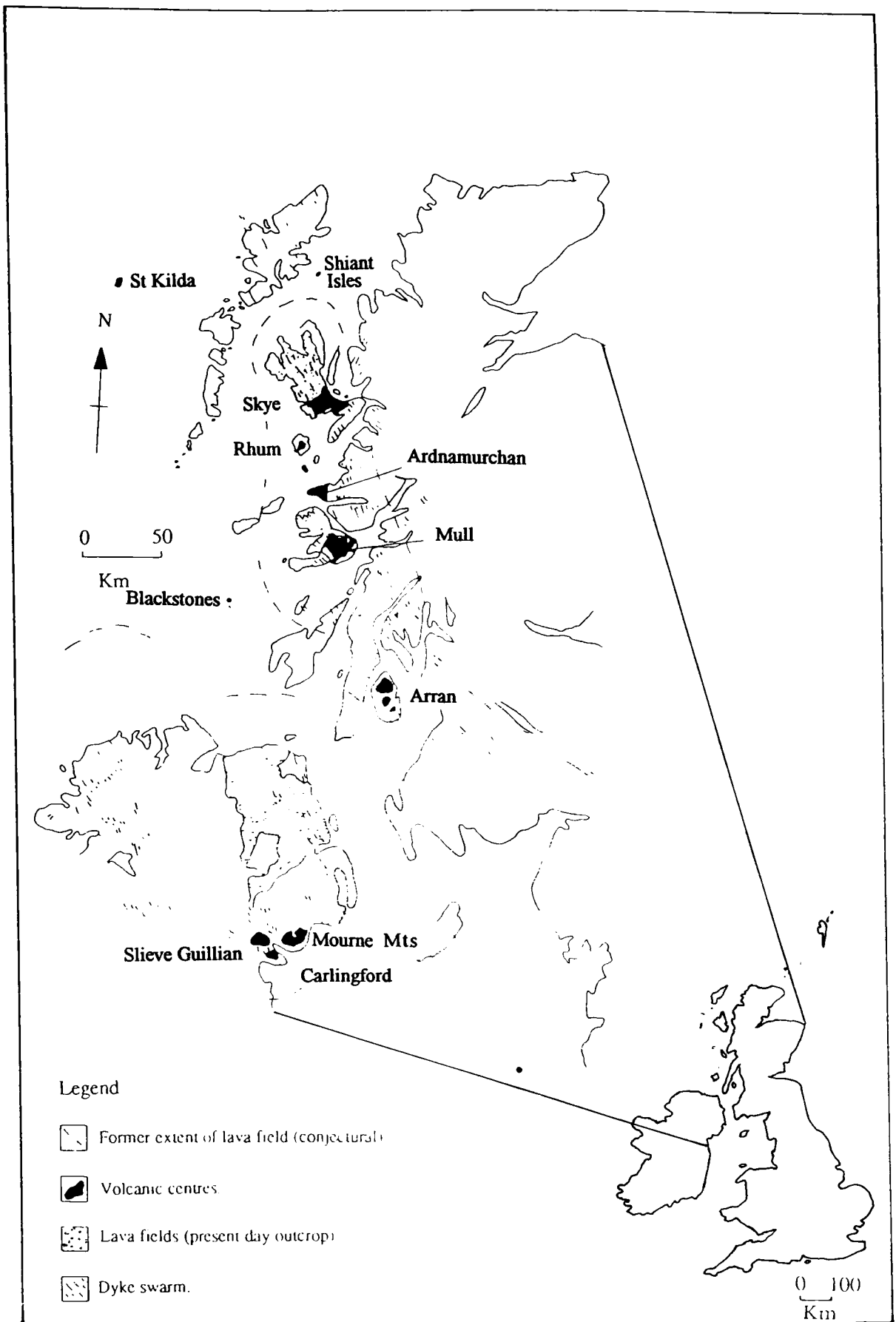


Figure 1.3 The British Tertiary Igneous Province (after Preston, 1982).

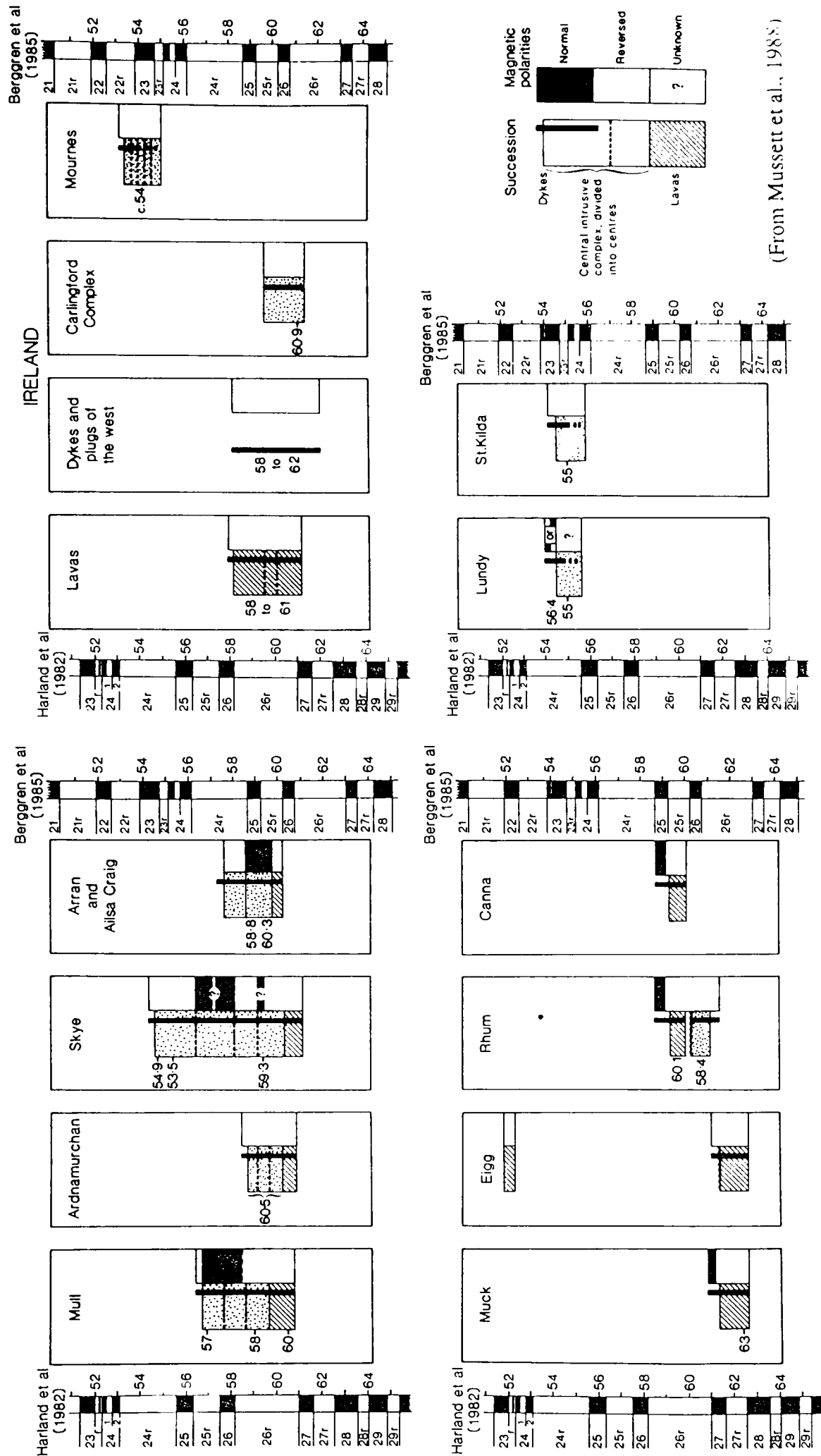


Figure 1.4 Summary of results of a study of the time and duration of activity in the British Tertiary Igneous Province. Each area is assigned a box; the central column summarizes the geological succession, while reliable dates are shown to the left and the magnetic polarities to the right. To either side of the boxes are shown the polarity time-scale according to Harland et al., (1982) and Berggren et al., (1985) (key is bottom right).

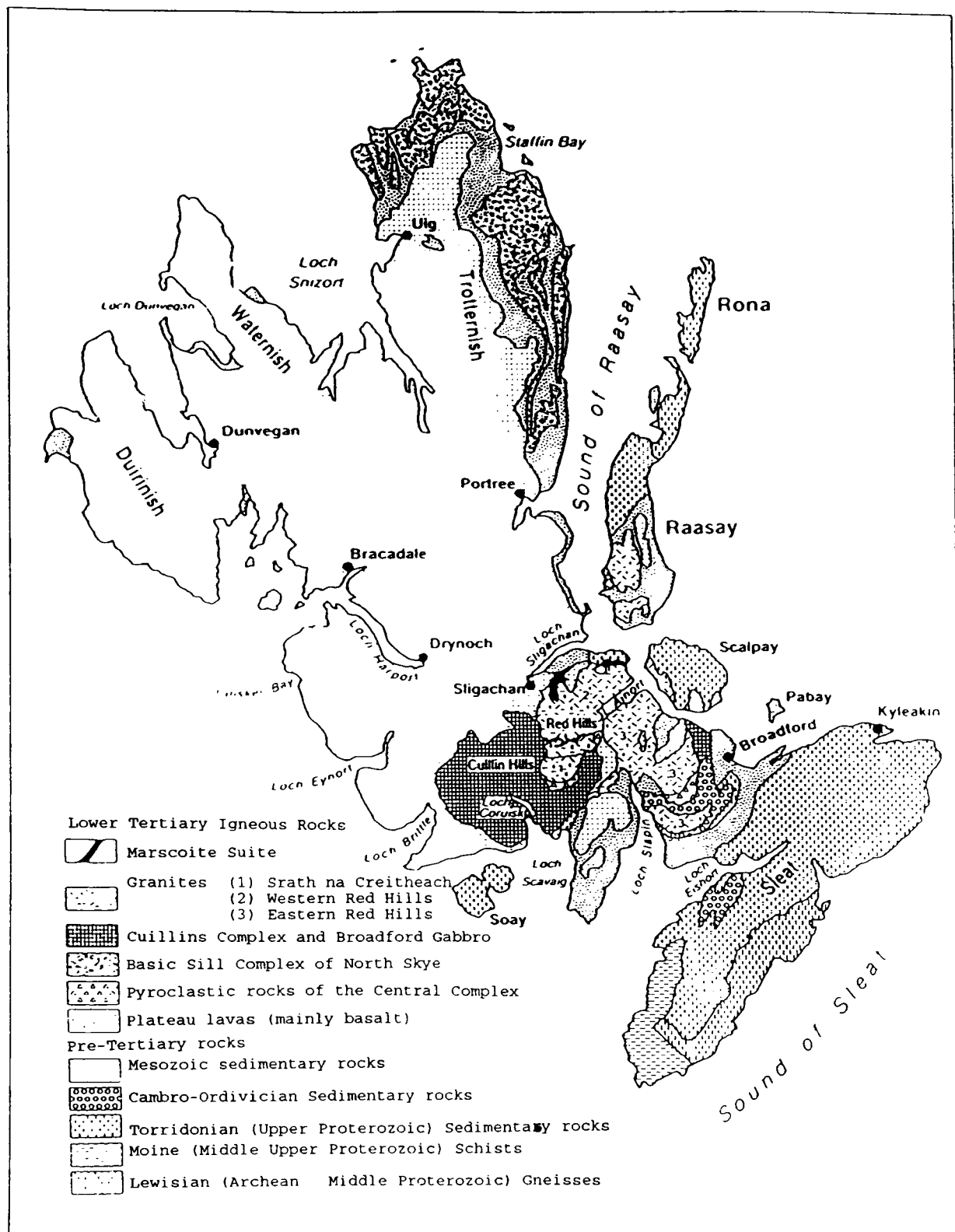


Figure 1.5 The Isle of Skye showing the geographic and stratigraphic position of the lavas.
(After Bell and Harris, 1986)

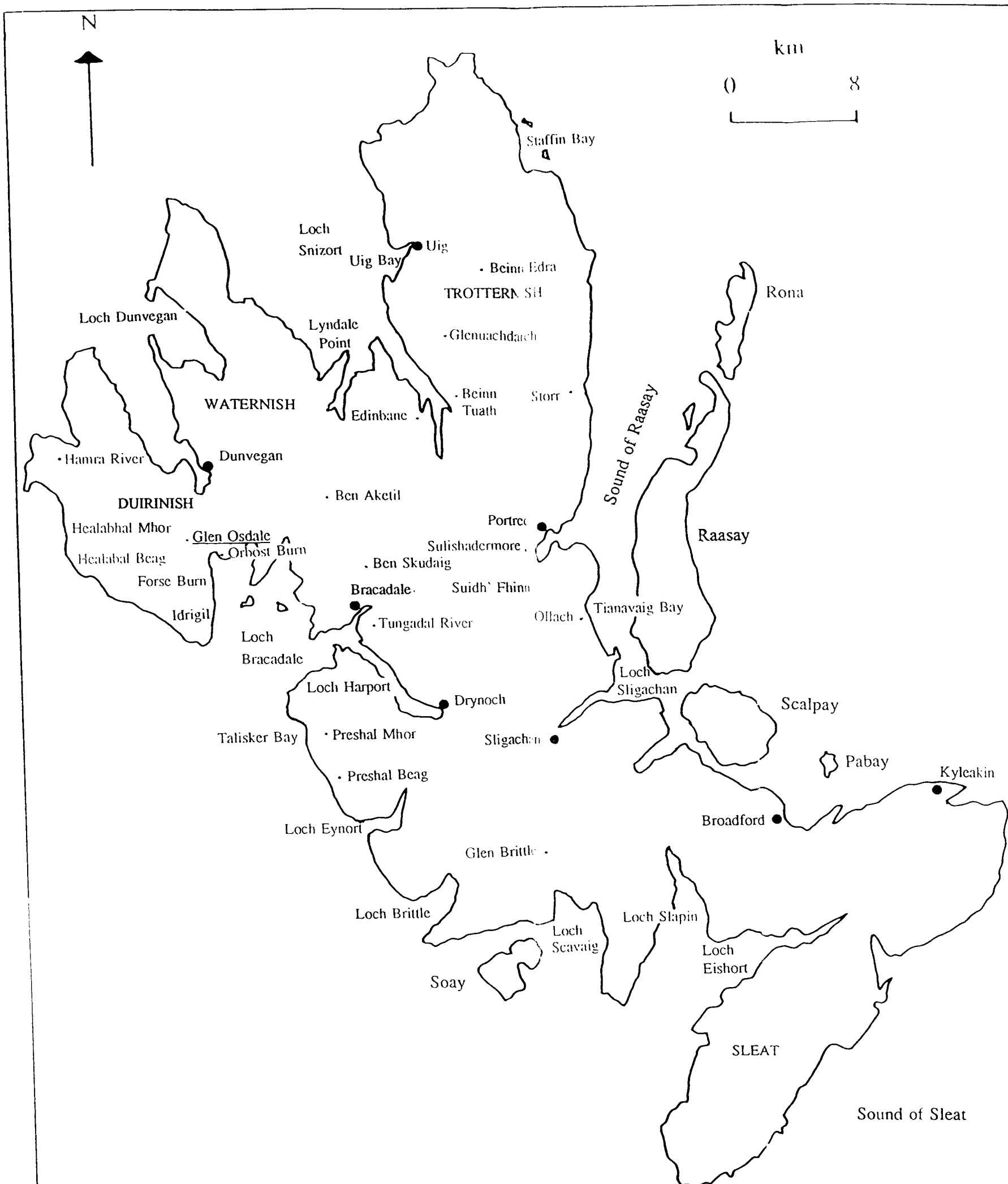


Figure 1.6 The Isle of Skye, major places (locality of King's (1976) plant bed underlined)

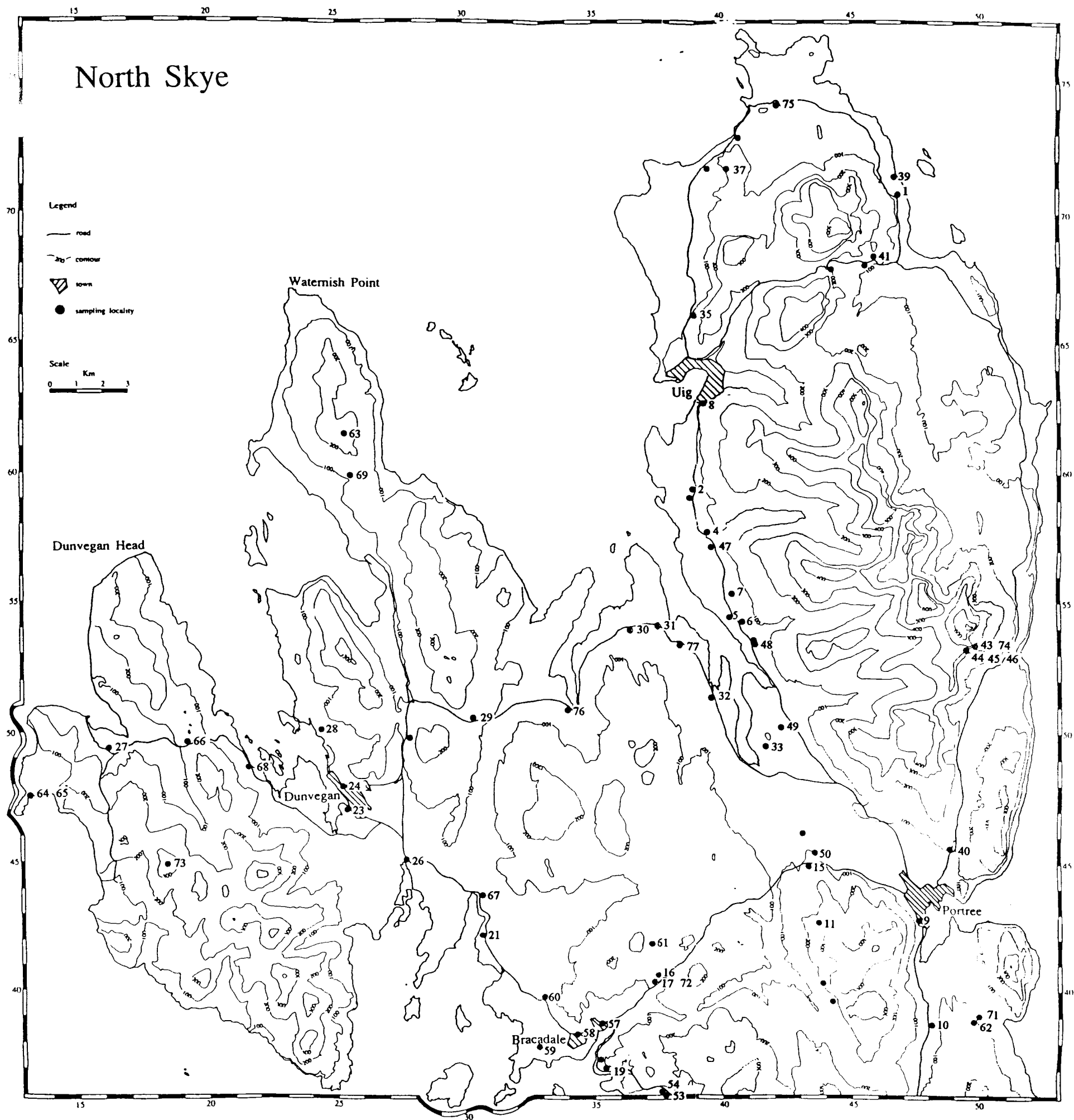


Figure 1.7 Area of study, showing sampling localities and locality numbers

Figure 1.8 The Skye Lava Field and Dyke Swarm.
(After Preston, 1982)

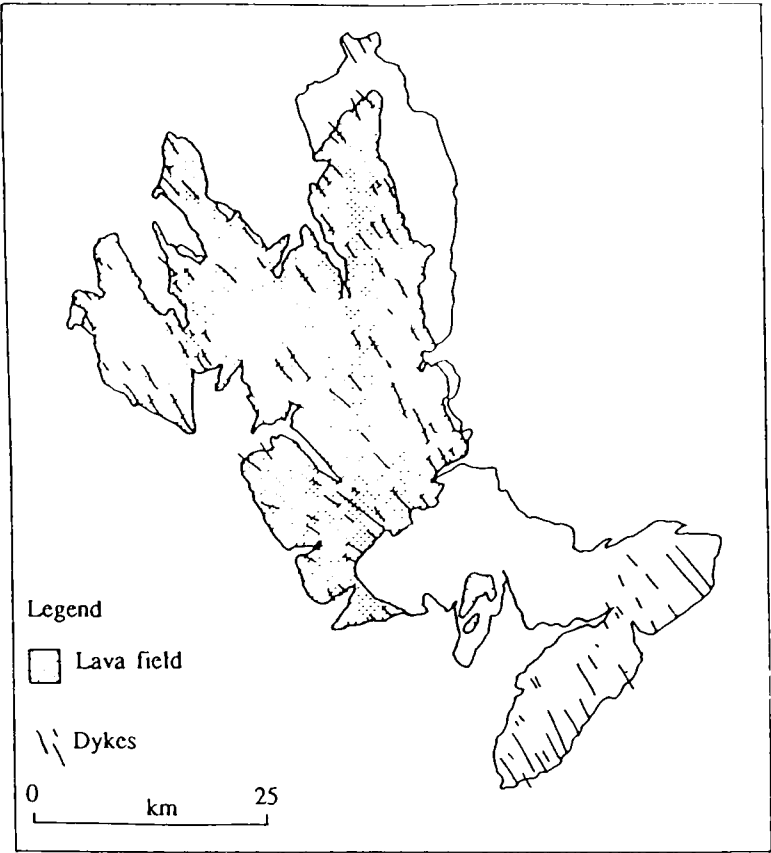


Figure 1.9 Schematic stratigraphic column of the main lithologies on Skye.
(Bell and Harris, 1986)

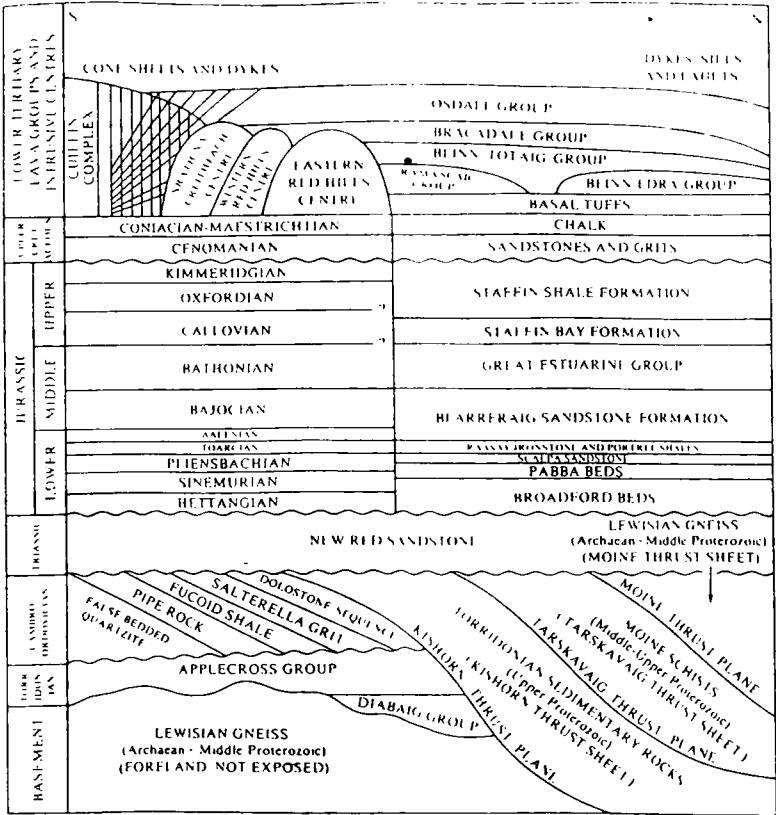


Figure 1.10 Cross section through the Skye lava field, showing the relationships of the stratigraphic units (Figure 1.10)
(Line of section marked on Figure 1.10) (After Anderson and Dunham 1966)

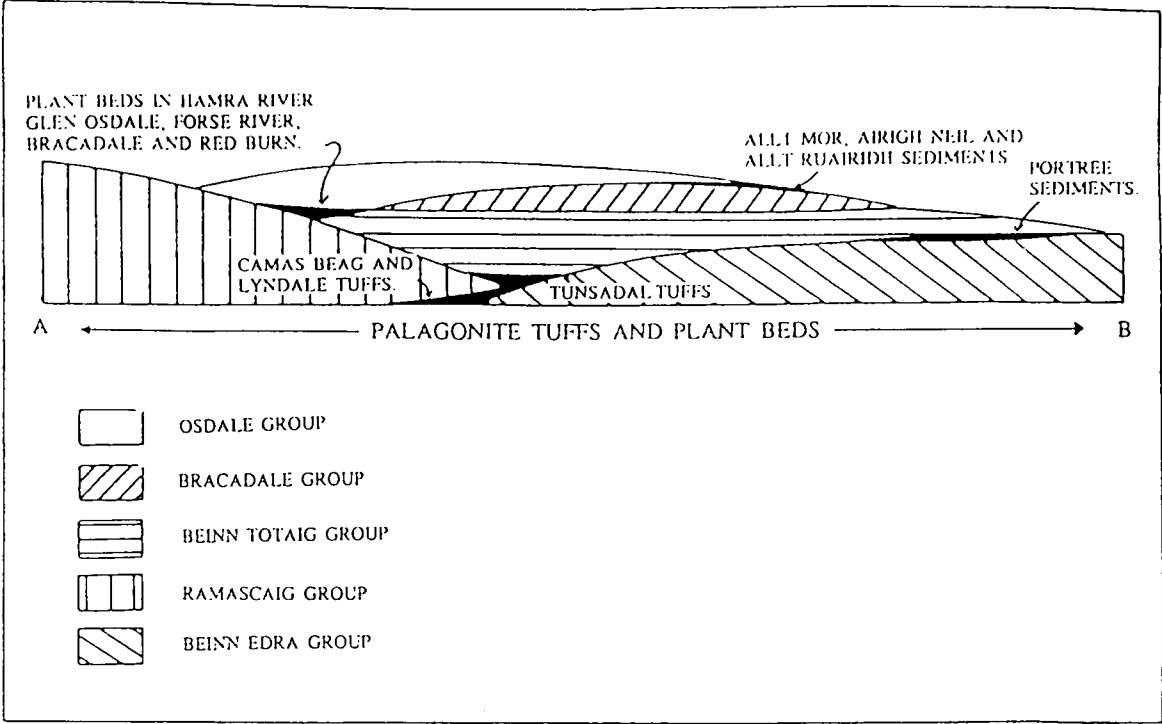
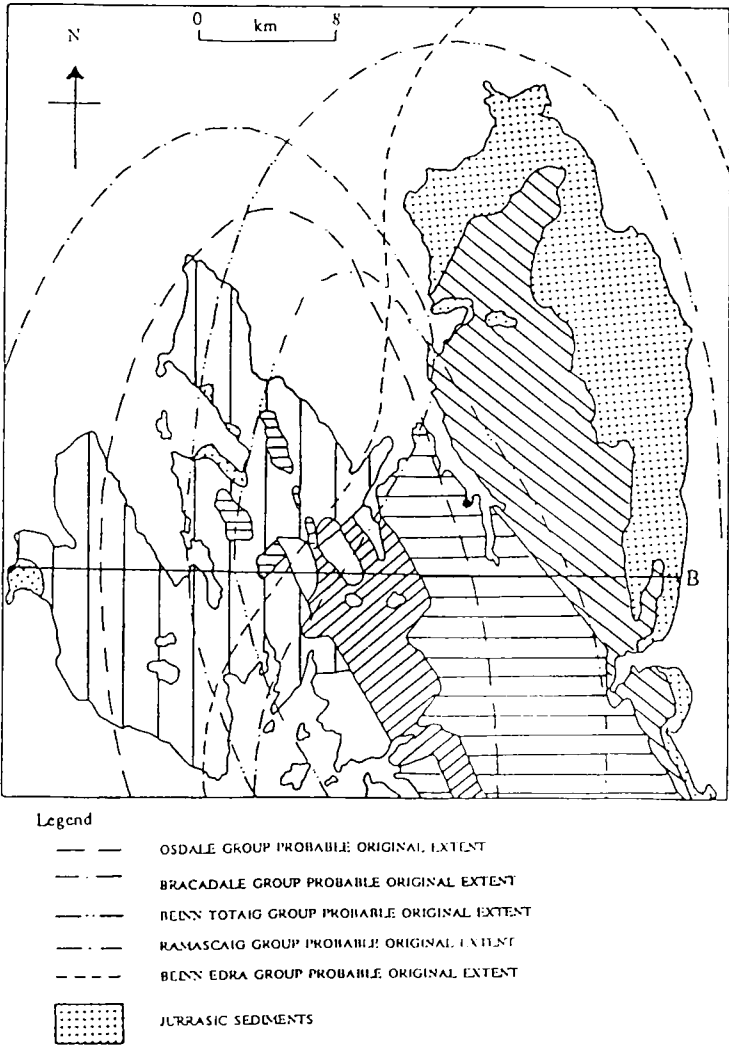


Figure 1.11 Sketch map of the lava field showing the stratigraphic units
(The suggested former limits are projected from the thickness of present day remnants)
(After Anderson and Dunham 1966)



PROVINCE	AGE Ma	MAXIMUM THICKNESS km	PRESENT AREA km ²
Keweenawan (Lake Superior)	1100-1200 (Late Precambrian)	12,000	>1,000,000
Siberian Platform	248-216 (Permo-Triassic)	3,500	>1,500,000
Karoo (South Africa)	206-166 (Jurassic)	9,000	140,000
Paraná (Brazil)	140-110	1,800	1,200,000
Etendeka (Namibia)	(Late Jurassic/Early Cretaceous)	900	78,000
North Atlantic Tertiary Province	65-50 (Late Cretaceous/Early Tertiary)	2,000	1,000,000
Deccan Traps (India)	Cretaceous-Tertiary boundary	>2,000	>500,000
Colombia River (north-west USA)	17-6 (Miocene)	>1,500	200,000
Snake River Plain (north-west USA)	0-17 (Quaternary)	-	50,000

Table 1.1 Ages and dimensions of the major continental flood-basalt provinces.
 (Data source: Wilson, 1989)

CHAPTER 2

HISTORY OF PETROGENETIC RESEARCH

2.1 Introduction

This chapter aims to summarise and critically assess the previous studies of the petrogenesis of the Skye lavas. For clarity the literature in this section has been divided. Topics such as fractional crystallisation, and crustal contamination are considered under separate headings.

A summary of the main conclusions reached by previous workers, the current state of knowledge including unresolved issues, and the resulting aims of this thesis are given at the end of this chapter.

2.2 The British Tertiary Igneous Province

Prior to the 1960s any consideration of the Skye lavas was as part of discussions of geochemical and petrogenetic concepts concerning the whole British Tertiary Igneous Province. The first work in the region was in the late 18th century and the early 19th century by Pennant, Jameson, Maccullough, Ami Boué, and others, who studied the rocks and minerals of the region. The first important paper on the province was the Mull Memoir (Bailey *et al.*, 1924). This authoritative work introduced several ideas which have subsequently remained central to geochemical and petrogenetic thinking. The concept of magma-types and magma-series was introduced. Bailey *et al.* (1924) postulated that the Mull lavas could be divided into nine magma types. The tendency at that time (in the early days of igneous petrological studies) was to avoid the complexity which would result from attempting to relate compositionally different

samples; by invoking evolutionary processes acting on a restricted number of parental compositions. Nonetheless, they did make a fundamental observation that basaltic magma was not a single entity, and instead several basaltic magmas needed to be defined in relation to their derivative products. Their terminology, plateau magma-type, and non-porphyritic central (NPC) magma-type, became synonymous with the terms alkali olivine basalt and tholeiite respectively (Kennedy, 1933; Tilley, 1950). The petrographic similarity between the lavas of various Tertiary centres led to the description of Hebridean lavas in terms of the two main magma-types in Mull. Although the original concept of Bailey *et. al.* (1924), of magma-types, was based solely on chemical criteria, the classification and grouping of samples was predominantly in terms of petrographic characteristics. This was because, at that time, whole rock geochemical analysis of samples was a laborious process. It involved wet chemistry and took two weeks to produce three analyses. Therefore, only ten of their 483 samples were chemically analysed. The magma-types concept obviously placed constraints on ensuing studies.

Once the magma-types concept had been defined, Bailey *et al.* (1924) attempted to relate the different magma-types to each other (this erroneous exploit led to much confusion in their study and in future researches). The discovery of the Glen More ring dyke (an intrusion which grades smoothly from a basic to acid composition within a vertical distance of approximately 500m), and the finding that the ring dyke analyses were very similar to those of the Mull magma-types influenced the thinking of Bailey *et al.* (1924). It led them to suggest that the magma-types could be related by fractional crystallisation. The NPC magma-type, with intersertal glass, was thought to be derived from the plateau magma-type by fractional crystallisation. The latter contained intersertal analcite and natrolite, so either assimilation of silicic crust or the precipitation of a diverse mineral assemblage was invoked to explain the different mesostasis of the two groups. In his book, *Evolution of the Igneous Rocks*, Bowen (1928) dismissed crustal contamination with associated fractional crystallisation, as a possible mechanism for generating the NPC magmas from the plateau magma-type, showing by graphical

analysis that it was quite unlikely that the NPC magma-type could be generated from the plateau magma-type by crustal assimilation alone. He ignored the comment of Bailey *et al.* (1924) that the plateau magma residuum was predominantly analcite and natrolite. He chose an atypical cone sheet sample, classified as plateau type on petrographic characteristics, to support his theory that the plateau magma-type could have a siliceous residuum. He employed his recent discovery that sub-calcic diopsides and enstatites melted incongruently to olivine in Fe-free, haplobasaltic synthetic systems in preference to petrographic observations; and concluded that the NPC magma-type could be generated from the plateau magma-type by fractional crystallisation of plagioclase and olivine.

The statement of Washington (1922) that magmas similar in composition to the BTIP NPC type were predominant throughout the flood basalt regions of the world, led Kennedy (1930) to suggest that they were primary basalts because of their "enormous bulk, worldwide distribution and remarkable uniformity". He inverted the scheme of Bailey *et al.* (1924) and proposed that the plateau magmas were derived by early separation and concentration of olivine and basic plagioclase from a NPC parent magma. Yet, he did not suggest how melting of the phenocrysts present in the NPC magma-type could occur to generate the phenocryst-free aphanitic plateau magmas mentioned by Bowen (1928). Presumably dissatisfied with his earlier theory Kennedy subsequently (1933) published a new hypothesis. He put forward a concept that revolutionized petrogenetic thinking - the NPC (renamed tholeiite) and Plateau magma-types (renamed olivine basalts, subsequently renamed alkali olivine basalt, Tilley, 1950) were independent parental liquids which evolved by fractional crystallisation to siliceous and feldspathoidal residua respectively. In the absence of detailed geophysical information about the state of the mantle region from which the two magma-types were generated Kennedy and Anderson (1938) proposed that two parental liquids were produced by melting of a tholeiitic layer and an olivine basalt layer, which they suggested were present in the lower crust.

During the Second World War (1939 to 1945) academic geological research ceased since investigations into coal and mineral deposits were commissioned as part of the war effort. In the post-war years the feeling of the British petrologists was that, drawing information from their current geological knowledge, the BTIP had been investigated adequately. Therefore, they turned their attention away from the BTIP to other igneous provinces, such as Hawaii (e.g. Powers, 1955). It was not until 1956 that the focus of petrogenetic research returned to Britain. The change of emphasis proved to be useful in the interpretation of the rocks of the BTIP. An important paper which discussed the igneous textures of the Skaergaard intrusion, Greenland, and their mechanisms of formation was published in the interim period by Wager and co-workers (e.g. Wager and Deer, 1939). The work had a great influence on petrogenetic thought resulting in an upsurge of interest in the new science of geochemistry. The concept of establishing the abundance and distribution patterns of elements in the earth, and the factors influencing their incorporation into common rocks and minerals had been addressed by Goldschmidt and co-workers in the 1920s and 1930s. Such work was continued by Wager and Deer (1939) who used optical emission spectrography (which was the main method for such investigations at that time) to determine the distribution of various trace elements in the rocks and minerals of the Skaergaard intrusion. Their study became a model for future geochemical researches. It emphasised the importance of having a clearly defined suite of igneous rocks for the study of the distribution of trace elements in magmatic systems. Experimental work on phase relations in silicate systems approximating to natural rocks had been produced from the geophysical laboratory of the Carnegie Institute since the 1920s. Although, the earliest of such experimental studies was performed by Hall in the late eighteenth century when he fused a dolerite to give support to the plutonists school of geological thought. The experimental work and the Skaergaard study were partly responsible for the renewed interest in igneous petrology in the 1940s, 1950s, and 1960s.

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demonstrated that petrological problems could be studied quantitatively, and so previous hypotheses based on little scientific evidence could be rigorously tested.

Other advances being made at that time included the use of X-ray crystallography to determine detailed information about the structure of minerals. Progress in experimental petrology occurred with the development of extremely strong steel alloys (originally produced for armaments in the Second World War), and apparatus which enabled experiments to be carried out in the presence of volatiles (e.g. Tuttle and Bowen 1958). Previous experiments had been limited to dry atmospheric pressures by the apparatus available, and the strength of the charge-capsules. The technological advances made it possible to subject the charge-capsules to extremely high pressures and temperatures comparable to mantle conditions, and also to consider the affects of volatiles on phase relations. Despite the initial resistance of some workers to experimental studies and laboratory based theories, igneous petrologists began to apply the new techniques to their studies. Nevertheless, experiments to determine the major constituents of rocks still involved painstaking gravimetric and volumetric analysis based on chemical separations. Some progress in the analysis of elements in whole rock samples was made in the 1950s and 1960s at Harwell Atomic Energy Research Establishment where the neutron activation analysis (NAA) technique was being investigated (this was before automated gamma ray spectrometry was developed). NAA was able to measure a range of elements accurately, e.g. the rare earth elements, the analysis of which had previously been a complicated procedure. In the late 1950s methods in X-ray crystallography were updated, and the X-ray goniometer diffractometer (which included subordinate apparatus for X-ray fluorescence spectrometry) was developed. At approximately the same time the increasing use of isotopic systems in geological age determinations led to research into the use of isotopes as cosmic and petrogenetic indicators.

From the mid 1950s onwards, the theories developed during the study of geologically different regions, and the new analytical techniques were applied to the rocks of the BTIP. The

acceptance that the NPC and plateau magma-types had separate parental liquids meant that the intra-suite chemical differences, resulting from fractional crystallisation, had to be distinguished from inter-suite differences. This was done by Wager (1956) who, having been persuaded to address the problem by Richey, employed his knowledge of the Skaergaard differentiated layered intrusion. He used Fe/Mg ratios and the composition of normative plagioclase to arrange lavas fractionating ferromagnesian minerals and plagioclase into an order of descending liquidus temperature. So the different stages of evolution of the NPC basalts, and the plateau basalts were identified, and the compositional diversity within each magma-type was summarised.

The main impediment to interpretation at this stage in the investigation of magma genesis was the lack of chemical analyses, because of difficulties in analytical methods.

The technological advances in X-ray fluorescence, mass spectrometry and experimental studies in the 1950s and 1960s made the compositional analysis of samples simpler (an adverse effect of this being that petrologists perhaps became less discerning when sampling). This resulted in a large amount of geochemical and isotopic data being produced, and used to address the questions posed by early workers, and more general petrological problems. By this time, the mid 1960s, the knowledge of important natural nuclear processes, and the factors affecting the natural fractionation of both radiogenic and non-radiogenic isotopes had significantly increased. It was recognised that the ratios of the different Sr isotopes evolved over long periods of time (as a result of the decay of ^{87}Rb to ^{87}Sr). Consequently, it was realised that some isotopic ratios could be used as petrogenetic indicators, which would be of particular use in distinguishing material of a mantle and a crustal origin. This realisation combined with a general improvement in the sensitivity and reliability of mass-spectrometers led to a whole new area of geological research into the isotopic characteristics of igneous rocks (with age determinations often being the by-product of such studies). An improvement in the reliability and precision of the X-ray fluorescence technique also occurred at about this time; this made

the analysis of the chemical composition of whole rock samples quicker and simpler. Following on from the experimental work of Tuttle and Bowen (1958), and others, a classic experimental study of natural and synthetic rock systems and the origin of basaltic magmas was made by Yoder and Tilley (1962). Once the behaviour of basaltic compositions at low pressures, and thus the affects of low pressure fractional crystallisation, had been established experimental petrologists investigated the high pressure phase relationships of basaltic compositions. Two key studies, by Green and Ringwood (1967) and O'Hara (1968), considered the melting behaviour of peridotites and basalts. Their works formed the basis of much of the later experimentation. Although the results of such studies do not usually provide a unique solution, because of potential variations in composition, pressure, temperature, and volatile contents, they do enable the construction of specific petrogenetic models which can be tested in other ways.

It was in the mid 1960s to the late 1960s (when the use of the analytical methods outlined above became prevalent) that attention focused on the BTIP once more and the third stage of the research in the BTIP began.

2.3 Skye

2.3.1 Introduction

During the 1960s the emphasis of the research on Skye was initially the petrogenesis of the granitic rocks, i.e. whether they were the products of fractional crystallisation of basaltic magmas or melts of sialic crust. Moorbath and Bell (1965) concluded that, since the Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the granites were significantly higher than those of the mantle derived basalts, the granites must have been generated by the fusion of sialic crust. They supported their hypothesis with the melting experiments of Brown (1963), the observation that there was a likely heat source (the volume of basic magma in the crust) (McQuillin and Tuson, 1963; Bell

1966), and the paucity of rocks of intermediate composition in the region. Although not strictly part of this study it is worth briefly summarising the history of the isotopic research of the Skye granites at this stage because the work affected the direction taken by later studies of the basaltic lavas. Thompson (1982a) and Moorbath and Thompson (1980) both present comprehensive reviews of the previous work on the Skye granites. The following section outlines the important points of the previous research. After the original study of Moorbath and Bell (1965), Moorbath and Welke (1969) employed Pb isotopic data to investigate the petrogenesis of the igneous rocks of Skye further. Somewhat unexpectedly they found that the majority of the rocks, including the ultra-basic and basic mantle-derived lavas, had some component (from 6 to 65%) of unradiogenic Pb from a ca. 3000 Ma source, in addition to a 60 Ma mantle type Pb signature. This led them to agree with Bell (1966) by concluding that both fractional crystallisation of the Tertiary basic magmas, and partial melting of sialic crust, had been important in the genesis of the granites. They proposed that the ancient Pb component in the Skye lavas was the result of selective contamination of the basic and ultrabasic magma by Archaean Lewisian basement (the unradiogenic-Pb characteristics of which had already been determined by Moorbath *et al.* 1967), thus producing a mixing line for the lavas which had a slope corresponding to an age of 3000 Ma. The realisation that hydrothermal alteration, such as that caused by the convective ground-water circulation associated with the Skye intrusive centres, could result in depletion of ^{18}O led to the proposal that some of the Sr and Pb characteristics of the Tertiary igneous rocks of Skye could have been modified (Taylor and Forester, 1971; Beckinsale, 1974; Beckinsale *et al.*, 1974; Pankhurst *et al.*, 1978; Forester and Taylor, 1977). However, later studies indicated that the cause of variations in Sr and Pb isotopic ratios were not merely the result of hydrothermal alteration (e.g. Beckinsale *et al.* 1978; Carter *et al.*, 1978). This was confirmed by Moorbath and Thompson (1980) who noted that the Beinn an Dubhaich granite had high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ancient unradiogenic Pb, but did not have depleted ^{18}O values.

The first experimental study to address the Skye lavas specifically was by Tilley and Muir (1962) who used a hypersthene (hy)-normative altered basalt and nepheline (ne)-normative fresh pyroxene crystals from within it as evidence for silica-saturation increasing as a result of hydrothermal alteration. They proposed that all previous samples analysed from the BTIP were affected by hydrothermal fluids, and prior to alteration had been ne-normative. In the early 1960s Tilley and co-workers showed that careful choice of petrographically-fresh samples allowed detailed studies to be made of the mineralogy, chemistry, and one-atmosphere melting relations of the alkali suite on Skye.

The first detailed geochemical study of the Skye lavas was by Thompson *et al.* (1972). They published 72 chemical analyses of petrographically fresh samples. One of their key findings was that both ne-normative and hy-normative lavas were present. Small but distinctive compositional differences were detected between the most primitive ne-normative and hy-normative lavas. Since positive correlations were observed between Si-saturation and elements known to be immobile during hydrous alteration, Thompson *et al.* (1972) concluded that weathering and hydrothermal alteration were not responsible for the variations in the normative character of the lavas. Morrison (1980) supported their opinion when she showed that Sr was the only element which was mobilised by the pervasive zeolite facies metamorphism of the lava pile; so, since variation in Sr content could not account for changes in the normative character of the lavas, hydrothermal alteration could not generate the range of Si-saturation of the Skye lavas. Thompson *et al.* (1972) therefore proposed that the lavas (now named the Skye Main Lava Series (SMLS)) really did lie across the critical plane of silica undersaturation. Having decided this, Thompson *et al.* (1972) employed the experimental results of Yoder and Tilley (1962) which had shown the critical plane of silica undersaturation in the system olivine-diopside-quartz/nepheline, corresponded to a thermal barrier in anhydrous systems at less than 8 kb pressure. Thompson *et al.* (1972) proposed that the lavas had evolved at pressures equivalent to the base of the lower crust, or uppermost mantle (at which pressure the divide is

inoperative), and had then been rapidly erupted without further fractionation.

The new data of Thompson *et al.* (1972) showed that both the hy-normative and ne-normative SMLS basalts had Plateau magma-type petrographic characteristics (i.e. olivine-phyric as opposed to aphyric like the non-porphyritic central magma-type). This led them to disregard the plateau magma-type (ne-normative, alkali basalt) and the non-porphyritic central magma-group (hy-normative, tholeiite) division of the lavas which had been defined by Bailey *et al.* (1924) (and renamed by Kennedy and Anderson, 1938; and Tilley, 1950) on the basis of the chemical and petrographical characteristics of the lavas. Instead, they divided the lavas solely on the basis of chemical criteria. They were more cautious than previous workers and did not apply their classification to the whole BTIP; this was because it was not clear whether the composition of the lavas was identical in the different regions e.g. Mull and Antrim. This point is still not entirely resolved, and it demonstrates how petrogenetic thinking had changed since the first studies of the BTIP, which inferred that the volcanic rocks of the North Atlantic Tertiary Province were all part of the same lava field (e.g. see Gass and Thorpe, 1976).

The detailed geochemical studies of the Skye basalts in the early 1970s led to the identification of two new magma-types (Preshal Mhor and Fairy Bridge) which, because they had basaltic petrography, had previously not been distinguished from the SMLS magma-type. Once the new magma-types had been identified an obvious question was "how are they related to the SMLS?". Each of the three magma-type showed internal chemical variation but, because of their compositional variations could not be related to either of the others by low pressure crystal-liquid fractionation. This resulted in Thompson and co-workers employing the hypothesis of Kennedy (1933) (which proposed that alkali basalts, and tholeiites had different parental liquids), i.e. they suggested that the magma-types may have had different parental liquids. The first new magma-type to be defined was identified by Thompson *et al.* (1972), it comprised a few flows of high-Ca, low-alkali olivine tholeiites intercalated with SMLS at the top of the lava pile. These lavas, named the Preshal Mhor (PM) magma-type, had

compositional similarities to Mid-Ocean Ridge Basalts (MORB). Only two localities of Preshal Mhor basalt have been found in the Skye lava field: both are within the Osdale stratigraphic division of Anderson and Dunham (1966); the first is at Edinbane (Figure 1.6), the second at Preshal Mhor (334300) and Preshal Beag (329279), (Esson *et al.*, 1975). A study of the dykes which cut the Skye lava field revealed however that the PM magma-type was abundant in the dykes of the Skye regional swarm (Mattey *et al.*, 1977). The third magma-type, the Fairy Bridge (FB), was identified in the Skye lava pile by Mattey *et al.* (1977). This magma type had compositional similarities to the major elements of the SMLS basalts and to the trace elements of the PM lavas, and it had a characteristic flat rare earth element (REE) profile. Only one lava flow of Fairy Bridge basalt (FB) has been found, (the type locality is at the Fairy Bridge (279514) near Dunvegan); but samples with the geochemical characteristics of the FB magma-type have been found in the Skye regional dyke swarm (Figure 1.8), (Mattey *et al.*, 1977). The preponderance of the PM magma-type, and FB magma-type in the dykes cutting the lava pile implies that they were erupted, and, possibly generated, later than the lavas of the SMLS magma-type; and that the PM and FB magma-types may have been abundant in an upper, now eroded, part of the lava pile. Also, the composition of the dykes led Mattey *et al.* (1977) (who observed that the majority of them were of the Preshal Mhor magma-type) to infer that the Preshal Mhor magmatism had been coincident with the period of maximum crustal extension on Skye.

Thus, the early geochemical studies revealed that what, from petrographic studies, had previously been thought of as a fairly uniform pile of basalts, could be divided into three compositionally distinct magma-types. This finding was to have an important affect on the interpretation of the petrogenetic evolution of the region.

Having defined the compositional characteristics of the magma-types research workers' attention focused on their petrogenesis.

2.3.2 Fractional crystallisation

2.3.2.1 Skye Main Lava Series

Before attempting to deduce detailed information about the mantle source region of the lavas the effects of fractional crystallisation on the composition of the lavas were considered.

The concept of settling of early formed crystals in a solidifying magma was first considered as early as 1825 by Scrope. After 1900 workers such as Schweig, Daly, and Harker proposed that crystal settling could cause magmatic differentiation. Yet, it was not until the experimental work of Bowen (1915) (which showed that gravitational settling of crystals, crystal zoning, and filter pressing were all important mechanisms in the differentiation of magmas) that the concept of fractional crystallisation became familiar to igneous petrologists and was considered to be an important petrogenetic process.

There had been some thought given to the process of fractional crystallisation in the evolution of the BTIP lavas in the attempt to relate the alkali basalt plateau magma-type and the tholeiitic Non-porphyrific central magma-type. Fractional crystallisation was also considered once it had been decided that the magma-types had independent parental liquids, to define intra-, and inter-suite variations. Yet, the first consideration of fractional crystallisation specifically in relation to the Skye lavas was not until 1966 by Anderson and Dunham in the Geological Survey memoir of the area. They inappropriately used the experimental results of Bowen and Schairer (1935) on the system MgO-FeO-SiO_2 to calculate temperatures of phases crystallising in a multi-component silicate melt. They stated that in a basaltic melt the first phase to crystallise would be magnesian olivine at 1890°C (the liquidus temperature for pure forsteritic olivine), followed by crystallisation of very calcic plagioclase at 1600°C (approximately the liquidus temperature of pure anorthite).

In the light of new whole rock and phenocryst analyses (the analysis of the latter made

easier by developments in the technology of the electron microprobe in the late 1950s and 1960s) Thompson *et al.* (1972) outlined the first detailed fractional crystallisation model for the Skye lavas, based on the separation of minerals observed as phenocryst phases within them. They did not identify any truly aphyric lavas but classified those with less than 5% phenocrysts as such. Their study of major element variations with increasing fractionation (assessed by the ratio $\text{FeO}+\text{Fe}_2\text{O}_3/\text{MgO}+\text{FeO}+\text{Fe}_2\text{O}_3$) led to the identification of two evolutionary lineages, a high-Si, low-Fe (hypersthene-normative) trend and low-Si, high-Fe (nepheline-normative) trend, in the Skye Main Lava Series (SMLS).

Trend 1 (ne-normative): SMLS basalt -> hawaiite -> mugearite -> benmoreite.

Trend 2 (hy-normative): SMLS basalt -> Si-rich, Fe-poor intermediates -> trachyte.

The compositional characteristics of the two lineages were linked to their phenocryst mineralogy i.e. the dominance of titaniferous magnetite over olivine in the high-Si lavas and vice versa in the low-Si lavas.

Thompson *et al.* (1972) projected the lavas into the basalt tetrahedron (nepheline-ne, olivine-ol, clinopyroxene-cpx, plagioclase-plag, quartz-qtz) from plag into ol-cpx-ne/qtz (in which the lavas trended across the ol-cpx join), and from ne/qtz into the plane ol-plag-cpx (in which the lavas plotted near the ol-plag-cpx cotectic). This led them to suggest that if the trends of the aphanitic lavas in the two projections were attributable to fractional crystallisation or partial melting processes, the separation or fusion of one or more pyroxenes may have played an important part in their genesis. They had not identified clinopyroxene in any of the more sparsely porphyritic lavas. They took this, in conjunction with the lavas lying across the critical plane of silica-undersaturation, and therefore the low pressure thermal divide close to it, to infer that the compositional variation in the aphanitic lavas was attributable to high pressure processes.

Thompson *et al.* (1972) noted that fractional crystallisation at relatively low pressures (i.e. when the thermal divide close to the critical plane of Si-undersaturation was operative)

would split the continuous spectrum of basalts into two groups: Si-saturated hy-normative basalts would give rise to Si-saturated derivatives and Si-undersaturated alkali basalts would give rise to ne-normative derivatives. Such a compositional divide was observed in the more evolved Skye lavas. Therefore, in order to investigate low pressure fractional crystallisation Thompson *et al.* (1972) carried out one-atmosphere pressure melting experiments on a representative suite of twenty one Skye lavas (one of which, SK971, the sample having a higher, 6°C, liquidus temperature for plagioclase, was later found to be of Fairy Bridge magma-type composition), the results of which are summarised below. No clear distinction was visible between the liquidus temperatures of the hy- and ne- normative basalts. However their derivatives were clearly separable, the latter having considerably higher liquidus temperatures than the former samples with a similar $\text{FeO}+\text{Fe}_2\text{O}_3/\text{MgO}+\text{FeO}+\text{Fe}_2\text{O}_3$. Another finding of the melting experiments was that a distinct break between the liquidus temperature - Fe enrichment trend of the aphyric and porphyritic basalts occurred at about 1220°C. The liquidus phase was olivine in all the olivine-phyric basalts. This led Thompson *et al.* (1972) to suggest that they were the products of low pressure crystal accumulation. Presumably because the presence of liquidus olivine was taken to be the result of an increase in olivine concentration in the magma, due to accumulation, thus raising the liquidus temperature for it - rather than it simply being the phase with the highest liquidus temperature in a complete melt of basaltic composition. It was found in the basalts that plagioclase did not begin to crystallise at a constant temperature. It had a liquidus temperature varying from 1190°C to 1205°C, which Thompson *et al.* (1972) took to be indicative that the basalts had a complex evolutionary history. Error bars on the temperatures produced by the above experiment are expected to be in the range $\pm 5^\circ\text{C}$ which would lessen the significance of the temperature range. The study of Thompson *et al.* (1972) showed that augite crystallised at relatively low temperatures, which was taken to confirm the petrographic observation that clinopyroxene did not exist as a phenocryst phase in the sparsely porphyritic basaltic Skye lavas. Somewhat unexpectedly the experiments showed that the

intermediate lavas always had plagioclase as their liquidus phase, but the members of the normative, high-Fe, low-SiO₂ trend always contained olivine microphenocrysts. If the composition of a silicate melt is such that olivine would crystallise from it, it would be expected that it would have the highest liquidus temperature. This apparently anomalous phenomenon had previously been noted by Tilley *et al.* (1965, 1966) who suggested that the plagioclase was inherited material collected by flotation in fractionation residua. Thompson *et al.* (1972) stated that the Skye lavas were not rich enough in plagioclase phenocrysts for that to be the explanation of their liquidus plagioclase. Yoder (1969) had proposed that the same anomaly in calc-alkaline lavas may have been the result of high P_{H₂O} in the system:- a rising P_{H₂O} resulting in a progressive lowering of the liquidus temperature of plagioclase relative to other minerals. So, a magma crystallising olivine and plagioclase together at appreciable P_{H₂O}, which was erupted quickly would not be in equilibrium at one atmosphere. Later fusing of the sample under anhydrous conditions would lead to supersaturation of the plagioclase which would then melt at a higher temperature than the olivine. From the results of their one-atmosphere melting experiments Thompson *et al.* (1972) suggested that this was the process affecting the intermediate Skye lavas. They supported their theory by noting the presence of hydrous phases such as biotite and amphibole in the lavas, which they suggested would contain dissociated water when erupted, thus permitting the possibility of late-stage oxidation within crystallizing flows by hydrogen leakage. Thus, Thompson *et al.* (1972) attributed the scatter in the SMLS data-set to the accentuation of small differences in parental magma compositions by fractional crystallisation. They noted that Si-poor intermediates were much more abundant than Si-rich intermediates, despite the more primitive lavas being of approximately equal abundance. They suggested that the latter may have undergone an increase in viscosity associated with their rise in Si content and fall in Fe content, thus inhibiting crystal-liquid separation.

Since the bulk compositions and liquidus temperatures of the primitive end-members of the two evolutionary trends were so similar it was suggested that the distinction between the

different fractionating assemblages (i.e. olivine in the ne-normative, high-Fe, low-Si trend and titanomagnetite in the hy-normative, low-Fe, high-Si trend) could be the result of variations in fO_2 in the magmas at crustal levels.

An evolutionary sequence of (upwards) basalt - hawaiiite - pause in activity - basalts - hawaiiites was recognised in the lower part of the Skye lava succession, with basaltic hawaiiites being virtually absent. However, no explanation was offered as to how the sequence may have developed.

The major conclusion of Thompson *et al.* (1972) was that there were two evolutionary trends in the SMLS lavas. The first trend was produced by alkali basalts (ne-normative) evolving by closed system, low fO_2 , fractional crystallisation deep in the crust, with the separating phenocryst assemblage maintaining a constant fO_2 value, thus enabling Fe-enrichment to occur. Under these conditions the alkali basalts evolved via low-Si, high-Fe intermediates to benmoreites. The second trend was produced by olivine tholeiites (hy-normative) evolving at upper crustal depths where the escape of H_2O , and the incorporation of meteoric O_2 (and possibly H_2O) caused fO_2 values to rise. Which would have resulted in cessation of olivine precipitation and subsequent separation of Fe-Ti oxides. Under these conditions the olivine tholeiites evolved via high-Si, low-Fe intermediates to trachytes.

Thompson (1972a) proposed that the compositional gap in the Skye lavas between basalt and hawaiiite (also found to exist in many other volcanic suites, Thompson, 1972a) originated in an eruptive process which resulted in discontinuous sampling at the surface of a series of magmas which were compositionally continuous at depth. He suggested that the crystal/liquid ratio could be the cause of the observed compositional gap. During the evolution from magnesian basalt to Mg-poor basalt the proportion of crystals could have been small enough to allow the escape of liquids, thus resulting in a continuum of compositions being represented at the surface. Continued crystallisation may have resulted in the residual liquid being trapped in

between the crystals of a virtual solid. So a compositional gap would result in the lavas until some effect (perhaps stresses associated with heating, cooling and magma production in the mantle beneath the volcanic area, or rising P_{H_2O}) resulted in the magma being able to reach the surface once more. Thus, a scenario was envisaged in which relatively minor upper mantle thermal disturbances, resulted in a heat sink developing because of the transfer of thermal energy to latent heat of fusion during the mantle melting. So a rise in the temperature of that area of mantle would have been temporarily prevented. Therefore, the thermally induced stresses helping the passage of magma to the surface would have been reduced, and since the mantle was only heating slowly few flows of the early basalt would be erupted at the surface. Later magma batches would stagnate and partially crystallize in the cooler mantle above their generation zone until they were released by some mechanism such as those discussed above (Thompson, 1972a).

Comments on natural fractionation patterns (as determined from one-atmosphere melting experiments) and simplified synthetic analogues for various suites of volcanic rocks including the Skye lavas by Thompson (1972b) revealed several interesting points regarding the fractional crystallisation of the SMLS. In comparisons between natural and experimental models the following simplifications were made, i. all differentiation processes other than crystal-liquid separation were ignored, ii. the natural systems were treated as isobaric and closed, with a single parent liquid giving rise to a daughter by crystal addition or subtraction. Since this is not strictly the case for many of the suites of volcanic rocks under study, including the Skye lavas, the one-atmosphere melting results are discussed with the proviso that they are likely to be only partially applicable to the genesis of the lavas concerned. Features which corresponded well between the natural fractionation and the simplified synthetic analogues were the kink in the bulk composition liquidus trend that divided the highly porphyritic, magnesian lavas and the sparsely porphyritic, less-magnesian lavas. Similarly the way the liquidus temperature of sub-

liquidus phases remain constant or fall slowly with increasing evolution of the bulk composition is readily explicable in terms of simple synthetic systems. Discrepancies however occurred in the behaviour of magnetite which, in the natural fractionation process, had a liquidus temperature that increased with the evolution of the magma until it became a liquidus phase, whereas in the synthetic system it was not present as a liquidus phase. This was attributed to less rapid falling of fO_2 in the natural system than in the simplified synthetic analogue, and resultant expansion of the magnetite stability field with falling temperature.

Thompson (1972b) proposed that the evolution of the Skye lavas without clinopyroxene appearing on their liquidus was discrepant. Since it would be expected that in a fractionating basaltic magma at low pressures olivine, plagioclase, and clinopyroxene would all reach the liquidus at an early stage of the process and fractionate together. However this statement should be qualified, by a statement "provided that the bulk composition of the magma is near to the ternary eutectic in the system olivine-plagioclase-clinopyroxene". Thompson (1972b) commented that, despite the best fit results of computer-generated extract calculations (in which, it should be noted, the best fit solutions are not necessarily correct) which were improved by the addition of clinopyroxene to the fractionating assemblage, clinopyroxene phenocrysts were not present in the lavas. He suggested that calcic-clinopyroxene would be needed in addition to olivine and plagioclase for the lavas to be driven along the observed evolutionary trends. From the results of high pressure melting experiments on an evolved Snake River Plain lava, in which clinopyroxene became a fractionating phase at anhydrous pressures of 7 kb to 10 kb, Thompson (1972b) suggested that the main differentiation of the Skye magmas took place at moderately high pressures. Then the magmas paused in a chamber at upper crustal levels long enough for the high pressure phenocryst phases to be dissolved and replaced by low pressure phases. This model was consistent with the previous proposal that olivine was replaced as the liquidus phase by plagioclase in the more evolved lavas because of raised P_{H_2O} in the fractionating system (supported by the presence of amphibole and biotite in the more evolved lavas). So, it was

concluded that anhydrous melting experiments would not be representative of the crystallisation history of the samples. The deviation of natural fractionating systems (as determined from one-atmosphere melting experiments) from fractionation patterns predicted by synthetic analogues was attributed to the influence of load pressure and P_{H_2O} during evolution. The main affects proposed were the depletion of augite, and concentration of plagioclase in the magma, thus resulting in anomalous behaviour in one-atmosphere melting experiments. Therefore, it was concluded that the interpretation of processes affecting igneous rocks by analogy with the results of experiments on synthetic analogues (simplified systems which have only four components, generally $CaO - MgO - Al_2O_3 - SiO_2$, O'Hara, 1968) was only possible when the samples had relatively unevolved compositions and the system was not complicated by the factors outlined above (Thompson, 1972b).

From the conclusions drawn from two-element variation diagrams, one-atmosphere melting experiments and crystal-extract calculations Thompson (1972a., 1972b.) reiterated the view of Thompson *et al.* (1972) that although olivine and plagioclase are the only phenocryst phases in the Skye lavas they could not explain the features of the basalt-hawaiite transition. To try to obtain a best fit fractional crystallisation model for the Skye lavas Thompson (1974a) used average basalt and hawaiite compositions, rather than true parent daughter pairs which were not discernable in the scatter/bundle of lineages of the data-set, in mixing calculations (such as those of Bryan *et al.*, 1969; and Wright and Doherty 1970). Least squares mixing calculations (Wright and Doherty, 1970) relating the major element concentrations of average magnesian basalt (MgO 11.70%, 17 samples), and average less magnesian basalt (MgO 8.41%, 11 samples) using an olivine and a plagioclase phenocryst composition from a magnesian basalt, showed that the best-fit crystal extract was 9.8% olivine (Fe_{84}) and 4.1% plagioclase (An_{79}). Using compositions of olivine and plagioclase fractionating from SK971 (originally thought to be representative of the SMLS basalts but later found to be a lava of the Fairy Bridge magma-

type), Thompson concluded, from least squares modelling, that the high sum of residuals, 6.71, negated the possibility of generation of an average hawaiite (MgO 4.75 wt%) from an average basalt (MgO 8.41 wt%) by their precipitation alone. He found that addition of a sub-calcic augite, such as that found to precipitate at 13 Kb from SK971 in high pressure experiments improved the sum of residuals to a better, but nonetheless quite imperfect, 1.23. Therefore, he concluded that the most suitable mineral assemblage for generating the hawaiite from the less-magnesian basalt was 8% olivine, 15% plagioclase and 21% aluminous sub-calcic augite (crystallised experimentally from SK971), with the fractionation occurring at a depth equivalent to 13 kb i.e. approximately 30-40 km.

A high pressure experimental study of one magnesian SMLS lava (Thompson 1974a) showed that there was a four-phase point (olivine, Ca-rich clinopyroxene, pigeonite, liquid) on its liquidus at 17 kb. This led Thompson (1974a) to conclude that the sample, and by analogy, the other high magnesian basalts were generated at depths equivalent to that pressure, i.e. approximately 60km, and were primary magmas. Consequently, the Mg-poor SMLS basalts which had previously been regarded by Thompson *et al.* (1972) as liquids equilibrated at relatively low pressures, into which olivine had accumulated to form the more magnesian porphyritic basalts, were reinterpreted. Thompson's high pressure work also revealed that the P-T diagram for a less-magnesian sample (SK971) had a four-phase (olivine, Ca-rich clinopyroxene, plagioclase, liquid) liquidus point at approximately 11 kb. This was suggested to be a cotectic point. Therefore, the Mg-poor SMLS basalts were proposed to have been the products of partial crystallisation of some batches of magnesian basalt primary magma. The magmas having been generated at approximately 60 km, 17 kb, then crystallized at a depth equivalent to 11 kb (approximately 40 km), i.e. approximately at the crust mantle boundary.

Although it had previously been noted that the scatter in the SMLS data-set ruled out the possibility of identifying and modelling parent-daughter pairs, Thompson (1974a) used the high pressure melting experiments performed on the Mg-poor basalt SK971 and a more

magnesian basalt to test the hypothesis of the evolution of the lavas by fractional crystallisation. He concluded that, assuming the magnesian basalt evolved by the precipitation of olivine + plagioclase + Ca-rich pyroxene between 1175°C and 1225°C in the pressure range 7 kb to 12 kb, the residual liquids which separated during that P-T range and erupted without further compositional change, would have phase relations like those of SK971. Comparison of the compositions of glasses (i.e. quenched residual liquid) from the magnesian basalt to SK971 and other Mg-poor basalts, showed that, although no pairs of compositions were comparable, the range of elements in the two were similar. Microprobe analyses of glasses from the Mg-poor basalt at 10 kb (near the P-T diagram four phase point) showed that a reduction in temperature of only 25°C resulted in a significant fall in MgO and rise in K₂O and P₂O₅, indicating that the sample was solidifying rapidly at that pressure. The major element compositions of the glasses were approximately equivalent to the composition of the hawaiites, with the exception of Fe which was not so enriched in the hawaiites because of the precipitation of titaniferous magnetite, but under the low fO₂ conditions in the experiment could rise to higher values. Minor discrepancies in the Ca and Na contents of the glasses and hawaiites could be resolved by crystallising more Ca-rich plagioclase from the Mg-poor basalt, an effect which would result from rising P_{H₂O} in the system (Yoder, 1969). So the hypothesis of increasing P_{H₂O} in the system as fractionation progressed was supported by Thompson (1974a). He proposed that high pressure melting experiments confirmed that an anhydrous model could not explain the genesis of the hawaiites. Therefore, an analogy for the genesis of the hawaiites was made with the hydrous study of Kushiro and Thompson (1972) on a mid-ocean ridge basalt (that had a similar phase relations to the Skye hawaiite under anhydrous conditions) which developed a four phase point at approximately 6 kb (equivalent to 20 km, i.e. within the crust) when its water content was increased to between 1.5% and 3.2%.

The major conclusions of Thompson regarding the fractional crystallisation history of the SMLS lavas as determined from experimental work and least squares mixing calculations

can be summarised as follows. He concluded that the SMLS magnesian basalts were primary magmas which had been generated at 17 kbars (approximately 60 km) and evolved to less-magnesian basalts by fractional crystallisation of 10% olivine and 4% plagioclase in a chamber near to the base of the crust, (11 kbars, 35 km): Fractionation of SMLS less-magnesian basalt to hawaiite was proposed to have occurred at approximately 20 km depth by crystallisation of 8% olivine, 15% plagioclase and 21% aluminous sub-calcic augite.

Further high pressure studies by Thompson (1974b), on the crystallisation behaviour of pyroxenes in a magnesian alkali basalt, and a transitional basalt (SK971, the Fairy Bridge lava) from Skye (and an olivine tholeiite, a tholeiitic andesite from the Snake River Plain, Idaho, U.S.A. and an augite leucitite from Lago di Albano, Italy) showed that Ca-poor clinopyroxene only precipitated from the alkali basalt at pressures of 14 kb to 18 kb. So for it to be in equilibrium with a normal mantle mineral assemblage it would have had to have been generated in that pressure range. The Ca-rich pyroxene which crystallized from all samples apart from the leucitite was Ca-poor augite to sub-calcic augite. The liquidus Ca-rich pyroxenes showed rising Al, Na, and falling Ti with increasing pressure and temperature. Compositional trends were observed in diagrams such as jadeite versus Ca-Tschermak's "molecule" in sets of pyroxenes formed under different P-T conditions. Thompson (1974b) naturally concluded that the bulk chemistry of the magma was the predominating influence on the composition of the pyroxenes crystallising from it. Therefore, he concluded that unless a suite of pyroxenes were known to be co-sanguineous it was probably pointless to try to deduce their relative P-T conditions of formation from their major element chemistry.

The fractionation model outlined for the SMLS by Thompson and co-workers on the basis of the major element chemistry of the lavas was investigated with respect to their trace element compositions by Thompson *et al.* (1980a). In attempting to choose a suitable index of

fractionation Thompson *et al.* (1980a) realised that all elements for which analytical data had been obtained were incorporated in significant amounts into at least one of the solid phases separating from the SMLS magmas between basalt and trachyte. They also noted that, whereas in many suites of volcanic rocks a plot of Y versus Zr approximates to a straight line passing through zero, for the SMLS basalts and hawaiites such a plot resulted in a fan shaped distribution. They attributed this to variation in the Y and Zr contents of the Skye primary magmas being enhanced by the fractionation of phases in which Y and Zr are incompatible. It was concluded that none of the elements usually considered to be incompatible in the minerals of basaltic fractionating assemblages could be used as an index of fractionation, and that the evolution of the SMLS occurred as a bundle of lineages rather than a single trend. Consequently, the ratio $\text{FeO}+\text{Fe}_2\text{O}_3/\text{FeO}+\text{Fe}_2\text{O}_3+\text{MgO}$ (F/F+M) was used as an index of fractionation. Analyses of magnesian basalts, less magnesian basalts and hawaiites were averaged and their evolution considered quantitatively. The sparse number of analyses of mugearites, benmoreites, Fe-poor intermediates and trachytes only allowed qualitative discussion of the evolution of their residua.

Two-element variation diagrams for the basalts showed that some elements, e.g. Y and Yb, correlated positively with F/F+M, and showed little variation at a given value of the parameter, whereas other elements showed large ranges in compositions at a given value of F/F+M. The variations observed at a given F/F+M ratio were summarised as follows; Ti, P, and Zr correlated positively with silica saturation, K correlated negatively with silica saturation, and Rb, Sr, Nb, Ce, Y, Yb, and Th did not vary systematically with Si saturation. The hawaiites and one mugearite which define the ne-normative, Fe-rich evolutionary trend were also found to have a wide range of element concentrations at a given F/F+M ratio, but were generally enriched in incompatible elements e.g. K, Rb, Ba, Nb, Ta, Th, Zr, and LREE relative to the less magnesian basalts. Relative to the hawaiites and mugearites the benmoreites were found to be enriched in K, Rb, Ba, Nb, Ta, Th, Zr, and LREE, depleted in Ti, and have

comparable contents of Sr, P, Y and HREE.

The hy-normative, Fe-poor intermediates resembled the Fe-rich benmoreites in their trace element abundances, except that they were depleted in Nd, Ta, Zr, Hf, Y and HREE. The most evolved lavas of the Fe-poor (hy-normative) evolutionary trend, the trachytes, had higher concentrations of K, Rb, and Ba than other SMLS lavas, P, Nb, Ta, Th and HREE in the hawaiite range, and Sr and Y abundances similar to those in the basalts.

Prediction of minor element behaviour (produced by the 14% crystallisation predicted from least-squares modelling of the major element concentrations of the magnesian and less magnesian basalts) modelled by Rayleigh fractionation showed that predicted trace element values in the SMLS less-magnesian basalt were close to the measured values. Taking the fractional crystallisation model of Thompson (1974a) which related the less-magnesian basalts and the hawaiites by 44% crystallisation, Thompson *et al.* (1980a) modelled the behaviour of minor elements between the two whole rock compositions. With the exception of Ta and Nb values of minor elements predicted by modelling were close to measured values. The anomalously high values of Ta and Nb were attributed to the presence of cumulus titanomagnetite, a phase in which both the elements are compatible because they substitute for Ti (minimum concentrations of 1000ppm Nb and 70ppm Ta were calculated for the titanomagnetites). Any enrichment in Ti caused by the accumulation of titanomagnetite was presumed to be masked by its variation in the SMLS primary magmas.

Having noted that incompatible minor elements varied by a factor of two in the primitive SMLS basalts Thompson *et al.* (1980a) stated that it was impossible to construct quantitative models of fractionation between hawaiite and benmoreite because too few analyses of the latter rock type were available to allow the calculation of a representative average (they analysed "every known flow of the sparsely represented rock types" - three flows Fe-poor mugearite; two flows Fe-poor benmoreite; one flow of trachyte). They tentatively outlined a qualitative fractional crystallisation model which was consistent with the available petrographic and

geochemical data: This was crystallisation of olivine, plagioclase, titanomagnetite, and apatite in the hawaiites, and in the benmoreites amphibole joining the fractionating assemblage. The depletion in the concentration of the REE was linked to the fractionation of apatite. However the observed steepening of the chondrite normalised REE patterns between the hawaiites and benmoreites (due to preferential extraction of HREE), was unexplainable by apatite fractionation since all the REE have a similar distribution coefficient for apatite. This, with the associated lack of enrichment in Zr, Hf, and Y relative to other incompatible trace elements, was attributed to fractionation of 0.10% to 0.15% zircon (found as a microphenocryst in one magnetite in one benmoreite) between the two groups.

Thompson *et al.* (1980a) observed that values of K, Rb, and Ba were enriched in the Skye trachyte relative to the benmoreites. Their compatibility in both biotite and alkali feldspar phenocrysts, present in the trachytes, ruled out their use as incompatible elements for calculating the amount of fractional crystallisation that would have been needed to generate the trachyte from a typical SMLS basalt. Even though they had concluded that none of the elements analysed for were incompatible throughout the whole evolution of the suite, they suggested that since the values of some of the elements not taken into crystallising phases in considerable amounts were about ten times greater in the trachyte than in the basalt approximately 90% fractional crystallisation must have occurred. It had been noted that Nb and Ta were compatible in titanomagnetite. Thompson *et al.* (1980a) noted a depletion of Nb and Ta in the hy-normative, Fe-poor intermediates relative to the members of the basalt - benmoreite trend. The depletion was attributed to the fractional crystallisation of titanomagnetite. In addition a reduction in the concentration of the REEs and Zr, Hf, and Y was taken to indicate that zircon had also been fractionated (possibly removed from the system by being incorporated into larger titanomagnetite phenocrysts) from the low-Fe intermediates.

There are no Eu anomalies in the chondrite normalised REE pattern of the more evolved members of the SMLS, despite plagioclase being a major fractionating phase. This was

suggested to be because Eu remained in a trivalent state (indicative of high fO_2 in the magma) throughout the fractional crystallisation of the suite (since it will only substitute for the Ca in plagioclase when in a divalent state) (Thompson *et al.*, 1980a).

Crustal contamination is discussed in detail in the next section, but under the topic of fractional crystallisation it is convenient to mention the work of Thirlwall and Jones (1983). During isotopic and elemental work which was aimed at deducing the crustal contamination processes affecting the Skye lavas these authors proposed an alternative model for the evolution of the Skye lavas, combining the processes of fractional crystallisation and crustal contamination. Having observed that the most primitive lavas were generally the most contaminated, they suggested that the primary magmas were all ne-normative, and that these magmas evolved by open system fractionation of olivine and plagioclase in a magma chamber near the base of the crust. The fractionation produced a wide range of incompatible element enrichments, perhaps up to ten times the primary magma values in the hawaiites, and resulted in a negative correlation between $F/(F+M)$ and MgO, Ni, and Cr, but caused little variation in the magmas SiO_2 concentrations. Magmas ranging in composition from magnesian basalt to hawaiite were periodically extracted from the chamber. It was proposed that the more magnesian, hotter magmas may have incorporated up to 15% cotectic melt of the Lewisian gneiss crustal material en route to the surface in feeder dykes, while the cooler more evolved magmas assimilated less crustal material. The crustal contamination increased the SiO_2 content of the lavas and modified their incompatible element concentrations, so that many incompatible element values were dominated by the crustal input. They proposed that the magmas which had undergone the most contamination were driven to hy-normative compositions. If this was the case there would be an extremely good positive correlation observed between Si-saturation and the elements and isotopes which have higher concentrations in the crust than in the magmas. It was suggested that the most contaminated magmas subsequently fractionated in crustal

chambers, possibly with associated assimilation of crustal material, to produce the low Fe-intermediates. Thirlwall and Jones (1983) tentatively proposed that the high-Fe intermediate benmoreites were the products of assimilation fractional crystallisation (see section 2.3.3) acting on the hawaiites but they had not analysed any samples to substantiate this theory.

In some of the most recent work on fractionation processes in the Skye lavas attention has been redirected to Thompson's (1972a) observation that a compositional gap exists in the SMLS between basalt and hawaiite (which he suggested may have been related to the viscosity of the magma, or the crystal/liquid ratio in the fractionating system). Recent work on the fluid dynamics of magma chambers has been considered in this context. In one of the most recent papers on the Skye lavas Cattell (1989) has attributed the gap to a density maximum in the basaltic-hawaiite magmas produced by their fractional crystallisation history. Taking the fractionation scheme suggested (from least squares modelling) by Thompson (1974a), Cattell proposed that the fractionation of olivine and plagioclase took place as a two stage process, initially only involving olivine then later, olivine and plagioclase fractionated in cotectic proportions (i.e. approximately 1:2). He assumed that since most lavas had few phenocrysts they had been erupted close to their liquidus temperature, and therefore whole rock densities were comparable to magma densities. Using the equations of Sparks and Huppert (1984) Cattell calculated that the density of the olivine and plagioclase fractionating assemblage to be $\sim 2.71 \text{ g cm}^{-3}$ i.e. lower than the basaltic liquid (approximately 2.75 g cm^{-3}), so the liquid densities would have increased during fractionation. However, the variation in $\text{TiO}_2\text{-P}_2\text{O}_5$ suggested that, at a later stage, $>10\%$ titanomagnetite had fractionated from basaltic-hawaiite to hawaiite. It was concluded that this would increase the density of the extract to above that of the liquid density, since crystallisation of only 5% titanomagnetite with a density of 4.40 g cm^{-3} would increase the density of the fractionating assemblage to 2.80 g cm^{-3} , thus making it 0.02 g cm^{-3} greater than the densest liquid erupted. Therefore, the fractionation of titanomagnetite would

cause a reduction in the residual liquid density from basaltic hawaiite to hawaiite, enabling the latter to be erupted. So, the absence of basaltic hawaiites in the lava pile was attributed to their high density. Cattell (1989) gave two reasons why the dense liquids would not rise. The first was that for a liquid to rise it must have positive buoyancy i.e. it must be less dense than the rock column overlying the magma chamber. The second was that the liquids may not be able to escape from the magma chamber, since as was shown by Sparks and Huppert (1984) if differentiation produces dense residual liquids these may become ponded at the base of the chamber beneath the less dense parental liquid. The latter proposal depended on the relative, not the absolute, densities of the liquids involved, and could therefore be invoked to explain the difference in maximum density of the Fe-rich (ne-normative) intermediates and the Fe-poor (hy-normative) intermediates. The densest Fe-rich intermediates are 0.05 g cm^{-3} denser than the densest Fe-poor intermediates, and would therefore be denser than most of the liquids within the compositional gap of the Fe-poor series. So, if the control on the positive buoyancy was the same for both suites of intermediates, i.e. the density of the overlying rock column, the compositional gap in the less-dense, Fe-poor suite should be much smaller than in the more-dense, Fe-rich suite but such a difference is not observed. As a consequence Cattell (1989) proposed that the two series had not differentiated in the same magma chamber. He concluded that his findings were consistent with previous high pressure experimental and isotopic work on the fractional crystallisation history and the composition of the crustal contaminant of the SMLS which had suggested that the more-dense, ne-normative, Fe-rich intermediates were trapped and had evolved at the base of the crust under a column of dense granulites. In contrast the less-dense, hy-normative, Fe-poor intermediates evolved in upper crustal magma chambers having risen through the granulites. However, Cattell decided that there was not enough information available about the Skye lavas to determine whether the difference in the depth of differentiation was enough to allow for the densest, ne-normative, Fe-rich intermediates being erupted despite their being denser than most of the liquids in the, density-induced, compositional

gap in the hy-normative, Fe-poor intermediates. So, he concluded that ponding of the more-dense, ne-normative, Fe-rich basaltic hawaiite within the chamber (because of an increase in the density of the residual liquid during fractional crystallisation of the magma, resulting from the precipitation of plagioclase before Fe-Ti oxides) was the most likely cause of the compositional gap observed in the SMLS lavas.

2.3.2.2 Preshal Mhor

Having identified the Preshal Mhor magma-type on Skye, Esson *et al.* (1975) continued the experimental work on the Skye lavas by performing one-atmosphere melting experiments on two Preshal Mhor basalts. From the results of their experiments they proposed a fractional crystallisation model for the PM lavas. Their results showed the sequence of crystallisation to be plagioclase, olivine, clinopyroxene, magnetite. It was suggested that if the microphenocrysts of plagioclase and olivine crystallised pre-eruption as oppose to syn- or post-eruption, the temperature of the erupting magma would have been in the range 1190-1210°C. Because of the small modal proportions of magnetite it was proposed that the solidus temperature would only have been slightly lower than the temperature at which magnetite began to crystallise, 1155°C, thus limiting the total range of crystallisation to approximately 100°C. It should be noted that if, as presumed by Esson *et al.* (1975), the plagioclase-olivine-clinopyroxene-magnetite-liquid equilibrium is univariant, the solidus temperature would be that at which the final phase (magnetite) came onto the liquidus. So the small modal proportion of magnetite would be a consequence of the magma having been erupted before the univariant reaction had gone to completion with the remaining liquid being quenched to groundmass phases; rather than, as suggested by Esson *et al.* (1975), it being the result of the system having a solidus temperature close to that of the co-precipitation point for olivine, plagioclase, clinopyroxene, and magnetite. Esson *et al.* (1974) suggested that the PM lavas were the products of further mantle melting of the volume of mantle which produced the SMLS lavas. They proposed that the magmas had

fractionated olivine during their ascent to the surface, but had been erupted in the plagioclase stability field, close to the plagioclase-olivine-liquid equilibrium surface. Since fractional crystallisation paths follow co-precipitational boundaries, such as that between the olivine and plagioclase field, the apparent crossing of the bulk composition into the plagioclase field was anomalous and needed an explanation. Several possible causes were suggested but the authors did not come to a decision as to which was the most likely. The apparent crossing of the bulk composition into the plagioclase field may have been the result of cumulus plagioclase in the system, because of crystallisation of the phases olivine and plagioclase with only the former being fractionated. Alternatively it could have resulted from a change in the position of the phase boundary as a result of changing conditions in the system e.g. increased volatile content; or it might be due to experimental error e.g. equilibrium not being reached in melting experiments.

2.2.2.3 Fairy Bridge

It was concluded by Matthey *et al.* (1977) that the Fairy Bridge (FB) lavas could not be related to the SMLS or PM lavas by low pressure fractionation processes. They deduced this from the differences in the FB rare earth element (REE) profiles (Chapter 4, Geochemistry).

The fractional crystallisation history of the Fairy Bridge (FB) lavas has not been studied since only one lava flow of the magma-type has been found (although there are occurrences of the magma-type in the regional dyke swarm).

2.3.3 Contamination

As discussed previously, after the recognition that there were two magma-types in the BTIP (Bailey *et al.*, 1924), i.e. the ne-normative plateau basalts and the hy-normative non-porphyrific central tholeiites, the aim of research workers in the region became to relate them to each other. The initial proposal of Bailey *et al.* (1924), was that assimilation of granitic

material could account for the generation of the tholeiitic NPC magma-type from the plateau magma-type. The idea of the involvement of a crustal component in what were subsequently called tholeiitic basalts was common throughout the early part of the twentieth century (e.g. see Thompson, 1982b). The concept of alkali basalts and tholeiites being related by fractional crystallisation with associated assimilation of crustal material persisted until the work of Kennedy (1933) which suggested that the two magma-types had separate parental magmas. In 1950 Tilley spent much of his review of magmatic evolution explaining why the generation of tholeiites by assimilation of sialic continental crustal material into alkali basalts was unacceptable as a worldwide concept, because tholeiitic magmas were erupted on ocean islands, e.g. Hawaii, where there was no continental crust present to take part in their genesis.

After the 1950s studies in the BTIP concentrated mainly on the granites and whether they were the products of fractional crystallisation of the basic magmas, fusion of crustal material, or a combination of both. The results of these classic studies have been summarized in section 2.3.1. Although the works are not directly related to the current study they are included in this review because of the influence that they had upon the direction taken by later studies of the petrogenesis of the lava pile.

In recent years, with developments in analytical techniques and the knowledge of isotopic systems the original basalt-crust question of the BTIP has been re-addressed; and the data tested in complex new models of magmatic evolution.

Two main contrasting styles of crustal contamination have been outlined for basaltic magmas. The first involves contamination with concurrent fractional crystallisation, and has been termed AFC (Assimilation and Fractional Crystallisation) by DePaulo (1981). This process is thought to occur in crustal magma chambers by heat loss from the magma fusing the wall rock. As a consequence of losing heat the magma crystallises. If the crystallisation is fractional suites of volcanic rocks which have been affected in this way show positive

correlations between indices of differentiation e.g. SiO_2 or MgO , and incompatible element ratios and Sr, Nd, and Pb isotopic ratios which reflect contamination. The second style occurs in provinces where magma chambers develop at the crust mantle boundary or within the mantle. If fractional crystallisation occurs in such chambers there is not necessarily associated assimilation of wall rock material since the surrounding material will be more refractory than upper crustal rocks that surround the AFC chamber discussed above. So, when magmas pass from these chambers to the surface they may become contaminated with crustal material, with the main control on the amount of contamination being the temperature of the magma. Therefore, suites of volcanic rocks which have evolved in this way will show negative correlations between differentiation indices and contamination indices. A model for how this style of contamination could occur was proposed by Devey and Cox (1987) who had observed that in the Podalpur Formation of the upper part of the Deccan CFB province the most mafic lavas were the most contaminated. They commented that the correlation could possibly be because the most mafic lavas were most abundant in the lower part of the sequence and the availability of the contaminant declined in the upper part of the sequence. But, they also noted that the most mafic magmas would be hottest and therefore able to assimilate more crustal material than the more evolved cooler magmas during their passage to the surface through dykes. They suggested that en route to the surface the importance of fractional crystallisation in magmatic differentiation would be diminished because of magmatic turbulence preventing crystal settling. This led them to define the process of AEC (Assimilation and *Equilibrium* Crystallisation), during which assimilation was accompanied by crystallisation but without the loss of crystals.

To consider the compositional effects of crustal contamination the nature of the crust beneath Skye must first be considered. Skye, and the other centres of the BTIP, lie to the west of the Moine Thrust which marks the western limit of the Caledonian tectonic activity; the crust

beneath Skye is therefore cratonic. It is mainly formed of Archaean Lewisian gneiss which has been geophysically divided into granulite-facies lower crust and amphibolite-facies upper crust, though the exact position of the divide and whether it is sharp or gradational is not clear (Bamford *et al.*, 1977). Whole rock Sm-Nd ages indicate an age of 2920 ± 50 Ma (Late Archaean) for the separation of the igneous precursor to the Lewisian from the mantle (Hamilton *et al.*, 1979). Later granulite- and amphibolite-facies metamorphism resulted in depletion of U relative to Pb and, in the granulites, Th relative to Pb and Rb relative to Sr (but REE, and therefore Sm and Nd, appear to have been unaffected). Consequently, almost all Lewisian material has low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, and the granulites also have low $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. The Lewisian amphibolite- and granulite-facies gneisses crop out on the Scottish mainland as Scourian and Laxfordian gneisses respectively. On Skye the Lewisian is overlain by a thin layer of Proterozoic (Torridonian) and Mesozoic sediments.

Analytical work has revealed a wide range of elemental abundances and isotopic ratios in the Skye lavas, and these data have been interpreted diversely. One extreme of opinion is that the compositional variations of the BTIP lavas were inherited at the time of their genesis from Archaean sub-cratonic mantle, and that no subsequent crustal interaction is necessary, thus implying mantle heterogeneity (Beckinsale *et al.*, 1978; Pankhurst and Beckinsale, 1979). Beckinsale and co-workers envisaged that the sub-Hebridean upper mantle had acquired a vertical compositional layering during the Lewisian craton-forming event. To explain the incompatible element concentrations and the Sr isotopic data, they suggested melting incompatible element-depleted garnet-lherzolite and incompatible element-enriched plagioclase-lherzolite. However, Thompson (1982a) noted that to explain the lava sequence observed on Mull (the area for which the model was proposed) mantle melting would have to start in the plagioclase stability field and progress downwards into the garnet stability field. If the compositional variations were attributable to a single event which had produced a heterogeneous

mantle, then it would be expected that pseudoisochrons obtained for different isotopic systems would give comparable ages for the mantle event; this is not the case for the lavas of the BTIP (see later this section).

In complete contrast, the other extreme of opinion is that the compositional variations in the BTIP lavas are the result of the interaction of the magmas with Archaean basic granulite-facies lower crust, followed by interaction with amphibolite-facies upper crust, so obliterating their original, sub-Moho, incompatible trace element and isotopic characteristics. This conclusion was reached by Wood (1980) in a controversial study which proposed the use of a triangular plot of Th-Hf-Ta to detect crustal contamination and, when used in conjunction with other trace element plots, as a tectonomagmatic discrimination diagram. Wood (1980) noted that the major and trace element concentrations of the lower crust were the subject of much debate, and proposed that they probably showed substantial regional variation. He suggested that there may have been a higher proportion of granulitic material (which is significantly less enriched in lithophile elements than average Lewisian gneiss) at depth than exposed at the surface. So granulitic material may have made a significant contribution to the contamination of mantle derived magmas as they entered a cratonic region. Since within-plate basalts were found to plot in a different region from crustal granulites, and the granulites had high Hf/Th and Hf/Ta ratios, he suggested that the Th-Hf-Ta diagram was suitable for the detection of lower crustal contamination. From studying the published data of Thompson and co-workers, Wood (1980) noted that most of the SMLS basalts plotted outside the "within-plate basalt" field, and that the hy-normative lavas had higher Th/Ta ratios than the ne-normative lavas (i.e. were nearer to the plotted position of the average granulite). He proposed that a group of five samples, comprising samples of hawaiite, mugearite and benmoreite from the two highest stratigraphic divisions of Anderson and Dunham (1966), with the lowest Hf/Th ratios (2.5-3.0), were the least contaminated SMLS samples. He supported this theory by showing that the low Hf/Th lavas had similar chondrite-normalised rare earth element patterns to some Iceland lavas (which would

have been unaffected by crustal contamination). Since most of the SMLS lavas showed low concentrations of Th and Ta relative to other within-plate basalts Wood (1980) proposed that their concentrations had been diluted by a low U, Th, and Ta contaminant i.e. basic granulite. Such contamination would be detectable in the plot of Th-Hf-Ta since Hf was enriched in granulite relative to mantle derived magmas. Wood went on to propose that bulk assimilation of basic granulite could have occurred in a lower crustal magma chamber, with concurrent fractional crystallisation, and replenishment, of the chamber by primitive material, buffering the major element concentrations so that they would not depart from a cotectic composition even with large amounts of crustal contamination. He suggested that a mantle-derived magma could assimilate up to 75% of basic granulite facies crust and still have more than 8% MgO. However, it would be expected that in an RTF (replenished, tapped, fractionating) open-system magma chamber the concentration of incompatible elements would be disproportionately enriched in the erupted magmas, and this is not observed in the SMLS basalts (Chapter 4, Geochemistry). In suggesting that the magmas could then erupt rapidly without equilibration in the upper crust, Wood (1980) did not suggest how the high pressure aluminous sub-calcic augite, which in the light of experimental work Thompson (1974a) had invoked to explain the fractional crystallisation history of the lavas, could have been dissolved, since Thompson found no sub-calcic augite as phenocrysts in the lavas. The hy-normative lavas were suggested to have resulted from further contamination of the magmas in the upper crust by 2-3% of Th-rich amphibolite facies crust (so, a clear positive correlation between silica-saturation and indicators of upper crustal contamination should be observed). Wood (1980) stated that a plot of Th/Ta versus Ce/Yb could be used to distinguish granulite and amphibolite contamination, and found that when plotted the hy-normative lavas trended towards silicic amphibolites. Consideration of the Th-Hf-Ta plot in conjunction with isotopic data led Wood (1980) to conclude that the data were in agreement with published Pb data, which indicated that the SMLS generally showed more than 50% contamination and in some cases as much as 90%. He proposed that

since assimilation of basic granulite would have little effect upon Sr or Nd isotopes, just decreasing their values slightly, it was not surprising that the different systems gave such different values for the amount of contaminant in mixing calculations. He made an important point, that variations in the amount of contamination determined from different isotopic systems and trace elements need not be the result of selective contamination, but instead could be caused by the variable sensitivities of the different geochemical parameters to the contamination involved. From plotting the Preshal Mhor lavas he concluded that they had assimilated, at most, 1% or 2% of upper crustal amphibolite. In conclusion Wood (1980) stated that there were two mantle derived parents for the Skye lavas - an alkali basalt, and a low-alkali tholeiite - both of which subsequently underwent contamination and fractional crystallisation to generate the range of major and trace element concentrations observed in the Skye lavas. Therefore, there would be no need to invoke separate parental liquids for the ne-normative, and hy-normative lavas, produced by varying degrees of mantle melting as had previously been suggested by Thompson and co-workers. He also stated that the Th-Hf-Ta diagram was extremely effective in estimating the degree of contamination, and the type of contaminant, something that no isotopic system could do.

In the same issue as the paper by Wood, Thompson *et al.* (1980b) presented a paper in which they stated that they had found that the Th-Hf-Ta diagram was unsuitable for discriminating between basalts erupted in various tectonic settings, and for detecting crustal contamination. They stated, with reference to the detection of contamination, the results from the Th-Hf-Ta diagram were inconsistent with isotopic data (possibly because the Th content of lower crustal rocks was too low to be a suitable detector of contamination). They also concluded that samples from several volcanic provinces of known tectonic setting plotted wholly or partially outside the appropriate fields.

It is best to assume that crustal contamination has had at least some affect upon the

isotopic composition of the lavas. Although mantle heterogeneity could in principle generate the observed differences, such a proposal is difficult to test because the composition of the mantle source is unconstrained. Thompson (1982b) noted that if the wide range of elemental and isotopic variations observed in the Skye lavas were the result of mantle metasomatism (the process of selective enrichment of the mantle in some elements; an excellent review of which is given by Menzies and Murthy, 1980) several intense metasomatic events would be needed within a small volume of mantle.

Isotopic studies have concentrated on the Rb/Sr, Sm/Nd, and U/Pb and Th/Pb system since they are the best established methods. In the following section the results of studies of the different isotopic systems are examined in more detail. Each system is reviewed separately and a synthesis of the available data is presented at the end of the section.

The initial Sr isotopic work on the Skye lavas was done by Moorbath and Bell (1965) who analysed twelve basic lavas, some dykes, and plutonics. They found that the lavas had values of $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ which ranged from 0.70320-0.70750. Following on from the preliminary Sr isotopic work of Moorbath and Bell (1965) on the Skye lavas, Moorbath and Thompson (1980) presented new, high-precision Sr isotopic data for forty five SMLS lavas, three Preshal Mhor lavas, seven Mull lavas, nine Skye dykes, seven Skye intrusives, and four Skye ferrodiorites. Their study has remained one of the principal works on the petrogenesis of the Skye lavas. Taylor and Forester (1971), and Forester and Taylor (1977) showed that hydrothermal alteration had depleted the ^{18}O contents of the greenschist facies rocks within a 4 km radius of the central intrusive complexes in Skye (and suggested that the Sr and Pb isotope compositions may also have been affected). Morrison (1980) showed that the Rb and Sr were mobile during the hydrothermal alteration of the Skye lavas. These two studies led Moorbath and Thompson (1980) to assess the affect that low grade zeolite facies hydrothermal

metamorphism upon the ratios before they investigated the variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios. Since they did not observe a correlation between $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ and $\text{H}_2\text{O}+$, and the $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ ratio of a petrographically altered sample was in the range of values of the fresh lavas, they concluded that Sr was only redistributed within individual flows during hydrothermal alteration.

Having ruled out hydrothermal alteration as a possible cause of the observed range of $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios they considered the likelihood that the differences were the result of local variations in the Rb/Sr ratio of the upper mantle beneath Skye which might have developed between the time of formation of the continental crust in the region (ca. 3000Ma, Mid-Late Archaean) and the Palaeocene (66.4 Ma to 57.8 Ma). If this had been the case, and the Rb/Sr ratio of the lavas had remained unchanged during their generation and passage to the surface, a pseudoisochron (i.e. a straight line, the gradient of which would give the age of the mantle event that produced the variation in the Rb/Sr ratio) should be detectable on a plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$. Moorbath and Thompson (1980) concluded that since the data for the primary lavas, and those under olivine control, was so scattered on such a plot, a pseudoisochron could not be detected for the Sr data of the Skye lavas. This conclusion was consistent with the previous work of Carter *et al.* (1978) who had combined Skye Sr and Nd isotopic data with that from other sites in the BTIP to try to detect a mantle pseudoisochron. In doing this they obtained different dates for the two isotopic systems, 1600 Ma (Early to Middle Proterozoic) from the Sr data and 6200 Ma from the Nd data. They therefore concluded that the observed range of initial isotopic values must be attributable to crustal contamination, rather than mantle heterogeneity in which a single mantle event affecting the two systems would give pseudoisochrons with the same age for the two isotopic systems. Moorbath and Thompson (1980) went on to assess the influence of crustal contamination on the Sr isotopic characteristics of the Skye lavas.

For the purpose of their study, Moorbath and Thompson (1980) divided the lavas into

two compositional groups - the SMLS lavas and the FB lava, and the PM lavas. They found that some of the SMLS basalts and the PM basalts had initial $^{87}\text{Sr}/^{86}\text{Sr}$ similar to MORB (0.70230-0.70340). Elemental evidence, i.e. correlations between K, Rb, Ti, P, Zr, Hf, Eu, Gd, and Tb (not all of which have higher concentrations in continental crustal material than in the basalts) and Si-saturation; and the lack of a clear correlation between $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ and SiO_2 or Si-saturation (a correlation which would be expected if the lavas had been contaminated with sialic crust) were taken to rule out simple bulk mixing of the basaltic magma and the Lewisian crust. It was suggested that to determine whether bulk crustal contamination of individual flows had occurred, a detailed flow by flow study would be required. An open system chamber such as that proposed by O'Hara (1977), in which magmas fractionally crystallise, are contaminated with wall rock material, are erupted, and are replenished, could result in non-systematic relationships, such as those observed in the Skye lavas, between $^{87}\text{Sr}/^{86}\text{Sr}$ and major elements. However the eruptive products of the system should show a positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and the incompatible elements. Since this was found not to be the case for the Skye lavas, Moorbath and Thompson (1980) concluded that they had not evolved in an O'Hara-type open system. A broad negative correlation between initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr in the SMLS basalts and ne-normative, Fe-rich benmoreites (but not the hy-normative Fe-poor intermediates and trachytes) was observed. When considered with other more compositionally diverse BTIP rocks it was found that the linear negative correlation of the basalts was part of a broad hyperbolic band (or series of curves), such as would be expected to result from interaction of primary magmas having mantle $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and variable Sr contents at the time of contamination with high $^{87}\text{Sr}/^{86}\text{Sr}$ crust. Consequently, Moorbath and Thompson (1980) suggested that the SMLS magmas had been selectively contaminated with material that had a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, similar to that of amphibolite-facies Lewisian gneiss. The existence of a negative correlation between initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr in the basalts and their derivatives led to the conclusion that the magmas must have evolved prior to contamination. Since, the evolved lavas must have reached their

final magmatic Sr contents before being exposed to the $^{87}\text{Sr}/^{86}\text{Sr}$ -rich contaminant. The contaminant would then have been preferentially incorporated into the hotter more magnesian, and lower-Sr lavas, so producing a negative correlation between the two variables. Therefore, it was suggested that the SMLS ne-normative, high-Fe intermediates evolved within $^{87}\text{Sr}/^{86}\text{Sr}$ -poor lower crust, and later interacted with ^{87}Sr -rich upper crust but with no accompanying fractional crystallisation, i.e. the second style of crustal contamination outlined above, AEC. Previous studies (Thompson *et al.*, 1972; Thompson 1974a) had suggested that the magmas had paused and equilibrated at upper crustal levels, but had not stayed there long enough for fractional crystallisation to occur. Thus, Moorbath and Thompson (1980) concluded that any interaction with the Lewisian upper crust must have been a fast process. They stated that the time-scale of the magma-crust interaction could be determined if the sizes and shapes of the upper crustal reservoirs, the water content, and the rate of uprise of the SMLS magmas were known, since that information would enable the calculation of the superheating of the magmas.

It was noted by Moorbath and Thompson (1980) that the SMLS hy-normative, low-Fe intermediates had much higher $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ than members of the ne-normative, high-Fe trend, and that the hy-normative lavas showed no clear correlation between $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ and total Sr content. They therefore postulated that the hy-normative, low-Fe intermediates evolved in the Lewisian upper crust, a theory consistent with the previous suggestions that the hy-normative lavas had fractionated under fairly high $P_{\text{H}_2\text{O}}$ and $f\text{O}_2$ conditions.

Moorbath and Thompson (1980) supplemented the sample set for the PM lavas for their study of the crustal contamination by considering some PM dykes from Skye and the only example of a PM lava from Mull (subsequently found to be a sill, Kerr A., pers comm. 1992). They found that the samples had a scattered distribution on a plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$, but showed a good positive correlation between $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ and Sr. The good correlation between the last two variables, and the previous evidence suggesting that the PM lavas had evolved by the fractional crystallisation of olivine and plagioclase at low pressure

(Thompson *et al.*, 1972; Esson *et al.*, 1975) led Moorbath and Thompson (1980) to conclude that the PM lavas had been contaminated with crustal material whilst fractionally crystallising within the upper crust (i.e. the first style of crustal contamination outlined above, AFC).

