

The Petrology of the Buckland Volcanic Province, Central Queensland, Australia

Thesis submitted for the degree of Doctor of Philosophy

by

Andrew Skae



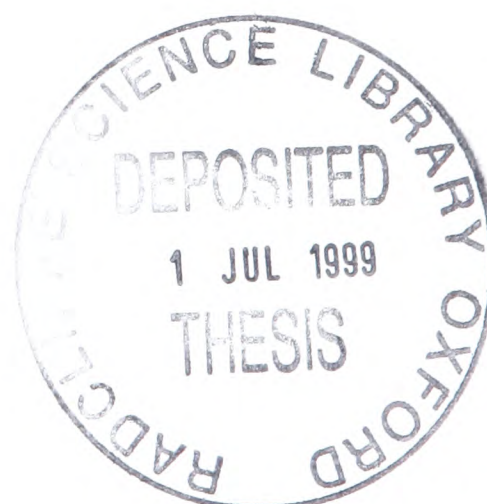
St. Edmund Hall

and

Department of Earth Sciences

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The Lord is my light.

Psalm 27 v.1

Dedicated to Keith Cox (1933-1998)

A smashing friend and supervisor

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The Living God.

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CENTRAL QUEENSLAND, AUSTRALIA

Andrew Skae

St. Edmund Hall and Department of Earth Sciences

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ABSTRACT

Cainozoic volcanism occurs in eastern Australia as a broad zone of discontinuous, small-volume, dominantly basaltic provinces. Central volcano provinces show a strong correlation between age and latitude, younging towards the south, hence the interpretation that they are related to a mantle hotspot. Previous work has interpreted the composition of lavas from these provinces using a four-component model involving material from a mantle plume, the shallow asthenosphere, continental lithosphere together with AFC processes in the lower crust.

The purpose of this thesis is to describe the petrology of the Buckland province, a relatively poorly-studied central volcano in central Queensland, and to constrain models for the petrogenesis of its lavas, assessing whether this is consistent with the four-component model outlined above. Mafic lava compositions show a wide range of silica saturation and degree of evolution. Highly undersaturated basanites are interpreted as being dominantly from the shallow asthenosphere, with the five most magnesian samples apparently containing a HIMU-like component. Comparison with experimental data demonstrates that the geochemistry of the most primitive basalts is consistent with decompressional melting within a plume whose T_P lies in the range 1410-1500°C and which has an above-average Fe/Mg. Evolved mafic lavas show geochemical and petrographic evidence for polybaric assimilation-fractional crystallisation in the crust. Megacrysts of plagioclase, orthopyroxene and clinopyroxene represent the extract assemblage from the lower crust (probably at pressures >10kbar, owing to the absence of olivine), while low-pressure crystallisation of olivine also took place. Both the elevation of the province (up to 1100m above sea level) and occurrence of high-pressure megacrysts are consistent with previous models of underplating at the crust-mantle boundary. Lavas from the neighbouring province of Springsure show greater evidence of AFC in the upper crust, while those from the northern part of the Mitchell province contain megacrysts of olivine which is suggestive of a slightly lower crystallisation pressure in the lower crust.

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EXTENDED ABSTRACT

Cainozoic igneous activity in eastern Australia is expressed as a broad zone of dominantly basaltic volcanic provinces which parallel the coastline. Individual provinces are small in volume and fall into two categories, namely central volcanoes which define a strong age-latitude correlation and lava fields which do not. The former are thus interpreted as the product of a mantle plume over which the Indo-Australian plate passed between ~35 and 1Ma ago. Geochemical and isotopic compositions of primitive basalts from these provinces overlap with OIB, consistent with a plume origin, while a wide range of evolved products, including trachybasalts and rhyolites, demonstrate the importance of AFC processes in the crust. Lava field provinces contain a greater proportion of primitive mafic compositions, whose geochemical and isotopic characteristics indicate that they are also derived from the convecting mantle. The absence of any systematic time-space relationship in these provinces suggests they are unrelated to the plume, but originate in the shallow asthenosphere. Some lavas show evidence of interaction with subduction-related lithosphere, a consequence of the subduction-accretion events that characterised the Palaeozoic-Mesozoic history of eastern Australia.

This study seeks to examine in detail the sequence of lavas and plugs which constitute the little-studied Buckland province in central Queensland. Previous work has indicated that its age and location are consistent with being related to the plume which, combined with the presence of a wide range of primitive and evolved lava compositions, indicates that it is a typical central volcano province. XRF data, microprobe analyses and Sr-Nd isotopes are used to characterise the lavas and to constrain the processes that generated them.

A thorough review of work carried out on Cainozoic volcanism is presented in the first chapter, covering a wide range of petrological and geophysical topics. These include seismic profiles which provide evidence for an layered crust-mantle transition zone; evidence from xenoliths demonstrates that this is the result of basaltic melts cooling and fractionating where they pond at the Moho. Such underplating accounts for the elevated topography of many of the volcanic provinces. Megacrysts, derived from the upper mantle and lower crust, are also found within the lavas and provide further evidence of high-pressure fractional crystallisation processes. Examples from central-southeastern

Queensland are lower crustal in origin, and include plagioclase. Lavas also show evidence of fractional crystallisation $\pm$ assimilation processes in the upper crust which generate further chemical diversity in the lavas. Models which interpret the petrogenesis of the lavas throughout eastern Australia are described which involve the modification of melts from a mantle plume and/or the shallow asthenosphere by interaction with the lithospheric mantle and the crust.

The new XRF data for the Buckland province are presented in Chapter 2. They show that the lavas range widely in composition, from primitive basanites (14% MgO and 41% SiO₂) to evolved trachybasalts and basaltic trachyandesites (3% MgO and 52% SiO₂). Most lavas contain between 4-7% MgO and are olivine tholeiites or hypersthene-normative trachybasalts. They are sub-divided for the purpose of this study on the basis of major element geochemistry. Mafic lavas containing <9% MgO behave in a coherent fashion, while more primitive basalts and basanites (26 in number) show considerable scatter. The five most mafic basanites ('12+ group' since their MgO content >12%) are silica- and iron-poor compared to the other basanites, and form a separate group. Sr-Nd data are also presented for the most mafic lavas. Comparison is made with lavas from elsewhere in eastern Australia. The wide range of compositions, including a continuous spread from nepheline- to quartz-normative types, is typical of central volcanoes throughout eastern Australia and of provinces in central-southeastern Queensland. Isotopic data for the 12+ group overlap with MORB and lavas from Tasmania, other basanites overlap with the field of lava field basalts from Queensland, while most basalts overlap with the proposed 'plume' composition. One outlying basalt sample overlaps with lavas from northern Queensland that have interacted with subduction-related lithosphere. The primitive basalts and basanites are similar in composition to plume and shallow lithosphere-derived lavas from other continental rift settings, comparison being made here with Cainozoic volcanics from the western US, western Europe and eastern China. Succeeding chapters deal with the petrology and petrogenesis of the three different groups.

The primitive basalts and basanites containing 9-12% MgO show evidence of minor fractional crystallisation (and possible assimilation in some of the basalts). Xenoliths of spinel lherzolite are found in the basanites which argue against significant residence of the lavas in the crust. The lavas are not primary, i.e. they do not have mg-numbers high enough to have been in equilibrium with mantle peridotite. It is argued that the discrepancy (lavas have mg-numbers between 62 and 67, while primary magmas should have values >68) is primarily due to the effect of fractional crystallisation of olivine. Lava compositions were recalculated to compensate for the extraction of olivine until they were in equilibrium with olivine of mantle composition (Fo_{87.5}) in order to permit comparison with experimentally-derived lherzolite melt data. Basalt compositions overlap with melts from nodule PHN-1611 (average olivine Fo_{87.5}: Kushiro, 1996), and were found to be consistent with decompressional melting of similar material (but with a higher Fe/Mg ratio) with a T_p between 1410 and 1500°C and with segregation taking place between 20 and 30 kbar. Basanite compositions do not overlap with any melts from anhydrous lherzolite within the range of experimental conditions, but appear to require the

presence of volatiles (>0.5 wt.% and $X^{\text{CO}_2} \geq 0.5$) to reproduce their low silica concentrations. Absence of sufficient data means that basanite generation cannot be constrained further.

Evolved mafic lavas are aphyric, olivine-phyric or megacryst-bearing. The latter group contains large ($<15\text{mm}$) crystals of plagioclase, orthopyroxene and clinopyroxene. These all show evidence of disequilibrium with their host lava, e.g. internal melting, evidence of resorption and mantles of intergrown olivine and clinopyroxene around orthopyroxene megacrysts. Compositionally they are identical to lower crustal examples from elsewhere in Queensland. Plagioclase crystals are the largest and most numerous, followed by orthopyroxene. The three petrographically-defined groups overlap geochemically and are distributed throughout the province in both space and time, thus it is argued that they are cogenetic. Geochemical trends of increasing TiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, and incompatible elements with falling MgO , together with decreasing CaO and variable SiO_2 are modelled by AFC using the three observed megacryst phases together with a range of contaminants. Two of these are based on lower crustal xenolith compositions from northern Queensland and a third from shale in southeastern Queensland which could plausibly exist (albeit with a different mineralogy) in the lower crust. Lavas from Springsure contain a higher proportion of phenocrysts than megacrysts, indicating the greater importance of low-pressure fractional crystallisation in this province than in Buckland. Their geochemistry is modelled with low pressure AFC of olivine $\pm$ plagioclase + clinopyroxene, and high-pressure fractional crystallisation of plagioclase, clinopyroxene and orthopyroxene. Samples from the northern part of the Mitchell province, just to the south of Buckland, contain sparse olivine and plagioclase megacrysts. The occurrence of olivine in the megacryst assemblage suggests that fractional crystallisation of these lavas took place at a lower pressure (perhaps in the middle-crust) than those from Buckland.

The five most mafic basanites appear to have an unusual isotopic composition which is shared only by Tasmanian lavas in eastern Australia. Their highly depleted Sr-Nd signature, radiogenic Pb-isotopes ($^{206}\text{Pb}/^{204}\text{Pb} \sim 19.2$: from one previously-published analysis only) together with their spidergram patterns suggest the involvement of HIMU-type material in their source. Interaction between depleted asthenosphere (i.e. MORB-source) and a HIMU-plume has been inferred for Tasmanian lavas, but geographical considerations mean that a source in the shallow asthenosphere is favoured for Buckland examples. A proposed model for the petrogenesis of basanites with a similar composition in the Massif Central involves mixing between depleted mantle and HIMU material residing in the asthenosphere after subduction during the Palaeozoic. Such a model is appealing for the Buckland examples owing to the episodes of subduction that took place at that time in eastern Australia.

A study of fifteen peridotite xenoliths retrieved from the basanites shows that all but one are fertile lherzolites whose compositions similar to other examples worldwide. The mineral chemistry of a single harzburgite (olivine: Fo_{91-92} ; spinel: $100\text{Cr}/(\text{Cr}+\text{Al})=60$) indicates that it has undergone partial melting. Variation with lava chemistry is also considered in time and space. Basanites are confined to the area west of the main Buckland shield and at the base of one of the main sequences, suggesting that

they mostly pre-date the main phase of plume-related volcanism. Consideration of extensively-sampled sequences suggests that there is no significant variation of lava geochemistry with time, although younger lavas tend to be slightly more SiO₂- and MgO-rich than older ones.

In summary, the lavas of the Buckland province are consistent with the petrogenetic models advanced by previous workers for volcanism in eastern Australia. They are dominated by plume-derived material which has been subsequently modified by polybaric fractional crystallisation $\pm$ crustal assimilation, giving rise to substantial crustal underplating. Rare basanites are thought to be derived from the shallow asthenosphere. Two compositions for this component are identified, a 'normal' composition that is similar to that observed in lava field provinces throughout eastern Australia, and a rare type which contains HIMU-type material.

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Chapter 1: Introduction and previous work

The purpose of this thesis is to describe the petrology of basaltic lavas from the Buckland province, a hitherto poorly-studied Cainozoic volcanic province in eastern Australia, and to constrain their petrogenesis.

This introductory chapter is divided into three sections. The first provides extensive background to the Cainozoic volcanism of eastern Australia, summarising a wide range of published observations and previous work about these continental volcanic provinces. It includes information about magma source components, the nature of the continental lithosphere, and the style of magma fractionation processes which have been recognised, together with models which have been advanced to explain these observations. The second section describes previous work carried out on the Buckland province, as well as the neighbouring provinces of Springsure and Mitchell with which comparison will be made in this study. The third section discusses the relevance and application of this previous work to the Buckland province and describes the aims of the project in greater detail.

1.1 INTRODUCTION TO CAINOZOIC VOLCANISM IN EASTERN AUSTRALIA

1.1.1 Province distribution and classification

Cainozoic intraplate volcanism extends for 4000 km as a broad zone of discontinuous, eroded volcanic provinces parallel to the eastern seaboard of Australia (Figure 1.1) which have been extruded through a wide variety of Proterozoic-Mesozoic lithospheric blocks. The volcanic centres tend to be associated with elevated regions, and commonly lie on the principal watershed of eastern Australia, the Great Dividing Range. Around fifty provinces have been recognised whose ages range from 60 Ma to 5000 a BP., whose total volume is estimated by Wellman and McDougall (1974) to be slightly greater than 20,000 km³. The volumes are relatively small compared to estimates for the Deccan Traps (>1,000,000 km³) and Mauna Loa volcano, Hawaii (40,000 km³) (data compiled by Johnson, 1989b). The provinces have been divided into two main types by Wellman and McDougall (1974), with further definition by more recent workers:

Central volcanoes which are dominated by sequences of relatively evolved, isotopically variable basalts and trachybasalts with small volumes of trachyte and rhyolite. Some form extensive, now eroded, shield structures.

Lava fields which are generally formed of more primitive, silica-undersaturated basic lavas, showing only minor evidence of associated differentiated products. They occur usually as small breccia pipes, diatremes and maars, and predominantly as extensive lava flows.

They can also be distinguished on a graph of age vs. latitude. Figure 1.2 (after Duncan and McDougall, 1989b) shows that the central volcano provinces fall on a straight line corresponding to a velocity of 65 ± 3 mm/yr. This has been interpreted as movement of the Indo-Australian plate, at that rate, over a fixed mantle hotspot (Vogt and Conolly, 1971). By contrast, the lava field provinces show no age-latitude correlation, but form two main groups. The first includes provinces north of 25°S , which range in age from 20-60 Ma and appear to be truncated by central volcano activity. The second includes those located south of 25°S which are younger than 5 Ma.

1.1.2 Pre-Tertiary geology

The Australian continent is dominated by Pre-Cambrian cratons whose eastern margin is marked by a dashed line in Figure 1.1. The geology of eastern Australia, by contrast, is dominated by Phanerozoic rocks.

Late-Proterozoic and early-Palaeozoic elements are known from isolated inliers of metavolcanic and metasedimentary rocks which range up to granulite facies, and are extensively intruded by S-type granites. The basement geology of eastern Australia is, however, dominated by intermittently outcropping Palaeozoic orogenic belts (see Figure 1.1). The Thompson (Queensland), Lachlan (Victoria and New South Wales (NSW)) and New England (Queensland and NSW) fold belts all comprise a mixture of metamorphosed volcanics, sediments and granites. The nature of the New England belt has led to its interpretation as the product of subduction, collision and back-arc development during continental accretion episodes in late Palaeozoic to early Mesozoic times (Veevers, 1984; Wyborn, 1989). The Thompson fold belt is much more poorly exposed, but the nature of the sedimentary record (marine in the Ordovician and shelf in the Devonian), volcanoclastic deposits and lavas suggests that this belt underwent a similar subduction-accretion history (Wyborn, 1989). The north-south trending Sydney-Bowen basin consists mostly of Permo-Triassic sediments which obscure the contact between the main fold belts, while sequences of Carboniferous-Cretaceous rocks form the sedimentary cover in other areas. Note from Figure 1.1 that several volcanic provinces lie at the boundaries between the different structural blocks.

Section 1.2.2 enlarges on these aspects with particular reference to the area of study.

1.1.3 Geophysical background

Wellman (1989) reviews the geophysical data which have been used to retrieve information about the eastern Australian lithosphere:

Seismic-refraction profiles suggest that the depth of the crust-mantle boundary (at which the P-wave velocity exceeds 8 km/s) varies from 35-55 km in eastern Australia, and is deeper below the highlands than the basins. An example of such a profile, from the Buckland province, is provided in Figure 1.3. Horizontal reflectors, caused by the interlayering of material of different seismic

velocities, are visible at three levels, at ~13 km, ~30 km and ~35 km. The deepest of these is interpreted as corresponding to the Moho discontinuity (Mathur, 1983). The petrological interpretation of this interlayering is discussed below (section 1.1.7).

Gravity and magnetic anomalies over several central volcanoes in eastern Australia suggest the presence of substantial intrusive complexes similar to those at Skye and Rum in the British Tertiary Volcanic Province (Wellman, 1986). The Tweed volcano, for example, has a maximum residual gravity anomaly of 40 mgal (compilation of Wellman, 1989), compared to 53 and 66 mgal in Skye and Rum respectively (compilation of Emeleus, 1991). In the study area, Mollan (1972) reports a positive Bouguer anomaly of 8 milligals just north of Springsure which he attributes to a buried intrusion. This is quite small compared to Skye and Rum, but comparable to Arran which has a 15 mgal anomaly over background (Emeleus, 1991).

There is a positive free-air anomaly over the highlands which, combined with other data, indicates that the topographic high is compensated at 40-60 km depth, i.e. the base of the seismically defined crust (Wellman, 1979). The lithosphere is relatively weak: T_e (elastic thickness) is 15-35 km for the eastern highlands, and is lowest in the southeast where the most recent vulcanism occurred (Zuber *et al.*, 1989). These workers note that the low T_e is compatible with crustal underplating, igneous intrusion and thermal perturbation events in eastern Australia.

Heat flow measurements for eastern Australia are provided by Cull (1982) and Cull and Conley (1983). These average 50-80 mW/m² (global average ~60 mW/m²), but reach 90 mW/m² in areas of Quaternary activity in northern Queensland and western Victoria.

Variation of shear wave velocity (V_s) with depth, based on Rayleigh wave data, is presented by Goncz and Cleary (1976). In eastern Australia (i.e. west of the cratonic interior) there is a decrease in V_s from ~4.5 km/s to ~4 km/s at a depth of 90 km (Figure 1.4). This could be interpreted as the depth of the top of the asthenosphere (e.g. by the definition of Isacks *et al.*, 1968). Similar profiles are observed in other 'tectonic' continental areas around the world (e.g. Dziewonski, 1971).

A cross-section of the shear wave velocity structure beneath Australia and the Tasman Sea, determined using surface wave overtone phase velocities, is provided in Figure 1.5 (after van Heijst, 1997), and is consistent with the observations outlined above. Relatively high velocities are observed beneath western and central Australia down to 200 km depth, compatible with the presence of a cold, dry Pre-Cambrian craton. By contrast, east Australian lithosphere has a slower velocity structure, probably since it is hotter and more hydrous and thus more attenuating than the craton.

1.1.4 Plate tectonic setting

Although the eastern Australian volcanics lie within the Indo-Australian plate, they have been influenced by late-Mesozoic-Recent extension and sea-floor spreading events. To the south, the Indo-Australian plate separated from the Antarctic plate 95 Ma ago. After a period of relatively slow movement, the plate has moved north during the last 44Ma at an average velocity of 60 mm/yr (actual

range ~50-72mm/yr: Duncan and McDougall, 1989a). At the same time (95 Ma), the Lord Howe Rise started to separate from Australia, producing the Tasman Sea; the main phase of spreading took place between 84 and 53 Ma (Weissel and Hayes, 1977). Further north the Coral Sea opened up between 63 and 53 Ma (Weissel and Watts, 1979). Figure 1.6 shows the current plate tectonic situation in the southwest Pacific region, and also shows the position of two seamount chains which lie off the coast of eastern Australian.

Lava field volcanism started 70 Ma ago, and the main phase of activity occurred between 55 and 30 Ma (Figure 1.2) and again after 5 Ma (Wellman and McDougall, 1974). Central volcanic activity took place between 34 Ma and the present day and this seems to coincide with the period of fast spreading between Australia and Antarctica (Duncan and McDougall, 1989a); by contrast there is no obvious correlation between plate boundary forces and timing of lava field volcanism.

1.1.5 Previous petrological work: lavas

Regional aspects

Ewart *et al.* (1988) and Ewart (1989a,b) give comprehensive summaries of the geochemical and isotopic characteristics of the Cainozoic lavas of eastern Australia, and models for their petrogenesis.

A wide variety of lava compositions has been extruded in eastern Australia, reflected in the compilation given in Table 1.1 where the rock names of Le Maitre (1989) are used. This variety is typical of continental intra-plate volcanism, as is the bimodal distribution of compositions with an intermediate 'gap' where lavas with silica contents between 55 and 65% are much rarer than mafic and silicic ones (e.g. Figure 1.22). Mafic compositions predominate in eastern Australia, and show geochemical continuity from nephelinites to quartz-tholeiites. Most intermediate-silicic compositions are silica-oversaturated trachytes and rhyolites; undersaturated types such as phonolites are rare.

Petrographically, most sampled mafic lavas are porphyritic. Olivine phenocrysts are the most abundant with less common plagioclase, augite and titanomagnetite. Groundmass minerals consist of plagioclase (zoning outward to anorthoclase/sanidine), augite, olivine, titanomagnetite and apatite. Subcalcic-augite and pigeonite occur in *qz*-tholeiite samples, as may orthopyroxene as phenocryst or groundmass phases. Ilmenite occurs in the groundmass of tholeiites and trachybasalts but rarely in more alkaline compositions, while groundmass nepheline is found in basanites and other strongly silica-undersaturated lavas. Amongst the silicic lavas, porphyritic varieties usually contain at least two Fe-endmember pyroxene/amphibole/ olivine phases (e.g. ferrohedenbergite, Fe-hastingsite, fayalite), one or more Fe-Ti oxides (ilmenite, titanomagnetite) and feldspar (anorthoclase, sanidine) $\pm$ quartz $\pm$ allanite. Groundmasses are dominated by feldspar and quartz.

Mafic samples show a wide range of silica saturation, from highly undersaturated leucitites to *qz*-tholeiites, and include alkali basalts and basanites with mg-numbers ($Mg^{2+}/(Mg^{2+}+Fe^{2+})$) high

enough to potentially be primary mantle melts. They are all enriched in incompatible elements with respect to MORB (Ewart *et al.*, 1988) which is typical of continental lavas: leucitites show the most enrichment and quartz-tholeiites the least. The primitive alkalic mafic lavas tend to have depleted Sr-Nd characteristics (i.e. low $^{87}\text{Sr}/^{86}\text{Sr}$ with high $^{143}\text{Nd}/^{144}\text{Nd}$), while more evolved samples exhibit more variable and 'evolved' Sr and Nd isotopic compositions. Regionally, lavas from Tasmania exhibit the most depleted isotopic compositions, overlapping with MORB; lavas from all other areas overlap with accepted OIB fields. Chemical variation in the primitive compositions appears to be due primarily to variation in source composition and degree of melting. Most are ascribed to some combination of OIB-like mantle plume $\pm$ shallow asthenosphere $\pm$ lithospheric mantle source. Tasmanian lavas are interpreted as asthenospheric and their isotopic signature (as well as that of certain undersaturated lavas from elsewhere, e.g. Rewan in the Buckland province) suggests the involvement of a 'St. Helena'-type HIMU source. The chemistry of certain lava field tholeiites suggests that they come from arc-modified lithosphere. Trace element and isotope modelling shows that most mafic compositions have undergone a degree of low-medium pressure assimilation-fractional crystallisation (AFC) processes, dominated by olivine $\pm$ augite $\pm$ plagioclase $\pm$ Fe-Ti oxide phenocrysts in the mafic lavas (Ewart *et al.*, 1988; Ewart, 1989a). This is supported by isotopic data: in central volcanoes, the geochemically evolved trachybasalts and tholeiites are more isotopically 'evolved' than primitive alkalic lavas, and exhibit wider variation. Megacrysts in numerous lavas (e.g. Ewart *et al.*, 1980: discussed in section 1.1.6) have been interpreted as accidental inclusions, or as high-pressure (from the lower crust or upper mantle) phenocrysts, thus indicating that fractional crystallisation in eastern Australia was polybaric.

Ewart (1989b) used the method and program of Ghiorso (1985) to estimate segregation pressures for different lava types from eastern Australia: quartz tholeiites 9-14 kbar; olivine tholeiites 14-16 kbar; alkali basalts 16-21 kbar; basanites 20-23 kbar; nephelinites 29-31 kbar. These are in broad agreement with other estimates (e.g. Green, 1989). Frey *et al.* (1978) estimated degrees of partial melting using major element and experimental data: olivine nephelinites/ basanites 5-7%; alkali basalts 11-15%; olivine tholeiites 20-25%. Ewart (1989b) used REE modelling to arrive at significantly lower estimates (as low as 0.5-2% for some undersaturated lavas). He noted, however, that the apparent discrepancy is consistent with models of trace element fractionation at low degrees of partial melting (e.g. McKenzie, 1985).

Silicic lavas show extreme patterns of trace element enrichment (e.g. Rb, Pb, Th) or depletion (e.g. Ba, Sr), and have 'evolved' Sr-Nd isotopic signatures (radiogenic Sr, unradiogenic Nd) compared to mafic compositions. Systematic increases in trace element depletion/enrichment in the whole rocks and minerals (e.g. increasing Fe/Mg up to iron end-member pyroxene and olivine) through the trachytes to the rhyolites suggest that fractional crystallisation processes are dominant in their petrogenesis. Modelling shows that they can be derived from mafic parental magmas, that crystallising assemblages are dominated by sanidine + plagioclase and that partition coefficients

change with ongoing fractionation. Crustal assimilation, usually combined with fractional crystallisation, appears to be commonly responsible for the enriched isotopic signatures of the silicic lavas. A small number of high-silica rhyolites from southeastern Queensland have a distinct chemistry and mineralogy which suggests that they were the result of localised crustal anatexis (e.g. Ewart, 1982).

Tasmanian and Victorian lavas

McDonough *et al.* (1985) studied samples ranging in composition from nephelinite to quartz tholeiite (and generally typical of east Australian mafic lavas) from Tasmania and the Newer Volcanics of Victoria, concentrating especially on the more primitive lavas (high Ni, Cr, mg-numbers). Examples from the two areas have similar incompatible element characteristics although those from Tasmania have generally more depleted Rb, Ba, Th, K and Nb. Isotopically, lavas from Tasmania have lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{143}\text{Nd}/^{144}\text{Nd}$ than those from Victoria. They note that, in common with many other Cainozoic intraplate basaltic provinces around the world (e.g. west Antarctica, Basin and Range, China), the isotopic compositions plot on the lower left side of the mantle array. The following conclusions are drawn:

1. Crustal contamination is insignificant in the primitive lavas on account of their geochemistry and the presence of lherzolite xenoliths which must have been conveyed rapidly from the mantle to the surface. Geochemically evolved mafic lavas (MgO contents down to 3.8%) have similar isotopic compositions to the primitive lavas, suggesting that they too are relatively uncontaminated.
2. Contamination by the lithospheric mantle is deemed to be minor, as the isotopic range of the lavas ($^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7026 to 0.7045; $^{143}\text{Nd}/^{144}\text{Nd}$ from 0.5127 to 0.5130) is much more restricted than the range shown by spinel lherzolites from Victoria which are interpreted as being lithosphere-derived ($^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7037 to 0.7085; $^{143}\text{Nd}/^{144}\text{Nd}$ from 0.5122 to 0.5132). Additionally, there is no evidence of melting within the xenoliths. Input of lithospheric mantle during magma generation is considered later.
3. Basalts in both areas show progressive decreases in incompatible element content with increasing silica saturation at approximately constant mg-number. Hence it appears that, in each area, varying degrees of partial melting of a single source could generate the whole range of compositions found there. The exact sources at the two areas are not thought to be the same, owing to differences in isotopic and incompatible element compositions.
4. The authors note that previous workers (e.g. Wellman and McDougall, 1974) have interpreted eastern Australian volcanism in terms of hotspot traces: either due to a deep-seated mantle plume or a shallower thermal perturbation. In order to constrain source components for the lavas which can explain their isotopic variation, a model for hotspot magmatism is considered, based on the Hawaiian model of Chen and Frey (1983, 1985). This involves source material from a mantle plume and the lithospheric mantle. An ascending mantle plume impinges on the base of the lithosphere and initiates

partial melting of it, the products of which mix with plume-derived melts ($\pm$ melts from the 'low velocity zone'). In Hawaii, the large-volume tholeiites have more enriched isotopic ratios than the alkalic lavas which overlap with MORB compositions. Since the tholeiites are the result of a higher degree of partial melting than the alkalic lavas the tholeiites are interpreted as being dominated by the plume component, while the alkalic lavas contain a component of melt from the MORB-composition oceanic lithosphere. Extrapolation to the continental environment is complicated by the presumed composition of the lithospheric mantle which is generally inferred to be more isotopically heterogeneous than the oceanic lithosphere. Plume compositions are assumed to be the same as those sampled in the ocean basins. The authors propose that lavas from the Newer Volcanics are the products of mixing between these two components, although a quantitative analysis is not possible owing to the heterogeneity of the lithospheric mantle. The model is illustrated in Figure 1.7.

NSW and Northern Queensland

O'Reilly and Zhang (1995) concentrated on primitive compositions from lava field provinces in NSW and northern Queensland. They noted that trace element patterns and isotope ratios suggest that an OIB - type source (similar to that which characterises the central volcano provinces) is a dominant component in the lavas. Some provinces show evidence of a significant contribution from other sources, generally residing in the sub-continental lithospheric mantle ('SCLM'), which can be related to the local tectonic environment. Northern Queensland lavas have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for given $^{143}\text{Nd}/^{144}\text{Nd}$ compared to the other provinces which, combined with evidence from trace element ratios, is interpreted as signifying input from subducted oceanic basalts and sediments. This is compatible with the situation of these lavas on the Hodgkinson-Broken River fold belt, which has been modelled in terms of late-Palaeozoic to Mesozoic subduction and accretion (e.g. Veevers, 1984). The Dubbo province (see Figure 1.1 for location) in NSW contains lavas with an enriched isotopic signature and elevated abundances of Ba, La & Nb compared to Sr and of light rare earth elements (LREE) compared to heavy rare earth elements (HREE). This is said to indicate input of melt from a metasomatised source, whose enriched isotopic signature has arisen following a long period of isolation - almost certainly in the SCLM. The province lies on an early-Palaeozoic tectonic block which is thought to have been unaffected by later orogenic processes, thus allowing isotopic isolation. Finally the authors cite the example of the Barrington province (NSW: see Figure 1.1) where OIB-like melts have been modified by interaction with apatite/amphibole-bearing metasomatised mantle, resulting in distinctive patterns of trace element depletion (Rb, K, Zr) and enrichment (Th, Nb, LREE). This province is situated on the Tamworth block, a late-Palaeozoic to Mesozoic fore-arc basin where such metasomatism could have taken place sufficiently recently to explain why isotope ratios for the lavas are not enriched like those at Dubbo.

1.1.6 Previous petrological work: xenoliths and megacrysts

“Eastern Australia contains the largest concentration of mantle xenoliths in the world” according to O’Reilly and Griffin (1987). Added to this is a wide range of crustal xenoliths as well as a diverse megacryst suite. The nature of all of these will be briefly discussed here.

Xenoliths are found in primitive (mg-number > 65, high Ni & Cr) nephelinites, basanites, alkali basalts and trachybasalts and rarely in olivine tholeiites, basaltic trachyandesites and trachytes. They are found throughout eastern Australia, but are most common in lava field provinces; they occur in lava flows, dykes, cinder cones and maars. Nodules retrieved from lava flows are generally 2-5cm in size, while examples from cinder cones and maars are generally 5-10 cm.

Mantle xenoliths

These are described in numerous papers and summarised in works such as O’Reilly and Griffin (1987), Griffin *et al.* (1987) and O’Reilly *et al.* (1989) which form the basis of this section. They have classified into three main groups, based on the classifications of Wilshire and Shervais (1975) and Frey and Prinz (1978).

Cr-diopside suite (‘Type I’ of Frey and Prinz, 1978). These make up 80-100% of the xenolith assemblage at any locality (Wass and Irving, 1976), and consist predominantly of spinel lherzolites which are usually anhydrous, but can be volatile-bearing (e.g. O’Reilly, 1987). Anhydrous lherzolites are composed of olivine (20-90%), clinopyroxene (10-30%), orthopyroxene (10-40%) and spinel ($\leq 5\%$). Garnet is rare. Hydrous examples consist of the four phases listed above $\pm$ amphibole (pargasite or kaersutite), mica (biotite or phlogopite), apatite and calcite. Volatile-bearing phases may be interstitial and rare ($< 1\%$ of the mode), or predominant ($> 90\%$). Distribution of the two xenolith types (anhydrous/hydrous) varies between provinces and between lava flows. Volatile-bearing examples have only been described from western Victoria and scattered provinces in NSW and northern Queensland.

Texturally, most Cr-diopside suite xenoliths from eastern Australia have a relatively undeformed ‘coarse’ microstructure. Others show evidence of recrystallisation (‘mosaic’ texture) and/or deformation (mildly deformed ‘porphyroclastic’ and highly sheared ‘mylonitic’ textures). While most xenoliths are geochemically and mineralogically ‘fertile’, others show evidence of having undergone partial melting and melt extraction resulting in high mg-number (> 91), high Cr/Cr+Al of spinel and decrease in modal clinopyroxene. Volatile-bearing xenoliths are generally less magnesian (mg-number of 87-88) than anhydrous examples, and are enriched in incompatible elements and LREE. The east Australian Cr-diopside suite xenoliths are similar to spinel lherzolites from around the world and are interpreted as fragments of lithospheric mantle wall-rock that is unmetasomatised (‘anhydrous’ types) or metasomatised (‘hydrous’ types).

Al-Augite suite (‘Type II’ of Frey and Prinz, 1978) Al-augite suite rocks comprise 0-20% of the xenolith assemblage at any locality and are found throughout the length of eastern Australia.

Wehrlite-types are the most common (90% of retrieved Al-augite suite xenoliths) and consist of clinopyroxene and olivine in variable proportions, $\pm$ spinel, feldspar, ilmenite, amphibole (primary or secondary), mica and apatite. They have igneous microstructures including cumulate and gabbroic textures, and are interpreted as either cumulates or as 'frozen' basaltic magma. Metapyroxenites are essentially pyroxene-rich examples of the wehrlite type which have undergone cooling from igneous temperatures to the ambient geotherm, resulting in re-equilibration and the development of metamorphic textures (Griffin *et al.*, 1984). A third type is represented by the apatite/amphibole series which consist of varying modal proportions of amphibole, apatite, clinopyroxene, mica, ilmenite, magnetite, carbonate and sulphides (including chalcopyrite, pyrrhotite, pyrite and pentlandite). They are interpreted (O'Reilly, 1987) as the crystallisation products of a magma enriched in incompatible elements and which fractionated in the mantle. Wehrlites and apatite/amphibole xenolith types have $^{87}\text{Sr}/^{86}\text{Sr}$ values consistently around 0.7037; metapyroxenites, by contrast, have ratios extending up to 0.7150 (O'Reilly, 1987).

Fe-rich Cr-diopside suite (see also Wilkinson and Binns, 1977). Xenoliths of this type most closely resemble those from the Cr-diopside suite, being predominantly spinel lherzolites. However, mineralogically they lie between the Cr-diopside and the Al-augite suites: olivines average Fo₈₆ (Cr-diopside olivines are Fo₈₈₋₉₂), while clinopyroxene compositions have higher Al, Fe and Ti contents than those from the Cr-diopside suite. Examples are found in six provinces in Victoria, central and northern NSW and northern Queensland. They are thought to result from interaction between lherzolite wall-rock and basaltic liquids, on the basis of evidence from large composite xenoliths. Smith and Boyd (1987) argue for a metasomatic origin for a lherzolite xenolith of similar composition from Lesotho.

Composite xenoliths are also important, especially in establishing which xenolith types coexist and thus allowing extrapolation of P-T data. It is noted that Cr-diopside examples can be veined by/ occur adjacent to Al-augite types, while wehrlite-series rocks are found in contact with metapyroxenites.

Crustal xenoliths

Xenoliths of crustal origin provide vital information about the nature of the lower crust, which can play an important role in the petrogenesis of magmas which undergo fractionation there. This section is divided into two parts. Firstly work by Griffin, O'Reilly and co-workers on crustal xenoliths from throughout eastern Australia will be discussed, while the second section describes in-depth studies of xenoliths retrieved from two provinces in northern Queensland by Rudnick and co-workers.

Eastern Australia This part summarises work published by Griffin and O'Reilly (1986, 1987), Griffin *et al.* (1987) and O'Reilly *et al.* (1989). They note that crustal xenoliths are less common than mantle-derived examples, but have nevertheless been retrieved from over 50 localities throughout eastern Australia. Examples of middle-upper crustal xenoliths are generally felsic and rare. Much more common are mafic examples from the lower crust, which are dominated by two pyroxene + plagioclase granulites, with rarer garnet-bearing varieties. These may have been modified during cooling/recrystallisation and a wide range of assemblages has been observed involving clinopyroxene, orthopyroxene, plagioclase, garnet, spinel and olivine. Most pressure-temperature estimates lie in the range 750-1100 °C and 7-17 kbar (e.g. O'Reilly and Griffin, 1985; Griffin *et al.*, 1987). Microstructures vary from unmodified igneous types (gabbroic, cumulate) to completely recrystallised metamorphic textures, of which the most common are foliated and deformed examples which are typical of global lower crustal mafic granulites (Griffin and O'Reilly, 1986). Grain sizes are generally < 4mm. A wide range of compositions is observed from nepheline- to quartz-normative, and overlapping the range of Cainozoic basalts. Isotopically (O'Reilly *et al.*, 1988) most granulites lie within the mantle array and within the range of ratios displayed by the host basalts (Figure 1.8). Exceptions are samples from northern Queensland which appear to have interacted with enriched continental crust, and those from Gloucester and Delegate provinces (Jurassic diatremes in NSW) which have high $^{87}\text{Sr}/^{86}\text{Sr}$ values thought to result from interaction with subducted continental or ocean floor/island arc material.

Most lower crustal xenoliths are considered to represent basaltic material intruded at the crust-mantle boundary during thermal events in the late-Palaeozoic-early Tertiary (age estimates from isochrons: O'Reilly *et al.*, 1988). Much of this is thought to be cumulate in nature owing to texture and geochemistry: observed high mg-numbers (>70), high Ca, Al, low alkali concentrations, and broad correlations between Cr & MgO and Sr & Al_2O_3 (but not CaO) suggest that fractionation assemblages were dominated by clinopyroxene and plagioclase (Griffin *et al.*, 1987). Other examples with lower mg-number (e.g. 58), and high Ti, P, Zr and Y are thought to be frozen basaltic liquids.

Northern Queensland Rudnick *et al.* (1986) and Rudnick and Taylor (1987) describe a wide compositional range of lower crustal xenoliths from two Cainozoic lava field provinces in northern Queensland. All of the nodules retrieved from Chudleigh and 80% of those from McBride (see Figure 1.1 for localities) are mafic granulites, consisting of plagioclase + orthopyroxene + clinopyroxene $\pm$ spinel $\pm$ garnet, which equilibrated at ~20-40 km depth. Geochemical study shows that they were formed by various processes, namely crystallisation of mafic magma, crystal accumulation, and partial melting of more felsic compositions to produce a mafic residue. The remainder of the McBride xenolith assemblage consists of intermediate-felsic compositions which also have high-grade mineralogies and textures. Their protoliths are interpreted as supracrustally-derived sediments, and felsic melts which are geochemically similar to Palaeozoic granitic rocks which crop out on the surface. Pb isotope work (e.g. Rudnick and Goldstein, 1990) interprets the rather radiogenic lead

composition of the mafic xenoliths (from both provinces) as the product of interaction (e.g. AFC) of magma with pre-existing rocks in the lower crust. Dating by ion microprobe analysis of zircons (Rudnick and Williams, 1987) shows that most of the McBride mafic and felsic xenoliths are Palaeozoic in age (~300Ma), while the metasediments are Proterozoic (<1570 Ma). These ages are similar to those of granites and sediments at the surface (the latter from the Pre-Cambrian Georgetown inlier). Isotopic evidence (Rudnick *et al.*, 1986) suggests that the mafic Chudleigh xenoliths are much younger, less than 100Ma old, and are related to an earlier phase of the Tertiary igneous activity.

Data from the McBride xenoliths are integrated into a model of a Palaeozoic continental margin subduction zone, as postulated by other workers on the basis of surface outcrop. Melting above the subducting slab generated mafic melts which intruded into, and intensely heated, the lower crust, causing partial melting and the generation of felsic melts (with corresponding mafic residues). Fractional crystallisation of the mafic magmas combined with assimilation of pre-existing crustal material resulted in the range of mafic compositions observed in the xenolith suite. Supracrustal sediments were thrust into the lower crust, where they were metamorphosed to granulite facies. Although not evident in the retrieved xenolith assemblage, a geochemically heterogeneous lower crust has also been inferred beneath the Chudleigh province. Calculated p-wave seismic velocities for the mafic granulites are higher than those in the observed seismic profile beneath the province (Rudnick and Jackson, 1995). This suggests that mafic granulite is interlayered with 'slower' quartz-rich material in the lower crust.

Megacrysts

Megacrysts are discussed in, *inter alia*, Irving (1974), Ewart *et al.* (1980), O'Reilly and Griffin (1987) and O'Reilly *et al.* (1989). A brief summary follows:

Occurrences are reported from over 200 localities in eastern Australia, from Tasmania to Queensland, within lava flows, dykes, cinder cones and maars. Assemblages are dominated by clinopyroxene, with anorthoclase/plagioclase, spinel, amphibole and orthopyroxene, and rarer ilmenite, magnetite, apatite, zircon, garnet and corundum. Their distribution throughout eastern Australia is presented in Table 1.2.

Megacryst compositions are discussed in Irving (1974) and O'Reilly and Griffin (1987). Clinopyroxenes are aluminous (5-10% Al_2O_3) with variable CaO (14-20%) and TiO_2 (0.5-3.0%), and compositions commonly vary within single localities. Irving (1974) interpreted the observed negative correlation of Al, Fe, Ca, Ti and Na with Si, Mg and Cr as the result of differentiation of the parent magma at depth. Feldspar is usually anorthoclase (average $\text{An}_{50}\text{Ab}_{50}$) and grades to labradorite. Spinel megacrysts are mostly spinel-hercynite in composition, with low TiO_2 and Cr_2O_3 ($\leq 1\%$). Amphiboles are predominantly kaersutitic. Orthopyroxene examples are aluminous enstatites ($\text{En}_{83}\text{-En}_{87}$) which contain 3-7% Al_2O_3 and 1.5-2.1% CaO. Most olivine megacrysts show evidence of strain

and are geochemically similar to olivine in spinel lherzolite xenoliths; they are thus interpreted as coming from disaggregated spinel lherzolite.

O'Reilly and Griffin (1987) note that available data show that while megacrysts do not lie within the $^{87}\text{Sr}/^{86}\text{Sr}$ range of their host lava, they do lie within the whole range of lavas from their host province thus suggesting that they could be genetically related to earlier magmas from the same eruptive episode. Clinopyroxene megacryst compositions overlap with those from upper mantle Al-augite suite xenoliths. Wass (1979) also described clinopyroxene with the same composition as coexisting megacrysts which rims Cr-diopside xenocrysts, suggesting that some of the clinopyroxene megacrysts are high-pressure precipitates. Together with the megacryst associations outlined above, the evidence suggests that some clinopyroxene megacrysts may be cognate, high-pressure liquidus phases while all other megacrysts come from the disaggregation of material which had already crystallised from earlier batches of magma (O'Reilly and Griffin, 1987) and which may have formed loose aggregates on the walls of the magma conduits (Irving, 1974).

Ewart *et al.* (1980) described megacrysts of orthopyroxene, clinopyroxene, feldspar, spinel, amphibole, olivine and mica from central and southern Queensland. They demonstrated thermodynamically that the megacrysts have compositions consistent with equilibration with their host magmas at 9-16 kbar, i.e. in the lower crust. This study is discussed in greater detail in section 1.2.3.

1.1.7 The nature of the east Australian lithosphere

A review of models for the structure and petrology of the east Australian lithosphere is presented by O'Reilly (1989), which is based on seismic (e.g. Mathur, 1983: Figure 1.3) and petrological evidence (mostly outlined above in section 1.1.6: e.g. Griffin *et al.*, 1984; O'Reilly and Griffin, 1985; Griffin *et al.*, 1987).

O'Reilly and Griffin (1985) and Griffin *et al.* (1987) used xenolith data (garnet websterites and lower-crustal mafic granulites) to construct geotherms for southeastern Australia and east-central Queensland, respectively. The two geotherms are more or less coincident and are also consistent with other xenolith data from throughout eastern Australia. The xenolith host rocks that they used range in age from 200 Ma to 4000 a BP., but probably only represent the geotherm at various periods of intense igneous activity during that time: host lavas for the southeastern geotherm are around 50,000 years old, while those for east-central Queensland are around 35-20 Ma old. The former is provided, together with other xenolith-derived continental geotherms for comparison in Figure 1.9. High temperatures and strong curvature between 10 and 25 kbar are consistent with magma intrusion around the crust-mantle boundary.

A model for the petrological structure of the eastern Australian lithosphere from O'Reilly and Griffin (1985) is shown in Figure 1.10 which is consistent with the available data. Coexistence of rock types was established using thermobarometry and composite xenoliths, while V_p , heat-flow and

other seismic data were also used to construct the model. The P-T data shown in Figure 1.10 indicates a broad maximum of granulite temperatures at 750-950 °C, i.e. 18-36 km, and for spinel lherzolites at 850-1050 °C, i.e. 25-45 km. The lherzolites dominate below ~30 km. This is consistent with interlayering between ~25-35 km (compare the seismic section Figure 1.3). The extent of underplating is illustrated by Cull *et al.* (1992), who model the empirical geotherm with a layer of basaltic magma 4 km thick (i.e. 10 x the maximum extruded thickness at any locality during the Cainozoic) intruded at around 28 km depth. At least some of the mafic lower crust must, however, pre-date the Cainozoic volcanism (e.g. because of mafic granulites found in Jurassic diatremes in NSW and in some of the first erupted lavas of the Cainozoic sequences). O'Reilly (1989) provides a plausible crustal development model for eastern Australia based on Powell (1983) which combines episodes of accretion with underplating during the Palaeozoic (Figure 1.11).

1.1.8 General tectonic and petrogenetic models

Recent general models for Cainozoic volcanism in eastern Australia have been developed by Lister and Etheridge (1989) and Sun *et al.* (1989). The former concentrate on tectonic aspects such as the nature of rifting, while the second paper discusses petrogenesis and recognition of basalt source components. O'Reilly and Zhang (1995) present a modified integration of the two models.

Detachment model for uplift and volcanism

Lister and Etheridge (1989) propose a model that seeks to explain features of tectonic style, uplift and timing of volcanism in eastern Australia, especially:

- 1) The nature of the rifting that took place between mainland Australia and the Lord Howe Rise, leading to the initiation of sea-floor spreading 80 Ma ago and formation of the Tasman Sea.
- 2) The mechanism of uplift of the eastern Highlands, which stand up to 1-2 km high today, over 50 Ma after the cessation of extension and up to 30 Ma after volcanic activity. Elevation has been more or less static throughout Cainozoic and Recent times (Wellman, 1987), and significant erosion since Permian times is discounted by fission track ages. There is a strong spatial relationship between volcanic provinces and the highlands.
- 3) The geodynamic processes in the mantle which gave rise to volcanism, and controlled its location and timing.

Geological observations and seismic surveys indicate that rifting was strongly asymmetrical. The authors present a detachment model based on the lithospheric-wedge 'Wernicke' model, with eastern Australia as an upper-plate passive margin (Figure 1.12). They envisage uniform stretching of the lower plate beneath the detachment which terminates in the crust, unlike the 'Wernicke' model where the lower plate is completely removed. This model accounts for the observed gross morphology of the rift, as well as some minor coastal geomorphological features on the mainland.

A necessary consequence of the model is a broad zone of upwelling asthenosphere beneath the rift axis and the stretched, thinned upper-plate lithosphere. Lister and Etheridge concluded that the thermal effect of this upwelling was insufficient to explain the elevation of the highlands, since a substantial amount of subsidence would have taken place following uplift due to the thermal time constant being on the order of a few million years: no such subsidence has been observed. However, they were able to show that substantial underplating of basic material could generate sufficient amounts of uplift provided that, during the period of extension, the upwelling asthenosphere had a potential temperature above the normal mid-ocean ridge figure of ~ 1300 °C and more like that observed at Iceland i.e. ~ 1500 °C. They suggest that convective upwelling of deep, hot material through the asthenosphere could have been induced by rapid lithospheric extension, or by pre-extension subduction and slab 'roll-back'. Such melts (which first reached the base of the lithosphere ~ 120 Ma ago) did not initially reach the surface, but were all underplated; further upward movement by the magmas was precluded by the prevalent lithospheric stress field. Favourable stress conditions for movement through the lithosphere did not arise until the rate of extension decreased: this was marked by the onset of sea-floor spreading (~ 95 Ma ago) and the creation of the Tasman Sea.

Lister and Etheridge (op. cit.) propose that diapirs rising from depths extending down to 400 km, at rates of 5-10 km/Ma, could take up to 100 Ma to reach the mantle solidus and undergo partial melting. Depending on density considerations, the prevalent lithospheric stress field, ascent rate etc., some of these melts would be extruded at the surface well over 100 Ma after the extensional event that initiated the upwelling. They also suggest that the independent appearance of a mantle plume (which has been invoked to explain the age-progressive central volcano provinces, e.g. Wellman and McDougall, 1974) in the same area shortly after a major extensional event requires a substantial coincidence; furthermore it is impossible that the deep mantle (where the plume would have originated) could have 'recognised' extensional events at the surface. They propose instead that the source of central volcanoes is attributable to melt segregation from the upwellings of chains of mantle diapirs (see Figure 1.13), triggered by an earlier lithospheric-extension event.

This hypothesis, however, also requires a substantial coincidence, namely that of an earlier significant extension event in exactly the same area. Furthermore, it does not adequately explain how the age-progressive nature of the provinces arise from the seemingly random spatial upwelling of the diapirs. Indeed O'Reilly and Zhang (1995) use the same figure to illustrate the generation and random geographical occurrence of the lava field provinces!

Four-component model dynamic model

Sun *et al.* (1989) confine their discussion primarily to geochemical and petrogenetic aspects of eastern Australia volcanism, and attempt to assess the roles of four source components (mantle plume, shallow asthenosphere, continental lithosphere and crust) in the generation of the Cainozoic

basalts. They also examine whether systematic differences exist between the central volcano and lava field provinces.

It is noted that alkali basalts from intraplate continental and oceanic settings are geochemically and isotopically similar, while tholeiites show differences, for example in exhibiting more 'evolved' isotopic signatures. Since they are generated at shallower depths and have lower ascent rates than alkali basalts, tholeiites are more susceptible to interaction with the lithosphere. This potentially explains why continental examples are isotopically 'evolved' and show greater geochemical evidence for AFC processes than oceanic examples. Evidence of this is seen in eastern Australia where primitive, xenolith-bearing alkalic magmas must have passed rapidly through the lithosphere without being contaminated. Tholeiitic liquids, which segregate at shallower depths and ascend at lower rates than alkalic ones, appear to have been more likely to underplate and intrude around the crust-mantle boundary, thereby generating the observed wider range of evolved magma compositions (e.g. Ewart *et al.*, 1988).

The upwelling of a mantle plume and its impingement on the base of the lithosphere leads potentially to the mixing of partial melts from the plume and the shallow asthenosphere, together with partial melts generated in the lithosphere in response to the increased heat flow. The heterogeneity of these components, especially the lithosphere, exerts strong controls on the compositional range of the resultant magmas. Compositional variation in the convecting mantle results from, for example, the input and mixing (by convection) of subducted slabs and delaminated lithosphere, as well as extraction of partial melts. These processes, together with interaction with the oceanic lithosphere (e.g. Chen and Frey, 1985) account for the isotopic and geochemical variation that is observed in ocean islands. Primitive basalts from eastern Australia show a similar chemical and isotopic variation to OIB, suggesting that they too could be derived from a similarly heterogeneous convecting upper mantle. Further complexity is introduced in the continental environment by the continental lithosphere, whose considerable geochemical and isotopic diversity is the result of, amongst other processes, accretion of arc/subduction-related material, underplating and trapping of basaltic melts, and passage of fluids from subducting slabs and the asthenosphere. Heterogeneity is maintained in the absence of convection, thus allowing the evolution of enriched isotopic ratios over long periods of time. Evidence of this compositional diversity in eastern Australia comes from the wide range of retrieved xenoliths and the outcrop of geochemically diverse early-Proterozoic to early-Palaeozoic basement, which has clearly been influenced by subduction-volcanic-accretion processes, as well as a major Gondwanan thermal event whose effects are visible in southeastern Australia.

Central volcano and lava field province lavas are characterised in terms of $^{87}\text{Sr}/^{86}\text{Sr}$ and some important incompatible trace element ratios in Table 1.3. Least-fractionated basalts from both province types are geochemically and isotopically similar to ocean island basalts, suggesting that plume and asthenospheric sources are dominant in their petrogenesis. Hofmann *et al.* (1986) demonstrated that OIB and MORB had remarkably consistent Ce/Pb and Rb/Cs ratios of 25 ± 5 and

80 ± 20 respectively. Significant deviations generally indicate input from the crust, lithosphere or the presence of recycled sediment within the convecting mantle. Table 1.3 shows that some east Australian basalts and especially tholeiites (in parentheses) can have significantly lower-than-mantle values of these ratios. Furthermore, values of Ba/Nb and La/Nb are higher than can be explained by fractional crystallisation (Figure 1.14), which is also attributable to crustal/lithospheric input.

The age-progressive central volcanoes were probably formed by a hot-spot, which is considered to have deep-mantle origin on the basis of geophysical evidence. Interaction of this plume with the lithosphere is envisaged in Figure 1.15, resulting in flooding of the shallow asthenosphere and directing of melt in structurally favoured directions. Influence of the plume component will consequently decrease with distance from the hotspot. Components are then characterised as follows (see also Figure 1.16):

Plume This composition is derived from the least-fractionated central volcano basalts (e.g. from Springsure), screened for crustal contamination (although this does not preclude the presence of some material from the shallow asthenosphere and lithosphere). Similar compositions are found in proximal lava field basalts of a similar age. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lie between 0.7036 and 0.7043, and $^{143}\text{Nd}/^{144}\text{Nd}$ between 0.5127 and 0.5129. These are compared with Hawaiian tholeiitic basalts, which are thought to represent their plume composition: 0.7035-0.7042 and 0.5127-0.5130 (Tatsumoto *et al.*, 1987) and Tasmanid guyots (Figure 1.5): 0.7038-0.7047 and 0.5124-0.5128 (McCulloch, 1988). Lead ratios are as follows: $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.34-18.82; $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.52-15.61; $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.25-38.82.

Shallow asthenosphere This component is defined by the compositions of alkalic lava field basalts which are older than nearby central volcanoes and thus not influenced by plume-derived material. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lie between 0.7026 and 0.7044, but most lie in the range 0.7030-0.7034. $^{143}\text{Nd}/^{144}\text{Nd}$ lies dominantly between 0.5129 and 0.5131. Lead isotope data is limited: $^{206}\text{Pb}/^{204}\text{Pb}$ generally lies between 18.34 and 18.82. However samples with $^{87}\text{Sr}/^{86}\text{Sr} < 0.7030$ (mostly Tasmanian lavas, but also a plug from the Buckland province), tend to have high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the range 19.13-19.66, similar to HIMU ocean island basalts, e.g. St. Helena.

Tholeiites from the Newer Volcanics of Victoria appear not to be related to a hotspot, and thus require an anomalously hot ($T_P \sim 1350^\circ\text{C}$) deep asthenospheric source. Upwelling of such material, isotopically similar to the plume component, could be related to the break-up of Gondwanaland.

Lithosphere This component is much harder to constrain than the previous two. It has been proposed (e.g. Nelson *et al.*, 1986; Ewart *et al.*, 1988) that the leucitites from NSW are the result of plume-induced melting of the lithosphere. They have 'evolved' Sr-Nd ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ in the range 0.7050-0.7056 and $^{143}\text{Nd}/^{144}\text{Nd}$ approximately 0.5125-0.5126). Lead isotopes are also quite distinctive, with relatively high $^{207}\text{Pb}/^{204}\text{Pb}$ values for their low $^{206}\text{Pb}/^{204}\text{Pb}$ (see Figure 1.16a). These isotopic ratios do

not necessarily reflect the composition of the lithosphere throughout eastern Australia, since xenolith evidence (e.g. Irving, 1980; O'Reilly, 1987) indicates that it is heterogeneous down to the cm scale. For example, a sample from Inglewood (SE Queensland) has similar Pb-isotope ratios to locally-outcropping Carboniferous sediments (Figure 1.16a) and is thus potentially the result of the melting of subduction-related lithosphere. Lavas from Mitchell (central Queensland: discussed later in this study) have elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ compared to the envisaged plume composition, as well as low Ce/Pb (~ 10). The most likely reason for this is the effect of AFC processes, but it could also be explained in terms of a strong input of subduction-related lithosphere (see Figure 1.16b). These cases suggest that the lithosphere in central-southeastern Queensland is isotopically distinct to that which gave rise to the leucitites in NSW.

In conclusion, Sun *et al.* (1989) argue that Cainozoic volcanism in eastern Australia can be interpreted in terms of interaction between mantle plume, shallow asthenosphere, lithosphere and crust (Figure 1.15). They suggest that the geographical deviation of some central volcanoes from a postulated single straight hotspot track is either a function of the geometry of the deep, vertical translithospheric fractures through which the magmas ascended, or requires up to three on-shore hotspots (Wellman and McDougall, 1974; Sutherland, 1983): see Figure 1.17. The discontinuous nature of the provinces is interpreted as resulting from the variable thickness of the lithosphere, which was too thick in some places to allow direct magma access to the surface.

O'Reilly and Zhang (1995) present slight modifications and refinements to the models. In a detailed geochemical study of a large number of primitive lava field basalts, they conclude that they are indistinguishable from OIB, and thus appear to be derived from the deep, rather than the shallow, asthenosphere. They suggest that a zone of deep upwelling (such as that proposed by Lister and Etheridge, 1989, for the central volcanoes: Figure 1.13) could explain the lava field volcanism, with their distribution being controlled by the structure of the lithosphere. Central volcanoes are the result of passage over a hotspot and the deviation of these provinces from a straight hotspot track is explained in terms of the 'thin-spot' model of Thompson and Gibson (1991): see Figure 1.18.

Johnson *et al.* (1989) combine the model of Sun *et al.* (1989) with other work presented in Johnson (1989a) to produce a general synthesis. The Australian continent, consisting of an ancient cratonic interior and an eastern zone of more recently accreted fold belts, has been deformed in the east as a result of intra-plate stresses. Extension was prevalent between 50 and 20 Ma which led to partial melting of the underlying asthenosphere, resulting in lava field volcanism localities controlled by the structure of the lithosphere. Short residence times in the lithosphere meant that few evolved lavas were produced. The northeastern edge of Australia started to pass over a deep mantle hotspot around 35 Ma ago, resulting in a discontinuous chain of central volcanoes. Melts were dominated by

plume-derived tholeiites which, partly owing to their density, tended to pond in the crust/lithosphere, resulting in the eruption of sequences of relatively differentiated lavas (with corresponding cumulates being produced in the lithosphere) and some anatectic felsic melts. Both types of volcanism waned around 20-15 Ma ago, perhaps due to a switch from dominantly tensional to compressional tectonism. More recent (<5 Ma) lava field volcanism in northern Queensland and Victoria is perhaps explained by the persistence of extensional regimes in those places. The ability of magmas to pass through the Australian lithosphere and generate the very unusual continental hotspot trace is almost certainly due to the fact that the lithosphere had been deformed and heated prior to passing over the hotspot.

1.2 INTRODUCTION TO THE FIELD AREA

1.2.1 General characteristics and age constraints

The area studied within this thesis is shown in Figure 1.19, encompassing three volcanic provinces, namely Buckland, Springsure and Mitchell, which lie between latitudes 23° 30' & 26° 30'S and longitudes 147° & 149°E. Each province is briefly described below, together with published age constraints:

Buckland

The main feature of this province is a strongly eroded shield structure, approximately 60 km across, with up to 300m of remaining basaltic lava thickness. Flows are approximately horizontal, forming flat-topped 'tableland' topography (Plate 1.1) whose elevation reaches 1100 m above sea level. Isolated minor basic intrusions, lava flows and volcanic plugs are also found, mostly to the west of the main structure (Figure 1.19; Plate 1.2). Three minor felsic intrusions have also been recorded (Mollan, 1972) close to the middle of the shield structure.

Sutherland *et al.* (1989b) provide a summary of available dates. One of the stratigraphically lowest flows in the northeast of the province was dated at 27 Ma by Elliot (1973). Griffin *et al.* (1987) dated anorthoclase megacrysts from the lowermost flow in the Battleship Spur section at 27 Ma, and an anorthoclase-rich phase from The Steeple (one of the felsic intrusions) at 25 Ma; they give the full age range of the main volcanic structure as 25-28 Ma, but suggest that the intrusions and volcanic plugs in the west of the province are older since they are more eroded.

Springsure

This province consists of a broad expanse of basaltic lavas, up to 330 m thick, which have been eroded to form tableland-remnants with plains of basaltic black soils (Plate 1.3). Elevation, in contrast to the Buckland province, does not exceed 630 m. A lower series of mafic lavas 70 m thick is overlain by mafic lavas, pyroclastics, and trachytic-rhyolitic lava flows and plugs (up to 250 m thick)

with a capping of unusual quartz-tholeiite (Ewart *et al.*, 1980). An area of acidic intrusions and flows, the Minerva Hills Volcanics, lies to the north of the town of Springsure.

Sutherland *et al.* (1989a) report that the oldest dated sample from the province is a *ne-mugearite* dyke, zircons from which have a fission-track age of 35 Ma. K/Ar ages from Webb and McDougall (1967) and Ewart (1982) constrain the main period of basaltic lava activity, including those which intercalate with felsic rocks, to 33-26 Ma; felsic samples have ages between 29 and 27 Ma, while the later phase of basaltic activity occurred between 26 and 24 Ma.

Mitchell

The areal extent of this province is considerably less than that of the two outlined above. Basaltic lavas occur in a discontinuous and rather sinuous outcrop pattern which has been ascribed (Exon, 1971; Sutherland *et al.*, 1989b) to extrusion and flow along the axial valley of the Merivale syncline. The thickness is greater in the northern part of the province (≤ 100 m) than in the south (average of 30 m).

Exon *et al.* (1970) dated several samples which yielded K/Ar ages between 20 and 23 Ma. They suggest that the youngest of these might be erroneous due to appreciable argon loss following glass devitrification.

Figure 1.20 shows a south-north section through the field area showing the thickness of the lava sequences together with dashed lines showing important topography and lava that lies just off-section. This clearly shows a gradual increase in the height of the base of the lava sequences in a northward direction through the Mitchell province to Buckland, and then a more abrupt reduction in height into the southern part of the Springsure province. The section is based on the published 1:250,000 topographic maps together with the BMR geological maps which do not show the presence of any fault or other structural feature that might explain the sudden change in height at the south of the Springsure province. This topographic variation will be discussed further in Chapter 6, together with its relation to lava geochemistry/thickness.

1.2.2 Pre-Tertiary geology

Figure 1.21 is a simplified geological map of the field area based on Bureau of Mineral Resources (BMR) map sheets SF 55-15, SG 55-3/4/7/11, and includes salient structural features.

Pre-Tertiary geology consists predominantly of sequences of fluvial to shallow non-marine conglomerate, sandstone and shale, with rare tuff, coal and marine limestones. They range in age from lower-Devonian to Cretaceous with an important regional unconformity between the Triassic and Jurassic series. This is said to mark a minor orogenic event in the Upper Triassic, which produced some of the folding observed on the map (Mollan, 1972). Borehole data in the Mitchell area indicates that the Mesozoic sequence is ~500 m thick and is underlain by Palaeozoic slates and phyllites. A

substantial granodiorite intrusion, upper-Devonian in age, outcrops to the northwest of Anakie (its southernmost tip is marked on Figure 1.21). Earlier, pre-Devonian lithologies in the field area are confined to the Anakie Metamorphics, consisting of schist (single muscovite K/Ar date of 458 Ma: Webb and McDougall, 1968), phyllite, slate, diorite and gneiss. These mostly crop out just north of Anakie, with a small occurrence 50 km west of Springsure.

Structural trends are predominantly north-south trending, and dips are generally gentle (i.e. $<15^\circ$).

Section 1.1.2 draws attention to the fact that a number of the Cainozoic volcanic provinces lie along the boundaries of the major structural blocks in eastern Australia. Reference to Figure 1.1 suggests that this is also the case for the three provinces considered in this study which apparently lie at the boundary of the Thompson Fold Belt and the Sydney-Bowen Basin. Wyborn (1989) suggests that this boundary is in fact the major structural break between the Thompson and the New England Fold Belts, and that the Sydney-Bowen Basin overlies the western parts of the latter.

1.2.3 Previous work

This section describes previous work which refers specifically to the area of study.

Ewart *et al.* (1980) describe lavas from several large central volcano provinces in central to southeastern Queensland, including Springsure. They all show a wide range of compositions which are bimodally distributed (Figure 1.22), but dominated by mafic compositions. Mafic lavas in Springsure are almost all hypersthene-normative, only one being silica-oversaturated. Phenocryst contents are low: the average is 6.7 wt.%, but over 40% of samples contain $\leq 2\%$. Springsure lavas contain phenocrysts of plagioclase (An₄₈-An₆₈, but often rimmed by K-feldspar), olivine (Fo₅₃-Fo₈₄) and augite of unusually aluminous composition. Groundmass minerals are plagioclase (An₆₅-sanidine), augite, olivine (Fo₄₈-Fo₆₆), Fe-Ti oxides and apatite. Ewart *et al.* (op. cit.) also report xenocrysts and megacrysts in a small number of lavas from nearly all the provinces they studied, the exception being Springsure. Xenocrysts of olivine (Fo₈₈-Fo₉₀), diopsidic augite, bronzite and spinel are found in close association with xenoliths of spinel lherzolite: they are thus interpreted as disaggregated lherzolite material. Megacrysts are generally $< 2\text{mm}$ in size, and recognised by the presence of reaction rims or resorption textures. Aluminous augite, aluminous bronzite (both rimmed by olivine + augite), plagioclase, anorthoclase (sieved and corroded), olivine, ilmenite, spinel are all reported. The unusually aluminous augite phenocrysts from Springsure (referred to above) are similar in composition to the aluminous augite megacrysts found in the other provinces, but lack any disequilibrium textures, hence their description as phenocrysts. These megacrysts are discussed in greater detail in Chapter 4.

Ewart *et al.* (op. cit.) attempted to assess the role of fractional crystallisation in producing the diverse chemistry of the lavas, and to test whether they represent predominantly primary or modified compositions. They carried out linear least squares modelling on tholeiitic lavas from two of the SE-

Queensland centres, and could model the chemical variation with fractionating assemblages of olivine + plagioclase $\pm$ Al-clinopyroxene $\pm$ magnetite $\pm$ ilmenite $\pm$ apatite, i.e. without orthopyroxene. They compared these assemblages with the experimentally-derived liquidus phase assemblages determined by Thompson on similar lavas from Skye (1974) and Snake River Plain (1975) (neither of which produce orthopyroxene) and found that they were comparable to empirically-determined assemblages from less than ~ 8 kbar. In order to test the primary nature of the lavas, Ewart *et al.* (op. cit.) employed the thermodynamic technique of Carmichael *et al.* (1977) and Nicholls (1977) which allows the calculation of the pressure and temperature at which a lava composition is in equilibrium with a given mineralogy using component activities. They tested three mineralogies: 1) "standard" upper mantle using compositions of olivine (Fo₈₉), clinopyroxene, orthopyroxene (Mg₈₉) and spinel from Cr-diopside suite Iherzolite; 2) Fe-enriched upper mantle (Wilkinson and Binns, 1977) consisting of the same minerals but with greater Fe/Mg ratios (olivine: Fo₇₉ and orthopyroxene: Mg₈₀); 3) "lower crust" model based on the megacrysts found in the lavas, specifically Al-augite, Al-orthopyroxene, spinel, olivine and plagioclase. Results show that the lower crust model produces the best fit, with calculated pressures lying in the range 7.2-16.3 kbar. (corresponding to 26-58 km depth: similar to the range of depths of underplating inferred in section 1.1.7) and temperatures in the range 995-1391 °C. There is no significant difference in the pressures and temperatures calculated for the five provinces: the six analysed Springsure lavas give an average temperature of 1201 ± 57 °C and 12.1 ± 1.6 kbar. (errors are 1σ). There is the suggestion, however, that the more silica-oversaturated lavas equilibrated at slightly lower pressures and alkaline lavas at greater pressures than the average.

The results are interpreted in terms of an underplating model in which discrete magma batches are intruded around the crust-mantle boundary. They undergo fractional crystallisation $\pm$ re-equilibration with country rock, with some liquids ascending to the surface, possibly via high-level magma chambers. The authors postulate the existence of a significant mafic granulite component in the lower crust, produced by Palaeozoic-Mesozoic volcanism and accretion; re-equilibration of Cainozoic mantle-derived magmas with such isotopically-diverse material could account for some of the isotopic variation recognised in the lavas. This model is illustrated in Figure 1.23, and is essentially the same as the one developed independently for the Karoo basalts of southern Africa by Cox (1980).

Further discussion together with detailed petrogenetic models for the silicic lavas from the same region is presented by Ewart (1982). Various types of silicic lavas are reported, mainly trachytes, rhyolites and comendites (peralkaline rhyolites). Examples from the Minerva Hills in Springsure consist of a complete range of trachytes-trachyrhyolites, typically with phenocrysts of anorthoclase-sanidine $\pm$ Na-plagioclase $\pm$ quartz $\pm$ ferrohedenbergite $\pm$ fayalite $\pm$ hastingsite $\pm$ accessory allanite + zircon + ilmenite + Ti-magnetite. Silicic lavas from the other centres discussed in the paper generally show a less complete range of compositions, but with similar phenocryst

assemblages. Trace element abundances in the acidic lavas show either: 1) enrichment right through to the rhyolites (Th, Rb, Pb); 2) strong depletions, especially in the rhyolites (Ba, Sr, V, Ni, Cr, Mg, Ca, P); 3) variable behaviour, though generally enriched in trachytes and some rhyolites (Zr, Ce, La, Zr, Y, Nb). Isotopic data are presented for mafic and silicic lavas. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally increase with degree of evolution, and vary within and between volcanic centres. Within provinces, there is consistent variation with silica-saturation: alkaline lavas average 0.70367, hypersthene-normative lavas average 0.70379 and quartz-normative lavas 0.70413. Examples from Springsure range from 0.70361-0.70386. A greater range is displayed in the silicic rocks: 0.70432-0.70589 in trachytes-trachyrhyolites and 0.70708-0.70863 in the rhyolites. Country rocks were also analysed: Carboniferous greywacke (0.71155-0.70868) and basalt (0.70346-0.71084) for SE Queensland, and mafic granulite xenoliths (0.70339-0.70422). Oxygen isotope data are also presented: $\delta^{18}\text{O}$ ranges from 4.89 (trachyte) to 10.44 (rhyolite). Springsure examples show little variation, lying between 6.23-6.74. A well defined correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ is noted in the silicic lavas.

Interpretation is given in terms of fractional crystallisation $\pm$ assimilation and crustal anatexis $\pm$ fractional crystallisation. The change in trace element behaviour from mafic to silicic lavas is interpreted to result from the change from a fractionating assemblage of plagioclase + olivine + Al-augite + Ti-magnetite + apatite to Na-plagioclase + sanidine $\pm$ Ti-magnetite + Fe-rich pyroxene/amphibole + accessory phases, together with changes in trace element partition coefficients in the silicic lavas. The accessory phases are shown to have a significant effect on the abundances of certain elements e.g. magnetite controls Nb & Zn and zircon controls Zr. $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{18}\text{O}$ compositions of some silicic lavas (e.g. Minerva Hills) can be modelled without recourse to crustal assimilation: owing to their high Rb/Sr ratios and minimal variation in $\delta^{18}\text{O}$, their isotopic signatures can be modelled by the action of fractional crystallisation on parental basaltic/trachybasaltic liquids within a magma chamber for $\leq 1\text{Ma}$. Other lavas are derived from concurrent crustal assimilation and fractional crystallisation of mafic parent liquids, while the rhyolites (with significantly different Pb-isotope ratios to mafic lavas in the same province) are interpreted as crustal melts $\pm$ variable assimilation-fractional crystallisation.

Bryan (1983) presented data for eleven lavas from the 'Carnarvon Range', i.e. the Buckland province. The samples range compositionally from alkali basalts through olivine tholeiites to a microsyenite and a rhyolite. The basic lavas contain 4 - 6.3% MgO and 46.8 - 49.3% SiO_2 with a regular variation in major elements, the microsyenite contains 0.2% MgO and 63.9% SiO_2 and the rhyolite 0.1% MgO and 74.7% SiO_2 . Basic lavas are fine-grained, with the exception of one gabbro, and are xenolith-free. The dominant texture is of olivine microphenocrysts in a groundmass of plagioclase laths (An_{60} at the core with rims of alkali feldspar), sub-ophitic augite with minor ilmenite/titanomagnetite. The gabbro consists of plagioclase (An_{50} - An_{59} at the core to alkali feldspar at the rim), rounded olivine (average Fo_{53}), sub-ophitic Ti-augite and minor ilmenite, fluorapatite,

hypersthene and biotite. The microsyenite is composed of rounded anorthoclase phenocrysts with microphenocrysts of ferrohedenbergite in a groundmass of alkali feldspar, magnetite, ferrohedenbergite and iddingsite (after fayalite?). Finally the rhyolite consists of rounded phenocrysts of quartz and feldspar (mosaic of alkali feldspar and albite/oligoclase) and biotite in a groundmass of alkali feldspar, biotite and quartz. The author noted that the lavas were generally similar in chemistry and mineralogy to examples from the Bunya mountains of southeast Queensland which he discusses in the same paper.

After describing the samples, Bryan (1983) sought to test the theory that they were linked by fractional crystallisation processes. He chose an average trachybasalt composition (4.1% MgO; 49.3% SiO₂) that could represent a residual liquid after ~50% fractional crystallisation. Mass balance calculations were then undertaken using compositions of olivine (Fo₅₃), plagioclase (An₆₀) and augite from the gabbro to estimate the weight fractions of each of the three minerals and the residual trachybasalt liquid in each of the mafic samples. The gabbro itself proved to 'contain' the lowest amount of the trachybasalt - 52%. This means that the average trachybasalt composition can be reproduced by 48% fractional crystallisation of olivine, plagioclase and augite (in the proportions 55:30:15; see Bryan, 1983, Table 9) acting on the gabbro composition. Other mafic lavas have higher calculated weight fractions of the trachybasalt, with an increasing fraction of augite. The series of mafic lavas is thus interpreted as the product of fractional crystallisation of olivine, plagioclase and augite acting on a composition similar to the gabbro. The increasing importance of augite with ongoing fractionation in the model is compatible with the inferred crystallisation of augite after olivine and plagioclase by textural analysis of the gabbro.

He also notes that the Carnarvon lavas show a demonstrable change from evolved to primitive compositions up-sequence, followed by the most evolved trachytes and rhyolites. This is interpreted in terms of the underplating and lower-crust fractionation model of Ewart *et al.* (1980): early-formed magmas had to pass through a substantial thickness of relatively cold upper mantle and crust before reaching the surface, and were thus more prone to fractionation than later-formed magmas passing through already-warmed crust.

Griffin *et al.* (1987) studied the xenolith suites found in several east-central Queensland provinces (between 20° and 27°S), using examples from the Buckland province, but not Springsure and Mitchell. A range of examples has been described from Boowinda Creek in the Buckland province, mostly derived from a basanite flow towards the base of the sequence at Battleship Spur (see Figure 2.1). They noted that spinel lherzolites make up 70-90% of the xenolith assemblages and are typical of east-Australian Cr-diopside suite xenoliths. Other upper mantle xenoliths were also retrieved, namely wehrlites (clinopyroxene + olivine ± garnet) and clinopyroxenites (2 pyroxenes ± garnet). Spinel lherzolites are interpreted as having been entrained in the upper mantle, while websterites (± garnet) are thought to represent basaltic cumulate material and frozen basaltic liquids.

They also reported lower crustal mafic granulites of two main types: two-pyroxene granulites (2 pyroxenes + plagioclase $\pm$ ilmenite $\pm$ magnetite $\pm$ quartz) and garnet granulites (2 pyroxenes + plagioclase + garnet *or* clinopyroxene + plagioclase + garnet + quartz $\pm$ biotite/olivine/magnetite/ilmenite/apatite). Some of these show cumulate textures, while others show a pronounced foliation. Lower crustal granulites vary widely in composition from basanite to *qz-tholeiite*, broadly equivalent to the range of lavas in the area. P-T estimates for the granulites and websterites fall along the geotherm previously defined by xenoliths from southeastern Australia (Figure 1.9).

O'Reilly *et al.* (1988) present isotopic data for lower-crustal xenoliths from east-central Queensland, shown in Figure 1.8. They form an array, most of which overlaps the field of lavas but which also extends towards more 'evolved' compositions (higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{144}\text{Nd}/^{143}\text{Nd}$). This is thought to reflect interaction of basaltic liquids with LREE-enriched, high-Rb/Sr basaltic lower crust. They note an unusual positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and mg-number, and a negative correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and mg-number. The authors also report that the three Boowinda Creek samples which they analysed suggest an isochron age of 450-500 Ma, consistent with Palaeozoic igneous activity.

1.3 DISCUSSION AND AIMS

1.3.1 Integration of the Buckland province into the regional picture

This section briefly summarises the foregoing introduction to assess what can be deduced from previous work about the Buckland province. The evidence suggests that the province has several characteristics in common with other Cainozoic central volcano provinces in eastern Australia:

1. it consists predominantly of basaltic lavas (olivine tholeiites, alkali basalts and basanites) with minor bodies of evolved felsic material.
2. it is topographically elevated and lies on the Great Dividing Range.
3. xenoliths retrieved from lavas in the province consist of anhydrous mantle lherzolites, websterites or lower crustal mafic granulites. P-T data from these xenoliths constrain a similar geothermal gradient to the one calculated for southeastern Australia.
4. local seismic reflection profiles indicate the presence of interlayered ultramafic-mafic material at the crust-mantle boundary beneath the province.
5. it lies on the straight line correlating the age of the central volcano provinces with latitude in Figure 1.2.

Points 2-4 support the existence of a significant underplate of basaltic material beneath the province, while point 5 confirms that magmatism in Buckland was related to a mantle hotspot.

Evidence for the presence of magmas from HIMU-related, shallow asthenosphere is provided by a volcanic plug from Rewan in the south east of the province.

Lavas from the neighbouring central volcano province of Springsure, together with other provinces in central-southeastern Queensland, show petrographical evidence of polybaric fractional crystallisation ($\pm$ crustal assimilation). Geochemical modelling indicates that processes operating in the lower crust were more important than those in the upper crust, and resulted in underplating at the crust-mantle boundary causing uplift. Least-fractionated mafic lavas from Springsure are used to define the characteristics of the 'plume' mantle source which dominates central volcano magmatism in eastern Australia.

Lavas (qz-tholeiites) from the Mitchell province have isotopic compositions distinct from the 'plume' composition referred to above, interpreted as the result of crustal AFC processes or interaction with subduction-related lithosphere.

Previous work therefore indicates that lavas from Buckland and the neighbouring provinces of Springsure and Mitchell show evidence of the participation of each of the four components which have been proposed for east Australian volcanism by Sun *et al.* (1989), namely plume, shallow asthenosphere, crust and lithosphere. The composition of the last reflects the Palaeozoic-Mesozoic history of subduction-accretion episodes throughout eastern Australia.

In areal extent, lava thickness and composition, Buckland shows most similarity with the Springsure province, and consequently would be expected to share the same petrological characteristics, i.e. plume-dominated melts which have undergone significant AFC (mostly in the lower crust).

1.3.2 Aims of the project

As outlined at the beginning of this chapter, the principal aim of this project is to describe the petrology of lavas from the Buckland province, which have not previously been studied in detail. Published data (summarised above) indicates that the province is typical of central volcano provinces in eastern Australia, consisting of a range of silica-saturated and undersaturated basaltic lavas, some of which are primitive i.e. they have high mg-numbers.

These primitive compositions are ideal for investigating source rock compositions and the conditions of melting under which magma generation took place, since they have undergone relatively little modification since segregation from their source. Numerous recent studies (e.g. Hirose and Kushiro, 1993; Kushiro, 1996) provide a wealth of data about the melting of a range of peridotite compositions. These have been applied successfully to the constraint of melting processes in plumes at other mafic igneous provinces (e.g. Skye: Scarrow and Cox, 1995), and will be used in this study. Application to primitive rocks from Buckland could also permit constraint of the potential temperature of the inferred plume which has not previously been attempted for lavas from eastern

Australia, and allow comparison with the estimates (~1450-1500°C) made by Lister and Etheridge (1989) on the basis of underplating calculations.

The petrology and petrogenesis of more evolved lavas will be addressed in detail, and compared to those from other central volcano provinces in central-southeast Queensland which show evidence for polybaric fractional crystallisation ($\pm$ assimilation).

Of additional interest is the extent of outcrop of strongly-undersaturated, HIMU-type lavas within the province. The previously analysed sample from Rewan (discussed above) is isotopically distinct from all other east Australian lavas, except examples from Tasmania, thus suggesting the presence of asthenospheric material of unusual composition beneath this part of central Queensland. Possible explanations for the presence of this source type will be discussed.

Other probes on the nature of magmatism may also be studied in the Buckland province. The analysis of ultramafic xenoliths allows assessment of the character of the lithospheric mantle beneath the province, while gross variations in geochemistry and height of the lava sequences across the Buckland, Springsure and Mitchell provinces can reveal useful information about variation in the extent of underplating, nature of melting and other magmatic processes in this part of central Queensland.

Finally, the conclusions of the chapters will be summarised and discussed in terms of the models for Cainozoic volcanism that have been advanced by previous workers.

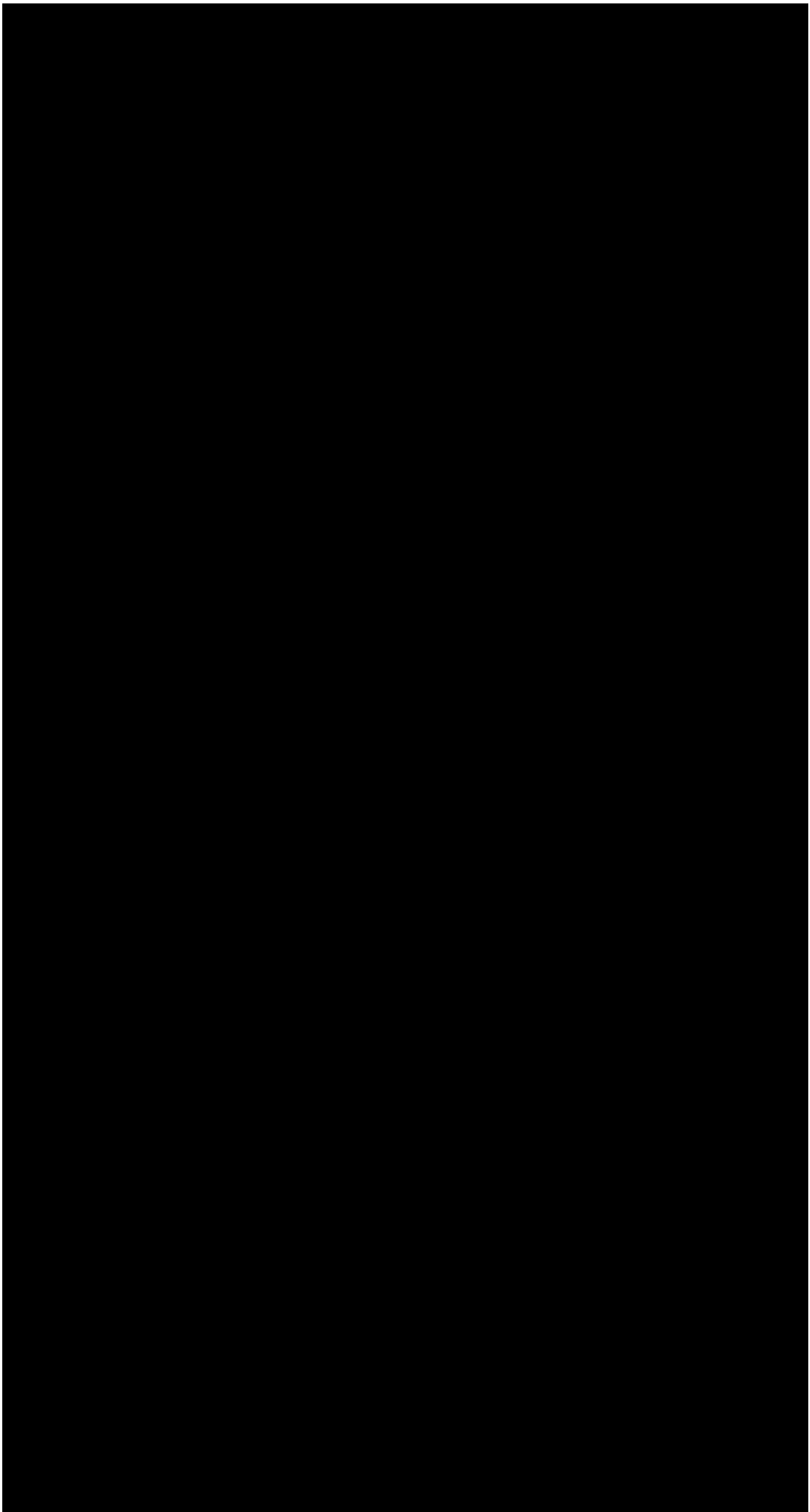


Figure 1.1 Map of eastern Australia showing Cainozoic volcanic provinces and principal tectonic units. Note the arcuate, discontinuous distribution of the provinces which are commonly located at tectonic boundaries. The three provinces which are the subject of this study are shown with bold capitals (e.g. **BUCKLAND**) and other provinces referred to in the text in lower case (e.g. McBride). Figure simplified from Ewart *et al.* (1988).

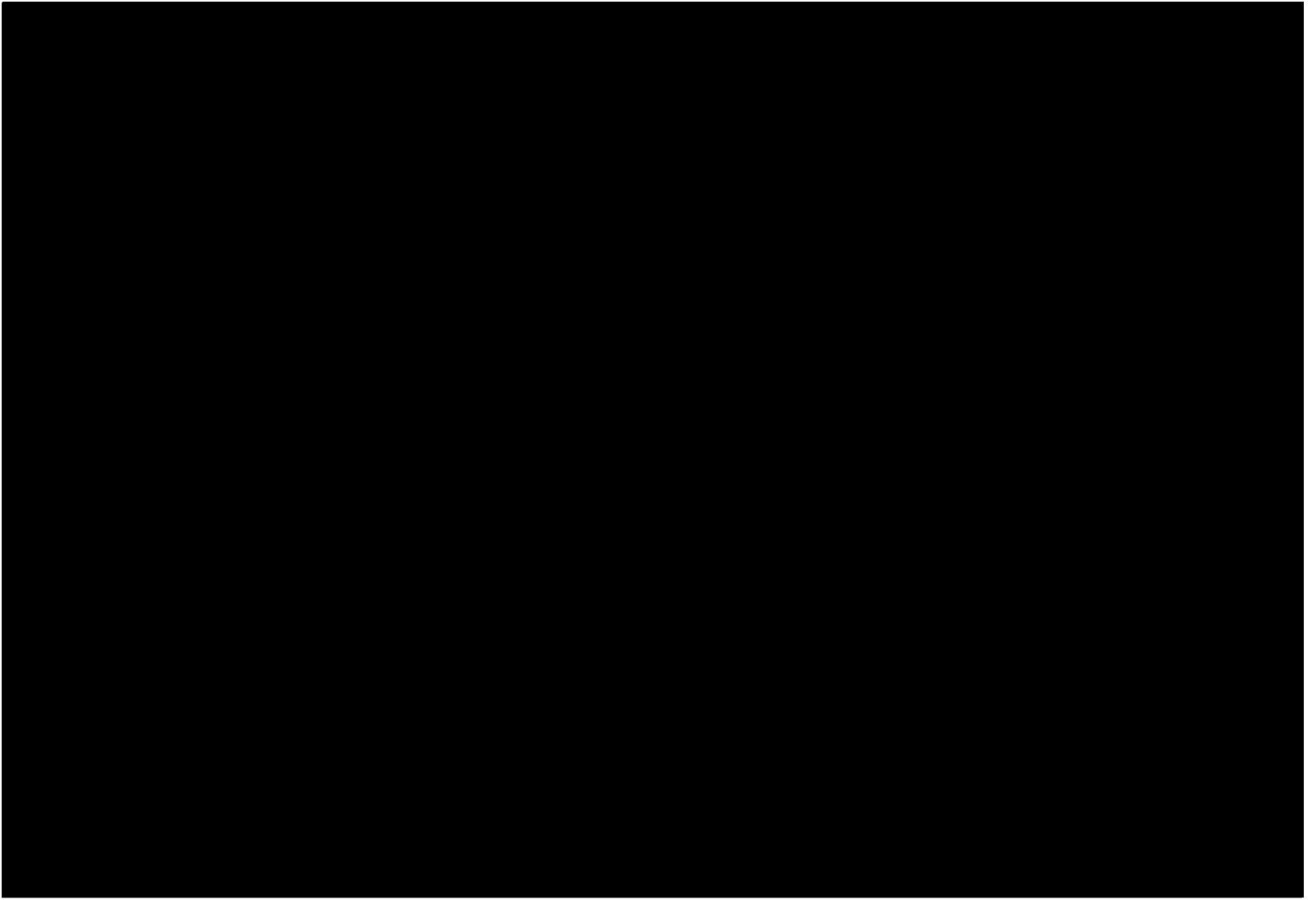


Figure 1.2 Age-latitude relationships shown by Cainozoic provinces in eastern Australia. Central volcanoes (filled circles) fit closely to a straight line corresponding to a velocity of 65mm/yr, while lava field provinces (open squares) show no correlation. The figure is redrawn from Duncan and McDougall (1989b).

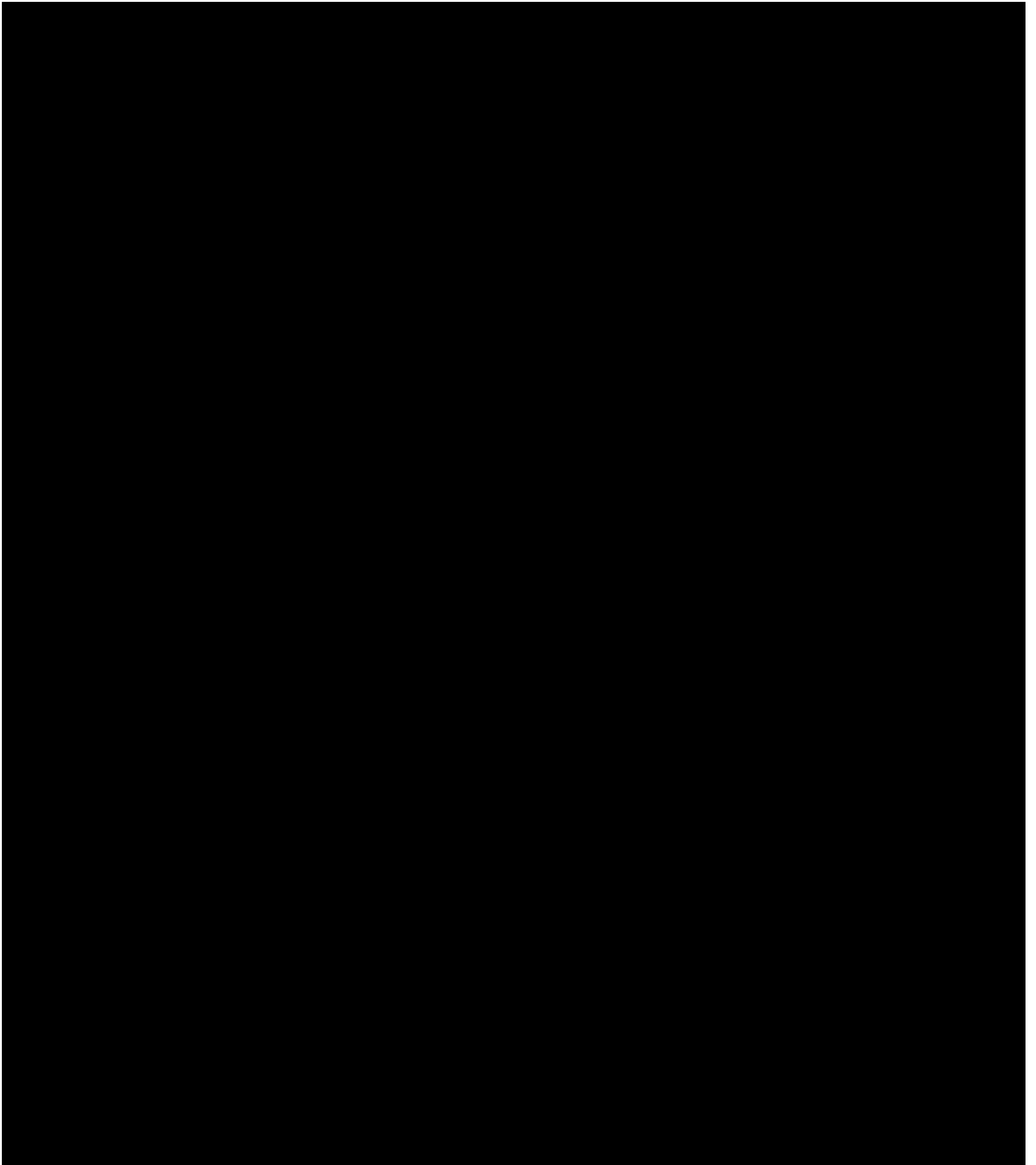


Figure 1.3 Unmigrated deep reflection seismic section from the southwestern part of the Buckland province. Reflections at the top of the section are thought to be Permo-Triassic sediments. There are three bands of reflectors (BR) at greater depths. The lowest of these (~35km) is interpreted to be the crust-mantle transition (Moho). D indicates diffractions. The figure and interpretation are from Mathur (1983). Vertical exaggeration is x3.