Assuming that contamination by Lewisian $^{87}\text{Sr}/^{86}\text{Sr}$ -rich upper crust would mask the mantle-derived values of the ratio in the magmas, Moorbath and Thompson (1980) concluded that their work supported the contamination hypothesis of Carter *et al.* (1978). Carter *et al.* (1978) had proposed a similar fractionation and contamination scheme for the SMLS lavas, based on Sr and Nd isotopic data. They had used $^{143}\text{Nd}/^{144}\text{Nd}$ data, in conjunction with $^{87}\text{Sr}/^{86}\text{Sr}$ results, to suggest selective contamination of the ne-normative SMLS magmas by granulite-facies Lewisian gneiss, and the hy-normative SMLS magmas by intermediate/acid granulite-facies Lewisian gneiss. A point made by Carter *et al.* (1978) was that although the evolutionary scheme involved fractional crystallisation at depth, where the lavas interacted with $^{87}\text{Sr}/^{86}\text{Sr}$ poor granulite-facies Lewisian crust, no high pressure clinopyroxene phenocrysts (suggested to be important in the evolution of the SMLS, Thompson, 1974a) were present in the lavas. To explain this they suggested that the lavas had paused and re-equilibrated in upper crustal chambers which had been previously lined with Tertiary basaltic magma.

In an attempt to devise a physical model for the contamination of the SMLS magmas Moorbath and Thompson (1980) considered the isotopic characteristics of the other igneous rocks on Skye. They observed that the gabbroic Cuillin complex had similar Pb and Sr isotopic values but lower ^{18}O than the lavas, and that xenoliths of ^{18}O depleted Lewisian gneiss occurred in the Skye intrusive complexes. From this evidence they proposed that, prior to the interaction with the Cuillins basic magmas, the Lewisian crust had been brecciated, and hydrothermally metamorphosed and metasomatised by a meteoric water convective system (which would have lowered the ^{18}O crustal values) that had been established by the injection of basaltic lava-forming magma into well-jointed H_2O saturated upper crust. So, the SMLS magmas may have partially equilibrated Pb and Sr from Lewisian gneisses during contact hydrothermal re-

metamorphism of hydrothermally altered gneiss near the sub-volcanic reservoirs. During this process fluids released as the wall rock dehydrated would have diffused towards the relatively anhydrous magma. Moorbath and Thompson (1980) therefore postulated a selective disequilibrium contamination mechanism which would have been terminated by the eruption of the magma batches.

The geochemical mechanisms of such a selective contamination model are not fully understood yet, but probably involve many complex and variable interactions with crustal material at various depths. At the base of the crust the lithospheric material probably has geochemical and isotopic characteristics similar to basaltic magmas. Therefore, interaction between basaltic magma and crustal material would only become apparent when the magma assimilated material with significantly different compositional characteristics, e.g. low U/Pb and high Rb/Sr; since this would result in unradiogenic Pb and radiogenic Sr characteristics, i.e. as observed in some of the SMLS lavas. A possible contaminant with suitable isotopic characteristics, through which the Skye Tertiary magmas passed during the Palaeocene approximately 60 Ma, would be the amphibolite-facies orthogneiss which constitutes a large proportion of the continental crust, possibly including the 2700-2900 Ma Lewisian basement of N.W. Scotland.

Carter *et al.* (1978) had suggested that between 5 and 50% of the Sr and Nd in the Skye lavas had been derived from either a Lewisian lower crustal granulite, or Lewisian upper crustal amphibolite. However, since Moorbath and Thompson (1980) found that the percentage of contaminant was not consistent with the SiO₂ contents of the lavas, they suggested that Sr and Nd would be preferentially extracted from the crustal material in partial melts. They noted that their selective contamination model depended on the availability of incompatible elements and volatiles in the country rock, and their subsequent expulsion which would result from heating by ascending magmas and magmas stored in crustal chambers. The crustal material must, therefore, have contained hydrous minerals from which the water could have been driven off

and scavenged incompatible elements from the country rock before it mixed with the magma. So, the Lewisian amphibolite-facies or granulite-facies rocks were shown to be suitable contaminants because they contained hydrous minerals such as amphibole, micas, and epidote, and biotite respectively. Also, if the crust had been shattered during the early stages of Tertiary magmatism, as had previously been suggested, and undergone hydrous retrogression to greenschist facies, the amount of fluid held in hydrous phases would have been increased, thus providing more fluids to be released in the thermal re-metamorphism by the basaltic magmas. In summarising, Moorbath and Thompson (1980) made an important point, that isotopic variations may well be inherent in the upper mantle and be represented in individual magma batches within a single province. However, any memory of such heterogeneities in the igneous products is likely to be concealed by the dominating compositional influence of the continental crust. So, additional types of geochemical data must also be used when investigating crustal contamination, and heterogeneities in the sub-continental lithospheric mantle.

The development of the Sm/Nd isotopic system led to further testing of contamination models originally based on Rb/Sr data, and to studies which combined data from the two systems. The major advantage of the Sm/Nd isotopic system over the Rb/Sr system is that the elements involved are not mobilised by hydrous alteration. The first $^{143}\text{Nd}/^{144}\text{Nd}$ work on the SMLS was by Carter *et al.* (1978), the results of which have been summarised above. A plot of $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ for the Skye lavas and the major potential crustal contaminants (Lewisian ultrabasic granulite, Lewisian intermediate and acid granulite, and Lewisian intermediate and acid amphibolite) led Thompson (1982a) to support the view of Carter *et al.* (1978) that, if the Skye lavas did not plot in the asthenospheric region because they had assimilated crustal material then intermediate (LREE-enriched) granulite-facies Lewisian crust, or acid (LREE-enriched) granulite-facies Lewisian crust, or both, had been the main contaminants. Nd isotopic data obtained by Thompson *et al.* (1980b) placed the PM samples

in the MORB field at 60 Ma (Palaeocene). This indicated that they were in the array of asthenospheric mantle isotopic compositions and so could not have interacted significantly with either the lithospheric mantle or the continental crust during their passage to the surface.

Dickin (1981) made a detailed study of the isotopic characteristics of the Tertiary igneous rocks of Skye, with particular emphasis on new Pb data, to try to obtain a clearer understanding of the problems left partially unresolved by the Sr isotopic work of Moorbath and Thompson (1980). The questions concerned the mechanism of selective contamination affecting the Skye lavas, the migration of trace elements during the interaction of magmas and continental crust, and the petrogenesis of the granites. A preliminary Pb isotopic study of the lavas by Moorbath and Welke (1969) had concluded that the basic magmas had interacted with crustal material. Dickin (1981) presented new Pb data for forty seven basic, intermediate, and acid Tertiary igneous rocks, and new Sr data for acid igneous rocks. Before addressing the granite question he attempted to assess the compositional effect, the mechanisms, and the depth of the crustal contaminant of the mantle-derived magmas. He disagreed with the conclusion of Wood (1980) (that the Skye lavas had undergone bulk contamination by basic granulite-facies gneiss) because the amount of contamination indicated by the Th-Hf-Ta data of Wood (1980) was not consistent with his Pb isotopic data. Dickin (1981) stated that element ratios were unsuitable for use in mixing calculations because of the large variations in element concentrations in magmas and crustal rocks. Instead he proposed that the use of isotopic systems was a much more valid approach, since the compositional variation of each component in the mixture would be more clearly defined. He also noted that bulk contamination of a non-superheated magma by refractory basic granulite was restricted by thermal constraints.

For the purpose of his study he divided the lavas into three groups, the SMLS ne-normative, high-Fe basalts and their differentiates, SMLS hy-normative, low-Fe intermediates, and the high-Ca, low-alkali basalts of the PM magma-type. The ne-normative, Fe-rich lavas had

large variations in their $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, whereas the hy-normative, Fe-poor lavas had a smaller range of compositions, and very unradiogenic Pb compositions. In contrast, the PM basalts had radiogenic Pb compositions.

On a plot of $(^{207}\text{Pb}/^{204}\text{Pb})_{60}$ versus $(^{206}\text{Pb}/^{204}\text{Pb})_{60}$ the Skye lavas, and acid intrusives, fell on a trend intermediate between MORB and averages of Lewisian gneiss. The slope of the line defined by the data gave an age of 2880 ± 70 Ma (Late Archaean) for the basic lava data, 2790 ± 200 Ma (Late Archaean) for the acid intrusive data and 2920 ± 70 Ma (Late Archaean) for the combined data-set.

A plot of $^{206}\text{Pb}/^{204}\text{Pb}$ versus Pb showed that the PM basalts clustered together, whilst the ne-normative Fe-rich lavas showed a weak negative correlation between the two variables and the hy-normative Fe-poor lavas a strong negative correlation.

Four possible explanations were suggested for the observed isotopic variations: post-solidification addition of Pb and Sr to the lavas by hydrothermal fluids, heterogeneities inherited from the mantle source, contamination of mantle derived magmas by crustal material, and derivation of the magmas by crustal anatexis.

A study by Dickin *et al.* (1980) had shown that the Pb isotopes of a Skye granophyre were only affected within 1.5 cm of major hydrothermal fractures. Some variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the vesicular tops of the basaltic lavas resulting from contamination by unradiogenic Sr carried in hydrothermal fluids in the greenschist-facies hydrothermal alteration zone on Mull, was observed by Hawkesworth and Morrison (1978). In the light of the previous work, Dickin was thus able to collect samples minimally affected by hydrothermal alteration, by sampling outside the zone of greenschist facies metamorphism, and collecting from flow centres rather than tops. He concluded that hydrothermal alteration was not the main cause of the isotopic variations in the SMLS or PM lavas.

Although Dickin (1981) recognised that lithospheric mantle heterogeneity could be responsible for some of the observed isotopic variations he thought it unlikely that it had caused

all the variation. This was because such a model would require that each lava flow had been produced by melting of an isolated and isotopically distinct mantle source region. Also, some of the hy-normative lavas had $^{206}\text{Pb}/^{204}\text{Pb}$ ratios which were too low to be derived from the mantle. So, he concluded that if variations had been inherited from the mantle source they were masked by later interactions with crustal material, and evidence other than Pb and Sr isotopic data would be needed to assess the extent to which heterogeneities in the mantle source had affected the composition of the Skye lavas.

The clear linear array between the estimated values of Lewisian gneiss and Tertiary Hebridean mantle for his Pb isotopic data, led Dickin (1981) to support the conclusion of Moorbath and Welke (1969) that the array was a mixing line. The coincidence of the age given by the slope of the line and ages determined for the granulite-facies Lewisian gneisses (approximately 2900 Ma and 2700 ± 60 Ma) was assumed by Chapman and Moorbath (1977) to provide further evidence in support of the mixing hypothesis. Assuming that the mantle source region of the Tertiary igneous rocks had the same $^{238}\text{U}/^{204}\text{Pb}$ ratio as the mantle source of the Lewisian crust (both having evolved since the formation of the earth as closed systems with constant values of the ratio) Dickin (1981) calculated growth curves for them. On a plot of $(^{207}\text{Pb}/^{204}\text{Pb})_{60}$ versus $(^{206}\text{Pb}/^{204}\text{Pb})_{60}$ he established that the mantle composition as calculated from growth curve modelling was much less radiogenic than the measured composition of the lavas. So, he concluded that the assumption that the Tertiary and Lewisian mantles had the same $^{238}\text{U}/^{204}\text{Pb}$ ratios was incorrect. He found that the mixing line of the Tertiary mantle and the Lewisian crust had a steeper slope than the Lewisian isochron, and that the Tertiary mantle plotted to the right of the Palaeocene 60 Ma geochron (i.e. had a higher $(^{206}\text{Pb}/^{204}\text{Pb})_{60}$ ratio). Dickin (1981) noted that the latter was characteristic of many ocean floor and ocean island basalts (e.g. Cohen *et al.*, 1980). He favoured the hypothesis of Cohen *et al.* (1980) that high $(^{206}\text{Pb}/^{204}\text{Pb})_{60}$ ratios of mantle-derived magmas resulted from modification of the Pb content of the mantle caused by the presence of radiogenic crustal material returned by subduction. The

alternative being the idea that high $^{206}\text{Pb}/^{204}\text{Pb}$ magmas were generated from mantle residual to gradual and episodic magma extraction crust-forming events (Cumming and Richards, 1975; Stacey and Kramers, 1975).

From plotting $(^{208}\text{Pb}/^{204}\text{Pb})_{60}$ versus $(^{206}\text{Pb}/^{204}\text{Pb})_{60}$ (variables which distinguish between Th-rich amphibolite-facies, and Th-poor granulite-facies crust) for the Skye lavas and acid intrusions, amphibolite- and granulite-facies gneiss, and an estimated composition of sub-Hebridean mantle, Dickin (1981) was able to calculate the relative contributions of the crust and the mantle to the Pb content of the lavas. He concluded that the ne-normative Fe-rich magmas had been contaminated by lower-crustal granulite-facies gneiss (which in some cases had contributed up to 90% of the Pb in the lavas) whereas the hy-normative, Fe-poor magmas had been contaminated by granulite-facies gneiss but had also assimilated a small amount of amphibolite-facies gneiss. In contrast the PM magmas had only undergone slight contamination by amphibolite-facies upper crust. Consideration of the isotopic character of the granulites led to the conclusion that (if the contamination had been by bulk granulite) they had Pb contents which were too low to explain the high degrees of Pb isotopic contamination calculated for the ne-normative, high-Fe lavas. So, instead, Dickin (1981) proposed that the Pb had moved selectively in a fluid phase. Contamination by silicate partial melt was ruled out, because the first melts of the gneisses would involve fusion of feldspar and quartz, but involvement of the latter had not been detected in the major element composition of the contaminated lavas (Moorbath and Thompson, 1980). Brown and Fyfe (1972) and Patchett (1980) stated that when there was no fluid free phase, hydrous mineral breakdown would be the first stage of melting. This led Dickin (1981) to conclude that the primary hydrous minerals in the Lewisian granulites, i.e. biotite, hornblende, and epidote, were the source of the unradiogenic Pb in the lavas and the U expected to be present in the minerals containing the Pb was held in zircon inclusions or the minerals would have radiogenic Pb isotopic characteristics produced by the decay of the U. Another proposed suitable contaminant was the U- and Th-poor, Pb-rich sulphide found in the

Lewisian granulites. A halide-rich fluid phase, such as that produced during magmatic differentiation or breakdown of hydrous crustal minerals, would be required to displace the Pb from the sulphide.

Patchett (1980) showed the heat from a small dyke could cause hydrous mineral breakdown which would produce a fluid that could be assimilated by later magma batches. Such a model would explain the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some of the ne-normative, Fe-rich lavas without the need for involvement of upper crustal amphibolite, which in any case Dickin had ruled out from his Pb data. Consideration of the Nd data of Carter *et al.* (1978) and Hamilton *et al.* (1979) led Dickin (1981) to conclude that the Nd isotopic characteristics of the lavas were not the result of bulk assimilation of crustal material by mantle derived magmas, since the composition of the lavas did not lie on a mixing line between the two. Instead he suggested that selective contamination of crustal Nd had occurred by the breakdown of light to middle REE-rich hydrous minerals (e.g. biotite or amphibole). Two important consequences of such a process would be that the REE patterns of the lavas would deviate from MORB like patterns; and unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the granites would not necessarily indicate their genesis from crustal rocks. In trying to explain the differences indicated for the type and amount contamination involved in the genesis of the lavas from the Sr, Nd, and Pb isotopic systems Dickin pointed out that the relative concentrations of the latter two would not be affected by magmatic differentiation. However he noted that the relative concentration of the former may be changed by the crystallisation of plagioclase. He also noted that if the contamination affecting the different systems was selective it could have occurred by the breakdown of different minerals, at different times, and different crustal depths so uncoupling the behaviour of the isotopic systems. Repeated contamination events at different stages of magmatic differentiation could produce compositionally scattered data from two-component mixing.

In summary, Dickin (1981) concluded that the high-Fe, ne-normative magmas differentiated and were contaminated at the base of the crust, and subsequently underwent

selective contamination as they paused briefly en route to the surface, whereas the low-Fe, hy-normative magmas were selectively contaminated in the granulite-facies lower crust, at a higher level than the high-Fe magmas. In contrast he proposed that the Preshal Mhor magmas had evolved in the upper mantle, and underwent minor selective contamination in the upper crust. His final conclusion regarded the Redhills granites, which he concluded were the products of assimilation of upper crustal material during the fractional crystallisation of mantle derived magmas which had previously undergone selective contamination in the lower crust.

It can be seen that having studied several isotopic systems various authors attempted to estimate the amount of crustal material which had been assimilated by the Skye lavas. Mixing calculations, based on the results from the different isotopic systems, indicated that there were large differences in the amount of contamination required to produce the observed compositional variations. Addition of up to 50% of the Sr and Nd from the contaminant in some of the samples was suggested by the studies of Carter *et al.* (1978) and Moorbath and Thompson (1980), whereas the Pb data indicate that up to 90% of the Pb in some samples was from the crustal contaminant (Dickin, 1981). In contrast, the range of CIPW normative silica saturation could be generated by assimilation of 15% amphibolite-facies gneiss (Morrison *et al.*, 1980). It should be noted that the presence of, for example, 90% Pb from the contaminant does not necessarily indicate addition of 90% of the contaminant to the original basaltic magma (indeed addition of such a large proportion crustal material would result in a composition far removed from basaltic). More correctly the absolute values of the relative concentrations of elements in the magma and contaminant should be considered, that is to say if, for example, the original magma contained no Pb addition of only 5% contaminant containing some Pb would result in 100% of the Pb in the mixture being from the contaminant. The question of the amount of crustal contamination of the Skye lavas is still, as yet, unresolved.

Previous workers have suggested various hypotheses to explain the differences in the

amount of crustal contamination indicated by the Sr, Nd, Pb, and Si-saturation data. The possibility of the differences being generated by assimilation of large quantities of crustal material in a long lived open system magma chamber (O'Hara, 1980), in which the major element composition of the liquid would be constrained by cotectic equilibria, was ruled out by Thompson (1982a). This was because the data of Moorbath and Thompson (1980) indicated post fractional crystallisation involvement of crustal Sr, which would not occur in a large crustal magma chamber. Selective contamination was proposed as the most likely explanation for the observed differences in the amount of contamination thought to be suggested by the Sr, Nd, and Pb isotopic systems. Thompson (1982a) outlined a model of selective contamination in which the breakdown of individual crustal minerals, such as biotite, would result in the migration of trace element-enriched fluids into the magma, thus enriching the magma in elements which were mobile in hydrous phases but without concomitant enrichment in elements that had significantly different concentrations in the crust from the mantle but were immobile in hydrous phases.

The differences in the amount of contamination indicated by the different isotopic systems continued to be a puzzle in the study of the Skye lavas. The data from the different isotopic systems and trace elements were combined to try to solve the problem. Once the characteristics of the various isotopic systems had been studied and quantified, and the likely contaminants identified, trace element data was employed to test the proposed crustal contamination models. Thompson *et al.* (1982) addressed the problem of the source of the low $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{206}\text{Pb}/^{204}\text{Pb}$ (needed to generate the observed isotopic characteristics of the lavas) in the granulite-facies crust. They divided the lavas into those which they considered to be uncontaminated, those contaminated by granulite-facies crust, and those contaminated by amphibolite-facies crust. They concluded that each group had a characteristic chondrite-normalised incompatible element pattern; resulting from the crustal contamination affecting the abundance ratios of Ba, Rb, Th, K, Sr, and the LREE, and had a negligible affect upon Nb, Ta,

P, Zr, Hf, Ti, Y, and the MREE. They modelled the incompatible trace element concentrations of the contaminated basalts, and concluded the data were consistent with addition of 15% to 20% Lewisian leucogneiss to uncontaminated basalt. To explain the major element data which suggested 5% to 10% contamination by the leucogneiss they postulated that the contaminant was a large fraction cotectic melt with plagioclase residua.

They took the presence of lower crustal Pb to indicate that crustal contamination had occurred. (However if, as suggested, Pb moved selectively in a vapour phase, then it would be possible for later magmas to pass through the crustal region and not assimilate Pb but still incorporate crustal material).

Although Thompson *et al.* (1982) were aware that contamination potentially occurred by partial melting of the crust they modelled total melting because it could be considered quantitatively, and the former could only be considered qualitatively. They found that the trace element characteristics of the granulite-facies contaminant could be modelled closely if a small amount of Scourian quartz alkali feldspar pegmatite was included in the mixture. The trace element characteristics of the amphibolite-facies contaminant were successfully modelled by addition of 20% average amphibolite-facies crust to an uncontaminated magma. The anomalously low Th values needed in the contaminant led to the suggestion that the easily-fusible leucocratic amphibolite-facies gneisses may have been disproportionately important in the contamination of the magmas.

Although the authors noted that their present study showed some of the elements they had previously used as indicative of mantle heterogeneity were in fact affected by crustal contamination, they concluded that the variations in the isotopically uncontaminated lavas indicated that their previous hypothesis, regarding mantle heterogeneity, was still correct.

In trying to deduce the amount of contamination which had affected the lavas they concluded that although trace element finger prints indicated 20% contamination, major element data suggested that no more than 5% to 10% crustal melt had been added to the lavas.

Correlations between Si-saturation and elements unaffected by crustal contamination lay in the range of primary variations expected from different degrees of melt. Noting that the sample used in their calculations was a fairly evolved small degree of melt which consequently had high incompatible element concentrations they stated that their calculations gave a maximum value for the amount of contamination (i.e. addition of material needed to reduce the incompatible elements to suitable concentrations). Therefore, they concluded that a value of 15% contamination was more likely for the less incompatible element-enriched basic magmas.

In conclusion they stated that most Lewisian granulite-facies gneisses plot far from the minimum melting point in the system $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-SiO}_2$, but potassic microcline leucogneisses, and pegmatites would melt at considerably lower temperatures than the granulites, particularly in the presence of water. They took this to support their suggestion that the leucogneisses had been important in the contamination of the Skye magmas.

Thompson (1982a) noted that progress could be made regarding the effect of crustal contamination upon incompatible trace elements such as Ba, Rb, Sr, and Th in the light of two recent developments. The first was the increase in the knowledge of the concentration of incompatible elements in igneous rocks and the determination of distribution coefficients for incompatible elements in mantle and basaltic phases. The second was the Pb isotopic study of Dickin (1981) which showed that on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ the lavas with the highest unradiogenic Pb (i.e. a large component of granulite-facies crust) also had the highest concentrations of radiogenic Sr, i.e. the data were inconsistent with the lower crustal evolution, upper crustal contamination model proposed by Moorbath and Thompson (1980). Since if, as they had suggested, the high $^{87}\text{Sr}/^{86}\text{Sr}$ resulted from interaction with $^{87}\text{Sr}/^{86}\text{Sr}$ -rich amphibolite-facies upper crust, then a Pb component from that source, i.e. high $^{208}\text{Pb}/^{204}\text{Pb}$, would also be expected, but was not detected in the lavas. In preference to the concept that the Sr had moved selectively without associated movement of Pb (a particularly mobile element), Thompson

(1982a) suggested that the radiogenic Sr had been incorporated into the lavas from the breakdown of a Rb-rich, $^{87}\text{Sr}/^{86}\text{Sr}$ -rich phase in the granulites, e.g. from biotite, or perhaps, a distinctive rock type (comprising the minerals needed to affect the isotopic ratios and incompatible element concentrations). This hypothesis explained the enrichment of K, Ba, and Rb of the $^{87}\text{Sr}/^{86}\text{Sr}$ rich lavas. Dickin (1981) had previously noted that (low- $^{206}\text{Pb}/^{204}\text{Pb}$, high- $^{87}\text{Sr}/^{86}\text{Sr}$) granulites were present in the Lewisian. Such rock types were compositionally suitable to be the contaminant. The positive correlation between ^{87}Sr and K indicated possible contamination by less refractory potassic leucocratic rock types found as veins, sheets and lenses in the Lewisian by Drury (1972), Sheraton *et al.* (1973) and Rollinson and Windley (1980).

When attempting to devise a physically and compositionally consistent model for the contamination of the SMLS magmas Thompson (1982a) took into consideration the previous work on major elements and isotopes, and the new trace element data of Morrison (1980). He considered the availability of the postulated low- $^{206}\text{Pb}/^{204}\text{Pb}$, high- $^{87}\text{Sr}/^{86}\text{Sr}$ contaminant in conjunction with recent theoretical work done on the behaviour of basaltic magma entering a stressed crust. The theoretical work showed that such a system would be likely to have a high surface to volume ratio with the magma being transported through a series of dykes and sills (Weertman, 1971; Vann 1978; Patchett 1980). Therefore, he concluded that in such a system, minor, less refractory, potassic, high- $^{87}\text{Sr}/^{86}\text{Sr}$ and low- $^{206}\text{Pb}/^{204}\text{Pb}$ veins, sheets and lenses could be extracted without involvement of the more refractory, predominantly sodic rock types. This was because the probability that even sparsely distributed veins of less refractory material would interact with basaltic material would be increased if the crust was cut by a swarm of dykes, since the plumbing system would have a high surface to volume ratio. Nevertheless the basic magma would have to come into contact with a large volume of Lewisian gneiss for such volumetrically minor rock types to be the major contaminant.

Thompson (1982a) attempted to explain all the available data, assuming that the presence of 90% radiogenic Pb in the system inferred 90% contamination of the lavas by the Pb

contributing phase. He therefore suggested that the near-total equilibration between Pb of the mantle-derived basic magmas and crustal material indicated that Pb moved selectively in a vapour of hydrous non-silicate fluid (such as that thought to be responsible for metasomatic events) between the major granulitic rock types and the basic magmas. If such vapours were involved in the contamination process one might expect that they would also have had an effect upon other mobile elements such as the large ion lithophiles (LILs) K, Sr, Ba, and Rb. Thus giving extremely high percentages of contaminant in mixing calculations, but their relative concentrations in the potential contaminant and the basaltic magma will be considered Chapter 7, Crustal Contamination.

As part of a collection of papers on CFBs and mantle xenoliths (Hawkesworth and Norry, 1983), published as a result of a Volcanic Studies Group conference, Thirlwall and Jones (1983) addressed the isotopic characteristics and contamination mechanisms of the Skye lavas. They attempted to unify the crustal contamination models for the lavas by considering previously published Sr, Nd, and Pb isotopic data, and elemental analyses (for which they presented a clear, concise summary of the previous work) in conjunction with some new Nd.

They stated that some of the uncontaminated samples had isotopic ratios similar to asthenospheric North Atlantic mantle material. The possibility that the isotopic range was generated in the sub-continental lithospheric mantle was dismissed because such a proposal would have required mixing of asthenospheric magma and lithospheric mantle (with a more diverse range of isotopic compositions than the asthenospheric source of the magmas), but no clear mixing relationships were observed. An alternative was that each flow sampled a discrete mantle source, this would be extremely unlikely in a region the size of Skye (Dickin, 1981).

It was concluded that the observed large variation in ϵ_{Nd} at a constant Sm/Nd ratio resulted from post-melting superimposition of ϵ_{Nd} variation on lavas with constant Sm/Nd (since to generate such a relationship by melting, the melting would have had to vary

systematically with ϵNd). Lewisian crust, or low ϵNd mantle material were proposed as the low ϵNd source.

A correlation between ϵNd and F/M (a ratio of $\text{FeO}/(\text{FeO}+\text{MgO})_{\text{molar}}$) led to the proposal that the mixing had occurred after the F/M variation had been produced by fractional crystallisation (an albeit unlikely alternative would be that the amount of subsequent fractional crystallisation was controlled by the degree of mixing). Since most of the basalt compositions would not have been in equilibrium with the mantle when they were completely liquid, it was concluded that a mixing event had occurred in the continental crust.

In considering the possible mechanism of contamination Thirlwall and Jones (1983) dismissed bulk assimilation and AFC, since the most primitive lavas were the most contaminated. The latter mechanism, for example, requires the reverse relationship. They concluded that the observed coherent isotopic variations of Sr, Nd, and Pb were difficult to produce by the selective contamination mechanism proposed by Dickin (1981). They also noted the effect that the contamination had on a wide range of incompatible elements in addition to the Sr, Nd, and Pb data. This led them to agree with the proposal of Thompson (1982a), and Thompson *et al.* (1982) that a crustal melt was the most likely contaminant.

Thirlwall and Jones (1983) suggested that $^{143}\text{Nd}/^{144}\text{Nd}$ should relate to the bulk chemistry of the melted rock type (as opposed to Sr and Pb which are potentially affected by post-consolidation processes). This would result in simpler relationships between $^{143}\text{Nd}/^{144}\text{Nd}$ and other compositional parameters. They also postulated that it should be possible to recognise elements which had not been affected by the contamination and therefore would provide evidence of the pre-contamination history of the basalts.

They found that there was a good positive correlation between ϵNd and Nd (which they concluded was equivalent to the correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr detected by Moorbath and Thompson, 1980), and a negative correlation between ϵNd and SiO_2 and Si-saturation. This led them to propose that the most primitive magmas had incorporated the most crustal material.

It was noted that only elements, or element ratios, which had restricted ranges prior to contamination could be used to determine the nature of the crustal melt. In considering the ratio of K/Zr as a possible contamination detector it was realised that the variation in the Zr content of the basalts was much greater than would have been expected from the amount of fractional crystallisation indicated by the reduction in Ni concentrations. Thirlwall and Jones (1983) therefore suggested that the high incompatible element concentrations had been produced during open system fractional crystallisation at the base of the crust.

The observed lack of variation in the Sm/Nd ratio with ϵNd constrained the ratio in the contaminant to be the same as that in the basalt (i.e. 0.24-0.25). From extrapolation of the straight mixing line on the plot of Sm/Nd versus ϵNd to intersect with the Scourian isochron it was concluded that the suggestion of Thompson *et al.* (1982), that the contaminant was a leucogneiss (Sm/Nd 0.12), was inconsistent with the new Nd data. An alternative proposal was made, that the intermediate or mafic bulk Lewisian crust had more suitable Sm/Nd ratios (i.e. >0.25 , since the ratio in the melt may have been less than in the source rock).

Having determined graphically that the most contaminated basalts had 75% Nd from a crustal source, and knowing that they contained 14 ppm Nd, their original Nd concentrations were calculated to have been approximately 3.5 ppm. SiO_2 restrictions on the proportion (15%) of crustal melt incorporated into the magmas enabled the calculation that the contaminant must have had about 70 ppm Nd, which was consistent with values for low volume melts of intermediate granulites. They stated that this was consistent with Dickin (1981) who found that up to 90% of the Pb in the contaminated basalts was from a crustal source, which eliminated the need to invoke separate selective movement of Pb. The good correlation of Nd and Sr led Thirlwall and Jones (1983) to suggest that 75% of the Sr could also have been from a crustal source, so also eliminating the need to have a contaminant with high $^{87}\text{Sr}/^{86}\text{Sr}$.

They concluded that for their model the incompatible trace elements had to have very low concentrations in the uncontaminated magmas. They suggested that play in their graphical

estimates of the amount of contamination could permit lower degrees of contamination and consequent higher values for the incompatible trace elements in the uncontaminated magmas. They also postulated that since Zr values were very high relative to Nd values, the former may have been added during the contamination process.

In summary, they outlined a petrogenetic model in which a mildly ne-normative mantle melt with low concentrations of incompatible trace elements underwent open system fractional crystallisation to hawaiite in a chamber at the base of the crust. Melts at varying stages of evolution were periodically extracted and underwent contamination proportional to their magmatic temperature en route to the surface through dykes. The most contaminated basalts would have been driven to hy-normative compositions which subsequently fractionated, and possibly assimilated upper-crustal acid Lewisian gneiss, to give the low-Fe intermediates.

The Thirlwall and Jones (1983) contamination model was tested against the Thompson *et al.* (1982) hypothesis in a combined study of Nd and a relatively new isotopic system $^{138}\text{Ce}/^{136}\text{Ce}$ (Dickin *et al.*, 1987). Dickin *et al.* (1987) proposed that $^{138}\text{Ce}/^{136}\text{Ce}$ would highlight time-integrated differences in the LREE and MREE. The ratio was investigated to assess whether it was geologically useful. Using the new isotopic data which enabled the modelling of REE patterns of the lavas, they modified the model of Thirlwall and Jones (1983) and concluded that the basaltic magmas had assimilated 8% to 5% melt from large degree melting of a Scourian granulite-facies sheet, or (possibly) by melting of an intermediate gneiss out of isotopic equilibrium. The contamination was proposed to have occurred during magmatic ascent through dykes and in sill complexes at distinct levels in the crust.

The $^{138}\text{Ce}/^{136}\text{Ce}$ data (five basic lavas and four hy-normative, low-Fe intermediates) showed that the lavas lay on mixing lines between mantle and Lewisian granite and dioritic gneiss, but not trondjemite (thus ruling out contamination by the predominant leucogneiss in the Lewisian complex).

They noted that to produce the observed Nd isotopic variations, 30% contamination by the granite, or >90% contamination by the diorite would be required. However, they stated that their figures were not quantitative since the mantle-derived end-member was probably more primitive than the one that they had used, and the crustal end members may have been enriched in REE by partial melting.

Dickin *et al.* (1987) noted that although bulk crust compositions were used in their calculations the actual contamination process probably involved partial melting of the crust (a possibility which they did not have detailed enough data to consider). From the results of melting experiments of Thompson (1981) they noted that the granitic potential contaminant had a small melting interval. At 755°C, 40°C above the solidus, it was 70% melted, so a 50% melt such as might be expected from dyke injection would produce a contaminant in which the REE concentrations were similar to the original rock. In contrast the diorite was only 15% melted at 755°C, and so a melt from it would be considerably enriched in LREE. From modelling the REE they found that the granite gave a better fit with the available data.

To assess the ascent model of contamination (in which assimilation of wall rock material was considered to be dependent on the temperature of the magma) proposed for magmas passing through dykes by Huppert and Sparks (1985), Dickin *et al.* (1987) compared the liquidus temperature of the basalts with the amount of contamination estimated from their model. They concluded that the amount of contamination was dependent on the temperature of the magma up to 1250°C, after which the contamination reached a level of about 10%. The hy-normative low-Fe intermediates were found to behave very differently from the other lavas, which was suggested to be because of AFC acting upon them.

Dickin *et al.* (1987) envisaged a plumbing system in which turbulent flow of magma through dykes prevented a chilled margin forming, so that crustal melt produced from the heat of the magma in the dyke could be assimilated. Density barriers at various levels in the crust could have resulted in the formation of sills, in which magma would pond, and possibly

assimilate crustal material, en route to the surface. It is interesting to note that in the same year a strong correlation between $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and Mg# had led Devey and Cox to similar conclusions for part of the Deccan sequence. The question of the timing of contamination is discussed further in Chapter 7, Crustal Contamination.

A study of xenoliths from the N.W. Highlands of Scotland led Menzies *et al.* (1987) to postulate that mantle metasomatism could have been partly responsible for the observed range in the isotopic compositions of the SMLS. From a chemical, and isotopic study of megacryst suites brought up to the surface in magmas which intruded the crustal rocks of north-west Scotland, comprising clinopyroxene, mica, magnetite, rutile, apatite, sanidine, anorthoclase, corundum, and zircon, and xenoliths of mafic granulites, peridotites, pyroxenites, and wehrlites. Menzies *et al.* (1987) concluded that the lower crust and upper mantle in that region were mineralogically complex. They noted that long term variable trace element ratios in the xenoliths were now recorded as extreme isotopic variations. The xenoliths were found to have Sr, and Pb isotopic compositions similar to lamproites and micaceous kimberlites respectively. In contrast, the Nd isotopic values were found to be very variable ($\epsilon\text{Nd} = -3.4$ to -32.6), and were more similar to values of garnet inclusions in diamonds and lamproitic-potassic volcanic rocks. Therefore, Menzies *et al.* (1987) suggested that the Hebridean lithospheric mantle had evolved very differently from the mantle source of the basaltic lavas of the BTIP. They based their hypothesis on the evidence of hydrous mantle nodules found in the Loch Roag dyke on Lewis, the Outer Hebrides. A comparative study was made of the composition of the ultramafic xenoliths with the host magma, and with xenoliths from other continental flood basalt provinces. The study showed that the Loch Roag xenoliths had high concentrations of incompatible elements Ba, La, Ce, and Nd relative to compatible elements, and were therefore termed enriched (Menzies *et al.*, 1987). Rb/Ba, Rb/Sr, and K/Ti ratios were similar in the xenoliths to their host basalt. The xenoliths had a wide range of $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51247-0.51097), and a

narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70415-0.70636). The large range in Nd values was attributed to a time-integrated variation generated over a period of 1000-1500 Ma. The restricted range of Sr values was presumed to reflect an original restricted range of Rb/Sr ratios in the xenoliths. The complex composition and texture of the xenoliths led Menzies *et al.* (1987) to suggest that they may be of multi-component origin, perhaps the result of mixing of Lewisian lithospheric peridotite and Tertiary asthenospheric melts (since such a combination would generate the vertical array observed on the plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$). To test this hypothesis the samples were analysed for Pb isotopes. The Pb data indicated that the mantle region from which the xenoliths were derived had a two-stage evolutionary history similar to that of micaceous kimberlites and lamproites, and that the mantle region had not been involved in MORB or OIB genesis. Menzies *et al.* (1987) considered that the suggestion of a spinel lherzolite source for the Tertiary lavas which had previously undergone a Permian extraction event (Thompson and co-workers) was consistent with their findings. This was because the Permian lavas were compositionally similar to Hawaiian nephelinites which required apatite and rutile to be residual mantle phases during their generation. Such minerals ($\pm$ zircon $\pm$ rutile $\pm$ apatite $\pm$ mica) were present as inclusions in the Loch Roag Dyke indicating that they could have been residual to the melting event generating the Permian lamproites. It was concluded that the Lewisian was underlain locally by chemically and isotopically heterogeneous lithospheric mantle with low $^{143}\text{Nd}/^{144}\text{Nd}$ (low Sm/Nd), low $^{87}\text{Sr}/^{86}\text{Sr}$ (low Rb/Sr), and low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and that in the light of evidence for mineralogical and chemical heterogeneity only time was needed produce isotopic variability. So, the Loch Roag xenoliths provided evidence that a series of metasomatic events had affected the mantle region beneath the BTIP. Therefore, Menzies *et al.* (1987) stated that it could not be assumed that the lithospheric mantle beneath the north-west Highlands had MORB- or OIB-like Sr, Nd, and Pb isotopic characteristics. The underlying asthenosphere could be MORB- or OIB-like, but mixing of such melts with heterogeneous lithospheric mantle could produce a series of volcanic rocks with elevated incompatible element concentrations and

isotopic ratios similar to ratios which would be produced by mixing with Lewisian crust.

It is clear that the question of the relative contributions of asthenospheric mantle, lithospheric mantle, and continental crust, to the composition of the Skye lavas has not, as yet, been fully resolved.

2.3.4 Magmatic plumbing system

Having established the compositional characteristics of the lavas, Thompson *et al.* (1972) considered the process of transportation of the lavas to the surface. Their proposal that there were two evolutionary trends in the SMLS led them to infer that the magmas must have been physically separated when they evolved. It was noted that magmas at varying points along both trends were extruded within a small area. To try to explain the temporal and compositional differences of the two trends, Thompson *et al.* (1972) rejected the possibility that the SMLS magmas had evolved in a large magma chamber. Instead they proposed a system of poorly connected sub-volcanic conduits and fissures (such as might be expected from the later studies of Patchett, 1980) which were sufficiently isolated to maintain the individual compositional characteristics of the magmas passing through them.

In the light of a polybaric fractionation model proposed by Thompson (1974a) and supported by Thompson *et al.* (1980a), Thompson (1982a) modified his original magmatic plumbing model (Thompson *et al.*, 1972). He suggested that the upwelling magmas ponded and stagnated near the Moho, and then again, briefly, in dykes and sills in the crust. The timing of contamination relative to differentiation by fractional crystallisation would, therefore, be constrained to occur post-crystallisation when the magmas moved upwards (possibly because of a reduction in the density of the magma as fractional crystallisation progressed) into the crustal dyke and sill complex. The high surface to volume ratio in the dykes and sills would enable contamination of the magmas by the dispersed, most-fusible, parts of the Lewisian crust

(Patchett, 1980). Such a model was consistent with the theoretical studies of Weertman (1971), Vann (1978), and Patchett (1980) which concluded that basalt entering a stressed sialic crust would do so as many dykes.

In accepting the dyke and sill plumbing model outlined above, Thompson (1982a) rejected the possibility of the SMLS being stored in a long lived open system magma chamber such as that proposed by O'Hara 1980 (in which complex elemental and isotopic characteristics may develop as a result of combined fractional crystallisation, assimilation of wall rock material, and replenishment of the evolving system with primitive magma). Such a chamber was rejected by Thompson (1982b) because of his assumption that such systems must be large, (although no such constraint was placed on their size by O'Hara, 1980). So Thompson inferred that assimilation of crustal wall rock material would have been of bulk crust, and therefore would not have been consistent with the hypothesis of selective contamination. He used the same line of reasoning to dismiss the elongate (whale-back) basic magma ridge model of Walsh *et al.* (1979).

2.3.5 Primary magmas

In any suite of basic volcanic rocks the parental magmas are potentially primary, i.e. not affected by differentiation processes such as fractional crystallisation, crustal contamination, magma mixing, liquid immiscibility or volatile loss during their passage to the surface. The identification of primary magmas is of great petrogenetic significance since, not only are they parental to the suite of rocks under investigation, they can also yield important information about their mantle source.

In the late 1960s and early 1970s petrologists researching the character of the mantle source regions of suites of basaltic rocks combined results from the newly devised experimental studies with geophysical (seismic profiles), and geological (xenolith compositions) knowledge

about the state of the mantle. Models of mantle melting were thus better constrained than they had been previously. Experimental studies enabled the determination of what would be in equilibrium with a given liquid under a range of pressure and temperature conditions, and volatile contents. Then knowledge of the state of the mantle made it possible to determine whether a sample could potentially have been in equilibrium with it i.e. was primary.

Thompson *et al.* (1972) had originally suggested that, since the MgO-rich SMLS basalts were highly porphyritic, they were the erupted products of accumulation of olivine phenocrysts into less magnesian liquids which were in equilibrium at relatively low pressures. The latter liquids being represented at the surface by the SMLS low-MgO basalts. One-atmosphere melting experiments by Thompson *et al.* (1972) showed that olivine was a liquidus phase in all the olivine-phyric basalts. This was suggested to support the crystal accumulation hypothesis. Presumably this was because the presence of liquidus olivine was taken to be the result of an increase in its concentration in the magma, due to accumulation, thus raising its liquidus temperature, rather than simply the result of the phase having the highest liquidus temperature in a melt of basaltic composition.

In an attempt to try to assess the extent to which high pressure processes had affected the genesis of the Skye lavas, and determine which phases would be in equilibrium with the magmas at high pressures, high pressure melting experiments were performed on three Skye lavas. Several lines of evidence resulting from the experimental work on one magnesian SMLS basalt, one low-Mg basalt thought to be representative of the SMLS (later found to be a different, FB, magma type), and a SMLS hawaiiite, led Thompson (1974a) to revise his earlier hypothesis (Thompson *et al.*, 1972) that the highly magnesian lavas were the products of crystal accumulation in the aphyric lavas. The first was that when the high-magnesian basalt sample was completely liquid it would have been in equilibrium with Fo₈₄ which Thompson suggested was equivalent to mantle olivines. It should be noted that mantle olivines are generally

considered to have a range of compositions from Fo₈₈ to Fo₉₄, BVSP, 1981). The second was the similarity in the composition of the near-liquidus olivine formed in the experiments with phenocryst cores analysed in the rocks. Olivine accumulation into a basaltic liquid would result in a change in its bulk composition so that, when it was remelted it would be in equilibrium with more magnesian olivines than the ones forming crystals in it. The third was that the olivines had Fe and Mg contents which gave values of K_D which suggested that they were in equilibrium with the present bulk composition of the lavas. Taking a Fe₂O₃ value slightly less than that measured in the rock (to allow for late magmatic oxidation) gave a K_D value of 0.33 which was in agreement with recent data for the coefficient. However, when a low pressure cumulate model was considered by calculating the K_D between phenocryst olivines in the magnesian basalt and the aphyric lava (SK 971, the Fairy Bridge lava taken to be a representative of a SMLS low-pressure basaltic liquid) an unreasonably low value of 0.22 was obtained for the coefficient (i.e. liquid too FeO-rich/MgO-poor, olivine too MgO-rich/FeO-poor). The fourth high pressure experimental result, leading Thompson to revise his view that the magnesian basalts were the products of crystal accumulation, was that an analysis of one aluminous Cr-spinel inclusion from an olivine phenocryst in the magnesian basalt was found to be more similar in composition to spinels in alpine peridotites than to spinels in magmatic stratiform intrusions. Compositionally-similar spinels in olivines from Small Isles (Canna, Eigg, Muck, and Rhum) basalts were found to be in reaction with the basaltic groundmasses where they were in contact with them (Ridley, 1972). The preceding observations and the compositional similarity of the Cr-spinel inclusions with spinels precipitated at 10 kb in experiments on a lunar basalt (Kushiro, 1972a) led Thompson (1974a) to propose that their unusual composition resulted from crystallisation at high pressures. He therefore suggested that the magnesian basalt was originally entirely liquid and although there were olivine (and Cr-spinel) phenocrysts present there was no significant loss by sinking between the time of separation of the magma batch and its eruption.

The P-T diagram for the magnesian-basalt showed a four phase point of liquid, olivine, Ca-poor pyroxene, and Ca-rich pyroxene, at approximately 17 kb. The absence of aluminous Cr-spinel despite its presence as inclusions in olivine in the rock was attributed to the low levels of fO_2 maintained in the capsule during the experimental runs. It was speculated that higher fO_2 levels may result in a five phase point at 17 kb.

Having presented evidence to suggest that the one magnesian basalt used in the experiments was a primary magma, Thompson (1974b) stated that there was almost no detailed information to allow the extension of the deductions made about its genesis to be extrapolated to other SMLS magnesian basalts. However, he then went on to propose that some ("if not all") the SMLS magnesian basalts had been slowly and near-adiabatically erupted without significant re-equilibration from their upper mantle source at approximately 60 km (depth equivalent to 17 kb) i.e. that they were primary magmas.

Variations in major and trace element concentrations of the SMLS lavas at a set F/F+M ratio (i.e. a set level of evolution) were considered to be original and were attributed to a combination of upper mantle compositional variation and variations in the degree of mantle melting producing the magmas (Thompson *et al.*, 1972). Thompson *et al.* (1980a) divided the incompatible trace elements into three groups on the basis of their compositional variation with Si-saturation, and Fe/Mg ratio. Y, and the HREE were found to correlate well with Fe/Mg, but did not correlate with silica-saturation. Assuming the variation in Si-saturation was attributable, and directly proportional, to variation in the degree of melt generating the lavas, Thompson *et al.* (1980a) proposed that the behaviour of Y, and the HREE was because of the elements being retained in the mantle diopside residual to the small degrees of mantle melt generating the lavas. Ti, P, Zr, Hf and the MREE were found to be almost twice as abundant in the ne-normative lavas as in the hy-normative lavas. Again a variation in the degree of melt was invoked since the elements would have been diluted in the larger degree hy-normative melt. Ba, Rb, Sr, Th, and the LREE did not correlate with silica-saturation. The observed variations in the ultra-

incompatible elements have been attributed to mantle heterogeneity resulting from Permian extraction of a very small amount of nephelinitic melt from the mantle region from which the Tertiary lavas were produced.

The hypothesis that primary magmas were present in the Skye lava pile was supported by Thompson (1980). He noted that the most magnesian PM and FB lavas were in equilibrium with olivine phenocrysts more forsteritic than Fo_{85} . He therefore concluded that they could be primary mantle melts from asthenospheric upper mantle. However, mantle olivines are generally considered to be more forsteritic than Fo_{92} , BSVP, 1981. This important question will be considered in more detail in Chapter 8, Magma Generation.

2.3.6 Mantle Source

Thompson *et al.* (1972) originally proposed that variable degrees of partial melting of a garnet phlogopite lherzolite at about 25 kb leaving residual phlogopite would cause variation in the Si-saturation content of the basalts of the SMLS. Such a model would also explain the SMLS basalts crossing the low pressure thermal divide in the normative system. This hypothesis also explained the negative correlation of Si-saturation (which is generally considered to increase proportionally to the degree of mantle melting) with Ti, P, Zr, Hf and the middle rare earth elements (MREE) (which, because they are incompatible in mantle phases, would have been concentrated in early formed small degrees of mantle melt and diluted as the degree of melting increased); and the unusual positive correlation of silica saturation with K. Thompson *et al.* (1972) postulated that the initial melt fraction varied from 5% to 10% to produce ne- and hy-normative magmas respectively. However, Thompson *et al.* (1980a) realised that liquids in equilibrium with phlogopite would be much more silica rich than the Skye lavas. They also noted that residual garnet would result in a large variation in the heavy rare earth elements (HREE) because they have a higher K_D in garnet than the light rare earth elements (LREE). In the absence of a large variation in the concentration of the HREEs Thompson *et*

al. (1980a) proposed that the SMLS basalts had been generated from a mantle source of spinel lherzolite with a minor amount of residual amphibole. Thompson (1974a) had suggested that the first fusion of the mantle region under Skye had given rise to the SMLS primary magmas. He supported the theory with the results of anhydrous high pressure melting experiments, mentioned previously, which showed that when completely liquid a magnesian Skye basalt was in equilibrium with olivine, sub-calcic augite, and pigeonite at 16.5 kb, 1370°C. The high pressure experiments showed that the maximum anhydrous pressure at which the sample was in equilibrium with an olivine-bearing upper mantle mineral assemblage was approximately 17 kb. This led Thompson (1974a) to propose a possible explanation for the multiple-saturation point observed at 16.5 kb 1370°C, that after melting to produce the SMLS magnesian basaltic magma the mantle at 16.5 kb (approximately 60 km depth) consisted of residual olivine, Ca-rich pyroxene and Ca-poor pyroxene. So it was possible that the sample could be in equilibrium with the upper mantle at 16.5 kb i.e. it could be a primary mantle melt. That is to say, the minerals which formed the multiple-saturation point on the liquidus of the sample at 16.5 kb were the most likely to be the major silicate phases in the upper mantle at that depth (depth in km = 3.03 x pressure in kb) i.e. approximately 60 km, below Skye.

The comparable ultra-incompatible element ratios, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ of some of the SMLS and PM magmas led Thompson *et al.* (1980a) to propose that the magmas had originated from the same mantle source. Thompson *et al.* (1980) tried to explain the time sequence of the different magma-types i.e. PM magmas being the product of a later stage of mantle fusion than the SMLS. This having been inferred from the PM magma-type occurring as lavas near the top of the SMLS pile, and as dykes cutting the SMLS lavas which suggested that they were feeders to stratigraphically higher, i.e. later lava flows. They outlined a model involving two increments of partial melting of spinel lherzolite mantle leaving a residuum of harzburgite.

The model of low-percentage melting of a spinel lherzolite source which was based on

major and trace element data was considered further by Thompson (1982b) in the light of new REE data. The data showed that the REE patterns of the SMLS magnesian basalts had $(\text{Ce/Yb})_N$ 2.56-4.72 i.e. not severely depleted in HREEs, and a small Eu anomaly. Assuming that the asthenospheric mantle source had chondritic relative REE abundances, Thompson (1982b) stated that the new data supported the spinel lherzolite mantle source hypothesis. He concluded that after the extraction of the SMLS magma, the residual lherzolite of the original asthenospheric peridotite would have been more magnesian, and depleted in light rare earth elements (LREE), incompatible trace elements, and major elements which were incompatible in mantle phases, e.g. Na and Ti. This led him to propose that the mantle residuum of the fusion event which generated the SMLS primary magmas could have been the source region for the Preshal Mhor magmas. Melting of mantle diopside, in which Y, and heavy rare earths (HREE) would have been retained (as deduced by Frey and Green, 1974), was invoked to explain the REE patterns of the PM lavas, i.e. HREE enriched relative to LREE. It was noted that melting of a mantle phase residual in the first fusion event was consistent with the sharp jump in composition between the two magma-types. Nevertheless, the inter-digitation of the SMLS and Preshal Mhor lavas at the top of the Skye volcanic succession still needed an explanation. Thompson (1982b) suggested that there could have been a time when parts of the mantle region beneath Skye were undergoing a second increment of fusion whilst others were still at the stage of first fusion. The single mantle hypothesis was validated further by Matthey (1979) who successfully used a complex dynamic melting model, involving incomplete melt extraction (Langmuir et. al., 1977), to model the generation of the SMLS magma-type, and the PM magma-type from a single upper mantle volume.

Having provided an explanation for the generation of the SMLS, and the PM magma-types, Thompson (1982b) considered the generation of the FB magma-type. From the preceding one-mantle model he proposed that there were three possible origins for the incompatible element depleted, flat chondrite-normalised REE pattern, FB magma-type. The first was melting

all the mantle diopside in a first increment partial fusion, thus leaving a harzburgite residuum, and giving the original chondritic REE, i.e. flat, patterns to the first fusion melt. The second was second increment partial fusion leaving some diopside in a lherzolite residuum, i.e. so that the HREE did not become significantly enriched relative to the LREE. Finally, melting of different areas of the mantle some of which had been partially depleted, and others of which were undepleted by previous extraction events so that the resulting FB compositional characteristics were produced by the mixing of LREE enriched and HREE enriched material.

Although the preceding models fit the available data, the sparse occurrence of the PM and FB magma types, and the only constraint on the timing of their generation and eruption relative to the SMLS and each other being the observation that the PM and FB magma-types occur in dykes cutting the SMLS lava pile, should be noted.

In a study of the trace element data of BTIP lavas Morrison *et al.* (1980) observed that the incompatible element abundances of BTIP basic rocks were low compared with alkali basalt suites worldwide, and that the concentrations of incompatible elements varied throughout the BTIP. To try to explain this Morrison *et al.* (1980) proposed that the sub-BTIP upper mantle had undergone a pre-Palaeocene magma extraction depletion event. They postulated that the site of the province had been affected by the closure of the Iapetus Ocean, which had occurred by subduction to the north-west, and had resulted in convective overturn in the mantle wedge above the subducting plate. It was suggested that the mantle source of the Tertiary lavas had "arrived" in the Province in the Carboniferous and Permian. Some strongly alkalic Permian lamprophyre dykes, which formed swarms throughout the region were found to be enriched in incompatible elements by approximately the same amount that the BTIP magmas were depleted in incompatible elements relative to world-wide alkali basalts. The Permian dykes were interpreted as the small degree melts produced during the first fusion of the mantle region

beneath the province. Morrison *et al.* (1980) proposed that regional tension in the Palaeocene, broadly associated with the opening of the North Atlantic, resulted in mantle upwelling. This caused a second stage of fusion of the mantle region which had previously produced the Permian lamproitic magmas. The small variation in the incompatible element abundances and ratios between the plateau-type basalts of Skye and Mull was attributed to Palaeocene lateral chemical mantle heterogeneity resulting from different amounts of extraction of the melts formed in the Permian first fusion of the mantle region. This hypothesis was supported by field evidence which showed that the dykes were more common in Mull than Skye. Mull being the area where the lavas had lower concentrations of incompatible elements.

In an attempt to explain the major local irregularities in chondrite-normalized incompatible element patterns of the low $^{87}\text{Sr}/^{86}\text{Sr}$, i.e. not crustally contaminated, BTIP lavas, Thompson (1982a) invoked the breakdown of a minor residual mineral of the Permian magmatic event (which retained REEs relative to P, Nb, and Th) in the episode of Tertiary magma genesis. However, $^{87}\text{Sr}/^{86}\text{Sr}$ is not a definitive indicator of crustal contamination because assimilation of granulite-facies lower crust would have little affect upon the ratio.

Thompson and Morrison (1988) developed the model outlined above to try to obtain a clearer understanding of the series of mantle events involved in the generation of the BTIP magmas. They proposed that the asthenospheric mantle region affected by the extraction of the Permian lamprophyre was welded onto the base of the lithosphere and was subsequently remobilised during stretching associated with the opening of the North Atlantic.

2.3.7 Tectonic setting

The magmatism of the BTIP has been linked with geodynamic processes related to the opening of the North Atlantic (e.g. White and McKenzie, 1989).

Decompression melting at the base of the lithosphere during adiabatic uprise of mantle peridotite within asthenospheric diapirs was proposed as the most likely source of primary

magmas in this region (Thompson, 1982a).

The tectonic controls on subsidence and faulting of a thinning crust outlined by Bott and Watts (1971) are thought to be responsible for early dyke injection phases and accumulation of very thick localised basaltic lava plateaux. Existing Mesozoic sedimentary basins may have influenced the position of the lava fields. (Thompson, 1982b)

2.4 Summary

The following points attempt to summarize the major conclusions reached by other workers so far.

The Tertiary basaltic lavas of Skye are part of the British Tertiary Igneous Province (BTIP), which is part of the larger North Atlantic Tertiary Province (NATP).

The lava pile lies either directly on Jurassic strata or on the earliest products of igneous activity on Skye, the basal palagonite tuffs.

The lavas are predominantly basaltic but there are some hawaiites, mugearites (including a big feldspar mugearite), and trachytes.

Classification and dating of plant remains, work on remnant magnetism and comparison with radiometric dates for later igneous intrusions (established from field relationships), indicate an early Tertiary age for the lavas.

The lava pile has been divided into five stratigraphic units from the presence of inter-basaltic sediments and plant horizons.

Three magma-types have been identified on Skye, they are the Skye Main Lava Series (SMLS), which comprises most of the Skye lava pile; the Preshal Mhor (PM) and the Fairy Bridge (FB) magmas both of which occur infrequently as lavas flows but are more common in dykes of the Skye regional swarm. Each magma-type shows internal chemical variation but

cannot be related to the others by low pressure crystal-liquid fractionation.

The high-magnesium SMLS basalts are postulated primary mantle melts.

Similar concentrations of elements which are ultra-incompatible in mantle phases and initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of the different magma-types led to the proposal of their derivation from a single mantle source.

A Permian magmatic depletion event in which small degrees of melt, enriched in elements incompatible in mantle phases, is proposed to account for the low values of incompatible elements in the Skye lavas relative to alkali basaltic provinces worldwide. The asthenospheric mantle residual to the Permian extraction event is suggested to have welded onto the base of the lithospheric mantle which was remobilised during stretching associated with the opening of the North Atlantic.

The SMLS are suggested to be derived from the volume of spinel lherzolite mantle which had undergone the Permian depletion event. Their variation in normative character has been attributed to varying degree of mantle partial melting. A further increment of fusion of the mantle residua of the SMLS is proposed to have produced the compositionally MORB-like PM basalts. It is unclear how the FB basalts were formed. Several theories have been proposed; melting of the mantle diopside in the SMLS residual lherzolite to leave a harzburgitic residuum, or second increment partial fusion leaving some mantle diopside in the lherzolitic residuum, or melting of areas of the mantle which have been partially depleted by, and others that are undepleted by, the previous extraction event have been suggested.

The two evolutionary lineages identified in the SMLS are thought to result from variations in their fractional crystallisation history.

The SMLS ne-normative basalts evolve to hawaiiite, mugearite and benmoreite. The trend from magnesian-basalt to hawaiiite is explained by crystallisation of 10% olivine and 4% plagioclase followed by crystallisation of 8% olivine, 15% plagioclase and 21% aluminous sub-calcic augite at 35km depth. The high pressure scheme has been tentatively extended to the

mugearites and benmoreites. The trend from SMLS hy-normative basalts to Si-rich, Fe-poor intermediates and trachytes, is thought to have occurred at shallower depths in a system where fO_2 values rose resulting in olivine precipitation being replaced by Fe-Ti oxides. An alternative suggestion invokes the assimilation of Lewisian granulite-facies crustal material to explain the two trends.

The compositional gap between basalt and hawaiite has been attributed to a density maximum in the magmas of that composition.

Contamination by Lewisian intermediate/acid granulite-facies crust has been invoked to explain the Skye lavas' Sr, Nd and Pb isotopic and elemental characteristics. The difference in proportion of contaminant needed to explain the variations observed in the different isotopic schemes has resulted in selective contamination, either by individual minerals or compositionally suitable rock types identified as veins and lenses in the Lewisian granulites, being suggested.

A magmatic plumbing system with a high surface to volume ratio, e.g. a system of dykes and sills, has been suggested for the lavas. It is consistent with experimental work on the behaviour of magma in a stressed crust, the separate fractionation trends of the SMLS hy- and ne-normative lavas and the selective assimilation of rock types which occur dispersed throughout the Lewisian crust.

The ultimate cause of the Skye lavas magmatism is postulated as geodynamic processes related to the opening of the North Atlantic. Subsidence and faulting of a thinning crust is thought to be responsible for early dyke injection phases and accumulation of localised basaltic lava plateaux. Decompression melting at the base of the lithosphere during adiabatic uprise of mantle peridotite within asthenospheric diapirs is suggested as the most likely source of the primary magmas in the Skye region.

2.5 Aims and structure of this thesis

From the study of the previous literature it can be seen that there are several fundamental questions regarding the Skye lavas that remain unanswered, or have not yet been satisfactorily answered. The questions can be considered under separate headings.

Petrography

Questions exist concerning:

- i. the inter- and intra-group compositional ranges of groundmass and phenocryst phases in the Skye Main Lava Series (SMLS) lavas, Preshal Mhor (PM) lavas, and Fairy Bridge (FB) lavas.
- ii. the deviation of modal proportions of phenocrysts from cotectic and eutectic proportions.
- iii. petrographic evidence of magma mixing.

Geochemistry

Questions exist concerning:

- i. the two distinct evolutionary trends versus a continuum of compositions.
- ii. the magnesian basalts having primary magma characteristics

Alteration and bole formation

Questions exist concerning:

- i. major and trace elements affected by post-consolidation alteration of the lavas.
- ii. major and trace elements affected by the weathering of the basalt tops to form boles.
- iii. the relative mobilities of the elements during the alteration processes.

Fractional crystallisation

Questions exist concerning:

- i. the implications of modelling the fractional crystallisation of the SMLS basalts as a two stage

process, with a different mineral assemblage either side of the compositional dog leg which occurs at 7 wt% MgO.

- ii. evidence to support the proposal that there is an evolutionary series of basalt-hawaiite-basalt-hawaiite in the SMLS lavas.
- iii. the major and trace compositions of the lavas indicating that, as has been suggested, the SMLS basalts underwent open system fractional crystallisation.
- iv. the fractional crystallisation history of the FB lavas.

Contamination

Questions exist concerning:

- i. the relative contributions of asthenospheric mantle, lithospheric mantle and continental crust to the SMLS lavas, PM lavas, and FB lavas.
- ii. the compositions of the asthenospheric mantle, lithospheric mantle, and crustal components.
- iii. the major and trace element compositions of the lavas consistent with crustal contamination models proposed on the basis of isotopes.
- ii. the assumption that some of the lavas have assimilated crustal material en route to the surface, and the nature, depth, and degree of involvement, and the composition of the contaminant(s).
- iii. the control on the amount of crustal material assimilated by the magmas.

Magma generation

Questions exist concerning:

- i. the exact relationship between the Iceland plume and the Skye lavas.
- ii. the geochemical and mineralogical composition of the source of the SMLS, PM, and FB magmas.
- iii. the depth at which, and to what degree, the various sources melted.

- iv. the nature of the plumbing system which brought the magmas to the surface.
- v. the composition of the mantle underneath the British Tertiary Igneous Province being mapped by comparing the elemental and isotopic characteristics of the Skye lavas with primary features with primary lavas from the other BTIP centres.

Stratigraphy

Questions exist concerning:

- i. the structure of the lava pile.
- ii. the stratigraphic units, distinguished on the basis of field relationships, being discernible by their petrographic characteristics.
- iii. the stratigraphic units, distinguished on the basis of field relationships, being discernible by their compositional characteristics.
- iv. the relationship between the previously defined stratigraphic units and the different magma-types i.e. the SMLS, PM, and the FB.
- iv. the evolution of the compositional characteristics of the lavas through time.

CHAPTER 3

PETROGRAPHY AND MINERALOGY

3.1 Introduction

In this chapter the main petrographic and mineralogical characteristics of the Skye lavas, as determined from inspection of thin sections and electron microprobe analysis, will be described. The petrography and mineralogy of the Skye lavas have been studied extensively (Chapter 2, History of Petrogenetic Research). Therefore this study does not present the first descriptions of the rocks of the area. Instead it aims to supplement what is already known about the lavas, by the petrographic description of a larger sample set, and the presentation of more mineral analyses than previous studies.

The data presented in this chapter will be utilised in Chapter 6, Fractional Crystallisation and Chapter 8, Magma Generation in which the petrogenesis of the lavas will be considered.

3.2 Previous Work

3.2.1 The Skye Main Lava Series

The Skye lavas range in composition from picritic-basalt to trachyte but the majority are basaltic. The lavas are mainly porphyritic, phenocrysts of olivine, plagioclase and clinopyroxene having been identified in the lavas as early as 1886 by Judd. The first detailed petrographic and mineralogical study of the lavas was by Harker (1904) in his classic work "The Tertiary Igneous Rocks of Skye", in which he concentrated on the southern section of the lava field. The study was predominantly descriptive, giving details of the textures and primary (olivine, plagioclase feldspar, clinopyroxene, iron oxides, and apatite) and secondary mineral

compositions of the Skye Main Lava Series (SMLS) lavas. Harker divided the lavas into four types on the basis of their mineralogy: olivine basalts, non-olivine basalts, hypersthene basalts (a type which has not been identified in the province by later workers), and augite andesites. Harker concluded that it was not possible to distinguish the lava-types systematically in the field and so did not subdivide the lavas on the map.

Harker's work formed the basis of many later studies, the most notable being the North Skye Memoir (Anderson and Dunham, 1966). In the Memoir the lavas were divided into six types (Hebridean olivine basalts, Vatternish Hebridean olivine dolerites, feldspar-porphyrific olivine basalts, mugearites, big feldspar mugearites, and trachytes) on the basis of texture and mineralogy. Anderson and Dunham considered all their lava-types to be recognisable in the field. Their petrological division of the lava field is summarised on the Geological Survey North Skye map (Sheet 80).

There are several other notable petrographic descriptions of the SMLS :-

Thompson *et al.* (1972) divided the lavas into five types (alkali olivine basalts, hawaiites, mugearites, benmoreites and trachytes) using CIPW normative characteristics. They then described the range in mineralogy within each chemically-defined group.

Williamson (1979) divided the SMLS basalts, hawaiites and mugearites on the basis of their phenocryst mineralogy. He defined, and gave detailed descriptions of, seven basalt groups (olivine (ol)+spinel, ol, ol+plagioclase (plag), clinopyroxene (cpx), ol+plag+cpx, plag macroporphyrific, and aphyric), six hawaiite groups (ol+plag+magnetite (mt) microporphyrific, ol+plag microporphyrific, plag macroporphyrific, coarse grained, composite, and aphyric), and five mugearite groups (ol+plag+mt microporphyrific, ol+mt microporphyrific, plag macroporphyrific, coarse grained, and aphyric). Preston (1982) summarised the mineralogical and chemical characteristics used by previous workers to define olivine basalts, tholeiitic basalts, hawaiites, mugearites, benmoreites, and trachytes of the SMLS.

3.2.2 The Preshal Mhor

The petrography of the Preshal Mhor (PM) basalts has been described by Esson *et al.*, (1975). They found the PM lavas to be petrographically comparable to the SMLS, but less porphyritic. Williamson (1979) gave a detailed petrographic and mineralogical description of his equivalents of the PM lavas, olivine and plagioclase porphyritic tholeiites. He noted that for a given Fe/Fe+Mg ratio (indicative of the stage of evolution of a sample) the tholeiites had more Ca-rich plagioclase, and Ca-rich, Fe-poor clinopyroxene than the SMLS basalts.

3.2.3 The Fairy Bridge

The Fairy Bridge (FB) basalts have not been described in detail petrographically or mineralogically. Matthey *et al.* (1977) commented that they could be distinguished by brown or purple-brown groundmass pyroxene containing numerous titanomagnetite inclusions, whereas the PM had pale green ophitic groundmass pyroxene and interstitial titanomagnetite.

3.3 Petrography

3.3.1 Skye Main Lava Series

3.3.1.1 Introduction

In the present study the SMLS samples were classified using their whole rock geochemical compositions. The divisions of the total alkalis (K_2O+Na_2O) versus SiO_2 diagram defined by Cox *et al.* (1979) were employed for the classification. Figure 3.1 shows the lavas are grouped into basalts (incorporating the high-MgO picrite basalts), which since they straddle the alkalic/sub-alkalic dividing line of Miyashiro (1978) are termed transitional basalts, trachybasalts, and trachytes.

3.3.1.2 Basalts

The principal basaltic phenocryst phase is olivine, which often contains microphenocryst inclusions of Cr-spinel. A large proportion of the lavas also contain plagioclase phenocrysts. Clinopyroxene and titanomagnetite occur in minor amounts, principally in the more evolved lavas. One example of a lava with a high modal proportion of large (up to 1.5 cm) plagioclase phenocrysts was analysed in the present study. The basalts with different phenocryst contents and proportions were not deemed sufficiently dissimilar, in terms of groundmass characteristics, mineral compositions, or whole rock geochemistry, to warrant division or separate description such as that carried out by Williamson (1979).

The basaltic groundmasses are predominantly holocrystalline, aphanitic microcrystalline. Occasional samples have a hypocrySTALLINE texture. Samples contain varying proportions of euhedral/subhedral olivine, plagioclase laths, granular or ophitic/sub-ophitic augite or titanaugite, equant titanomagnetite, and mesostasis zeolites (Plate 3.1).

It has been suggested previously that the alkalic and sub-alkalic basalts (synonymous with alkali basalt and tholeiite, or nepheline (ne) and hypersthene (hy) normative basalts respectively) can be distinguished by the presence of purple-brown titanaugite and pale purple-brown, weakly titaniferous augite or augite respectively (Thompson, 1982b). In the present study it has been observed that the alkalic (ne-normative) lavas do indeed generally have more coloured, purple-brown, groundmass augite and larger (average diameter 0.2 mm as compared with 0.08 mm) and more abundant groundmass opaques than the sub-alkalic (hy-normative) lavas.

3.3.1.3 Trachybasalts

The trachybasalts are texturally and mineralogically similar to the basalts. Their equivalent phases are generally more evolved (Appendix B, Tables 3.1, 3.2, 3.3, and 3.4).

3.3.1.4 Trachytes

The trachytes have phenocrysts of augite and sub-calcic augite, illmenite, plagioclase, alkali feldspar and biotite: Their groundmasses comprise plagioclase, alkali feldspar, biotite, Fe oxides and secondary minerals (Appendix B, Tables 3.2, 3.3, and 3.4, Plate 3.2).

3.3.2 Preshal Mhor

The Preshal Mhor (PM) lavas are basaltic and are petrographically similar to the SMLS basalts. They contain phenocrysts of olivine, plagioclase and sparse clinopyroxene. The only noticeable petrographic differences being that they are less porphyritic than the SMLS, and that chrome spinel microphenocrysts are not present as inclusions in the olivine phenocrysts. Groundmasses are holocrystalline, aphanitic microcrystalline, containing varying proportions of euhedral/subhedral olivine, plagioclase laths, granular or sub-ophitic augite or moderately titaniferous augite, anhedral/euhedral titanomagnetite, pyrite (which may be secondary), and secondary minerals (Plate 3.3).

3.3.3 Fairy Bridge

The Fairy Bridge (FB) lavas are basaltic, and are petrographically analogous to the SMLS basalts and the PM lavas having, phenocrysts of olivine (with Cr-spinel inclusions) $\pm$ plagioclase $\pm$ clinopyroxene. Groundmasses are holocrystalline, aphanitic and microcrystalline composed of varying proportions of euhedral/subhedral olivine, plagioclase laths, subophitic or ophitic purple-brown titanaugite, anhedral/euhedral titanomagnetite, pyrite (which may be secondary) and secondary minerals (Plate 3.4). The only distinguishing petrographic features of the FB lavas are the olivine phenocrysts being commonly skeletal and having embayed textures, the plagioclase phenocrysts being significantly more Ca-rich than those in the SMLS basalts (An_{90} as compared with An_{78}), and the presence of pyrite.

3.3.4 Intrusives

The seven dykes and one sill collected in the present study have basaltic petrographic characteristics. The dykes are compositionally equivalent to the SMLS and PM lavas. Their petrography is also comparable but, as would be expected since they cool more slowly, they have a coarser groundmass texture (Plate 3.5).

The sill has a typical basaltic mineral assemblage of olivine, plagioclase, clinopyroxene and opaques. Its texture is equi-granular with minerals in the range 1-1.5 mm diameter.

3.4 Mineralogy

3.4.1 Introduction

In the absence of evidence to suggest that the SMLS, PM, and FB lavas have sufficiently different ranges in mineral composition, size or shape to warrant separate discussion; and because of the paucity of compositional analyses of PM and FB minerals of the phases for each category (Appendix C, Tables 3.1, 3.2, 3.3, and 3.4, Plates 3.3 and 3.4) the properties of minerals will be described irrespective of magma-type categories.

3.4.2 Olivine

3.4.2.1 Occurrence and texture

The olivines are primarily subhedral and occur within the groundmasses and as individual phenocrysts, as monomineralic glomerocrysts, and less frequently, bi or trimineralic glomerocrysts with plagioclase, clinopyroxene or titanomagnetite (Plate 3.6 a,b,c). The crystal diameters vary in size from 0.1 mm (groundmass and microphenocrysts) to 4 mm, with the majority of phenocrysts being in the range 0.6-1.0 mm. Skeletal textures are seen occasionally, usually affecting large (>1 mm) crystals. Such textures can result from rapid crystal growth, or disequilibrium between crystals and liquid. Disequilibrium is also suggested by the presence

of internal structures, a line dividing a single crystal on either side of which the birefringence colours are different. Occasionally the phenocrysts show trachytoid texture parallel to aligned groundmass plagioclase or phenocryst plagioclase or both. The phenocrysts commonly have 0.02-0.2 mm inclusions of chrome spinel, whereas plagioclase and zeolite inclusions are present very occasionally.

The main alteration product of olivine is iddingsite. It either completely replaces crystals or exists around crystal edges or within cracks or both. Other alteration products include chlorite, Fe oxides, and bowlingite (the unoxidized state of iddingsite, Deer *et al.*, 1966) which sometimes replaces the centres of crystals the edges of which are iddingsitized.

3.4.2.2 Composition

94 olivine phenocrysts and 42 groundmass olivines were analysed from 21 and 18 representative samples respectively using the electron microprobe. The data are presented in Appendix C. The principles of analysis are outlined in Appendix C. The majority of analyses were of a single spot at the centre of a crystal. Traverses from the centre to edge of phenocrysts were also performed on 31 crystals.

A broad positive correlation is observed in the Skye lavas between the forsterite (Fo) content of the olivine and the MgO content (taken to be indicative of level of evolution) of the whole rock (Figure 3.2). NiO, TiO₂, Cr₂O₃ (possibly present due to contamination from Cr-spinel inclusions), MnO, occur in minor amounts (< 0.1 wt %) in the olivines. These elements have a high error:concentration ratio and are generally close to their detection levels.

The phenocrysts vary in composition from Fo₈₈ to Fo₆₂. The groundmass crystals range in composition from Fo₈₂ to Fo₄₀ with the majority falling into two groups between Fo₆₂₋₅₄ and Fo₈₂₋₇₂ (Figure 3.3.a, Figure 3.3.b). Zoning is rare, occasional crystals show normal zoning (Figure 3.4) which mainly affects their extreme outer edge, suggesting that it is the result of late stage quenching. Only one crystal analysed in the present study showed reverse zoning (Figure

3.4.c), possibly the result of magma mixing or crystal settling in a compositionally zoned magma chamber.

Representative analyses of five olivine phenocrysts and five groundmass olivines are presented in Table 3.1.

3.4.3 Plagioclase

3.4.3.1 Occurrence and texture

The plagioclase laths occur within the groundmass and as individual phenocrysts, as monomineralic glomerocrysts, and occasionally associated with olivine or augite in biminerallitic glomerocrysts (Plates 3.7.a, 3.7.b, 3.6.c). The laths vary in length from <0.1 mm (groundmass and microphenocrysts) to 15 mm (megacryst in big feldspar mugearite). Most of the phenocrysts are in the range 0.5-1.0 mm. Very few crystals show evidence of resorption. There is little evidence (2 samples) of orientation of plagioclase phenocrysts parallel to aligned groundmass plagioclase laths. Lamellar twinning is common as is, to a lesser extent, carlsbad twinning. Inclusions, which include titanomagnetite, apatite, olivine, augite and groundmass, are sparse.

The plagioclases, although generally fresh, sometimes alter to fine grained zeolitic material, and less frequently to chlorite (Plate 3.8).

3.4.3.2 Composition

41 plagioclase phenocrysts and 69 groundmass plagioclases were analyzed in 19 and 28 representative samples respectively. These data are presented in Appendix C. The majority of analyses were of a single spot at the centre of a crystal. Traverses from the centre to edge of phenocrysts were performed on 8 crystals.

A broad positive correlation is observed in the Skye lavas between the An content of the plagioclase and the MgO content of the whole rock (Figure 3.5).

The phenocrysts vary in composition from anorthite An_{90} in the picritic basalts to alkali feldspar An_{20} and orthoclase Or_{25} in the trachytes. The groundmass laths vary in composition from An_{79} to Or_{40} (Figure 3.6.a, Figure 3.6.b). Some phenocrysts show very faint concentric normal or oscillatory zoning. The latter is attributable to variation in the diffusion rate and degree of superheating at the crystal liquid interface, as discussed by Sibley *et al.* (1976). A sharp compositional change close to the crystal edge, similar to that seen in the olivine phenocrysts, is observed in some plagioclase phenocrysts (Figure 3.7).

Representative analyses of five plagioclase phenocrysts, five groundmass plagioclases and the phenocryst and groundmass alkali feldspars analyzed in the trachytes are presented in Table 3.2.

3.4.4 Clinopyroxene

3.4.4.1 Occurrence and texture

Clinopyroxene phenocrysts are sparse in the Skye lavas. They are usually subhedral to anhedral, and occur both individually, and as monomineralic and biminerallitic glomerocrysts with olivine or plagioclase (Plates 3.9.a, 3.9.b, 3.6.c). The phenocrysts vary in diameter from 0.3-1.5 mm, the majority being in the range 0.3-0.8 mm. Inclusions of opaques and plagioclase are common. The crystals occasionally partially enclose plagioclase and olivine phenocrysts. Phenocrysts sometimes show oscillatory zoning. Sector and simple twinning occurs occasionally.

Clinopyroxene is a common groundmass phase in the Skye lavas. The crystals have a granular, sub-ophitic or ophitic habit, they are generally less than 0.2 mm in size.

The clinopyroxenes are frequently altered to chlorite.

3.4.4.2 Composition

11 clinopyroxene phenocrysts and 53 groundmass clinopyroxenes were analysed from

5 and 28 representative samples respectively. The data are presented in Appendix C.

Although compositional evolutionary trends are observed in other clinopyroxene series (Figure 3.8) no such trends, or consistent elemental variations with evolution of the whole rock geochemistry are observed in the phenocryst or groundmass clinopyroxenes of the Skye lavas (Figure 3.9).

The phenocrysts and groundmass crystals are predominantly salite, there are occasional crystals of augite and, in the trachytes, sub-calcic augite (Figures 3.10.a, 3.10.b). Pink, purple and brown colouration in some of the groundmass clinopyroxenes indicates an elevated Ti content.

Analyses of five clinopyroxene phenocrysts and five groundmass clinopyroxenes, which cover the compositional range, are presented in Table 3.3.

3.4.5 Fe oxides

Octahedral Fe oxides are common in the groundmass of the basalts and occur as phenocrysts in the trachytes. The Fe oxides range in size from 0.05-0.4 mm. 4 phenocryst and 56 groundmass Fe oxides were analyzed from 1 and 27 representative samples respectively (Appendix C, Figure 3.11, Table 3.4). The Fe oxides are predominantly titanomagnetite; one magnetite crystal and two illmenite crystals were analysed in a basalt and a trachyte respectively.

3.5 Alteration and secondary mineralogy

There is evidence for alteration of most SMLS, PM and FB lavas by one or more of the following processes: iddingsitization of olivine, chloritization of augite, and zeolitization of groundmass minerals (Plates 3.10.a, 3.10.b, 3.10.c). Pyrite is present in the PM and FB lavas but, from textural evidence, it not possible to determine whether it is primary or secondary.

Amygdaloidal lavas are common and have vesicles infilled by zeolites, quartz, or calcite (Plates 3.11.a, 3.11.b, 3.11.c).

3.6 Relative proportion of phenocrysts

The modal proportions of phenocryst phases, as determined by point counting, are presented in Table 3.5, and illustrated on triangular diagrams Figure 3.12 and 3.13.

Table 3.6 summarises point counting results obtained by varying the area of sample covered, and the number of points counted for each area. The variation in the proportion of phenocrysts in two slides of the same sample shows the importance of covering as large an area of sample as possible. The results demonstrate that varying the density of points, for example from 500 to 1000, has little effect on the modal proportions obtained. For each sample, 2000 points were counted over two thin sections.

Olivine is the most abundant phenocryst phase, having modal proportions varying from 0 to 23.38%. Plagioclase phenocryst proportions range from 0 to 20.90% (with the exception of a big-feldspar basalt, 30.50%), and those of clinopyroxene phenocrysts are between 0 and 3.45%.

The variation in phenocryst proportions, and the deviation the olivine/plagioclase ratio from cotectic proportions will be discussed in Chapter 6, Fractional Crystallisation.

Having considered the petrographic characteristics of the Skye lavas their compositional characteristics are now considered in Chapter 4, Geochemistry.

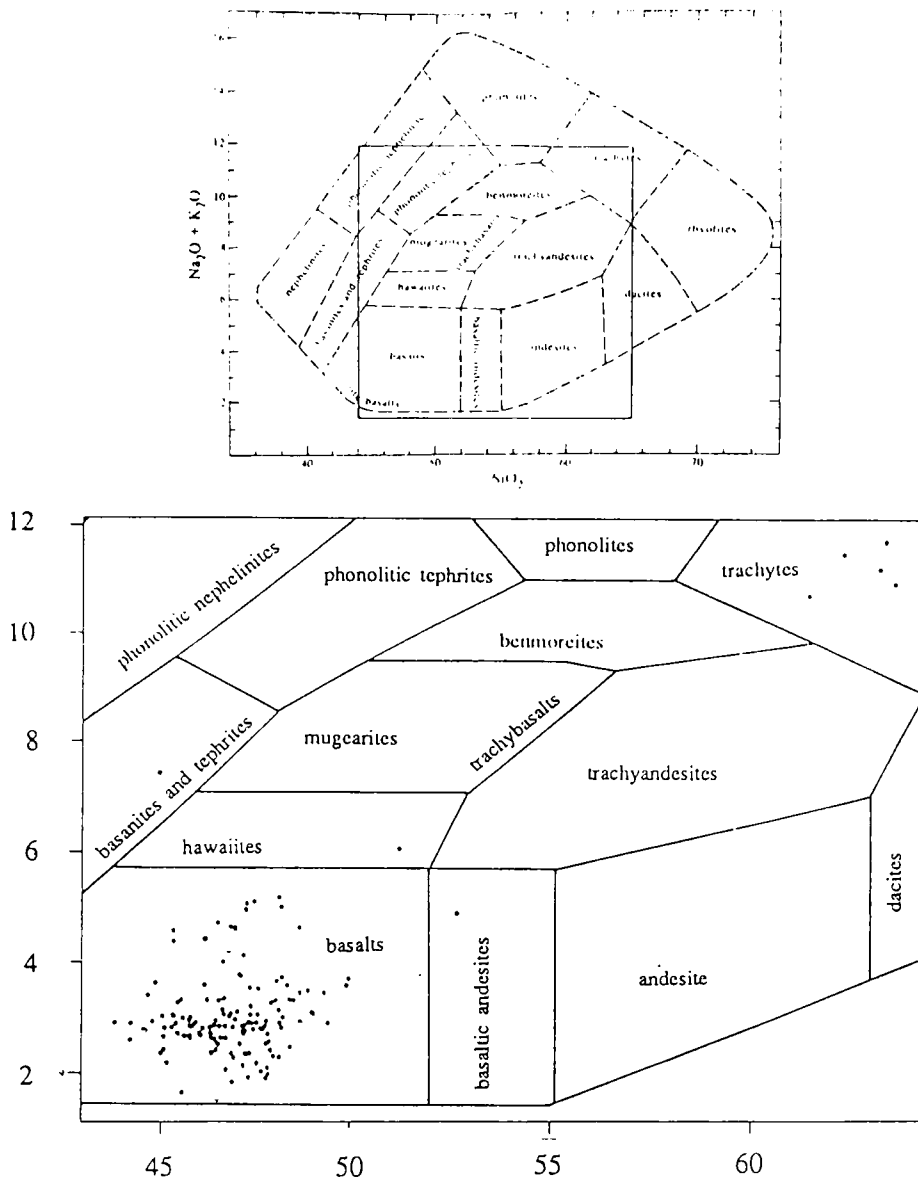


Figure 3.1 Total alkalis versus silica diagram. Nomenclature of normal (i.e. non-potassic) volcanic rocks. The boundaries are not intended to be sharp, the field labelled are intended to show the approximate areas in which the different rock types plot.

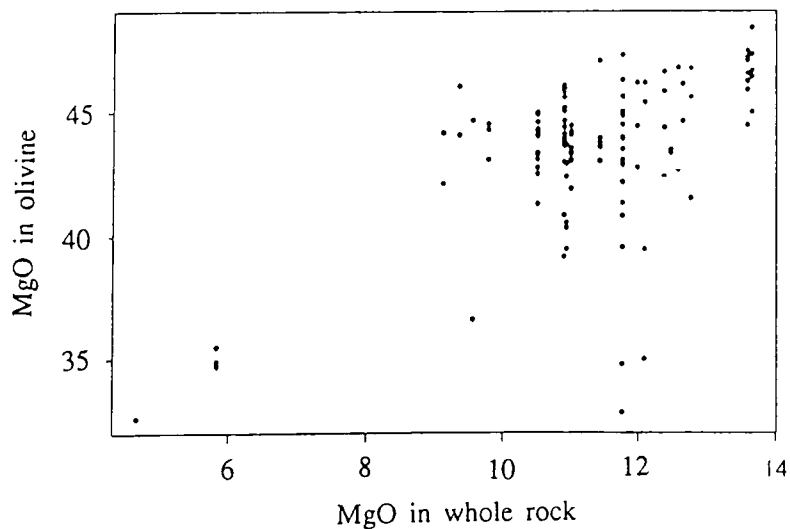


Figure 3.2 Olivine forsterite (Fo) content versus the MgO content of the whole rock, there is a very broad positive correlation between the two variables. (Element concentrations are in wt% oxide.)

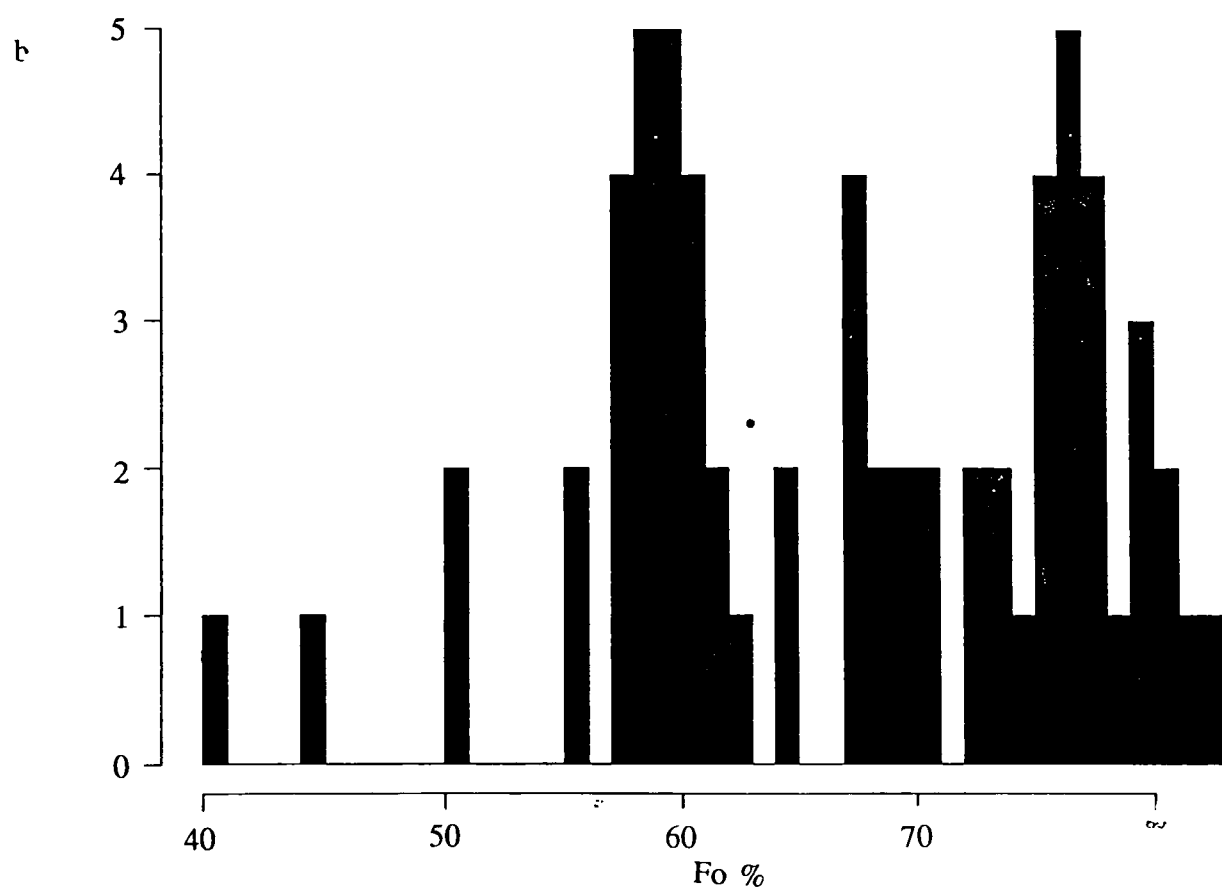
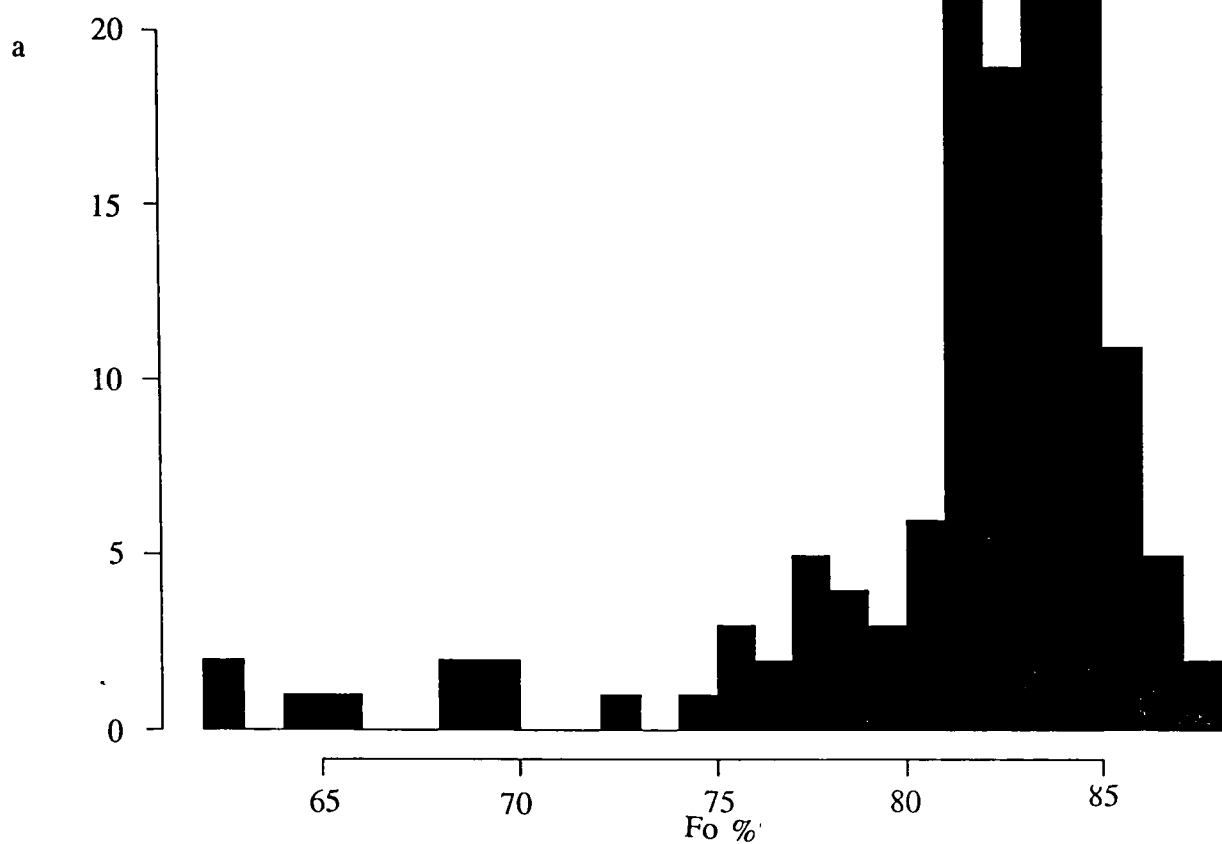


Figure 3.3 Histograms of the variation in olivine phenocryst and groundmass compositions.
 a. phenocryst olivine.
 b. groundmass olivine.

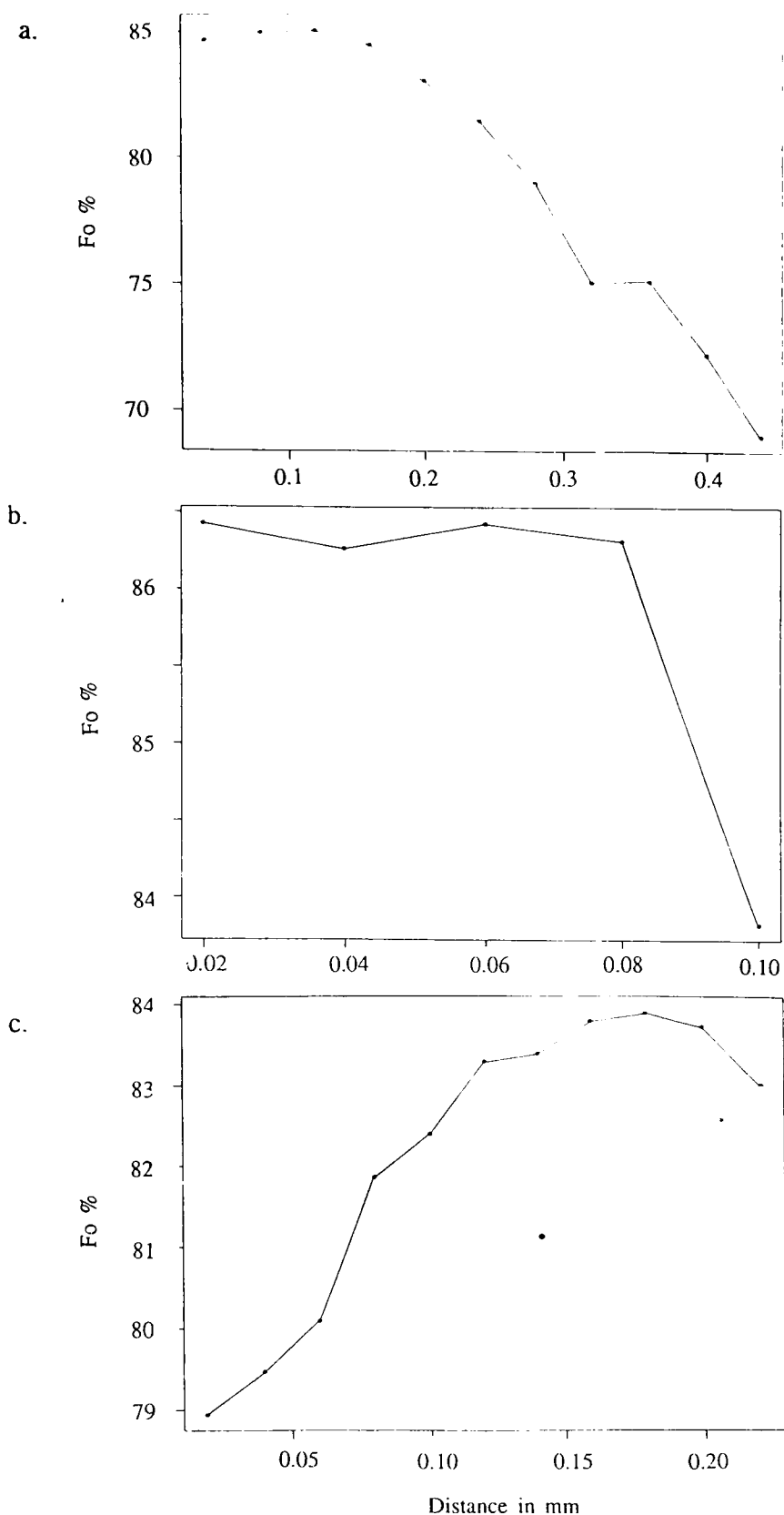


Figure 3.4

Variation in the forsterite content in traverses from the centre to the edge of olivine phenocrysts. (Solid lines joining spot analyses are not supposed to imply a compositional profile).

- Normal zoning, ie a reduction in Fo content from the crystal centre to edge (JHS33)
- Normal zoning at the very edge of the crystal (JHS 129).
- Reverse zoning, an increase in the Fo content from the crystal centre to edge (JHS37)

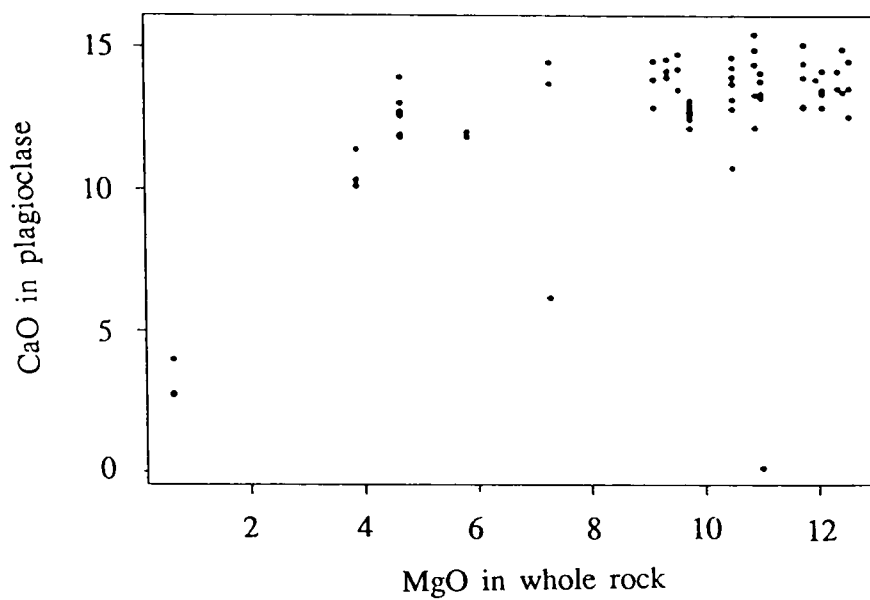


Figure 3.5 Plagioclase CaO content versus the MgO content of the whole rock. There is a broad positive correlation between the two variables. (Element concentrations are in wt% oxide.)

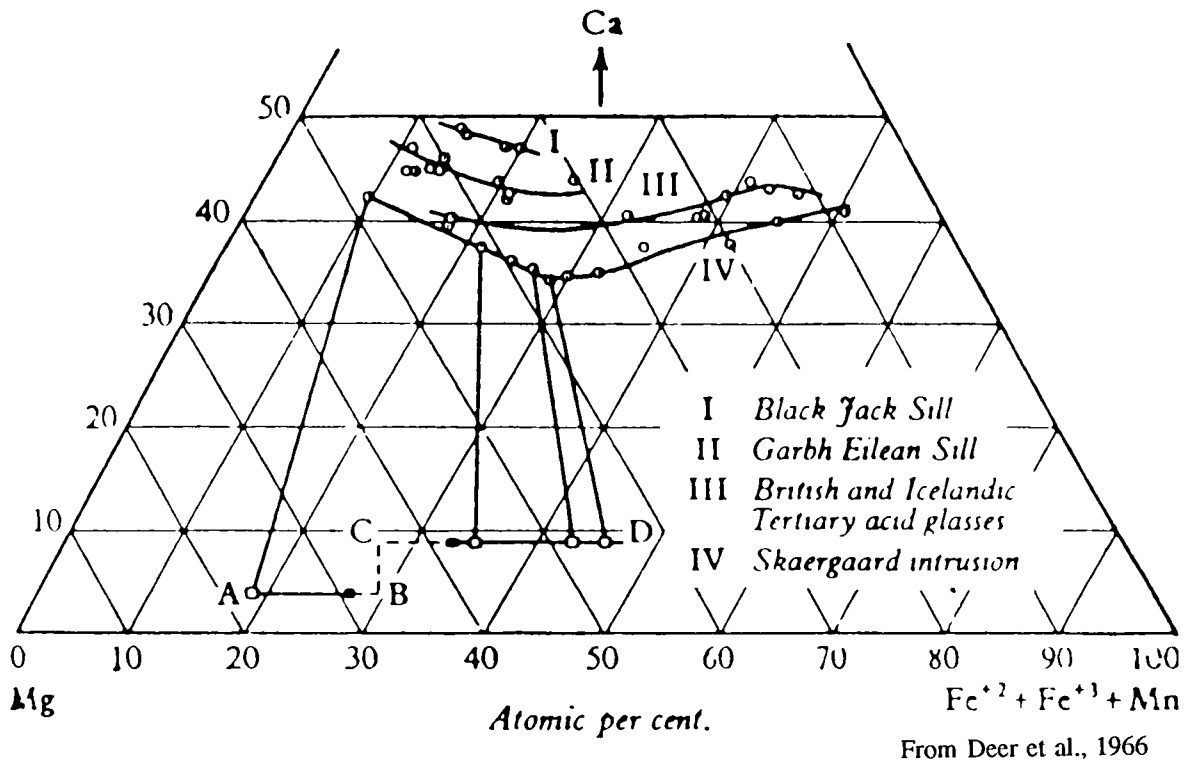


Figure 3.8 Trends of pyroxene crystallisation.
 I Differentiated teschenite sill, Gunnedah, New South Wales.
 II Garbh Eilean sill, Shiant Isles.
 III British and Icelandic Tertiary acid glasses.
 IV Skaergaard intrusion.
 Line A-B crystallisation trend of primary orthopyroxenes.
 Line C-D crystallisation trend of inverted pigeonites.
 Tie-lines are shown for 4 coexisting pyroxene pairs from the Skaergaard intrusion.