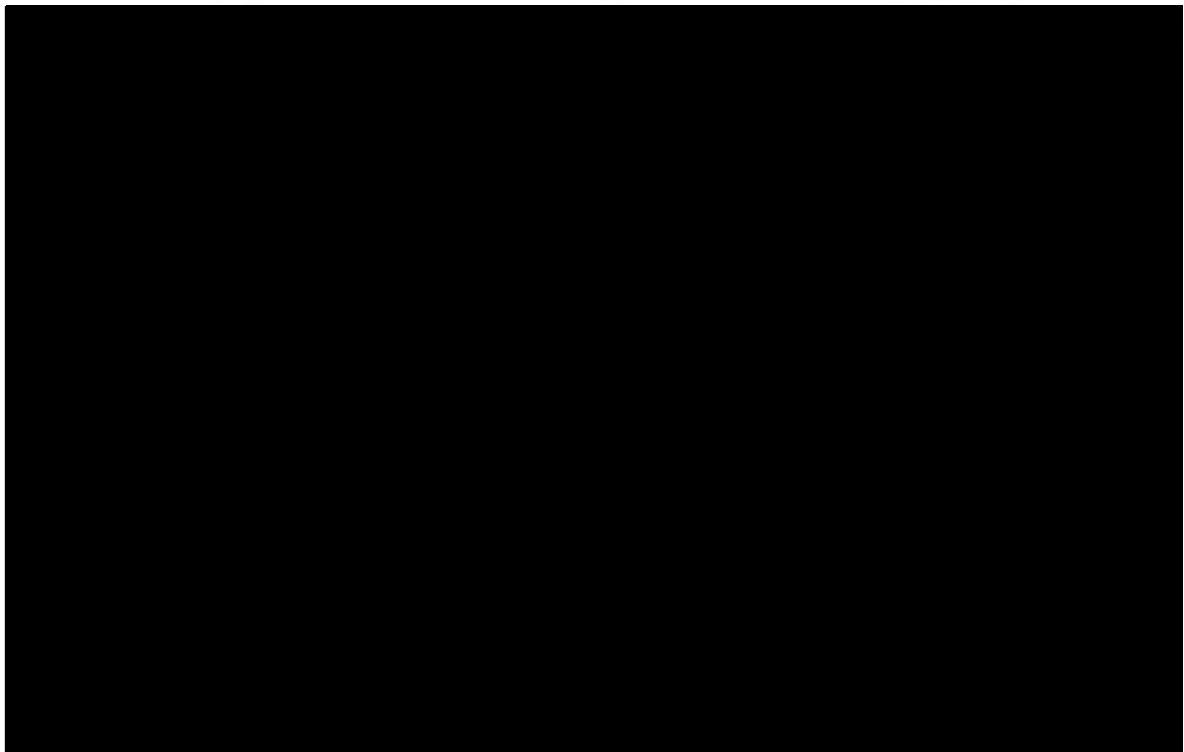


Figure 1.4 Upper mantle shear wave (V_s) models based on Rayleigh wave phase velocity data for the ‘east’ (non-cratonic) and ‘west’ (cratonic) regions of Australia. The figure is reprinted from Goncz and Cleary who note that the model becomes less reliable below 200km. See the text for discussion.

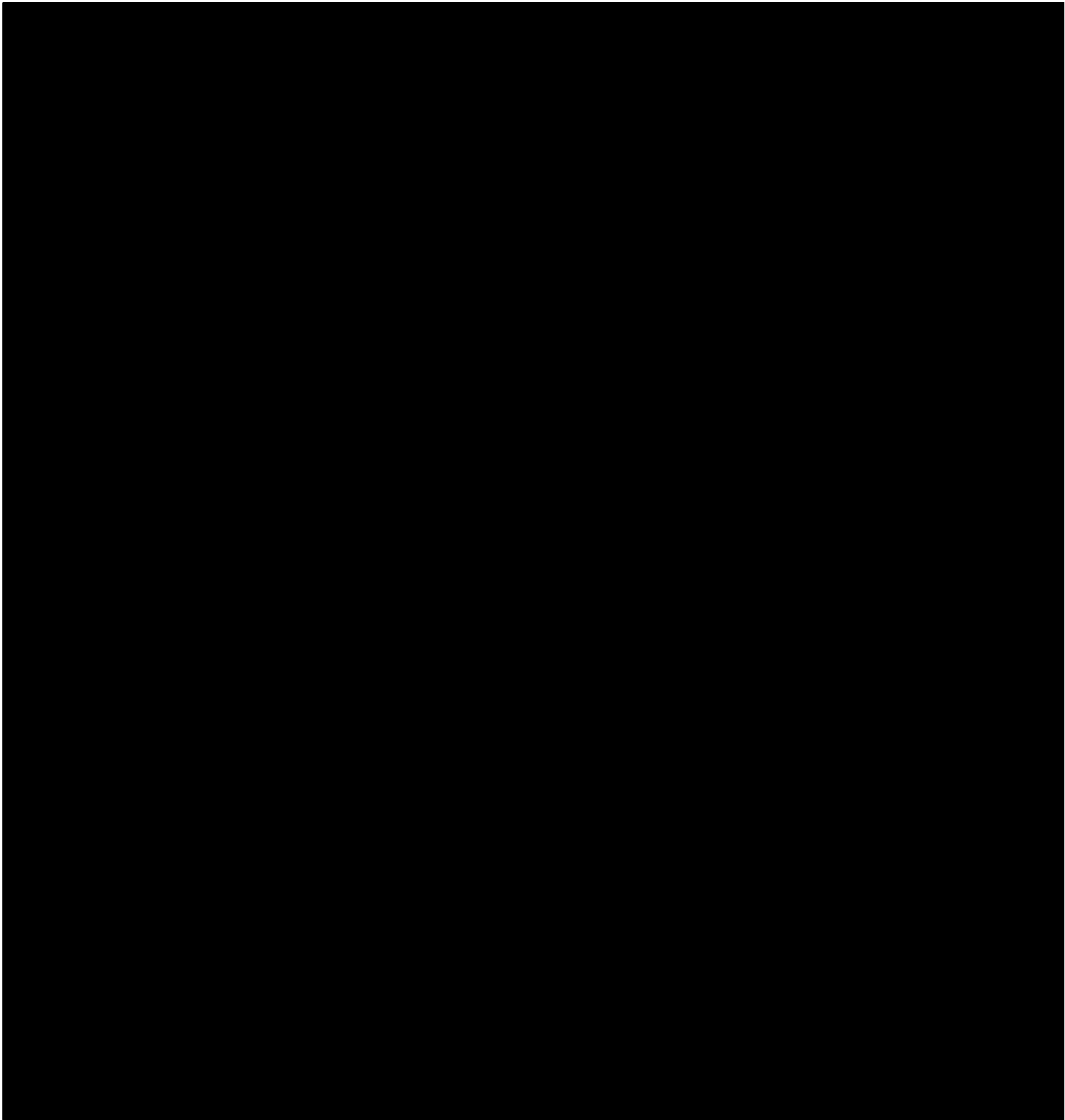


Figure 1.6 General plate tectonic features of the eastern part of the Indo-Australian plate reprinted from Duncan and McDougall (1989a). Filled circles represent central and leucitite-suite provinces on land, and seamounds in the Tasman Sea.

Figure 1.5 Velocity structure beneath Australia (after van Heijst, 1997) determined using surface wave overtone phase velocities. See the text for details. The horizontal resolution of the cross-section is on the order of hundreds of km, hence the apparent discrepancy with the craton-fold belt sketch map of Australia to the same scale (O'Reilly and Griffin, 1987).

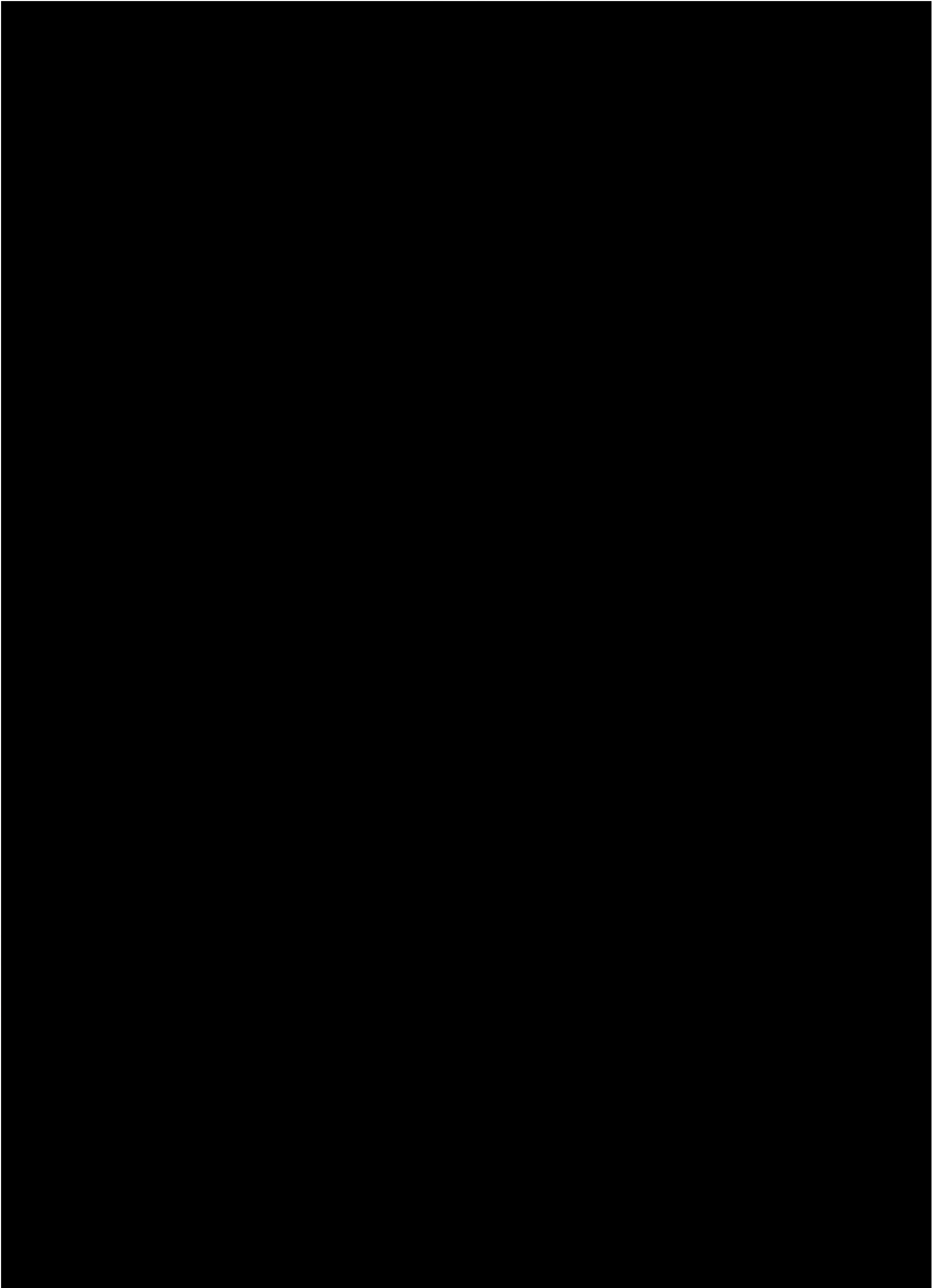




Figure 1.7 Model for intraplate magmatism in oceanic and continental settings from McDonough *et al.* (1985), based on the model of Chen and Frey (1983, 1985). An ascending hot mantle plume impinges on the base of the lithosphere, initiating melting within it. Resultant magmas are consequently a mixture of the two components. Plume compositions are likely to be the same in both settings, but the lithosphere is quite different: the oceanic type having a broadly MORB-type, isotopically depleted compositions, but the continental type being much more heterogeneous and generally more isotopically enriched. The isotopic composition for the continent illustrated here is based on spinel lherzolite xenoliths found in the Newer Volcanics of Victoria.



Figure 1.8 Sr-Nd isotopic characteristics of granulite xenoliths from eastern Australia. While many overlap with the field of host basalts (grey shading) others lie outside it. Possible explanations for this are discussed in the text. Figure is reprinted from O'Reilly *et al.* (1988).

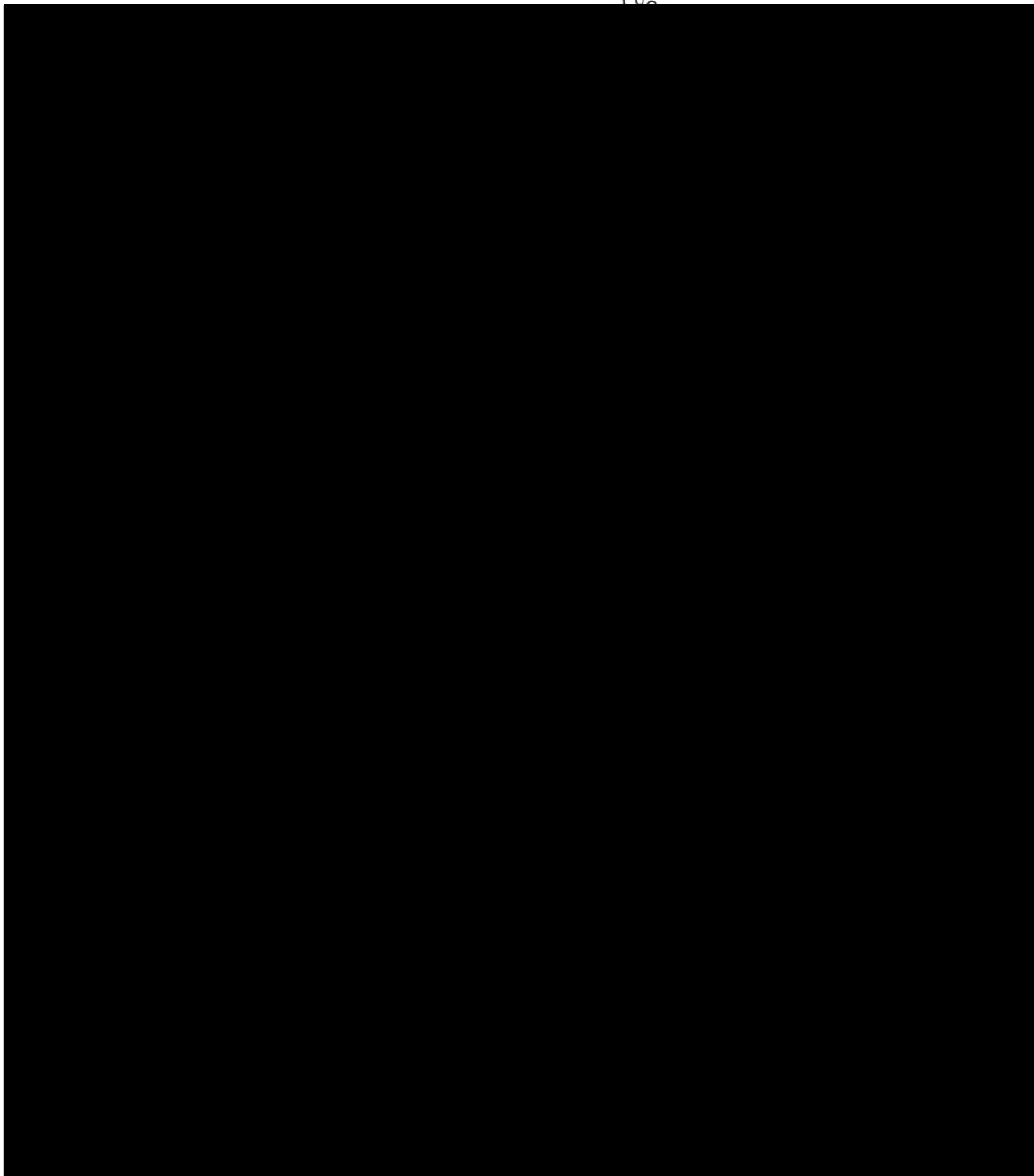


Figure 1.9a Pressure-temperature estimates from east Australian granulite and spinel lherzolites together with the southeast Australian geotherm defined by garnet websterites from Victoria (O'Reilly and Griffin, 1985). A seismic reflection profile (from Mathur, 1983) is also provided with the average regional crust-mantle boundary, defined by the predominance of spinel lherzolite, marked as 'CMB'. The figure is taken from O'Reilly *et al.* (1988).

Figure 1.9b Comparison of the southeast Australian geotherm of O'Reilly and Griffin (1985) with other geotherms from different tectonic environments around the world. Figure reprinted from O'Reilly (1989), based on a figure in Jones *et al.* (1983). The 'Alkaline Province Geotherm' links overlapping PT estimates from granulites from alkaline provinces in east Australia, Germany and Tanzania (Jones *et al.*, op. cit.).

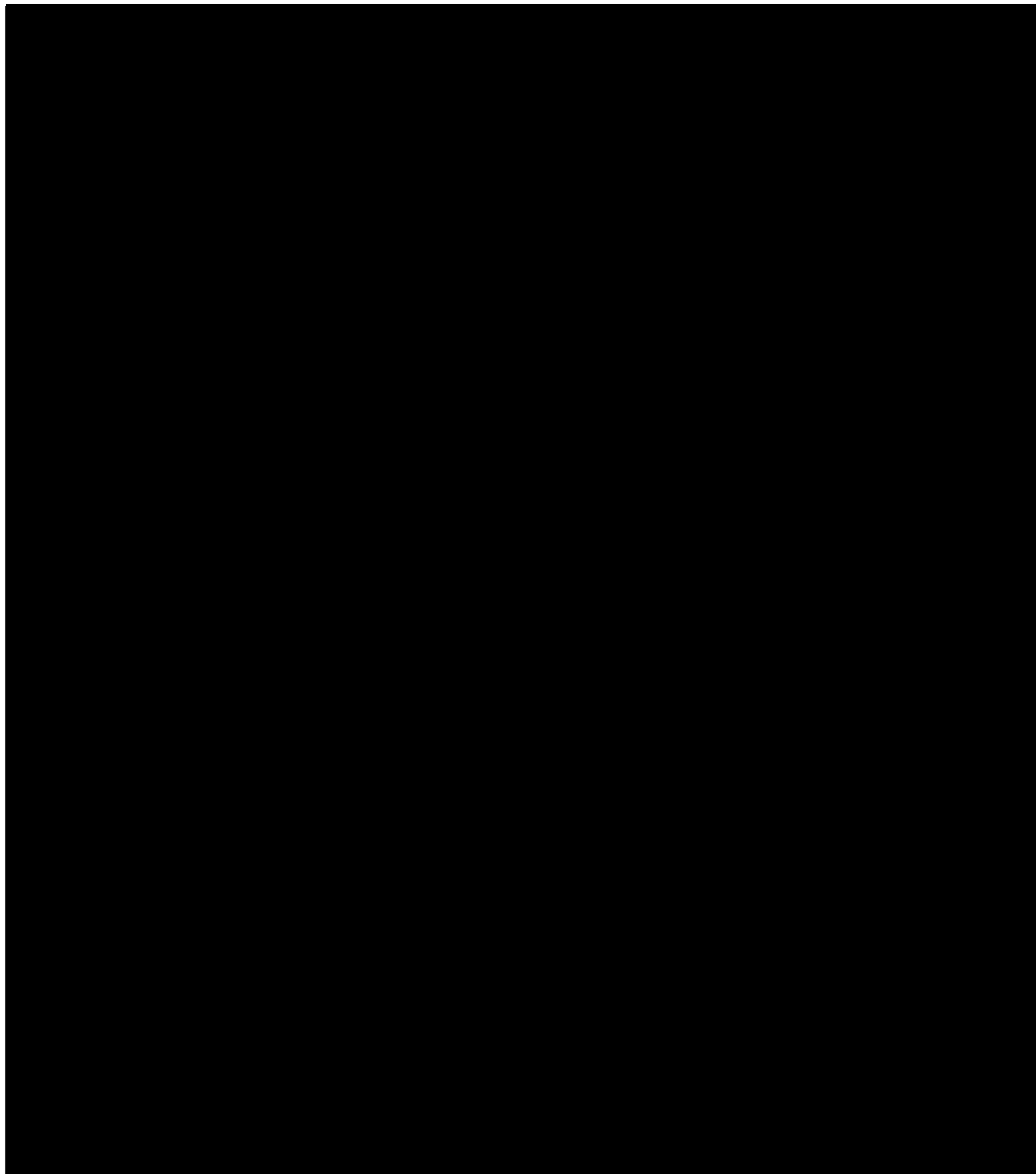


Figure 1.10 Models for the petrological structure of the east Australian lithosphere constrained by rock density (based on observed P-wave velocities) and xenolith data. From O'Reilly (1989).

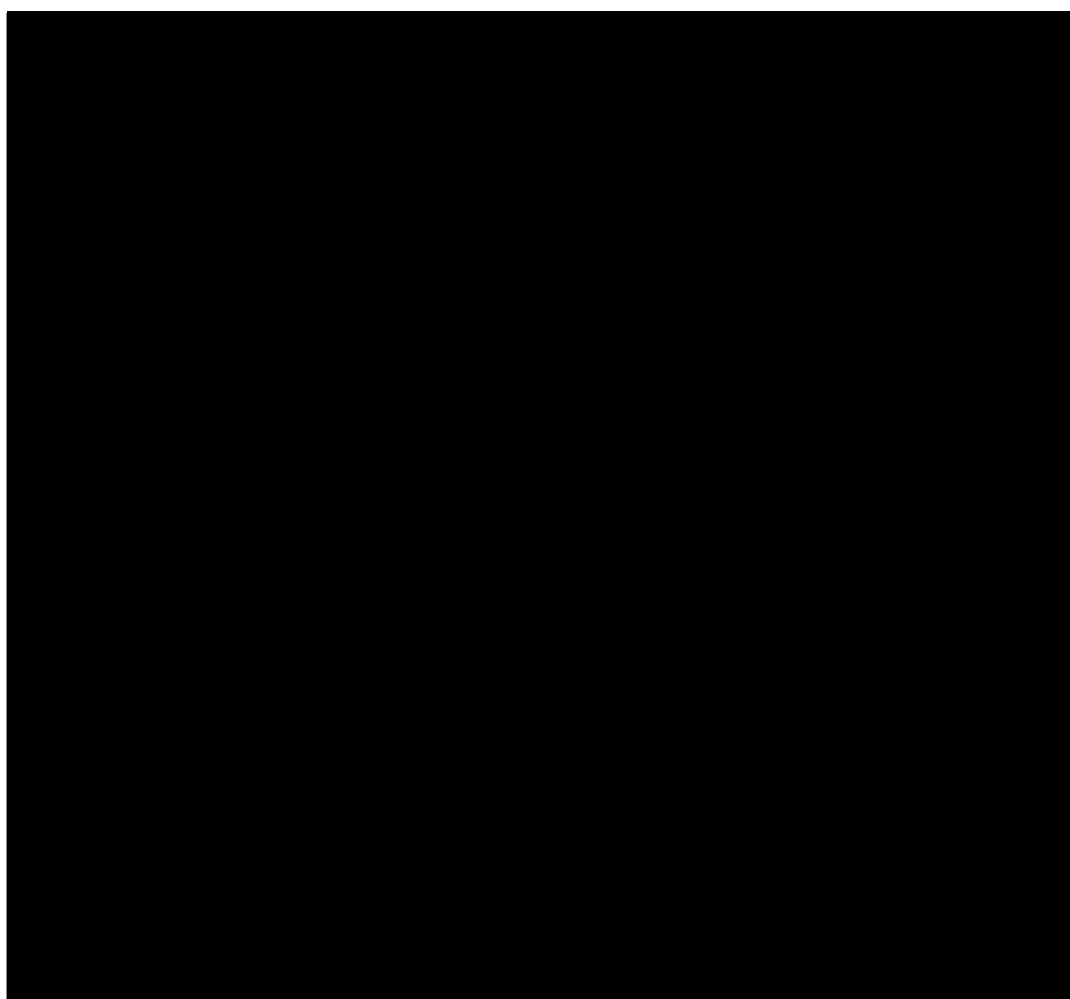


Figure 1.11 Cartoon taken from O'Reilly (1989), modified from Powell (1983) showing a possible crustal development model which results in a mafic lower crust, as is observed in eastern Australia. Mafic material is emplaced both tectonically and intrusively. Subduction/accretion episodes took in eastern Australia during the Palaeozoic (e.g. forming the New England fold belt), and there is also evidence for the intrusion of magma around the crust-mantle boundary during the Palaeozoic Mesozoic (approximately dated using isochrons: O'Reilly *et al.*, 1988).

Figure 1.12 Detachment model for the rifting event that resulted in the separation of eastern Australia from the Lord Howe Rise, which adequately explains the observed gross morphology of the region, e.g. its asymmetry. Extension and thinning took place by pure shear beneath the upper-plate margin, and gave rise to a broad region of asthenospheric upwelling beneath the upper-plate as well as the spreading ridge. Reprinted from Lister and Etheridge (1989).

Figure 1.13 Cartoon of the ‘plume swath’ model which Lister and Etheridge (1989) use to explain the age-progressive volcano provinces. Chains of rising diapirs or convective upwellings ascend from the asthenosphere, triggered by a rapid lithospheric extension event which preceded the one which led to the formation of the Tasman Sea. Hotspot traces are produced as the lithosphere drifts over the chains: in the illustration three hotspot traces will be produced from the three upwellings that are shown.

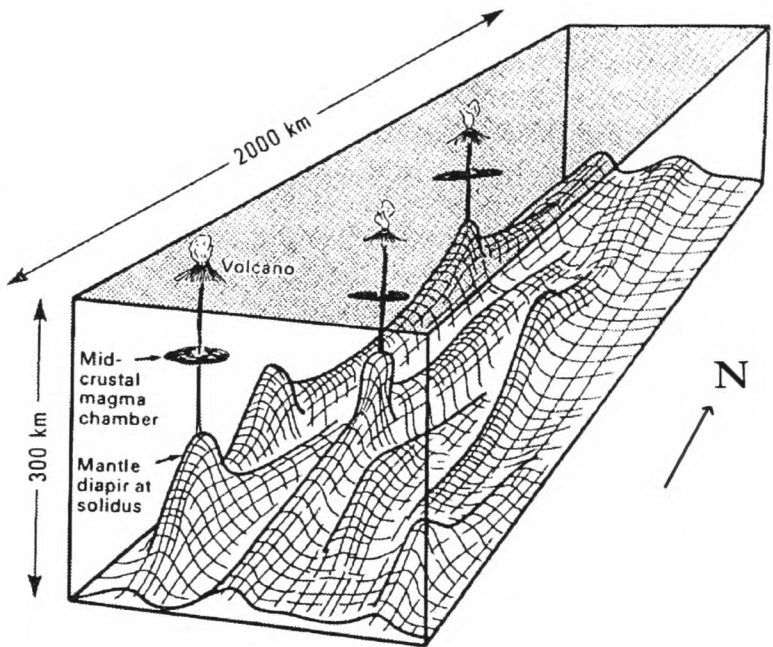


Figure 1.14 Positive correlations between Ba/Nb, La/Nb and $^{87}\text{Sr}/^{86}\text{Sr}$ for basalts from eastern Australia and various ocean islands. Input from the lithosphere or the crust can result in the increase of all three ratios. Reprinted from Sun *et al.* (1989).

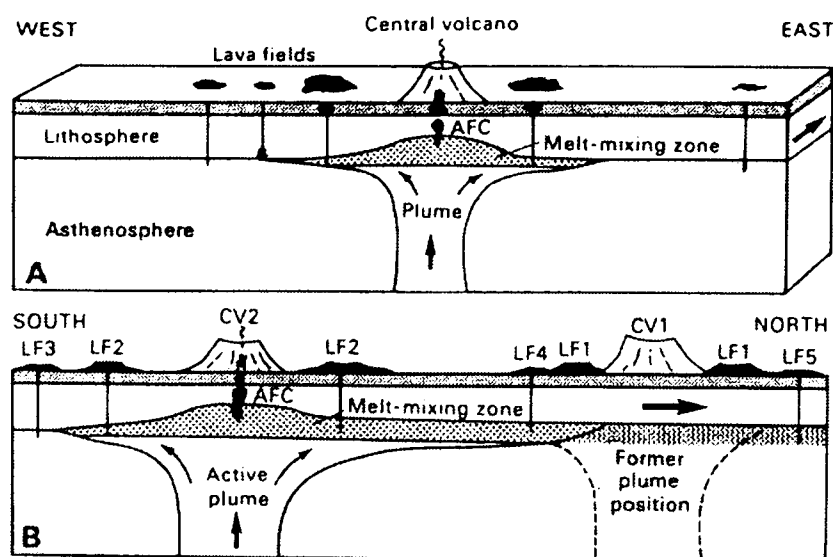
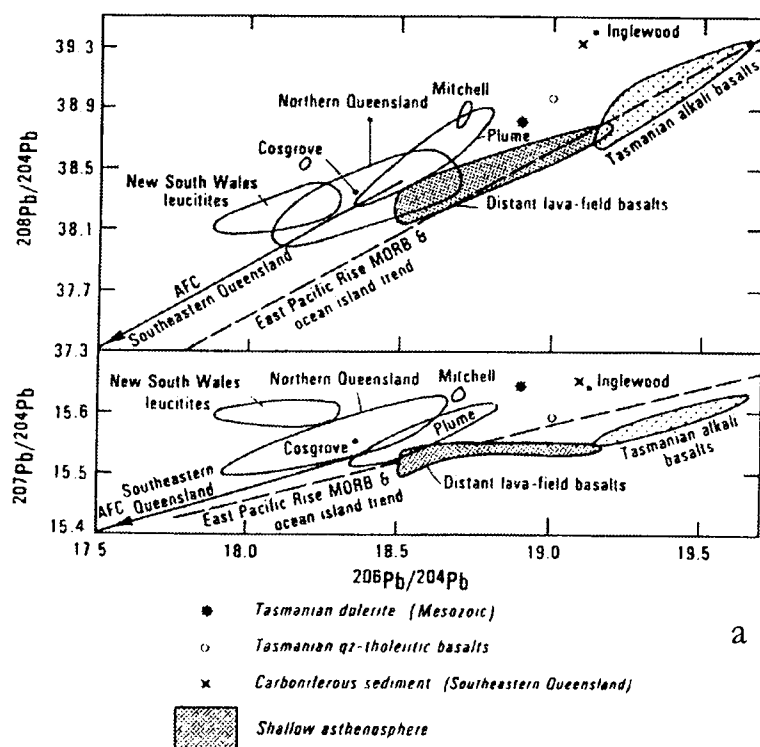
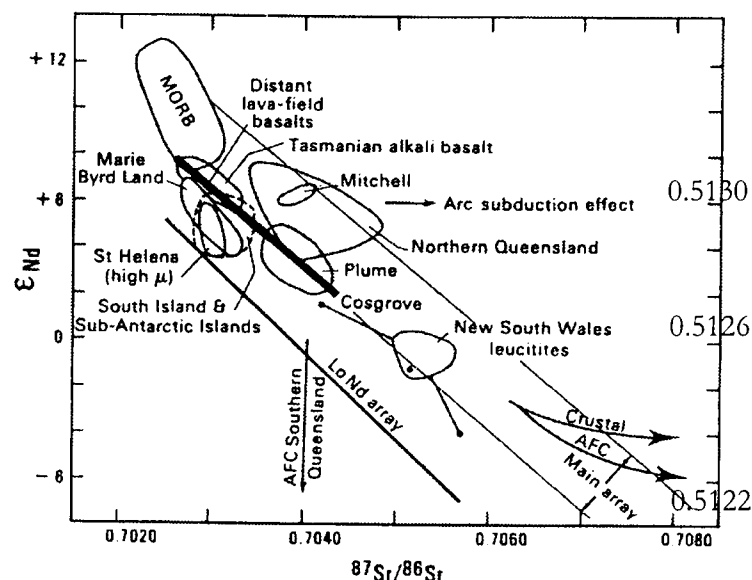


Figure 1.15 Illustration of the model presented by Sun *et al.* (1989) for Cainozoic volcanism in eastern Australia, involving the interaction of mantle plume, shallow asthenosphere, lithosphere and crust. Material from the ascending plume is channelled between the shallow asthenosphere and the lithosphere, permitting interaction of these components. The plume source dominates the central volcano (CV) basalts, as well as nearby lava field (LF) basalts of the same age (CV1 and LF1 etc.). Some lava field basalts in advance of the mantle plume (e.g. LF3) are derived from sources (asthenosphere $\pm$ lithosphere) that have not yet been affected by the plume, while later lava field basalts erupted well after the passage of the plume may be derived from plume-modified asthenosphere and lithosphere. Channelling of plume material may lead to the eruption of other lava field provinces (LF4) that are distant from the current plume position but adjacent to older lava field provinces.



a



b

Figure 1.16 Isotopic compositions of the inferred mantle plume (from least-fractionated central volcano lavas), shallow asthenosphere (distant lava fields, e.g. LF3 in Figure 1.15), and lithosphere (leucitites) components proposed by Sun *et al.* (1989), together with selected MORB and OIB for comparison. Reprinted from Sun *et al.* (op. cit.), where the data sources are given.

Approximate $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are provided alongside the ϵNd values.



Figure 1.17 Illustration of the multiple-hotspot hypothesis of Wellman and McDougall (1974) and Sutherland (1983). They propose that central volcano and leucitite provinces in eastern Australia result from the impact of three hotspots (numbers 1-3), rather than the channelling of magma away from the main trace of a single hotspot (e.g. Figures 1.15, 1.18). Of the three proposed hotspots, only number 2 can be located in its present position NE of Tasmania (Wellman, 1989). Filled circles are dated volcanoes, open circles are undated. Reprinted from Sun *et al.* (1989).

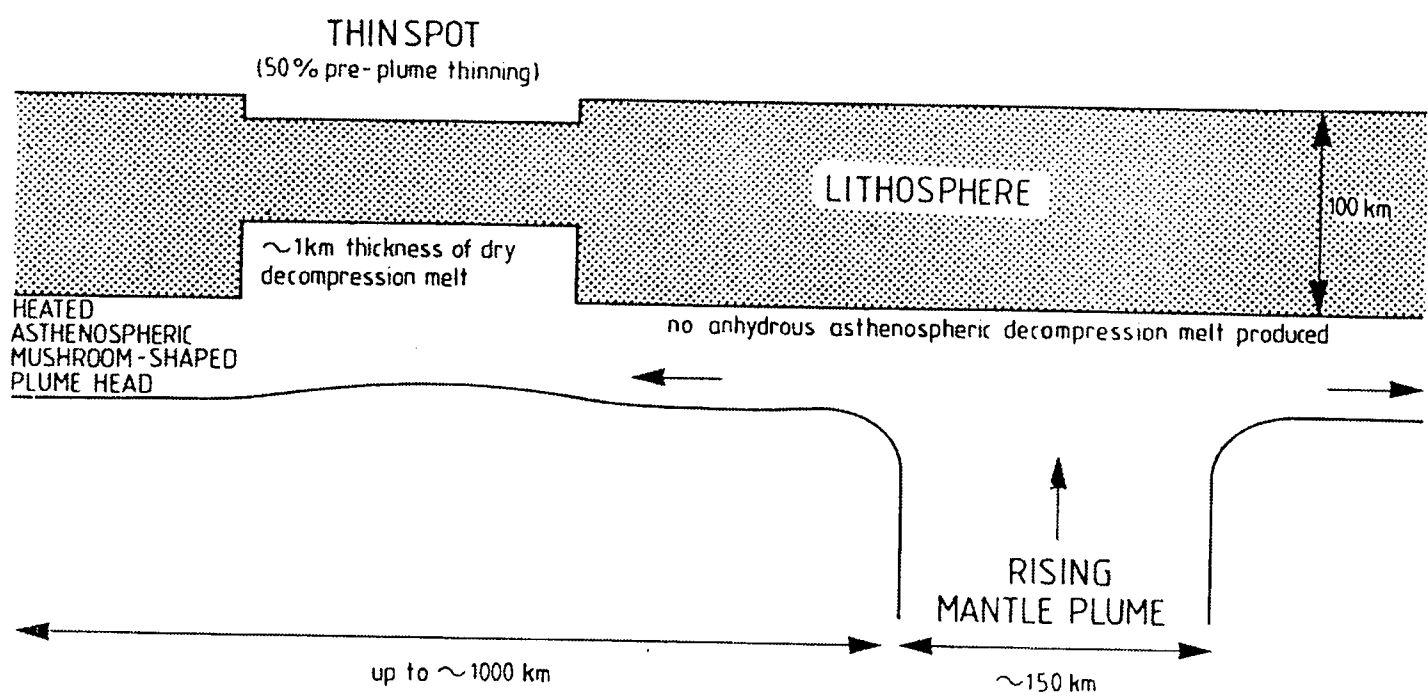


Figure 1.18 Sketch of the ‘thin-spot’ model of Thompson and Gibson (1991), reprinted from their paper. A mantle plume rising beneath thick lithosphere is deflected along the base of it, with decompression and partial melting taking place where the lithosphere thins. This model could explain the non-linear distribution of the central volcano provinces in eastern Australia, and their derivation from a single hotspot.

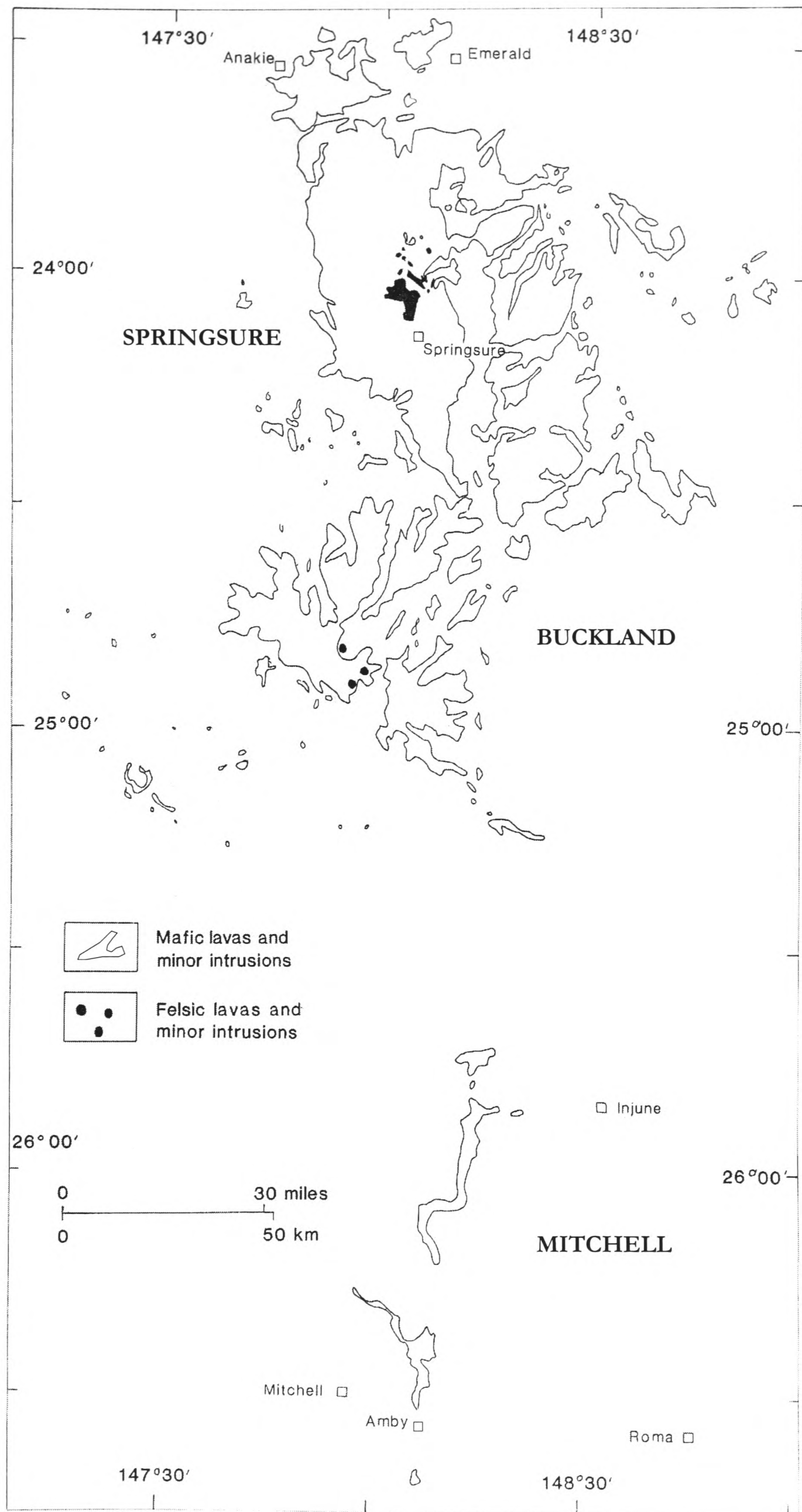


Figure 1.19 Map of the area of study, showing the relative positions of the Buckland, Springsure and Mitchell provinces, distribution of Cainozoic igneous rocks, and principal settlements. After Sutherland (1989).

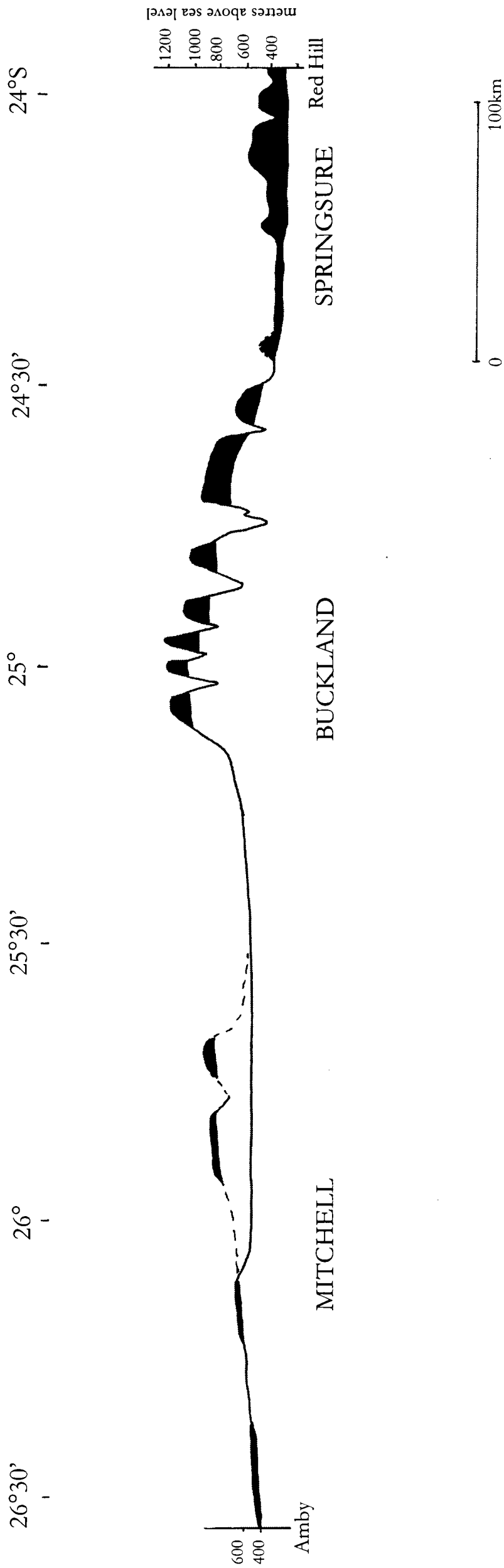


Figure 1.20 Sketch section through the field area, from Amby in the south to Red Hill in the north and passing through the main Mitchell Buckland and Springsure sequences. Important sequences that actually lie off-section e.g. north Mitchell, are shown with dashed lines. Note the gradual increase in height and thickness of the lava through Mitchell and into Buckland while the Springsure lavas, of comparable thickness to those from Buckland, are less elevated. Based on regional 1:250,000 and BMR geological 1:250,000 maps.

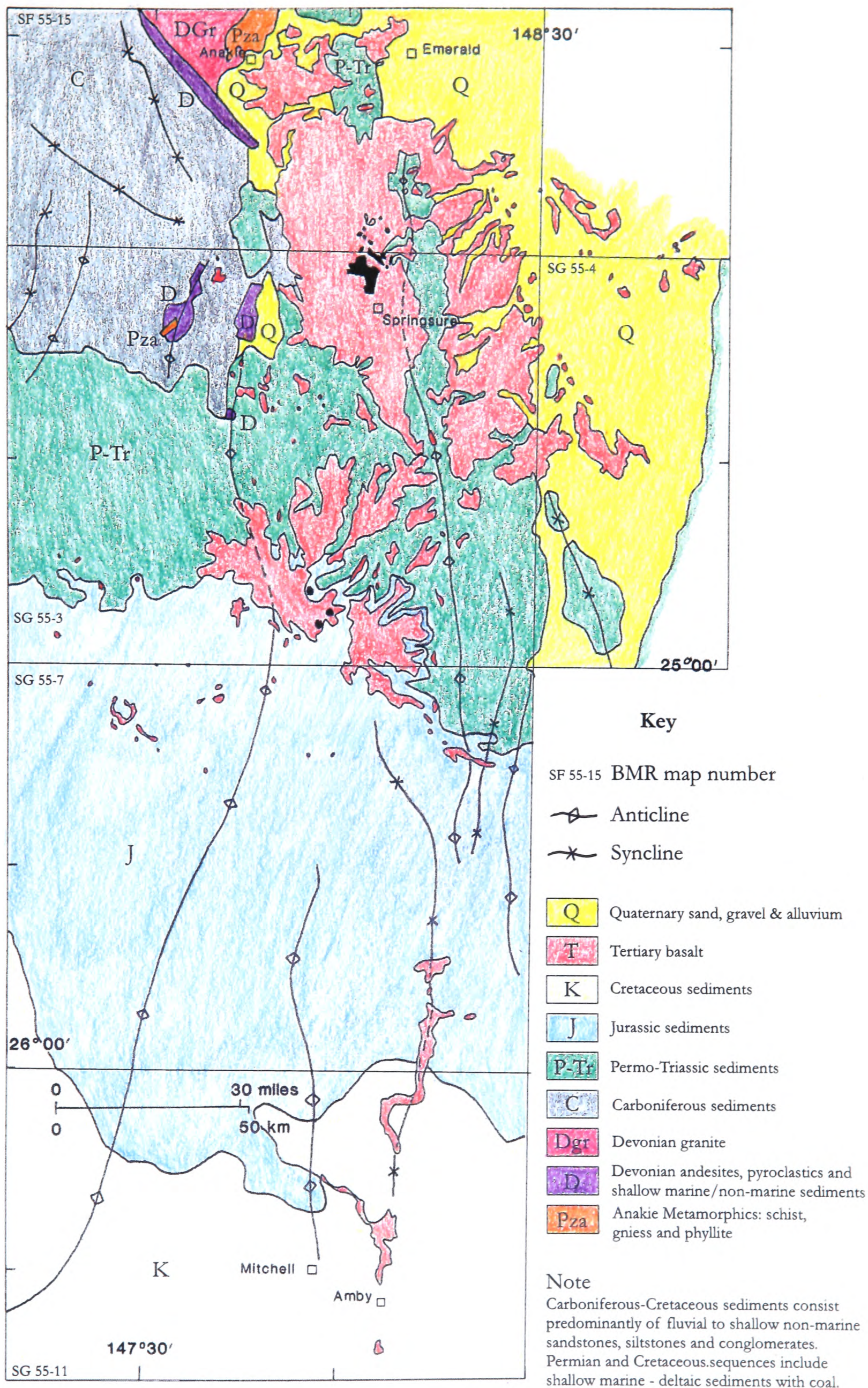


Figure 1.21 Geological sketch map of the study area, based on BMR 1:250,000 maps SF 55-15, SG 55-3, 4, -7, -11.



Figure 1.22 Histogram of the SiO_2 content of analysed Cainozoic volcanic rocks from central-southeastern Queensland, reprinted from Ewart *et al.* (1980). The strongly bimodal distribution of lava compositions is clearly demonstrated.

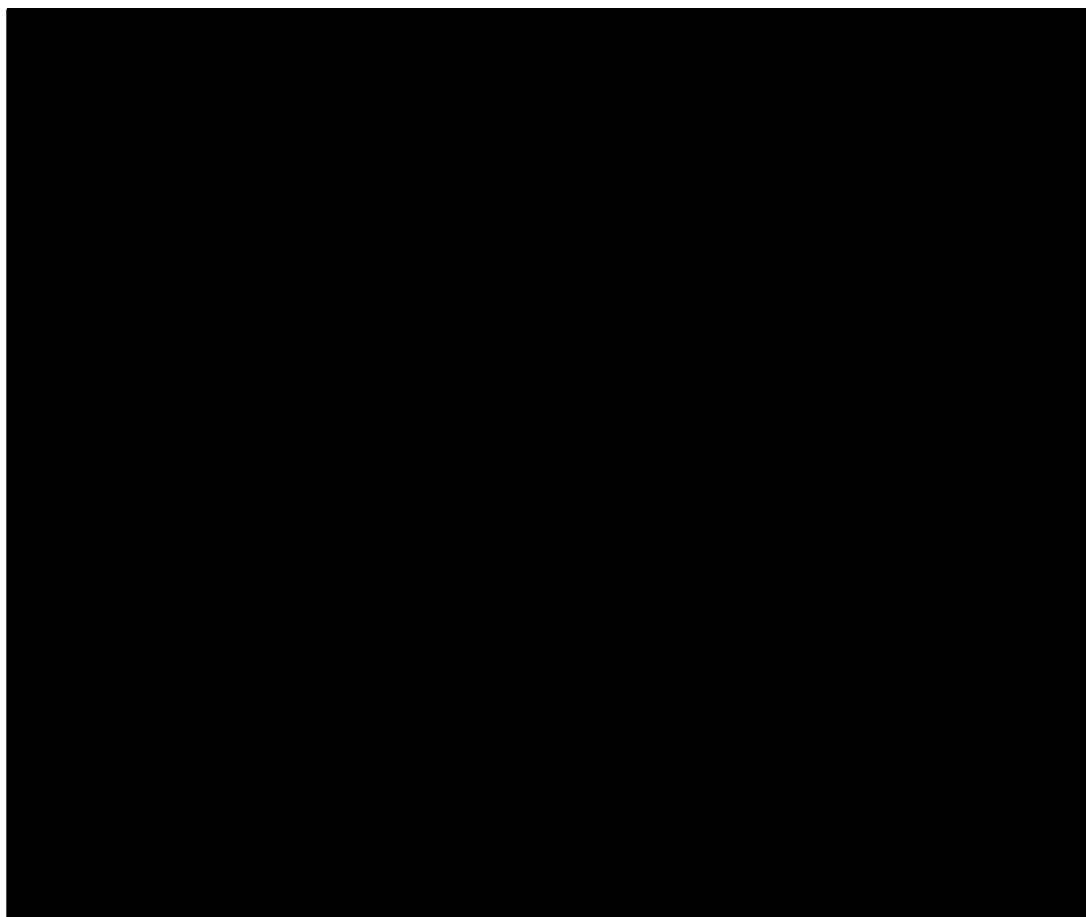


Figure 1.23 Cartoon showing the magmatic underplating model for the petrogenesis of central volcano lavas in central-southeastern Queensland from Ewart *et al.* (1980). Ascending magma ponds in the lower crust where it cools and crystallises high-pressure mineral phases (which are brought to the surface as megacrysts). The wide range of magma compositions produced in the lower crust may be further modified by higher-level fractionation processes before eruption. A product of the extensive underplating is uplift of the surface, hence the elevated topography of many central volcano provinces.

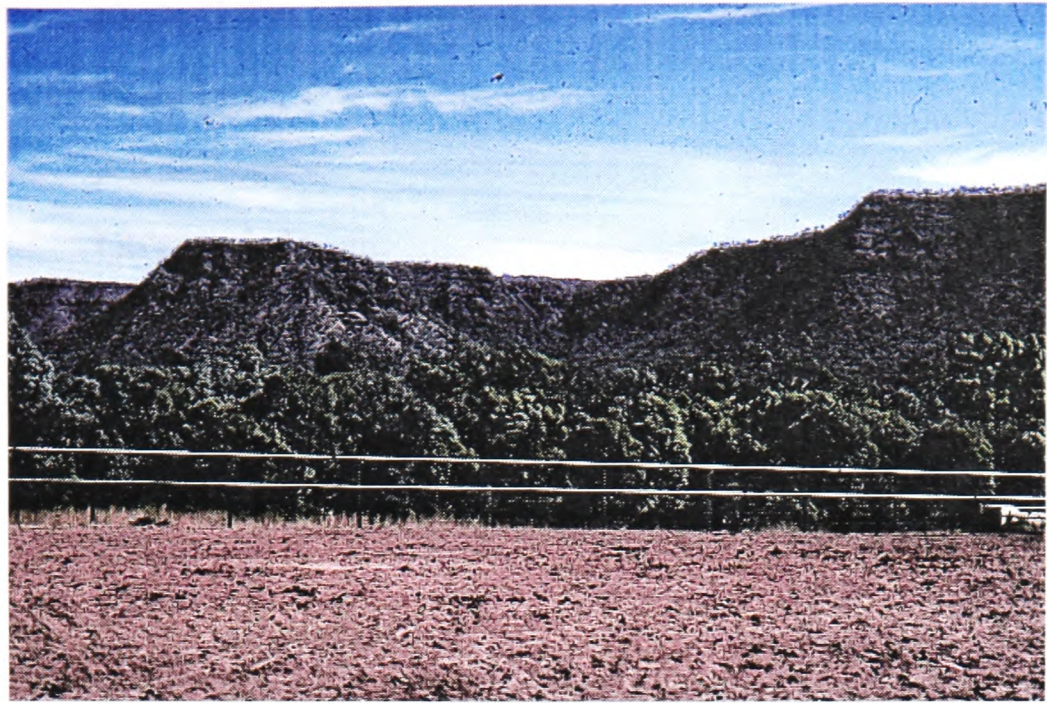


Plate 1.1 Photo of typical tableland topography at Vandyke in the Buckland province. Note the near-horizontal lava flows.



Plate 1.2 Photo illustrating the scenery to the west of the main Buckland shield. Eroded volcanic plugs rise up to 300m above the floor of the flat-lying schlerophyll forest.



Plate 1.3 An illustration of the scenery around Springsure with flat-topped features of lava rising from low-lying plains of black soil where the lava flows have been eroded away.

Nephelinites and leucitites	5.7
Basanites	9.6
Alkali basalts	5.3
Olivine tholeiites	13.0
Quartz tholeiites	8.4
Trachybasalts/ andesitic trachybasalts	40.3
Trachytes and rhyolites	17.7

Chapter 2: Data collection, analysis and comparison

2.1 SAMPLING STRATEGY

The aim of the fieldwork carried out in May-June 1995 was to sample the lavas of the Buckland province as comprehensively as possible, with particular emphasis on complete sections through the lava pile, and to supplement these with samples from the Springsure and Mitchell provinces in order to investigate inter-province variation over relatively small (~200 km) distances.

The sub-tropical grassy and open sclerophyll forest, poor outcrop and difficulty of access due to lack of vehicle tracks restricted the choice of sample localities. Therefore collecting was attempted at sections which had been sampled by previous workers (e.g. Battleship Spur in Buckland), but mainly at places which showed good sampling potential, i.e. those which were accessible with a four-wheel-drive vehicle, where a good thickness of lava was present (estimated using the geological and topographical maps), where there was potentially reasonable exposure (usually suggested by the presence of a creek) and finally subject to the permission of the relevant landowner (almost invariably given). Assistance was also given by the rangers of the Queensland National Parks and Wildlife Service (which owns sizeable amounts of land in the area) who know local landowners as well as likely sampling localities.

Three main sections were sampled in Buckland: at Battleship Spur, Carnarvon and Van Dyke (Figure 2.1). Smaller sections were collected at other localities where accessibility or outcrop precluded fuller sampling, while still other individual samples were taken from road cuttings, quarries etc. where opportunities presented themselves. In the Springsure province, sections were sampled along the east-west Rolleston Road, at Mt. Walleroo and also at Mt. Catherine in the extreme south of the province. Individual samples were also taken at numerous other localities, including representative felsic plugs and domes north of the town of Springsure. In the southern part of Mitchell, samples were taken at the roadstone quarries near Amby and at various localities to the north where the lava thickness is generally no greater than 30 m. In the northern part of the province, samples were taken from Womblebank Gap where the road follows an eroded gap through the lava flows. A full list of samples with grid reference localities is provided in Appendix A, while Figure 2.1 shows the principal sampling localities on a map of the field area.

A brief summary of the geochemistry of the lavas according to their geography is presented in section 2.2.5, while a more detailed study of geographical and up-sequence variation is given in Chapter 6. Ultramafic xenoliths were retrieved from lava flows and plugs at several localities and are also described in Chapter 6.

2.2 WHOLE-ROCK GEOCHEMISTRY

2.2.1 Introduction

This section outlines the geochemical characteristics of the 153 samples which were analysed in this study, and subdivides them for more detailed discussion in subsequent chapters. Major and trace element compositions were determined by X-ray fluorescence (XRF) methods (see Appendix B for the methodology and full data-set); all analyses totalled between 99% and 101% and were normalised to 100% (anhydrous: all Fe as Fe₂O₃) for plotting and comparative purposes.

2.2.2 Classification

The samples are classified according to the Total Alkalis (Na₂O+K₂O) vs. Silica (TAS) diagram of Le Maitre (1989), shown in Figure 2.2.

The frequencies for each rock type are:

Basalt	67
Trachybasalt	48
Basanite	20
Basaltic andesite	6
Rhyolite	5
Basaltic trachyandesite	4
Trachyte	2
Phonotephrite	1

There is clearly a broad range of compositions represented by the lavas. The greatest number are basaltic/trachybasaltic with a peak on the boundary at 50% SiO₂/5% Total Alkalis. There are examples of rather primitive compositions - the silica undersaturated basanites - while highly evolved rocks, namely trachytes and rhyolites are all oversaturated. The samples form a bimodal distribution strongly skewed towards the mafic compositions, which is typical of eastern Australian volcanic provinces and other continental lava sequences world-wide (section 1.1.5).

The 67 basalts were further divided on the basis of their normative characteristics: alkali basalts being nepheline normative, olivine tholeiites hypersthene normative, and quartz tholeiites quartz normative. Frequencies for these are given below:

Alkali basalt	9
Olivine tholeiites	54
Quartz tholeiites	4

The CIPW norms of the mafic samples (calculated assuming $\text{Fe}_2\text{O}_3/\text{FeO} = 0.2$) are illustrated graphically in Figure 2.3 where they are projected onto the *ne-di-ol-hy-qz* planes. There is a virtually unbroken spread of silica saturation from the most undersaturated basanites (which contain 22% normative nepheline) to oversaturated basaltic andesites (which contain 10% normative quartz), although it is clear that the majority lie within the saturated *ol-di-hy* sector of the diagram. It is noteworthy that two thirds of those that lie in the undersaturated *ne-di-ol* sector are primitive compositions, containing $> 9\%$ MgO. Most mafic samples contain normative andesine; the principal exceptions being the basanites and the *qz*-tholeiites which contain normative labradorite.

2.2.3 Major and trace element characteristics

In Figure 2.4 major element oxides and trace elements are plotted against MgO which can be regarded as a measure of the degree of crystal-liquid fractionation, since removal of the common fractionating phases olivine and clinopyroxene from basaltic melts reduces the MgO content of the residual liquid. The main characteristics of the data are summarised below:

Major elements: Silica content increases from 40 to 55% through the mafic compositions, although it appears to be more or less constant at $\sim 50\%$ between 5 and 8% MgO. Titanium and iron (as Fe^{3+}) decrease from 15 to 9% MgO, and then increase as MgO continues to fall; concentrations are low in the evolved trachytes/rhyolites. Aluminium increases with falling MgO, and reaches 15-17% in the evolved lavas; CaO decreases over this interval, and drops finally to $<0.1\%$ where $\text{MgO} < 0.1\%$ (i.e. below the limits of detection). Sodium, potassium and phosphorus correlate positively with MgO where $\text{MgO} > 9\%$, but negatively in more evolved mafic compositions. Na and K reach 5-6% in the felsic rocks, while concentrations of P fall below detection limits.

First Transition series elements: Nickel and chromium show the positive linear covariance with MgO which is usual for compatible trace elements during fractional crystallisation or partial melting in basaltic systems; concentrations of both elements fall below detection limits at 2-3% MgO. Copper behaves similarly, but with a great deal more scatter. Cobalt concentrations fall steadily with MgO and are as scattered as Cr, but concentrations drop to only 2-12 ppm in the felsic compositions. Vanadium concentrations are scattered between 100 and 180 ppm for nearly all samples; the most evolved mafic samples contain ~ 50 ppm, dropping below detection limits in the trachytes and rhyolites. In contrast to all the above, zinc behaves more like the incompatible trace elements described below: concentrations rise steadily from ~ 100 to ~ 150 ppm as MgO decreases throughout the mafic compositions, while the evolved trachytes/rhyolites contain between 100 and 300 ppm.

Incompatible elements: In general it is to be noted that rather scattered, but generally positively correlating trends are seen for samples with 9-12 % MgO. In mafic samples with MgO<9% there is less scatter and the correlation between elements and MgO is negative. In the evolved trachytes and rhyolites, concentrations are either higher than in the mafic samples (Rb, Nb, Zr, Y, Ga, Pb, Th and U), or lower (Ba and Sr: both close to detection limits). Note also that the concentrations of incompatible elements in these evolved samples can vary by up to a factor of two e.g. Zr from 450 to 900 ppm and Rb from 120 to 180 ppm. Interestingly, concentrations of Zr form two populations in the felsic samples - one containing 450-600 ppm and another 850-900 ppm. This is not observed for any other elements.

The possibility of hydrothermal alteration is examined in Figure 2.5 which contains plots of three mobile elements (Na, K, Ba) and one immobile element (Nb) against 'loss on ignition' (weight % of volatiles lost during heating of each sample at 1000 °C overnight). Systematic alteration would be expected to result in correlations between the two variables in mobile element plots, but clearly no such correlations are observed. Furthermore, the immobile element plot is very similar to the mobile element ones. These observations argue against significant alteration of the samples.

2.2.4 Isotopic data

All samples containing > 9% MgO have been analysed for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ten of which have been analysed additionally for $^{143}\text{Nd}/^{144}\text{Nd}$. A description of the analytical methodology and the data, complete with age correction to 25 Ma, is provided in Appendix D.

The ten samples analysed for both isotopic ratios are presented in Figure 2.6, with fields for OIB (Thompson *et al.*, 1998) and Pacific & Indian MORB (Ferguson and Klein, 1993) shown for comparison. The $^{87}\text{Sr}/^{86}\text{Sr}$ characteristics are discussed more fully in Chapters 4 and 5.

2.2.5 Subdivision into smaller units

A relatively large data-set such as presented in this study cannot be analysed as one unit, but clearly needs to be divided into more manageable subsets. Non-analytical parameters such as geographical location cannot accomplish this satisfactorily. It is clear, however, from Figure 2.4 and the brief descriptions presented above that different geochemical trends are shown by the data within different ranges of MgO content. Consequently the data-set is divided into four groups on this basis: evolved felsic compositions which contain concentrations of MgO scarcely above detection limits, mafic samples which contain 2.5-9% MgO (hereafter referred to as '2.5-9 group'), 9-12% MgO ('9-12 group') and those exceeding 12% ('12+ group'):

1. The first of these groups consists of the trachytes and rhyolites which contain high concentrations of SiO_2 (68-73%), negligible MgO , and either highly depleted or enriched trace element concentrations (e.g. Ba below detection limit; 850 ppm Zr).
2. The 2.5-9 group encompasses the majority of the analysed samples, and consists of basaltic compositions which appear to be related by crystal-liquid fractionation processes, wherein compatible element concentrations decrease and incompatible element concentrations increase with decreasing MgO content.
3. An inflexion visible on plots of several elements vs. MgO (e.g. TiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, Nb and Zr) at 9% MgO marks the lower limit of the 9-12 group. Behaviour of elements here is quite different to that in the 2.5-9 group, and it is to be noted that only SiO_2 and Al_2O_3 concentrations increase with decreasing MgO , while *all* others (major and trace) behave in the opposite manner. Hence the interesting and unusual observation that compatible and incompatible trace elements such as nickel and barium behave in the same fashion.
4. Samples in the '12+' group contain more than 12% MgO and form a set distinct from the 9-12 group, containing lower concentrations of $\text{Fe}_2\text{O}_3\text{T}$ and incompatible trace elements, and exhibiting more 'normal' basaltic trends, i.e. compatible and incompatible trace elements showing broadly positive and negative correlations respectively with MgO .

The geochemical characteristics these groups will be discussed at greater length in the following chapters.

2.2.6 Geographical variation

A brief description is given here of the principal petrological characteristics of the three provinces, a summary of which is given in Table 2.1 below.

Buckland The main sequences are dominated by olivine tholeiites and trachybasalts, with occasional flows of basanite (Battleship Spur only) and alkali basalt. The region of volcanic plugs and intrusions to the west of the main shield, at around 25°S, consists almost entirely of silica undersaturated compositions - mostly basanites.

Springsure Mafic lavas are almost invariably silica saturated in this province, with only two oversaturated basaltic andesites and one alkali basalt. Evolved felsic compositions are more common than in the other provinces (Buckland has three minor mapped intrusions, and Mitchell none), with a concentration of rhyolite/trachyte plugs and lava flows occurring in the Minerva Hills, north of the town of Springsure.

Mitchell Lavas from the southern part of the province, around Mitchell and Amby, are all silica oversaturated, consisting of *qz*-tholeiites and basaltic andesites. The northern part, in contrast, consists of trachybasalts, a basaltic andesite and a basaltic trachyandesite, 40% of which are silica-oversaturated.

	Buckland	Springsure	N. Mitchell	S. Mitchell
Basanite	21(16)			
Alkali basalt	6(3)	2		
Phonotephrite	1(1)			
Trachybasalt	35(1)	8	5	
Olivine tholeiite	41(2)	13		
Basaltic trachyandesite		3	1	
Quartz tholeiite	1(0)			3
Basaltic andesite		2	1	3
Trachyte		2		
Rhyolite		5		
Total	105(23)	35	7	6

Table 2.1 Geographical distribution of analysed lava types. Numbers in brackets in the Buckland section refer to samples from the area of plugs and intrusions west of the main structure. The Mitchell province is divided into two to emphasise the difference between compositions in the north (~25°45’S) and the south (south of 26°15’).

2.3 GEOCHEMICAL COMPARISON WITH OTHER AREAS

The characteristics of Cainozoic volcanism in eastern Australia were comprehensively reviewed in Chapter 1, and showed that Buckland appeared to be a typical central volcano-type province. This proposal will be investigated in this section using the geochemical data described in section 2.2. Comparison will also be made with volcanic centres from around the world (western US, western Europe and eastern China) which share characteristics with east Australian provinces, being dominantly mafic in character, Cainozoic in age and related to extension and rifting. These centres contain primitive lava compositions which have been used to develop models for their origin, and which could provide useful clues to the petrogenesis of primary Buckland lavas.

2.3.1 Eastern Australia

Evidence presented in Chapter 1 showed that the Buckland province shares important characteristics with central volcano provinces for which the primary magma source is considered to be a plume. The wide spread of compositions in these provinces is held to result from the action of AFC processes in the crust (e.g. Ewart *et al.*, 1988). It is clear from Figure 2.7 that the spread of lava compositions from strongly-undersaturated to mildly oversaturated in Buckland is similar to the variation shown in other central volcano provinces, and typical of other provinces in central-southeastern Queensland. Trace element concentration patterns of primitive (to minimise the effect of AFC) lavas from Buckland are shown in Figure 2.8 and clearly overlap with other examples of the same lava types from provinces (central volcano and lava field) throughout eastern Australia.

Isotopic comparison between the analysed Buckland lavas and lavas from different parts of eastern Australia is made in Figure 2.10a. The main array of Buckland basanites and basalts overlaps with Queensland central volcano provinces only at the 'evolved' basaltic end, while the basanites show more affinity with samples from Queensland lava field provinces. Of the two outlying Buckland samples, the most isotopically depleted lies in the fields of MORB and Tasmanian lavas, while the other lies in the field of northern Queensland lavas whose isotopic characteristics are attributed to interaction with subduction-modified lithosphere (e.g. O'Reilly and Zhang, 1995). Least-fractionated (i.e. primitive compositions) from central volcano provinces have been used (Sun *et al.*, 1989) to characterise the composition of the plume which generated them. This 'plume' composition is based on more data than is shown in Figure 2.10 and lies in the range $^{87}\text{Sr}/^{86}\text{Sr} = 0.7035\text{--}0.7043$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.5127\text{--}0.5129$. Three of the five analysed Buckland basalts lie within this range.

In summary, the wide range of lava compositions in the Buckland province compares with that of other central volcano provinces, while trace element patterns are similar to examples from the same rock types throughout eastern Australia. Isotopic data suggest the involvement of several different components in the petrogenesis of the Buckland lavas. Some basalt samples overlap with the proposed 'plume' composition, while basanites show more affinity to lava field provinces which are thought to be dominated by a shallow asthenospheric component (Sun *et al.*, 1989; O'Reilly and Zhang, 1995). The compositions of outlying samples are compatible with the involvement of MORB-like material and subduction-related lithosphere.

2.3.2 Western US

A sudden change in plate movement ~30 Ma ago brought subduction and related calc-alkaline magmatism in the western US to an end. The subsequent uplift and extensional tectonic regime is characterised by basaltic volcanism continuing to Recent times (Fitton *et al.*, 1991).

Lavas show a wide range of major element compositions, extending from *qz*- to *ne*-normative. Young (<5Ma) lavas from the Basin and Range province are indistinguishable from OIB-type compositions (trace elements: Fitton *et al.*, op. cit.; Kempton *et al.*, 1991), suggesting an origin in the

asthenosphere. Lavas from all other provinces deviate from OIB in both trace element abundances (elevated Ba and Sr; depleted Ti and Nb) and isotopic ratios (higher $^{87}\text{Sr}/^{86}\text{Sr}$; lower $^{143}\text{Nd}/^{144}\text{Nd}$). Fitton *et al.* (1991) note that these shifts cannot be accounted for by crustal contamination, but propose that they demonstrate interaction of primary asthenospheric melts with subduction-modified lithosphere. Fluids driven off a subducting slab are rich in Ba and Sr, but poor in Ti and Nb (due, in part, to the role of oceanic pelagic sediment), and these characteristics are imparted to the overlying lithosphere. Subsequent extension (together with the interaction of a hotspot, e.g. at Snake River) results in the ascent of magmas from the asthenosphere which interact with the modified continental lithosphere. The relative lack of contribution from the lithosphere in the young (<5Ma) Basin and Range lavas is explained by the purging of mobile fractions from the lithosphere by previous magmatic activity, thus rendering it much less susceptible to later melting. A further lithospheric component, derived from the infiltration of very small-degree potassic, carbonate-rich partial melts from the asthenosphere, accounts for the low- $^{143}\text{Nd}/^{144}\text{Nd}$ and low-La/Nb characteristics of some ultrapotassic lavas.

Comparison is made between these lavas and basanites from the 9-12 and 12+ groups in Figures 2.9 and 2.10, and Table 2.2. There is significant overlap between compositions of lavas from Buckland (both basanites and basalts) and young (<5Ma) lavas from the Basin and Range province which are indistinguishable from OIB. The location of some of the Buckland basalt isotopic compositions outside the field of Basin and Range lavas, and in the field of 'Eastern Transition Zone' lavas suggests that they show evidence for minor interaction with subduction-modified lithosphere. Alternatively it demonstrates that the convecting mantle beneath eastern Australia is more heterogeneous than below the western US.

2.3.3 Western Europe - Massif Central

Rift-related volcanic provinces dominated by primitive alkalic lavas are found throughout Europe and are described in numerous papers, e.g. Downes (1984, 1987), Wilson and Downes (1991, 1992), Wilson *et al.* (1995). Lithospheric blocks in western Europe, which have complex histories of magmatism and deformation, were 'welded' together by subduction-accretion events up to, and including, the Hercynian orogeny (360-325 Ma). A major rifting and uplift event in the Oligocene was preceded by minor volcanism between 65-35 Ma and followed by the main phase of activity from 20 to 0.04 Ma. Decompression and melting in the mantle is thought to have developed in response to lithospheric flexure following nappe emplacement, or due to small hotspots. The location of volcanic centres appears to be strongly controlled by the lithospheric structure, commonly occurring close to the boundaries between different blocks.

Alkali basalts and basanites from the Massif Central contain >7% MgO, and lie at the low-silica end of two fractionation series: alkali basalt-trachybasalt-trachyte-rhyolite and basanite-tephrite-phonolite (see Figure 2.7). Megacrysts of amphibole and clinopyroxene are found in these primitive

lavas together with xenoliths of spinel lherzolite and harzburgite from the upper mantle, and mafic cumulates and granulites (Hercynian in age?) from the lower crust. Trace element data (Wilson and Downes, 1991) are provided in Figure 2.9, and Sr-Nd isotopic data in Figure 2.10 for volcanic centres throughout western Europe (Downes, 1984). Sr-Nd data define a linear trend from isotopically 'depleted' basanites and alkali basalts (including Massif Central lavas) to 'enriched' potassic compositions, which include leucitites and leucite nephelinites from the Rhenohercynian province of Germany. The lavas are interpreted (Wilson and Downes, 1992) as the product of mixing between an isotopically depleted upper-asthenospheric component ("A"), and a lithospheric component ("B"). On the basis of isotopic characteristics, this depleted component is modelled as a mixture between HIMU St-Helena-type and MORB-like material, with the HIMU-like component deriving from the recycling of oceanic crust in the asthenosphere or from enriched material at the base of the lithosphere. The samples whose spidergrams are shown in Figure 2.9 are dominated by this asthenospheric component. The lithospheric component is derived from the partial melting of material which had been metasomatised during a pre-Hercynian magmatic event producing phlogopite/amphibole-bearing lherzolite, examples of which are found as xenoliths. Mixing between the two components occurred as the rising asthenospheric magmas, generated by decompression, heated and mobilised the low-solidus, metasomatised component in the lithosphere.

There are several points of similarity with the Buckland province. The pre-eruption history of the lithosphere in western Europe is similar to eastern Australia involving a number of subduction-accretion episodes. Geochemical and isotopic comparison between the lavas is made in Figures 2.7, 2.9 and 2.10. Basanites from Buckland are very similar to examples from the Massif Central in terms of TAS characteristics, spidergrams and Sr-Nd ratios. Overlap between basalts is less pronounced, as Massif Central examples are poorer in silica and have 'spikier' spidergram patterns. The involvement of a plume, as proposed for Australian central volcanoes, is not required in western Europe nor has it been ruled out.

2.3.4 Eastern China

Fan and Hooper (1991) describe the basaltic volcanism that occurs discontinuously over 3000 km in eastern China from 80 Ma to Recent. Provinces are small, being rarely greater than 100km across and 400m thick. They occur in an extensional setting, associated with a NE-NNE trending fault system parallel to the coast. The authors propose that extension resulted from back-arc spreading owing to subduction of the Pacific plate beneath the Eurasian plate during the Cainozoic. Magmatism is ascribed to asthenospheric upwelling in response to this extension, with no evidence for the involvement of a plume.

Alkali basalts dominate the sequences, (Figure 2.7e), but leucitites, olivine nephelinites, basanites, olivine tholeiites and quartz tholeiites are also found. Lavas are mostly aphyric but contain

some olivine and clinopyroxene phenocrysts, as well as xenoliths of spinel- and garnet-lherzolite, harzburgite, clinopyroxenite (Fan and Hooper, 1989). Fan and Hooper (1991) recognise primitive lavas with mg-number of 60-68, 200-300 ppm Ni and 10-13% MgO. Examples of these are given in Table 2.2. They note that these primitive lavas are similar to lavas from southeastern Australia (Frey *et al.*, 1978) in terms of major element geochemistry. The high Al_2O_3 -content of the included clinopyroxene phenocrysts indicates that fractional crystallisation took place at high pressures (upper mantle to lower crust). They propose that the alkaline lavas result from the partial melting of garnet lherzolite (at >79 km depth) and the tholeiites from spinel lherzolite at a shallower depth (<66 km).

Song *et al.* (1990) analysed interbedded alkali basalts and tholeiites from Hannuoba, near Beijing. Normative characteristics (from Zhi *et al.*, 1990) are given in Figure 2.7, and isotopic data in Figure 2.10. Isotopic compositions lie within the field of OIB lavas, but show variation in line with their major element geochemistry. Specifically, alkaline lavas have a relatively 'depleted' isotopic composition, while isotopic ratios become more 'evolved' (i.e. higher $^{87}\text{Sr}/^{86}\text{Sr}$; lower $^{143}\text{Nd}/^{144}\text{Nd}$) through the transitional basalts to the tholeiitic basalts. They argue that the alkaline lavas are derived from an asthenospheric source, while mixing of this with an isotopically enriched EMI-like component accounts for the isotopic composition of the transitional and tholeiitic basalts. Xenoliths from the lithospheric mantle show considerable compositional heterogeneity and overlap with the isotopic composition of the tholeiitic basalts, suggesting that the 'evolved' component resided in the continental lithosphere.

Geochemical comparison with the Buckland lavas shows significant overlap in major element compositions with lavas from China. Spidergrams of primitive Buckland lavas show closer similarity to Chinese basanites and alkali basalts than to olivine tholeiites. The array of Chinese isotopic compositions parallels that of the Buckland lavas, but shifted towards higher $^{87}\text{Sr}/^{86}\text{Sr}$ values. The data suggest that the composition of the asthenosphere beneath eastern China is richer in radiogenic Sr than beneath eastern Australia, and that the trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and decreasing $^{143}\text{Nd}/^{144}\text{Nd}$ in the Buckland lavas could reflect the involvement of an isotopically 'evolved' component.

2.3.5 Conclusions

The conclusions of the comparisons above can be drawn together as follows:

1. The lavas in this study overlap those from other eastern Australian Cainozoic volcanics in terms of major/trace elements and isotopic ratios. The spread of compositions (nepheline- to quartz-normative) is similar to that observed in other central volcano provinces and is interpreted as the result of AFC processes. Most primitive Buckland compositions overlap with fields of central volcano provinces (interpreted as 'plume'-derived) or lava field provinces (interpreted as shallow asthenospheric). Outliers overlap with MORB or subduction-modified lavas, suggesting that a range

of source components have contributed to the Buckland lavas, although dominated by the convecting mantle.

2. Comparison of the primitive lavas in this study with examples from extensional continental settings around the world confirms this conclusion. Basanites from Buckland are very similar to those from the Massif Central, while basalts are similar to alkali basalts from eastern China and western US. In all cases, the geochemical characteristics of primitive lavas have been ascribed to a dominantly asthenospheric source. Minor lithospheric input is observed in each region, and commonly has a subduction-related geochemical signature, consistent with the pre-volcanic history of the region. This is especially apparent in the western US where subduction ceased only ~30 Ma ago. Overlap between isotopic compositions of basalts from Buckland and those which have interacted with subduction-modified lithosphere (e.g. in the western US) could be interpreted in terms of a more heterogeneous asthenosphere beneath eastern Australia. This could result from recycling of enriched material following subduction events in the Palaeozoic.

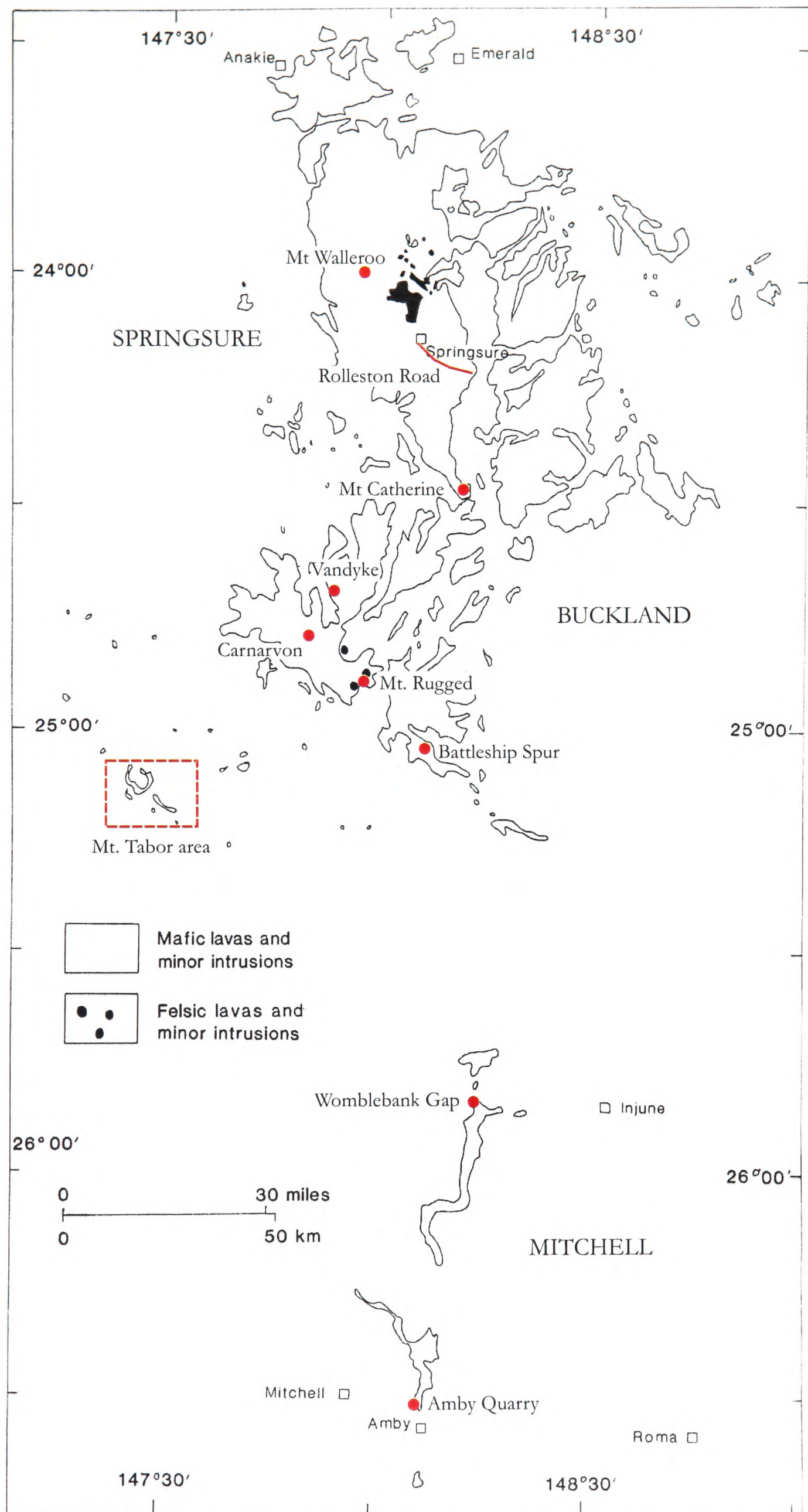


Figure 2.1 Map of the field area showing the main sampling localities from each province.

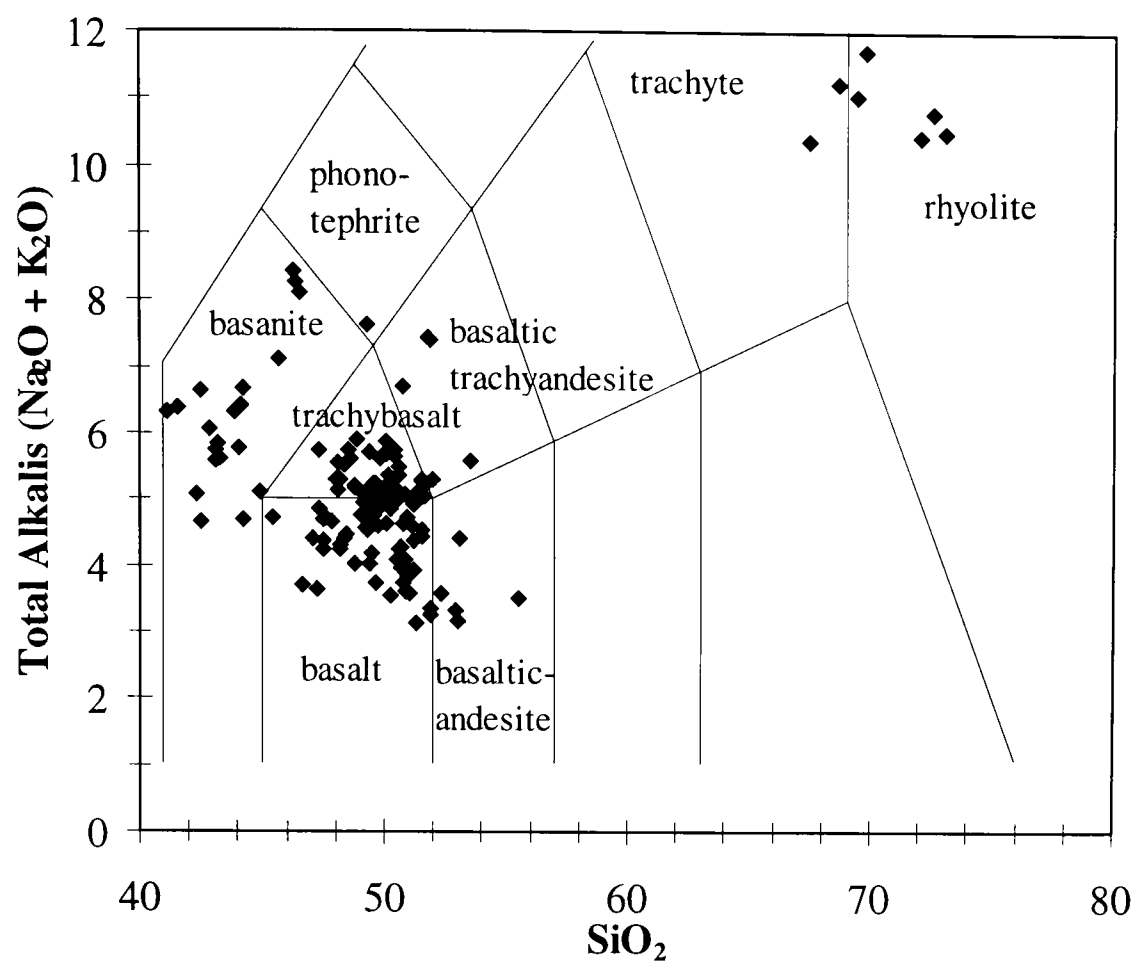


Figure 2.2 Classification of all analysed samples according to the TAS scheme of Le Maitre (1989).

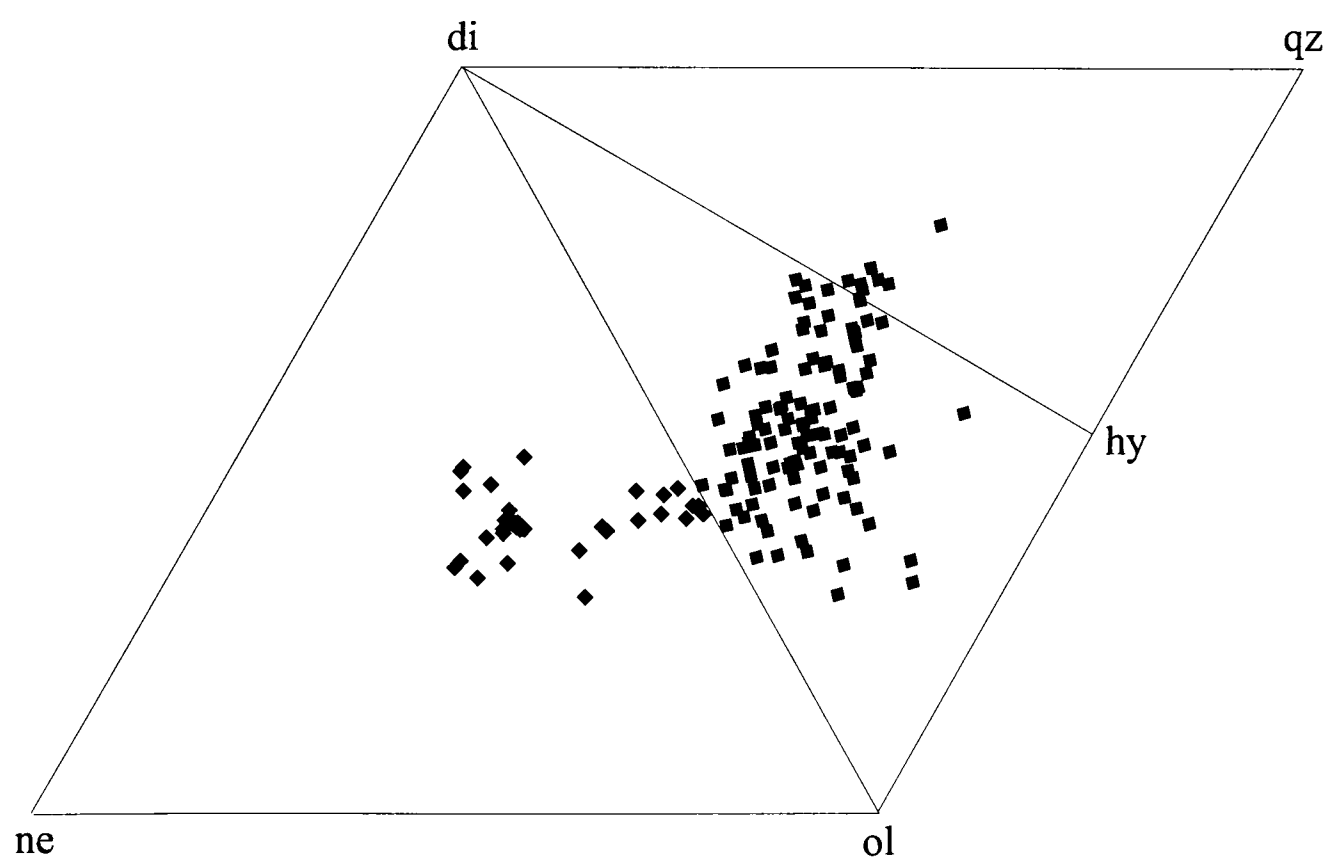


Figure 2.3 Normative characteristics of the analysed mafic samples (MgO > 2.8%) projected onto *ne-di-ol-hy-qz*, assuming Fe₂O₃/FeO=0.2. There is continuous spread from strongly silica undersaturated basanites to oversaturated tholeiites and basaltic andesites.

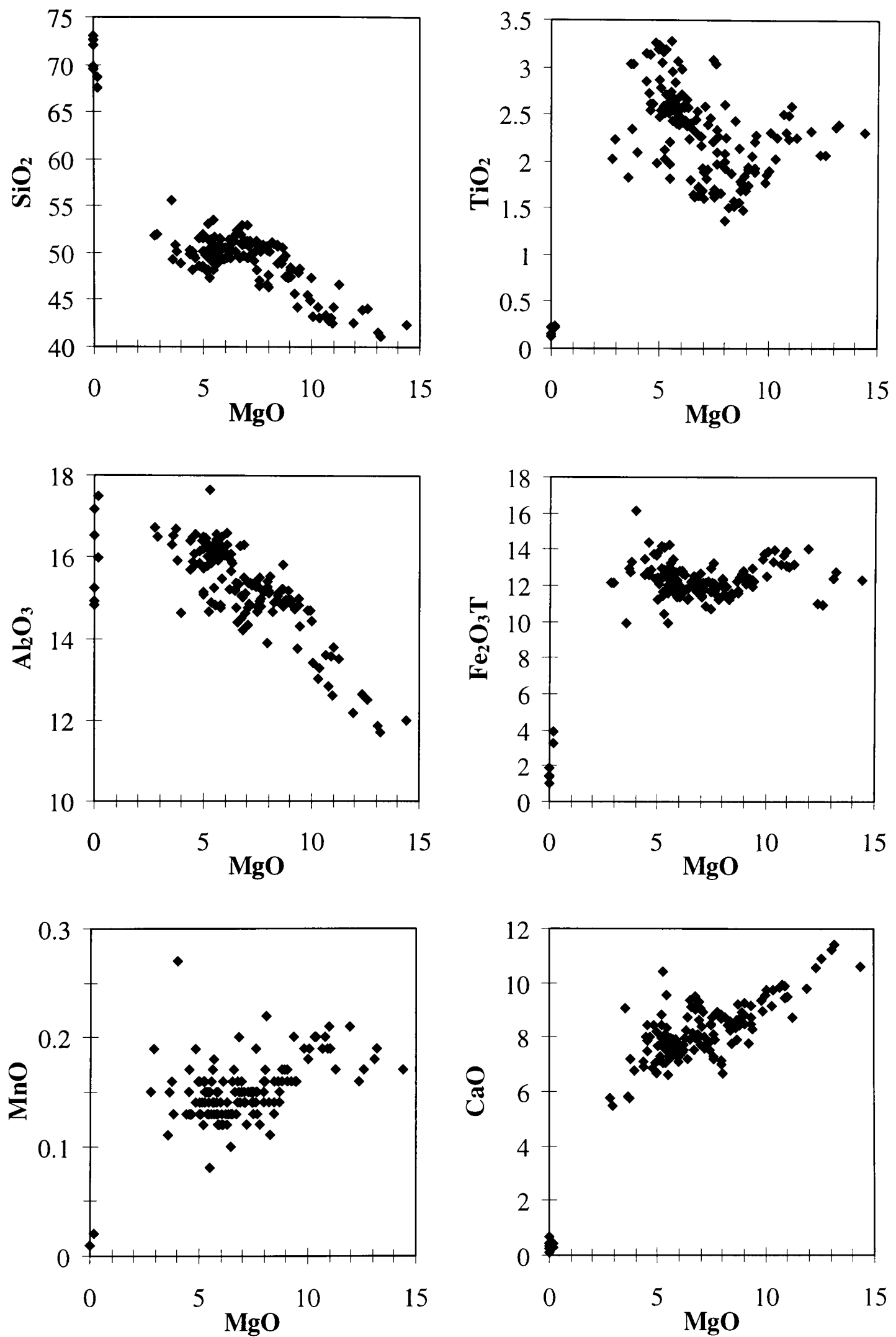


Figure 2.4 Graphs of major element oxides and trace elements against MgO for all the analysed samples.

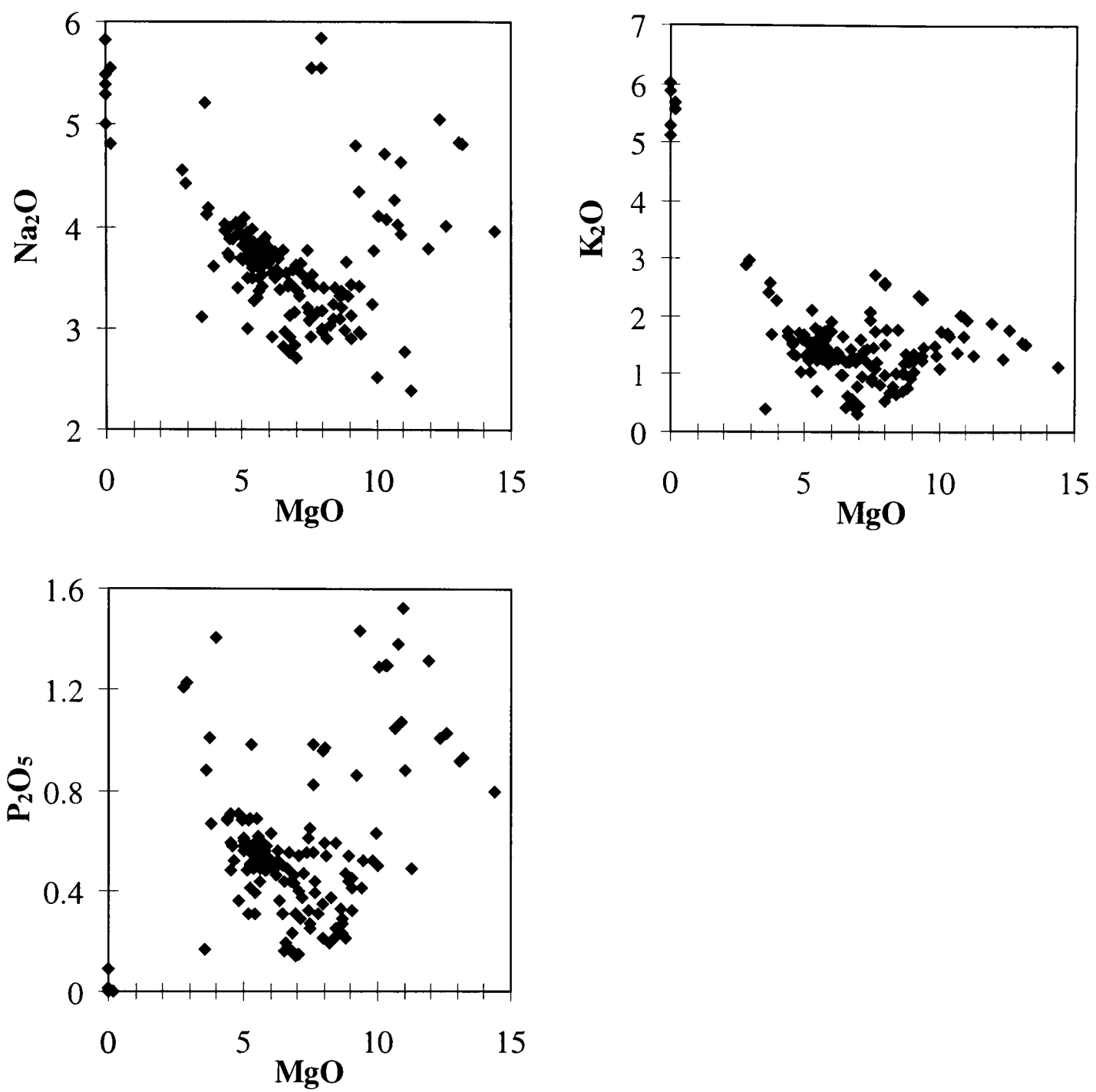


Figure 2.4 (cont.) Graphs of major element oxides and trace elements against MgO for all the analysed samples.

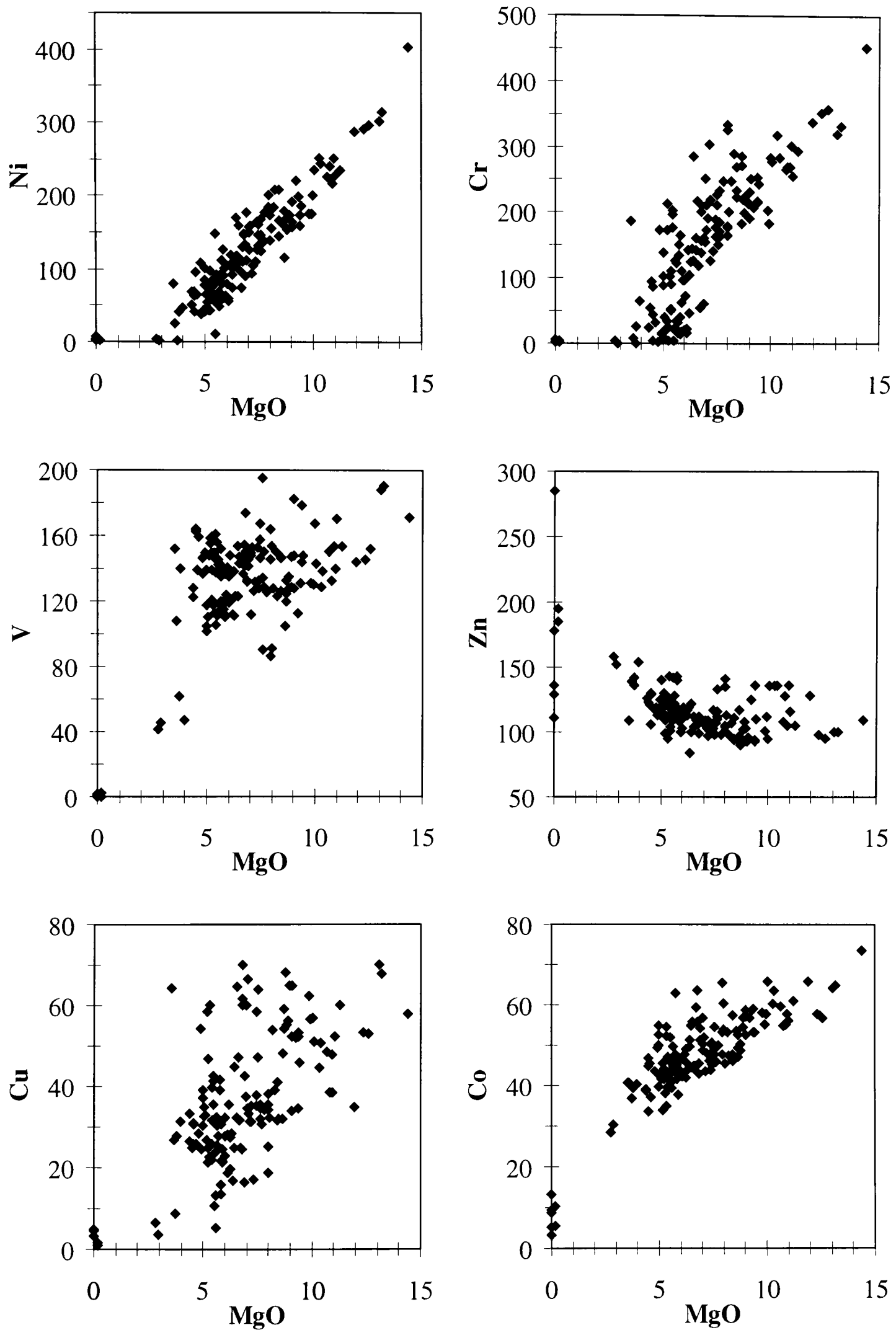


Figure 2.4 (cont.) Graphs of major element oxides and trace elements against MgO for all the analysed samples.

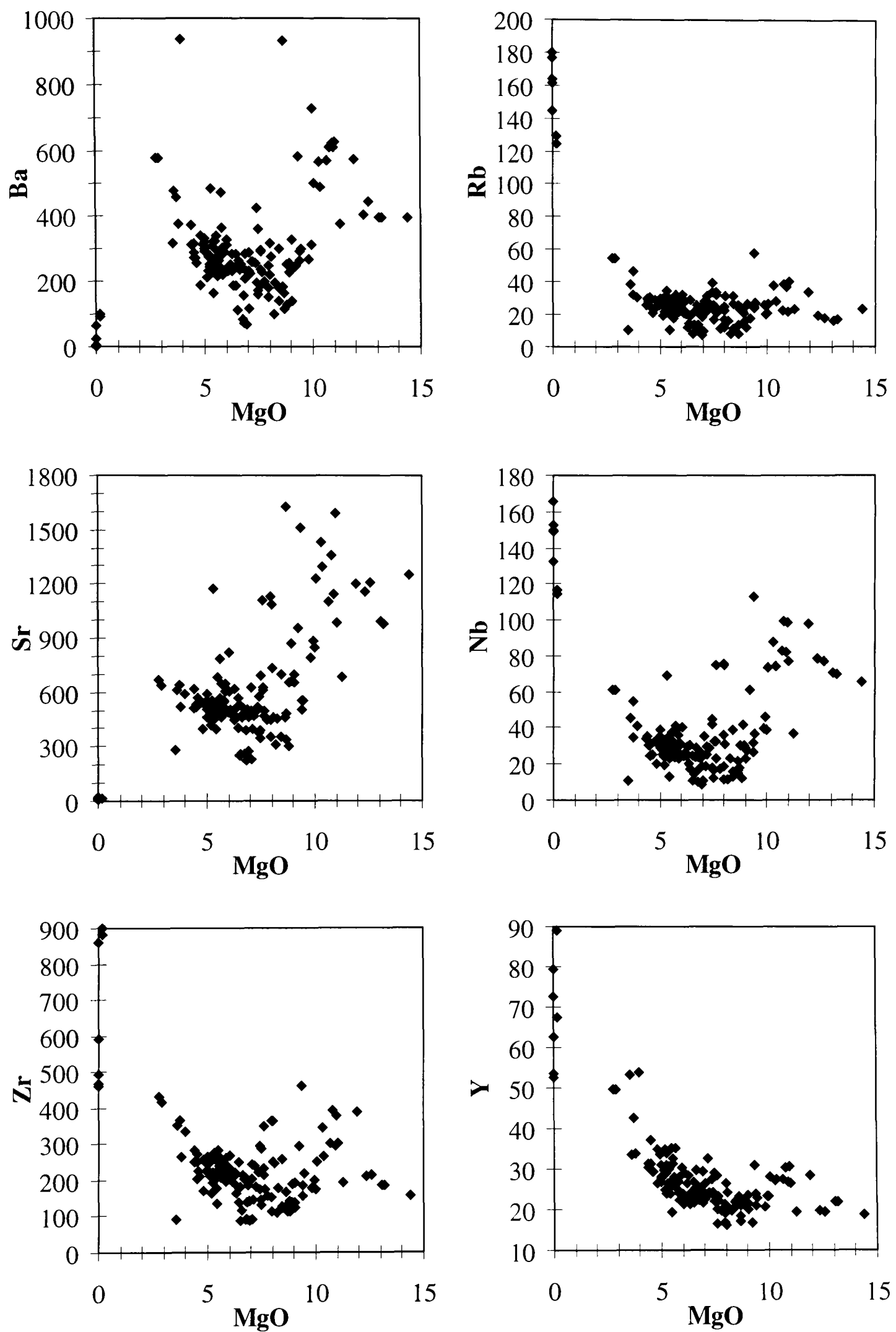


Figure 2.4 (cont.) Graphs of major element oxides and trace elements against MgO for all the analysed samples.

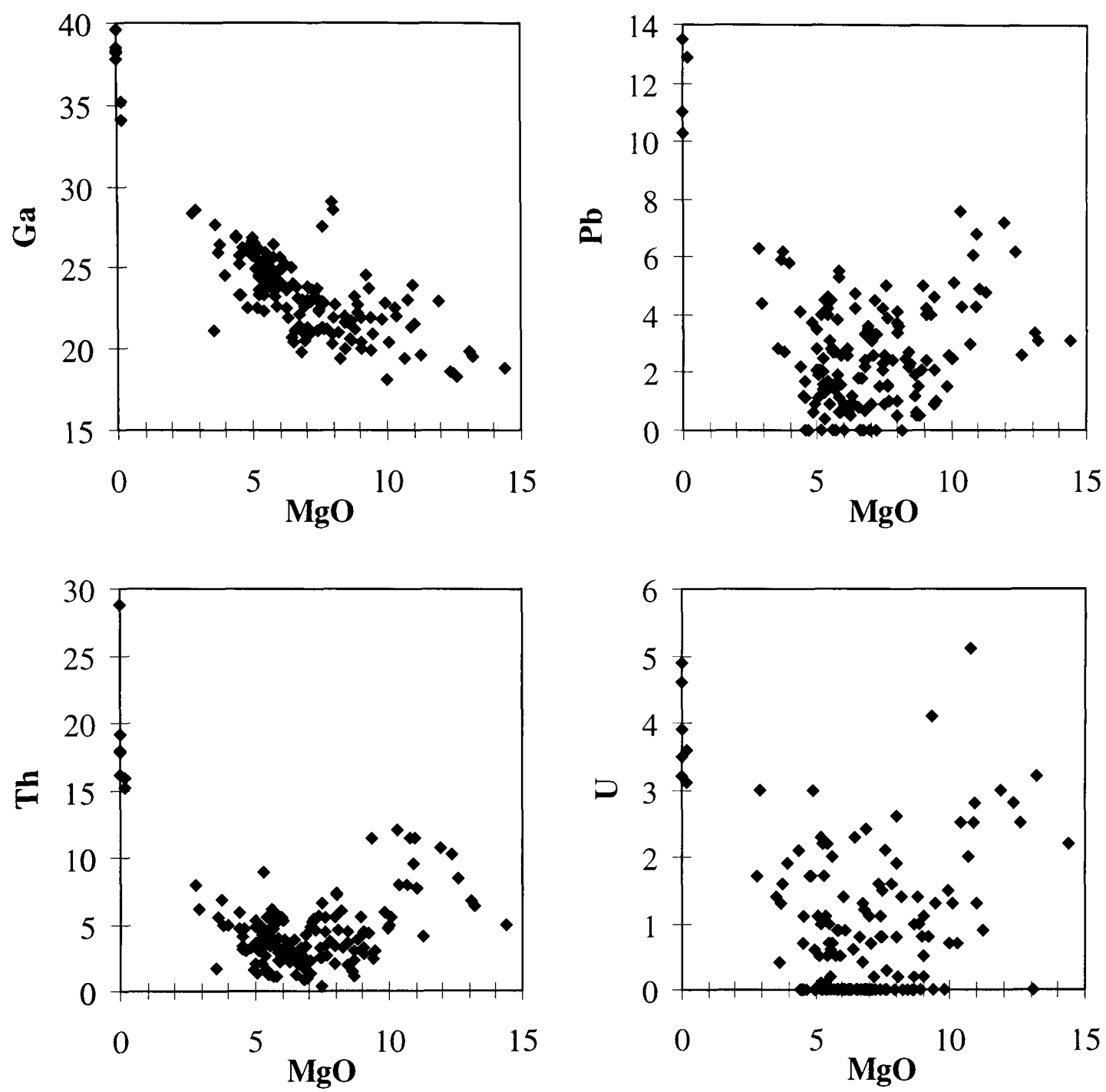


Figure 2.4 (cont.) Graphs of major element oxides and trace elements against MgO for all the analysed samples.

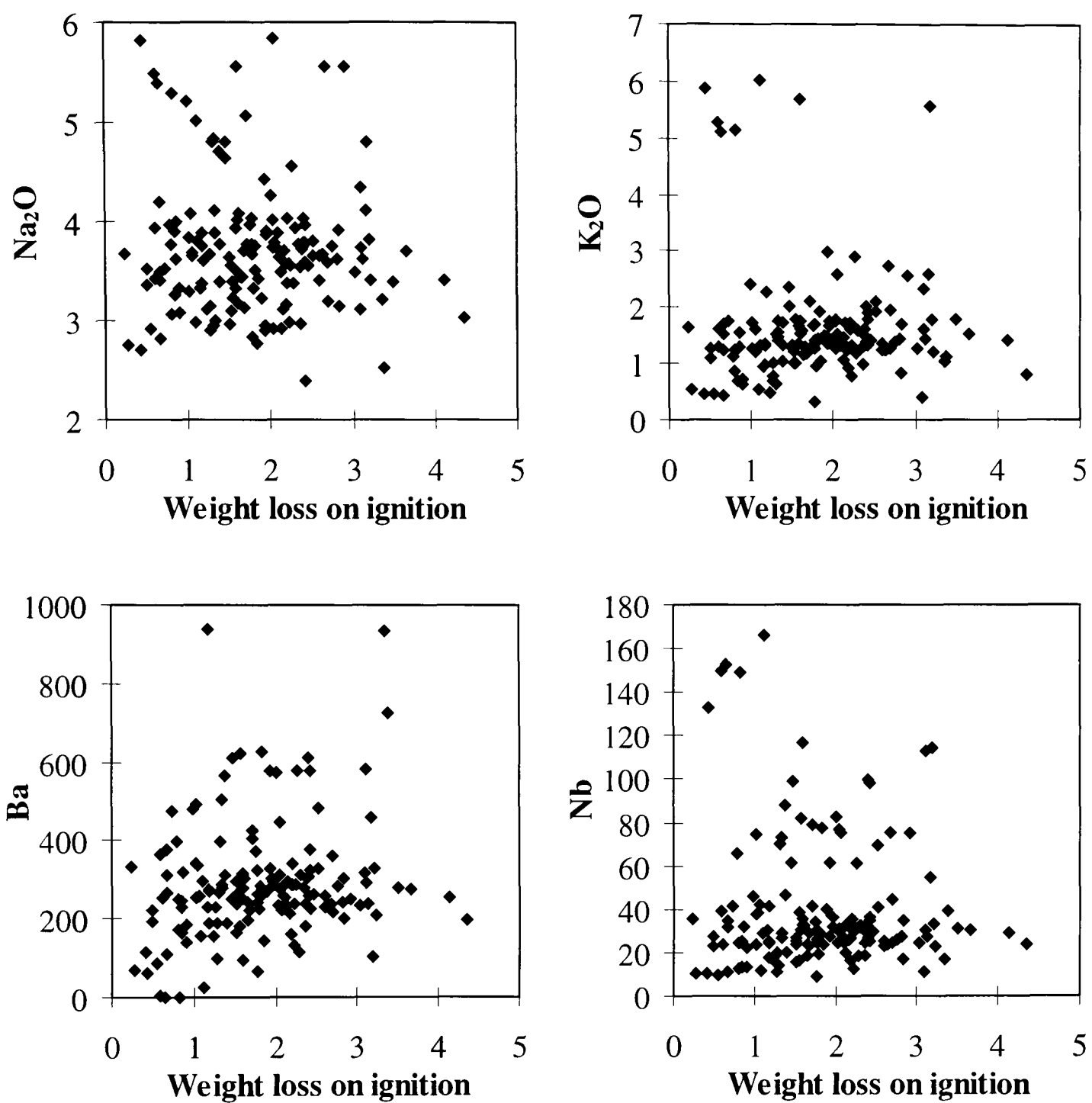


Figure 2.5 Graphs of mobile elements Na, K and Ba and immobile element Nb against weight loss on ignition (%: see the text for details). No correlation is shown between variables in the mobile element plots, suggesting that no significant hydrothermal alteration has taken place. This is supported by the close similarity of the plot involving niobium, an immobile high field-strength element.

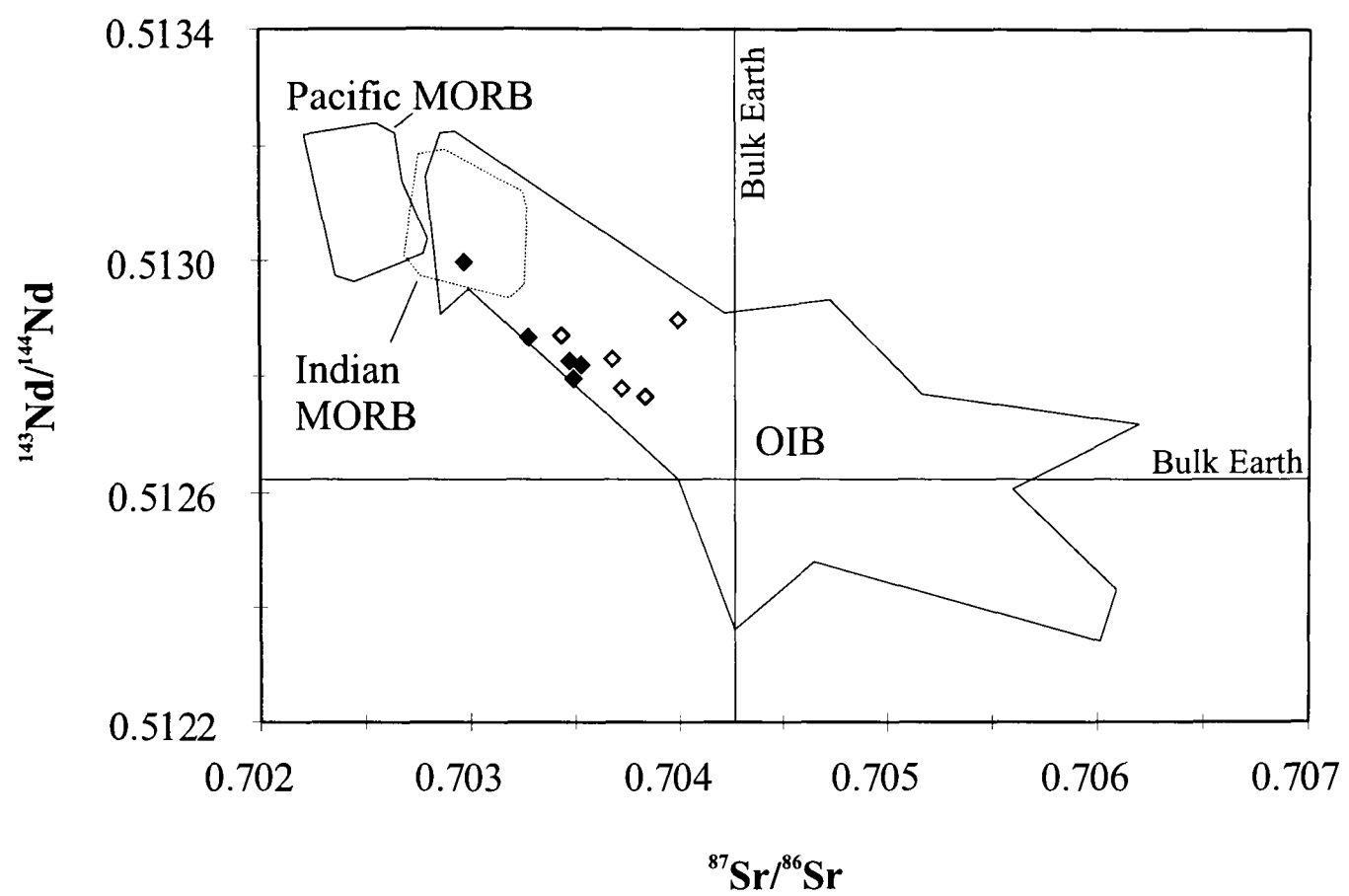


Figure 2.6 Sr-Nd isotope compositions of the ten samples analysed for both isotopic ratios within this study. Filled diamonds are basanites and open diamonds basalts. Fields for MORB are taken from Ferguson and Klein (1993) and OIB from Thompson *et al.* (1998).

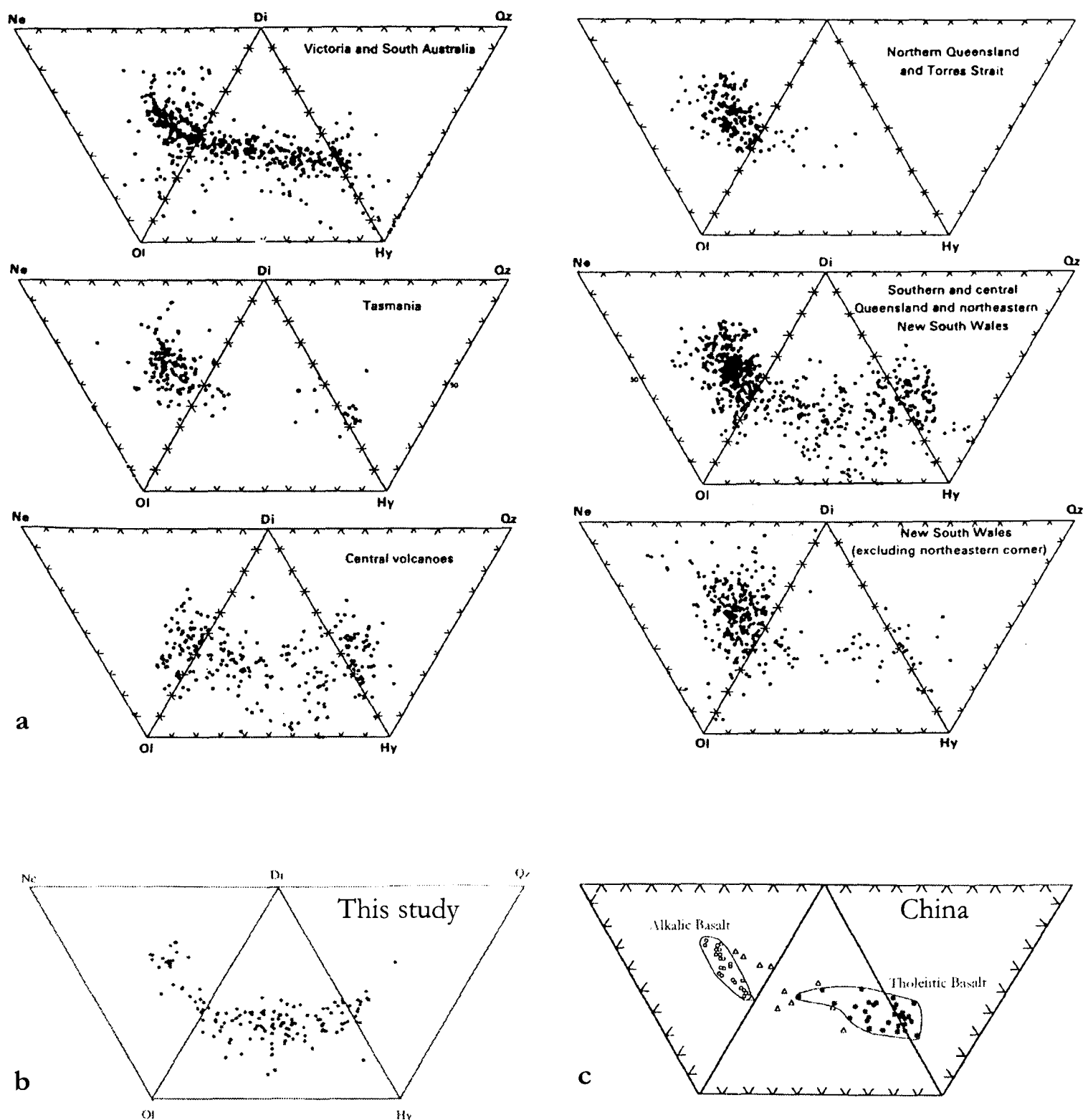


Figure 2.7 Comparison between CIPW norm characteristics of the samples in this study (**b**) with lavas from eastern Australia (**a**) and the Hannuoba province of eastern China (**c**). Lavas from this study are clearly typical of east Australian central volcanoes and of lavas from southern-central Queensland, and also overlap the fields of tholeiitic and alkalic basalts from China. (**b**) is simply a replotted form of Figure 2.3 to allow comparison with the other published figures. (**a**) is reprinted from Ewart (1989a), and (**c**) from Zhi *et al.* (1990). The key for (**c**) is asterisks = tholeiitic basalts, triangles = transitional basalts, circles = mantle xenoliths.

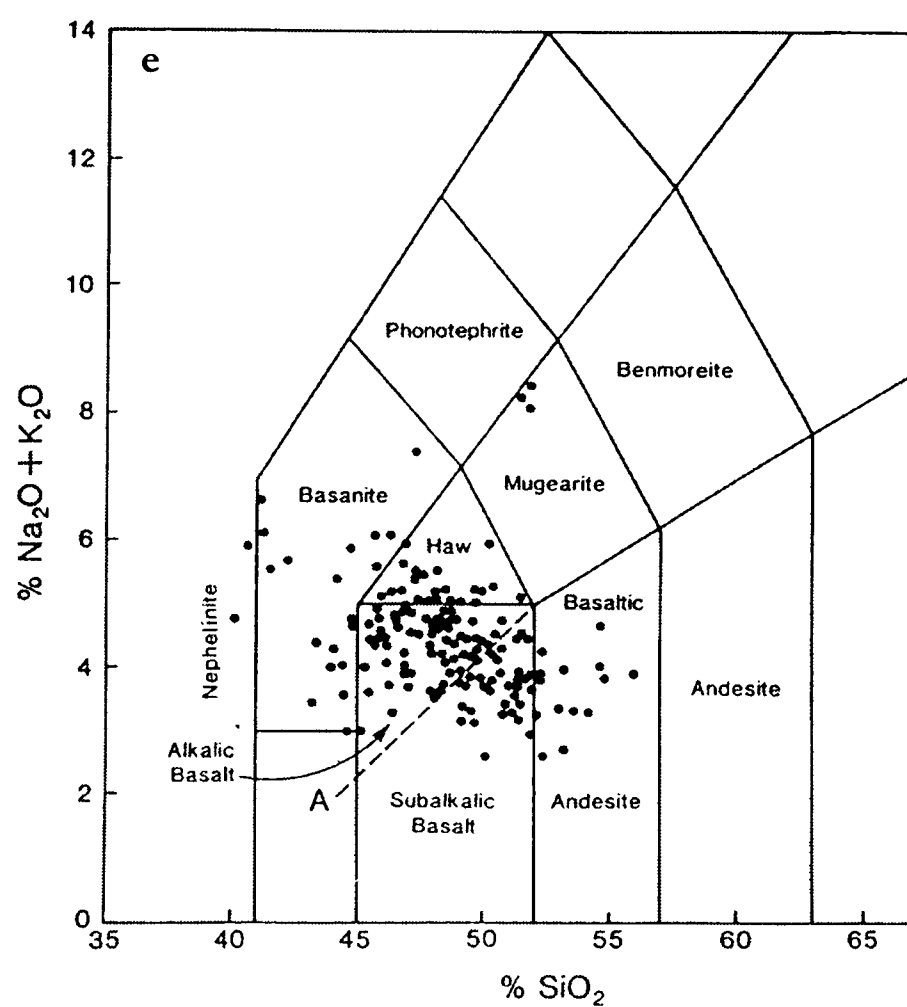
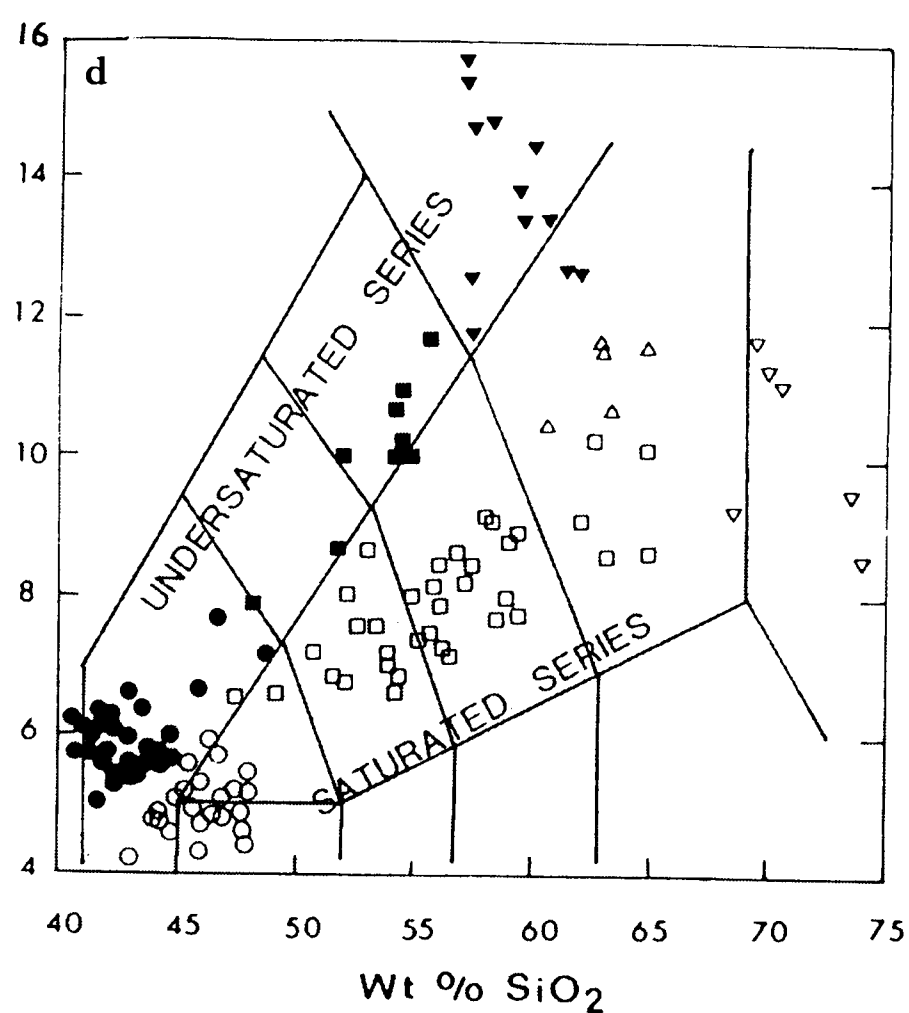


Figure 2.7d,e TAS plots for lavas from the Massif Central (Downes, 1984) and eastern China (Fan and Hooper, 1991). Comparison with Figure 2.2 shows that Queensland basalts are similar to those from China, but slightly more siliceous than those from France. Queensland basanites, however, are comparable to the basanites from the 'undersaturated series' of the Massif Central

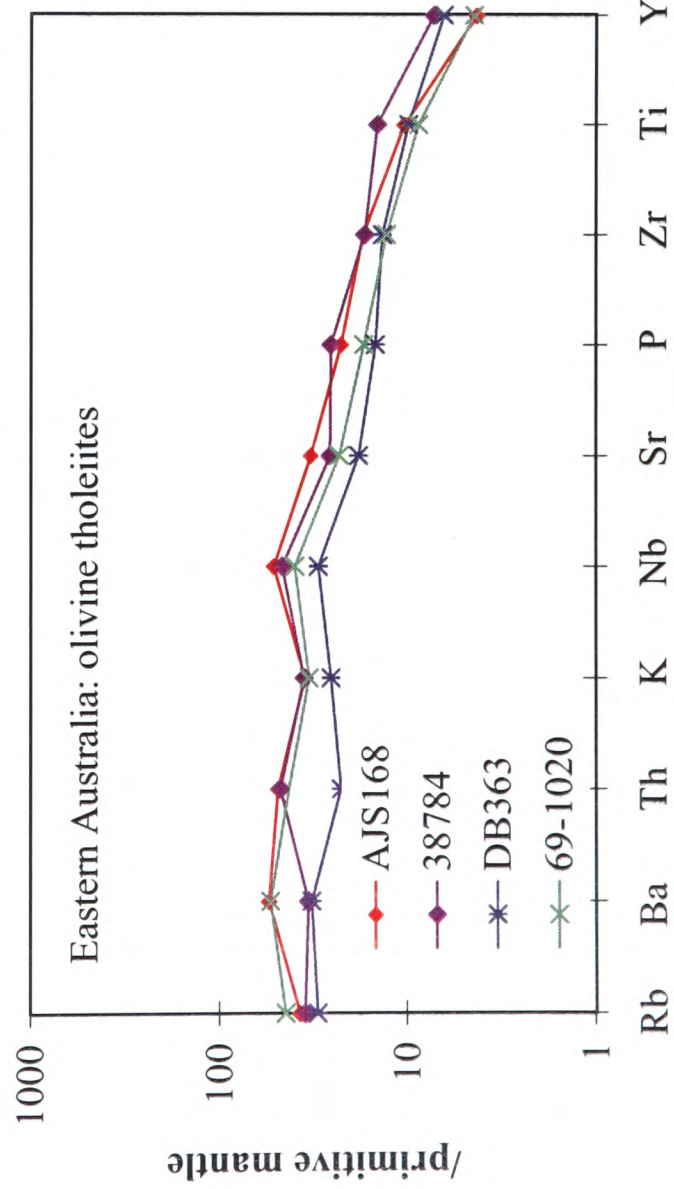
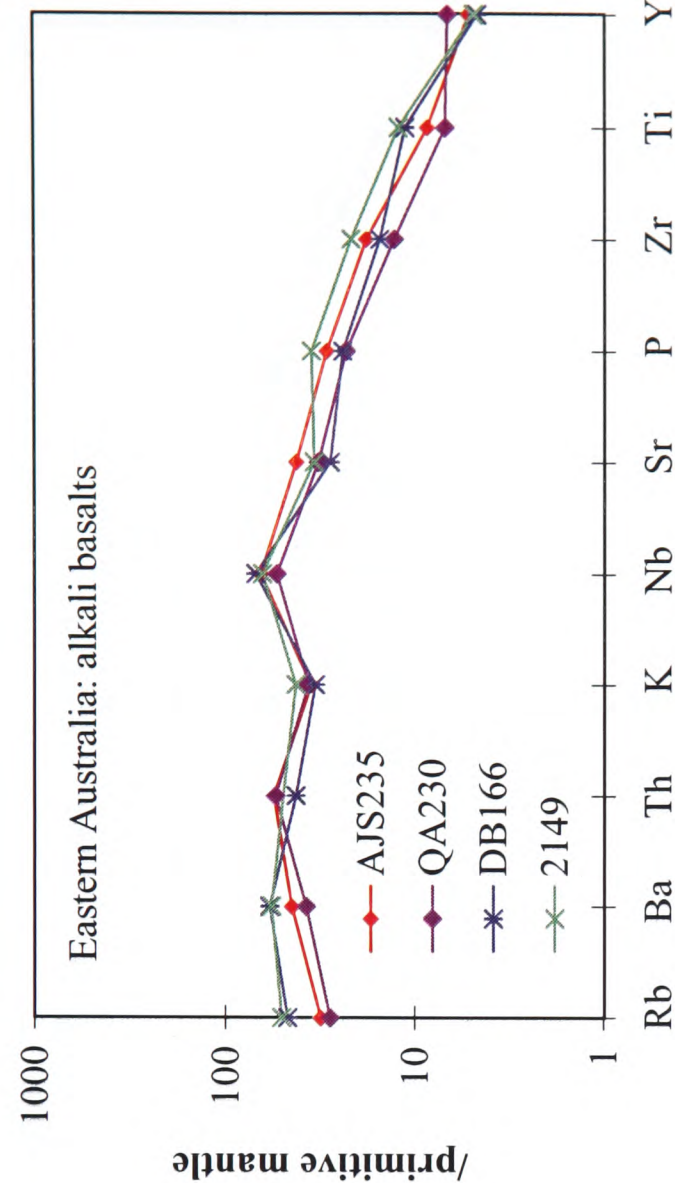
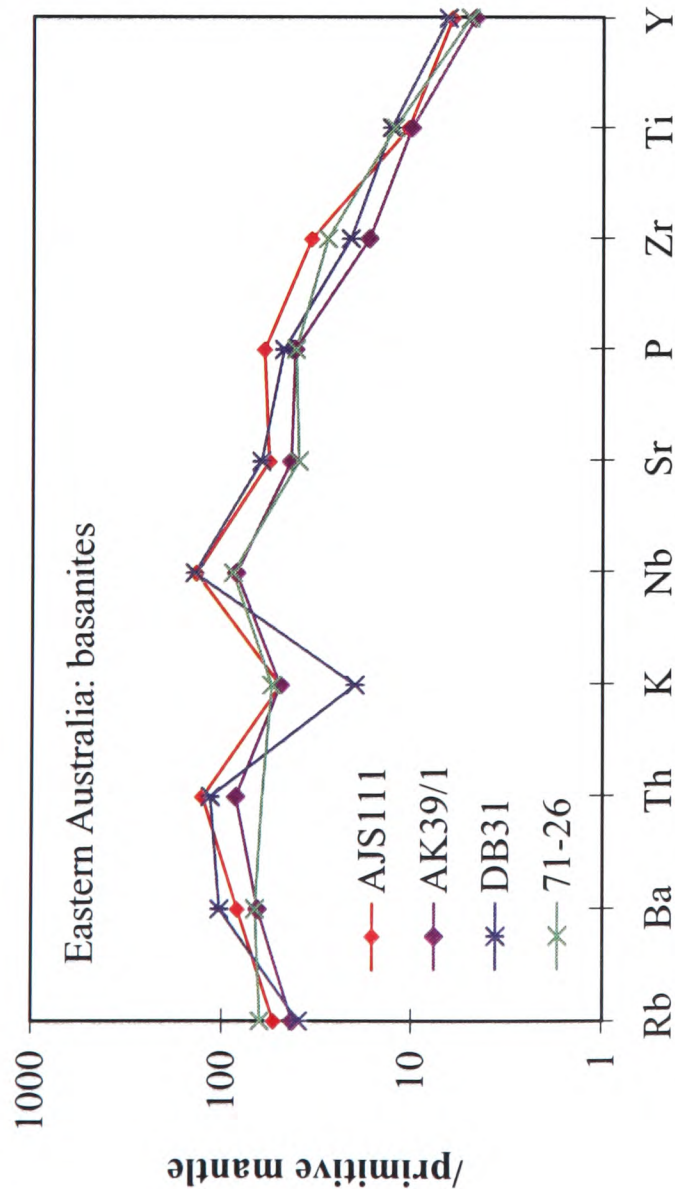


Figure 2.8 Spidergrams comparing examples of a basanite, alkali basalt and olivine tholeiite from the area of study with examples of other Cainozoic lavas from eastern Australia. Those in maroon are from Queensland, namely AK39/1 from Anakie, QA230 from Yatton Creek (Ewart *et al.*, 1988) and 38784 from Bunya (Ewart and Grenfell, 1985). Those in blue are from Dubbo, NSW (O'Reilly and Zhang, 1995), while those in green are from the Newer Volcanics of Victoria (McDonough *et al.*, 1985). Examples are confined to those containing >8.5% MgO in order to minimise the effects of fractional crystallisation/AFC processes. Normalising constants are taken from Sun and McDonough (1989).

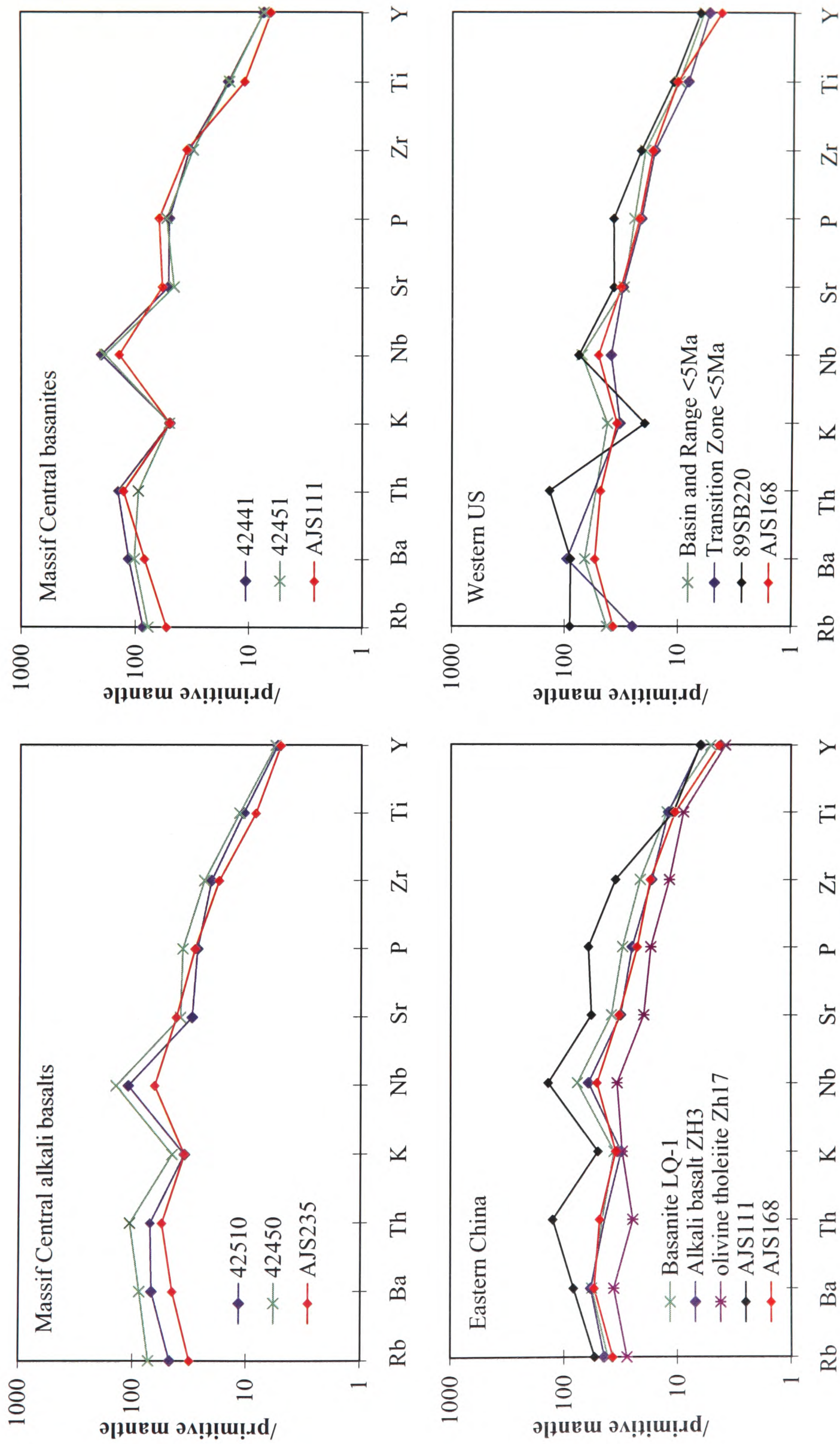


Figure 2.9 Spidergrams to compare examples of a basanite (AJS111), alkali basalt (AJS235) and olivine tholeiite (AJS168) from the area of study with examples from the Massif Central (Wilson and Downes, 1991), Eastern China (Fan and Hooper, 1991; Zhi *et al.*, 1990) and Western US (Transition Zone and Basin and Range are averages: Fitton *et al.*, 1991; 89SB220 is a basanite from the Espanola Basin in the Rio Grande rift which has been interpreted (Gibson *et al.*, 1992) as being largely asthenospheric, like the late Basin and Range lavas). Normalising constants are from Sun and McDonough (1989).

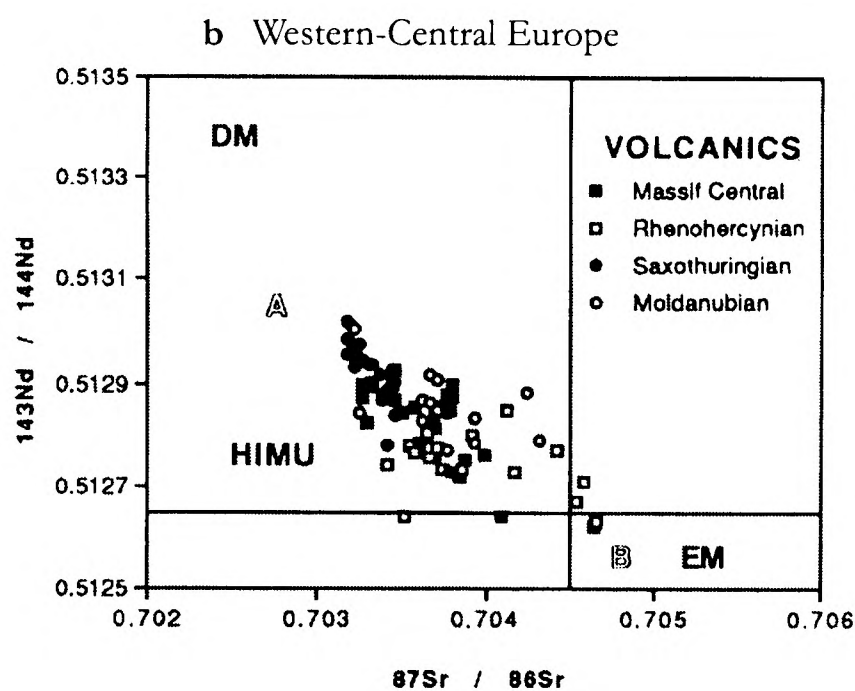
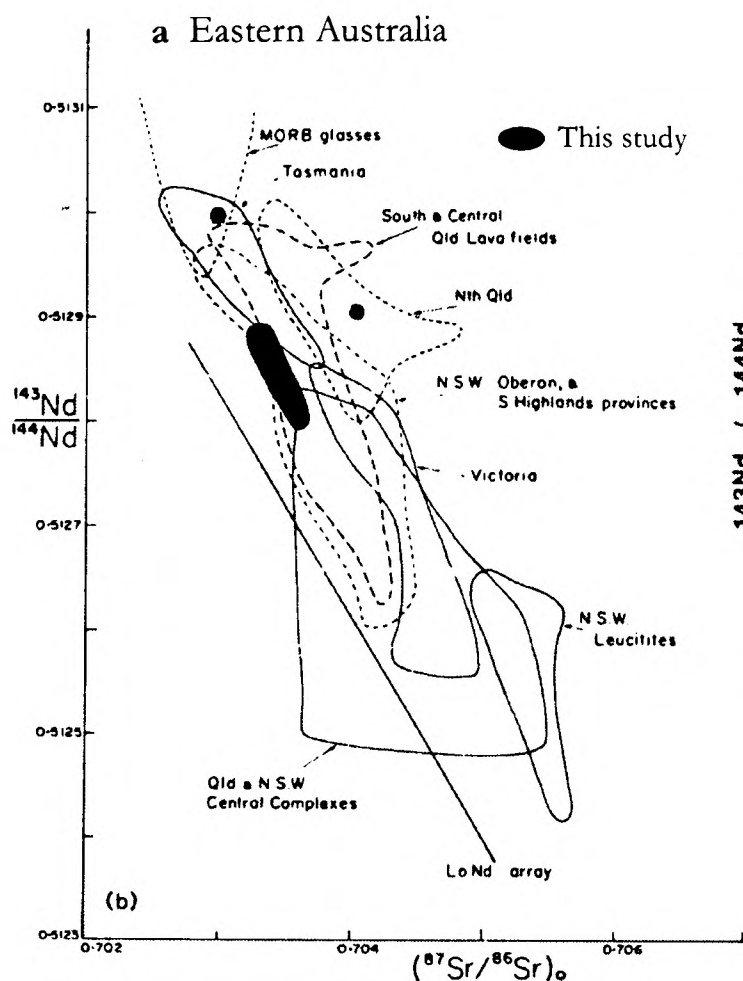


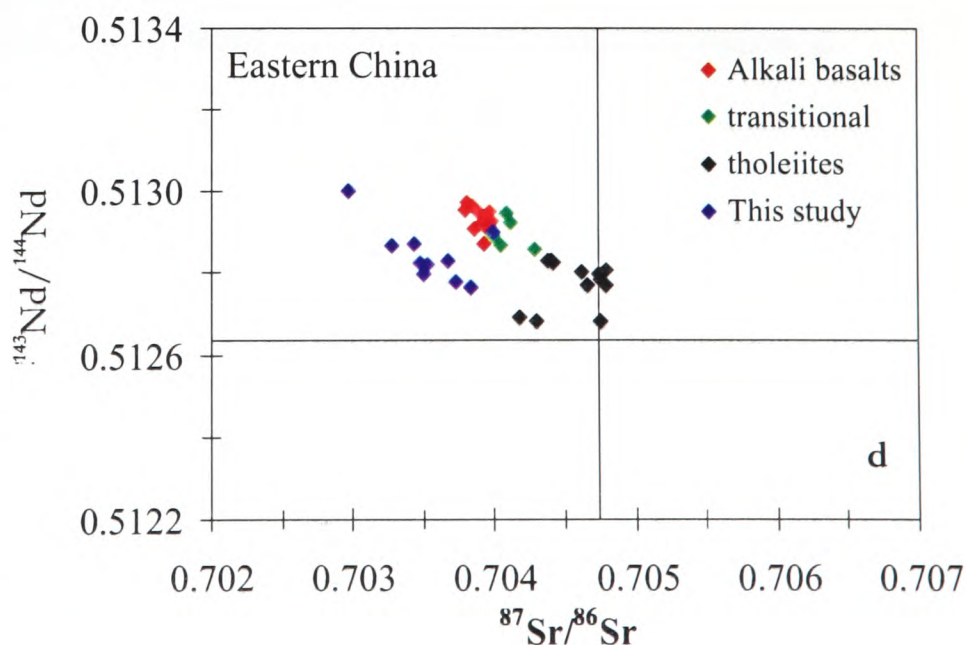
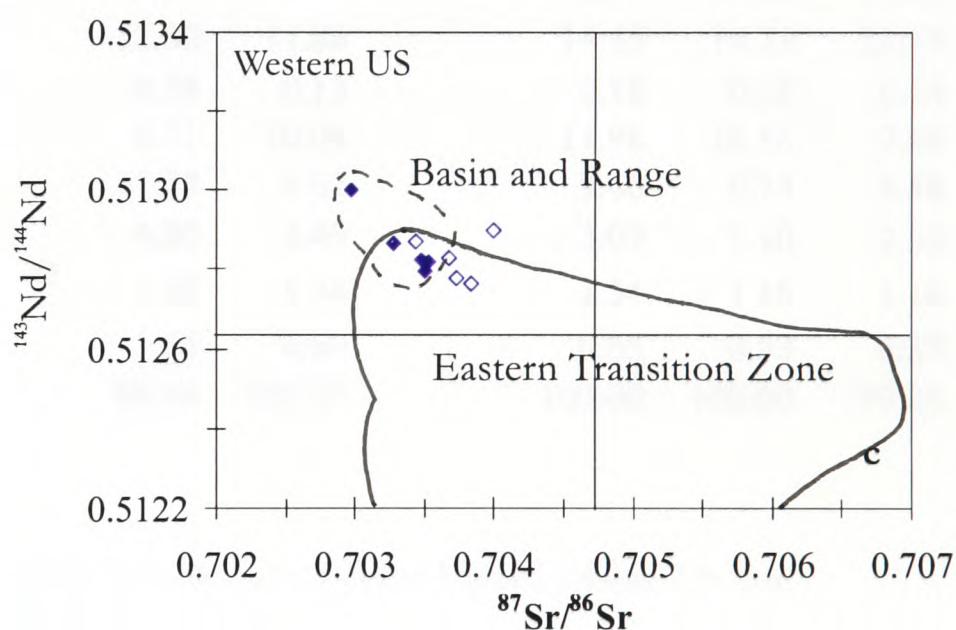
Figure 2.10 Comparison between the analysed isotopic data from this study and:

a) generalised fields of Cainozoic volcanics from throughout eastern Australia (Ewart *et al.*, 1988).

b) lavas from Western - Central Europe (Wilson and Downes, 1992) which are interpreted in terms of mixing between asthenospheric component "A" (depleted mantle + HIMU) and enriched lithospheric component "B".

c) young (<5Ma) lavas from the Basin and Range of the western US which are interpreted as asthenospheric (Fitton *et al.*, 1991), and lavas from the Eastern Transition Zone which contain variable amounts of isotopically enriched lithosphere. Data from Kempton *et al.* (1991). Filled diamonds = basanites from this study, and open diamonds = basalts.

d) lavas from the Hannuoba province of China, which show mixing between asthenospheric (alkali basalts) and lithospheric (tholeiites) components. Data from Song *et al.* (1990).



	This study				Eastern Australia		
	AJS111	AJS 235	AJS168	AJS143	71-26*	DB166	38784*
	Bas	AB	OT	OT	Bas	AB	OT
SiO ₂	42.50	44.91	46.63	48.19	44.89	45.87	47.83
TiO ₂	2.32	1.85	2.25	1.91	2.69	2.42	3.10
Al ₂ O ₃	12.18	14.69	13.51	14.84	12.50	13.35	14.06
Fe ₂ O ₃ T	14.04	13.70	13.19	12.31	13.02	13.07	12.49
MnO	0.21	0.19	0.17	0.17	0.17	0.17	0.16
MgO	11.91	9.92	11.25	9.05	11.46	13.08	8.50
CaO	9.79	8.97	8.75	8.82	8.24	9.08	8.81
Na ₂ O	3.79	3.77	2.39	2.90	4.08	2.26	3.17
K ₂ O	1.88	1.33	1.32	1.37	2.06	1.27	1.32
P ₂ O ₅	1.32	0.63	0.49	0.41	0.89	0.52	0.55
Total	99.94	99.96	99.94	99.96	100.00	101.09	100.00

	Western US			Massif Central		Eastern China		
	Transition Basin &	89SB220		42441	42510	LQ-1*	ZH-3*	Zh17
	Zone	Range	Bas	Bas	AB	Bas	AB	OT
SiO ₂	48.76	46.71	43.24	41.22	46.79	43.64	46.66	50.94
TiO ₂	1.82	2.19	2.45	3.22	2.36	2.63	2.56	1.89
Al ₂ O ₃	15.54	15.66	12.24	13.32	13.99	12.91	11.78	15.01
Fe ₂ O ₃ T	11.51	11.54	14.04	12.50	11.86	14.15	14.73	11.19
MnO	0.17	0.18	0.20	0.18	0.15	0.18	0.18	0.14
MgO	8.05	8.04	12.99	9.71	10.04	11.98	10.56	7.88
CaO	9.01	9.18	11.13	11.73	9.62	9.46	9.75	8.48
Na ₂ O	3.35	3.57	2.79	4.20	3.49	3.07	2.10	2.82
K ₂ O	1.24	1.61	0.75	1.88	1.34	1.34	1.16	1.16
P ₂ O ₅	0.47	0.54	0.82	1.68	0.60	0.65	0.53	0.37
Total	99.92	99.22	100.65	99.64	100.24	100.00	100.00	99.88

Table 2.2 Major element analyses for some of the samples considered in Figures 2.8 and 2.9. For references, see the captions to Figures 2.8 and 2.9.

Bas signifies a basanite, AB an alkali basalt and OT an olivine tholeiite.

*Iron recalculated to Fe₂O₃T and the whole analysis normalised to total 100% for ease of comparison.

Chapter 3: Petrology and petrogenesis of the 9-12 group

3.1 AIMS AND INTRODUCTION

3.1.1 Aims

The purpose of this chapter is to detail the petrology and petrogenesis of the 21 samples whose MgO contents lie between 9 and 12% and which form a distinct group, as explained in Chapter 2. Their importance is twofold:

1. Due to their comparatively primitive nature, they have the potential to reveal the composition of their source(s) and details of the melting process(es) that generated them.
2. Consideration of Figure 2.4 indicates that samples with ~9% MgO could be parental to the more evolved mafic samples (MgO 3-9%), and thus the nature of their petrogenesis has implications for all the other mafic lavas in this study.

3.1.2 Classification

The samples are classified as basanites or basalts according to the Total Alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) vs. Silica (TAS) scheme of Le Maitre (1989), the relevant section of which is shown in Figure 3.1. Samples 232 and 235 lie either side of the boundary and both have some intermediate geochemical traits: sample 235 lies just on the silica-poor side of the boundary but will be treated as a basalt subsequently for convenience. Basalts are divided into alkali basalts (*ne*-normative) and olivine tholeiites (*hy*-normative).

The colour scheme used in these figures i.e. basanites as filled red diamonds, alkali basalts as green and olivine tholeiites as black, will be used throughout the chapter.

3.1.3 Geographical distribution

Figure 3.2 shows the distribution of the samples across the field area. Three important points can be made:

First, they are confined to the Buckland and Springsure provinces. Secondly, the basanites are restricted to an area west of the main Buckland lava sequences, where they are characterised in outcrop by eroded volcanic plugs (see Plate 1.2) and occasionally as lava flows. Three basanites which contain < 9% MgO (see Chapter 4) all occur within the Battleship Spur section marked on Figure 3.2. Thirdly, the basalts are widely distributed throughout Buckland and Springsure, and occur only as lava flows (with the exception of the Mt. Tabor intrusion). The tholeiites are confined to the Springsure province, while the alkali basalts occur in Springsure (1 sample), south Buckland (3) and the Mt. Tabor area (1).

3.1.4 Age constraints

Unfortunately, little can be said with confidence on this aspect as none of the new sample set has been dated. A brief discussion follows, based on observed field relations and previously published data.

Buckland

In a compilation of previous published and unpublished dates, Griffin *et al.* (1987) give the age range of the main central volcano as 25-28 Ma (using the K-Ar method). However, basanites such as AJS 126 which form plugs close to the main lava pile are not represented compositionally within it. This suggests either that the plugs are the remains of feeders to now-eroded, stratigraphically-higher basanite lava flows, or that they represent minor intrusions which may pre-date, post-date or be synchronous with the lava pile. Griffin *et al.* (1987) suggest that the more eroded nature of the igneous bodies in the area west of the shield (i.e. towards the Mt. Tabor area) is consistent with an age greater than the main volcano. However the original lava pile probably thinned away from the main shield centre and was thus more easily eroded away. The only cross-cutting relationship observed in the field involves the Mt. Tabor intrusion referred to above (AJS 102) which intrudes into basanitic lava flows. This could suggest that basaltic activity post-dated basanitic, provided that the intrusion is contemporaneous with basalt extrusion. A compositionally very similar coarse-grained sample (AJS 236) is found in the main lava pile at Battleship Spur 50 km to the east (occurring just above a flow dated at 27.3 Ma; Griffin *et al.*, 1987). The poor accessibility of the exposure makes it hard to verify whether this is a lava flow or a sill. If the latter is the case then it would suggest a period of minor basaltic intrusive activity at this latitude after the main period of basaltic and basanitic extrusion. Basanite lava flows are rare in the main Buckland sequences, being confined to one thick flow (whose MgO content <9) towards the base of the Battleship Spur sequence (see Figure 2.1 for location).

A plausible chronology, which fits the sparse evidence, consists of early basanite magmatism which overlaps briefly with the eruption of the main basaltic sequences. These are post-dated by a minor basic intrusive phase.

Springsure

Sutherland *et al.* (1989a) give the age range of the main sequence of basaltic extrusion in Springsure as 33-26 Ma. Ewart (1982) provides ages (25.2 and 25.4 ± 0.2 Ma) for two lavas from the eastern part of the Rolleston Road section, from which lavas AJS143 and 144 were sampled. Other Springsure samples lie towards the base of their respective sequences.

3.2 PETROGRAPHY

Table 3.1 details the modal analyses of these samples, which petrographically fall into three main categories, namely dolerites (AJS 102, 236), aphyric basalts (AJS 167, 168, 175, 182, 232, 235), and porphyritic basanites and basalts.

3.2.1 Dolerites

They consist of olivine, clinopyroxene, plagioclase and Fe-Ti oxide in the approximate proportions 20:18:57:5. Olivine crystals are euhedral and up to 1.5 mm long, commonly occurring in small aggregates; there is minor alteration to chlorite. Compositions lie in the range Fo₅₆-Fo₆₅. Plagioclases (An₄₉-An₅₉) are elongate and up to 3mm long. Intergranular/ophitic clinopyroxene (Ca₄₇Mg₃₈Fe₁₅-Ca₄₇Mg₄₁Fe₁₂) is slightly pink in colour and shows minor zoning due to variation in TiO₂ content (1.63-3.07%). Oxide minerals have a platy habit in AJS 102; some hexagonal/octagonal basal sections are visible and range in diameter up to 0.5 mm. Ilmenite in AJS 236 is, by contrast, ophitic. Tubular apatite needles (<0.3 mm) are commonly observed within plagioclase crystals in AJS 236: they are much less common in AJS 102. Alkali feldspar is also present in minor amounts in AJS236. Sample AJS 102 has an intergranular texture while AJS 236 has an ophitic texture (see Plate 3.1).

3.2.2 Aphyric basalts

These all contain euhedral olivine crystals (Fo₇₇-Fo₈₂) whose lengths vary between 0.09 and 1 mm, with an average of 0.3 mm. Minor alteration to iddingsite or chlorite is visible along cracks. Elongate plagioclase crystals (An₄₀₋₅₈) range up to 1 mm in length, but are usually ~0.5 mm. Clinopyroxene (Ca₄₆Mg₃₅Fe₁₉-Ca₄₆Mg₄₁Fe₁₃) occurs as intergranular or ophitic crystals. Intergranular examples rarely exceed 0.15 mm in length, while ophitic ones range up to 0.75 mm in length but more commonly lie between 0.3-0.4 mm. Compositionally, clinopyroxene in most samples displays the pink colour (and occasionally the hourglass twinning) characteristic of titanaugites (TiO₂ content varies between 1.80 and 3.73 %). These crystals are usually zoned, with the edges being more deeply coloured than the cores. Fe-Ti oxides occur as plates up to 0.4 mm across. Apatite is a commonly occurring accessory mineral: needle-shaped, high relief crystals are observed in plagioclase crystals. Proportions of phases in these samples vary greatly: olivine from 8-23%, clinopyroxene from 20-36%, plagioclase from 39-52% and Fe-Ti oxide from 4-11%. Plate 3.2 is a photomicrograph of sample AJS235.

3.2.3 Porphyritic basanites and basalts

Phenocryst assemblages are dominated by olivine (57-100%), crystals of which range up to 2 mm in length, but average ~0.25 mm; compositionally they lie between Fo₆₈ and Fo₈₄ in the basanites and Fo₇₂ and Fo₈₄ in the basalts. Augite is a rarer phenocryst phase, and varies compositionally according to the type of host lava. Basanite examples lie in the range Ca₄₉Mg₃₉Fe₁₂-Ca₅₁Mg₃₇Fe₁₂ with

1.81-2.97% TiO₂, while basalt examples lie in the range Ca₄₃Mg₄₆Fe₁₁-Ca₄₅Mg₄₃Fe₁₂ with 0.86-1.27% TiO₂. Plagioclase (An₅₄-An₆₆ in the basanites: An₆₃-An₆₆ in the basalts) is the least common phenocryst phase.

The groundmass (74-96% of total rock volume) consists of olivine + clinopyroxene ± plagioclase ± nepheline ± orthoclase ± Fe-Ti oxide, of which the latter is Ti-magnetite in the probed basanite samples AJS 39, 112. Crystals are mostly > 0.05 mm long and coarse enough to allow minerals to be distinguished at x10 magnification. The texture of the groundmass is most commonly intergranular, although nepheline (which is found in the basanites) is invariably ophitic and commonly contains needles of apatite. Minor alkali feldspar has been identified in AJS 112 where it occurs with nepheline. Plate 3.3 is a photomicrograph of basanite AJS101.

3.2.4 Xenoliths and megacrysts

These are found in a number of the basanites and basalts (see Table 3.2). Xenoliths comprise anhydrous spinel lherzolites (discussed in detail in Chapter 6), while the megacrysts are olivine which exhibits corroded and strongly zoned rims. Four microprobe analyses are given in Table 3.2 below, together with a phenocryst composition (the most magnesian of those probed from the basanites) and an example from a spinel lherzolite. Clearly, the first three megacrysts plausibly represent xenocrysts derived from the disaggregation of lherzolite nodules. The rim composition however, could reflect re-equilibration with the lower temperature/pressure liquidus composition illustrated by the phenocryst analysis.

	Megacrysts				Phenocryst	Xenolith
Analysis	18.11	18.3	17.3*	17.A*	17.1	6.9
			core	rim		
SiO ₂	40.60	41.37	41.60	41.23	40.15	41.02
FeO	12.04	10.08	10.11	13.31	14.87	9.35
MnO	0.22	0.14	0.18	0.12	0.14	0.10
MgO	48.10	49.27	49.26	46.81	45.08	49.17
CaO	0.06	0.03	0.01	0.09	0.21	0.06
NiO	0.27	0.42	0.41	0.38	0.20	0.41
Total	101.29	101.31	101.57	101.94	100.68	100.11
Fo content	87.7	89.7	89.7	86.2	84.4	90.3

* analyses 17.3 and 17.A are from the core and rim respectively of the same crystal.

Table 3.2 Compositions of analysed olivine megacrysts from lavas of the 9-12 group, with a magnesian phenocryst and an example from a spinel lherzolite xenolith for comparison. The analysis numbers refer to those used in Appendix C where the full analyses are provided.

3.3 GEOCHEMISTRY

Major and trace element data for the samples discussed in this chapter are provided in Table 3.3. The geochemical variation shown by the different lava types is represented in Figures 3.3, 3.4 and 3.5, and is discussed below.

3.3.1 Major elements

Major element oxides are plotted against MgO in Figure 3.3. Although there is a certain degree of overlap between lava types, basanites typically have higher concentrations of TiO_2 , $\text{Fe}_2\text{O}_3\text{T}$, MnO, MgO, CaO, Na_2O , K_2O and P_2O_5 than the basalts, and lower amounts of SiO_2 and Al_2O_3 . However, a certain amount of overlap in TiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, MnO and CaO between basanites and basalts indicates that the variation of these elements with MgO is independent of lava type. The two basalt types have similar concentrations of all elements except sodium which is more abundant in the alkali basalts than in the tholeiites. A variable amount of scatter is shown by the samples, being most obvious in the plot of Na_2O vs. MgO.

Mg-numbers ($100 \times \text{atomic Mg}^{2+}/\text{Mg}^{2+}+\text{Fe}^{2+}$, assuming $\text{Fe}_2\text{O}_3 = \text{FeO}/0.2$) of both basanites and basalts lie in the range 62-67, which indicates that they are not primary mantle melts (they should be greater than 68 to be in equilibrium with mantle olivines in the range Fo_{88-92} ; Irving and Green, 1976; Frey *et al.*, 1978).

In certain plots, e.g. Al_2O_3 and $\text{Fe}_2\text{O}_3\text{T}$ vs. MgO, linear trends involving basanites and basalts are defined, suggesting that the different lava types could be cogenetic. This is discussed in detail in section 3.3.4.

CIPW norms

In Figure 3.4 the normative characteristics of the samples (calculated assuming $\text{Fe}_2\text{O}_3/\text{FeO}=0.2$) are projected onto the *ne-di-ol-hy-qz* plane. All but one of the basanites (AJS 99) form a small group in the centre of the *ne-di-ol* triangle. The tholeiitic basalts form a small group in the *hy-ol-di* triangle, close to the boundary of silica undersaturation, while the alkali basalts define a linear trend between the basanites and the tholeiites. Alkali basalts AJS 232 & 235 that straddle the basanite-basalt divide in the TAS classification (section 3.1.2) are the most undersaturated of the basalts and they overlap the outlying basanite, AJS 99.

3.3.2 Trace elements

Plots of MgO against analysed trace elements are presented in Figure 3.5, and their characteristics are discussed below.

First Transition Series

Nickel and chromium concentrations vary in proportion to MgO contents, and are generally higher in the basanites than the basalts, and in turn higher in the tholeiites than the alkali basalts for a given MgO content. Vanadium and cobalt concentrations overlap in the basalts and basanites. Copper is more abundant in the basalts, while zinc is more abundant in the basanites.

Incompatible elements

Concentrations of incompatible elements are consistently higher in the basanites than in the basalts, while alkali basalts and olivine tholeiites have similar abundances. Concentrations in the basanites are more scattered than in the basalts, an observation which is well illustrated by the plots of Ba and Nb vs. MgO.

Typical spidergrams for each lava type are shown in Figure 3.6, and are normalised to the primitive mantle values of Sun and McDonough (1989). Basanite patterns are characterised by a distinct negative potassium anomaly, with niobium invariably having the highest normalised abundance of the plotted elements. Basalts have flatter patterns, as shown by AJS 102 and 144 in Figure 3.6b. There are a few examples of both alkali basalts (e.g. AJS 235) and olivine tholeiites (AJS 168) which show slightly negative potassium anomalies and have similar patterns to the basanites, albeit with lower normalised abundances (e.g. Figure 3.6a).

Incompatible element ratios are plotted in Figure 3.7. Ratios between pairs of highly incompatible elements (i.e. where bulk $D < 0.01$), e.g. Ba, Rb, Nb, K, Zr should be relatively unchanged during processes such as melting and fractional crystallisation (e.g. Weaver, 1991), since insignificant relative fractionation between the elements will occur. However, they may be modified by contamination by material whose ratios are significantly different to those of the primary liquid. Consequently they are used to infer source characteristics of primitive lavas. The plots in Figure 3.7 show that the basanites and basalts have generally distinct ranges of these ratios, although minor overlap is observed in certain cases (e.g. Ba/Nb).

3.3.3 Isotopes

All the samples were analysed for $^{87}\text{Sr}/^{86}\text{Sr}$ and nine for $^{143}\text{Nd}/^{144}\text{Nd}$ (basanites AJS 101, 104, 108 & 113; basalts AJS 102, 144, 182, 235 & 236). Age-corrected data are provided in Table 3.3.

Figure 3.8 plots $^{143}\text{Nd}/^{144}\text{Nd}$ against $^{87}\text{Sr}/^{86}\text{Sr}$ showing that the samples define a linear group which lies within the field of ocean island basalts (Thompson *et al.*, 1998), but projects on the low- $^{87}\text{Sr}/^{86}\text{Sr}$ side of the OIB array. The basanites project on the low- $^{87}\text{Sr}/^{86}\text{Sr}$ side of the total group. AJS 182 forms a prominent outlier with an elevated $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.703990) compared to the other samples.

Selected plots of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. major and minor trace elements are given in Figure 3.9 which, unlike Figure 3.8, includes the $^{87}\text{Sr}/^{86}\text{Sr}$ data for the whole 9-12 group. They show the basanite $^{87}\text{Sr}/^{86}\text{Sr}$ to lie between 0.7030 and 0.7037, alkali basalts between 0.7034 and 0.7040 and olivine tholeiites all at ~ 0.7036 . Overlap between basanites and alkali basalts involves the samples which overlap in the normative plot (Figure 3.4): basanite AJS 99 has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and lowest normative nepheline content of the basanites, while AJS 232 and 235 have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ and highest normative nepheline content of the alkali basalts.

3.3.4 Relationship between the basanites and basalts

It was noted in section 3.3.1 that the major element data define linear trends involving the basanites and the basalts (e.g. Al_2O_3 , CaO vs. MgO) which suggested that the two lava types might be cogenetic. However, there are several lines of evidence which argue against this possibility:

1. A single fractionating mechanism (as implied by approximately linear trends in Figure 3.3) could not be reconciled with the complete overlap in mg-number of the basanites and basalts (indicating overlap of degree of fractionation) but massive variation in normative nepheline content.
2. The two groups have different isotopic values, trace element ratios and spidergram patterns, although with minor overlap (e.g. AJS235). These geochemical parameters are all considered to reflect the source characteristics of primitive basaltic rocks such as these. They consequently indicate that the basanites and basalts have different sources.
3. Any cogenetic hypothesis would have to account for the difference in isotope and trace element ratios shown by the basalts and basanites. This requires interaction with material which has a different composition to the primary magma. Hypotheses involving AFC of basanitic liquid to produce the basalts, however, is inconsistent with the overlap in MgO and mg-numbers of the two lava types.
4. Although there is evidence for fractional crystallisation, this need only have occurred within the separate groups, and modelling demonstrates that the trends (e.g. apparent increase in SiO_2 , Al_2O_3 and decrease in CaO with falling MgO content) could not be generated by any combination of the observed phenocryst phases (nor indeed unobserved phases such as amphibole or phlogopite). However, a hypothesis involving AFC of basanitic liquid to produce the basalts is inconsistent with the overlap in MgO and mg-numbers of the two lava types. Mg-numbers overlap completely (Table 3.3), and are thus consistent with two separate fractionation trends.

Consequently the apparent trends shown in Figure 3.3 are interpreted as an artefact of the dataset. However, the occurrence of magma mixing is indicated by the intermediate geochemical and isotopic characteristics of AJS235 between the basanites and basalts referred to in the sections above.

3.3.5 Comparison with published data

Comparison was made between lavas from the 9-12 group and examples from eastern Australia in Chapter 2, using trace element and isotopic data. These showed that the basanites showed strong similarity to lava field basalts from Queensland (interpreted as being derived from the shallow asthenosphere: Sun *et al.*, 1989), while basalts lie at the isotopically depleted end of the field of Queensland central volcano lavas, and within the 'plume' field defined by other primitive central volcano samples. Note that some further support for these comparisons comes from trace element ratios: Ba/Nb for the basanites is 4-7 (lava field provinces 4-13: Table 1.3) and basalts 6-12 (central volcanoes 8-13). In line with the conclusions of Sun *et al.* (1989), the preliminary conclusion can be drawn that the basalts are typical 'plume'-derived central volcano lavas, while the basanites are dominated by a shallow asthenospheric source.

3.3.5 Preliminary interpretation

The geochemical and isotopic data detailed above show that:

1. The major and trace element data show considerable scatter, as found in all east Australian Cainozoic provinces (e.g. Ewart, 1982).
2. Mg-numbers of both basanites and basalts lie in the range 62-67, which indicates that although they are primitive, they cannot be primary mantle melts. Petrographic evidence indicates that some fractional crystallisation of olivine $\pm$ clinopyroxene $\pm$ plagioclase has taken place.
3. Alkali basalts and olivine tholeiites are chemically very similar and aside from minor differences in their normative characteristics (the result of slight variations in their silica and alkali contents) and in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (constant in the tholeiites, variable in the alkali basalts), they are indistinguishable.
4. The basanites show a greater degree of scatter than the basalts, but are characterised by low silica contents, high incompatible trace element concentrations (on average double those of the basalts) and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Spidergram patterns are also distinct from the basalts having a pronounced negative potassium anomaly.
5. Derivation of basanites and basalts from the same source is unlikely. For example, although the mg-numbers of the two lava types overlap, they differ in isotopic compositions, spidergram patterns, incompatible trace element ratios and major element chemistry (especially silica). The first three of these are important indicators of the composition of the source of primitive lavas. Consequently the apparent trends observed in certain major element plots (e.g. Al_2O_3 and CaO vs. MgO) are not the product of common fractionation mechanisms, but rather an artefact of the fact that the basanites are richer in CaO and MgO , and poorer in Al_2O_3 and SiO_2 compared to the basalts. Overlap in certain parameters, e.g. isotopes and spidergrams (e.g. AJS235) suggests that some mixing occurred.

3.4 PETROGENESIS: INTRODUCTION

The aim of the final sections of this chapter is to establish petrogenetic models for the basanites and basalts which can account for their geochemical and isotopic characteristics. For continental basaltic rocks, this could involve any combination of: variation in source composition, variation in depth/degree of melting, magma mixing, fractional crystallisation $\pm$ assimilation processes in the mantle and crust, and post-eruptive alteration. These will be dealt with in reverse order in order to identify the parental compositions of the lavas, thus permitting comparison with experimentally-derived melt compositions which can be used to constrain source composition and the nature of melting. First, a brief introduction is given to computer modelling methods which will be referred to subsequently in the text.

3.4.1 Computer modelling

The 'modelling' referred to in subsequent sections refers to computer modelling using the DARTS software package of Duncan and Ewart (unpublished). This permits numerical modelling of various processes, including closed-system fractional crystallisation, and assimilation-fractional crystallisation (AFC), and forward modelling from a given magma composition with extraction of a given amount of inputted phase compositions. Fractional crystallisation hypotheses can be tested using least squares techniques which calculate major element fits between a starting and residual magma composition for given phase compositions; it calculates the best-fit phase proportions, F (fraction of melt remaining) and degree of fit (r^2). This is based on the techniques of Bryan *et al.* (1969) and the GENMIX program of Le Maitre (1981).

Also used is the OLFRACT calculation program of Cox (unpublished). This uses the equations of Roeder and Emslie (1970) and Pearce (1978) to adjust lava compositions for the fractional crystallisation of olivine, in effect replacing the olivine. It is possible to add olivine until the desired liquid MgO content is reached, or until equilibrium is reached with olivine of a chosen composition.

3.4.2 Alteration

In Section 2.2.3, the absence of a positive correlation between weight loss on ignition due to heat expulsion of volatiles (LOI) and concentration of mobile elements was ascribed to the absence of significant hydrous alteration of all the samples. However, it is prudent here to look specifically at the 9-12 group data-set, since it is possible that any correlation between LOI and mobile elements for these samples could be hidden within the scatter of all the other samples. To this end, mobile elements Rb, Ba and Na₂O are plotted against LOI in Figure 3.10. Clearly no correlation is visible, and a further plot involving Nb - an immobile HFSE (high field-strength element) - shows similar scatter to the more mobile LIL elements. Consequently it seems unlikely that significant alteration has taken place.

3.4.3 Fractional crystallisation ± assimilation

As outlined above, the mg-numbers of the basanites and basalts indicate that they are not primary mantle melts. Petrographic evidence points towards variable fractional crystallisation of olivine ± clinopyroxene ± plagioclase. Since these phases are euhedral and were thus in equilibrium with their host liquid immediately before eruption, they appear to result from low-pressure crystallisation. Olivine clearly dominates the phenocryst assemblages (Table 3.1), but significant accumulation of olivine cannot explain the elevated MgO contents of these lavas owing to the absence of correlation between volume % of olivine phenocrysts and MgO (Figure 3.11). Vectors indicating the effect of 10% fractional crystallisation of a combination of observed phenocrysts is shown in Figure 3.12, and could plausibly explain some of the geochemical variation within the lava groups. In the absence of any megacrysts (observed in alkaline lavas from provinces in NSW and Victoria: Binns *et al.*, 1970; Irving, 1974) there is no evidence of high-pressure fractional crystallisation. Xenocrysts of olivine in some of the basanites have already been shown to be disaggregated lherzolite crystals.

Evidence of other magma-modification processes, such as contemporaneous assimilation with fractional crystallisation, or interaction with the lithosphere during ascent are harder to constrain. Significant AFC in the xenolith-bearing lavas can be ruled out, since the presence of these nodules precludes a substantial crustal residence time when such contamination could occur (e.g. Spera, 1980). The xenoliths (lithosphere-derived: e.g. Griffin *et al.*, 1987) are all anhydrous (Chapter 6) and thus there is no evidence for interaction with any geochemically-mobile material in the lithosphere which could have significantly modified the compositions of these lavas. Furthermore, spidergrams of the basanites are comparable to examples from ocean islands, indicating little change in trace element ratios since segregation from their source.

Most of the basalts do not contain xenoliths (Table 3.1), and thus could have undergone assimilation with fractional crystallisation in the crust. Variation in isotopic characteristics, specifically that the tholeiites (none of which contain xenoliths) have $^{87}\text{Sr}/^{86}\text{Sr}$ values ~ 0.7038, while alkali basalts range from 0.7034 (xenolith-bearing sample AJS235) to 0.7040, can be interpreted in two ways. First that they reflect the isotopic heterogeneity of a common source, or secondly that they represent variable amounts of AFC acting on their parental liquids. Upper crustal sediments found in southeastern Australia could provide an appropriate assimilant composition, having $^{87}\text{Sr}/^{86}\text{Sr}$ ~ 0.719 (Ewart, 1982).

It is concluded that the dominant process which modified the compositions of the liquids which were parental to the 9-12 group was fractional crystallisation of olivine. Consequently, in order to estimate the compositions of these parental liquids to permit comparison with experimental melting data, the OLFRACT program of Cox (unpublished) was used to replace fractionated olivine in the lavas. Lavas were modified to be in equilibrium with mantle olivine of composition Fo_{87.5}, which is the average

of the compositions of the three mantle xenolith compositions considered by Hirose and Kushiro (1993) and Kushiro (1996) in their melting studies. Correction to either of the other values (Fo_{85} and $\text{Fo}_{89.1}$) makes little difference to the modified lava compositions. Examples of these compositions are shown in Figure 3.13, where the basanites and basalts define separate linear trends in plots of SiO_2 , Al_2O_3 , Sr and Nb vs. MgO.

3.4.4 Lherzolite melting and the role of H_2O and CO_2

This is a brief review of recent experimental work carried out on the melting of spinel- and garnet-bearing lherzolite with a view to understanding the generation of the basalts and basanites of the 9-12 group. Although the presence of volatiles (mainly H_2O and CO_2) can clearly have a profound effect on melt compositions and especially on silica concentrations, the effects are still not fully understood.

Lherzolite (spinel- or garnet-bearing, depending on pressure: transition at ~27-30 kbar.) in the upper mantle is now widely accepted as the source rock for the generation of anhydrous basaltic magmas (see, for example, reviews in Wilson, 1989 and Hall, 1996). Various workers have sought to study and constrain the conditions of melting of lherzolite in terms of pressure, temperature, presence of volatiles and degree of partial melting in order to experimentally derive the range of basaltic compositions which are observed.

Melting of anhydrous peridotite

Hirose and Kushiro (1993) and Kushiro (1996) studied the melting of three relatively fertile lherzolite nodules assuming them to be representative of basalt source compositions. Two are spinel-bearing (KLB-1 from New Mexico and HK-66 from Hawaii) while the other is garnet-bearing (PHN-1611 from Lesotho). The compositions of these xenoliths are presented in Table 3.4. Hirose and Kushiro (op. cit.) and Kushiro (op. cit.) subjected them to a range of upper mantle pressures and temperatures, and used aggregates of diamond to segregate the melts produced, whose compositions they determined after quenching. They were able to generate a wide range of basaltic compositions (see, for example, Table 3.5 and Figure 3.14). The data show that lowering the degree of melting, or increasing the pressure, results in increasingly silica-undersaturated melts, while increasing the degree of melting generates liquids of progressively greater silica saturation. Clearly melting of anhydrous lherzolites at up to 30 kbar and 1500 °C can produce a wide range of alkalic and tholeiitic basalts and picrites ($\text{MgO} \geq 15\%$), but not liquids containing $\leq 44\%$ SiO_2 (i.e. including basanites). Extrapolation of the data to higher pressures suggests that melts containing 44% silica would not be generated below 38 kbar, and 42% (the concentration in some of the basanites) until ~50 kbar. However extrapolation of the data 20 kbar above the limits of the experiments cannot be justified in the absence of any melting data in this pressure range.

The effect of volatile phases on melting of peridotite

The presence of the volatile species H_2O and CO_2 in the source, either within mineral phases or interstitially, is known to have a dramatic effect on melting by a considerable reduction of the solidus temperature, an increase in the degree of partial melting, and a change in melt composition. Recent melting experiments carried out on hydrous spinel lherzolite (Hirose and Kawamoto, 1995; Hirose, 1997) show, for example, that addition of 0.3 wt.% H_2O to lherzolite reduces its solidus temperature from ~1250 to just below 1100 °C at 10 kbar with the generation of 7% partial melt. Hydrous ($\text{H}_2\text{O} > 3\%$) andesitic melts are produced at low temperatures (<1100 °C) while at higher temperatures basaltic melts similar to those generated under anhydrous conditions are derived.

Mysen and Boettcher (1975b) melted spinel lherzolite under various volatile compositions. Where $X^{\text{H}_2\text{O}}=1$, andesitic melts are produced between 7-22 kbar. With decreasing $X^{\text{H}_2\text{O}}$ in favour of CO_2 , basalts are formed with progressively lower silica saturation until at $X^{\text{H}_2\text{O}}=0.2$ basanitic melt is produced (1150 °C, 15 kbar). This increase in X^{CO_2} also increases the Ca, Al and alkali contents of the melt, while increasing the pressure generates progressively more silica-undersaturated liquids and decreases Ca and Al contents. Eggler (1978) noted that when total $\text{CO}_2+\text{H}_2\text{O}$ is small (<0.5 wt.%), the initial product of partial melting is nephelinitic, regardless of $\text{CO}_2/\text{H}_2\text{O}$ ratio. Above 0.5%, compositions between andesite (where $X^{\text{H}_2\text{O}}=1$) and basanite (where $X^{\text{CO}_2}=1$) are generated at 20 kbar.

Summary

It is possible to produce alkali basalt and ol-tholeiite from the same source by varying the pressure and/or the degree of melting of anhydrous lherzolite (higher pressure and lower degree of melting lead to more alkalic melts). This will be discussed in more detail in the next section with regard to the basalts of the 9-12 group. Basanitic melts can be produced from volatile-bearing peridotite at pressures ≥ 15 kbar where $X^{\text{H}_2\text{O}} \leq 0.2$ and $\text{H}_2\text{O}+\text{CO}_2 \geq 0.5$ wt.%. Eggler (1978) noted from experiments that these volatiles commonly reside in lherzolite within the amphibole pargasite. It is interesting to note that negative potassium anomalies (as observed in the basanites: Figure 3.6) are commonly attributed to the presence of residual amphibole or in the source of a magma.

3.5 PETROGENESIS OF THE BASALTS**3.5.1 Comparison of basalt compositions with experimental liquids**

This section addresses the question of whether the empirically-derived melt compositions of Hirose and Kushiro (1993) and Kushiro (1996) can be used to constrain the conditions of melting of the basalts from the 9-12 group. These workers carried out melting experiments on three different lherzolite compositions (Table 3.4) and demonstrated the importance of source chemistry in determining melt

composition. Average olivine composition from the three xenoliths is wide-ranging: Fo_{89.1} (a typical upper mantle value) in KLB-1, Fo_{87.5} in PHN-1611 and Fo₈₅ in HK-66 (average olivine).

The compositions of basalts modified for the extraction of olivine clearly overlap with the experimental melt compositions (Table 3.5). The silica-poor basalts (45-46% SiO₂) show closest similarity to melts produced at 30 kbar, and silica-rich basalts (47-48% SiO₂) to melts produced at 20kbar.

In Figure 3.14, the modified basalt contents of SiO₂, Al₂O₃, FeO(T), MgO and CaO are plotted together with melt compositions for the three nodules PHN-1611, HK-66 and KLB-1. The latter two are represented by fields on three of the plots to reduce clutter. Melts more siliceous than 49% (corresponding to pressures <20 kbar for PHN-1611 and <15 kbar for HK-66 and KLB-1) are omitted, since all the basalts under consideration contain < 48.2% silica. Of interest is the strongly linear nature of the basalt data-points. This feature cannot be modelled in terms of fractional crystallisation of olivine $\pm$ clinopyroxene $\pm$ plagioclase (using basalt phenocryst compositions) from the most silica-poor, magnesia-rich sample. Consequently it would appear to represent a melting trend.

The plot of MgO vs. SiO₂ in Figure 3.14 shows that four points (runs KH3, KH2, 467,464) from PHN-1611 lie along the observed basalt trend. They also lie more or less along the trend in the plot of Al₂O₃ and approximately parallel to the trend in the plot of FeO, but containing ~1.5% less of this oxide than the basalts. There is little overlap in the CaO plot, and indeed the trends diverge with increasing SiO₂. The data in Table 3.5 also show that the four runs exhibit a pattern of increasing melt fraction (F) with decreasing pressure and temperature as the silica content of the liquid falls. Coincidentally, the gradient of the line between the points on a P-T graph (Figure 3.15) is 2.3 °C/km, which is similar to the solid + liquid adiabatic gradients of 2.3 °C/km (Scarrow and Cox, 1995) and 2.6 °C/km (McKenzie and Bickle, 1988). This suggests that the range of basalt compositions could plausibly be generated by decompressive melting.

However, as demonstrated above, there is not complete geochemical overlap between the experimental runs and the modified basalt compositions. The FeO compositions of all the PHN-1611 melts are ~1.5% below the basalts, considered to represent a significant difference. Additionally, the poor overlap in terms of CaO must be explained:

FeO

The difference in concentrations can be explained in terms of the Fe/Mg ratio of the lherzolite source. Hirose and Kushiro (1993) noted that melts from HK-66 (mg-number of 85.3) are more Fe-rich than KLB-1 (mg-number of 89.6) which they ascribed to the higher FeO content of the starting compositions. This can be seen in the FeO-SiO₂ plot in Figure 3.14. The higher iron contents of the basalts suggest that they were derived from source with a higher Fe/Mg ratio i.e. a lower mg-number

value than PHN-1611. The plot in Figure 3.14 suggests that their source could have an mg-number comparable to HK-66, since the basalts plot in the high-Fe part of the field of HK-66 melts.

CaO

Hirose and Kushiro (1993) also noted that CaO contents of melts depend on the composition of the source. Again the difference can be seen in Figure 3.14 where the CaO content of melts from KLB-1 (CaO=3.44%) is greater than that from HK-66 (CaO=2.97%). Consequently it could be argued that melting of a source lherzolite with a lower CaO content than PHN-1611 could be responsible for the reduced CaO contents of the basalts.

Figure 3.14 also shows that run KH4 has the lowest CaO content of all the PHN-1611 runs, and is comparable with the basalts. This run is derived from the lowest temperature (1460 °C) of the 30 kbar runs, and the residue contains garnet. The next highest CaO concentration is from the next highest temperature run at 30 kbar i.e. KH3, which also contains residual garnet, but presumably a smaller amount than KH4 since it underwent a higher degree of melting). The low-CaO content of these liquids is thus ascribed to calcium being retained within the garnet. Clearly the low calcium content of the whole basalt array cannot be interpreted in this way as garnet is not stable at pressures below ~27-30 kbar. Spinel, which replaces garnet as the primary Al-bearing mineral in lherzolite at lower pressures, contains minimal calcium and thus has no effect on calcium release into melts.

Consideration of a geochemically depleted source composition is ruled out since, although such compositions are relatively CaO-poor compared to fertile lherzolite, they also have lower Fe/Mg ratios and lower concentrations of Al₂O₃ (the product of having already undergone melting). Consequently melts of such a composition would be relatively low in Al₂O₃ and poor in FeO, while the modified basalt compositions appear to be derived from a source with above-average Fe/Mg, although they do have below-average Al₂O₃ contents.

3.5.2 Nodule geochemistry

Smith and Boyd (1987) note that PHN-1611 shows evidence of the metasomatic introduction of Ti, Fe, Na and P shortly before ascent, and thus does not represent 'normal' primitive mantle. In eastern Australia, O'Reilly and Griffin (1987) record the occurrence of Fe-rich lherzolites which contain olivines of average composition Fo₈₆ from five Tertiary provinces between northern Queensland and Victoria. They interpret them as the result of interaction between lherzolite wall rock and basaltic liquids on the basis of large heterogeneous xenoliths which they observed. However Kushiro and co-workers, who have published several melting studies on the high-Fe/Mg nodule HK-66 make no mention of its condition, other than to refer to it as 'dry peridotite' (Takahashi and Kushiro, 1983). It is therefore impossible to state with confidence whether such high-Fe/Mg material exists to any significant extent in the convecting mantle, i.e. in sufficient volume to generate basalts by decompressive melting in a plume.

3.5.3 Isotopic variation in the basalts

As noted in section 3.2.3, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7038$ in the tholeiites, but 0.7034-0.7040 in the alkali basalts. This variation is significant, especially as the two basalt types overlap in all other geochemical characteristics. It is possible that the common source material is isotopically heterogeneous and that the tholeiites which have been sampled coincidentally all have the same isotopic composition. Alternatively it could reflect regional variation, since all the samples with $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7038$ (i.e. the tholeiites + AJS 182) are from Springsure, while those with $^{87}\text{Sr}/^{86}\text{Sr} < 0.7038$ are from Buckland. This suggests that the plume possible changed composition with time as the volcanism moved south from Springsure to Buckland. A further possibility, and the most likely, is the role of AFC which was discussed in section 3.4.3.