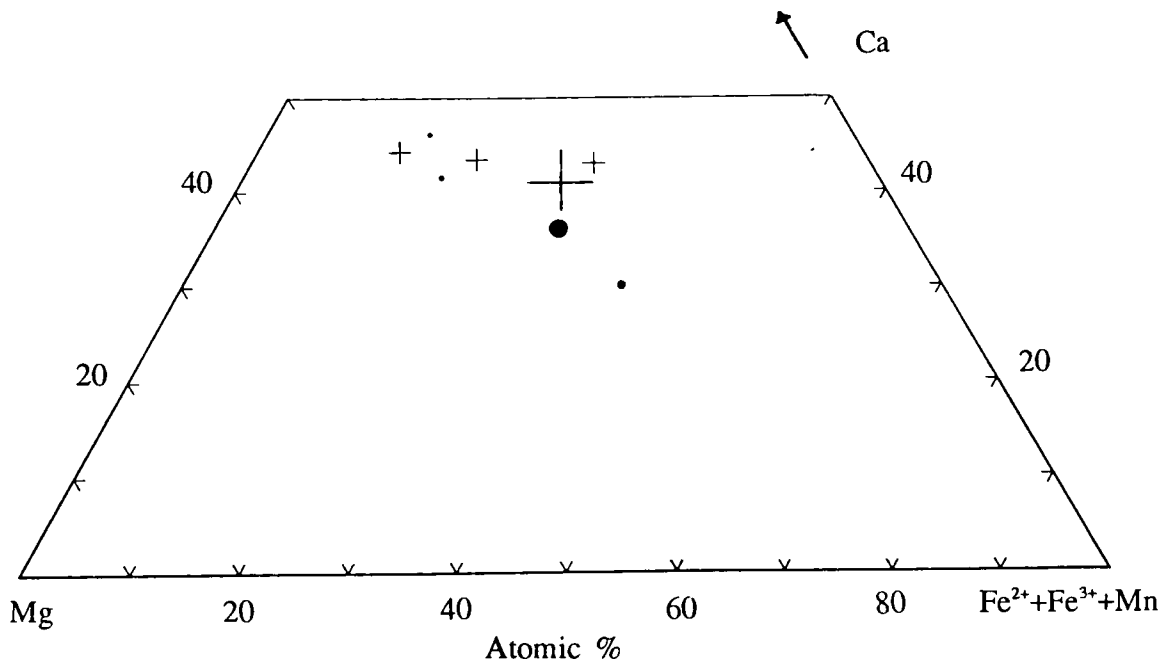


Figure 3.9 Phenocryst (large symbols) and groundmass (small symbols) pyroxenes from the SMLS showing that they have no compositional trend with evolution of the whole rock composition.
 (+ primitive lavas with olivine and Cr spinel phenocrysts,
 • more evolved lavas with olivine, plagioclase and clinopyroxene phenocrysts).

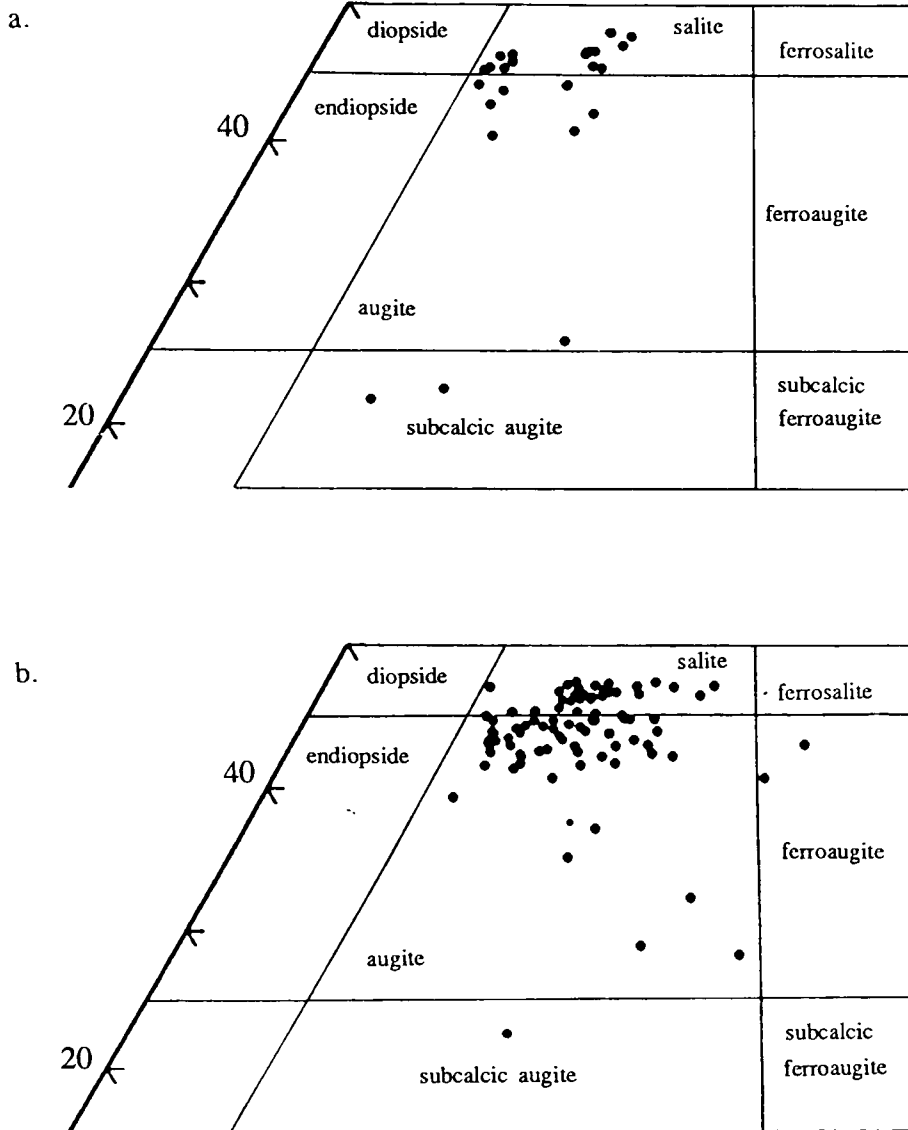
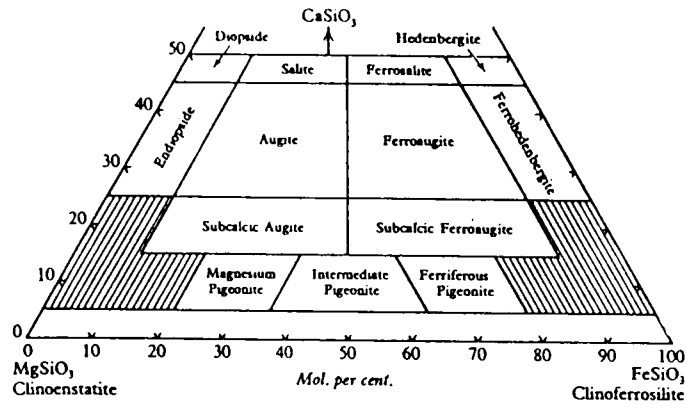


Figure 3.10 Variation in clinopyroxene phenocryst and groundmass compositions.
a. phenocryst clinopyroxenes.
b. groundmass clinopyroxenes.
The diagram above shows the position of the main diagram within the pyroxene quadrilateral. Most analyses lie in the salite/high Ca-augite part of the diagram.

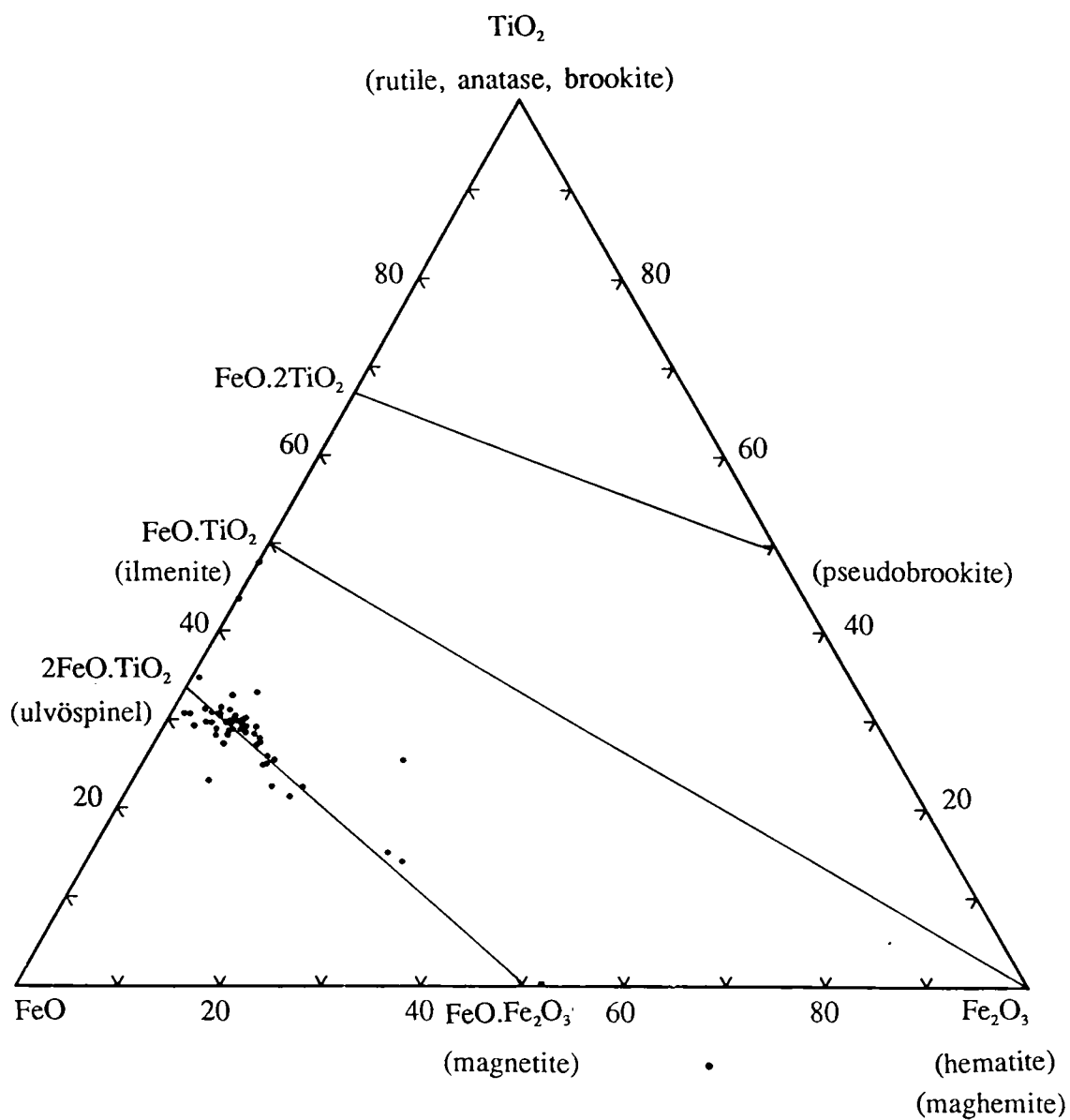


Figure 3.11 Variation in groundmass Fe oxide composition.

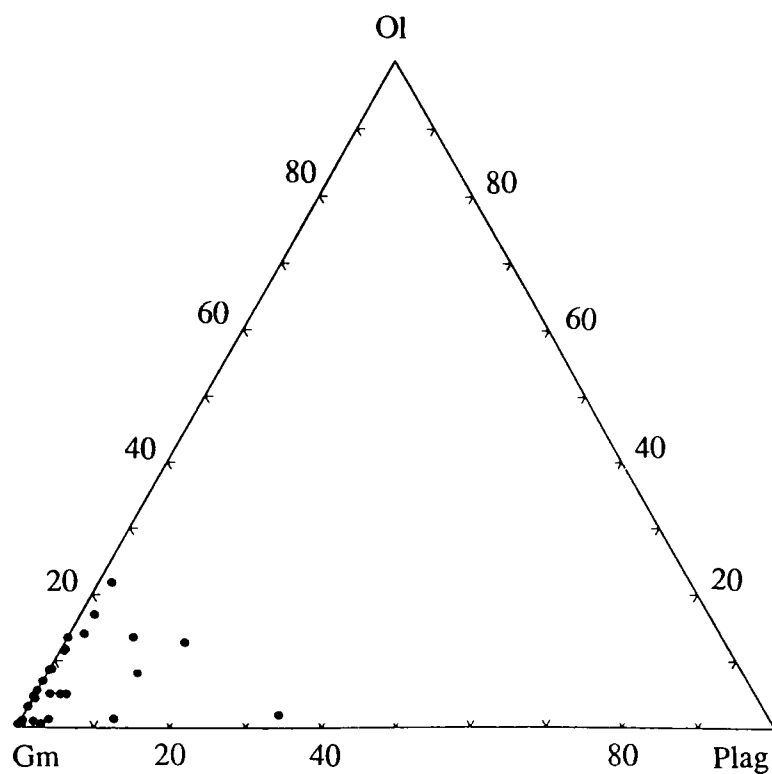


Figure 3.12 Relative proportions of groundmass and phenocryst olivine and plagioclase in selected lavas. Data are taken from Table 3.5

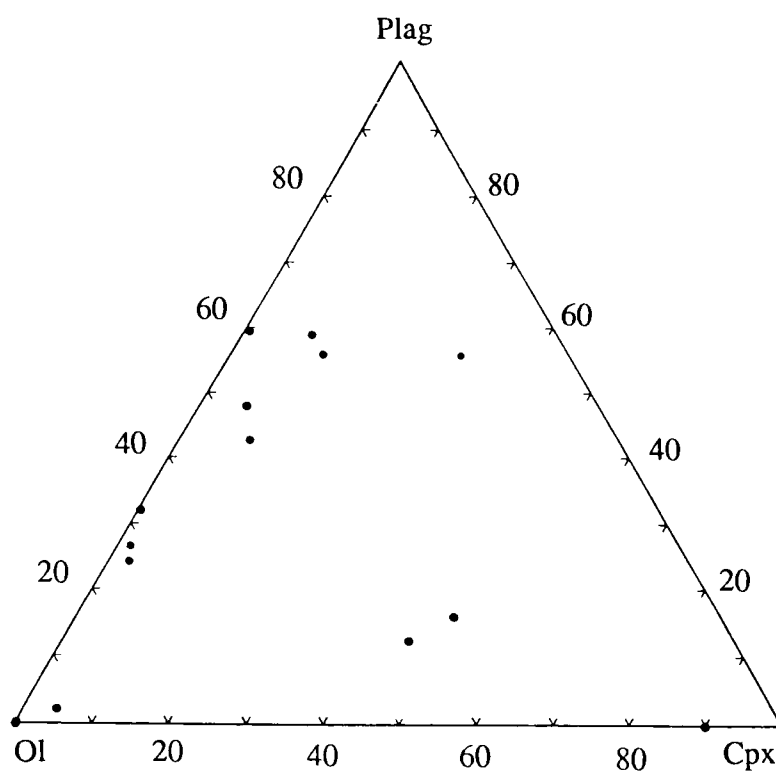


Figure 3.13 Relative proportions of phenocryst olivine, plagioclase, and clinopyroxene in selected lavas. Data are taken from Table 3.5

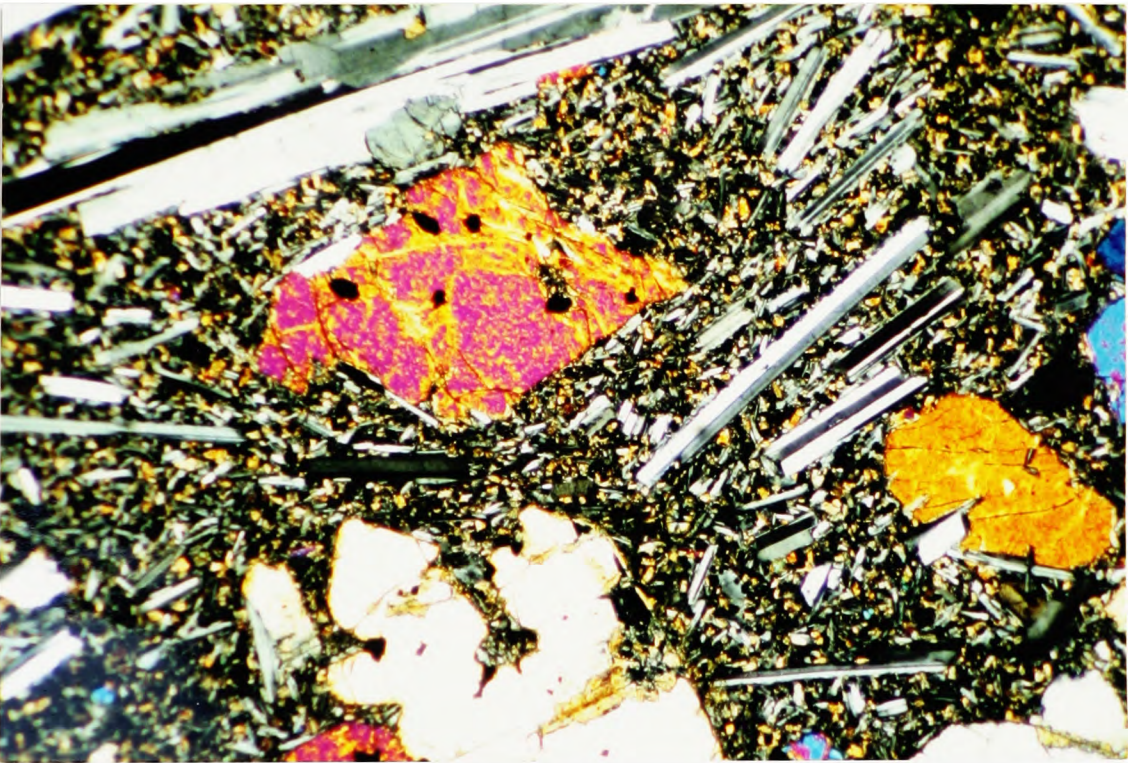
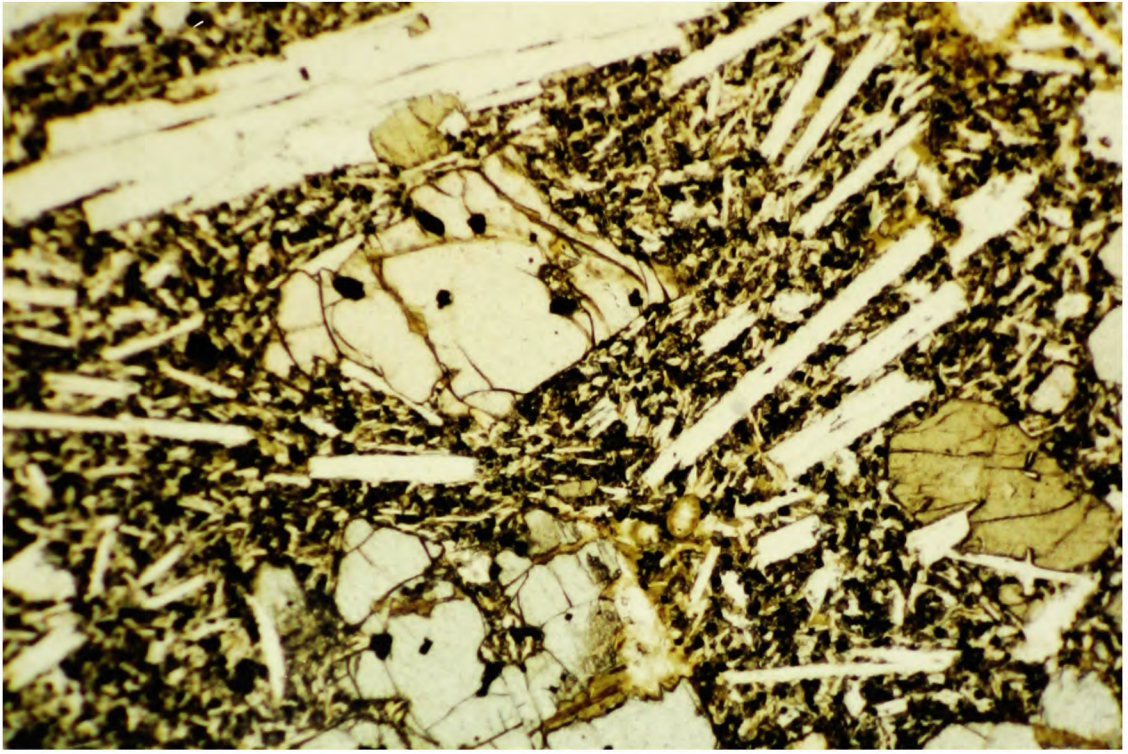


Plate 3.1

Views of a typical SMLS basalt (JHS 158) in plane polarised light and under crossed polars. This sample is representative of the phenocryst and groundmass mineralogy of the SMLS basalts; it shows phenocryst olivine (with inclusions of chrome spinel), plagioclase and clinopyroxene, and groundmass olivine, plagioclase, clinopyroxene and titanomagnetite.

Fields of view : 2.4mm x 3.6mm.

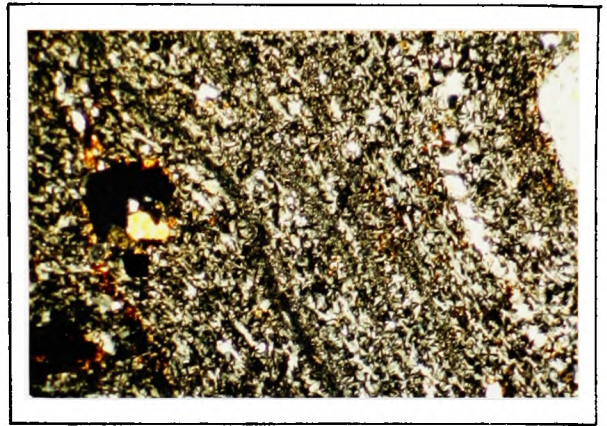
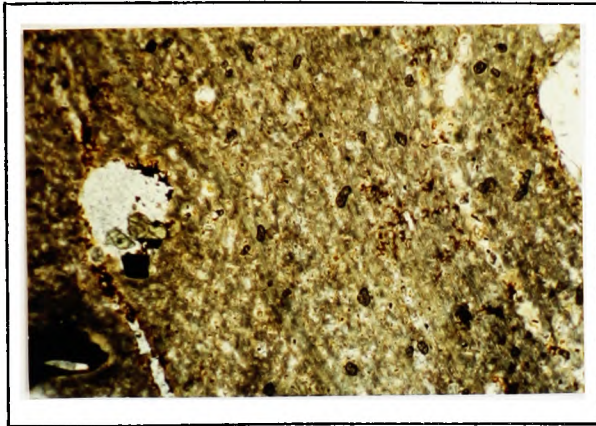


Plate 3.2.a

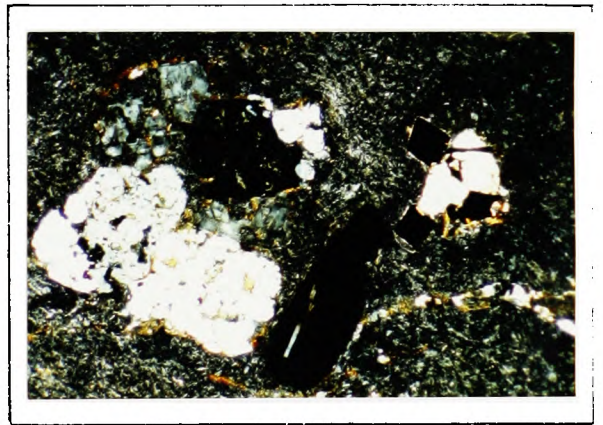


Plate 3.2.b

Views of typical SMLS trachytes (JHS54 and JHS57) in plane polarised light and under crossed polars. These samples are representative of the phenocryst and groundmass mineralogy of the SMLS trachytes; they show phenocrysts of alkali feldspar, sub-calcic augite, and titanomagnetite, groundmasses are extremely fine grained plagioclase laths and opaques can be identified.

Fields of view : 2.4mm x 3.6mm.



Plate 3.3

Views of a PM basalt (JHS 202) in plane polarised light and under crossed polars. The sample is mineralogically similar to the SMLS basalts comprising olivine, plagioclase, clinopyroxene and titanomagnetite, but is it less porphyritic. Fields of view : 2.4mm x 3.6mm.

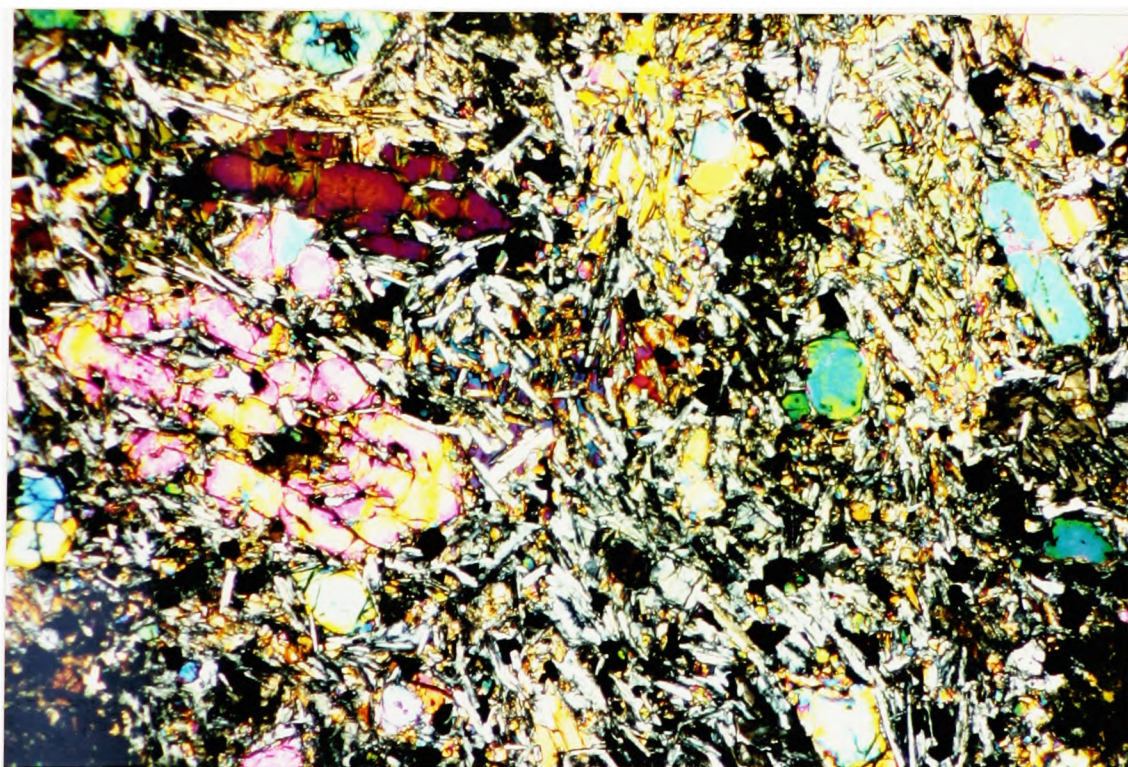
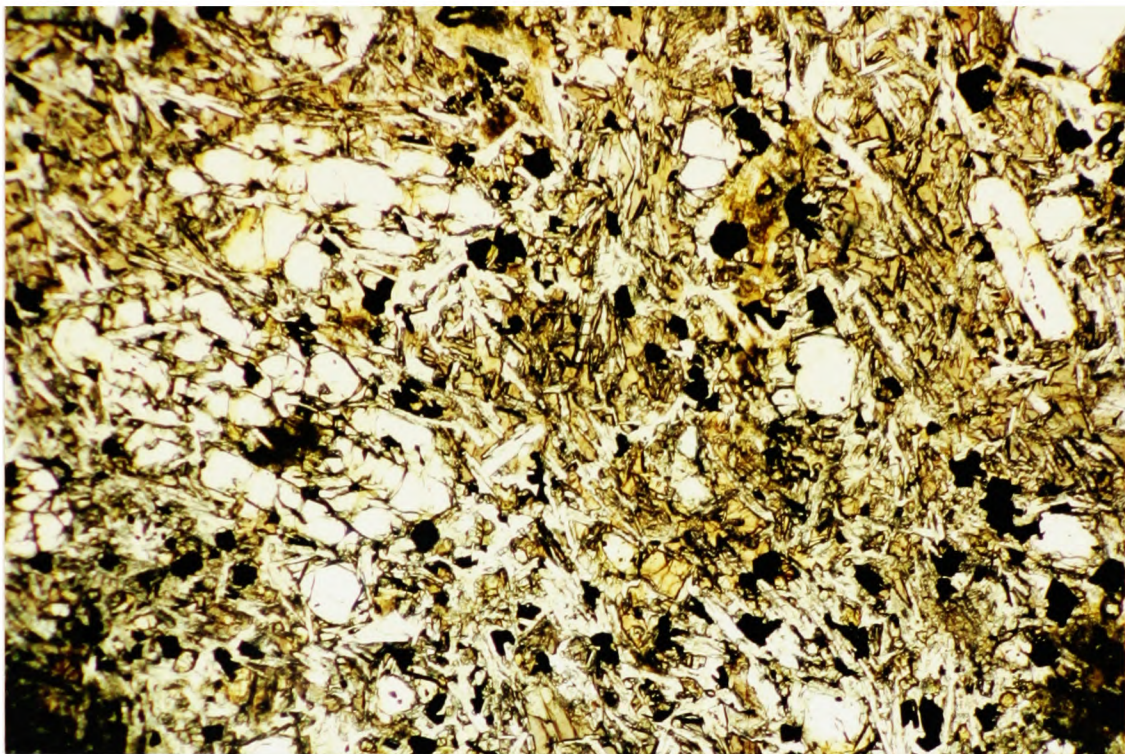


Plate 3.4

Views of a FB basalt (JHS 184) in plane polarised light and under crossed polars. The sample is mineralogically similar to the SMLS basalts comprising olivine, plagioclase, clinopyroxene and titanomagnetite, but the olivine phenocrysts are more skeletal. Fields of view : 2.4mm x 3.6mm.

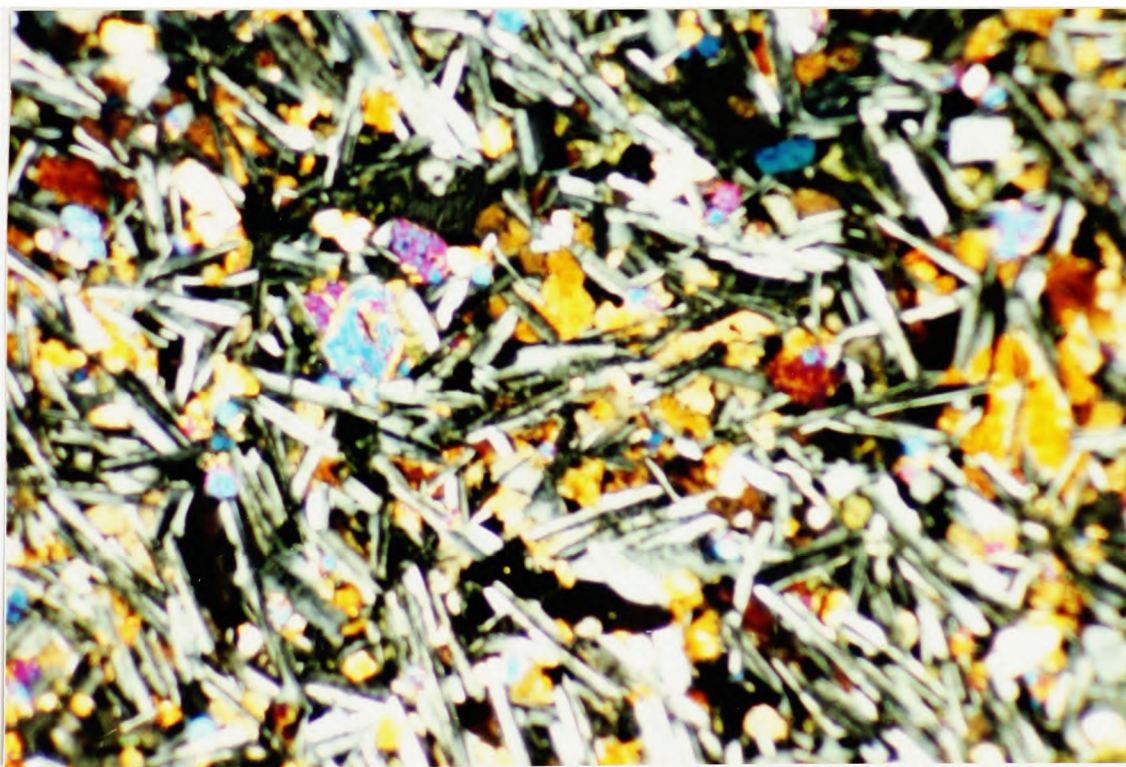
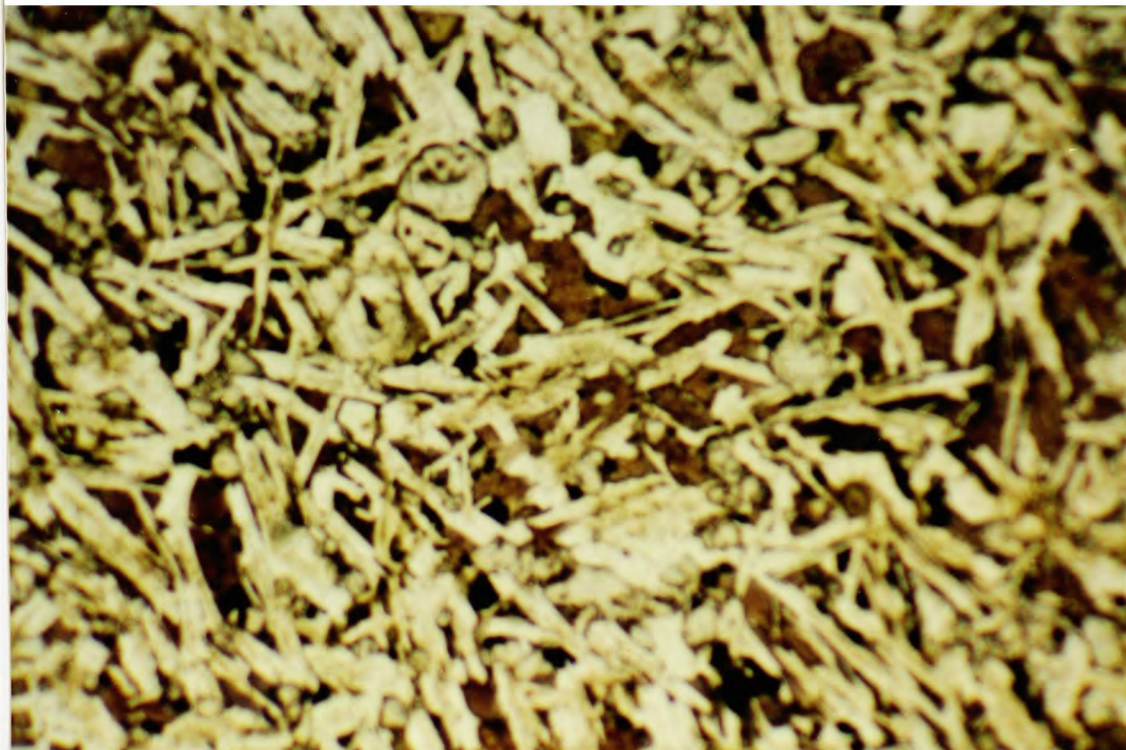


Plate 3.5

Views of a dyke (JHS 155) in plane polarised light and under crossed polars. The sample is mineralogically similar to the SMLS basalt comprising olivine, plagioclase, clinopyroxene and titanomagnetite, but it has a coarser texture.



Plate 3.6.a

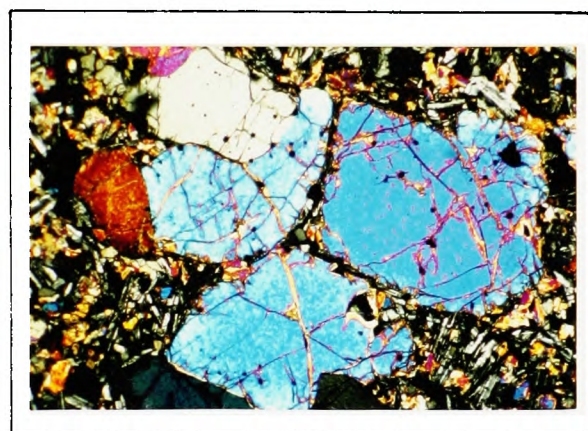
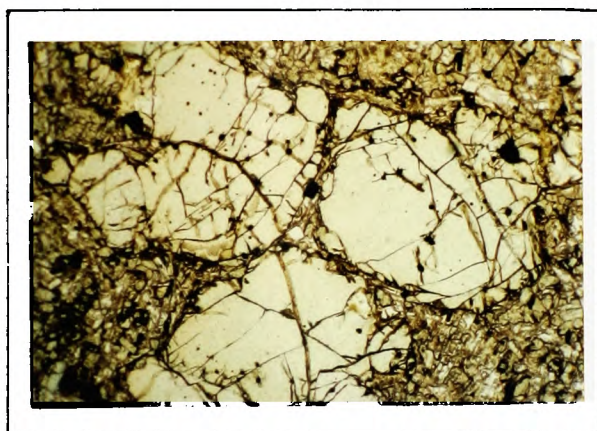


Plate 3.6.b

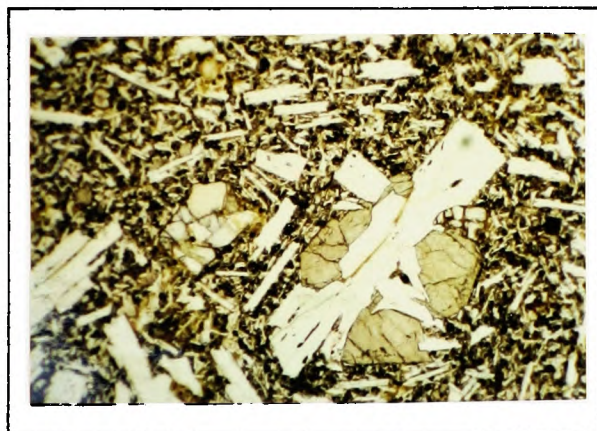


Plate 3.6.c

Views in plane polarised light and under crossed polars of
 a. individual olivine phenocrysts (JHS 229).
 b. a monomineralic olivine glomerocryst (JHS 15).
 c. a trimineralic (with plagioclase and clinopyroxene) olivine glomerocryst (JHS 158).
 Fields of view : 2.4mm x 3.6mm.



Plate 3.7.a

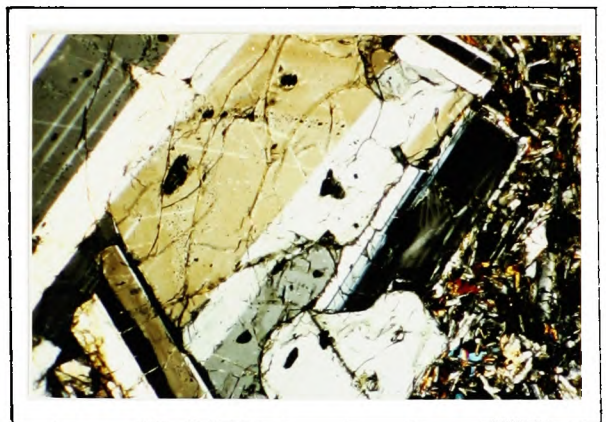
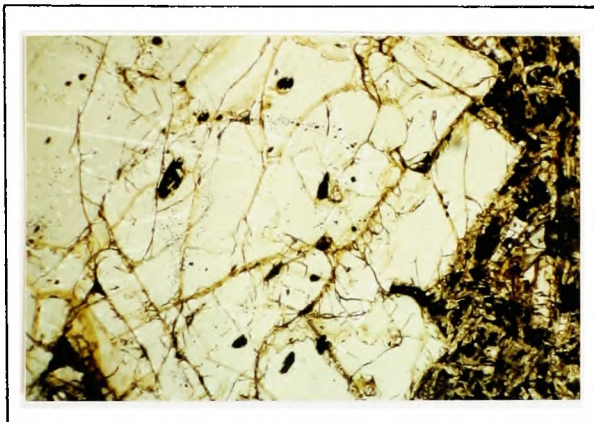


Plate 3.7.b

Views in plane polarised light and under crossed polars of
 a. individual plagioclase phenocrysts (JHS 146).
 b. a monomineralic plagioclase glomerocryst in a big feldspar basalt (JHS 212).
 Fields of view : 2.4mm x 3.6mm.

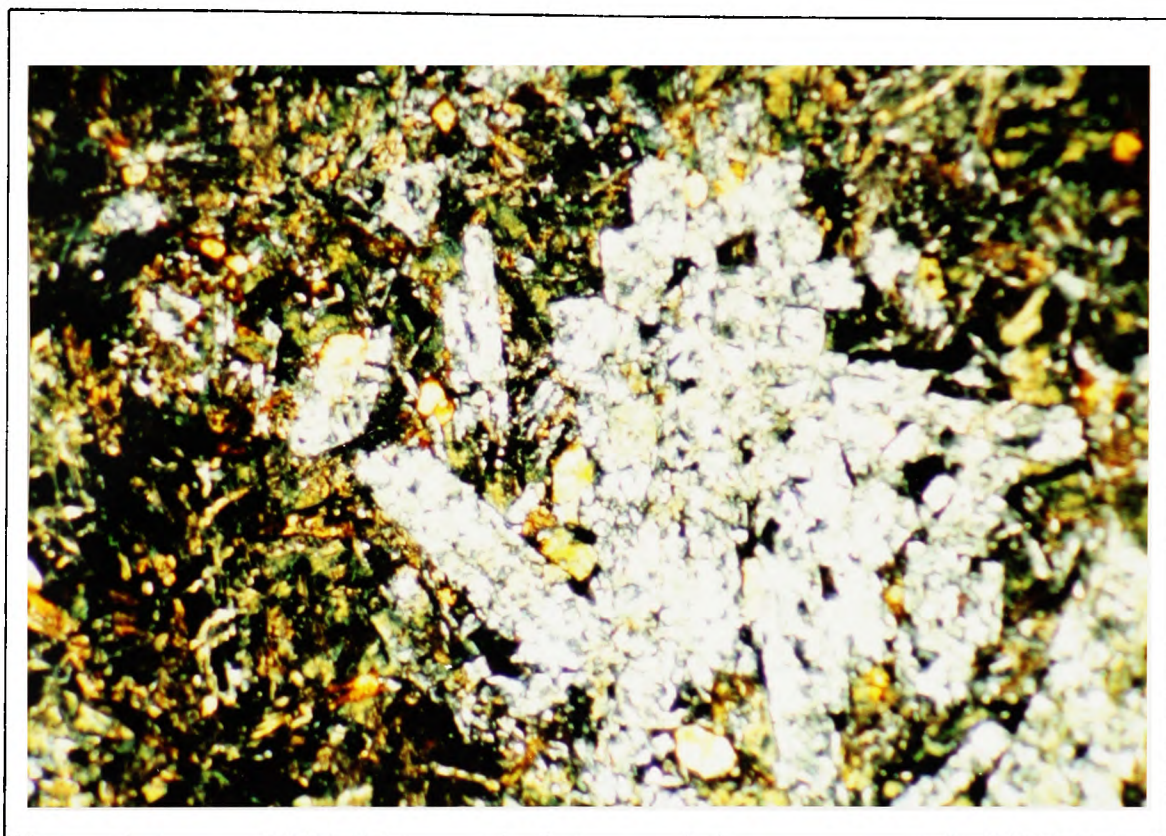


Plate 3.8

View under crossed polars of alteration of plagioclase phenocrysts to zeolites, and groundmass material to chlorite and iddingsite.

(JHS 149)

Field of view : 2.4mm x 3.6mm.

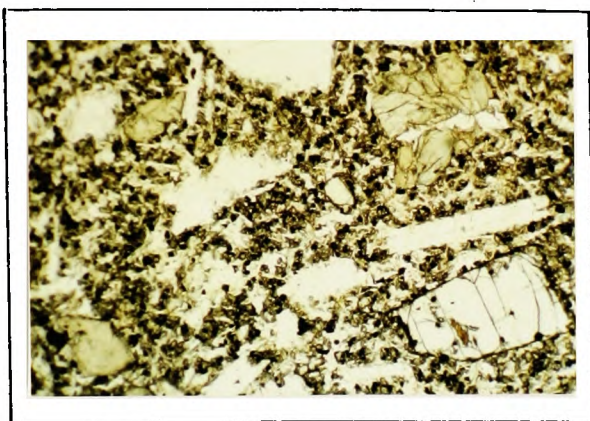


Plate 3.9.a

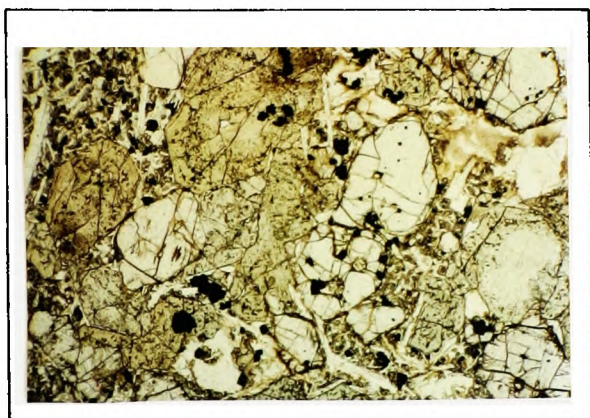


Plate 3.9.b

Views in plane polarised light and under crossed polars of
a. individual clinopyroxene, and plagioclase, phenocrysts (JHS 154).
b. a glomerocryst composed largely of clinopyroxene, but with some olivine (JHS 154).
Fields of view : 2.4mm x 3.6mm.



Plate 3.10.a

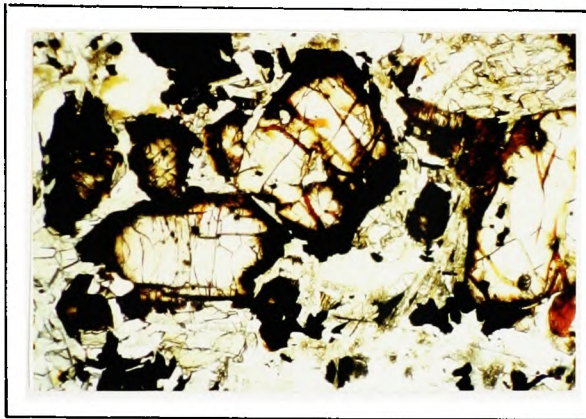


Plate 3.10.b

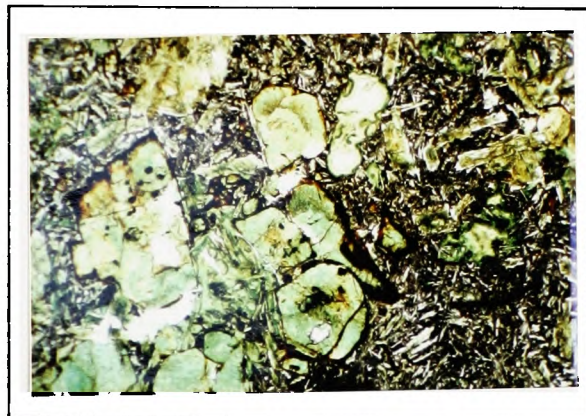


Plate 3.10.c

Views in plane polarised light and under crossed polars of secondary minerals in the Skye lavas.

- a. alteration of olivine to iddingsite and groundmass clinopyroxene to chlorite (JHS 66).
- b. alteration of olivine to iddingsite and Fe oxides (JHS 171).
- c. alteration of olivine to chlorite (JHS 236).

Fields of view : 2.4mm x 3.6mm.

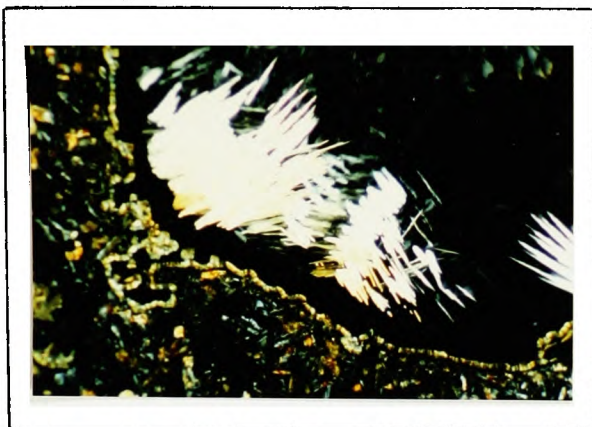


Plate 3.11.a

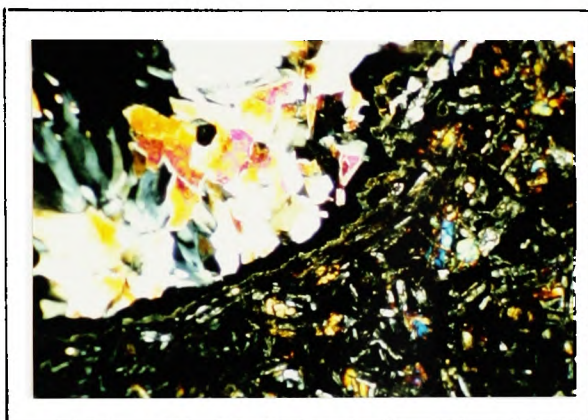


Plate 3.11.b

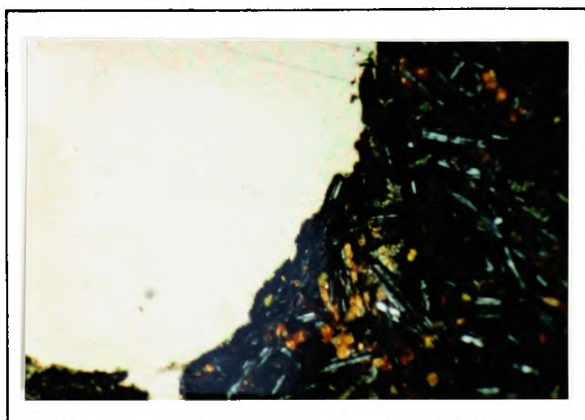


Plate 3.11.c

Views under crossed polars of amygdales in the Skye lavas.

a. fibrous zeolite (JHS41)

b. blocky zeolite (JHS44)

c. calcite (JHS132)

Fields of view : 2.4mm x 3.6mm.

	JHS10 SMLS basalt	JHS39 SMLS basalt	JHS148 SMLS basalt	JHS211 SMLS basalt	JHS184 FB basalt
SiO₂	38.63	36.62	38.89	35.04	37.75
FeO	27.47	26.28	19.23	40.39	35.13
MnO	0.45	0.36	0.24	0.76	0.67
MgO	32.43	34.79	41.25	23.32	28.07
CaO	0.49	0.53	0.05	0.38	0.50
Cr₂O₃	0.03	0.00	0.05	0.01	0.00
NiO	0.09	0.09	0.23	0.04	0.04
Total	99.59	98.67	100.34	99.94	98.16

Table 3.1.a Five representative groundmass olivine compositions.

	JHS39 SMLS basalt	JHS100 SMLS trachybasalt	JHS146 SMLS basalt	JHS211 SMLS basalt	JHS184 FB basalt
SiO₂	40.01	36.49	38.62	37.61	37.87
FeO	16.21	28.30	15.10	20.76	18.51
MnO	0.20	0.72	0.20	0.32	0.24
MgO	44.18	35.50	46.08*	40.57	42.98
CaO	0.02	0.31	0.02	0.23	0.27
Cr₂O₃	0.05	0.00	0.03	0.06	0.02
NiO	0.27	0.01	0.29	0.19	0.23
Total	101.20	101.33	100.58	99.74	100.12

Table 3.1.b Five representative phenocryst olivines.

	JHS39 SMLS basalt	JHS56 SMLS trachyte	JHS100 SMLS trachybasalt	JHS148 SMLS basalt	JHS184 FB basalt
SiO₂	56.06	64.04	54.28	49.82	50.80
TiO₂	0.13	0.45	0.11	0.11	0.08
Al₂O₃	28.30	17.93	28.66	30.13	28.72
FeO	0.74	1.83	0.80	1.07	2.38
MnO	0.18	0.07	0.00	0.01	0.03
MgO	0.11	2.08	0.00	0.06	1.54
CaO	11.53	0.84	12.34	13.54	12.06
Na₂O	4.89	6.42	4.33	3.58	3.76
K₂O	0.38	6.17	0.23	0.26	0.19
Total	102.17	99.83	100.79	98.58	99.56

Table 3.2.a Four representative groundmass plagioclases, and one groundmass alkali feldspar.

	JHS39 SMLS basalt	JHS56 SMLS trachyte	JHS100 SMLS trachybasalt	JHS146 SMLS basalt	JHS184 FB basalt
SiO₂	50.46	64.05	55.47	50.45	49.60
TiO₂	0.08	0.09	0.15	0.04	0.08
Al₂O₃	30.80	22.60	28.52	31.00	32.13
FeO	0.61	1.07	0.95	0.55	0.54
MnO	0.00	0.01	0.00	0.01	0.01
MgO	0.17	0.31	0.29	0.19	0.06
CaO	14.54	4.02	12.05	14.60	14.49
Na₂O	3.21	7.37	4.29	3.02	2.94
K₂O	0.12	1.83	0.21	0.12	0.17
Total	99.99	101.35	101.93	99.98	100.47

Table 3.2.b Five representative phenocryst plagioclases.

	JHS39 SMLS basalt	JHS100 SMLS trachybasalt	JHS142 SMLS basalt	JHS211 SMLS basalt	JHS184 FB basalt
SiO₂	48.45	52.63	47.67	50.08	49.12
TiO₂	1.29	1.48	2.00	1.45	3.01
Al₂O₃	5.65	3.66	3.42	1.95	5.59
FeO	7.20	7.94	14.13	11.70	9.27
MnO	0.15	0.25	0.30	0.31	0.16
MgO	14.20	14.03	9.97	13.08	12.27
CaO	21.52	20.14	20.55	20.00	21.20
Na₂O	0.34	0.80	0.62	0.45	0.58
Cr₂O₃	0.88	0.00	0.02	0.02	0.05
Total	100.70	100.93	98.68	99.04	101.25

Table 3.3.a Five representative groundmass clinopyroxene compositions.

	JHS31 SMLS basalt	JHS39 SMLS basalt	JHS56 SMLS trachyte	JHS67 SMLS basalt	JHS142 SMLS basalt
SiO₂	46.36	50.78	45.39	47.45	51.34
TiO₂	3.46	0.95	0.00	3.08	0.00
Al₂O₃	5.33	5.83	9.71	4.70	3.35
FeO	10.63	0.06	12.53	9.75	7.33
MnO	0.18	0.14	0.47	0.16	0.21
MgO	11.03	15.30	13.81	12.12	15.34
CaO	21.59	18.71	10.19	21.40	20.26
Na₂O	0.63	0.41	3.06	0.51	0.31
Cr₂O₃	0.03	0.57	0.00	0.10	0.55
Total	99.25	100.70	99.03	99.27	98.63

Table 3.3.b Five representative phenocryst clinopyroxenes.

	JHS39 SMLS basalt	JHS110 SMLS trachybasalt	JHS146 SMLS basalt	JHS211 SMLS basalt	JHS184 FB basalt	JHS56 SMLS trachyte	JHS56 SMLS trachyte
SiO ₂	0.33	0.96	0.00	0.03	0.03	0.00	0.00
TiO ₂	25.57	44.38	28.97	18.80	24.41	11.42	34.29
Al ₂ O ₃	3.40	0.86	1.31	1.01	2.54	1.05	0.24
FeO	63.41	43.41	63.77	71.14	63.77	77.76	57.83
MnO	1.24	0.83	0.66	0.41	0.60	1.63	2.20
MgO	0.47	1.64	1.05	1.49	3.68	0.95	1.61
CaO	0.04	0.15	0.18	0.05	0.26	0.00	0.00
Na ₂ O	0.03	0.20	0.00	0.06	0.03	0.03	0.00
K ₂ O	0.04	0.08	0.05	0.05	0.04	0.06	0.05
Cr ₂ O ₃	0.04	0.00	0.04	0.22	1.20	0.00	0.01
NiO	0.00	0.04	0.03	0.11	0.11	0.01	0.03
Total	94.57	92.55	96.06	94.53	96.67	92.91	96.26

Table 3.4 Five representative groundmass Fe-oxides, and two phenocryst Fe-oxides (JHS56).

Sample number	OI	Plag	Cpx	Opq	Gm
1	14.00	0.00	0.00	0.00	84.00
8	14.00	2.00	0.00	0.00	84.00
9	21.75	1.80	0.00	0.00	76.45
10	16.85	1.95	0.00	0.00	81.20
12	15.70	0.00	0.00	0.00	84.30
15	6.95	0.00	0.00	0.00	96.05
16	2.85	5.25	0.80	0.00	91.10
18	3.25	0.95	3.45	0.00	92.35
19	6.05	0.00	0.00	0.00	93.50
21	5.65	0.00	0.00	0.00	94.35
22	8.45	0.00	0.00	0.00	91.55
23	13.45	0.00	0.00	0.00	86.55
26	12.00	0.00	0.00	0.00	88.00
31	8.50	0.15	0.00	0.00	91.35
33	14.00	20.90	0.20	0.00	64.90
35	14.65	0.00	0.00	0.00	85.35
37	18.65	0.00	0.00	0.00	81.35
39	4.95	8.65	1.85	0.00	84.55
40	11.85	0.00	0.15	0.00	88.00
41	0.00	0.00	0.00	0.00	100.00
44	4.95	4.05	0.00	0.00	91.00
46	5.00	1.90	0.00	0.00	93.10
47	4.90	0.00	0.00	0.00	95.10
49	2.40	0.00	0.00	0.00	97.60
58	2.50	0.00	0.00	0.00	97.50
60	12.35	0.00	0.00	0.00	87.65
64	10.25	0.00	0.00	0.00	89.75
66	11.45	0.60	0.00	0.00	87.95
67	1.95	0.90	2.75	0.00	94.40
69	0.40	0.45	0.00	0.00	99.15
70	21.45	0.00	0.00	0.00	78.55
73	9.50	0.00	0.00	0.00	90.50
75	13.95	0.00	0.00	0.00	86.05
76	4.90	0.00	0.00	0.00	95.10
80	6.70	0.00	0.00	0.00	93.30
81	1.10	3.60	0.00	0.00	95.50
82	4.20	0.00	0.00	0.00	95.80
84	5.45	0.05	0.00	0.00	95.50
85	4.55	0.00	0.00	0.00	95.45
87	12.75	0.00	0.00	0.00	80.25
89	17.10	0.00	0.00	0.00	82.90
92	9.60	0.00	0.00	0.00	90.40
94	1.80	0.00	0.00	0.00	98.20
95	0.00	0.00	0.00	0.00	100.00
97	0.30	0.05	0.00	0.00	99.65
100	0.90	0.35	0.00	0.00	98.75
103	6.85	0.10	0.00	0.00	93.50
104	5.00	0.00	0.00	0.00	95.00
108	4.40	0.00	0.00	0.00	95.60
124	0.00	0.00	0.00	0.00	100.00
129	11.90	0.00	0.00	0.00	88.10
130	11.70	0.65	0.00	0.00	93.05
136	17.95	0.00	0.00	0.00	82.05
142	16.30	0.40	0.75	0.00	82.55
146	8.15	11.90	0.00	0.00	79.95
148	19.90	0.00	0.00	0.00	80.10
149	12.80	15.75	0.00	0.00	71.45
153	13.15	13.75	1.70	0.00	71.40
154	15.10	13.40	2.80	0.00	68.70
159	18.70	0.00	0.00	0.00	81.30
160	23.38	0.00	0.00	0.00	76.61

contd.....(caption on next page)

Sample number	OI	Plag	Cpx	Opq	Gm
162	20.80	0.00	0.00	0.00	79.20
163	23.25	0.00	0.00	0.00	76.75
164	11.40	0.00	0.00	0.00	88.60
166	4.65	0.00	0.00	0.00	95.35
167	0.00	0.00	0.00	0.00	100.00
171	22.95	0.00	0.00	0.00	77.05
172	0.00	0.75	0.00	0.00	99.25
175	0.00	0.00	0.00	0.00	100.00
182	4.20	0.40	0.00	0.00	95.40
184	8.65	0.35	0.00	0.00	91.00
186	0.00	0.00	0.00	0.00	100.00
188	0.90	0.30	0.00	0.00	98.80
190	0.00	0.05	0.00	0.00	99.95
197	13.40	0.15	0.00	0.00	86.45
201	11.65	0.00	0.00	0.00	87.45
202	1.20	12.15	0.00	0.00	86.70
210	13.40	0.00	0.00	0.00	86.60
211	1.20	0.00	0.00	0.00	98.65
212	1.80	33.50	0.00	0.00	64.70
213	0.65	0.25	0.00	0.00	99.10
214	0.85	1.75	0.00	0.00	97.40
215	0.10	0.00	0.00	0.00	99.90
216	5.85	0.00	0.00	0.00	94.15
217	0.45	2.95	0.00	0.00	96.60
218	4.90	0.00	0.00	0.00	95.10
219	5.10	0.00	0.00	0.00	94.90
220	2.90	0.00	0.00	0.00	97.10
221	1.95	0.00	0.00	0.00	98.05
222	3.00	0.05	0.00	0.00	96.95
223	0.05	0.00	0.45	0.00	99.50
225	17.20	0.00	0.00	0.00	82.80
226	19.70	0.00	0.00	0.00	80.30
227	17.00	0.00	0.00	0.00	83.80
229	18.00	0.00	0.00	0.00	82.00
230	20.75	0.00	0.00	0.00	79.25
232	20.60	0.05	0.00	0.00	79.35
233	22.30	7.45	0.80	0.00	69.45
234	15.56	7.40	0.05	0.00	76.99
236	13.55	8.65	0.00	0.00	77.80
237	13.80	5.15	0.30	0.00	80.75
239	4.95	3.25	0.00	0.00	91.80
244	0.00	0.00	0.00	0.00	100.00

Table 3.5 Modal proportions of groundmass and phenocryst olivine, plagioclase, clinopyroxene, and titanomagnetite in the Skye lavas. Data presented are means of data obtained by point counting two thin sections of each sample.

	No of points	OI %	Plag %	Cpx %	Mgt %	Gm
JHS1.a	500	14.0	0.0	0.0	0.0	86.0
JHS1.a	1000	13.6	0.0	0.0	0.0	86.4
JHS1.b	500	15.3	0.0	0.0	0.0	84.7
JHS1.b	1000	19.3	0.0	0.0	0.0	80.7

Table 3.6 Result of point counting two thin sections of JHS1. The number of points counted on each thin section is less significant in determining representative modal proportions than the total area covered.

CHAPTER 4

GEOCHEMISTRY

4.1 Introduction

In this chapter the major and trace element, rare earth element (REE), Sr-isotope and Nd-isotope compositional properties of the Skye lavas will be described. The lavas have previously been divided into three groups on the basis of their composition (Chapter 2, History of Petrogenetic Research, section 2.3.1), the Skye Main Lava Series (SMLS), the Preshal Mhor basalts (PB), and the Fairy Bridge basalts (FB). A lot is known about the compositional characteristics of the SMLS, the PM, and the FB lavas from the wealth of previous research on the rocks of the area (Chapter 2, History of Petrogenetic Research). Consequently, the current chapter takes a different approach from that expected to be taken if the study had produced the first major geochemical data-set for the igneous rocks of the area. Compositional variations in the new, larger, data-set are described here, as they would be in the latter type of study. However, the emphasis of the chapter is assessment of the conclusions of previous workers, in the light of the new data. SMLS lava, PM lava, FB lava, dyke, and sill data will be considered separately in the following sections.

A comparison of the composition of the Skye lavas will be made with that of samples from the British Tertiary Igneous Province (BTIP), the North Atlantic Tertiary Province (NATP), and other continental flood basalt (CFB) provinces.

Consideration of the petrogenesis of the lavas will be left until Chapter 8, Magma Generation.

4.2 Chemical compositions

4.2.1 Major and trace elements

4.2.1.1 Introduction

Whole rock element compositions have been determined for 151 lavas, sixty boulders, five dykes and one sill by the X-Ray Fluorescence (XRF) technique. Major and trace elements were measured on glass beads and pressed powder pellets respectively. Analytical procedures, accuracy and precision are given in Appendix B and the data are tabulated in Appendix B. Representative major and trace element analyses and CIPW normative compositions are given in Tables 4.1 and 4.2.

Inspection of two-element variation diagrams of the Skye lavas indicates that there is a considerable amount of compositional scatter in the data-set. One of the key questions of the current chapter is whether SMLS, PM, FB lavas are really compositionally distinct, i.e. separate populations as opposed to variants of a compositional continuum, and if distinct, how can a sample be classified into one of the three groups using chemical criteria? It is possible to distinguish the SMLS, the PM, and the FB lavas by their concentrations of rare earth elements (section 4.3.2 REE). However, REE analysis is an expensive and laborious procedure which prohibits the analysis of all the samples in the present study. Therefore, a different method classification is needed. Those samples which had been analysed for REE were used to define SMLS, PM, and FB compositional groups. Various combinations of element-element and element-ratio diagrams were plotted to try to identify some characteristics of the elements measured by XRF analysis which could distinguish the SMLS, the PM, and the FB groups. However, no such characteristics were identified. Therefore, a statistical procedure, discriminant function analysis (DFA), was employed to differentiate between the three magma types. The purpose of DFA is to produce linear combinations of major and trace elements contents which best distinguish pre-defined groups. Samples that had been analysed for REE elements were used to define three compositional groups. Major and trace element data for these analyses

were input into DFA. The DFA produced a set of discriminant variables, the most information about the data-set being given by the elements Ca, Ti, and Zr, and contained in variables one and two which when plotted divide the SMLS, the PM, and the FB lavas quite neatly (Figure 4.1). The remaining data were then put through the computational matrix which had been calculated using REE-defined groups. In this way all samples were classified as either SMLS, PM, or FB (Figure 4.1).

4.2.1.2 The Skye Main Lava Series

4.2.1.2.a Previous work

This group constitutes the bulk of the Skye lava pile. The first compositional analysis was published by Harker (1904) in his time-honoured work, *The Tertiary Igneous Rocks of Skye*. Early studies focused on the significance of the transitional normative nature of the basalts in relation to petrogenetic processes affecting the whole BTIP (Chapter 2 section 2.2). Major element analyses and CIPW norms were published for fourteen lavas in the North Skye Memoir (Anderson and Dunham, 1966). With the exception of some experimental work by Tilley, Yoder, and Schairer (1965, 1966), the first major work on the geochemistry of the Skye Main Lava Series (SMLS) was by Thompson *et al.* (1972). They presented major element and CIPW normative analyses for 76 lavas. A standard Fe_2O_3 content ($\text{Na}_2\text{O}+\text{K}_2\text{O} < 4\%$, $\text{Fe}_2\text{O}_3=1.5\%$; $\text{Na}_2\text{O}+\text{K}_2\text{O}=4-7\%$, $\text{Fe}_2\text{O}_3=2\%$; $\text{Na}_2\text{O}+\text{K}_2\text{O} > 7\%$, $\text{Fe}_2\text{O}_3=2.5\%$) was used for the calculation of CIPW norms. The lavas were found to comprise nepheline (ne) and hypersthene (hy) normative samples, and were therefore described as transitional basalts. Thompson *et al.* (1972) recognised two compositional divisions within the SMLS; in the first, predominantly ne-normative hawaiites, mugearites and benmoreites defined a single coherent trend, whereas in the second, trachytes lie at the end of a lineage of predominantly hy-normative, Si-rich, Fe-poor intermediates. The major element ranges in the magnesian aphyric basalts of the two divisions are summarised in Table 4.3; and the variations in the major element concentrations of all samples in the two divisions, as observed by Thompson *et al.* (1972) are given Table 4.4.

The absolute variation in concentrations of a comprehensive set of trace elements in the SMLS, determined by Thompson *et al.* (1980a) is presented in Table 4.5. Many trace elements, K, Ti, P, Rb, Sr, Ba, Nb, Ta, Zr, Hf, and Th have concentrations which vary by up to a factor of two for a given Fe/Mg ratio, Table 4.6 shows two typical ranges between samples from trend 1 and 2.

4.2.1.2.b Major and trace elements

In contrast to the findings of Thompson *et al.* (1972) two clearly discernible evolutionary trends cannot be identified in the data of the present study. These data form a continuum of compositions. The SMLS lavas have, therefore, been divided on the basis of normative character; ne- and hy-normative lavas taken to correspond to trends 1 and 2 of Thompson *et al.* (1972) respectively. Norms were computed using a standard oxidation state of 15% for the calculation of FeO and Fe_2O_3 from Fe measured as Fe_2O_3 ($\text{FeO} = ((0.85 \times \text{Fe}_2\text{O}_3\text{T})/1.1)$) (after Brooks, 1976).

The samples with highest values of normative hypersthene and highest values of normative nepheline are end-members of the continuum of compositions identified in the present study. The end-members have distinctive differences in the concentrations of most elements. These differences are described below under the groupings ne-normative and hy-normative. However, it should be borne in mind that there is a continuum and, for most elements, some overlap in their concentrations in the hy-normative and the ne-normative lavas. SiO_2 is lower in the ne-normative lavas than in the hy-normative lavas, varying from 44.57-46.41% compared with 46.64-63.44%. TiO_2 is higher in the ne-normative lavas (2.49-3.52%) than in the hy-normative lavas, (1.40-0.75%). The ne-normative lavas have slightly lower Al_2O_3 (12.39-17.11%) than the hy-normative lavas (13.87-17.85%). $\text{Fe}_2\text{O}_3\text{T}$ is considerably higher in the ne-normative lavas (14.35-15.92%) than in the hy-normative lavas (12.52-3.79%). The most

primitive ne-normative lavas are marginally less magnesian than the hy-normative lavas, 13.16% compared with 13.65%, and they also have a more restricted MgO range, 4.41% in the most evolved ne-normative lavas and 0.64% in the hy-normative lavas. However, this difference may be due to incomplete sampling. CaO is slightly higher in the ne-normative lavas (9.57-7.14%) than in the hy-normative lavas (8.80-1.38%). K₂O is higher and Na₂O lower in ne-normative lavas. Total alkalis (Na₂O+K₂O) are approximately the same for the primitive lavas of the ne-normative and hy-normative groups, 2.78% and 2.63% respectively; but, the evolved lavas have very different values, 4.72% and 11.73% respectively. P₂O₅ is higher in the ne-normative lavas 0.33-0.50%, compared with 0.15-0.23% in the hy-normative lavas.

The ne-normative lavas have higher concentrations of Co (70.70-41.40 ppm), V (328.10-144.60 ppm) and Sr (671.60-604.50 ppm). With the exception of the trachytic hy-normative lavas, the ne-normative lavas also have higher Zn (99.90-70.40 ppm), Ba (506.50-280.40 ppm), Rb (17.90-16.70 ppm), Zr (185.70-293.60 ppm), Nb (15.50-17.70 ppm), Pb (4.90-5.40 ppm), Th (2.40-3.10 ppm) U (1.30-0.00); and lower Cu (88.20-15.00 ppm) and Cr (670.00-6.10 ppm).

The hy-normative lavas have lower concentrations of Co (65.40-0.00 ppm), V (237.30-21.50 ppm) and Sr (220.60-241.00 ppm). The hy-normative trachytes have the following element concentrations, Zn (111.60 ppm), Ba (3055.40 ppm), Rb (80.20 ppm), Zr (450.30 ppm), Nb (21.00 ppm), Pb (21.60 ppm), Th (2.30 ppm) and U (0.00 ppm) Cu (4.70 ppm) and Cr (0.90 ppm). The hy-normative lavas have lower Zn (84.50-73.90 ppm), Ba (124.70-202.40 ppm), Rb (11.30-14.80 ppm), Zr (100.90-251.30 ppm), Nb (4.80-14.40 ppm), Pb (0.30-2.50 ppm), Th (1.20-2.50 ppm) and U (1.30-0.00); and higher Cu (130.50-21.10 ppm) and Cr (706.10-7.80 ppm) than the ne-normative lavas.

The ne-normative and hy-normative lavas have comparable Ni (407.90-31.00 ppm : 413.90-1.50 ppm), Ga (20.40-16.40 ppm : 19.20-21.90 ppm), and Y (18.00-51.90 ppm : 17.50-39.00 ppm).

4.2.1.2.c Compositional scatter

Inspection of two-element variation diagrams reveals that many elements have a range of concentrations for any given MgO content (Figure 4.2). Having assumed that MgO content is linearly related to the liquidus temperature of basalt and so to its stage of fractional crystallisation and level of evolution; two groups of samples with restricted MgO contents (10-11% and 12-13%) were defined for study of the compositional scatter. In these two groups, fractional crystallisation can be assumed to have had a minimal effect upon the composition of the basalts. Inspection of the two restricted-MgO groups revealed that within each group there are statistically significant inter-element correlations between many of the elements; to summarize elements generally considered to be incompatible in mantle phases correlate negatively with SiO_2 (Figure 4.3). Having recognized statistically significant inter-element correlations in the high-MgO data-sets, correlations within data-sets with lower MgO contents (but still under olivine control, i.e. greater than 7% MgO, Chapter 6, Fractional Crystallisation) were identified. In this way planar arrays present in the SMLS data-set were defined. The significance of the inter-element correlations is discussed in detail in Chapter 6, Fractional Crystallisation, Chapter 7, Crustal Contamination, and Chapter 8, Magma Generation.

4.2.1.2.d MORB normalization diagrams

The general principles and use of spider diagrams, in which incompatible major and trace elements are normalised against either mid-ocean ridge basalts (MORB) (e.g. Pearce, 1983) or chondrite (e.g. Sun, 1980; Thompson *et al.*, 1983), are outlined in Section 4.3.6 (spider diagrams). The characteristic patterns of the Skye lavas for the former are described in this section and the latter in Section 4.3.2 (rare earth elements).

On the basis of their MORB normalized spider diagram patterns the Skye lavas can be divided into two, somewhat arbitrary, groups (Figure 4.4). The first group comprises those samples which have a value of Rb_N which is less than the averaged value of K_2O_N and Ba_N ; and

the second, samples which have a value of Rb_N greater than the averaged value of K_2O_N and Ba_N . The SMLS is composed of examples of both groups. The FB and PM show only the second pattern type. The variation in pattern shape is assumed to result from enrichment of Ba relative to the other LIL elements. There is no clear correlation between the MORB-normalized pattern shape and the normative character of the SMLS samples. This suggests that the process controlling the behaviour of Ba is different from that which produced the inter-element correlations observed in the restricted-MgO data-sets. The significance of the variation in Ba concentration in the SMLS lavas is considered in Chapter 7, Crustal Contamination.

4.2.1.3 The Preshal Mhor

The Ca-rich, alkali-poor, olivine tholeiite, Preshal Mhor basalts were first identified by Thompson *et al.* (1972). Further studies, on lava flows and dykes of the Skye regional swarm, (Esson *et al.*, 1975; Matthey *et al.*, 1977; Thompson *et al.*, 1980a), have shown that the PM basalts have compositional similarities with basalts erupted at mid-ocean ridge systems (Tables 4.1 and 4.2, section 4.2.2 rare earth elements).

Trace element studies (Esson *et al.*, 1975; Matthey *et al.*, 1977; Thompson *et al.*, 1980a) have shown that, relative to the SMLS basalts, the PM basalts typically have low concentrations of elements which are incompatible in mantle phases for example, large-ion lithophile (LIL) and high field strength (HFS) elements (Table 4.2).

Five lavas of PM composition have been identified in the present study. Representative major and trace element compositions are presented in Tables 4.1 and 4.2. The PM samples have high SiO_2 (46.81-47.91%), Al_2O_3 (15.98-14.02%) and CaO (12.81-12.70%); low TiO_2 (0.99-1.30%), Na_2O (1.75-2.13%), K_2O (0.08-0.17%) and P_2O_5 (0.07-0.10%); and comparable Fe_2O_3T (12.45-14.02%), relative to SMLS samples with similar MgO (8.75-7.33%).

With respect to trace elements the PM lavas have high Cu (148.90-170.80 ppm), Y

(21.10-20.30 ppm); low Zn (71.20-84.20 ppm), Ni (94.00-72.30 ppm), Co (58.60-58.50 ppm), Cr (226.70-125.00 ppm), Ba (60.00-57.60 ppm), Rb (6.80-8.90 ppm), Sr (121.30-144.80 ppm), Zr (51.00-69.50 ppm) and Nb (3.00-4.60 ppm); and similar V (246.00-327.70 ppm), Ga (17.80-18.40 ppm), Pb (2.60-0.90 ppm) and Th (1.40-0.10 ppm) compared with the SMLS lavas.

It should be noted that, although tholeiitic, the PM basalts are not analogous to the non-porphyrific central (NPC) magma type of Mull (Chapter 1, Introduction, section 1.5.1). The PM basalts have Y/Zr ratios which are too high, and $(\text{Ce/Yb})_N$ which are too low (section 4.2.2.3).

Previously the PM lavas have only been found in the highest stratigraphic division of the Skye lava pile, the Osdale division of Anderson and Dunham (1966) (Chapter 1, Introduction, section 1.4.4). Thompson *et al.* (1972) postulated that the PM lavas may have been more common in the upper, now eroded, parts of the Skye volcanic sequence. In the present study several new flows of PM lava have been identified; these occur within lower stratigraphic units (Ramascaig, Beinn Totaig and Bracadale) of Anderson and Dunham (1966).

The significance of the PM lavas in the interpretation of the Skye volcanic cycle will be considered in Chapter 8, Magma Generation.

4.2.1.4 The Fairy Bridge

This group was originally recognised by Matthey *et al.* (1977). It is common in the regional dyke swarm but, to date, only one flow has been identified. Thompson *et al.* (1980) stated that this group has major element compositions which are in the range of the SMLS (Tables 4.1 and 4.4).

The FB magma-type can be distinguished from the SMLS and the PM lavas by small differences in trace element concentrations. Some elements (Sr, Nb, Ta) are in the range of composition of the SMLS whereas others (Rb, Zr, Hf, Th) are in the PM compositional range

(Thompson *et al.*, 1980a), (Tables 4.2 and 4.5).

In the present study four new FB lava flows have been recognised. Representative major and trace element analyses are presented in Tables 4.1 and 4.2. Although the FB lavas have similar SiO₂ (46.65-44.98%), TiO₂ (1.18-1.96), Al₂O₃ (13.63-16.15%) and Fe₂O₃T (12.26-14.63) to the SMLS and PM samples their MgO content is slightly higher (14.73-9.55%). The FB lavas can be distinguished from the PM lavas by their relatively low CaO (10.06-9.01%) and from the SMLS by their low Na₂O (1.85-2.09%), K₂O (0.20-0.27%) and P₂O₅ (0.10-0.16%).

Previously only found in the Ramascaig stratigraphic division, the present study has identified FB lavas in the higher Beinn Totaig and Osdale units of Anderson and Dunham (1966).

The significance of the FB lavas in the interpretation of the Skye volcanic cycle will be considered in Chapter 8, Magma Generation.

4.2.1.5 Other Skye lavas

A few samples have been identified in the Skye lava pile which do not fall into the above categories.

A mafic lava with a high modal proportion of large plagioclase phenocrysts occurs at several localities in Northern Skye. Aphyric margins of such flows have hawaiitic and mugearitic compositions (Tilley *et al.*, 1967). However, analysis of the groundmass of the central portion has shown it to have major and trace element concentrations similar to a SMLS basaltic hawaiite (Thompson *et al.*, 1980a). Whole rock major and trace element analyses of highly plagioclase porphyritic lavas are given in Tables 4.1 and 4.4, and Tables 4.2 and 4.5 respectively.

Anderson and Dunham (1966) noted the presence of tholeiitic pillow lavas at the base of the volcanic pile near Portree. Previous workers have noted that major element analyses

(Table 4.4) place these lavas in the compositional field of the SMLS, but trace elements such as Ti, P, Sr, Y, and Yb (Table 4.5) exhibit closer similarities with flows at the base of the Mull lava pile (Bailey *et al.*, 1924; Morrison, 1978; Beckinsale *et al.*, 1978).

4.2.1.6 Dykes

The lavas are preserved in a shallow faulted oval basin with a long axis running north west/south east parallel to a regional dyke swarm (Figure 1.8). An authoritative account of the geochemistry, relative abundance and spatial distribution of the dykes of the Skye regional swarm is given by Matthey *et al.* (1977). The dykes can be divided, like the lavas, into the three magma-types, SMLS, PM, and FB. Since the dykes are compositional equivalents of the lavas their geochemical characteristics are within the range of the lavas and therefore do not merit separate description. The dykes comprise 70% PM, 15% SMLS and 15% FB (Matthey *et al.*, 1977).

Seven dykes were collected in the present study. Three of the dykes are compositionally equivalent to the SMLS, the remaining four are equivalent to the PM lavas.

The predominance of the PM magma type in the dyke swarm, described in the literature (Matthey *et al.*, 1977), may be a reflection of the function of the dykes as feeders to the lavas. Dykes feeding the early lavas may have been concealed by later lava flows, thus resulting in the magma composition of the final stage of volcanism being disproportionately represented in the dyke swarm (Figure 4.6).

4.2.1.7 Sills

Contrary to the beliefs of early workers on Skye (e.g., Harker 1904), later studies (Wilson, 1937; Anderson and Dunham, 1966) have shown there is no evidence to suggest an intrusive origin for the hard, jointed, central portions of the Skye lava flows. There are,

however, sills of basaltic material within the Jurassic strata underlying the lava pile in Trotternish. A recent study by Gibson (1990) has shown these sills, designated the Little Minch Sill Complex, to have been emplaced during the Palaeocene. The sills have similar compositional characteristics to the SMLS, although, some have been shown to be cumulus enriched in olivine.

One sill was analysed in the present study. It has major and trace element compositions which are consistent with the hypothesis of cumulus olivine enrichment of a parental magma similar in composition to a SMLS basalt (Tables 4.1 and 4.2).

4.2.2 Rare Earth Elements

4.2.2.1 Introduction

It was decided to treat the rare earth elements (REE) separately from the other trace elements because they form a distinct coherent group, and because they are analysed by a different method. The REE concentrations of twenty four representative samples were analysed at Royal Holloway and Bedford New College, University of London, using the inductively coupled plasma (ICP) technique. Analytical procedures, accuracy and precision are outlined in Appendix D and the data are tabulated in Appendix D. Representative REE and chondrite normalised REE abundances are presented in Table 4.8 and in Figure 4.6 respectively.

Each of the three magma types identified on Skye, SMLS, PM and FB, has a distinctive chondrite normalized rare earth element profile (Figure 4.6). In the present study a fourth pattern type has been identified (Figure 4.6). Samples which have the fourth pattern shape have major and trace element characteristics typical of SMLS basalts.

4.2.2.2 The Skye Main Lava Series

The SMLS are generally enriched in light rare earth elements (LREE) relative to heavy rare earth elements (HREE). Thompson *et al.* (1980a) noted that there is a considerable range in REE concentrations in samples with similar major element compositions. Consequently, chondrite normalised REE patterns vary in slope and curvature (Figure 4.7). Mean Ce_N values and $(Ce/Yb)_N$ ratios show a general increase of 25 to 200 and 3.5 to 11 respectively, from basalt to benmoreite/trachyte (Thompson *et al.*, 1980a).

From the data of this study two distinctive chondrite normalised REE patterns are discernible for the SMLS samples (Figure 4.6). The first pattern has a steep LREE slope $(Ce/Sm)_N$ 1.6, typical HREE Yb 9 and Ce/Yb ratios of 4.5. The second pattern has a much flatter LREE end $(Ce/Sm)_N$ 1.2, significantly lower values of HREE Yb 1 and Ce/Yb ratios in the range of 24. There is no coherent relationship between the two divisions of the SMLS established in section 4.2.1.2.b, on the basis of their normative character, or their MORB normalisation pattern, and the two patterns observed here. However, the samples were analysed for REE in two batches and there is a direct correlation between the batch in which the sample was analysed and its pattern shape. It is therefore assumed that the division results from an error in the sample preparation or analysis, rather than a primary magmatic process. Investigation of the cause of the division is unfortunately beyond the scope of the present study. However, since the second group of samples have exceptionally low concentrations of heavy REE (HREE), in most cases less than chondritic values, it is assumed that the error occurred during the analysis of this batch. Samples which have the second pattern type are, therefore, disregarded. Investigation of the variation in the slope of the first pattern type has revealed that there is a broad negative correlation between the REE concentrations and the Si-saturation of the samples (Figure 4.8).

4.2.2.3 The Preshal Mhor

The PM lavas are depleted in LREE relative to HREE in chondrite normalised plots (Figure 4.6). This group is more restricted in REE composition than the SMLS, previous work has given a value of 7 for Ce_N and a $(Ce/Yb)_N$ ratio of 0.5 (Thompson *et al.*, 1980a).

The PM lavas analysed in this study have Ce_N 6.877-9.647 and 1.741-0.885 Ce/Yb .

4.2.2.4 The Fairy Bridge

This magma-type is best distinguished from the SMLS and PM by its flat chondrite normalised rare earth element profiles (Mattey *et al.*, 1977) (Figure 4.6), Ce_N 20 and $(Ce/Yb)_N$ values typically being 1.8-2.0.

The two FB samples analysed here for REE have Ce_N 15 and 25 and $(Ce/Yb)_N$ 1.87 and 1.66.

4.2.2.5 Other Skye lavas

The highly plagioclase porphyritic lavas have Ce_N values of 70 and $(Ce/Yb)_N$ ratios of approximately 6, much higher than the SMLS (Figure 4.6).

An analysis of a basal tholeiitic pillow lava has a Ce_N value of 28 and a $(Ce/Yb)_N$ ratio of 4.5 (Figure 4.6), (Thompson *et al.*, 1980a).

4.2.3 Sr Isotopic compositions

4.2.3.1 Introduction

Sr isotope measurements were carried out on 30 of the Skye lavas. The analytical method and the procedure for recalculation of $^{87}Sr/^{86}Sr$ values to initial ratios at 60 Ma is discussed in Appendix E. The data are presented in Appendix E.

The purpose of carrying out Sr isotope analyses was threefold: initially to determine the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ between the three magma-types, secondly to assess the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ within each magma-type, and finally, to determine to what extent the range of $^{87}\text{Sr}/^{86}\text{Sr}$ observed is attributable to alteration, or contamination, or both. Consideration of the processes of alteration and contamination will be left until Chapter 5, Alteration and Bole Formation and Chapter 7 Crustal Contamination. The observed range of $^{87}\text{Sr}/^{86}\text{Sr}$ values will be described in this section.

4.2.3.2 The Skye Main Lava Series

The SMLS has a moderately wide range of initial $^{87}\text{Sr}/^{86}\text{Sr}$. Previous studies have shown a range in $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ from 0.70306 to 0.70571 (Moorbath and Thompson, 1980; Thompson *et al.*, 1982).

26 SMLS samples were analyzed for Sr isotopes in this work. Their $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ values range from 0.70312, similar to those obtained from samples from mid-ocean ridge systems (MORB), to 0.70532. The observed range in the SMLS $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is fairly small relative to many other continental flood basalt province e.g. 0.7040-0.7120 Paranà, Brazil and 0.7040-0.720 Deccan, India (Wilson 1989, Cox pers. comm., 1992).

The lack of a clear correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ (Figure 4.9) negates the possibility of ascertaining a pseudoisochron (commonly interpreted as an inhomogeneous enrichment of the mantle in ^{87}Rb at some time prior to the generation of the magmas) for the Sr data. Previous work has shown considerable disagreement in isochron dates obtained for the SMLS from different isotopic systems. This has resulted the isochrons being considered to be pseudoisochrons and, in view of the different dates, processes other than a single mantle enrichment event being invoked to explain the range of isotopic ratios in the Skye lavas (Chapter 2, History of Petrogenetic Research, section 2.3.3).

4.2.3.3 The Preshal Mhor

Previous studies have found PM lavas to have initial $^{87}\text{Sr}/^{86}\text{Sr}$ similar to MORB, 0.70307 to 0.70351 (Moorbath and Thompson, 1980).

In the present study three PM lavas were analysed for Sr isotopes, their $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ values are consistent with previous work, they range from 0.70300-0.70336.

4.2.3.4 The Fairy Bridge

Only one FB lava has been analysed previously for Sr isotopes, it had $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ 0.70468.

The two FB lavas analysed here have lower initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70355 and 0.70375.

4.2.3.5 Other Skye lavas

No highly plagioclase porphyritic basalts have been analysed for Sr isotopes in this or previous studies. The basal tholeiitic pillow lava has a $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ ratio of 0.70487.

4.2.4 Nd Isotopic compositions

4.2.4.1 Introduction

Nd isotope measurements were carried out at the Open University on 17 of the Skye lavas; the analytical method and procedure for recalculation of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios to 60 Ma are discussed in Appendix F. The data are presented in Appendix F. The Nd isotopic work was performed for the same reasons as the Sr isotope work.

4.2.4.2 The Skye Main Lava Series

Previous work has shown the SMLS to have a wide range of initial $^{143}\text{Nd}/^{144}\text{Nd}$, 0.51308-0.51116 (Dickin *et al.*, 1987).

Eight SMLS samples were analyzed for Nd isotopes in this work. Their $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ values range from, 0.51301 (similar to MORB) to 0.51210. The range of Nd isotope values for the SMLS is comparable to that of other continental flood basalt provinces e.g. $^{143}\text{Nd}/^{144}\text{Nd}$ 0.51275-0.51225 Paraná, Brazil and 0.5130-0.5122 Deccan, India (Wilson 1989).

There is no clear correlation between the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio and Sm/Nd, or $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ and Sm/Nd (Figure 4.10). Thus neither an isochron nor a pseudoisochron can be identified for the Skye lavas. If there had been a correlation between the Nd isotopic ratios and Sm/Nd, this could have been the result of heterogeneity of the Sm/Nd ratio of the mantle source at some time prior to the generation of the magmas, or mixing of two isotopically distinct components.

4.2.4.3 The Preshal Mhor

The PM lavas have $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic values comparable to MORB. The results of previous studies range from 0.51313-0.51287 (Dickin *et al.*, 1987).

The $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ ratios obtained for the two PM samples analysed in the present study, 0.51298-0.51297, are just outside the range of values determined by previous workers.

4.2.4.4 The Fairy Bridge

No FB samples have been analysed for Nd in previous studies.

The two samples analysed here have $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ 0.51271-0.51294.

4.2.4.5 Other Skye lavas

The highly plagioclase porphyritic basalt and the basal tholeiitic pillow lavas have not been analysed for Nd isotopes.

Figure 4.11 (ϵNd versus ϵSR plot) shows inter and intra magma-type variations for the

Sr and Nd isotopic data of the present study. These variations are discussed in Chapter 7, Crustal Contamination.

4.3 Comparison of the Skye lavas with other continental flood basalts

4.3.1 Introduction

Tables 4.9 and 4.10 show average compositions of the three Skye magma-types and average and representative analyses from the British Tertiary Province (BTIP), the North Atlantic Tertiary Province (NATP) and other continental flood basalt provinces (CFB). MgO, being at least approximately linearly related to the liquidus temperature of basalts, was assumed to be indicative of the stage of evolution of a sample. Thus samples with a similar MgO content are assumed to be at a comparable level of evolution.

In this section comparisons of compositions will be made between each of the Skye magma types and BTIP, NATP and CFB samples.

4.3.2 Previous work

Morrison *et al.* (1980) compared the transitional SMLS basalts with samples from world-wide alkali basalt suites (Figure 4.12). The comparison showed that the SMLS basalts had similar concentrations of major element to the alkali basalts but lower concentrations and ratios of incompatible elements, more similar to world-wide olivine tholeiites.

It should be noted that there is a difference in the CIPW normative characteristics of the samples of the present study and those of the previous studies of Thompson and co-workers. Thompson *et al.* (1972) stated that the SMLS samples were nepheline and hypersthene normative in approximately equal proportions. In this study the majority of the SMLS samples fall into the latter category. The variation in normative character of the samples is the result of a difference in the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio used for the calculation of the CIPW norms (Section

4.2.1.2.a). The lower Fe_2O_3 content used by Thompson *et al.* (1972) produces less magnetite in the early stages of the calculation, thus leaving more FeO to be calculated as diopside in which SiO_2 is also a component, this results in less SiO_2 being available in the final stages of the calculation and so reduces the Si-saturation values of the lavas. Thus fewer of the lavas have hy-bearing norms.

4.3.3 Major and trace elements

Since the SMLS basalts have already been compared with typical alkali basalts (Morrison *et al.*, 1980, Figure 4.12); comparisons will be made here between the compositions of the Skye PM lavas, Skye FB lavas, the predominantly, albeit mildly, tholeiitic SMLS basalts, and other BTIP lavas, NATP lavas, and basalts from other CFB provinces.

The data in Table 4.9 show the averages of the SMLS plateau lavas and other BTIP plateau lavas have comparative contents of most major and trace elements, but Rb and Zr values are higher in the Skye lavas. The SMLS hy-normative and ne-normative lavas are compositionally most similar to the Antrim plateau lower basalts and the Canna plateau respectively.

As would be expected, the Skye PM lavas are most like the Mull Preshal Mhor basalts.

The sample of FB is more magnesian than the lavas chosen for the comparative study. Nevertheless it has a similar major element composition to the other BTIP lavas. However, many trace elements (Cu, V, Rb and Zr) have much higher, up to double, concentrations in the FB sample than in other BTIP plateau lavas. No analyses of basalts comparable to the Skye FB lavas have been found in the BTIP literature.

The SMLS hy-normative and ne-normative lavas are similar to other NATP basalts from Iceland (Table 4.10). No NATP analogies have been found for the PM lavas in the present

study. The FB lavas are broadly comparable with a Rockall trough lava (Table 4.10).

Southern hemisphere and Deccan lavas tend to have higher SiO_2 and K_2O and lower Na_2O and Sr than the SMLS basalts; the Deccan and Paraná high-Ti basalts also have much higher Ti and Y values. Basalts from Kirwan (Antarctica), Kenya, and Siberia are compositionally similar to the hy-bearing SMLS lavas, whereas basalts from the Snake River Plain (USA) and Hawaii provinces are comparable to the ne-bearing SMLS lavas (Table 4.10). No CFB basalts analogous to either the Skye PM or FB lavas have been found in the literature. However, it is worth noting that the former are compositionally similar to plume type mid-ocean ridge basalts (Table 4.10).

Having looked generally at the compositional similarities between the SMLS, PM and FB basalts and other CFB lavas, the relationships observed will be investigated in more detail using various element plots and trace element variation diagrams.

4.3.4 Total alkalis versus silica diagram

Figure 4.13 shows all the Skye lavas plotted on a total alkalis ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) versus SiO_2 (TAS) diagram, Figure 4.14 shows the Skye lavas and other basalts from Tables 4.9 and 4.10 plotted on a TAS diagram.

SiO_2 and $\text{K}_2\text{O} + \text{Na}_2\text{O}$ are two of the most important and useful chemical parameters used to assess compositional variations and similarities in magmas. Assuming lavas plotted are reasonably fresh ($\text{H}_2\text{O}^+ < 3.5\%$) (since the alkalis are mobile during weathering) the TAS diagram can be used for general classification of non-potassic volcanic rocks (Figure 4.13). The basalt field is divisible into alkali and sub-alkali (tholeiitic) fields (Miyashiro, 1978). However, the division is gradational and samples which plot near to the boundary are termed transitional; the SMLS comes under this term.

Here the TAS diagram is used for comparison of the compositional characteristics of the samples.

On the TAS diagram the SMLS hy-normative and ne-normative basalts plot in two fields (the latter having lower SiO_2 and higher $\text{K}_2\text{O} + \text{Na}_2\text{O}$) between which there is some overlap (Figure 4.14). The PM and FB lavas plot at the alkali-poor and alkali-rich extremes of the SMLS ne-normative and hy-normative fields respectively.

In Figure 4.15 the SMLS and Skye PM lavas cluster with their proposed analogues. Similarities between the Skye basalts and other lavas which plot in the SMLS hy-normative and ne-normative fields are also shown. The hy-normative lavas are comparable to basalts from Kenya, Horringbaai (Karoo, S.Africa), Kirwan (Antarctica) and Siberia. The ne-normative lavas have chemical compositional affinities with Hawaiian and Ethiopian basalts. The difference of lower SiO_2 with comparable or higher $\text{K}_2\text{O} + \text{Na}_2\text{O}$ between the Skye samples and many other CFB province basalts is demonstrated on the TAS diagram.

4.3.5 AFM diagram

The AFM diagram is a triangular plot of alkalis ($\text{K}_2\text{O} + \text{Na}_2\text{O}$), iron ($\text{FeO} + \text{Fe}_2\text{O}_3$) and magnesium (MgO). It can be used to distinguish between tholeiitic suites (which show a marked Fe-enrichment) and calc-alkaline suites (which trend directly across the diagram which is probably usually the result of suppression of Fe-enrichment by early crystallisation of Fe oxides) (Figure 4.15).

The SMLS hy-normative and ne-normative lavas fall on a single trend in the AFM diagram (Figure 4.15). They show Fe-enrichment relative to alkalis. The difference in composition between the most primitive SMLS basalts and the PM and FB basalts is highlighted

on the AFM diagram.

The primitive SMLS basalts have affinities with the trend of Hawaiian tholeiites; the more evolved SMLS lavas have an Fe enrichment pattern similar to Thingmuli lavas (Figure 4.15).

Figure 4.16 shows trends of some of the SMLS analogues and, for comparison, other CFB suites. The Small Isles (Canna, Rhum, Muck and Eigg), Mull, Ireland, Faeroes, Iceland and Siberia have very similar element concentrations and trends to the Skye lavas. Other CFB suites, the Karoo, Paraná, Colombia River (N.W USA), Greenland and Deccan (India) show more Fe- enrichment with evolution, and the Deccan primitive basalts are generally more magnesian than the Skye basalts.

4.3.6 Spider diagrams

Spider diagrams are produced by normalizing major and trace elements which are incompatible (concentration in mineral/concentration in liquid < 1) in mantle phases or phases crystallising from basalts (i.e. olivine, clinopyroxene and plagioclase) against either mid-ocean ridge basalts (MORB) (e.g. Pearce, 1983) or chondrite (e.g. Sun, 1980; Thompson *et al.*, 1983). The principles of both systems are comparable, the former will be described here because it is the system used in this section. Figure 4.17 shows the elements used in MORB normalisation diagrams. The elements are arranged according to their petrogenetic properties of mobility, due to low ionic potential, and incompatibility during mantle melting. Mobile elements, Sr, K, Rb, and Ba are placed on the left of the diagram, and immobile elements e.g., P, Zr, Ti and Y on the right. Combining the factors of mobility and incompatibility the elements are graded on a scale of 1 to 15. The elements are then arranged so that the incompatibilities of both mobile and immobile elements increase from the outside to the centre of the pattern (Figure 4.17). A representative restricted range of elements were selected for use in this study (Figure 4.17). With the exception of Sr, which is compatible in plagioclase, all the elements used are

incompatible in fractional crystallisation and mantle partial melting processes. Such processes will, therefore, change the level but not the shape of the spider diagrams. Processes such as mantle source region enrichment or contamination of the lavas by crustal material are invoked to explain pattern shape changes.

Spider diagram patterns may be used to distinguish lavas from different tectonic settings. Subduction related magmas may have enriched concentrations of mobile elements and depleted immobile elements relative to MORB (Figure 4.18). Such patterns are often attributed to enrichment of mobile elements in the mantle wedge by dehydration of the subducting slab, so eliminating the need to invoke crustal contamination to explain the observed element concentrations (Best, 1975; Hawkesworth *et al.*, 1977; Saunders and Tarney, 1979). Within-plate basalts (WPBs) are generally relatively enriched, relative to MORB, in all elements except Y and Yb. WPBs show most enrichment in mobile elements. This results in a concave downwards pattern which is thought to be the result of the relative compatibility of elements in their garnet lherzolite source (Pearce, 1983) (Figure 4.18). Continental calc-alkaline basalts erupted at active continental margins are typically extremely enriched in large ion lithophile (LIL) elements (Figure 4.18). Pearce (1983) noted that to yield comprehensive and meaningful conclusions spider diagrams patterns must be considered in conjunction with isotopic and major element chemistry.

Figure 4.19 shows MORB normalised spider diagrams for the Skye lavas, and Figure 4.20 shows their proposed analogues, and other CFB lavas.

Each of the three magma types identified on Skye, SMLS, PM and FB, has a distinctive MORB normalised element profile (Figure 4.19). The patterns of the Skye lavas and their proposed analogues resemble each other and are more like the within-plate basalt patterns than the island arc tholeiites or continental calc-alkaline basalts patterns (Figure 4.19). Other CFB

samples plotted for comparison also clearly resemble the within-plate basalts most strongly (Figure 4.20 and Figure 4.18). However, other CFB basalts show much greater enrichment in K_2O and Rb than the Skye lavas.

4.3.7 Palaeotectonic setting diagrams

It has been suggested by various authors (Pearce and Cann, 1973; Floyd and Winchester, 1975; Pearce *et al.*, 1975; Wood *et al.*, 1979; Shervais 1982; Pearce, 1982; Mullen, 1983; Meschede, 1986) that if compositional characteristics of modern volcanic rocks can be correlated with a particular tectonic setting then such data can be used to identify the tectonic setting of ancient volcanic suites. Various major, minor and trace element concentrations have been proposed as diagnostic of certain tectonic settings. This has resulted in numerous tectonomagmatic discrimination diagrams (TMD) being suggested. Such diagrams can be divided into three types (Duncan, 1987) :-

- (i) Those using relatively immobile minor and trace elements measured by X-ray fluorescence (XRF), the most commonly used being ternary plots, e.g., Ti/100-Zr-Y.3 (Pearce and Cann, 1973).
- (ii) Those that use major and minor elements e.g., TiO_2 -MnO.10- P_2O_5 .10 (Mullen, 1983).
- (iii) Those that use immobile trace elements measured by instrumental neutron activation analysis (INAA), e.g. Th-Hf/3-Ta (Wood *et al.*, 1979).

TMD diagrams are unlikely to give unequivocal determinations of tectonic settings since the composition of volcanic rocks is dependent on their source composition and mineralogy, depth and degree of partial melt, mechanism of partial melting, and fractionation and contamination processes they may have undergone on the way to the surface. The compositional characteristics of volcanic rocks can only be used as indicative of tectonic setting when some or all of the above factors are unique to a particular setting. With the accumulation of compositional data it has been found that rocks known to be from a particular tectonic setting

sometimes plot within another field in the TMD diagrams (Duncan, 1987). Therefore, the field boundaries should not be interpreted too rigidly.

Figure 4.21 shows that the SMLS lavas fall in the within-plate basalt (WPB) field and the field containing ocean-floor basalts, calc-alkaline basalts and low-K tholeiites (OFB, CAB and LKT); the PM lavas are within the LKT field and the FB lavas fall in the OFB/CAB/LKT field. Figure 4.22 shows some of the proposed analogues for the Skye lavas and other continental flood basalt provinces. Mitchell (1988) noted that samples from the Falkland Islands predominantly lie in the OFB/CAB/LKT field and that high Ti basalts from the northern Karoo and Paraná do not plot clearly in the WPB field. This anomaly has also been observed in other high- and low-Ti lavas e.g. the north Lebombo and southern Lebombo, and Lesotho (Cox, 1983).

So, in summary the SMLS lavas are much less tholeiitic than the great majority of CFBs. Isotopically they are rather uniform and have rather low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ compared with several other provinces particularly the Ferrar (Antarctica), the Paraná (Brazil) and the Deccan (India).

4.4 Summary and conclusions

The Skye lavas range in composition from picritic basalts to trachytes. They can be divided into three magma-types on the basis of compositional differences: the Skye Main Lava Series (SMLS), Preshal Mhor (PM) and Fairy Bridge (FB).