3.5.4 Mantle potential temperature

An estimate of the potential temperature of ascending material can be made by extrapolation of the solid + liquid adiabat and the solidus up pressure/temperature. Their intersection represents the pressure and temperature at which the upwelling material reached its solidus and started to melt. The potential temperature (T_p) can therefore be estimated by the extrapolation of a line of gradient $0.6^\circ\text{C}/\text{km}$ (the gradient of the solid adiabat given in McKenzie and Bickle, 1988) to the temperature axis, since T_p is the temperature that mantle material would have at the Earth's surface if it could be brought there adiabatically and without melting. This is illustrated in Figure 3.15, which also shows the considerable potential source of error in the estimate. This arises chiefly due to the similarity in gradient of the extrapolated solidus curve and the solid + liquid adiabat at pressures above 25 kbar, and thus any slight change in the gradients of these lines will dramatically change the position of the intersection. The lines intersect, as drawn, at 45 kbar/ 1590°C , which corresponds to a T_p of ascending material of $\sim 1500^\circ\text{C}$. However, the solidus curve at ≤ 30 kbar is estimated from Figure 3 of Kushiro (1996) by extrapolating isobaric runs to the temperature axis (i.e. $F=0$) on a graph of melt fraction (F) vs. temperature. This does not take into account any near-solidus effects such as isothermal eutectic melting which would give rise to slightly higher estimates for the solidus temperature at each pressure. In turn this would result in an intersection with the solid + liquid adiabat at < 45 kbar. Additionally, the linear extrapolation of the solidus above 30 kbar is questionable: first because it is not linear below 30 kbar and also because of evidence for a curved solidus displayed by nodule KLB-1 (e.g. Takahashi, 1986; Zhang and Herzberg, 1994) which also forms cusps at ~ 10 and ~ 27 kbar. Furthermore, since the degree of melting for each run was calculated from the K_2O content of the melt (assuming potassium to be perfectly incompatible in the melt), then all the estimates of F are likely to be subject to small error owing to instrument error, minor K partitioning etc. Consequently, the lower limit of the possible range of intersection pressures can be constrained to no higher than approximately above 30 kbar, since run KH2 was definitely generated above the solidus. The T_p of material intersecting with the solidus at 30

kbar. is 1410 °C. Although the mantle T_P has thus been rather only approximately constrained to between 1410 and 1500 °C, this is still important as the range is significantly above the value for average mantle (1280 °C: McKenzie and Bickle, 1988).

3.5.5 Estimated eruption temperatures

The method of Roeder and Emslie (1970) can be used to estimate eruption temperatures for olivine-phyric basalts and also the temperature at which olivine appears on the liquidus. In this study, the method can only be applied to two samples AJS 143 and 144 since all others are aphyric. Groundmass compositions are calculated using the known volume of phenocrysts (modal analysis: Table 3.1) and their compositions (Appendix C). The corrected analyses are then recalculated in mole %, and plotted in Figure 3.16 (Cox *et al.*, 1979 after Roeder and Emslie, 1970) from which an estimate of the eruption temperatures can be read (AJS 143: 1165 °C; AJS 144: 1140 °C). These lie within the range of measured temperatures for basalts (e.g. Macdonald, 1972), and also permit estimates to be made of the temperature gradient which the liquids experienced between segregation and eruption. Comparison of the basalt compositions with melts from PHN-1611 suggest they segregated at ~21-22kbar/1410 °C. Temperature gradients to the surface are then calculated as 3.5 and 3.8 °C/km for samples AJS 143 and 144 respectively, which are close to those calculated by Scarrow and Cox (1995) for the primitive lavas of the Skye Main Lava Series (~3 °C/km). They also lie within the limits calculated by Huppert and Sparks (1985) for mafic magmas ascending through the crust in dykes (2.5 - 5 °C/km), although this requires that they remain below their liquidus temperatures. Recalculation of the uncorrected (for olivine) but recalculated (mole %) analyses provides points on Figure 3.16 which are estimates for the temperature at which olivine appears on the liquidus (AJS 143: 1240 °C; AJS 144: 1250 °C). Note that the diagram predicts the liquidus olivine compositions to be ~Fo₈₅ which is very close to the most magnesian phenocryst analysed in these samples (Fo₈₄).

3.5.6 Comparison with Tasmanid seamounts

These form a linear chain off the coast of eastern Australia and demonstrate an age-latitude correlation comparable to the central volcanoes on land (section 1.1.1; Figures 1.2, 3.17). Eggins *et al.* (1991) note that the chemistry of lavas recovered from the seamount changes from alkali basalts to tholeiites, with an increase in Ba/Nb, a change in spidergram pattern, and more enriched isotopic ratios (i.e. lower ¹⁴³Nd/¹⁴⁴Nd and higher ⁸⁷Sr/⁸⁶Sr). The authors argue that this results from the interaction of a deeply derived EMI plume (dominating the tholeiite geochemistry) with “long-term depleted” upper mantle source material (from the asthenosphere or oceanic lithosphere). Figures 3.18 and 3.19 demonstrate that the basalts discussed in this study show greater geochemical similarity to the Tasmanid alkali basalts than to the plume-derived tholeiitic melts. This indicates that the contemporaneous mainland and Tasmanid plumes had different compositions.

3.6 PETROGENESIS OF THE BASANITES

It was noted in section 3.4.4 that basanites cannot be generated by melting of anhydrous peridotite within the range of P and T in the experiments (up to 1500°C and 30kbar.). Basanitic melts were, however, produced from spinel lherzolite (composition B in Table 3.4) in the presence of volatiles where $X^{\text{CO}_2} \geq 0.2$ by Mysen and Boettcher (1975). Unfortunately there is not the wealth of data providing compositions of melts generated under conditions of high X^{CO_2} that there is for melting under anhydrous conditions, or even conditions of high- $X^{\text{H}_2\text{O}}$. Consequently, a detailed assessment of the conditions of melting under which the basanites formed is not possible.

Mysen and Boettcher (op. cit.) provide only four melt compositions which have the low contents of silica characteristic of the basanites in this study: these are provided in Table 3.6, with the compositions of two basanite samples modified for the effects of olivine extraction. The silica content of the two runs at 1100°C and $X^{\text{CO}_2}=0.5$ are similar to that of sample AJS126, although there is poor overlap with other elements e.g. FeO and MgO. The run at $X^{\text{CO}_2}=0.2$ has a similar silica content to sample AJS100, but overlap between MgO and CaO is poor.

It is impossible, in the absence of further data, to establish whether these differences are a function of lherzolite composition, temperature, pressure and X^{CO_2} or degree of melting. Comparison with the first two experimental runs, which have the same T and X^{CO_2} , suggests that the silica content of the melt is independent of pressure (unlike anhydrous melting where it increases as the pressure falls), while Al_2O_3 and CaO decrease and FeO and MgO increase. However neither the fraction of melt in each case nor the residual phase assemblage are provided, both of which can strongly affect the composition of liquids.

In conclusion, melts with basanitic composition can be generated at much more reasonable P-T in the presence of CO_2 than is possible in anhydrous conditions. However, in the absence of further data it is impossible to place any further constraint on the conditions of basanite formation other than to note that similar liquids to the proposed parental basanite compositions can be produced at X^{CO_2} between 0.2 and 0.5, pressure between 10 and 20 kbar and temperature between 1100 and 1150°C.

3.7 CONCLUSIONS

The evidence presented in this chapter suggests that the basanites and basalts which constitute the 9-12 group are derived from different sources.

The major element geochemistry of the alkali basalts and olivine tholeiites of the group is consistent with derivation by the decompressive melting of lherzolite (garnet $\rightarrow$ spinel) with a lower mg-number, and lower CaO content than the experimentally melted PHN-1611. Segregation took place between 30-20 kbar (~100-65 km), with the most silica undersaturated melts coming from the highest pressures and lowest degrees of partial melting (~10%). Subsequently, the magmas underwent fractional crystallisation of olivine (8-16%), with minor clinopyroxene and plagioclase crystallisation (evident

from petrography); minor AFC cannot be ruled out, especially in the tholeiites. The P-T trajectory of melt segregation is compatible with melting of mantle material whose potential temperature lies between 1410-1500 °C. Comparison with other plume-related volcanic settings suggests that the actual T_P probably lies at the low end of this range. For example, Scarrow and Cox (1995) estimated the potential temperature of the plume which generated the much thicker (~1500m) Skye lavas as ~1440°C, although the greater thickness on Skye could be a result of greater thinning of the lithosphere thus permitting a higher degree of melting.

The basanites, by contrast, appear to be the result of melting of volatile-bearing lherzolite. The conditions of melting cannot be constrained in detail, but basanites can be generated at pressures ≥ 15 kbar and where $X^{H_2O} \leq 0.2$ and $H_2O+CO_2 \geq 0.5$ wt.%. The volatiles possibly resided in pargasitic amphibole which, if it remained in the lherzolite residue after melting, would account for the negative K-anomaly observed in the spidergrams of these lavas. The basanites are similar in isotopic and trace element ratios to examples from lava field provinces which have been interpreted as shallow-asthenospheric in origin since they are unrelated to the plume and yet undoubtedly originated in the convecting mantle. It is feasible that the Buckland basanites are older than the plume-related volcanism, although they overlap at the base of the Battleship Spur section (section 3.1.4) where lavas of intermediate origin between alkali basalt and basanite occur (e.g. AJS235). These could be the product of mixing between the two magma types. Furthermore, the required volatile conditions for basanite generation are thought to exist in the asthenosphere (e.g. Olafsson and Eggler, 1983).

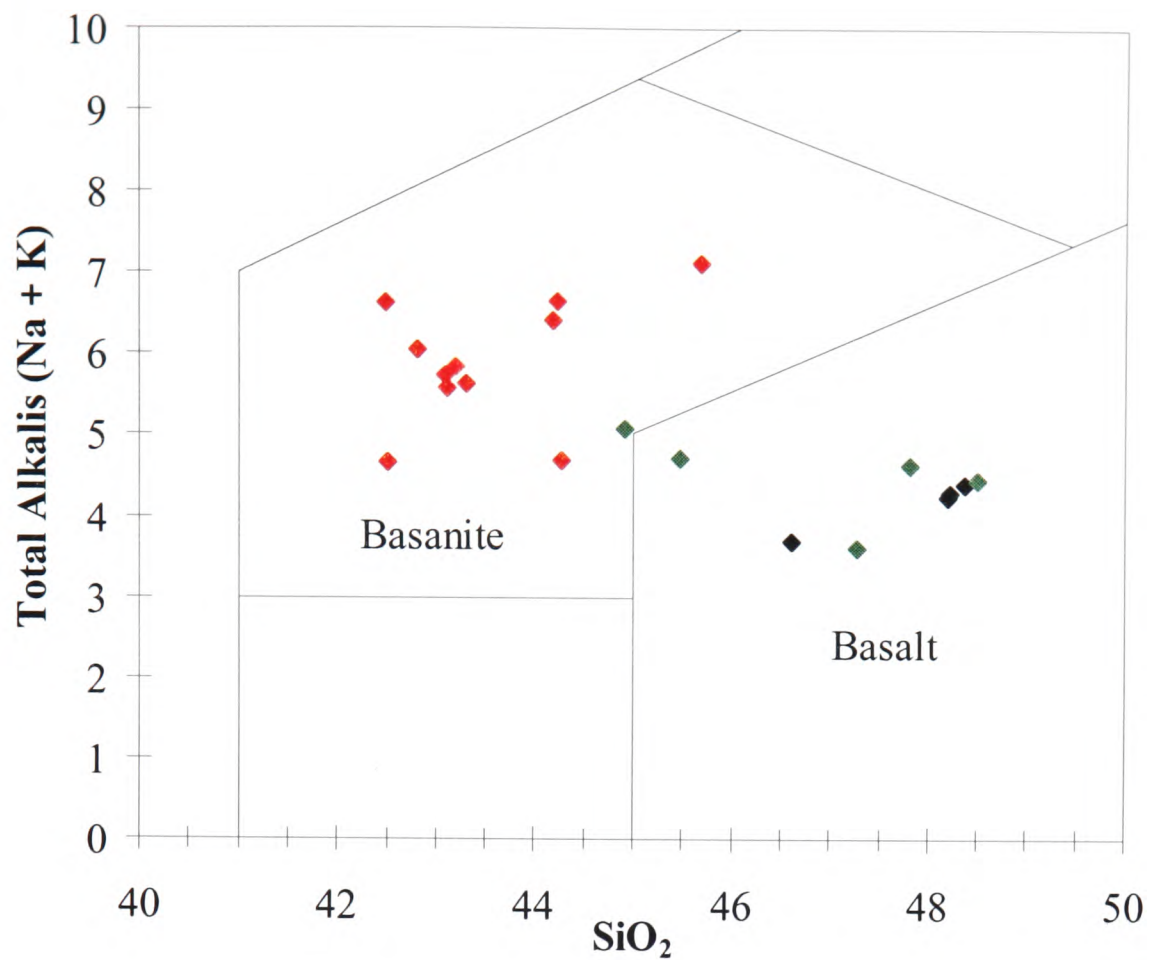


Figure 3.1 Classification of the 9-12 group using the TAS grid of Le Maitre (1989). The basalts are subdivided into nepheline-normative alkali basalts (green) and hypersthene-normative olivine tholeiites (black).

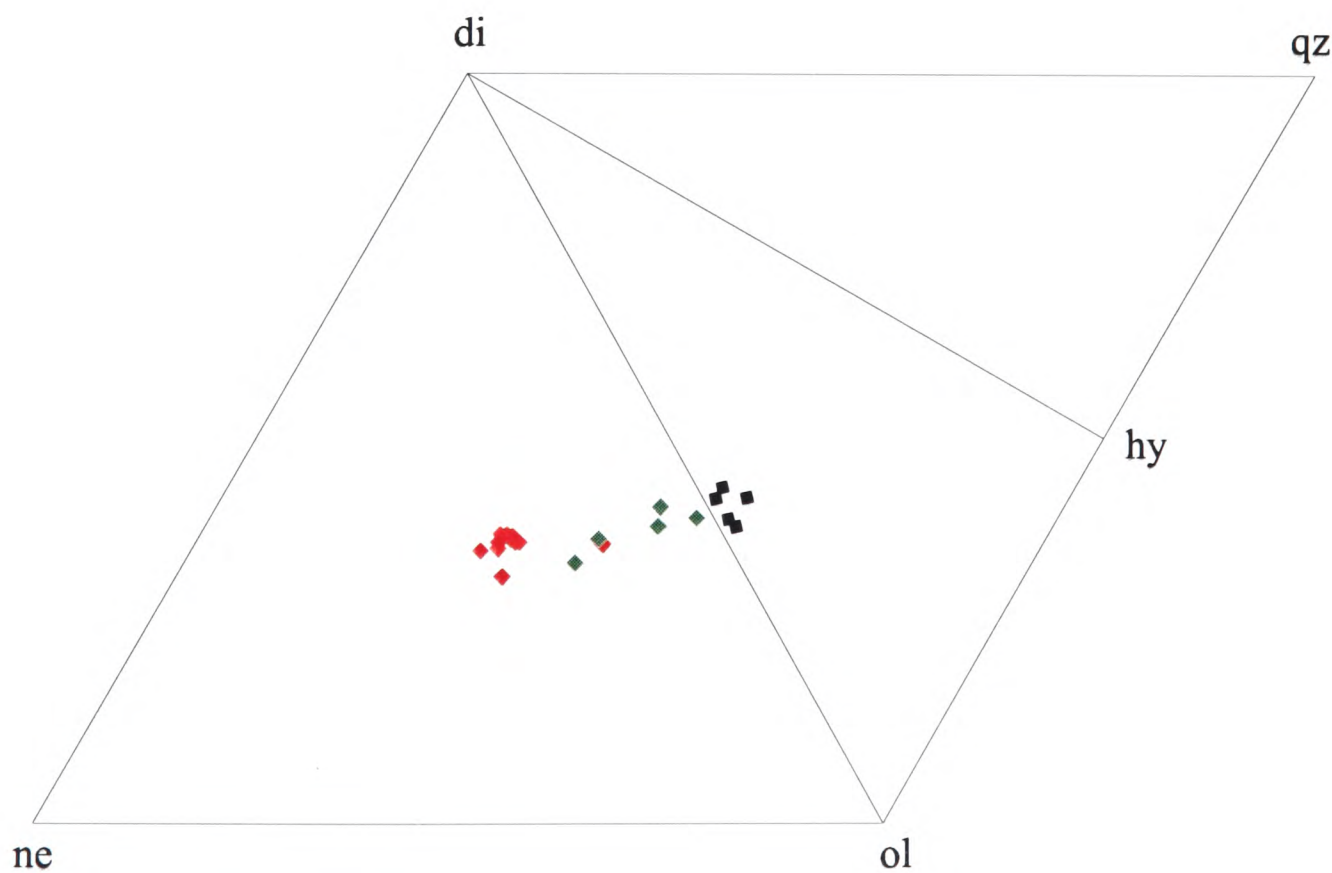


Figure 3.4 CIPW norms (assuming $\text{Fe}_2\text{O}_3/\text{FeO} = 0.2$) of the 9-12 group lavas projected onto *ne-di-ol-hy-qz*. Ornament is as Figure 3.1 above.

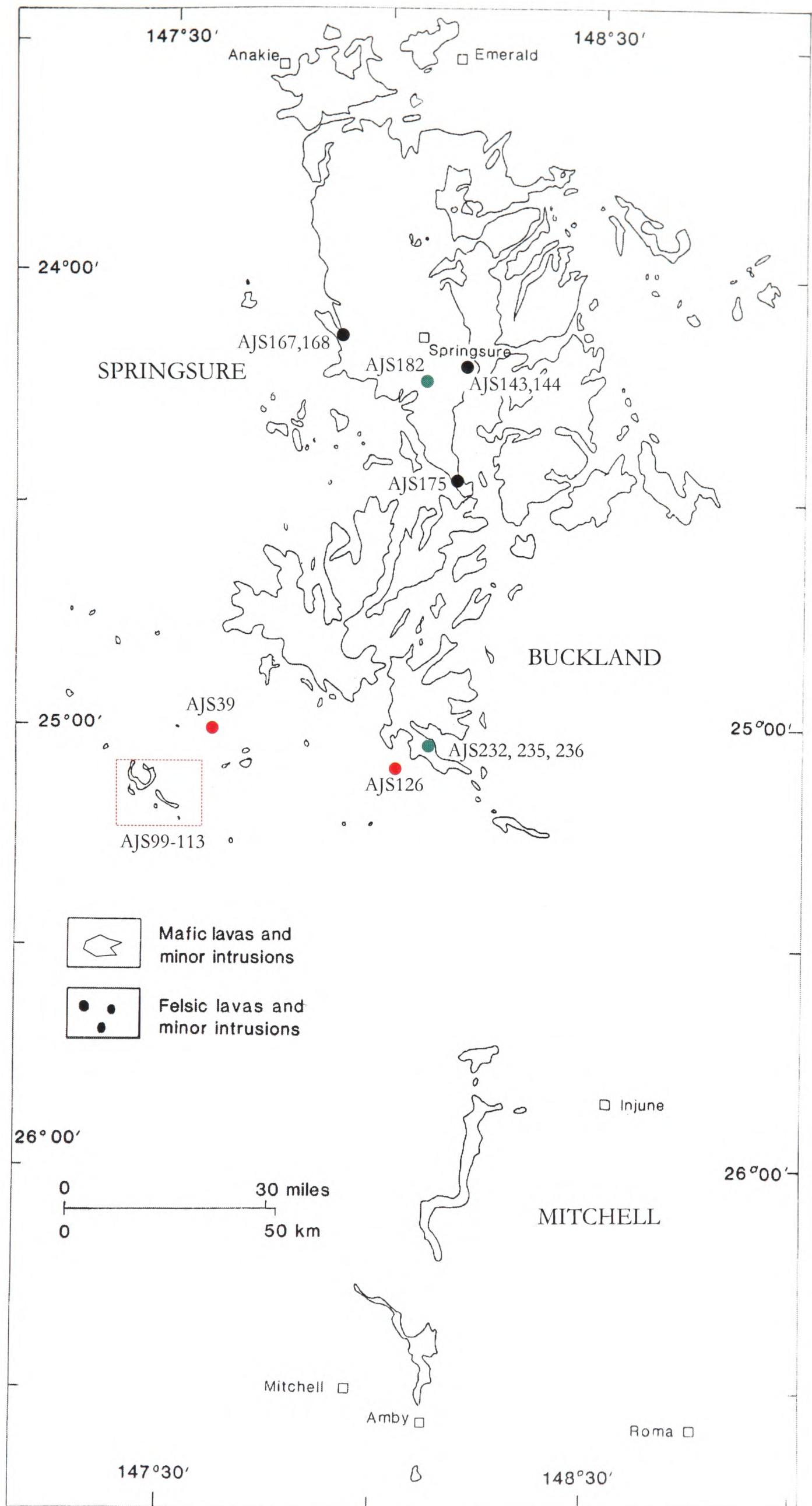


Figure 3.2 Map showing the location of samples from the 9-12 group. Red spots represent basanites, green spots alkali basalts and black spots olivine tholeiites. Note that the basanites **are confined to ~25°S**, while the olivine tholeiites all come from Springsure.

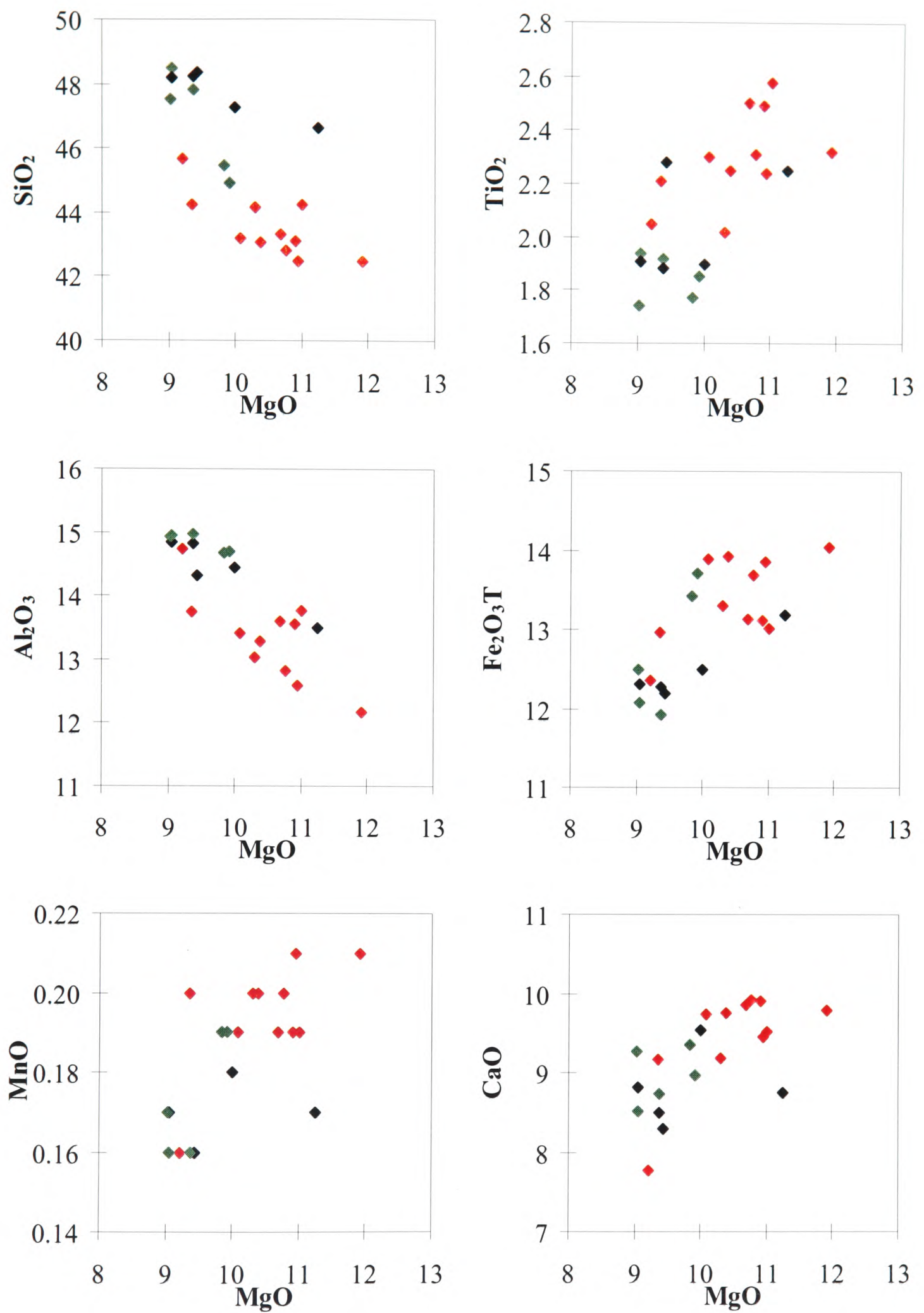


Figure 3.3 Major element oxides against MgO. Red spots represent basanites, green spots alkali basalts, and black spots olivine tholeiites.

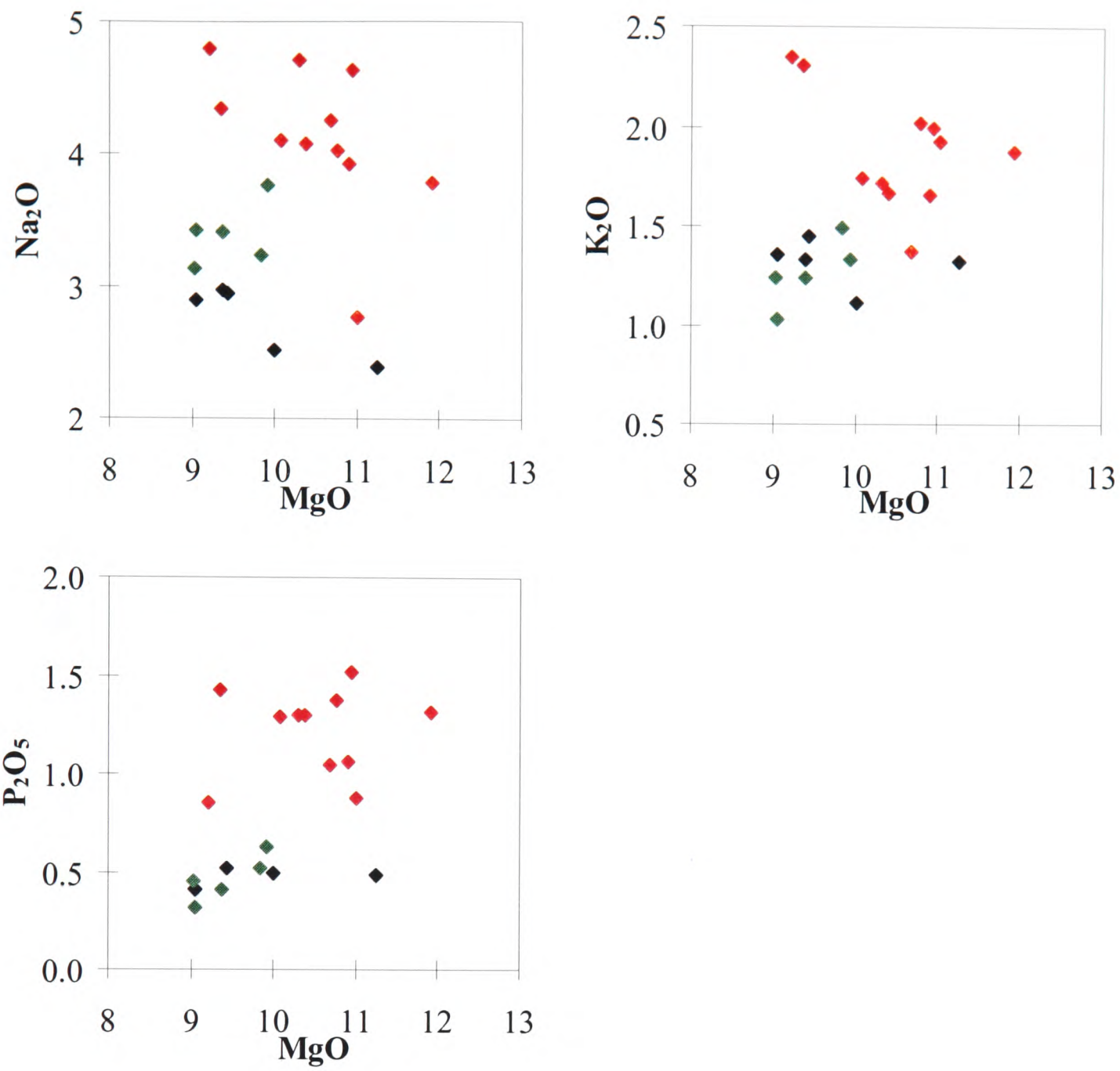


Figure 3.3 (cont.) Major element oxides against MgO. Red spots represent basanites, green spots alkali basalts, and black spots olivine tholeiites.

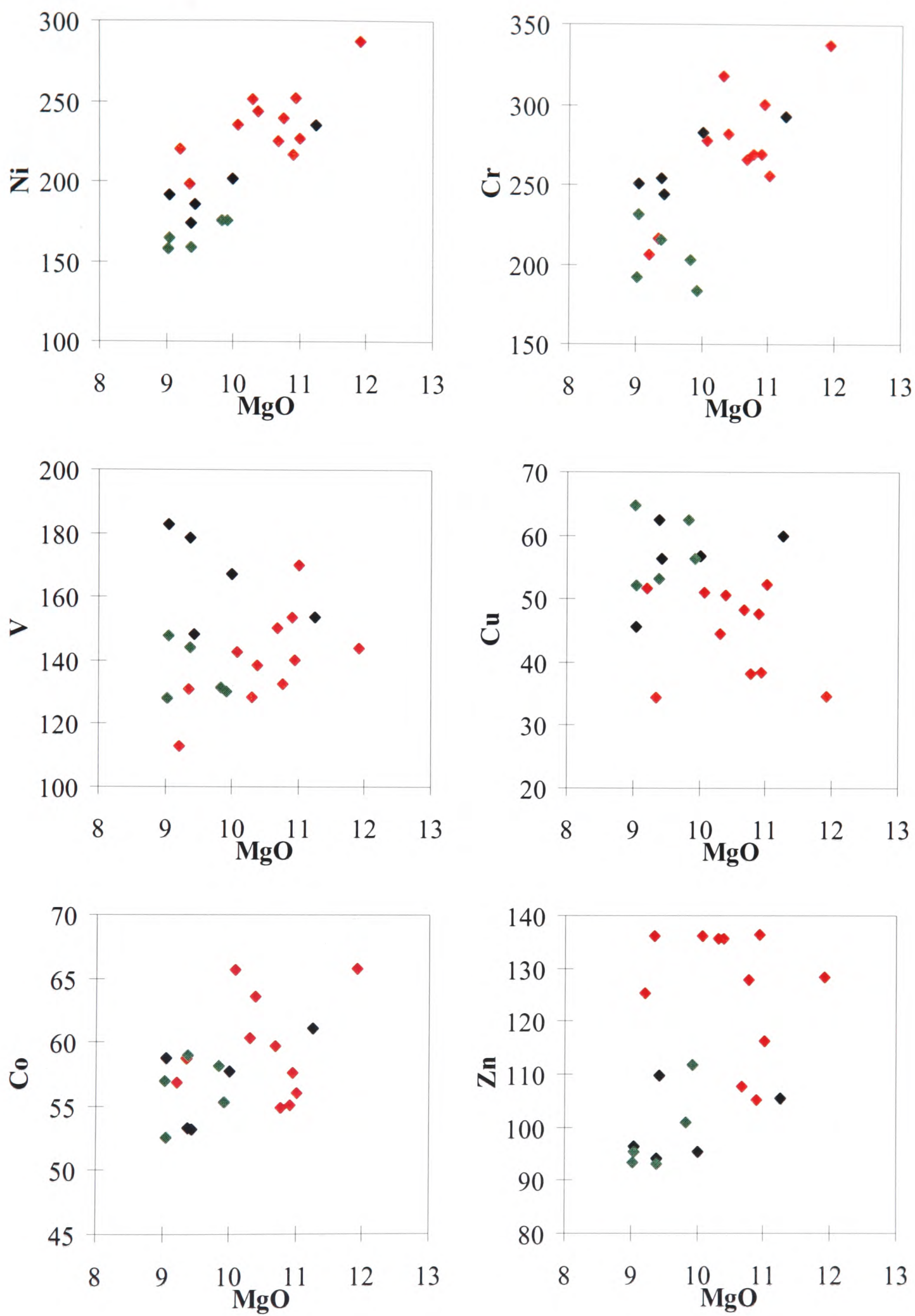


Figure 3.5 Trace element concentrations against MgO. For legend, see Figure 3.3.

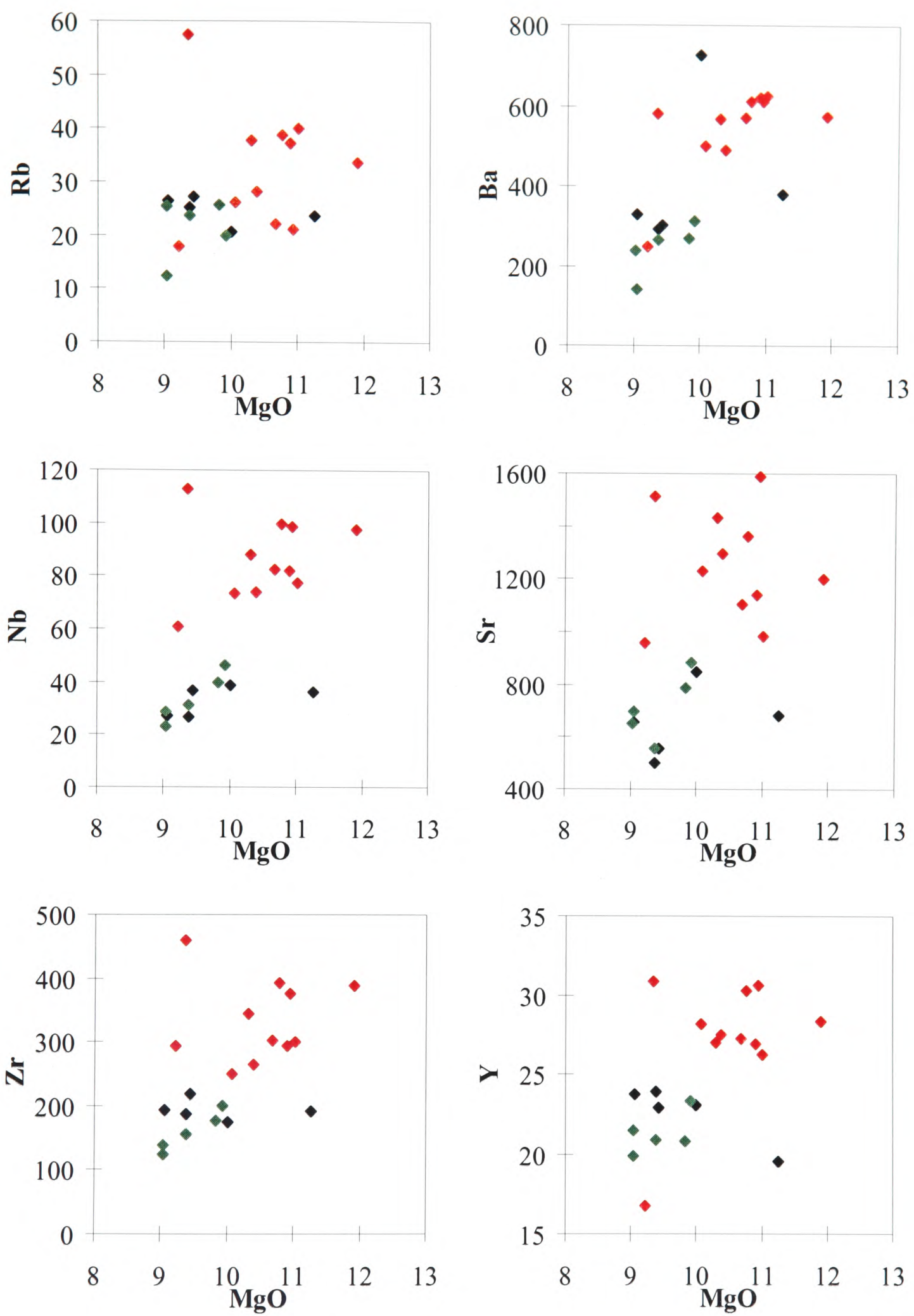


Figure 3.5 (cont.) Trace element concentrations against MgO. For legend, see Figure 3.3.

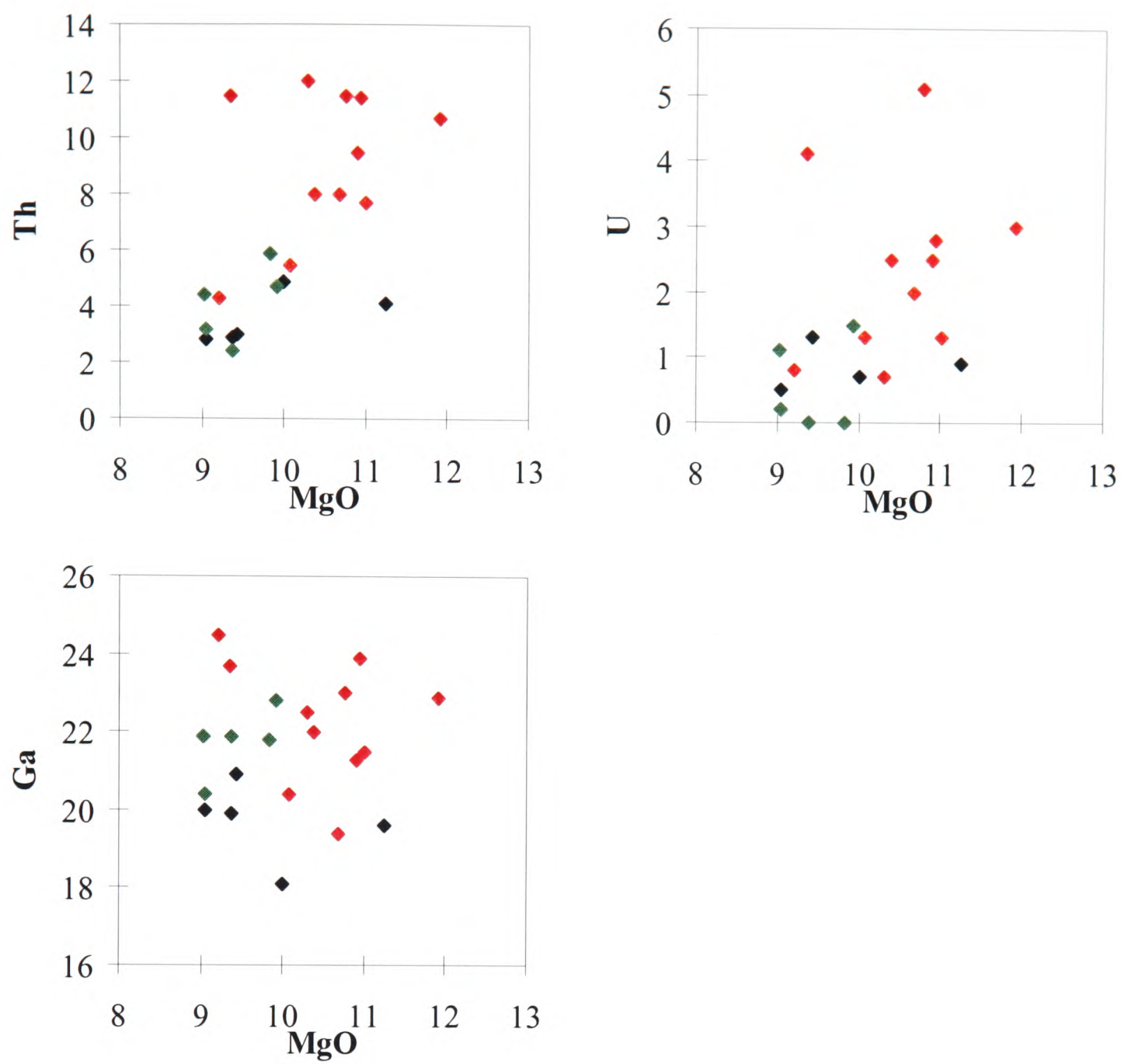


Figure 3.5 (cont.) Trace element concentrations against MgO. For legend, see Figure 3.3.

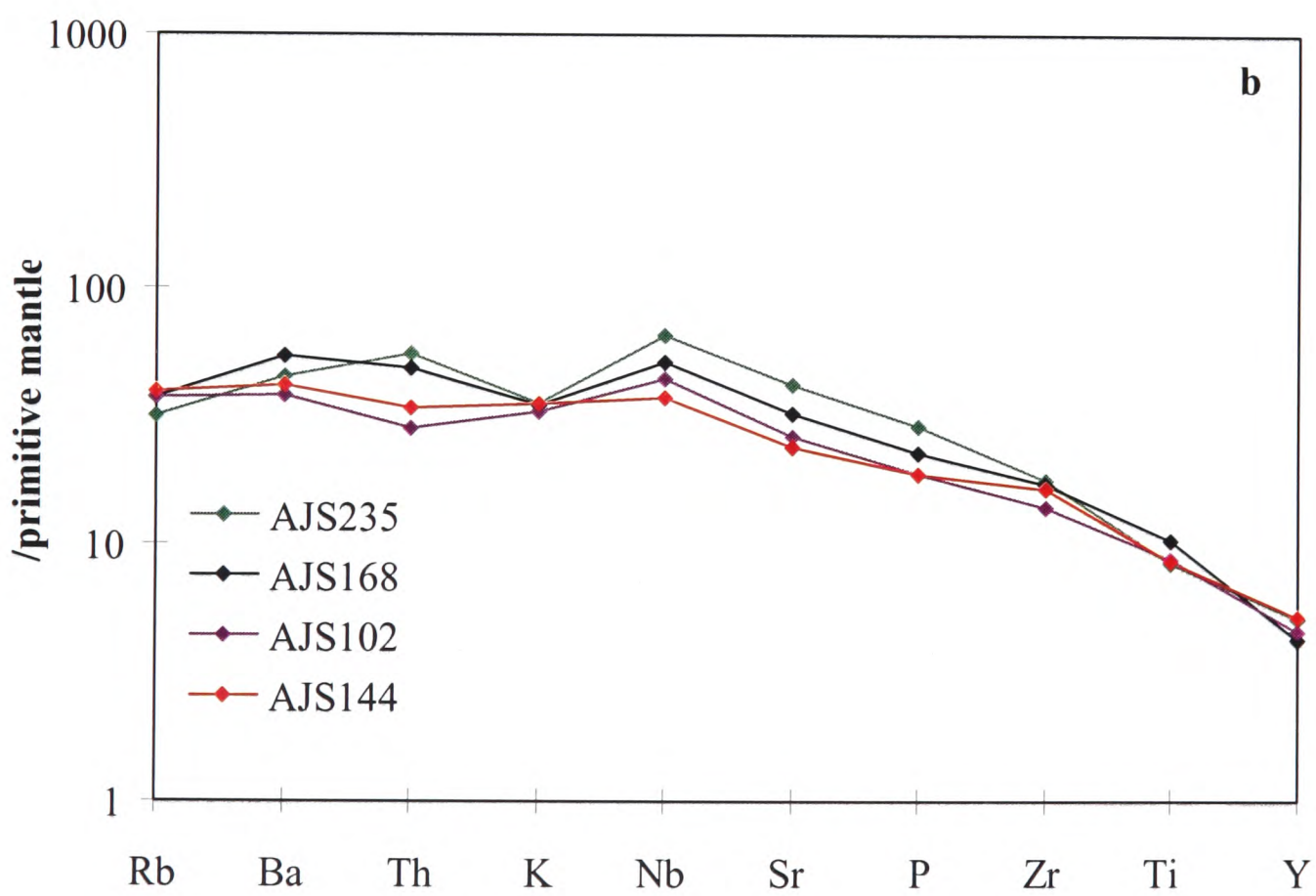
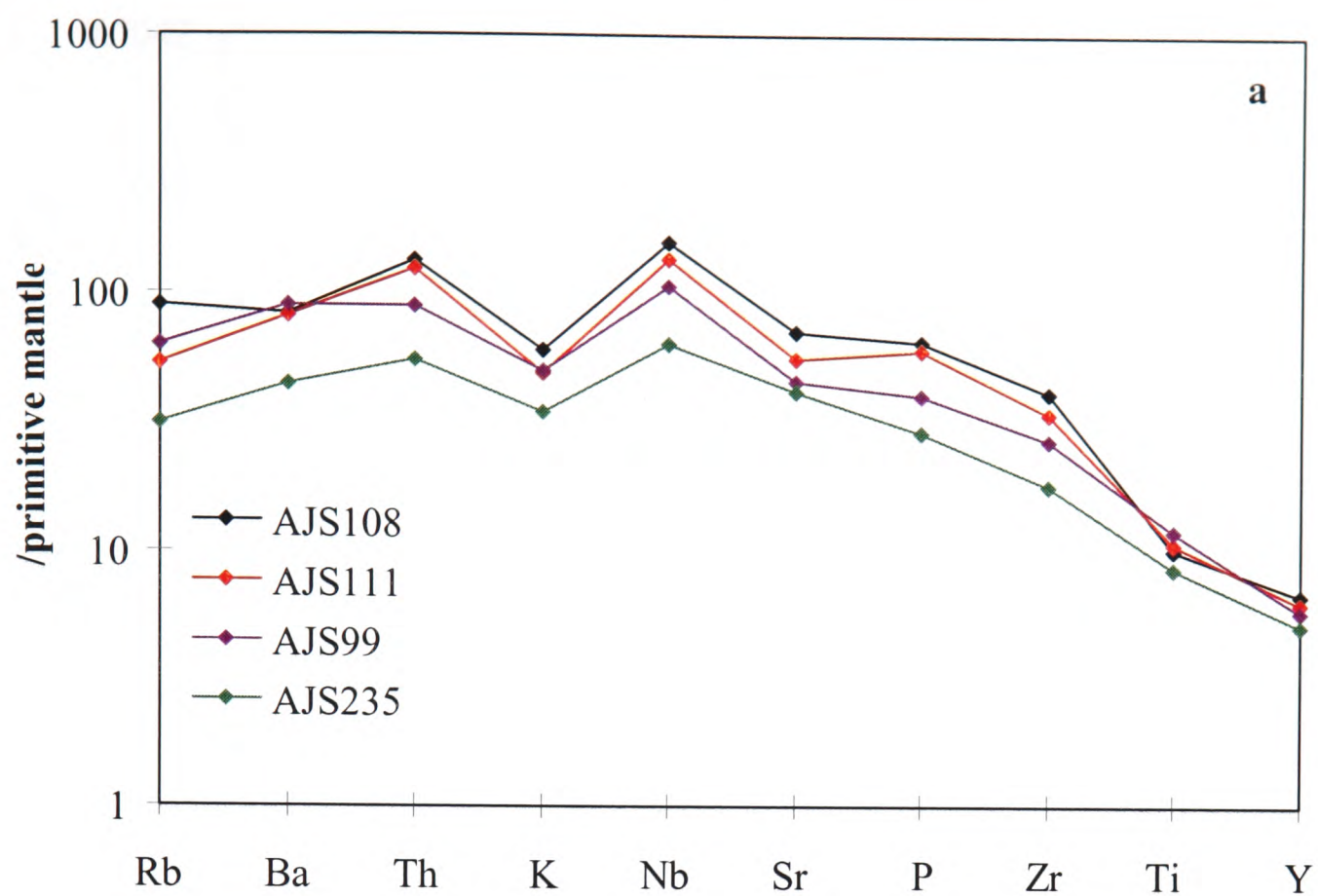


Figure 3.6 Spidergrams of selected samples from the 9-12 group, normalised to the primitive mantle concentrations of Sun and McDonough (1989).

a) Basanites AJS 108, 111 and 99 with alkali basalt AJS 235 for comparison.

b) Alkali basalts AJS 235 and 102; olivine tholeiites AJS 168 and 144.

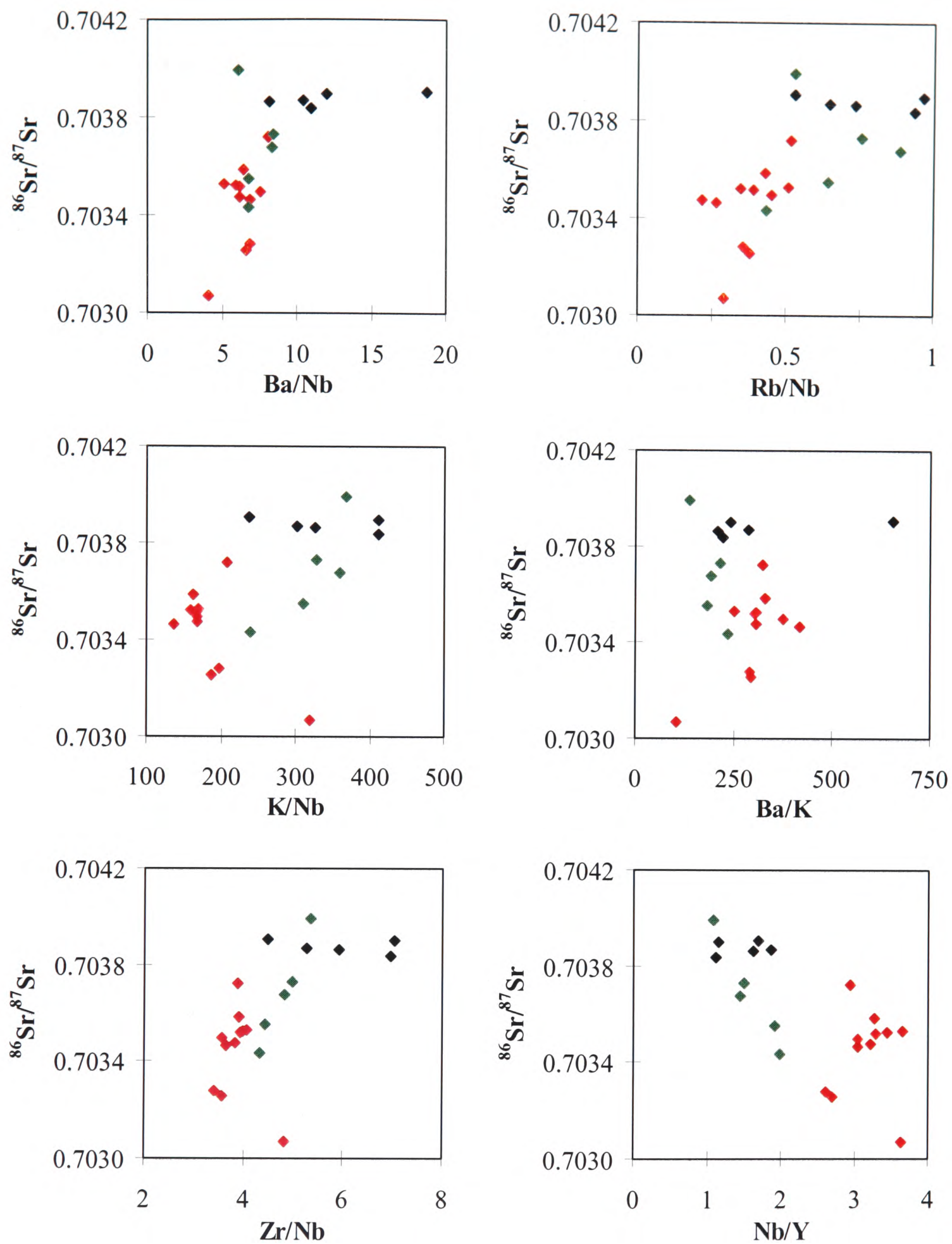


Figure 3.7 $^{87}\text{Sr}/^{86}\text{Sr}$ vs. incompatible element ratios for basanites and basalts. Note that they tend to form distinct groups. Olivine tholeiite AJS 175 forms an outlier in the plots involving Ba owing to its elevated Ba content (727 ppm).

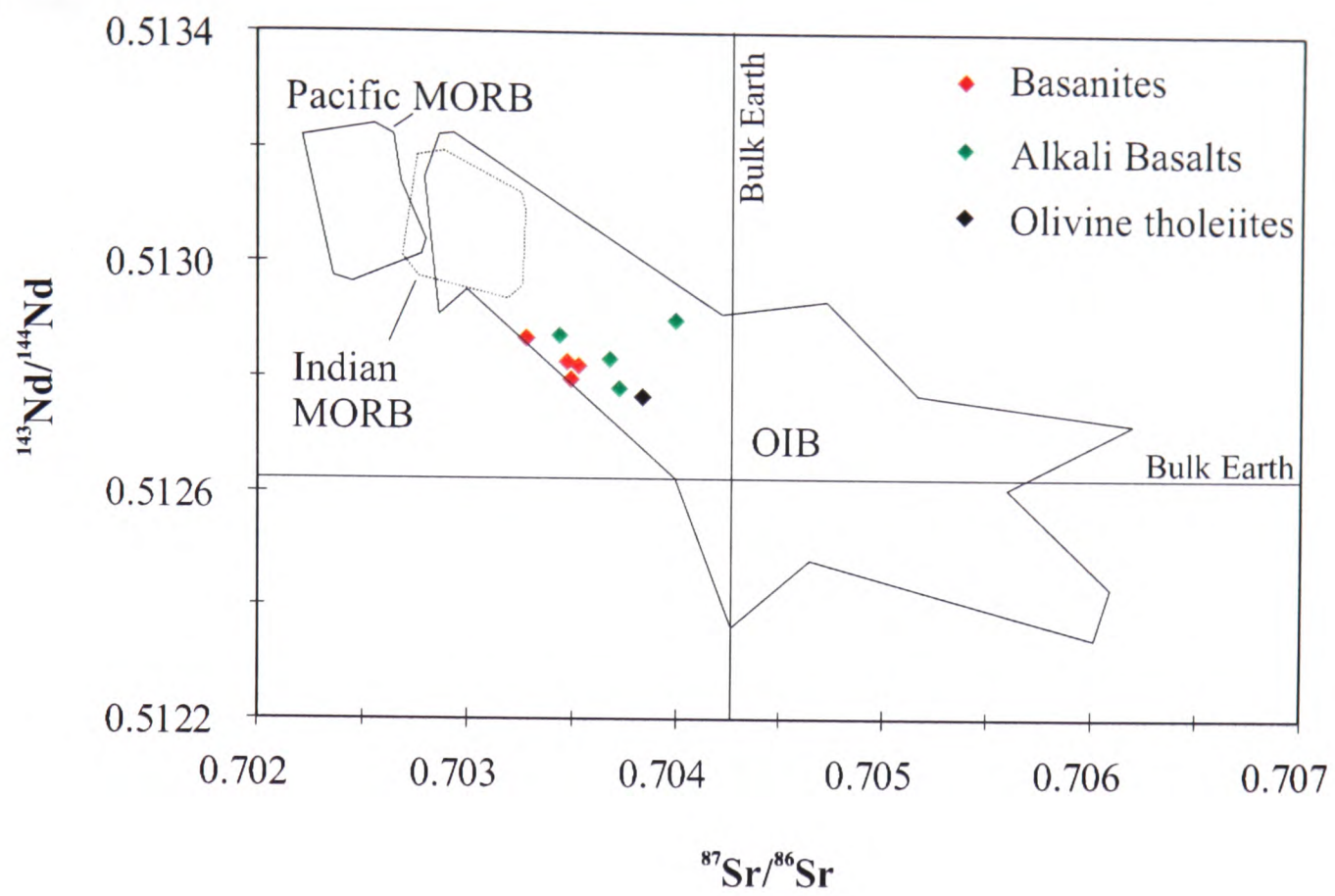


Figure 3.8 Sr-Nd isotope compositions of the 9 analysed samples from the 9-12 group. Fields for MORB are taken from Ferguson and Klein (1993) and OIB from Thompson *et al.* (1998).

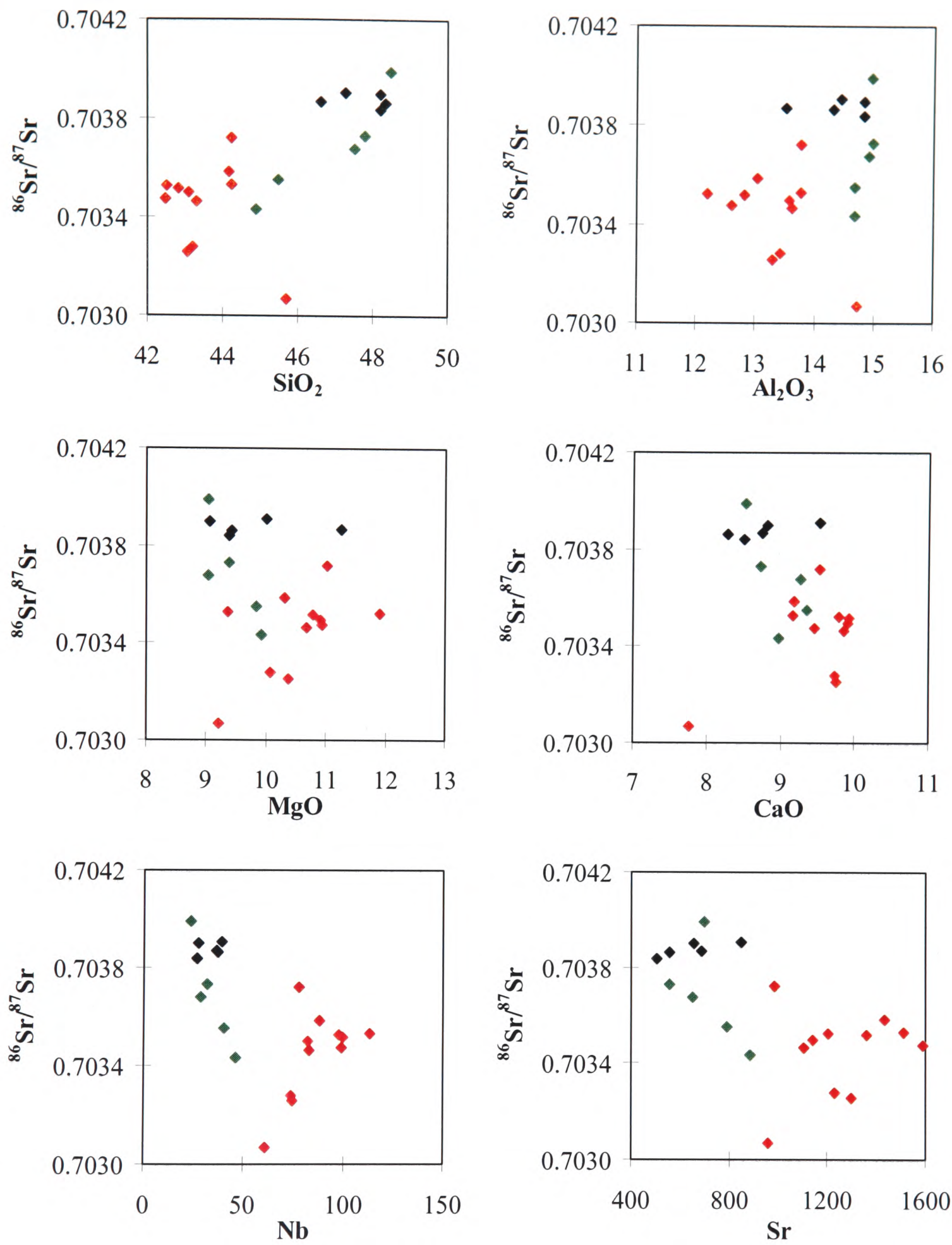


Figure 3.9 $^{87}\text{Sr}/^{86}\text{Sr}$ vs. selected major element oxides and trace elements.

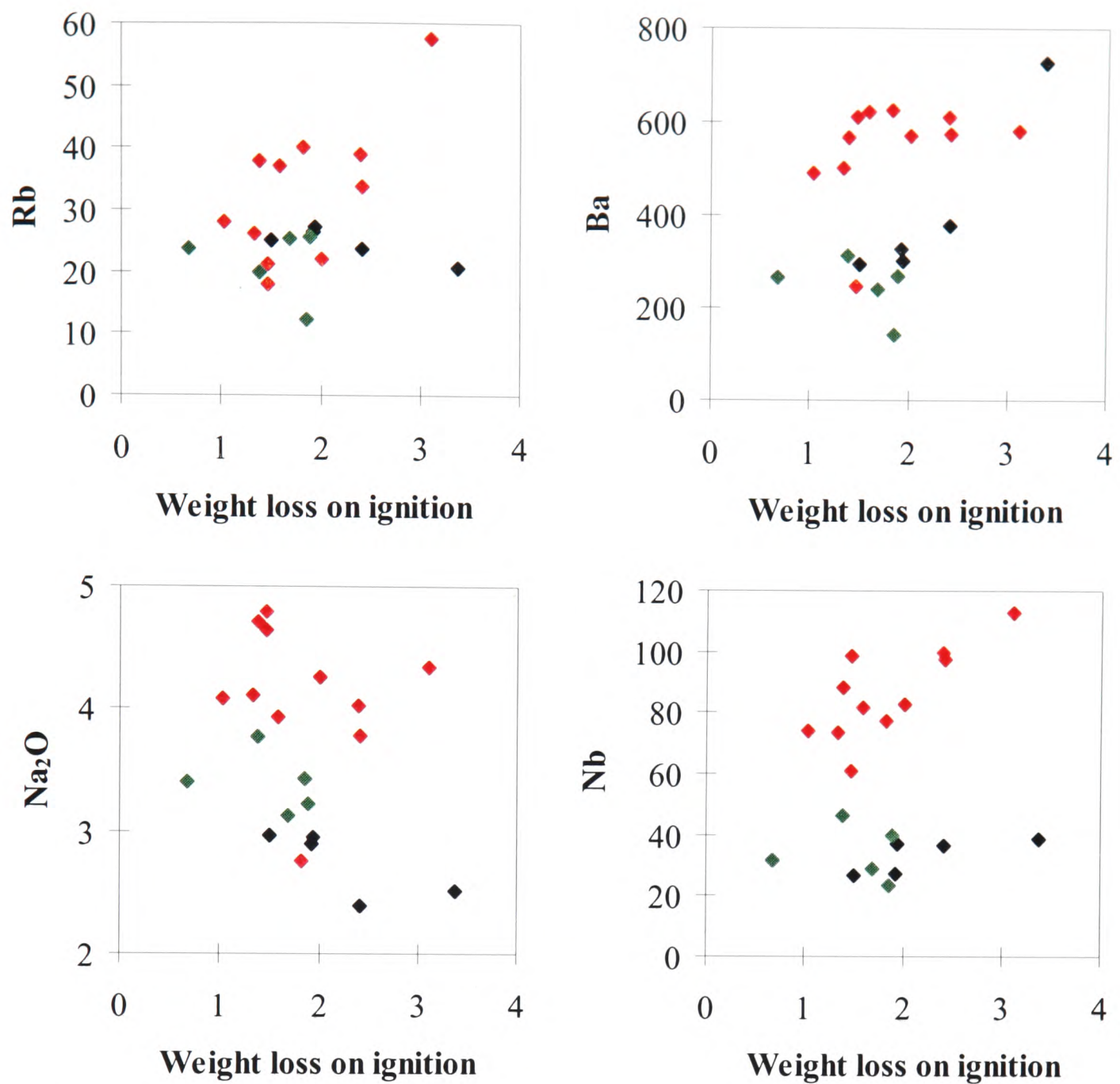


Figure 3.10 Plots of elements vs. weight loss on ignition (wt. %). The lack of strong positive correlations between the mobile elements (Rb, Ba, Na) and weight loss suggest that hydrous alteration of the samples was not significant. The similarity of the plot involving immobile element Nb tends to confirm this conclusion.

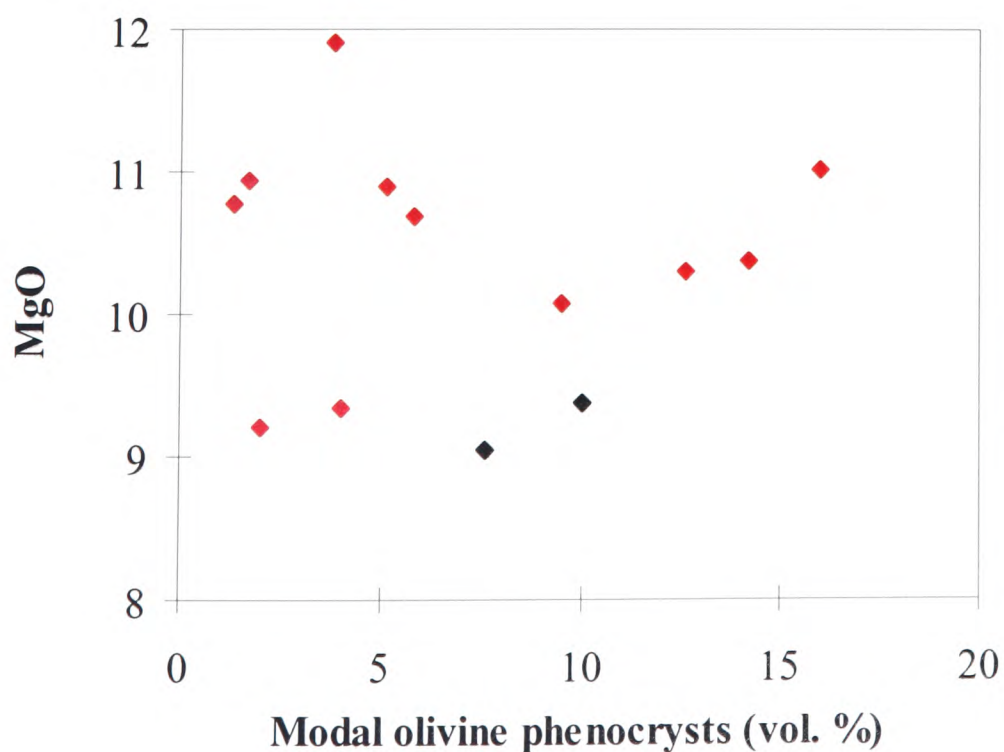


Figure 3.11 Plot of MgO against volume of olivine phenocrysts determined by point counting (Appendix F). All basanites are porphyritic, while only two basalts are. The absence of a positive correlation between the indices argues against significant olivine accumulation.

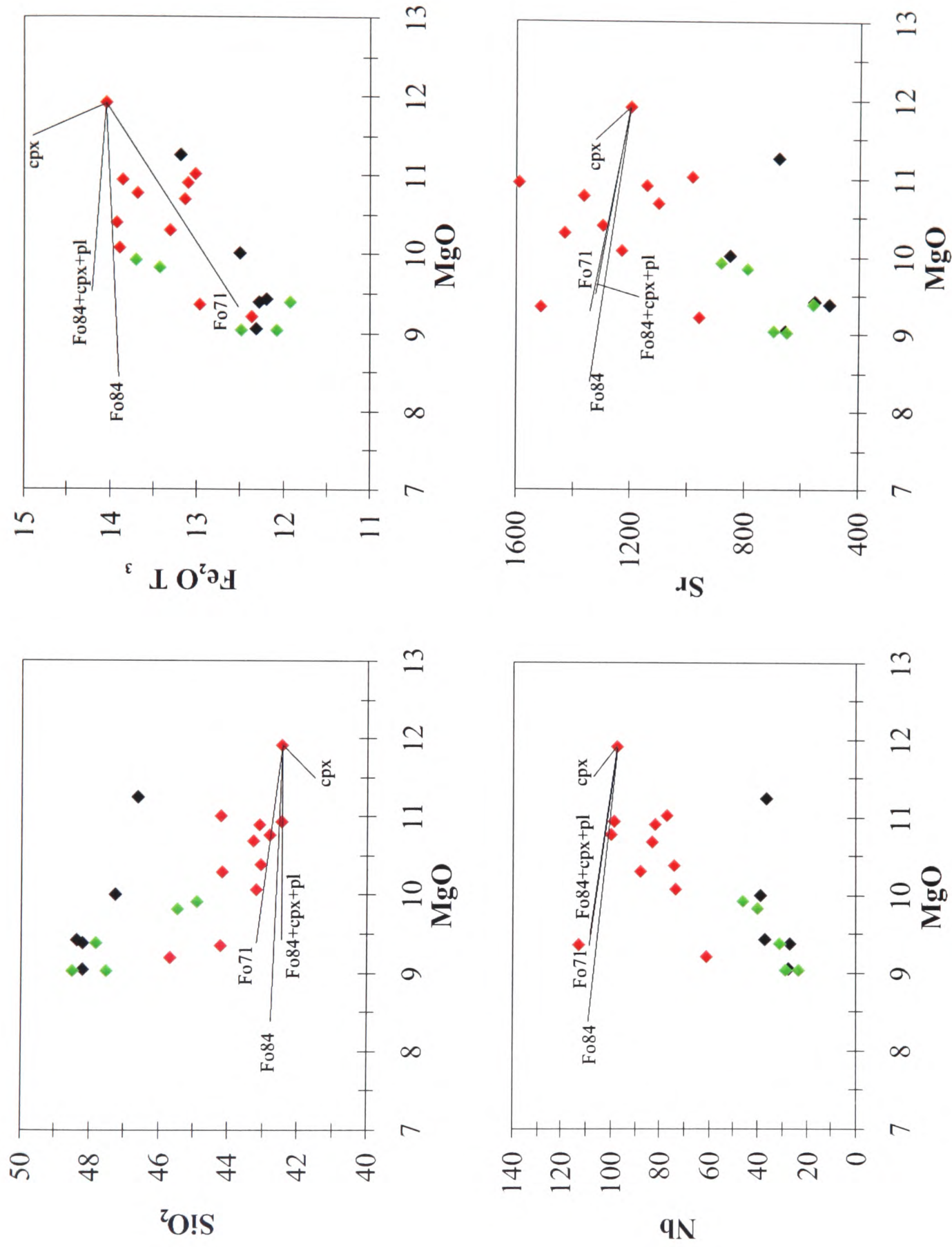


Figure 3.12 Vectors to show the effect of fractional crystallisation acting on sample AJS 111. Four phenocryst compositions are used: olivine compositions Forsterite 84 and 71; clinopyroxene and plagioclase of composition An66. The three-phase assemblage is proportioned 70% Fo84, 10% clinopyroxene and 15% An66 (the phenocryst proportions which occur in sample AJS 144). $F=0.9$ in each case.

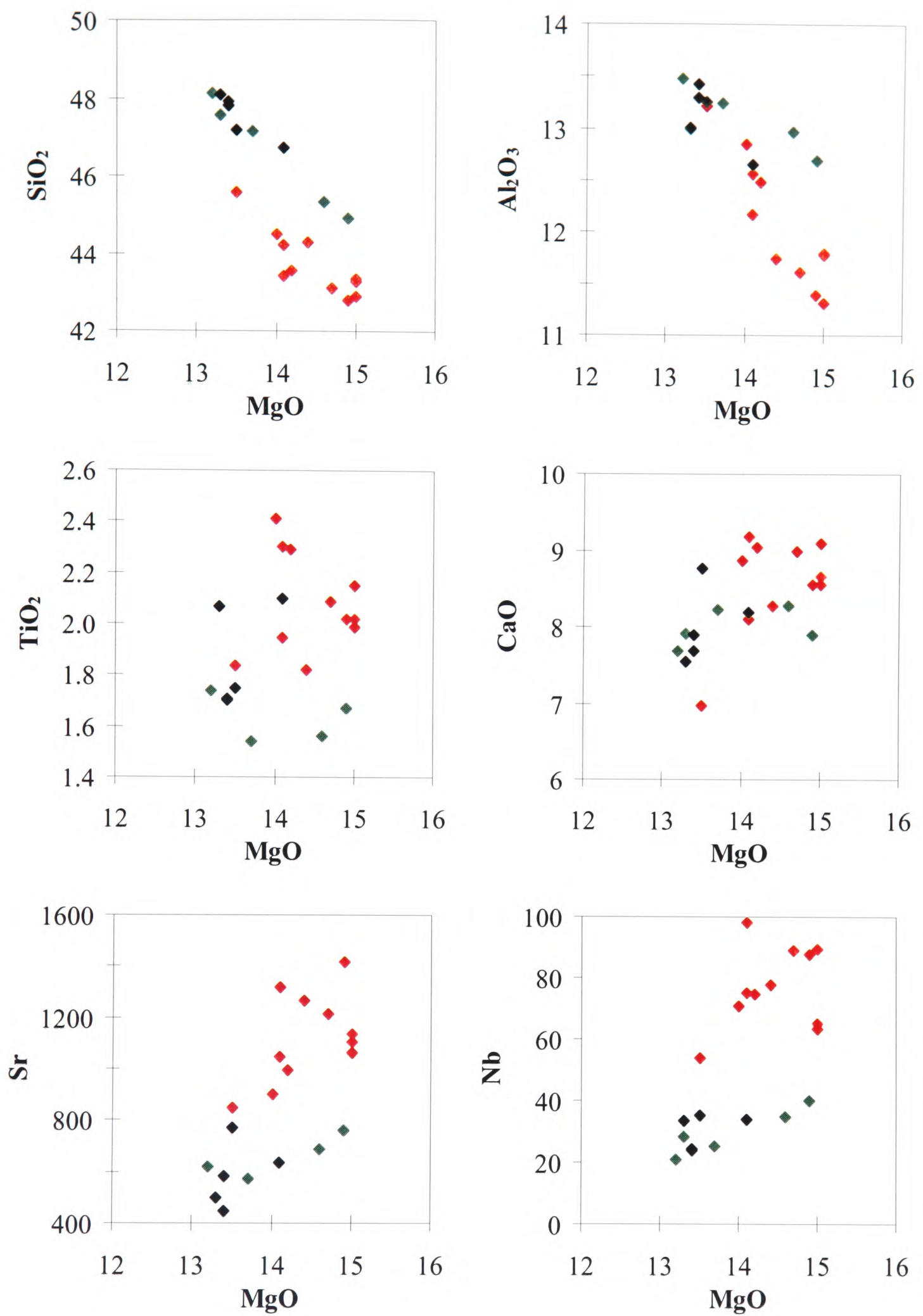


Figure 3.13 Plots of selected major and trace elements vs. MgO for samples corrected for olivine fractionation (see text for details).

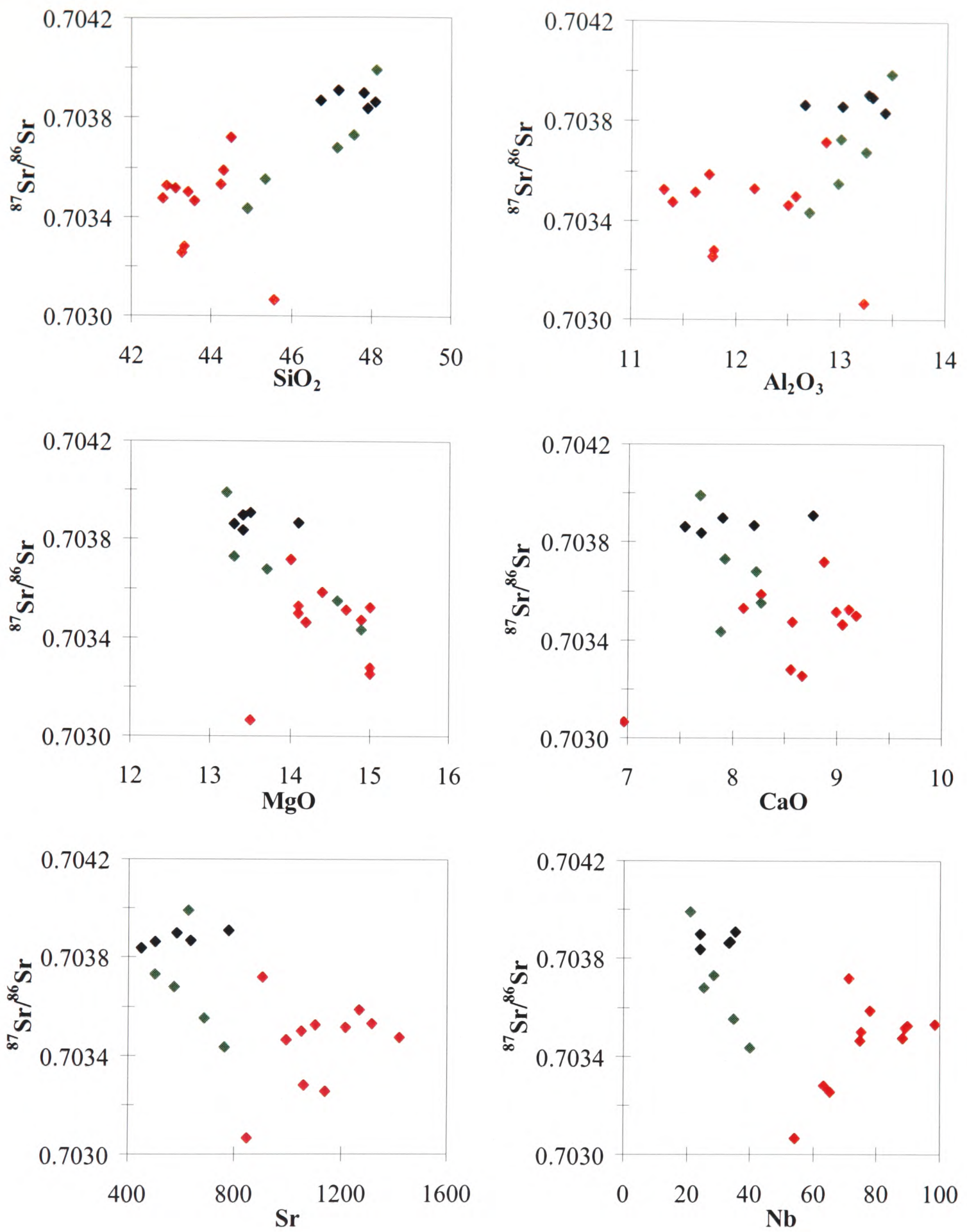


Figure 3.13(cont.) Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ against selected major and trace elements for samples corrected for olivine fractionation (see text for details).

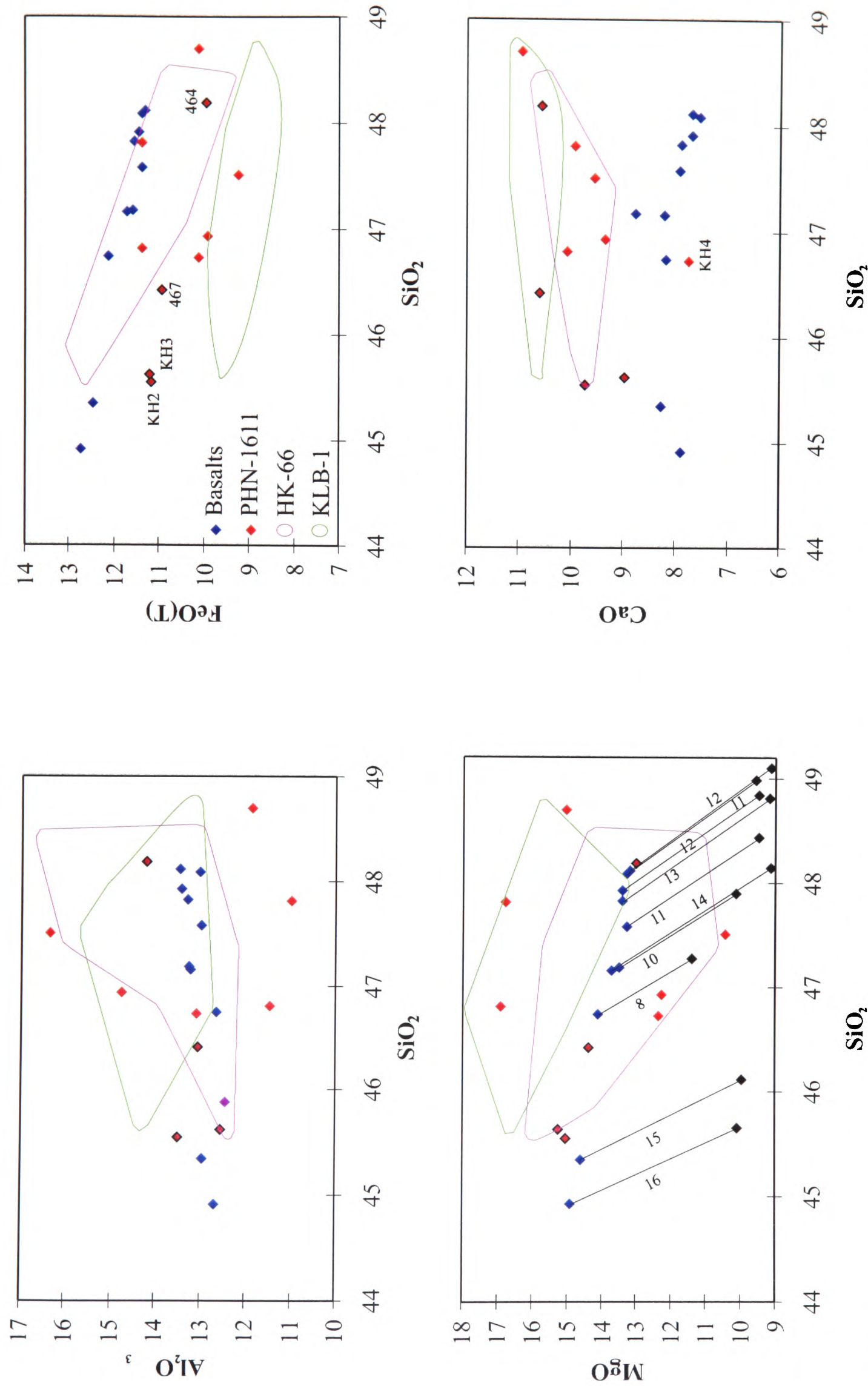


Figure 3.14 Comparison of the experimentally-derived melts of lherzolites HK-66 and KLB-1 (Hirose and Kushiro, 1993) and PHN-1611 (Kushiro, 1996) with the basalts of the 9-12 group which have been adjusted to be in equilibrium with olivine of composition $\text{Fo}_{87.5}$ (see text for details). For clarity, only the fields of HK-66 and KLB-1 melts are shown. The plot of MgO vs. SiO_2 includes the unadjusted basalt compositions (black dots) with tie-lines connecting them to their respective olivine-compensated compositions, together with the amount of olivine (%) that was added. The four runs from PHN-1611 which are referred to in the text (464, 467, KH2, KH3) have black outlines in each plot and are labelled in the plot of FeO-SiO_2 .

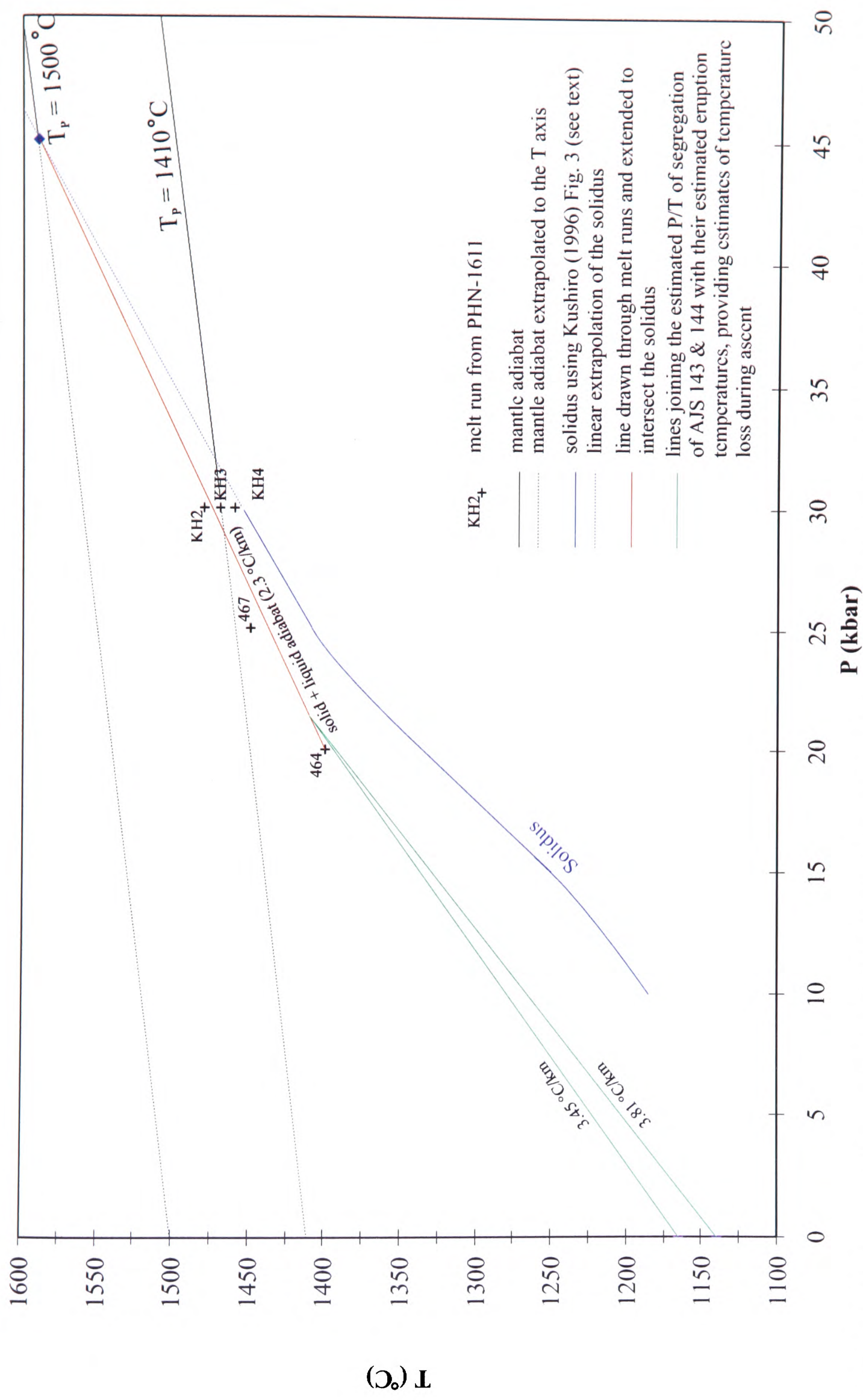


Figure 3.15 Pressure - Temperature graph indicating the main aspects of the argument presented in the text for the derivation of the basalts under study from the adiabatic melting of mantle with a T_p between 1400-1500 °C. Figure 3.14 draws attention to the similarity of the basalt compositions (compensated for olivine extraction) and melt runs 464, 467, KH2 and KH3 from the experimental partial melting of PHN-1611 by Kushi (1996). This figure shows that a line drawn through the melt-run data has a gradient of 2.3 °C/km, similar to other estimates of solid+liquid adiabats (see text for details). Continuation of this red line until it intersects the extrapolated solidus of PHN-1611 allows an upper estimate to be made of the mantle T_p assuming a gradient of 0.5 °C/km. The lower T_p estimate is made by assuming the solidus forms a cusp at 30 kbar (e.g. Takahashi, 1986), intersecting the solid adiabat just up-pressure of KH3.

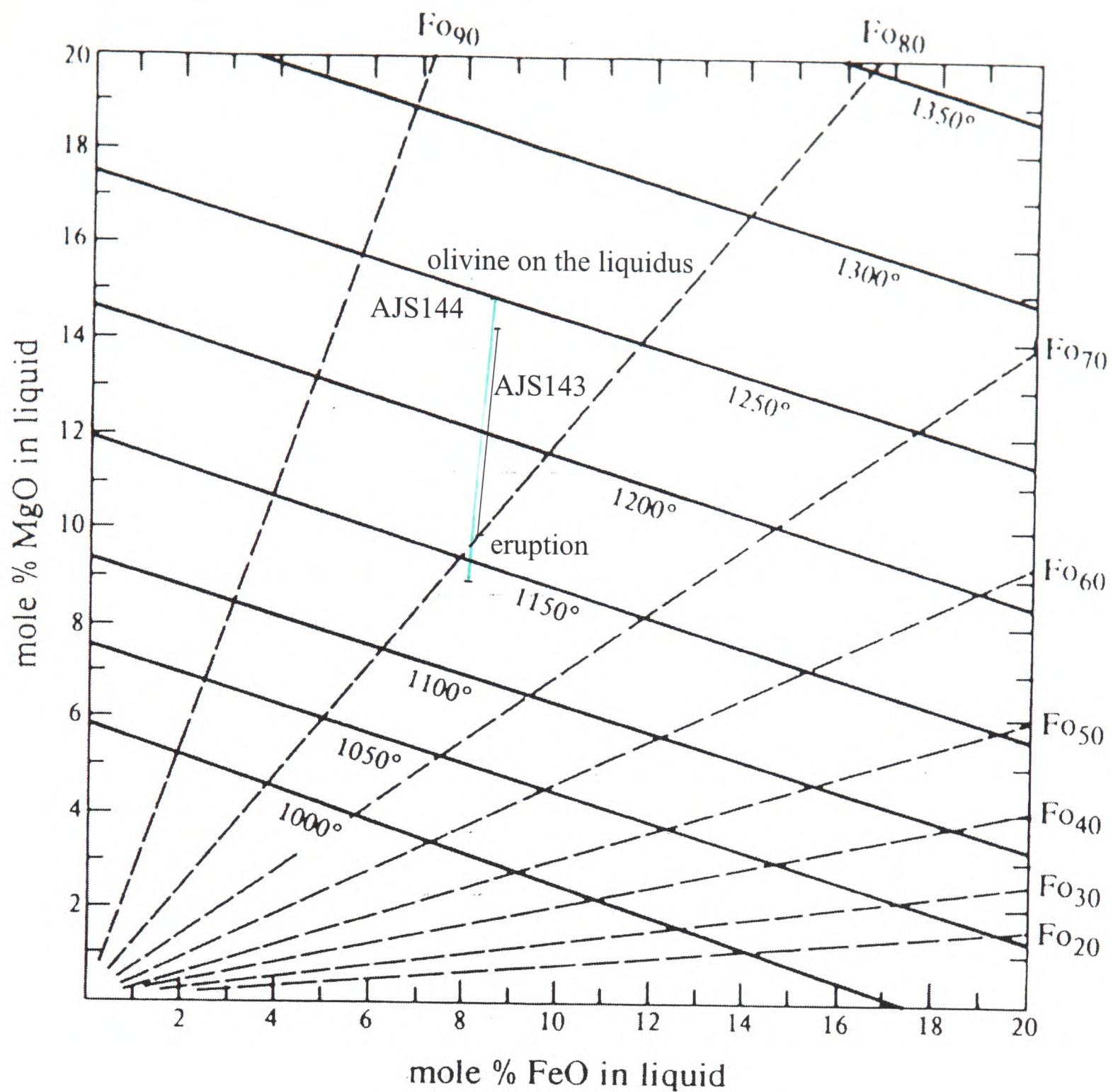


Figure 3.16 Estimated temperatures of the appearance of olivine on the liquidus, and of eruption for samples AJS143 (black) and AJS144 (green). The plot is taken from Cox *et al.* (1979), and was constructed using the method of Roeder and Emslie (1970).

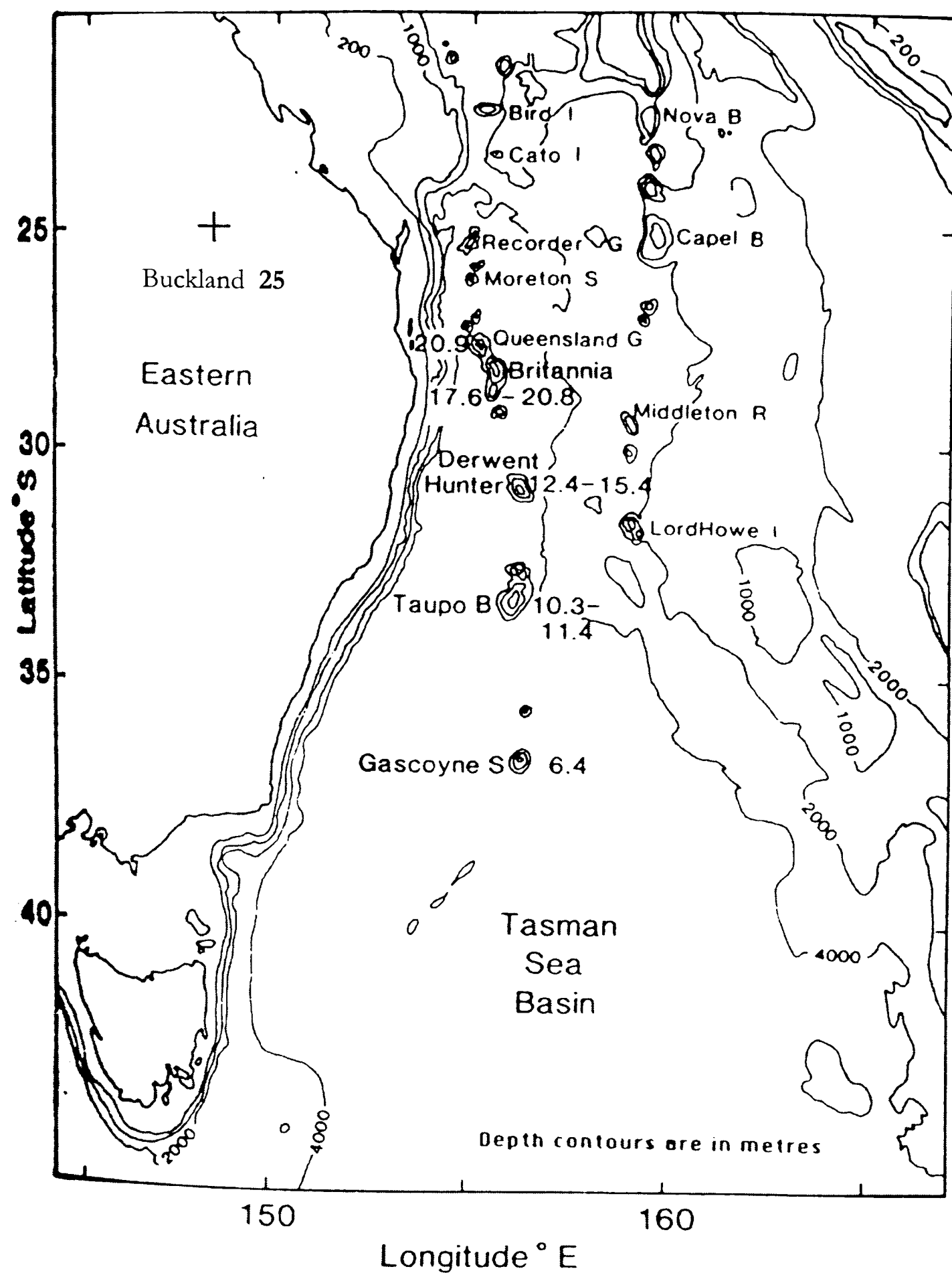


Figure 3.17 Location of the Tasmanid seamount chain ($\sim 155^{\circ}$ E) from Eggins *et al.* (1991). The Lord Howe chain is also shown, slightly to the east. Figures by individual seamounts are K/Ar age determinations (McDougall and Duncan, 1988). The approximate position of the Buckland province is also shown, together with an average age determination. G = guyot; S = seamount; B = bank; R = reef; I = island.

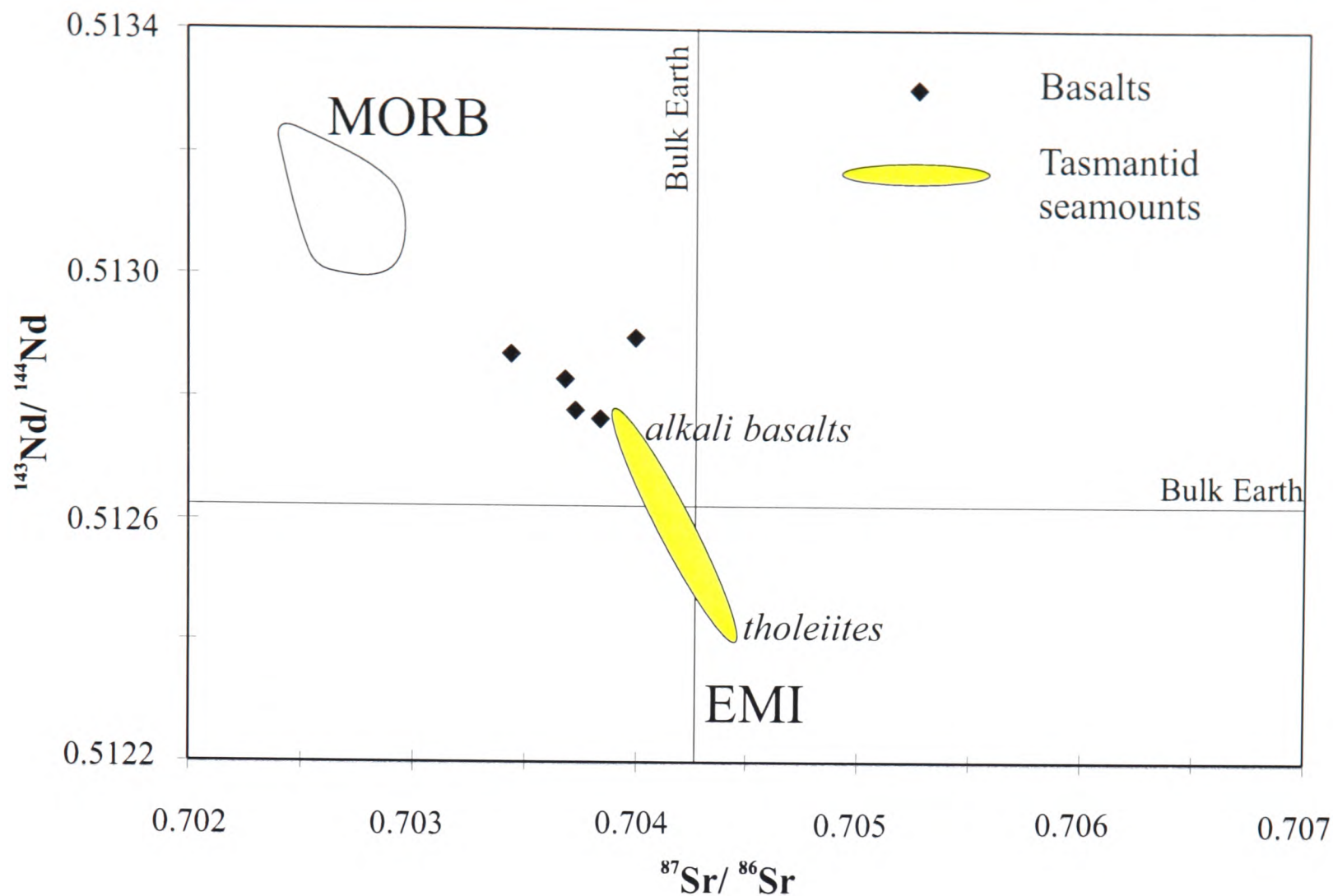


Figure 3.18 Graph comparing the Sr-Nd characteristics of the basalts from the 9-12 group with samples from the Tasmantid seamount chain (data from McCulloch, 1988). Samples from the chain are interpreted (Eggins *et al.*, 1991) as the result of mixing between a plume of EMI composition (characterised by the *tholeiites*) and depleted asthenosphere (by the *alkali basalts*). The latter nearly overlap with the basalts under study.

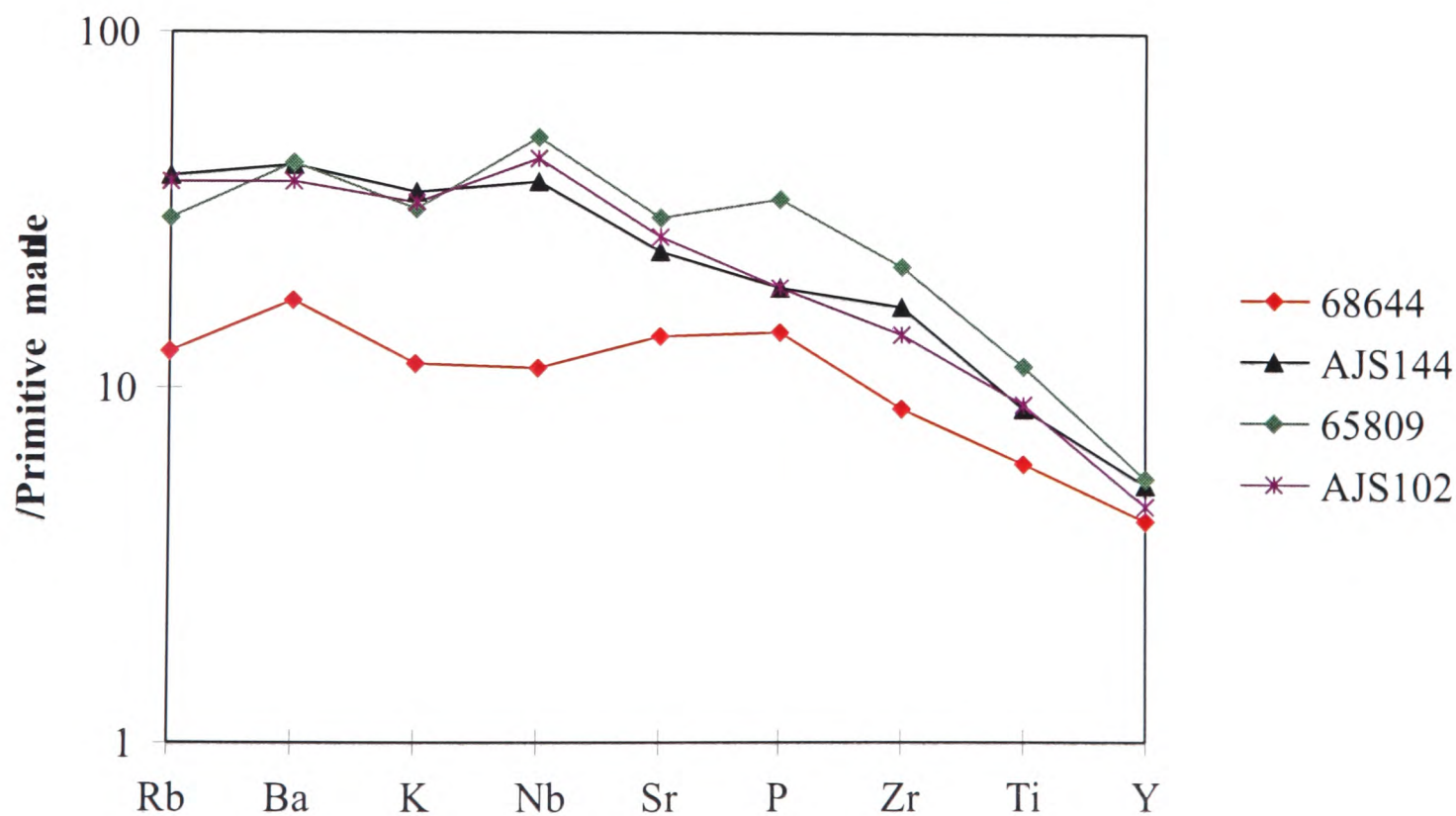


Figure 3.19 Comparison of basalt spidergrams (alkali basalt AJS 102 and olivine tholeiite AJS 144) with samples from the Tasmantid seamount chain (alkali basalt 65809 and tholeiite 68644). Both basalt types show greater similarity to the Tasmantid alkali basalt than to the tholeiite. Normalisation factors are from Sun and McDonough (1989).

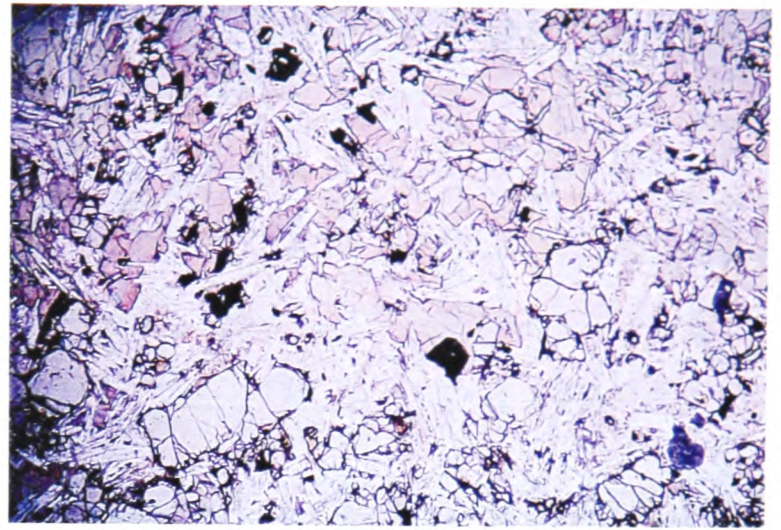


Plate 3.1 Photomicrographs in XPL and PPL of dolerite AJS236. Olivine and plagioclase are enclosed within oikocrysts of pink clinopyroxene. Field of view is 7.5mm across.

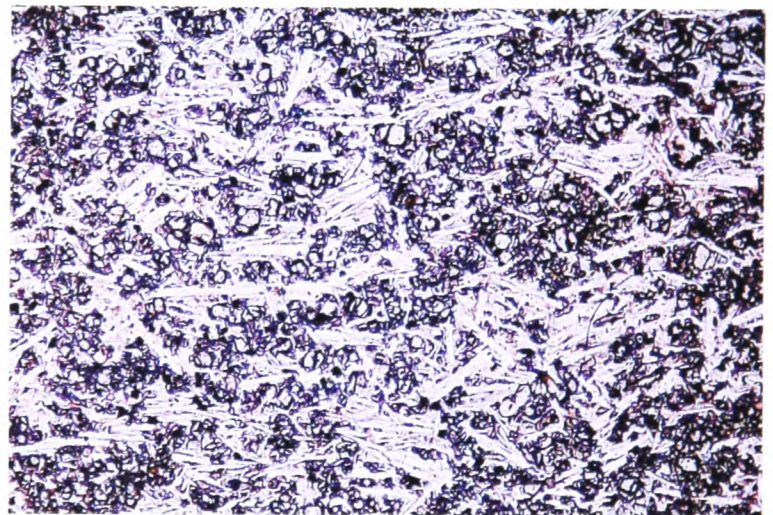
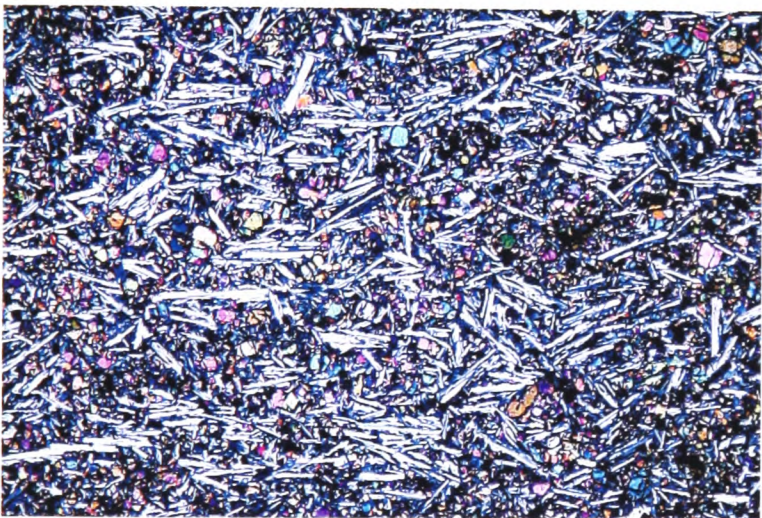


Plate 3.2 Photomicrographs of one of the aphyric lavas, AJS235, which consists of elongate plagioclase crystals which define a left-to-right flow direction, olivine, intergranular clinopyroxene and Fe-Ti oxide. Field of view is the same as Plate 3.1.

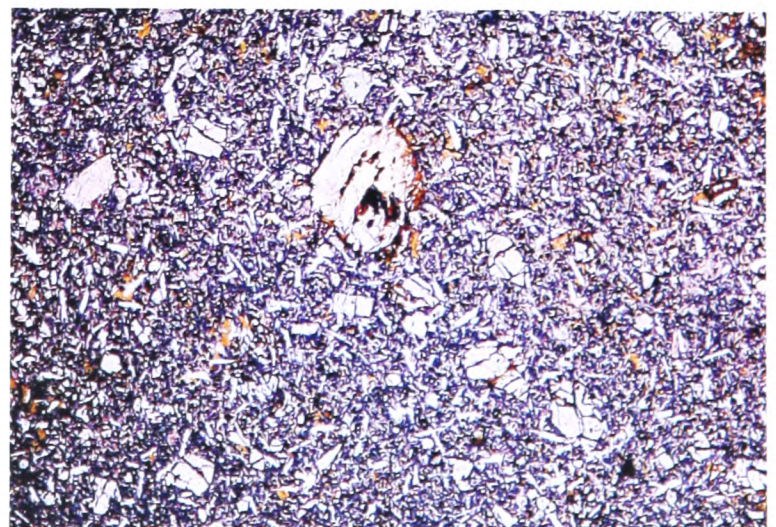
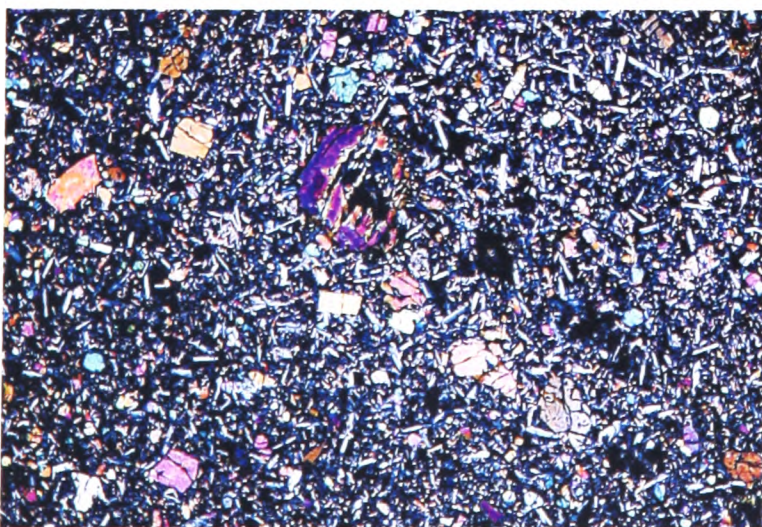


Plate 3.3 Photomicrographs of a porphyritic basanite, AJS101. Phenocrysts of olivine, clinopyroxene and plagioclase can be observed, together with an olivine megacryst, whose compositions ($\sim\text{Fo}_{90}$ and $\sim 0.03\%$ CaO) suggests that they are derived from disaggregation of mantle lherzolite, examples of which are also found in this sample. The groundmass is composed of olivine, clinopyroxene, plagioclase, Fe-Ti oxide) and nepheline. Field of view is the same as Plates 3.1 and 3.2.

Modal Analyses
 All are 1000 point averages

Aphyric samples

	Sample	Olivine	Cpx	Plag	Oxide ^a	g'mass	Xenoliths	Olivine M
Dolerites:	102	18.9	17.7	51.1	5.0	7.3		
	236	21.5	18.0	53.5	3.9	3.1		
Basalts:	167	9.9	30.5	43.9	10.7	5.0		
	168	17.5	21.0	39.1	10.1	12.3	X	
	175	8.6	35.5	49.0	4.8	2.1		
	182	16.7	21.1	52.1	6.6	3.5		
	232	22.5	24.6	44.5	5.2	3.2		
	235	16.1	26.1	50.7	5.3	1.8	X	

Porphyritic samples

		Phenocrysts						
Basanites:	39	12.6	2.9			84.5	X	X
	99	16.0		4.6		79.4	X	X
	100	14.2	2.2	4.4		79.2		X
	101	9.5	2.6	2.3		85.6	X	X
	104	5.1		0.3		94.6	X	X
	106	5.8	0.7			93.5	X	
	108	4.0	0.1			95.9	X	X
	111	3.8	0.5			95.7		X
	112 ^b	1.3				98.7	X	X
	113	1.7	0.4			97.9	X	
	126	2.0				98.0	X	X
Basalts:	143	7.6	1.0	1.6		89.8		
	144	10.0	1.4	2.5		86.1		

a Microprobe analyses (Appendix C) indicate that AJS236 contains ilmenite, while AJS39 and 112 contain Ti-magnetite.

b Groundmass of 112 contains 14.8% olivine, 35.3% clinopyroxene, 35.6% nepheline, 9.8% oxide and 4.5% unidentifiable/altered material (1000 point average).

g'mass: groundmass figures include alteration

Xenoliths: spinel lherzolite nodules

Olivine M: Olivine megacrysts

X indicates the presence of xenoliths or megacrysts identified in the field or in thin section.

Table 3.1 Modal analyses for samples from the 9-12 group. All are 1000 point averages.

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	TA	LOI	mg#	<i>ne</i>	Ni	Cr
Basanites																	
AJS111	42.50	2.32	12.18	0.06	14.04	0.21	11.91	9.79	3.79	1.88	1.32	4.67	2.42	66	15.38	287.4	337.6
AJS99	44.26	2.58	13.78	0.04	13.04	0.19	11.01	9.52	2.77	1.93	0.88	4.70	1.83	66	6.98	227.3	255.6
AJS113	42.48	2.24	12.60	0.05	13.86	0.21	10.94	9.46	4.64	2.00	1.52	6.64	1.47	65	19.38	252.0	300.3
AJS104	43.12	2.49	13.57	0.05	13.11	0.19	10.90	9.91	3.93	1.66	1.07	5.59	1.58	66	14.66	216.9	269.0
AJS112	42.82	2.31	12.82	0.05	13.67	0.20	10.77	9.93	4.03	2.02	1.38	6.05	2.40	65	16.29	239.9	269.3
AJS106	43.31	2.50	13.61	0.05	13.13	0.19	10.68	9.85	4.26	1.37	1.05	5.63	2.01	66	15.05	225.3	265.7
AJS100	43.08	2.25	13.30	0.04	13.93	0.20	10.38	9.77	4.08	1.67	1.30	5.75	1.03	64	14.69	243.8	282.3
AJS39	44.18	2.02	13.03	0.05	13.31	0.20	10.30	9.18	4.71	1.72	1.30	6.43	1.38	64	16.17	250.9	317.8
AJS101	43.20	2.30	13.42	0.05	13.89	0.19	10.07	9.74	4.11	1.74	1.29	5.85	1.33	63	14.72	235.4	277.4
AJS108	44.23	2.21	13.76	0.04	12.96	0.20	9.35	9.16	4.35	2.31	1.43	6.66	3.11	63	15.10	198.1	216.1
AJS126	45.68	2.05	14.73	0.03	12.36	0.16	9.21	7.77	4.80	2.35	0.86	7.13	1.46	64	15.25	220.1	206.5

Basalts																	
AJS168	46.62	2.25	13.51	0.06	13.19	0.17	11.25	8.75	2.39	1.32	0.49	3.71	2.42	67		235.7	292.7
AJS175	47.27	1.90	14.44	0.05	12.50	0.18	10.00	9.53	2.52	1.11	0.50	3.63	3.38	65		201.3	282.9
AJS235*	44.91	1.85	14.69	0.04	13.70	0.19	9.92	8.97	3.77	1.33	0.63	5.10	1.38	64	9.49	176.0	183.2
AJS232*	45.47	1.77	14.68	0.04	13.42	0.19	9.83	9.36	3.23	1.49	0.52	4.72	1.89	64	6.96	175.5	202.6
AJS167	48.36	2.28	14.32	0.04	12.20	0.16	9.43	8.29	2.95	1.45	0.52	4.40	1.94	63		185.7	243.9
AJS102*	47.81	1.92	14.98	0.04	11.92	0.16	9.38	8.73	3.41	1.24	0.41	4.65	0.67	63	2.46	159.0	215.7
AJS144	48.22	1.88	14.83	0.04	12.28	0.16	9.38	8.50	2.97	1.33	0.41	4.30	1.51	63		173.6	253.8
AJS143	48.19	1.91	14.84	0.04	12.31	0.17	9.05	8.82	2.90	1.36	0.41	4.26	1.93	65		191.9	250.7
AJS182*	48.49	1.94	14.96	0.04	12.07	0.16	9.04	8.52	3.43	1.03	0.32	4.46	1.85	64	0.47	164.5	231.7
AJS236*	47.52	1.74	14.92	0.04	12.49	0.17	9.03	9.27	3.13	1.24	0.45	4.37	1.68	63	1.88	157.6	191.6

Table 3.3 Major and trace element data for the basanites and basalts of the 9-12 group, normalised to total 100% and arranged in order of decreasing MgO. LOI refers to weight loss on ignition (see section 3.4.1). *ne* refers to the amount of normative nepheline calculated for the sample assuming Fe₂O₃/FeO=0.2. Basalts marked with an * are alkali basalts, the remainder are olivine tholeiites (classification discussed in section 3.1.2). mg#=mg-number.

	Rb	Ba	Nb	Sr	Zr	Th	U	Y	V	Ga	Zn	Cu	Co	Pb	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd (age-corrected)
Basanites																
AJS111	33.9	576.1	97.8	1201.9	388.5	10.7	3.0	28.4	144.3	22.9	128.5	34.7	65.8	7.2	0.703524	
AJS99	40.0	626.1	77.4	983.9	300.1	7.7	1.3	26.3	170.3	21.5	116.4	52.4	56.0	4.9	0.703721	
AJS113	21.3	610.2	98.6	1588.5	376.1	11.4	2.8	30.6	140.2	23.9	136.5	38.4	57.6	4.3	0.703475	0.512826
AJS104	37.2	621.2	82.0	1142.6	293.4	9.5	2.5	26.9	153.6	21.3	105.3	47.7	55.1	6.8	0.703498	0.512798
AJS112	38.9	611.6	99.7	1361.6	391.9	11.5	5.1	30.3	132.6	23.0	127.8	38.3	54.9	6.1	0.703518	
AJS106	22.1	571.9	82.9	1104.0	301.5	8.0	2.0	27.3	150.5	19.4	107.7	48.3	59.7	3.0	0.703465	
AJS100	28.2	490.8	74.3	1297.5	264.4	8.0	2.5	27.5	138.8	22.0	135.8	50.7	63.6	4.3	0.703256	
AJS39	37.9	567.2	88.1	1433.0	343.9	12.0	0.7	27.0	128.6	22.5	135.7	44.6	60.3	7.6	0.703586	
AJS101	26.2	502.5	73.4	1230.9	251.0	5.5	1.3	28.2	143.0	20.4	136.1	51.0	65.7	5.1	0.703281	0.512869
AJS108	57.6	582.7	113.0	1513.3	459.8	11.5	4.1	30.9	131.1	23.7	136.2	34.6	58.8	4.6	0.703530	0.512822
AJS126	17.9	248.9	61.0	957.9	294.0	4.3	0.8	16.8	113.1	24.5	125.5	51.8	56.9	4.0	0.703068	

Basalts																
AJS168	23.6	378.9	36.4	684.4	191.7	4.1	0.9	19.5	153.7	19.6	105.4	60.0	61.1	4.8	0.703868	
AJS175	20.6	726.9	38.8	850.3	174.2	4.9	0.7	23.1	167.1	18.1	95.4	56.7	57.7	2.5	0.703907	
AJS235*	20.0	313.0	46.2	883.4	200.0	4.7	1.5	23.3	130.3	22.8	111.7	56.4	55.3	2.6	0.703434	0.512872
AJS232*	25.6	270.3	39.8	789.2	176.3	5.9	0.0	20.8	131.6	21.8	101.0	62.4	58.1	1.5	0.703551	
AJS167	27.2	301.3	37.0	554.7	218.5	3.0	1.3	22.9	148.2	20.9	109.7	45.7	53.2	1.0	0.703863	
AJS102*	23.8	265.0	31.4	556.8	156.4	2.4	0.0	20.9	144.1	21.9	93.1	53.1	59.0	2.1	0.703730	0.512779
AJS144	25.1	294.0	26.8	502.3	186.6	2.9	0.0	23.9	178.6	19.9	94.0	52.3	53.3	0.9	0.703838	0.512767
AJS143	26.5	328.6	27.4	656.6	193.1	2.8	0.5	23.7	182.8	20.0	96.4	34.0	58.8	4.2	0.703898	
AJS182*	12.4	141.6	23.3	696.1	124.2	3.2	0.2	21.5	147.9	20.4	95.4	52.1	52.6	2.4	0.703990	0.512899
AJS236*	25.5	238.9	28.7	652.2	138.1	4.4	1.1	19.9	128.3	21.9	93.3	64.8	57.0	4.0	0.703677	0.512832

Table 3.3(ctd) Trace element data for the 9-12 group. Isotopic ratios are corrected to 25Ma (see Appendix D). Basalts marked with an * are alkali basalts, the remainder are olivine tholeiites (classification discussed in section 3.1.2).

	Spinel lherzolites					Garnet lherzolite
	KLB-1	HK-66	average	Buckland	B	PHN-1611
SiO ₂	44.18	48.02	44.20	45.00	43.7	44.54
TiO ₂	0.16	0.22	0.13	0.11	0.2	0.25
Al ₂ O ₃	3.59	4.88	2.05	3.13	4	2.80
FeO(T)	8.10	9.90	8.29	10.00	8.98	10.24
MnO	0.12	0.14	0.13	0.17	0.12	0.13
MgO	39.22	32.35	42.21	38.67	37.4	37.94
CaO	3.44	2.97	1.92	2.53	3.5	3.32
Na ₂ O	0.30	0.66	0.27	0.36	0.38	0.34
K ₂ O	0.02	0.07	0.06	0.01	0.01	0.14
P ₂ O ₅	0.03	0.07	0.03	0.02	<0.01	
Cr ₂ O ₃	0.31	0.25	0.44		0.4	0.29
NiO	0.25	n.d.	0.28			
Total	100.02	99.53	100.01	100.00*		100.00*

Mineralogy (wt.%)

olivine	58	27				60
opx	25	57				10
cpx	25	14				20
spinel	2	2				10
					garnet	
Fo content	89.1	85.0				88.3-86.3

References

HK-66, KLB-1: Hirose and Kushiro (1993)
Average: average of 384 spinel-lherzolite samples from Maaløe and Aoki (1977)
Buckland: spinel lherzolite BWD-5 from the base of the lava sequence at Carnarvon Gorge. Analysis from Griffin *et al.* (1987).
B: Starting material for volatile-present melting of Mysen and Boettcher (1975a)
PHN-1611: Smith and Boyd (1987).

* Iron recalculated to FeO(t) and total normalised to 100%.

Table 3.4 Compositions of the lherzolite nodules HK-66, KLB-1 and PHN-1611 which are referred to in this chapter. A worldwide average spinel lherzolite composition and one from the field area are provided for comparison.

Basalt compositions

	AJS235*	AJS232*	AJS168	AJS236*	AJS175	AJS143	AJS144	AJS102*	AJS167	AJS182*
SiO ₂	44.92	45.35	46.74	47.16	47.18	47.82	47.92	47.58	48.09	48.12
TiO ₂	1.67	1.56	2.10	1.54	1.75	1.71	1.70	2.07	2.07	1.74
Al ₂ O ₃	12.70	12.97	12.65	13.24	13.26	13.29	13.42	13.00	13.01	13.48
FeO	12.73	12.47	12.13	11.72	11.60	11.54	11.46	11.39	11.38	11.31
MgO	14.90	14.60	14.10	13.70	13.50	13.40	13.40	13.30	13.30	13.20
CaO	7.89	8.27	8.19	8.22	8.76	7.90	7.69	7.92	7.54	7.68
Na ₂ O	3.31	2.86	2.23	2.78	2.31	2.60	2.69	3.09	2.68	3.09
K ₂ O	1.17	1.32	1.24	1.10	1.02	1.22	1.21	1.13	1.32	0.93

Original compositions have been corrected to be in equilibrium with mantle olivine Fo_{87.5} using OLFRACT (see text for details)
* alkali basalts: remainder are olivine tholeiites

Melt runs for PHN-1611 for P ≥ 20 kbar (Kushiro, 1996)

Run	462	464	465	468	467	471	474	KH2	KH3	KH4
P (kbar)	20	20	20	25	25	25	30	30	30	30
T (°C)	1450	1400	1350	1500	1450	1425	1500	1480	1470	1460
F	25	16.3	6.4	24.1	14.7	6.8	18.1	11.3	7.5	2.9
Residual phases	ol,opx, (cpx)	ol,opx, cpx	ol,opx, ol,opx, cpx,spl	ol,opx	ol,opx, cpx	ol,opx, ol,opx, cpx,spl	ol,opx	ol,opx, ol,opx, cpx	ol,opx, cpx,grt	ol,opx, cpx,grt
SiO ₂	48.69	48.19	47.50	47.81	46.42	46.93	46.81	45.55	45.63	46.73
TiO ₂	1.00	1.25	1.91	0.92	1.47	1.90	1.03	1.60	2.00	2.23
Al ₂ O ₃	11.86	14.21	16.36	11.00	13.05	14.77	11.45	13.49	12.54	13.09
FeO	10.12	9.96	9.24	11.38	10.95	9.91	11.37	11.18	11.20	10.14
MgO	15.01	13.01	10.43	16.76	14.36	12.28	16.89	15.01	15.24	12.35
CaO	10.94	10.56	9.55	9.93	10.59	9.34	10.08	9.74	8.98	7.74
Na ₂ O	1.29	1.46	2.49	1.01	1.68	2.41	1.25	1.80	2.06	2.55
K ₂ O	0.56	0.86	2.18	0.58	0.95	2.07	0.77	1.24	1.88	4.91

Table 3.5 Basalt compositions compensated for olivine extraction, together with melt compositions from PHN-1611 at P ≥ 20 kbar.

Basanites			Experimental melt data				
			X ^{CO2}	0.5	0.5	0.2	0.25
			T (°C)	1100	1100	1150	1070
			P (kbar)	10	20	15	10
	AJS100	AJS126					
SiO ₂	43.27	45.58		45.6	45.8	43.5	40.7
TiO ₂	1.99	1.84		1.0	0.7	0.5	0.6
Al ₂ O ₃	11.78	13.22		18.9	12.0	10.5	17.4
FeO	12.87	11.57		6.0	9.9	13.0	3.5
MgO	15	13.5		5.9	18.3	10.7	14.5
CaO	8.66	6.97		18.5	10.2	13.8	18.5
Na ₂ O	2.62	4.31		3.8	2.8	7.6	4.6
K ₂ O	1.48	2.11		0.1	0.1	0.4	0.3

Table 3.6 Comparison of basanite lavas AJS100 and 126 adjusted for olivine extraction and compositions of liquids generated by the melting of spinel lherzolite in the presence of volatiles (Mysen and Boettcher, 1975b). Undersaturated liquids were only produced where X^{CO2}≥0.5 and P≥10 kbar. Na₂O contents of the melts were calculated by mass balance owing to inaccuracy of analysis. The melts show some similarity to the basanites (e.g. SiO₂), but it is hard to establish whether the differences are a function of source composition or conditions of P, T or X^{CO2} in the absence of more data.

Chapter 4: Petrology and petrogenesis of the 2.5-9 group

4.1 INTRODUCTION

This is the largest of the groups defined on the basis of MgO content in Chapter 2 (section 2.2.5), and comprises 120 analysed samples. They are geochemically and petrographically diverse, and consequently will be subdivided and discussed as separate sub-groups.

Major element oxides and trace elements are plotted against MgO for the whole dataset in Figure 4.1, and clearly show substantial scatter. In an attempt to divide the group into smaller units with the aim of discerning any underlying trends, the samples are coloured according to province, with the Buckland samples split into those from the main lava sequences and those from isolated plugs and flows to the west of the main shield. This four-fold division (Buckland shield, Buckland plugs, Springsure and Mitchell) brings more order to the data, and this chapter will follow these divisions.

4.2 BUCKLAND SHIELD

4.2.1 Introduction and classification

Numerically this is the largest of the four sections, consisting of 72 samples. Three samples are basanites, while the remainder are basalts which are classified petrographically as aphyric, olivine-phyric or megacryst-bearing basalts. The basanite samples are derived from a thick flow towards the base of the Battleship Spur sequence (see Figure 2.1) and, owing to their strong geochemical and petrographical similarity to the basanites discussed in Chapter 3, can be considered as slightly low-MgO examples of the same group, and will not be further discussed in this chapter. The other types are found throughout the province and show no obvious geographical or stratigraphical concentrations.

Classification of the lavas is made using the TAS classification grid of Le Maitre (1989), shown in Figure 4.2. The samples are coloured according to their petrographic characteristics outlined above. The basanites form a distinct group, while the other samples are intermingled and straddle the basalt-trachybasalt boundary. Note that the olivine-phyric lavas lie generally at the high-silica end of this array.

4.2.2 Petrography

Aphyric samples

Lavas from this group of 35 samples contain olivine, plagioclase, clinopyroxene and Fe-Ti oxide ($\pm$ altered/devitrified glass) in an intergranular-ophitic texture. Olivine crystals (<0.6 mm in length) are invariably iddingsitised at the rims, while in some samples they are completely altered. Compositions lie in the range Fo₅₇-Fo₆₂. Plagioclase crystals are elongate (aspect ratio ~ 5 -8), up to 0.6 mm long, and rarely define a trachytic texture, probably related to the direction of flow of the lava (see Plate 3.2 for an example from the 9-12 group); compositions lie between calcic andesine and labradorite (An₄₇-An₅₆). Clinopyroxene is augitic in composition (Ca₄₄₋₄₅Mg₃₆₋₃₇Fe₁₈₋₂₀) and occurs as small crystals (<0.3 mm) where the texture is intergranular, and as larger crystals (<1 mm) partially enclosing plagioclase where the texture is ophitic. Plates 4.1a and 4.1b show examples of each textural type.

Olivine-phyric samples

Thirteen samples contain phenocrysts of olivine set in a groundmass of plagioclase, clinopyroxene, Fe-Ti oxide and altered/devitrified glass. Phenocryst size ranges up to 4mm, but is more commonly in the range 1.5-3mm. Most are euhedral (Plate 4.2a), but rare examples are strongly embayed, although some crystals contain both straight and embayed faces (e.g. Plate 4.2b). Samples AJS 12 and 239 (from the same lava flow) contain generally small (<0.8 mm), completely iddingsitised skeletal olivine phenocrysts which are set in a fine grained (<0.5 mm) groundmass (Plate 4.2c). Alteration of the phenocrysts is variable: they are unaltered in sample AJS 77, altered only at the rims in other samples, and $>50\%$ altered in the remaining samples (see Table 4.1 below for details). Modal amounts of olivine phenocrysts range from 4.0% to 13.5%, while their composition lies in the range Fo₇₇-Fo₈₃; analysis of rim compositions is confounded by alteration. Small aggregates or 'glomerocrysts' of phenocrysts occur in 8 of the samples; they consist of 2-6 crystals, and are rare, there being only one or two such glomerocrysts per slide where observed.

Groundmass olivine is more Fe-rich than the phenocrysts, lying in the range Fo₅₂-Fo₆₅. Plagioclase crystals are typically elongate with a high aspect ratio (~ 8) and range from sodic to calcic labradorite (An₅₀-An₆₆). In very rare instances (one or two examples in each of four samples: AJS 52, 91, 118, 202) approximately equant plagioclase crystals up to 1mm in size are found which show extensive internal melting (see Plate 4.2d). Clinopyroxenes are augites, with compositions in the range Ca₄₃₋₄₅Mg₃₉₋₄₂Fe₁₄₋₁₇. Interstitial glass may be present ($<10\%$ by volume) and is invariably altered, sometimes showing spherulitic devitrification textures. Groundmass textures are intergranular-ophitic.

Sample	Modal phen. (Vol. %)	Alteration	Phenocryst size (mm)	Groundmass size (mm)	Glom.	Skeletal olivine
AJS12	7.3	complete	<1.5	<0.4		X
AJS52	9.7	>50%	<3	<1.5		
AJS77	13.5	none	<3	<0.8	X	
AJS84	5.8	rims	<1.2	<0.5		
AJS91	9.4	rims	<2	<1	X	
AJS118	4.2	rims	<3	<2	X	
AJS121	5.7	rims	<1.8	<0.7	X	
AJS178	7.0	>50%	<2	<1	X	
AJS197	4.9	>50%	<4	<1		
AJS200	6.7	rims	<2	<0.5	X	
AJS202	6.0	rims	<1.5	<1.0	X	
AJS239	7.7	complete	<2.0	<0.5		X
AJS240	4.0	>50%	<3	<1.5	X	

Table 4.1 Petrographic characteristics of the olivine-phyric lavas. Modal analyses are 1000 point averages. Samples AJS12 and 239 are from the same flow. ‘Glom.’ indicates the occurrence of glomerocrysts.

Megacryst-bearing samples

The remaining 24 samples contain large (up to 18mm long) crystals of plagioclase, clinopyroxene and orthopyroxene which show various disequilibrium textures (e.g. reaction rims, sieving, rounded forms) and are set in a finer-grained (< 1mm) groundmass. The objective term ‘megacryst’ is used to describe these crystals, since they could be non-cognate *xenocrysts* or high-pressure cognate *phenocrysts* (e.g. section 1.1.6).

Modal analyses for the megacryst-bearing lavas are provided in Table 4.2. Most samples (15 in number) contain less than 2% by volume of megacrysts, and only 6 of them contain more than 5% by volume (including 75% of those samples which contain all three megacryst species). It is likely that the abundances are overestimates, since slides were often made of the area of rock which appeared have the greatest abundance of megacrysts. Plagioclase examples are the most common, occurring in 20 out of the 24 samples; orthopyroxene is found in 15 and clinopyroxene in 8. In terms of relative proportions, plagioclase is the sole megacryst phase in 9 rocks, while it comprises >70% of the assemblage in 9 more: proportions are plotted in Figure 4.3.

Plagioclase megacrysts are elongate and long (<18mm). Composition is uniform (calcic andesine to sodic labradorite: An₄₇-An₅₃), but narrow (~0.1mm) optically discontinuous rims (often

marked by a trail of tiny inclusions) are more calcic ($An_{55}-An_{58}$), and overlap with the calcic end of groundmass compositions ($An_{42}-An_{58}$). Disequilibrium with the groundmass is demonstrated by:

1. the rounded, anhedral habit of the crystals.
2. the occurrence of strongly embayed examples, e.g. in Plate 4.3a.
3. rare occurrences of sieve textures, interpreted (e.g. Cox *et al.*, 1979) as the result of internal melting e.g. in Plate 4.3b.

Rare examples have also been found which show evidence of solid-state deformation, e.g. undulose extinction and kinked twin-lamellae (Plate 4.3b,c).

Orthopyroxene is found as equant crystals up to 5mm in size which are invariably jacketed by an intergrowth of olivine and clinopyroxene, in which the clinopyroxene occurs rarely as a single crystal (Plate 4.3d) but most commonly as several crystals (Plate 4.2e). The proportion of intergrowth jacket to orthopyroxene core varies widely, up to the point where there is no remaining orthopyroxene (Plate 4.2e). Compositionally, the megacrysts lie in the range $Ca_{3-4}Mg_{70-80}Fe_{16-26}$ (enstatite) and Al_2O_3 contents vary between 3.1-4.8%, although individual samples are homogeneous and show no exsolution. Evidence of recrystallisation at two opposite ends of crystal is shown in Plate 4.2d. The recrystallised areas have a different composition to the unrecrystallised: $Ca_4Mg_{75}Fe_{21}$ and 1.1% Al_2O_3 compared to $Ca_4Mg_{79}Fe_{17}$ and 3.3% Al_2O_3 . The decrease in alumina content is compatible with recrystallisation at a lower pressure than that of the original crystallisation (e.g. Binns *et al.*, 1970). Rim textures comparable to those described above are also observed in the Nuanetsi picrites of Zimbabwe (Cox and Jamieson, 1974; Cox *et al.*, 1979: Figure 7.7): chemical and empirical evidence suggests that these orthopyroxenes crystallised at 6-12 kbar and the formation of the rim is thought to result from quenching at low pressures where olivine and clinopyroxene are in equilibrium with the host liquid.

Clinopyroxene examples occur as rounded, occasionally twinned crystals up to 2 mm long: exsolution lamellae are not observed. Outer rims, commonly marked by inclusions (including iddingsitised olivine), are optically discontinuous with the cores (Plate 4.3f). In other instances, an optically continuous 'spongy'-textured rim ~0.2mm wide is present, e.g. Plate 4.3g. Pike and Schwarzman (1977) interpreted similar rims which they observed around clinopyroxenes in spinel lherzolites as the result of partial melting (compare Plates 6.4, 6.5 for examples from Buckland lherzolites). Compositions lie in the range $Ca_{31-41}Mg_{44-56}Fe_{11-18}$ (augite) and Al_2O_3 content is 3.9-6.7%; zoning is insignificant. Rim compositions are MgO- and Al_2O_3 -poor compared to the cores they enclose, e.g. $Ca_{41}Mg_{45}Fe_{13}/2.2\%$ Al_2O_3 enclosing $Ca_{34}Mg_{52}Fe_{13}/5.9\%$ Al_2O_3 in sample AJS120. Groundmass compositions lie in the range $Ca_{43-45}Mg_{37-41}Fe_{14-20}$, (Al_2O_3 between 2.6 and 4.3%).

The groundmass contains olivine (Fo_{49-74}), clinopyroxene (augite), plagioclase (labradorite), Fe-Ti oxide (ilmenite in sample AJS 120) and glass (usually altered). Crystals range in size up to 0.6 mm and form an ophitic-intergranular texture.

Aggregates As well as containing individual megacrysts, these lavas are also host to aggregates of plagioclase, clinopyroxene and orthopyroxene crystals. Examples of these are found in 7 of the 24 megacryst-bearing lavas (detailed below in Table 4.3: Plate 4.4a-c), and notably these are 7 of the 8 most megacryst-rich samples. Three come from the Vandyke section, three from Carnarvon, and one from Mt. Percy (near Battleship Spur), thus they occur throughout the Buckland shield (see Figure 2.1 for localities). The number of crystals which form an aggregate ranges from 2 to 11, and they display the same size range, disequilibrium textures and compositions as the individual megacrysts. Aggregates range in size from 2mm-1cm, and can involve any combination of the three phases, however plagioclase is dominant in terms of size (no pyroxene crystals exceed 3mm) and occurrence (it features in all but four of the thin sections described below in Table 4.3). Strain-related features are observed in rare instances, specifically undulose extinction of plagioclase and sub-grains in orthopyroxene. Plate 4.4a illustrates a unique instance where clinopyroxene appears to be forming from a reaction between adjacent orthopyroxene and plagioclase crystals. Table 4.3 below summarises the main characteristics of the aggregates observed in thin section:

Sample	Aggregate size (mm)	Plagioclase number: size	Orthopyroxene number: size	Clinopyroxene number: size
80	8	3 : 0.4-4 mm		1 : 1.5mm
	5	2 : 3-5 mm		
	1.5	1 : 1 mm		1 : 0.5mm
81	10	1 : 4 mm	3 : 1-2mm	
	7	5 : 1.5-6mm		
	6	5 : 0.5-2.5mm		
92	10	8 : 1-8mm	3 : 1mm	
	10	2 : 1-10mm	1 : 1mm	
	5		1 : 2mm	1 : 3mm
	2	1 : 2mm	1 : 1mm	
120	2			2 : 2mm
199	10	1 : 10mm		1 : 1mm
204	3		3 : 1mm	
	2		3 : 0.25-1mm	
210	10	1 : 10mm		1 : 0.5mm
	5		1 : 0.5mm	4 : 1-4mm

Table 4.3 Details of sixteen crystal aggregates observed in thin sections of samples AJS 80, 81, 92 (2 sections), 120 (2 sections), 199, 204, and 210 (2 sections).

4.2.3 Comparison with megacrysts from other provinces

Eastern Australia

The megacryst compositions are compared to examples retrieved from Cainozoic provinces in eastern Australia in Figure 4.4, incorporating data from Binns *et al.* (1970), Irving (1974), Irving and Frey (1984), Griffin *et al.* (1987) and Ewart *et al.* (1980), of which the latter includes analyses from the Springsure province.

Irving (1974) and Irving and Frey (1984) identify a range of megacrysts from alkaline lavas (nephelinites - basanites - alkali basalts - trachybasalts) in southeastern Australia. These consist of relatively common aluminous clinopyroxene, kaersutite, feldspar (especially anorthoclase) and somewhat rarer aluminous orthopyroxene, biotite/phlogopite, apatite, zircon and corundum. There is considerable variation in megacryst abundance, proportions and composition between flows and provinces, and only clinopyroxene is essentially ubiquitous. Experimental work indicates that the pyroxenes and amphibole are near-liquidus phases of their host lavas at high-pressures, but that anorthoclase, mica and zircon could only be in equilibrium with more evolved liquids. Systematic geochemical trends in clinopyroxene megacrysts are interpreted as the result of some fractionation. Also present in the same lavas are upper mantle xenoliths of the Cr-diopside and Al-augite suites (see section 1.1.6). The latter, interpreted as 'frozen' basaltic melt or basalt-derived cumulates which crystallised at 10-20 kbar, contain pyroxenes of a similar composition to that of the megacrysts. The authors conclude that the pyroxene and amphibole megacrysts are probably disaggregated Al-augite suite material which crystallised from magmas of similar composition to the host liquids, while the other megacrysts precipitated from more evolved magmas and were then mixed with the more primitive alkaline lavas which ultimately reached the surface. They suggest that the absence of a systematic relationship between megacryst assemblage and host composition, and variation in megacryst composition result from random sampling of the crystals by the host magmas. Consequently any attempts to ascribe petrogenetic significance to megacryst proportions are flawed.

Binns *et al.* (1970) describe megacrysts retrieved from ten lavas, each from different localities in four northeastern NSW volcanic provinces. All but two lavas are undersaturated, the remainder contain ~2% normative hypersthene. They contain varying proportions of clinopyroxene, orthopyroxene, olivine, kaersutite, titanobiotite, spinel, magnetite, ilmenite, plagioclase and anorthoclase, some of which are restricted to certain rock types and localities. Crystals range in size up to 6cm, but most lie between 1-3 cm. Compositionally they are homogeneous and distinct from any groundmass compositions or examples in lherzolite nodules (which have been found at each locality bar one). Exsolution and deformation textures are rare/non-existent. Clinopyroxene examples are almost ubiquitous, ranging from sub-calcic to calcic in composition (14-19% CaO: 7-10% Al₂O₃), and showing chemical variation among different crystals within single lavas. Orthopyroxenes are restricted to the

hypersthene-normative lavas, and contain 4-8% Al_2O_3 , while spinel occurs in the undersaturated samples. Plagioclase megacrysts are confined to only two localities and are more sodic than groundmass compositions. Composite megacrysts are rare, although one xenolith of olivine-gabbro is reported. The authors argue that the megacrysts are unlikely to be accidental inclusions of disaggregated material since they tend to occur only as single crystals, they display no evidence of strain and have a large grain size compared to crystals within included igneous xenoliths. They are thought to be cognate owing to a correlation between some megacryst types and host lava compositions, e.g. orthopyroxene and spinel referred to above. The absence of exsolution is ascribed to quenching from high temperature, while the rims which occur on the crystals result from re-equilibration with the host lava at lower pressures prior to eruption. They suggest that Ca in clinopyroxene rises with falling pressure, while Al falls, and note that it is probable that most crystallisation took place around the upper-mantle/lower-crust boundary. The sodic nature of the plagioclase crystals is interpreted as a pressure effect since Green (1968) and Green and Ringwood (1968) noted that liquidus plagioclase becomes more sodic with increasing pressure.

Griffin *et al.* (1987) provide mineral analyses for clinopyroxene and orthopyroxene in pyroxenites and granulites which have been interpreted as cumulates or 'frozen' basaltic liquids from the upper-mantle/lower-crust. These xenoliths have been retrieved from various volcanic provinces in Queensland (see Chapter 1) including Buckland.

Ewart *et al.* (1980) describe megacrysts which they found in olivine tholeiites-trachybasalts from several central-southeastern Queensland provinces. Assemblages consist of aluminous augite, aluminous orthopyroxene, olivine, ilmenite, plagioclase and spinel; nodules of lherzolite are rare. Size of megacrysts is mostly < 2mm. Orthopyroxene examples are rimmed by reaction rims of olivine + clinopyroxene. Olivine is rare. Plagioclase is strongly sieved and corroded and found at two localities; they are andesine in composition and rimmed by labradorite similar in composition to coexisting phenocrysts. Thermodynamic calculations suggest that the compositions of these phases are consistent with their being in equilibrium with their host liquids at 7.2-16.3 kbar (av.12.4) and 995-1391 °C (av. 1192) i.e. in the lower crust.

Some comparisons may be drawn between the examples discussed above and the Buckland samples. In terms of lava and megacryst composition/size, the closest similarity may be drawn with the examples from Queensland presented by Ewart *et al.* (1980): both sets of lavas are hypersthene normative (with the exception of 3 nepheline normative examples from Buckland) and range from relatively primitive to evolved compositions (Ewart *et al.*, op. cit.: mg-numbers 60-30; Buckland: 62-43), while megacryst pyroxene and plagioclase compositions overlap almost completely (Figure 4.4).

From this can be drawn the conclusion that the Buckland megacrysts, just like the examples discussed by Ewart *et al.* (op. cit.), were probably in equilibrium with their host liquids at lower-crustal conditions. Spinel and olivine megacrysts, noted in rare instances by Ewart *et al.* (op. cit.) are absent from the Buckland lavas.

Comparison with the work of Binns *et al.* (1970), Irving (1974) and Irving and Frey (1974) reveals significant differences between the examples which they studied and the Buckland samples. Host lavas in NSW and Victoria are nearly all undersaturated basanites, nephelinites, alkali basalts and their alkaline derivatives, while megacryst assemblages are much more diverse. This latter point is probably related to the host composition, since volatile-rich alkaline magmas may easily crystallise hydrous phases such as mica and amphibole, while Binns *et al.* (1970) suggest that the confinement of spinel to undersaturated lavas and orthopyroxene to saturated lavas in the Newer Basalts is a result of high-pressure phase equilibria. Rarer apatite, zircon and anorthoclase are not found at Buckland; their presence in Victoria and NSW is attributed to the mixing of alkaline basaltic magmas with more evolved lavas from which these phases could have precipitated. Figure 4.4 shows that while Buckland clinopyroxenes have similar Ca-Mg-Fe compositions to examples from Victoria, they have lower Al contents, suggestive of crystallisation at a lower pressure (Binns *et al.*, 1970): indeed Irving (1974) and Irving and Frey (1984) constrain the crystallisation pressures of Victorian pyroxenes to 10-20 kbar.

Another striking difference between Buckland samples and those from NSW/Victoria regards the abundance of upper mantle xenoliths of the Al-augite suite (NSW and Victoria) and Cr-diopside suite (Victoria only): no xenoliths of any description are found in the Buckland samples. Irving (1974) and Irving and Frey (1984), noting the overlap in compositions between megacryst pyroxenes and those in the Al-augite suite rocks, suggest disaggregation of these xenoliths as the main source of clinopyroxene megacrysts. Binns *et al.* (1970) reach a different conclusion since their lavas lack Al-augite suite xenoliths and the megacrysts show no compositional overlap with Cr-diopside suite nodules. Noting the lack of strain effects in their megacrysts and the fact that megacrysts are always individual crystals, they conclude that they are high-pressure phenocrysts.

These latter points have some bearing on the Buckland examples, which do show strain effects (in plagioclase and orthopyroxene), and do form composite bodies. Comparison with the data of Griffin *et al.* (1987) shows that derivation of Buckland megacrysts by disaggregation of locally-derived lower-crustal/upper-mantle mafic xenoliths is inconsistent with the mineralogy of these xenoliths (clinopyroxene + orthopyroxene $\pm$ garnet, i.e. no plagioclase) and the geochemistry of the pyroxenes (Figure 4.4).

In conclusion, comparison with published megacryst data from eastern Australia shows that the Buckland megacrysts show closest similarity to examples from other Queensland provinces which crystallised in the lower crust. By analogy with the disaggregation hypothesis put forward for

megacrysts in Victoria, it is plausible that the disaggregation of the aggregates found in some of the Buckland lavas could account for the occurrence of the megacrysts. Irving (1974) and Irving and Frey (1984) suggest that the random incorporation of such material at depth resulted in the observed non-systematic distribution of megacrysts in their lavas, and thus it is possible that the same mechanism could account for their non-systematic variation in Buckland. The domination of the Buckland megacryst assemblages by plagioclase is apparently very unusual.

China and Yemen

Alkali basalts from the Hannuoba province of China (discussed in Chapter 2) contain megacrysts of clinopyroxene, anorthoclase, and rare garnet and titanomagnetite, as well as abundant upper-mantle xenoliths, even in lavas with MgO contents as low as 5.7% (Zhi *et al.*, 1990). Major and trace element variation in the lavas can be explained by the extraction of a clinopyroxene-dominated assemblage with additional garnet and titanomagnetite in the upper mantle, with subsequent entrainment of wallrock. Interbedded tholeiitic lavas contain neither megacrysts nor xenoliths. These clearly show little similarity to the Buckland examples.

Cox *et al.* (1993) described alkali basalts from Shuqra in Yemen which contain megacrysts (< 1cm across) of olivine, aluminous (8-10% Al_2O_3) diopside, kaersutite, spinel, plagioclase and apatite as well as phenocrysts of olivine, augite and labradorite. The lavas containing 5-11% MgO do not contain xenoliths. The presence of kink-bands in olivine and the occurrence of aggregates of various combinations of the megacryst phases suggest that the megacrysts are derived from disaggregated plutonic rocks. Variation in whole-rock compositions can be modelled by mixing between alkali basalt melt and restite material represented by the megacrysts. It is envisaged that remelting of a suite of lower-crustal hydrous, alkalic picritic-gabbroic-syenogabbroic intrusions following a thermal event (e.g. injection of hot, picritic magma) produced the relatively evolved alkali basalts, while the more primitive liquids represent melt + restite. The megacryst mineralogy is clearly more comparable to the assemblages reported from Victoria and NSW than to Buckland: indeed Cox *et al.* (op. cit.) draw analogies between Shuqra and eastern Australia, suggesting that the processes which apparently took place in Yemen may also have occurred in eastern Australia. Furthermore, following the postulation of a complex interlayering of lherzolite and intruded basaltic material around the eastern Australian Moho (see section 1.1.7), they suggest that melting of this basaltic material could result in the destabilisation of adjacent lherzolite bodies, thus explaining the occurrence of alkali basalts, basanites and nephelinites containing abundant peridotite xenoliths in Australia and world-wide.

Although there are some similarities between the Shuqra lavas and the Buckland lavas, e.g. evidence of strain in the megacrysts and the occurrence of aggregates, a similar model cannot be invoked for the Buckland lavas. It would require generation of the evolved Buckland lavas by partial

melting of a protolith consisting of the Buckland megacryst assemblage, i.e. plagioclase + clinopyroxene + orthopyroxene. This is not possible since these three phases can crystallise together from a basaltic parent liquid (e.g. to form norite), hence basalt can be considered as a combination of plagioclase + clinopyroxene + orthopyroxene + residual liquid. Consequently partial melting, or even complete melting, of a plagioclase + clinopyroxene + orthopyroxene rock could not generate a basaltic melt.

4.2.4 Lava geochemistry

Major element oxide and trace element data for the Buckland shield lavas (excluding the three basanite analyses) are plotted against MgO in Figure 4.5. The data clearly show considerable scatter: for example, samples containing 6% MgO also contain between 49.0-51.5% SiO₂, 11-13% Fe₂O₃T, 7.2-8.7% CaO and 15-30ppm Rb. The data form linear trends in most of the plots in Figure 4.5, e.g. increasing TiO₂, Fe₂O₃T & incompatible elements, and decreasing CaO, Ni, Cr with falling MgO. The data appear to form two separate groups in the graph of Al₂O₃-MgO: a low-Al group at MgO > 6% and a high-Al group at MgO < 6%, although this may be an artefact of the sampling. The data also form a distinct fan-shaped pattern in the plot of SiO₂ vs. MgO, which ranges from ~50.5% SiO₂ at 9% MgO to 48.0-51.5% SiO₂ at 4.5% MgO.

The following section assesses whether the scatter in the data could be related to geographical variation or differences between the three petrographically-defined groups discussed above.

Geographical variation

This is assessed by considering lavas from three sequences which were sampled in the Buckland shield, namely Vandyke in the north, Carnarvon in the centre, and Battleship Spur in the south (see Figure 2.1 for a location map). Plots for each sequence are provided in Figure 4.6, showing SiO₂, Al₂O₃, CaO and Rb vs. MgO. The Battleship Spur sequence contains some lavas from the 9-12 group (Chapter 3) which are not included in Figure 4.6. Comparison with the equivalent plots for the whole data-set (Figure 4.5) clearly demonstrates that the geochemical scatter is a province-wide feature.

Variation in the petrographically-defined groups

Comparison is made in the same way as for geographical variation, and the plots are presented in Figure 4.7. The three petrographically-defined groups, while showing some overlap, do show some important geochemical differences. Aphyric lavas are MgO-poor (<6%), Al₂O₃-rich (mostly >15.8%) and show a wide variation in SiO₂ content (lavas containing 5% MgO range between 48 and 51% SiO₂). Megacryst-bearing lavas have MgO contents evenly spread between 4 and 8% MgO, Al₂O₃ contents between 14.5 and 16.5% and a 'fan-shaped' SiO₂-MgO pattern similar to that displayed by the whole data-set. Olivine-phyric samples are MgO-rich (>6%), generally SiO₂-rich (>50%) and Al₂O₃-poor. To

summarise, megacryst-bearing samples reflect the geochemical variation of the whole data-set, while the aphyric ones reflect the MgO-poor section of the data-set and the olivine-phyric the MgO-rich section.

Figure 4.8 demonstrates that there is no systematic geochemical distribution of lavas with the same megacryst assemblage. For example, those that contain plagioclase only (green diamonds) have widely spread MgO, SiO₂ and Al₂O₃ concentrations. However, olivine-phyric lavas are typically MgO- and SiO₂-rich, and include lavas with very high (>51%) SiO₂ contents.

An important point to address is whether the three groups are cogenetic, i.e. they are all derived from the same range of parental magmas. As described above, the three petrographically-defined groups are spread throughout the province and interbedded within the three main sequences; furthermore they are intermingled in the TAS plot (Figure 4.2) and in the plot of normative characteristics (Figure 4.9). These observations, combined with the overlap between the MgO-rich portion of the megacryst-bearing lavas and the olivine-phyric lavas, and between the MgO-poor portion of the megacryst-bearing lavas and the aphyric lavas, suggest that they are cogenetic.

4.2.5 Lava petrogenesis

Fractional crystallisation

The linear geochemical trends displayed by the lavas in most of the plots in Figure 4.5 suggest that they are linked by a common crystal-liquid fractionation process. The observed enrichment in incompatible elements with falling MgO together with enrichment in TiO₂, Al₂O₃, Fe₂O₃T, depletion in CaO, Ni, Cr and unchanging *average* SiO₂ are commonly associated in basaltic systems with the extraction of the 'gabbroic' phase assemblage olivine + clinopyroxene + plagioclase at low pressures (the suppression of Fe-Ti oxide crystallisation accounts for the enrichment in Fe and Ti). The absence of any kinks in the plots of lava data in Figure 4.5 suggests that no change of extraction assemblage took place during fractionation, although subtle changes (e.g. phase proportions, mineral solid-solution) could be masked by the scatter. Note from Figure 4.5 that Sr has a much lower enrichment factor (1.2) than other incompatible elements (~3 in Ba, Nb, Zr), which is consistent with the extraction of plagioclase.

However, the petrography of the lavas (section 4.2) is at variance with this suggestion. Instead of containing well-formed phenocrysts of olivine + plagioclase + clinopyroxene with low-pressure compositions, some of the lavas actually contain megacrysts of plagioclase, clinopyroxene and orthopyroxene, whose compositions are consistent with crystallisation at high pressures (~10 kbar: section 4.2.3) from liquids of a similar composition to their host lavas. Only a small number of samples contain olivine phenocrysts, and these occur in isolation without any plagioclase or clinopyroxene examples. Furthermore, while *average* silica content of the lavas changes little with falling MgO, the actual pattern is much more complex.

It is plausible that extraction of the observed megacryst assemblage could account for the observed geochemical trends with orthopyroxene acting as a high-magnesium substitute for olivine at high pressures (consistent with the contraction of the olivine + liquid field at the expense of the orthopyroxene + liquid field with increasing pressure: e.g. Cox *et al.*, 1979). However there is a significant and important difference in SiO₂ content between the two phases. The approximately unchanging SiO₂-content of lavas with ongoing fractional crystallisation that is observed in many basaltic sequences occurs because the low silica content of the olivine (~40%) counterbalances the high-silica (~55%) content of the plagioclase in the extract. Consequently, the extract has a silica content comparable to that of a basaltic parent liquid. Orthopyroxene contains ~53% silica, and so the extraction of plagioclase + clinopyroxene + orthopyroxene from a similar basaltic parent composition will result in a decrease in silica content in the resultant evolved liquids. As described above, the SiO₂-MgO pattern shown by the Buckland samples is fan-shaped, thus it is plausible that the extraction of plagioclase + clinopyroxene + orthopyroxene from a parental composition containing ~50% SiO₂ and 9% MgO could account for the trend of decreasing silica shown by some of the data. It is unlikely that it could generate trends of unchanging or increasing silica which are shown by the rest of the data, thus apparently requiring the involvement of a silica-poor phase such as olivine.

Fractional crystallisation modelling

Modelling using the DARTS program (least-squares mixing) was carried out in an attempt to quantify this hypothesis, and assess the potential role of olivine. Owing to the scatter of the data, any successful modelling result will merely represent an average solution for what are probably numerous overlapping liquid lines of descent resulting from the extraction of slightly differing phase proportions from a range of 'parental' liquids. This overlapping is to be expected given that the lavas were extruded over a distance of ~75 km and ~3 Ma (Griffin *et al.*, 1987). It is also feasible that fractional crystallisation took place over a range of pressures: as noted above, Ewart *et al.* (1980) calculated that megacrysts retrieved from several provinces throughout central-southeastern Queensland could have been in equilibrium with their host liquids at pressures between 7 and 16 kbar.

In order to take into consideration the geochemical scatter of the data, especially the variation in silica, the modelling considers fractional crystallisation from two 'parental' compositions containing 9% MgO towards three 'evolved' compositions containing 4.5% MgO (Table 4.4 and Figure 4.5). These compositions were estimated by eye, since linear-regression techniques give poor results in the presence of this amount of scatter. Average megacryst compositions were used for the extracts (Table 4.4) owing to the difficulty of accounting for mineral solid-solution with ongoing fractional crystallisation, while a forsterite-rich phenocryst from an olivine-phyric lava was used in the absence of any olivine megacrysts. Results are given in Table 4.5 and summarised below:

End-member Mg4.5/1:	best fit from Mg9/1 is:	37% plag, 36% cpx, 19% opx, 9% ol:	$\Sigma r^2=0.25$
	next best from Mg9/2 is	35% plag, 33% cpx, 32% opx	$\Sigma r^2=0.48$
	next best from Mg9/1 is	32% plag, 38% cpx, 30% opx	$\Sigma r^2=1.31$
End-member Mg4.5/2:	best fit from Mg9/2 is	34% plag, 40% cpx, 18% opx, 8% ol	$\Sigma r^2=0.12$
	next best from Mg9/1 is	37% plag, 43% cpx 20%ol	$\Sigma r^2=0.40$
	next best from Mg9/2 is	30% plag, 43% cpx, 28% opx	$\Sigma r^2=1.06$
End-member Mg4.5/3:	best fit from Mg9/2 is	39% plag, 27% cpx, 10% opx, 24% ol	$\Sigma r^2=0.50$
	next best from Mg9/2 is	40% plag, 30% cpx, 30% ol	$\Sigma r^2=0.91$
	next best from Mg9/1 is	40% plag, 26% cpx, 34% ol	$\Sigma r^2=1.40$

F lies in the range 0.48-0.57 for modelling towards Mg4.5/1 and /2, and 0.63-0.67 for Mg4.5/3.

In each case, the best fitting assemblage contain all four phases. However, some wariness is required in accepting these results at face value. First, since they are best-fit solutions they are non-unique, since the next-best fit (which is not given in the DARTS output) may in fact be a more geologically reasonable solution e.g. in terms of phase assemblage. Secondly, a characteristic of least-squares mixing modelling is that addition of extra phases to a fractionating assemblage commonly results in a better fit, regardless of whether it is supported by petrographical evidence. For example, in the case of the modelling the end-member Mg4.5/1 from Mg9/1 the quality of fit (Σr^2) for a three phase assemblage of plagioclase + clinopyroxene + orthopyroxene is 1.31 while the addition of olivine to the assemblage results in a much better fit of 0.25. Although it is possible that extraction of the four-phase assemblage represents what actually occurred during petrogenesis, it is also possible that the result is meaningless which is a reasonable conclusion in the absence of any olivine megacrysts. Thirdly, solutions which give a poor fit ($\Sigma r^2>1$) may still have some relevance to the petrogenetic modelling of these lavas, since the three evolved end-members have been arbitrarily defined. For example, a solution which gives a poor fit to one of the three evolved end-members on account of excessively high SiO₂ in the residual liquid may be a good fit to one of the lavas which has a slightly higher silica content than the target composition. Note the similarity in the phase proportions of the second and third best fits for target end-members Mg4.5/1 and /3, even though they start at different primitive end-members and produce Σr^2 values either side of 1.

Bearing in mind these factors, it is notable that while the three-phase assemblage orthopyroxene + plagioclase + clinopyroxene provides a good fit for generating the silica-poor end-member Mg4.5/1, the best-fitting three-phase assemblage that can derive the other two end-members is olivine + plagioclase + clinopyroxene. The modelling thus suggests that olivine played an important role in the fractional crystallisation processes that produced these lavas, despite its absence from the observed

megacryst assemblage. If olivine was actually involved in the petrogenesis of the lavas then some mechanism is required to account for its absence from the megacryst assemblage. If it was not involved, then a more complex process than fractional crystallisation must have taken in order account for the generation of the medium- to high-silica evolved lavas. This latter possibility is assessed in the next section.

Assimilation-Fractional Crystallisation

In this section the possible role of crustal contamination in the petrogenesis of the Buckland lavas is considered. Assimilation of a high-silica contaminant alongside fractional crystallisation of an olivine-absent extract could plausibly result in the enrichment of silica in the residual liquids and thus be of considerable relevance to these lavas.

As outlined in Chapter 1, petrological (i.e. from xenoliths) and seismic evidence indicates that the lower crust in the Buckland area, and indeed much of eastern Australia, consists primarily of mafic (basaltic) granulite, with increasing interlayering of lherzolite with depth. Silica contents of such granulites retrieved from the Buckland province and analysed by Griffin *et al.* (1987) are too low (44.6-48.1%) for them to be considered as possible high-silica contaminants in the modelling of Buckland lavas. Very few xenoliths of intermediate-felsic composition from the lower-crust have been reported from eastern Australian provinces (none from central-southern Queensland), although Rudnick and Taylor (1987) suggest that this is at least partly due to preferential sampling by geologists. However, the influence of such compositions at depth may be seen in the enriched isotopic characteristics of some mafic granulite xenoliths throughout eastern Australia which are thought to result from the action of AFC processes in the lower crust (e.g. Ewart *et al.*, 1980; Rudnick *et al.*, 1986).

Rudnick and Taylor (1987) describe a wide compositional range of xenoliths found at a single cinder cone in northern Queensland (in the McBride province near Cairns). The xenolith assemblage is dominated by mafic compositions (~80%), but also includes intermediate and felsic granulites. On the basis of mineralogy and geochemistry, these are interpreted as metamorphosed sediments (supracrustal in origin) and granodiorites respectively; the granodiorites show strong similarities to subduction-related Palaeozoic examples which crop out locally. The rocks have high-grade mineralogies and evidence for derivation from 7-10 kbar, i.e. the lower crust. Reference to Figure 1.1 shows that the McBride province lies on a completely different tectonic block to the Buckland province, and indeed lies on upper crust of Proterozoic age, thus it is perhaps questionable whether the lower crust beneath Buckland could be of a similar composition to that at McBride. However, subduction-accretion mechanisms are invoked for the primary origin of all the eastern Australia tectonic blocks (section 1.1.2), and thus it is plausible that the mid-lower crust beneath Buckland could be composed of subduction-related granites and sediments. This is backed up to some extent by the outcrop of the Retreat Granite, a Palaeozoic intrusion near Anakie, just 100 km north of Buckland (Figure 1.21). Consequently the intermediate and felsic

xenolith compositions of Rudnick and Taylor (op. cit.) are used here to simulate the lower crust beneath Buckland. Major and trace element data for the xenoliths are provided below (Table 4.6). Two compositions are given for each xenolith type: these are averaged for use in AFC modelling.

	Intermediate metasediments			Felsic granodiorites			Shale
	83-157	85-101	Average	83-160	83-162	Average	
SiO ₂	54.22	55.12	54.67	64.00	66.98	65.49	69.85
TiO ₂	1.46	0.56	1.01	0.91	0.56	0.74	0.60
Al ₂ O ₃	19.65	19.54	19.60	15.75	14.31	15.03	15.68
Fe ₂ O ₃ T	10.93	12.80	11.87	6.54	7.66	7.10	4.27
MnO	0.15	0.34	0.25	0.16	0.28	0.22	0.05
MgO	6.23	5.25	5.74	2.98	2.71	2.85	1.26
CaO	4.60	3.89	4.24	4.31	1.59	2.95	1.51
Na ₂ O	2.18	1.95	2.07	3.34	1.45	2.40	2.70
K ₂ O	0.35	0.38	0.37	1.56	4.24	2.90	3.99
P ₂ O ₅	0.23	0.15	0.19	0.45	0.21	0.33	0.09
Rb	3	0.9	2	91	134	113	183
Ba	445	361	403	585	1580	1283	661
Sr	276	164	220	205	205	205	248
Nb	6.6	20	13	8.1	16	12	5.3
Zr	381	77	229	199	206	203	147
Y	35	47	41	33	67	50	31
Rb/Nb			0.2			9.4	35
Zr/Nb			18			17	28
Ba/Rb			202			11	3.6

Table 4.6 Compositions of intermediate (metasedimentary) and felsic (granodioritic) xenoliths from the McBride province of northern Queensland (Rudnick and Taylor, 1987). ‘Shale’ is a composition averaged from Palæozoic shale and greywacke from southeastern Queensland (Lohe, 1980: data from Ewart, 1989a). Iron has been recalculated to Fe(III) in each case and the analyses normalised to 100% for use in AFC modelling.

AFC modelling (least-squares mixing) was carried out to test whether extraction of the observed megacryst assemblage together with assimilation of intermediate or felsic lower crustal material could generate the whole compositional range of evolved end-members. The results are provided in Table 4.7.

Compared to fractional crystallisation modelling (Table 4.5), much better major element fits ($\Sigma r^2 < 1$) are established for modelling of the evolved end-members Mg4.5/1 and /2 using the olivine-absent extract plagioclase + clinopyroxene + orthopyroxene. The best fits are achieved with the most

silica-rich ('felsic') contaminant, which is predictable due to the silica-rich character of the three-phase extract. Also of note is the general consistency of phase proportions and F for these good felsic fits (runs 2,4,6 in Table 4.7): plagioclase between 33-36%, clinopyroxene between 32-37% and orthopyroxene between 30-31%; F between 0.56-0.63. Note the correlation of r with difference in silica content between parent and target compositions: $r=0.09-0.11$ for runs 2 and 6 where the silica difference is 1%, but 0.24 in run 4 where the silica difference is 2%. This is to be expected since raising the silica content of the liquid by 2% requires more assimilation than to raise it by 1%. Runs 1,3,5 using the intermediate composition give poorer fits than the equivalent runs using the felsic composition. One is very poor (run 3: $\Sigma r^2=3.86$), while the other two have fair fits ($\Sigma r^2<1$) as well as similar phase proportions and F to the felsic runs.

The modelling suggests that the major element characteristics of the end-member compositions Mg4.5/1 and 4.5/2 can be modelled from the parental compositions Mg9/1 and 9/2 respectively by AFC processes using the olivine-absent megacryst assemblage. Although the felsic contaminant produces better fits, the results using the intermediate composition are quite similar in terms of F , r and phase proportions. Trace element ratios are used below to assess whether the actual variation in these ratios is compatible with the AFC models and to determine whether it is possible to distinguish between the contaminants.

Ratios involving Rb, Ba, Nb and Zr are considered. Being highly incompatible in basaltic systems, they show comparable enrichments with fractional crystallisation which explains why ratios such as Rb/Nb, Zr/Nb and Ba/Rb vary negligibly during the extraction of plagioclase + clinopyroxene + orthopyroxene. Since the ratios of these elements in the contaminants are substantially different to average ratios in the basalts (Table 4.6; Figure 4.10), AFC involving these contaminants would be expected to have a significant effect on these ratios in the residual liquid.

Vectors illustrating the results of modelling towards Mg4.5/1 and /2 are provided in Figure 4.10. Clearly most of the variation resulting from AFC lies within the scatter of the lava compositions (but cannot account for all of it: some probably results from variation in parental liquid composition), and thus the AFC modelling appears to be reasonable. The greatest variation in each ratio arises from runs 3 and 4 (parent Mg9/1, target Mg4.5/2), which have the highest amount of assimilation ($r=0.23$ and 0.24). Ratios of Rb/Nb and Ba/Rb from these runs exceeds the variation shown by most of the lavas by a factor of x2, and thus it is likely that lavas with compositions close to Mg4.5/2 are more likely to be derived from parental liquids approximating Mg9/2 rather than 9/1 which does not involve such a high value of r . It is clearly impossible to rule out the involvement of the intermediate assimilant.

The high-silica lavas

The previous sections have shown that it is possible to model the gross geochemical characteristics of many of the Buckland lavas by assimilation-fractional crystallisation of the observed

megacryst phases plagioclase + clinopyroxene + orthopyroxene with a felsic ($\pm$ intermediate) contaminant. The samples which extend between the end-members Mg9/2 and Mg4.5/3 in MgO-SiO₂ space have so far evaded all attempts to establish their petrogenesis owing to their apparent trend of silica enrichment with falling MgO. This section considers this problem in greater detail, and evaluates whether the failure of modelling attempts thus far is a result of the rather arbitrary choice of the geochemistry of the evolved end-member Mg4.5/3.

Selected geochemical parameters for the twelve lavas which contain >50.8% SiO₂ are plotted against MgO in Figure 4.11. Although the data form linear trends in certain plots (e.g. Al₂O₃, Na₂O), they are more scattered in other plots (e.g. Fe₂O₃T, CaO), while Nb appears to show no correlation with MgO. The samples come from throughout the Buckland province and contain examples of all three petrographically-defined groups. It is possible that the geochemical scatter which is visible in some of the plots in Figure 4.11 results from variation (in time and space) of 'parental' magma composition, phase proportions, assimilant composition etc. It is notable that the samples all occur in the upper half of their respective sequences, suggesting that any process(es) that link them did not commence until the latter stages of the active eruptive life of the province.

A clue that the samples do have a common petrogenetic mechanism is provided by the plot of Rb/Nb vs. MgO, which seems to show a good correlation with MgO (although with such a small number of points this is obviously influenced by outliers). Even discounting the samples with the highest and lowest Rb/Nb contents, the ratio approximately doubles as MgO falls from 8% to 4.5%. The previous section has shown that the effect on Rb/Nb ratios of AFC involving the felsic contaminants of Rudnick and Taylor (1987) is less dramatic than this (i.e. a factor of 1.4 where $r \sim 0.1$), while fractional crystallisation without assimilation has essentially no effect on the ratio. Is it possible that the 'high-silica' samples all underwent AFC involving a contaminant which has a higher silica content and Rb/Nb ratio than the felsic granodioritic composition? A possible contaminant which fulfils these criteria is a shale/pelite: such rocks are rich in silica and Rb (substituting for K in clay minerals and micas) and low in Nb. Although such xenoliths were not reported from northern Queensland by Rudnick and Taylor (1987), clay-rich sediments are commonly associated with subduction/accretion zones, and might be expected to occur in the lower crust (albeit with a high-grade mineralogy) along with the metasedimentary xenoliths that were retrieved from the McBride province. Modelling is thus carried out using an average Palaeozoic greywacke/shale sediment from southeastern Queensland (Table 4.6: Lohe, 1980; data provided in Ewart, 1989a).

As discussed in a previous section, a disadvantage of least-squares modelling is that only the statistically best fitting result appears in the output, although the next best fit might be more geologically reasonable. This form of modelling is consequently very sensitive to the exact target composition and it is possible that better fits would be achieved if the Mg4.5/3 end-member composition were slightly adjusted. It is possible to overcome this problem by using the constraints provided by the

AFC modelling results for the rest of the lavas. Since the high-silica group is indistinguishable from the other lavas in terms of petrography and most geochemical parameters, any fractionation model for the high-silica group should have similar phase proportions and values of F and r to the models proposed for the other lavas.

Since the least-squares modelling which targeted Mg4.5/3 generally gave best-fit results which involved low proportions of clinopyroxene, the phase proportions used here are the most clinopyroxene-poor of the successful felsic-contaminant runs in Table 4.7. (i.e. 36% plagioclase, 32% clinopyroxene, 32% orthopyroxene: run 2, from Mg9/1 to Mg4.5/1). Different values of r (0.20, 0.15, 0.10) and F (0.65, 0.60 and 0.55) are used which span the range of AFC runs using the felsic contaminant in Table 4.7.

Results are provided in Table 4.8 and Figure 4.11. The closest approximation to AJS195 is the run which is emboldened in Table 4.8, with $r=0.2$ and $F=0.65$, which has well-fitting major and trace element concentrations, and shows strong enrichment in Rb/Nb. Of course this solution is non-unique, and merely allows a general conclusion to be drawn, namely that the high-silica lavas appear to have undergone a similar degree of AFC to the other lavas, with similar phases and phase proportions, but with a different contaminant. It is plausible that this represents the establishment of a new magma chamber some time into the period of extrusion of the Buckland lavas, and at a similar depth to the other chambers (indicated by the consistency of phase proportions and megacryst petrography).

In conclusion, modelling shows that the major and trace element variation in the Buckland lavas can be interpreted in terms of fractional crystallisation of plagioclase + clinopyroxene + orthopyroxene (approximate proportions 36:33:31) with concomitant assimilation of a felsic granodioritic/ intermediate metasedimentary or metapelite (for the 'high-silica' lavas) composition in the lower crust. The high-pressure conditions are inferred by megacryst compositions, texture and by the presence of orthopyroxene.

Phase proportions

The ability of relatively fixed proportions of orthopyroxene, plagioclase and clinopyroxene in the extract assemblages to generate the observed geochemical variation of the lavas (with variation in assimilation) provides a degree of internal consistency to the models. However, it is important to test whether this assemblage and these proportions are geologically reasonable in terms of high-pressure phase equilibria.

Accounts of high-pressure (<30kbar) melting experiments carried out on basaltic compositions under anhydrous conditions are found in, for example, Green and Ringwood (1967) and Thompson (1974, 1975). Unfortunately the starting compositions which these authors use, while including alkali basalts, olivine tholeiites and trachybasalts, are all much poorer in silica (45-48%) than the proposed

'parental' compositions for the Buckland lavas (~50%). Thompson (1975) does not report the crystallisation of any orthopyroxene from melts of the olivine tholeiite and tholeiitic andesite from the Snake River Plain. This phase does not crystallise from Skye trachybasalt or transitional basalt, but does appear in the runs for an alkali basalt where it always occurs with olivine (indeed olivine is the primary liquidus phase up to 17 kbar).

Green and Ringwood (1968) reported olivine as the primary liquidus phase for experiments on an olivine tholeiite, an olivine basalt and an alkali olivine basalt at pressures up to 11.3 kbar. In the olivine tholeiite, orthopyroxene was the second phase to crystallise at 9 and 11.3 kbar, while at 13.5 kbar (where olivine does not crystallise), orthopyroxene and clinopyroxene dominate the extract assemblage, with plagioclase joining late in the crystallisation sequence ($F < 0.5$); spinel also crystallises at this pressure. No phase proportions are provided, however, with the exception of the presence of 15% plagioclase at 13.5 kbar together with orthopyroxene, clinopyroxene and minor spinel. Cox *et al.* (1979) note that orthopyroxene enters the crystallisation sequence at 9 kbar at an earlier stage in the olivine tholeiite than in the alkali olivine basalt: they ascribe this to the higher silica content of the former composition.

These comparisons show that it is possible to crystallise orthopyroxene, clinopyroxene and plagioclase together at high pressures: at ~13.5 kbar from an olivine tholeiitic parent. The extent of plagioclase crystallisation at these pressures is clearly lower than is required by the petrogenetic modelling above (~15% compared to ~36%). Amount of plagioclase crystallisation increases down pressure, and it is possible, therefore, that crystallisation of a more silica-rich parent (appropriate for the Buckland lavas) at a lower pressure than 13.5 kbar would permit a greater extent of plagioclase crystallisation, and the occurrence of orthopyroxene as a primary liquidus phase.

4.2.6 Magma and crystal density calculations

Comparison of the phase proportions derived from modelling with the relative proportions of megacrysts in the lavas (Table 4.2) shows a dramatic discrepancy, especially in the overabundance of plagioclase compared to pyroxene in the rocks. Calculations by Kushiro (1980) suggested that plagioclase would be less dense than a host olivine tholeiite at pressures > 4 kbar, and would thus be expected to float. Such a possibility is appealing with regard to the Buckland megacrysts, as it could explain the overabundance of plagioclase megacrysts.

In order to assess the role of relative density of crystal phases compared to host magma, estimates were made of magma and megacryst density. These are calculated for lower-crustal conditions, since it is assumed that this is the level at which fractionation took place, on the basis of the similarity between megacryst compositions from Buckland and those studied by Ewart *et al.* (1980) interpreted as being in equilibrium with host magma at ~12 kbar and the absence of olivine (discussion of phase equilibria above).

Densities of megacryst phases at 10 kbar. and 1000 °C (the limit of available temperature data) were calculated using 1 atm./25 °C values from Deer *et al.* (1992) and corrections made for temperature and pressure using thermal expansion and compressibility data from Skinner (1966) and Birch (1966) respectively. These data, however, are generally provided for endmember compositions, and only rarely for intermediate minerals e.g. bronzite and labradorite. Consequently, while estimates are made for minerals as close to the observed megacryst compositions as possible, estimates are also made for the end-member compositions to examine the full range of possible densities. Density estimates are given in Table 4.9.

The MELTS program of Ghiorso and Sack (1995), which uses thermodynamics to model magma crystallisation at specified conditions of temperature, pressure, water content etc., was used to estimate magma density at 10, 5 and 2 kbars, in both anhydrous and hydrous conditions for the end-member composition Mg9/1. The output (summarised in Figure 4.12) also gives densities of liquidus phases which are slightly lower than those calculated in Table 4.9. This is probably due to the fact that the MELTS runs were carried out for temperatures above 1000 °C: the tables used to calculate the volume change in Table 4.9 do not provide data for temperatures > 1000 °C, although a thermal expansion coefficient is given for Fo₁₀₀ at 1200 °C which suggests that volume expansion will be greater (and thus density lower) at the higher temperature, as borne out by the MELTS output.

Some general conclusions may be drawn:

1. Magma density lies in the range 2630-2780 kg/m³ for dry and wet melts over 2-10 kbar. These figures compare well with the estimates of Kushiro (1980) within the same pressure range (2650-2760 kg/m³: see Figure 4.12). The effect of the presence of water is to reduce the density slightly: from 2710-2730 (anhydrous) to 2670-2690 kg/m³ (0.5% H₂O) and 2630-2660 kg/m³ (1.0 % H₂O) at 5 kbar.
2. Ferromagnesian mineral densities at 10 kbar, 1000 °C are much greater than the range of estimates for magma at all pressures, and would thus be expected to sink under these conditions. Magma viscosity estimates (from the MELTS output) are ~40-500 poises (4-50 Pa.s) at 10kbar, showing variation with temperature (1380-1160°C) and melt composition. Settling velocities, calculated using Stokes' equation, are large over this viscosity range: between 21 and 1.8 m/hour for a 2mm orthopyroxene crystal with a density of 3250 kg/m³. These are much higher values than those calculated by Wager and Brown (1968) for the Skaergaard intrusion, for example a 2mm clinopyroxene (density 3280 kg/m³) was calculated to sink at 0.073m/hour. However, the viscosity value used by Wager and Brown (op. cit.) is an order of magnitude greater than the highest MELTS estimate (3000 poises i.e. 300 pa.s), reflecting the different P-T conditions in this shallow magma chamber.
3. The estimate for plagioclase (~An₅₀) density in Table 4.9 (i.e. 2710 kg/m³) lies slightly below the density estimate for magma at 5-10 kbar (anhydrous), but slightly above the estimates for hydrous melts at 5 kbar. Plagioclase densities calculated by MELTS (see Figure 4.12) are lower than those for magma

under all conditions except at 2kbar/0.5% H₂O, indicating that this phase floats in the magma at medium-high pressures.

To conclude, density modelling suggests that ferromagnesian crystal phases such as orthopyroxene and clinopyroxene are much denser than their host magma at all pressures and would be expected to sink. Plagioclase crystals are likely, however, to have a slightly lower density than the host liquid at all modelled conditions except 2 kbar (hydrous), and would thus float under these conditions. Settling rates for the pyroxenes are considerable, although based on the assumption that the magma behaves as a Newtonian liquid (i.e. crystals do not have to overcome a threshold force, e.g. by attaining a certain weight) before settling. Effective separation of plagioclase from pyroxene could thus easily have taken place and contributed to the disproportionate abundance of plagioclase in the megacryst assemblages (mostly >70%), far outweighing its proportion in modelled fractionating assemblages (~40%).

4.2.7 Conclusions and model

AFC modelling suggests that the full geochemical range of the Buckland lavas containing <9% MgO can be accounted for by extraction of plagioclase + clinopyroxene + orthopyroxene in the approximate proportions 36:33:31 with assimilation of a range of intermediate-silica rich contaminants. This is interpreted as occurring at high pressures >9kbar (?) owing to the similarity of megacryst compositions with examples which have crystallised at these pressures, and to the absence of olivine from the extract assemblage. The presence of olivine phenocrysts in some of the lavas indicate that some low-pressure crystallisation also took place in some of the lavas. This can be explained by the expansion of the olivine + liquid field and contraction of the orthopyroxene + liquid field with reducing pressure. Liquids in equilibrium with orthopyroxene + plagioclase + clinopyroxene at high pressure may lie in the olivine + liquid field at 1 atm (e.g. CMAS projections in Cox *et al.*, 1979).

A tentative model is presented to account for all the observations:

Fractional crystallisation ($\pm$ assimilation) of primitive liquids took place in the lower crust. 'Parental' liquids containing ~9% MgO and 50-51% SiO₂ and almost certainly the result of fractionation themselves, undergo further AFC involving orthopyroxene + clinopyroxene + plagioclase. Owing to variation in relative density, pyroxenes sink at a faster rate than plagioclase (which probably has approximately neutral buoyancy). On being forced out of the chamber, a magma batch takes a random selection of included crystals (but a greater abundance of plagioclase than pyroxene since this phase is floating/scarcely sinking) or no crystals at all (aphyric lavas). Some pieces of wallrock may also be incorporated into the liquid: these are composed of precipitates from this magma or previous batches of similar composition and are dominated by plagioclase owing to its buoyancy. Some settling

probably occurs during ascent to the surface of the dense pyroxene phases. Some batches pause for a long enough period in the upper crust to crystallise some olivine before eruption. Hence aphyric lavas may represent batches which left the magma chamber without crystals or from which all crystals settled during transport.

4.3 COMPARISON WITH LAVAS FROM SPRINGSURE AND MITCHELL

In this section, geochemical and petrographic comparisons are made between the Buckland lavas studied in detail in section 4.2 (above) and lavas from Springsure and Mitchell which also contain <9% MgO. Table 2.1 shows that Springsure, in common with the Buckland shield sequence, is dominated by silica-saturated olivine tholeiites and trachybasalts, while Mitchell lavas are saturated to slightly oversaturated in the north, and mildly oversaturated in the south. It is thus plausible that Springsure lavas have a similar petrogenetic history to those from Buckland, while lavas from Mitchell have a different history.

4.3.1 Springsure

Geochemistry

It can be seen from Figure 4.1 that most lavas from Springsure have similar abundances of all the plotted major element oxides and trace elements to those from the Buckland shield, but show a greater degree of scatter. For example, Springsure lavas which contain 7% MgO have concentrations of SiO₂ between 49-53% and Rb between 10-45ppm, compared to equivalents from Buckland which contain 49-51% SiO₂ and 23-30ppm Rb. Two other distinctions can be made. First, that lavas reach a greater degree of evolution in Springsure, since the most evolved Springsure sample contains 2.8% MgO compared to 3.8% in Buckland, although this could be a sampling effect. Secondly, that the clear trends of Ti and Fe enrichment that characterise the Buckland lavas are not apparent in Springsure, where concentrations of TiO₂ are widely scattered but Fe₂O₃ shows little variation with decreasing MgO.

The similarity of the geochemistry of Springsure lavas to those from Buckland is compatible with a similar petrogenetic history, although the presence of an Fe-Ti oxide in the fractionating assemblage is suggested by the non-enrichment of Fe. Furthermore, these processes appear to have proceeded to a greater extent than in Buckland. The greater degree of scatter in Springsure could be explained by all or some of the following:

- 1) A wider range of parental liquid compositions for lavas in Springsure than in Buckland.
- 2) Different, or a wider range of, assimilant compositions.
- 3) A greater variation of extract phases and proportions.

These will be considered in greater detail below.

Petrographically, the lavas from Springsure are aphyric (10 samples), porphyritic (8) or megacryst-bearing (6), although two of the latter group also contain phenocrysts of olivine. Aphyric samples consist of olivine, clinopyroxene, plagioclase and Fe-Ti oxide in an ophitic/intergranular texture, with crystal size ranging from 0.1-1mm. Characteristics of the porphyritic and megacryst-bearing lavas are summarised below in Tables 4.10 and 4.11. The groundmass assemblage in these groups comprises olivine, plagioclase, clinopyroxene and Fe-Ti oxide in an ophitic/intergranular texture.

Sample	Phenocrysts				Groundmass	
	Olivine%	plagioclase%	cpx %	Size	Volume%	size
148	8.6	21.6	4.6	<2mm	65.2	~0.1mm
150	5.7			<1mm	94.3	<0.2mm
156	1.8			<1mm	98.2	<0.6mm
157	3.0			<1.5mm	97.0	<0.6mm
164	1.7	0.7		<2mm	97.6	<0.4mm
173	3.2			<0.5mm	96.8	<0.1mm
176	2.9			<2mm	97.1	~0.4mm
183	8.7	13.8	4.1	<1mm	73.4	<0.1mm

Table 4.10 Principal petrographic characteristics of porphyritic lavas from Springsure, including volume % of phenocrysts. Phenocrysts in sample AJS173 are skeletal in habit.

Sample	Megacrysts					G'mass
	orthopyroxene	plagioclase	clinopyroxene	volume %	size	size
159		2 crystals		0.5	<2mm	~0.15mm
165	1			1.6	6mm	<0.2mm
174			1	1.9	6mm	<0.1mm
177		1		0.2	2mm	<0.3mm
188	9		1 (0.03%)	1.4	<4mm	<1mm
228	1			1.5	4mm	<0.4mm

Table 4.11 Principal petrographic characteristics of megacryst-bearing lavas from Springsure, including number of megacrysts per thin section, and their total volume. Samples AJS174 and 228 also contain olivine phenocrysts <1.5mm long, and 1.9% and 7% by volume respectively.

Comparison with Buckland lavas is made below using percentages of the different petrographic types found in each province:

	Aphyric	Megacryst-bearing	Porphyritic
Buckland	49	33	18
Springsure	42	25 ^a	33 ^a

^a Two megacryst-bearing lavas from Springsure also contain olivine phenocrysts.

The principal difference between lavas from the two provinces concerns porphyritic lavas. They are more abundant in Springsure than in Buckland, and have more diverse phenocryst assemblages consisting of olivine ($\pm$ plagioclase) or olivine + clinopyroxene + plagioclase. In contrast, olivine is the only phenocryst phase which is found in Buckland lavas.

Lavas from Springsure which contain >9% MgO are aphyric or contain phenocrysts of olivine + clinopyroxene + plagioclase (Table 3.2). Samples AJS148 and 183 which contain the three-phase phenocryst assemblage are geochemically similar (high-MgO and low-SiO₂) to these examples from the 9-12 group. However, phenocryst proportions in the more primitive lavas are more olivine-rich (olivine >> plagioclase > clinopyroxene) than in samples AJS148 & 183 (plagioclase > olivine > clinopyroxene).

Megacryst-bearing samples are less common in Springsure than in Buckland - only 6 samples contain megacrysts, and the modal volume of these crystals does not exceed 1.9%. Only one of the samples (AJS188) contains more than one megacryst phase: the rarity of poly-phase assemblages could be an artefact of sampling. Two orthopyroxene and one clinopyroxene megacryst were analysed. The orthopyroxenes are similar to examples from Buckland, but are slightly more magnesian (Ca₄Mg₇₉₋₈₃Fe₁₃₋₁₇/3% Al₂O₃), while the clinopyroxene proved to be a low-Ca example (Ca₂₆Mg₅₈Fe₁₆/5% Al₂O₃) unlike the augites invariably seen in Buckland. Clinopyroxene megacrysts appear to be rare in Springsure, as Ewart *et al* (1980) did not recognise any clinopyroxene *megacrysts* (with disequilibrium textures) in the Springsure which they sampled, but only high-Al (4-6%) *phenocrysts* which they interpreted as high-pressure precipitates which were brought to the surface too rapidly to undergo any re-equilibration with their host liquids.

It is clear that the Springsure lavas show evidence for both high- and low-pressure crystal fractionation processes, just like Buckland lavas. However, the fact that porphyritic samples are more abundant than megacryst-bearing samples suggests that low-pressure fractionation was of greater importance in the petrogenesis of the Springsure lavas. The relative paucity of megacrysts could be the result of resorption during low-pressure fractionation.

Previous work and data

As outlined in Chapter 1, Ewart *et al.* (1980) analysed samples from six central volcano provinces in southeastern-central Queensland, including Springsure. They noted that lavas had low phenocryst abundances (mode < 2%, mean 6.7%) which were dominated by olivine (in 93% of assemblages in rocks containing < 52% SiO₂) and plagioclase (75% of assemblages), with smaller amounts of augite (20%) and Fe-Ti oxide (30%). In Springsure, phenocryst compositions lie in the ranges Fo₅₃-Fo₈₄, An₄₈-An₆₈ and augite Ca₄₂₋₄₇Mg₄₀₋₄₅Fe_{13/4}-6% Al₂O₃. As noted above, megacrysts were observed in lavas from the other Queensland provinces, but not from Springsure. Modelling showed that the observed range of lava compositions could be explained by high-pressure fractional crystallisation of olivine + plagioclase + clinopyroxene + magnetite ± ilmenite ± apatite.