PM lavas have been identified in the Ramascaig, Beinn Totaig, and Bracadale stratigraphic units. Previously PM lavas had only been found in the highest stratigraphic unit, the Osdale group. FB lavas, previously only found in the Ramascaig stratigraphic unit, have been identified in the higher Beinn Totaig and Osdale units.

The SMLS comprises hy-normative and ne-normative samples, and are thus termed transitional basalts. Distinct compositional variations exist between the most hy-normative and the most ne-normative SMLS lavas. There is a continuum of compositions between the hy-normative and ne-normative end-members. The continuum is represented by inter-element correlations between samples that are at a similar stage of evolution, and planar arrays in the data-set as a whole.

The PM lavas are tholeiitic basalts. They have high CaO and low total alkalis (K_2O and Na_2O) relative to the SMLS.

The FB lavas are tholeiitic basalts. They have subtle major and trace element differences from the SMLS and PM basalts.

Big feldspar basalts and basal tholeiitic pillow lavas occur in the Skye lava pile.

The dykes of a regional swarm which trends approximately NW-SE comprise SMLS, PM and FB magma-types in the proportions 15:70:15. The sills which occur in the Jurassic strata underlying the lava pile and near its base are compositionally similar to the SMLS, some have been cumulus enriched in olivine.

The SMLS, PM and FB magma-types all have characteristic REE profiles: LREE enriched relative to chondrite, LREE depleted relative to chondrite and flat, respectively.

The SMLS lavas have a wide range of initial $^{87}Sr/^{86}Sr$ (0.70312-0.70532). The PM and FB lavas are more restricted compositionally, $^{87}Sr/^{86}Sr$ - 0.70300-0.70336 and $^{87}Sr/^{86}Sr$ - 0.70355-0.70375 respectively. A pseudo-isochron is not detectable from the Sr isotope data of the Skye lavas. The SMLS lavas have a wide range of initial $^{143}Nd/^{144}Nd$ (0.51301-0.51210). The initial $^{143}Nd/^{144}Nd$ of the PM lavas ranges from 0.51298-0.51297 and those of the FB lavas from 0.51271-0.51294. A pseudoisochron is not detectable from the Nd isotope data of the Skye lavas.

The SMLS and FB basalts show greatest compositional affinities to within plate basalts, whereas the PM basalts are most like ocean floor basalts. Comparison with other BTIP, NATP

and CFB lavas has shown that the SMLS hy-normative lavas have the greatest compositional affinities with Antrim lower basalts, Icelandic, Kirwan (Antarctica), Kenyan and Siberian basalts. Whereas the SMLS ne-normative basalts have greatest compositional affinities with Canna plateau basalts, Icelandic, Snake River Plain (USA) and Hawaiian basalts. The Skye PM lavas are compositionally most similar to Mull PM lavas and plume, enriched (E-type) MORB. The Skye FB lavas show some affinities with a sample from the Rockall trough but no direct analogies have been found in the literature.

It is worth noting that the Skye lavas are compositionally complex. Two-element variation diagrams are very scattered. Subsequent Chapters 5 to 8 address the main processes which have affected the lavas: alteration, fractional crystallisation, crustal contamination and variation in degree of melt and composition of the mantle source. Sloman (1987) remarked that when a lava suite has undergone a complex evolution it is unlikely that a complete understanding of the history will be gained; however the processes dominant in controlling the compositional variation may be recognised.

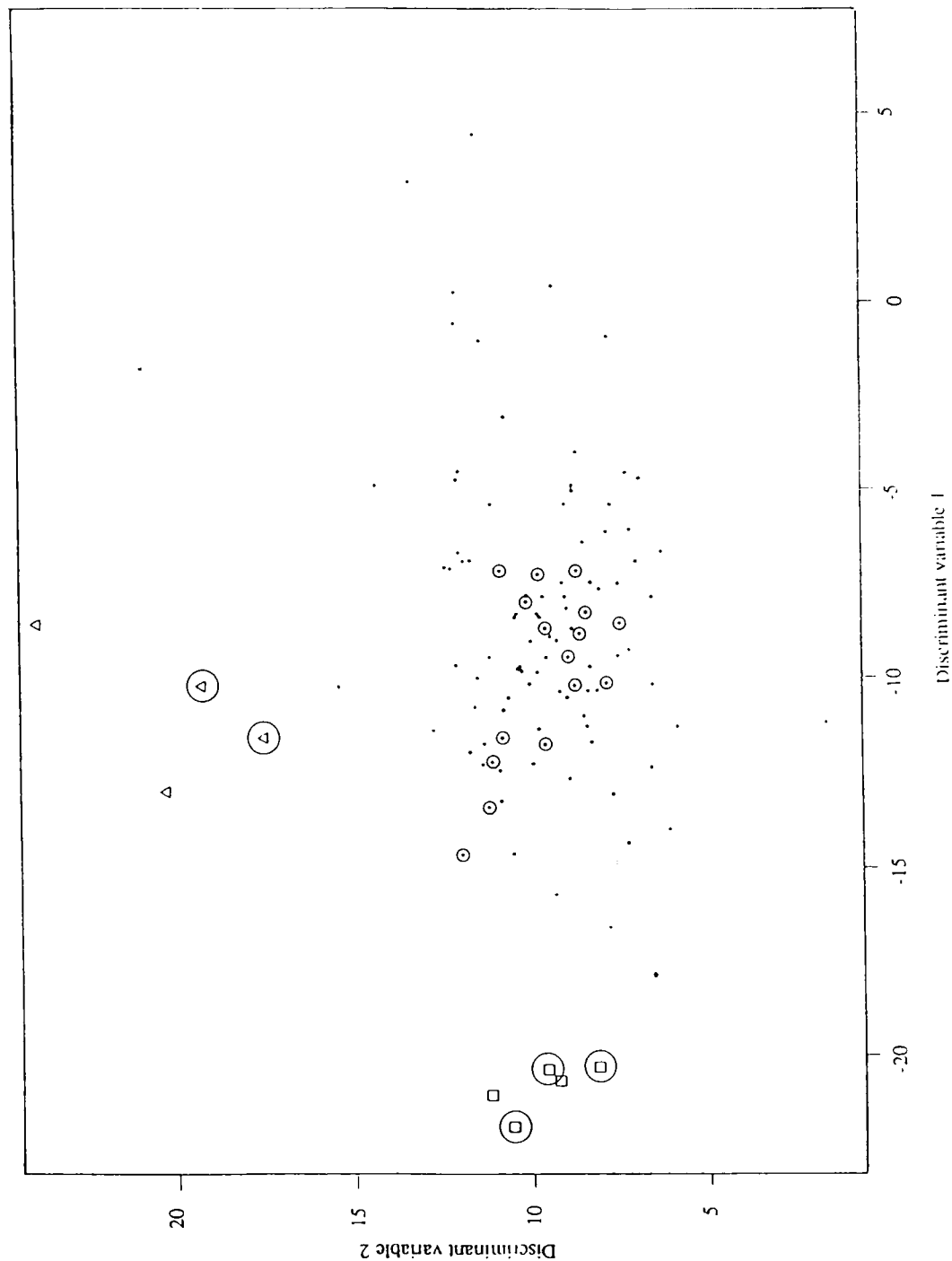


Figure 4.1 Division of the three Skye magma types using discriminant function analysis (see text for details).
 Circled samples are those which defined the groups used in the discriminant function analysis
 dots - Skye Main Lava Series samples
 open squares - Preshal Mhor samples
 open triangles - Fairy Bridge samples

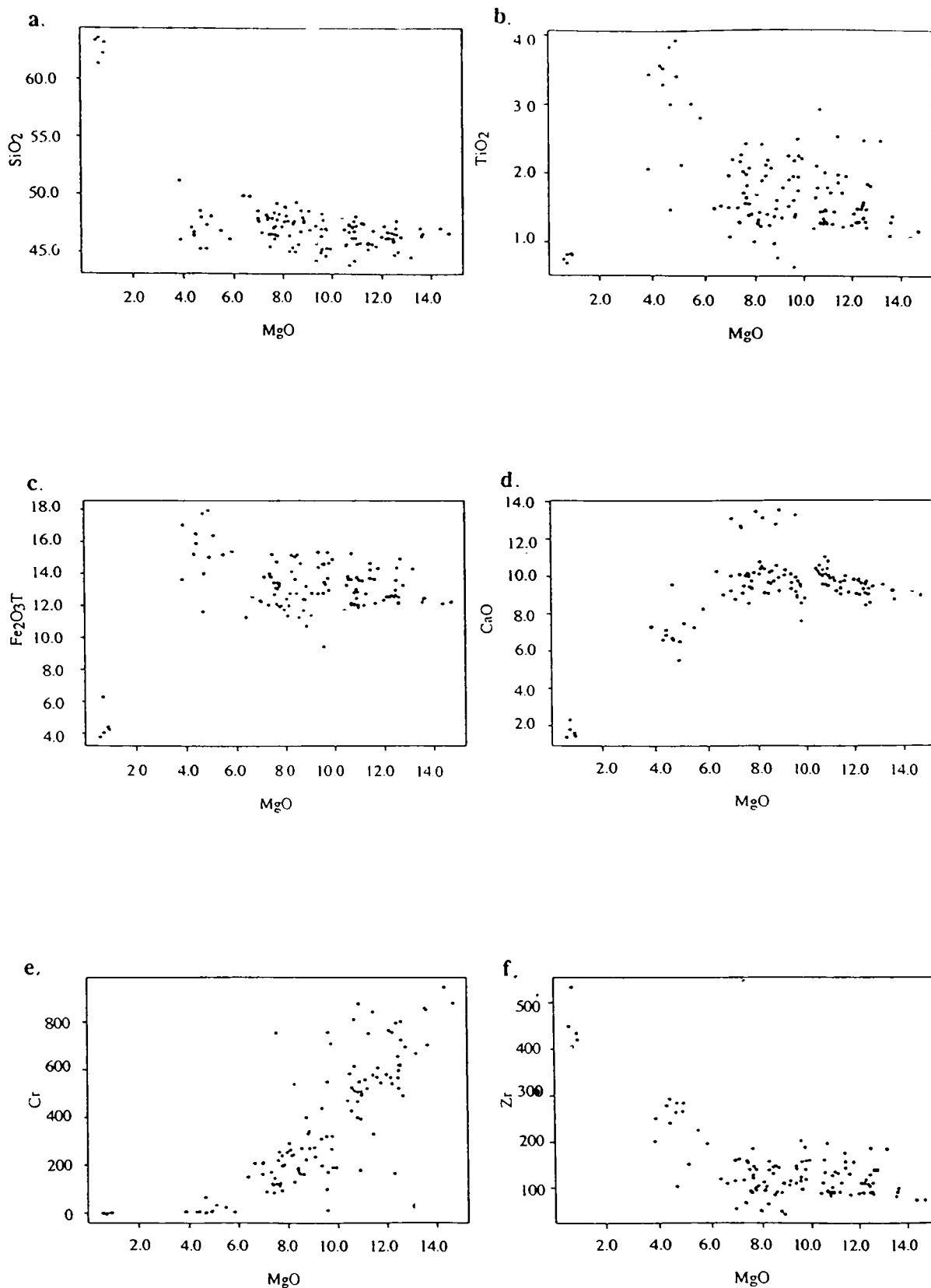


Figure 4.2

Two-element variation diagrams showing scatter in element concentrations at constant values of MgO. (Element concentrations are in wt % oxide)

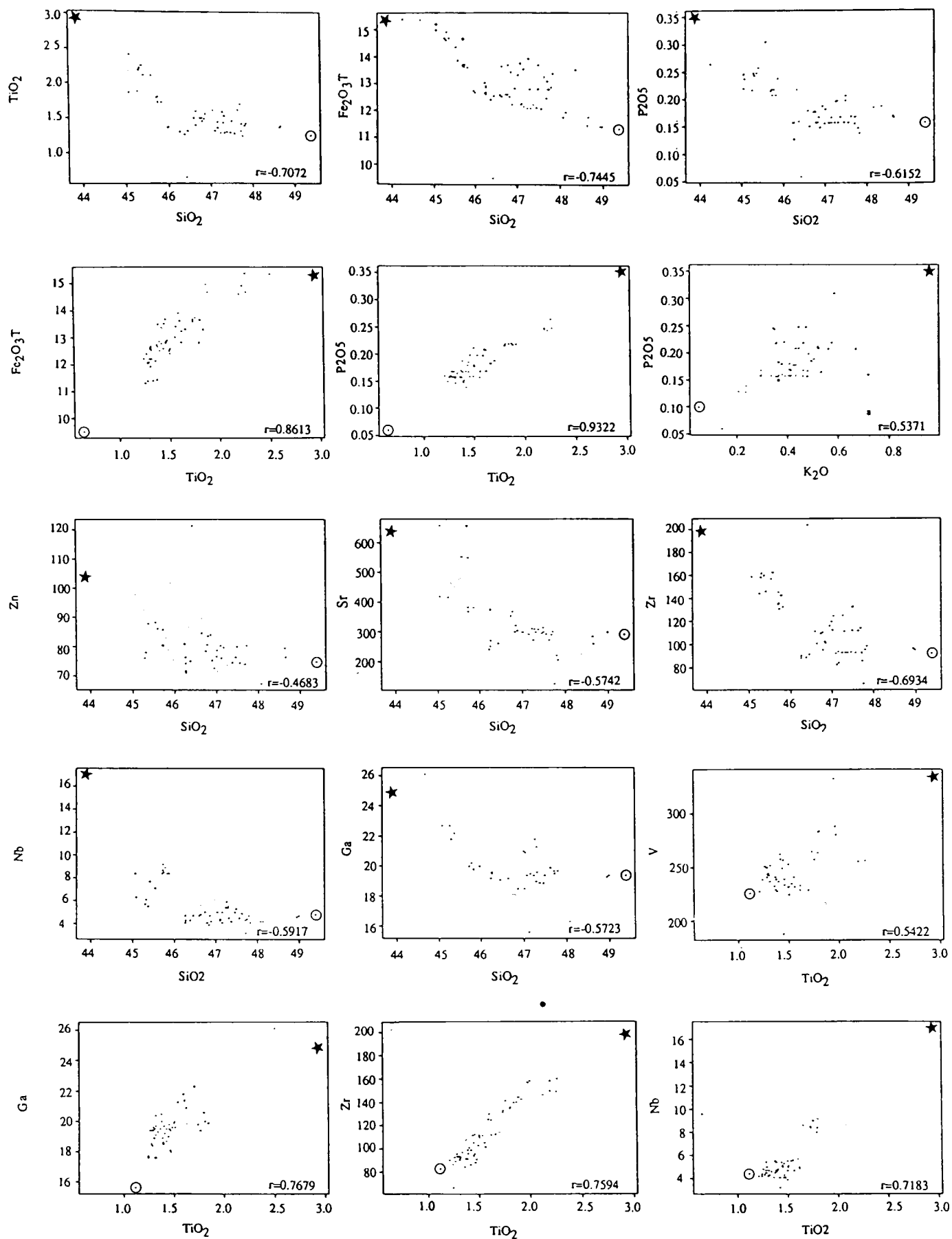


Figure 4.3 continued.....

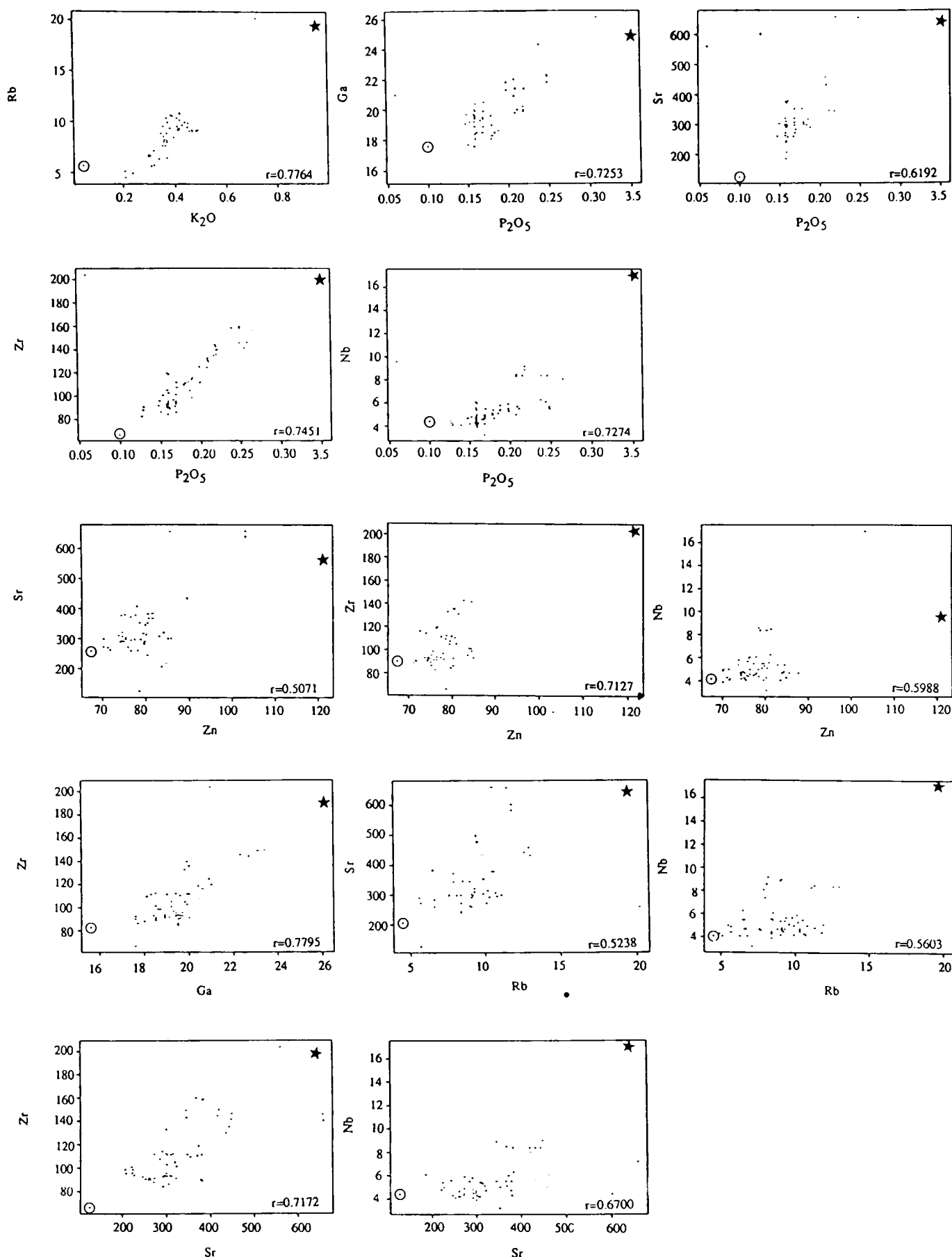


Figure 4.3 Inter-element correlations for a 15 wt % MgO dataset created by the addition of olivine to all samples under olivine control, i.e. more than 7wt% MgO (see Chapter 6 Fractional crystallisation for details).
 closed star - ne-normative end member.
 open circle - hy-normative end member.
 r = correlation coefficient, all correlations are significant at the 99% level.

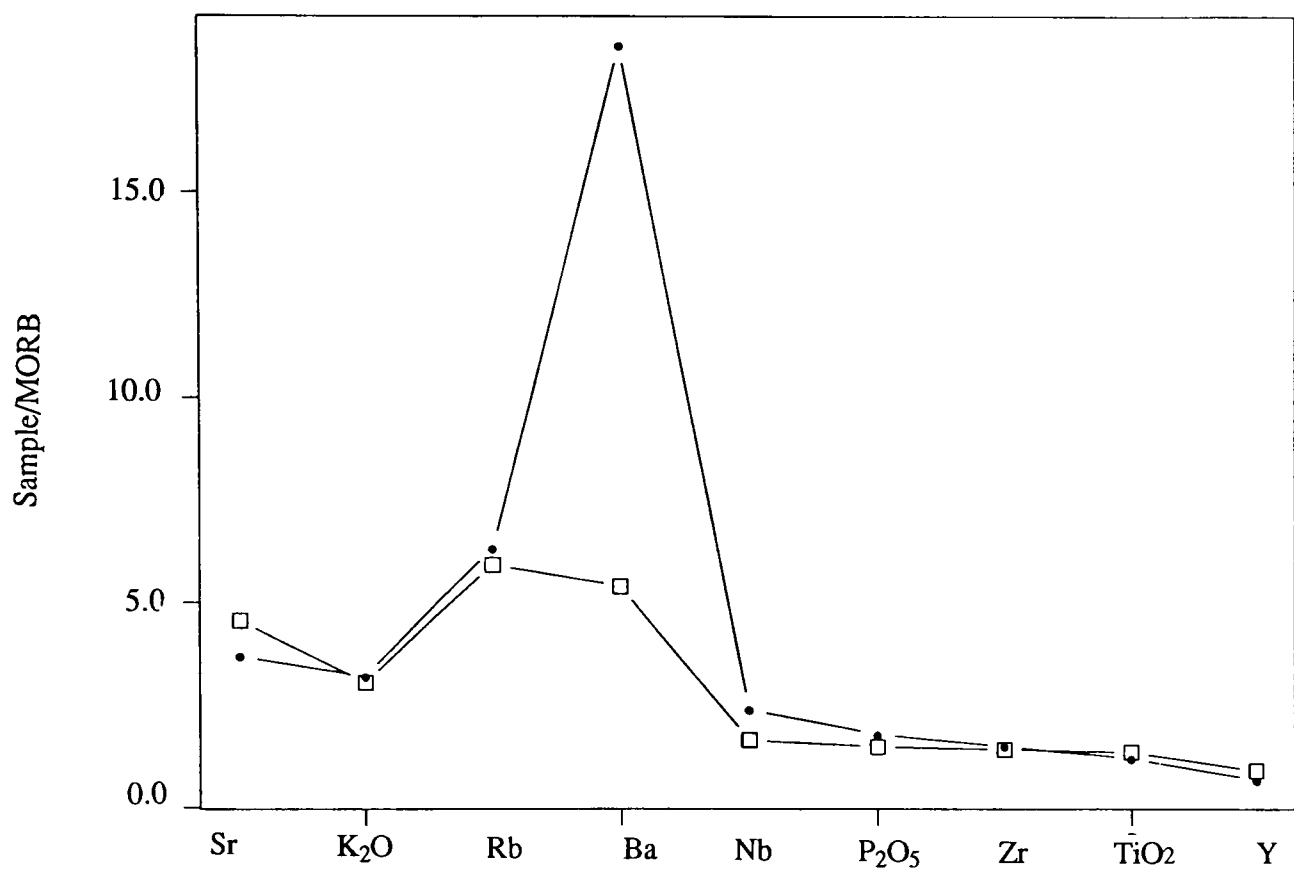
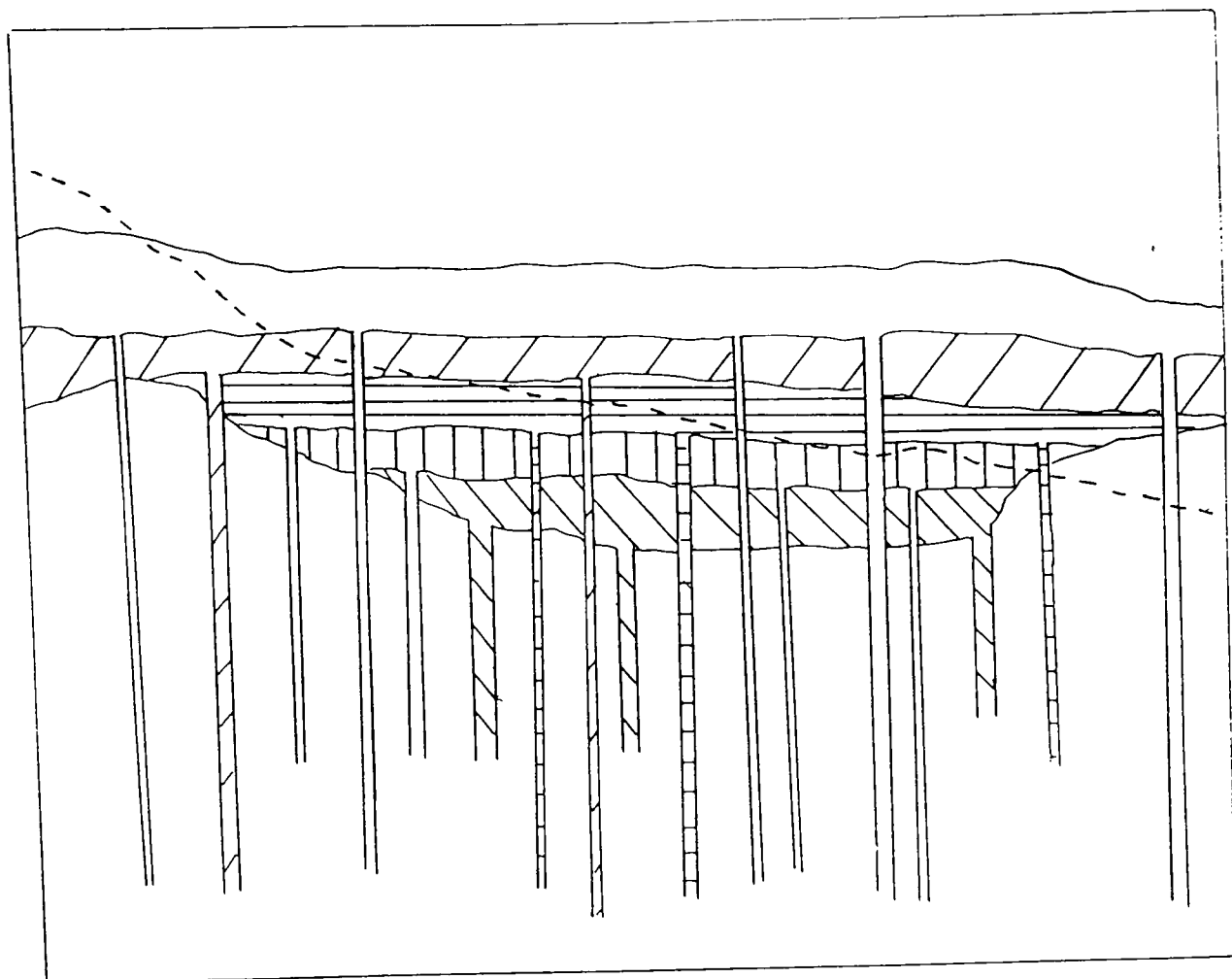


Figure 4.4 The two characteristic pattern shapes of Skye lavas normalised to Mid-Ocean Ridge basalt (MORB).

(sample numbers • JHS154, □ JHS184)



Legend

--- Present day erosion level

Figure 4.5 Cartoon of feeder dykes and a lava pile, showing how late stage magma compositions can be disproportionately represented in a dyke swarm.

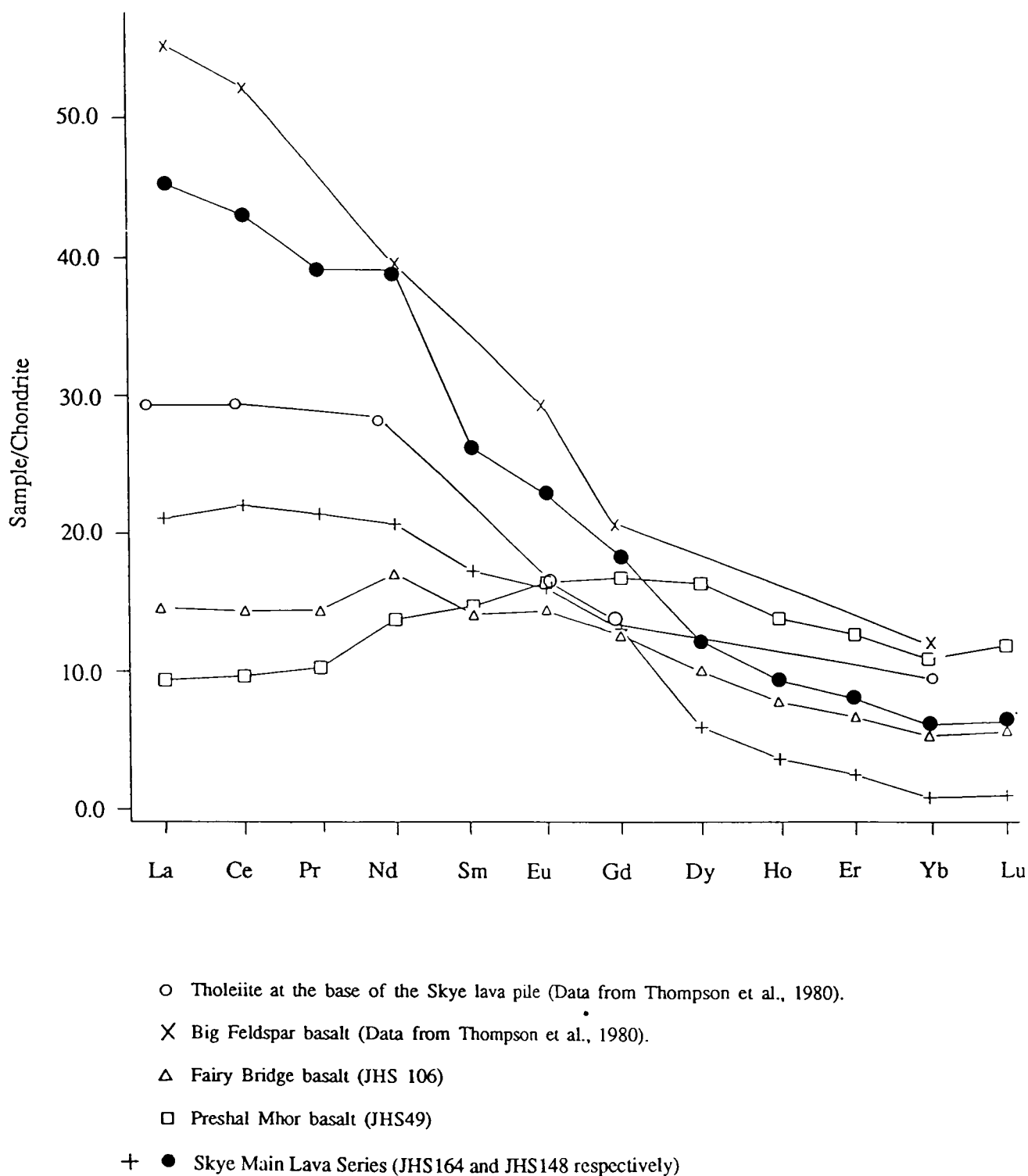


Figure 4.6 Characteristic chondrite normalised rare earth element patterns of the Skye lavas.

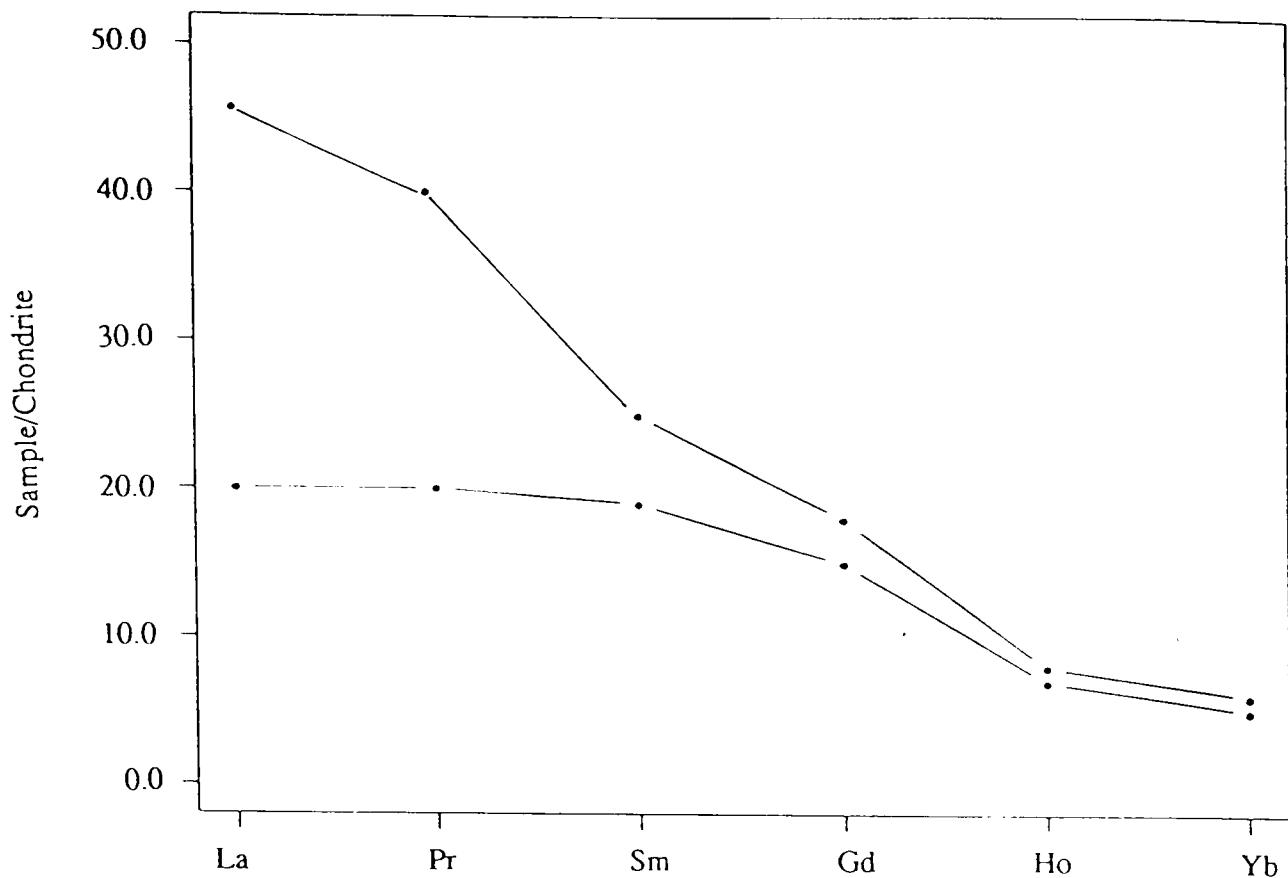


Figure 4.7 Variation in the slope and curvature of the chondrite normalised rare earth element profiles in a restricted MgO set of SMLS basalts.
(sample numbers flat pattern JHS89, steep pattern JHS148)

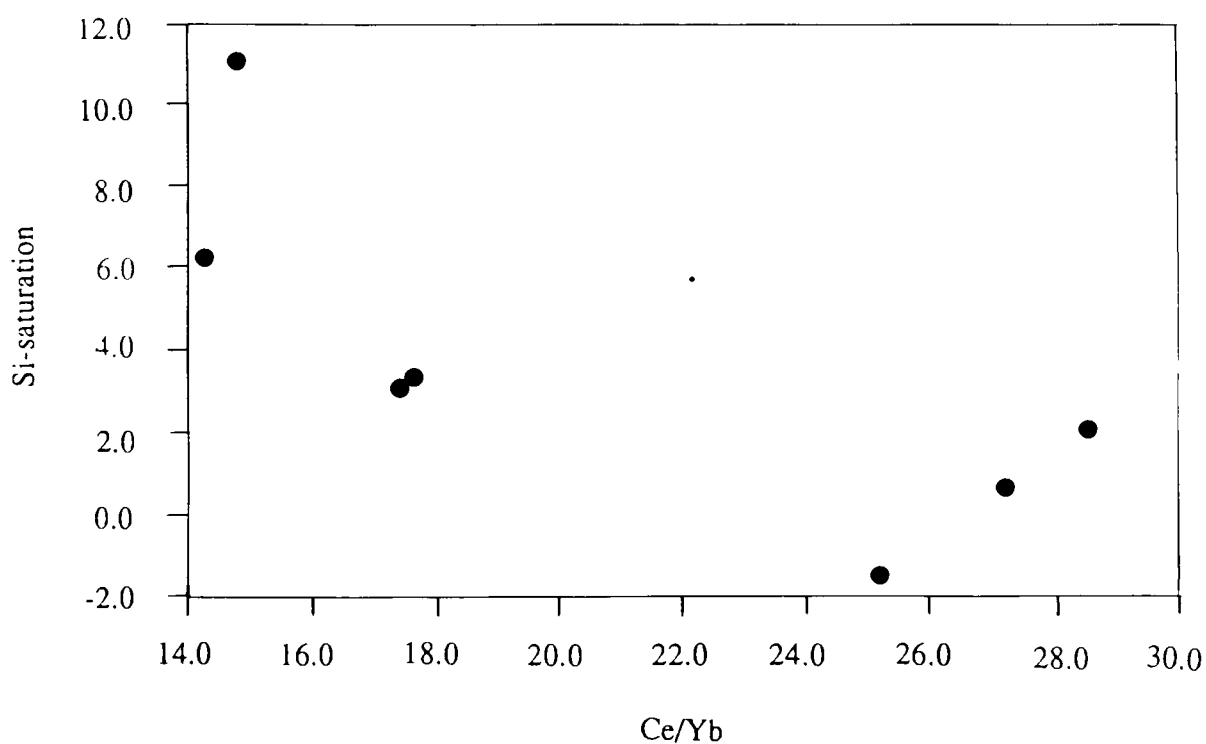


Figure 4.8 Ce/Yb versus Si-saturation for seven SMLS lavas.

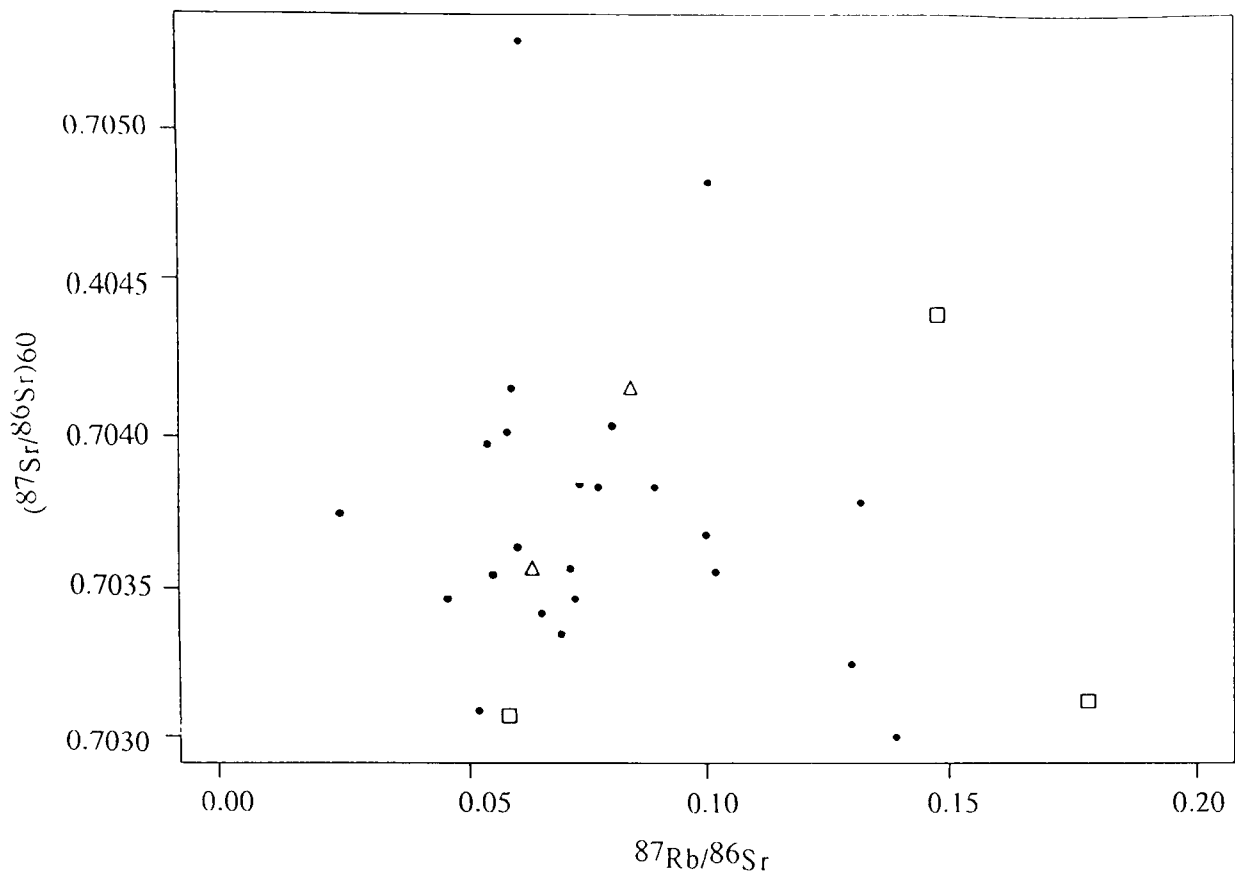


Figure 4.9 $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$.
There is no clear correlation between the two variables.
(Symbols as in Figure 4.6)

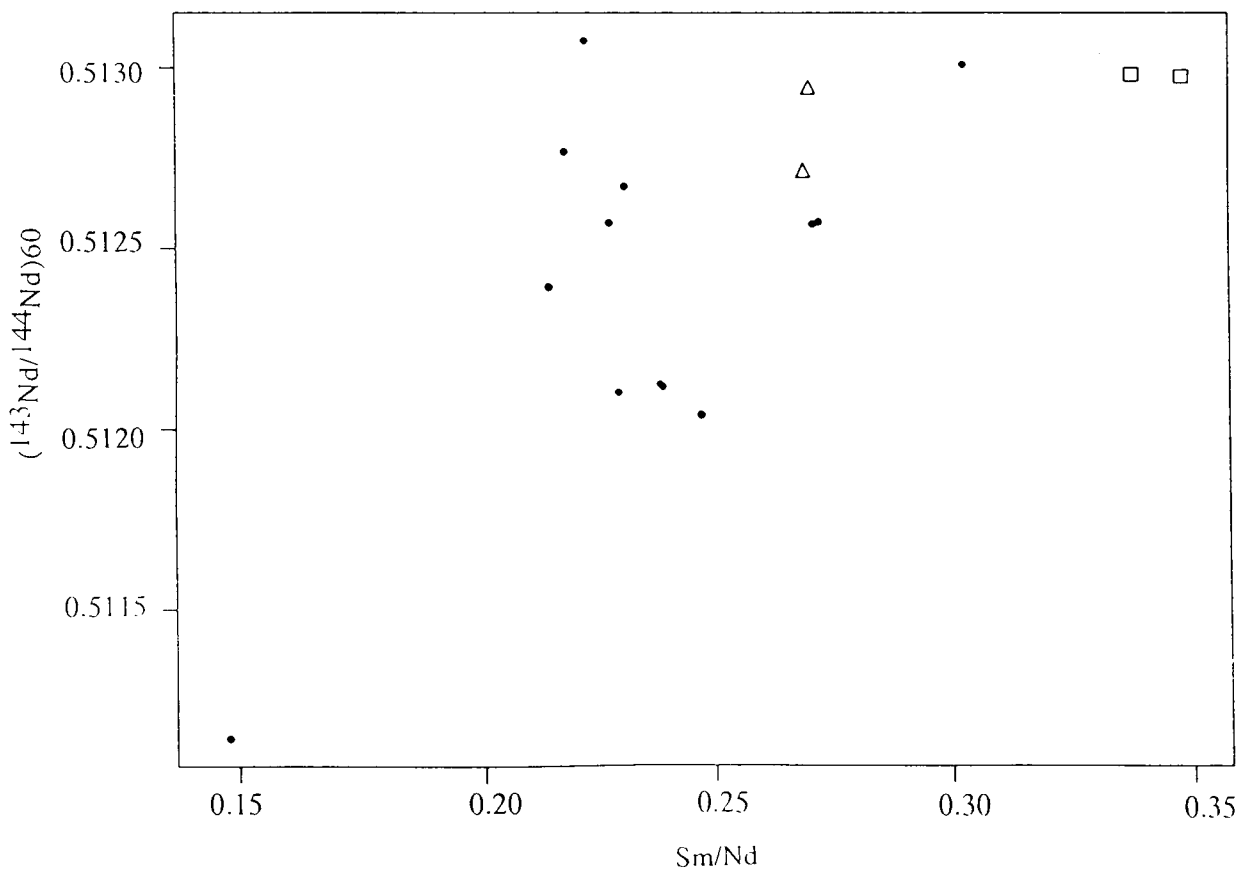


Figure 4.10 $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ versus Sm/Nd.
There is no clear correlation between the two variables.
(Symbols as in Figure 4.6)

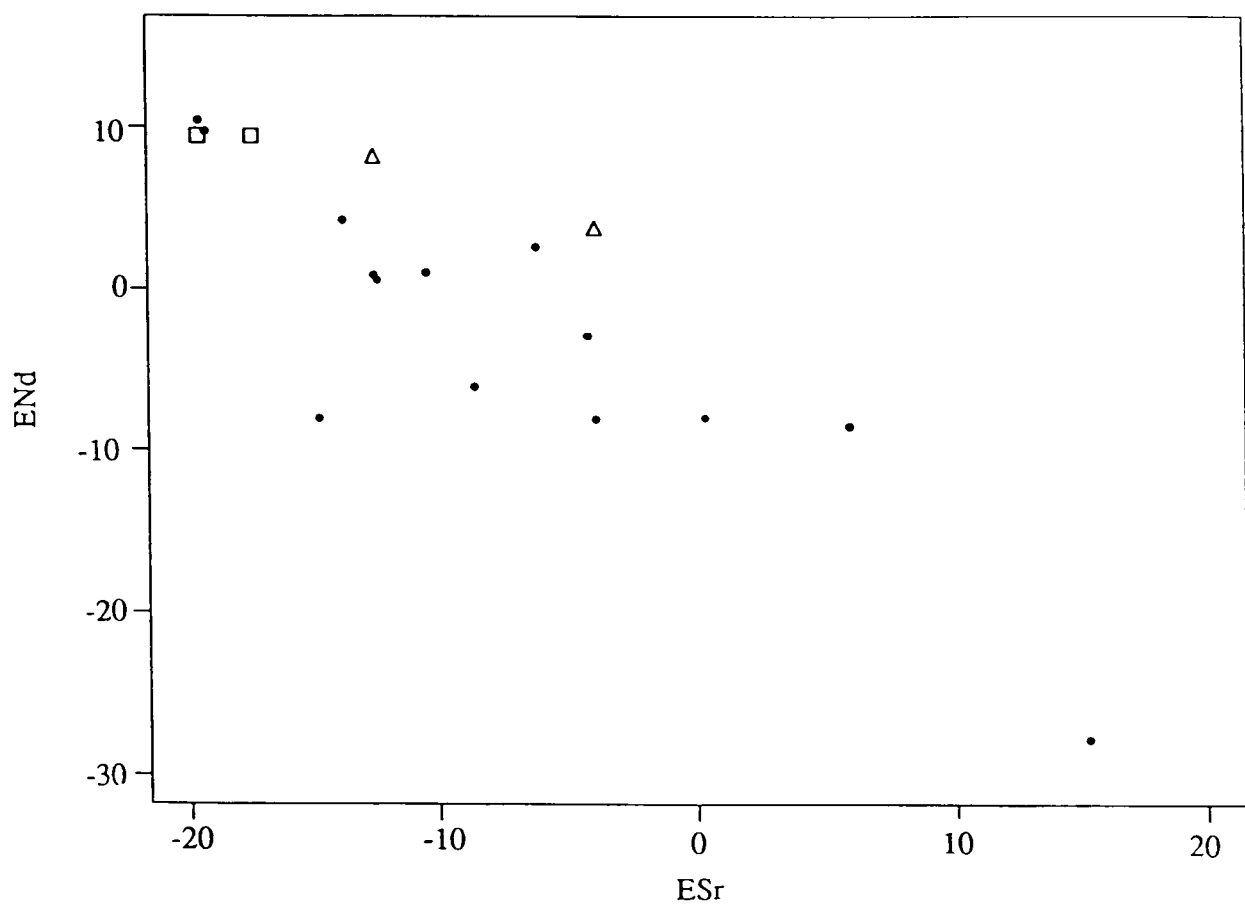
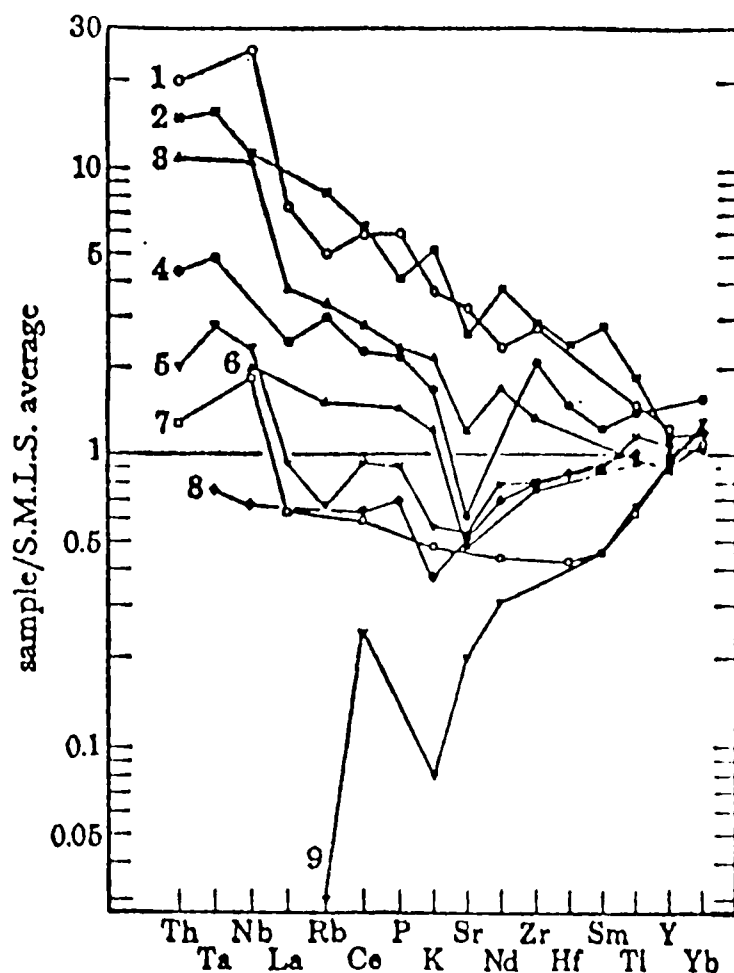


Figure 4.11 ENd versus ESr showing the intra and inter magma type isotopic variations.
(Symbols as in Figure 4.6)



Morrison et al., 1980

Figure 4.12 Comparison of incompatible element abundances in SMLS basalts and other lavas. The SMLS average (MgO=8.41%) to which other lavas are normalised is the mean of the less-magnesian basalts (Thompson et al., 1979). MgO concentrations in the other samples range from 8.12 to 8.99%, except for MS144 (7.68%).

- Legend :
- 1, Nephelinite (4168), New South Wales (Kesson 1973)
 - 2, Camptonite (MS144), Dornie, Loch Duich (Morrison et al., 1980)
 - 3, Alkali olivine basalt (27417), New South Wales (Kesson, op.cit)
 - 4, Olivine tholeiite (72-3B), Snake River Plain (Leeman and Vitaliano, 1976)
 - 5, Olivine tholeiite (V11), eastern Iceland (Wood, 1978)
 - 6, Olivine tholeiite (AJ32), Anjouan, Comores (Flower, 1973)
 - 7, Tholeiitic basaltic glass (523-1 GL), Famous area, Mid-Atlantic Ridge (Langmuir et al., 1977)
 - 8, Average of M.P.G. basalt with mean MgO 8.33% close to SMLS basalt (Morrison et al., op.cit.)
 - 9, Tholeiitic basalt glass (319-21/27-30cm), D.S.D.P. Leg 34, Nazca Plate, eastern Pacific (Hart, 1976)

In addition the following alkali olivine basalts plot along essentially the same line as number 3 in the diagram : 0030436 (MgO=8.79%), Dunedin, New Zealand (Price and Chappeli, 1975); M33 (MgO=8.42%), Maderia (Hughes and Brown, 1972). A Kilauean olivine tholeiite K10037, with MgO=8.37% (Gunn, 1971), plots close to the SMLS average.

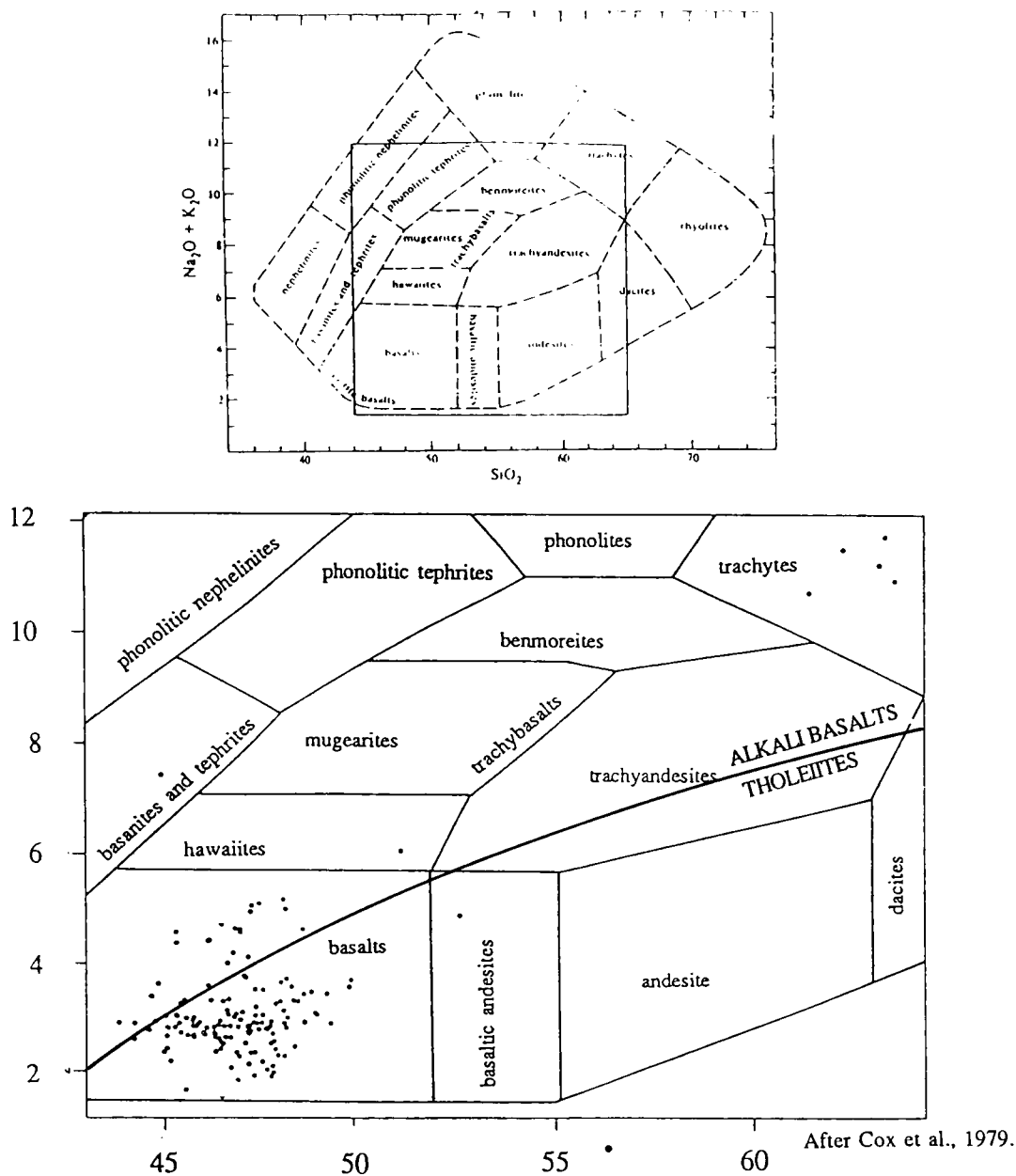
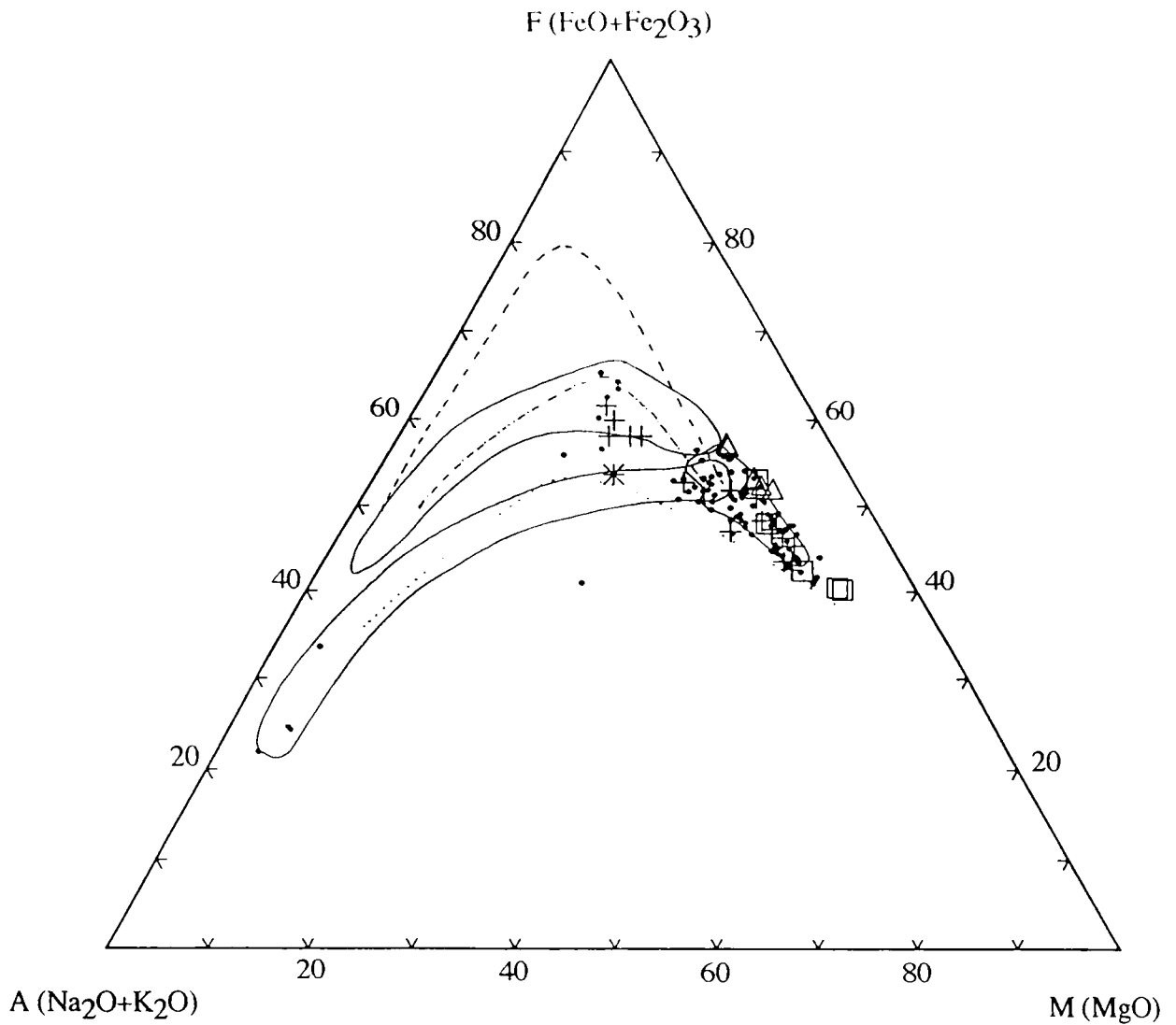


Figure 4.13 Total alkalis versus silica diagram. Nomenclature of normal (i.e. non-potassic) volcanic rocks. The boundaries are not intended to be sharp, the fields labelled are intended to show the approximate areas in which the different rock types plot.



Legend

- + SMLS Ne normative lavas
- SMLS Hy normative lavas
- Preshal Mhor basalts
- △ Fairy Bridge basalts
- * Big feldspar basalt
- - - Skaergaard trend
- . - . Thingmuli trend
- Hawaii alkali trend
- Thompson et al. (1972) less than 5% phenocrysts.
- Thompson et al. (1972) trend 1.
- Thompson et al. (1972) trend 2.

Figure 4.15

AFM diagram.

The three Skye magma types lie on a single trend of Fe enrichment.

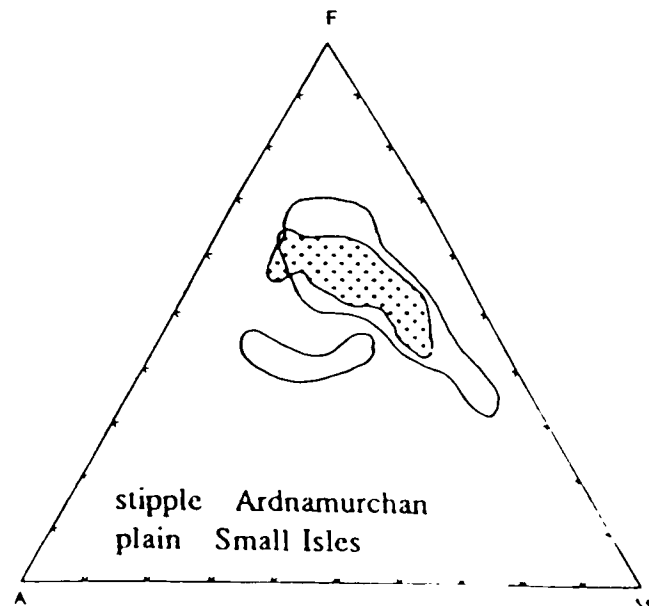
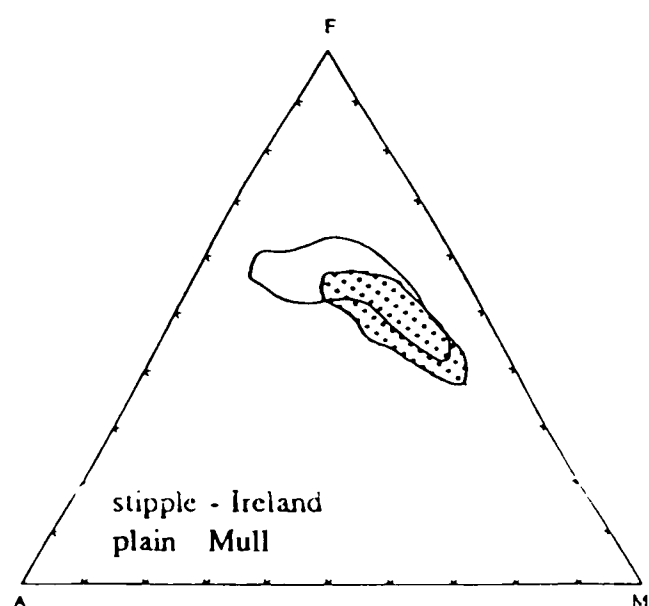
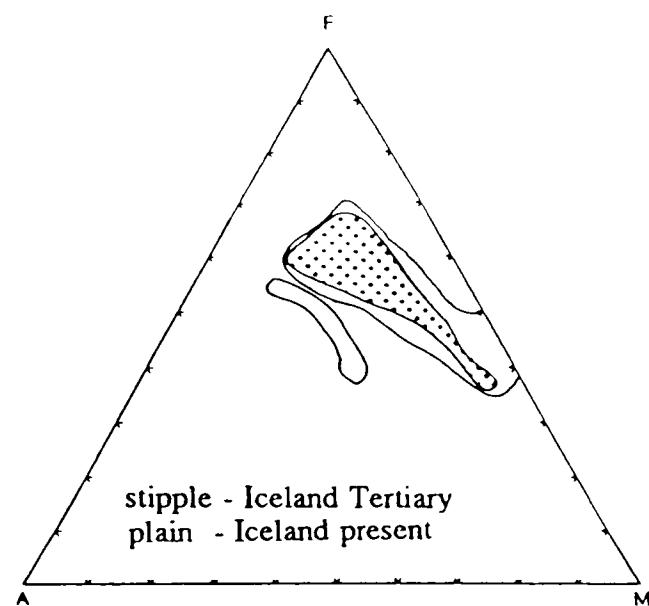
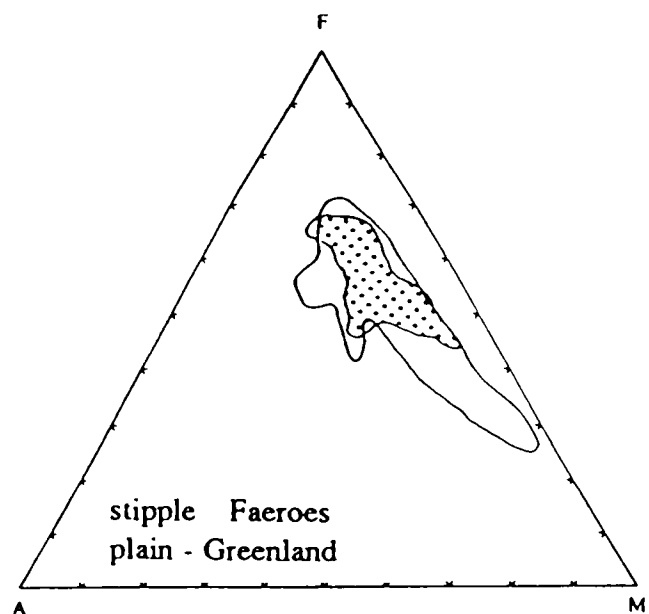
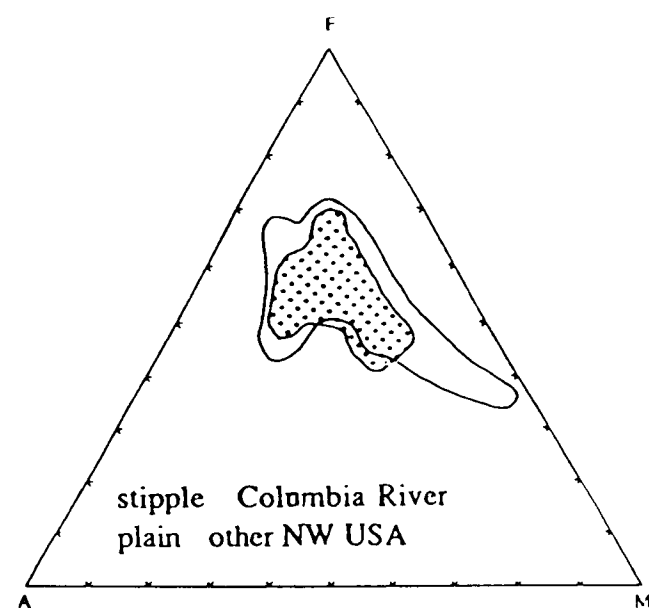
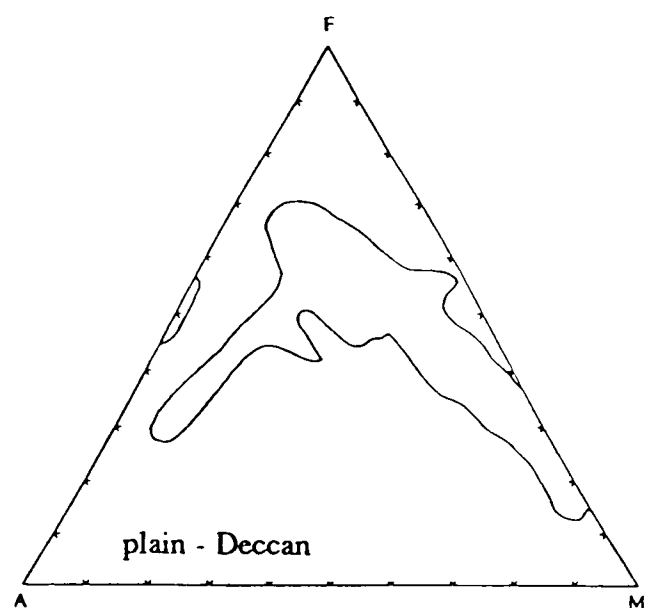
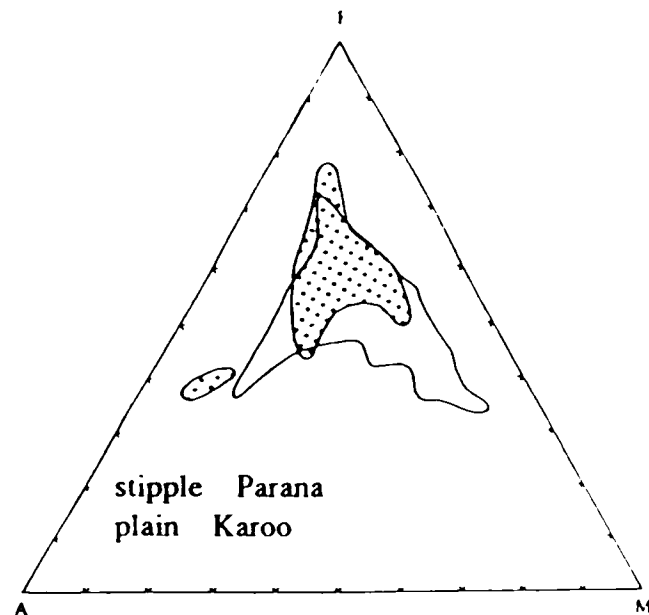
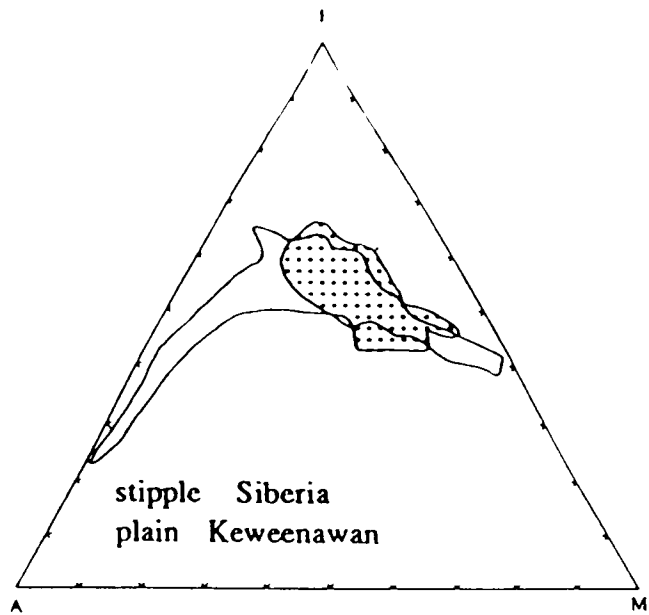


Figure 4.16 AFM diagrams for basalts from other continental flood basalt provinces, the North Atlantic Tertiary Province, and the British Tertiary Igneous Province.

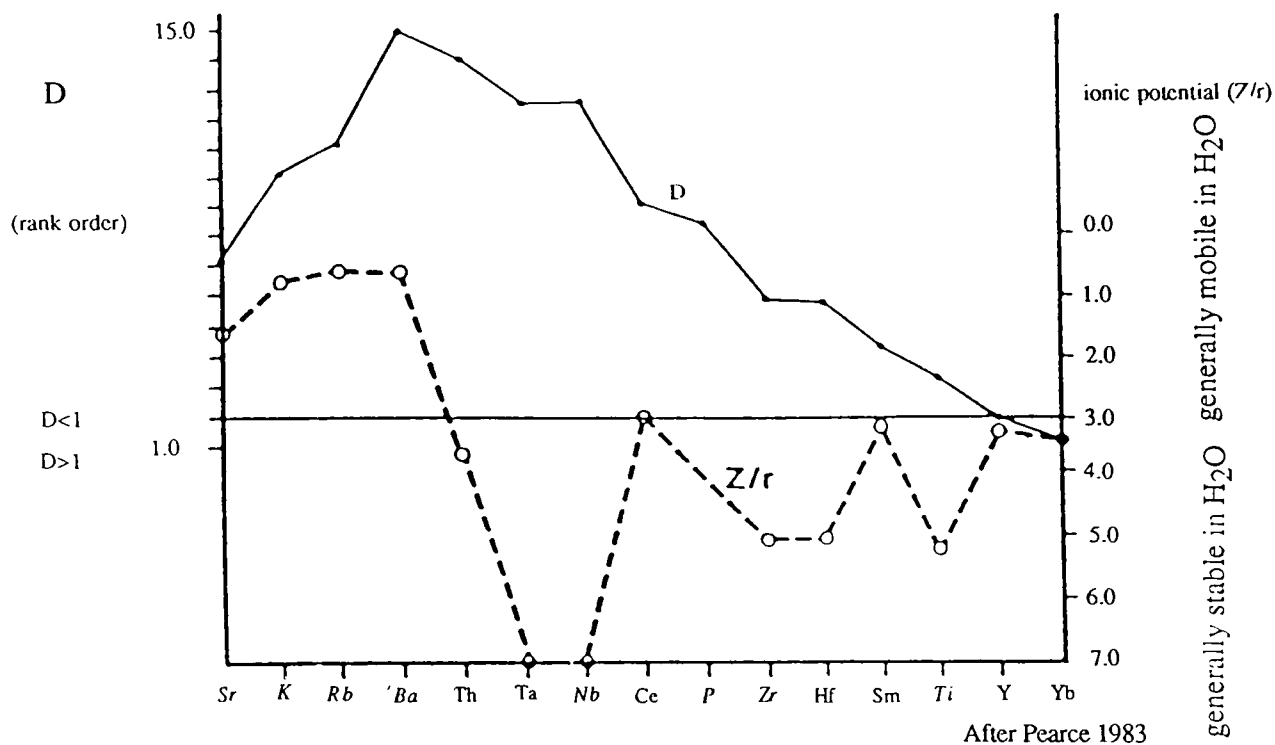
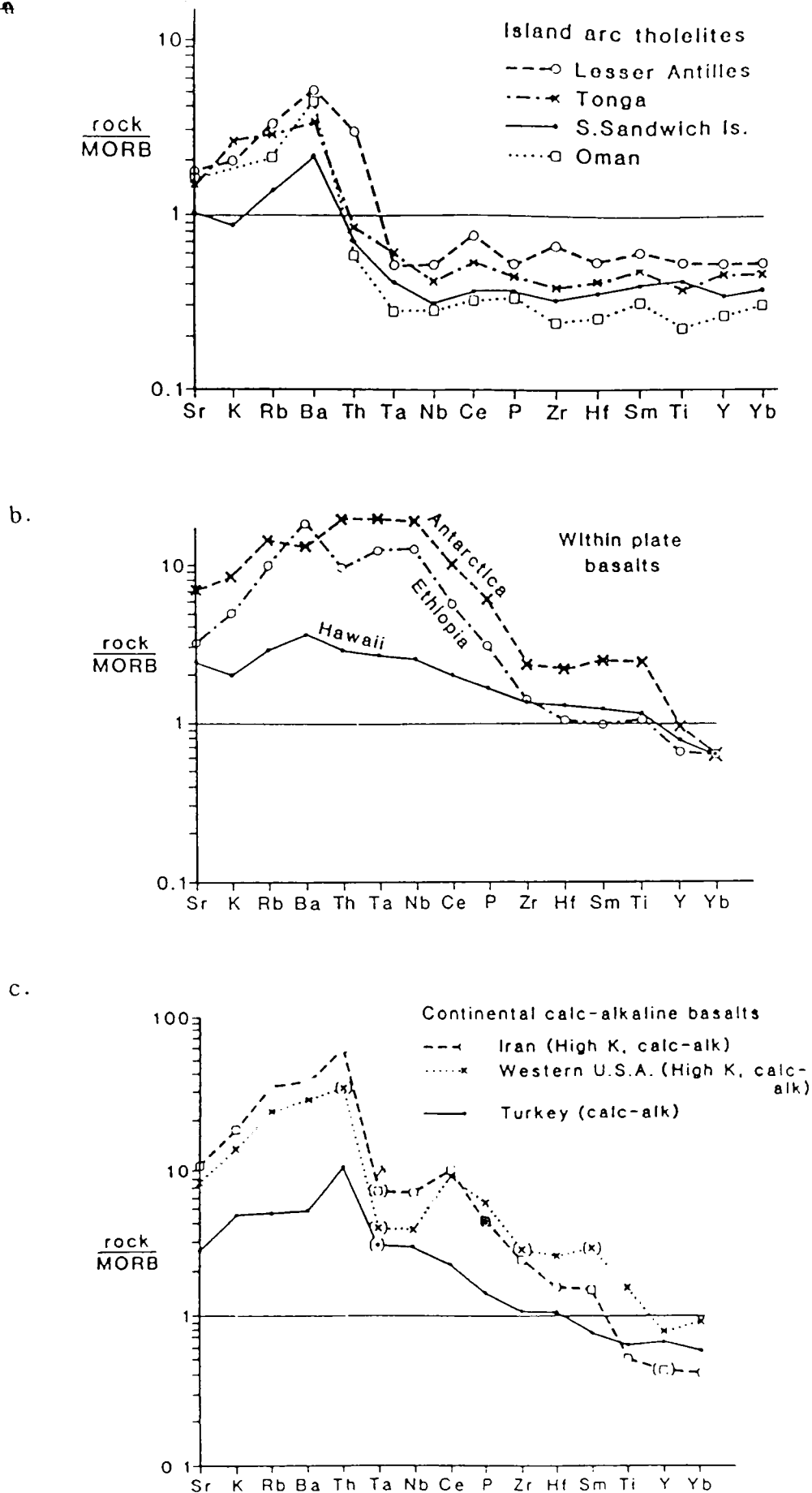


Figure 4.17 Element generally used in MORB normalisation diagrams and the petrogenetic variables that determine their ordering in the geochemical patterns as described by Pearce (1980).

(z = ionic charge of element in its normal oxidation state

r = ionic radius

D.= bulk distribution coefficient for element between garnet lherzolite and melt)



After Pearce 1983

Figure 4.18

Typical MORB normalisation patterns for basalts from various tectonic settings.

a. subduction zones.

b. within plates.

c. destructive continental margins.

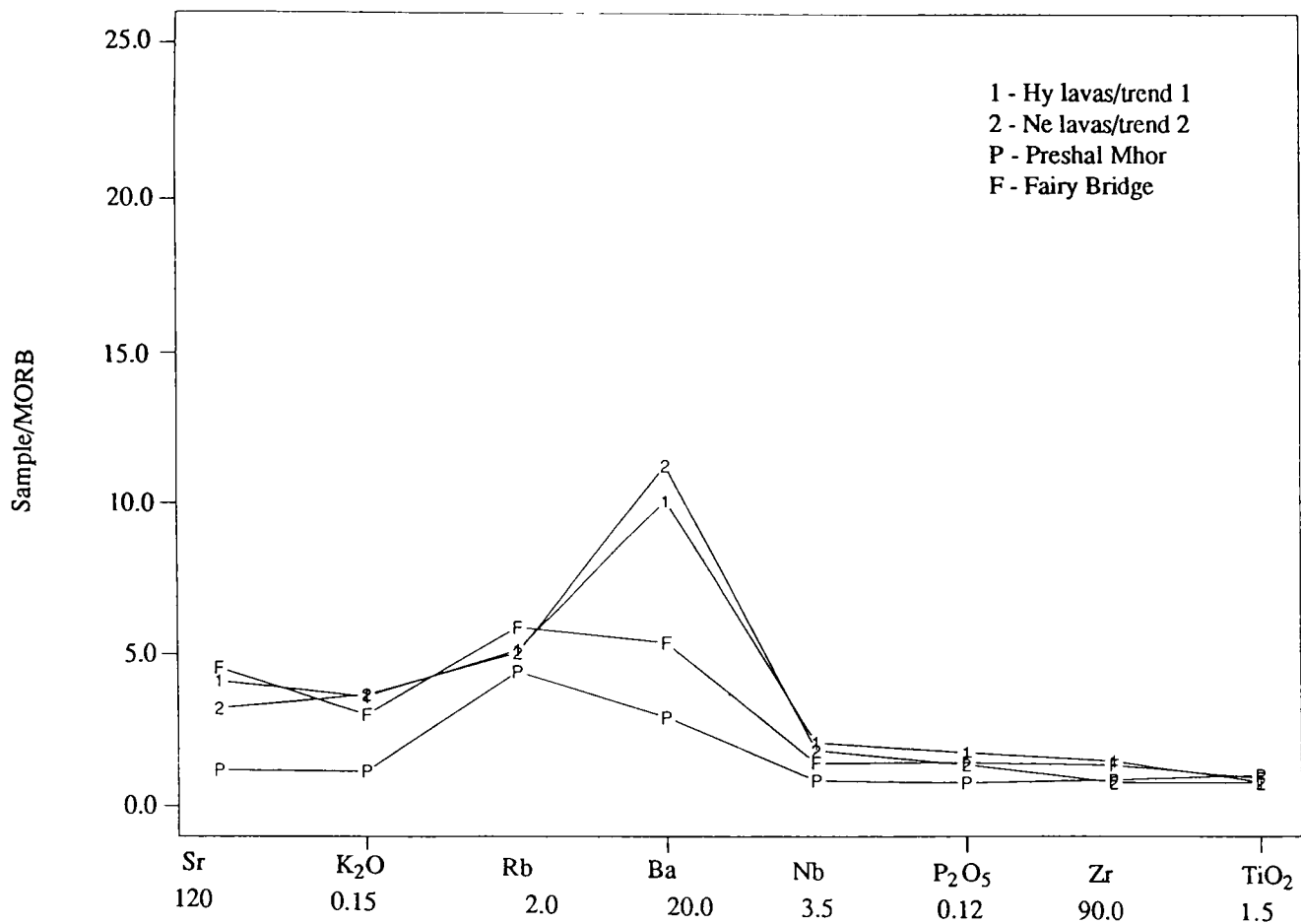


Figure 4.19 MORB normalisation diagram for the three Skye magma types, averages of samples from the SMLS trends 1 (Ne normative) and 2 (Hy normative) are shown separately.

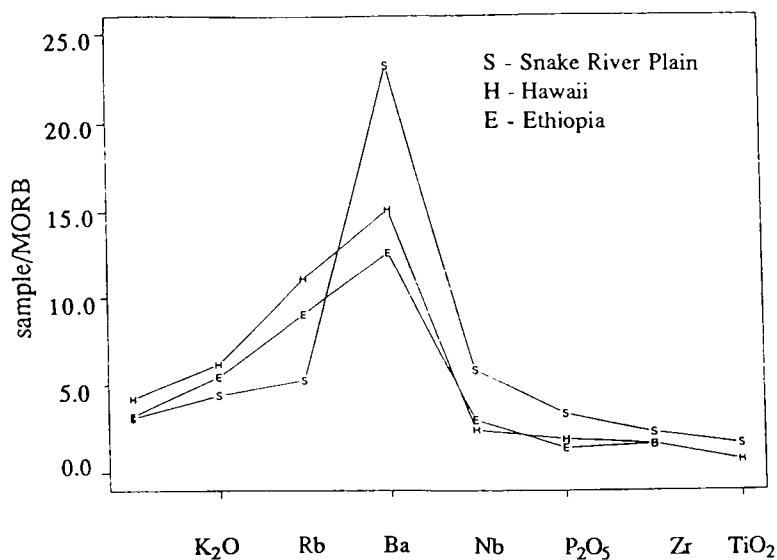
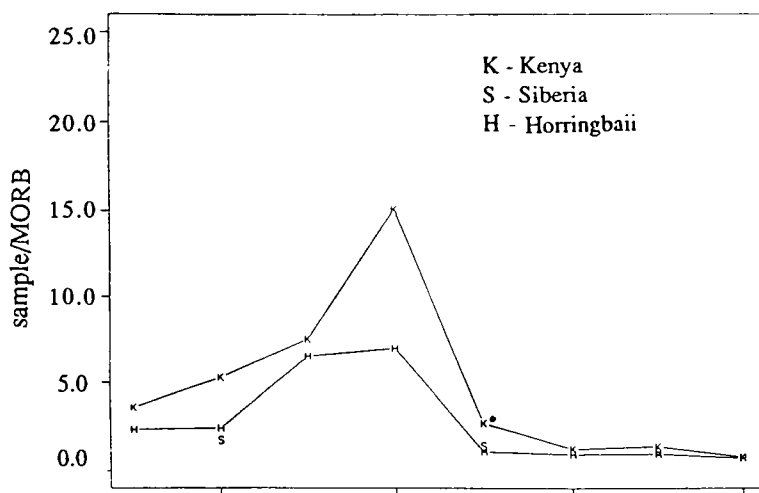
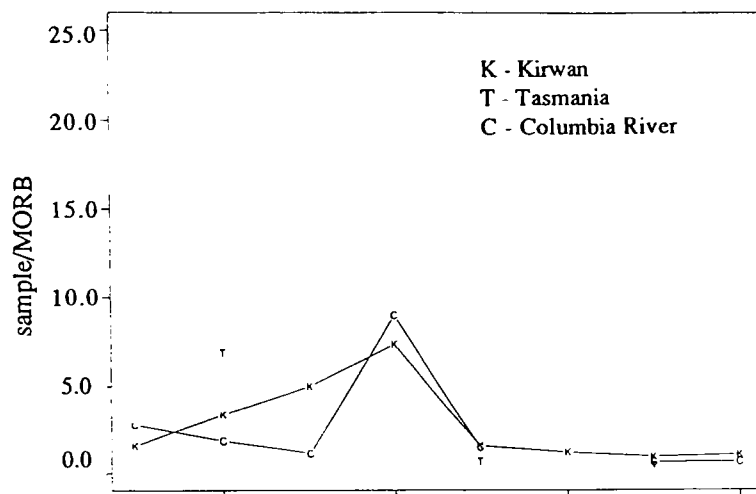
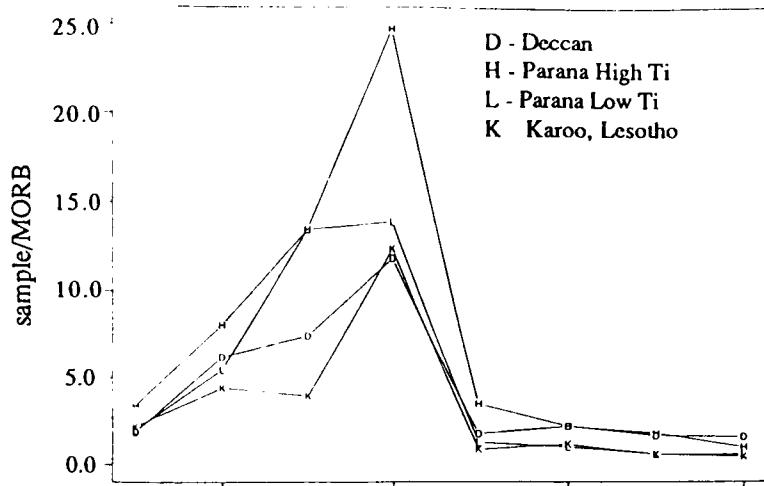


Figure 4.20

..... continued

(caption on next page)

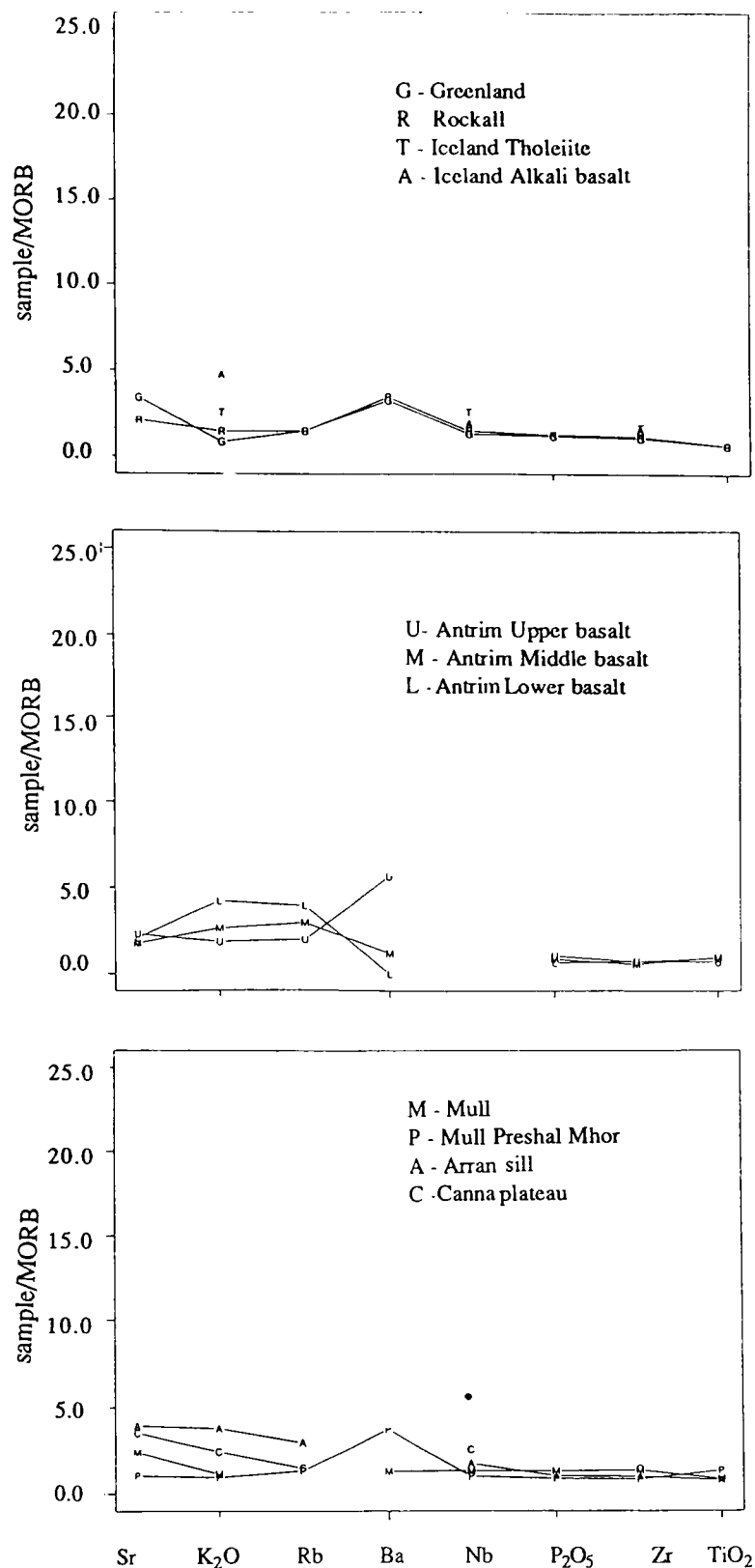


Figure 4.20 MORB normalisation diagrams for basalts from other continental flood basalt provinces, the North Atlantic Tertiary Province, and the British Tertiary Igneous Province. (Line segments are missing where data were unavailable in the literature, data are from Table 4.10.)

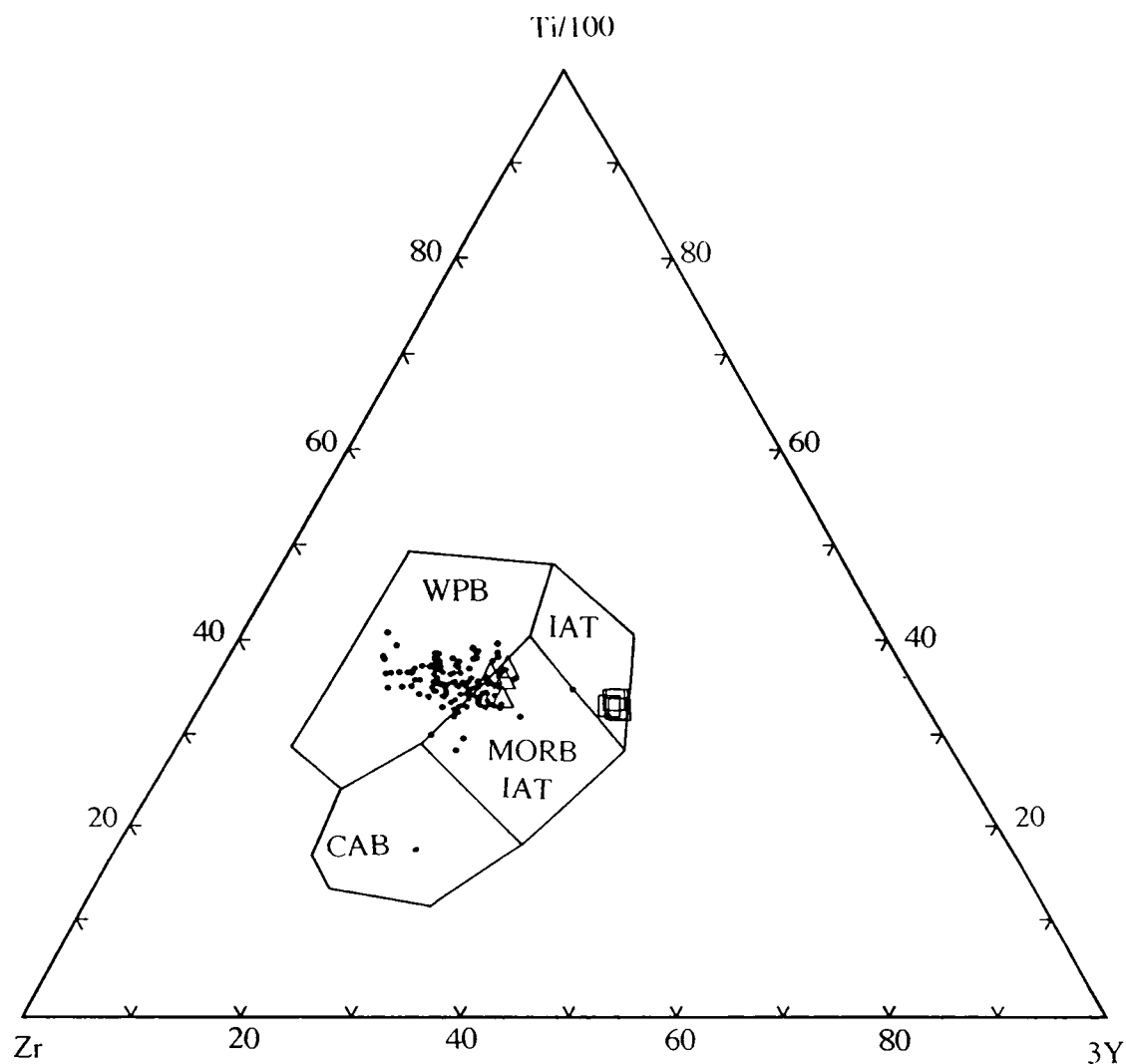


Figure 4.21 Palaeotectonic setting diagram $\text{Ti}/100$ Zr 3Y
 The three Skye magma types are shown, symbols as in Figure 4.6.

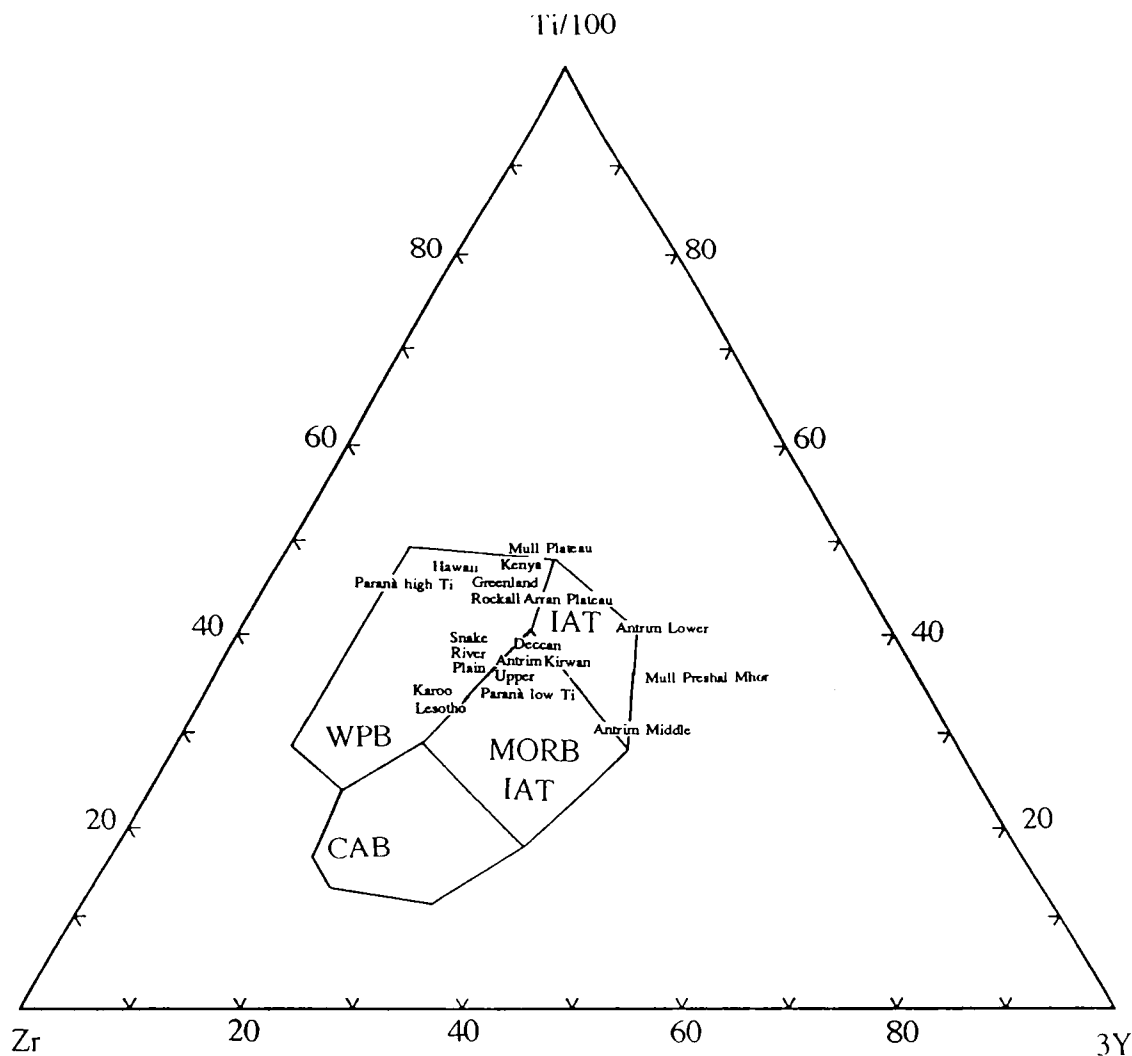


Figure 4.22 Palaeotectonic setting diagram Ti/100 Zr 3Y. Basalts from other continental flood basalt provinces, the North Atlantic Tertiary Province, and the British Tertiary Igneous Province are labelled (the first letter of each label marks the composition of that sample). (Horringbairi sample plots in the same position as the Greenland sample)

	SMLS Ne-normative	SMLS Hy-normative	Preshal Mhor	Fairy Bridge	Big feldspar lava	Sill
SiO ₂	44.57 - 46.41	46.64 - 63.44	46.81 - 47.91	46.65 - 44.98	48.60	44.58
TiO ₂	2.49 - 3.52	1.40 - 0.75	0.99 - 1.30	1.18 - 1.96	1.47	1.21
Al ₂ O ₃	12.39 - 17.11	13.87 - 17.85	15.98 - 14.02	13.63 - 16.15	18.89	11.21
Fe ₂ O ₃ T	14.35 - 15.92	12.52 - 3.79	12.45 - 14.02	12.26 - 14.63	11.67	13.63
MnO	0.17 - 0.23	0.18 - 0.14	0.21 - 0.22	0.14 - 0.19	0.16	0.19
MgO	13.16 - 4.41	13.65 - 0.64	8.75 - 7.33	14.73 - 9.55	4.66	19.70
CaO	9.57 - 7.14	8.80 - 1.38	12.81 - 12.70	9.01 - 9.96	9.58	7.07
Na ₂ O	1.94 - 4.05	2.27 - 6.37	1.75 - 2.13	1.85 - 2.09	3.69	1.77
K ₂ O	0.84 - 0.67	0.36 - 5.36	0.08 - 0.17	0.20 - 0.27	0.94	0.22
P ₂ O ₅	0.33 - 0.50	0.15 - 0.23	0.07 - 0.10	0.10 - 0.16	0.27	0.12
Qtz	0.00 - 0.00	0.00 - 0.70	0.00 - 0.00	0.00 - 0.00	0.00	0.00
Or	5.11 - 4.03	2.17 - 32.30	0.54 - 1.08	1.32 - 3.07	5.65	1.32
Ab	15.39 - 33.18	18.95 - 53.98	14.81 - 18.02	15.65 - 33.08	28.60	14.98
An	22.55 - 26.46	26.19 - 4.30	35.52 - 28.20	28.24 - 27.77	32.21	22.00
Ne	0.60 - 0.59	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	1.60	0.00
Di	18.36 - 4.76	12.82 - 0.88	22.29 - 27.79	12.59 - 4.83	11.26	9.84
Hy	0.00 - 0.00	4.83 - 5.85	11.24 - 13.25	15.93 - 9.92	0.00	5.91
Ol	28.70 - 20.30	28.16 - 0.00	7.47 - 1.84	17.57 - 4.43	14.57	39.01
Il	4.73 - 6.69	2.62 - 1.44	1.18 - 2.49	2.26 - 6.53	2.79	2.30
Mt	2.48 - 3.00	2.33 - 0.71	5.15 - 6.09	5.15 - 8.34	2.02	2.93
Ap	0.79 - 1.16	0.35 - 0.56	0.19 - 0.25	0.25 - 0.95	0.65	0.28
Cc	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00	0.00

Table 4.1 Representative major element and CIPW normative compositions for the Skye lavas, this study.
(All Fe expressed as Fe₂O₃, all major element analyses recalculated to 100% for comparative studies)

	SMLS Ne-normative		SMLS Hy-normative		Preshal Mhor	Fairy Bridge	Big feldspar lava	SIII
Zn	99.90	70.40	84.50 - 111.60		71.20 - 84.20	70.30 - 84.50	66.80	79.80
Cu	88.20	15.00	130.50	4.70	148.90 - 170.80	100.80 - 109.90	46.60	86.00
Ni	407.90	31.00	413.90	1.50	94.00 - 72.30	473.00 - 189.70	45.60	738.80
Co	70.70	41.40	65.40	0.00	58.60 - 58.50	71.90 - 66.70	39.40	88.50
Cr	670.00	6.10	706.10	0.90	226.70 - 125.00	880.10 - 101.50	66.40	1566.90
V	328.10	144.6	237.30	21.50	246.00 - 327.70	214.30 - 278.60	192.40	193.10
Ba	506.50	280.40	124.70	-3055.40	60.00 - 57.60	81.00 - 210.30	816.20	121.00
Ga	20.40	16.40	19.20	21.90	17.80 - 18.40	15.40 - 17.40	21.40	15.60
Rb	17.90	16.70	11.30	80.20	6.80 - 8.90	5.90 - 13.10	16.70	9.80
Sr	671.60	604.50	220.60	241.00	121.30 - 144.80	692.70 - 914.80	765.30	238.80
Y	18.00	51.90	17.50	39.00	22.10 - 30.30	17.20 - 27.20	24.10	14.10
Zr	185.70	293.6	100.90	450.30	51.00 - 69.50	74.50 - 116.20	104.70	76.00
Nb	15.50	17.70	4.80	21.00	3.00 - 4.60	3.40 - 5.40	4.60	4.10
Pb	4.90	5.40	0.30	21.60	2.60 - 0.90	1.50 - 2.60	2.30	1.20
Th	2.40	3.10	1.20	2.30	1.40 - 0.10	0.00 - 2.70	0.60	2.50
U	1.30	0.00	0.80	0.20	0.00 - 0.00	0.20 - 0.00	0.00	0.00

Table 4.2 Representative trace element compositions for the Skye lavas, this study.