Ewart (1982) discussed the petrogenesis of mafic and silicic lavas from the same six provinces in central-southeastern Queensland. He noted that most of the highly variable chemistry of the mafic lavas across the whole region and within individual centres could be explained by the action of fractional crystallisation. However, he observed a broad correlation between extent of fractionation and ⁸⁷Sr/⁸⁶Sr value, with the most evolved mafic lavas having the highest ⁸⁷Sr/⁸⁶Sr (in Springsure variation in MgO is 4-10% and variation in ⁸⁷Sr/⁸⁶Sr is 0.703610-0.703860). Bearing in mind the high ⁸⁷Sr/⁸⁶Sr of locally outcropping Carboniferous sediments (0.711-0.717) and volcanics (0.710), the increase in ⁸⁷Sr/⁸⁶Sr with fractionation was interpreted as the result of minor crustal assimilation.

Modelling

In summary, petrographic evidence suggests that the following have occurred, to a greater or lesser extent, in the Springsure lavas:

- 1) Low-pressure fractional crystallisation of olivine ± plagioclase.
- 2) Low-pressure fractional crystallisation of olivine + plagioclase + clinopyroxene.
- 3) High-pressure fractional crystallisation of a combination of orthopyroxene, clinopyroxene and plagioclase.

There is also geochemical evidence for fractional crystallisation e.g. in the enrichment of incompatible elements with falling MgO (Figure 4.1) and from the modelling of Ewart *et al.* (1980) and Ewart (1982). Isotopic data suggest that some crustal contamination has also taken place.

Modelling was carried out in an attempt to assess whether these fractional crystallisation (± assimilation) hypotheses are consistent with lava geochemistry. Figure 4.13 shows plots of the geochemistry of Springsure lavas together vectors representing different fractional crystallisation and AFC models which are based on the petrographic evidence summarised above. The plots also include five lava analyses published by Ewart *et al.* (1980), as well as AJS144 which contains 9.38% MgO and which was used as a 'parental' composition in two of the models (see Table 3.1 for its composition).

Details of the three assemblages which were modelled are given below:

1. 10% crystallisation of olivine (Fo₈₄) from sample AJS144.

2. Low-pressure AFC of olivine (Fo₈₄) + clinopyroxene + plagioclase (An₆₃) + magnetite acting on sample AJS144 and using the 'shale' contaminant of Table 4.6. This model was constructed in an attempt to fit the open square data points in Figure 4.13 which represent compositions of lavas sampled along the Rolleston Road, east of Springsure town (see Figure 2.1), and which form linear geochemical trends. Samples AJS144 and 148 contain phenocrysts of olivine + clinopyroxene + plagioclase, while AJS150 contains olivine only. Compositions of olivine, plagioclase and clinopyroxene phenocrysts from AJS 144 were used in the model, together with magnetite from Ewart *et al.* (1980). In order to investigate the extent of contamination which could have taken place in the Springsure lavas, the starting composition (AJS144) was assigned the ⁸⁷Sr/⁸⁶Sr ratio 0.70361 and the target composition (AJS145) the ratio 0.70386, thus covering the range of ⁸⁷Sr/⁸⁶Sr values displayed by Springsure lavas presented in Ewart (1982). The 'shale' contaminant was assigned the ⁸⁷Sr/⁸⁶Sr ratio 0.719, from a SE Queensland shale (sample 38683 in Ewart, 1982). The most successful model, which reproduces most of the geochemical variation as well as increasing the ⁸⁷Sr/⁸⁶Sr ratio from 0.70361 to 0.70386, is shown on Figure 4.13. Phase proportions are 24.7% olivine, 28.0% clinopyroxene, 39.6% plagioclase and 7.7% magnetite, while F (fraction of melt remaining)=0.5 and r (mass of assimilant/mass of crystals)=0.05.

3. High-pressure AFC of orthopyroxene + clinopyroxene + plagioclase with the 'felsic' contaminant (Table 4.6), using a model from the Buckland section above (run 6 in Table 4.7). Starting composition is the Buckland 'primitive' end-member Mg9/2, phase proportions are 29.6% orthopyroxene, 36.6% clinopyroxene and 33.8% plagioclase; F=0.56 and r=0.09.

It is clear that these models can account for a significant amount of the scatter and trends that are observed in the major and trace element data, while model 2 can also reproduce the observed isotopic variation. Obviously with variation in parental compositions (e.g. higher TiO₂, CaO, Sr), and allowance for the effects of mineral solid-solution in the extract phases a greater proportion of the data points could be modelled.

Conclusions

Springsure lavas show evidence for polybaric crystal-fractionation just like examples from Buckland, but appear to have undergone a greater amount of low-pressure fractionation. This could have resulted in ‘overprinting’ of any evidence of earlier high-pressure fractional crystallisation, specifically the resorption of megacrysts, and given rise to the substantial geochemical scatter of the lavas.

4.3.2 Mitchell*Geochemistry*

Inspection of Figure 4.1 shows that the Mitchell lavas form two main geochemical groups, at ~7% MgO and ~5.5% MgO, with one outlier at 3.5% MgO. Compared to Buckland lavas with the same MgO contents, the Mitchell lavas are silica-rich and alumina-poor. The 7% MgO group is depleted in incompatible trace elements compared to Buckland samples: in most cases, e.g. P_2O_5 , Ba, Sr, abundances are ~50% of those from Buckland. CaO concentrations are relatively high. The group at ~5.5% MgO overlaps almost completely with Buckland lavas in terms of trace element and major element abundances. Exceptions to this are SiO_2 , where concentrations partially overlap the most silica-rich Buckland lavas, and Al_2O_3 where concentrations are ~1% lower than equivalent Buckland lavas.

Selected elements are plotted against MgO in Figure 4.14, with lavas from the northern part of the province (~25°45'S) and from the southern part (south of 26°15') having different ornaments. Clearly there is a strong correlation between location and geochemistry of the samples. The samples containing ~7% MgO are almost all to be found in the south, together with the most evolved sample (which is also incompatible-element poor) and one lava containing ~5.5% MgO.

The geographical proximity and geochemical similarity of the northern lavas to those from Buckland suggest that they are related, or even represent ‘overspill’ material from that province. Those from the south are distinctly incompatible element-poor and mildly oversaturated, and show little overlap with Buckland samples, suggesting that they are unrelated. Later sections will examine these possibilities in greater detail.

Petrography

Petrographically, the lavas fall into two groups:

The lavas containing ~7% MgO are aphyric and are composed of plagioclase, clinopyroxene (augite and pigeonite), Fe-Ti oxide ± olivine. Plagioclase crystals are elongate and up to 1mm in length, while pyroxene ranges up to 1.5mm in length as ophitic crystals or as intergranular, elongate crystals (aspect ratio ~10). Glass (commonly devitrified/altered) comprises up to 10% by volume.

The lavas which contain ~5.5% MgO consist of olivine crystals (commonly skeletal) up to 1mm in size, elongate plagioclase up to 0.8mm long and rare elongate clinopyroxene. The groundmass is glassy, rarely devitrified/altered and comprises up to 70% by volume. Sample W1 contains a plagioclase megacryst 1.5mm long which shows patchy extinction and an internal melting texture, and an anhedral olivine crystal 1mm long with strongly zoned rims (a feature not shared by the other olivine crystals). Sample W2 contains a 7mm long xenolith of sandstone (well-sorted: apparently quartz-only), with a grain size of 0.05-0.2mm (see Plate 4.5). The xenolith has a margin 0.15mm wide which consists of elongate, moderately-birefringent crystals (clinopyroxene?) and a pale brown alteration product.

In summary, the lavas from Mitchell fall petrographically into the same groups which have been previously defined geochemically. The incompatible-poor group which contain ~7% MgO contains aphyric lavas, while the incompatible-element-rich group (~5.5% MgO) contains both skeletal olivine crystals and rare megacrysts. The olivine crystals in the ~5.5% group are commonly skeletal, while plagioclase and rare clinopyroxene crystals are elongate, suggesting that all may be quench phenomena, rather than the products of low-pressure fractional crystallisation. Rare megacrysts of olivine and plagioclase indicate a phase of high-pressure fractional crystallisation. A role for crustal assimilation in the petrogenesis of the group is suggested by the inclusion of a sandstone xenolith. Alternatively, this could derive from any of the locally outcropping Mesozoic sandstones (some of which are notably quartz-rich) and been acquired by the lava as it extruded from its vent.

Previous work and data

Sun *et al.* (1989) show that the isotopic characteristics of *qz*-tholeiites (MgO~7%) from the Mitchell province are distinct from the average 'plume' composition for eastern Australia (see Figure 1.16). They have notably high $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ as well as low Ce/Pb (~10) compared to the least fractionated central volcano province lavas (including those from Buckland and Springsure) which are considered to represent the average 'plume' composition. Sun *et al.* (op. cit.) state that the Mitchell lavas probably gained their elevated Pb-isotope ratios from the action of AFC processes involving continental crust, although they note that this cannot be easily distinguished from the interaction of their parental magmas with subduction-related lithosphere.

Reference to the published isotopic data of Ewart *et al.* (1988) shows that these distinctive isotopic characteristics are shown by the lavas from *south* Mitchell. Isotopic data for only one north Mitchell sample is provided, whose $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are significantly lower (15.56 and 38.46 respectively) than those for south Mitchell lavas, and plot in the 'plume' field of Sun *et al.* (op. cit.) (Figure 1.16).

The different isotopic characteristics of the lavas containing 7% MgO (mostly south Mitchell) and those containing 5.5% (mostly from north Mitchell) suggests that the two groups have different petrogenetic histories.

Petrogenesis

It is clear from Figure 4.14 that the two main geochemical groups cannot be connected by any reasonable fractional crystallisation model involving the removal of a crystal extract from the ~7% group to generate the ~5.5% group. The plot of K_2O vs. MgO indicates that any extract could not have an MgO content above ~7.2% (because K_2O content cannot be negative!). Consideration of other plots, e.g. Al_2O_3 and Fe_2O_3 vs. MgO shows that ~90% crystallisation of an extract containing 7.2% MgO would be needed to derive the most evolved member of the ~5.5% group from the most primitive member of the ~7% group. This figure is unreasonably high, since it would involve a tenfold enrichment of incompatible element concentrations, thus Zr would be expected to rise from ~90ppm in the ~7% group to ~900ppm in the ~5.5% group: inspection of Figure 4.13 shows that this is clearly not the case. This evidence, combined with a significant difference in isotopic characteristics, indicates that the two groups have different petrogenetic histories, and will be dealt separately in the following sections.

~5.5% group

The similarity of these lavas to those from Buckland suggests that they could also be the product of dominantly high-pressure AFC processes acting on similar parental magma compositions. However, the observed megacryst phase assemblage is different in Mitchell, being olivine + plagioclase as opposed to orthopyroxene + plagioclase + clinopyroxene in Buckland. Of course it is possible that the actual megacryst assemblage in Mitchell lavas includes other phases as well, e.g. clinopyroxene, which did not happen to be recovered during sampling. The occurrence of olivine in a Mitchell lava is an important difference compared to the Buckland lavas, and suggests that the conditions of crystallisation for the Mitchell lavas were different to those for Buckland lavas. The expansion of the olivine + liquid field and contraction of the orthopyroxene + liquid field with decreasing pressure suggests that fractionation of the Mitchell magmas operated at lower pressures than the Buckland magmas (see section 4.2.5 for a fuller discussion of this).

Modelling was carried out to test whether the geochemistry of the ~5.5% Mitchell lavas could be reproduced by fractional crystallisation ($\pm$ assimilation) of olivine + plagioclase (+ other phases?) from the same parental liquids as the Buckland lavas. The 'primitive' end-member magma compositions Mg9/1 and Mg9/2, which were used to model the range of Buckland compositions, were used as parental compositions. Least squares mixing calculations were carried out using the observed megacryst phases olivine + plagioclase, together with orthopyroxene and clinopyroxene on the basis that these phases were involved in the petrogenesis of Buckland lavas and might have also been involved in

Mitchell, but happened not to be sampled. Assimilation of a range of crustal assimilants was considered, using the same compositions as those used for modelling of the Buckland lavas, i.e. 'intermediate', 'felsic' and 'shale': Table 4.6.

Results of the modelling are provided in Table 4.12. Runs which used the starting composition Mg9/1 or which included orthopyroxene in the extract gave poor fits ($\Sigma r^2 > 1$) or negative phase proportions, which are geologically unreasonable. However, good fits were achieved using end-member Mg9/2 and the phase assemblage olivine + plagioclase + clinopyroxene. AFC modelling using each of the three assimilants gives slightly better fits than plain fractional crystallisation, and with little change in phase proportions or values of F. Mass of assimilant/mass of crystals (r) is low in each case (0.04-0.07).

Owing to the similarity of these results, it is difficult to say which is the most likely representation of the petrogenesis of these lava compositions, although it is unlikely that lavas which underwent 40% fractional crystallisation in the mid-lower crust did not undergo some contamination. Since the three assimilant compositions show considerable variation in trace element ratios (see Table 4.6), it should be possible to use these criteria to decide which is the most likely contaminant composition. However, the amounts of assimilation calculated in the modelling are too low for significant divergence in the Ba/Nb and Rb/Nb of the calculated residual liquids to take place which might allow discrimination between contaminants. Vectors plotted in Figure 4.14 show that the calculated trace element ratios lie close to the range of actual ratios.

Use of isotopic ratios to distinguish between contaminants is confounded by the absence of any data for these specific assimilant compositions. It is possible, however, to test whether this amount of AFC is reasonable by calculating the change in $^{87}\text{Sr}/^{86}\text{Sr}$ that it would cause. Calculations show that AFC with $F=0.68$ and $r=0.05$ using a contaminant whose $^{87}\text{Sr}/^{86}\text{Sr}$ is 0.715 (average of Carboniferous sediments from Queensland: Ewart, 1982) would raise the $^{87}\text{Sr}/^{86}\text{Sr}$ of a liquid from 0.70350 to 0.70360. As noted above, Ewart *et al.* (1988) provides a $^{87}\text{Sr}/^{86}\text{Sr}$ analysis for one north Mitchell lava: 0.70363 (sample AE46). If this lava composition was produced by the AFC model calculated above, then its parent liquid would have had a $^{87}\text{Sr}/^{86}\text{Sr}$ of ~ 0.70353 , which lies within the range of 'primitive' Buckland lavas (lavas containing $>9\%$ MgO: Chapter 3) and the 'plume' compositions of Figure 1.13. This indicates that the AFC model is reasonable.

~7% group

The origin of these lavas is much more problematical than for the ~5.5% group. Lavas are aphyric, thus there are no phenocrysts or megacrysts to indicate the nature of low- or high-pressure crystal-liquid fractionation processes. Nor are there any 'primitive' lavas which share the same distinctive depletion in incompatible elements which could indicate the nature of their parental liquids. Isotopic data shows that they are quite different to lavas from north Mitchell, Buckland or Springsure,

and are interpreted as the products of considerable crustal AFC or interaction with subduction-related lithosphere (Sun *et al.*, 1989).

Experimental data show that the silica saturation of melts from anhydrous fertile spinel lherzolite increases with increasing degree of melting and decreasing pressure (e.g. Hirose and Kushiro, 1993). Melting in the presence of H₂O likewise produces silica-rich melts, and lowers the solidus temperature (Hirose and Kawamoto, 1995). Either could provide a plausible reason for the oversaturation of the lavas.

The published isotope data for the ~7% group (Figure 1.16) shows some similarity to data for arc-related lavas from the Tonga-Kermadec islands of the western Pacific which are shown in Figure 5.9 (Ewart *et al.*, 1998). Note also from Figure 1.16b that the Mitchell lavas have high-¹⁴³Nd/¹⁴⁴Nd and high-⁸⁷Sr/⁸⁶Sr, thus plotting to the high-⁸⁷Sr/⁸⁶Sr side of lava field basalts which are presumed to derive from the shallow asthenosphere. Consequently these data are consistent with the interaction of asthenospheric melts with arc-subduction material. By contrast, AFC involving significant crustal contamination would be expected to significantly reduce the ¹⁴³Nd/¹⁴⁴Nd of the residual liquids (see vectors in the bottom right-hand corner of Figure 1.16b).

The geochemical characteristics of the lavas from south Mitchell could thus be explained by a high degree melting, possibly at lower pressures than Buckland examples, followed by interaction with the lithosphere. The low abundances of incompatible elements in the lavas shows that they would have been very susceptible to significant shifts in isotopic ratios.

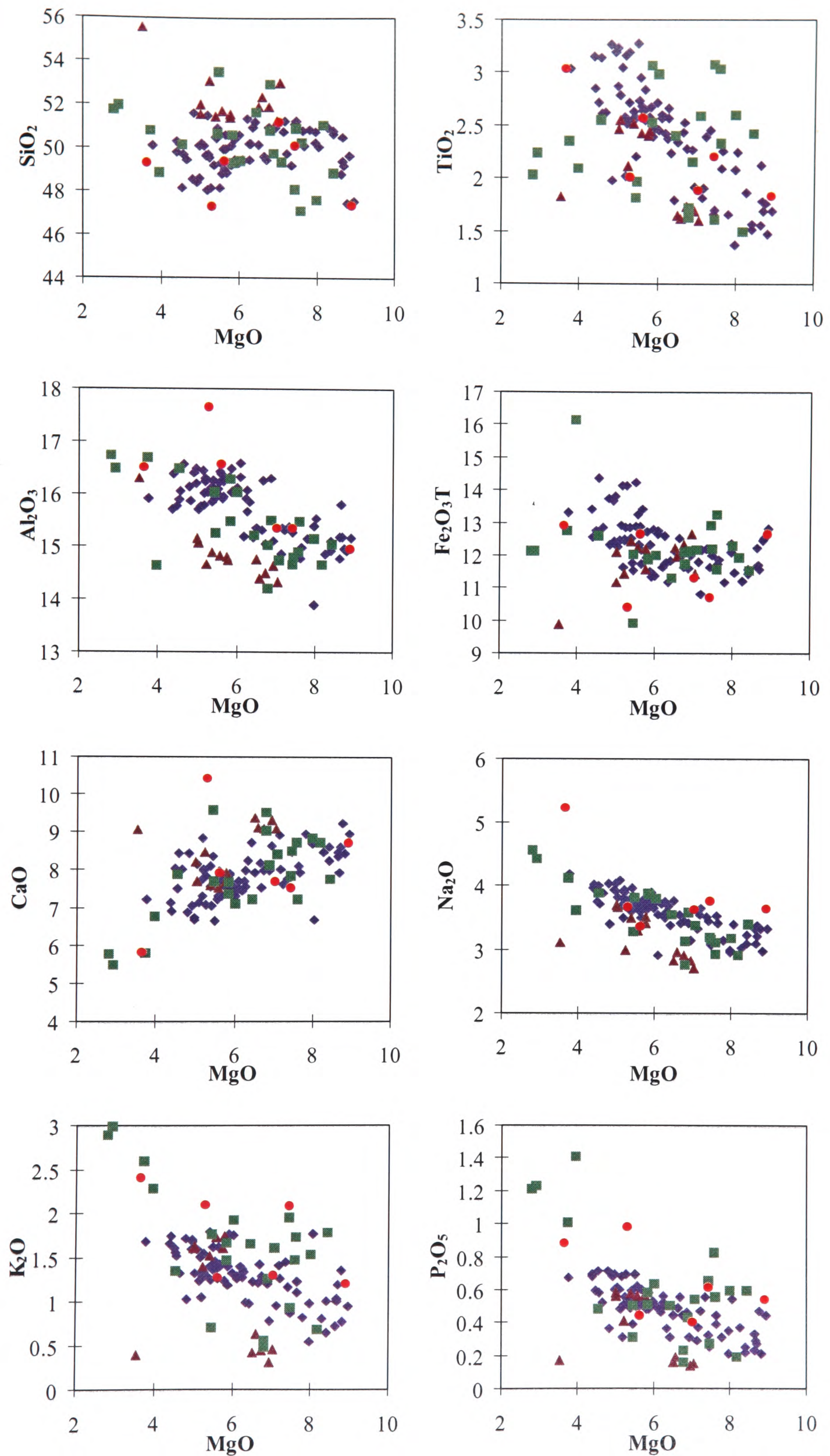


Figure 4.1 Graphs of major element oxides and trace elements vs. MgO for the evolved mafic samples. Those from the Buckland shield are in blue, those from the area west of the Buckland shield in red, Springsure lavas in green and Mitchell lavas in maroon

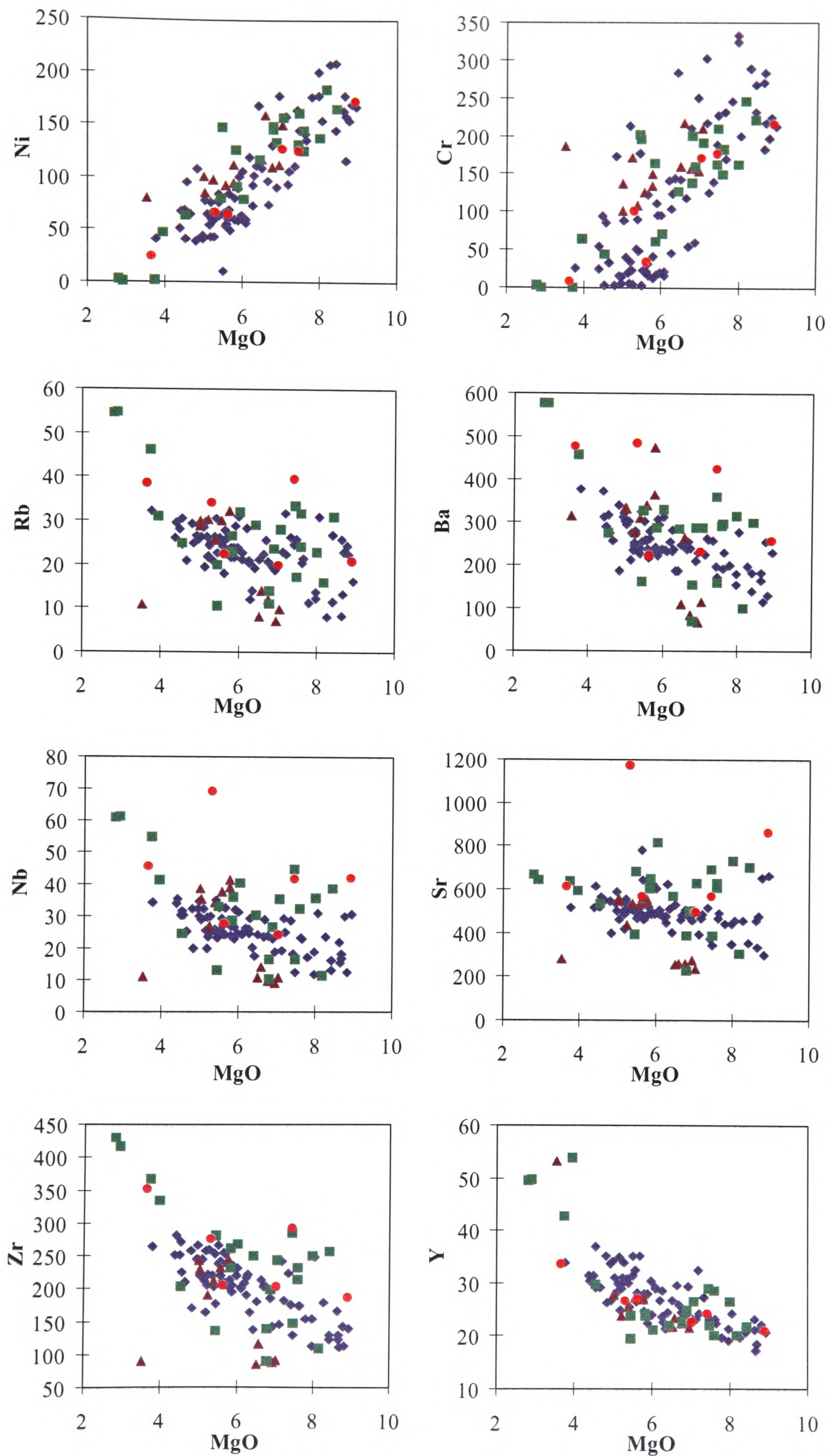


Figure 4.1(cont) Graphs of major element oxides and trace elements vs. MgO for the evolved mafic samples. Those from the Buckland shield are in blue, those from the area west of the Buckland shield in red, Springsure lavas in green and Mitchell lavas in maroon

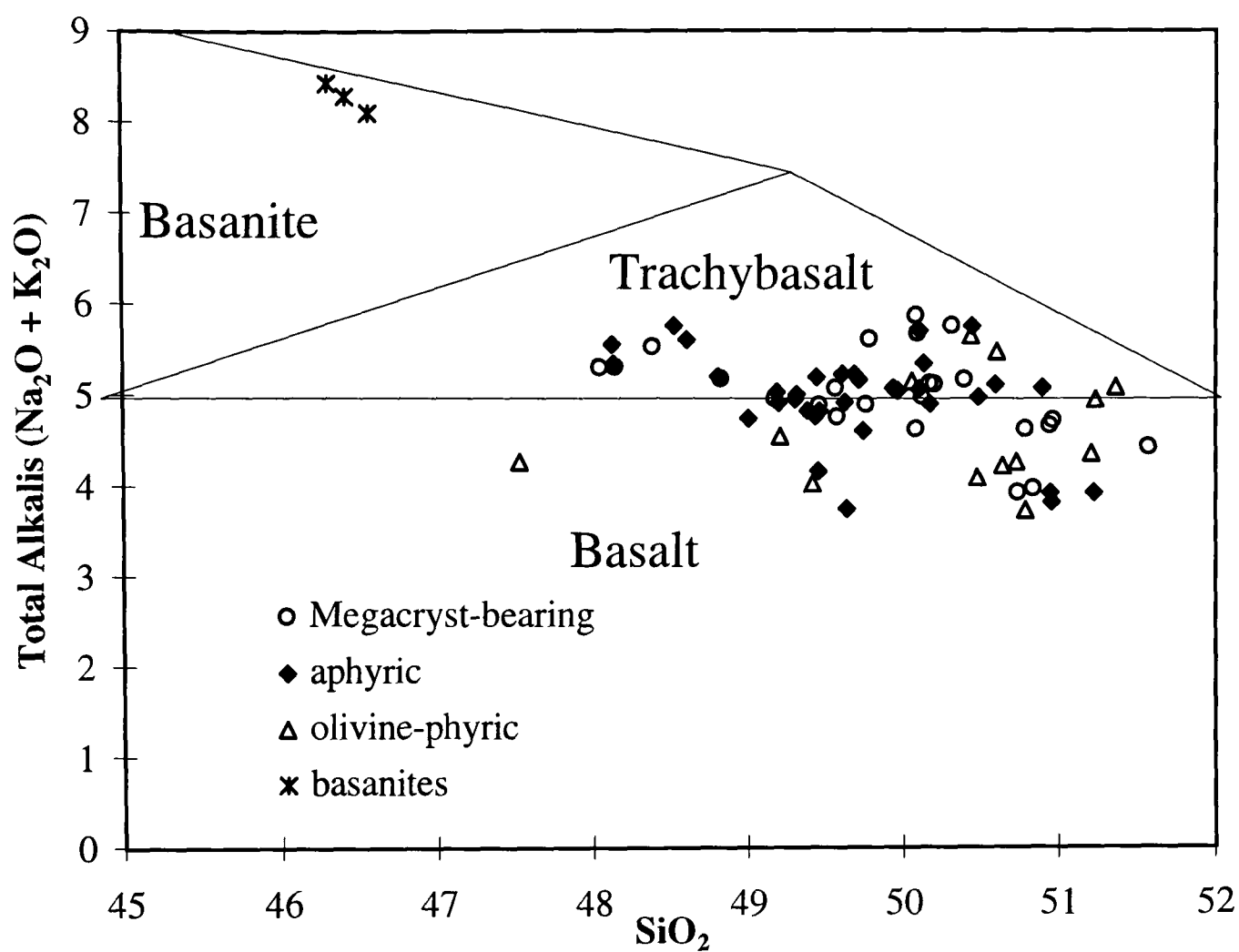


Figure 4.2 Classification of the Buckland samples which contain $\text{MgO} < 9\%$, using the TAS grid of Le Maitre (1989). The samples are ornamented according to the petrographic characteristics described in the text.

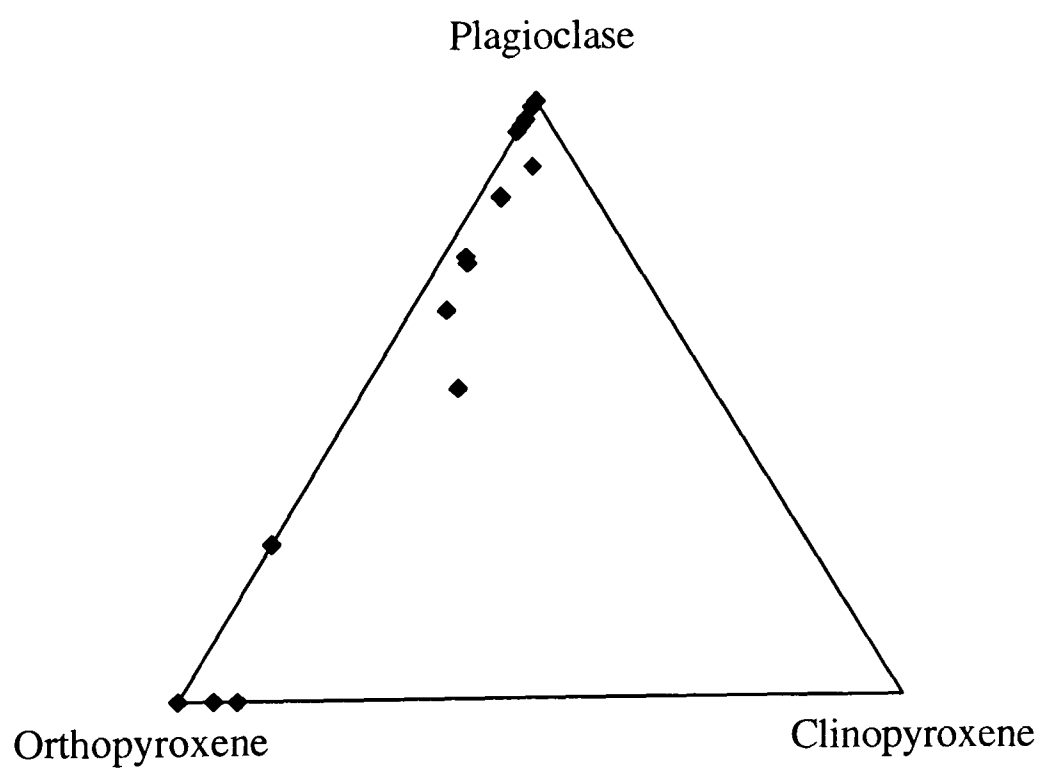
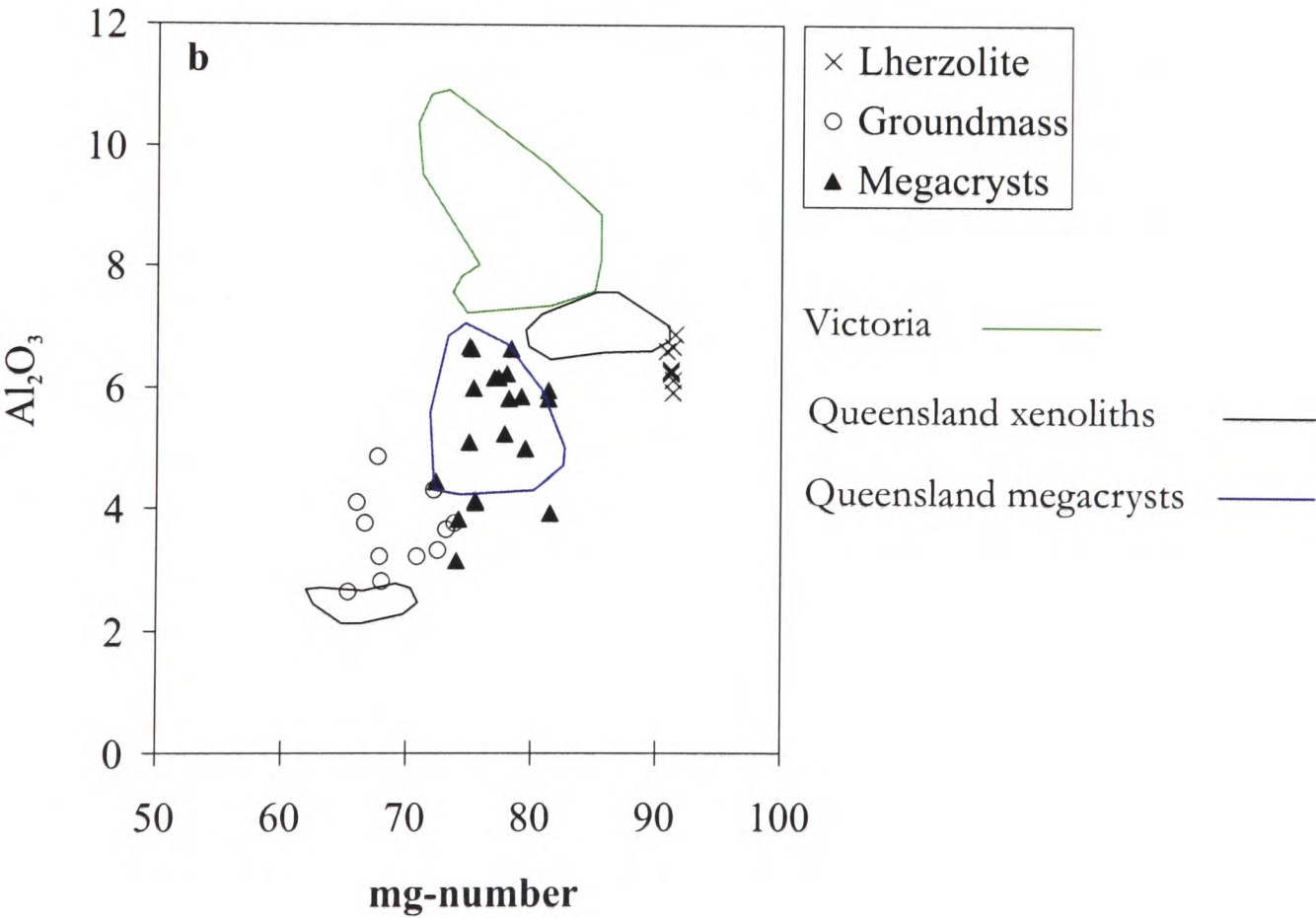
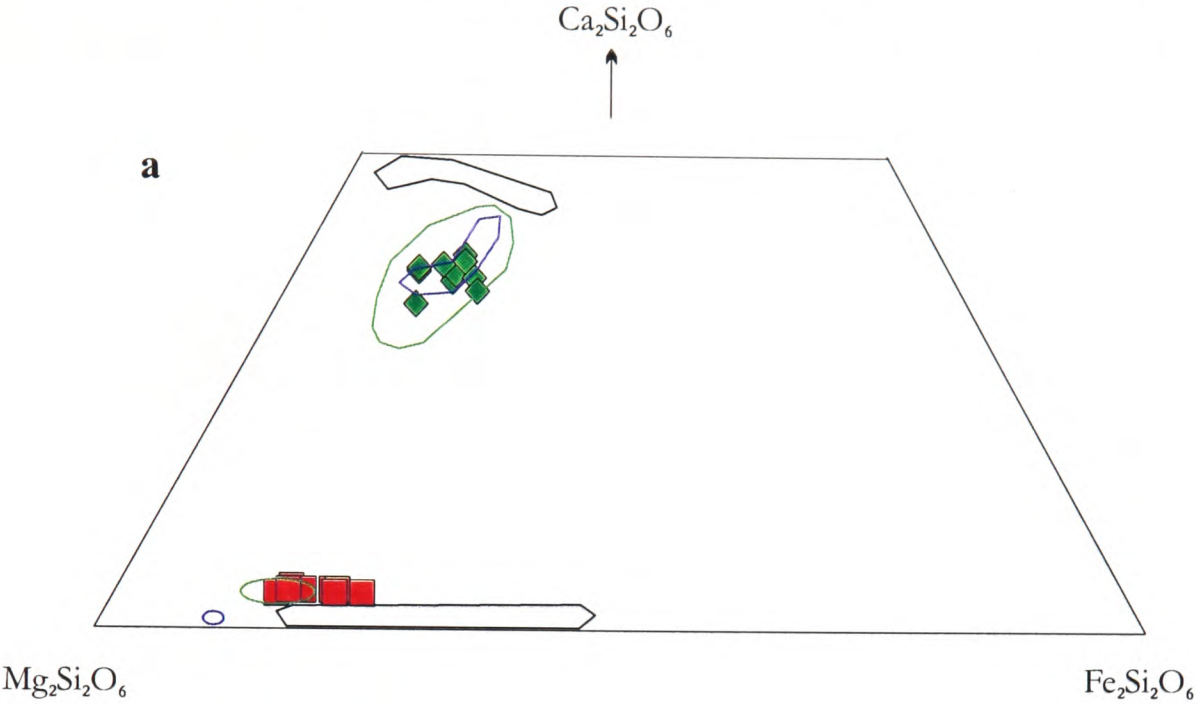


Figure 4.3 Graphical representation of the relative proportions of phases in the megacryst assemblages detailed in Table 4.2. Plagioclase clearly dominates the assemblages, while clinopyroxene is much rarer than orthopyroxene

Figure 4.4a Compositions of Buckland clinopyroxene (green diamonds) and orthopyroxene (red diamonds) megacrysts. Comparison is made with:
 Megacryst pyroxenes from Victoria (Irving, 1974; Irving and Frey, 1985): green field
 Megacryst pyroxenes from provinces in east-central Queensland (Ewart *et al.*, 1980): blue field
 Pyroxenes from granulite and pyroxenite xenoliths from central Queensland (Griffin *et al.*, 1987): black field



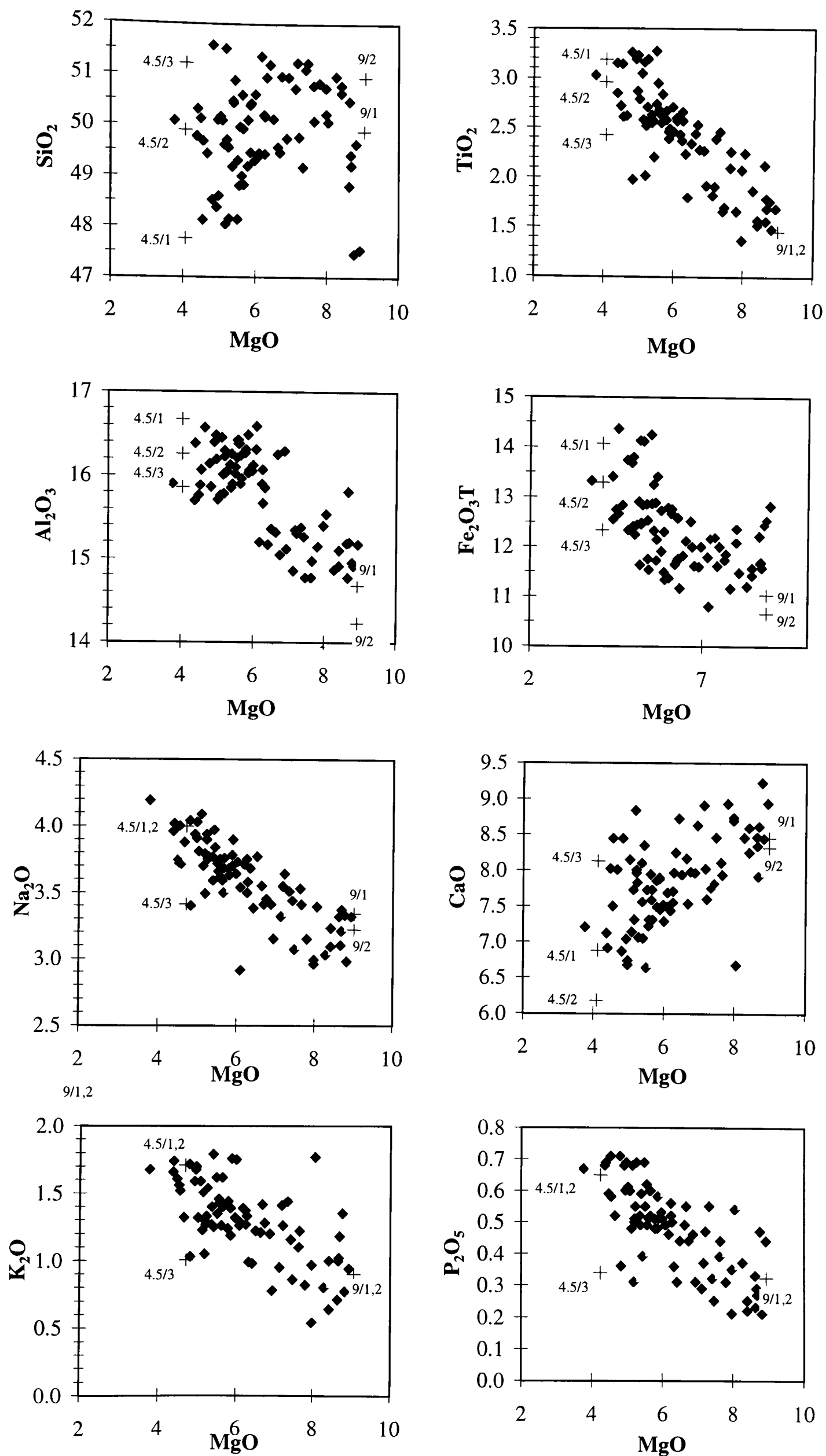


Figure 4.5 Major and trace element variation in the lavas from the Buckland shield. Also shown are the compositions of end-members used in fractional crystallisation ± assimilation modelling, Mg9/1, 9/2, 4.5/1, 4.5/2 & 4.5/3. See Table 4.4 for their full compositions.

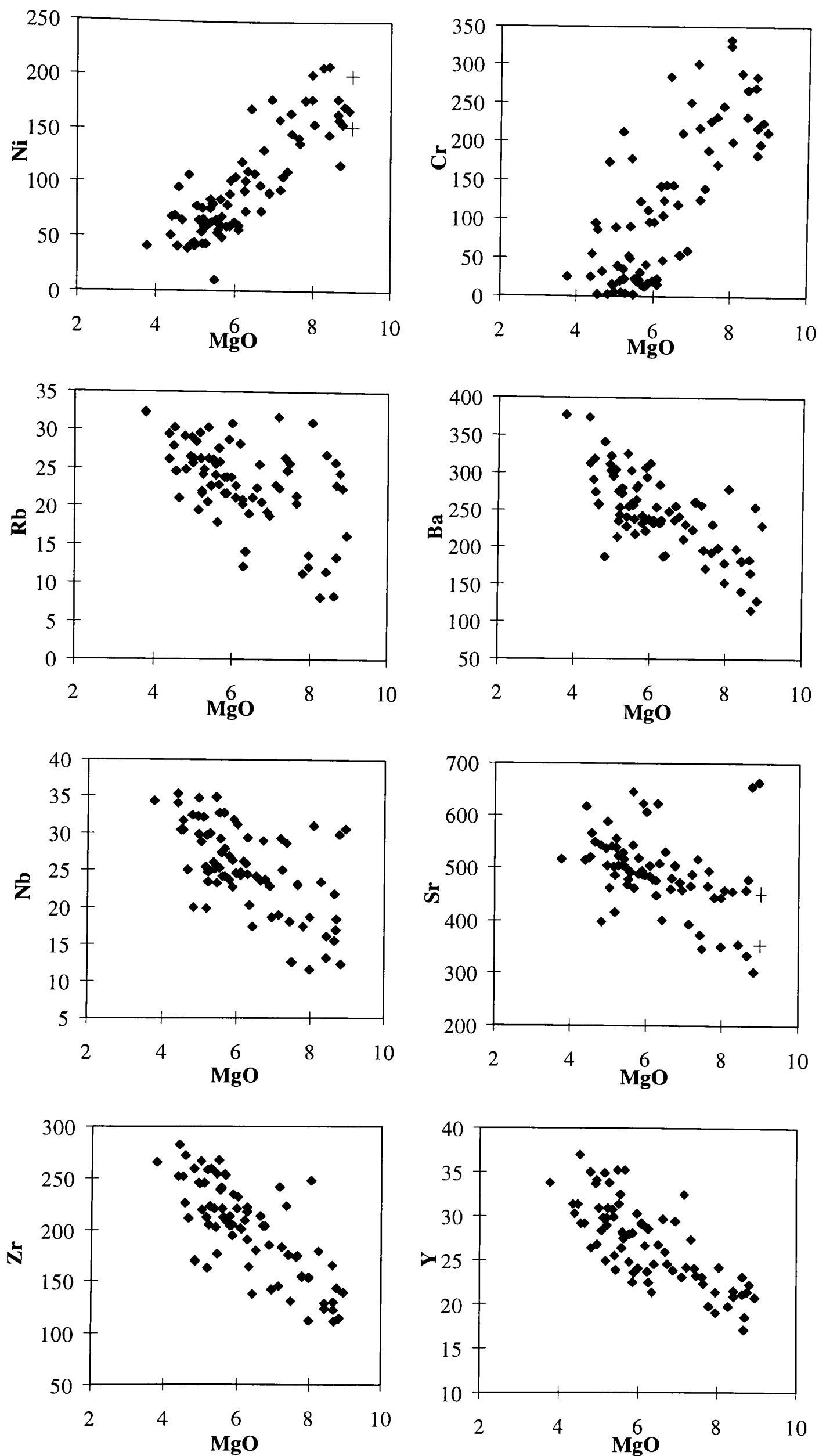


Figure 4.5(cont.) Major and trace element variation in the lavas from the Buckland shield, together with initial Ni and Sr concentrations for the 'parental' end-members.

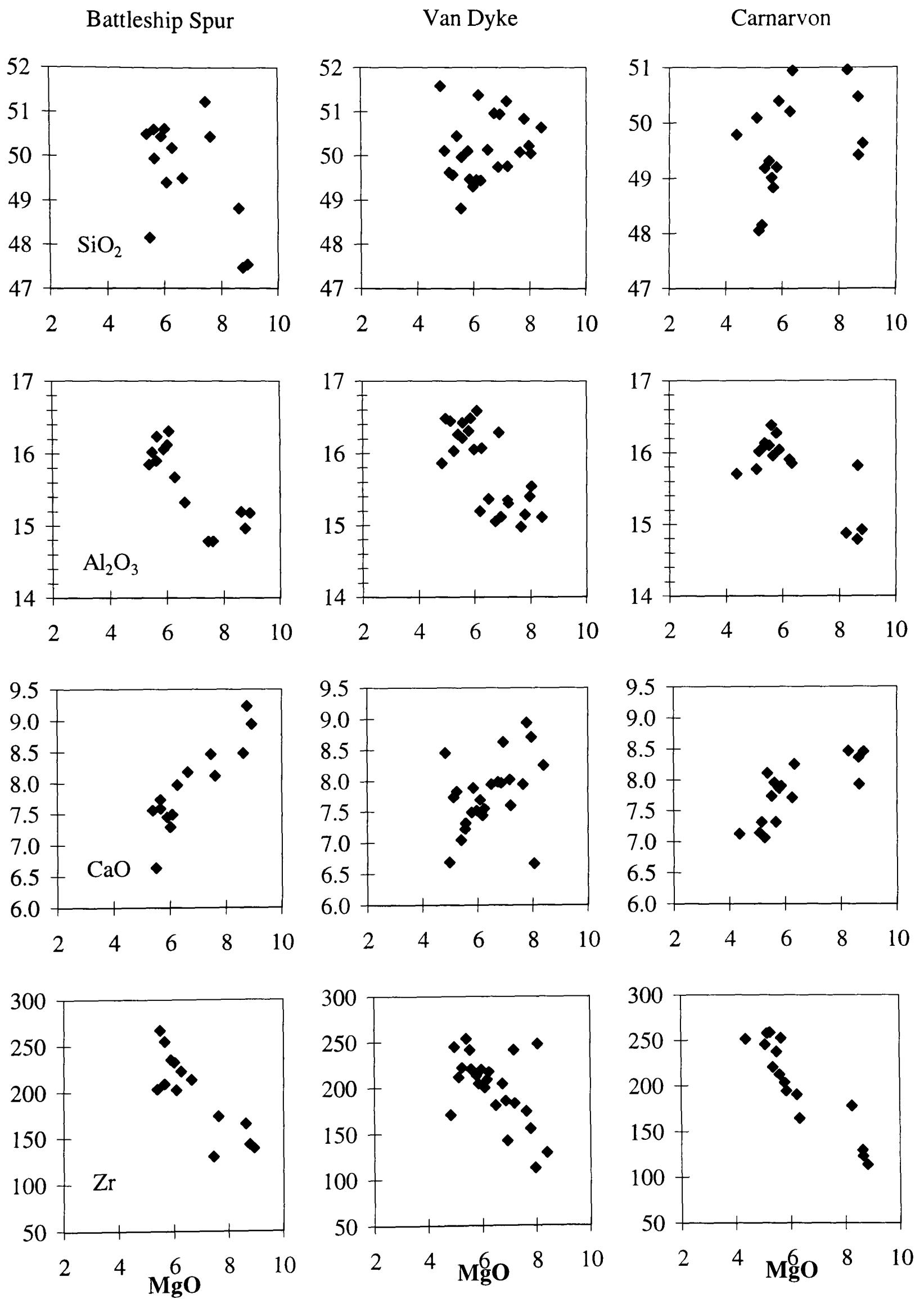


Figure 4.6 Graphs of selected element oxides and a trace element vs. MgO (x-axis) for each of three sections from the Buckland province (see Figure 2.1 for a location map).

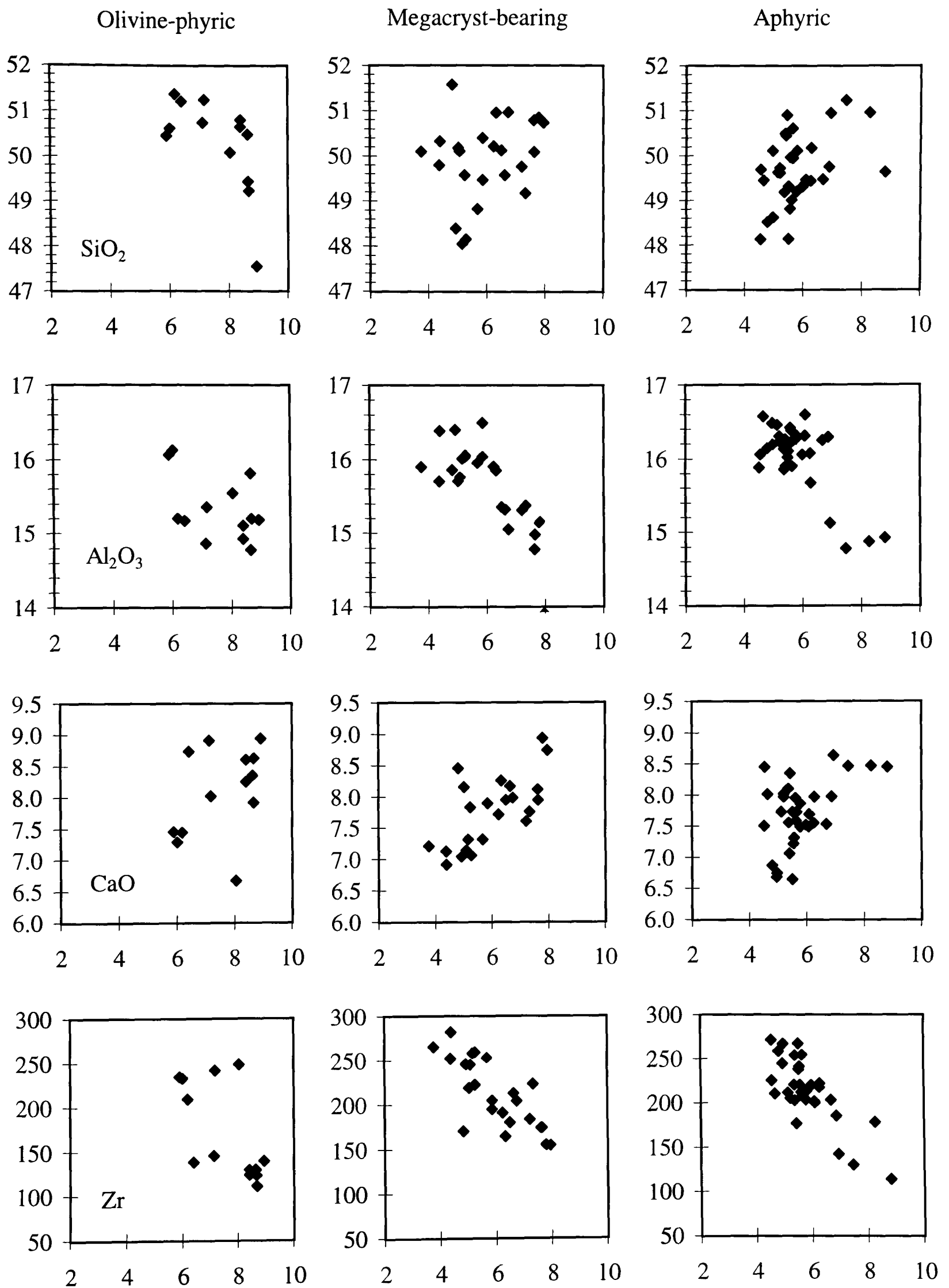


Figure 4.7 Graphs of various element oxides and a trace element vs. MgO (x-axis) for each of the three petrographically-defined groups.

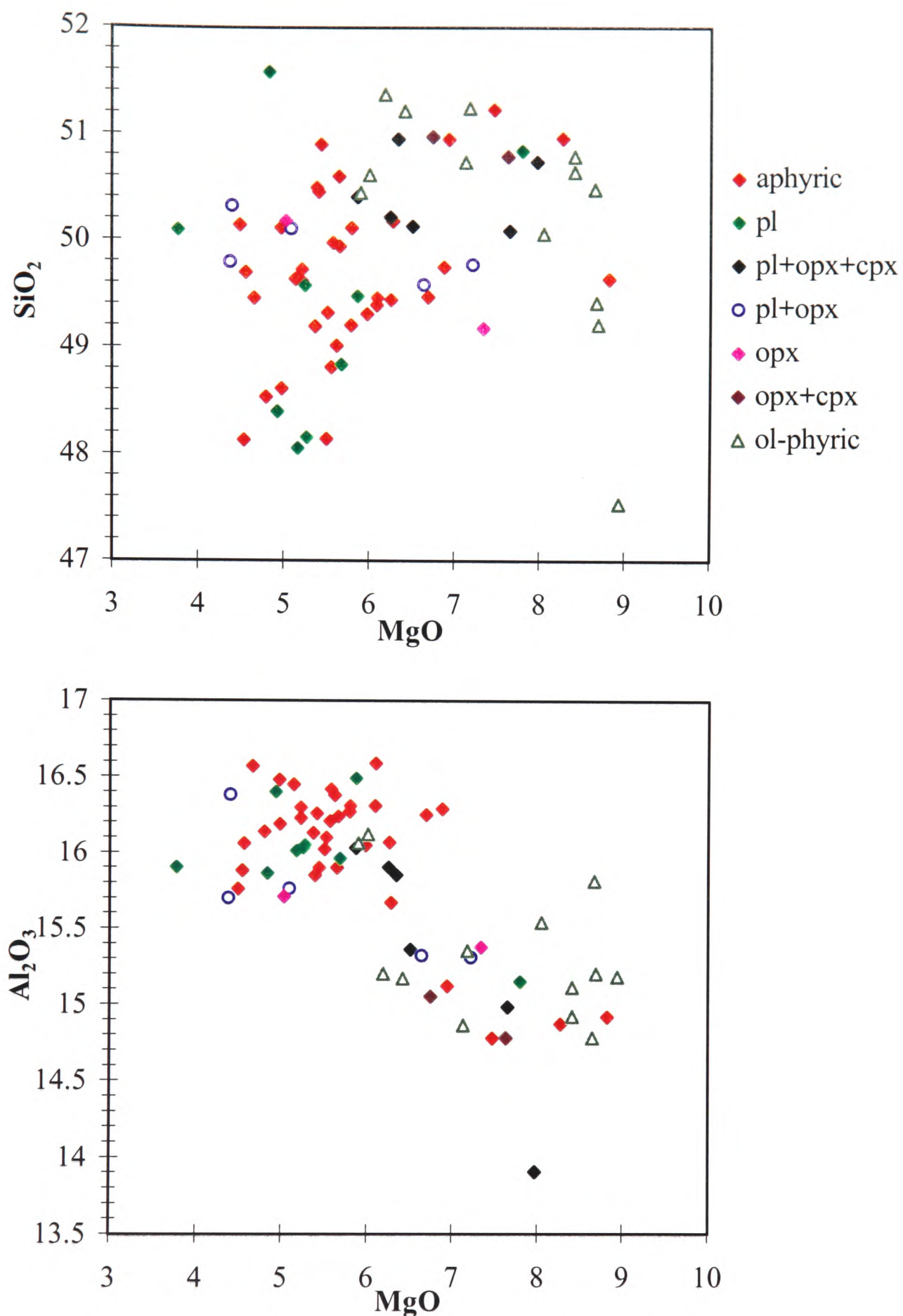


Figure 4.8 Plots to show the distribution of the different petrographic types with lava geochemistry, namely aphyric, olivine-phyric and the different megacryst assemblages involving plagioclase (pl), orthopyroxene (opx) and clinopyroxene (cpx). Note that aphyric lavas have relatively low MgO contents, olivine-phyric types are generally high in MgO and SiO_2 , while lavas with plagioclase-only megacryst assemblages show considerable geochemical variation.

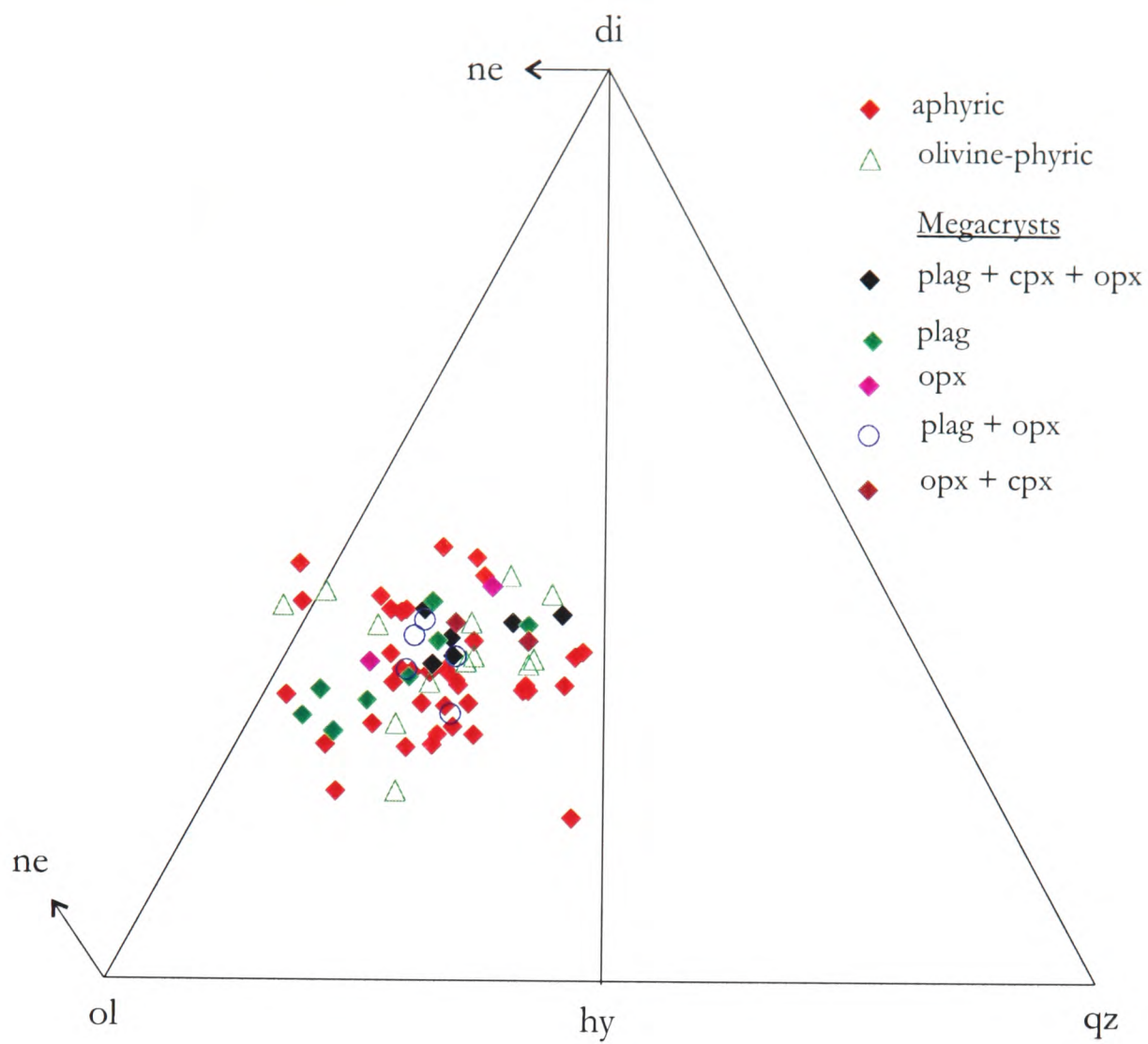


Figure 4.9 CIPW norm characteristics of the Buckland lavas considered in this chapter which are ornamented according to their petrographic classification (see the text). Note the extensive overlap between groups.

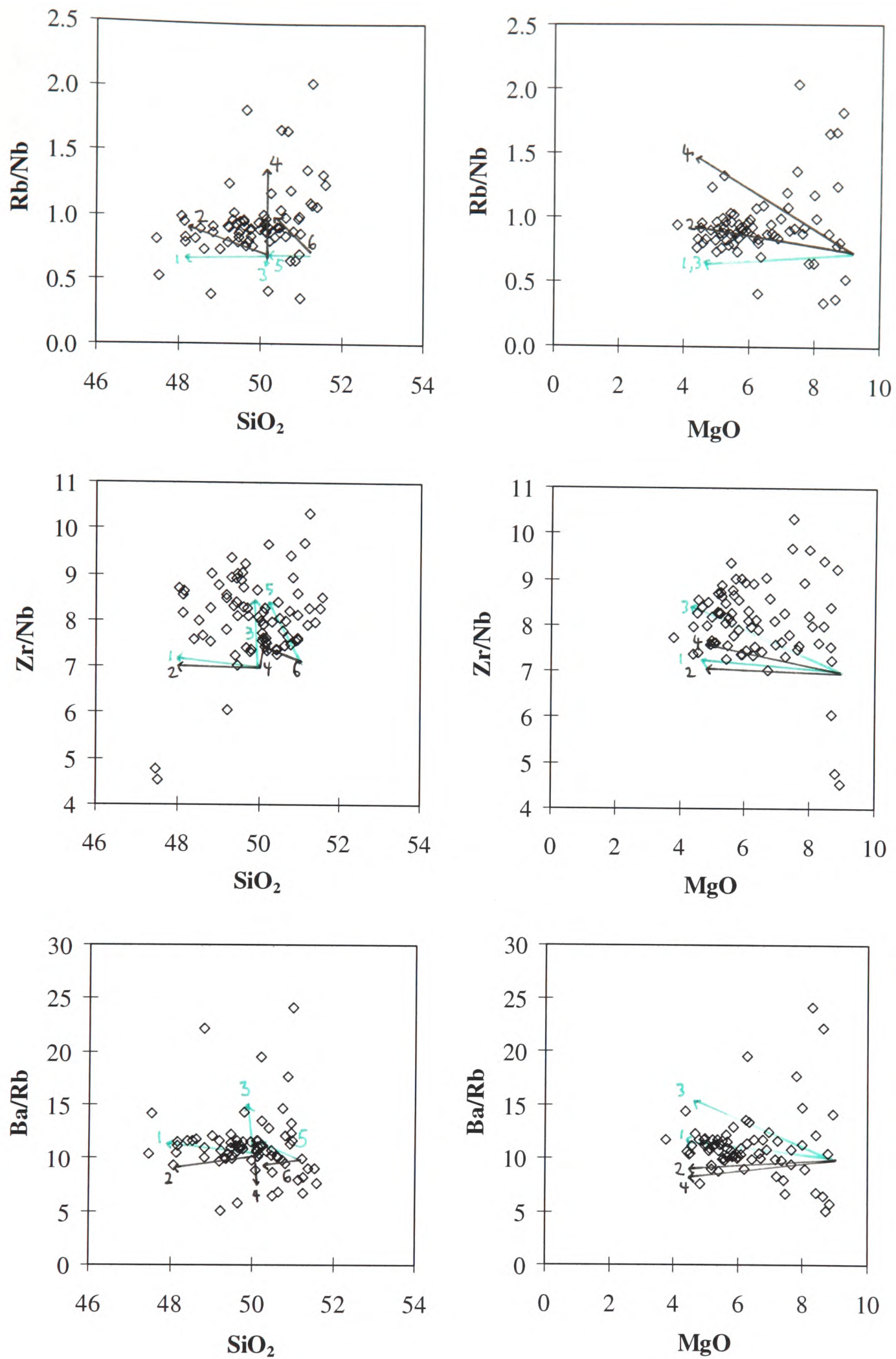


Figure 4.10 Variation in the ratios of selected incompatible trace elements within the group. Vectors indicate the effect of AFC on parental compositions Mg9/1 (50% SiO_2) and Mg9/2 (51% SiO_2), and are labelled according to the run details provided in Table 4.7. Those runs which involve the intermediate assimilant are green, while those which involve the felsic assimilant are black. No vectors are given for runs from Mg9/2 in the plots vs. MgO to avoid cluttering

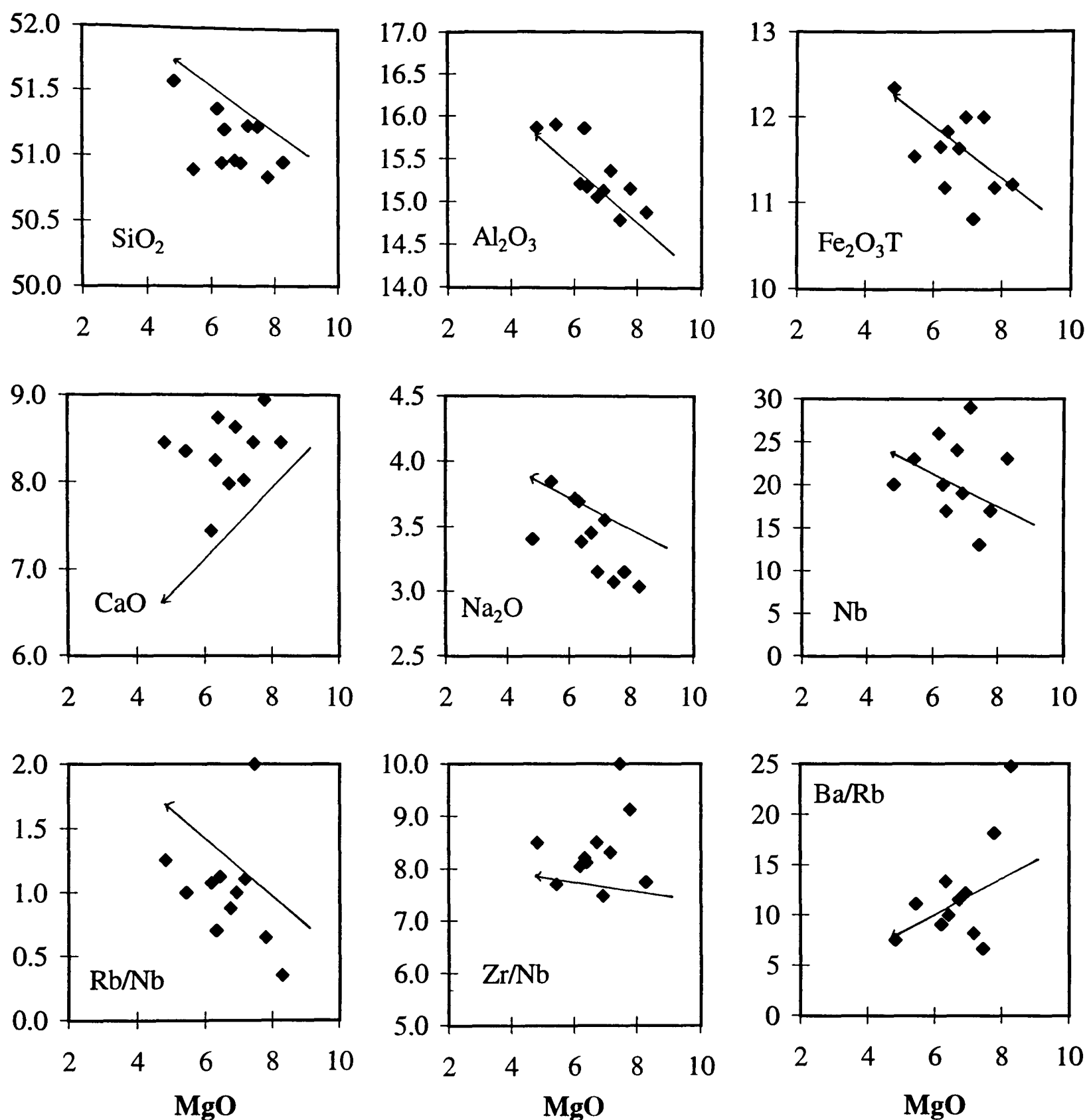


Figure 4.11 Selected major element oxides, trace elements and trace element ratios plotted against MgO for the the 'high-silica' samples which contain $>50.8\%$ SiO_2 . Vectors indicate the effect of AFC involving the 'shale' composition (Table 4.6) acting on the 'parental' end-member $\text{Mg}9/2$. Full details of this AFC model are provided in Table 4.8: run 1, which is clearly capable of explaining some of the geochemical trends shown by these lavas. The Nb concentration (15ppm) and values of Rb/Nb (0.7), Zr/Nb (8.5) and Ba/Rb (10) are typical of Buckland lavas which contain 51% SiO_2 and 9% MgO (see Figures 4.5 & 4.9).

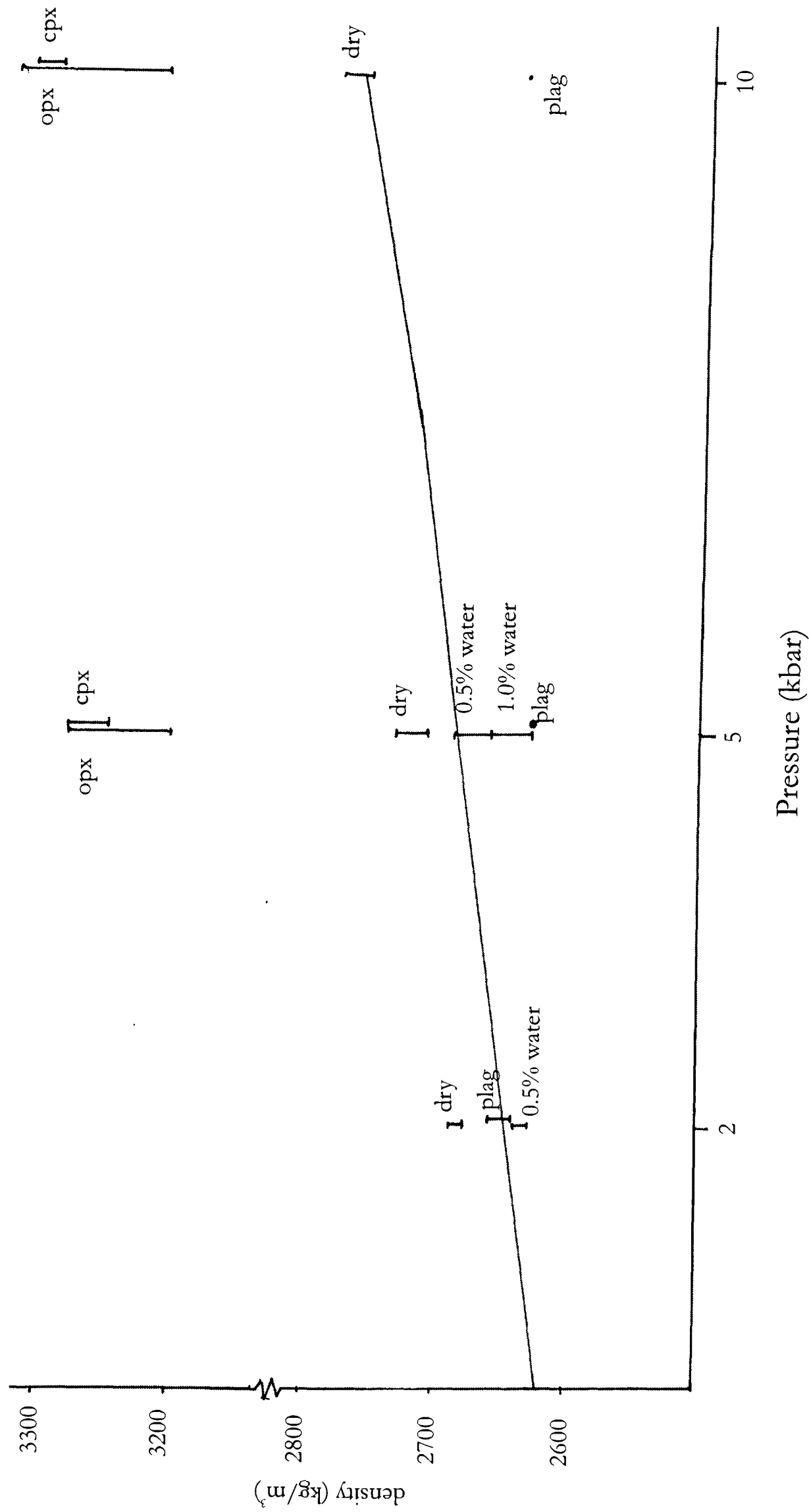


Figure 4.12 Graphical representation of the MELTS outputs for cooling of a magma with the same composition as Mg9/1 (Table 4.4). Ranges of density for the magma under different volatile conditions are labelled 'dry', '0.5% water' or '1% water' according to their volatile content. The curve shows the calculated density of an olivine tholeiite by Kushiro (1980). Densities of coexisting phases are also shown. Clearly the pyroxenes are much denser than the liquid under all pressures, while plagioclase is only denser than volatile-bearing magma at low pressures.

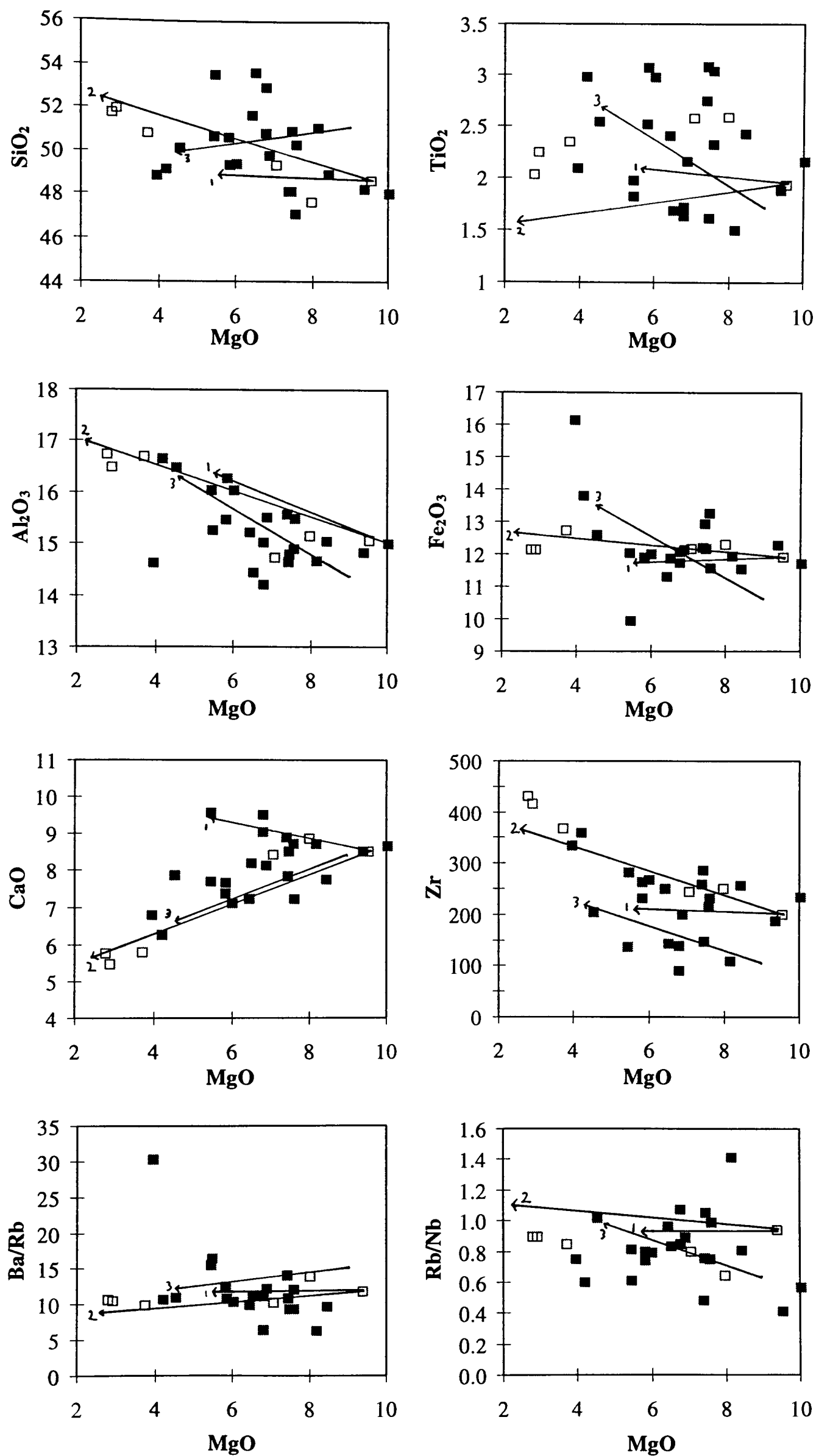


Figure 4.13 Geochemical variation in lavas from Springsure. Included are five analyses from Ewart *et al.* (1980) and AJS144 (from the 9-12 group: Chapter3) which is used as a 'parental' composition in some of the petrogenetic modelling. Open squares come from the Rolleston Road section (Figure 2.1) and clearly form linear trends in these plots. Vectors represent the fractional crystallisation models described in the text, numbered 1-3.

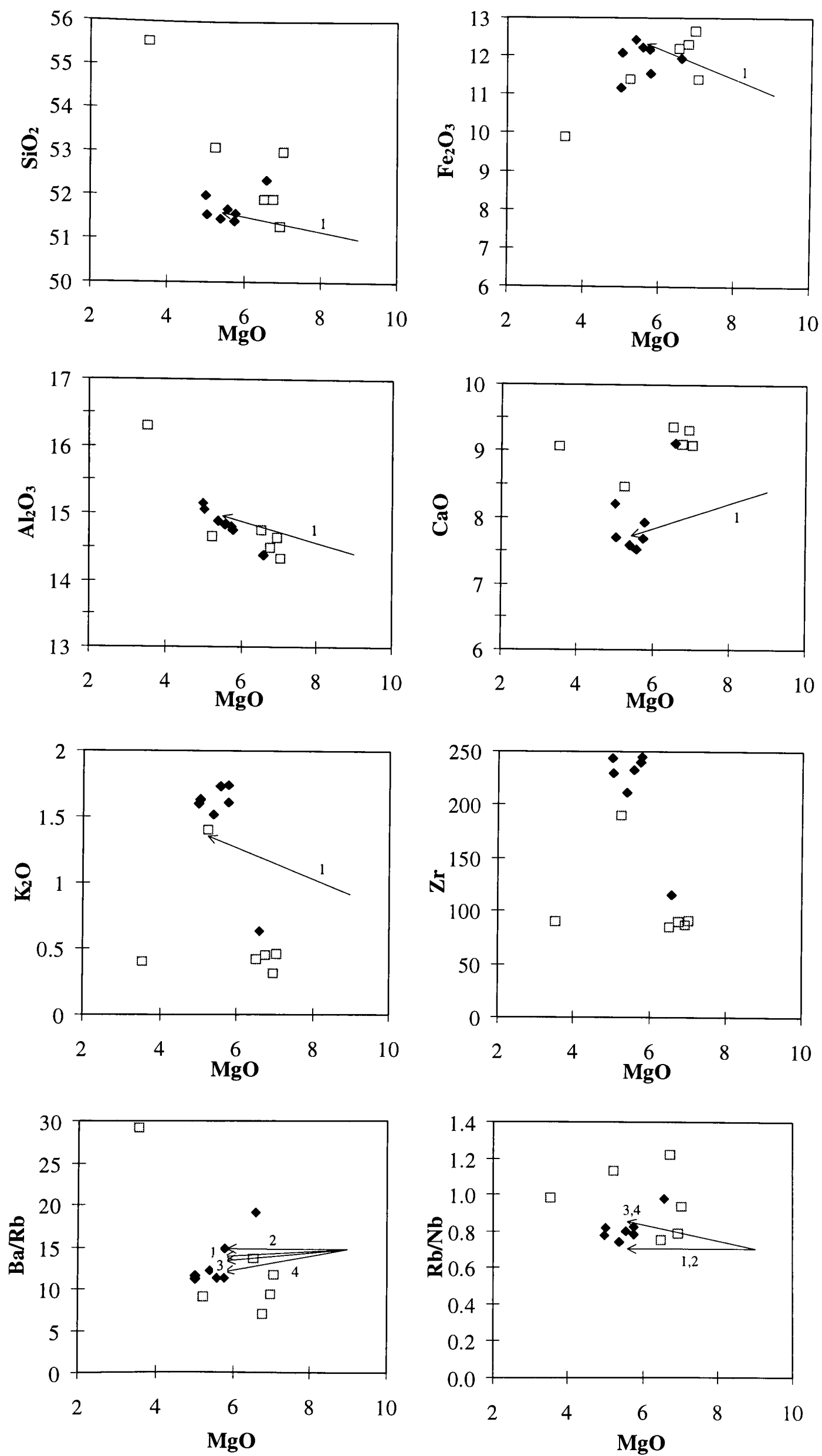


Figure 4.14 Geochemical variation in lavas from north Mitchell (filled diamonds) and south Mitchell. Vectors represent fractional crystallisation $\pm$ assimilation from end-member composition Mg_{9/2}, and are labelled by run number in Table 4.12.



Plate 4.1a Photomicrographs of an intergranular-textured aphyric lava (AJS256) in XPL and PPL .Field of view is 7.5mm across.

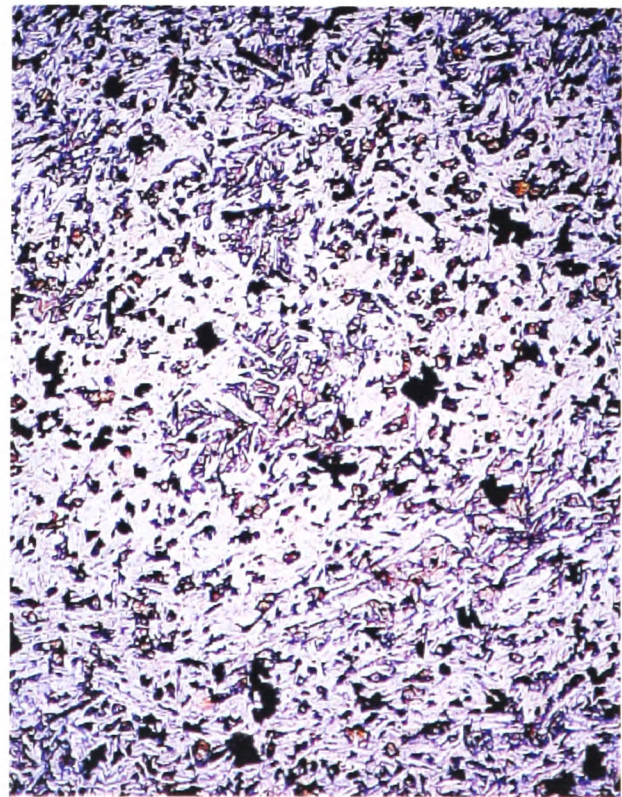
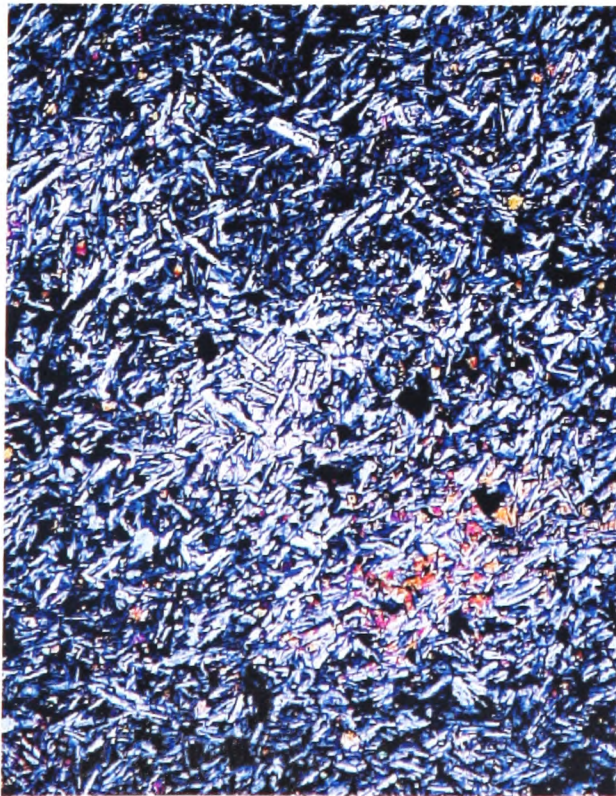


Plate 4.1b Photomicrographs of an ophitic-textured aphyric lava (AJS248) in XPL and PPL Field of view is 7.5mm across..

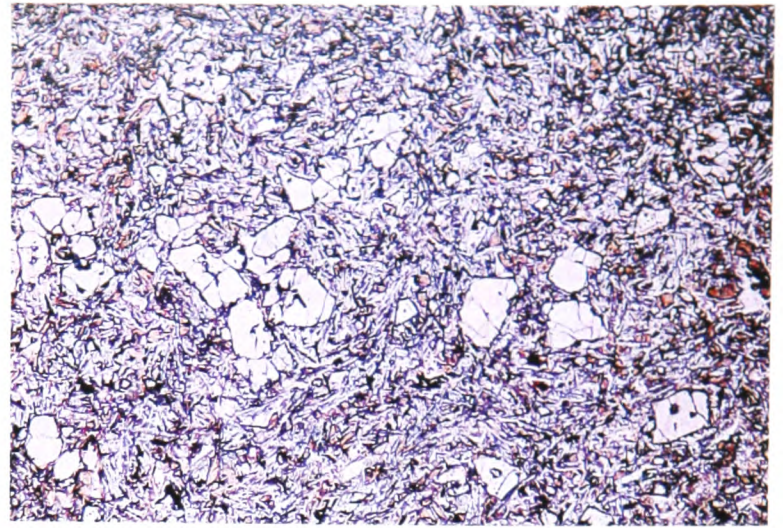


Plate 4.2a Photomicrographs of olivine-phyric sample AJS77. Olivine phenocrysts are unaltered and some form glomerocrysts. The groundmass consists of olivine, plagioclase, clinopyroxene, and Fe-Ti oxide. Field of view is 10mm across.

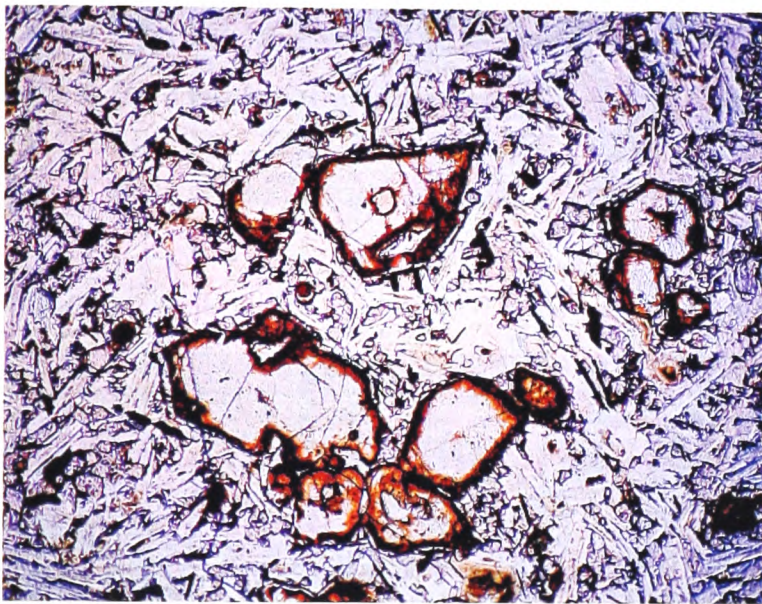


Plate 4.2b Photomicrograph of olivine phenocrysts in AJS200 which show iddingsitised rims. Note that the large crystal in the lower left of the picture has straight and embayed faces. Field of view is 4mm across.

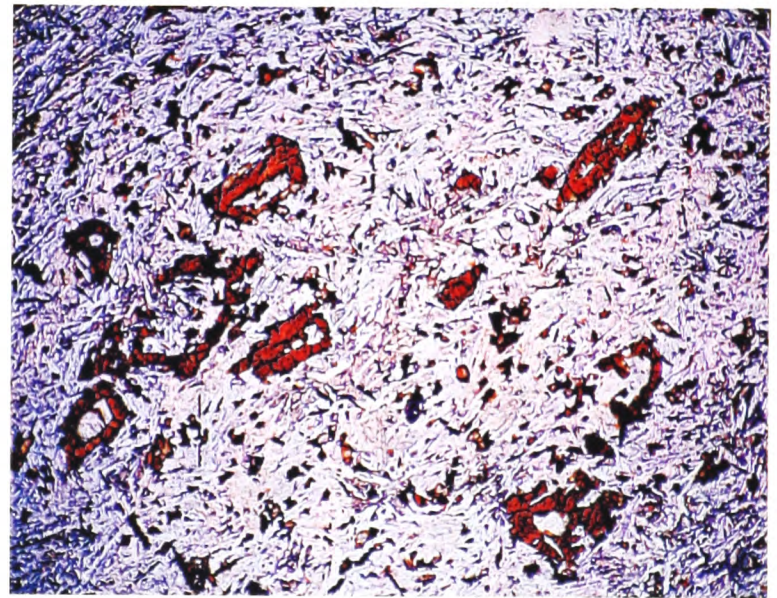


Plate 4.2c Photomicrograph of olivine phenocrysts with a skeletal habit in sample AJS239. The crystals are completely altered. Field of view is 4mm.

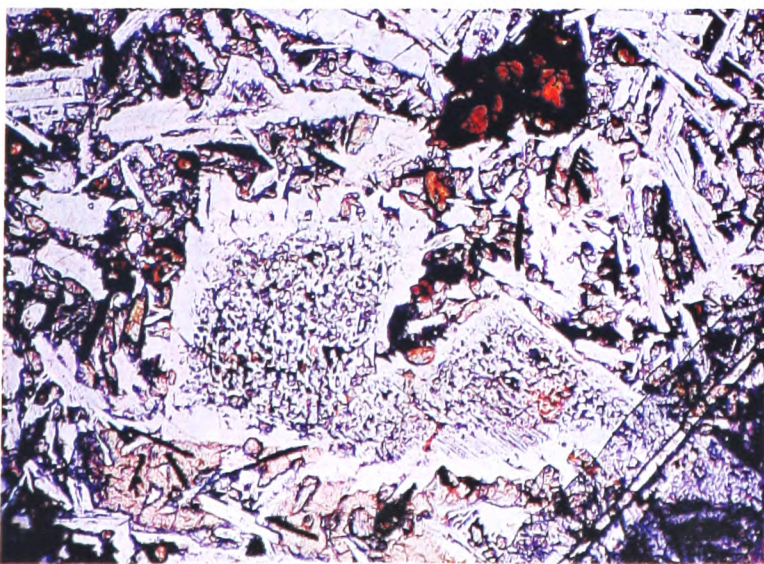


Plate 4.2d Rare plagioclase megacryst from sample AJS52 showing an internal melting 'sieve' texture. Groundmass consists of elongate plagioclase, clinopyroxene and completely altered olivine. Field of view is 4mm.



Plate 4.3a Large, rounded plagioclase megacryst in sample AJS120. The optical continuity of the 'islands' with the main body suggests that this is a strongly embayed single crystal. Field of view is 14mm.

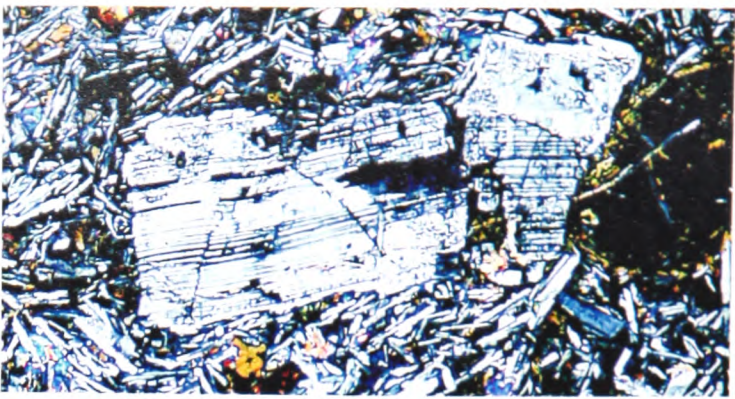


Plate 4.3b Plagioclase megacryst 4mm long in sample AJS203 showing deformation of twin lamellae and internal melting.

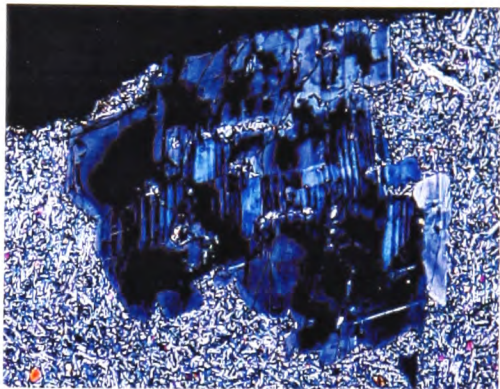


Plate 4.3c Two further examples of plagioclase megacrysts exhibiting signs of lattice deformation. The first is from sample AJS81 (3mm long) and shows an undulose pattern of extinction, while the second from AJS92(4mm across) shows deformation of twin lamellae as well as undulose extinction.

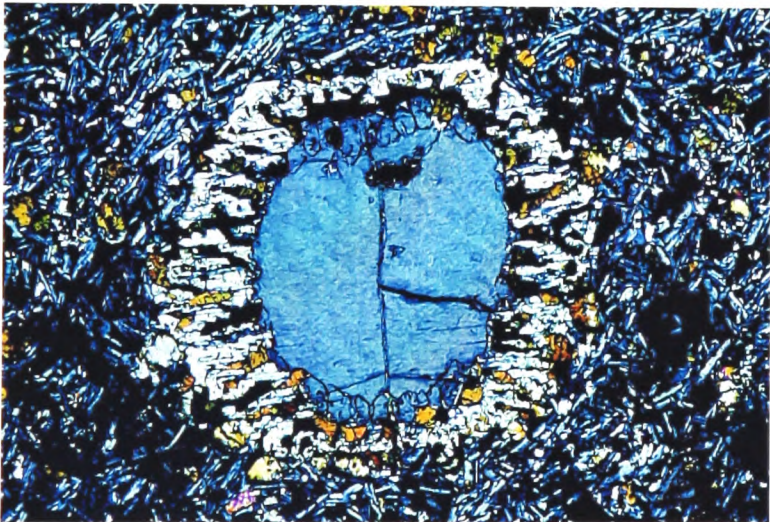


Plate 4.3d An orthopyroxene megacryst from sample AJS120. It is mantled by an intergrowth of olivine (iddingsitised and elongate) and clinopyroxene which unusually consists of a single, optically continuous crystal. Recrystallisation has taken place at the top and bottom of the orthopyroxene; these areas have a lower Al_2O_3 content than the rest of the crystal (1.1% compared to 3%: see the text for details). Field of view is 3mm across.

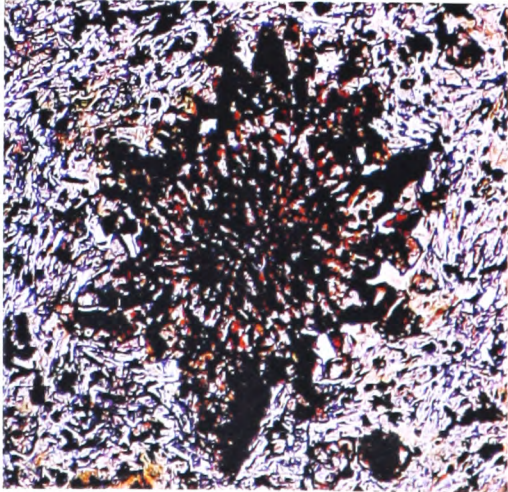
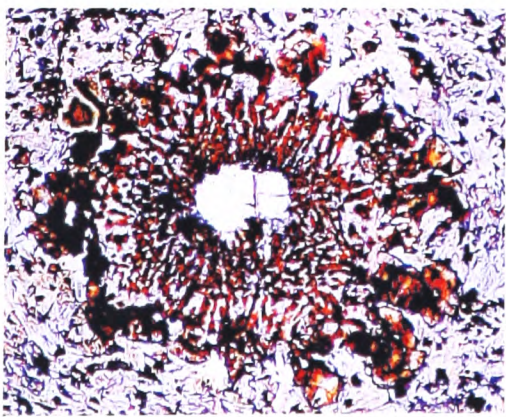
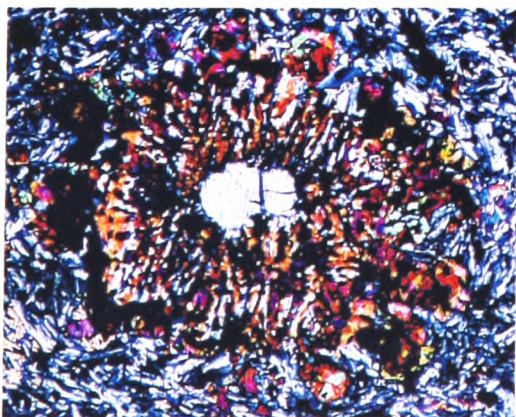


Plate 4.3e These three photomicrographs from sample AJS64 are more typical of the appearance of orthopyroxene megacrysts in the lavas which were studied. They have a greater proportion of mantle than does the example in 4.3d, and include the limiting case (third photo) where there is apparently no remaining orthopyroxene. The first two photos are XPL and PPL shots of the same megacryst: Field of view is 1mm for each shot.

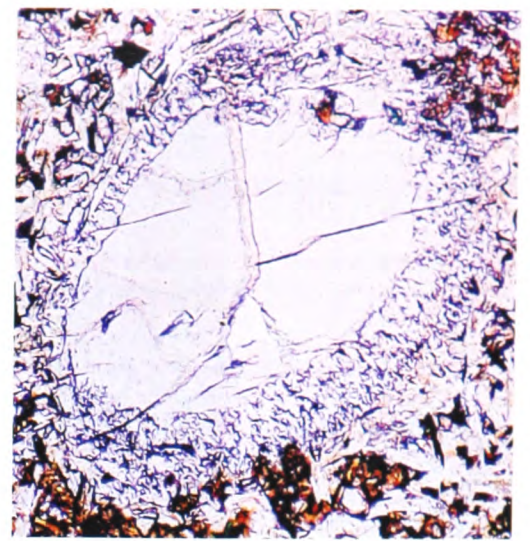
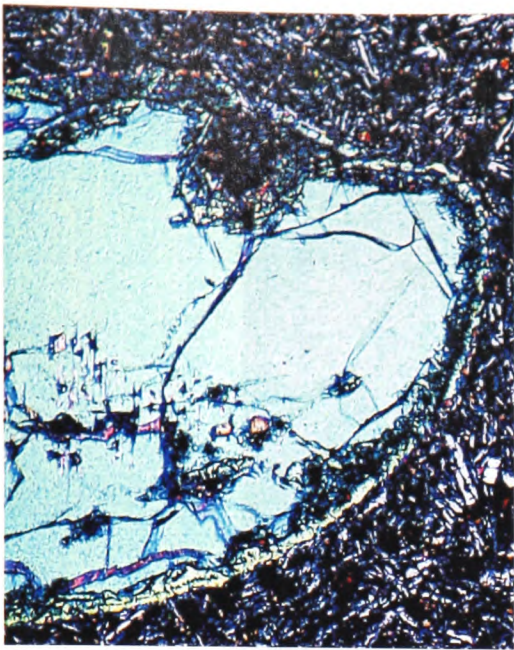


Plate 4.3g Clinopyroxene with a 0.2 mm 'spongy' rim which is optically continuous with the core: see the example in Plate 4.4a. This is interpreted as a partial melting texture (see the text for details). Field of view 1.4mm.

Plate 4.3f A clinopyroxene megacryst from sample AJS210 in XPL and PPL. Note that the rim, optically discontinuous from the core, is separated from it by an irregular zone of inclusions which includes altered olivine. Field of view is 2mm across.

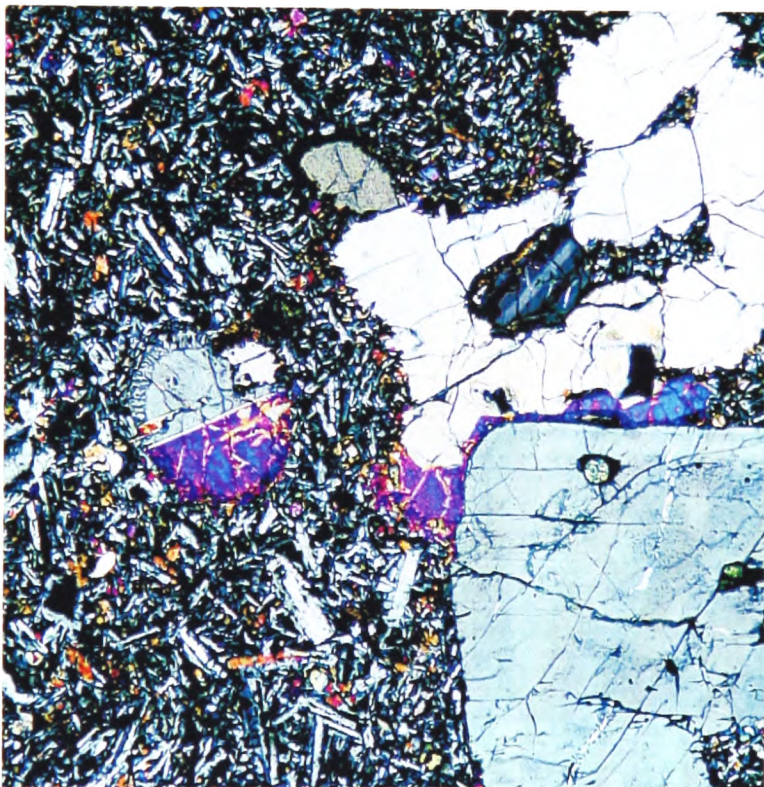


Plate 4.4a Photomicrographs (XPL and PPL) of an aggregate of plagioclase, orthopyroxene and clinopyroxene, as well as a megacryst of twinned clinopyroxene, from sample AJS81. Note that the clinopyroxene forms a narrow band between plagioclase and orthopyroxene, suggesting that it could be a reaction product. Field of view is 5mm.

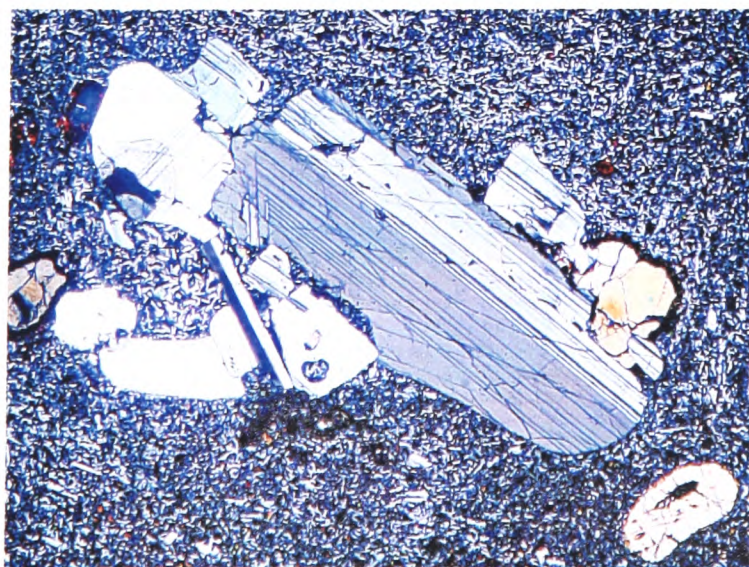


Figure 4.4b Aggregate consisting predominantly of plagioclase with minor orthopyroxene. Note that the latter are indistinguishable from individual megacrysts of the same species. From sample AJS92A. Field of view is 10mm.

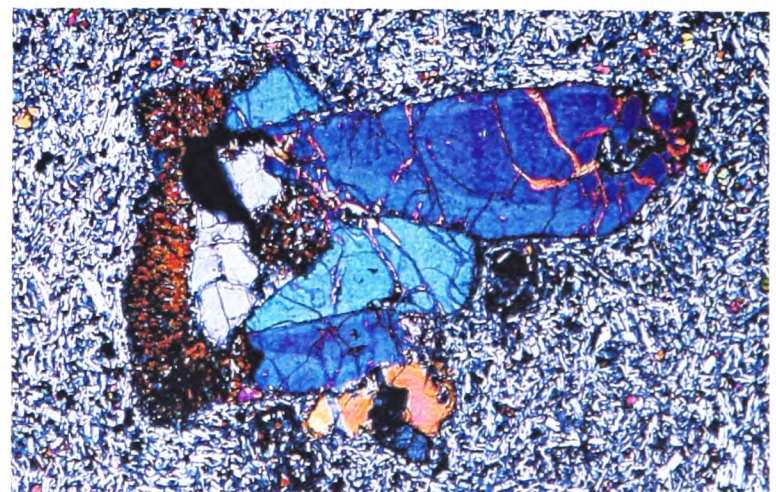


Plate 4.4c Aggregate of clinopyroxene and orthopyroxene in sample AJS210. The two mineral types can be distinguished by the rim around the orthopyroxene as well as the difference in birefringence. Field of view 6mm.

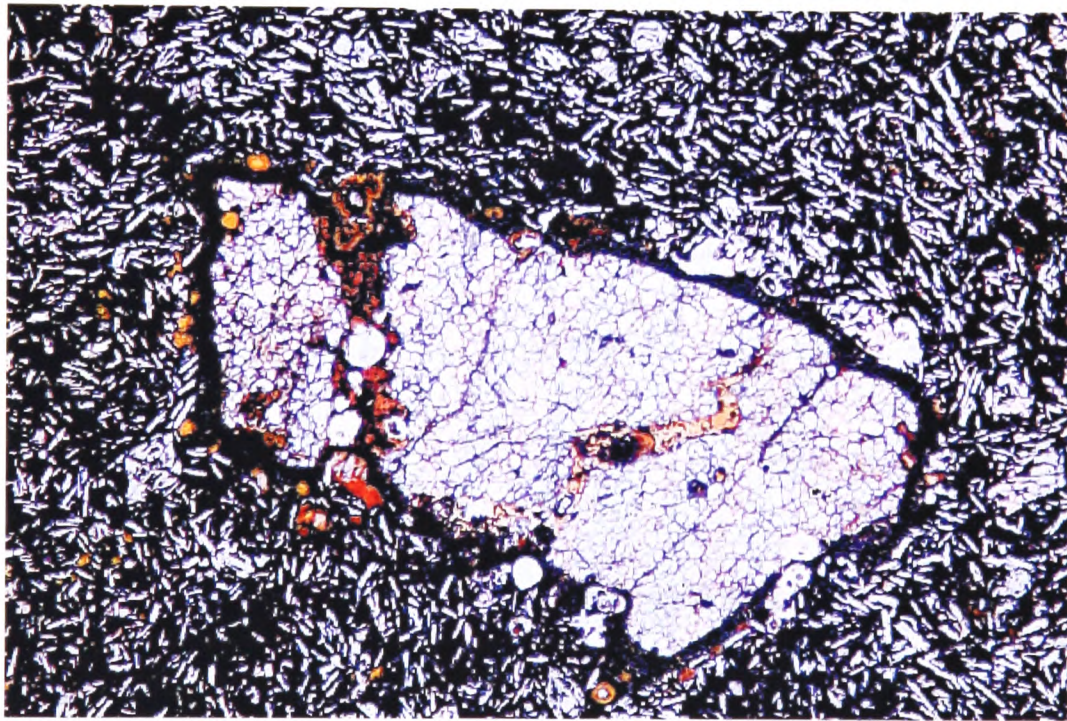


Plate 4.5 Sandstone xenolith 7mm across which was found in sample AJSW2. It is the only xenolith of crustal origin found during fieldwork and subsequent rock cutting, and consists of grains of silica within the size range 0.05-0.15mm. A narrow (0.15mm) margin consists of an intergrowth of moderately birefringent clinopyroxene(?) and a brown alteration product.

Sample	Plag vol. %	Opx vol. %	Cpx vol. %	Total	Relative Proportions
1		1.8	0.15	1.95	0:92:8
6		0.1		0.1	0:100:0
8	0.28	0.01		0.29	97:3:0
54M	2.8			2.8	100:0:0
64		0.08		0.08	0:100:0
73	0.014	0.04		0.054	26:74:0
78	0.005			0.005	100:0:0
79	0.2			0.2	100:0:0
80*	6.0	0.89	0.21	7.11	84:13:3
81*	7.2	2.2	0.37	9.77	73:23:4
89	0.76			0.76	100:0:0
92*	11	0.7	0.6	12.3	89:6:5
97	0.4	0.02		0.42	95:5:0
98	11	0.1		11.1	99:1:0
120*	1.7	1.1	0.44	3.24	52:35:13
195	0.08			0.08	100:0:0
198	1.4	0.44	0.04	1.88	74:23:3
199*	2.7	0.1		2.8	96:4:0
203	0.7			0.7	100:0:0
204*		4.3	1.27	5.57	77:0:23
207	1.3			1.3	100:0:0
210*	3.5	1.6	0.31	5.41	65:30:5
211	0.9			0.9	100:0:0
255	0.6			0.6	100:0:0

Table 4.2 Modal analyses of the megacryst-bearing samples. Numbers are given as percent by volume, and in nearly all cases are based on one thin section only: this probably results in an overestimate of the total amounts of megacrysts in the samples for the reasons given in the text. Relative proportions are given in the final column and are plotted in Figure 4.3.

* indicates the presence of crystal aggregates, which are included in the modal analyses.

End-members					
	Mg9/1	Mg9/2	Mg4.5/1	Mg4.5/2	Mg4.5/3
SiO ₂	50.00	51.00	48.00	50.00	51.50
TiO ₂	1.70	1.70	3.20	3.00	2.50
Al ₂ O ₃	14.80	14.40	16.70	16.30	15.90
Fe ₂ O ₃	11.20	10.90	14.10	13.40	12.50
MnO	0.16	0.16	0.14	0.14	0.14
MgO	9.00	9.00	4.50	4.50	4.50
CaO	8.50	8.30	7.00	6.30	8.20
Na ₂ O	3.40	3.30	4.00	4.00	3.40
K ₂ O	0.90	0.90	1.70	1.70	1.00
P ₂ O ₅	0.34	0.34	0.66	0.66	0.36
	opx	cpx	olivine		plagioclase
SiO ₂	53.52	50.15	38.38		56.97
TiO ₂	0.25	0.94			
Al ₂ O ₃	3.06	6.12			26.79
Fe ₂ O ₃	13.72	9.11	19.56		0.26
MnO	0.23	0.25	0.24		
MgO	27.43	15.37	41.61		
CaO	1.65	17.25	0.21		9.77
Na ₂ O	0.14	0.77			5.81
K ₂ O					0.40
P ₂ O ₅					
mg#	79	77	81	An	48

Table 4.4 Compositions of magma end-members used for petrogenetic modelling in this chapter: the method for determining them is discussed in the text. Also provided are compositions of the phases used in the modelling calculations. The orthopyroxene, clinopyroxene and plagioclase analyses are average megacryst compositions, while olivine (which is not observed as a megacryst phase) is a phenocryst composition from the olivine-phyric group.

mg#=100(Mg/Mg+Fe) where all iron is Fe(ii). An refers to anorthite content.

Phases:	C+O+P Mg9/1	C+O+P+Ol	C+P+Ol	C+O+P Mg9/1	C+O+P+Ol	C+P+Ol	C+O+P Mg9/1	C+O+P+Ol	C+P+Ol	Target compositions	
start comp.	mg4.5/1	mg4.5/1	mg4.5/1	mg4.5/2	mg4.5/2	mg4.5/2	mg4.5/3	mg4.5/3	mg4.5/3	mg4.5/1	mg4.5/2
target comp.											
SiO ₂	47.37	48.06	49.45	48.51	NO	49.78	49.30	NO	50.56	48.00	mg4.5/2
TiO ₂	2.70	2.83	2.84	2.37	RESULT	2.67	2.04	RESULT	2.43	3.20	50.00
Al ₂ O ₃	17.17	16.70	16.09	17.49		16.54	17.11		16.04	16.70	3.00
Fe ₂ O ₃ T	13.99	14.27	14.35	13.00		13.62	11.44		12.25	14.10	16.30
MnO	0.16	0.17	0.17	0.14		0.16	0.14		0.17	0.14	13.40
MgO	5.00	4.50	4.50	5.68		4.52	5.97		4.43	4.50	0.14
CaO	7.13	7.07	6.39	6.55		6.55	8.30		8.51	7.00	4.50
Na ₂ O	4.36	4.23	4.04	4.34		4.10	4.10		3.84	4.00	6.30
K ₂ O	1.51	1.55	1.54	1.37		1.46	1.15		1.27	1.70	4.00
P ₂ O ₅	0.61	0.63	0.63	0.54		0.59	0.44		0.51	1.70	1.70
										0.66	0.66
Σr ²	1.31	0.25	3.07	5.9		0.4	10		1.4		
F	0.56	0.54	0.54	0.63		0.57	0.78		0.67		
Plag	32	37	41	23		37	10		40		
Cpx	38	36	40	53		43	43		26		
Opx	30	19		24			47				
Ol		9	19			20			34		
Initial Ni(ppm)											
200	58	46	46	77		46	84		41		
150	43	34	34	58		35	63		31		
Initial Sr (ppm)											
450	581	563	539	586		550	548		512		
350	452	437	420	456		423	426		398		

Table 4.5 Results of fractional crystallisation modelling starting from the two primitive end-member magma compositions Mg9/1 and Mg9/2 given in Table 4.4 and shown graphically in Figure 4.5. The least-squares mixing option from the DARTS program (see section 3.4.1) was used. Each column gives the inputted extract phases (C=clinopyroxene, O=orthopyroxene, P=plagioclase and Ol=olivine: compositions given in Table 4.4), start and target megma end-members, together with the calculated residual liquid composition, degree of fractionation (F: fraction of melt remaining) and phase proportions. Σr² is the calculated quality of fit, being the sum of squares of the difference between the target composition and the calculated evolved liquid composition:a good fit lies between 0 and 1. NO RESULT denotes runs where the best fit solution involved addition rather than subtraction of one of the phases in the assemblage, and are thus unreasonable.

Phases: start comp.	C+O+P Mg9/2	C+O+P+Ol	C+P+Ol	C+O+P Mg9/2	C+O+P+Ol	C+P+Ol	C+O+P Mg9/2	C+O+P+Ol	C+P+Ol	Target compositions		
target comp.	mg4.5/1	mg4.5/1	mg4.5/1	mg4.5/2	mg4.5/2	mg4.5/2	mg4.5/3	mg4.5/3	mg4.5/3	mg4.5/1	mg4.5/2	mg4.5/3
SiO ₂	48.42	NO	51.17	51.37	50.05	51.37	49.91	51.38	51.92	48.00	50.00	51.50
TiO ₂	2.99	RESULT	2.82	2.72	2.77	2.72	2.31	2.52	2.50	3.20	3.00	2.50
Al ₂ O ₃	16.37		15.37	15.80	16.33	15.80	16.54	15.60	15.39	16.70	16.30	15.90
Fe ₂ O ₃ T	14.26		13.90	13.43	13.54	13.43	11.83	12.20	12.16	14.10	13.40	12.50
MnO	0.16		0.17	0.16	0.16	0.16	0.15	0.17	0.17	0.14	0.14	0.14
MgO	4.24		4.83	4.65	4.50	4.65	5.30	4.42	4.48	4.50	4.50	4.50
CaO	7.00		5.71	5.81	6.35	5.81	8.14	8.06	7.84	7.00	6.30	8.20
Na ₂ O	4.25		3.87	3.95	4.13	3.95	4.04	3.78	3.71	4.00	4.00	3.40
K ₂ O	1.65		1.54	1.50	1.54	1.50	1.28	1.33	1.32	1.70	1.70	1.00
P ₂ O ₅	0.67		0.63	0.61	0.62	0.61	0.50	0.54	0.53	0.66	0.66	0.36
Σr ²	0.48		14		0.12	2.5	4.6	0.51	0.91			
F	0.5		0.54	0.56	0.54	0.56	0.68	0.63	0.64			
Plag	35		40	37	34	37	25	39	40			
Cpx	33		43	45	40	45	32	27	30			
Opx	32				18		43	10				
Ol			17	18	8			24	30			
Initial Ni(ppm)												
200	45		51	50	48	50	65	41	41			
150	34		38	37	36	37	48	31	31			
Initial Sr (ppm)												
450	592		544	553	580	553	558	526	520			
350	460		423	430	450	430	434	409	404			

Table 4.5(cont.)

Run number:	1	2	3	4	5			6
Parent:	Mg9/1				Mg9/2			
Target:	Mg4.5/1	Mg4.5/1	Mg4.5/2	Mg4.5/2	Mg4.5/3	Mg4.5/3	Mg4.5/1	Mg4.5/2
Assimilant:	Inter	Felsic	Inter	Felsic	Inter	Inter	Felsic	Inter
Plagioclase	36.92	36.28	38.00	36.82	41.48		NO	33.80
Clinopyroxene	29.95	32.26	28.60	33.67	11.64	RESULT	RESULT	36.61
Orthopyroxene	33.14	31.46	33.40	29.51	46.88			29.59
Residual liquid:								
SiO ₂	47.76	48.03	49.33	50.02	51.25			50.03
TiO ₂	2.64	2.77	2.25	2.55	2.27			2.72
Al ₂ O ₃	17.16	16.69	17.46	16.38	15.69			16.32
Fe ₂ O ₃ T	14.31	14.23	13.68	13.56	12.16			13.51
MnO	0.18	0.17	0.20	0.18	0.19			0.17
MgO	4.82	4.49	5.29	4.52	4.47			4.86
CaO	7.19	7.05	6.67	6.37	8.07			6.45
Na ₂ O	3.96	4.19	3.49	3.96	3.61			3.97
K ₂ O	1.41	1.72	1.15	1.86	1.78			1.43
P ₂ O ₅	0.58	0.64	0.49	0.60	0.52			0.58
Σr ²	0.86	0.24	3.80	0.28	0.97			0.87
r	0.20	0.09	0.58	0.24	0.44			0.15
F	0.61	0.56	0.80	0.63	0.77			0.61
								0.11
								0.09
								0.56
								0.86
								0.25
								0.69

Table 4.7 Results of least-squares mixing calculations to model the petrogenesis of evolved end-members Mg4.5/1, /2 and /3 by assimilation-fractional crystallisation from 'parental' end-members Mg9/1 and /2. Assimilants are averages of intermediate metasedimentary and felsic granodioritic lower-crustal xenoliths analysed by Rudnick and Taylor (1987): see Table 4.6 for analyses and see the text for discussion. Phase compositions are averages of analysed megacrysts: data provided in Table 4.4. Analyses of residual liquid compositions are provided here: Σr² is a measure of the quality of fit to the actual target composition, r = mass of assimilant/mass of crystals, and F is the fraction of melt remaining. NO RESULT denotes a geologically unreasonable result was given, e.g. negative values of r for Mg9/2 - Mg4.5/1. The three best fits (in bold) all involve the felsic contaminant and show good consistency of phase proportions.

r	0.20	0.20	0.20	0.15	0.15	0.15	0.10	0.10	0.10		
F	0.65	0.60	0.55	0.65	0.60	0.55	0.65	0.60	0.55	mg4.5/3	AJS195
SiO ₂	51.73	51.91	52.11	51.09	51.11	51.14	50.52	50.41	50.27	51.50	51.88
TiO ₂	2.44	2.62	2.82	2.43	2.61	2.81	2.42	2.60	2.80	2.50	1.98
Al ₂ O ₃	15.80	16.13	16.52	15.67	15.98	16.33	15.56	15.84	16.17	15.90	15.86
Fe ₂ O ₃ T	12.36	12.71	13.12	12.49	12.87	13.31	12.60	13.00	13.48	12.50	12.37
MnO	0.15	0.15	0.14	0.15	0.15	0.15	0.16	0.16	0.16	0.14	0.14
MgO	4.80	3.80	2.61	5.29	4.41	3.36	5.73	4.95	4.03	4.50	4.83
CaO	6.53	6.10	5.60	6.85	6.50	6.09	7.13	6.85	6.52	8.20	8.45
Na ₂ O	3.84	3.96	4.12	3.82	3.95	4.10	3.81	3.93	4.08	3.40	3.40
K ₂ O	1.82	2.04	2.31	1.67	1.86	2.07	1.54	1.69	1.87	1.00	1.03
P ₂ O ₅	0.54	0.58	0.64	0.53	0.58	0.63	0.53	0.57	0.63	0.36	0.36
Rb	40	47	55	33	38	44	26	30	34		
Ba	298	331	370	274	302	335	252	276	303		
Nb	23	25	27	23	25	27	23	25	27		
Sr	414	426	440	413	425	440	413	426	440		
Zr	205	223	245	199	217	237	195	211	230		
Y	31	33	36	30	32	34	29	31	33		
Rb/Nb	1.7	1.9	2.0	1.4	1.5	1.6	1.1	1.2	1.3		
Zr/Nb	7.9	7.9	8.0	7.6	7.7	7.7	7.5	7.4	7.5		
Ba/Rb	7.5	7.0	6.7	8.3	7.9	7.6	9.7	9.2	8.9		

Table 4.8 Compositions of residual liquids generated by forward AFC modelling from 'parental' end-member Mg9/2 for different values of F (fraction of melt remaining) and r.(mass of assimilant/mass of crystals). In each case the phase proportions are 36 % plagioclase, 32% clinopyroxene and 32% orthopyroxene. End-member and phase compositions are provided in Table 4.4 and the shale composition is provided in Table 4.6. The initial trace element ratios assigned to the parent composition are Rb/Nb=0.7, Zr/Nb=7.5 and Ba/Rb=15. The closest approximation to end-member 4.5/3 is emboldened, and is graphically illustrated in Figure 4.11. Compositions of Mg4.5/3 and AJS195, a lava composition from the low-MgO end of the high-silica group are also shown.

Density (at STP)		Thermal expansion	Compressibility (volume)		Density at 10 kbar, 1000°C
<u>Plagioclase</u>		Vol. increase (%)	Vol decrease (%)		ρ (kg/m ³)
An46	2690*	An44	An48	1.04	An~46
Ab	2620	Ab99	Ab100	1.8	Ab
<u>Pyroxene</u>					
Augite	3190	Augite	Augite	1.02	Augite
Diopside	3220*	Diopside	Diopside	1.07	Diopside
En85	3330	Enstatite80	Enstatite88	1.01	Enstatite

Notes

Densities at STP taken from Deer *et al.* . (1992).

Thermal expansion coefficients from Skinner (1966) and Compressibility from Birch (1966).

a Volume % increase of 4.88 at 1200°C also shown

b Taken from Frisillo and Buljan (1972) in the absence of data in Skinner

* Estimates of density assuming linear composition-density relationship between end-members

Table 4.9 Calculation of the densities of plagioclase and pyroxene at 1000°C and 10 kbar in order to assess relative sinking velocities of these phases, observed as megacrysts in the lavas under study, at lower crustal conditions. Unfortunately, the tables of thermal expansion and compressibility do not always provide data for exactly the same composition of any phase, but they are unlikely to differ by a significant amount. The calculations clearly show that the effect of the temperature increase outweighs that of the pressure increase, resulting in slightly lower densities than are observed at STP.

run	1	2	3	4	Target
Assimilant:	none	inter	felsic	shale	AJSW2
olivine	26.3	26.9	25.9	25.8	
plagioclase	43.1	44.8	44.1	44.3	
clinopyroxene	30.6	28.3	30.0	29.9	
F	0.66	0.68	0.67	0.67	
r	-	0.07	0.04	0.04	
SiO ₂	51.52	51.62	51.79	51.79	51.68
TiO ₂	2.43	2.40	2.41	2.42	2.43
Al ₂ O ₃	14.91	14.93	14.80	14.79	14.83
Fe ₂ O ₃ T	12.38	12.42	12.35	12.34	12.26
MnO	0.17	0.18	0.17	0.17	0.13
MgO	5.55	5.57	5.58	5.58	5.56
CaO	7.65	7.63	7.53	7.52	7.52
Na ₂ O	3.59	3.50	3.54	3.55	3.30
K ₂ O	1.28	1.25	1.32	1.33	1.73
P ₂ O ₅	0.52	0.51	0.51	0.51	0.56
Σr^2	0.36	0.33	0.25	0.25	
Ba/Rb	14.0	14.8	13.5	12.1	
Zr/Nb	8.3	8.5	8.4	8.4	
Rb/Nb	0.68	0.67	0.78	0.82	

Table 4.12 Results of least-squares mixing calculations for the modelling of sample AJSW2 (~5.5% MgO) by fractional crystallisation (run 1) and AFC (runs 2-4)). The Buckland 'parental' end-member Mg9/2 is used (Table 4.4), together with phase compositions from Buckland lavas (Table 4.4). The program calculates best-fitting phase proportions, F (fraction of melt remaining) and r (mass of assimilant/mass of crystals). Starting ratios of Ba/Rb, Zr/Nb and Rb/Nb are 15, 8.3 and 0.7 respectively. Assimilants are the intermediate, felsic and shale compositions of Table 4.6. Attempts which used the other Buckland starting composition Mg9/1 or involved orthopyroxene gave poor fits ($\Sigma r^2 \gg 1$) or negative phase proportions.

Chapter 5: Petrology and Petrogenesis of the 12+ group

5.1 AIMS AND INTRODUCTION

5.1.1 Aims

The five samples discussed here form a group which is geochemically distinct from the less-magnesian 9-12 group, as discussed in section 2.2.5. The aim of the chapter is to describe the petrology of the samples and discuss models for their petrogenesis, including the question of whether they are related to basanites from the 9-12 group.

5.1.2 Classification

All five samples plot in the basanite field of the TAS classification of Le Maitre (1989), although samples AJS 20/21 lie very close to the basanite-nephelinite boundary (see Figure 5.1).

5.1.3 Geographical Location

The five samples come from three localities in the Buckland province: AJS 27 from Mt. Eddystone, AJS 20/21 from Mt. Ogilvie and AJS R1/R2 from Rewan (see Figure 5.2). The first two localities lie within 8 km of each other while the third lies 60 km to the NE. Note that all the localities lie between latitudes 25° and 25°15'S in common with the basanites from the 9-12 group described in Chapter 3. All localities are volcanic plugs which have been eroded to form steep-sided hills (Plate 1.2).

5.1.4 Age constraints

None of the sample set has been dated, and there are no cross-cutting relationships with dated lavas at any of the three localities that might indicate whether they pre- or post-date the eruption of the main Buckland lava sequences. It was argued in Chapter 3 that the basanites from the 9-12 group are generally older than the main sequences but overlap with the earliest basalts, e.g. at the base of the Battleship Spur sequence.

5.2 PETROGRAPHY

5.2.1 Lavas

The samples are all olivine phyric, and modal analyses for the samples are given in Table 5.1 below. Olivine crystals are classified as megacrysts (up to 3.1% of rock volume) and phenocrysts (up to 16%). Distinction is made on the basis of texture: megacrysts have corroded, strongly zoned rims, commonly display kink-banding, and are up to 5mm long, while phenocrysts are euhedral and smaller (< 1.5mm). Plate 5.1 shows an example of each. The groundmass in all samples is composed of olivine,

clinopyroxene, nepheline and Fe-Ti oxide in the approximate proportions 20:35:35:10; crystals rarely exceed 0.2mm in length. Plagioclase appears to be absent from all of the samples.

Sample	Olivine		Groundmass
	phenocrysts	megacrysts	
20	4.9	1.6	93.5
21	5.7	2.2	92.1
27	10.2	3.1	86.7
R1	16	1.4	82.6

Table 5.1 Modal proportions (volume %) of the 12+ group, from 1000 point averages.

5.2.2 Mineral chemistry

Microprobe analyses (Appendix C) show that megacryst compositions lie within the range Fo₈₆-Fo₉₁ and phenocrysts in the ranges Fo₇₈-Fo₈₂ and Fo₈₅-Fo₈₇. The cause of the bimodal distribution of phenocryst compositions is uncertain, but is perhaps an artefact of the small size of the sample (32 crystals). Megacrysts have higher NiO/CaO ratios (greater than 3) than phenocrysts (less than 2). A plot of NiO/CaO vs. Fo content of the olivines (Figure 5.3) shows that NiO/CaO ratio spans a much greater range in the megacrysts (between 13 and 3) than in the phenocrysts, and that megacrysts define a trend from high-Fo and high-NiO/CaO towards the composition of the tightly grouped phenocrysts at ~Fo₈₅. This variation could be the result of re-equilibration of megacrysts with their host magma during transport.

Analyses of two nepheline crystals from sample AJS 20 are given in Appendix C.

5.2.3 Xenoliths

Xenoliths of spinel lherzolite, as well as aggregates of olivine ± clinopyroxene ± orthopyroxene ± spinel occur in the samples, and range in size from 1mm to 5cm. These are described in more detail in section 6.2. It is to be noted that the olivine megacrysts referred to above overlap compositionally with the olivine crystals found in the xenoliths. Furthermore, the occurrence of kink-bands in the megacrysts indicates that they have undergone solid-state deformation, and it is therefore likely that the megacrysts are derived from disaggregated lherzolite xenoliths.

5.3 GEOCHEMISTRY

In this section the geochemical characteristics of the 12+ lavas will be described, and compared with the 9-12 group (see Chapter 3). It is clear that there is some *intra*-locality variation since sample

AJS 21 is not identical to 20, nor R2 to R1: this will be discussed in section 5.3.4. All the geochemical data discussed in this section are provided in Table 5.2.

5.3.1 Major and trace element characteristics

Major elements are plotted against MgO in Figure 5.4, in which the basanites from the 9-12 group are also shown. All of the lavas in the group have high mg-numbers (71-73) consistent with being in equilibrium with olivine from mantle lherzolite (mafic liquids in equilibrium with mantle olivine of composition Fo₈₈-Fo₉₂ have mg-numbers greater than 68: Irving and Green, 1976; Frey *et al.*, 1978).

The samples are highly silica-undersaturated, containing more than 17% normative nepheline (Figure 5.5), while AJS20 and 21 also contain ~7% normative leucite.

Trace elements are plotted against MgO in Figure 5.6. Concentrations of Ni and Cr are high (300-400 ppm and 320-450 ppm respectively), consistent with the high MgO content of the samples.

Concentrations of incompatible elements show generally little variation within the group, and no consistent variation with MgO: for example, abundances of Nb, Zr and Th all rise with decreasing MgO content, while other elements show no common pattern.

5.3.2 Isotopic characteristics

Within this study, all five samples were analysed for ⁸⁷Sr/⁸⁶Sr, and AJS 27 additionally for ¹⁴³Nd/¹⁴⁴Nd (see Table 5.1). Other data come from Ewart *et al.* (1988) who analysed a sample from Rewan (whence AJS R1 and R2 were taken) for Sr, Nd and Pb isotopes.

It is fair to assume that the samples which have not been analysed for Nd isotopes (AJS20, 21, R1 and R2) or Pb isotopes (AJS20, 21, 27, R1, R2) have similar values to those which have been analysed. The lavas in the 12+ group are very similar in terms of major and trace element geochemistry, while their ⁸⁷Sr/⁸⁶Sr ratios are all similar to the Rewan composition analysed by Ewart *et al.* (1988).

Data from AJS27 and the Rewan sample are plotted in Figure 5.7, where generalised composition fields of mafic lavas from eastern Australia are also shown (from Ewart *et al.*, 1988). The two samples clearly have a very depleted Sr-Nd isotopic signature, which overlaps with MORB and lavas from Tasmania. Pb-isotopic ratios of the Rewan sample are also extreme (Figure 5.7b), overlapping only with the field of Tasmanian lavas. The group thus appear to have an isotopic composition which is unique in mainland east Australia.

5.3.3 Comparison with the 9-12 group

Figures 5.4 and 5.6 allow geochemical comparison to be made between the 12+ group and the basanites from the 9-12 group. There is clearly some overlap of major element abundances, but average

concentrations of SiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, MnO , K_2O and P_2O_5 are lower in the 12+ group than in the 9-12 group. Average CaO and, by definition, MgO contents are higher in the 12+ group, while concentrations of TiO_2 and Na_2O overlap completely.

Further differences between the two groups are evident in terms of trace element abundances. Samples from the 12+ group have higher concentrations of Ni , Cr , Cu than those from the 9-12 group, and lower concentrations of Zn , Rb , Ba , Zr , and Y (amounts which are similar, incidentally, to *basalts* from the 9-12 group). There is overlap in the abundances of the other trace elements, although the 12+ group samples show much less variation. The similarity of spidergrams for the two groups (Figure 5.8b) indicates that they have comparable ratios of incompatible trace elements.

Isotopic comparison is made using Figure 5.7 and Figure 2.10, from which it is clear that lavas from the 12+ group have a more 'depleted' signature (lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{143}\text{Nd}/^{144}\text{Nd}$) than the 9-12 group. There is insufficient data to compare the 12+ group with the 9-12 group using isotopes of lead (none of the 9-12 group has been analysed for these isotopes), although Ewart *et al.* (1988) provide data for a basanite from the Battleship Spur section which contains ~8% MgO and is geochemically similar to examples from the 9-12 group. It has a significantly different Pb isotopic signature to the 12+ group ($^{206}\text{Pb}/^{204}\text{Pb}=18.491$; $^{207}\text{Pb}/^{204}\text{Pb}=15.488$; $^{208}\text{Pb}/^{204}\text{Pb}=38.195$), and lies at the low- $^{206}\text{Pb}/^{204}\text{Pb}$ end of the field of Central Queensland lavas in Figure 5.7b.

The low abundance of silica in the 12+ group suggests, following the arguments presented in Chapter 3, that they result from the melting of volatile-bearing lherzolite where $X^{\text{CO}_2} \geq 0.5$. The differences in major element geochemistry compared to the basanites from the 9-12 group are likely to result from a different bulk composition of the source rock, and potentially from differences in degree of melting, depth of melting and X^{CO_2} . Such material must reside in the asthenosphere owing to its significantly different isotopic composition compared to lithosphere-related melts in eastern Australia.

5.3.4 Intra-locality variation

It is clear that there is some geochemical variation between samples from the same locality, for example AJS R2/R1 differ in Na_2O content by 1%, and AJS 20/21 in SiO_2 by 0.5%. This probably reflects a combination of analytical error (see Appendix B) and chemical heterogeneity within the plug, and perhaps even different magma batches. The latter is hard to confirm since exposure did not allow detailed study of the plugs. However it is unlikely that small geochemical differences would be manifested in such a way as to be distinguishable in the field.

5.4 PETROGENESIS

5.4.1 Introduction

As described in Section 5.3.1, the samples from the 12+ group all have sufficiently high mg-numbers to have been in equilibrium with mantle olivine, and thus plausibly to be primary mantle melts.

Clearly, however, the presence of olivine phenocrysts indicates that some fractional crystallisation of this phase has taken place, but the high mg-numbers of the lavas suggest that it is unlikely to have occurred to any significant extent. The observed non-linear variation in major and most trace element with MgO in the samples indicates that they do not lie on a common fractionation trend or trends, e.g. extraction of olivine. Vectors demonstrating the effect of 10% fractional crystallisation of olivine are shown in Figure 5.4. They show additionally that the variation in SiO₂ and Fe₂O₃T within the group cannot be accounted for by olivine extraction, nor indeed that the group be the product of olivine accumulating in basanites from the 9-12 group. Although this latter suggestion might explain the lower SiO₂ and higher MgO contents of the 12+ group, it is not compatible with their higher CaO and lower ⁸⁷Sr/⁸⁶Sr. Furthermore, there is no correlation between phenocryst volume (Table 5.1) and MgO content of the samples, and indeed one of the least magnesian samples (AJSR1) contains the greatest volume of olivine phenocrysts. It is possible that phenocrysts were not removed from the crystallising magma (i.e. equilibrium crystallisation), or that a process of compensated crystal settling occurred (Cox and Bell, 1972; Cox *et al.*, 1979) whereby crystals which settled from a magma batch were replaced by others settling from above, resulting in little change in the bulk composition of the batch.

Crustal contamination, if it occurred at all in the group, must have been minor owing to the highly magnesian geochemistry and depleted isotopic signature of the lavas, and the similarity of their spidergrams to ocean island basalts (e.g. St. Helena: Figure 5.8b) which cannot have been modified by continental crust. Furthermore, the presence of mantle xenoliths up to 5cm long indicates that the residence time of ascending magmas in the crust must have been short (and thus the opportunity for contamination minimal).

These geochemical and isotopic criteria also argue against significant interaction of primary asthenospheric melts with the continental lithosphere, which is considered to be isotopically 'evolved' in eastern Australia (arc-modified lithosphere has ⁸⁷Sr/⁸⁶Sr > 0.704 and lithosphere-derived leucitites have ⁸⁷Sr/⁸⁶Sr > 0.7045 and ¹⁴³Nd/¹⁴⁴Nd < 0.5127: see Chapter 1), and indeed around the world (e.g. Gibson *et al.*, 1992). Interaction with subduction-modified lithosphere commonly results in enrichment of Ba and Sr, and depletion of Nb and Ti compared to asthenospheric liquids (e.g. Western US: Fitton *et al.*, 1991). These features are clearly not observed in the 12+ group where Nb has the highest normalised abundance of all the trace elements in the spidergrams (Figure 5.8a). Leucitites in eastern Australia are significantly enriched in Rb and Ba compared to Nb, features not shared by the 12+ group.

Consequently, the most likely model for the petrogenesis of the 12+ group is that they are near-primary melts from the asthenosphere which have undergone minor olivine fractionation during ascent. It is also clear that they could not represent parental liquids to basanites from the 9-12 group because of the significant difference in Sr-Nd isotopic compositions (and probably Pb-isotopes). The presence of mantle xenoliths in lavas from both groups rules out the possibility that the difference in isotopes could be attributed to the effects of crustal contamination.

The aim of the following section is to characterise the source material of the 12+ group.

5.4.2 Isotopic and trace element constraint on source composition

As noted previously, information about the chemistry of the source of a primitive lava can be obtained directly from its isotope values and ratios of highly-incompatible trace elements, since minimal fractionation of these ratios takes place during melting (Weaver, 1991). This requires that significant contamination by material in the lithosphere or crust (by compositions with significantly different isotopic values and trace element ratios to the primary magma) has not taken place. Significant contamination has already been ruled out for the 12+ group.

It has been shown in Figure 5.7 that the isotopic characteristics of the 12+ group are similar to those of lavas from Tasmania which have been interpreted as the result of mixing between depleted MORB-like and HIMU-type material (Ewart *et al.*, 1988; Lanyon *et al.*, 1993). Comparison of trace element and isotopic characteristics of the 12+ group with selected oceanic compositions is made in Figures 5.8b and 5.9. It can be seen that the group projects between MORB and HIMU-type oceanic basalts (St. Helena and Mangaia-Rurutu) in Sr-Nd-Pb isotope space. Furthermore, in terms of ratios of highly-incompatible trace elements (Table 5.3, below), the 12+ group are much more similar to lavas from Tasmania and HIMU-type oceanic basalts than to the other oceanic source components, for example in their low Zr/Nb. An important role for arc-related material, typified by Tonga-Kermadec lavas, which project close to the 12+ group in Sr-Nd-Pb isotope space, can be ruled out by the characteristically low-Nb contents of these lavas, resulting in significantly different trace element ratios to the 12+ group, e.g. $Zr/Nb > 15$, $Ba/Nb > 50$, $Rb/Nb > 2$ and $Ba/Th > 200$ (Ewart *et al.*, 1998).

	Zr/Nb	Ba/Nb	Ba/Th	Rb/Nb	K/Nb
12+ group	2.35-2.78	5.15-6.05	40-80	0.22-0.35	134-191
Tasmanian lavas	3.3-4.0	2.2-5.4	12-114	0.12-0.75	133-285
HIMU	3.2-5.0	4.9-6.9	49-77	0.35-0.38	77-179
Pacific N-MORB	>17	1.7-8.0	30-205		210-350
EMI	4.2-11.5	11.4-17.8	103-154	0.88-1.17	213-432
EMII	4.5-7.3	7.3-13.3	67-84	0.59-0.85	248-378

Table 5.3 Incompatible trace element ratios for the 12+ group (this study), lavas from Tasmania (Lanyon *et al.*, 1993), HIMU, EMI and EMII-type OIB (Rollinson, 1993) and Pacific N-MORB (Saunders *et al.*, 1988; Wilson, 1989).

Furthermore, although Sr-Nd-Pb data indicate that the 12+ group could be explained as a mixture of MORB+EMI/EMII, the trace element ratio data do not corroborate this hypothesis since the low Zr/Nb and K/Nb ratios could not be reproduced by such combinations.

These comparisons indicate that the 12+ group could be derived from a source containing a mixture of HIMU and MORB material which probably resides in the shallow asthenosphere since the isotopic composition of the inferred east Australian 'plume' (probably from the deep mantle) is quite different to the 12+ lavas (e.g. Figure 1.16). The same conclusion was reached by Ewart *et al.* (1988) for the sample from Rewan and lavas from Tasmania. However, the paucity of data means that this cannot be stated with confidence. Although there is certainly overlap in trace element ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ data between the 12+ group and HIMU-like lavas, a single analysis is insufficient to prove that the 12+ group really do have the required HIMU-like Pb-isotope signature.

5.4.3 Source of the HIMU composition

Tasmania

Lanyon *et al.* (1993) propose that the occurrence of HIMU-type lavas in Tasmania is attributable to the Balleny hotspot which currently resides beneath the Balleny Islands on the Antarctic Circle to the SE of Tasmania. Plate-tectonic reconstructions indicate that this plume resided beneath Tasmania when volcanism commenced there in the early-Tertiary. Lanyon *et al.* (op. cit.) propose that the intermediate composition of Tasmanian and Balleny Island lavas between MORB and HIMU means that the plume is HIMU in composition and mixed with MORB material in the shallow asthenosphere, or reflects the primary composition of the plume. Clearly this plume cannot be invoked to account for the isotopic characteristics of the 12+ group which lie 1800km to the north of Tasmania, and which did not even leave any trace in southeastern mainland Australia.

Western Europe

As discussed in Chapter 2, some basanites from western Europe (including the Massif Central) plot along a mixing line between an isotopically depleted asthenospheric component and an enriched lithospheric component. Wilson and Downes (1992) account for the composition of the asthenospheric end-member by the mixing of depleted mantle (i.e. MORB-source) and HIMU-type material. They propose that the latter could derive from recycled subducted slab material in the upper asthenosphere, or follow the lithosphere-derived model of Hawkesworth *et al.* (1990). Here, high-U/Pb, low-Rb/Sr melilititic partial melts build up at the base of the continental lithosphere, leading to the development there of HIMU isotopic characteristics. Mobilisation of this material during extension events could generate melilititic melts with HIMU characteristics, examples of which are observed in western European volcanic centres. Wilson and Downes (1992) note that a HIMU-like plume does not need to be invoked.

The latter model is appealing for explaining the composition of the 12+ group lavas. Although the lithospheric source model for the development of HIMU characteristics can be ruled out owing to the absence of melilititic rocks in eastern Australia, the model which involves mixing of recycled subducted slab in the shallow asthenosphere is plausible owing to the history of pre-Cainozoic subduction events in eastern Australia.

Development of HIMU characteristics

Chauvel *et al.* (1995) discuss the development of HIMU material in the western Pacific, noting that these characteristics in ocean island basalts can be modelled with ~25% recycled subducted slab material (isolated for ~2Ga) + 75% MORB. The distinctive HIMU-type isotopic characteristics build up in the slab as a consequence of pre-subduction hydrothermal activity which leaches Pb from the slab and re-precipitates it within sulphides on top of the oceanic crust. During subduction these sulphides are preferentially removed by dissolution, while fluids also remove Rb. Over a long period of time the high U/Pb and low Rb/Sr of the slab material results in unusually enriched Pb isotope ratios and depleted Sr isotope ratios. Chauvel *et al.* (op. cit.) note that the incorporation of <5% of pelagic sediment in the slab can prevent these HIMU characteristics from developing, owing to high concentrations of Pb, U and Th in these sediments. The EMI and EMII source components develop in this way, differing in composition according to the type of sediment which is incorporated (pelagic or terrigenous). The rarity of HIMU around the world can thus be explained by the fact that:

1. subducting slabs usually carry some sediment with them and thus develop EMI or EMII characteristics in the mantle.
2. slabs which are subducted without sediment are unlikely to remain isolated from EMI or EMII material in the convecting asthenosphere for the long periods of time (~2Ga) required to allow the isotopic characteristics to fully mature.

Discussion and conclusion

Wilson and Downes (1992) note that the Pb-isotope ratios of depleted component “A” (see Figure 2.10) in lavas from western Europe do not require the involvement of ‘extreme’ HIMU material, with $^{206}\text{Pb}/^{204}\text{Pb} > 20$ as typified by St. Helena, and propose that the required isotopic characteristics could have developed over 500 Ma from material subducted during the Variscan orogeny. It is reasonable that slab material of a similar age could reside beneath eastern Australia dating from one of the subduction episodes that occurred during the Palaeozoic. The apparent rarity of HIMU-type lavas in eastern Australia could be explained by:

- 1) Artefact of sampling, since the 12+ group represents only a tiny proportion of the total volume of lava in the Buckland province.

2) The fact that most oceanic crust carries some sediment with it during subduction and thus develops different, non-HIMU isotopic characteristics. The widespread distribution of lavas derived from the shallow asthenosphere throughout eastern Australia which have less depleted Sr-Nd and less radiogenic Pb than HIMU (e.g. basanites from the 9-12 group, most lava field basalts/basanites) confirms this suggestion. The average composition of the shallow asthenosphere beneath eastern Australia thus represents MORB + isotopically enriched components such as EMI- and EMII-like material.

5.5 CONCLUSION

The five basanite samples which form the 12+ group seem to be characterised by low $^{87}\text{Sr}/^{86}\text{Sr}$, high- $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and enrichment in Nb compared to other incompatible elements. They are apparently isotopically distinct from all other mainland provinces in eastern Australia, but overlap with the field of Tasmanian lavas. However, this clearly requires support from further Nd- and Pb-isotope analysis. Lavas from Rewan and Tasmania had previously (Ewart *et al.*, 1988) been interpreted as melts from the shallow asthenosphere with a significant HIMU-like component. This conclusion is confirmed in this chapter, and the source of the HIMU-component is thought to be recycled Palaeozoic subducted slab material.

It is proposed that the magmatic activity characterised by the 12+ group is older than the main phase of plume-related extrusion in Buckland. A similar age is unlikely because of the great volume of compositionally-different plume-derived material in the upper mantle at that time which would dilute any entrained HIMU-like asthenospheric component. A younger age can perhaps be ruled out because the HIMU-type material would be unlikely to remain isolated during the large-scale melting promoted by the plume but be homogenised with the rest of the asthenosphere. Additionally, the basanite activity typified by the 9-12 group appears to be older than/just overlap with the main phase of Buckland volcanism.

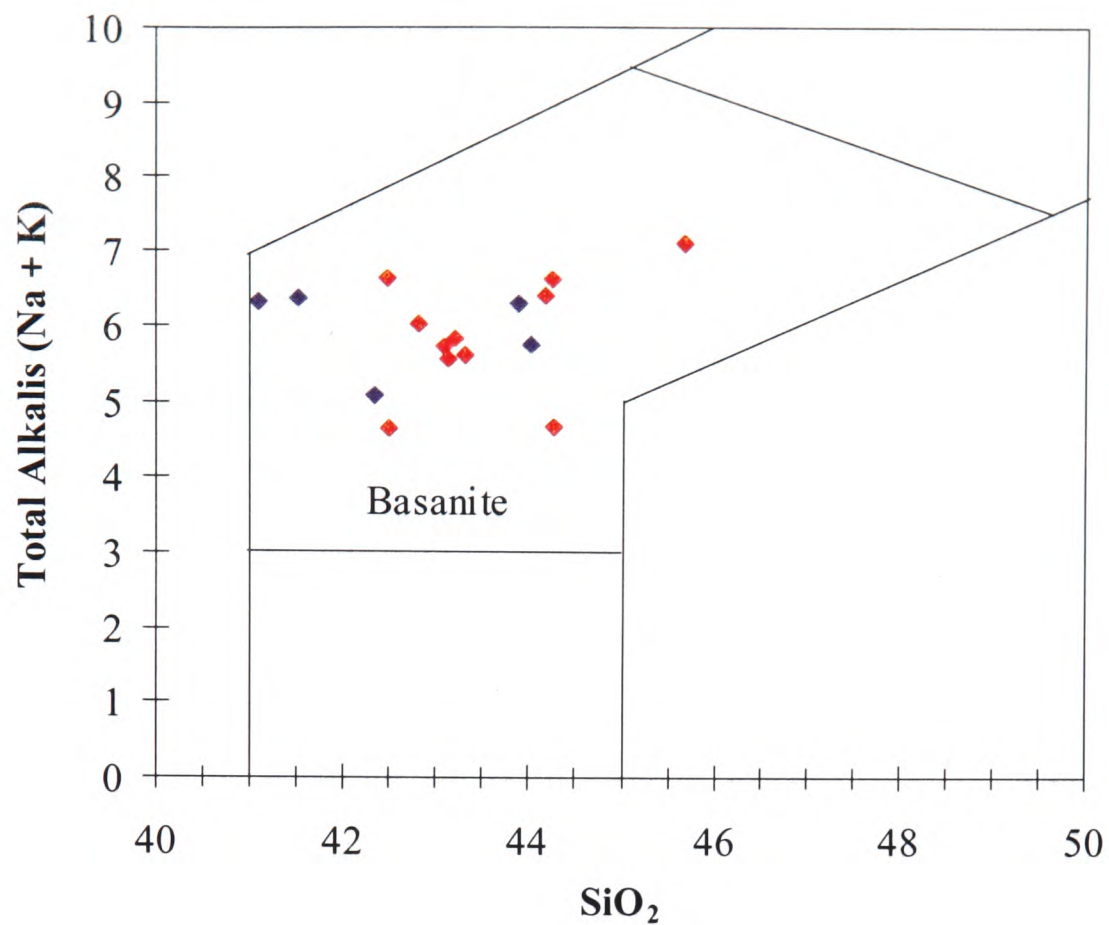


Figure 5.1 Classification of the 12+ group (blue spots) using the grid of Le Maitre (1989). Basanites from the 9-12 group are shown for comparison (red spots).

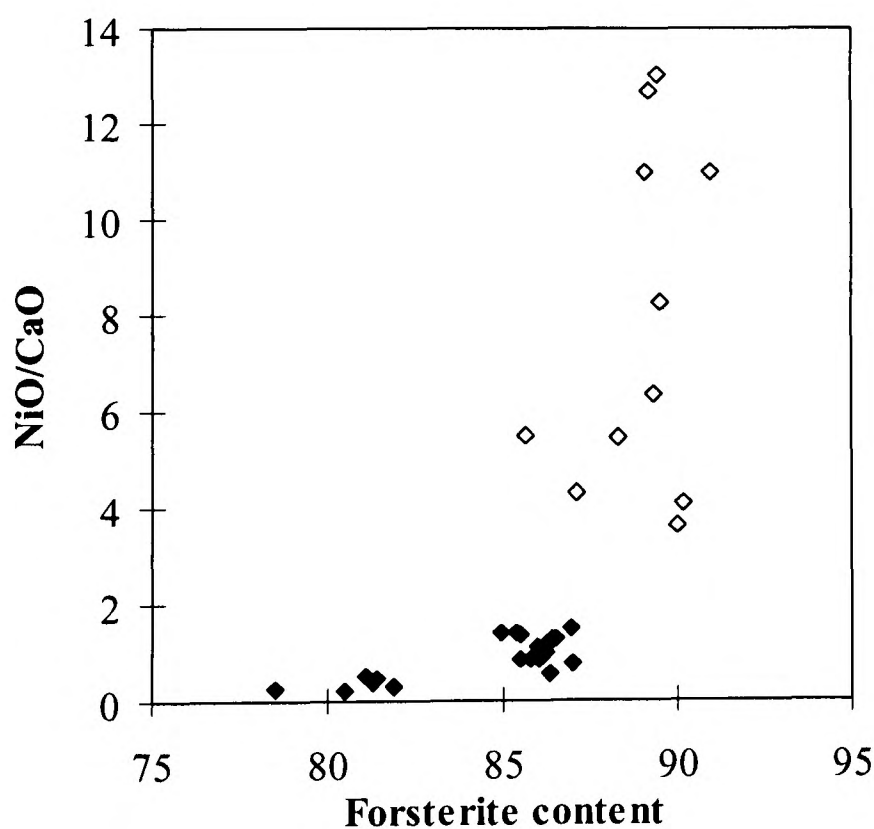


Figure 5.3 NiO/CaO vs. forsterite content of olivine crystals found in the 12+ group. They are petrographically identified as megacrysts (open spots) and phenocrysts (filled spots). The bimodal distribution of the phenocrysts could be a sampling effect.

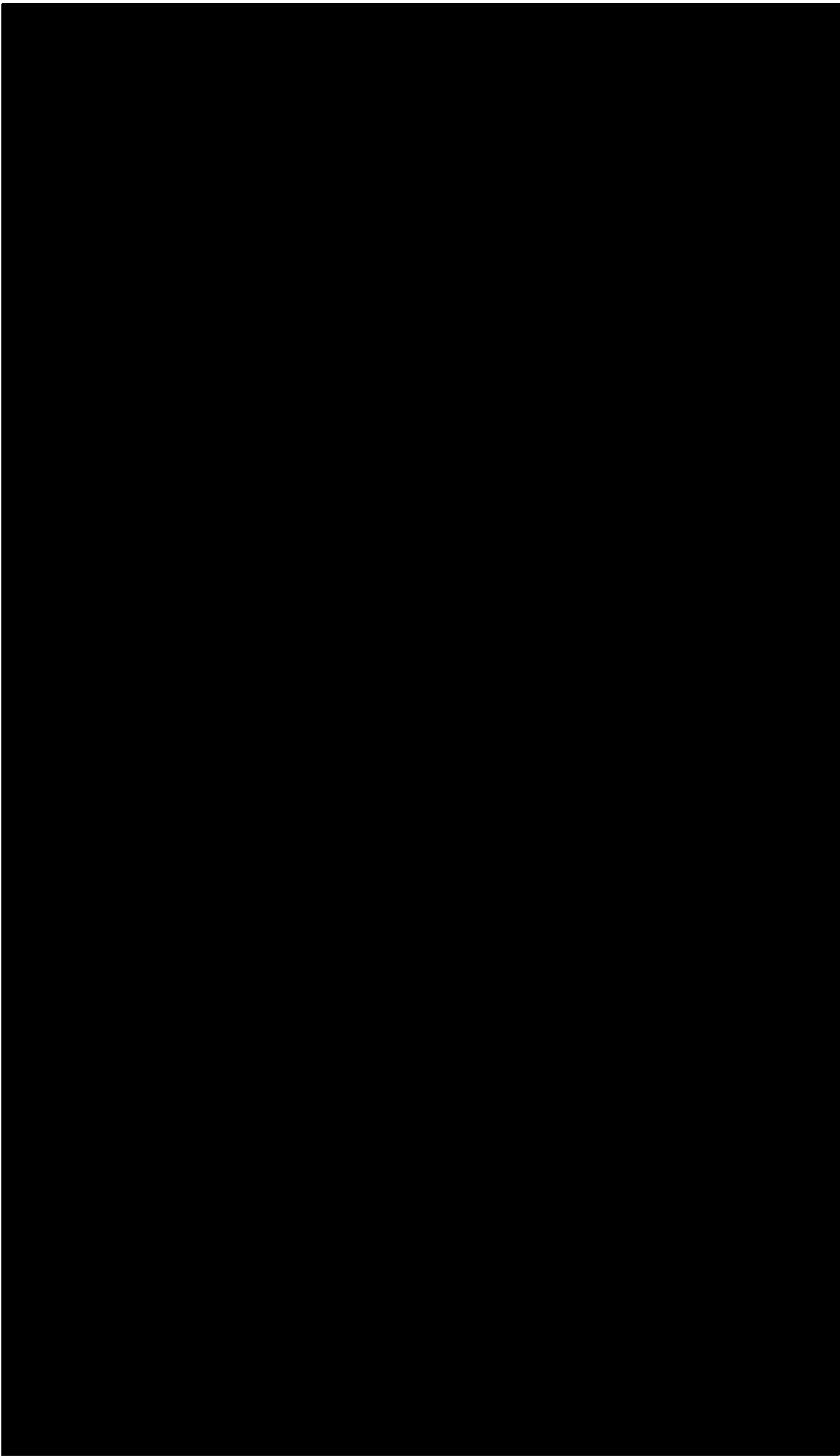


Figure 5.2 Map showing the location of samples from the 12+ group. Note that they crop out at the same latitude as basanites from the 9-12 group (Figure 3.2).

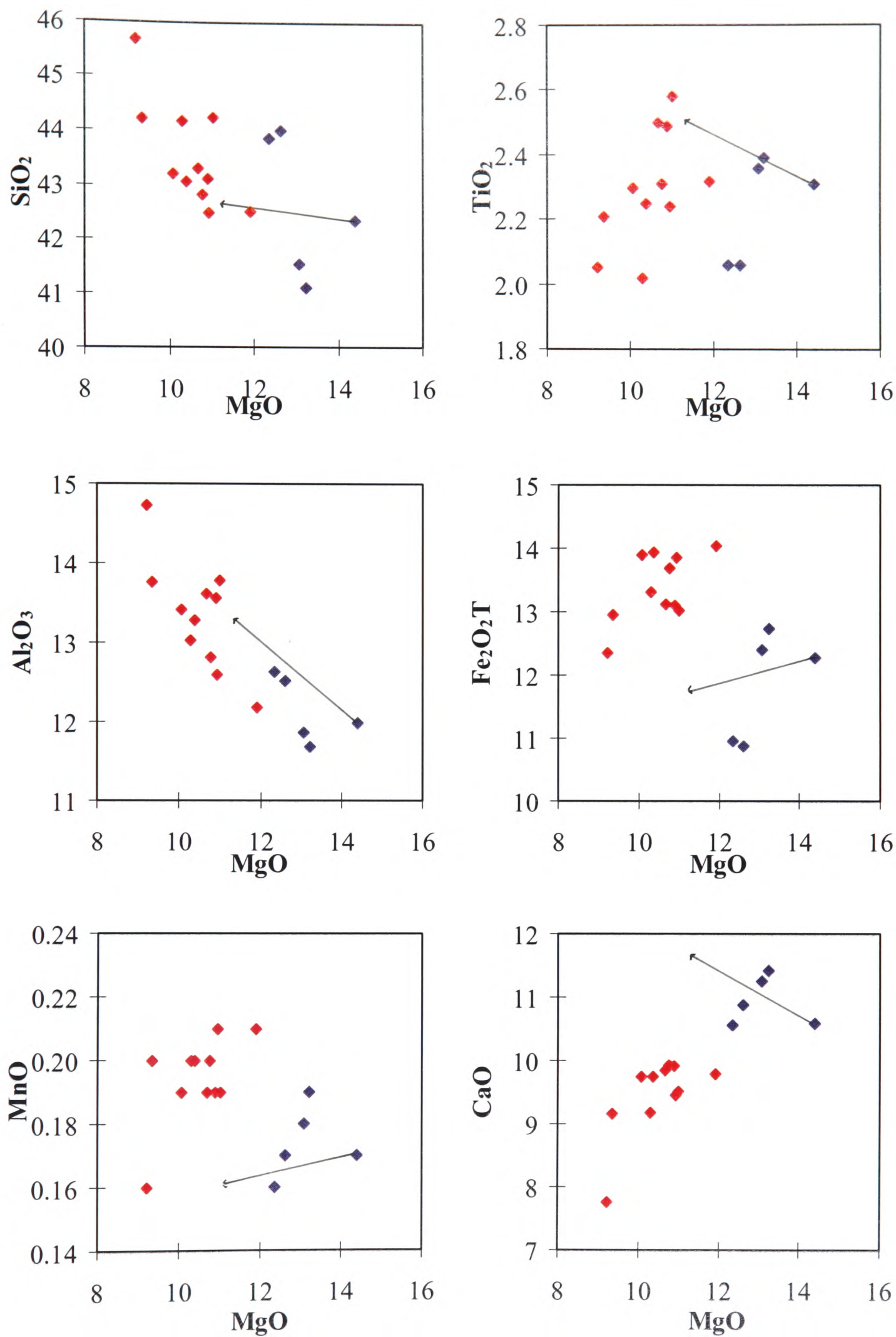


Figure 5.4 Plots of major element oxides vs. MgO. The 12+ group are shown in blue, and basanites from the 9-12 group are shown in red. Vectors indicate the effect of 10% fractional crystallisation of olivine (Fo₈₄).

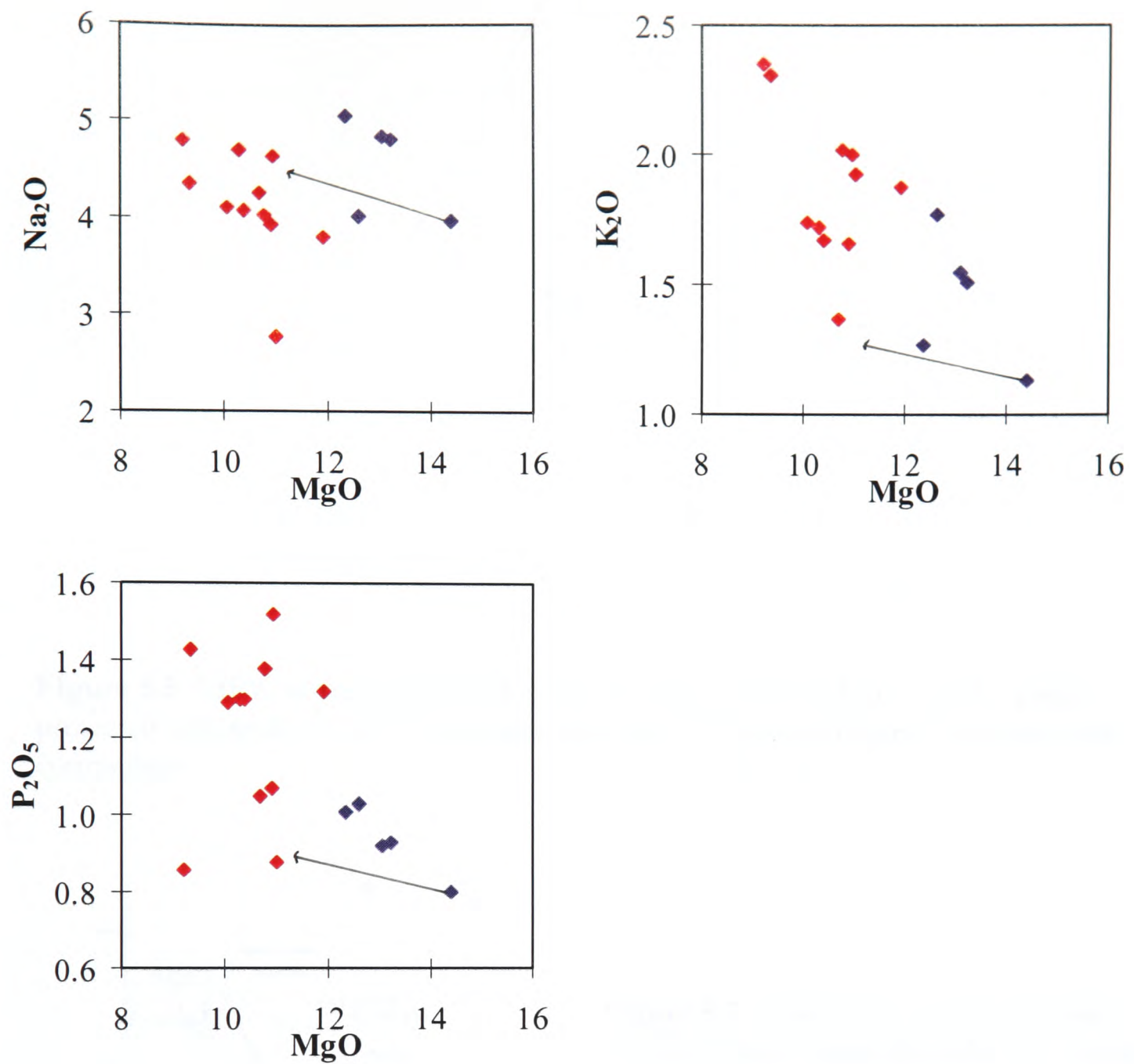


Figure 5.4(ctd) Plots of major element oxides vs. MgO. The 12+ group are shown in blue, and basanites from the 9-12 group are shown in red. Vectors indicate the effect of 10% fractional crystallisation of olivine (Fo₈₄).

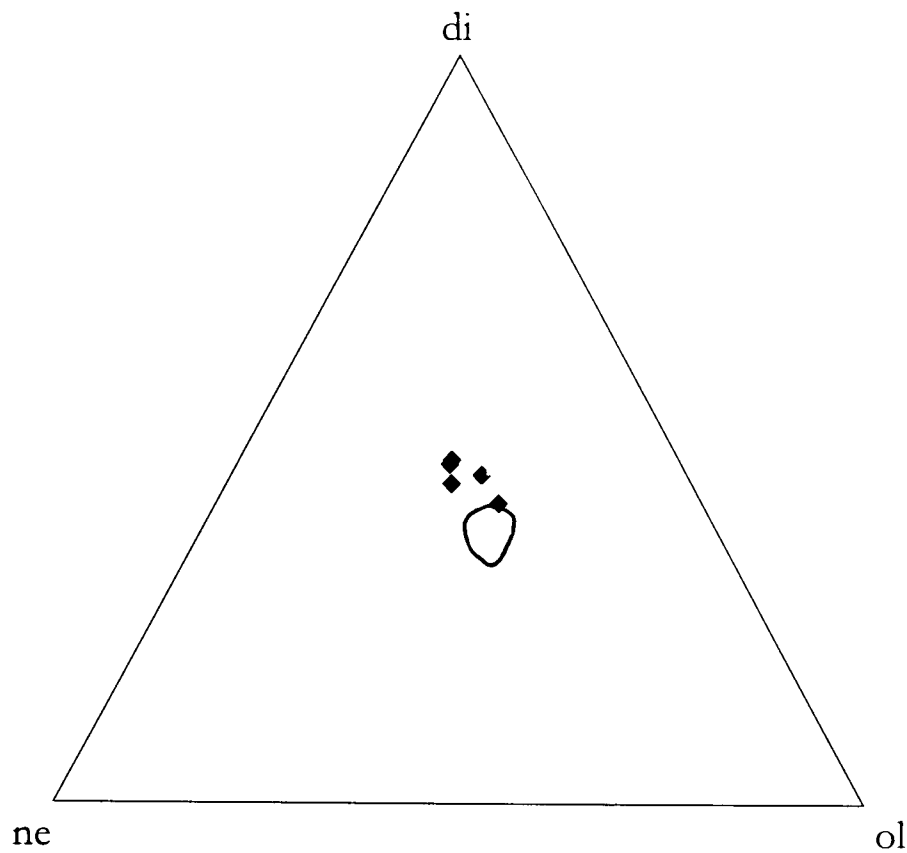


Figure 5.5 CIPW norms (calculated assuming $\text{Fe}_2\text{O}_3/\text{FeO}=0.2$) of the 12+ group projected into *ne-di-ol*. Field of basanites from the 9-12 group (Figure 3.4) shown for comparison.

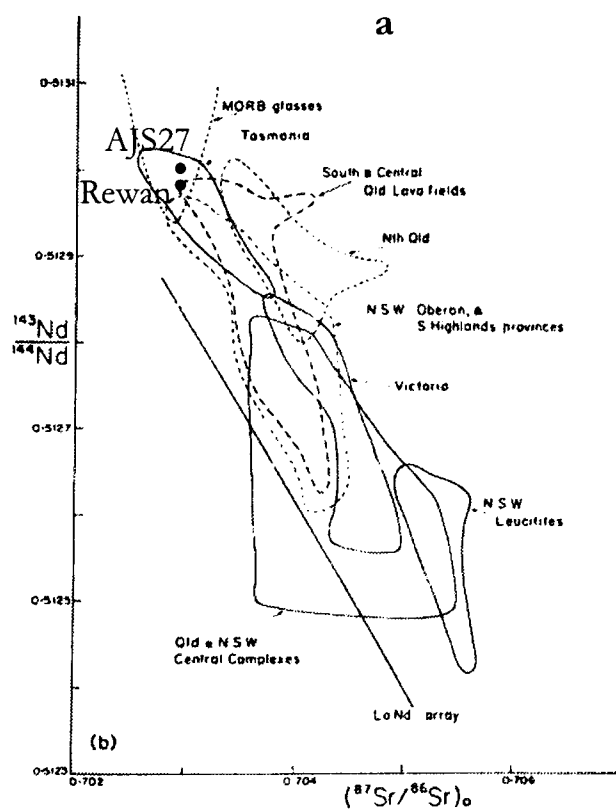
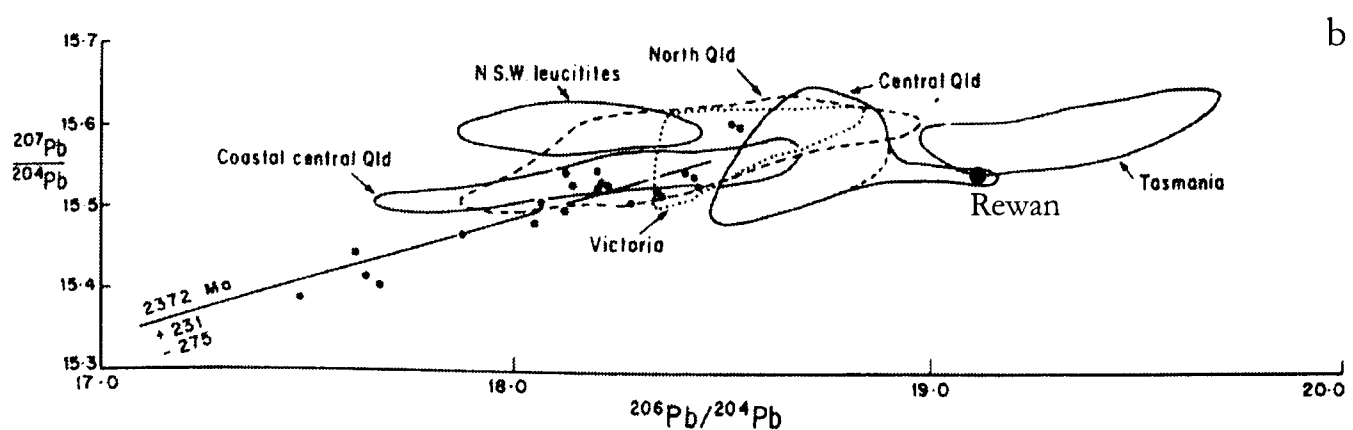


Figure 5.7 Comparison of the isotopic compositions of lavas from the 12+ group with generalised regional fields of east Australian mafic lavas from Ewart *et al.* (1988). Samples are AJS27 (this study) and a sample from Rewan (=AJSR1 and R2) analysed by Ewart *et al.* (1988).

a) $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$

b) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$

Note that they show closest similarity to lavas from Tasmania.



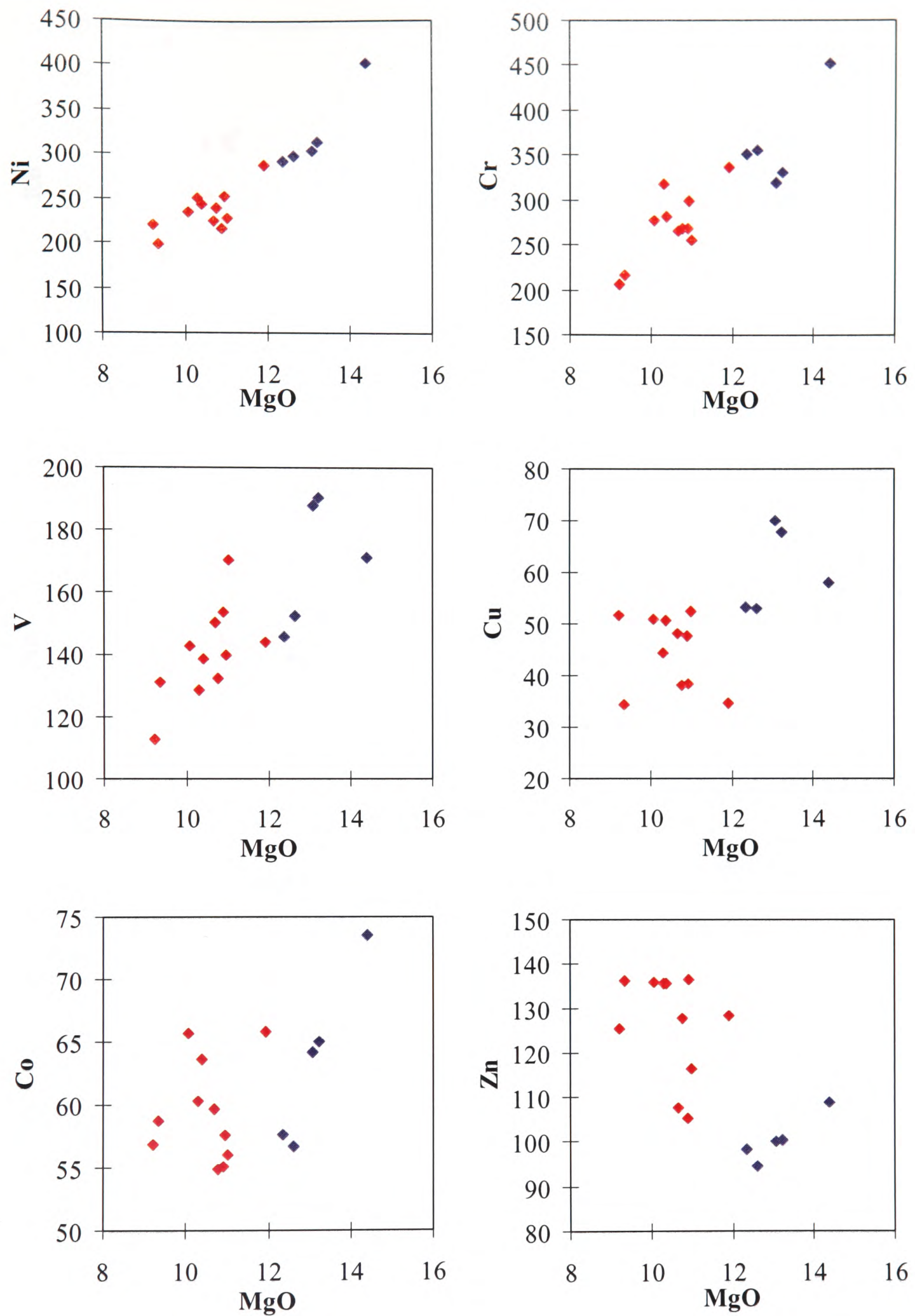


Figure 5.6 Plots of trace elements vs. MgO. The 12+ group are shown in blue, and basanites from the 9-12 group are shown in red. Vectors, where shown, indicate the effect of 10% fractional crystallisation of olivine (Fo84).

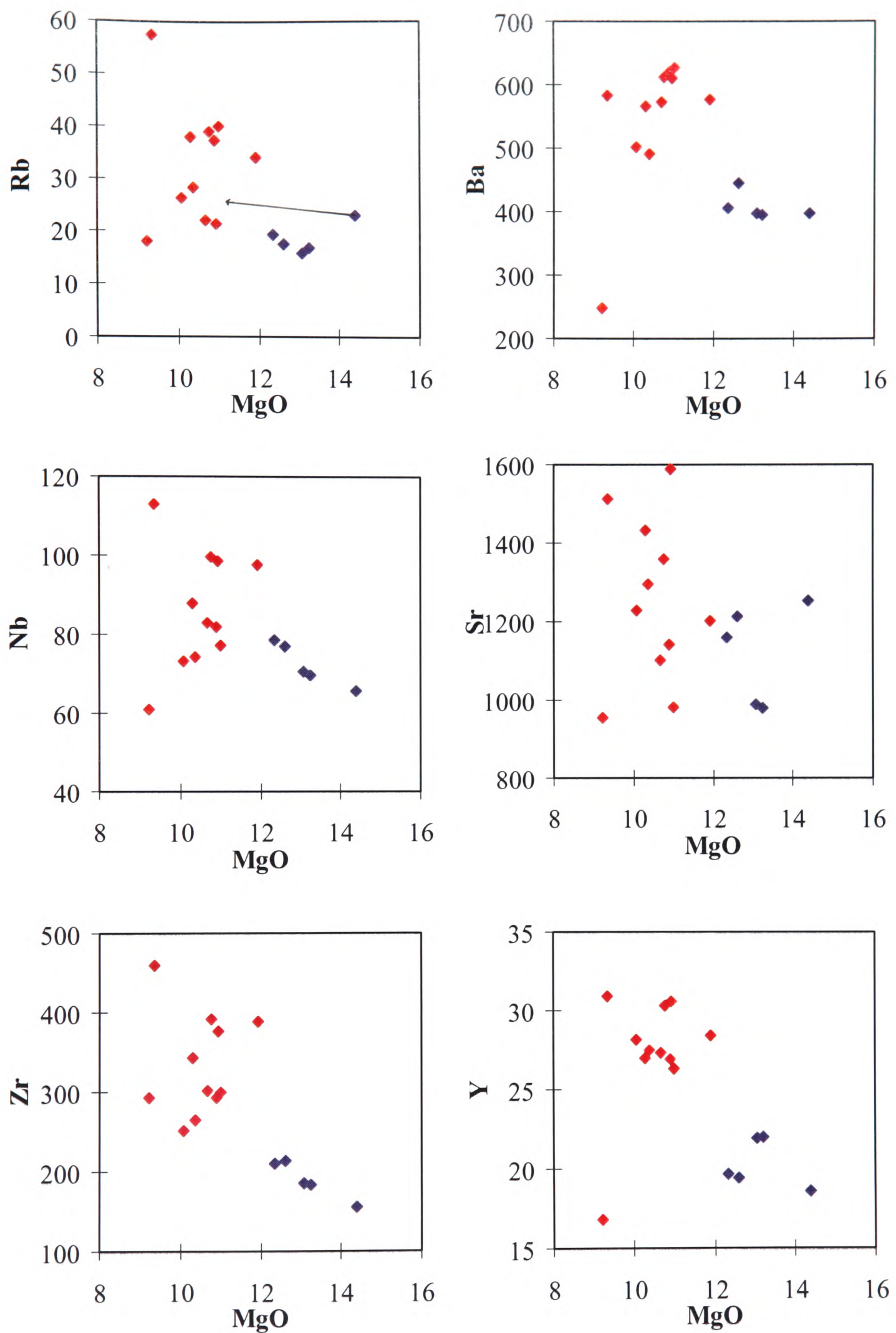


Figure 5.6(ctd) Plots of trace elements vs. MgO. The 12+ group are shown in blue, and basanites from the 9-12 group are shown in red. Vectors, where shown, indicate the effect of 10% fractional crystallisation of olivine (Fo84).

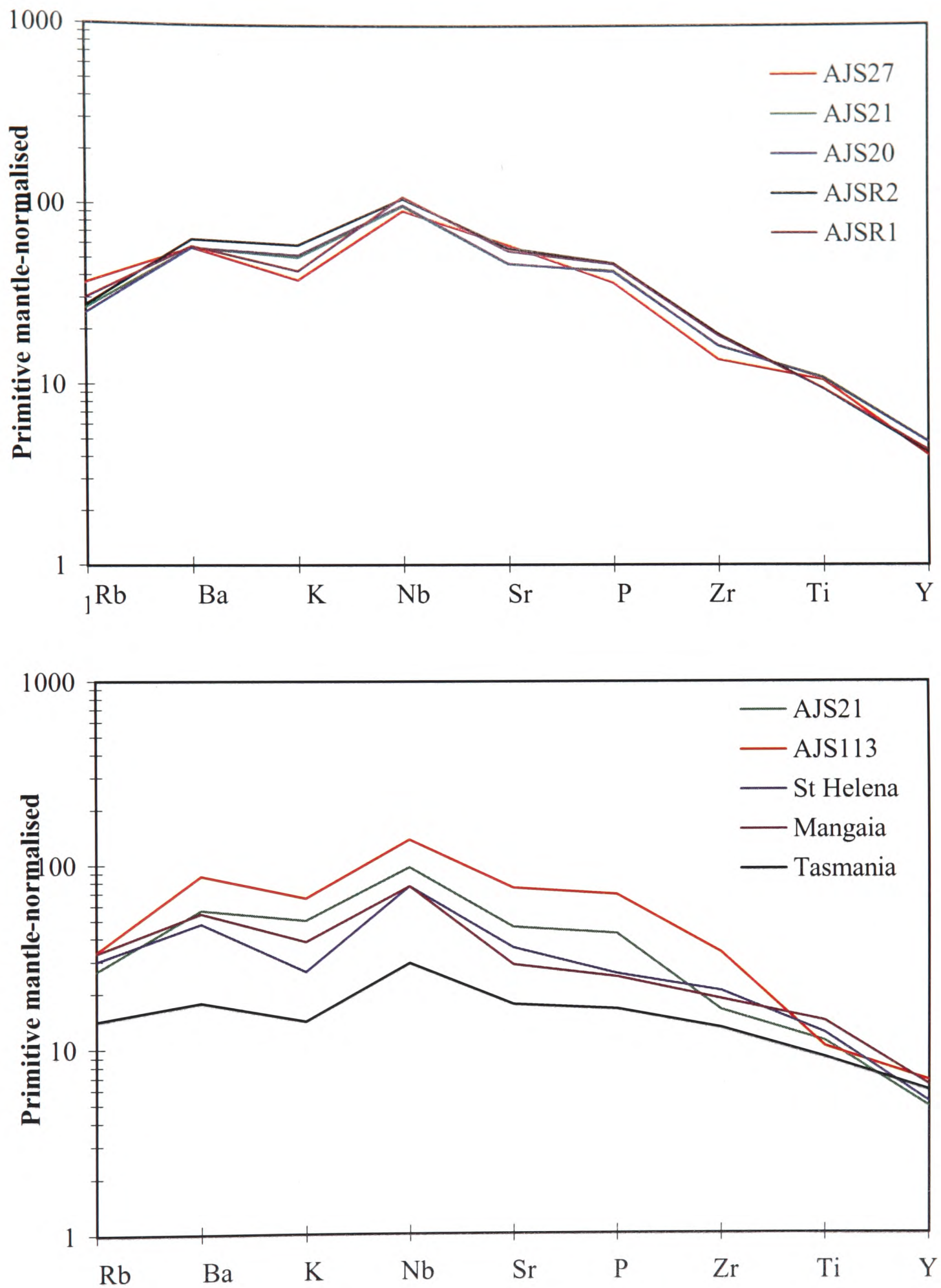


Figure 5.8a Spidergrams for the 12+ group, normalised to the primitive mantle values of Sun and McDonough (1989).

b Comparison of a representative of the 12+ group with HIMU-type lavas from St. Helena, Mangaia (Palacz and Saunders, 1986), Tasmania (Frey *et al.*, 1978) and a representative basanite from the 9-12 group (AJS113).

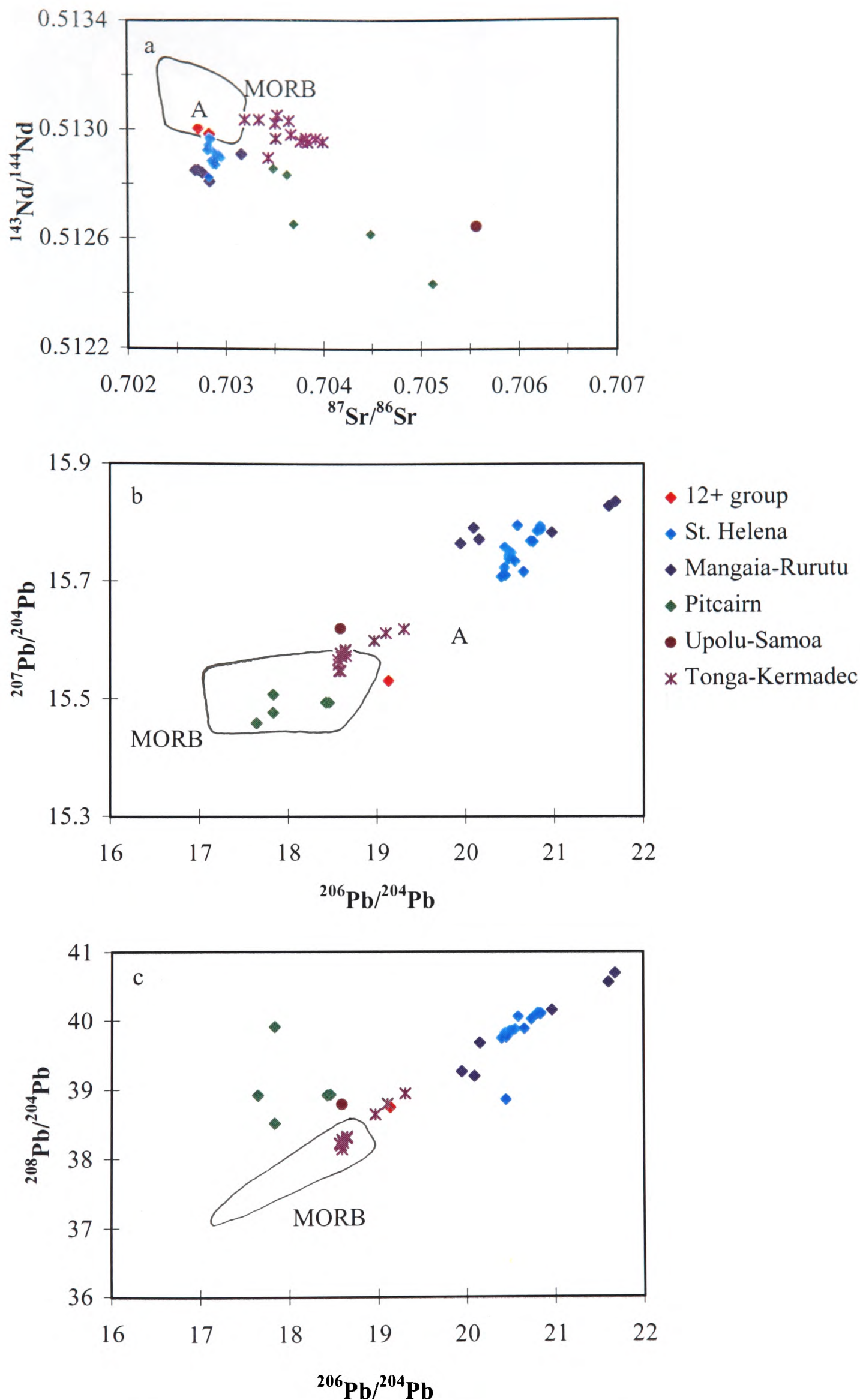


Figure 5.9 Comparison of 12+ data, using Sr-Nd-Pb isotopes, with HIMU lavas from St. Helena (Chaffrey *et al.*, 1989) and Mangaia-Rurutu (Palacz and Saunders, 1986), EMI-related lavas from Pitcairn (Woodhead and McCulloch, 1989), EMII-related lavas from Upolu-Samoa (Rollinson, 1993), Arc-related lavas from Tonga-Kermadec (Ewart *et al.*, 1998) and field of Indian & Pacific MORB from Ferguson and Klein (1993). "A" is the proposed asthenospheric end-member for western European lavas (Wilson and Downes, 1992). The key is the same for each plot.