	Trend 1	Trend 2
SiO₂	44.60 - 45.10	46.30 - 47.80
TiO₂	2.20 2.50	1.40 1.70
Al₂O₃	14.00 - 17.00	14.00 - 17.00
FeO+Fe₂O₃	12.41 - 14.10	10.70 - 12.60
MgO	8.10 - 10.30	6.90 8.40
CaO	8.50 - 9.20	9.30 - 10.30
Na₂O	3.10 - 3.40	2.60 3.00
K₂O	0.20 - 0.50	0.30 - 0.90
P₂O₅	0.25 - 0.27	0.18 0.25

Table 4.3 The major element ranges of the two divisions of the SMLS.
 (element concentrations are in weight percents, only aphyric samples were used
 in determining the ranges)
 (Data from Thompson et al., 1972).

	SMLS Trend 1	SMLS Trend 2	Preshal Mhor	Fairy Bridge	Basal pillow lava	Big feldspar lava
SiO ₂	45.17 - 59.14	46.84 - 62.14	47.55	47.12	50.47	50.85
TiO ₂	2.08 - 0.82	1.54 - 0.91	1.13	1.38	1.15	1.29
Al ₂ O ₃	14.80 - 16.77	14.05 - 16.29	15.07	17.22	15.59	17.57
Fe ₂ O ₃ T	13.76 - 8.81	12.01 - 5.30	11.97	12.97	10.99	10.93
MnO	0.20 - 0.28	0.18 - 0.13	0.26	0.19	0.11	0.10
MgO	10.77 - 0.96	12.90 - 1.29	9.14	7.72	7.97	5.25
CaO	9.81 2.93	9.85 - 2.09	12.79	9.77	10.99	9.41
NaO ₂	2.75 - 6.08	2.12 - 5.79	1.89	3.02	2.39	3.44
K ₂ O	0.39 - 3.54	0.40 - 5.73	0.10	0.43	0.24	0.89
P ₂ O ₅	0.26 - 0.67	0.11 - 0.54	0.10	0.18	0.09	0.26
Qtz	0.00 - 1.55	0.00 - 2.25	0.00	0.00	0.00	0.00
Or	2.31 20.56	2.36 - 33.03	0.59	2.54	1.36	5.08
Ab	18.74 - 50.60	17.77 - 47.81	15.82	25.12	19.63	27.92
An	26.77 - 7.87	27.43 - 1.43	32.02	31.01	30.05	28.60
Ne	2.41 0.00	0.00 - 0.00	0.00	0.19	0.00	0.00
Di	16.02 - 1.32	16.14 - 4.20	23.77	12.09	18.02	11.95
Hy	0.00 - 9.11	6.05 - 2.29	13.21	0.00	21.18	11.40
Ol	25.43 - 0.00	23.13 - 0.00	4.80	21.34	1.17	4.32
Il	3.93 - 1.54	2.91 1.69	2.13	2.60	2.11	2.36
Mt	2.18 - 3.63	2.18 - 3.63	5.54	2.18	2.18	2.90
Ap	0.57 1.44	0.24 - 1.16	0.22	0.39	0.20	0.55
Cc	0.11 0.21	0.11 0.00	0.23	0.14	0.00	0.00

Table 4.4 Representative major element and CIPW normative compositions for the Skye lavas.

(All Fe expressed as Fe₂O₃, all major element analyses recalculated to 100% for comparative studies)

Data sources: Thompson et al., 1972; Esson et al., 1975; Thompson et al., 1980)

	SMLS Trend 1	SMLS Trend 2	Preshal Mhor	Fairy Bridge	Basal pillow lava	Big feldspar lava
Ba	108.0 -1790.0	127.0 -2289.0	33.0		-	-
Rb	6.0 - 70.0	9.0 - 79.0	1.0	0.0	1.0	7.0
Sr	455.0 - 481.0	279.0 - 271.0	123.0	420.0	293.0	807.0
Y	20.0 61.0	23.0 34.0	26.0	27.0	18.0	26.0
Zr	137.0 - 405.0	94.0 388.0	60.0	68.0	104.0	106.0
Nb	9.0 59.0	- 22.0	3.0	6.0	6.0	7.0
Th	0.8 - 6.5	0.7 2.9	0.3	0.3	1.1	1.1
Ta	0.7 4.6	0.2 1.1	0.2	0.2	0.3	0.4
Hf	3.6 11.0	2.4 10.0	1.6	2.0	3.0	3.2

Table 4.5 Representative trace element compositions for the Skye lavas.
(Data sources: Thompson et al., 1980; Esson et al., 1975; Thompson et al., 1982)

	Trend 1	Trend 2
K₂O	0.29	0.45
TiO₂	2.49	1.64
P₂O₅	0.27	0.22
Rb	1.00	1.00
Sr	583.00	711.00
Ba	70.00	177.00
Nb	8.00	3.00
Ta	0.42	0.18
Zr	176.00	115.00
Hf	4.94	3.03
Th	0.59	0.28

Table 4.6 Trace element compositions of two SMLS basalts both with
 $\text{FeO}+\text{Fe}_2\text{O}_3/\text{FeO}+\text{Fe}_2\text{O}_3+\text{MgO} = 0.63$.
(similar variations in trace element compositions are observed in the data-set for a range of Fe/Mg ratios)
(Samples SK940, SK970. Data sources: Thompson et al., 1972; Thompson et al., 1980; Thompson et al., 1982)

	Ne-normative	Hy-normative
K₂O	0.31	0.70
TiO₂	2.50	1.40
P₂O₅	0.30	0.23
Rb	14.80	12.70
Sr	614.80	352.80
Ba	273.60	264.60
Nb	10.50	4.10
Zr	189.10	91.00
Th	2.30	0.90

Table 4.7 Trace element compositions of two SMLS basalts both with $\text{FeO}+\text{Fe}_2\text{O}_3/\text{FeO}+\text{Fe}_2\text{O}_3+\text{MgO} = 0.61$, this study.
(similar variations in trace element compositions are observed in the data set for a range of Fe/Mg ratios)
(Samples JHS33, JHS84)

	SMLS REE Group 1	SMLS REE Group 2	Preshal Mhor	Fairy Bridge
La	14.06	6.53	2.90	4.52
Ce	34.82	17.80	7.79	11.60
Pr	4.78	2.61	1.25	1.76
Nd	23.49	12.41	8.25	10.24
Sm	5.10	3.36	2.87	2.75
Eu	1.68	1.17	1.20	1.05
Gd	4.75	3.38	4.34	3.27
Dy	3.92	1.91	5.27	3.2
Ho	0.66	0.26	0.99	0.55
Er	1.68	0.52	2.65	1.40
Yb	1.28	0.18	2.27	1.11
Lu	0.20	0.03	0.38	0.18

Table 4.8 Representative rare earth element concentrations for the Skye lavas, this study.
(element concentrations are in ppm).

	SMLS Plateau Ne	SMLS Plateau Hy	Skye Preshal Mhor	Skye Fairy Bridge	Mull Plateau	Mull Preshal Mhor	Arran sill	Canna Plateau	Antrim Plateau Lower Basalt	Antrim Plateau Middle Basalt	Antrim Plateau Upper Basalt
SiO ₂	46.03	47.82	47.99	44.27	46.09	48.39	48.50	46.61	48.55	51.33	49.24
TiO ₂	2.22	1.17	1.29	2.02	2.08	1.27	1.51	2.24	1.19	0.88	1.17
Al ₂ O ₃	16.34	16.57	14.08	15.60	15.57	15.55	15.99	16.33	17.21	14.42	16.34
Fe ₂ O ₃ T	14.52	12.77	13.94	13.81	13.08	14.38	11.86	14.09	11.76	11.21	11.67
MnO	0.17	0.17	0.22	0.19	0.18	0.23	0.15	0.19	0.15	0.15	0.15
MgO	7.42	7.41	7.34	10.89	8.67	6.20	8.85	7.04	7.82	7.91	8.09
CaO	9.30	9.90	12.66	10.06	11.63	11.25	8.87	9.24	9.93	11.65	10.71
Na ₂ O	3.13	2.80	2.12	2.45	2.32	2.46	3.47	3.57	2.72	2.05	2.33
K ₂ O	0.54	0.55	0.17	0.45	0.17	0.14	0.58	0.38	0.67	0.40	0.29
P ₂ O ₅	0.25	0.22	0.10	0.17	0.16	0.12	0.21	0.31			
Zn	85.45	80.31	83.60	75.20					63.00	67.00	73.00
Cu	78.70	83.19	172.45	143.70					57.00	99.00	52.00
Ni	144.60	143.05	72.75	237.10	152.00	73.00		81.00	120.00	52.00	134.00
Cr	117.45	206.70	121.95	181.50	260.00	47.00			160.00	132.00	245.00
V	256.05	262.55	324.50	305.50					176.00	212.00	160.00
Ba	201.85	225.25	58.50	107.70	26.00	75.00			0.00	120.00	0.00
Rb	10.30	10.10	8.85	11.80		2.70	6.00	3.00	8.00	6.00	4.00
Sr	494.15	386.86	141.85	546.90	293.00	125.00	475.00	426.00	251.00	213.00	280.00
Y	23.80	22.98	30.35	27.20	25.00	40.00	23.00		28.00	30.00	22.00
Zr	158.30	122.22	68.85	128.30	119.00	78.00	92.00		61.00	79.00	96.00
Pb	3.35	3.20	1.90	0.00					0.00	24.00	114.00

Table 4.9 Representative major and trace element analyses for lavas from the British Tertiary Igneous Province.

(Data sources: Skye data, this study (Ne average of 2 analyses, Hy 2 average of 19 analyses, Preshal Mhor average of 2 analyses; Mull, Arran, and Canna, Thompson, 1982; Antrim, Lyle, 1980)

	Green land	Rockall Trough	Iceland tholeiite	Iceland alkali basalt	Paraná high-Ti	Paraná low-Ti	Karoo Lesotho	Kirwan	Tasmnia	Snake River Plain	Colombia River
SiO ₂	48.76	46.18	47.28	46.82	50.82	52.50	50.61	51.11	53.30	45.57	48.89
TiO ₂	1.73	1.88	2.54	2.40	2.79	0.96	0.95	1.45	0.65	3.31	0.96
Al ₂ O ₃	12.98	15.53	15.00	15.51	14.15	15.43	14.46	14.87	15.40	14.53	16.97
Fe ₂ O ₃ T	14.62	13.41	13.97	12.64	13.49	9.33	12.09	12.52	9.94	16.52	11.03
MnO	0.16	0.17	0.21	0.22	0.20	0.16	0.16	0.20	0.15	0.21	0.20
MgO	8.25	10.05	6.78	7.50	4.81	7.63	7.89	5.85	6.72	6.41	7.89
CaO	11.66	7.94	10.95	11.06	9.40	10.87	10.69	10.52	11.06	9.30	11.10
Na ₂ O	1.55	4.42	2.56	2.90	2.70	2.14	2.32	2.77	1.65	2.82	2.49
K ₂ O	0.14	0.23	0.38	0.71	1.21	0.82	0.68	0.51	1.03	0.65	0.28
P ₂ O ₅	0.17	0.19	0.31	0.23	0.43	0.16	0.11	0.19	0.08	0.69	0.18
Zn		85.00								131.00	
Cu		60.00								50.00	
Ni		249.00			58.00	123.00	90.00			44.00	
Cr		451.00			96.00	314.00	350.00			107.00	156.00
V		274.00					350.00		-		
Ba	65.00	69.00			490.00	280.00	250.00	147.00		464.00	180.00
Rb	3.00	3.00			27.00	27.00	8.00	10.00		10.40	2.30
Sr	407.00	251.00			404.00	232.00	260.00	189.00		370.00	338.00
Y	20.00	20.00			32.00	19.00	15.00	32.00		48.00	20.00
Zr	109.00	117.00			205.00	94.00	109.00	109.00		295.00	
Pb		7.00								3.00	4.00

Table 4.10 continued (caption on the next page)

	Deccan	Kenya	Siberia	Hawaii	Ethiopia	Horring -baal	E-type MORB	N-type MORB
SiO ₂	50.56	47.50	47.37	45.96	47.25	46.86	51.18	50.40
TiO ₂	2.57	2.09	1.66	2.38	2.32	1.45	1.69	1.36
Al ₂ O ₃	13.38	14.88	14.06	14.05	14.08	15.25	16.01	15.19
Fe ₂ O ₃ T	13.79	12.74	14.41	13.77	12.22	13.39	9.40	10.01
MnO	0.17	0.20	0.30	0.19	0.19	0.19	0.16	0.18
MgO	5.12	6.88	8.07	9.39	9.85	7.84	6.90	8.96
CaO	9.62	11.94	11.54	10.24	10.19	12.29	11.49	11.43
Na ₂ O	2.65	2.67	2.17	2.82	2.73	2.28	2.74	2.30
K ₂ O	0.93	0.79	0.26	0.92	0.92	0.36	0.43	0.09
P ₂ O ₅	0.22	0.32	0.17	0.28	0.35	0.13	0.15	0.14
Zn	149.00							
Cu	202.00							
Ni	44.00	76.00			75.00		132.00	177.00
Cr	44.00	83.00			370.00		225.00	346.00
V								
Ba	239.00	300.00		300.00	250.00	139.00	86.00	<20.00
Rb	15.00	15.00		22.00	18.00	13.00	10.30	2.30
Sr		428.00		500.00	382.00	279.00	155.00	98.00
Y	219.00	24.00		21.00		22.00	39.00	37.00
Zr	50.00							
		112.00		166.00	121.00	84.00	121.00	97.00
Pb	203.00							
	-		-	1.00	-	-	-	-

Table 4.10 Representative and average major and trace element analyses for lavas from the North Atlantic Tertiary Province and other Continental Flood Basalt Provinces.

(Data sources: Greenland, Gill et al., 1988; Rockall, Morton et al., 1988; Deccan, Paraná, Snake River Plain, Kenya, Hawaii, Ethiopia, Wilson, 1989; Karoo, Iceland, Colombia River, BSVP, 1981; Kirwan (Antarctica), Tasmania, Horringsbaai (S.Africa), in Mitchell, 1988; E-type and N-type MORB, Humphris et al., 1985)

CHAPTER 5

ALTERATION AND BOLE FORMATION

5.1 Introduction

In this chapter the effect of post-consolidation alteration on the composition and petrography of the lavas will be assessed, since before considering the genesis of the lavas in terms of pre-eruptive processes it is essential to know the extent to which late-stage alteration may have affected them.

A typical Skye lava flow comprises four zones: a basal amygdaloidal layer, a massive central portion possibly showing columnar jointing, a purple rotted amygdaloidal upper layer, and a capping red or brown bole (fossil soil horizon).

In the absence of any compositional or petrographic evidence to suggest that the boles are not sub-aerially weathered flow tops (e.g. such horizons could, alternatively, be the products of alteration of pyroclastic material) it has been assumed that the transition from the massive central portion of the flow to the bole is a continuum from reasonably compositionally fresh to extremely altered basalt. The identification of secondary minerals in thin sections of the massive central portions of the lava flows indicates that most of the lavas have been subjected to varying degrees of post-consolidation alteration (Chapter 3, Petrography and Mineralogy, Plates 3.8, 3.10).

The hydrothermal alteration of the Skye lavas has been attributed to their burial in a rapidly accumulating lava pile through which hot fluids were circulating (King, 1976).

5.2 Previous work

A detailed study of the secondary minerals of the Skye lavas and their zeolite zonation patterns was made by King (1976). His work concentrated on the zeolites. He proposed that the formation of the zeolites was caused by burial in the rapidly thickening lava pile through which hydrothermal fluids were circulating, and not the products of circulation of fluids associated with the gabbroic Cuillin complex to the south of the lavas. He concluded this because secondary minerals associated with faults caused by the Cuillin complex occur as overgrowths on amygdales already present in the lavas. From determining to what depth the lavas would have to have been buried for the different zeolite zones (thomsonite-chabasite, analcite, mesolite and laumontite) to form, he calculated that the lava pile may have been up to 2000 m thick (as compared with the present day 700 m estimated maximum thickness). His summary of secondary mineralogies and that of the present study are presented in Table 5.1.

King proposed that vertical movement of fluids was subordinate to lateral movement. The composition of a lava flow was, therefore, important in the determination of the secondary mineral assemblage because element movement occurred predominantly on a local scale, thus overriding any regional compositional pattern. From a study of eight lava flow profiles and one bole, he described the compositional variations occurring during alteration of the lavas. He grouped elements into those which increase in concentration with increasing alteration up flow, H_2O^+ , Fe_2O_3 , Al_2O_3 , those which decrease in concentration up flow, SiO_2 , MgO , CaO , Na_2O , Rb , Sr , Ba , Ga , Y , and those whose concentration was constant throughout the flow, K_2O , TiO_2 , MnO , P_2O_5 , Zr , Nb , Cr , Ni . Lateritization of the flow top to produce a bole was noted to leach SiO_2 , CaO , MgO , but not Al_2O_3 , TiO_2 , and Fe_2O_3 . King stated that there were three significant aspects of chemical alteration of the Skye lavas. The first was the irregular distribution of elements in flows implying rearrangement of components at a later stage than primary inherited heterogeneities. The second was that the overall chemistry of fresh flow centres and altered bases and tops suggested that introduction and removal of components was subordinate to

redistribution of components. Finally, he proposed that the alteration took place via a fluid which was responsible for both mass and heat transfer.

The extent of the redistribution of components was assumed to be a function of the rate of dissolution of the primary phase and growth of secondary phases compared with the flow rates of the aqueous fluids.

King (1976) concluded that the main factors affecting the formation of secondary minerals were the availability of a particular component in the original rock, the mineral-solution interaction and the PH_2O and temperature at which the reaction occurred, and the time available for the reaction to occur. Finally, he emphasised the importance of the composition of the fluid, the rate of water flow, and the permeability and porosity of the host rock.

5.3 Assessment of the degree of alteration

In this study the amount of alteration to which the lavas have been subjected has been assessed in two ways. The first of which was the measurement of structurally bound water (H_2O^+). The method for doing this is outlined in Appendix B. H_2O^+ content is often used as an indication of alteration in volcanic rocks (Floyd, 1976; Hart *et al.*, 1974; Humphris and Thompson, 1978; Thompson, 1973; Wolery and Sleep, 1976). The second method was to study the samples in thin section and visually estimate the modal proportion of secondary minerals in their groundmasses. In this way an alteration index similar to that devised by Sloman (1987) was established. Sloman ranked her samples from 1 to 6, based on the modal proportion of secondary minerals in thin section. She found that element concentrations and isotopic ratios varied more systematically with the petrographic alteration index (A.I) than with the more conventional measure of alteration, H_2O^+ . In the present study the Skye lavas have been ranked from 1 to 10, 1 representing an apparently completely fresh basalt, and 10 a bole. The alteration index and H_2O^+ of the samples are presented in the data tables in Appendix B.

There is a broad positive correlation between the two measures of alteration, petrographic A.I and H_2O+ (Figure 5.1). The scatter shown in Figure 5.1 is reduced when the two variables of a particular lava flow, the sub-aerially weathered top of the flow, and the overlying flow are plotted (Figure 5.2)(such profiles are henceforth referred to as lava flow-bole-lava flow profiles). There appears to be little difference in how element concentrations and isotopic ratios vary with A.I and H_2O+ (Figures 5.3 and 5.4); therefore, the latter, more conventional, measure of alteration is used in the present study. To try to eliminate the effects of post-consolidation alteration on the composition of the lava, only samples with less than 3.5% H_2O+ were used in the petrogenetic studies in Chapter 6, Fractional Crystallisation, Chapter 7, Crustal Contamination, and Chapter 8, Magma Generation.

5.4 The effect of alteration and bole formation on major and trace elements

In the present study fifty lava flow and overlying bole sample pairs were collected. The average basalt and average bole element concentrations are compared here to try to assess the behaviour of elements during the bole formation process (Figure 5.5). Redistribution of elements within the bole layer may occur on a large lateral scale since relative to the over-lying and under-lying basalts the boles form a porous layer which could act as a conduit for any fluids within the lava pile. It is assumed that the process of bole formation essentially involves the removal of elements in solution. The removal may be a complex process involving either straight aqueous solution, or mineral breakdown followed by fixing of the elements in secondary minerals such as clays, or both. Whatever the complexities of the process each element shows an "effective solubility". High solubility implies strong depletion in the bole relative to the underlying flow. In contrast relatively insoluble elements are concentrated in the bole as other elements are removed. Thus, the elements showing the greatest increases in concentration in the bole relative to the underlying flow are assumed to be the least soluble. If it is assumed that

such elements are completely insoluble their concentrations can be used to estimate the minimum amount of the original rock which has been removed in solution. For example, Widdowson (1990) found that, in his study of the regional laterites of the Deccan province, Cr was usually the element showing greatest concentration in the laterite relative to the bed-rock. A laterite showing double the concentration of Cr relative to the bed-rock was assumed to be formed by the removal of at least 50% of the original mass of fresh rock.

Widdowson (1990) carried out very detailed studies on the Deccan laterites, which unfortunately cannot be emulated in the present work. He was able to arrange elements in a sequence of relative effective solubilities. It is emphasised that because he studied laterites developed on a regional scale after the complete cessation of vulcanism, the lateritization process was far more advanced than anything demonstrated by the Skye boles. For example, extreme Deccan laterites consist almost entirely of Al- and Fe-oxides, having been almost completely stripped of Si, Ca, Mg and other important elements. In the Skye case, although it is clear for example that Si has on average been removed, the lowest values for SiO_2 found in the boles are ca. 42.5 wt% as compared with ca. 47 wt% in the under-lying flow. Evidently the lateritization process is much less advanced on Skye - and climatic differences aside - this is attributed to there being relatively little time available between the eruption of one flow and the next. However, as the following study shows, the lateritization processes in the two provinces do seem to have many features in common.

The results of the element solubility study of the Skye lavas can be summarised as follows: components which increase in concentration in the bole relative to the underlying flow are TiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , Zn, Cu, Ni, Cr, Ga, Rb, Y, Zr, Nb, Th, U, and H_2O^+ . Those that decrease in concentration in the bole relative to the underlying flow are SiO_2 , MgO, CaO, Na_2O , P_2O_5 , Co, V, Ba, Sr (Figure 5.5). It appears that Al_2O_3 behaves in a more complex way than many other elements increasing in concentration in the average bole relative to the average basalt despite being expected to be mobilised during the alteration of the basalts. One

explanation is that Al is initially mobilised and subsequently held in secondary clay minerals and zeolites.

In attempting to quantify the relative solubilities of the different elements, the question of whether the element concentrations were normally distributed was investigated, since skewed data may produce anomalous results if the averages of the two data-sets are compared. In the bole data-set some elements have a distinct skew in the distribution of their concentration. Those elements enriched by the bole formation process are skewed towards high values and those depleted by the bole formation process are skewed towards low values. Thus the skews emphasise the geochemical effects of the bole formation process. Nevertheless enrichment factors were calculated (enrichment factor = conc in average bole/conc in average basalt). Thus it was possible to rank the elements from least soluble (most enriched) to most soluble (most depleted) (Table 5.2). If it is assumed that bole formation essentially involves the removal of elements, the amount of material removed can be calculated from the enrichment factor of the most enriched, least soluble element. Pb has an enrichment factor of 4.364 which corresponds to removal of 77% of the original rock. However, in the zone of weathering Pb readily forms solute cations which may either react with suitable anions to form insoluble compounds, or take part in processes of absorption and ionic exchange with the insoluble constituents of the soil minerals, particularly the clay fraction (Goldschmidt, 1958). So it is not clear whether 77 % of rock has been removed by the bole forming process or whether Pb has been leached from an area larger than an underlying flow and concentrated in the bole. The enrichment factors of other insoluble elements such as Nb and Zr indicate that at least 50 % of the original rock was removed in the bole formation process.

The enrichment factors of the Skye lavas were compared with those of a study of the geochemical effects of weathering and lateritization of the basalts of the Deccan traps, India (Widdowson, 1990) (Table 5.3). Spearman rank correlation coefficients were calculated between the relative solubility ranking of an element in this study and its ranking in Deccan

kaolinitized basalt, altered basalt, bole, weakly lateritized basalt, moderately lateritized basalt, and strongly lateritized basalt. All the correlations were significant above the 95% level but statistically the most significant correlation in the element solubility ranking was between the Deccan bole and the Skye average bole (Table 5.4).

5.5 The effect of alteration and bole formation on mineralogy

The least altered basalts show fresh groundmasses and phenocryst olivine. The most altered basalts, some of which are at zeolite facies metamorphic grade, have olivine which is pseudomorphed by iddingsite, bowlingite, chlorite, Fe oxides and occasionally serpentine, talc, and carbonates; calcic plagioclase is replaced by zeolites, and pyroxene is occasionally replaced by chlorite and hematite (Table 5.1). The boles show almost complete replacement of their primary basaltic mineralogy by clay minerals, but relict phenocryst textures are observed occasionally.

The elements which are soluble during the alteration of the basalts (Al_2O_3 , CaO, and Na_2O) are also those which form the major components of the amygdaloidal zeolites: thomsonite, chabasite, analcite, mesolite, and laumontite (Tables 5.5 and 5.6). This observation supports the theory of King (1976) that introduction of material was subordinate to the local redistribution of material during hydrothermal alteration and lateritization of the lavas.

5.6 Summary and conclusions

A typical Skye lava flow comprises four zones: a basal amygdaloidal layer, a massive, possibly columnar jointed central portion, a purple amygdaloidal upper layer, and a capping red or brown bole (fossil soil horizon). The boles are assumed to be sub-aerially weathered basaltic flow tops.

The presence of secondary minerals indicates most of the lavas have undergone some post-consolidation alteration. The alteration of the lavas is attributed to their burial in a rapidly accumulating lava pile, through which hot fluids were circulating.

The amount of alteration to which the lavas have been subjected was quantified in two ways: the H_2O+ of the sample and the modal proportion of groundmass secondary minerals. There is an extremely good positive correlation between the two measures of alteration.

In a study of lava flow-bole profiles the elements were ordered from most enriched (least soluble) to most depleted (most soluble). The sequence is Pb, Th, Nb, Zr, TiO_2 , Zn, Y, Fe_2O_3 , Cu, Al_2O_3 , Rb, Ga, Cr, Ni, Co, SiO_2 , Sr, V, Ba, Na_2O , MgO, and CaO. The relative solubility rankings of the elements for the Skye boles are comparable to those determined for the Deccan laterites, although the former are obviously a lot less altered than the latter.

Secondary mineralogies show that olivine is pseudomorphed by iddingsite, bowlingite, chlorite, Fe oxides and occasionally serpentine, talc, and carbonates; calcic plagioclase is replaced by zeolites, and pyroxene is occasionally replaced by chlorite and hematite. The boles show almost complete replacement of their primary basaltic mineralogy by clay minerals, but relict phenocryst textures are observed occasionally.

The elements which are soluble during alteration form the main constituents of the amygdaloidal zeolites (Chapter 3, Petrography and Mineralogy).

In conclusion the petrogenetic significance of elements which are soluble during alteration (Si, Al, Ca, Na and Sr and the large ion lithophile elements K, and Rb) should be treated with caution and the Sr isotope data interpreted with care in those samples with high values of A.I. and H_2O+ . In order to try to eliminate the effects of post-consolidation alteration on the composition of the lava only samples with less than 3.5% H_2O+ are used in the petrogenetic studies in the following chapters.

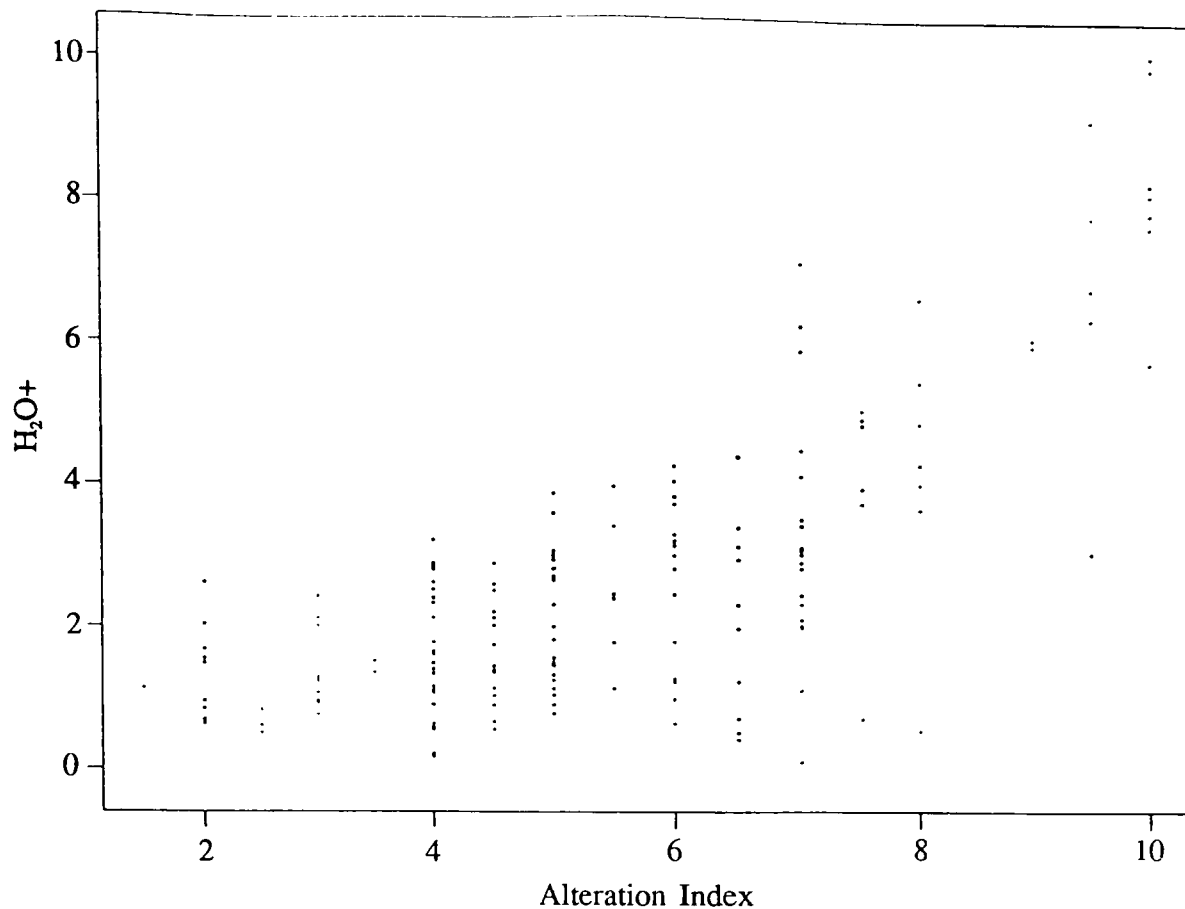


Figure 5.1 H₂O⁺ (in wt%) versus alteration index (A.I) for all the Skye lavas. There is a broad positive correlation between H₂O⁺ and A.I.

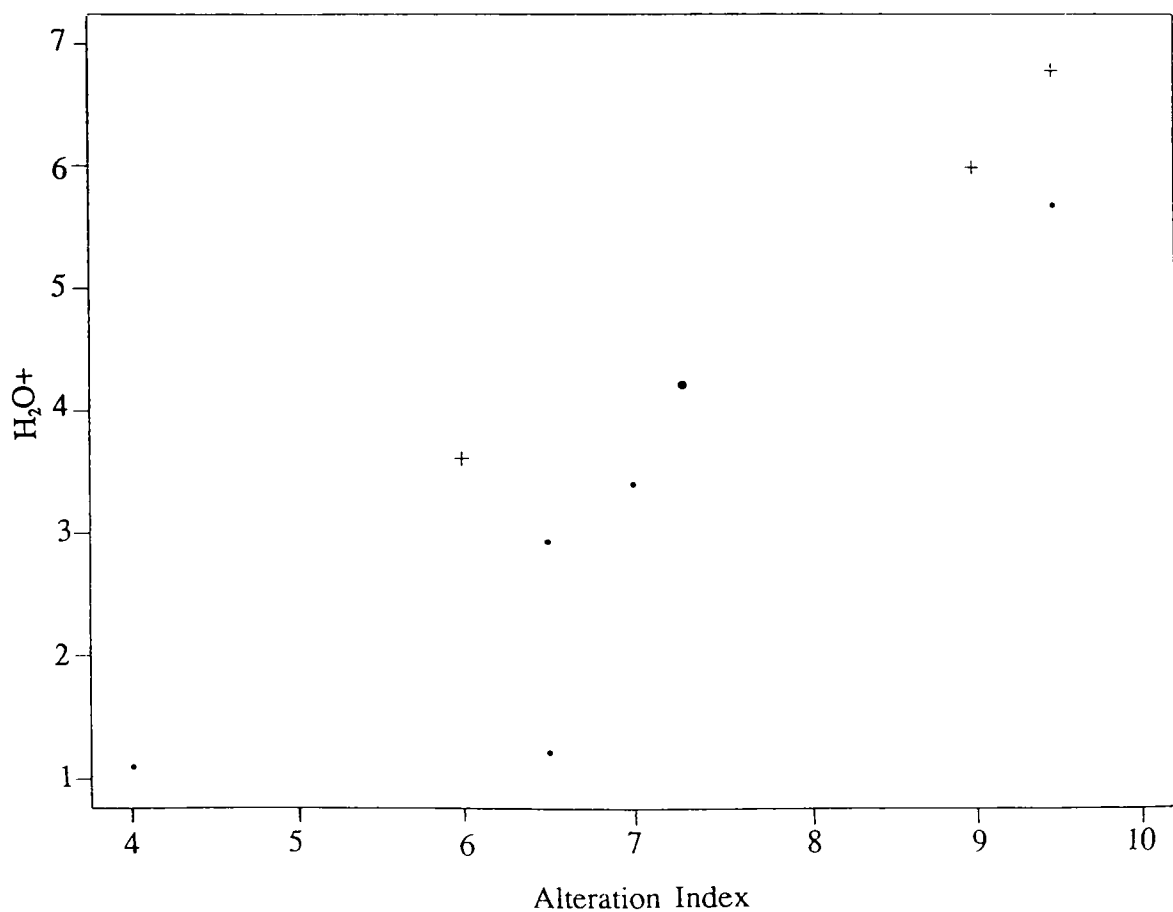


Figure 5.2 H₂O⁺ (in wt%) versus alteration index (A.I) for two flow-bole profiles. (● JHS76-JHS81; + JHS159-JHS163).

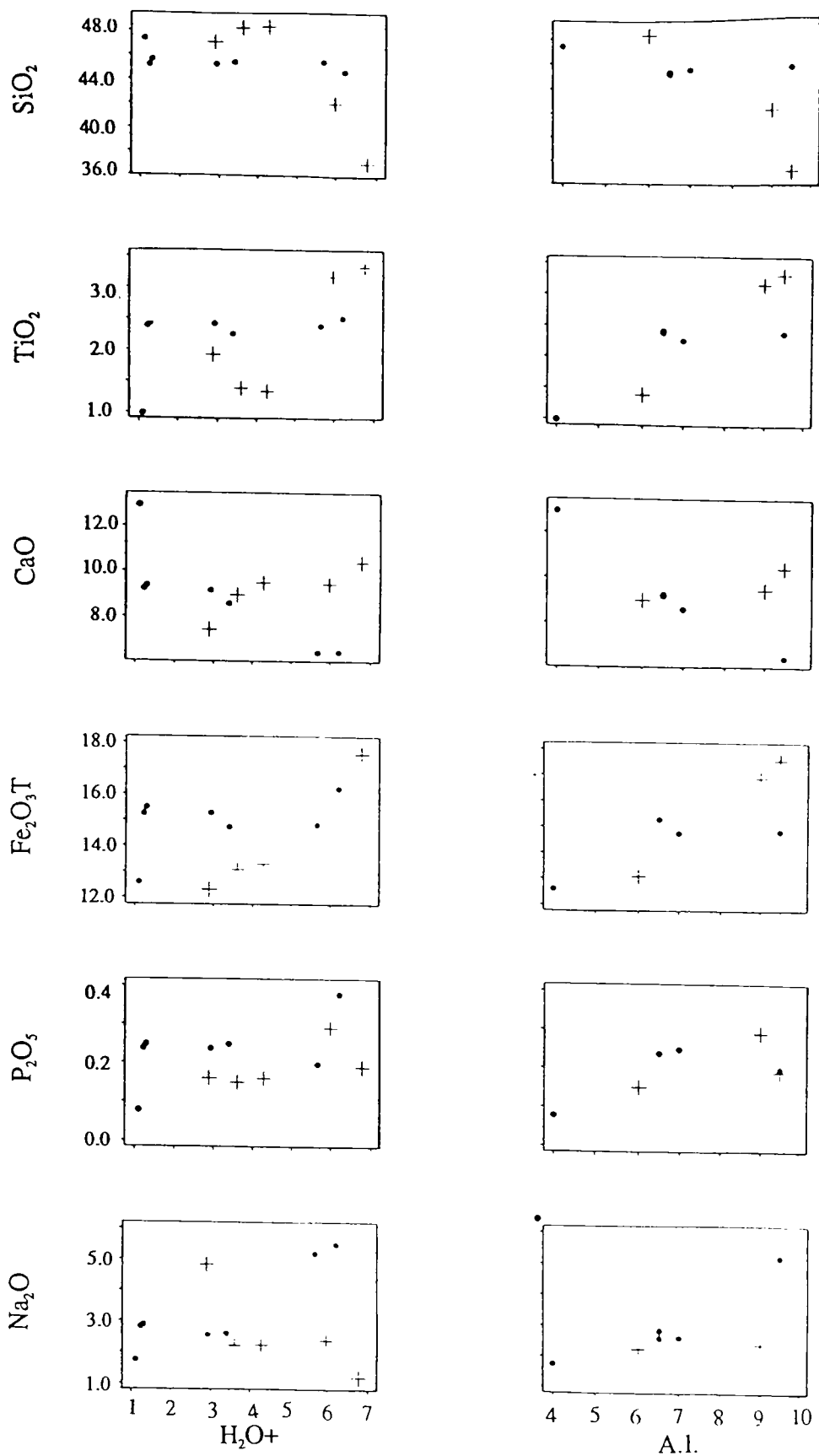


Figure 5.3 Plots of selected major and trace elements versus alteration index (A.I.) and H_2O+ for two flow-bore profiles (see text for details) (JHS76-JHS81, JHS159-JHS163). Major element concentrations are in wt% oxides; trace element concentrations are in ppm.

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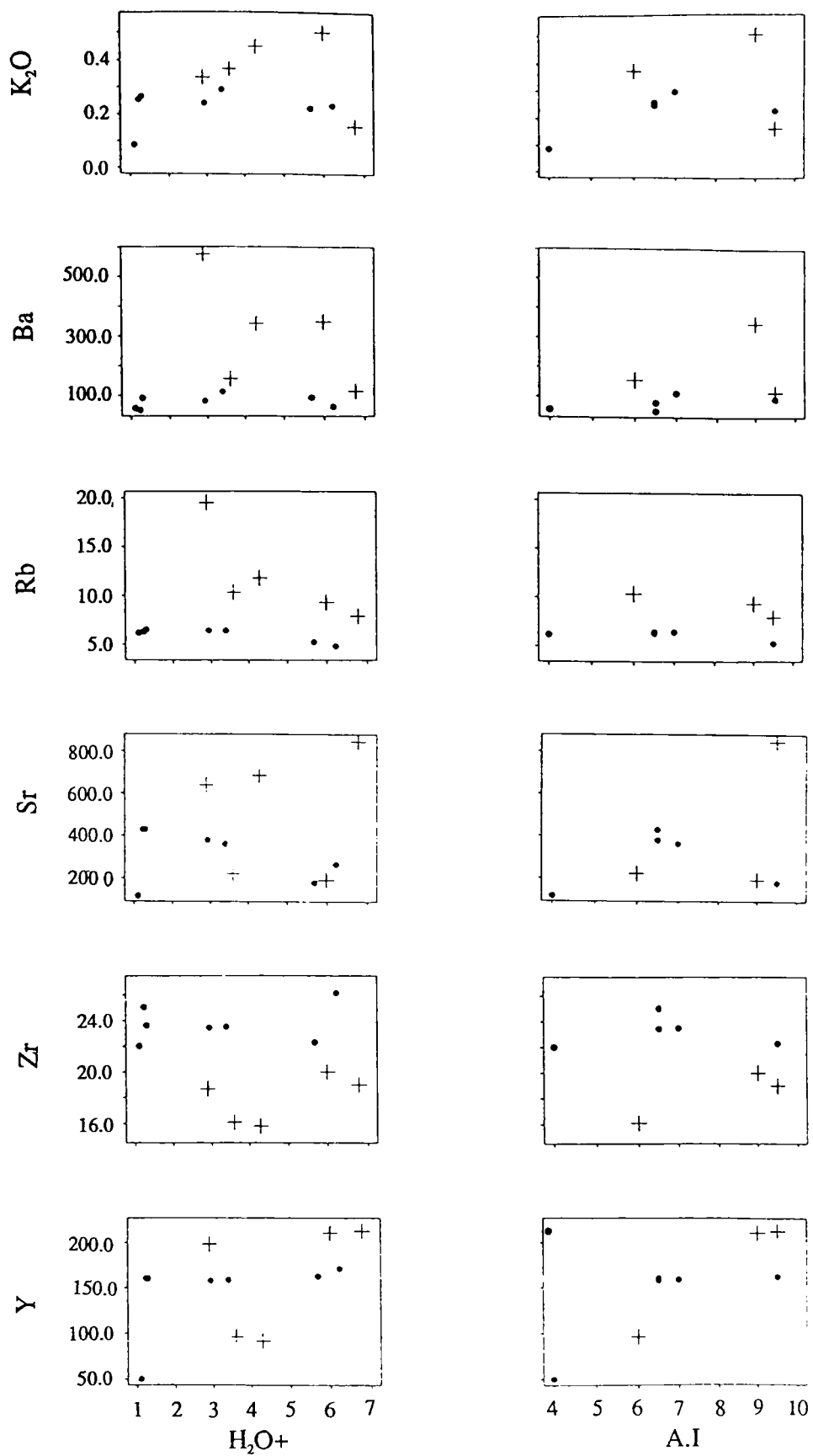


Figure 5.3 continued. See previous page for figure caption.

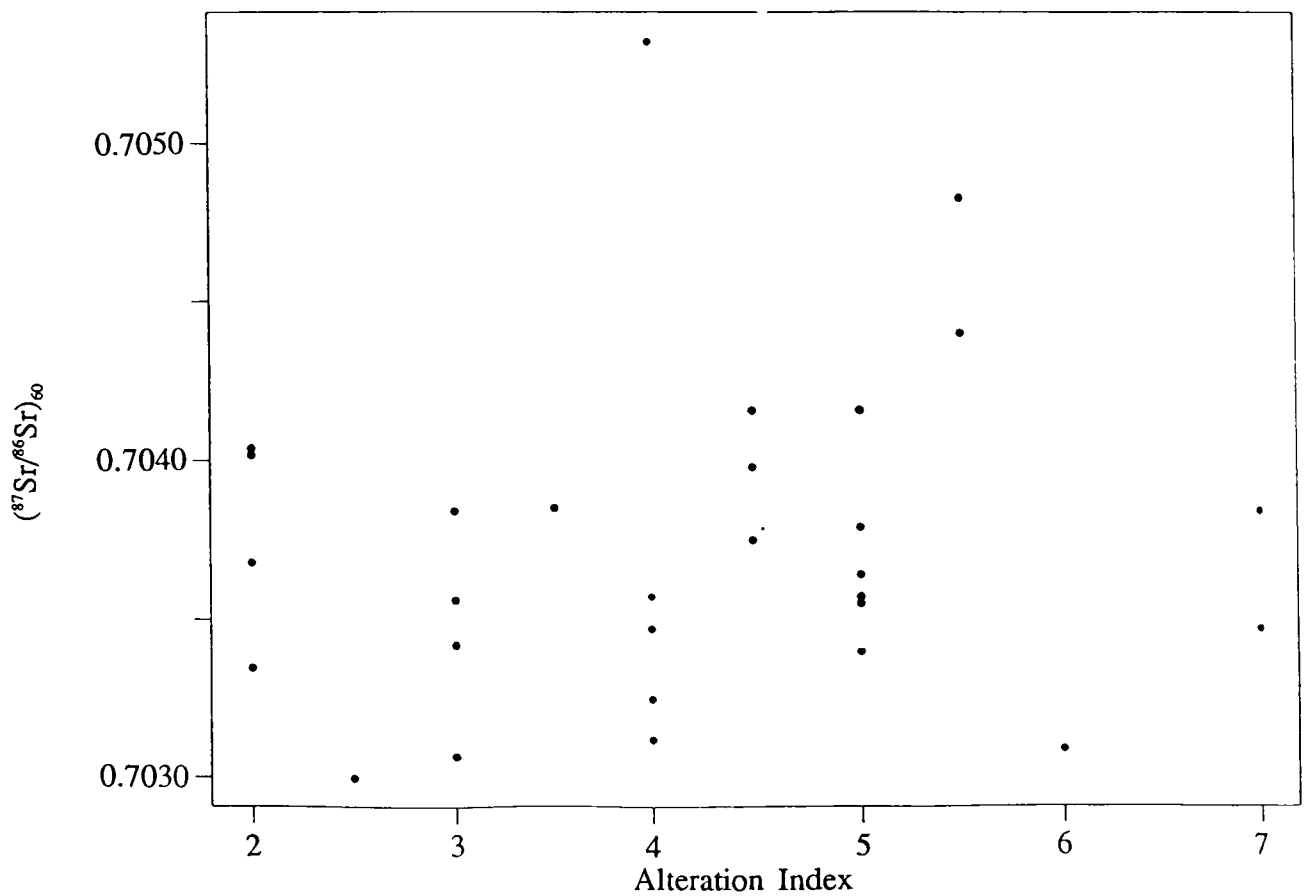
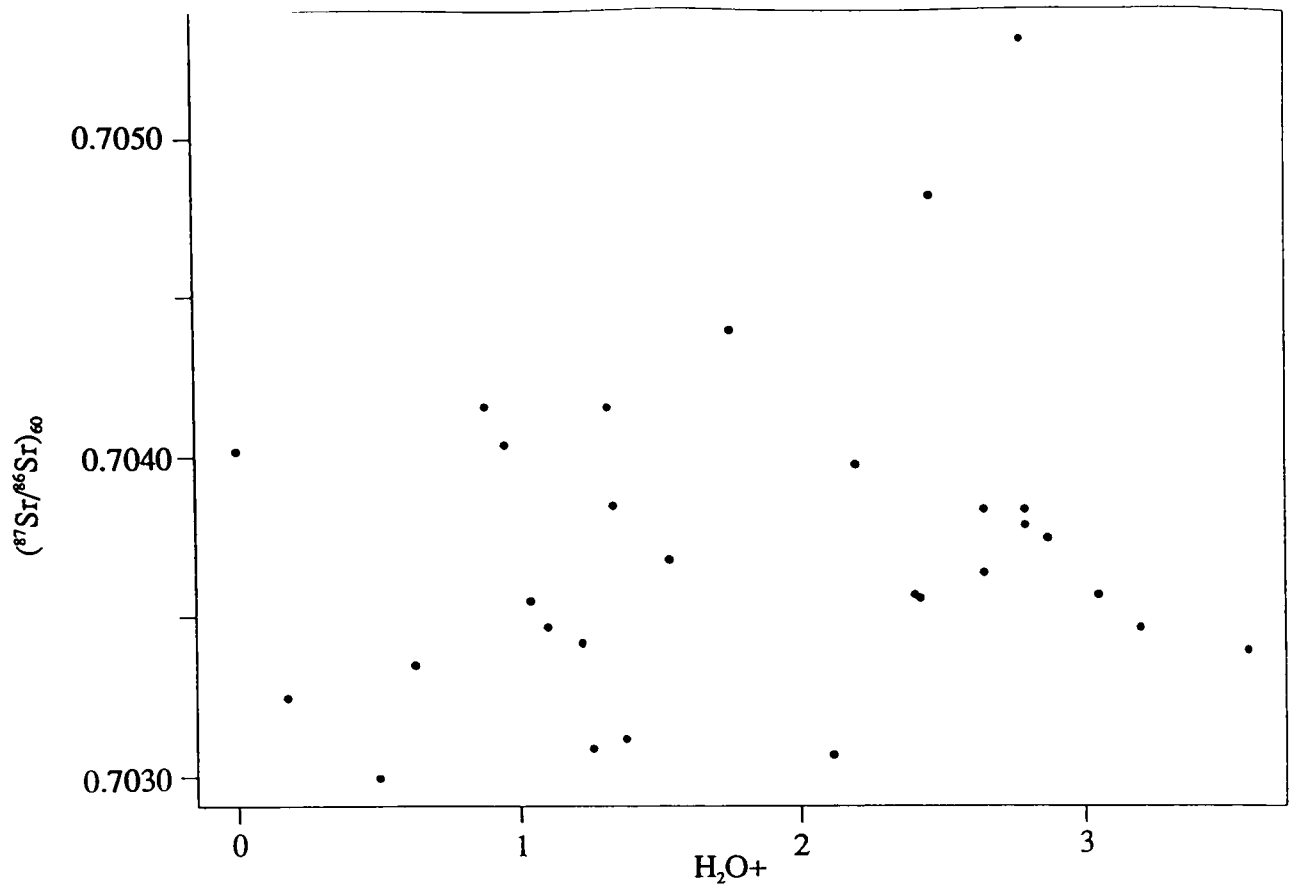


Figure 5.4.a Variation of Sr-isotope initial ratio with alteration index and with H_2O^+ . See text for discussion.

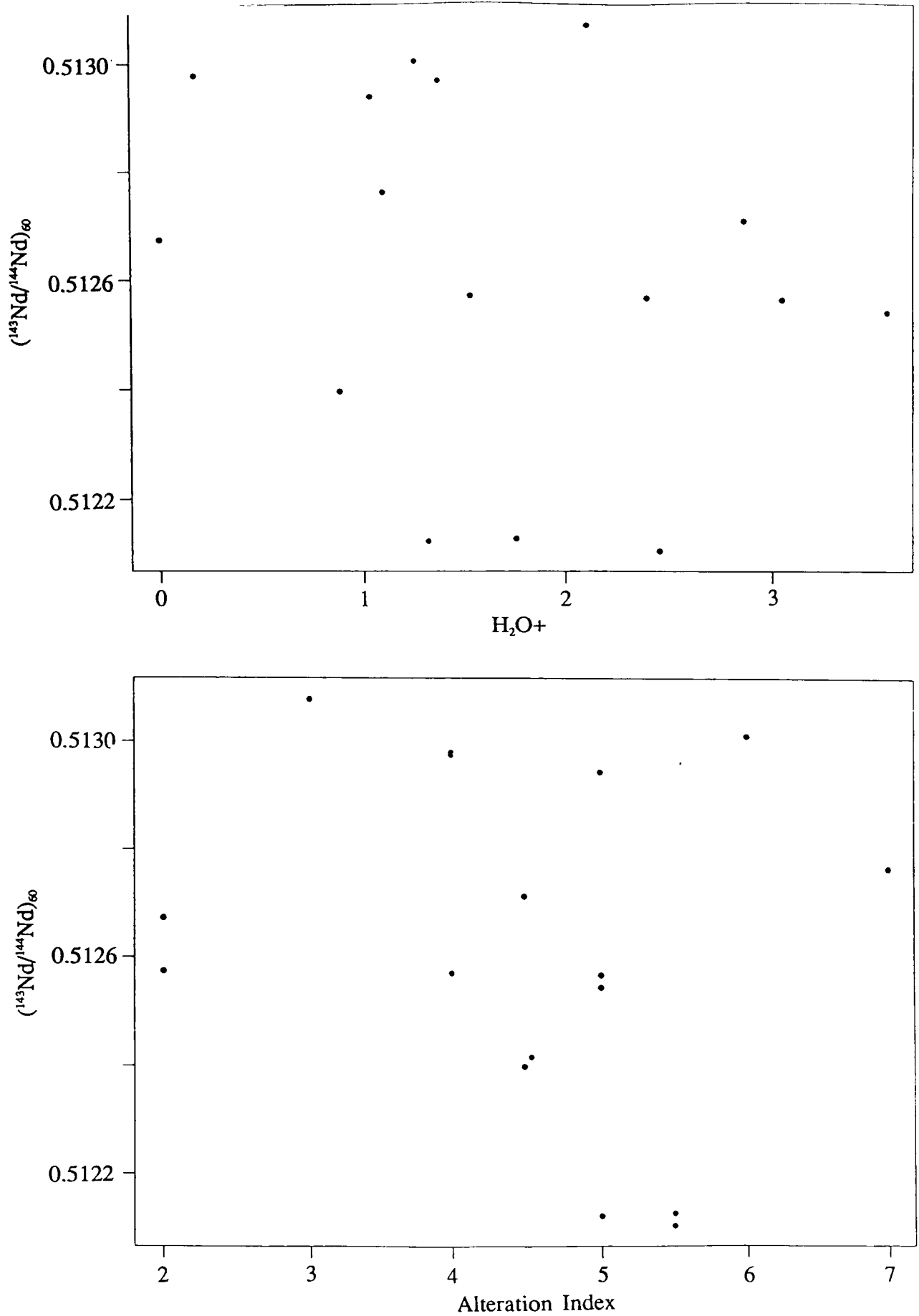


Figure 5.4.b

Variation of Nd-isotope initial ratio with alteration index and with H_2O^+ .
See text for discussion.

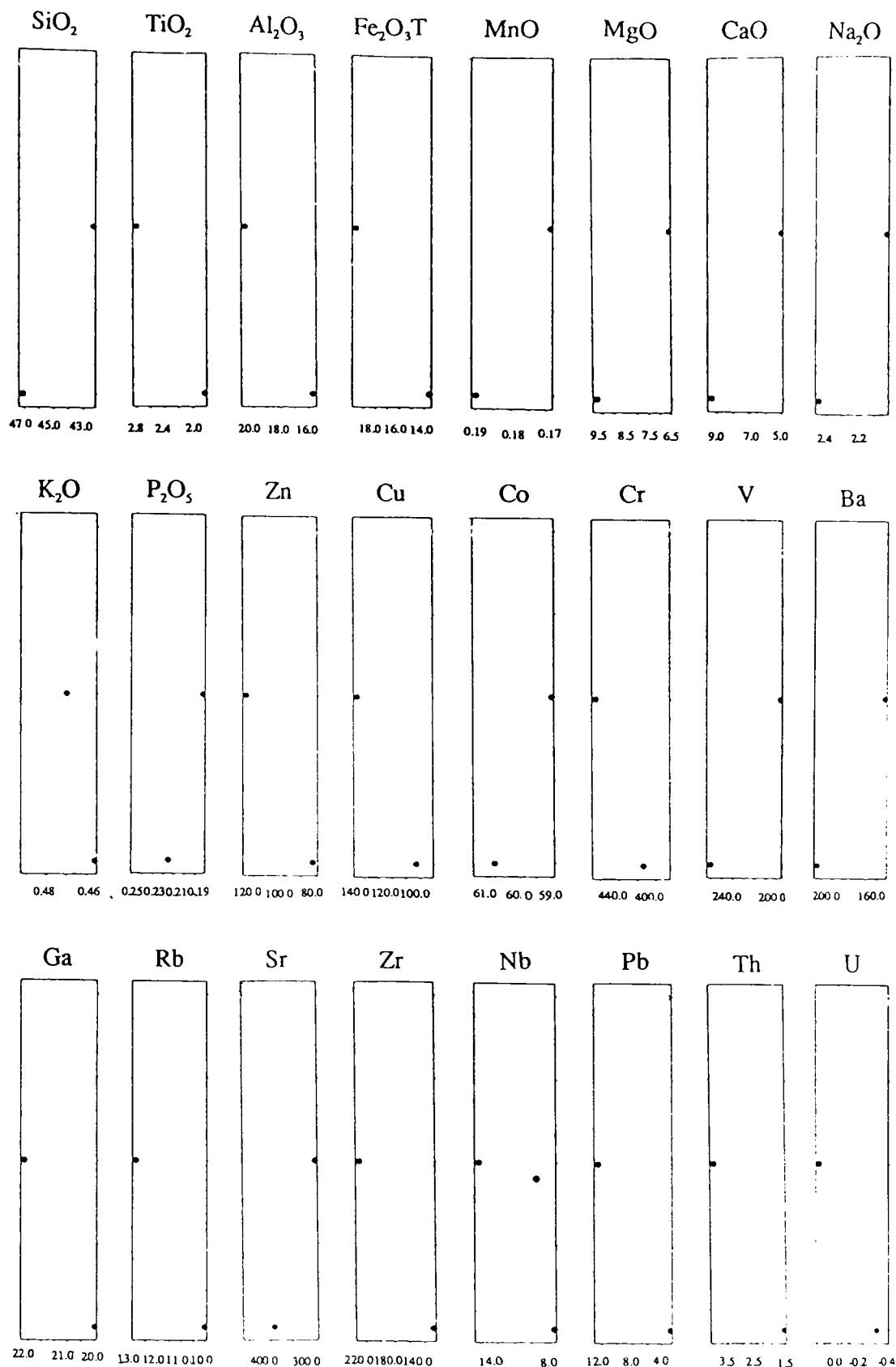


Figure 5.5 Average lower flow average bole sample profiles showing variations in the concentration of selected elements.
 (The average bole is the upper sample in all graphs)
 Major element concentrations are in wt% oxide; trace element concentrations are in ppm.
 See text for discussion.

OLIVINE
MgO, FeO, Si₂O
(minor MnO, Al₂O₃)

SERPENTINE MgO, SiO₂.
(minor Fe₂O₃, Al₂O₃)
IDDINGSITE MgO, SiO₂, Fe₂O₃.
BOWLINGITE SiO₂, FeO, Fe₂O₃, Al₂O₃.

AUGITE
FeO, MgO, CaO, SiO₂, Al₂O₃.
(minor TiO₂, MnO, Na₂O)

CHLORITE MgO, FeO, SiO₂, Al₂O₃.
(minor CaO, Na₂O, MnO)
HEMATITE Fe₂O₃.

PLAGIOCLASE
CaO, Na₂O, Al₂O₃, SiO₂.
(minor K₂O)

ZEOLITES CaO, Na₂O, SiO₂, Al₂O₃.

Table 5.1 Summary of the primary and secondary mineralogies of the Skye lavas and their compositions.

	F	Relative mobility
Pb	4.364	least mobile
Th	2.550	
Nb	2.170	
K₂O	2.010	
Zr	1.779	
TiO₂	1.517	
Zn	1.494	
Y	1.446	
Fe₂O₃	1.441	
Cu	1.406	
Al₂O₃	1.310	
Rb	1.286	
Ga	1.132	
Cr	1.120	
Ni	1.055	
Co	0.970	
SiO₂	0.898	
Sr	0.758	
V	0.755	
Ba	0.716	
Na₂O	0.687	
MgO	0.677	
CaO	0.542	most mobile

Table 5.2 Order of increasing solubility of elements.
(F=concentration in bole/concentration in basalt).

Altered basalt		Bole		Kaolinitized		Weakly lateritized		Moderately lateritized		Strongly lateritized	
	F		F		F		F		F		F
Pb	1.96	Ba	2.12	Al ₂ O ₃	1.57	Pb	2.88	Pb	10.87	Cr	12.97
Ba	1.90	K ₂ O	2.00	Pb	1.56	Ba	2.30	Cr	7.13	Pb	7.92
TiO ₂	1.86	Rb	1.58	Cr	1.56	Fe ₂ O ₃	2.04	Fe ₂ O ₃	3.46	Fe ₂ O ₃	3.51
Cr	1.83	Pb	1.57	Fe ₂ O ₃	1.55	Al ₂ O ₃	2.01	Rb	3.24	V	3.00
Fe ₂ O ₃	1.82	Nb	1.35	TiO ₂	1.53	TiO ₂	1.91	V	2.98	Al ₂ O ₃	2.68
Al ₂ O ₃	1.80	Y	1.35	MnO	1.46	Ni	1.90	Ba	2.89	Nb	1.96
Ni	1.67	Cu	1.31	Ba	1.45	Cr	1.89	MnO	2.47	Zr	1.65
MnO	1.52	Al ₂ O ₃	1.28	Ni	1.33	V	1.84	Al ₂ O ₃	1.81	TiO ₂	1.27
Zr	1.47	TiO ₂	1.26	Y	1.22	Zr	1.56	Nb	1.61	P ₂ O ₅	1.21
Cu	1.44	Fe ₂ O ₃	1.14	Zr	1.21	Cu	1.49	Co	1.50	Ba	0.91
V	1.44	Zr	1.12	Cu	1.20	Nb	1.49	Ni	1.45	Rb	0.91
Nb	1.38	Zn	1.07	Zn	1.15	P ₂ O ₅	1.11	P ₂ O ₅	1.44	MnO	0.58
Y	1.27	MnO	1.05	Nb	1.15	Zn	1.10	Zr	1.39	Ni	0.56
Co	1.24	SiO ₂	1.03	Co	1.10	MnO	1.10	TiO ₂	1.32	Co	0.49
Zn	1.22	P ₂ O ₅	0.96	V	1.05	Co	1.05	K ₂ O	1.06	K ₂ O	0.48
P ₂ O ₅	1.00	Co	0.92	P ₂ O ₅	0.94	Rb	0.94	Cu	0.88	Y	0.45
Rb	0.89	Ni	0.90	Rb	0.91	Y	0.90	Zn	0.71	Zn	0.41
SiO ₂	0.82	Sr	0.89	SiO ₂	0.90	SiO ₂	0.74	SiO ₂	0.39	Cu	0.31
K ₂ O	0.27	Cr	0.84	K ₂ O	0.53	K ₂ O	0.21	Y	0.32	SiO ₂	0.15
MgO	0.21	MgO	0.71	MgO	0.47	MgO	0.12	Sr	0.09	Sr	0.07
Sr	0.17	V	0.68	Sr	0.34	Sr	0.12	MgO	0.04	Na ₂ O	0.03
CaO	0.07	CaO	0.48	CaO	0.31	CaO	0.04	Na ₂ O	0.04	MgO	0.01
Na ₂ O	0.03	Na ₂ O	0.37	Na ₂ O	0.25	Na ₂ O	0.03	CaO	0.01	CaO	0.00

Table 5.3 Order of increasing solubility for Deccan basalts affected by weathering and lateritisation, data from Widdowson, 1990.
(F = concentration in altered sample/concentration in basalt).

Comparison of SMLS average bole with the samples of Widdowson 1990	Spearman rank correlation coefficient	Significance level (%)
Altered basalt	0.5338	95
Deccan bole	0.6303	99
Kaolinitized	0.6072	99
Weakly lateritized	0.5026	95
Mod lateritized	0.4174	95
Strongly lateritized	0.5709	99

Table 5.4 Spearman rank correlation coefficients between the SMLS average bole and the samples of Widdowson 1990.

THOMSONITE	$\text{NaCa}_2[(\text{Al},\text{Si})_5\text{O}_{10}]_2 \cdot 6\text{H}_2\text{O}$	LOW GRADE
CHABAZITE	$\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 6\text{H}_2\text{O}$	
STIBLITE	$(\text{Ca},\text{Na}_2,\text{K}_2)[\text{Al}_2\text{Si}_7\text{O}_{18}] \cdot 7\text{H}_2\text{O}$	
ANALCITE	$\text{Na}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$	HIGH GRADE

Table 5.5 Compositions of the amygdaloidal zeolites of the Skye lavas (After King, 1976)

	1	2	3	4	5
SiO₂	54.94	41.64	46.97	48.78	56.24
TiO₂	0.02	0.06	0.00	0.00	0.00
Al₂O₃	23.30	27.99	27.39	18.04	17.16
FeO	0.12	0.32	0.03	0.00	0.00
MnO	0.01	0.01	0.00	0.00	0.00
MgO	0.02	0.08	0.00	0.00	0.00
CaO	0.26	11.86	9.06	9.77	8.56
Na₂O	13.01	2.96	6.43	0.98	0.00
K₂O	0.07	0.04	0.04	0.60	0.32
Cr₂O₃	0.02	0.00	0.02	0.00	0.00
NiO	0.00	0.00	0.00	0.00	0.00
Total	91.86	84.96	89.94	78.00	83.30

Table 5.6 Analyses of zeolites from the Skye lavas.

1. Analcite this study, JHS211 - electron microprobe analysis.
2. Thomsonite this study, JHS9 electron microprobe analysis.
3. Mesolite this study, JHS100 electron microprobe analysis.
4. Chabazite from King 1976
5. Stilbite from King 1976

CHAPTER 6

FRACTIONAL CRYSTALLISATION

6.1 Introduction

6.1.1 Fractionation Processes

In an attempt to determine the nature and degree of mantle source melting which occurred to produce the Skye lavas it is necessary to try to account first for the fractionation processes which have affected the lavas since their generation. The effects of post-solidification alteration have already been assessed (Chapter 5, Alteration and Bole Formation) and removed from consideration. In this chapter the compositional variation observed within each magma type (Chapter 3, Petrography and Mineralogy, and Chapter 4, Geochemical Characteristics) will be considered, and the process of fractional crystallisation assessed as a mechanism for generating the observed ranges in element concentrations.

For reasons which will become apparent later, consideration of the effects of other processes such as crustal contamination and heterogeneities inherited from variations in the composition or degree of melt of the mantle source is left until Chapters 7 and 8.

6.2 Two-element variation diagrams

6.2.1 Introduction

To assess the compositional variation in the Skye lavas in relation to their phenocryst phases, element concentrations in the lavas of the three different magma-types (SMLS, PM and FB) and representative microprobe analyses of phenocrysts were plotted against a fractionation index (MgO) (Figures 6.1.a-j, 6.2.a-i, 6.3.a-i).

6.2.2 Skye Main Lava Series

In the plots of SMLS compositions porphyritic and aphyric lavas were distinguished (Figure 6.1). It can be seen that the SMLS data-set is compositionally scattered. The aphyric lavas do not define a clear liquid line of descent, but an evolutionary trend can be identified from average analyses. The most important feature of the evolutionary trend is an inflection at approximately 7 wt% MgO (most obvious on the MgO versus CaO plot). This indicates that the crystallisation history of the SMLS should be considered as a two stage process involving two different fractionating mineral assemblages, which has not been done in previous studies. Preliminary inspection of the two-element variation diagrams shows that the first stage of crystallisation is consistent with the removal of olivine ($\pm$ Cr-spinel), whereas the second stage appears to have involved the removal of a Ca-rich phase, either plagioclase or clinopyroxene, or both. On the plot of MgO versus Cr_2O_3 the first trend runs directly away from clinopyroxene and appears to have no involvement of olivine; however, if the composition of Cr-spinel (found as microphenocryst inclusions in the olivine phenocrysts, Chapter 3, Petrography and Mineralogy) is considered it can be shown that the Cr_2O_3 trend is consistent with the fractionation of olivine + Cr-spinel in the proportion 98:2 (a ratio which is in agreement with visual estimates of the proportion of Cr-spinel in the olivines).

6.2.3 Preshal Mhor

The data-set for this magma type is much smaller and is compositionally more restricted than the SMLS (Figure 6.2). However, in many of the two-element plots a trend, consistent with either the removal of olivine + plagioclase or the removal of olivine + plagioclase + clinopyroxene can be provisionally identified.

6.2.4 Fairy Bridge

The data-set for this magma type is small and compositionally restricted (Figure 6.3).

Within the small range of MgO content, many elements behave coherently and suggest that the lavas have evolved by the removal of olivine $\pm$ plagioclase.

6.3 Mixing calculations

6.3.1 Introduction

The crystal fractionation models proposed from the inspection of the two-element variation diagrams were tested using the method of Wright and Doherty (1970). A computer program (Kenwood5, Hodges 1990) was used to determine whether whole rock major element compositions, presumed to represent primitive and evolved lavas, could be related by extraction or addition of some combination of the minerals olivine, plagioclase and clinopyroxene. The program was found to give the best results for the determination of the composition of the primitive lava by addition of the minerals (extract) to the evolved lava (residual liquid), rather than as in nature extraction of the minerals from the primitive lava.

Since the SMLS aphyric lavas do not define a clear liquid line of descent (Figures 6.1.a-j), average analyses of SMLS lavas at various MgO contents were taken to be representative of primitive and evolved liquids in the numerical calculations. The compositional scatter in the SMLS data-set made the use of average analyses preferable to the use of individual samples since specific pairs of the latter may not lie on the same liquid line of descent. Numerical calculations performed on the average primitive and average evolved compositions thus minimised the effect of the compositional scatter giving a generalised evolutionary model for the whole suite. A range of phenocryst compositions was used in the modelling to try to assess the effects of mineral solid solutions upon the solutions of the extract/addition calculations. For the first stage of the SMLS evolution (13 wt% MgO - 7 wt% MgO) three olivine and plagioclase compositions were used, i.e. the most basic (found to approximate to the compositions of the first minerals to crystallise in the magma as determined using the method

of Nathan and Van Kirk, 1978, and a K_D based on experimental results of Roeder and Emslie, 1970) and least basic electron microprobe phenocryst analyses, and a composition intermediate to these. A single clinopyroxene composition was used since it was representative of the range present in the lavas. For the second stage of the SMLS evolution (7 wt% MgO - 4 wt% MgO) three olivine and plagioclase compositions (basic, evolved and intermediate) were employed in the modelling. The composition of clinopyroxene to be used presented more of a problem since there were no electron microprobe analyses available for it. The composition of a clinopyroxene from the most evolved lava in which it had been analysed (9 wt% MgO) and a groundmass clinopyroxene composition were used. The PM lavas have such a restricted compositional range that one olivine, plagioclase and clinopyroxene composition (determined using the method of Nathan and Van Kirk, 1978, because no electron microprobe data were available) were employed. It was found that varying the composition of the mineral phases used in the modelling did not have a significant effect on the mineral proportions of the solution. The primitive mineral phase compositions produced the solutions with the lowest sum of squares of residuals, these results are presented in Table 6.1 and 6.3. It can be seen that the evolution of the various suites in terms of crystal fractionation can be explained satisfactorily by more than one mineral assemblage; however, the different mineral assemblages require different crystal:liquid proportions.

The data used in the major element modelling are presented in Tables 6.2.a and 6.2.b.

6.3.2 Skye Main Lava Series

The data presented in Table 6.1 show the results of modelling the fractional crystallisation of the SMLS lavas as a two stage processes. For each of the assemblages the value of F (fraction of liquid remaining) was affected by solid solution in the mineral compositions, but the intra-mineral assemblage compositional variations are smaller than those between the different mineral assemblages, only the solutions of the most primitive minerals are

presented here. For the first stage of evolution of the suite, i.e. 13 wt% MgO to 7 wt% MgO, fractionation of olivine alone would produce most of the observed compositional variations by 14% fractional crystallisation. Addition of Cr-spinel (found as microphenocryst inclusions in the olivine phenocrysts) to the fractionating assemblage has very little effect on the amount of crystallisation calculated for any of the assemblages but tends to lower the sum of squares of residuals slightly. The assemblage olivine and clinopyroxene also produces a reasonable fit and would require 18.5% fractional crystallisation, with the minerals in the proportions 70:30. The proportions required, however, eliminate this assemblage because the linear trend of the first stage indicates fractionation of a single assemblage (two assemblages would result in a dog-leg in the trend) and no phase diagram allows the precipitation of olivine and clinopyroxene in the above proportions as a single assemblage. The compositional variations observed in the second stage of evolution, i.e. from 7 wt% MgO to 4.5 wt% MgO can be explained by either 39% fractionation of olivine and plagioclase in the proportions 33:67, or 45% fractionation of olivine, plagioclase, and clinopyroxene in the proportions 23:50:27.

6.3.3 Preshal Mhor

The data presented in Table 6.3 show the results of modelling the fractional crystallisation of the PM lavas. The data are consistent with the removal of 1.5% olivine, or 21% olivine and plagioclase in the proportions 32:68. The latter assemblage has a much lower sum of squares of residuals.

6.3.4 Fairy Bridge

It was decided not to perform mixing calculations on the FB lavas because of their restricted compositional range and the variation in the concentration of elements such as Fe_2O_3 and TiO_2 . In view their MgO contents (~ 13 wt%) and the similarity of their major element concentrations to those of the SMLS it is suggested that they evolved by the fractional

crystallisation of olivine.

The results of mixing calculations give the best fit mineral assemblages and proportions for the compositions under consideration, however the best fit solution is not necessarily the correct solution. So the fractionating assemblages outlined above could account for the observed compositional variations but the correctness of the mineral assemblages and proportions needs to be tested further. To do this the positions of the whole rock and groundmass compositions in the normative basalt tetrahedron (ol-cpx-plag-SiO₂) (Figure 6.4) were investigated.

6.4 Phase relations

6.4.1 Introduction

The normative basalt tetrahedron (ol-cpx-plag-SiO₂) can be used as an approximate substitute for experimental work, and analogies can be drawn between it and the synthetic system Forsterite (Fo)-Diopside (Di)-Anorthite (An)-Silica (SiO₂). But, it is only to the early stages of basaltic crystallisation that the phase diagrams of the normative system can be applied with any degree of certainty (Cox *et al.*, 1979). The reader is referred to Cox *et al.* (1979) for a more detailed discussion of the limitations of the normative basalt tetrahedron system.

Tholeiitic basalts (i.e. containing normative hypersthene) can be considered in the simple normative system if they satisfy the, somewhat arbitrary, criteria of Cox *et al.* (1979).

- i. normative plagioclase at least as calcic as An₅₀.
- ii. the ratio $(\text{FeO} + \text{Fe}_2\text{O}_3) / (\text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3) < 0.7$.
- iii. K₂O < 1 wt%.
- iv. normative quartz (Q) parameters < 10 (to avoid encountering hypersthene or silica bearing equilibria early in the crystallisation sequence).

Criteria i. and ii. ensure that the compositions are basalt-like and are therefore suitable to be considered in terms of experiments performed on basalts. Criterion iii. ensures that the dramatic effects of K on phase relations in basaltic systems are avoided. Criterion iv. ensures that samples lie close to the ternary plane ol-cpx-plag in the quaternary (ol-cpx-plag-SiO₂), so projection from SiO₂ leads to minimal distortion.

Samples satisfying the above criteria can be considered in the ol-cpx-plag pseudoternary plane projection from SiO₂ in the quaternary system ol-cpx-plag-SiO₂. Figure 6.4 shows the SMLS, PM, and FB whole rock compositions in the projections from SiO₂ onto the plane ol-cpx-plag, from plag onto the plane ol-qtz-di, and di onto the plane ol-qtz-an. Figures 6.5 show the aphyric (i.e. less than 5% phenocrysts) SMLS, the PM lavas, and the FB lavas, and their respective extracts. The most obvious feature of the porphyritic lavas is that both the SMLS and FB basalts lie across the ol-cpx-plag plane, which approximates to the position of a thermal divide at pressures less than 8 kb, whereas the PM samples only plot on the Si-rich side of the ol-cpx-plag plane. This may suggest that the SMLS and FB magmas were generated at higher pressures than the PM magmas (Chapter 8, Magma Generation). Two primitive SMLS basalts were selected and each was paired with an evolved SMLS basalt with comparable Si-saturation characteristics. The plotting position of the pairs in the basalt tetrahedron (Figure 6.4) highlighted two features of the data-set. The first was that the primitive samples spread out parallel to the ol-di join; thus suggesting that compositional variations, parallel to the ol-di join, could be primary, possibly resulting from different degrees of mantle partial melting. The second was that in all the projections both evolved samples lay on a trend away from the primitive lavas which, allowing for solid solution effects and given that the diagram is a projection, is consistent with the removal of olivine by fractional crystallisation.

The porphyritic and aphyric SMLS basalts, and the FB basalts plot predominantly in the ol field, although some samples plot on or near the ol-plag cotectic. The samples can therefore be presumed to have been in equilibrium with ol, or ol and plag at or near one-atmosphere

pressure, a finding which is consistent with the results of the mixing calculations. The PM basalts plot around the ol-plag-cpx ternary eutectic, indicating equilibration with all three mineral phases.

From the evidence presented so far it would seem that the compositional variation of the SMLS basalts and FB basalts can be attributed to fractional crystallisation of olivine ($\pm$ Cr spinel) followed by olivine ($\pm$ Cr spinel) and plagioclase $\pm$ clinopyroxene. The PM basalts appear to have had a different fractional crystallisation history which involved the crystallisation of olivine and plagioclase ($\pm$ clinopyroxene).

To investigate the fractionation models further it was decided to determine which phases would be in equilibrium with the liquids of the whole rock samples (which are potentially affected by crystal accumulation) at the time of eruption. Groundmasses were assumed to approximate to quenched liquids, and the compositions of the former were calculated and taken to represent the compositions of the latter. The results of mass balance calculations are considered here. Groundmass compositions were estimated for twenty representative SMLS basalts using the equation:

$$A_{GM} = (A_{WR} - (A_{PL} \cdot X_{PL}) - (A_{CPX} \cdot X_{CPX}) - (A_{OL} \cdot X_{OL})) / X_{GM}$$

where

A_{WR} is the whole rock element wt%

$A_{PL,CPX,OL}$ mineral element wt%

$X_{GM,PL,CPX,OL}$ refers to the mass fraction of groundmass, plagioclase, clinopyroxene, and olivine determined by modal analyses.

When plotted in the normative basalt tetrahedron the liquid compositions were found to be predominantly in apparent equilibrium with olivine or plagioclase at one-atmosphere (Figure 6.6). Unexpectedly some samples plotted within the plagioclase field, indicating that at one atmosphere pressure they were in equilibrium with plagioclase alone. The petrographic and

mixing-calculation evidence does not support this. So it is presumed that either not enough plagioclase was extracted in the calculations of groundmass compositions, or that too much olivine was extracted, i.e. the compositions in the plagioclase field are not representative of quenched liquid compositions. With the exception of the plagioclase-rich samples the groundmass data supports the fractional crystallisation model proposed from the study of the whole rock compositions.

6.4.2. High pressure phase relations

The above data give information about the low pressure anhydrous phase relations of the SMLS, PM, and FB lavas, but to assess fully the potential compositional affects of fractional crystallisation on a suite of rocks the high pressure phase relations should also be examined, since these may give important information about the deeper origins of the magmas, and their possible fractionation at depth. Such considerations are of paramount importance for a suite of rocks, such as the SMLS, which have previously had their evolution explained by high pressure processes. In the absence of experimental data the effects of increasing pressure were considered in general terms by studying the changes in phase boundary and primary phase field positions in synthetic systems such as the Forsterite (Fo)-Diopside (Di)-Anorthite (An)-Silica (SiO_2) system (e.g. Walker *et al.*, 1979) (Figure 6.7). With increasing pressure the olivine and plagioclase fields contract and the clinopyroxene, orthopyroxene, and spinel fields expand up to 15 kb. At pressures above 15 kb the orthopyroxene and spinel fields contract because of the expansion of the garnet field. The presence of the spinel field ruled out the possibility of direct comparison between the normative and synthetic system but a general comparison indicates that the configuration of the fields is such that at high pressures SMLS and FB whole rock and groundmass/liquid compositions could have been in equilibrium with clinopyroxene. Cr-spinel inclusions in olivine phenocrysts in the SMLS and FB basalts show that spinel was an early fractionating phase which is indicative of initial crystallisation at pressures higher than one

atmosphere when the spinel field would be larger. To say more than this on the subject of high pressure phase relationships is beyond the scope of this study since further discussion would require detailed experimental work.

6.4.3 Hydrous phase relations

Having considered the dry high pressure phase relations, hydrous phase relations will be considered for completeness. The characteristic feature of basaltic phase relations in the presence of volatiles is the depression of both the solidus and the liquidus temperatures relative to dry systems. If the volatile phase is H₂O then melts generated tend to be more silica saturated, whereas if the volatile phase is CO₂ melts tend to be more silica undersaturated. Increased pressure in the presence of volatiles results in the contraction of the plagioclase field (Yoder, 1969). So liquids will be produced which are richer in normative plagioclase than dry eutectic melts. Such liquids will lie within the plagioclase field if considered in terms of dry phase relations (which may be appropriate if the magmas dehydrate en route to the surface). It is not proposed that the SMLS, FB, or PM lavas have had a high pressure hydrous stage during their genesis, since if a process such as that outlined above were to occur it would be expected that a large amount of plagioclase would fractionate prior to olivine, or clinopyroxene, or both. There is only one rock which lies firmly in the plagioclase field, a big feldspar basalt, JHS212, collected from a hill top north east of Bracadale, and this is likely to be a plagioclase flotation cumulate.

6.5 Relationship between observed and fractionating phenocryst assemblages

6.5.1 Introduction

Fractional crystallisation can be non-selective, i.e. the phases are removed in the proportions in which they crystallise, or selective, i.e. phases are not removed in the proportions

in which they crystallise. The former can occur by crystal settling or convective fractionation, whereas the latter can probably only result from selective crystal settling. The mechanism of fractional crystallisation can, therefore, potentially, give some insight into the pre-eruptive processes acting upon the magmas and the conditions under which the processes occurred.

6.5.2 Skye Main Lava Series

Two-element variation diagrams, mixing calculations, and phase relations all indicate that, in the basic lavas, i.e. >7 wt% MgO, olivine was the principal fractionating phase. Yet most of the lavas contain phenocrysts of olivine and plagioclase, with occasional minor clinopyroxene. In a system where both olivine and plagioclase are present it would be expected that both phases would fractionate. Figure 6.8, in which groundmass and whole rock compositions are compared, demonstrates that this was not the case in the SMLS basic lavas. The groundmass compositions, calculated by mass balance, are linked to their whole rock compositions by tie-lines. If the phenocrysts present in the lavas were those responsible for producing the bulk compositional trend, i.e. non-selective fractionation, the whole rock groundmass tie-lines would be parallel to the main trend.

Another feature of the SMLS lavas which is apparently anomalous is the variation in the proportion of phenocrysts, and the deviation from cotectic proportions noted in Chapter 3, Petrography and Mineralogy. The proportions of phenocrysts in selected representative samples are shown in Figures 3.12 and 3.13. The lavas generally have a higher olivine:plagioclase ratio than cotectic proportions. When considered in conjunction with the evidence which suggests that olivine ($\pm$ Cr-spinel) was the sole fractionating phase, the high olivine:plagioclase ratio could be the result of one, or more, of the following processes.

Initial crystallisation and imperfect fractionation of olivine above the liquidus temperature of plagioclase.

Initial high pressure fractionation of olivine followed by crystallisation of olivine and

plagioclase without fractionation, resulting from compensated crystal settling (i.e. loss of crystals by settling with concomitant replacement by crystals settling from above, Cox and Bell, 1972). In this way an evolutionary trend could have been generated whilst the magmas were fractionating (olivine), then as crystallisation proceeded the magmas could have passed to a non-fractionation stage (olivine + plagioclase).

Plagioclase not influencing the evolutionary trend can be attributed to crystallisation of olivine and plagioclase with fractionation of the former but not of the latter.

The third possibility requires that the density of the host magma is equal to, or greater than, the density of the plagioclase, but less than that of the olivine. It is well established in the literature that this can indeed be the case (Bottinga and Weill 1970; Campbell, 1978).

6.5.3 Density calculations

6.5.3.1 Skye Main Lava Series

A recent study by Cattell (1989) considered the density of the fractionating mineral assemblage relative to the residual liquid density to try to explain the compositional gap observed in the SMLS data-set at basaltic-hawaiite compositions. He proposed that the fractionation of olivine and plagioclase took place as a two stage process, initially only involving olivine, and later olivine and plagioclase fractionated in cotectic proportions (i.e. approximately 1:2). He assumed that since most lavas had few phenocrysts they had been erupted close to their liquidus temperature, and therefore whole rock densities were comparable to magma densities. Using the equations of Sparks and Huppert (1984) Cattell calculated the density of the olivine and plagioclase fractionating assemblage to be $\sim 2.71 \text{ g cm}^{-3}$ i.e. lower than the basaltic liquid (approximately 2.75 g cm^{-3} , Cattell, 1989). So liquid densities would have increased during fractionation. There were, however, two fundamental flaws in this study. The first was that Cattell assumed that the fractional crystallisation model proposed by Thompson (1974a) was correct, something which has not been substantiated by the present

study. The second was that he assumed whole rock densities were comparable to magma densities, but since most of the lavas are porphyritic this may not be the case.

In the present study the whole question of the density of the SMLS magmas is readdressed with a view to explaining the fractional crystallisation mechanism affecting the SMLS basic magmas and the conditions under which it took place. It is assumed (for reasons outlined previously, section 6.4.1) that groundmass compositions approximate to quenched liquid compositions. The densities of twenty representative groundmass compositions have been calculated and compared with experimentally determined densities for the potential crystallising mineral phases, i.e. olivine, plagioclase and clinopyroxene. The absolute values of the calculated densities may not be precise but errors involved are likely to be consistent for all the calculations, so the relative values of calculated densities can be taken to be significant. An oxidation state of 15% was assumed for the calculation of FeO and Fe₂O₃ from total Fe measured as Fe₂O₃ (Brooks, 1976). Magmatic temperatures at one atmosphere were estimated from Nathan and Van Kirk (1978) (Figure 6.9).

A range of solutions were calculated and it was found that varying the depth of crystallisation from 0 km, 0 Kb to 45 km, 13.5 kb (the approximate limit of plagioclase stability) had a minimal affect upon the value of the density, i.e. $\pm 0.01 \text{ g/cm}^3$. The densities of the whole rocks were generally greater than those of the groundmasses/liquids, both are in the range 2.56 g/cm^3 to 2.73 g/cm^3 (Figure 6.10, one-atmosphere anhydrous conditions) which is the lower half of the range expected for basaltic liquids (2.55 g/cm^3 to 2.8 g/cm^3). This was expected since magmatic density is directly related to the magmatic Fe content, and the Skye lavas are transitional basalts, i.e. do not show the Fe-enrichment trend evident in tholeiitic suites. The calculated densities are considered to be maximum values because any increase in volatile content, or a depth related temperature increase would reduce the magmatic density. The lack of correlation between MgO and density is attributed to the low density of the magma relative to the fractionating mineral assemblage (olivine (Fo₇₅) 3.51 g/cm^3). In a

magmatic system where the density of the magma is greater than the phases fractionating, e.g. plagioclase crystallising from an Fe-rich tholeiitic liquid, an increase in density would be expected with increasing fractionation.

From the above data it can be concluded that plagioclase, An_{65} to An_{90} has densities of 2.63 g/cm^3 to 2.70 g/cm^3 at typical pressures of magmatic fractional crystallisation, i.e. 0 kb to 10 kb. These densities are in the range of the SMLS whole rock densities, so plagioclase may or may not fractionate depending upon the exact composition of the plagioclase and the magma. In any case, from Stokes' law (only valid for spherical crystals, the tabular shape of plagioclase crystals would reduce the settling velocity further), olivine would have had a much higher settling velocity than the plagioclase.

$$V = \frac{2}{9} \frac{gr^2}{\eta} \frac{\rho_s - \rho_L}{\eta}$$

where

g acceleration due to gravity
r radius of the sphere
 $\rho_{s/L}$ density of the solid/liquid
 η viscosity of the liquid

The settling of the plagioclase could, potentially, have been suppressed by the yield strength of the magma, but it is unlikely that this would have been sole cause of the apparent fractionation of olivine without concurrent fractionation of plagioclase.

Another hypothesis is that olivine fractionated without concurrent fractionation of plagioclase, followed by crystallisation of olivine and plagioclase without their fractionation possibly because of increased magmatic turbulence.

Alternatively compensated crystal settling, i.e. loss of crystals by sinking balanced by addition of crystals from above, could have occurred to mask late stage fractionation. Compensated crystal settling is more likely to occur in conduits, e.g. dykes. This is consistent with previous ideas regarding the magmatic plumbing system of the Skye lavas, i.e. many dykes cutting the continental crust. So an evolutionary trend could have developed by fractional

crystallisation of olivine in a magma chamber at depth. Magmas could have been extracted at varying stages of evolution and transported to the surface through dykes in which compensated crystal settling of olivine and in some cases plagioclase (consistent with the lower pressure environment) occurred.

Mitchell (1988) gave a detailed account of the potential affect of the association of plagioclase and denser ferromagnesian minerals in glomerocrysts in a system in which the plagioclase had negative or zero buoyancy. He concluded that only a small percentage of ferromagnesian minerals would be required to increase the density sufficiently for the plagioclase to fractionate. This would not appear to be the case here because in the SMLS basic lavas plagioclase glomerocrysts are generally monomineralic (Section 3.4.3.1, plate 3.7.b).

6.5.3.2 Preshal Mhor

The results of density calculations on two Preshal Mhor lavas, under anhydrous low pressure conditions are shown in Figure 6.10. The data are consistent with the evolution of the PM lavas by the crystal settling of olivine and plagioclase $\pm$ clinopyroxene.

6.5.3.3 Fairy Bridge

The densities of two FB lavas were calculated for anhydrous low pressure conditions. The results, Figure 6.10, are consistent with the evolution of the lavas by fractional crystallisation of olivine, or olivine and plagioclase.

6.6 Eruptive temperatures

The fractional crystallisation paths of silicate liquids can be predicted by computer simulation using equations derived by Nathan and Van Kirk (1978). By making the assumption that the suite of lavas are the products of magma undergoing equilibrium crystallisation the

equations enable the prediction of the liquidus temperature of the anhydrous minerals magnetite, olivine, hypersthene, augite, quartz, plagioclase, orthoclase, leucite, and nepheline; and the composition of the minerals in terms of solid solution end-members. The results of computer simulation of the equilibrium crystallisation of representative SMLS, PM, and FB lavas are presented in Figure 6.9. Assuming that the phenocrysts present in the rocks are those that were crystallising from the magmas when they were erupted, the eruptive temperature of the SMLS would have been ~ 1215°C (olivine + plagioclase), the PM magmas would have been ~ 1200°C (olivine + plagioclase + clinopyroxene) and the FB magmas ~ 1250°C (olivine alone).

A noteworthy feature of the computer simulation of the equilibrium crystallisation path of the SMLS is the coincidence of plagioclase becoming a liquids phase at 7 wt% MgO, and the inflection in the data-set at 7 wt% MgO.

6.7 Summary and conclusions

Two-element variation diagrams show that there is an inflection in the SMLS data-set at approximately 7 wt% MgO, thus necessitating consideration of the compositional evolution as a two-stage process. From the inspection of two-element variation diagrams of the SMLS the first stage of crystallisation is consistent with the removal of olivine ($\pm$ Cr-spinel), or olivine ($\pm$ Cr-spinel) and clinopyroxene in the proportions 90:10. The second stage of crystallisation appears to have involved removal of olivine and plagioclase ($\pm$ clinopyroxene) in the proportions 25:75. The PM data are consistent with the evolution of the PM lavas by fractional crystallisation of either olivine and plagioclase in approximately cotectic proportions (20:80), or olivine and plagioclase and clinopyroxene in approximately eutectic proportions (20:25:65). The compositionally restricted data for the FB lavas suggest that they evolved by the removal of olivine.

Mixing calculations showed that for the SMLS first stage of evolution, fractional

crystallisation of 14% olivine would produce the observed compositional variations from a parental magma with 13 wt% MgO. The SMLS second stage of evolution can be explained by either 39% crystallisation of olivine and plagioclase in the proportion 33:67, or 45% crystallisation of olivine, plagioclase and clinopyroxene in the proportions 23:50:27 from a parental magma with 7 wt% MgO. The PM lavas are consistent with the removal of 15% olivine alone or 21% olivine and plagioclase in the proportions 32:68 from a parental magma with 9 wt% MgO.

The SMLS and FB basalts lie across the ol-cpx-plag plane (which approximates to the position of a low-pressure thermal divide) in the normative basalt tetrahedron, whereas the PM basalts only plot on the Si-rich side of the ol-cpx-plag plane. In the normative basalt tetrahedron the SMLS primitive basalts are scattered parallel to the ol-di join suggesting that the compositional scatter could be primary. Allowing for solid solution effects, the primitive-evolved compositional trends in the SMLS in the basalt tetrahedron are consistent with the crystallisation of olivine alone. At one-atmosphere pressure the SMLS and FB basalts plot predominantly in the olivine field with some samples on or near the ol-plag cotectic, whereas the PM basalts plot at the ol-plag-cpx ternary eutectic. SMLS groundmass and aphyric whole rock compositions were taken to approximate to liquid compositions and when plotted in the normative basalt tetrahedron were found to be in equilibrium with olivine, olivine and plagioclase, or plagioclase. From consideration of changes in phase field relations with increasing pressure it was concluded that at high pressure SMLS and FB whole rock and groundmass/liquid compositions could have been in equilibrium with clinopyroxene.

SMLS whole rock-groundmass tie-lines do not parallel the bulk compositional evolutionary trend, thus demonstrating that the phenocrysts present in the samples, i.e. olivine and plagioclase, were not responsible for the compositional evolution. In the absence of suitable mineral-liquid density contrasts depending on the plagioclase and magma compositions and their densities the deviation of the olivine-plagioclase modal ratio from cotectic proportions was

attributed to initial fractionation of olivine, followed by crystallisation of olivine and plagioclase without their fractionation, either because of magmatic turbulence or compensated crystal settling. This is consistent with ideas regarding the magmatic plumbing system of the Skye lavas, i.e. many dykes cutting the continental crust.

Assuming that the SMLS magmas were fractionating olivine and may have just begun to fractionate plagioclase at the time of their eruption, their temperature at one atmosphere would have been $\sim 1215^{\circ}\text{C}$. Presuming that the PM lavas were fractionating olivine, plagioclase, and clinopyroxene at the time of their eruption, their temperature at one-atmosphere pressure would have been $\sim 1200^{\circ}\text{C}$. If, as suggested, the FB lavas were precipitating olivine ($\pm$ Cr-spinel) they would have had an eruptive temperature of $\sim 1250^{\circ}\text{C}$.

6.8 Unexplained compositional scatter

Having considered the compositional effects of fractional crystallisation upon the SMLS basalts, it must be concluded that a considerable amount of scatter exists in the SMLS data-set which cannot be accounted for by the above process. To try to quantify the scatter and determine the process(es) generating it the effects of fractional crystallisation were removed. Lavas under olivine control, i.e. greater than 7 wt% MgO, were calculated back to a potentially primary MgO content of 15 wt% by the addition of olivine. The equations of Pearce (1987) were used to calculate suitable olivine compositions.

To ensure that compositions were not a function of the addition of olivine, all elements were plotted against F (amount of olivine added to the sample to calculate it back to 15 wt% MgO). It was found that some elements correlated with F, and for most samples the correlation is easily explained. A positive correlation between Ni and F indicates that too much Ni has been added during the calculation, i.e. the distribution coefficient used, 10, was too high. FeO has a positive correlation with F whereas Fe_2O_3 has a negative correlation with F. This can be

attributed to all the Fe added from the olivine being FeO, resulting in the FeO/Fe₂O₃ ratio being too high. A negative correlation between F and MnO, Zn, Cu and Co indicates that their concentration in the 15 wt% data-set are too low. This is a result of their distribution coefficient being close to 1 for olivine. The simplistic computer program, however, treated them as incompatible so their concentration decreased as more olivine was added, when in fact addition of olivine would have maintained or slightly increased their concentrations. A negative correlations of V and Rb are inexplicable since neither element is compatible in olivine, the only phase used to calculate the 15 wt% data-set

The importance of two-element variation diagrams in the analysis of geochemical data has already been discussed (section 6.2). For the current data-set in which 27 elements were determined (sometimes more if REE are included), over 350 variation diagrams may be plotted. The characteristics of the plots can be summarised by calculating the regression line, the intercept of the regression line, and the inter-element correlation coefficients. The correlation coefficients indicate how scattered the data-set is, i.e. whether a discernable trend exists. So, a correlation coefficient matrix outlines most of the petrogenetic information attainable from the 350 plus two-element variation diagrams.

The means, ranges, and standard deviations of elements in the 15 wt% MgO data-set are presented in Table 6.4. The correlation coefficients of the 15 wt% MgO data-set are presented in Table 6.5. Correlation coefficient patterns were plotted for the incompatible and semi-incompatible elements arranged with the LIL (K, Rb, Ba, and Sr) elements at the left, the HFS elements (Nb, Zr, P₂O₅, TiO₂, and Y) in the middle and Zn and Cu at the right, in Figure 6.11. The correlation coefficient patterns can be divided into three groups on the basis of pattern shape. First, SiO₂ and Al₂O₃, concave upwards pattern which has negative correlations with all the incompatible elements, the strongest correlations being with the HFS elements. Second, TiO₂, Fe₂O₃, FeO, P₂O₅, Zn, Co, V, Ga, Sr, Zr, Nb, and to a lesser extent Y, a group of patterns which have concave downwards patterns and show positive correlations with all the

incompatible elements and slope to the left as a result of having stronger correlations with the HFS than the LIL elements. This pattern shape is almost a mirror image of correlation coefficient pattern of group one. Third, K_2O , Ba, Rb, elements which have patterns that slope to the right because they have a stronger positive correlation with the LIL elements than the HFS elements. Several elements, MnO, CaO, Na_2O , Cu, Ni, Cr and Pb, do not correlate significantly with any of the incompatible elements.

If the process(es) that generated the inter-element correlations can be identified, this should shed light on the petrogenetic history of the SMLS. The possibility that crustal contamination could have produced the correlations is now investigated.

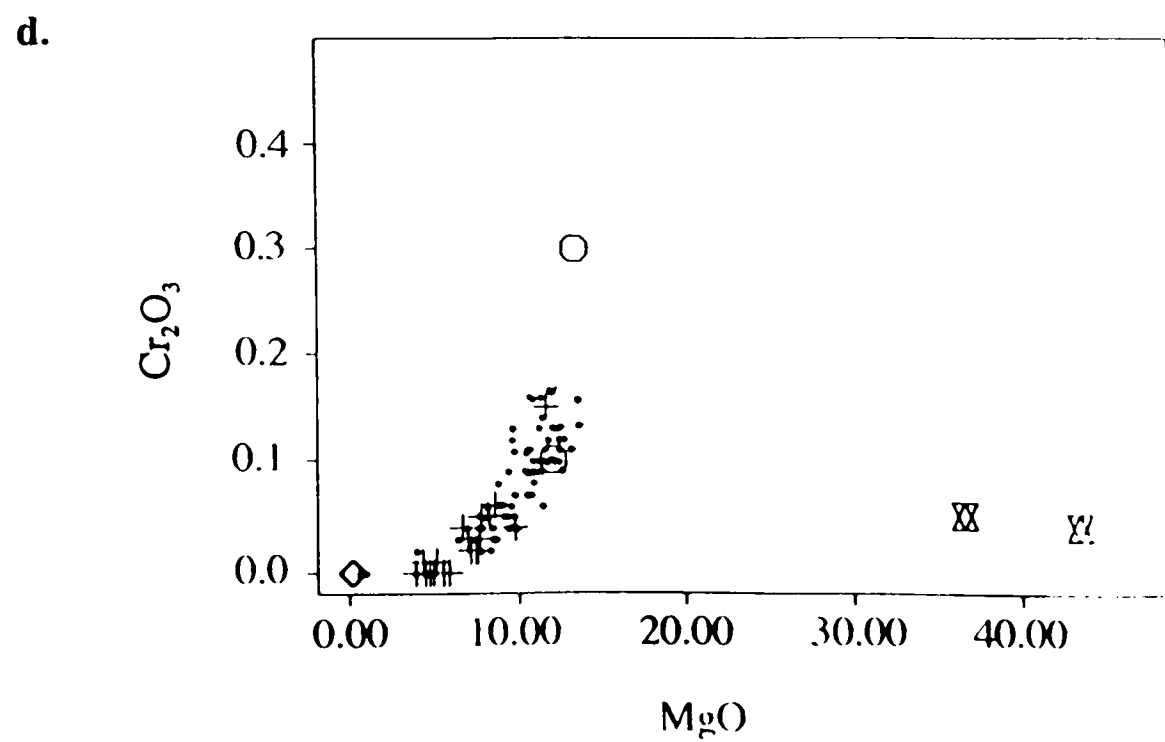
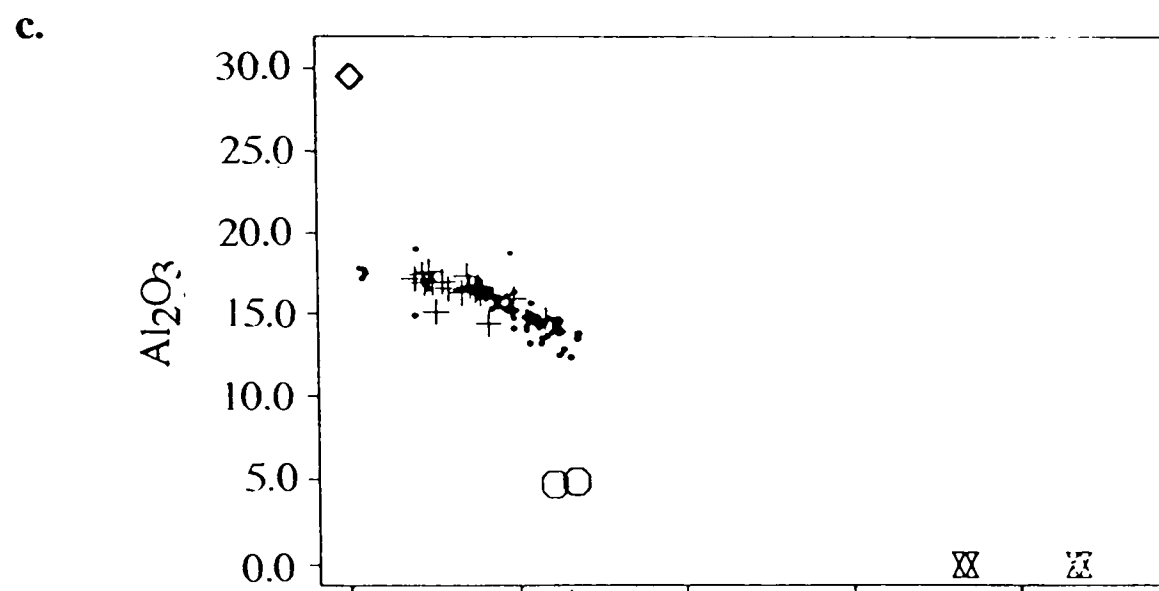
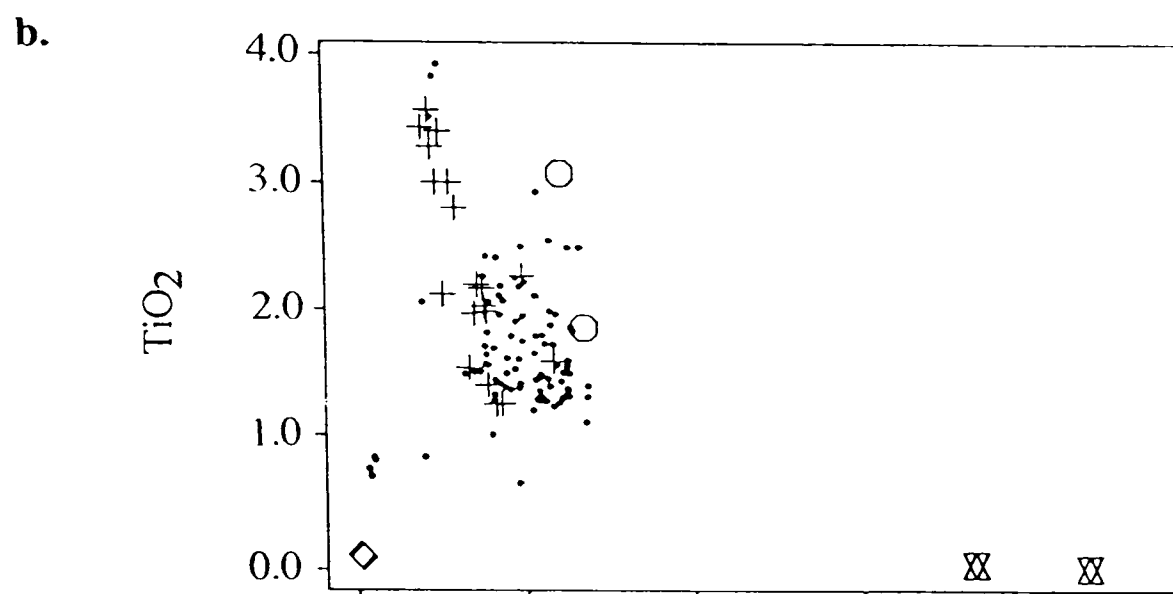
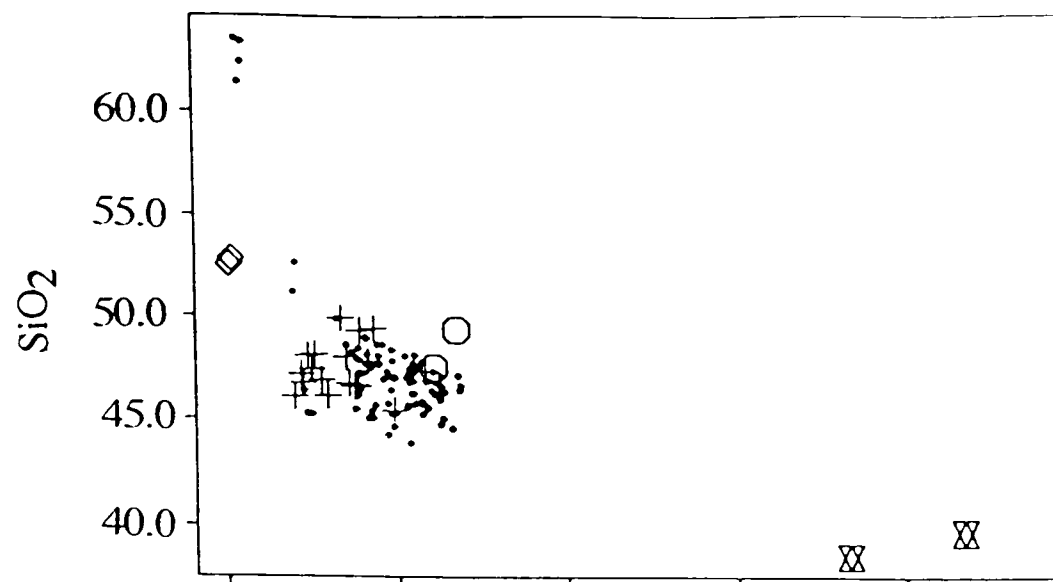
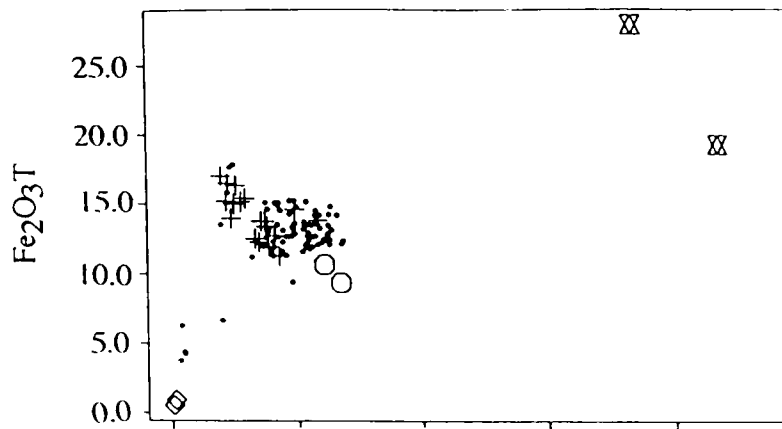
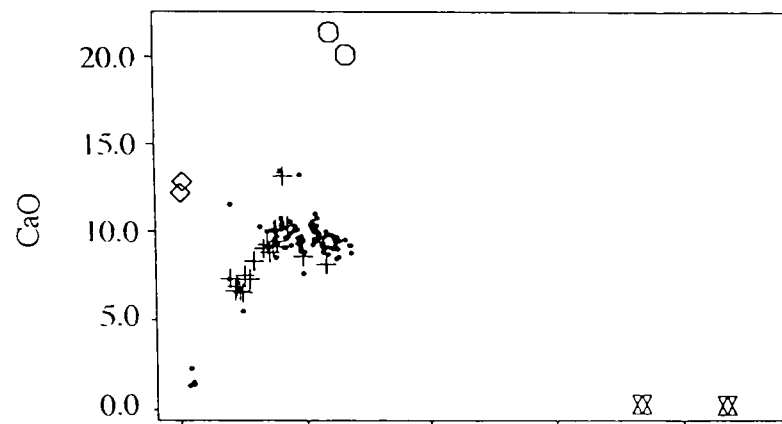


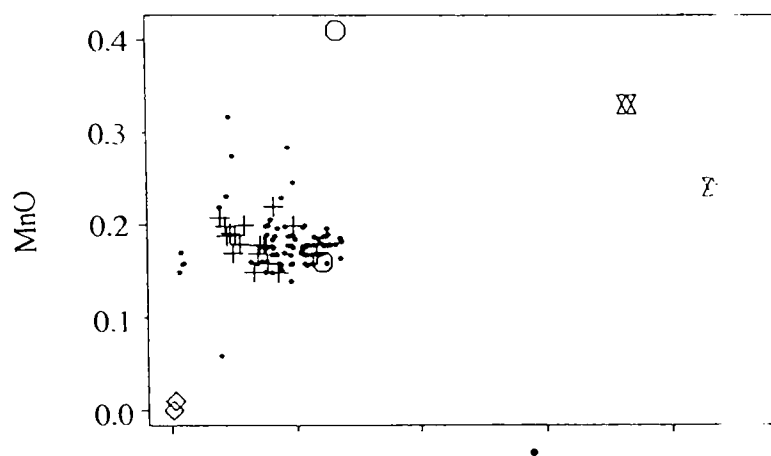
Figure 6.1 continued.... see two pages on for caption



f.



g.



h.

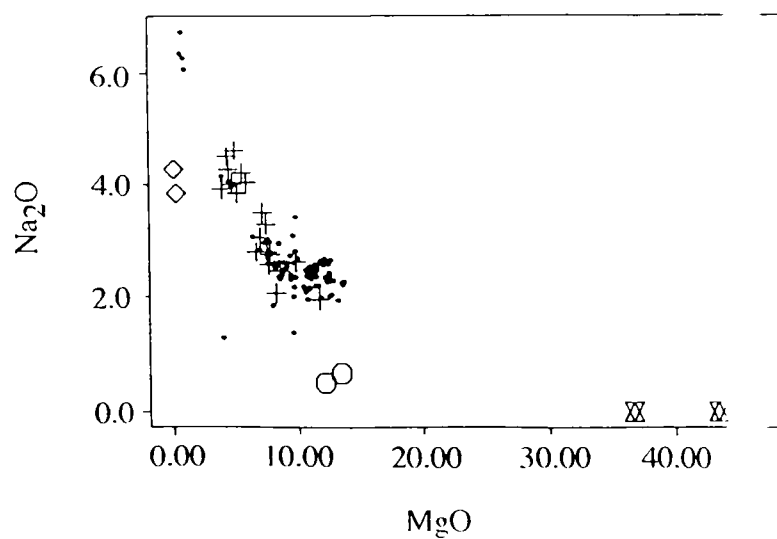
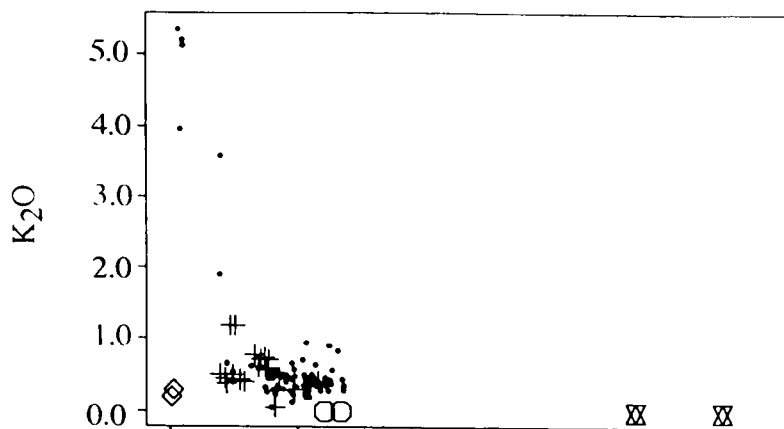


Figure 6.1 continued.... see next page for caption

i.



j.

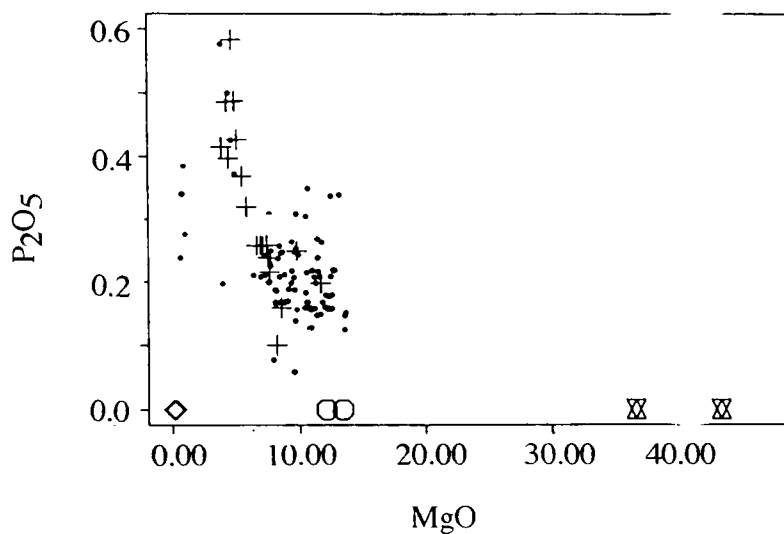


Figure 6.1 Major element oxide versus an index of fractionation, MgO , plots for the Skye Main Lava Series lavas.

Symbols: dots = porphyritic lavas (> 5% phenocrysts), crosses = aphyric lavas, overlaid triangles = olivine phenocrysts, diamonds = plagioclase phenocrysts, octagons = clinopyroxene phenocrysts.

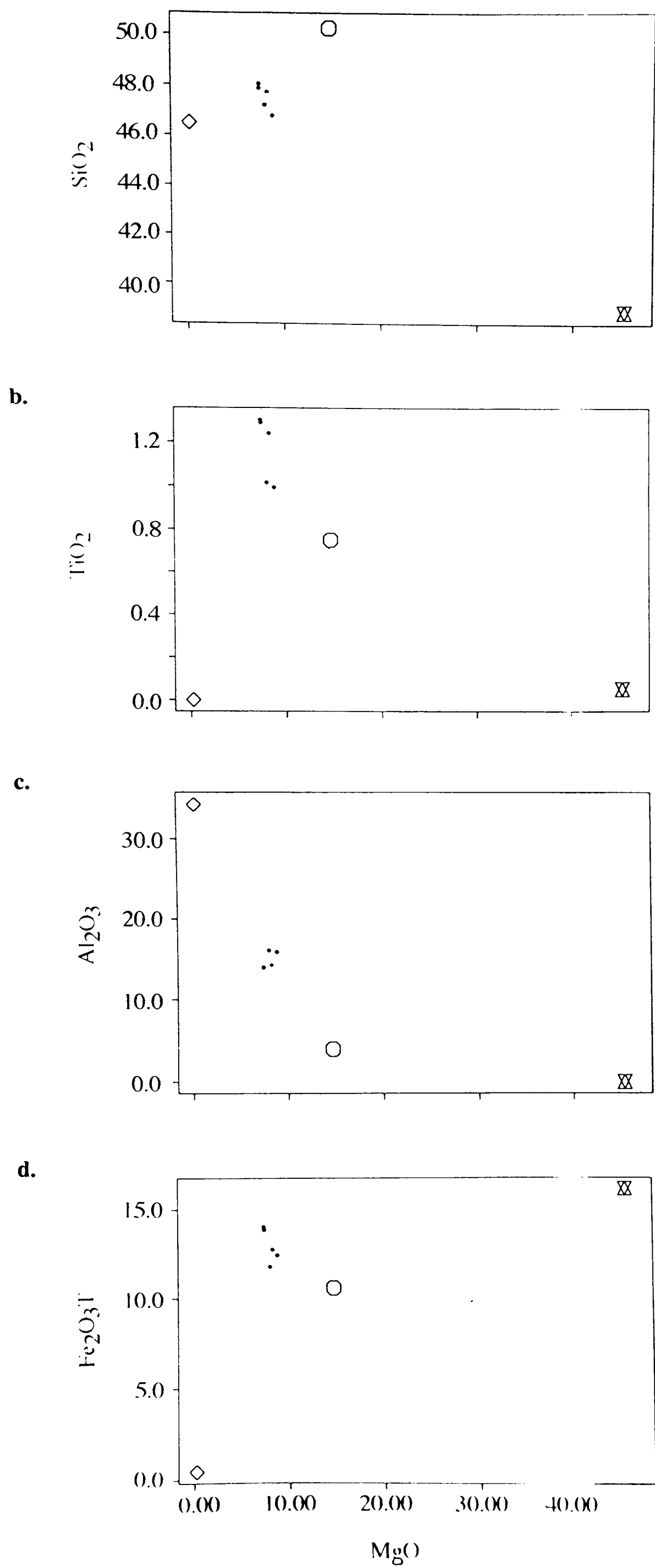


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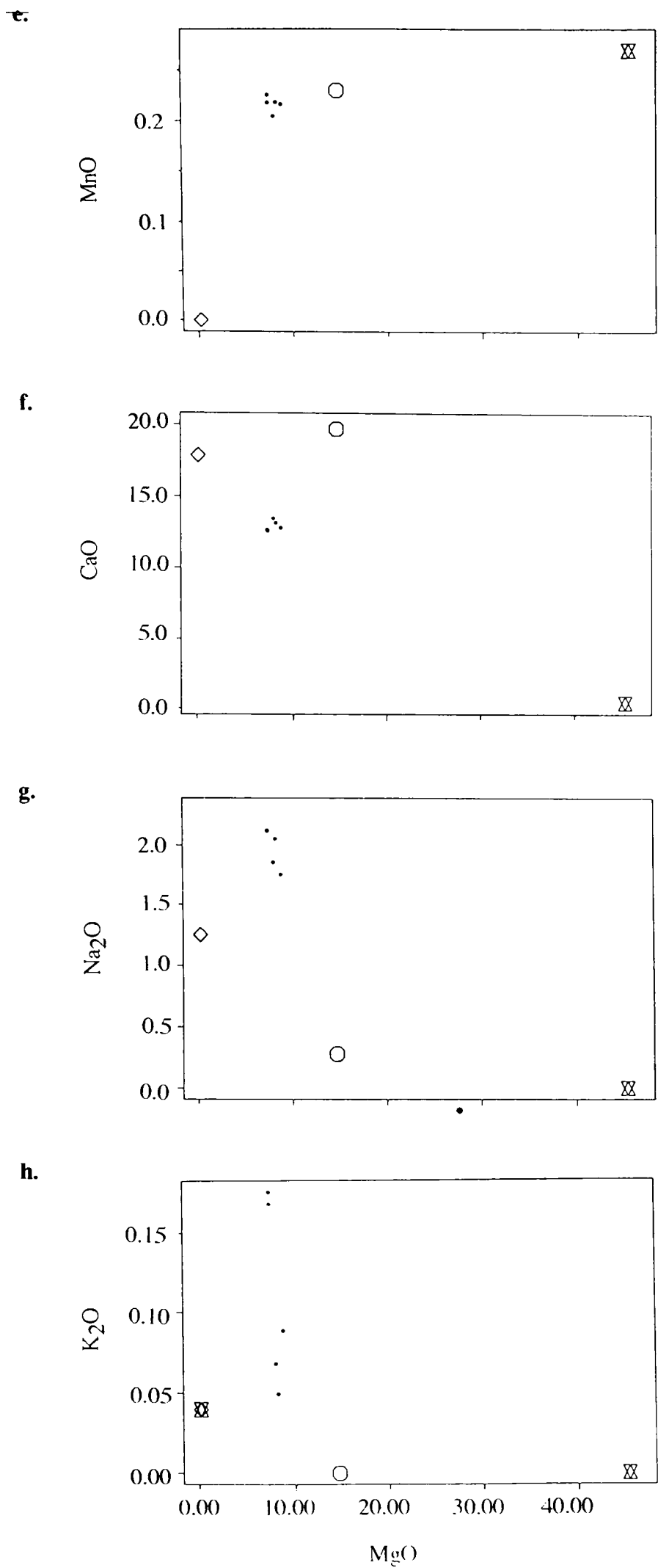


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i.

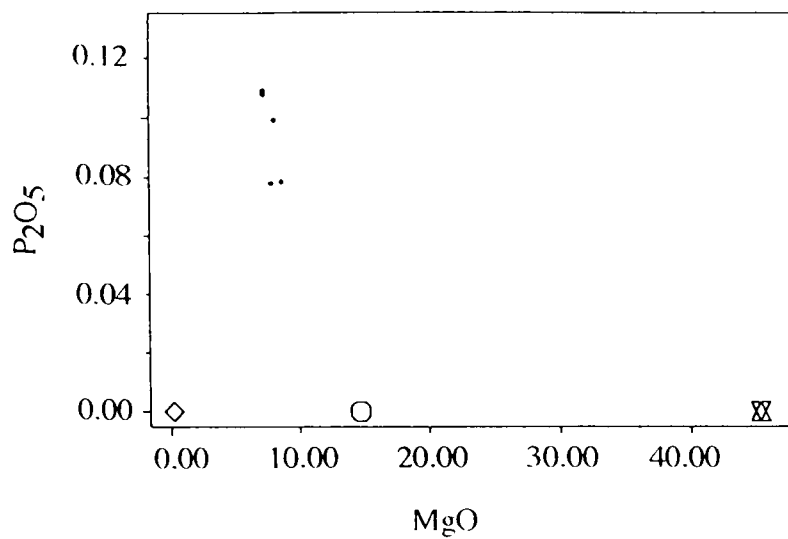


Figure 6.2 Major element oxide versus an index of fractionation, MgO, plots for the Preshal Mhor lavas.

Symbols: as for Figure 6.1.

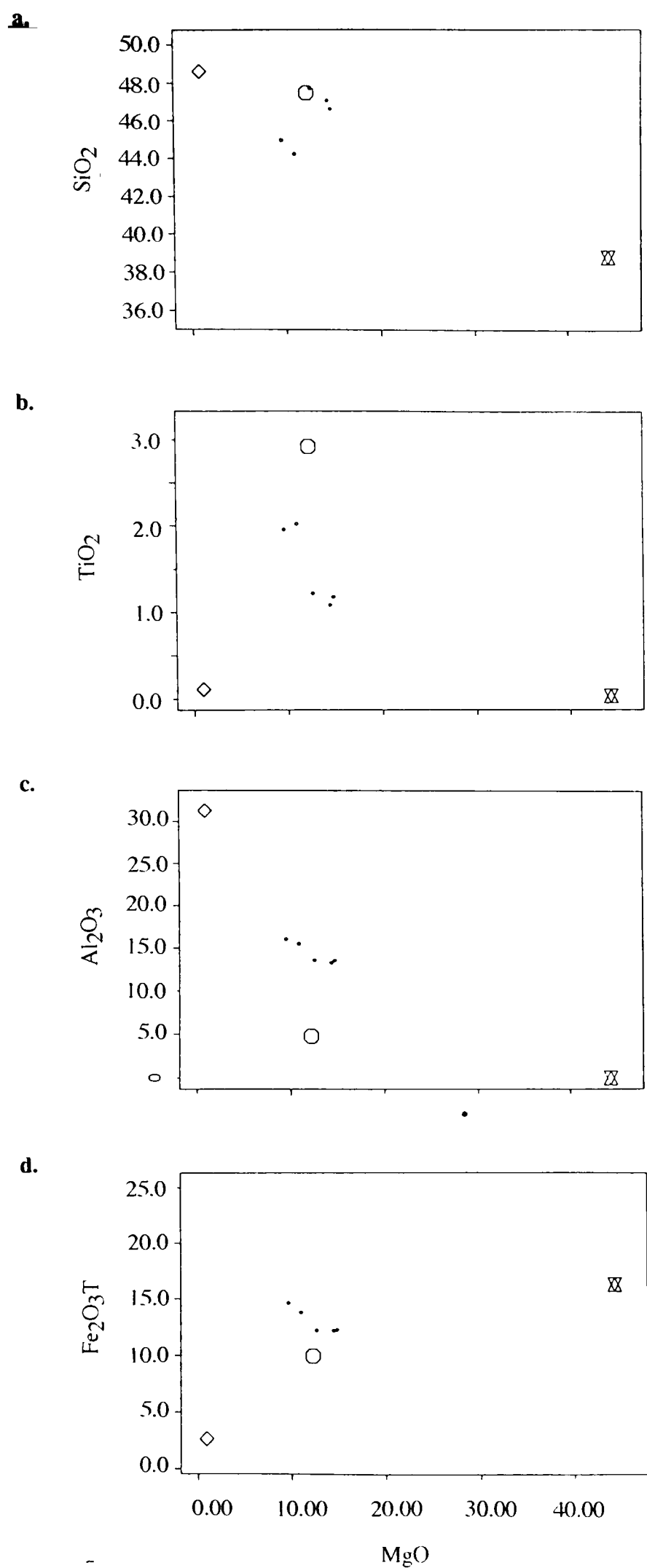


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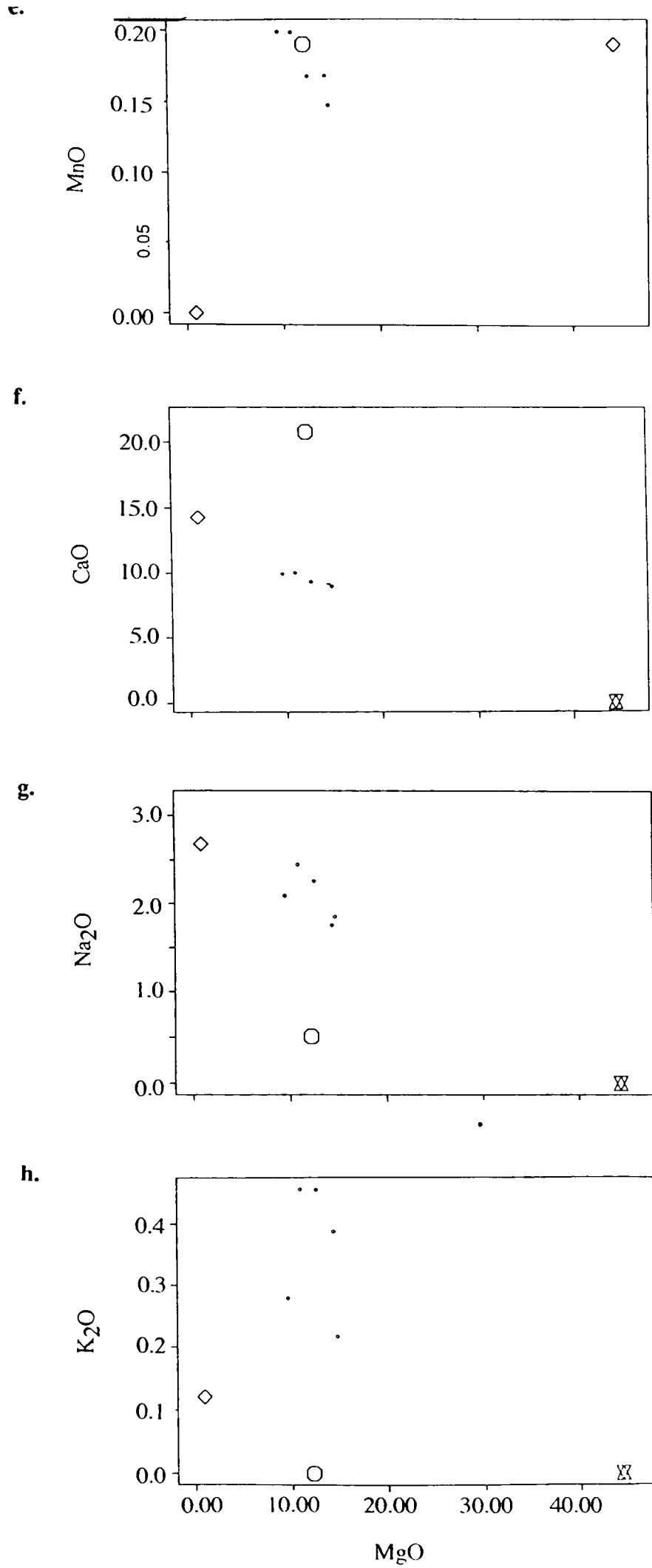


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i.

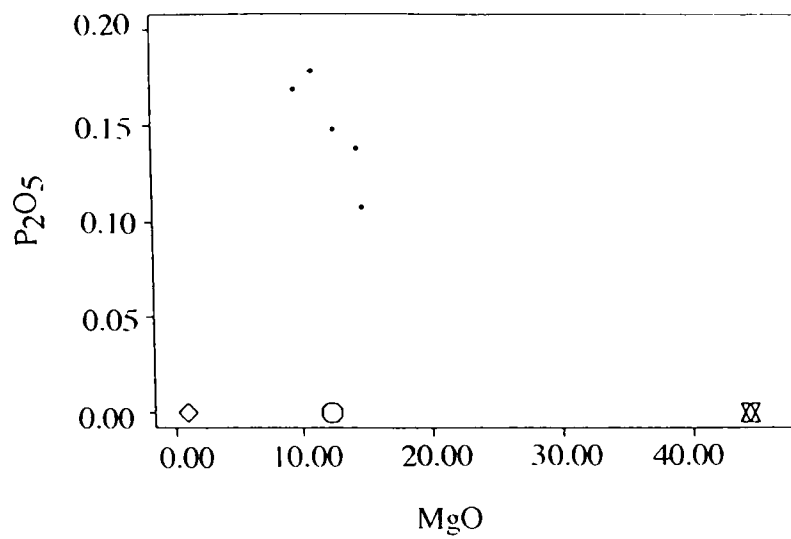
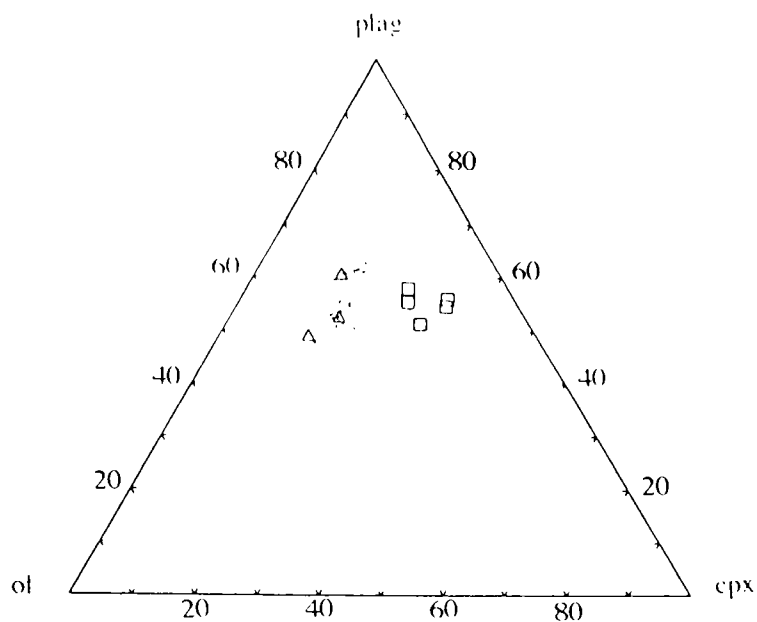


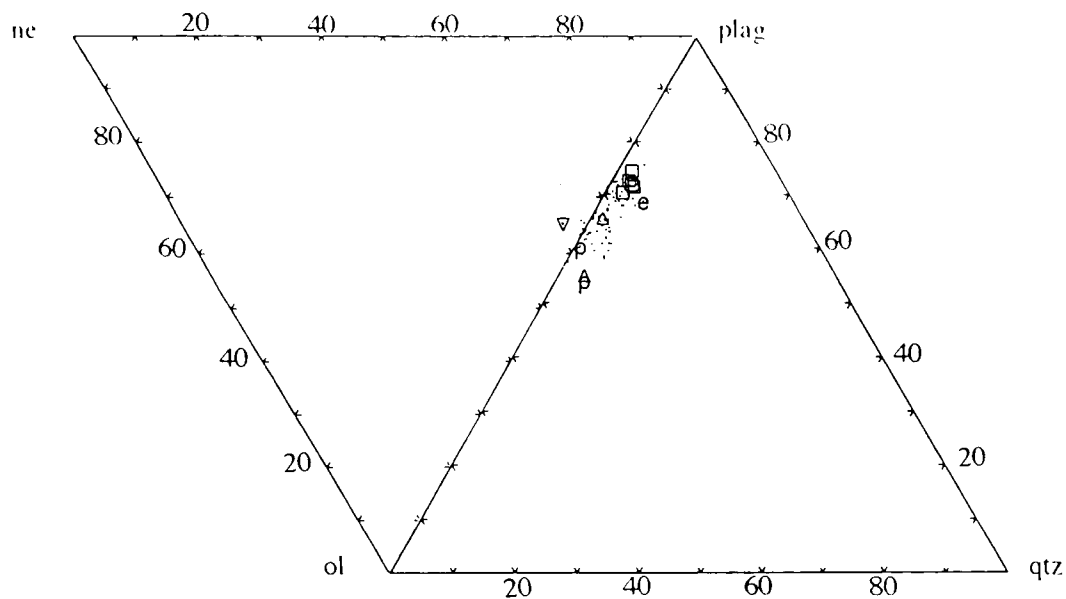
Figure 6.3 Major element oxide versus an index of fractionation, MgO, plots for the Fairy Bridge lavas.

Symbols: as for Figure 6.1.

a.



b.



c.

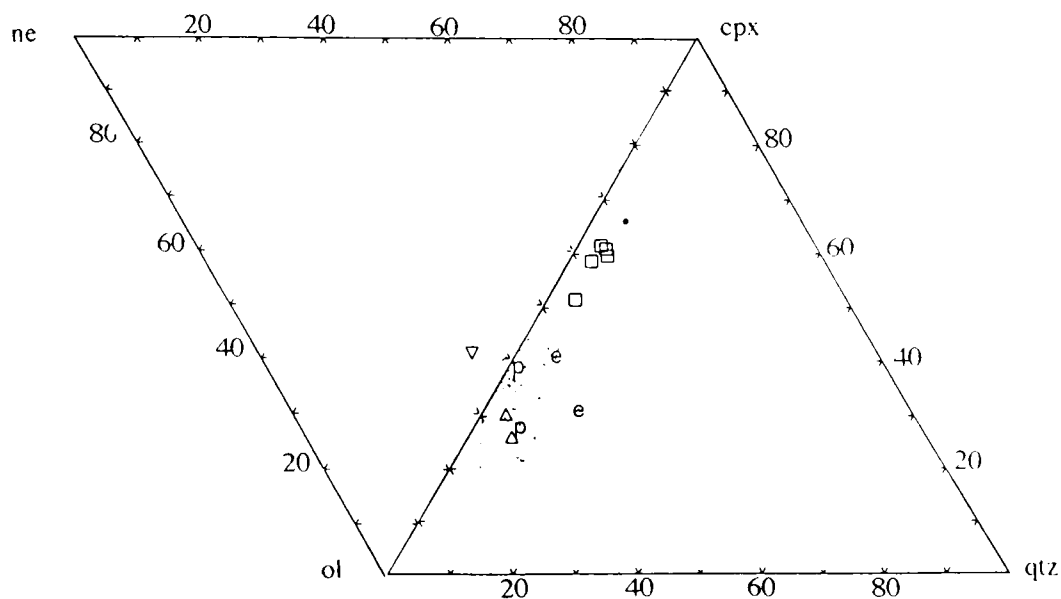
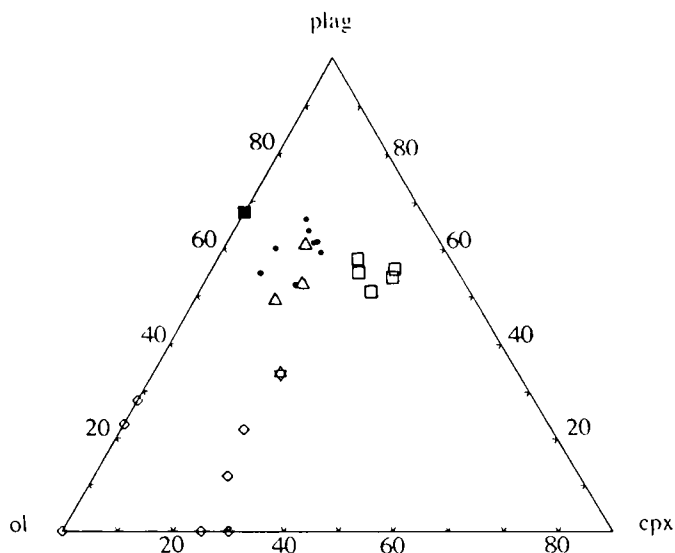


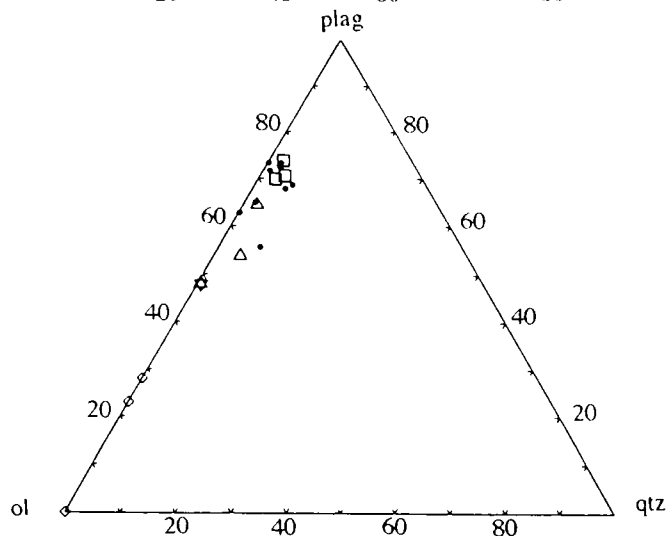
Figure 6.4 Projection of the SMLS, PM, and FB lavas in the basalt tetrahedron from:
a. quartz onto olivine-clinopyroxene-plagioclase.
b. clinopyroxene onto nepheline/quartz-olivine-plagioclase.
c. plagioclase onto nepheline/quartz-olivine-clinopyroxene.

symbols: dots - SMLS lavas, p_1e_1 and p_2e_2 SMLS primitive - evolved basalt pairs (see text for details)
open squares - PM lavas
open triangles - FB lavas

a.



b.



c.

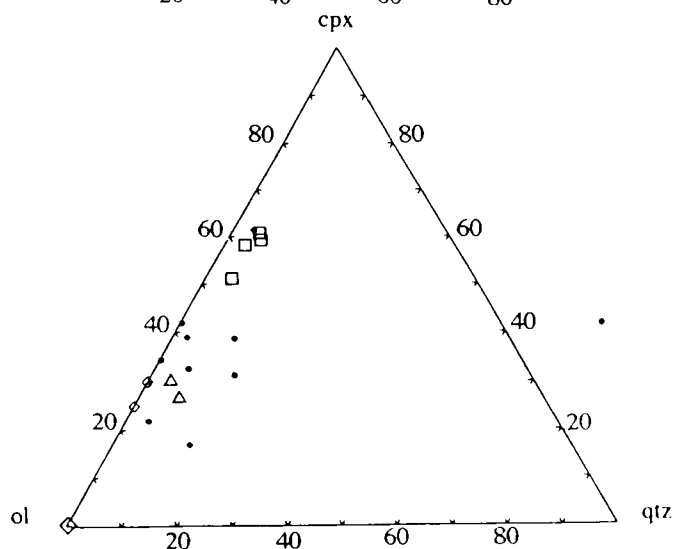


Figure 6.5 Projection of the SMLS, PM, and FB lavas in the basalt tetrahedron from:
a. quartz onto olivine-clinopyroxene-plagioclase.
b. clinopyroxene onto nepheline/quartz-olivine-plagioclase.
c. plagioclase onto nepheline/quartz-olivine-clinopyroxene.

symbols: SMLS dots - aphyric lavas (<5% phenocrysts)
 diamonds - mixing calculation extract solutions
PM open squares - lavas
 closed squares - mixing calculation extract solutions
FB open triangles - lavas
 stars - mixing calculation extract solutions

(in b. SMLS and PM extract at 100% ol; in c. SMLS, PM, and FB extract at 100% ol)

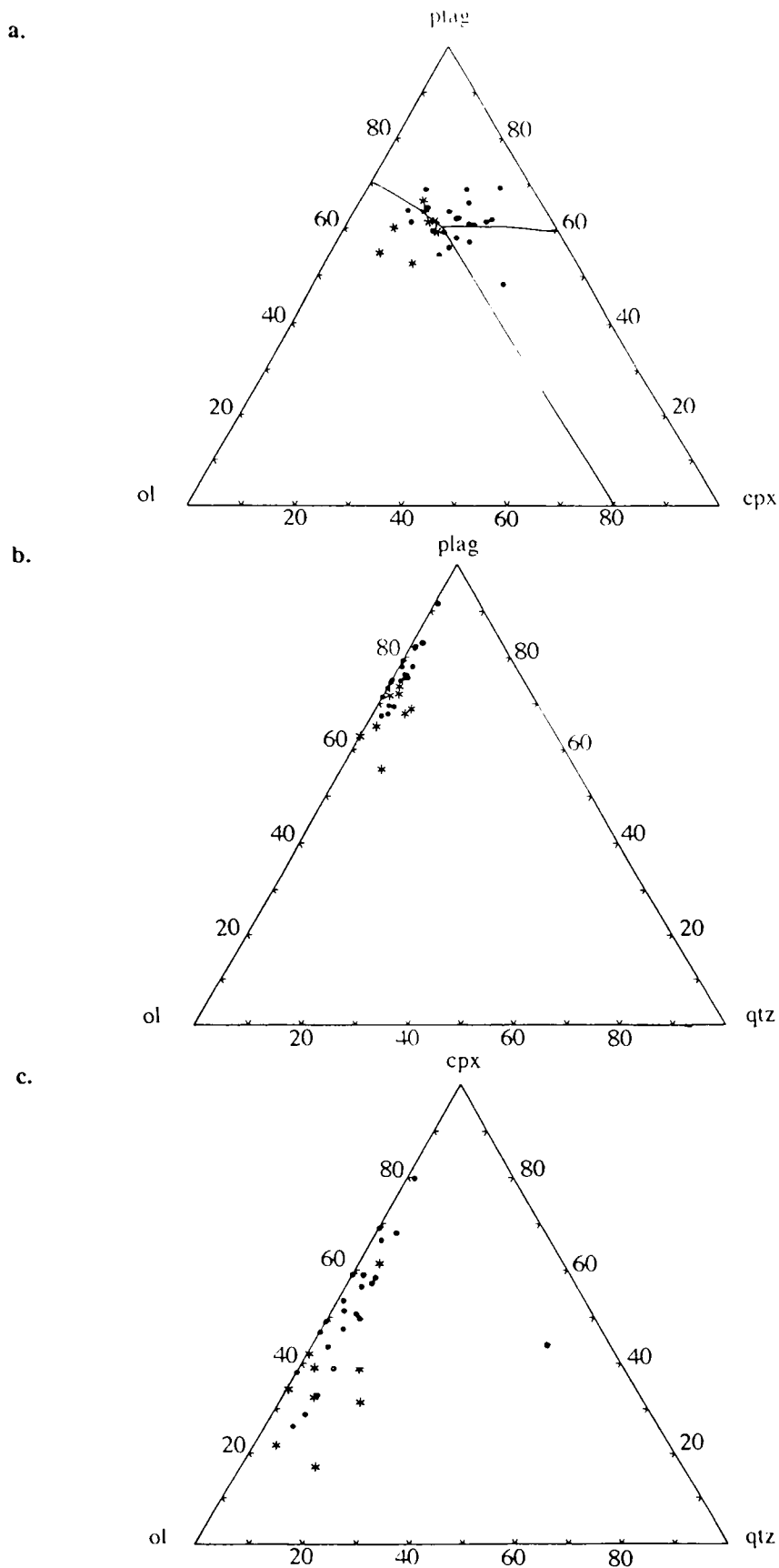


Figure 6.6

Projection of the SMLS aphyric lavas, and groundmass compositions (calculated by mass balance, see text for details) in the basalt tetrahedron from:

- quartz onto olivine-clinopyroxene-plagioclase.
- clinopyroxene onto nepheline/quartz-olivine-plagioclase.
- plagioclase onto nepheline/quartz-olivine-clinopyroxene.

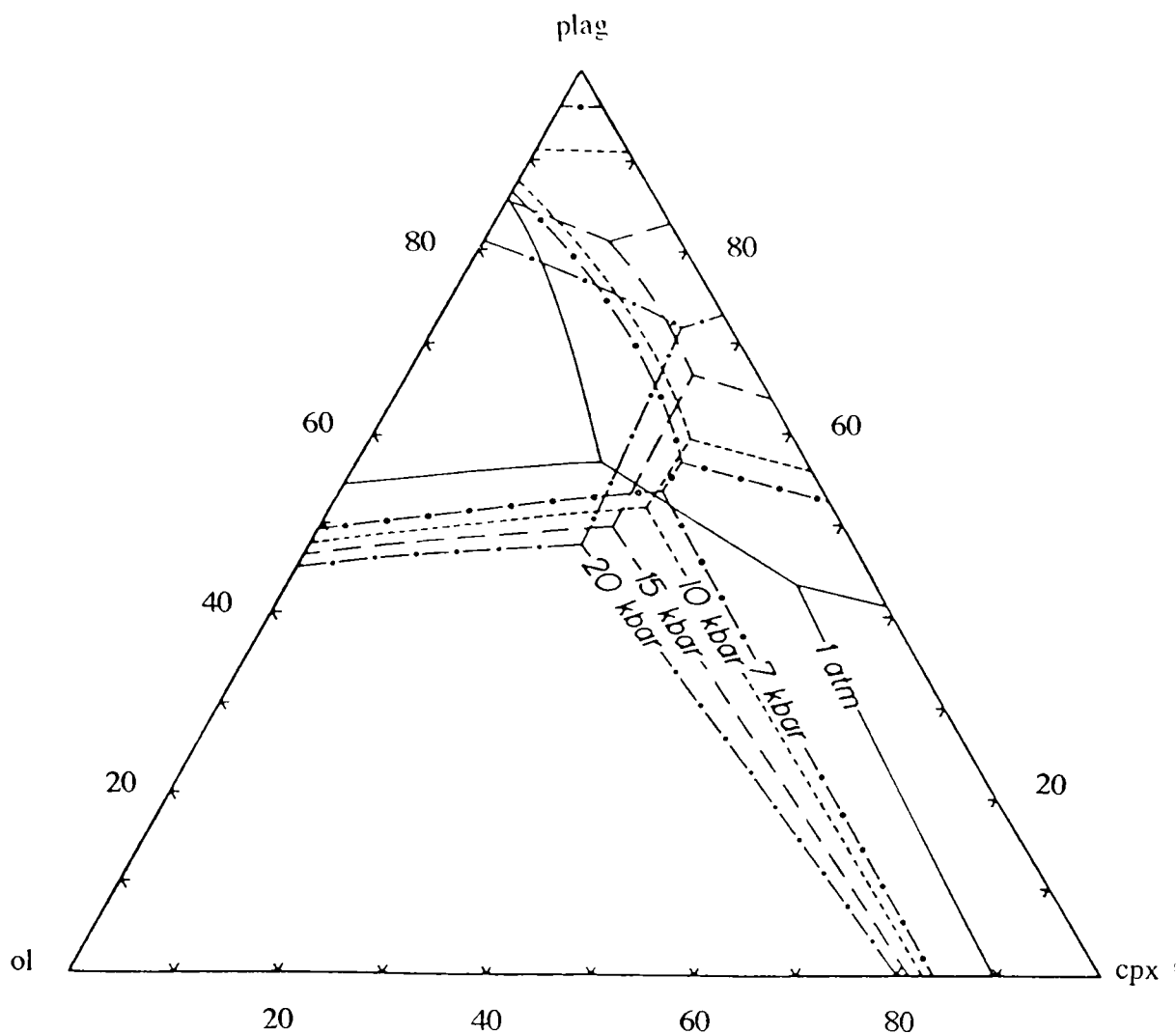
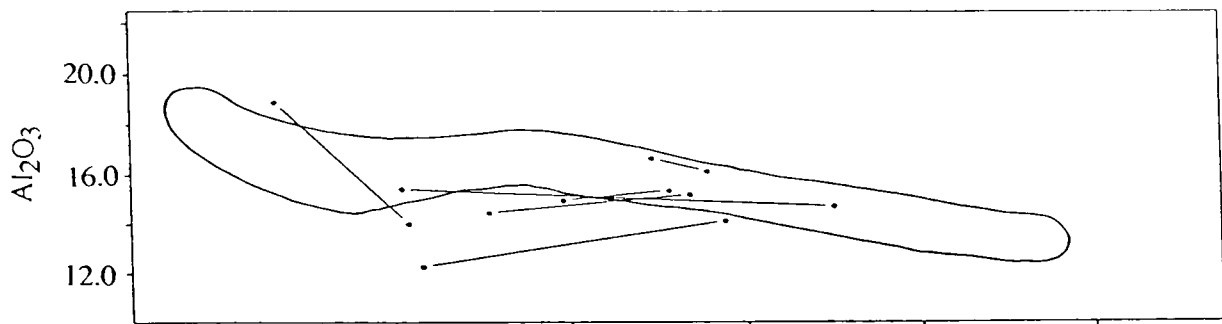


Figure 6.7

Projection from quartz onto the plane olivine-clinopyroxene-plagioclase showing the phase relations at various pressures, derived from experimental results.
(Walker et al., 1979)

a.



b.

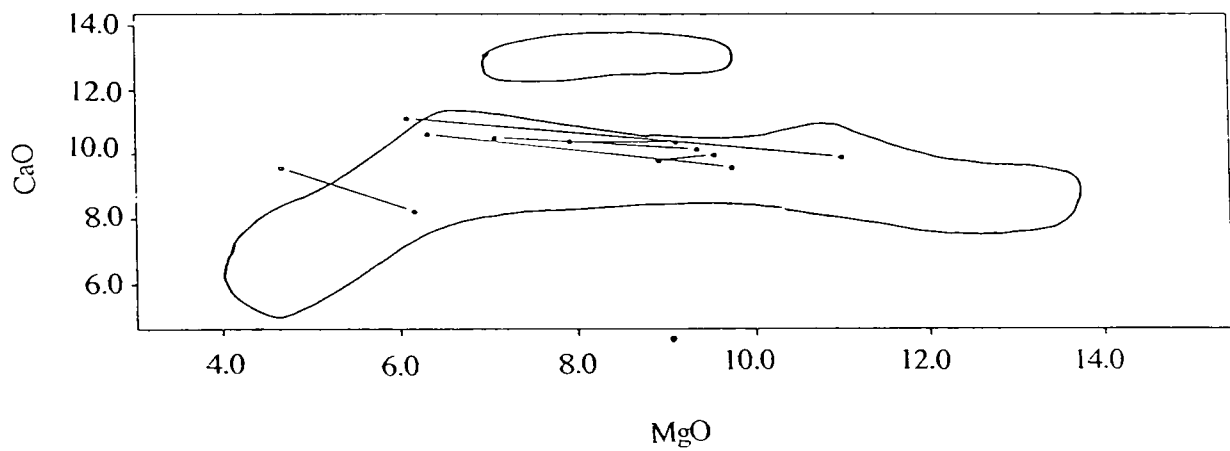


Figure 6.8 Groundmass whole rock tielines for selected SMLS samples.
Envelopes enclose the whole dataset.

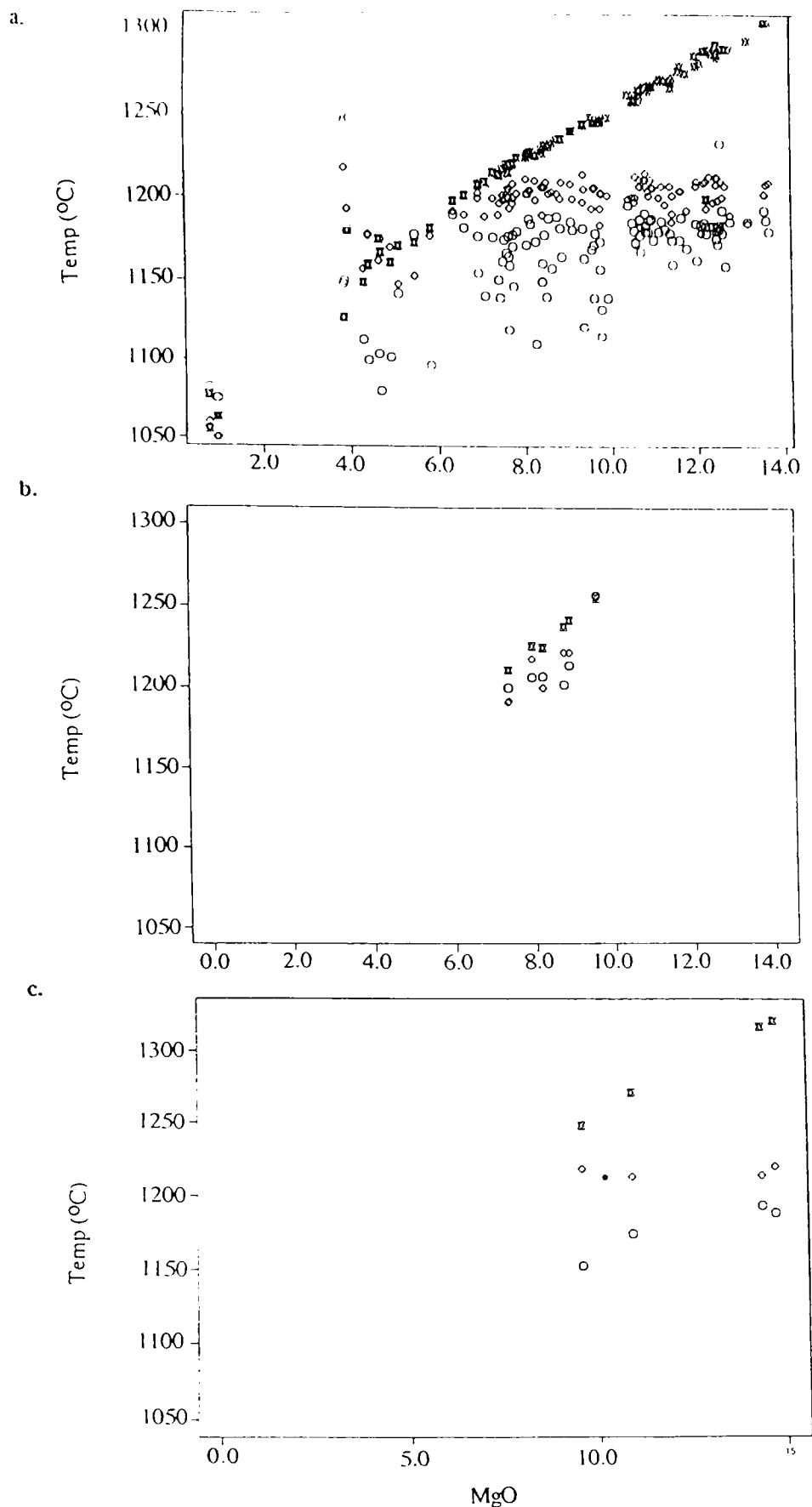


Figure 6.9 Liquidus temperatures of olivine (overlaid triangles), plagioclase (diamonds) and clinopyroxene (octagons) at one-atmosphere pressure for:

- a. SMLS
- b. PM
- c. FB

(calculated using the equations of Nathan and Van Kirk, 1978)

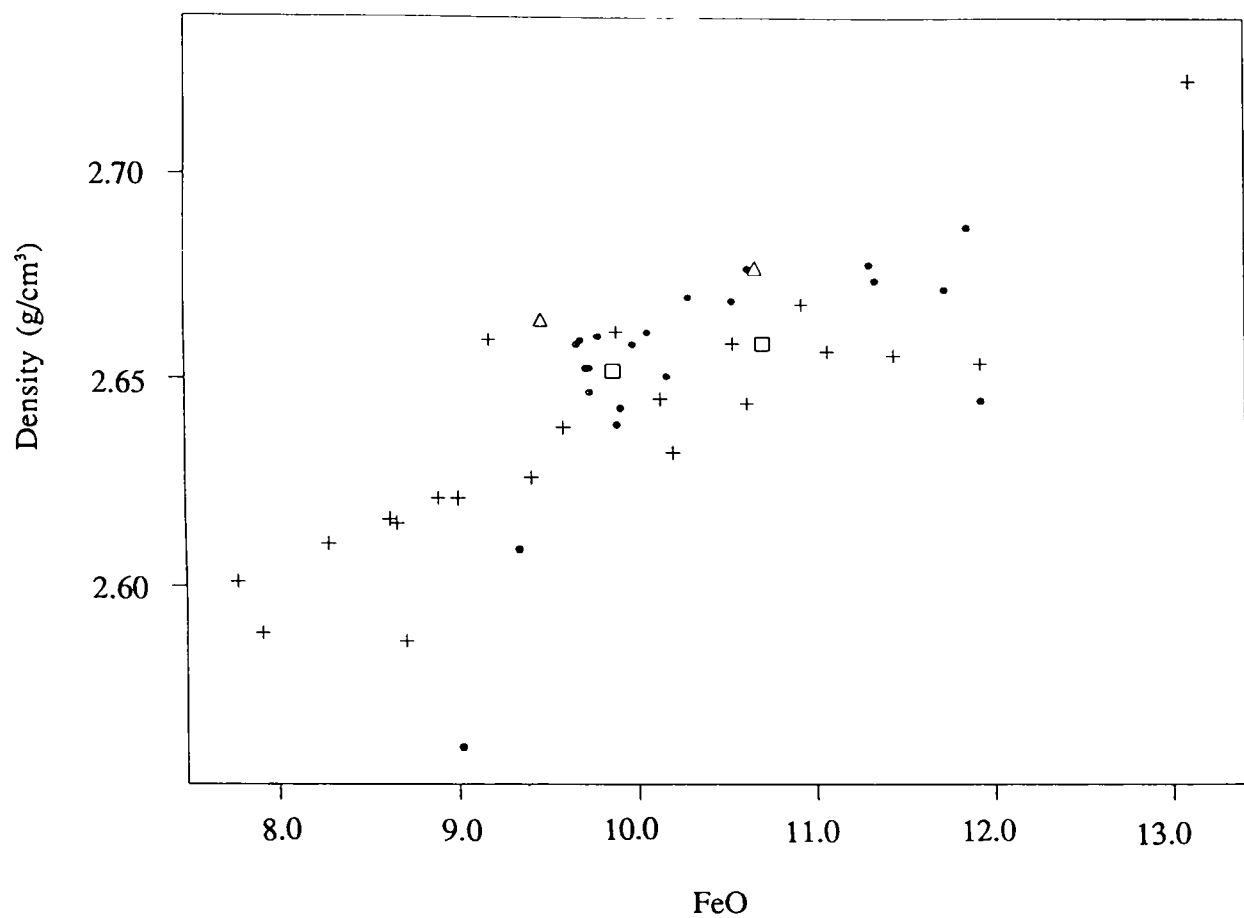


Figure 6.10 FeO versus density.

Symbols: as for Figure 6.1.

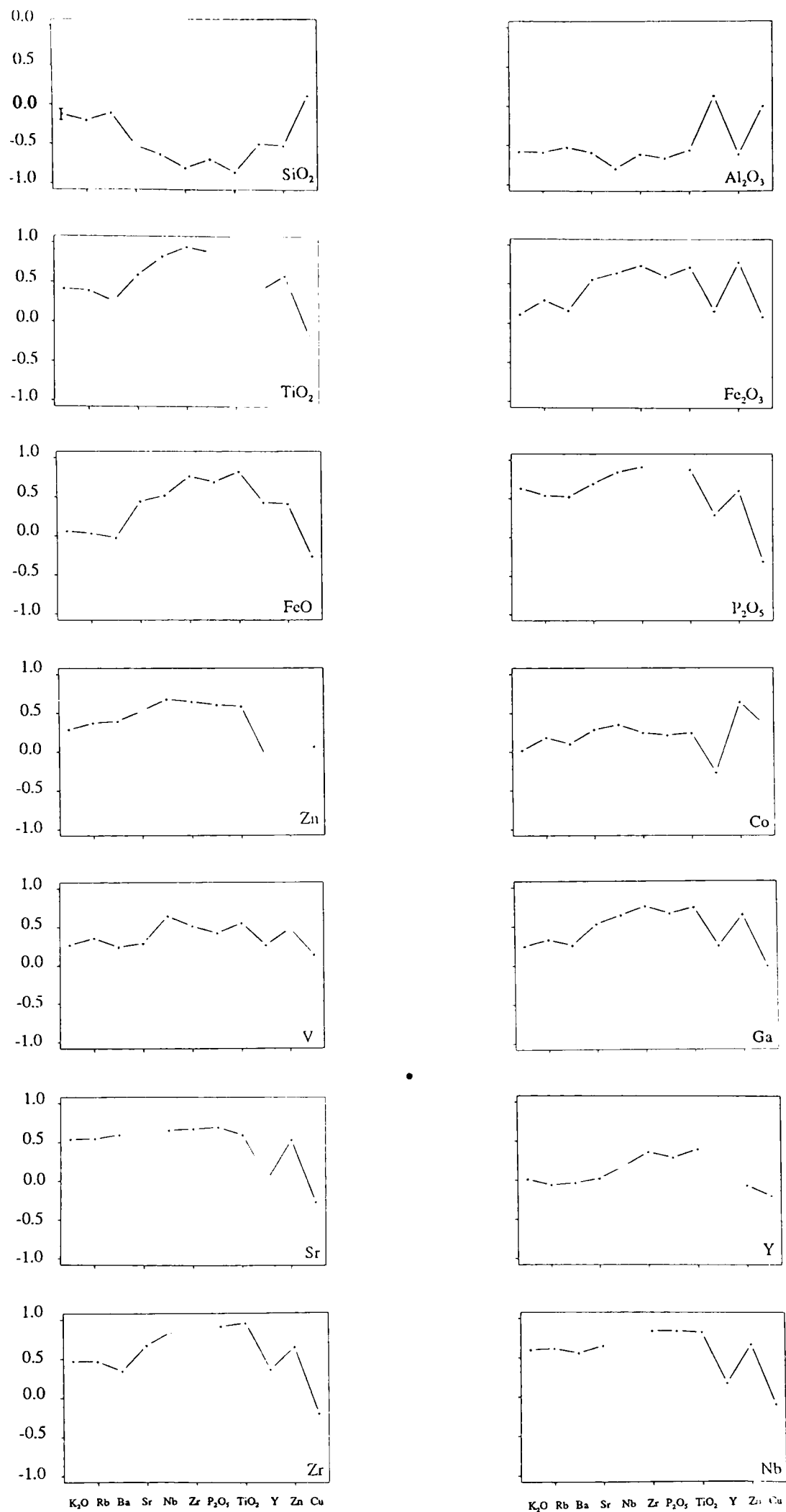


Figure 6.11 caption on next page

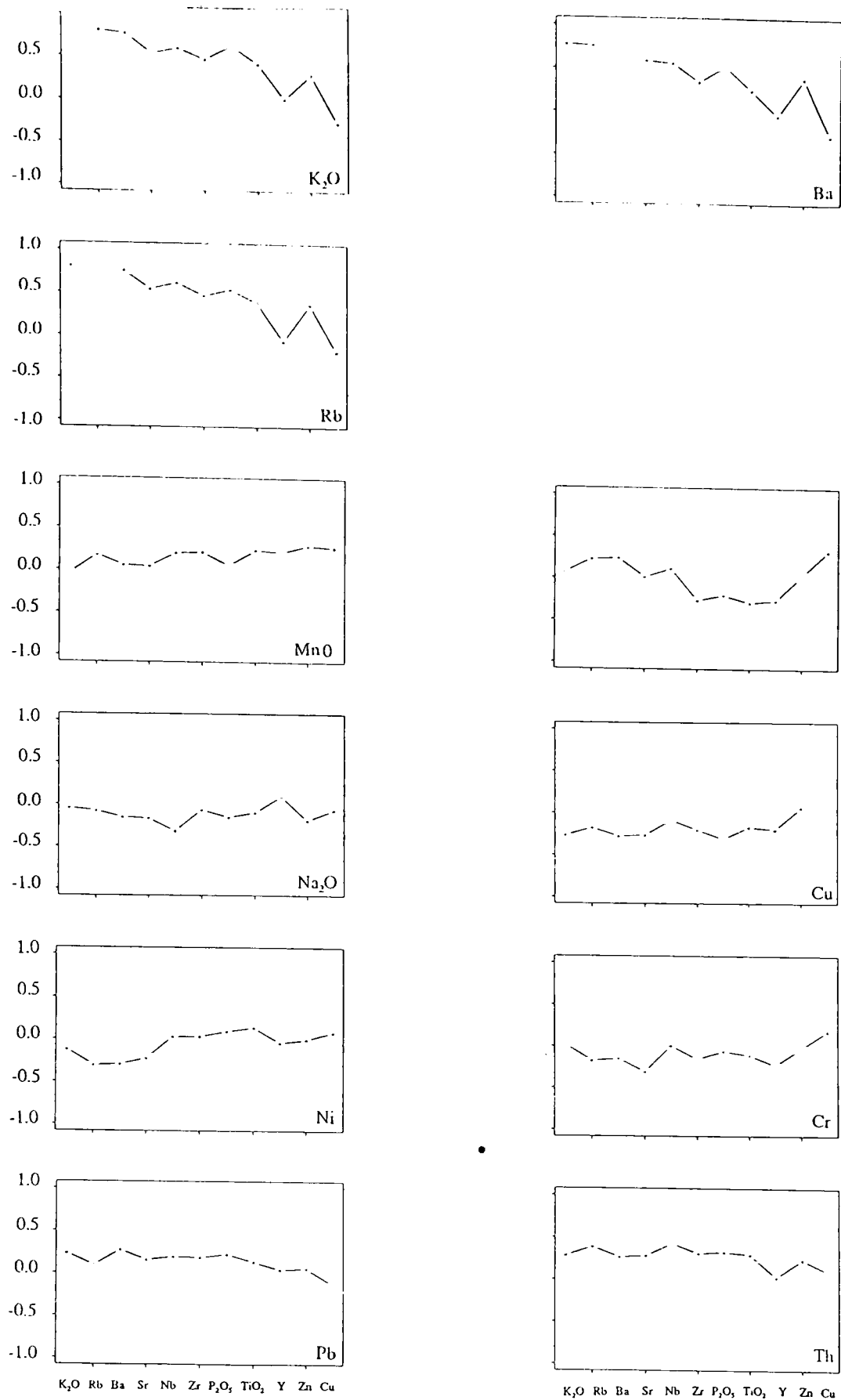


Figure 6.11 Correlation coefficient patterns for the SMLS 15 wt% MgO data-set
(see text for details)

INPUT DATA					SOLUTION				
Evolved end-member	OI	Plag	Cpx	Target	Extract %	Olivine %	Plag %	Cpx %	Sum of squares
7 MgO	1			13 MgO	13.59	100.00			0.7767
7 MgO	1	1		13 MgO	13.40	101.30	-0.30		0.7804
7 MgO	1		1	13 MgO	17.28	74.34		25.63	0.1595
7 MgO	1	1	1	13 MgO	16.75	75.90	-0.02	26.49	0.1564

Table 6.1.a. Results of Wright and Doherty modelling of the SMLS basic lavas.

INPUT DATA					SOLUTION				
Evolved end-member	OI	Plag	Cpx	Target	Extract %	Olivine %	Plag %	Cpx %	Sum of squares
4.5 MgO	1	1		7 MgO	36.69	35.07	64.92		6.9008
4.5 MgO	1	1	1	7 MgO	43.60	26.67	46.83	26.49	0.8047

Table 6.1.b Results of Wright and Doherty modelling of the SMLS less basic lavas.

	Ol	Plag	Cpx	13 wt% MgO average	7 wt% MgO average	4.5 wt% MgO average
SiO ₂	40.56	53.32	46.58	46.26	47.60	47.50
TiO ₂		0.06	1.28	1.55	1.78	2.98
Al ₂ O ₃		30.68	4.55	13.96	16.55	16.87
FeO	14.50	0.79	7.65	12.99	12.99	15.15
MnO	0.19	0.01	0.16	0.18	0.17	0.20
MgO	47.21	0.04	14.06	12.63	7.39	4.64
CaO	0.26	14.20	21.71	9.28	9.82	7.33
Na ₂ O		3.13	0.31	2.33	2.84	3.91
K ₂ O		0.15	-	0.45	0.55	0.94

Table 6.2.a SMLS data used in Wright and Doherty modelling.

	Ol	Plag	Cpx	9 wt% MgO average	7.5 wt% MgO average
SiO ₂	39.78	53.32	54.46	48.08	46.81
TiO ₂	-	-		1.29	0.99
Al ₂ O ₃		32.58		14.14	15.98
FeO	17.76		0.00	13.86 •	12.45
MnO	0.00	-	0.00	0.21	0.21
MgO	44.07		15.95	7.35	8.75
CaO	-	15.34	25.46	12.62	12.81
Na ₂ O	-	2.82		2.12	1.75
K ₂ O	-	0.00		0.16	0.08

Table 6.2.b PM data used in Wright and Doherty modelling.

INPUT DATA					SOLUTION				
Evolved end-member	OI	Plag	Cpx	Target	Extract %	Olivine %	Plag %	Cpx %	Sum of squares
7.5 MgO	1		-	9 MgO	1.54	100.00			9.1672
7.5 MgO	1	1		9 MgO	21.42	31.36	68.64		1.0549
7.5 MgO	1	1	1	9 MgO	21.26	31.58	68.81	-0.003	1.0493

Table 6.3 Results of Wright and Doherty modelling of the PM lavas.

	Mean	Range			Std dev
SiO ₂	45.93	43.46	-	47.98	0.957
TiO ₂	1.46	1.04	-	2.55	0.339
Al ₂ O ₃	13.10	11.60	-	14.12	0.503
FeO	2.60	2.14		3.17	0.226
Fe ₂ O ₃	10.41	9.13	-	12.40	0.850
MnO	0.14	0.11	-	0.20	0.016
MgO	15.00	15.00	-	15.00	0.000
CaO	8.42	6.57	-	9.79	0.610
Na ₂ O	2.17	1.72	-	2.95	0.200
K ₂ O	0.38	0.17		0.85	0.130
P ₂ O ₅	0.16	0.10	-	0.31	0.043
Zn	70.67	57.68	-	96.27	8.240
Cu	84.14	25.09	-	137.05	20.480
Ni	921.91	124.43	-	3392.00	249.360
Co	54.47	37.56		70.30	8.290
Cr	1391.64	14.38	-	5097.00	667.950
V	223.47	178.25	-	310.66	27.830
Ba	183.50	7.30		570.86	83.520
Ga	17.69	14.33		22.32	1.560
Rb	8.59	2.99		17.76	2.980
Sr	334.84	136.54		653.91	112.980
Y	17.68	14.48		22.57	1.610
Zr	105.01	71.71	-	175.83	26.310
Nb	5.53	2.65		14.95	2.580
Th	2.54	0.00	-	5.19	1.170
U	1.21	0.00		3.23	0.782
Pb	1.14	1.04	-	1.26	0.060

Table 6.4 Mean, range, and standard deviation for all samples in the 15 wt% MgO data-set.

	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Zn	Cu	Ni	Co	Cr	V	Ba	Ga	Rb	Sr	Y	Zr	Nb	Pb	Th	U
SiO ₂	0.852	0.296	-0.799	-0.859	-0.305	-	0.184	0.142	-0.124	-0.686	-0.517	0.113	-0.103	-0.302	0.237	-0.508	-0.103	-0.709	-0.199	-0.516	-0.491	-0.799	-0.627	-0.099	-0.240	-0.028
TiO ₂	-	-0.548	0.725	0.822	0.236	-	-0.292	-0.097	0.415	0.881	0.586	-0.166	0.135	0.247	-0.111	0.548	0.256	0.745	0.391	0.593	0.398	0.952	0.828	0.128	0.292	0.081
Al ₂ O ₃	-	-	-0.508	-0.284	0.072	-	-0.319	0.320	-0.577	-0.655	-0.603	0.003	-0.054	-0.430	-0.202	-0.494	-0.516	-0.421	-0.586	-0.578	0.139	-0.602	-0.785	-0.136	-0.337	0.271
FeO	-	-	-	0.642	0.405	-	-0.035	-0.210	0.115	0.602	0.789	0.093	0.000	0.699	-0.156	0.562	0.166	0.688	0.297	0.562	0.165	0.746	0.650	-0.029	0.234	-0.461
Fe ₂ O ₃	-	-	-	-	0.019	-	-0.511	-0.085	0.062	0.689	0.408	-0.265	0.348	0.140	-0.088	0.247	-0.022	0.589	0.031	0.440	0.427	0.762	0.515	0.023	0.075	0.381
MnO	-	-	-	-	-	-	0.013	0.166	-0.039	0.054	0.290	0.270	-0.291	0.350	-0.265	0.476	0.055	0.300	0.174	0.041	0.211	0.209	0.198	-0.046	0.021	0.470
MgO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	-	-	-	-	-	-	-0.534	0.070	-0.202	0.037	0.324	-0.245	0.268	0.111	0.259	0.238	-0.149	0.225	0.012	-0.264	-0.265	0.113	0.048	0.252	-0.539	
Na ₂ O	-	-	-	-	-	-	-	-0.045	-0.155	-0.191	-0.067	-0.184	-0.300	-0.219	-0.113	-0.154	0.001	-0.077	-0.168	0.097	-0.065	-0.321	0.141	-0.147	0.132	
K ₂ O	-	-	-	-	-	-	-	0.631	-	0.286	-0.265	-0.121	0.020	0.019	0.271	0.772	0.248	0.805	0.539	0.008	0.469	0.601	0.229	0.281	-0.067	
P ₂ O ₅	-	-	-	-	-	-	-	-	-	0.603	-0.306	0.901	0.217	-0.060	0.419	0.524	0.666	0.539	0.692	0.290	0.912	0.845	0.216	0.322	0.079	
Zn	-	-	-	-	-	-	-	-	-	-	0.062	-0.005	0.646	-0.026	0.480	0.394	0.649	0.371	0.531	-0.062	0.643	0.676	0.054	0.232	-0.472	
Cu	-	-	-	-	-	-	-	-	-	-	-	0.081	0.351	0.177	0.140	-0.274	-0.007	-0.177	-0.264	-0.195	-0.199	-0.084	-0.131	0.090	-0.409	
Ni	-	-	-	-	-	-	-	-	-	-	-	-	0.160	0.766	-0.512	-0.297	-0.136	-0.304	-0.226	-0.044	0.029	0.026	-0.034	-0.124	0.408	
Co	-	-	-	-	-	-	-	-	-	-	-	-	-	0.204	0.397	0.104	0.288	0.187	0.288	-0.266	0.250	0.351	-0.180	0.112	-0.680	
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.056	-0.152	-0.271	-0.178	-0.311	-0.233	-0.155	0.005	-0.010	-0.105	0.106	
V	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.243	0.454	0.357	0.291	0.264	0.511	0.642	0.095	0.275	-0.387	
Ba	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.261	0.755	0.591	-0.035	0.343	0.558	0.268	0.260	-0.225	
Ga	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.332	0.530	0.250	0.760	0.645	0.127	0.160	-0.143	
Rb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.541	-0.060	0.467	0.615	0.090	0.383	-0.326	
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.022	0.669	0.652	0.151	0.277	-0.169	
Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.360	0.177	0.038	0.026	0.295	
Zr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.846	0.177	0.305	-0.011	
Nb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.186	0.422	-0.177	
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.134	0.050	
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.204	

Table 6.5 Correlation coefficient matrix for all samples in the 15 wt% MgO data-set.

CHAPTER 7

CRUSTAL CONTAMINATION

7.1 Introduction

The concept that en route to the surface magmas may come into contact with, and interact with, wall rock material, with which they are not in chemical equilibrium, has long been familiar to igneous petrologists. Many igneous rocks contain inclusions of foreign material which show evidence of having been attacked by the magma. Interaction between upwelling magmas and wall rocks results in the modification of the composition of both. This may prevent information being obtained about the ultimate source region of the magmas, instead the composition of the magmas may only give information about the conditions of last attempts at equilibration.

The range of Sr, Nd, and Pb isotopic data in the Skye Main Lava Series, Preshal Mhor, and Fairy Bridge lavas of Skye could result from inherited source characteristics, of a heterogeneous, possibly metasomatised, source, or mixing of basic magma and crustal, or mantle lithospheric material.

To date, the behaviour of the non-radiogenic elements during lithospheric contamination has been relatively neglected. This study attempts to assess the conclusions of previous workers in the light of new Sr- and Nd-isotopic data, and major and trace element data. There is, however, only enough information to do this for the SMLS samples. The PM and FB samples analysed in the present study all have asthenospheric Sr and Nd isotopic characteristics, i.e. a lithospheric component cannot be detected on the basis of the isotopic characteristics of the lavas. Other workers have found evidence for crustal contamination of the PM lavas. The reader is referred to Moorbath and Thompson (1980) for a detailed discussion of lithospheric

contamination of the PM lavas (Chapter 2, History of Petrogenetic Research, section 2.3.3). The crustal contamination of the PM and FB lavas is not considered here.

7.2 Identification of contaminated and uncontaminated magmas

To assess the compositional affect of contamination and determine the nature and volume of the contaminant(s) the compositional variation within the SMLS lavas not attributable to hydrothermal alteration or fractional crystallisation was considered.

Several approaches were used to try to identify samples contaminated with lithospheric material.

7.2.1 Isotopic data

A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$, Figure 7.1, shows that some of the Skye lavas plot within the mantle array, i.e. the range of compositions which can be generated from the asthenospheric mantle. Samples which plot outside this region do so because their $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are too low rather than because they have elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The position of the SMLS in relation to asthenospheric samples, i.e. mid-ocean basalts and ocean island basalts, and mantle and crustal lithospheric samples is shown in Figure 7.1.

The Sr isotope data are presented in Figures 7.1 and 7.2. The Skye lavas which plot in the same region as OIB and MORB samples can be regarded as possibly-uncontaminated asthenospheric basalts. However, particularly in view of evidence to suggest that Sr isotopic values may be affected by late stage hydrothermal alteration (Chapter 5, Alteration and Bole Formation), this proposal was investigated further with reference to the Nd-isotopic system, and major and trace elements.

The Nd isotope data are presented in Figures 7.1 and 7.3. Some of the Skye lavas have asthenospheric $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic characteristics, whereas other lavas trend towards crustal compositions.

7.2.2 Ba/TiO₂ as an indicator of deviation from asthenospheric compositions

Isotopic analysis is a laborious and expensive process which necessitates the careful selection of a few representative samples. Therefore, isotopic analyses are not available for all samples in this study and, although ideally it would be desirable to identify contamination in this way, other compositional indicators of contamination have to be employed. The major and trace element characteristics of those lavas within the mantle array and the field defined by OIB in Figure 7.1 were thus compared with those lavas that plotted outside the mantle array and the field defined by OIB. Ba and TiO₂ were found to show the greatest percentage difference between the mean of the samples which plot within the mantle array and the mean of samples which plot outside it. The absolute abundances of Ba and TiO₂ cannot be used as an indices of contamination because they vary with fractional crystallisation (increasing in concentration with the evolution of the suite because they are incompatible in the fractionating phases, olivine and plagioclase) as well as with contamination. To try to eliminate the effect of fractional crystallisation, the ratio of TiO₂ and Ba was examined, since the ratio of two incompatible elements is expected to remain constant during fractional crystallisation but could vary during contamination, depending on the relative concentrations of elements in the magma and the contaminant. It was found that the mean of the ratio Ba/TiO₂ is significantly different between the isotopically-defined asthenospheric (Ba/TiO₂ < 90) and non-asthenospheric (Ba/TiO₂ > 90) samples. Since $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are generally accepted as useful indices of degree of contamination it was decided to investigate whether there was a correlation between them and Ba/TiO₂ (Figures 7.4 and 7.5 respectively). A broad positive correlation, significant at the 95% level, does indeed exist between Ba/TiO₂ and ($^{87}\text{Sr}/^{86}\text{Sr}$)_i. However Sr data should be interpreted

with care because Sr may be mobilised during hydrothermal alteration (Chapter 5, Alteration and Bole Formation). More significantly a clear negative correlation, significant at the 99.9% level, is found between Ba/TiO_2 and $(^{143}\text{Nd}/^{144}\text{Nd})_i$ (Figure 7.5). In view of this relationship it can be concluded that the Ba/TiO_2 ratio of a sample can be used to detect the presence of a lithospheric component, i.e. deviation from asthenospheric compositions. For convenience in the following discussion those samples with a value of Ba/TiO_2 less than 90 are taken to be essentially asthenospheric whereas samples with a value of Ba/TiO_2 greater than 90 are assumed to have some significant lithospheric component.

7.2.3 MORB normalization diagrams

The general principles of these diagrams has been outlined in Chapter 4 (Geochemistry, section 4.3.6 Spider diagrams). The SMLS lavas are divided into four groups on the basis of their Ba/TiO_2 ratios, >90 , 90-50, 50-15, and <15 . The divisions, which were chosen somewhat arbitrarily, divided the samples quite neatly into four pattern types. The first group, $\text{Ba/TiO}_2 > 90$, has a distinct peak at Ba relative to the other incompatible elements this gives the pattern a shape comparable to basaltic magma contaminated by crustal material (e.g. Pearce, 1983) (Figure 7.6). The second group, Ba/TiO_2 90-50, has a much less prominent Ba peak, or an OIB-like pattern. The third group, Ba/TiO_2 50-15, has fairly flat MORB-normalised patterns with a small peak at Ba and occasionally Rb, and Sr. The fourth group, $\text{Ba/TiO}_2 < 15$, which comprise only two SMLS samples, has virtually flat MORB-normalised patterns.

7.3 Composition and amount of contaminant

7.3.1 Introduction

The nature and amount of contamination affecting the Skye lavas has been the subject of much discussion (e.g. see Thompson, 1982b). Previous work has focused on isotopic systems

to try to decipher the effect of contamination by mantle (e.g. Menzies *et al.*, 1987) or crustal (e.g. Dickin 1981) lithospheric material. In the present study new major and trace element data are used in conjunction with new isotopic data to try to determine the compositional effect of lithospheric contamination upon the Skye lavas.

A thorough search of the literature produced a comprehensive range of major and trace element analyses for potential lithospheric contaminants. It was decided therefore that analysis of potential contaminants by the author was unnecessary.

A large sample set of potential crustal compositions was found in the literature. The data-set includes average bulk, average lower, and average upper crustal compositions and an extensive range of Lewisian rock types.

The mantle xenoliths were all collected from the N.W Highlands and the Hebrides. They comprise a compositionally diverse group of spinel lherzolites and pyroxenites (Hunter and Upton, 1987).

7.3.2 Mixing calculations

The means of all samples with $\text{MgO} > 7 \text{ wt\%}$ and $\text{Ba/TiO}_2 < 90$, and $\text{MgO} > 7 \text{ wt\%}$ and $\text{Ba/TiO}_2 > 90$ were taken to be representative averages of the uncontaminated lavas and the contaminated lavas respectively. In the light of previous studies of crustal contamination of continental flood basalts which show that the contamination is usually related to the amount of fractionation by one of two processes: assimilation fractional crystallisation (AFC - when the most evolved lavas are the most contaminated) or assimilation equilibrium crystallisation (AEC - when the most primitive lavas are the most contaminated) the question of whether there was a link between the amount of contamination and the amount of fractionation was investigated before mixing calculations were performed. If such a link exists, it could distort the averages

of one of the data-sets, with the result that simple mixing calculations based on the averages of the two data-sets could give spurious information about the composition of the contaminant (Figure 7.7). The contaminated SMLS data-set does indeed have a very slightly higher MgO content than the uncontaminated data-set (10.32 as compared with 10.04). So the mixing relationship can be thought of in the following terms: original magma + contaminant = evolved magma - olivine i.e. original magma + contaminant + olivine = evolved contaminated magma. To compensate for this difference, olivine was included in the mixing assemblage to encourage the program to produce the compositional differences by a combination of both contaminant and olivine addition to the uncontaminated magma.

The data used in the mixing calculations are presented in Table 7.1. The results of the mixing calculations are presented in Table 7.2. In all cases the sum of squares of residuals was reduced when olivine was added to the mixing assemblage. The mix of 5.8% average Lewisian granulite, 1.4% olivine, and 92.8% average uncontaminated lava gave the best fit with the average contaminated lava, but it should be noted that all samples gave solutions with sum of squares of residuals of less than one.

An attempt was made to consider the results of the major and trace element mixing calculations using REE data. The results obtained indicated that different amounts of contamination by the average crustal contaminants are required by each REE. This suggests that either the contamination process affecting the REEs was not one of bulk assimilation of average crust (a model which fits the major and trace element data surprisingly well), or the REE have different concentrations in the contaminant relative to the magma, or more REE data are required to obtain a reasonable result.

In the light of previous isotopic and elemental studies, which showed that different elements indicated different amounts of contamination, the percentage of each element that was derived from a lithospheric source was calculated (Table 7.3). For a set amount of contamination, here 5%, the percentage contributions of lithospheric material are quite variable

since they are dependant on the relative concentration of the element in the magma and the contaminant. The findings demonstrate that it is not necessary to invoke separate selective movement of elements, such as Pb, to explain the presence of a large contribution from a lithospheric component (e.g. Dickin, 1981). The data presented here do not explain the differences in the amounts of contamination suggested by the different isotopic systems, (Sr and Nd 50%, Pb 90%), but it can be seen that modelling of a slightly different contaminant could produce the relative contributions required.

In conclusion, the results of the major and trace element mixing calculations indicate that contamination by Lewisian crustal material could produce the elemental differences between the uncontaminated and the contaminated lavas. But, these results must be considered with other evidence because from the mixing calculations alone it is not clear whether the major contaminant of the SMLS magmas was the Lewisian granulite-facies lower crust or the Lewisian-amphibolite facies upper crust. The Sr and Nd isotopic data of this (Figure 7.1) and other studies (e.g. Carter *et al.*, 1978) indicate that many of the lavas have $^{143}\text{Nd}/^{144}\text{Nd}$ ratios which are too low to have been derived from the asthenospheric mantle. This can be attributed to the addition of Lewisian granulite-facies crust but not to the addition of Lewisian amphibolite-facies crust (Figure 7.1). Thus, the contaminant is constrained to be granulite-facies Lewisian crust.

The exact composition and amount of contaminant affecting the SMLS magmas cannot be constrained. This in itself is not important because the contaminant has been characterised sufficiently for its compositional effect to be recognised and removed, thus potentially enabling study of the primary, mantle-derived, compositional features of the lavas (Chapter 8, Magma Generation).

7.4 Correlation coefficient patterns

7.4.1 Introduction

Cox and Clifford (1982) demonstrated the value of calculation of inter-element correlation coefficients when assessing compositional variations in a suite of volcanic rocks. In Chapter 6 (Fractional Crystallisation, section 6.7) a 15 wt% MgO data-set was created to try to quantify the scatter in the data-set that was not attributable to fractional crystallisation. It was found that distinct, statistically-significant correlation coefficients exist between many of the elements. In this chapter it is investigated whether the inter-element correlations are the result of crustal contamination. Having calculated the correlation coefficients (Table 6.5) and plotted the correlation coefficient patterns for the whole data-set ($n=79$) (Figure 6.11), the samples were divided into those assumed to be contaminated by lithospheric material (i.e. $\text{Ba/TiO}_2 > 90$; $n=56$) and those assumed to be uncontaminated (i.e. $\text{Ba/TiO}_2 < 90$; $n=23$). The inter-element correlation coefficient patterns of the uncontaminated lavas and the contaminated lavas were then compared.

7.4.2 Uncontaminated samples

The element means, ranges and standard deviations for the 15 wt% MgO uncontaminated data-set are given in Table 7.4. The inter-element correlation coefficients in this group are presented in Table 7.5. The correlation coefficient patterns can be divided into three groups on the basis of pattern shape. First typified by SiO_2 there is a concave upwards pattern which has negative correlations with all the incompatible elements, the strongest correlations being with the HFS elements. Second, TiO_2 , Fe_2O_3 , FeO , P_2O_5 , Zn , Sr , and Zr , have positive correlations with all the incompatible elements and show concave downwards patterns which slope to the left as a result of having stronger correlations with the HFS than the LIL elements. The third group contains K_2O , Ba , Rb , and to some extent Ga (a mixture of pattern shape two and three), this pattern shape slopes to the right because of the stronger positive correlation with the LIL

elements than the HFS elements. Some elements, Al_2O_3 , MnO , CaO , Na_2O , Y , Cu , Ni , Co , Cr , V , do not correlate significantly with the incompatible elements. Despite being a much smaller data-set for pattern shapes one to three the magnitudes of the correlations in this data-set are similar to those in the whole data-set.

7.4.3 Contaminated samples

The same procedure was followed for the contaminated lavas as for the uncontaminated lavas. The element means, ranges and standard deviations for the 15 wt% MgO contaminated data-set are given in Table 7.6. The inter-element correlation coefficient matrix for the crustally contaminated 15 wt% data-set is presented in Table 7.7. The correlation coefficient patterns can be divided into three groups on the basis of pattern shape. The first pattern shape is shown by SiO_2 and Al_2O_3 , which have a concave upwards pattern and negative correlations with all the incompatible elements, the strongest correlations being with the HFS elements. The second pattern shape is shown by TiO_2 , Fe_2O_3 , FeO , P_2O_5 , Zn , Co , V , Ga , Sr , Zr , Nb , Pb , and Th all of which show positive correlations with the incompatible elements and have a concave downwards pattern which slopes to the left as a result of having stronger correlations with the HFS than the LIL elements. The third group contains, K_2O , Ba , Rb , elements which have patterns that slope to the right since they have a stronger positive correlation with the LIL elements than the HFS elements. Some elements, MnO , CaO , Na_2O , Y , Cu , Ni , Cr , do not correlate significantly with the incompatible elements.

7.4.4 Effects of lithospheric contamination on the correlation coefficient patterns of the uncontaminated samples

Somewhat surprisingly it was found that the patterns of the contaminated and the uncontaminated samples were similar to each other and to the whole 15 wt% MgO data-set. It had been expected that the investigation of correlation coefficients would reveal that the

whole data-set and the contaminated lavas were compositionally most similar, and that lithospheric contamination was the dominant effect controlling the compositional characteristics of the lavas. The presence of the same trends in the uncontaminated lavas as in the contaminated lavas suggests on the contrary, that the inter-element correlations are not essentially the result of contamination. This hypothesis is supported by the observation that, for some elements, addition of a lithospheric component to the uncontaminated lavas draws the data in the wrong direction to produce the observed trends. Processes possibly responsible for the inter-element correlations are discussed in Chapter 8, Magma Generation. Here the effects of contamination on the trends present in the uncontaminated lavas are considered.

The viability of various contaminant(s) generating the differences in the correlation coefficients between the contaminated and uncontaminated data-sets was constrained by considering the positions of the potential contaminants, identified by the mixing calculations, (Tables 7.1 and 7.2), relative to the trends in the uncontaminated data-set on two-element variation diagrams. As was noted by Cox and Clifford (1982) the capacity of a second process to blur the initial trend, i.e. reduce the inter-element correlations, is entirely dependent on the geometrical relationships concerned. The differences in correlations between the uncontaminated data-set and the contaminated data-set can be divided into 3 categories, those which stay approximately the same with contamination, those which improve with contamination, and those which deteriorate with contamination. Inspection of the two-element plots of the different groups reveals that for the first two categories the range of potential contaminants lies along the extension of the original trend, or parallel to it. For the last group the range of compositions of potential contaminants lies at right angles to the original trend. It is difficult to identify the actual contaminant(s) affecting the Skye magmas in this way because by varying the amount of contaminant, most of the rock types considered could produce the observed trends. Discrepancies in the amounts of contamination needed to produce the

contaminated trends could eliminate certain potential contaminants, but such differences are better considered using detailed mixing calculations, the results of which are given above, rather than visual estimates from two-element plots.

7.5 Mechanism and timing of contamination

7.5.1 Introduction

In the present study the nature and behaviour of magma is considered in conjunction with the results of mixing calculations to try to present a model of contamination which is consistent with all the available data and knowledge of magmatic behaviour currently available.

7.5.2 Thermal considerations

A paper by Patchett (1981) considered the thermal effects of basalt passing through the continental crust, and the implications for the contamination of magmas. He used a simple conduction-based heat-flow model to calculate the thickness of the zone of crustal rock adjacent to basalt sheets which would undergo hydrous mineral breakdown, and partial melting. He came to two major conclusions. The first was that emplacement of basaltic magma into the crust results in a wide zone of partial fusion, and aqueous fluid circulation, at most crustal levels. The second was that crustal contamination of basaltic magma is most effective when the magmatism is episodic on a 0.1 to 1,000 year time scale. It was noted that the circulation of fluids may have the effect of dissipating the heat of the magma quite quickly resulting in the zone affected by the fluids being wide but the zone of partial melting being narrow. The greatest uncertainty in prediction of the width of the total melting (next to the magma), partial melting (near the region of magma), and hydrous mineral breakdown zones was concluded to be in the lower crust. In the light of results of mixing calculations for the SMLS, which suggest that lower crustal granulites were assimilated by asthenospheric melts, Patchett's observation

that mantle lithosphere and lower crustal granulites do not contain a free fluid phase nor a significant amount of hydrous minerals and therefore might not melt at temperatures below 1000°C, is particularly important in the interpretation of the contamination of the SMLS magmas.

The stack of lava flows on Skye, thought to have been erupted over a period of 1 Ma (e.g. Mussett, 1988), indicate that the passage of magma through the crust must have been episodic and occurred through dykes in a tectonically-active stressed crust. So the magmatic system had a high surface to volume ratio, i.e. ideal conditions for the assimilation of crustal material by basaltic magma.

Extrapolation of liquidus temperatures determined for the SMLS basalts at one atmosphere pressure using the equations of Nathan and Van Kirk (1978) to depths equivalent to the lower granulitic crust (approximately 40 km, Taylor and McLennan, 1985), using the temperature gradient 2.7°C/km (e.g. Mitchell, 1988), showed that the asthenospheric magmas would have had liquidus temperatures in the range 1450°C. The liquidus and solidus temperatures of the lower crust are 850°C and 1200°C respectively. Therefore, the proposed assimilation of lower crustal granulite by the SMLS asthenospheric magmas is consistent with the thermal data.

From the data presented above it is concluded that the predominant contamination mechanism affecting the Skye lavas is whole-rock assimilation of granulite crustal material adjacent to the body of magma at the depth of the lower crust.

7.5.3 Mechanical considerations

The model outlined above does not, however, explain one aspect of the SMLS basalts geochemical characteristics. It would appear that the magmas passed from the lower crust to the surface without assimilating a significant amount of upper crustal material (Lewisian

amphibolite-facies gneiss in the Skye region) which is generally considered to be more fusible than lower crustal material. This anomaly could be the result of several processes some of which are considered here.

A reduction in the magmatic temperature, and an increase in the amount of suspended crystals (a direct consequence of which would be an increase in the magmatic viscosity), could result in a change in the rheology of the magma in the dykes, the consequences of which are discussed below.

The Reynolds number is a dimensionless expression of the flow behaviour of magma, i.e. whether it is turbulent or laminar.

$$\text{Reynolds no} = \frac{(\text{speed of magma}) \times (\text{width of conduit}) \times (\text{density of magma})}{(\text{viscosity of magma})}$$

Reynolds numbers of $< 10^3$ indicate laminar flow which would result in the development of chilled margins on the dyke walls, whereas numbers $> 10^3$ indicate that the magma would be flowing turbulently and thermally eroding the dyke walls. The amount of country rock that a magma assimilates is directly proportional to its Reynolds number.

Tectonic activity could have facilitated an easy passage to the surface for the magmas so that there was little contact with wall rock material. Or, if a scenario of upper mantle lower crustal contamination is envisaged to have occurred whilst picritic basalts were ponded near the crust-mantle boundary because they were denser than the surrounding rocks, some time would have been available to assimilate the country rocks. Whereas during rapid rise to the surface through dykes little time would be available for interaction with the surrounding rocks.

7.5.4 Relationship between amount of contamination and degree of evolution

The two main end-member processes of crustal contamination (between which it is expected some combinations of the two may occur) affecting CFB province magmas have been described in detail in Chapter 2, History of Petrogenetic Research, section 2.3.3. The first end-

member process of contamination is Assimilation Fractional Crystallisation (AFC) when contamination accompanied by concurrent fractional crystallisation results in the most evolved magmas being the most contaminated. The second end-member process is Assimilation Equilibrium Crystallisation (AEC) when contamination is accompanied by crystallisation without fractionation of the precipitating phases, which results in the most primitive, hottest, magmas being the most contaminated. The style of contamination affecting a suite of igneous rocks can be detected quite effectively using major and trace element, and isotopic data. A plot of an index of fractionation, e.g. MgO, versus an isotopic ratio indicative of contamination, e.g. $^{87}\text{Sr}/^{86}\text{Sr}$, can be used to distinguish the two styles of contamination. For a suite affected by AFC the data-set will show the more evolved lavas being more scattered towards the composition of the contaminant. In contrast a suite of igneous rocks affected by AEC will show the primitive samples scattered towards the composition of the contaminant and less scatter in the evolved samples. Since $^{143}\text{Nd}/^{144}\text{Nd}$ has been shown to be a more accurate measure of the degree of contamination of the SMLS lavas than $^{87}\text{Sr}/^{86}\text{Sr}$, MgO was plotted against $^{143}\text{Nd}/^{144}\text{Nd}$ (Figure 7.8). This plot shows no obvious correlation between the two variables. Nevertheless, a plot of MgO versus Ba/TiO₂ shows a suggestion of a positive correlation, indicating that the most primitive magmas are the most contaminated (Figure 7.9). When the Ba/TiO₂ versus MgO plot is considered with the results of the mixing calculations that showed the average contaminated lava was more magnesian than the average uncontaminated lava it is proposed that there is a link between the amount of contamination and the degree of evolution in the Skye lavas. The most basic lavas are the most contaminated. This is consistent with the results of previous workers who have concluded that the most basic lavas are the most contaminated (Thirlwall and Jones, 1983). However more isotopic data are needed to test this hypothesis further. The link between the amount of contamination and degree of evolution is consistent with the conclusions regarding the location and timing of contamination.

A magmatic plumbing model is proposed on the basis of the above results: Magnesian magmas ponded at the crust-mantle boundary where they assimilated granulite-facies lower crust. The magmas subsequently passed to the surface through dykes cooling, evolving by fractional crystallisation, and thus becoming less magnesian and more viscous. Consequently the magmatic flow regime in the dykes was laminar which resulted in minimal assimilation of wall rock material.

7.6 Summary and Conclusions

On a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ some of the SMLS plot within the array of values which can be derived from the mantle, others plot outside it because they have $^{143}\text{Nd}/^{144}\text{Nd}$ ratios which are too low. All the PM and FB lavas analysed in the present study plot within the array of values which can be derived from the asthenospheric mantle. From this it is concluded that the asthenospheric mantle was an important source in the generation of the Skye lavas.

The Ba/TiO_2 ratio of a sample was found to be a good indicator of the amount of lithospheric material contaminating the asthenospheric magmas. Samples with $\text{Ba}/\text{TiO}_2 > 90$ were taken to be contaminated by lithospheric material and samples with $\text{Ba}/\text{TiO}_2 < 90$ were taken to be uncontaminated by lithospheric material.

Lavas under olivine control, i.e. > 7 wt% MgO, were calculated back to a potentially primary MgO content of 15 wt%, by the addition of olivine. It was found that the correlation coefficient patterns of the contaminated and uncontaminated samples were similar to each other and to the whole 15 wt% data-set. Thus indicating that the contamination had not had a major affect upon the compositional characteristics of the data-set.

Mixing calculations were performed using an average uncontaminated lava, an average contaminated lava, an average olivine composition (to compensate for the difference in the MgO

content of the two data-sets), and a range of crustal compositions; average crust, average lower crust, average upper crust, average Lewisian granulite, and average Lewisian amphibolite. All assemblages had solutions with sum of squares of residuals of less than one.

For a set amount of contamination, here 5%, the percentage contributions of lithospheric material are perceived to be quite variable. This is because they are dependent on the relative concentrations of the element in the magma and the contaminant. Thus it is not necessary to invoke separate movement of elements to explain the presence of apparently large contributions from lithospheric components, when individual elements are considered.

Consideration of the results of major, trace, and RE element mixing calculations in conjunction with isotopic data lead to the conclusion that the Lewisian granulite-facies crust was the most likely contaminant of the SMLS lavas.

The stack of lava flows on Skye and an associated dyke swarm (presumed to feed the lava flows) indicate that the magmatism was episodic through a tectonically stressed crust ideal conditions for the assimilation of crustal material by basaltic magmas.

Thermal arguments are consistent with the proposed assimilation of Lewisian granulite, with the predominant contamination mechanism affecting the Skye lavas being whole-rock assimilation of crustal material adjacent to the body of magma.

The broad positive correlation between Ba/TiO_2 and MgO has led to the conclusion that for the lavas with >7 wt% MgO , the amount of contamination is inversely related to the degree of evolution.

The above results confirm the findings of previous workers (e.g. Moorbath and Thompson, 1980; Dickin, 1981; Thompson, 1982b) that the Skye lavas have assimilated crustal material. However, having quantified the compositional effect of the crustal contamination it is concluded that it was not the principal control on the composition of the SMLS lavas. The lavas which have been identified as essentially uncontaminated (i.e. $Ba/TiO_2 < 90$) are now

investigated to try to identify the process(es) responsible for the compositional scatter in the SMLS data-set.

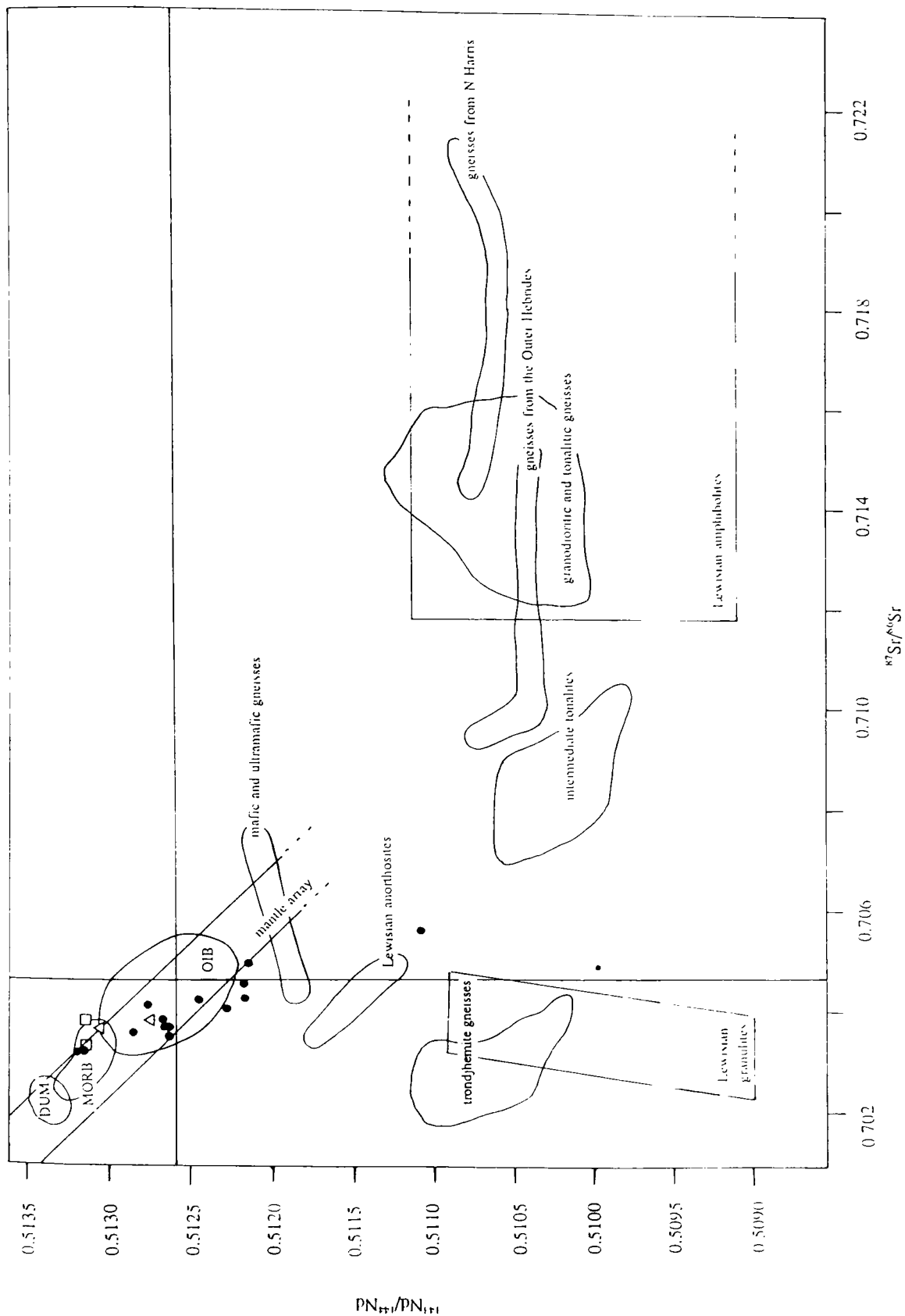


Figure 7.1 $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ showing the lavas analysed in the present study and the major potential crustal contaminants. (crustal data from Whitehouse, 1988; positions of mantle fields from Wilson, 1989)

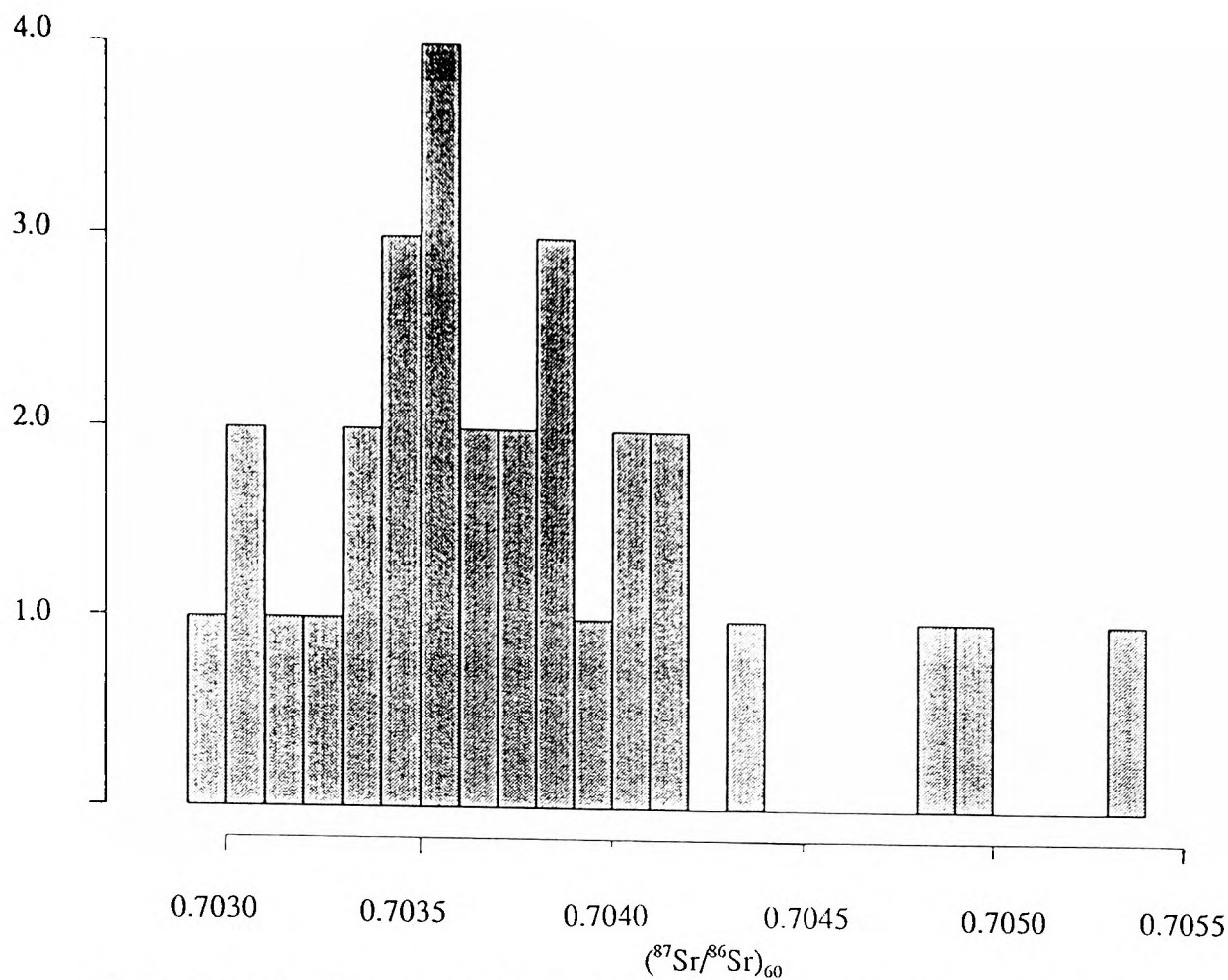


Figure 7.2 Histogram of $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ for the lavas analysed in the present study.

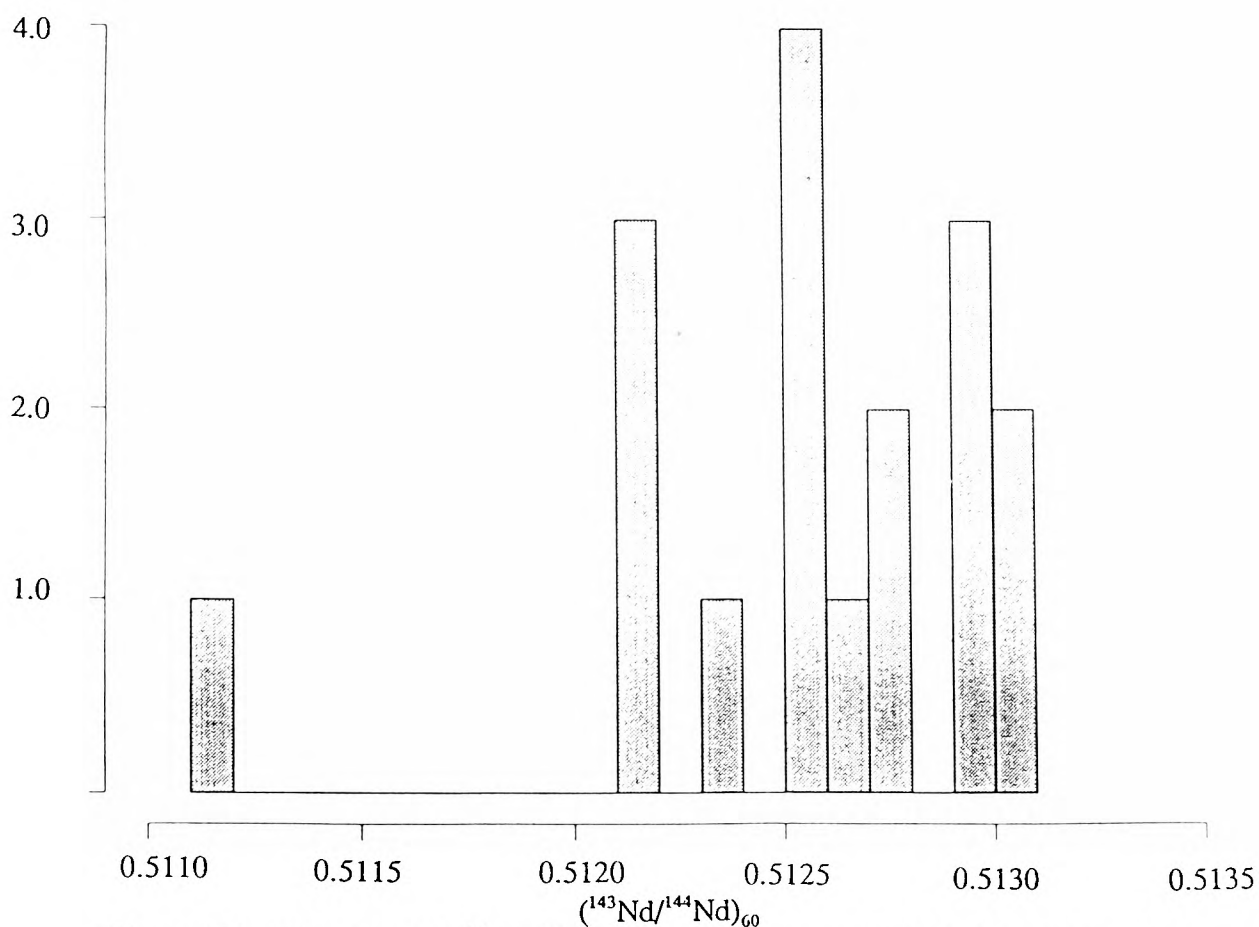


Figure 7.3 Histogram of $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ for the lavas analysed in the present study.

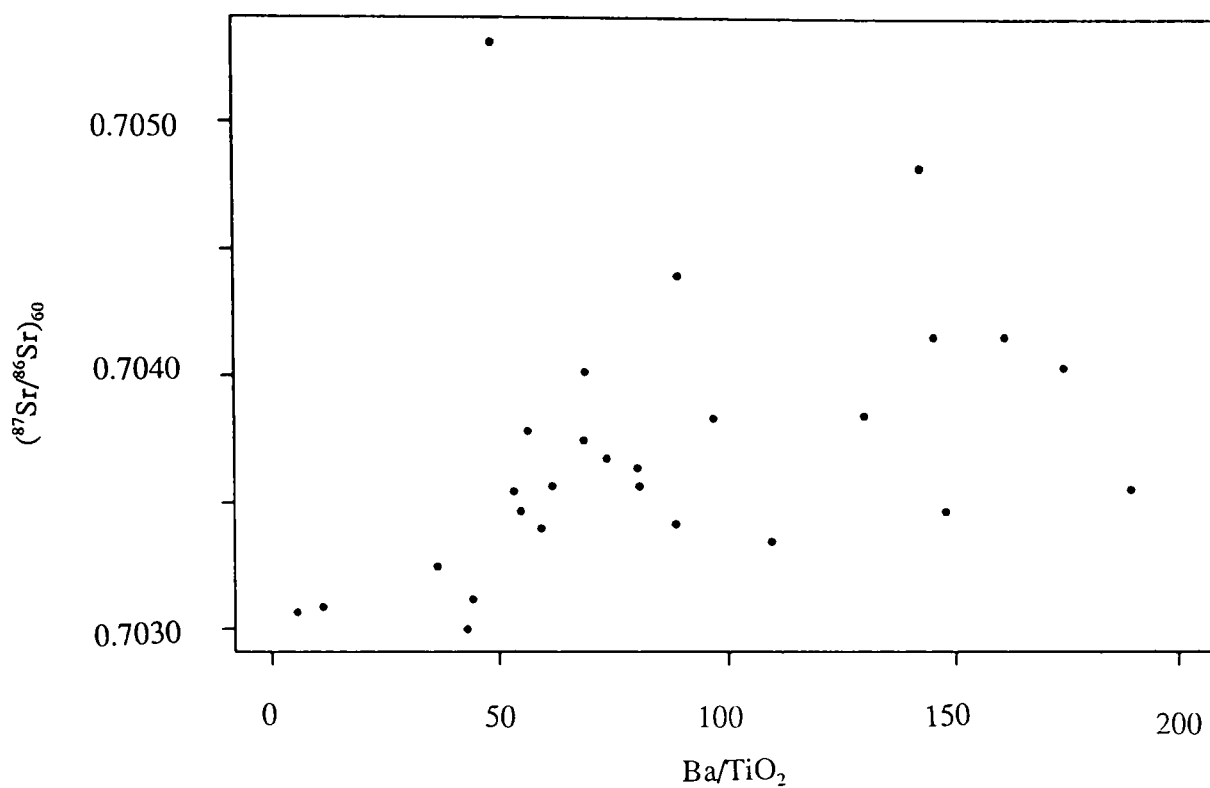


Figure 7.4 Ba/TiO_2 versus $(^{87}\text{Sr}/^{86}\text{Sr})_{60}$ for lavas analysed in the present study.

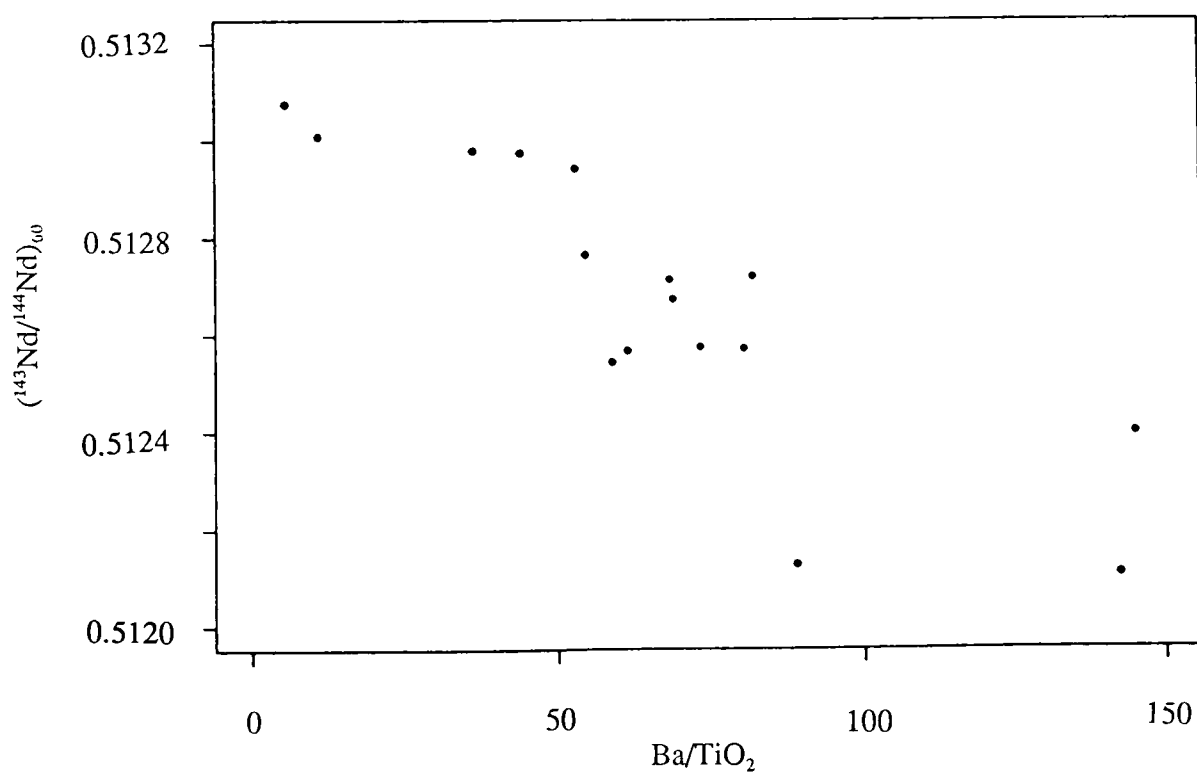


Figure 7.5 Ba/TiO_2 versus $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ for lavas analysed in the present study.

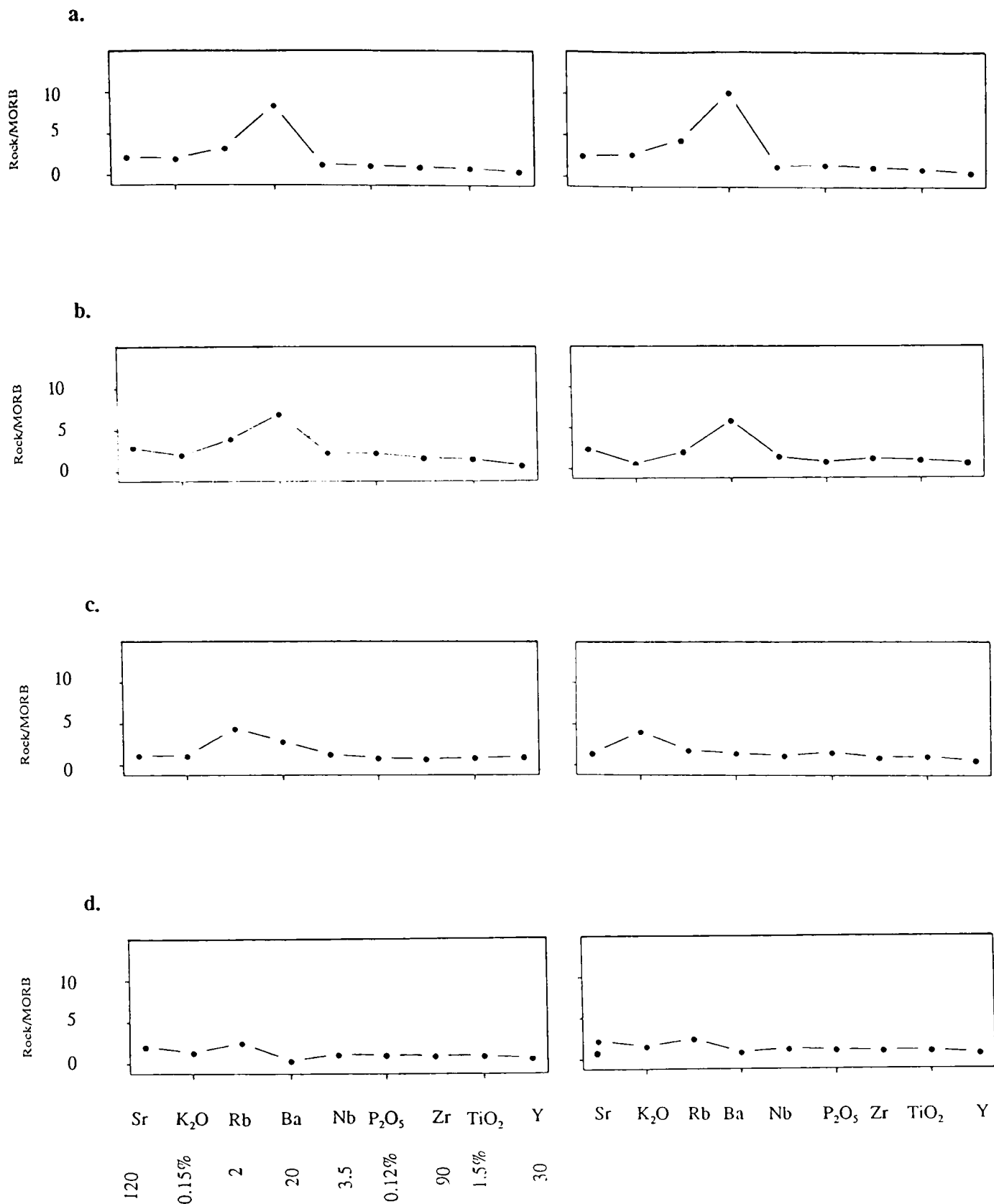


Figure 7.6

MORB normalised diagrams showing two examples of each of the pattern shapes of the Ba/TiO₂ groups

- a. Ba/TiO₂ > 90
- b. Ba/TiO₂ 50-90
- c. Ba/TiO₂ 15-50
- d. Ba/TiO₂ < 15

(normalisation factors, shown above d., from Pearce, 1983)

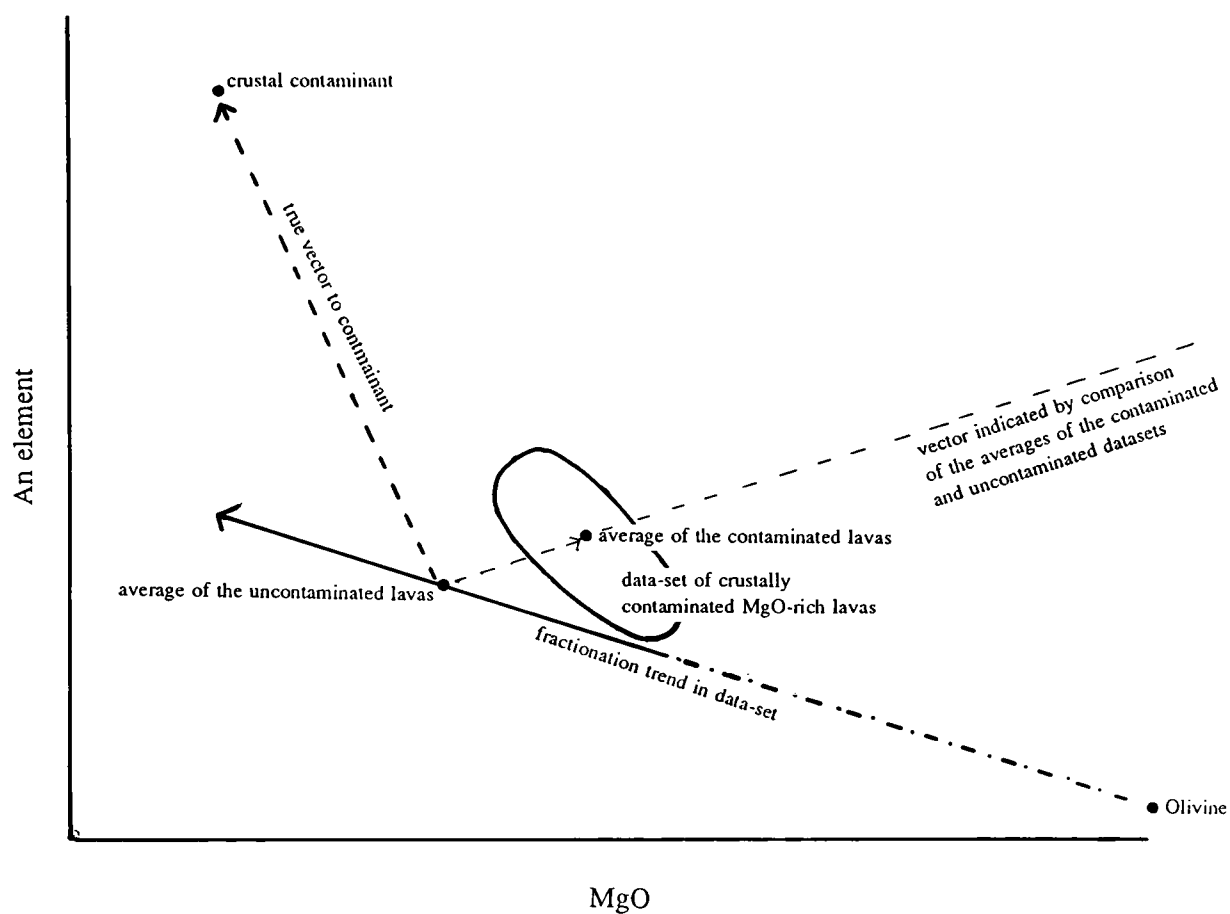


Figure 7.7 Schematic diagram of how preferential contamination of the MgO rich magmas could produce unrepresentative mixing averages.

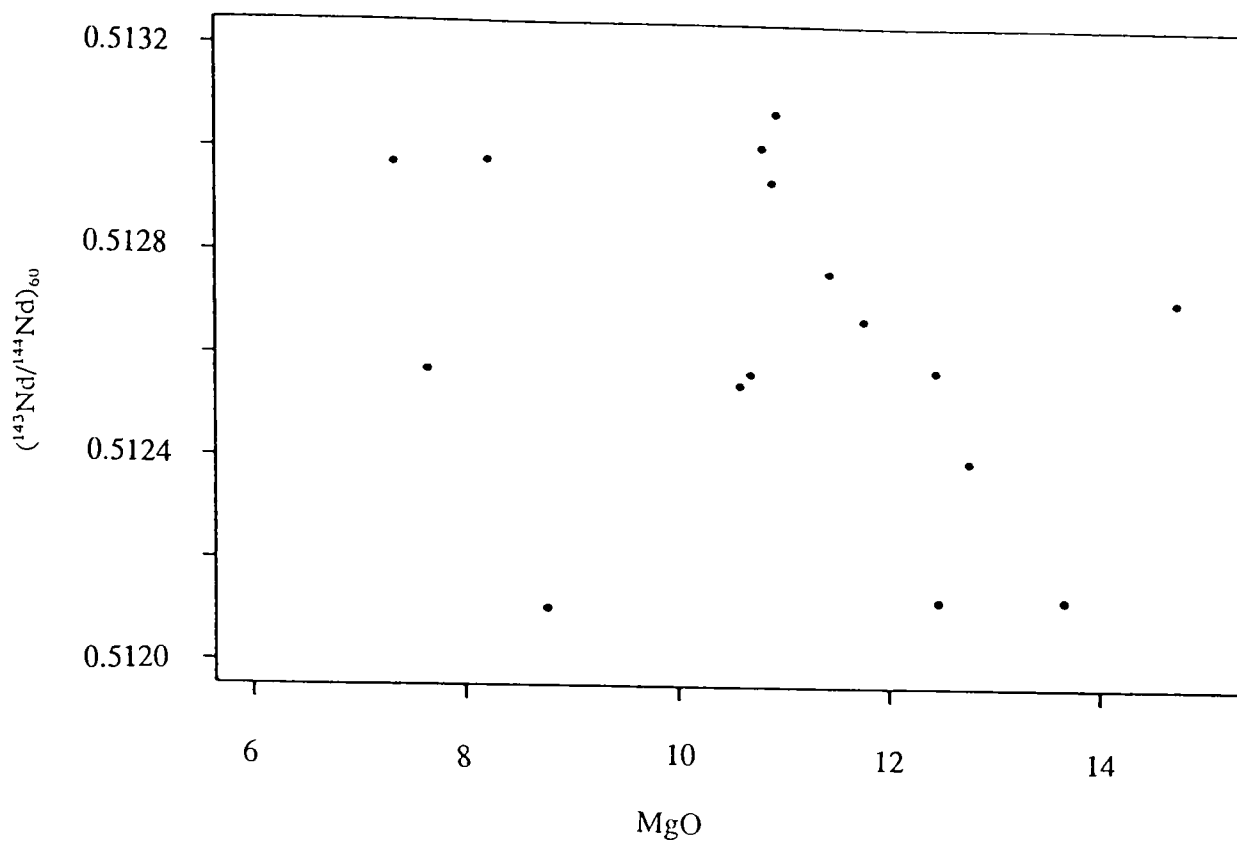


Figure 7.8 MgO versus $(^{143}\text{Nd}/^{144}\text{Nd})_{60}$ for lavas analysed in the present study.

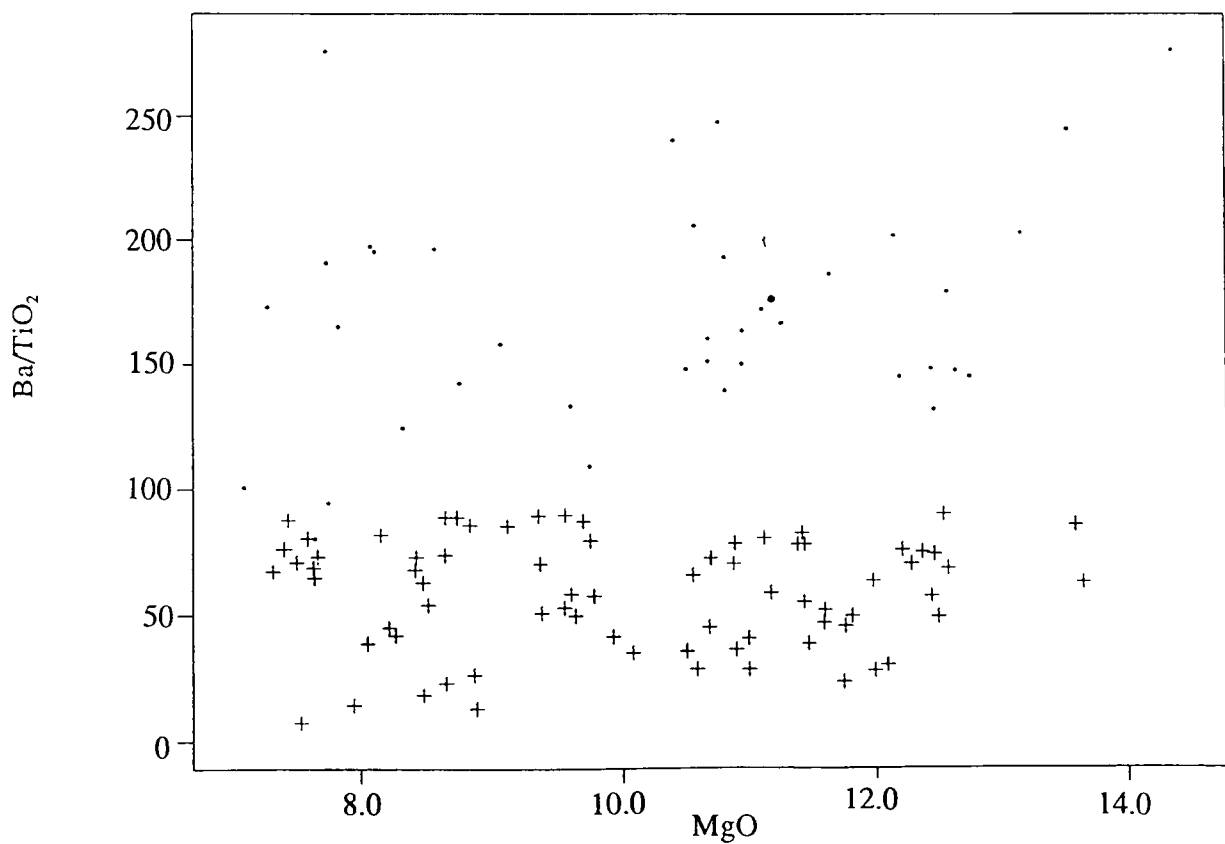


Figure 7.9 MgO versus Ba/TiO₂ for lavas analysed in the present study.

symbols: crosses - samples with Ba/TiO₂ < 90, dots - samples with Ba/TiO₂ > 90.

	Average cont lava	Average uncont lava	Olivine	Average crust	Average upper crust	Average lower crust	Average Lewisian amphibolite	Average Lewisian granulite
SiO ₂	47.24	46.39	40.56	57.50	66.00	54.40	68.10	63.00
TiO ₂	1.51	1.78		0.90	0.50	1.00	0.35	0.55
Al ₂ O ₃	15.13	15.29		15.90	15.20	16.10	16.30	16.10
Fe ₂ O ₃	12.68	13.55	14.50	10.01	4.95	11.66	3.64	5.47
MgO	10.32	10.04	17.21	5.30	2.20	6.30	1.43	3.50
CaO	9.73	9.57	0.26	7.40	4.20	8.50	3.27	5.76
Na ₂ O	2.42	2.48		3.10	3.90	2.80	5.00	4.53
K ₂ O	0.48	0.40		1.10	3.40	0.34	2.15	1.03
P ₂ O ₅	0.18	0.20						
Ni	265.69	282.26		105.00	20.00	135.00	20.00	58.00
Ba	285.34	173.30		250.00	550.00	150.00	710.00	760.00
Rb	10.70	9.07		32.00	112.00	5.30	74.00	11.00
Sr	424.89	376.20		260.00	350.00	230.00	580.00	570.00
Y	20.39	20.96		20.00	22.00	19.00	7.00	9.00
Zr	113.83	123.58		100.00	190.00	70.00	190.00	200.00

Table 7.1 Data used in the crustal contamination mixing calculations.

Contaminant type	Contaminant %	Uncontaminated lava %	Olivine %	Sum of squares of residuals
Average crust	6.87	93.13	0.00	0.8872
Average crust	9.16	89.27	1.57	0.5366
Average upper crust	3.82	96.18	0.00	0.8421
Average upper crust	4.71	93.95	1.34	0.5694
Average lower crust	9.14	90.86	0.00	0.9372
Average lower crust	13.14	85.08	1.78	0.5197
Average Lewisian amphibolite	3.41	96.59	0.00	0.8615
Average Lewisian amphibolite	4.25	94.38	1.37	0.5798
Average Lewisian granulite	4.62	95.38	0.00	0.8165
Average Lewisian granulite	5.83	92.17	1.44	0.5069

Table 7.2 Results of crustal contamination mixing calculations.

	% contribution from contaminant
SiO₂	1.79
TiO₂	17.33
Al₂O₃	1.05
Fe₂O₃	6.86
MnO	5.88
CaO	1.64
Na₂O	2.47
K₂O	16.66
P₂O₅	11.11
Zn	2.21
Cu	16.70
Ni	0.23
Co	5.64
Cr	4.08
V	8.14
Ba	39.26
Ga	2.82
Rb	15.23
Sr	11.45
Y	2.79
Zr	8.56
Nb	9.62
Pb	17.02

Table 7.3 Percentage contribution of lithospheric material to each element concentration in the contaminated data-set.

(% contribution from contaminant = difference between the contaminated and the uncontaminated element concentration expressed as a percentage of the uncontaminated concentration.)

	Mean	Range			Std dev
SiO ₂	45.46	44.18	-	46.79	0.810
TiO ₂	1.59	1.21	-	1.97	0.250
Al ₂ O ₃	13.21	12.16		14.12	0.420
FeO	2.69	2.32	-	3.00	0.170
Fe ₂ O ₃	10.97	9.68	-	12.40	0.790
MnO	0.14	0.11	-	0.20	0.020
MgO	15.00	15.00	-	15.00	0.000
CaO	8.16	6.57	-	9.79	0.760
Na ₂ O	2.14	1.86	-	2.95	0.230
K ₂ O	0.29	0.17	-	0.49	0.080
P ₂ O ₅	0.16	0.10		0.24	0.030
Zn	70.10	57.68	-	91.70	8.130
Cu	91.97	49.03	-	137.05	23.070
Ni	1205.40	567.20	-	3392.00	645.370
Co	55.62	39.48	-	67.92	7.310
Cr	1564.42	715.00		5097.00	104.96
V	228.03	188.48	-	286.52	26.190
Ba	97.11	7.30		156.30	41.500
Ga	17.87	14.56		21.89	1.570
Rb	6.59	2.99	-	10.86	1.940
Sr	288.67	136.54	-	425.55	87.700
Y	18.14	14.77		21.19	1.520
Zr	110.54	76.52		150.11	22.910
Nb	5.42	3.47		8.19	1.520
Pb	2.04	0.28		4.93	1.120
Th	1.03	0.00		2.57	0.730
U	1.16	1.03	-	1.25	0.056

Table 7.4 Mean, range, and standard deviation for all uncontaminated samples (Ba/TiO₂ < 90) in the 15 wt% MgO data-set.

	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Zn	Cu	Ni	Co	Cr	V	Ba	Ga	Rb	Sr	Y	Zr	Nb	Pb	Th	U	
SiO ₂	0.852	-0.030	-0.692	-0.853	0.007	-	0.321	-0.128	-0.014	-0.728	-0.409	0.606	0.215	0.140	0.573	-0.008	-0.319	-0.552	-0.193	-0.800	-0.525	-0.788	-0.457	-0.179	-0.075	-0.268	
TiO ₂		0.112	0.589	0.832	0.107	-	-0.663	0.460	0.260	0.870	0.389	-0.640	-0.116	-0.218	-0.488	-0.012	0.423	0.597	0.328	0.764	0.470	0.931	0.513	0.275	0.000	0.350	
Al ₂ O ₃			-0.288	-0.069	0.461	-	-0.500	0.394	-0.101	-0.160	-0.493	0.013	-0.213	-0.615	-0.372	-0.240	-0.127	-0.085	-0.094	-0.157	0.537	-0.087	-0.450	0.065	0.149	0.196	
FeO				0.577	0.208	-	-0.146	0.076	-0.158	0.551	0.716	-0.275	-0.330	0.503	-0.488	0.262	0.345	0.603	0.348	0.565	0.311	0.708	0.461	-0.287	-0.110	-0.363	
Fe ₂ O ₃					-0.209	-	-0.542	0.115	0.085	0.808	0.387	-0.747	0.172	-0.096	-0.290	-0.262	0.412	0.399	0.098	0.729	0.275	0.785	0.451	0.314	-0.112	0.568	
MnO						-	-0.287	0.536	-0.152	-0.133	0.040	0.270	-0.568	-0.056	-0.538	0.383	0.073	0.262	0.295	-0.084	0.393	0.113	0.049	-0.193	-0.130	-0.449	
MgO							-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
CaO							-0.713	-0.265	-0.528	-0.079	0.435	-0.161	0.295	0.213	0.281	-0.355	-0.251	-0.193	-0.258	-0.314	-0.560	-0.108	-0.284	0.214	-0.455		
Na ₂ O								0.303	0.228	0.142	-0.034	-0.091	-0.220	-0.206	0.260	0.190	0.313	0.269	0.049	0.343	0.362	0.153	0.241	-0.214	0.044		
K ₂ O									0.434	0.028	-0.217	0.211	-0.182	0.197	-0.119	0.318	0.099	0.469	0.316	-0.204	0.239	0.227	0.148	-0.133	0.247		
P ₂ O ₅										0.482	-0.652	0.057	-0.042	-0.266	-0.229	0.598	0.531	0.397	0.826	0.211	0.925	0.632	0.316	0.077	0.360		
Zn											-0.084	0.013	0.581	-0.056	0.199	0.421	0.624	0.266	-0.167	-0.187	-0.663	-0.197	-0.593	-0.331	-0.234	0.101	-0.565
Cu												-0.039	0.317	0.251	0.321	-0.462	-0.432	-0.451	-0.314	-0.427	-0.186	-0.116	0.409	-0.127	0.526		
Ni													0.197	0.832	-0.401	-0.165	-0.432	-0.451	-0.202	-0.336	-0.023	0.080	-0.380	-0.171	-0.599		
Co														0.332	0.211	-0.592	0.059	-0.023	-0.560	-0.559	-0.493	-0.188	0.272	-0.159	0.174		
Cr															-0.144	-0.283	-0.512	-0.438	-0.560	-0.559	-0.493	-0.188	0.272	-0.159	0.174		
V																-0.118	0.214	0.195	-0.065	0.137	0.001	0.229	-0.247	-0.222	-0.536		
Ba																	0.482	0.695	0.546	0.022	0.570	0.744	0.023	-0.068	0.104		
Ga																		0.551	0.576	0.105	0.705	0.521	0.001	-0.052	-0.149		
Rb																			0.492	-0.100	0.468	0.469	-0.242	-0.066	-0.264		
Sr																				0.306	0.843	0.565	0.118	0.070	0.259		
Y																					0.341	0.059	0.037	0.071	0.010		
Zr																						0.638	0.185	0.018	0.182		
Nb																							0.183	0.014	0.050		
Pb																								0.132	0.640		
Th																									-0.030		

Table 7.5 Correlation coefficient matrix for the uncontaminated samples (Ba/TiO₂ < 90) of the 15 wt% MgO data-set.

	Mean	Range			Std dev
SiO ₂	46.11	43.46	-	47.98	0.940
TiO ₂	1.41	1.04	-	2.55	0.350
Al ₂ O ₃	13.06	11.60	-	13.98	0.530
FeO	2.54	2.14	-	3.17	0.230
Fe ₂ O ₃	10.18	9.13	-	12.10	0.760
MnO	0.14	0.11	-	0.17	0.014
MgO	15.00	15.00	-	15.00	0.000
CaO	8.54	6.99		9.32	0.500
Na ₂ O	2.18	1.72	-	2.77	0.190
K ₂ O	0.42	0.21		0.85	0.130
P ₂ O ₅	0.16	0.11		0.31	0.046
Zn	71.00	59.27		96.27	8.290
Cu	81.35	25.09	-	118.22	18.720
Ni	800.63	124.43	-	1448.00	218.880
Co	54.29	37.56		70.30	8.520
Cr	1308.89	14.38	-	2771.00	416.92
V	222.10	178.25		310.64	28.260
Ba	219.67	138.64	-	570.86	6.890
Ga	17.63	14.33	-	22.32	1.550
Rb	9.43	3.95		17.76	2.950
Sr	354.40	219.11	-	653.91	116.900
Y	17.51	14.48		22.57	1.620
Zr	102.48	71.71		175.83	27.560
Nb	5.58	2.65	-	14.95	2.920
Pb	2.75	0.00		5.19	1.150
Th	1.29	0.00	-	3.23	0.790
U	1.13	1.04		1.25	0.061

Table 7.6 Mean, range, and standard deviation for all crustally contaminated samples (Ba/TiO₂ > 90) in the 15 wt% MgO data-set.

	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Zn	Cu	Ni	Co	Cr	V	Ba	Ga	Rb	Sr	Y	Zr	Nb	Pb	Th	U
SiO ₂	0.840	0.455-0.805	-0.837	-0.478	-	-	-0.001	-0.733	-0.604	0.039	-0.128	-0.404	0.163	-0.654	-0.470	-0.781	-0.435	-0.610	-0.456	-0.803	-0.714	-0.214	-0.374	0.119		
TiO ₂	-0.765	0.736	0.830	0.266	-	-	-0.094	-0.257	0.684	0.930	0.686	-0.119	0.190	0.337	0.026	0.690	0.604	0.806	0.609	0.690	0.343	0.964	0.916	0.189	0.420	-0.030
Al ₂ O ₃	-	-0.622	-0.494	-0.091	-	-	-0.190	0.318	-0.689	-0.788	-0.638	-0.031	-0.122	-0.391	-0.207	-0.592	-0.656	-0.547	-0.689	-0.664	0.000	-0.780	-0.854	-0.148	-0.453	0.236
FeO	-	0.634	0.541	-	-	-	0.110	-0.293	0.365	0.652	0.862	0.149	0.014	0.745	-0.047	0.632	0.476	0.723	0.483	0.687	0.085	0.754	0.714	0.137	0.387	-0.571
Fe ₂ O ₃	-	-	0.075	-	-	-	-0.491	-0.122	0.402	0.778	0.505	-0.262	0.318	0.179	-0.084	0.409	0.388	0.705	0.311	0.609	0.434	0.791	0.635	0.094	0.251	0.269
MnO	-	-	-	-	-	-	-0.368	-0.088	0.055	0.124	0.451	0.276	-0.134	0.597	0.001	0.548	0.214	0.331	0.238	0.138	0.110	0.223	0.264	0.083	0.137	-0.606
MgO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	-	-	-	-	-	-	-0.504	-0.001	-0.098	0.073	0.423	-0.144	0.320	0.110	0.316	0.224	-0.079	0.247	-0.002	-0.171	-0.103	0.180	0.118	0.232	-0.572	
Na ₂ O	-	-	-	-	-	-	-0.249	-0.314	-0.358	-0.051	-0.358	-0.051	-0.278	-0.328	-0.235	-0.265	-0.464	-0.135	-0.271	-0.298	0.013	-0.217	-0.468	0.059	-0.143	0.209
K ₂ O	-	-	-	-	-	-	0.755	0.380	-0.174	0.061	0.129	0.097	0.493	0.766	0.392	0.809	0.527	0.185	0.696	0.527	0.185	0.696	0.736	0.112	0.339	-0.022
P ₂ O ₅	-	-	-	-	-	-	0.645	-0.184	0.241	0.290	0.114	0.624	0.689	0.721	0.621	0.683	0.322	0.928	0.615	-0.025	0.705	0.712	0.065	0.330	-0.526	
Zn	-	-	-	-	-	-	0.145	0.031	0.670	0.028	0.586	0.512	0.022	-0.077	0.036	-0.057	-0.066	-0.268	-0.113	-0.032	0.012	0.175	-0.236	-0.031	0.337	
Cu	-	-	-	-	-	-	-0.026	0.360	0.021	0.022	-0.077	0.036	-0.057	-0.066	-0.268	-0.113	-0.032	0.012	0.175	-0.236	-0.031	0.337				
Ni	-	-	-	-	-	-	0.135	0.631	-0.095	0.081	0.047	0.018	-0.016	0.124	0.118	0.175	-0.236	-0.031	0.337							
Co	-	-	-	-	-	-	0.149	0.430	0.264	0.348	0.305	0.443	-0.267	0.312	0.400	-0.098	0.211	-0.737								
Cr	-	-	-	-	-	-	-0.016	0.074	-0.115	0.057	-0.144	-0.077	0.035	0.132	-0.185	-0.028	-0.001									
V	-	-	-	-	-	-	0.544	0.531	0.512	0.435	0.295	0.660	0.744	0.264	0.466	-0.359										
Ba	-	-	-	-	-	-	0.412	0.694	0.581	0.143	0.598	0.723	0.141	0.283	-0.166											
Ga	-	-	-	-	-	-	0.372	0.571	0.296	0.780	0.698	0.213	0.252	-0.147												
Rb	-	-	-	-	-	-	0.490	0.049	0.618	0.698	0.018	0.462	-0.265													
Sr	-	-	-	-	-	-	0.008	0.716	0.690	0.072	0.294	-0.204														
Y	-	-	-	-	-	-	0.338	0.213	0.117	0.052	0.344															
Zr	-	-	-	-	-	-	0.912	0.235	0.424	-0.090																
Nb	-	-	-	-	-	-	0.190	0.507	-0.202																	
Pb	-	-	-	-	-	-	0.086	-0.079																		
Th	-	-	-	-	-	-	-0.225																			

Table 7.7 Correlation coefficient matrix for all crustally contaminated samples (Ba/TiO₂ > 90) in the 15 wt% MgO data-set.

CHAPTER 8

MAGMA GENERATION

8.1 Introduction

Some of the main aims of the petrogenetic study of igneous rocks are the characterization of the source region of the magmas and the conditions of partial melting, and the evaluation of the relationship between magma generation processes and tectonic processes. Such processes can, however, only be considered once the extent to which the primary, mantle-derived, magmas have been affected by secondary processes has been assessed. Previous chapters (Chapter 5 Alteration and Bole Formation, Chapter 6 Fractional Crystallisation, and Chapter 7 Crustal Contamination) have attempted to quantify the effects of the secondary processes affecting the Skye lavas. In the present chapter the processes involved in magma generation are considered.

The partial melting of mantle material produces basic or ultrabasic primary magmas, the generation of which appears to be restricted to a narrow depth range within the upper 100-200 km of the mantle. Although in detail their precise depths of origin are poorly constrained (Wilson, 1989).

The compositions of primary magmas depend upon their source composition and mineralogy, and the depth and degree of partial melting. In the present study an inverse approach is taken, i.e. the geochemical characteristics of the lavas are used to deduce details of the conditions of magma generation.

A brief outline of the main characteristics of the mantle is given in Chapter 1 (Introduction, section 1.2.3). Knowledge of the structure, physical properties, and chemical composition of the mantle is limited. The study of the velocity of seismic waves has placed

some constraints on density and other physical properties. Information about the geochemical properties has been obtained from basalts, ophiolite complexes, and mantle xenoliths.

The major element characteristics of primary mantle-derived magmas are not particularly sensitive indicators of tectonic setting. Trace elements and Sr-Nd-Pb isotopic signatures, however, are generally good indicators of the environment of magma generation. In the present study both major and trace elements characteristics are used to try to obtain information about the conditions of magma generation.

Most CFB volcanism is associated with extensional tectonics which appear to be the consequence of lithospheric stretching associated with the upwelling of deep hot mantle material. The characterization of CFB mantle source regions is hindered by uncertainties regarding the extent of modification of magmas by interaction with continental crust, and by the lack of detailed knowledge about chemical and isotopic heterogeneities in the sub-continental lithospheric mantle.

In this chapter the compositional characteristics of the Skye lavas with primary magma characteristics are first outlined, then the conditions of magma generation are considered.

8.2 Parental and Primary magmas

8.2.1 Identification of parental and primary magmas

In the absence of any experimental data from the present study the nature of the magnesian basalts was investigated using petrographic and geochemical evidence, and the results of experiments performed by other workers.

The majority of the SMLS magnesian basalts (arbitrarily defined as lavas with more than 9 wt% MgO) do not have the glassy, aphyric texture often associated with quenched primary mantle melts. The SMLS magnesian basalts are generally highly porphyritic, having more than

10 modal % olivine phenocrysts and very occasional plagioclase phenocrysts. Very few of the lavas show skeletal phenocryst textures (indicative of rapid crystallisation in a melt with few nuclei).

Many of the Skye lavas do however have geochemical characteristics associated with primary magmas ($MgO > 10$ wt%, $Mg/Mg+Fe$ 0.7-0.83, $Ni > 400$ -500 ppm, Ni/MgO 33-39) (BSVP, 1981). Nevertheless, the detection of a crustal lithospheric component (Chapter 7, Crustal Contamination) reveals that most of the primitive SMLS lavas are not strictly primary magmas. The potentially primary nature of the basalts not contaminated by crustal material was therefore investigated using a K_D of 0.3 ± 0.03 for the distribution of Fe and Mg between the olivine and the melt (Roeder and Emslie, 1970).

$$K_D = \frac{X_{Ol}^{FeO} \times X_{Liq}^{MgO}}{X_{Liq}^{FeO} \times X_{Ol}^{MgO}}$$

where

$$X_{Ol}^{FeO}, X_{Ol}^{MgO} = \text{Conc of FeO, MgO - olivine.}$$

$$X_{Liq}^{FeO}, X_{Liq}^{MgO} = \text{Conc of FeO, MgO - melt.}$$

No whole-rock compositions were found to represent liquids potentially capable of equilibration with olivine of mantle composition (i.e. $>Fo_{92}$). Most samples, however, were found to be potentially capable of equilibration with olivine more Fo-rich than the phenocrysts present in the rock. Such a relationship can be indicative of accumulation of cognate olivine into a basaltic liquid. This process makes the magma composition more magnesian, so that when the whole rock composition is considered it will appear to have been in equilibrium with a liquidus olivine which is more magnesian than the olivine phenocrysts present. Such a relationship can, however, also be generated if a highly magnesian magma undergoes equilibrium, or quasi-equilibrium, crystallisation so that the phenocrysts are made over to less

magnesian compositions as crystallisation proceeds. Assuming that the crystallisation process affecting the SMLS lavas is not perfect equilibrium crystallisation, the former hypothesis is employed and it is concluded that cumulus enrichment of olivine eliminates many of the magnesian basalts not affected by crustal contamination from being primary.

If it is considered that precipitation in a magma chamber is more likely to be a combination of fractional and equilibrium crystallisation rather than solely the latter, it is expected that some early formed phenocrysts would be preserved. These phenocrysts would be the most magnesian found, and would have been in equilibrium with the magmas parental to the whole suite. Superimposition of the range of olivine compositions found as phenocrysts in the lavas (electron microprobe analyses) on a plot of whole rock wt% MgO versus whole rock equilibrium olivine composition reveals the MgO content of the magma in equilibrium with the first formed olivine (Figure 8.1). In this way the parental magma of the SMLS lavas can be identified as having ca. 14 wt% MgO and a Mg/Fe ratio of 52.5 (assuming 15% oxidation).

On the basis of the above rigorous petrographic and geochemical criteria only two SMLS lavas and one FB lava were identified as primary. This result is of importance in the interpretation of the genesis of the Skye lavas since it questions the previous hypothesis that all the SMLS magnesian lavas are primary magmas (Thompson, 1974a). The discovery has a rather negative consequence, i.e. very few primary magmas are available for study.

The implications of the petrographic and compositional characteristics of the primary magmas for the mantle source mineralogy, type and degree of mantle melting and processes operating during the passage of the magmas to the surface is considered in the following section. Having addressed such questions with respect to the small number of available samples, the proposed models are then tested on a larger data-set of highly magnesian basalts. The larger data-set was produced by the arithmetical addition of olivine (assumed to be the sole fractionating phase for lavas > 7 wt% MgO, Chapter 6, Fractional Crystallisation) to all analyses

that have $\text{MgO} > 7 \text{ wt\%}$ and which show no evidence of having been contaminated with lithospheric material ($\text{Ba/TiO}_2 < 90$) until all analyses contain 15 wt% MgO. The results of this study are presented in section 8.2.3 below.

8.2.2 Primary magma phase relations

The three potential primary magmas were plotted in the $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ (CMAS) system (Figure 8.2)(several non-primary highly magnesian lavas were plotted and found to fall in the same place as the primary lavas). The samples plot very close to the cotectic curve where liquid is in equilibrium with clinopyroxene, orthopyroxene, and olivine (lherzolite mineral assemblage) at 15 kb (approximately 45 km). Whether the magmas were generated at a depth of 45 km, or were generated at greater depth and then paused and equilibrated at 45 km cannot be determined from the plotting position of the lavas in the CMAS system. All that can be concluded from the above results is that the magmas probably last equilibrated at a depth equivalent to 15 kb and a temperature of $\sim 1380^\circ\text{C}$ (O'Hara, 1968; Green and Ringwood, 1967). The conclusions reached using the CMAS system were checked by plotting the samples in the projections of Faloon and Green (1988) (Figure 8.3). The plotting position of the samples in these diagrams is consistent with their position in the CMAS system.

The above results are consistent with the results of a melting experiment carried out on one magnesian SMLS sample (Thompson, 1974a). The presence of a four phase point (ol+opx+cpx+liquid) on the liquidus of the sample at 17 kb, 1360°C , led Thompson (1974a) to conclude that the sample was a primary magma generated by partial melting of a Fe-rich lherzolite. The potential primary magmas under consideration in the present study may represent greater degrees of melting than Thompson's sample or the latter may have evolved somewhat by the fractional crystallisation.

8.2.3 Primary magma compositional variation

The range of whole rock element concentrations of the two SMLS potential primary magmas are presented in Table 8.1. The range of compositions of the uncontaminated (i.e. $90 \text{ Ba/TiO}_2 < 90$) samples of the 15 wt % MgO data-set is presented in Table 7.4. Variation in the composition of 15 wt% MgO lavas implies that some factor in their magmatic generation was changing, e.g. the composition of the source, the depth of melting, or the degree of melting. Source heterogeneity could be investigated by comparison of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of those lavas of the true primary magma, if the ratios were similar it could be assumed that the lavas had been derived from the same source. It might be possible to detect variations in the depth of magma generation using REEs if the melting zone extends from a depth where the aluminous phase is garnet (in which LREE and MREE are incompatible but HREE are compatible) to a shallower depth where the aluminous phase is spinel (in which all REEs are incompatible). Unfortunately the former possibility cannot be investigated in the present study because too few primary magmas have been identified and analysed for Sr and Nd isotopes; the latter possibility is investigated in section 8.4 below.

Creation of a 15 wt% MgO data-set (by the addition of olivine to lavas with more than 7 wt% MgO, i.e. under olivine control) to investigate the compositional scatter in the SMLS which could not be explained by fractional crystallisation effects, revealed that there were statistically significant inter-element correlations in the data-set (Chapter 6, Fractional Crystallisation section 6.8). The possibility that addition of lithospheric material had produced the correlations was investigated in Chapter, 7 Crustal Contamination and found unlikely to be the case (Chapter 7, Crustal Contamination, section 7.4). Therefore, the possibility that the correlations were generated at the time of magma production is investigated. The 15 wt% MgO data-set inter-element correlations could be the result of source heterogeneity, or variation in the depth of melt, or the degree of melt. The first possibility is essentially untestable with the data available in the present study. The possibility of variation in the depth of melting was

investigated using the results of polybaric melting experiments on a range of peridotitic materials. Jaques and Green (1980) and Takahashi and Kushiro (1983) found that for the mantle source compositions under experimental investigation (pyrolite, Tinaquillo lherzolite, spinel lherzolite) some, but not all, of the inter-element correlations could be produced by varying the depth of mantle fusion. Representative results from Jaques and Green (1980) and Takahashi and Kushiro (1983) are presented in Table 8.2. To try to minimise compositional variations resulting from effects other than different depth of fusion only samples produced by similar degrees of melting and, where known, having the same residues, were compared. The most obvious difference between the inter-element correlations of the 15 wt% MgO data-set and the major element compositional range produced by varying the pressure of melting is the behaviour of TiO_2 and K_2O . In the 15 wt% MgO data-set TiO_2 and K_2O correlate negatively with SiO_2 , but in the experimental data both elements maintain a constant concentration as SiO_2 decreases with increasing depth of fusion. This apparently eliminates variation in depth of melting as the cause of the observed inter-element correlations, and the compositional effects of variation in the degree of melt at a constant depth were thus investigated. Some representative experimental results of Jaques and Green (1980) and Takahashi and Kushiro (1983) are presented in Table 8.3. The experimental results show that the inter-element correlations of the 15 wt% MgO data-set can indeed be generated by varying the degree of fusion at a constant depth of magma generation. The peridotite compositions investigated show that, at pressures greater than 5 kb, with increasing degrees of fusion, percentage melts in the range 10 - 40%, SiO_2 increases in concentration in the melt (as does MgO, the behaviour of which cannot be tested in the present study) whereas elements generally considered to be incompatible in mantle phases, e.g. K_2O and Na_2O , decrease in concentration as they are diluted by larger melt fractions. At low pressures, ≤ 10 kb, Fe behaves like SiO_2 increasing in concentration with increasing degrees of fusion; but at higher pressures, ≥ 15 kb, Fe decreases in concentration with increasing fusion. Since Fe correlates negatively with SiO_2 in the 15 wt%

MgO data-set it is proposed that the SMLS were generated at a depth equivalent to, or greater than, 15 kb.

Consideration of the range in concentration of the elements which decrease in concentration with increasing fusion suggests that the high-SiO₂, low-incompatible element lavas were produced by approximately 1.6 times the degree of melt of the low-SiO₂ high-incompatible element lavas. The absolute degree of melting cannot be determined without knowledge of the depth of fusion. This is because many element concentrations are dependent on the depth as well as the degree of fusion, a point discussed further in section 8.4. An exception to the variations in concentrations of elements considered to be incompatible in mantle phases is Y. It does not correlate with any other element. The lack of correlation results from the limited variation in Y (approximately 20 ppm in all the basalts). Since Y is highly compatible in garnet (K_D 40) it is suggested that this behaviour is consistent with the above suggestion that the SMLS were generated at pressures $\geq$ 15kb, with some garnet retained in the source.

The successive stripping off of the compositional effects of post-consolidation alteration, fractional crystallisation and crustal contamination, has enabled assessment of the primary compositional variation in the SMLS data-set. Consideration of the compositional variation in conjunction with the results of experiments that investigated the melting behaviour of peridotites has led to the conclusion that the compositional scatter in the SMLS data-set is the result of the processes of crustal contamination, fractional crystallisation, and post-solidification alteration acting upon a primary melting trend.

8.3 The relative influences of crustal stretching and mantle temperature upon melt generation

Having determined a pressure of last equilibration for the primary magmas (ca. 15 kb),

the role of crustal stretching and mantle temperature in magma generation were investigated. In a study of melt generation during lithospheric extension, McKenzie and Bickle (1988) concluded "extension of the continental lithosphere generates little melt unless $\beta > 2$ and $T_p > 1380^\circ\text{C}$ " (where β is the final surface area/initial surface area, and T_p is the mantle potential temperature, i.e. the temperature that the mantle would have if compressed or expanded to some constant reference point). McKenzie and Bickle (1988) postulated an average mantle potential temperature of 1280°C , but this rises to 1480°C in hot mantle jets, i.e. plumes. Use of the McKenzie and Bickle (1988) equations to calculate the volume and composition of magma generated by lithospheric extension is somewhat problematic since it requires knowledge of the variation and composition of the melt fraction as a function of pressure and temperature. In their paper the relevant geophysical observations are outlined and geotherms are obtained from parameterised convective models. Empirical functions are used to describe the liquidus and solidus, and the melt fraction parameterised by a variation from 0 on the solidus to 1 on the liquidus. From parameterisation of the composition of the melt fraction major elements the expected magma composition produced by adiabatic upwelling can be calculated.

As a preliminary, the equations of Nathan and Van Kirk (1978) were used to calculate the one-atmosphere liquidus temperature of the Skye primary magmas. However, both the lavas contain phenocrysts so it is obvious that the magmas did not erupt exactly at the liquidus temperature, i.e. some cooling and crystallisation had taken place prior to eruption. To try to determine the erupted temperature of the potential primary magmas the Nathan and Van Kirk (1978) equations were used to model equilibrium crystallisation of olivine until an amount of olivine equivalent to the modal proportion of olivine was present. This modelling gave erupted temperatures of $\sim 1220^\circ\text{C}$ depending on the amount of crystallisation considered to have taken place. Such an erupted temperature corresponding to minimum mantle potential temperatures of $\sim 1290^\circ\text{C}$ (Figure 8.4).

The SMLS data were considered in terms of the experimental results of Green and Ringwood (1967). The experiments studied the melting behaviour of an olivine tholeiite, an olivine basalt, an alkali olivine basalt, and a picrite. The olivine basalt is compositionally the most similar to the SMLS potential primary magmas, but has an MgO content which is slightly too low, i.e. 12.73 % compared with 14 % (Figure 8.1). Assuming a linear relationship between whole rock MgO content and liquidus temperature (Table 8.3), interpolation of the olivine basalt and picrite data gave a liquidus temperature of 1380°C for a 14 wt% MgO composition at 15-17kb, this corresponds to a mantle potential temperature of 1430°C.

Figure 8.5 summarizes the results of McKenzie and Bickle (1988) regarding total melt thickness in relation to stretching factor and the mantle potential temperature. Interpolation between the data for 1380°C and 1480°C mantle potential temperatures suggested a potential temperature of 1430°C. For this temperature and a lithospheric thickness of 70-100 km the melt thickness predicted from the maximum β factor calculated for the Skye dyke swarm, 1.2 (Speight *et al.*, 1982) is 2 km. This is consistent with the maximum Skye lava pile thickness of 2 km suggested by King (1976) on the basis of regional zeolite facies metamorphism of the lavas by burial in the rapidly accumulating lava pile. On the basis of the above mantle potential temperature a melt fraction of ~ 15% is implied from Figure 8.4. This is consistent with the melting percentage suggested by major element compositions of liquids in equilibrium with various peridotite compositions at 15 kb (Faloon and Green, 1983; Takahashi and Kushiro, 1980). The 15% melt fraction proposed in Figure 8.4 is also close to the percentage melting suggested by the inversion of REE data (10%) (see section 8.4 below).

Assuming adiabatic upwelling of magma to the point of segregation from the point of melt generation, places the beginning of melting at 30 kb, i.e. ~ 100 km. This depth is just beneath the spinel - garnet transition, as calculated by McKenzie and Bickle (1988).

Since McKenzie and Bickle (1988) propose 1280°C as the average mantle potential temperature, the above data suggest that the mantle temperature was higher than normal during

the production of the SMLS primary magmas. Thus it can be inferred that the mantle region under Skye was within the area affected by the plume, now situated under Iceland, at the time of the generation of the magma which gave rise to the Tertiary basaltic lava flows. Figure 8.5 shows that an increase in the mantle potential temperature reduces the amount of stretching required to produce a certain volume melt. The position of Skye on the edge of the thermal effect of the plume (Figure 8.6) suggests several possibilities for the production of the SMLS, FB, and PM magmas.

A model of melt generation proposed by Thompson and Morrison (1987) suggested that there was no plume related increase in the mantle potential temperature related to the melt generation. According to the McKenzie and Bickle (1988) theory, this would require a β factor of $\gg 2$. Study of the Hebridean dyke swarm (Figure 1.8) has led to the determination of β factors in the range 1.04 to 1.20 (Speight *et al.*, 1982), i.e. from the results of McKenzie and Bickle (1988), not enough to cause mantle melting without a thermal component. The presence of a thermal component in the generation of the Skye magmas, as opposed to a pure stretching model such as that proposed by Thompson and Morrison (1988), is supported by the high proportion of samples near the base of the lava pile that are contaminated with lithospheric material (Chapter 7, Crustal Contamination). Interaction between the magma and lithosphere may be more likely to occur in a system where the magma is percolating than in a system where the melt production resulted purely from lithospheric extension where it might be expected that the magma would have an easy passage to the surface thus minimizing magma-lithosphere interaction.

8.4 Inverse theory

8.4.1 Introduction

A recent series of papers by McKenzie and co-workers have outlined a new inverse

technique for the study of melt generation. Their main aim in doing this was to constrain the physical processes of melt generation in the mantle in order to attain a clearer understanding of how melts map isotopic anomalies in the mantle as reflected in ocean island rocks (McKenzie pers. comm. 1991). At first sight the technique appears rather complicated involving the use of high-powered computer work-stations. Yet, when the aims of the technique, and the way in they are achieved are considered, it is realised that it is a similar method to that previously used by geochemists and igneous petrologists performing petrogenetic modelling. A summary of what the technique attempts to do and how it goes about doing it is given below. The technique is considered here because it may prove to be extremely important in the study of the petrogenesis of igneous rocks. As with any complex computer modelling it should be borne in mind that the results of such a technique cannot be considered in isolation from the results of other field based, geochemical, and petrographic studies. Apart from providing a control on the reliability of the results produced by the computer modelling, such data enable the distinction of systematic composition variations in a data-set from unsystematic compositional scatter.

McKenzie and co-workers use their program to calculate the melt distribution required to produce the REE concentrations in a wide variety of terrestrial (and extra-terrestrial) magmas. The program assumes that the mean composition of a suite of lavas represents the point and depth average of the melt. Ideally three or more samples are averaged. A smaller number of samples may not represent the point and depth average adequately, which might produce spurious results. An educated guess at the expected melt distribution is entered into the program (the melt distribution input is generally determined by selecting a melt distribution profile of a data-set which has comparable REE profiles to the data-set in question) along with a specification of the depth to the top of the melting region. Having defined the region in which melting may take place, the composition of the source, and the partition coefficients, the REE data are inverted to obtain information about the conditions of melt formation. It can be

seen that the inversion technique is essentially the same as the procedure of defining a mantle source region. The inversion calculates the range of compositions of melt that may be generated from the source and compares these with observed compositions. The only difference with the computer modelling being that several hundred solution fits can be tested in a matter of minutes rather than arduously testing a few fits in a day by hand calculation.

Trace elements, specifically REE, were used to study the melting processes because their activities in the melt and the melt residue can be assumed to be proportional to their concentrations. So the REE distribution between the melt and the matrix can be described by partition coefficients using Henry's law. From the melting model obtained from the REE concentrations the program calculates the major and minor element concentrations using the parameterization of Watson and McKenzie (1991).

McKenzie and co-workers considered the importance of their new technique to be the information given about the melt distribution as a function of depth as well as the melt fraction involved. The technique differs from that of previous models of mantle melting in several ways, first by modelling fractional melting of a depth range as opposed to batch melting at a fixed depth. This was considered to be more valid geologically because it is thought that melt volumes of greater than approximately 1% do not remain in contact with their source minerals. Also it would be expected that, if generated by a thermal perturbation, i.e. a plume, or by decompression melting, e.g. a ridge, mantle melting would occur over a range of depths.

With the exception of komatiites and lunar basalts it was found that the results of inverse theory calculations on the magmas studied by McKenzie and O'Nions (1991) were consistent with what is known about melt production by decompression melting, or in small volume melting of previously enriched parts of the mechanical boundary layer. It was concluded that melt generation within the earth is the result of a few simple processes. It results predominantly from adiabatic decompression, with the melt composition being controlled by how close the

upwelling material comes to the surface. In light of the clearer understanding of the physical processes involved in melt generation obtained from their inversion study McKenzie and O'Nions (1991) suggested that "useful results can be obtained by applying inverse theory to most problems in igneous petrology" !

The REE inversion technique is continually being updated in an attempt to try to simulate the conditions of mantle melt generation more closely. Modifications of the inversion program include consideration of melt production over a depth range upon the composition of the melt, inversion of a wider range of elements, and correction for the effects of fractional crystallisation involving calculation of the amount of material removed adjustment of the REE values and recomputation of the inversion (White *et al.*, submitted).

In the present study a version of the program which considers adiabatic decompression affects is used.

8.4.2 Inversion of the REE data of the Skye lavas

The inversion technique outlined in the preceding section was applied to five SMLS lavas, three PM lavas, and two FB lavas. The results of the study are presented in Table 8.4 and Figures 8.7 and 8.8. To summarize it was found that best fits between observed and calculated REE concentrations were obtained when the SMLS average lava was derived from a primitive mantle source and the PM average lava was derived from a depleted mantle source. Neither source gave a close fit for the FB lavas so they may have been derived from some mixture of primitive and depleted mantle. The SMLS data produced the smallest melt thickness and degree of melt at the greatest depth (1.9 km, 10%, 110-80 km), the FB produced more melt with a slightly higher degree of melt at a shallower depth (2.8 km, 11%, 105-70 km) and the PM data produced the greatest amount and degree of melt at the shallowest depth (5.49 km, 15%, 65-95 km). These results are in keeping with the findings of the detailed geochemical study (section 8.2-8.3).

8.6 Summary and conclusions

Most of the SMLS magnesian (> 9 wt% MgO) lavas do not have geochemical or petrographic primary magma characteristics.

Assuming that the most magnesian olivine phenocryst microprobe analyses were first-formed crystals from the parental SMLS melt, a parental composition of 14 wt% MgO was identified.

Inter-element correlations in an artificial 15 wt% MgO data-set, created by the addition of olivine to samples under olivine control, were found to result from variation in the degree of mantle melting. This led to the conclusion that the scatter in the SMLS data-set resulted from secondary processes such as fractional crystallisation and crustal contamination acting upon a primary melting trend in which the high-Si, low-incompatible element lavas were generated by 1.6 times the percentage melting of the low-Si, high-incompatible lavas.

The SMLS magmas last equilibrated at a pressure of 15 kb and a temperature of 1380°C. This corresponds to a mantle potential temperature of 1430°C (considerably higher than the average mantle potential temperature of 1280°C proposed by McKenzie and Bickle, 1988).

The above geophysical data predict a melt thickness of 2 km, a melt fraction of 15 %, and a depth of beginning of melt generation of ~ 100 km, just within the garnet zone, for the SMLS lavas.

By inversion of the Skye lavas REE data, using a new technique of McKenzie and co-workers, it was calculated that the SMLS lavas represent the smallest melt thickness and degree of melting at the greatest depth (1.9 km, 10%, 110-80 km), the FB lavas represent a larger melt thickness with a slightly higher degree of melting at a shallower depth (2.8 km, 11%, 105-70 km), and the PM lavas resulted from the greatest amount and degree of melting at the shallowest depth (5.49 km, 15%, 65-95 km).

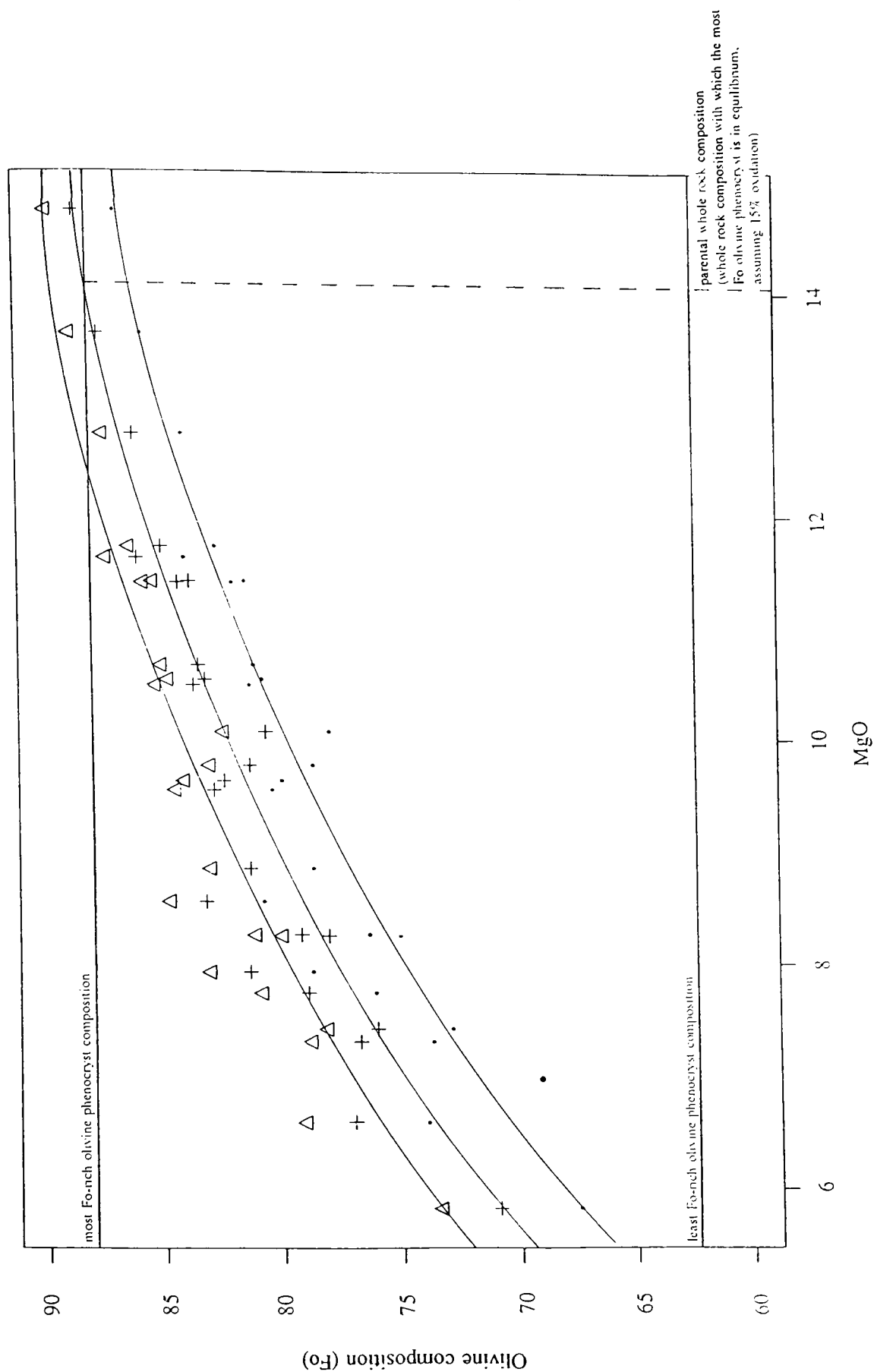
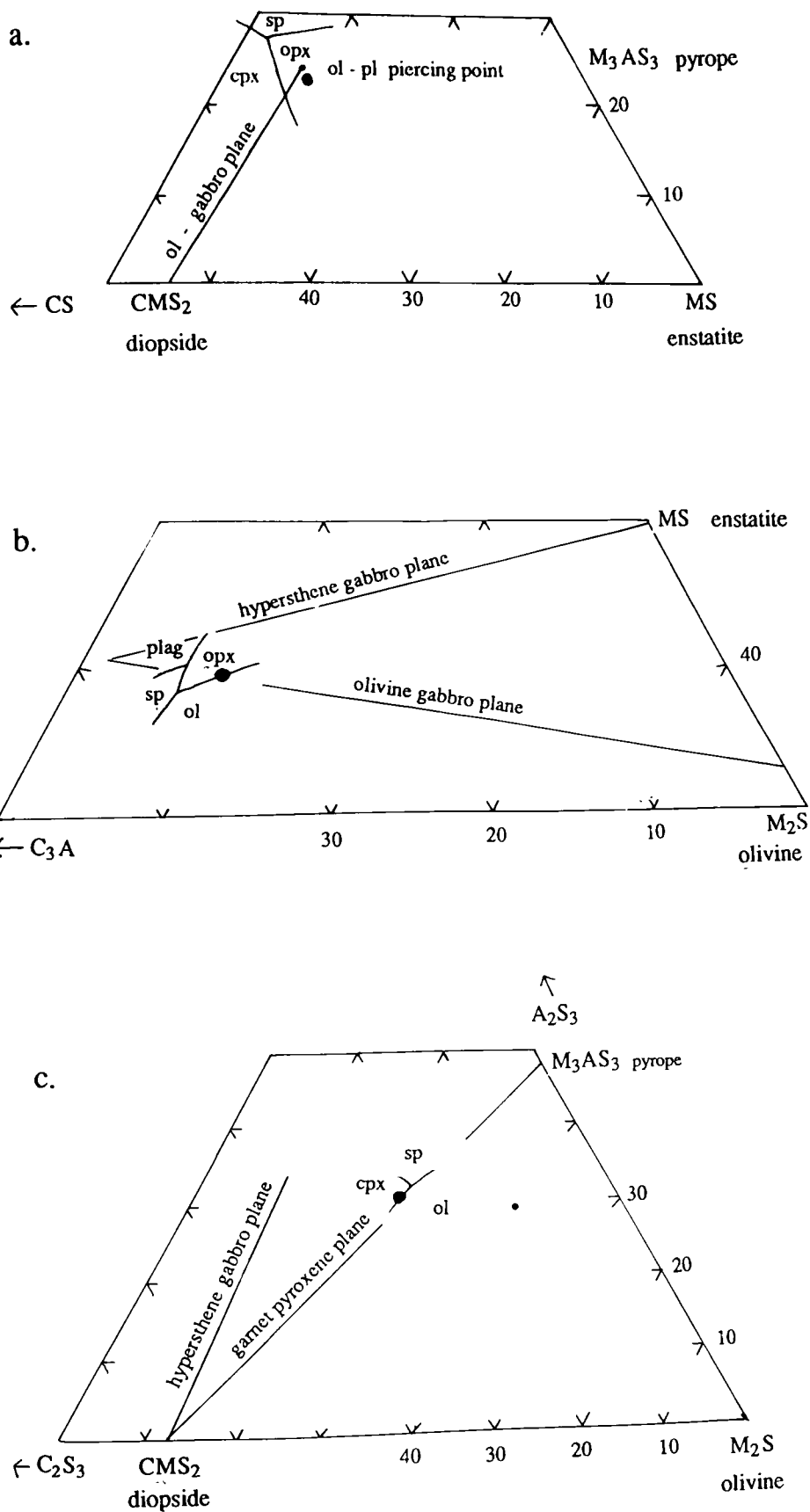


Figure 8.1 Whole rock MgO (wt%) versus composition of the first olivine to crystallise from the whole rock. (olivine compositions calculated using the equations of Nathan and Van Kirk, 1978)

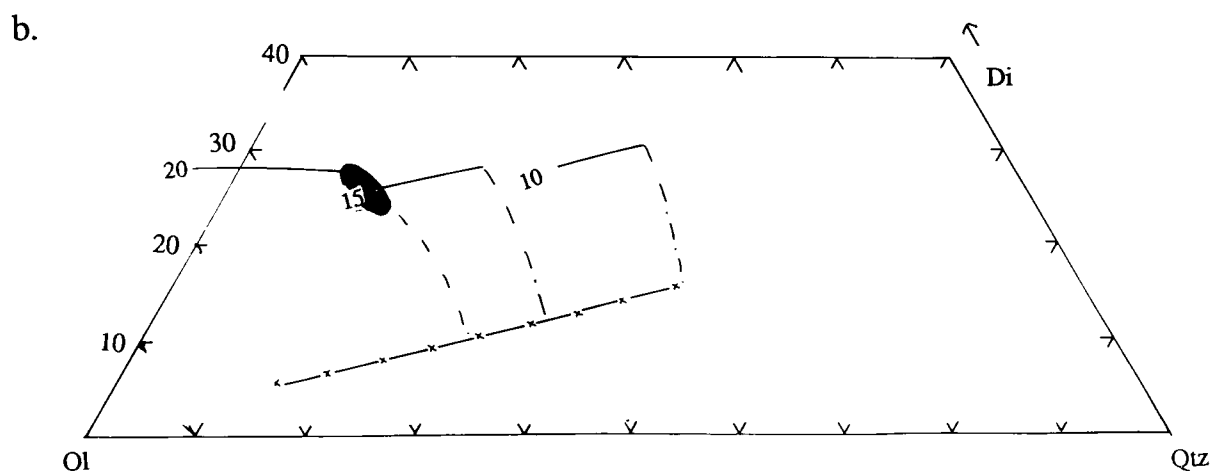
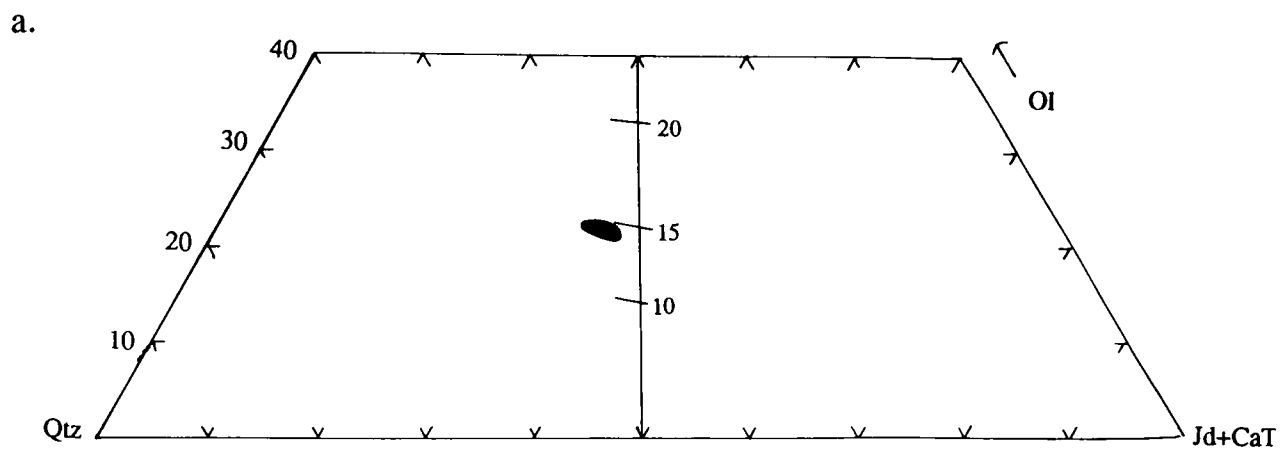
symbols: dots - 0% oxidation, crosses - 15% oxidation, open triangles - 25% oxidation .



15 Kb phase boundaries shown.

Figure 8.2 Projection of the Skye potential primary magmas in the CMAS system using phase boundaries and algorithms of O'Hara 1968.

- a. CS-MS-A from Ol.
- b. C_3A -M-S from Di.
- c. C_2S_3 - A_2S_3 -M-S from Enst.



locus of lines in equilibrium with :

- ol, cpx, opx. .
- - - ol, opx.
- x - x - ol.

Figure 8.3 Projection of the Skye potential primary magmas into
 a. Qtz-Jd+CaTs-Ol from Di.
 b. Ol-Qtz-Di from Plag.
 using the equations of Faloon and Green, 1989.

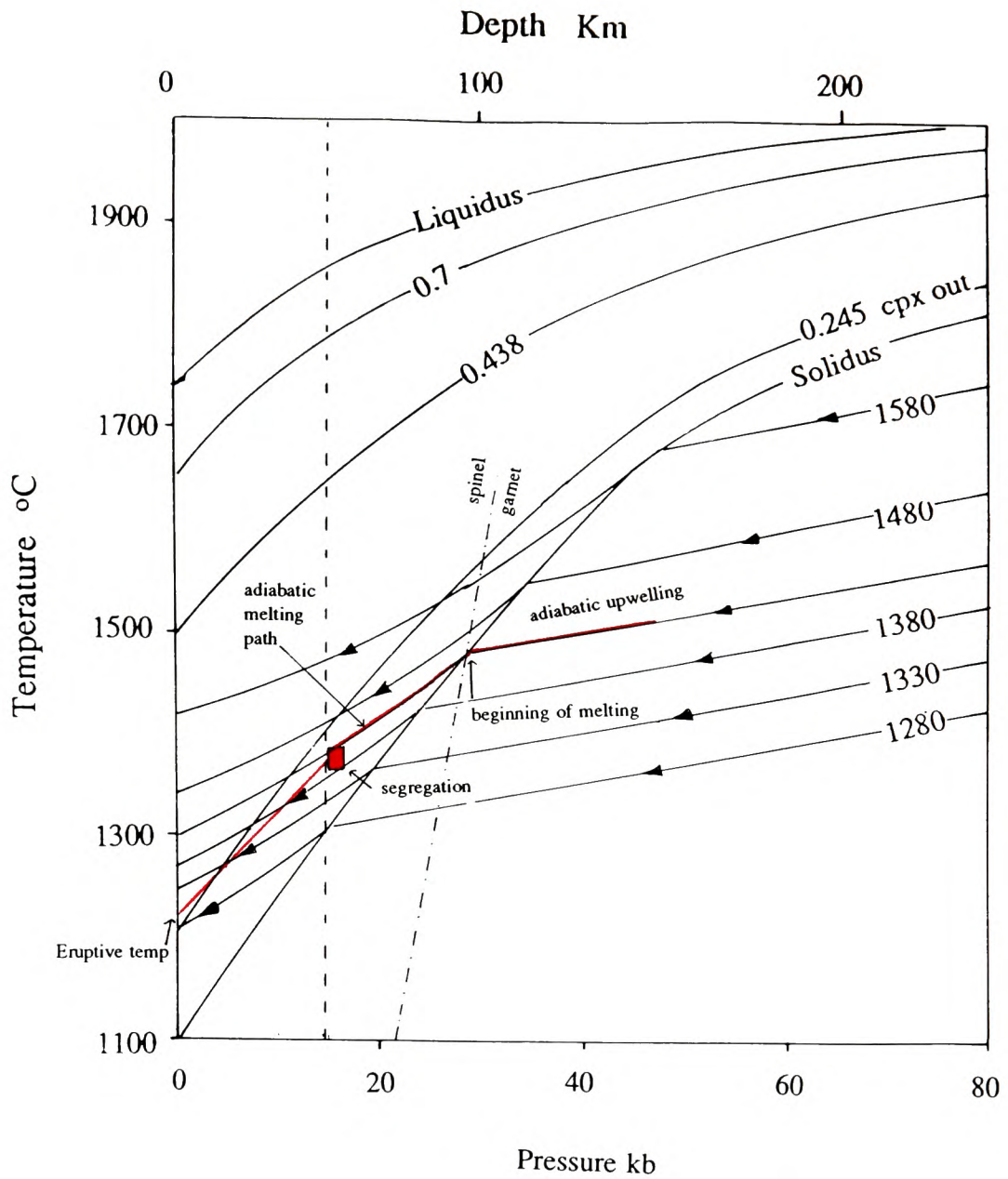
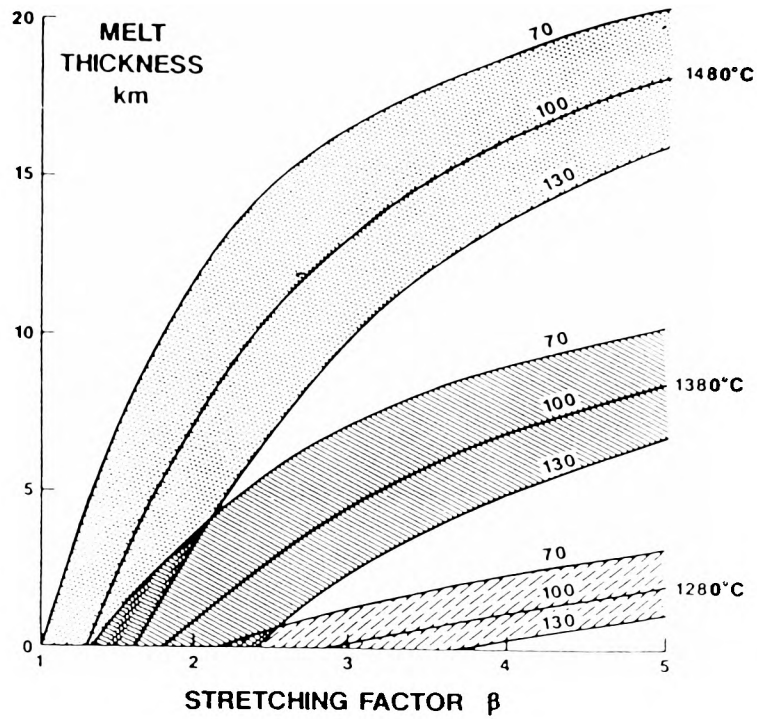


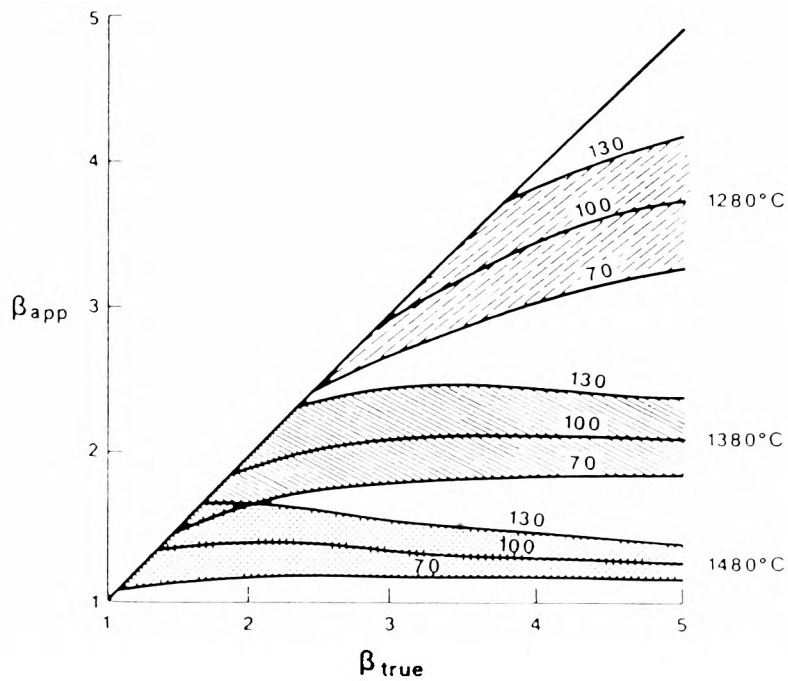
Figure 8.4 Pressure-Temperature conditions of melt generation and segregation.
(Error bars on P and T of segregation are shown by a box)

symbols: dashed line - 15kb
dot dashed line - spinel/garnet transition zone (from McKenzie and Bickle, 1988).

a.



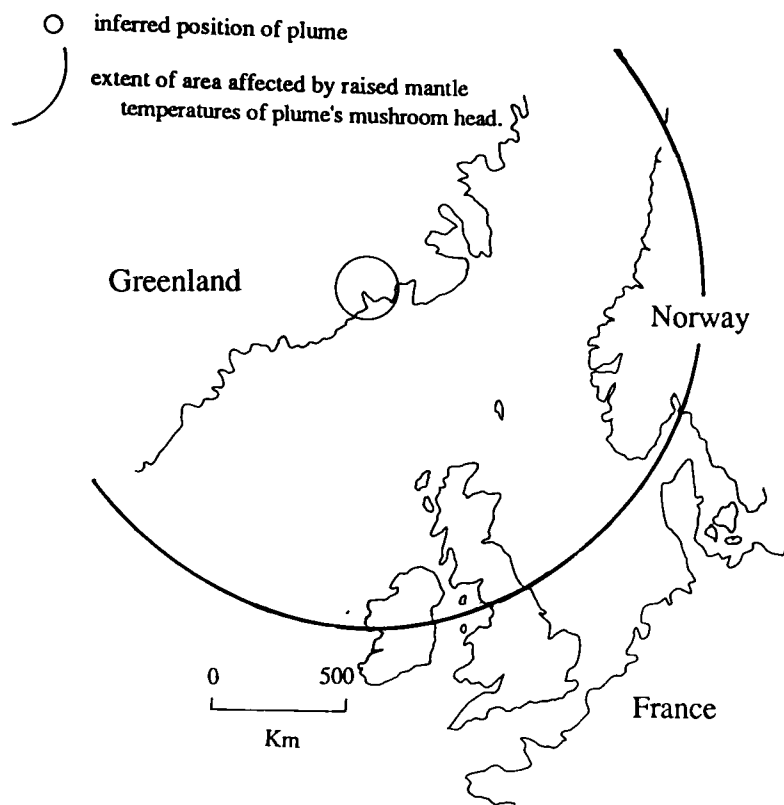
b.



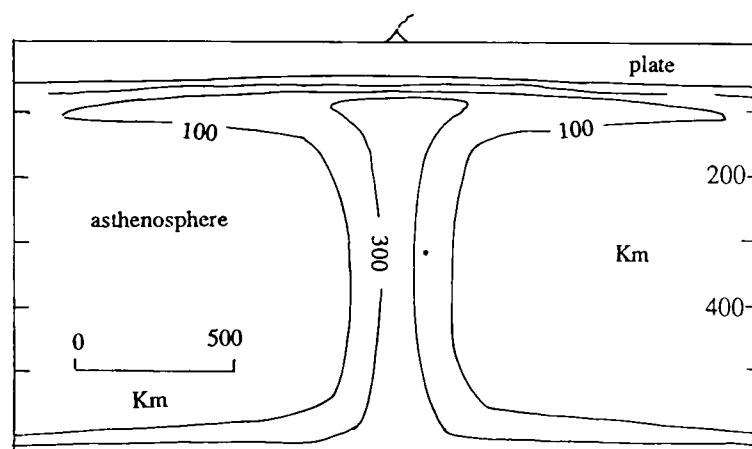
From McKenzie and Bickle 1988.

Figure 8.5 a. Total melt thickness generated by various amounts of extension, β . The numbers against the curves give the thickness of the mechanical boundary layer, and the temperatures on the right are the interior potential temperatures. b. The apparent extension β_{app} as a function of the true extension β_{true} for the examples in a. (calculated by McKenzie and Bickle, 1988 using their equation 25).

a.



b.



After White and Mc Kenzie 1988.

Figure 8.6 a. Early Tertiary reconstruction of the North Atlantic region.
b. Schematic diagram of temperature variations in a plume.

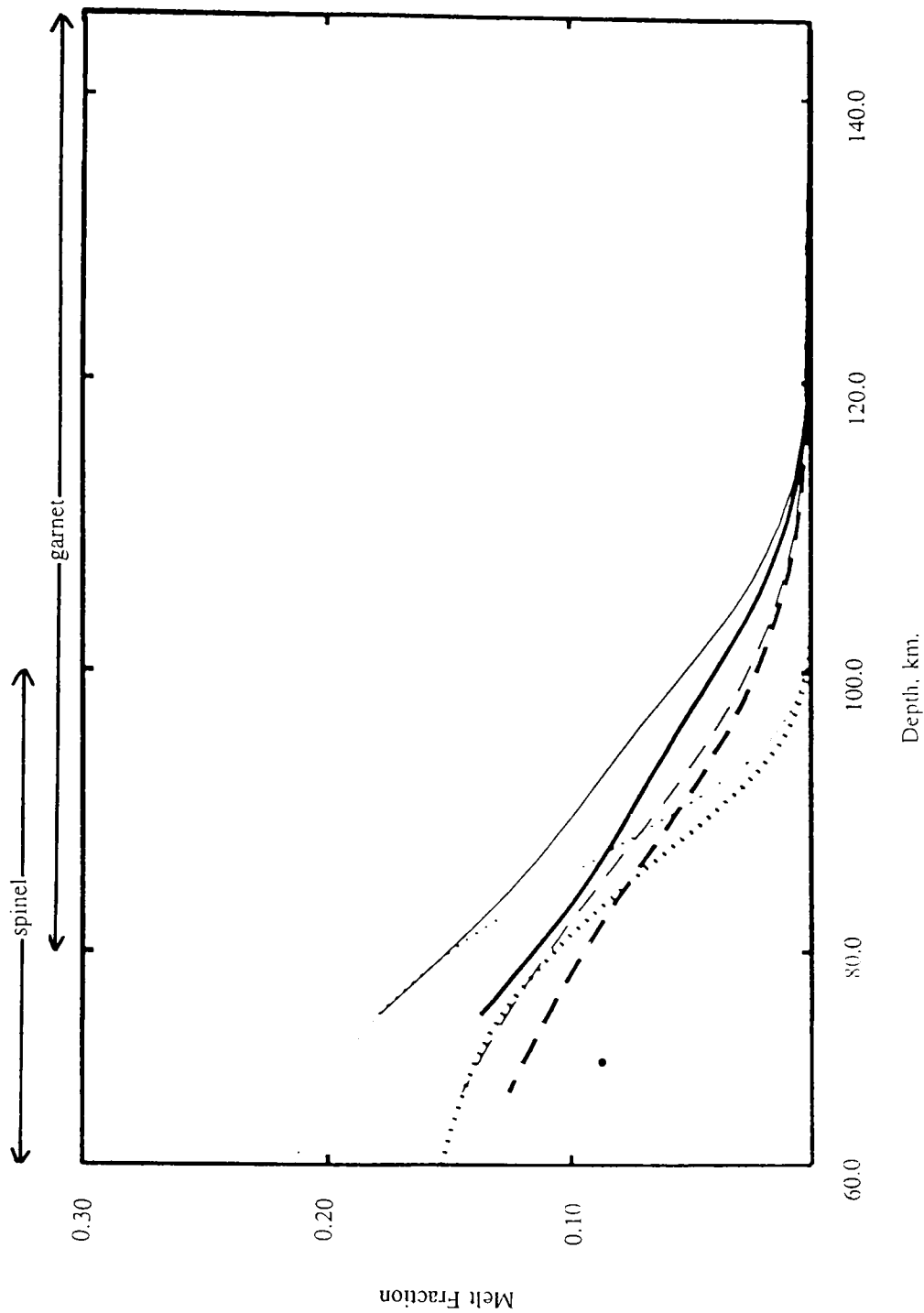


Figure 8.7 Depth versus melt fraction, results of inverse theory modelling of melt generation.

symbols:

continuous lines - SMLS, dotted lines - PM, dashed lined - FB.

thick lines - melt fraction predicted from REE data input.

thin lines - 'true' melt fraction, corrected for fractionation from thick lines (using major elements) to give primary melt fractions.

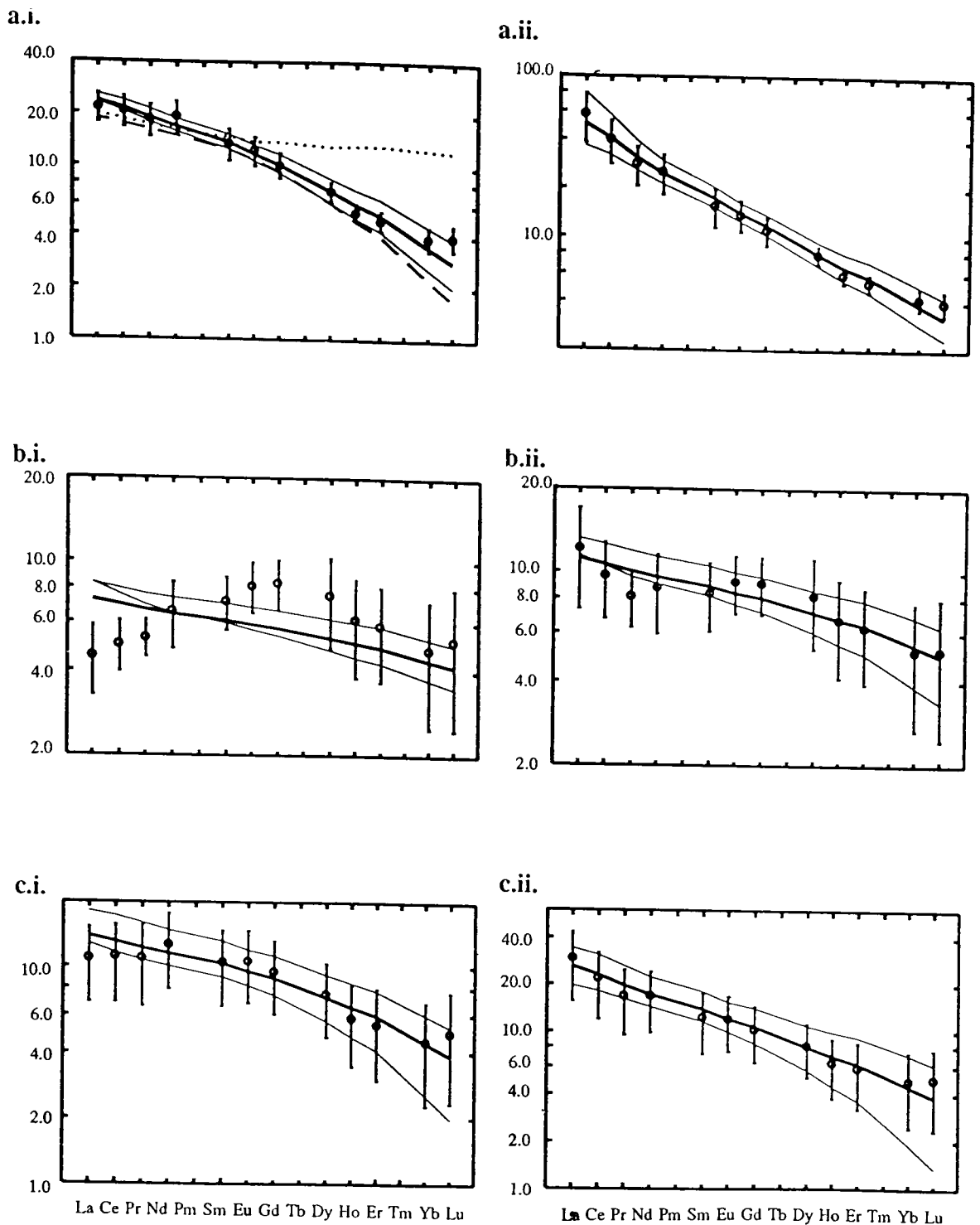


Figure 8.8

Results of inversion of REE data.

- Circles ratio of measured REE concentrations and mantle type used for the inversion (error bars are shown).
- Thick line values of REE calculated from the melt distribution (see Figure 8.6).
- Thin lines REE concentrations calculated from the estimated upper and lower bounds respective to the melt fraction.
- Dotted line in a.i. inversion result if all melting is forced to occur in the spinel field.
- Dashed line in a.i. inversion result if all melting is forced to occur in the garnet field.

- a.i. SMLS, primitive mantle, top of the melting zone 75 km.
- a.ii. SMLS, depleted mantle, top of the melting zone 75 km.
- b.i. PM, primitive mantle, top of the melting zone 65 km.
- b.ii. PM, depleted mantle, top of the melting zone 65 km.
- c.i. FB, primitive mantle, top of the melting zone 70 km.
- c.ii. FB, depleted mantle, top of the melting zone 70 km.

	JHS1	JHS201
SiO₂	46.45	46.64
TiO₂	1.31	1.40
Al₂O₃	13.82	13.87
Cr₂O₃	0.15	0.13
Fe₂O₃T	12.54	12.52
MnO	0.18	0.18
MgO	13.59	13.65
CaO	9.26	8.80
Na₂O	2.22	2.27
K₂O	0.30	0.36
P₂O₅	0.14	0.15
Zn	78.10	84.50
Cu	118.70	130.50
Ni	423.30	413.90
Co	71.10	65.40
Cr	853.30	706.10
V	71.10	237.30
Ba	120.00	124.70
Ga	19.10	19.20
Rb	6.60	11.30
Sr	261.20	220.60
Y	16.50	17.50
Zr	91.90	100.90
Nb	4.70	4.80
Pb	2.80	0.30
Th	1.30	1.20

Table 8.1 SMLS potential primary magmas.

Sample name	MPY-87	MPY-87	MPY-87	MPY-90-40	MPY-90-40	MPY-90-40	MPY-90-40	KRB	KRB	KRB	KRB	KRB	KRB	KRB
Pressure kb	8	12	20	12	15	18	30	5	8	10.5	15	20	25	30
% melt	27.00	28.00	28.00	23.00	25.00	22.00	33.00	-	-	-	-	-	-	-
Temp °C	1350.00	1450.00	1475.00	1375.00	1420.00	1450.00	1600.00	1225.00	1225.00	1290.00	1275.00	1375.00	1425.00	1520.00
SiO ₂	52.63	49.64	47.39	49.86	49.11	47.88	46.72	54.40	50.91	50.27	49.14	47.80	48.77	46.50
TiO ₂	0.58	0.59	0.60	0.69	0.69	0.66	0.55	1.99	1.41	1.45	1.59	1.55	1.66	1.79
Al ₂ O ₃	14.50	14.34	14.26	17.18	15.88	15.16	12.71	16.20	16.16	15.37	17.48	15.60	15.32	12.91
FeO	7.39	8.58	9.44	6.74	7.38	8.12	8.40	6.64	7.98	8.95	8.59	9.91	8.70	11.03
MgO	11.63	13.83	15.46	11.13	12.97	14.58	19.31	7.91	8.00	10.18	8.45	11.20	12.18	16.56
CaO	11.14	11.10	10.94	• 11.96	11.69	11.64	10.60	8.78	10.29	9.61	7.63	9.71	8.80	7.25
Na ₂ O	1.66	1.65	1.60	2.06	1.87	1.56	1.19	2.03	2.81	2.52	4.00	3.33	3.09	2.72
K ₂ O	-	-	-	-	-	-	-	0.95	0.72	0.79	1.55	1.00	1.26	1.23
Cr ₂ O ₃	0.41	0.59	0.28	0.34	0.37	0.36	0.51	0.42	0.22	-	-	0.31	0.30	-
Total	99.99	100.32	99.97	99.96	99.96	99.96	99.99	99.44	98.78	99.32	98.58	100.64	100.32	100.23

Table 8.2 Experimental conditions and compositions of liquids equilibrated with various peridotite compositions, different depths of melting, constant degree of melting.
 (Data from Jaques and Green, 1980; Takahashi and Kushiro, 1983)

Sample no	MPY-87	MPY-87	MPY-87	MPY-90-40	MPY-90-40	MPY-90-40	KRB	KRB	KRB
Pressure kb	20	20	20	15	15	15	30	30	30
% melt	12.00	17.00	24.00	5.00	25.00	28.00	-	-	-
Temp °C	1420.00	1430.00	1450.00	1360.00	1420.00	1450.00	1520.00	1540.00	1550.00
SiO ₂	47.03	46.94	47.52	50.50	49.11	49.19	46.50	47.84	47.32
TiO ₂	1.00	0.70	0.73	0.82	0.69	0.59	1.79	1.10	1.16
Al ₂ O ₃	16.62	15.44	14.39	18.00	15.88	14.58	12.91	11.85	11.34
FeO	9.67	9.83	9.62	7.00	7.38	7.36	11.03	10.12	10.64
MgO	12.99	14.24	14.51	10.00	12.97	14.42	16.56	18.47	18.91
CaO	9.93	10.53	10.98	9.60	11.69	11.79	7.25	8.08	6.19
Na ₂ O	2.63	2.30	1.84	3.50	1.87	1.67	2.72	1.84	1.88
K ₂ O	0.12	-	-	-	-	-	1.23	0.55	0.68
P ₂ O ₅	-	-	-	-	-	-	-	0.07	0.15
Total	99.99	100.18	99.97	100.24	99.96	99.98	100.23	100.29	98.64

Table 8.3 Experimental conditions and compositions of liquids equilibrated with various peridotite compositions, different degree melts at constant pressure.
(Data from Jaques and Green, 1980; Takahashi and Kushiro, 1983)

Magma type	Mantle type	Top of melting zone (km)	Base of melting zone (km)	RMS error	% Melt	% Fractn	True melt thickness	Spinel in/ Garnet out (km)	Good fit between measured and invmel calculated
SMLS	primitive	75	140	1.130	10	23.54	2.57	100/80	✓
SMLS	depleted	75	115	0.927	6	21.70	1.64	100/80	
PM	primitive	65	95	2.430	25	29.16	9.11	100/80	
PM	depleted	65	95	1.223	15	28.49	5.49	100/80	✓
FB	primitive .	70	105	1.019	13	14.52	3.53	100/80	
FB	depleted	70	115	0.646	9	13.33	2.35	100/80	
FB	50:50 mix	70	105	0.790	11	14.35	2.80	100/80	✓

Table 8.4 Summary of best fit invmel results from inversion of REE data using the equations of McKenzie and O’Nions (1991).

CHAPTER 9

CONCLUDING REMARKS AND SUGGESTIONS FOR FUTURE WORK

The detailed review of history of research of the Skye lavas (Chapter 2, History of Petrogenetic Research) revealed many unresolved issues. In the completion of a D.Phil. one cannot hope to answer all unanswered questions relating to an area which has been a focus of geological study for over 200 hundred years. The present study has addressed the main issues relating to petrogenesis of the Skye lavas, but some of the unresolved points have been outside the scope of this work. The sparsity of Preshal Mhor and Fairy Bridge lavas analysed in the present study has made any interpretation of their genesis somewhat tenuous. A larger sample set, perhaps from the dyke swarm, could provide enough data for assessment of the models suggested here on the basis of few data.

The most important unresolved issue is the validity of the stratigraphic division of the lava pile by Anderson and Dunham (1966). The present work has not found any compositional or petrographic evidence to support the previous stratigraphic division of the lavas. The relation of the compositional (with particular reference to the three magma-types) and petrographic characteristics of the lavas to the stratigraphy is needed in view of two recent works which reinterpret the structure of the pile (England, pers. comm. 1990; Smythe, pers. comm. 1991).

Consideration of evolution of the compositional characteristics of the lavas with time requires detailed flow by flow sampling of the volcanic pile. Unfortunately much of the Skye lava pile is poorly exposed, or exposed in inaccessible cliff sections. McLeod's Tables at Healadhail Mhor and Healabal Beag, and the accessible cliff sections round north western Duirinish (Figure 1.6) may provide suitable lava flow successions for such a study.

Finally, it may be possible to map the composition of the mantle underneath the British Tertiary Igneous Province (BTIP) by comparison of the elemental and isotopic characteristics of the Skye lavas having primary features, with primary lavas from other BTIP centres. The recent resurgence of research interest in the BTIP may enable such a study.

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APPENDIX A

SAMPLING TECHNIQUE AND SAMPLING LOCALITIES

Technique

In the present study lava flows and, where possible, pairs of lava flows separated by a bole (fossil soil) were collected. The presence of a between-flows bole indicates that there has been a time gap (during which the bole formed) between the two eruptive events. The rationale behind collecting lavas from either side of a bole was to place a time constraint on geochemical and petrographic variations. Several profiles from a fresh flow centre upwards through altered basalt into bole were sampled with a view to study of the mobility of elements during the alteration of the lavas.

Localities

The localities of all the samples collected in this study are listed here. Grid references are those of the Ordnance Survey of Great Britain (North Skye, sheet 23). The nature of the sample is listed (abbreviations given below). If the sample was collected from a glacial landslide block off the lava field, rather than being in situ, this has been listed (abbreviation LS). The magma-type to which the sample has been assigned is given. For completeness the position of the sample in the stratigraphy of Anderson and Dunham (1966) is given in the final column.

Sample description abbreviations:

F	Flow
B	Bole
D	Dyke
S	Sill
G	Gabbro
SED	Sediment

Magma-type abbreviations:

SMLS	Skye Main Lava Series
PM	Preshal Mhor
FB	Fairy Bridge

Stratigraphic Unit abbreviations:

O	Osdale
B	Bracadale
BT	Beinn Totaig
R	Ramascaig
BE	Beinn Edra

Table A

Sample no	Locality	Grid Ref	Sample type	Landslip block	Magma type	Strat division
1	1	46807070	F	Y	SMLS	BE
2	1		B		SMLS	BE
3	1		F		SMLS	BE
4	1		B		SMLS	BE
5	1		B		SMLS	BE
6	1		F		SMLS	BE
7	1		B		SMLS	BE
8	1		F		SMLS	BE
9	1		F		SMLS	BE
10	1		F		SMLS	BE
11	1		F		SMLS	BE
12	2	39005940	F	Y	SMLS	BE
13	2		B		SMLS	BE
14	2		B		SMLS	BE
15	2		F		SMLS	BE
16	4	39605720	F	N	SMLS	BE
17	4		B		SMLS	BE
18	4		F		SMLS	BE
19	5	40355450	F	N	SMLS	BE
20	5		B		SMLS	BE
21	5		F		SMLS	BE
22	6	40755420	F	N	SMLS	BE
23	7	40455525	F	N	SMLS	BE
24	7		B		SMLS	BE
25	7		F		SMLS	BE
26	7		F		SMLS	BE
27	7		F		SMLS	BE
28	7		F		SMLS	BE
29	7		F		SMLS	BE
30	7		D			BE
31	8	39306270	F	N	SMLS	BE
32	8		B		SMLS	BE
33	8		F		SMLS	BE
34	8		B		SMLS	BE
35	8		F		SMLS	BE
36	8		B		SMLS	BE
37	8		F		SMLS	BE
38	8		B		SMLS	BE
39	8		F		SMLS	BE
40	9	47704280	F	N	SMLS	BE
41	10	47953870	F	N	SMLS	BT
42	10		B		SMLS	BT
43	10		F		SMLS	BT
44	11	43654270	F	N	SMLS	BT
45	11		B		SMLS	BT
46	11		F		SMLS	BT
47	15	43304497	F	N	PM	BT
48	15		B		PM	BT
49	15		F	•	PM	BT
50	16	37454035	F	N	SMLS	BT
51	16		F		SMLS	B
52	17	37404025	F	N	SMLS	B
53	17		B		SMLS	B
54	17		F		SMLS	B
55	17		B		SMLS	B
56	17		F		SMLS	B
57	17		B		SMLS	B
58	19	35353695	F	N	SMLS	B
59	19		B		SMLS	B
60	19		F		SMLS	B
61	19		B		SMLS	B
62	19		F		SMLS	B
63	19		B		SMLS	B
64	19		F		SMLS	B
66	19		F		SMLS	B
67	21	30804215	F	N	FB	O
68	21		B		SMLS	O
69	21		F		SMLS	O
70	23	25404710	F	N	SMLS	R
71	23		F		SMLS	R
72	23		F		SMLS	R

73	24	25204780	F	N	SMLS	R
74	24		B		SMLS	R
75	24		F		SMLS	R
76	26	27754980	F	N	SMLS	BT
77	26		B		SMLS	BT
78	26		B		SMLS	BT
79	26		B		SMLS	BT
80	26		F		SMLS	BT
81	26		F		PM	BT
82	27	16104935	F	N	SMLS	R
83	27		B		SMLS	R
84	27		F		SMLS	R
85	28	24305000	F	N	SMLS	R
86	28		B		SMLS	R
87	28		F		SMLS	R
88	28		F		SMLS	R
89	28		F		SMLS	R
90	28		F		SMLS	R
91	28		F		SMLS	R
92	29	30355050	F	N	SMLS	BT
93	29		B		SMLS	BT
94	29		F		SMLS	BT
95	30	36505405	B	N	SMLS	BT
96	30		B		SMLS	BT
97	30		F		SMLS	BT
98	31	37505410	F	N	SMLS	BT
99	31		B		SMLS	BT
100	31		F		SMLS	BT
101	32	39655140	F	N	SMLS	BT
102	32		B		SMLS	BT
103	32		F		SMLS	BT
104	33	41604950	F	N	SMLS	BT
105	33		B		SMLS	BT
106	33		F		FB	BT
107	33		B		SMLS	BT
108	33		F		SMLS	BT
109	35	38806500	F		SMLS	BE
110	35		B		SMLS	BE
111	35		F		SMLS	BE
112	37	40157175	SED	N		
113	37		SED			
114	37		SED			
115	37		SED			
116	37		SED			
117	37		SED			
118	37		SED			
119	37		SED			
120	37		SED			
121	37		SED		-	
122	37		SED			
123	37		SED			
124	37		F		SMLS	BE
125	39	46707130	F	Y	SMLS	BE
126	39		F		SMLS	BE
127	39		B		SMLS	BE
128	39		F	•	SMLS	BE
129	39		F		SMLS	BE
130	40	48804550	F	N	SMLS	BE
131	40		F		SMLS	BE
132	40		F		SMLS	BE
133	40		F		SMLS	BE
134	40		F		SMLS	BE
135	40		B		SMLS	BE
136	40		F		SMLS	BE
137	41	45906850	F	Y	SMLS	BE
138	41		B		SMLS	BE
139	41		F		SMLS	BE
140	41		B		SMLS	BE
141	41		B		SMLS	BE
142	41		F		SMLS	BE
143	41		B		SMLS	BE
144	41		F		SMLS	BE
145	43	49775330	D	N		
146	43		F		SMLS	BE
147	43		B		SMLS	BE
148	43		F		SMLS	BE
149	44	49555320	F	N	SMLS	BE
150	44		B		SMLS	BE

151	44		B		SMLS	BE
152	44		B		SMLS	BE
153	44		F		SMLS	BE
154	44		F		SMLS	BE
155	45	49505320	D	N	-	
156	46	49405317	F	N	SMLS	BE
157	46		B		SMLS	BE
158	46		F		SMLS	BE
159	46		F		SMLS	BE
160	46		F		SMLS	BE
161	46		B		SMLS	BE
162	46		SED			BE
163	46		F		SMLS	BE
164	47	39375767	F	N	SMLS	BE
165	47		B		SMLS	BE
166	47		F		SMLS	BE
167	48	41155350	F	N	SMLS	BE
168	48		B		SMLS	BE
169	48		F		SMLS	BE
170	49	42305020	F	N	SMLS	BT
171	50	43704550	F	N	FB	BT
172	53	37903600	F	N	SMLS	BT
173	53		B		SMLS	BT
174	53		B		SMLS	BT
175	53		F		SMLS	BT
176	54	36113699	D	N		BT
177	54		F		SMLS	BT
178	57	35203865	F	N	SMLS	B
179	57		B		SMLS	B
180	57		F		SMLS	B
181	58	34303820	D	N		O
182	59	32903770	F	N	SMLS	O
183	59		B		SMLS	O
184	59		F		FB	O
185	60	33003970	B	N	SMLS	O
186	60		F		SMLS	O
187	60		B		SMLS	O
188	60		F		SMLS	O
189	60		D			O
190	61	37234178	F	N	SMLS	BT
191	62	49763880	F	N	SMLS	R
192	63	25306140	F	N	SMLS	
193	64	13254740	F	N	SMLS	
194	64		F		SMLS	
195	64		SED			
196	65	13204780	G	N	SMLS	
197	66	19254950	F	N	SMLS	R
198	66		F		SMLS	R
199	66		B		SMLS	R
200	66		F		SMLS	R
201	66		F		SMLS	R
202	67	30554370	F	N	PM	R
203	67		B		SMLS	R
204	67		F		SMLS	R
205	68	21104950	F	N	SMLS	R
206	68		B		SMLS	R
207	68		F		SMLS	R
208	69	25805990	F	N	SMLS	R
209	69		B		SMLS	R
210	69		F		SMLS	R
211	71	49903950	F	N	SMLS	BE
212	72	37404040	F	N	SMLS	B
213	72		F		PM	B
214	72		F		SMLS	B
215	73	18474487	F	N	SMLS	R
216	73		F		SMLS	R
217	73		F		SMLS	R
218	73		F		SMLS	R
219	73		F		SMLS	R
220	73		F		SMLS	R
221	73		F		SMLS	R
222	73		F		SMLS	R
223	73		F		SMLS	R
224	73		F		SMLS	R
225	74	49255315	F	N	SMLS	BE
226	74		F		SMLS	BE
227	74		F		SMLS	BE
228	74		B		SMLS	BE

229	74		F		SMLS	BE
230	74		F		SMLS	BE
231	74		B		SMLS	BE
232	74		F		SMLS	BE
233	74		F		SMLS	BE
234	74		F		SMLS	BE
235	74		B		SMLS	BE
236	74		F		SMLS	BE
237	74		F		SMLS	BE
238	74		B		SMLS	BE
239	74		F		SMLS	BE
240	75	42307410	F	Y	SMLS	BE
241	75		B		SMLS	BE
242	75		F		SMLS	BE
243	76	34105100	B	N	SMLS	B
244	76		B		SMLS	B
245	76		F		SMLS	B
246	77	38605340	F	N	SMLS	BT
247	77		B		SMLS	BT
248	77		F		SMLS	BT
249	77		B		SMLS	BT
250	77		F		SMLS	BT
251	77		F		SMLS	BT

APPENDIX B

WHOLE ROCK ANALYSES AND ANALYTICAL TECHNIQUES

The analytical methods used in the analyses of whole rock compositions are outlined here. Information about the accuracy and precision of the techniques is given.

Major and trace elements analyses were performed on a Philips PW1400 X-ray fluorescence spectrometer, with data processing using the X14 package on a PDP11 minicomputer. The x-rays were generated using a Rh tube. The analysing crystals used were LiF 220, LiF 200, PE and PX1. The machine was calibrated using USGS standards. Major element analyses were corrected by the X14 package using De Jongh's formula. Trace element mass absorption was determined using the Rh Compton scatter peak. The elements Co, Cr, V, and Ba were corrected for the Fe, Mn, and Ti absorption edges and line overlaps.

The major elements were obtained on fused glass beads. The beads contained 1g of rock powder and 5g of flux. The rock powder was heated at 150°C for at least twelve hours (twenty four hours for the bores) to remove all H₂O-, that is non-structurally bound H₂O. The powders were then weighed, heated to 1000°C overnight, and then reweighed. The weight difference was taken to be H₂O+, i.e. structurally bound H₂O. The beads were made with the flux Spectroflux 100B, which was predried at 600°C for at least twelve hours. The dried rock powder and flux were mixed and fused for five minutes at 1175°C in a zirconia grained Pt-5% Au alloy crucible. The mixture was stirred once, after two and a half minutes. The melt was then poured into a Pt-Au alloy casting mould and quenched over a jet of air. Because the mould was rather old and scratched, and possibly as a result of the composition of the flux (Whittingham, 1991), the melt tended to stick to the mould as it cooled resulting in shattering upon solidification. This was avoided by addition of a speck of lithium borate to the melt upon removal from the furnace, and agitation of the mould as the mixture cooled. The crucible was cleaned for five minutes between each fusing in a solution of boiling six molar HCl. The mould was also cleaned occasionally in the HCl solution.

Samples which had major element totals of less than 98.5% or greater than 101.5% were reanalysed. All major element analyses were normalised to 100% volatile free. The data were normalised on the assumption that there is a linear relationship between the concentration of an element in the bead and the analysis total, irrespective of why the total is not 100. The precision, i.e. reproducibility, of repeat analyses of a bead, shows that the total is related to the bead rather than the XRF analysis. The total is sensitive to the ratio of rock powder to flux (since the XRF is calibrated for a ratio of 1:5) (Devey, 1986). The ratio may be altered by flux

boiling off whilst the mixture is in the oven. Devey (1986) found that analyses of a single sample which had different totals because of variation in the rock powder to flux ratio resulting from different fusing times had almost identical major element concentrations when the analyses were normalised. So it is assumed that normalisation is a valid procedure.

Trace elements were obtained on pressed powder pellets which comprised 10.0 g of rock powder and 1.0 ml of Moviol glue. The rock powder and moviol were homogenised using a mortar and pestle. The mixture was put into a steel piston and subjected to 10^5 Pa of pressure for thirty seconds. The pellets were removed from the steel piston and then dried at 60°C for at least twelve hours (at least twenty four hours for the boles) before being analysed in XRF spectrometer.

The 216 major and trace element analyses performed during this study are given in Table B. The original, i.e. unnormalised major element analyses are given here.

Table B
Whole rock major and trace element analyses

	JMS1	JMS3	JMS6	JMS8	JMS9	JMS10	JMS11	JMS12	JMS13	JMS14	JMS18	JMS19	JMS21	JMS22	JMS23	JMS25	JMS26	JMS27	JMS28	JMS29
SiO ₂	47.37	45.09	45.36	46.54	47.22	47.37	47.19	47.31	48.01	44.54	49.98	47.41	48.04	49.32	44.92	47.99	47.71	47.81	47.60	47.77
TiO ₂	1.34	2.30	1.67	1.50	1.52	1.44	1.52	1.58	1.24	1.32	1.49	1.29	1.41	1.48	1.24	1.29	1.30	1.10	1.30	1.31
Al ₂ O ₃	14.10	14.48	14.44	14.07	14.06	13.95	14.41	14.94	14.80	14.81	16.43	16.11	16.32	16.57	14.58	15.07	15.25	15.12	15.21	15.23
Cr ₂ O ₃	0.16	0.04	0.16	0.13	0.13	0.13	0.13	0.13	0.13	0.16	0.16	0.15	0.16	0.16	0.16	0.17	0.17	0.17	0.17	0.17
Fe ₂ O ₃ T	12.79	15.66	13.81	12.57	12.74	12.43	12.71	11.56	11.14	12.73	11.28	11.50	11.98	12.34	12.23	12.18	12.22	12.21	12.19	12.33
MnO	0.19	0.29	0.17	0.19	0.19	0.17	0.19	0.17	0.17	0.18	0.16	0.15	0.16	0.16	0.17	0.17	0.17	0.17	0.17	0.17
MgO	13.86	9.55	11.26	12.56	12.50	12.11	12.32	11.51	10.41	12.36	6.35	8.15	7.79	8.35	11.65	11.29	10.94	11.07	10.76	10.77
CaO	9.45	9.53	8.90	9.07	9.43	9.11	9.12	8.85	10.43	9.70	10.25	10.89	10.16	10.80	10.10	9.86	10.27	10.16	10.09	10.18
Na ₂ O	2.21	2.14	2.49	2.44	2.47	2.49	2.48	2.48	2.01	2.29	3.07	2.64	2.75	2.58	2.61	2.41	2.54	2.52	2.52	2.40
K ₂ O	0.11	0.1	0.04	0.41	0.44	0.38	0.40	0.38	0.40	0.37	0.33	0.47	0.57	0.51	0.37	0.41	0.47	0.42	0.42	0.42
F ₂ O ₃	0.15	0.21	0.04	0.18	0.18	0.18	0.18	0.17	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Total	101.48	101.81	100.71	99.88	101.01	100.16	100.88	100.97	99.97	100.61	99.68	100.85	99.41	102.37	100.06	100.89	101.13	101.03	100.71	100.88
H ₂ O ⁺	1.13	1.50	1.79	1.03	1.60	1.07	1.64	4.01	1.54	1.48	1.56	2.00	1.68	1.51	1.33	0.90	1.13	0.88	1.07	0.42
A	3.50	3.50	3.50	4.00	3.00	4.00	3.00	4.00	3.00	4.00	3.00	4.00	3.00	4.00	3.00	4.00	3.00	4.00	3.00	4.00
Zn	78.10	90.50	81.70	85.70	78.50	83.80	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00
Cu	118.70	72.70	128.50	107.00	70.10	85.50	89.20	95.90	68.30	75.00	63.00	120.90	83.00	89.50	104.90	104.50	90.60	104.10	84.80	90.40
Ni	421.10	262.10	424.00	381.10	340.00	338.60	345.90	376.40	207.20	61.90	64.90	155.90	129.90	122.20	128.20	274.80	278.10	273.90	283.80	278.70
Co	71.10	48.00	64.00	62.90	62.20	64.70	64.70	64.70	51.70	40.60	46.40	47.70	55.10	57.60	61.80	59.90	61.00	61.10	61.70	60.20
Cr	85.30	200.70	609.00	804.90	797.70	767.00	751.60	813.30	472.40	168.10	151.70	266.90	204.20	243.40	610.90	523.90	509.50	510.60	513.90	514.50
V	217.20	276.10	130.10	253.30	232.30	249.60	274.70	232.20	227.80	210.50	266.50	215.80	216.20	258.90	238.90	230.40	241.10	210.00	243.80	244.00
Ba	120.00	139.70	116.70	204.50	224.10	211.00	226.40	98.60	291.00	280.10	293.50	252.50	236.70	245.70	97.30	88.70	248.10	210.50	207.10	196.40
Ka	19.10	21.10	14.00	18.30	18.10	19.00	19.60	18.50	16.30	20.40	21.70	19.40	20.50	19.80	17.70	18.40	19.40	19.60	18.90	18.40
Hf	6.40	7.90	4.00	9.10	9.90	9.30	11.60	6.70	20.20	7.90	11.90	7.60	14.10	11.90	9.90	10.30	9.30	9.20	10.80	10.70
Sr	261.70	344.00	191.40	153.90	308.90	368.80	321.70	259.10	372.20	369.40	259.30	327.80	318.60	304.30	292.80	311.60	299.20	295.50	307.90	307.90
T	16.50	21.50	17.70	18.00	18.00	18.10	17.60	21.00	18.40	22.60	21.10	19.50	22.10	20.10	18.50	20.10	20.60	20.20	19.80	19.80
Zr	91.90	149.30	103.60	111.50	109.70	111.50	110.70	101.50	90.20	118.80	120.20	95.60	105.90	105.00	86.40	93.30	93.20	93.30	93.80	93.50
Nb	4.70	8.10	4.80	4.70	5.00	5.40	5.10	4.70	4.20	6.00	5.60	4.70	5.10	4.20	4.50	5.40	5.40	4.50	5.00	4.20
Pb	2.80	8.00	1.50	4.70	2.30	3.00	3.50	1.50	3.70	5.60	2.10	2.10	2.20	3.40	4.60	2.90	3.20	4.70	3.20	2.70
Th	1.30	0.40	1.60	0.30	1.90	0.00	0.00	0.00	1.00	1.50	1.50	1.30	0.40	1.10	2.10	3.60	1.70	0.90	0.00	1.60
U	0.60	0.30	0.00	0.00	0.00	1.40	1.20	0.00	0.00	0.00	0.00	0.00	0.60	0.50	0.50	0.00	0.50	0.00	1.10	1.00

	JMS31	JMS33	JMS35	JMS37	JMS39	JMS40	JMS43	JMS44	JMS46	JMS47	JMS49	JMS50	JMS52	JMS54	JMS56	JMS58	JMS60	JMS64	JMS66	JMS67
SiO ₂	45.09	44.79	45.91	46.56	47.23	47.05	48.14	48.02	48.17	48.78	48.41	64.19	63.91	63.06	63.54	66.14	48.16	47.89	47.91	45.14
TiO ₂	1.87	2.51	2.56	1.85	1.81	1.50	1.43	1.99	1.73	1.33	1.30	0.83	0.83	0.85	0.76	4.01	1.43	1.49	1.63	1.97
Al ₂ O ₃	11.93	14.18	13.31	12.93	15.47	14.65	16.20	15.53	14.32	14.28	14.24	17.56	17.70	18.00	17.88	17.66	15.21	15.01	16.21	16.21
Cr ₂ O ₃	0.09	0.05	0.09	0.12	0.05	0.10	0.03	0.04	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.13	0.13	0.06	0.02
Fe ₂ O ₃ T	14.98	15.39	11.82	13.18	12.90	12.57	12.90	13.83	12.80	12.68	12.10	19.50	22.10	22.10	22.10	18.50	17.40	17.40	17.40	17.40
MnO	0.18	0.19	0.18	0.18	0.20	0.18	0.17	0.17	0.15	0.23	0.22	0.16	0.16	0.16	0.15	0.28	0.16	0.17	0.23	0.20
MgO	12.65	9.78	11.47	12.82	9.18	10.94	8.55	8.52	7.57	7.47	7.41	0.78	0.99	0.95	0.65	4.99	9.71	11.82	8.92	9.59
CaO	8.60	9.61	9.74	9.54	10.43	10.46	10.32	9.21	10.09	12.94	12.71	1.82	1.47	1.62	1.39	5.52	9.84	8.23	9.30	10.00
H ₂ O ⁺	2.05	8.81	2.38	2.31	2.63	2.56	2.65	3.00	2.72	2.17	2.14	6.03	6.15	6.36	6.38	4.10	2.20	1.85	2.52	2.10
K ₂ O	0.39	0.59	0.65	0.54	0.30	0.32	0.57	0.62	0.18	0.17	0.17	5.00	5.57	5.62	5.37	0.00	0.54	0.20	0.32	0.28
P ₂ O ₅	0.22	0.31	0.27	0.22	0.19	0.16	0.17	0.21	0.20	0.11	0.11	0.30	0.28	0.39	0.24	0.38	0.14	0.16	0.17	0.17
Total	100.06	100.24	100.39	100.49	100.60	100.46	100.87	101.09	101.41	101.81	100.68	100.78	101.00	101.16	100.15	101.88	100.68	100.61	100.58	100.34
H ₂ O ⁺	3.20	0.63	2.64	0.88	2.41	0.93	0.57	3.38	2.68	1.19	0.90	4.41	4.44	4.44	4.44	4.10	3.20	3.97	2.78	3.20
A	4.00	2.00	3.00	3.00	3.00	3.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Zn	103.30	95.90	89.60	87.00	72.60	70.20	80.30	92.80	87.10	84.20	84.20	84.20	84.20	84.20	84.20	84.20	84.20	84.20	84.20	84.20
Cu	84.00	134.70	94.70	86.50	88.60	123.70	82.10	70.90	117.10	170.80	174.10	0.00	4.70	1.10	4.70	24.50	108.40	147.10	113.40	109.90
Ni	382.70	234.40	332.00	358.10	168.80	293.60	138.20	94.90	503.00	72.30	73.20	0.20	2.40	1.80	1.50	19.70	501.00	489.60	269.50	189.70
Co	74.50	64.70	64.40	68.50	64.30	59.30	57.60	49.50	72.30	58.50	54.80	4.70	1.00	0.00	0.00	44.80	72.70	66.70	64.80	66.70
Cr	494.20	269.40	580.00	698.10	237.06	552.00	169.60	182.70	755.70	125.00	118.40	0.00	1.40	1.60	0.90	5.60	757.70	148.90	284.70	101.50
V	216.70	255.50	209.50	303.90	263.80	276.70	262.40	268.30	245.80	327.70	321.10	18.60	18.60	23.70	21.50	224.00	253.70	248.70	229.00	278.60
Ba	275.60	273.60	246.40	267.00	340.00	155.80	188.40	218.60	30.00	57.60	59.40	319.50	304.20	1185.20	305.40	112.60	98.80	46.80	78.70	210.30
Ka	21.40	26.10	23.80	19.90	20.60	19.90	19.50	22.00	18.00	18.40	19.30	21.20	22.50	21.90	20.60	18.70	18.70	18.20	19.90	17.40
Rb	10.50	14.80	17.00	11.80	14.90	8.40	7.10	11.10	3.70	8.90	8.80	74.80	79.20	78.20	80.20	15.70	6.80	5.30	5.70	13.10
Sr	458.30	614.80	549.70	583.20	421.50	300.10	352.40	239.60	168.80	144.80	138.90	324.50	273.00	290.00	241.80	434.10	204.50	180.50	272.30	514.80
T	17.56	23.00	18.60	18.80	20.00	19.50	21.50	19.20	20.50	30.30	30.30	35.40	35.40	41.30	39.00	39.00	18.30	20.70	20.90	27.20
Zr	140.00	189.10	177.10	139.90	116.40	102.90	86.30	133.00	94.60	69.50	68.20	406.40	420.50	435.60	450.30	266.60	98.70	97.20	111.90	116.20
Nb	7.20	10.50	14.30	10.00	8.00	3.90	3.20	8.30	4.40	4.60	4.00	19.00	19.60	20.40	21.00	10.40	4.10	3.60	4.90	5.40
Pb	0.00	1.50	3.60	3.40	2.30	2.30	2.30													

	JMS234	JMS236	JMS237	JMS239	JMS240	JMS242	JMS246	JMS24W	JMS250	JMS251
S102	46 15	46 42	46 17	47 26	46 75	46 50	45 56	47 63	46 51	48 19
T102	1 75	1 83	1 75	2 10	2 02	0 65	1 83	1 46	1 40	1 72
A1203	14 44	14 04	14 48	16 17	13 95	18 83	17 13	15 35	17 94	16 05
Cr203	0 10	0 07	0 10	0 10	0 05	0 13	0 04	0 09	0 11	0 06
Kr2017	11 42	11 07	13 33	13 24	14 28	9 52	12 78	13 67	14 47	12 59
MNO	0 18	0 18	0 18	0 18	0 15	0 14	0 15	0 20	0 17	0 17
NH2	11 71	11 57	11 21	8 71	10 56	5 59	6 51	10 64	7 34	8 14
Ca20	9 84	8 43	10 07	8 16	9 16	13 31	10 59	9 38	9 70	10 25
MZ0	2 23	2 51	2 39	4 00	01	1 39	3 09	2 12	2 27	2 58
P205	0 44	0 14	0 53	0 62	0 65	0 14	0 48	0 26	0 29	0 31
FZ05	0 21	0 21	0 21	0 19	0 24	0 06	0 22	0 17	0 14	0 19
Tot +1	100 71	100 82	100 76	100 76	100 51	100 16	98 05	101 01	100 22	101 05
M20+	3 07	4 92	3 45	5 05	1 71	2 19	6 65	3 59	9 44	2 31
A 1	2 00	7 50	5 00	7 50	7 50	4 50	8 00	5 00	6 00	4 00
Zn	81 50	74 90	79 00	73 20	84 60	121 48	2 50	70 40	70 50	74 00
Cu	117 50	135 90	96 40	112 40	84 50	36 00	139 10	73 50	104 00	141 80
M1	304 30	297 20	288 00	174 00	450 60	17 90	114 70	487 30	192 80	167 50
Co	65 80	57 80	66 50	49 30	72 40	39 50	62 40	73 20	69 10	50 60
Cr	571 40	355 50	560 50	268 80	715 00	13 20	459 70	529 30	15 50	294 80
V	274 20	298 20	265 00	373 20	280 50	203 50	283 90	188 30	211 70	229 30
Ca	204 60	116 80	240 40	270 80	297 80	1431 00	102 30	85 20	201 70	116 50
Ba	18 70	20 00	19 80	19 80	20 10	21 00	18 50	19 50	17 30	22 50
Nb	11 30	8 30	13 00	9 00	13 60	13 10	5 60	5 50	8 40	5 40
Sr	367 80	493 20	412 10	177 50	198 80	263 40	226 50	970 40	290 40	
Y	21 40	21 20	21 80	24 70	20 00	42 10	23 00	17 40	26 40	22 60
Zr	130 90	112 60	132 40	128 70	141 70	201 70	105 40	94 10	76 10	114 40
M1	9 50	5 80	8 40	6 10	10 40	4 40	5 20	5 00	6 10	5 00
U1	1 40	0 00	4 70	4 30	7 10	4 70	2 00	0 70	1 40	4 20
Pa	2 50	1 40	2 20	2 90	2 10	1 80	1 00	2 00	1 40	2 50
U	0 20	0 40	0 00	0 00	0 10	0 00	0 00	0 00	0 40	0 20

	JHS2	JHS4	JHS7	JHS1	JHS14	JHS17	JHS20	JHS24	JHS32	JHS34	JHS36	JHS38	JHS42	JHS45	JHS48	JHS53	JHS55	JHS59	JHS61	JHS63
SiO2	44.71	47.43	41.37	43.45	35.91	49.04	48.74	47.53	44.47	41.94	41.18	46.03	40.69	47.97	47.28	49.86	46.98	19.87	27.33	47.87
TiO2	1.93	1.43	2.48	2.04	3.81	1.61	1.69	1.51	2.40	3.36	3.73	2.30	2.23	2.72	1.85	1.25	1.34	23.66	0.42	1.89
Al2O3	20.42	22.19	23.20	19.86	21.90	17.98	21.33	16.28	15.58	19.26	18.68	14.94	22.26	22.81	15.64	19.11	20.96	10.26	11.51	14.86
Cr2O3	0.20	0.14	0.04	0.14	0.14	0.02	0.04	0.12	0.09	0.06	0.10	0.11	0.05	0.04	0.01	0.05	0.06	0.10	0.04	0.11
Fe2O3T	18.78	14.48	18.28	17.46	25.67	12.43	16.53	14.97	17.40	24.22	20.32	15.85	19.41	17.31	14.21	13.66	16.36	38.73	49.10	16.29
MnO	0.19	0.11	0.26	0.21	0.19	0.15	0.07	0.16	0.22	0.18	0.17	0.18	0.17	0.18	0.16	0.07	0.16	0.11	0.19	0.12
MgO	7.52	5.99	7.99	8.51	5.15	6.24	6.42	9.85	8.19	3.43	5.52	10.30	6.21	5.07	7.00	7.26	7.37	4.63	8.19	12.95
CaO	2.43	2.57	4.78	6.60	4.78	10.60	3.83	7.71	8.14	1.79	6.06	7.54	6.17	2.57	11.05	6.77	4.99	0.75	2.30	3.77
Na2O	2.99	4.98	1.03	1.34	1.62	1.18	0.69	1.47	2.99	4.66	3.81	2.49	1.65	0.32	2.39	1.63	1.37	1.65	0.52	1.68
K2O	0.61	0.57	0.27	0.17	0.61	0.29	0.54	0.19	0.27	0.93	0.23	0.08	0.95	0.83	0.17	0.13	0.24	0.13	0.06	0.18
P2O5	0.17	0.02	0.23	0.15	0.12	0.42	0.05	0.15	0.20	0.12	0.13	0.14	0.15	0.13	0.16	0.13	0.10	0.08	0.28	0.20
Total	101.32	101.04	102.08	100.77	100.86	101.60	101.45	101.65	100.83	101.73	100.72	103.05	101.74	100.51	101.17	100.81	101.08	98.57	98.94	100.82
Zn	120.10	116.30	165.70	105.10	155.80	83.00	91.80	90.10	114.40	258.20	174.00	111.20	110.50	118.80	84.10	81.30	103.10	111.50	62.00	88.90
Cu	140.20	141.20	199.30	129.10	332.80	108.80	168.10	117.40	124.90	438.80	127.80	133.70	139.90	110.80	189.30	165.90	176.00	132.80	259.60	162.10
Ni	569.90	427.70	153.30	417.10	233.90	66.10	111.80	427.60	392.40	404.20	322.40	358.60	109.10	127.10	92.80	87.80	104.40	77.70	353.40	361.90
Co	80.70	54.80	56.00	67.40	61.00	36.40	34.10	67.00	73.00	78.20	65.50	71.20	39.40	83.90	58.20	36.40	62.40	36.30	71.90	66.20
Cr	956.30	671.50	221.70	688.20	848.40	144.70	248.10	623.90	606.80	611.60	500.00	498.70	326.80	266.70	69.00	339.10	377.00	681.10	287.50	626.30
V	71.40	100.80	106.40	304.40	175.89	156.20	115.20	239.70	274.00	145.60	229.50	252.70	149.90	285.40	291.70	320.90	340.30	767.90	691.10	239.40
Ba	324.30	236.70	139.80	97.40	189.40	166.20	143.30	122.40	110.60	244.40	111.90	35.40	263.90	163.40	37.30	216.80	129.00	35.00	35.00	8.00
Ga	17.50	17.90	23.10	22.10	26.00	16.10	17.80	18.30	20.90	24.70	17.90	19.90	18.10	21.30	19.50	21.10	25.20	50.90	25.90	15.40
Rb	14.00	16.30	7.50	4.40	12.60	6.30	6.30	3.80	6.40	37.20	11.80	4.30	25.30	15.30	5.90	2.10	5.50	19.20	14.60	3.70
Sr	37.40	92.30	54.70	186.20	579.00	582.20	601.00	207.30	387.10	120.30	276.60	118.70	407.60	220.40	300.50	257.80	160.50	111.20	67.40	106.80
Y	25.20	25.60	27.90	17.90	20.30	21.00	10.80	22.40	21.70	45.00	25.40	21.90	24.30	25.60	31.60	18.10	23.80	34.20	39.70	19.00
Zr	129.50	113.90	190.90	132.50	249.50	120.50	146.00	99.30	171.60	253.10	256.70	146.60	243.60	181.30	110.70	93.60	97.00	329.30	127.10	117.40
Nb	5.00	5.80	9.90	5.50	28.40	5.70	7.30	4.60	9.30	22.40	22.80	11.50	11.80	11.00	5.60	3.50	4.60	58.50	4.20	4.10
Pb	5.20	2.40	6.70	3.70	30.20	4.80	52.30	5.20	4.60	16.90	11.20	4.30	19.70	2.90	1.80	2.90	4.70	30.10	2.30	4.50
Th	2.00	2.20	5.40	0.50	2.60	1.00	1.50	1.60	1.10	6.00	3.60	2.00	1.70	1.00	1.40	2.50	2.600	2.40	1.00	3.50
U	0.00	0.10	2.00	0.60	1.90	0.70	0.00	0.00	0.00	0.80	0.40	0.20	0.00	1.60	0.00	0.00	0.00	1.30	2.10	0.00

	JHS68	JHS74	JHS78	JHS79	JHS83	JHS86	JHS93	JHS96	JHS99	JHS102	JHS105	JHS107	JHS110	JHS127	JHS135	JHS138	JHS140	JHS141	JHS143	JHS147
SiO2	39.20	49.03	44.38	44.79	50.37	45.20	43.07	48.01	41.49	47.17	45.17	37.16	42.81	35.80	35.95	47.26	48.50	41.84	41.14	30.05
TiO2	3.39	1.81	2.49	2.37	1.91	1.93	4.98	2.53	4.55	2.17	1.65	3.66	2.20	3.19	3.26	1.65	0.94	2.33	2.35	3.81
Al2O3	28.62	19.35	17.52	16.13	19.01	21.08	25.58	25.41	22.03	19.15	15.93	26.03	27.17	25.51	22.08	17.00	19.70	22.46	20.07	25.22
Cr2O3	0.02	0.08	0.03	0.01	0.05	0.03	0.01	0.01	0.00	0.06	0.18	0.21	0.10	0.10	0.03	0.09	0.02	0.14	0.06	0.07
Fe2O3T	20.73	13.51	16.08	15.11	14.01	16.38	18.92	16.43	21.26	17.43	16.82	25.96	17.13	24.20	21.47	13.28	14.82	19.31	20.02	28.75
MnO	0.11	0.14	0.19	0.21	0.12	0.16	0.14	0.09	0.15	0.13	0.20	0.08	0.13	0.13	0.35	0.16	0.19	0.13	0.14	0.14
MgO	3.49	7.01	6.78	8.84	5.54	6.61	2.42	2.74	2.24	5.97	14.53	4.92	4.06	3.22	4.20	12.04	11.21	7.92	7.02	4.22
CaO	3.02	6.60	6.42	9.17	6.44	6.28	3.16	2.37	3.23	6.03	4.39	0.78	4.82	5.15	9.33	6.50	3.18	3.66	7.03	6.12
Na2O	0.89	1.99	5.46	2.81	1.74	1.90	0.58	1.13	4.33	1.38	0.72	0.21	0.96	1.82	2.63	1.35	0.84	1.35	1.72	1.28
K2O	0.31	0.30	0.23	0.25	0.53	0.21	0.92	1.06	0.39	0.28	0.25	0.86	0.42	0.70	0.38	0.44	0.37	0.64	0.26	0.18
P2O5	0.18	0.13	0.37	0.23	0.23	0.15	0.14	0.14	0.27	0.18	0.09	0.07	0.13	0.13	0.26	0.20	0.16	0.15	0.13	0.06
Total	101.15	100.72	101.08	101.13	100.95	101.04	100.44	100.20	100.82	102.96	100.91	100.63	100.71	100.30	100.16	101.16	101.34	100.88	101.72	100.03
Zn	134.70	87.50	105.90	87.70	86.80	101.50	185.70	138.60	93.10	103.70	76.50	87.50	145.10	181.40	205.60	72.20	76.30	161.00	147.70	147.50
Cu	140.60	121.20	91.10	99.60	179.40	156.90	46.40	17.30	0.00	143.30	180.40	219.20	239.30	156.80	78.90	102.80	126.70	293.30	147.40	184.60
Ni	168.50	195.40	235.20	220.70	117.00	199.70	40.50	18.60	4.90	140.50	536.80	192.40	232.90	292.40	193.70	295.40	331.90	642.20	244.40	172.80
Co	55.90	46.20	64.90	68.40	40.80	61.60	20.40	34.20	45.80	45.00	68.80	30.20	58.80	67.60	71.30	57.40	64.60	83.80	60.10	52.90
Cr	157.80	446.00	229.90	133.60	296.90	260.60	123.10	88.20	4.90	322.80	731.80	943.50	490.20	601.70	259.00	397.90	160.90	772.10	315.50	493.50
V	272.60	264.50	171.30	307.20	255.30	236.70	91.10	72.60	112.90	214.10	252.20	236.40	120.10	92.00	170.10	208.60	103.20	158.40	200.40	88.40
Ba	125.80	189.30	63.70	52.90	375.20	100.90	120.10	84.60	88.70	153.80	42.50	136.50	92.50	212.30	150.20	195.70	120.20	168.60	81.50	99.40
Ga	24.90	18.70	18.00	21.00	24.00	18.20	33.70	31.10	19.90	22.50	16.90	19.40	24.60	29.10	38.90	17.30	18.50	20.00	18.80	39.90
Rb	8.30	4.80	4.90	6.40	8.10	4.50	17.80	16.60	11.40	8.40	6.90	24.70	5.40	27.30	8.20	6.60	7.30	22.60	11.60	11.20
Sr	242.20	240.80	269.40	432.60	403.80	319.40	128.30	182.80	336.10	217.00	159.90	382.90	848.50	464.30	559.20	435.80	195.70	164.30	229.60	384.60
Y	54.10	22.50	26.20	25.10	28.70	28.00	141.50	44.50	40.70	22.90	22.50	25.40	22.50	37.90	35.70	19.80	15.50	22.90	27.40	20.60
Zr	313.70	123.80	172.10	161.50	123.50	110.00	640.00	638.30	336.60	175.40	102.20	226.10	156.50	473.90	315.20	134.90	107.60	191.40	173.70	266.80
Nb	12.90	5.60	6.00	5.60	5.60	4.60	62.90	73.50	15.90	7.20	4.30	12.90	9.50	22.50	22.70	8.60	4.90	10.40	11.20	15.30
Pb	12.60	2.80	4.10	3.50	4.90	6.30	80.30	57.70	2.30	7.00	2.90	9.40	5.30	18.50	11.60	4.00	5.60	5.60	16.70	16.90
Th	1.90	0.70	0.40	1.10	1.20	1.20	39.10	46.50	0.90	2.50	0.70	5.00	2.60	6.30	3.10	0.00	1.20	2.50	4.50	4.20
U	0.00	0.00	0.30	0.50	0.00	0.00	1.30	0.10	0.50	0.60	0.00	0.40	0.00	0.30	0.00	0.00	0.70	1.00	1.50	1.80

	JHS150	JHS152	JHS157	JHS161	JHS168	JHS173	JHS174	JHS179	JHS183	JHS187	JHS199	JHS203	JHS206	JHS209	JHS228	JHS231	JHS235	JHS238	JHS241	JHS249
SiO2	38.44	42.81	34.72	37.18	46.06	55.33	34.99	34.86	39.63	42.05	22.16	42.85	45.76	42.13	38.02	44.96	40.82	42.73	45.25	40.92
TiO2	3.30	2.44	3.06	3.32	2.95	3.37	6.15	5.58	5.76	4.09	65.71	2.95	2.54	2.25	3.20	1.87	2.28	2.40	2.14	2.65
Al2O3	19.72	20.70	22.46	17.04	21.72	24.97	22.56	19.84	27.90	22.31	20.21	20.81	23.95	20.46	18.63	15.98	18.83	19.90	22.54	25.6*
Cr2O3	0.12	0.10	0.12	0.12	0.05	0.02	0.01	0.07	0.00	0.00	0.30	0.03	0.10	0.10	0.12	0.08	0.13	0.09	0.09	0.07
Fe2O3T	25.32	18.09	23.28	17.62	21.38	7.18	32.26	33.35	24.83	20.66	43.09	19.19	15.11	24.68	18.58	14.20	18.41	18.13	16.53	21.5*
MnO	0.16	0.21	0.23	0.24	0.06	0.06	0.02	0.10	0.06	0.19	0.15	0.21	0.12	0.17	0.17	0.17	0.24	0.15	0.19	0.07
MgO	7.43	6.10	9.47	12.47	4.68	3.79	1.48	3.05	1.90	4.05	2.60	4.92	4.87	8.07	7.82	10.16	11.14	8.33	6.49	4.89
CaO	3.60	3.65	3.76	10.44	2.10	3.41	1.27	2.43	0.07	3.96	3.66	6.42	4.97	1.72	10.77	8.41	4.94	3.07	5.64	2.14
Na2O	0.39	4.76	2.22	1.20	0.19	0.31	0.15	0.25	1.92	1.74	1.09	1.88	1.32	0.13	2.13	3.93	2.42	4.35	0.50	1.13
K2O	1.38	0.74	0.49	0.16	0.70	1.02	0.69	0.40	0.08	0.35	0.05	0.31	0.99	0.13	0.33	0.05	0.25	0.63	0.46	0.78
P2O5	0.09	0.37	0.13	0.19	0.05	0.48	0.33	0.00	70.00	0.58	0.09	0.37	0.21	0.07	0.16	0.11	0.48	0.14	0.11	0.08
Total	101.20	99.74	101.82	99.70	101.12	100.74	100.04	100.30	99.63	99.00	99.83	100.52	101.67	101.03	100.18	100.78	100.33	100.52	100.93	101.28
Zn	178.60	160.00	190.70	114.30	88.70	31.90	57.50	88.80	130.50	113.90	132.00	114.40	125.90	115.60	122.50	93.20	199.00	187.30	113.90	126.80
Cu	198.20	187.30	210.80	89.00	134.30	46.00	9.50	24.50	79.10	37.60	69.20	117.90	209.50	121.50	197.00	111.40	217.10	157.70	132.20	233.30
Ni	806.70	461.70	662.40	409.90	97.30	25.30	22.00	63.40	28.40	6.10	177.40	152.20	243.50	243.50	389.00	314.80	572.30	522.60	358.40	181.90
Co	98.80	81.60	108.20	79.50	35.60	18.10	23.60	30.70	12.90	43.20	45.20	54.70	56.10	57.40	69.90	67.20	85.60	84.70	63.90	34.70
Cr	755.70	551.30	758.60	569.40	319.70	133.60	104.60	441.10	154.00	0.20	2214.00	236.80	425.70	548.50	720.50	417.10	760.00	547.90	445.20	386.80
V	165.20	205.20	115.70	246.70	102.30	438.00	368.30	320.20	84.90	103.30	260.30	248.90	57.00	190.70	234.70	197.30	334.10	257.80	195.00	153.30
Ba	249.40	116.50	298.70	114.00	204.50	61.00	350.50	106.30	337.70	209.60	36.50	230.40	149.40	82.90	281.20	36.40	135.70	121.70	95.00	168.80
Ga	28.50	19.40	21.20	25.50	19.40	31.10	25.60	31.40	35.70	25.50	39.10	26.20	21.30	24.50	24.30	18.60	21.90	19.80	20.10	19.10
Rb	44.70	20.90	13.70	7.90	17.90	42.60	38.70	19.90	15.50	13.20	14.00	8.80	10.40	7.00	8.30	3.80	9.30	20.40	6.00	20.90
Sr	187.30	126.10	392.80	844.20	214.80	175.90	153.50	228.30	128.60	331.30	411.40	575.30	341.20	101.70	802.50	202.30	191.60	122.10	380.70	297.00
Y	41.10	23.50	23.00	19.00	23.00	29.10	44.30	144.60	47.20	45.30	13.40	27.80	33.90	27.40	19.00	18.60	21.40	21.60	20.60	36.40
Zr	227.70	208.30	239.30	212.60	199.20	302.10	695.00	795.50	1590.00	351.10	253.80	240.50	171.40	129.00	200.40	139.20	189.30	209.30	146.10	202.10
Nb	7.60	10.60	9.10	18.80	9.70	13.20	57.80	76.00	146.10	40.10	40.20	12.20	7.20	7.00	17.30	8.80	11.10	9.70	9.70	9.70
Pb	1.00	10.80	5.30	12.60	7.70	6.80	34.70	47.10	73.00	2.50	24.20	6.50	2.30	12.40	6.80	4.30	3.90	3.20	6.50	6.70
Th	0.20	4.00	0.90	3.40	0.00	1.30	2.90	7.70	18.20	2.70	2.50	2.40	1.80	2.30	3.20	0.00	0.60	0.00	0.60	0.90
U	0.00	1.70	0.50	0.00	0.70	0.00	0.00	0.60	2.20	0.10	0.08	0.10	0.80	0.00	0.00	0.00	0.60	0.00	0.60	0.90

APPENDIX C

MINERAL ANALYSES AND ANALYTICAL TECHNIQUES

Minerals were analysed on polished, 30 µm thick, thin sections. Before analysis the sections were coated with a 200 µm thick layer of carbon to prevent charge build-up. The mineral analyses were performed using a Cambridge Instruments Microscan 9 electron microprobe. The microprobe has two wavelength dispersive spectrometers. The machine is controlled by an Opus p.c. The machine was calibrated by running standards before each session of mineral analysis. The Opus p.c converted measured element concentrations to true element percentages using ZAF corrections.

The operating conditions of the machine were : beam size 0.5-1.0 µm, the beam current was 4×10^{-8} A, accelerating potential was 20 kV. Only analyses with totals of greater than 98.5% or less than 101.5% were used.

The 336 mineral analyses performed during this study are given in Table C.

Table C
Mineral analyses

Groundmass olivines

	10	100	103	103	145	145	145	146	146	146	148	148	148	184	184	184	184	184	201	210	211	
MgO	32.43	14.59	21.52	42.32	35.01	38.76	35.01	40.62	36.46	37.40	42.13	43.10	41.25	28.30	27.83	37.72	28.84	28.48	28.07	40.80	33.99	44.12
SiO2	38.63	53.53	37.94	40.11	36.14	37.82	36.14	35.40	34.94	38.16	39.32	39.31	38.89	35.79	34.75	38.50	35.81	36.92	33.75	35.98	37.72	38.77
CaO	0.49	20.63	0.66	0.27	0.36	0.38	0.36	0.38	0.42	0.39	0.38	0.35	0.42	0.50	0.51	0.31	0.58	0.58	0.50	0.34	0.52	0.24
Cr2O3	0.03	0.03	0.01	0.03	0.03	0.03	0.03	0.00	0.05	0.04	0.04	0.04	0.05	0.01	0.01	0.02	0.01	0.02	0.00	0.03	0.02	0.03
MnO	0.45	0.23	0.60	0.39	0.50	0.45	0.50	0.33	0.40	0.40	0.24	0.23	0.24	0.65	0.66	0.35	0.66	0.59	0.67	0.28	0.46	0.20
FeO	27.47	8.06	37.29	18.03	28.76	22.90	28.76	22.19	27.42	24.69	18.15	18.19	19.23	35.29	35.51	24.26	35.09	32.81	35.13	21.16	29.12	16.31
NiO	0.09	0.00	0.04	0.15	0.12	0.15	0.12	0.10	0.10	0.07	0.23	0.24	0.23	0.09	0.07	0.12	0.07	0.12	0.04	0.22	0.13	0.29
Total	99.59	97.07	98.06	101.30	100.97	100.49	100.97	99.05	99.81	101.18	100.55	101.49	100.34	100.63	99.34	101.30	101.06	99.52	98.16	98.81	101.96	99.96

	211	211	211	211	211	211	212	31	35	35	35	37	37	39	46	67	8	81	81	87	87	89
MgO	45.39	45.24	28.81	23.32	27.43	21.96	35.12	40.35	40.43	40.06	34.92	28.99	30.86	37.39	38.59	34.79	27.84	41.19	43.81	27.84	32.75	26.39
SiO2	39.56	39.12	34.98	35.04	34.95	32.74	37.51	37.79	38.67	40.28	38.45	36.32	36.32	37.32	37.43	36.62	36.34	39.29	38.55	36.82	36.52	39.66
CaO	0.23	0.23	0.35	0.38	0.32	0.31	0.31	0.32	0.44	0.40	0.46	0.50	0.72	0.49	0.41	0.53	0.46	0.41	0.38	0.62	0.40	0.60
Cr2O3	0.02	0.02	0.03	0.01	0.01	0.01	0.03	0.05	0.02	0.00	0.02	0.05	0.09	0.02	0.03	0.00	0.02	0.06	0.03	0.02	0.02	0.00
MnO	0.19	0.19	0.57	0.76	0.61	0.74	0.55	0.29	0.29	0.28	0.39	0.63	0.87	0.41	0.37	0.36	0.59	0.31	0.28	0.75	0.69	0.53
FeO	14.67	15.57	34.18	40.39	35.58	42.47	28.11	22.49	21.94	0.56	157.73	14.01	33.05	25.89	24.00	24.28	33.90	19.45	17.96	31.91	28.24	31.97
NiO	0.33	0.29	0.10	0.04	0.07	0.09	0.09	0.21	0.16	0.18	0.10	0.07	0.10	0.07	0.09	0.09	0.09	0.09	0.11	0.06	0.09	0.07
Total	100.39	100.66	99.02	99.94	98.97	98.32	101.74	101.50	101.95	101.76	101.82	101.35	101.94	101.59	100.92	98.67	99.24	100.80	101.12	98.02	98.73	99.22

	89	9
MgO	27.90	24.51
SiO2	37.04	39.71
CaO	0.42	2.76
Cr2O3	0.03	0.02
MnO	0.59	0.56
FeO	33.83	32.33
NiO	0.07	0.09
Total	99.88	99.98

Phenocryst olivines

	1	1	1	1	1	10	10	10	10	100	100	100	129	129	129	129	129	129	129	
MgO	47.09	46.27	46.57	47.21	46.23	44.47	34.99	39.48	46.19	46.20	35.50	34.70	34.88	42.87	40.85	44.48	44.90	41.35	39.75	46.32
SiO2	40.33	40.60	40.40	40.56	40.64	39.50	37.65	38.88	37.75	39.60	36.49	35.60	35.55	39.07	38.28	39.08	39.13	37.22	38.22	38.75
CaO	0.26	0.26	0.27	0.26	0.30	0.31	0.29	0.25	0.28	0.27	0.31	0.82	0.28	0.26	0.27	0.21	0.24	0.25	0.24	0.23
Cr2O3	0.02	0.02	0.05	0.00	0.04	0.02	0.05	0.02	0.05	0.05	0.00	0.00	0.02	0.05	0.03	0.03	0.07	0.05	0.03	0.07
MnO	0.19	0.20	0.22	0.19	0.20	0.24	0.41	0.36	0.23	0.23	0.72	0.74	0.74	0.26	0.30	0.19	0.19	0.27	0.31	0.22
FeO	13.50	13.97	13.84	13.19	13.57	15.30	27.63	22.70	15.58	14.99	28.30	27.78	28.21	18.04	20.56	16.60	15.39	19.88	22.18	13.78
NiO	0.32	0.29	0.29	0.35	0.30	0.29	0.21	0.22	0.26	0.29	0.01	0.03	0.00	0.24	0.21	0.26	0.33	0.17	0.19	0.33
Total	101.79	101.69	101.71	101.81	101.36	100.18	101.31	101.93	100.34	101.63	101.33	99.90	99.87	100.79	100.50	100.85	100.25	99.19	100.74	99.70

	129	129	129	129	129	129	129	129	142	142	142	142	142	142	142	142	142	145	145	
MgO	43.98	39.97	43.52	45.63	44.84	32.83	42.94	45.02	41.34	43.36	43.11	44.22	44.98	44.61	44.10	44.23	44.03	45.00	45.05	43.82
SiO2	39.04	38.37	39.18	39.94	37.51	36.49	38.69	38.58	37.41	38.46	38.55	37.68	38.58	37.88	38.61	38.66	38.52	38.57	38.54	37.92
CaO	0.23	0.31	0.24	0.23	0.21	0.39	0.31	0.23	0.31	0.28	0.28	0.27	0.26	0.26	0.27	0.26	0.27	0.26	0.23	0.26
Cr2O3	0.05	0.07	0.05	0.08	0.05	0.02	0.05	0.08	0.05	0.02	0.02	0.05	0.03	0.03	0.05	0.05	0.03	0.10	0.02	0.04
MnO	0.23	0.24	0.26	0.19	0.20	0.53	0.24	0.19	0.30	0.27	0.26	0.26	0.23	0.20	0.20	0.20	0.23	0.19	0.19	0.20
FeO	16.78	15.71	17.38	13.50	15.63	30.64	17.62	15.39	19.33	17.58	17.52	16.15	15.15	15.89	15.09	14.63	16.24	15.29	15.21	16.58
NiO	0.33	0.33	0.26	0.33	0.33	0.15	0.21	0.33	0.15	0.20	0.21	0.24	0.24	0.26	0.27	0.24	0.21	0.29	0.29	0.29
Total	100.64	95.00	100.89	99.90	98.77	101.05	100.06	99.82	98.89	100.17	99.95	98.87	99.47	99.13	98.59	98.21	99.53	99.70	99.60	99.14

	146	146	153	153	153	153	153	153	153	153	153	153	184	184	184	184	184	184	184	184
MgO	45.05	43.82	43.04	41.94	44.21	44.10	43.33	43.39	43.35	43.56	44.46	43.32	43.90	45.91	43.87	42.98	44.11	43.65	40.87	44.66
SiO2	38.54	37.92	37.79	38.60	38.21	39.38	39.29	39.43	38.59	38.32	39.77	38.93	38.76	39.64	38.97	37.87	38.64	39.09	37.98	37.51
CaO	0.23	0.26	0.23	0.30	0.24	0.23	0.24	0.23	0.24	0.26	0.23	0.24	0.24	0.27	0.23	0.27	0.23	0.24	0.27	0.26
Cr2O3	0.02	0.04	0.03	0.02	0.05	0.03	0.03	0.03	0.03	0.05	0.02	0.03	0.03	0.03	0.02	0.03	0.02	0.03	0.05	0.03
MnO	0.19	0.20	0.23	0.26	0.22	0.23	0.23	0.27	0.24	0.20	0.22	0.23	0.23	0.22	0.22	0.20	0.24	0.23	0.24	0.27
FeO	15.21	14.58	17.92	18.17	16.16	18.94	16.15	17.60	17.59	17.41	16.44	17.45	16.63	14.74	16.75	18.51	15.19	17.30	20.66	16.33
NiO	0.29	0.29	0.24	0.18	0.29	0.23	0.26	0.16	0.24	0.24	0.21	0.21	0.26	0.27	0.29	0.23	0.27	0.26	0.13	0.26
Total	99.60	99.14	99.48	99.67	99.38	101.14	100.13	101.21	100.30	100.02	101.35	100.41	100.05	101.07	100.34	100.12	98.70	100.83	100.21	99.24

	184	184	184	184	184	201	201	201	211	211	211	211	211	212	35	35	35	39	39	67	67
MgO	45.97	46.10	44.40	45.05	43.78	46.42	46.69	47.33	40.35	39.49	40.57	42.95	32.60	43.60	43.95	43.76	44.18	42.16	36.63	44.67	
SiO2	38.16	38.68	38.84	38.67	38.59	40.26	40.91	41.13	37.20	36.52	37.61	38.55	39.79	39.43	39.38	39.57	40.01	39.33	38.51	40.02	
CaO	0.24	0.23	0.26	0.23	0.31	0.26	0.24	0.24	0.30	0.27	0.23	0.24	0.62	0.27	0.27	0.27	0.26	0.33	0.31	0.21	
Cr2O3	0.03	0.03	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.05	0.06	0.02	0.02	0.02	0.04	0.02	0.02	0.02	0.04	0.02	
MnO	0.18	0.18	0.19	0.20	0.20	0.16	0.18	0.16	0.30	0.32	0.32	0.27	0.33	0.23	0.22	0.27	0.20	0.27	0.33	0.22	
FeO	14.56	14.40	16.25	15.27	15.76	12.46	12.58	12.25	20.75	22.32	20.76	17.69	26.40	16.76	16.65	16.71	16.21	19.39	25.36	15.55	
NiO	0.26	0.30	0.26	0.29	0.29	0.38	0.39	0.33	0.16	0.16	0.19	0.21	0.07	0.32	0.29	0.32	0.27	0.18	0.16	0.30	
Total	99.40	99.92	100.23	99.73	98.96	100.01	101.11	101.35	99.09	99.13	99.74	99.93	99.83	100.65	100.85	100.97	101.20	101.70	101.39	101.01	

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	76	76	76	79	8	81	81	81	87	87	89	89	89	9
MgO	44.54	44.31	43.11	44.62	42.68	45.28	46.40	45.39	46.19	44.44	43.36	43.49	43.38	45.83
SiO2	40.16	39.76	39.97	39.53	39.24	40.91	38.82	38.85	40.50	39.96	39.86	39.62	39.64	39.22
CaO	0.23	0.24	0.24	0.21	0.26	0.43	0.36	0.38	0.24	0.26	0.27	0.28	0.27	0.24
Cr2O3	0.04	0.02	0.02	0.04	0.03	0.05	0.05	0.05	0.00	0.02	0.02	0.02	0.02	0.02
MnO	0.23	0.24	0.26	0.32	0.30	0.26	0.20	0.23	0.15	0.24	0.24	0.23	0.23	0.23
FeO	14.33	16.35	17.39	16.70	16.63	15.27	15.65	15.02	16.17	17.30	16.62	17.37	15.46	
NiO	0.32	0.22	0.23	0.23	0.20	0.14	0.18	0.08	0.35	0.30	0.26	0.24	0.29	0.31
Total	101.98	101.27	100.94	101.70	101.26	103.41	100.63	101.20	101.48	101.43	101.36	100.56	101.25	101.49

Groundmass plagioclases

	10	103	103	129	129	129	129	129	184	184	142	142	142	142	142	145	145	146	146	146
Na2O	4.33	3.95	4.39	4.81	3.51	4.97	4.18	6.66	3.58	3.51	3.40	4.70	5.39	5.49	5.03	5.04	7.81	3.93	3.76	4.57
MgO	0.04	1.40	0.23	3.06	1.66	1.26	0.08	0.02	0.06	0.06	0.23	0.08	0.15	0.10	0.15	1.22	0.04	0.83	1.54	1.70
Al2O3	28.66	27.10	28.13	25.89	26.91	27.38	29.71	25.19	30.13	30.48	30.83	28.91	27.61	27.52	28.21	25.41	18.47	28.91	28.72	27.08
SiO2	54.28	51.98	54.72	53.65	51.25	53.04	51.62	57.84	49.82	50.13	49.03	53.42	53.39	54.65	53.81	55.47	65.95	50.75	50.80	52.00
K2O	0.23	0.24	0.43	0.73	0.17	0.32	0.20	0.95	0.26	0.19	0.15	0.24	0.31	0.35	0.29	0.99	5.41	0.19	0.19	0.25
CaO	12.34	11.37	11.64	8.21	13.45	9.64	12.50	6.79	13.54	13.59	13.94	11.33	10.46	10.02	10.78	8.46	0.72	12.47	12.06	10.83
TiO2	0.11	0.09	0.13	0.17	0.36	0.13	0.13	0.21	0.11	0.09	0.09	0.21	0.15	0.15	0.13	0.09	0.04	0.11	0.08	0.08
MnO	0.00	0.03	0.00	0.03	0.04	0.03	0.00	0.03	0.01	0.01	0.04	0.01	0.01	0.03	0.01	0.00	0.01	0.01	0.03	0.01
FeO	0.80	3.07	1.32	1.95	2.24	1.95	0.82	0.77	1.07	0.81	0.84	1.03	0.88	1.01	0.75	2.20	0.97	1.56	2.38	2.08
Total	100.79	99.23	100.99	98.50	99.59	98.72	99.24	98.46	98.58	98.87	98.55	99.33	98.35	99.32	99.16	98.88	99.42	98.76	99.56	98.60

	148	148	153	153	153	153	201	210	210	211	211	211	211	211	211	211	211	212	212	212
Na2O	4.13	3.55	4.28	3.92	5.41	4.95	4.03	1.58	4.16	4.09	5.04	4.02	4.84	7.67	6.68	3.82	4.41	4.71	0.17	5.41
MgO	0.88	2.65	1.31	0.13	0.93	1.75	0.17	10.07	3.37	0.13	0.12	0.17	0.13	0.06	0.06	0.10	0.13	1.52	16.52	2.16
Al2O3	28.65	25.42	27.61	29.51	25.26	23.90	32.34	11.14	23.57	29.59	29.61	29.87	28.75	22.22	25.41	30.18	29.15	26.14	0.55	23.63
SiO2	51.39	50.13	51.71	51.20	55.61	55.77	50.51	48.38	53.81	50.91	52.02	51.89	53.62	63.87	57.54	51.14	51.89	51.98	38.69	53.97
K2O	0.19	0.19	0.30	0.19	0.42	3.13	0.23	0.08	0.61	0.24	0.19	0.20	0.31	2.72	0.70	0.24	0.27	0.37	0.07	1.02
CaO	12.19	11.76	11.24	12.89	9.07	6.64	13.50	16.98	10.37	12.53	11.42	12.73	11.21	3.43	7.59	12.83	12.00	9.51	6.41	7.15
TiO2	0.13	0.37	0.17	0.17	0.15	0.15	0.11	2.04	0.28	0.09	0.08	0.09	0.11	0.15	0.15	0.09	0.09	0.07	0.38	0.13
MnO	0.01	0.04	0.01	0.00	0.01	0.03	0.03	0.19	0.04	0.01	0.01	0.01	0.03	0.01	0.00	0.01	0.00	0.07	1.00	0.04
FeO	1.49	4.62	2.08	0.98	1.66	2.87	0.81	9.38	4.57	1.03	0.69	0.74	0.74	0.51	0.56	0.77	0.81	4.51	36.41	5.07
Total	99.06	98.73	98.71	98.99	98.52	99.19	101.73	99.84	100.78	98.62	99.18	99.72	99.74	100.64	98.69	99.18	98.75	98.88	100.20	98.58

	212	33	33	35	35	35	35	35	37	37	37	39	49	49	56	67	67	69	69	79
Na2O	4.14	4.04	5.89	7.26	4.59	4.04	3.04	3.87	7.66	4.30	3.93	5.73	2.98	3.22	6.42	4.22	3.82	5.01	5.45	3.52
MgO	3.81	0.29	0.15	0.14	0.17	0.19	1.65	0.74	0.16	0.08	0.06	5.66	0.32	0.40	2.08	0.29	0.13	3.80	0.82	8.46
Al2O3	21.46	29.27	25.70	24.13	27.93	29.15	28.91	29.01	23.30	29.05	29.40	20.28	31.08	30.49	17.93	31.21	30.87	17.14	22.20	17.97
SiO2	49.31	51.96	57.44	60.79	54.35	52.33	49.53	52.09	61.75	52.64	51.53	53.48	50.35	51.09	64.04	50.38	50.05	53.15	49.52	58.30
K2O	0.21	0.32	0.70	1.58	0.39	0.23	0.17	0.23	1.50	0.29	0.24	0.61	0.17	0.07	6.17	0.24	0.17	0.33	0.53	0.36
CaO	7.33	12.08	8.04	5.84	11.18	12.75	12.71	12.41	4.98	12.37	12.92	4.04	14.22	13.87	0.84	12.20	13.48	11.62	6.82	4.89
TiO2	0.15	0.11	0.15	0.17	0.17	0.15	0.09	0.15	0.17	0.11	0.11	0.09	0.04	0.06	0.45	0.13	0.13	1.93	3.43	1.17
MnO	0.20	0.03	0.01	0.01	0.01	0.04	0.03	0.01	0.00	0.01	0.00	0.18	0.03	0.00	0.07	0.03	0.01	0.16	0.23	0.08
FeO	12.20	1.04	0.82	0.59	0.77	0.54	2.12	1.23	0.67	0.87	0.94	8.61	0.85	1.26	1.83	0.88	0.74	7.48	11.68	11.88
Total	98.81	99.14	98.90	100.51	99.56	99.42	98.25	99.74	100.19	99.72	99.13	98.68	100.04	100.46	99.83	99.58	99.40	100.62	100.68	98.63

	79	8	8	8	81	81	87	89	9
Na2O	3.65	4.98	3.82	4.25	3.90	3.25	4.04	7.81	3.59
MgO	2.69	1.54	0.10	0.56	0.21	0.40	0.54	0.64	7.63
Al2O3	26.31	26.34	29.82	28.74	29.30	30.46	27.48	19.55	13.11
SiO2	50.53	53.14	52.07	52.00	52.46	50.64	53.41	64.26	54.61
K2O	0.20	0.37	0.20	0.21	0.06	0.06	0.31	3.16	0.25
CaO	10.82	10.05	13.11	12.40	12.95	14.02	12.63	3.36	15.10
TiO2	0.21	0.19	0.09	0.09	0.06	0.06	0.26	0.17	0.75
MnO	0.10	0.03	0.01	0.01	0.03	0.07	0.01	0.03	0.12
FeO	3.88	2.77	0.98	1.56	1.21	1.46	1.30	1.03	6.08
Total	98.39	99.41	100.20	99.82	100.18	100.42	99.98	100.01	101.24

Phenocryst plagioclase

	10	10	10	10	100	103	103	103	129	129	129	142	142	145	145	146	146	146	153	153
Na2O	3.45	3.57	3.85	3.19	3.80	2.99	6.69	2.86	4.06	3.82	3.36	3.19	3.45	3.21	3.16	3.41	3.49	3.02	3.63	3.45
MgO	0.10	0.15	0.27	0.70	1.30	0.09	0.99	1.20	0.08	0.06	0.08	0.34	0.19	0.19	0.19	0.19	0.15	0.19	0.15	0.11
Al2O3	30.26	30.29	29.94	30.10	27.98	30.66	23.33	29.08	30.50	30.63	30.54	30.78	30.66	31.08	31.27	30.55	30.26	31.00	30.36	30.63
SiO2	50.19	51.23	52.13	49.86	53.66	50.39	60.01	51.08	50.60	50.72	49.99	49.83	50.95	49.20	49.90	50.92	50.71	50.45	50.56	50.68
K2O	0.17	0.15	0.18	0.15	0.20	0.19	1.01	0.17	0.20	0.19	0.15	0.14	0.13	0.08	0.07	0.13	0.12	0.12	0.12	0.13
CaO	14.23	13.41	12.93	13.55	11.86	14.49	6.21	13.74	12.94	12.97	13.97	14.32	13.74	14.46	14.63	14.21	13.97	14.60	13.37	13.25
TiO2	0.06	0.06	0.06	0.06	0.11	0.06	0.15	0.06	0.11	0.11	0.09	0.06	0.08	0.06	0.06	0.06	0.06	0.04	0.09	0.06
MnO	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.00	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01
FeO	0.68	0.64	0.81	1.21	1.72	0.72	2.22	1.92	0.72	0.81	0.64	0.80	0.78	0.54	0.52	0.55	0.61	0.55	0.54	0.52
Total	99.15	99.50	100.71	98.82	100.63	99.60	100.62	100.14	99.21	99.35	98.83	99.47	99.99	98.83	99.81	100.03	99.38	99.98	98.82	98.84

	153	153	153	153	184	184	184	33	33	33	39	39	39	56	56	67	67	69	69	69
Na2O	3.57	3.25	3.76	5.55	3.16	2.94	2.45	3.94	4.27	3.89	3.29	3.94	3.21	7.37	7.25	2.90	2.68	5.57	5.57	4.78
MgO	0.17	0.13	0.15	0.64	0.04	0.06	0.09	0.11	0.11	0.11	0.13	0.15	0.17	0.31	0.27	0.04	0.92	0.06	0.23	0.13
Al2O3	30.78	31.42	30.52	26.40	31.56	32.13	32.44	29.65	29.53	29.77	30.57	29.25	30.80	22.60	20.42	31.04	31.29	27.43	27.33	27.93
SiO2	49.76	49.87	50.89	56.64	50.20	49.60	47.59	52.20	52.53	52.22	50.98	52.33	50.46	64.05	63.92	49.63	48.63	57.28	55.23	54.07
K2O	0.13	0.12	0.14	9.23	0.19	0.17	0.09	0.20	0.20	0.20	0.12	0.18	0.12	1.83	3.04	0.12	0.12	0.23	0.24	0.18
CaO	13.83	14.13	13.40	0.17	14.42	14.94	15.50	12.66	12.19	12.68	13.90	12.92	14.54	4.02	2.81	14.79	14.27	10.12	10.15	11.45
TiO2	0.06	0.09	0.08	0.00	0.08	0.08	0.06	0.11	0.11	0.09	0.06	0.08	0.08	0.09	0.24	0.09	0.11	0.13	0.15	0.15
MnO	0.01	0.01	0.03	0.04	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.04	0.01	0.03
FeO	0.61	0.61	0.55	1.52	0.71	0.54	0.58	0.43	0.48	0.49	0.64	0.59	0.61	1.07	1.46	0.71	2.63	0.45	1.21	0.81
Total	98.92	99.63	99.52	100.23	100.37	100.47	98.81	99.31	99.42	99.45	99.70	99.45	99.99	101.35	99.42	99.69	100.69	101.28	100.14	99.51

	79	8	8	81	81	81	81	87	89	89	9
Na2O	3.52	3.13	3.52	1.07	1.25	2.31	1.09	3.41	3.27	2.91	3.73
MgO	8.46	2.23	8.46	0.30	0.22	0.32	0.22	0.08	0.72	0.15	0.11
Al2O3	17.97	28.73	17.97	34.51	34.32	32.38	34.19	30.23	29.21	70.50	30.45
SiO2	50.10	49.14	50.10	45.45	46.50	47.41	45.10	52.42	51.11	51.55	51.78
K2O	0.36	0.19	0.36	0.04	0.04	0.06	0.04	0.15	0.19	0.15	0.20
CaO	4.89	12.60	4.89	18.02	17.84	15.17	18.02	13.91	11.45	14.97	13.59
TiO2	1.17	0.06	1.17	0.02	0.00	0.02	0.02	0.08	0.06	0.06	0.08
MnO	0.01	0.08	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01
FeO	11.88	2.71	11.88	0.45	0.45	0.64	0.48	0.64	1.32	0.64	0.64
Total	98.63	98.80	98.63	100.36	100.42	98.94	99.78	100.93	100.00	101.31	100.59

	100	100	103	129	184	142	142	142	145	145	153	153	153	184	201	201	210	210	210	211
Na2O	0.80	1.45	0.52	0.73	0.61	0.37	0.62	0.28	12.41	12.62	0.51	0.52	0.58	0.46	0.51	0.36	0.65	0.52	0.45	0.45
Al2O3	14.03	9.97	13.99	11.77	11.89	13.10	9.97	15.22	4.69	4.78	11.80	12.73	12.27	14.55	12.81	14.54	11.86	11.93	13.08	13.08
SiO2	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63	52.63
CaO	20.14	15.52	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14	20.14
TiO2	1.48	1.42	1.12	3.37	2.68	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83	20.83
Cr2O3	0.00	0.00	0.09	0.00	0.02	0.02	0.02	0.02	0.02	0.02	1.56	2.52	3.01	1.55	1.91	1.61	1.61	1.61	1.61	1.61
FeO	0.25	0.16	0.18	0.19	0.16	0.19	0.30	0.12	11.30	10.45	0.33	0.19	0.15	0.26	0.30	0.14	0.29	0.30	0.31	0.31
Total	100	99.14	101.08	98.50	98.51	102.13	98.68	98.39	98.43	98.66	99.27	101.18	101.25	100.74	101.61	101.54	101.71	101.88	98.96	98.96

	211	211	211	211	212	212	33	33	33	33	35	37	39	39	39	46	46	49
Na2O	0.29	0.31	0.33	0.29	0.46	0.52	0.47	0.80	0.7	0.58	0.35	0.37	0.39	0.39	0.39	0.46	0.46	0.49
HgO	15.28	15.18	15.16	14.67	12.50	11.69	13.09	10.23	14.88	12.12	12.10	10.66	0.69	0.36	0.34	0.37	0.31	0.27
SrO	2.89	3.56	2.12	3.94	4.17	3.45	4.07	3.56	5.04	4.63	7.26	5.38	4.98	3.39	5.65	4.61	3.14	2.16
SiO2	51.02	51.25	51.10	50.23	50.01	48.94	48.81	48.60	50.26	50.23	46.37	46.44	46.42	50.54	48.45	49.85	51.60	49.10
CaO	20.68	20.36	20.16	18.47	20.08	19.56	21.98	21.11	20.24	20.31	21.25	21.04	21.25	21.51	21.52	21.78	21.47	21.06
TiO2	0.83	0.90	0.70	0.84	1.02	0.98	1.16	1.12	1.14	1.12	4.3	3.62	3.82	1.14	1.29	1.05	0.85	1.05
Cr2O3	0.40	0.69	0.03	0.22	0.03	0.02	0.02	2.15	1.14	1.12	0.00	0.20	0.02	0.55	0.88	0.88	0.48	0.02
HfO	0.18	0.18	0.23	0.16	0.18	0.27	0.15	0.24	0.46	0.45	0.07	0.20	0.23	0.18	0.21	0.15	0.15	0.15
FeO	7.23	7.22	7.22	7.79	11.85	13.16	11.81	12.34	0.21	0.23	0.22	10.87	11.53	6.94	7.20	6.61	6.63	9.91
Total	94.54	98.65	98.87	98.85	101.82	99.68	99.48	99.13	100.17	99.86	99.81	99.10	99.46	99.15	99.70	99.68	98.38	98.65

	49	49	67	67	67	69	69	69	81	81	81	87	89
Na2O	0.24	0.48	0.52	0.60	0.53	0.37	0.44	0.51	0.61	0.78	0.52	0.41	1.53
HgO	16.02	13.89	13.08	11.73	11.80	2.16	5.53	1.51	11.54	11.53	14.64	15.00	11.62
Al2O3	3.52	4.69	5.20	4.61	6.50	26.49	16.75	27.26	4.46	2.91	2.59	3.54	6.15
SiO2	51.77	50.83	48.47	48.10	44.21	51.91	51.77	50.41	50.49	50.89	50.15	50.04	51.79
CaO	2.04	2.11	2.16	2.11	21.45	9.21	10.73	8.39	20.18	19.56	20.20	20.73	18.79
TiO2	0.64	1.11	2.34	3.65	4.24	0.35	0.63	0.30	2.74	2.74	1.05	1.21	0.31
Cr2O3	0.14	0.02	0.39	0.02	0.00	0.02	0.00	0.00	0.02	0.00	0.34	0.52	0.02
MnO	0.12	0.25	0.18	0.22	0.18	0.03	0.0	0.06	0.26	0.29	0.22	0.22	0.31
FeO	7.62	10.07	8.99	10.64	10.29	5.19	10.18	5.66	11.16	12.67	9.08	7.22	7.97
Total	100.56	99.21	100.81	100.19	99.23	100.73	100.14	98.79	101.36	100.61	98.88	98.73	99.18

	142	153	39	39	56	56	56	67	67	67	67
Na2O	0.31	0.29	0.41	0.41	3.06	1.22	3.44	0.51	0.45	0.51	0.29
HgO	15.34	14.72	15.30	14.39	13.01	13.35	17.58	12.12	12.13	12.19	12.49
Al2O3	3.35	3.03	5.83	5.53	9.71	52.70	52.37	4.70	5.58	4.77	5.61
CaO	57.28	59.95	50.78	49.07	45.39	20.75	9.50	47.45	47.08	47.43	47.06
TiO2	20.26	21.63			10.39	0.39	0.88	21.40	20.96	20.71	21.73
Cr2O3		1.11	0.95	1.18	0.87	0.02	0.02	3.08	3.17	2.92	3.15
Cr2O3	0.55	0.22	0.57	0.66	0.00	0.28	0.00	0.00	0.00	0.00	0.22
MnO	0.21	0.14	0.14	0.11	0.47	9.70	10.38	0.16	0.19	0.19	0.19
FeO	7.33	7.42	7.90	6.94	12.53	0.00	0.00	9.75	9.33	9.91	9.64
Total	98.63	98.51	100.70	99.60	99.03	100.94	99.25	99.27	99.38	98.77	100.44

	0	1	2	129	229	129	129	184	184	184	184	142	142	142	142	153	153	153	201	210	212
Na2O	0.00	0.08	0.00	0.57	0.05	0.05	0.05	0.03	0.03	0.03	0.03	0.00	0.06	0.03	0.03	0.10	0.00	0.08	0.03	0.06	0.05
MgO	1.08	1.03	0.73	0.99	1.90	4.56	0.55	3.68	2.61	1.87	2.44	0.32	0.26	0.64	1.93	1.93	3.48	1.33	1.49	1.39	
Al2O3	0.74	1.10	0.66	0.99	1.21	5.72	1.55	2.54	1.81	1.56	1.78	0.47	0.26	0.46	1.75	2.12	3.80	4.44	2.37	2.17	0.99
SiO2	0.10	0.41	0.20	0.76	0.13	2.83	0.77	0.03	0.21	0.10	0.03	0.95	0.41	0.09	4.78	0.21	4.35	0.15	0.03	0.03	
K2O	0.05	0.05	0.04	0.12	0.06	0.05	0.05	0.04	0.06	0.05	0.06	0.05	0.05	0.06	0.05	0.05	0.04	0.05	0.05	0.05	
CaO	0.05	0.01	0.11	1.27	0.06	0.35	0.15	0.26	0.01	0.17	0.17	0.61	0.02	0.05	0.91	0.07	1.21	0.04	0.05	0.05	
Cr2O3	2.12	2.43	2.75	0.97	25.00	0.01	28.14	24.41	26.99	25.95	26.73	25.74	26.14	26.75	24.93	21.24	17.13	21.15	18.80	27.27	
TiO2	0.04	0.08	0.06	0.03	0.03	0.83	0.30	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
MnO	2.10	1.66	1.68	0.86	0.80	0.58	0.78	0.60	0.68	0.74	0.61	0.85	1.04	1.26	1.34	0.64	0.58	0.68	0.41	1.78	
FeO	63.96	66.51	63.99	56.65	64.83	54.54	63.22	63.77	62.57	63.82	63.05	67.23	65.07	64.78	57.73	66.30	58.98	66.30	71.14	62.94	
NiO	0.01	0.11	0.06	0.09	0.06	0.14	0.07	0.11	0.09	0.11	0.09	0.01	0.01	0.01	0.00	0.04	0.03	0.06	0.06	0.11	0.03
Total	95.35	95.27	95.12	96.50	94.95	95.16	95.39	96.67	95.80	94.54	94.99	96.33	95.52	95.85	95.94	96.34	93.87	96.40	94.53	94.60	

	212	212	212	212	31	31	31	33	35	35	37	39	49	56	67	67	67	69	69	81
Na2O	0.05	6.31	0.00	0.00	2.91	0.00	0.05	0.02	0.00	0.11	0.03	0.03	0.11	6.25	0.00	0.16	0.11	0.23	0.03	0.00
MgO	0.88	1.09	2.38	2.02	6.39	1.78	40.43	42.98	2.85	0.62	0.47	1.02	0.66	0.08	2.96	2.39	1.36	2.43	1.70	1.35
Al2O3	0.60	15.91	1.46	1.96	12.42	1.38	0.05	0.11	0.87	0.85	1.88	1.39	2.12	19.18	0.23	1.88	1.52	1.77	2.64	2.79
SiO2	0.46	57.72	0.08	0.20	26.84	0.59	39.31	39.87	1.96	0.13	0.28	0.36	0.05	63.19	0.00	0.49	0.20	4.36	1.46	0.50
K2O	0.06	4.49	0.05	0.07	0.48	0.05	0.02	0.04	0.11	0.06	0.05	0.06	0.05	5.72	0.05	0.05	0.10	0.06	0.05	0.05
CaO	0.09	1.33	0.02	0.14	1.83	0.07	0.37	0.31	0.66	0.00	0.11	0.07	0.01	0.97	0.00	0.21	0.06	0.62	0.31	0.11
TiO2	25.93	5.26	32.29	28.77	10.35	47.64	0.04	0.04	27.74	28.47	28.46	29.01	17.50	0.18	27.70	28.28	29.69	27.24	25.08	15.36
FeO	0.06	0.06	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
MnO	1.34	0.31	0.47	0.53	0.18	0.86	29.27	0.24	0.90	0.85	3.10	4.40	0.61	0.07	0.64	0.58	0.64	0.61	0.64	0.61
FeO	64.94	13.52	58.32	60.90	36.25	43.94	19.09	16.72	57.76	65.63	61.73	62.61	73.02	1.82	63.69	60.44	58.71	56.08	60.07	73.07
NiO	0.04	0.05	0.01	0.06	0.01	0.04	0.00	0.24	0.29	0.01	0.04	0.00	0.03	0.00	0.06	0.03	0.10	0.01	0.01	0.04
Total	94.59	101.08	95.42	94.74	97.72	96.34	100.00	100.65	94.00	96.75	96.21	96.02	94.23	98.06	97.23	94.78	96.67	93.48	93.33	93.78

	81	87	89	89	9
Na2O	0.03	1.11	0.00	0.03	0.00
MgO	0.63	1.15	0.29	0.73	1.46
Al2O3	2.78	3.71	1.15	1.33	1.10
SiO2	0.21	6.38	0.05	0.25	0.13
K2O	0.05	0.25	0.04	0.05	0.06
CaO	0.04	0.59	0.00	0.07	0.14
TiO2	17.96	17.81	28.14	25.94	26.03
Cr2O3	0.04	0.11	0.06	0.27	0.45
MnO	0.58	0.91	0.41	3.98	2.38
FeO	71.84	61.78	64.36	59.97	62.84
NiO	0.00	0.06	0.01	0.07	0.06
Total	93.66	93.86	95.51	94.49	94.65

	56	56	56
Na2O	0.00	0.00	0.00
MgO	1.61	1.10	0.99
Al2O3	0.24	0.22	0.68
SiO2	0.00	0.00	0.03
K2O	0.05	0.05	0.04
CaO	0.00	0.00	0.00
TiO2	34.29	34.20	10.90
Cr2O3	0.01	0.03	0.01
MnO	2.20	2.28	1.96
FeO	57.83	58.23	81.47
NiO	0.03	0.03	0.01
Total	96.26	96.14	96.09

APPENDIX D

RARE EARTH ELEMENT ANALYSES AND ANALYTICAL TECHNIQUES

Rare earth element concentrations were determined by inductively coupled plasma spectrometry. About 0.3 g of each sample was accurately weighed into a PTFE bomb, and subjected to dissolution in concentrated HF. When dissolution was complete, the samples were evaporated to dryness, and 5 ml of H_3BO_3 solution (saturated in 2.5M HCl) were added. The samples were heated to 150°C for two hours, again evaporated to dryness, and then heated to 150°C with 1.5 M HCl.

Quartz columns with a bed of AG50-X12 200-400 mesh cation exchange resin of 0.4 by 3.5 cm size were pre-equilibrated with 1.5M HCl. The solutions were loaded onto the columns, and after washing with 3 x 0.5 ml 1.5M HCl were eluted with 7 ml 5.1M HCl. This was collected in a PTFE beaker, and evaporated to dryness. Quantitative transfer of samples was ensured at all stages.

The columns were re-equilibrated with 1.5M HCl. For the second stage of the preparation, each sample was dissolved in 0.4 ml 1.5M HCl and loaded onto the same column as before. After washing with 3 x 0.2 ml 1.5M HCl, a further 9.5 ml 1.5M HCl was passed through the columns before eluting the REE with 2 ml 5.1M HCl. The solutions were evaporated to dryness and the residue dissolved in a few drops of concentrated HNO_3 . Shortly before the samples were run, the concentrated HNO_3 was evaporated off and about 3 ml of 1M HNO_3 (accurately weighed) was added to each one.

Analyses were carried out on a PV8060 ICP OES machine at Royal Holloway and Bedford New College, Egham. The running specifications being: REE program 0.39 A, plasma setting 110 mm Hg, auxillary gas 5, carrier gas 90. Four standards were run before each batch of samples, and after every eight samples to monitor machine drift.

The REE were analysed in two batches, the second of which were found to have extremely low concentration of heavy REE, i.e. below chondritic concentrations. It is assumed that the low concentrations result from an error in the sample preparation or analysis, rather than a primary magmatic process. Investigation of the cause of the division is unfortunately beyond the scope of the present study. Only those samples analysed in the first batch were used in petrogenetic models of this study.

The 24 rare earth element analyses performed during this study are given in Table D.

Table D

Rare earth element analyses

	JHS37	JHS47	JHS54	JHS66	JHS73	JHS82	JHS89	JHS106	JHS129	JHS146
La	15.578	2.904	107.490	5.767	10.596	12.765	6.418	4.521	12.867	10.660
Ce	35.970	7.795	195.884	16.800	24.914	30.074	16.821	11.603	32.586	27.869
Pr	4.900	1.253	25.394	2.407	3.422	3.959	2.202	1.763	4.783	3.750
Nd	24.216	8.253	102.254	11.660	17.325	16.984	10.292	10.247	25.314	16.567
Sm	5.183	2.873	15.122	3.197	3.966	3.743	2.457	2.758	5.832	3.994
Eu	1.714	1.207	3.989	1.103	1.432	1.158	0.819	1.055	1.930	1.284
Gd	4.872	4.341	10.195	3.059	4.253	3.051	2.258	3.270	5.552	3.699
Dy	4.107	5.273	7.869	1.592	4.195	1.655	1.549	3.210	4.363	2.055
Ho	0.694	0.993	1.448	0.213	0.759	0.238	0.221	0.558	0.727	0.283
Er	1.699	2.659	4.066	0.439	2.019	0.519	0.542	1.401	1.734	0.565
Yb	1.260	2.277	3.465	0.176	1.690	0.249	0.310	1.115	1.287	0.218
Lu	0.198	0.382	0.616	0.025	0.286	0.032	0.044	0.181	0.196	-0.013

	JHS148	JHS158	JHS164	JHS184	JHS201	JHS202	JHS204	JHS210	JHS211	JHS213
La	14.067	7.166	6.535	7.658	8.870	1.746	10.756	7.143	12.496	2.878
Ce	34.827	21.104	17.808	20.050	21.424	5.557	30.259	19.345	27.689	7.736
Pr	4.780	3.161	2.614	3.133	2.975	1.016	4.255	2.723	3.749	1.241
Nd	23.491	14.724	12.417	17.404	15.010	5.081	19.739	12.351	18.743	8.096
Sm	5.108	3.975	3.366	4.706	3.575	1.969	4.917	3.363	4.160	2.735
Eu	1.680	1.335	1.176	1.754	1.255	0.841	1.560	1.146	1.434	1.151
Gd	4.753	3.661	3.382	5.500	3.875	3.032	3.853	3.333	4.260	4.120
Dy	3.920	2.081	1.912	5.416	3.807	2.604	1.371	1.518	4.033	5.091
Ho	0.669	0.285	0.261	0.989	0.682	0.460	0.154	0.179	0.724	0.971
Er	1.680	0.618	0.523	2.687	1.801	1.270	0.260	0.327	1.917	2.645
Yb	1.284	0.275	0.180	2.297	1.501	0.826	0.071	0.074	1.590	2.303
Lu	0.205	0.039	0.033	0.390	0.246	0.127	0.012	0.015	0.256	0.396

	JHS216	JHS223	JHS230	JHS248
La	4.146	11.567	7.648	6.363
Ce	13.512	29.215	21.925	17.054
Pr	2.134	4.152	3.200	2.367
Nd	10.441	21.355	14.787	10.309
Sm	3.163	4.849	4.066	2.685
Eu	1.167	1.705	1.364	0.891
Gd	3.577	4.894	3.875	2.354
Dy	2.579	4.493	1.861	0.955
Ho	0.384	0.786	0.229	0.115
Er	0.875	2.047	0.421	0.229
Yb	0.430	1.661	0.127	0.051
Lu	0.061	0.267	0.013	0.013

APPENDIX E

Sr ISOTOPE ANALYSES AND ANALYTICAL TECHNIQUES

Sr isotope analysis was performed on 36 samples in a VG Aldermaston Micromass 30 mass spectrometer. The Sr was extracted from the samples by dissolution of 0.2 g of rock powder in 10 ml of HF and a few drops of HNO₃; this solution was evaporated to dryness. 8 ml of 6M HCl was added to the dry material and the mixture was evaporated to incipient crystallinity. 4 ml of 2.5M HCl was added to the crystals, this solution was then centrifuged at 2000 rpm for 10 minutes to remove any solid residue which may have been present. The centrifuged solution was run through columns containing Dowex X8 resin. 1 ml of solution was washed into the resin using two 1 ml 2.5M HCl washes, and then 35 ml of 2.5M HCl was passed through the column and discarded. A further 11 ml was passed through the columns and collected. This solution was evaporated to a small drop to which a few drops of aqua regia (75% HCL + 25% HNO₃) were added to remove organic carbon. The solution was then evaporated to dryness, leaving a small speck of SrCl₂.

Having extracted the Sr from a sample it was transferred to a filament by the following procedure. A drop of 0.2M H₃PO₄ was placed on the filament. The speck of SrCl₂ was dissolved in a drop of quartz-distilled water and placed on the filament on top of the H₃PO₄. The filament was heated gently to dry it, then briefly degassed at a dull red heat.

The mass spectrometer analysed each sample in blocks of twelve readings, and a cumulative standard error was calculated. Each sample was run for at least five blocks or until the standard error was down to 2.5×10^{-5} . The system was controlled by in-house software on an Amstrad PC-1640 HD20. The results were corrected to the Eimer and Amend international standard (0.70800), for which the reproducibility figure for the mass spectrometer was 0.70820.

The (⁸⁷Sr/⁸⁶Sr)_{initial} ratio at 60 Ma was derived from the machine ratio (present day ⁸⁷Sr/⁸⁶Sr) using the following calculation. The Rb and Sr content used were those from the XRF analysis.

$$\frac{Sr^{87}}{Sr^{86}}_{initial} = \frac{Sr^{87}}{Sr^{86}}_{present} - \frac{Rb^{87}}{Sr^{86}} (e^{\lambda t} - 1)$$

where $\lambda = 1.42 \times 10^{-11} \text{ yr}^{-1}$
 $t = 60 \times 10^6 \text{ yr}$

Steiger and Jäger (1977)

where Ab(x) is the isotopic abundance of x, and Wx is the atomic mass of natural x.

$$\frac{Rb^{87}}{Sr^{86}} = \frac{Rb}{Sr} \times \frac{Ab(Rb^{87}) \times W_{Sr}}{Ab(Sr^{86}) \times W_{Rb}}$$

Now, $Ab(^{87}Rb) = 0.278346$

$W_{Rb} = 85.46776 \text{ g mole}^{-1}$

Catanzaro et al. (1969)

and it is necessary to determine:

$Ab(^{86}Sr)$ = isotopic abundance of ^{86}Sr in the sample

W_{Sr} = atomic mass of Sr in the sample.

To calculate $Ab(^{86}Sr)$:

		<i>abundances</i>	
$^{84}Sr/^{88}Sr$	$= 0.006756$	$Ab(^{84}Sr)$	$= 1/b \times 0.006756$
$^{86}Sr/^{88}Sr$	$= 0.119400$	$Ab(^{86}Sr)$	$= 1/b \times 0.119400$
$^{88}Sr/^{88}Sr$	$= 1.000000$	$Ab(^{88}Sr)$	$= 1/b \times 1.000000$
$^{87}Sr/^{88}Sr$	$= (^{87}Sr/^{86}Sr) \times (^{86}Sr/^{88}Sr) = a$	$Ab(^{87}Sr)$	$= a/b$

$$\text{sum} = b$$

$$\text{sum} = 1.0000$$

and to calculate W_{Sr} :

$$\begin{aligned} & \text{atomic weight} \\ & \text{of isotope} \\ & Ab(^{84}Sr) \times 83.9134 + \\ & Ab(^{86}Sr) \times 85.9092 + \\ & Ab(^{88}Sr) \times 87.9056 + \\ & Ab(^{87}Sr) \times 86.9088 = W_{Sr} \end{aligned}$$

Table E presents the measured and calculated initial $^{87}Sr/^{86}Sr$ ratios for the 36 samples analysed.

Table E

Sr isotope analyses

	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{present}}$	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}}$
JHS1	0.70391	0.70385
JHS31	0.70351	0.70347
JHS33	0.70341	0.70335
JHS35	0.70392	0.70384
JHS37	0.70421	0.70416
JHS39	0.70365	0.70356
JHS47	0.70327	0.70312
JHS54	0.70558	0.70492
JHS66	0.70537	0.70531
JHS73	0.70492	0.70483
JHS82	0.70391	0.70384
JHS89	0.70423	0.70416
JHS106	0.70377	0.70375
JHS129	0.70407	0.70402
JHS146	0.70411	0.70404
JHS148	0.70353	0.70347
JHS158	0.70348	0.70342
JHS164	0.70362	0.70357
JHS184	0.70360	0.70355
JHS201	0.70453	0.70440
JHS202	0.70312	0.70300
JHS204	0.70369	0.70364
JHS210	0.70377	0.70368
JHS211	0.70312	0.70307
JHS213	0.70336	0.70325
JHS216	0.70314	0.70309
JHS223	0.70363	0.70357
JHS230	0.70390	0.70379
JHS242	0.70403	0.70398
JHS248	0.70346	0.70340

APPENDIX F

Nd ISOTOPE ANALYSES AND ANALYTICAL TECHNIQUE

Nd isotope analysis was performed on 17 samples at the Open University, Milton Keynes.

The laboratory environment at the Open University, where the Nd isotope chemical preparation and analysis were performed, had a small positive pressure generated by an air circulation unit equipped with particle filters. All reagents were of Analar grade but their purity was improved as follows: HCl and HNO₃ were double-distilled using quartz stills and then further purified in sub-boiling teflon stills (TD); HF and HBr were cleaned up by just using the teflon two-bottle stills. A MilliporeTM reverse osmosis system was used to supply (RO) water.

All sample digestions and subsequent evaporations were performed in teflon beakers (Sr and Nd) or teflon SavalexTM screw-top bombs (Pb) within laminar-flow "fume"cupboards. Evaporations were carried out within a teflon evaporation hood with air circulation under a thermal lamp. The routine for cleaning the teflon beakers was as follows:(i) thorough rinsing with RO H₂O until visibly clean; (ii) add 5 ml 1.5M HNO₃, leave standing overnight; (iii) soak in hot (80°C) concentrated HNO₃ for at least 24 hours; (iv) soak in RO H₂O for 24 hours; (v) add 10-15 ml 6M HCl, heat under lamps for 15 mins. After each stage of the cleaning procedure, the beaker was rinsed with RO H₂O.

Before loading samples for the mass spectrometer, filaments had to be made and outgassed. Filaments were first cleaned, boiled in RO H₂O and then dried in a vacuum oven. The filaments were prepared by welding a strip of Ta or Re ribbon across pins mounted in the filament housing, and these were then outgassed, in batches of eight, for 5 mins at 4.5A in a vacuum of $< 2 \times 10^{-5}$ torr.

100-150 mg of rock powder was weighed into a teflon beaker. About 2 ml 15M TD HNO₃ followed by 8 ml 40% TD HF were added and the sample was left to digest overnight, prior to evaporating to dryness. A further 2 ml 15M TD HNO₃ was added and evaporated, followed by the addition of 2 ml 6M TD HCl, checking to ensure complete dissolution before evaporating. The sample was then redissolved in 2 ml 1.5M HCl and centrifuged to remove any residue. 1 ml of this solution was loaded onto a preconditioned cation exchange column containing 10 ml Bio-Rad AG 50 Wx8, 200-400 mesh resin. The sample was washed in with 2 x 1 ml 2.5M HCl and then eluted with 43 ml 2.5M HCl. 10 ml 2.5M HCl was then washed through the column. Nd was obtained by further washing with 1 ml RO H₂O and eluting 21 ml 3M HNO₃. An additional 20 ml 3M HNO₃ was then collected and this contained the Nd

along with the other MREE and Ba. After evaporating to dryness, the extract was dissolved in 1 ml 0.25M HCl and left standing overnight in a covered beaker. This was then loaded onto a pre-conditioned ion-exchange reverse chromatatography column which was prepared by mixing 1 g of teflon powder (Votalef 300LD PL micro) with 100 mg HD-EHP {Di(2-ethylhexyl)orthophosphoric acid}. The sample was washed in with 2 x ml 0.25M HCl and then eluted with a further 8 ml 0.25M HCl. Nd was then collected with 4 ml 0.25M HCl in a clean teflon beaker and evaporated to dryness, ready for loading.

Nd was loaded in a filtered loading bay. Nd was dissolved in a drop of TD H₂O and loaded onto a "double" Ta filament on which a small nick had been made in order to concentrate the Nd in the centre of the filament.

The sample was gently dried out, using a current of 1 A.

Nd isotopic ratios were analysed on a Finnigan MAT261 multi-collector mass spectrometer. Sample runs were controlled automatically using Finnigan software on a HP 9836 computer. The in-house software used was developed by D.W. Wright and P.W.C. van Calsteren.

The (¹⁴³Nd/¹⁴⁴Nd)_{initial} ratio at 60 Ma was derived from the machine ratio (present day ¹⁴³Nd/¹⁴⁴Nd) using the following calculation. The Sm and Nd contents used were those from the ICP analysis.

$$\frac{Nd^{143}}{Nd^{144}}_{initial} = \frac{Nd^{143}}{Nd^{144}}_{present} - \frac{Sm^{147} e^{-\lambda t}}{Nd^{144}}$$

where $\lambda = 0.654 \times 10^{-11} \text{ yr}^{-1}$

it was assumed that the ICP measured Sm/Nd ratio approximated to ¹⁴⁷Sm/¹⁴⁴Nd.

Table F presents the measured and calculated initial ¹⁴³Nd/¹⁴⁴Nd ratios for the 17 samples analysed.

Table F

	$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{present}}$	$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{initial}}$
JHS37	0.512482	0.512398
JHS47	0.513113	0.512976
JHS54	0.511208	0.511149
JHS73	0.512196	0.512106
JHS89	0.512218	0.512124
JHS106	0.512821	0.512715
JHS129	0.512765	0.512675
JHS148	0.512852	0.512767
JHS164	0.512676	0.512569
JHS184	0.513051	0.512945
JHS201	0.512222	0.512128
JHS210	0.512683	0.512576
JHS211	0.513166	0.513079
JHS213	0.513114	0.512981
JHS216	0.513131	0.513012
JHS223	0.512661	0.512572
JHS248	0.512648	0.512545