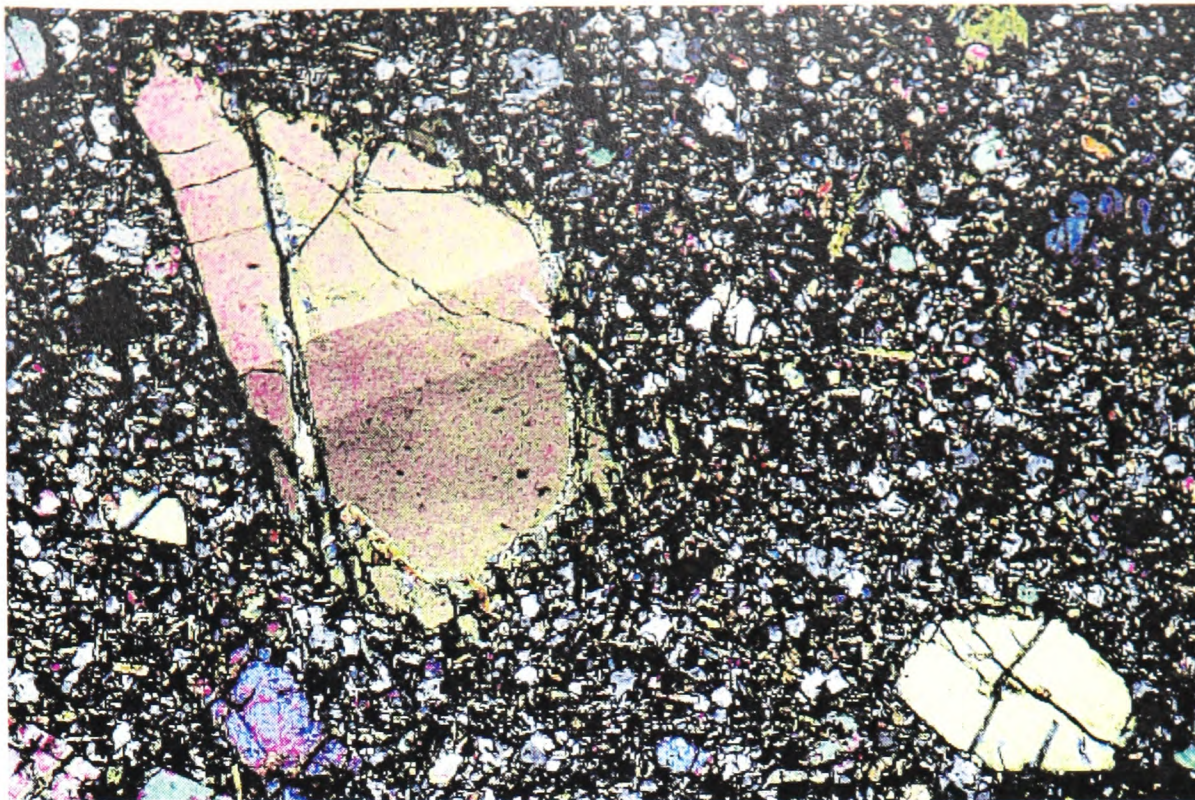


Plate 5.1 Photomicrograph of sample AJS21 showing a large, kink-banded corroded olivine megacryst derived from the disaggregation of lherzolite material, and smaller euhedral olivine phenocrysts. The groundmass consists of olivine, clinopyroxene, nepheline and Fe-Ti oxide. Field of view is 4mm across.

[illegible]

Chapter 6: Sequences, xenoliths and topography

In the previous chapters, the lavas under study have been classified and examined according to their geochemical characteristics (mostly MgO content). The purpose of this chapter is to study other aspects of the lavas which have been briefly alluded to in previous sections, namely within-sequence variation, the nature of the ultramafic xenolith suite and regional variation in geochemistry and topography. These characteristics can reveal useful information about chronological and regional variation in lava geochemistry, the nature of the lithosphere beneath the field area and the extent of underplating. These factors are all useful in constraining any model for the volcanism in Buckland, Springsure and Mitchell.

6.1 WITHIN-SEQUENCE VARIATION

6.1.1 Introduction

This section assesses chronological and geographical variation in the Buckland province using three comprehensively-sampled sequences. The sequences are from Vandyke, Carnarvon and Battleship Spur (see Figure 2.1 for locations) and span 50 km of the Buckland shield. It has already been noted (Table 2.1; section 4.2.4) that there is considerable overlap in rock type and geochemistry from these sequences, but this section aims to examine them in greater detail, and to consider whether any correlation of flows between the sequences is possible. Another aim is to test whether the observation of Bryan (1983) that compositions of lavas from just southeast of the Carnarvon section become more primitive up-sequence is evident elsewhere in the province.

6.1.2 Data presentation and description

Figure 6.1 presents up-sequence variation in lava composition for the Vandyke, Carnarvon and Battleship Spur sequences. A number of geochemical parameters have been chosen to illustrate variation in major elements, trace elements (compatible and incompatible) and trace element ratios. Variation in the silica saturation of lavas is assessed using the Saturation Index (SI) of Fitton *et al.* (1991) derived from the CIPW norm scheme. Lavas with $SI < 0$ are nepheline-normative, with $SI > 0$ hypersthene-normative, and $SI > 10$ quartz-normative. Heights are given in metres above sea level for the middle of each analysed lava flow. In some cases more than one sample has been taken from a given lava flow: comparison allows assessment of within-flow variation.

Clearly the data show considerable scatter and trends are commonly uncertain. Consequently they can only be used to examine gross geochemical trends, for example that the average Al_2O_3 content of lavas at the top of a sequence is greater than those at the bottom. Characteristics of the three sequences are summarised below:

1. Lavas from Vandyke show a slight increase in average SiO_2 and MgO composition with increasing height up the sequence, together with a slight decrease in Fe_2O_3 , while average values for other plotted parameters remain approximately constant, e.g. Sr at ~500ppm, Nb/Y~1.0. The scatter of the data is greater in the lavas above 870m than in those below: this is especially obvious for the incompatible elements, e.g. K_2O , TiO_2 and Nb. This height also marks a change in the average Al_2O_3 content of the lavas in the sequence: below 870m it is ~16.25%, while above 870m it is ~15%.
2. Compositions of the Carnarvon lavas show a bi-modal distribution which is well illustrated in the plots of MgO , Na_2O , Al_2O_3 and Nb. Most lavas show little geochemical variation throughout the sequence e.g. MgO ~5-6%, Al_2O_3 ~16%, Nb ~22-30ppm, while samples from 948m, 952m, 1040m and 1045m have dramatically different compositions e.g. MgO between 8 and 9%, Al_2O_3 ~15% and Nb ~11-20ppm. These distinct lavas are sub-alkaline in character, with high SI (~5) and low concentrations of incompatible elements. The majority of lavas from Carnarvon, however, are similar to those from the lower part of the Vandyke section (high- Al_2O_3), while the distinct sub-alkaline lavas compare to high- MgO , subalkaline types in the upper part of the Vandyke section (e.g. at 855m).
3. The basal part of the Battleship Spur sequence consists of lavas which are geochemically distinct from all other lavas in the sequence, as well as those from Vandyke and Carnarvon. They comprise five lava flows (seven samples) of primitive (mg-number=60-63) alkali basalt and basanite at heights below 950m and at 1000m. These lavas have lower Zr/Nb ratios (between 4 and 5) than any other lavas from this or the other sections (between 6 and 11). They are the most silica undersaturated (SI <-4) of all the lavas from the three sequences, and also possess relatively low TiO_2 (<2%) and Al_2O_3 (14.5-15.2%). The group overlaps with other lavas in most other geochemical parameters (e.g. concentrations of Fe_2O_3 , Na_2O , K_2O), although the two basanite samples in the group (AJS233 & 234 at 896 & 907m) contain extremely high concentrations of incompatible elements (e.g. ~75ppm Nb, 1100ppm Sr).

The remaining lavas from Battleship Spur (~100m thickness) show up-sequence trends of increasing MgO (5-9%) and Na/K (2.0-4.5), and decreasing concentrations of Al_2O_3 , K_2O and incompatible elements.

6.1.3 Correlation

It is clear that correlation of lava flows across the province is not possible using height above sea level: the Vandyke sequence extends from 760-950m while the base of the other two sequences lies at 900-950m. There is overlap in height between the upper, 'normal'-Zr/Nb section of the Battleship Spur section and lavas from Carnarvon between the heights of ~950 and 1100m. However, lavas from

Carnarvon show a different pattern of up-sequence variation to those from Battleship Spur: they show little average variation in MgO, Al₂O₃, Nb and Sr compared to the significant changes observed in these parameters at Battleship Spur.

It is possible, however, that correlation can be made between lavas of a comparable height above the base of their respective sequences. The lower part of the Battleship Spur section cannot be correlated with the other sections (owing to its distinct geochemistry), nor can the trends of dramatically (within ~100m) increasing MgO, decreasing K₂O etc. of the upper part. As noted above, there is a general similarity between the lower (height < 870m) part of the Vandyke section (~100m thick) and the non-subalkaline lavas from Carnarvon (~150m thick). Close inspection of the sections in Figure 6.1 shows that the geochemical overlap between the two groups is very good, although there is more variation in the Carnarvon section, for example in SiO₂ (48.0-50.9% compared to 48.4-50.2% at Vandyke) and Al₂O₃ (15.6-16.4% compared to 16.0-16.5). This overlap suggests that these sequences could have been extruded at the same time, despite the discrepancy in height; however this conclusion needs to be substantiated by radiometric dating.

6.1.4 Discussion and conclusions

It is possible to correlate much of the Carnarvon section with the lower half of the Vandyke section. While it is possible that this is the result of flows from a single vent covering the ~12km between the sections, the substantial discrepancy in height of the sections (Carnarvon: 950-1100m and Vandyke: 770-870m) makes it more likely that separate vents close to each section were served by the same ascending magma batches. The Vandyke sequence above 870m is not represented at Carnarvon, presumably due to subsequent erosion.

The sequence from Battleship Spur cannot be correlated with the other two sequences 40-50km to the north west. The base of the section consists of alkali basalts and basanites which have distinctly low Zr/Nb ratios, suggesting the involvement of different source material to the rest of the lavas considered here (see Chapter 3). Note that the Battleship Spur section lies at ~25°S, a latitude where undersaturated alkaline lavas are common: this is discussed in greater length in section 6.3. In the upper, silica-saturated part of the section, lavas show an increase in MgO contents with height, consistent with the observation of Bryan (1983) for lavas further to the north. This is also observed over a greater height interval at Vandyke, where samples at the top of the section are, on average, more MgO-rich (and SiO₂-rich) than those at the base.

6.2 ULTRAMAFIC XENOLITHS

6.2.1 Introduction

As outlined in chapters 3 and 5, ultramafic xenoliths have been observed in a number of primitive ($\text{MgO} > 9\%$) lavas from the Buckland province. The aim of this section is to describe them petrographically and geochemically, to assess their distribution across the field area and draw some conclusions about the nature of the lithosphere beneath the Buckland province.

6.2.2 Xenolith distribution

Xenoliths were retrieved from seven localities (see Figure 6.2) which are confined to a narrow band between 25° - $25^\circ 15'S$. These include basanite plugs from Rewan, Mt. Eden, Mt. Ogilvie, Mt. Eddystone, Bally Letheridge and around Mt. Tabor, and basanite/alkali basalt lava flows at Battleship Spur and at Mt. Tabor. Alkali basalt hosts are in the minority, consisting of AJS235 from Battleship Spur. Nodules in these rocks are much less abundant than in basanite hosts. The greater abundance of xenoliths in basanite hosts compared to alkali basalts is a typical feature throughout eastern Australia (Wass and Irving, 1976; O'Reilly *et al.*, 1989). The greatest number of xenoliths was sampled from Rewan, Battleship Spur and Mt. Tabor, although this xenolith distribution is quite clearly an artefact of the distribution of the host basanites, since the localities which lie between these named localities are small, isolated volcanic plugs.

Individual nodules up to 5 cm in length are found in the field, but most of these are strongly weathered rendering them useless for geochemical analysis. The fifteen nodules considered in this study were mostly found during rock cutting, hence they are small (0.5-3 cm: most are $< 1\text{cm}$) but also very fresh. They have been studied petrographically and mineralogically (by microprobe analysis only), and are described below.

6.2.3 Petrography

All but three of the nodules are spinel lherzolites, whose relative mineral proportions are usually olivine $>$ orthopyroxene $>$ clinopyroxene $>$ spinel (see Table 6.1 below). Systematic modal analysis was not attempted owing to the small nodule size and large grain size ($< 7\text{mm}$), hence the presence of a large crystal could strongly bias the apparent phase proportions. However, analysis of the largest sample AJS114N gave the proportions 59% olivine, 27% orthopyroxene, 13% clinopyroxene and 1% spinel, which lie within the range for typical eastern Australian examples (O'Reilly *et al.*, 1989). Two other samples are lherzolites without spinel (AJS15 and 28N), while the remaining sample (AJS 113A) is a spinel harzburgite which contains only one small crystal of clinopyroxene. Modal analysis for this harzburgite yielded the proportions 79% olivine, 20% orthopyroxene and 1% spinel.

The lherzolites are coarse-equant in texture (Harte, 1977), which is equivalent to the protogranular texture of Mercier and Nicolas (1975). Average grain size is 1-3 mm, although olivine

and orthopyroxene crystals in certain samples range up to 5mm (AJS 124N, REWAN1) and 7mm (AJS234B). Evidence of strain is confined to wide (~0.5-1mm) kink-banding in olivine; there is no deformation of the prominent Ca-rich exsolution lamellae which are visible in many orthopyroxene crystals. Grain boundaries are mostly irregular or curved, but straight ones are also found which are associated with 120° triple-point boundaries. Spinel is almost invariably associated with orthopyroxene. See Plate 6.1.

Sample	Phases and relative abundance	Crystal size (mm): range (mode)	Olivine mg-number	Spinel 100 (Cr/Cr+Al)
15	ol>opx>cpx	1-3 (2)	88.8-89.2	-
15N	opx>ol=cpx>spl	0.2-4 (1)	89.2-89.3	8.9-9.1
28N	ol>opx>cpx	0.2-4 (3)	88.9-89.1	-
39	ol=opx>cpx>spl	0.2-3 (1)	89.2-89.5	9.2-9.5
105N	ol>opx>cpx>spl	0.1-2 (1)	89.4-89.6	9.8-10.4
112	ol>opx>cpx>spl	0.2-5 (1)	89.1-89.4	9.0-9.2
113A	ol>opx>spl>>cpx	0.1-3 (1)	91.0-91.8	60.2-60.4
114N	ol>opx>cpx>spl	0.2-2 (1.5)	90.1-90.5	21.2
124B	ol>opx>cpx>spl	0.4-5 (3)	88.9-89.9	17.4-17.9
124N	ol>opx>cpx>spl	0.5-5 (3)	89.7-90.0	16.7-17.8
234B	opx>ol>cpx>spl	0.4-7 (1.5)	89.5-90.3	9.7-9.8
R2	ol,opx,cpx,spl	0.4-2 (1)	89.9-90.0	13.1-14.1
REWAN1	ol>opx>cpx>spl	0.5-5 (3)	89.6	10.0-10.1
REWAN2	ol>cpx>spl	0.2-4 (1.5)	88.7-90.3	10.1-10.3

Table 6.1 Characteristics of the fifteen ultramafic nodules discussed in this section. Owing to the small size of the nodules relative to constituent crystals, modal proportions were not calculated.

Sample AJS113A has a coarse-tabular texture (Plate 6.2) consisting of equant-elongate crystals of olivine and orthopyroxene, with minor spinel and one crystal of clinopyroxene which is identifiable by its twinning. Olivine shows evidence of strain in the form of kink-bands (>0.5mm wide). Exsolution is not present in the orthopyroxene crystals, some of which partially enclose crystals of olivine. Spinel occurs mostly as a large (1.5mm) ‘holly-leaf’ crystal, but also as tiny (0.1mm) fragments enclosed within olivine. Grain size varies between 0.5-3mm, and grain boundaries are dominantly irregular or curved.

The nodules contain some striking mineral textures. Plate 6.3 shows a reaction texture (visible in five samples) between orthopyroxene and the host melt. The expansion of the olivine+liquid field and

contraction of the orthopyroxene+liquid field with decreasing pressure in the basaltic system (e.g. Cox *et al.*, 1979) results in the decompressional breakdown of the pyroxene and the formation of an intergrowth of olivine + clinopyroxene aligned with its exsolution planes. Note that the reaction is either a two stage process or it has occurred at two separate occasions: the inner 'zone' is fine-grained ($\leq 0.1\text{mm}$), while the outermost 'zone' is coarser ($\sim 0.2\text{mm}$) and includes small crystals of Fe-Ti oxide which are comparable in distribution and size to those in the host lava. The composition of the olivine in this outer zone ($\sim \text{Fo}_{84}$) overlaps with the compositions of phenocrysts in the host ($\text{Fo}_{76}\text{-Fo}_{86}$).

A narrow ($\sim 0.1\text{mm}$) spongy border is visible around individual clinopyroxene crystals in some samples (e.g. AJS105: Plate 6.4). This is interpreted (e.g. Pike and Schwarzman, 1977) as a partial melting texture, and indeed a similar texture is observed around the rims of some clinopyroxene megacrysts in the more evolved ($\text{MgO} < 9\%$) lavas discussed in Chapter 4 (e.g. Plate 4.3g). Plate 6.5 shows a low-birefringence example from another nodule (AJS28N) which has undergone a greater degree of melting.

6.2.4 Geochemistry

Microprobe analyses were carried out on each of the fifteen samples: ranges of olivine and spinel compositions are given in Table 6.1, and spinel and pyroxene compositions are plotted in Figure 6.3.

In the lherzolites, olivines lie in the range $\text{Fo}_{88.8}\text{-Fo}_{90.5}$, and contain 0.30-0.45% NiO and 0.01-0.07% CaO. Orthopyroxenes are Al-rich enstatites, with mg-numbers in the range 89.7-90.7, while clinopyroxenes are Cr-rich (0.6-0.9% Cr_2O_3) diopsides. Figure 6.3 demonstrates that there is very little variation in pyroxene composition, with the exception of one low-Ca clinopyroxene (10.8% CaO) in lherzolite nodule AJS105N. The Cr/Cr+Al ratio of spinels lies in the range 9-21, and thus they can be termed 'Al-spinels' following the classification of Carswell (1980): see Figure 6.4. Examples of mineral compositions are given in Table 6.2.

The solitary harzburgite (AJS113A) contains olivine and orthopyroxene whose mg-numbers are significantly higher than those in the lherzolites (91.0-91.8; 92.3-92.4 respectively). Nickel content in the olivine (0.38-0.41%) is comparable to that in the lherzolites, while CaO content is slightly higher (0.03-0.12%). Spinel in AJS113A has a much higher Cr/Cr+Al ratio (~ 60) than the lherzolites, and is termed Cr-spinel (Carswell, 1980). Comparison is made between typical orthopyroxene and spinel compositions from the harzburgite and lherzolite AJS15N in Table 6.2. Note that the Al_2O_3 content of the orthopyroxene from the harzburgite is significantly lower than the example from the lherzolite.

6.2.5 Comparison and interpretation

As noted in section 1.1.6, the majority (>80%) of xenoliths recovered from other provinces in eastern Australia are from the Cr-diopside suite and are typical of examples of this suite world-wide (e.g. O'Reilly *et al.*, 1989). These consist predominantly of anhydrous spinel lherzolites with a coarse-equant to weakly-porphyroclastic texture and grain size from 1-10mm. Common features are kink-banding in olivine (composition: Fo₈₈-Fo₉₂) and exsolution lamellae in orthopyroxene. The xenoliths in this study clearly share these features. Overlap of orthopyroxene and spinel compositions from Buckland with world-wide spinel-bearing lherzolites (including examples from eastern Australia) is shown in Figure 6.4.

Griffin *et al.* (1987) described spinel lherzolites from east-central Queensland, including the Buckland province. These xenoliths are all anhydrous and show no evidence of strong deformation; petrologically they are similar to other Cr-diopside lherzolites from eastern Australia. The authors provide two analyses of xenoliths from Buckland which are presented below (Table 6.3), together with a world-wide average spinel lherzolite composition (Maaløe and Aoki, 1977) and the model basalt-source material 'pyrolite' (e.g. Jaques and Green, 1980). The Buckland samples have greater abundances of Al₂O₃, CaO, Na₂O and lower MgO, Mg/Mg+Fe and Cr/Cr+Al than the continental average, and are similar to the 'pyrolite' composition. This suggests that they are relatively fertile or undepleted compositions: extraction of basaltic melt from such material results in more refractory bulk compositions with lower Al₂O₃, CaO, Na₂O and higher MgO, Mg/Mg+Fe and Cr/Cr+Al.

Although Griffin *et al.* (1987) do not provide any mineral analyses from these xenoliths which would facilitate comparison with the xenoliths in this study, it is likely that they have a similar compositions. Mg-number of lherzolites is controlled by constituent olivine (and orthopyroxene) compositions, and there is clearly overlap between the values for the lherzolites (89) and the olivine microprobe analyses from this study (88.8-90.5). Furthermore, the spinels that have been analysed in this study contain low Cr/Cr+Al ratios (9-21) which are typical of undepleted lherzolites.

Opx-spinel thermometry carried out by Griffin *et al.* (1987) on the Queensland lherzolites yielded temperatures in the range 900-1050°C. They used the geotherm which they had calculated using garnet granulites and websterites from the same localities in Queensland in order to estimate pressures for the lherzolites. These lie in the range 9-16 kbar (26-50 km), i.e. upper mantle - lowermost crust.

The solitary harzburgite, with its distinctive refractory phase assemblage and mineral chemistry must have a bulk chemistry significantly different from the fertile lherzolites. The high MgO content of constituent olivine and orthopyroxene and low Al₂O₃ content of spinel and orthopyroxene indicate that the bulk composition of the harzburgite will be relatively MgO-rich and Al₂O₃-poor compared to the lherzolites. The near-absence of clinopyroxene must also result in a lower CaO content in the harzburgite.

	BWD-5	BWD-10	Hawaiian Pyrolite	Average continental
SiO ₂	44.49	43.84	45.2	44.15
TiO ₂	0.11	0.10	0.71	0.07
Al ₂ O ₃	3.1	3.28	3.54	1.96
FeO	8.9	8.67	8.47	8.28
MnO	0.17	0.15	0.14	0.12
MgO	38.24	37.66	37.5	42.25
CaO	2.50	3.20	3.08	2.08
Na ₂ O	0.36	0.37	0.57	0.18
K ₂ O	0.01	-	0.13	0.05
P ₂ O ₅	0.02	0.01	-	0.02
Cr ₂ O ₃	0.40	0.39	0.43	0.44
l.o.i.	1.96	1.66	-	-
Total	100.20	99.35	99.97	99.60
100Mg/Mg+Fe ^a	89	89	89	90
100Cr/Cr+Al	8.0	7.4	7.5	12.9

Table 6.3 Comparison of analysed spinel lherzolites from the Buckland province (Griffin *et al.*, 1987), with the model Hawaiian pyrolite composition of Jaques and Green (1980) and average global continental spinel lherzolite composition (Maaløe and Aoki, 1977). Note the close similarity of the Buckland samples to the fertile pyrolite composition, suggesting that they have undergone little/no partial melting.

^a Fe=all iron as Fe²⁺.

Phase equilibria suggest, and experiments prove (e.g. Jaques and Green, 1980; Hirose and Kushiro, 1993), that progressive melting of spinel lherzolite can result in the complete consumption of spinel and clinopyroxene leaving a harzburgitic residue. Obviously the exact order of mineral consumption is determined by the relative rates of melting and initial modal proportions of the different phases. Jaques and Green (1980) demonstrated that melting is accompanied by an increase in the mg-number of the residual olivine and in the Cr/Cr+Al ratio of remaining spinel. Specifically, their melting experiments on Hawaiian pyrolite at 15 kbar result in an increase in mg-number of olivine from a little under 88 (just above the liquidus) to 89, and of spinel from a Cr/Cr+Al of <25 (specific value not provided) to 60 after 25% melting. By analogy, it is plausible that the harzburgite AJS113A could represent the residue from the melting of a fertile spinel lherzolite containing olivine with an mg-number of ~90-90.5 and spinel with a Cr/Cr+Al ratio of ~20, i.e. comparable to the mineral compositions of

AJS114N (Table 6.2). It is impossible to date the timing of such a partial melting event with the available data. While the most obvious conclusion is that it is related to Cainozoic volcanism, the occurrence of subduction-accretion episodes in eastern Australia during the Palaeozoic-Mesozoic (Chapter 1) raise the possibility that AJS113A dates from a subduction-related magmatic phase prior to the Cainozoic.

6.2.6 Discussion and conclusions

Of the xenoliths studied here, fourteen are anhydrous, undepleted and relatively unstrained examples of Cr-diopside suite lherzolites which are geochemically and petrographically similar to other examples from east-central Queensland and eastern Australia. Comparison with previously-published data for nodules from the same area suggests that they are derived from the shallow lithospheric mantle (~25-50km depth). Their anhydrous nature clearly renders them incapable of representing the source rock of their host basanites, which are thought to derive from volatile-bearing lherzolite (Chapter 3). They cannot represent the source material of rarer alkali basaltic hosts, since major element data suggest that the lavas segregated at depths greater than 25-50km (Chapter 3).

The solitary analysed harzburgite has a refractory mineralogy, in both modal terms (clinopyroxene is very rare) and geochemical terms (olivines have high mg-numbers; spinel has high Cr/Cr+Al). Comparison with experimental data suggests that its geochemistry is consistent with it being the residue of ~25% melting of fertile lherzolite.

Xenolith localities are clearly dictated by the occurrence of basanite lava flows and plugs (discussed in the next section). Although restricted to latitude 25°S, xenoliths are found over a distance of ~90 km in the field area although xenolith occurrence is not evenly spread along this length. There is no clear systematic variation in xenolith composition across the area (see Table 6.3 below), although this may reflect the uneven sampling imposed by exposure.

	WEST		EAST		
Locality	Mt. Tabor	Bally Letheridge	Mt. Eden	Battleship Spur	Rewan
Longitude	147°30'E	147°37'	148°6'	148°10'	148°15'
Samples	105-113	39	124B,124N	15,15N,234B	R2, REWAN1,2
Olivine	89.1-91.8	89.2-89.5	88.9-90.0	88.8-90.3	88.7-90.3
Spinel	9.0-60.4	9.2-9.5	16.7-17.9	8.9-9.8	10.0-14.1

Table 6.3 Table showing east-west variation in xenolith composition across the field area. ‘Olivine’ compositions are 100(Mg/Mg+Fe) and ‘Spinel’ compositions are 100(Cr/Cr+Al). All samples come from basanite plugs or flows within latitudes 25° and 25°10’S. See Figure 6.2 for exact locations.

In conclusion, this small study seems to suggest that the lithospheric mantle in this part of Queensland consists mostly of fertile spinel lherzolite with smaller amounts of depleted harzburgite, the residue from previous melting events. This is consistent with the average continental lithosphere composition of Maaløe and Aoki (1977), which lies between fertile and depleted spinel lherzolite compositions. However, bearing in mind the notorious heterogeneity of the continental lithospheric mantle (e.g. Irving, 1980; O'Reilly, 1987; Gibson *et al.*, 1992), and the very small size of the sample considered here (15 nodules), it is very possible that the sub-Buckland lithosphere shows more geochemical variety than is shown by these xenoliths.

6.3 VARIATION IN TOPOGRAPHY AND GEOCHEMISTRY ACROSS THE FIELD AREA

6.3.1 Introduction

Evident from the foregoing chapters are variations in geochemistry (e.g. basanite distribution) and lava thickness/height (section 1.2.1) across the field area. The aim of this section is to describe these in more detail and examine whether they reveal any useful information about magmatic processes in the lithosphere beneath the field area. Regional variation in height/thickness and geochemistry are considered together as it will be argued that they are inextricably linked in the model for lava petrogenesis.

6.3.2 Lava height and thickness

Variation in lava thickness and height of the base of the lava pile is shown in Figure 1.20, which is a north-south sketch-section from Amby in the south to just north of Springsure (see Figure 6.2 for location). Where the section does not pass through important sequences, for example north Mitchell, these sequences are shown with a dashed line. Lava thickness is estimated by comparison between the 1:250,000 topographic maps and BMR geological maps. Unfortunately this method is susceptible to considerable error for two reasons:

1. First, the geological map for the field area is based only on 'several traverses' (Buckland) or 'numerous traverses' (Springsure), i.e. they have not been mapped in detail.
2. Secondly, since the basalt flows commonly form steep cliff sections, it can be very hard to estimate the height of the base of the lava where the contours are very closely spaced. Since the contour interval is 50m, it is quite possible that the error on the estimates is at least $\pm 50\text{m}$.

Height of the lava base

This shows a gradual increase from ~400m a.s.l. near Amby to ~1000m in Buckland, followed by a sharper reduction to ~300m in Springsure. Local variation in height was referred to in section 6.1, where it was noted that the base of the lava at Carnarvon is at 950m, while at Vandyke, just 12km to

the NNE, it is at 770m. This northward reduction in height is sharper than estimated from the cross-section Figure 1.20 and is ascribed to the undulose nature of the pre-eruption landscape.

Thickness

Having established the variation in height of the lava base, it is a simple step to estimate the thickness by using spot heights which indicate the highest points of the basalt exposure. This varies along the section from ~30 m in south Mitchell to ~100m in north Mitchell to ~300m in Buckland and Springsure. Within-province variation, especially evident for Springsure, is clearly due to erosion. Considerable fluvial incision is evident in the Buckland province although the visual effect in Figure 1.20 is amplified by the vertical exaggeration of the section. Lava thickness is more constant across Buckland than across Springsure: this is presumably an artefact of a difference in erosion style.

6.3.3 Geochemical variation

The geochemistry of the lavas from the field area has been discussed in detail in the previous chapters (3-5), and it is clear that there is some regional, inter-province variation. In terms of rock type, this variation can be summarised as below (see Table 2.1 for greater detail):

South Mitchell: *qz*-normative tholeiites and basaltic andesites.

North Mitchell: Predominantly trachybasalts, a basaltic trachyandesite and a basaltic andesite.

Buckland (main shield sequences): Predominantly *ol*-tholeiites and trachybasalts, with rarer basanites, alkali basalts and a *qz*-tholeiite.

Buckland (plugs and sequences to the west of the main shield, including Mt. Tabor): Predominantly basanites, with sub-ordinate alkali basalts, *ol*-tholeiites, a trachybasalt and a phonotephrite.

Springsure: Predominantly *ol*-tholeiites and trachybasalts, with rarer alkali basalts, basaltic andesites (*qz*-normative) and basaltic trachyandesites (*hy*-normative).

Geochemical variation is shown in Figure 6.5 where selected geochemical parameters are plotted against a measure of latitude, specifically distance (km) north of 26°30'S. Parameters considered are:

- saturation index (SI), a measure of silica saturation where $SI < 0$ for nepheline normative samples (Fitton *et al.*, 1991)
- Mg-number, which provides a measure of the degree of fractionation of a sample.
- Zr, to indicate variation in the concentration of incompatible elements.
- Nb/Y, used as a source discriminator in Chapter 3.

Variation in each parameter is summarised below:

Saturation index: Average SI of basalts decreases from ~15 in south Mitchell, to ~8 in north Mitchell to ~5 in most of Buckland (the main shield) and the whole of Springsure. SI does not fall below -2, with the exception of 10 alkali basalts from ~25°S (from both the main shield and the area to the west, including Mt. Tabor) which range between -2 and -15. Basanites (2 samples from the Battleship Spur sequence in the main shield, the remainder from the area to the west) form a distinct group whose SI < -20.

There is thus a strong correlation between SI and geographical location: SI decreases northward through Mitchell to Buckland and Springsure, and there is a region of mildly-strongly undersaturated compositions at ~25°S which extends across the field area from 147°30' to 148°15'E.

Mg-number: Basaltic samples from Mitchell lie in the range 45-60, while those from Buckland and Springsure show a greater range: 40-65 and 35-65 respectively. Mg-number is evenly distributed throughout Buckland, while Springsure lavas divide into two groups (35-40 and 50-65) which are interbedded in the north of the province. Basanites are primitive, with values between 62 and 74.

Zr: Abundance of this element lies in the range ~100-300 for nearly all basaltic samples. Most lavas from south Mitchell contain ~100ppm (typical of *qz*-tholeiites), most from north Mitchell ~200-250ppm, while those from Buckland and Springsure show an even distribution between 100-300ppm. Four Springsure samples containing 330-430ppm are the four most evolved samples from that province (mg-number between 35-40), thus the elevated incompatible element abundances reflects a higher degree of fractional crystallisation than other lavas. Basanites have high abundances of incompatible elements: Zr varies between 250 and 450 ppm. Their high mg-numbers indicate that this is a primary feature of the liquids.

Nb/Y: This lies between 0.2-2.0 in all but one of the basalts, but between 2.5-4.5 in the basanites. It is argued in Chapter 3 that this reflects different sources for the basanites and the basalts.

In conclusion there is significant variation in lava geochemistry with geographical location. The thick sequences in Buckland and Springsure are composed primarily of *ol*-tholeiites and trachybasalts which have values of SI predominantly between 0 and 5 (i.e. *hy*-normative), range from primitive (mg-number=65) to evolved (mg-number~40), and contain moderate amounts of incompatible elements (Zr between ~100 and 300ppm). Lavas from north Mitchell show some overlap with those from Buckland in all the geochemical parameters considered, but have slightly higher SI values. Those from south Mitchell are all silica-oversaturated and relatively depleted in incompatible elements (Zr slightly below 100ppm). Basanites with a distinct chemistry (SI<-20), mg-number mostly>62, Zr mostly 250-450ppm and Nb/Y>2.5 found span the width of the field area, but are confined to latitude 25°-25°15'S. They

crop out mostly to the west of the Buckland shield, although where they occur within the shield (e.g. Battleship Spur) they lie at the base of the sequence (Figure 6.2). Some alkali basalts at this latitude show below-average SI values (-2 to -15).

6.3.4 Discussion

Excepting the basanites and alkali basalts at $\sim 25^\circ\text{S}$, there is clearly a correlation between lava thickness and saturation index throughout the area of study (i.e. small thickness - high SI). Furthermore, an apparent correlation of these two variables with height of the lava base exists for Mitchell and Buckland, but not for Springsure. This section considers interpretations for these observations, discussing firstly the factors that affect lava thickness, composition and height.

What influences rock thickness/volume?

1. Temperature and pressure of melting: experimental melting of anhydrous peridotite (e.g. Hirose and Kushiro, 1993) shows that melt volume increases with rising temperature and with falling pressure. A greater volume of melt is generated during adiabatic decompression of mantle above its solidus if it has a high potential temperature (T_P) than low one (McKenzie and Bickle, 1988), other factors being equal.
2. Rate of extension: extension promotes the rise of hot asthenospheric material to replace the lithosphere removed by thinning. At high stretches where thinning is considerable, asthenospheric material can rise to shallower levels than at low stretches, thus permitting a greater overstepping of the peridotite solidus and a greater degree of melting.
3. Residence in the lithosphere: this is a function of the density difference between magma and country rock, and the nature of the lithospheric stress field. Magma may pond in the lithosphere or crust if it is denser than the country rock, and will not ascend until it has become less dense by fractional crystallisation of mafic phases such as olivine. The greater the density difference between magma and country rock, the greater the extent of fractional crystallisation that is required before it can ascend to the surface. If the prevailing lithospheric stress field is compressional, then magma will not be able to ascend to the surface, and it will crystallise and underplate the crust. Lister and Etheridge (1989) argue that this was the case in eastern Australia before the commencement of eruption at the surface, leading to the formation of a considerable underplated layer around the Moho (see Chapter 1).

What influences the silica-saturation of lavas?:

1. Degree and depth of melting: silica saturation of melts increases with degree of melting and decreasing pressure for anhydrous source rocks: Hirose and Kushiro (1993).

2. The extent of assimilation of silica-rich material: increasing assimilation will increase the silica content of the lava. However, concomitant fractional crystallisation will tend to elevate concentrations of Na₂O, K₂O etc. which act to *decrease* the silica saturation. The 'high-silica' lavas discussed in Chapter 4 whose SiO₂ contents increase with falling MgO and which are interpreted as having assimilated silica-rich material, show no systematic increase in saturation index.
3. The volatile content of the source rock: This has been discussed in Chapter 3, where it was noted that H₂O-bearing source rocks produce oversaturated liquids under most conditions (e.g. at subduction zones), while CO₂-bearing source rocks generate undersaturated liquids.
4. The fertility of the source rock: i.e. the extent of prior depletion of the source by partial melting episodes. These melting events tend to reduce/remove Ca, Al and Na-bearing phases (clinopyroxene and spinel) leaving a residue of olivine and orthopyroxene. Such refractory compositions have higher solidus temperatures than fertile lherzolite, and produce iron-rich, silica-oversaturated liquids.

What influences the height of the lava base?

1. Pre-eruption topography: as outlined above, there is evidence for this in the order of 100-200m over 12km by comparison of the Carnarvon and Vandyke sections in the Buckland province.
2. Thermal uplift as a result of volcanism: Lister and Etheridge (1989) argue that, since the thermal decay constant is low in eastern Australia (a few tens of Ma), a negative correlation should be observed between the age and height of volcanic provinces in eastern Australia. This, however, is not observed, and consequently thermal uplift is not thought to contribute significantly to the current elevation of the volcanic provinces.
3. Uplift owing to underplating: this results from the accretion of relatively low density basaltic material at the base of the crust where it replaces denser ultramafic material. This is potentially substantial: Lister and Etheridge (op. cit.) calculated that 5-15km of underplate (consistent with seismic evidence in eastern Australia) can account for 400-1400m of permanent uplift (although Cull *et al.*, 1993 estimate the actual thickness of underplated material as ~4km on the basis of thermal modelling).

The similarities in geochemistry and lava thickness/volume in the Buckland and Springsure provinces suggest that there were no substantial differences in the petrogenetic processes which operated in these two provinces, while similarities in lava petrography suggests that lavas from both provinces have undergone polybaric fractionation. Significant differences in T_P of the plume or amount of extension are unlikely between these adjacent provinces. Consequently, the difference in height between the two provinces must be ascribed to either pre-eruption topography or variation in the amount of underplating. It is clear from the figures of Lister and Etheridge (1989) above that a difference in height of ~500 m in the lava base between Buckland and Springsure translates to a difference in the amount of

underplated material of ~5km. Such a dramatic difference in crustal underplate over a distance of ~50 km is clearly unreasonable. First because the rigidity of the lithosphere would result in the uplift being spread over a greater distance than 50 km, and secondly because such a significant difference in the amount of underplate beneath two adjacent provinces which have very similar magmatic histories is unreasonable, even though there is more petrographic evidence for high-pressure fractional crystallisation in lavas from Buckland than in those from Springsure. Consequently, the cause of the difference in lava height across the two provinces is interpreted as an artefact of the pre-eruption landscape of the area.

Lava sequences in Mitchell thin towards the south (to ~30m) and show a gradual increase in normative quartz content. There is no evidence that they represent the remains of a thicker and more widespread sequence, and thus an explanation is required for their gradual geochemical change and volumetric reduction away from Buckland. Note that there are no further volcanic provinces to the south of Mitchell: the locus of central volcano activity switched to the west, including the contemporaneous (24-21 Ma) Tweed volcano by the coast on the Queensland-NSW border. As outlined in Chapter 1, the non-linear distribution of the age-progressive central volcanoes is interpreted as the result of the channelling of magmas by trans-lithospheric fractures away from the zone of plume melting (Figure 1.15). Thus it is possible that if the Tweed volcano ~500 km to the east was receiving large quantities of magma (<440m of remaining lava thickness), then these fractures were preferentially channelling material to the east rather than the west, hence the paucity of lava in the Mitchell province.

It is argued in Chapter 4 that the primary cause of the relatively high silica saturation of the Mitchell lavas is an increase in partial melting / decrease in the depth of melting compared to lavas from Buckland, although it could result from the melting of more geochemically-depleted material. The isotopic characteristics of the province (see Figure 1.16) are distinct from the postulated eastern Australia plume composition, and it has been argued (Sun *et al.*, 1989) that this could result from interaction with subduction-related lithosphere and/or AFC involving subduction-related crust.

The reduction in height towards the south can be readily interpreted, owing to the decrease in lava volume, in terms of a reduction in underplating away from Buckland.

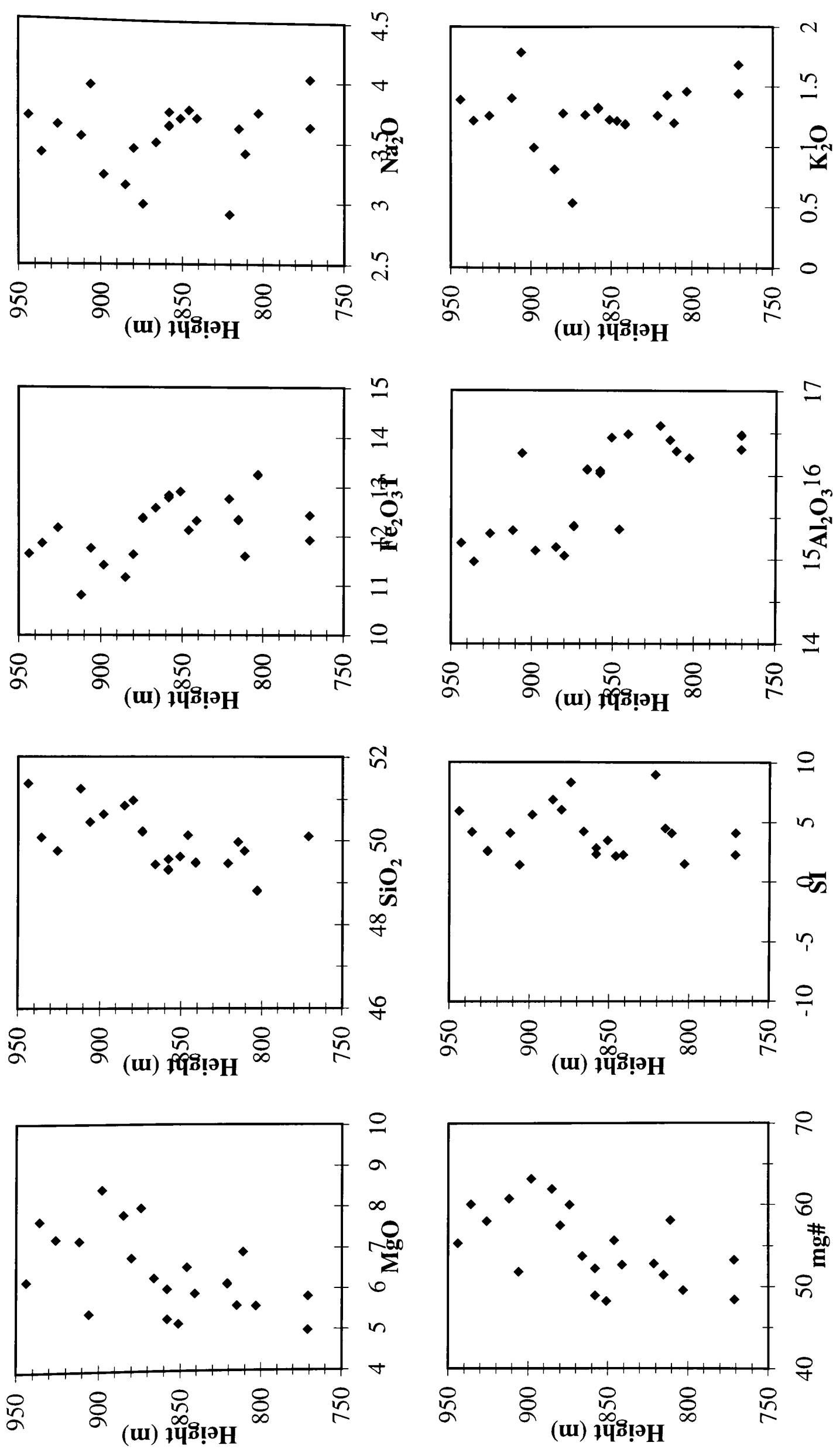


Figure 6.1a Up-sequence variation in lava composition with height above sea level at **Vandyke**.

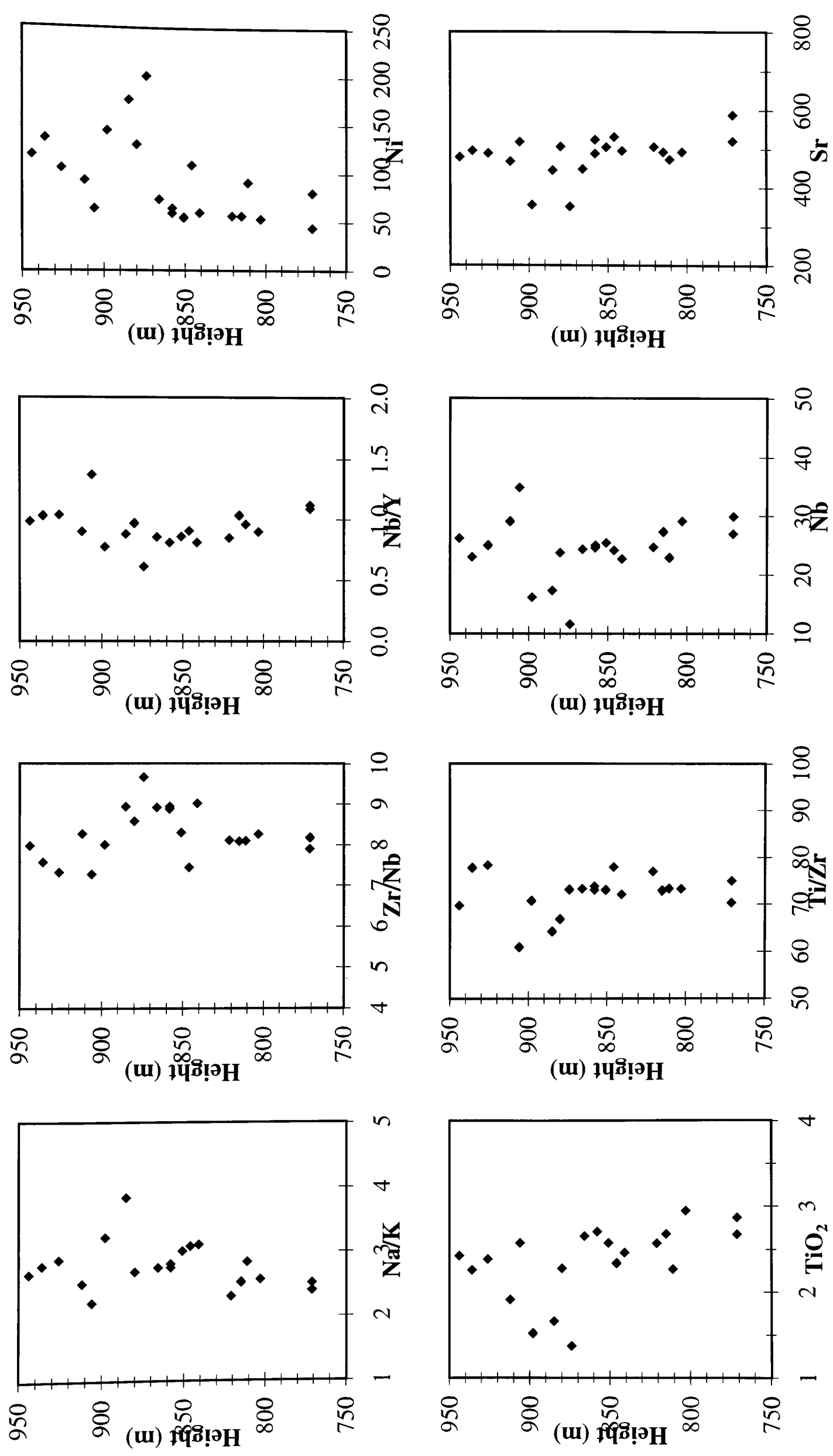


Figure 6.1a Up-sequence variation in lava composition with height above sea level at **Vandyke**.

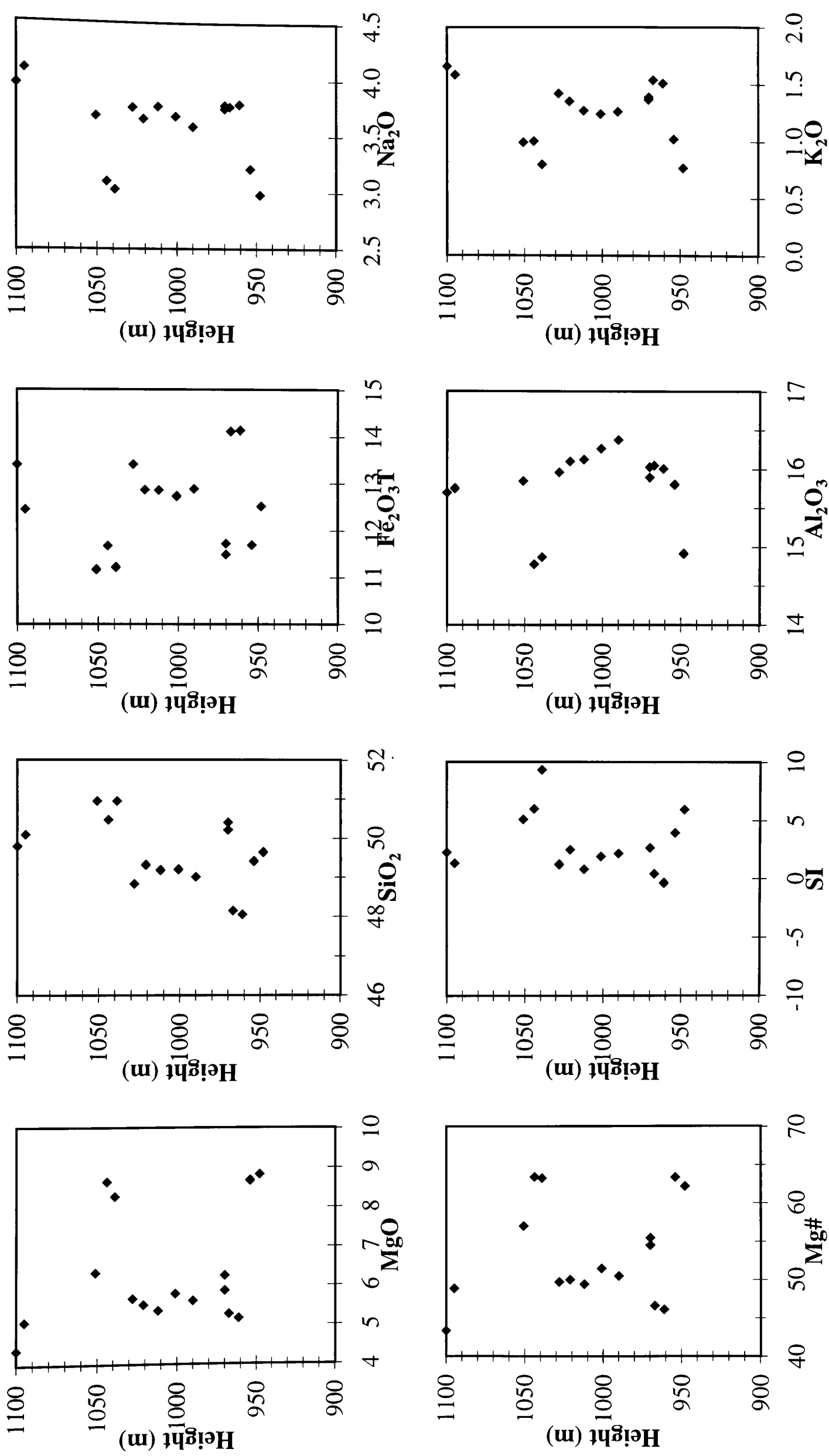


Figure 6.1b Up-sequence variation in lava composition with height above sea level at **Carnarvon**.

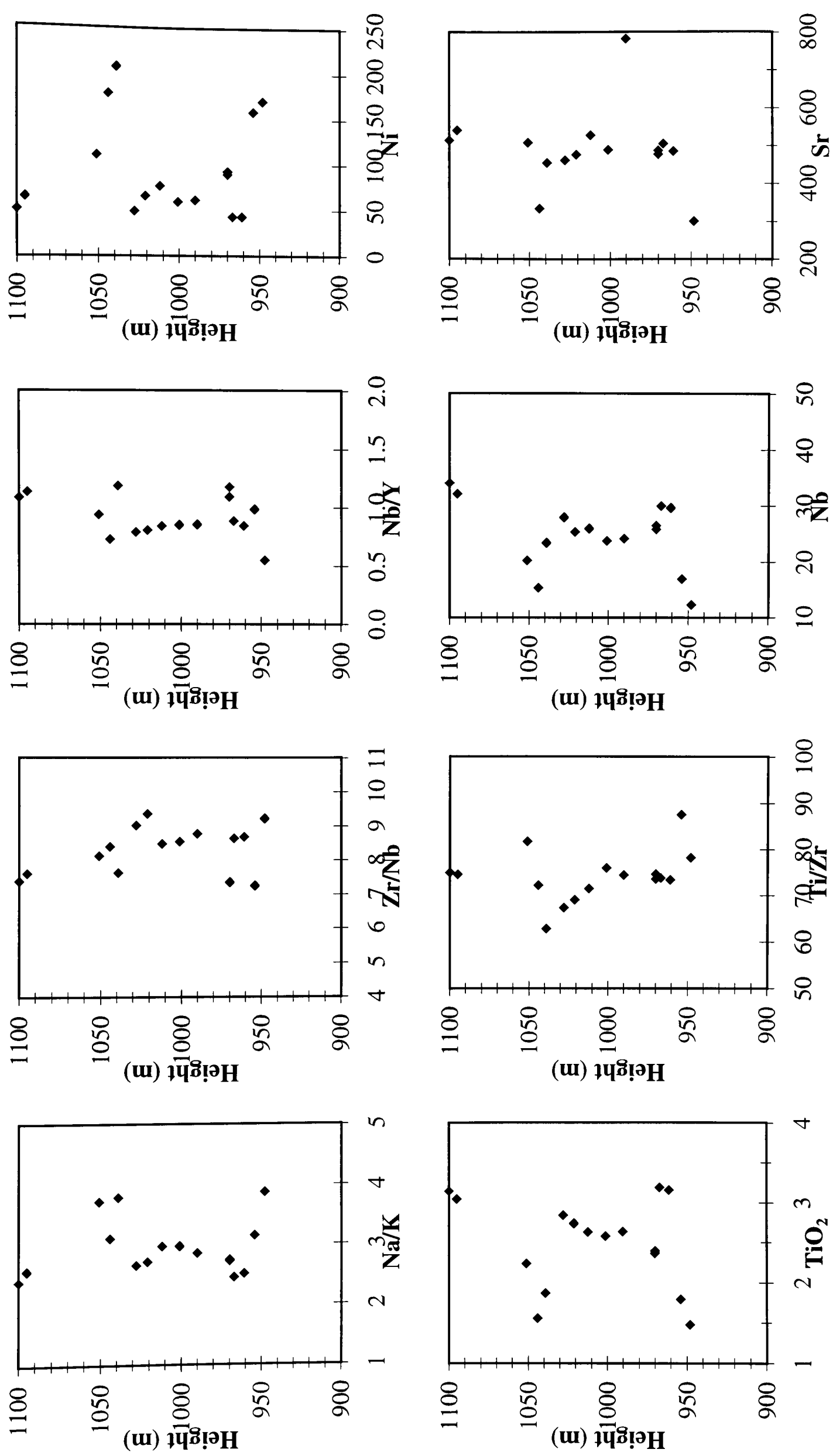


Figure 6.1b Up-sequence variation in lava composition with height above sea level at **Carnarvon**.

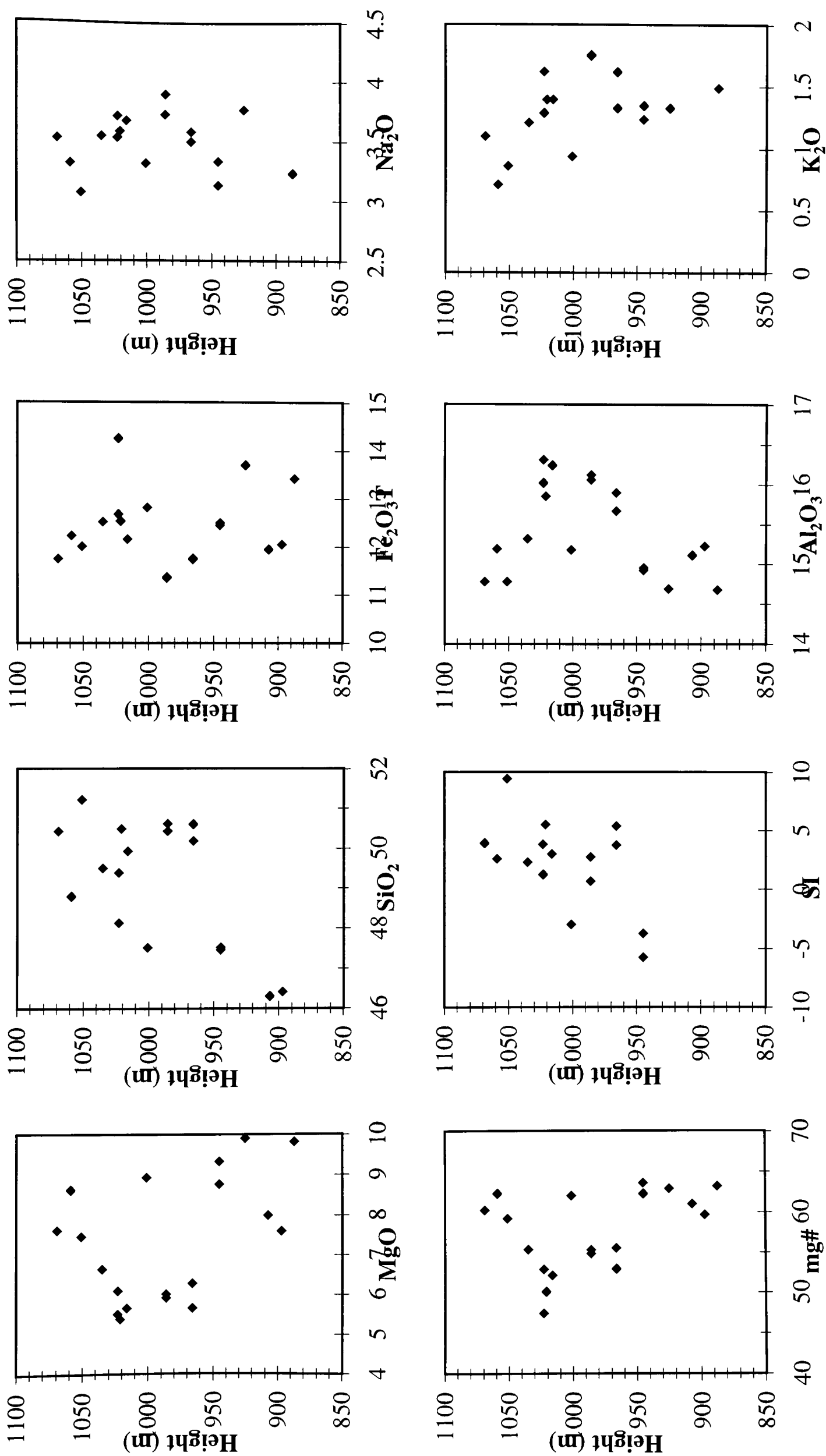


Figure 6.1c Up-sequence variation in lava composition with height above sea level at Battleship Spur.

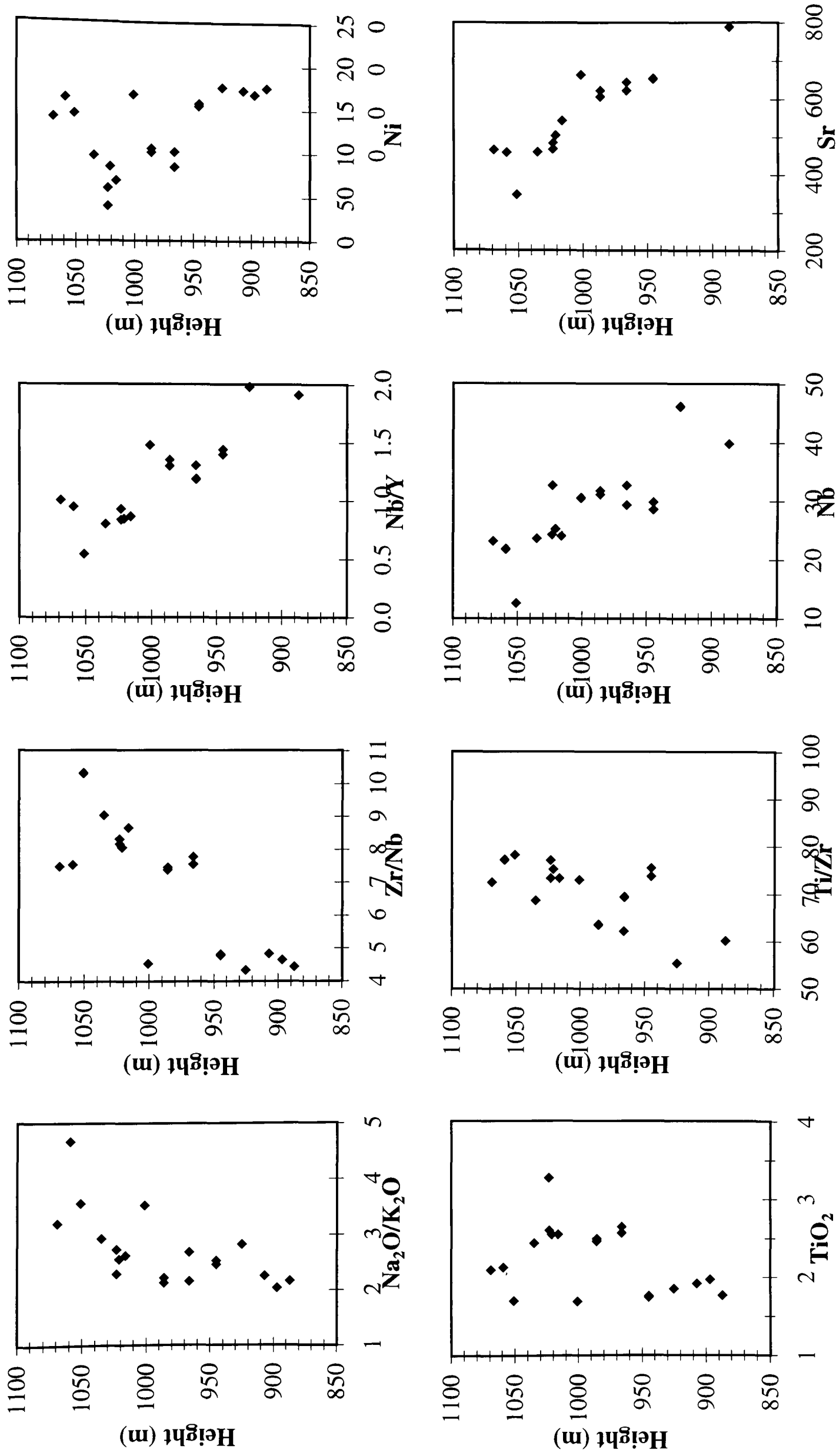


Figure 6.1c Up-sequence variation in lava composition with height above sea level at **Battleship Spur**.

Figure 6.2 Map of localities of analysed xenolith samples. ‘n.a.’ refers to other xenolith-bearing samples from the same locality.

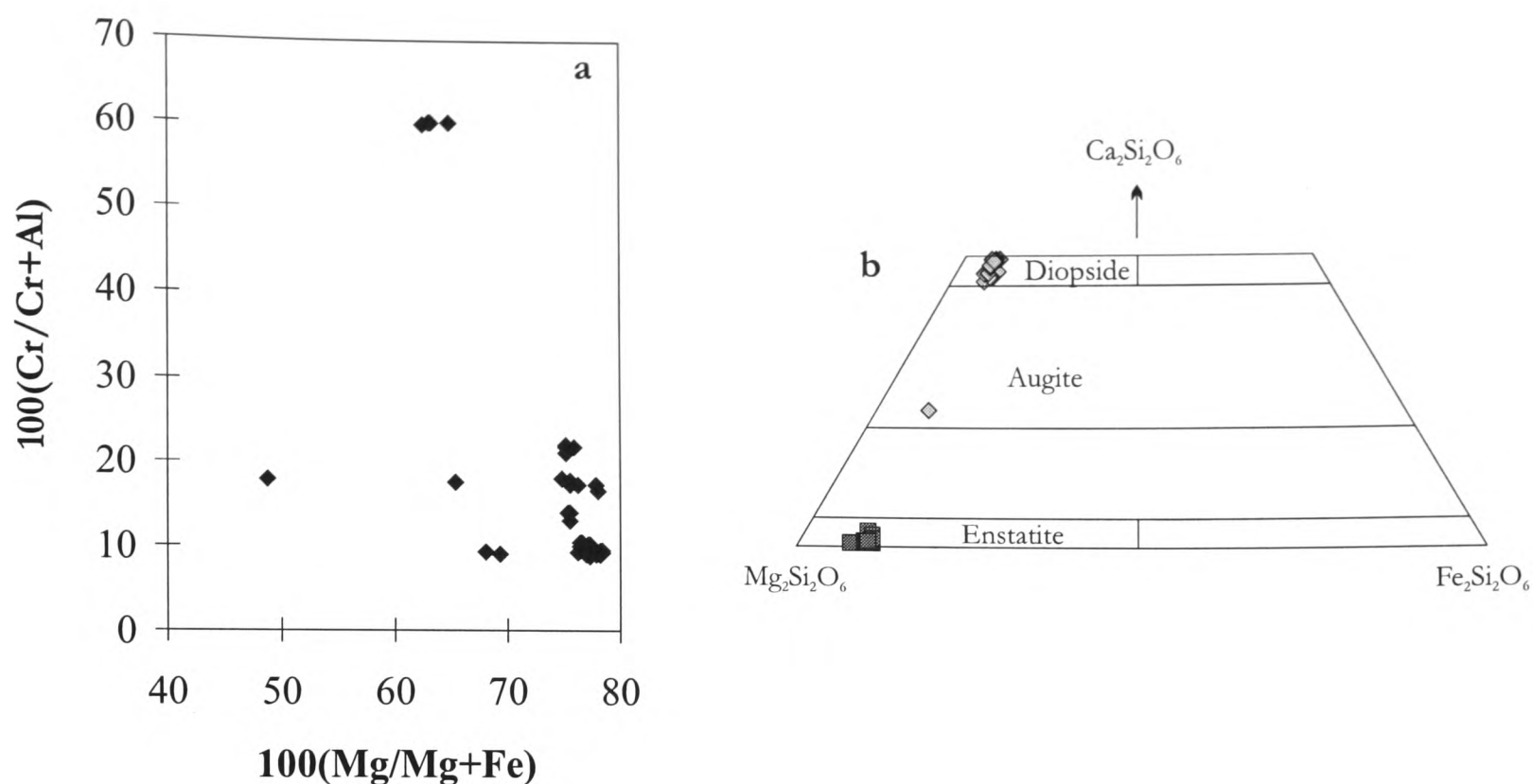


Figure 6.3 Plots to illustrate variation in the composition of spinel (a) and pyroxene (b) in the analysed lherzolites and harzburgite. The $100(\text{Cr}/\text{Cr}+\text{Al})$ value of spinel in the lherzolite lies between 9 and 21, while in the harzburgite (AJS113A) it is ~ 60 , typical of depleted peridotite. Clinopyroxenes (diamonds) and orthopyroxenes (plotted together for convenience) show little variation in composition, with the exception of one low-Ca clinopyroxene from sample AJS105N (see Table 6.2 for a full analysis). The composition of orthopyroxenes from the harzburgite have a slightly higher $100\text{Mg}/\text{Mg}+\text{Fe}$ value than do those from lherzolite.

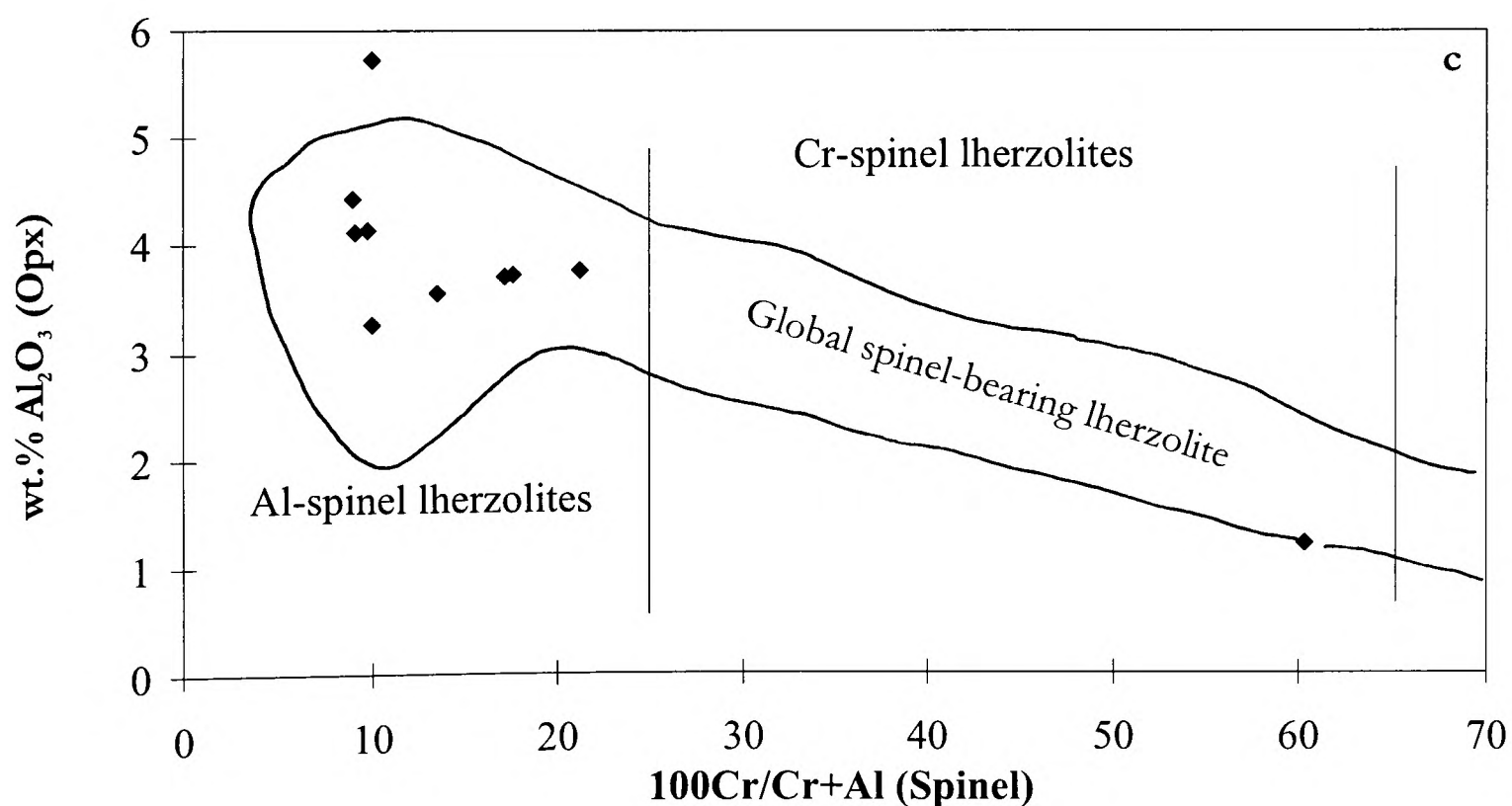


Figure 6.4 Plot of Al_2O_3 in orthopyroxene vs. $100(\text{Cr}/\text{Cr}+\text{Al})$ in coexisting spinel for the analysed Buckland lherzolites and harzburgite, together with the classification of Carswell (1980). Comparison is made with spinel-bearing lherzolites from around the world using the field of compositions from Carswell (1980). The harzburgite compositions (low- Al_2O_3 in orthopyroxene and high $100\text{Cr}/\text{Cr}+\text{Al}$ in spinel) are clearly similar to those from depleted lherzolite..

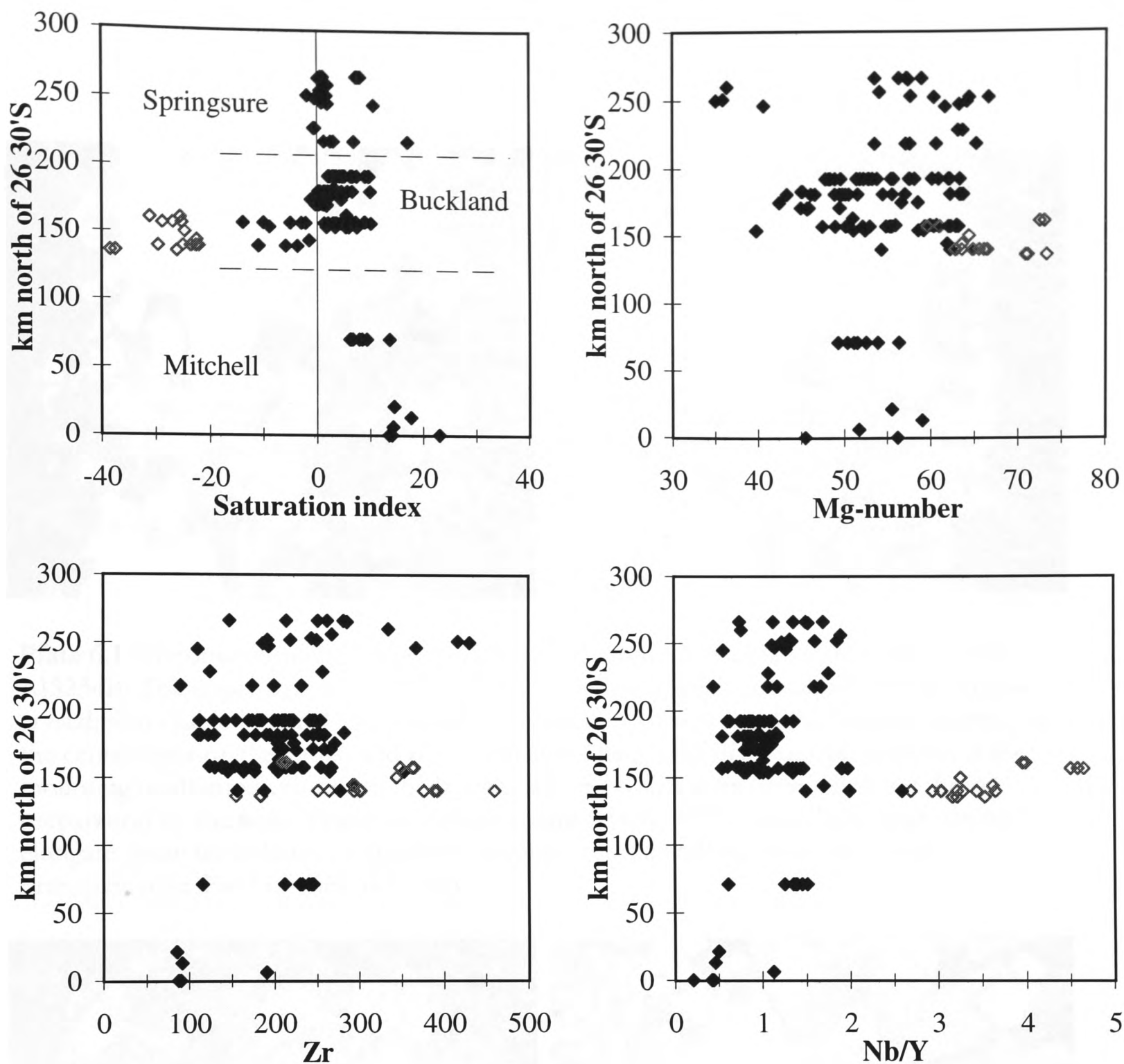


Figure 6.5 Plots showing variation of selected geochemical parameters throughout the field area. The y-axis is a measure of latitude, being distance north of Amby (see Figure 1.19 for location). 0km corresponds approximately to 26°30'S, 150km to 25°S and 250km to 24°S. The provinces are labelled in the first plot. Samples with a saturation index of <0 are nepheline normative. Basanites are shown as open diamonds, and all other lava types as filled diamonds

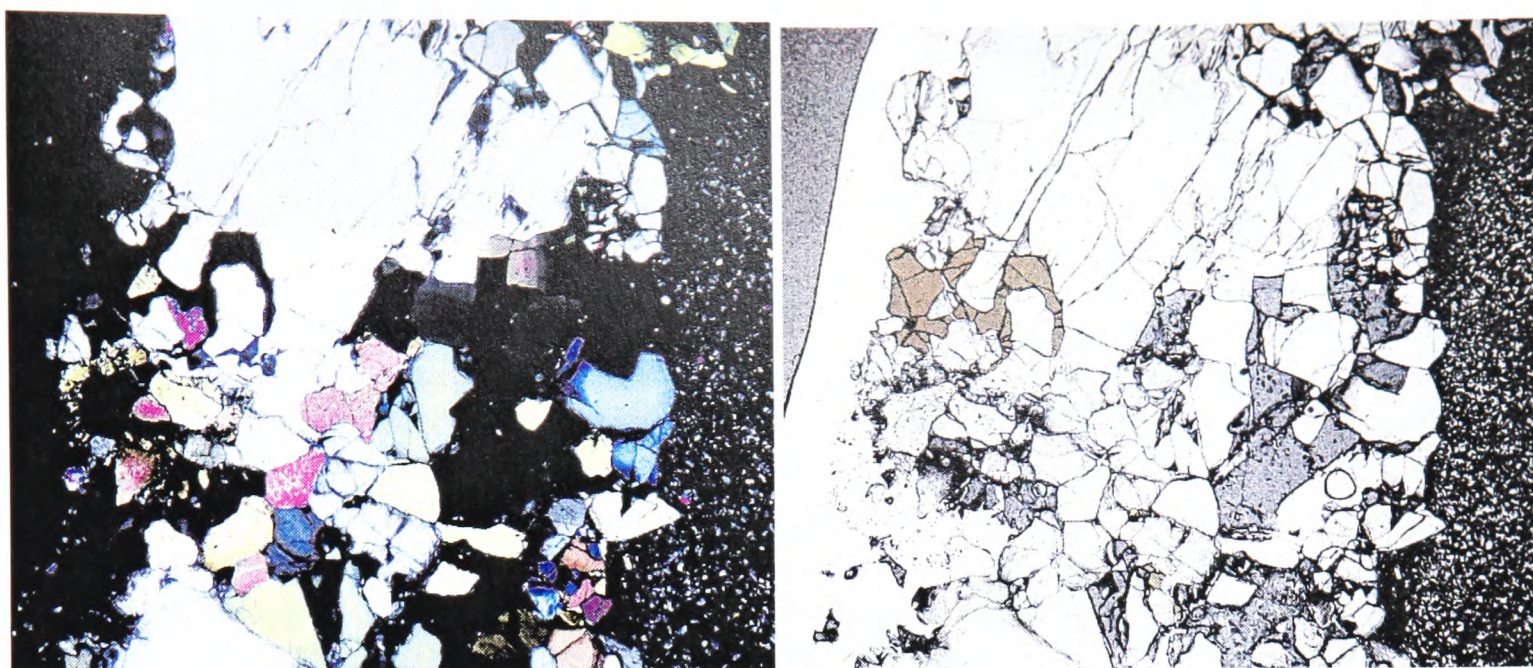


Plate 6.1 Photomicrographs of a typical lherzolite from the Buckland province (sample AJS234B). The upper part of the shots is dominated by a large, unstrained orthopyroxene crystal; also visible is spinel (brown in PPL, isotropic), olivine (e.g. kink-banded example in the centre-right of the shots) and clinopyroxene. The grey (PPL) isotropic material is the mounting medium which fills in the lacunae where crystals have been fallen out during preparation of the slide. Texture is coarse-equant (Harte, 1977) since the crystals are not elongate, grain boundaries are generally irregular-curved and spinel occurs within orthopyroxene. Field of view is 11mm.

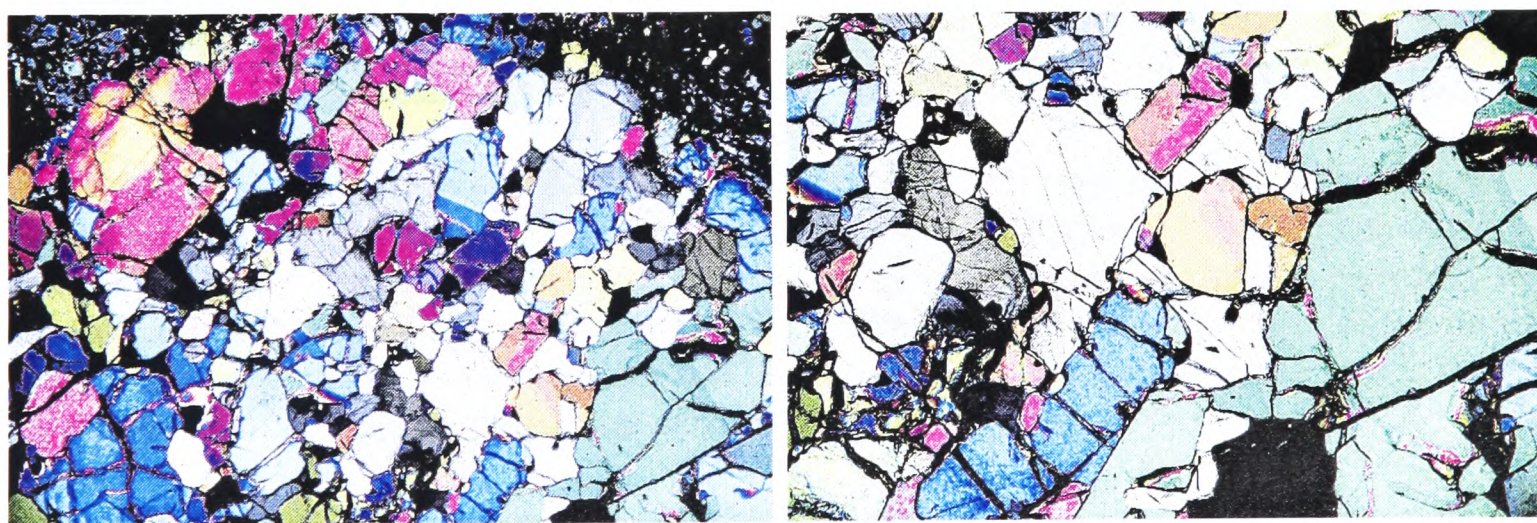


Plate 6.2 Photomicrographs in XPL showing the mineralogy and texture of the harzburgite sample AJS113: the second shot is a close up of the bottom right-hand corner of the first. Olivine crystals have moderate birefringence and several crystals are elongated, loosely defining a fabric from bottom-left to top-right.. Low-birefringence orthopyroxene crystals are also present, and in some instances (see the second photo) partially enclose olivine crystals. The sample also contains spinel and one tiny clinopyroxene crystal which are not visible in these photos. Field of view in the left-hand picture is 10mm across, while in the other it is 4.5mm.



Plate 6.3 Photomicrographs of the texture produced by the decompressive reaction between orthopyroxene and liquid. Note from the PPL shot that the pyroxene has a corroded upper margin, and that the reaction products appear to be aligned with the exsolution lamellae of the orthopyroxene. The innermost zone of reaction products is very fine-grained; the middle zone consists of olivine and clinopyroxene ~ 0.1 mm in size, while the outermost zone contains olivine of comparable composition to phenocrysts in the lava, and Fe-Ti oxide crystals of comparable size and distribution to those in the lava groundmass. Note the kink-banded olivine crystal on the right of the picture. Field of view is 2.5 mm.

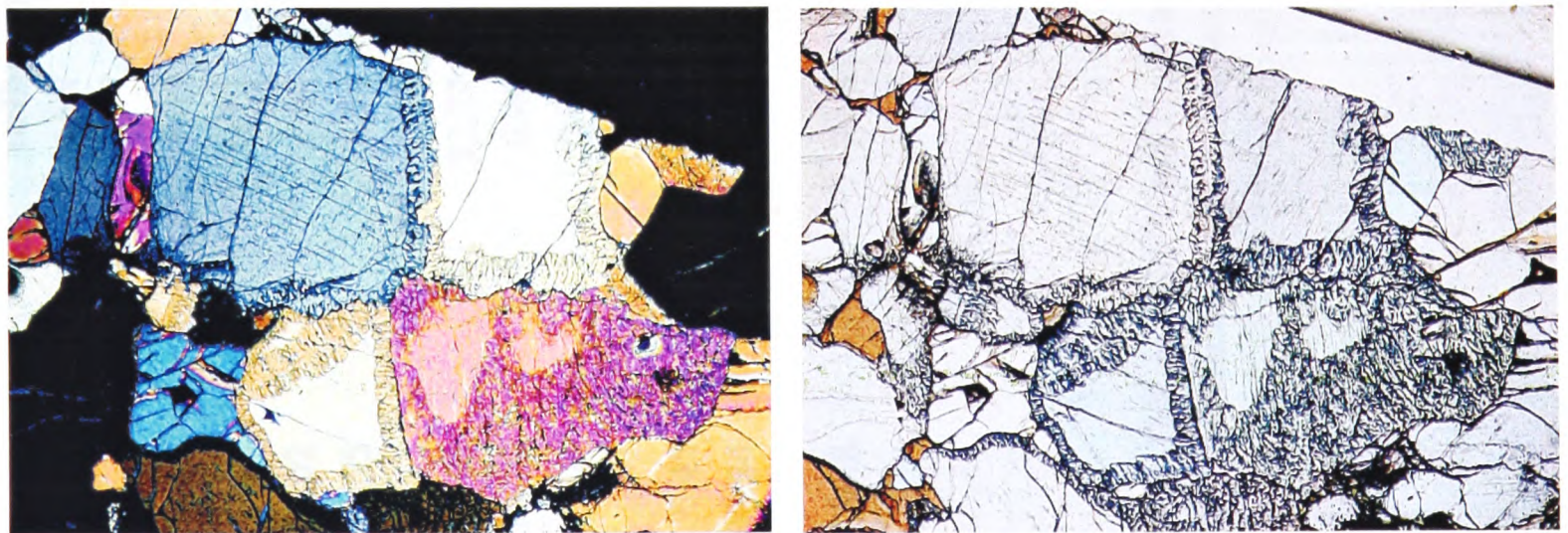


Plate 6.4 Photomicrographs in XPL and PPL from AJS105N showing four adjacent clinopyroxene crystals with 'spongy' borders. This texture is interpreted (e.g. Pike and Schwarzman, 1977) as a result of partial melting. Note the variation in width of the border, and that it is especially well developed in the lower right-hand crystal of the four which is presumably closer to the heat source (i.e. the host magma) than the other crystals. The upper left-hand crystal of the four is the low-Ca clinopyroxene discussed in the text, an analysis of which is given in Table 6.2. Field of view is 4 mm.

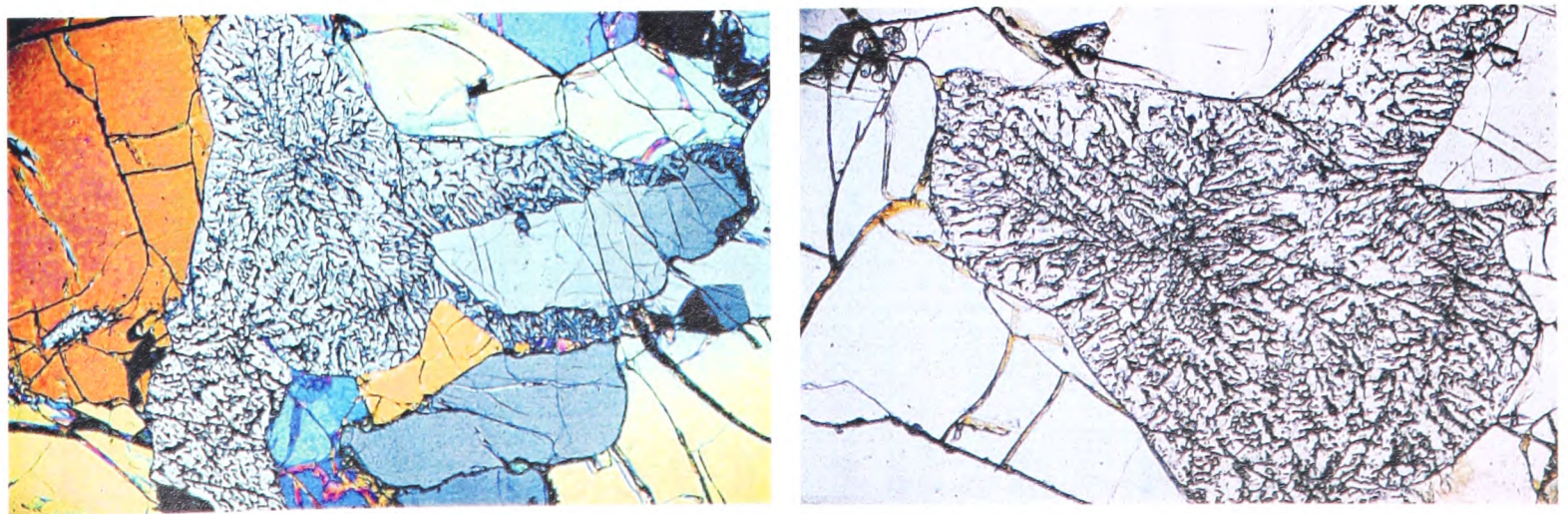


Plate 6.5 Photomicrographs of a low-birefringence augite from AJS28N which shows the same partial melting texture as the clinopyroxenes in Plate 6.4, albeit to a greater extent. The PPL shot is a close-up of the upper part of the XPL shot, rotated $\sim 45^\circ$ anti-clockwise. Fields of view are 4.5 mm (left-hand photo) and 2.5 mm.

Sample	olivine		clinopyroxene		orthopyroxene		Spinel	
	15N	113A	105N	105N	15N	113A	15N	113A
SiO ₂	40.73	41.15	52.30	54.12	55.05	57.46		
TiO ₂			0.53	0.32	0.11	0.02	0.11	0.06
Al ₂ O ₃			6.57	5.02	4.10	1.29	58.95	21.57
FeO(T)	10.47	8.24	2.49	4.55	6.59	5.16	10.71	15.28
MnO	0.10	0.11			0.18	0.14		
MgO	48.65	50.33	14.04	22.58	32.77	34.52	20.43	14.58
CaO	0.01	0.04	20.53	10.80	0.40	0.42		
Na ₂ O			2.03	1.00	0.04	0.06		
NiO	0.39	0.42					0.37	0.07
Cr ₂ O ₃			0.82	0.45	0.31	0.38	8.75	48.61
Total	100.35	100.29	99.31	98.84	99.55	99.45	99.32	100.17
Mg#	89.2	91.6	91.0	89.8	89.9	92.3	77.3	63.0
Cr#							9.1	60.2

Table 6.2 Some typical mineral compositions from Iherzolites 15N and 105N and Harzburgite 113A, allowing comparison to be made between the two rock types. Olivines and orthopyroxenes from the Harzburgite have higher Mg# values but lower Al₂O₃ (orthopyroxene), while spinels have much higher Cr#. The two clinopyroxene analyses from 105N are for a typical Cr-diopside and a rare low-Ca example. Mg# = 100 * Mg / (Mg + Fe) and Cr# = 100 * Cr / (Cr + Al).

Chapter 7: Conclusions

This chapter summarises the conclusions of the previous chapters, and integrates them into existing models for the development of Cainozoic volcanism in eastern Australia. Suggestions for future work are also made.

7.1 SUMMARY

1. Analysed samples from the Buckland province show a wide range of mafic compositions, ranging from magnesium-rich basanites to evolved trachybasalts and basaltic andesites. There is a continuous spread in silica saturation from nepheline- to quartz-normative compositions.
2. The most primitive basanites (the 12+ group) typically have lower SiO_2 and $\text{Fe}_2\text{O}_3\text{T}$ concentrations than the other examples, and contain lower abundances of incompatible trace elements. They are interpreted as near-primary mantle melts owing to their high mg-numbers (71-73), and could not represent the products of olivine accumulating in the less primitive (9-12 group) basanites. Isotopic and trace element data suggest that their source involved a HIMU-type arc component, although more Pb-isotope data are required to confirm this. Models for the generation of HIMU material involve hydrothermally-altered subducted slabs which require isolation in the asthenosphere for their characteristic isotopic composition to mature. The history of subduction-accretion events in the Palaeozoic-Mesozoic history of eastern Australia means that such material could have been present beneath the Buckland province during the Cainozoic.
3. Other basanites, which contain 9-12% MgO, show greater variation in major element geochemistry than the more mafic 12+ group. They have similar spidergrams, but a more enriched Sr-Nd signature which overlaps with the composition of shallow asthenosphere-derived lava field provinces from elsewhere in Queensland. Lherzolite xenoliths found in the lavas indicate that these lavas did not reside for a significant amount of time in the crust, since they would have settled out from the magma owing to their size and density. Comparison with sparse experimental data indicates that they probably result from the melting of lherzolite in the presence of volatiles. Previous workers note that production of basanitic melts requires $X^{\text{CO}_2} \geq 0.5$.
4. Major element compositions of primitive alkali basalts (from Buckland) and olivine tholeiites (from Springsure) were recalculated for olivine extraction to bring them into equilibrium with mantle peridotite. These adjusted compositions are consistent with generation by the adiabatic melting of four-phase lherzolite whose potential temperature lies in the range 1410-1500°C, with segregation

taking place between ~30-20 kbar (100-60 km depth). In terms of isotope and trace element geochemistry they are indistinguishable from OIB and overlap with the 'plume' field of Sun *et al.* (1989). The data do not rule out the possibility of some lithospheric or crustal interaction.

5. Relatively evolved basaltic compositions (2.5-9% MgO) are dominant in the Buckland province, and are divided petrographically into aphyric, olivine-phyric and megacryst-bearing groups. Megacrysts are compositionally identical to cognate lower crustal megacrysts in other central-southeastern Queensland provinces. These petrographically-defined groups show complete geochemical overlap, and are interbedded with each other throughout the province, and are thus interpreted as cogenetic. Their geochemistry has been successfully modelled by AFC processes, involving the extraction of plagioclase + clinopyroxene + orthopyroxene in the approximate proportions 36:33:31, with contamination by granodioritic and pelitic assimilants, although the involvement of another 'intermediate' composition used in the modelling cannot be ruled out. The effect of the pelitic assimilant is only recognised in lavas from the upper levels of lava sequences, suggesting the initiation of a new magma chamber, or the growth of a pre-existing one towards the end of the extrusive event. These fractionation processes are considered to take place at lower crustal conditions, owing to the compositions of the megacrysts, and due to the fact that orthopyroxene crystallises instead of olivine. Minor upper-crustal fractional crystallisation is indicated by the olivine-phyric lavas.
6. Comparison with similarly evolved basaltic lavas from the neighbouring provinces of Springsure and Mitchell suggests that they underwent similar AFC processes. Megacrysts are rarer in Springsure lavas than in Buckland, while porphyritic types are more abundant. This points to a more important role for high-level AFC processes in the petrogenesis of the Springsure lavas. A further variation is seen in Mitchell where an olivine megacryst has been retrieved and lavas from the northern part of the province show strong geochemical similarity to Buckland lavas 70km to the north (although they are poorer in Al_2O_3). The major element geochemistry of these lavas can be modelled by AFC of olivine + plagioclase + clinopyroxene from the same 'parental' composition as many of the Buckland lavas. Middle-lower crustal fractionation is implied by the presence of olivine and plagioclase as megacrysts, although the occurrence of olivine in the extract suggests that fractionation took place at a slightly lower pressure than in Buckland.
7. Mildly silica-oversaturated compositions from south Mitchell are very incompatible element-poor compared to lavas from the other provinces, and have distinctive isotopic compositions (radiogenic Sr and Pb). They are interpreted as the product of higher-degree melting at lower pressures than Buckland and Springsure lavas, while subsequent interaction with arc-related lithosphere/crust

accounts for their isotopic composition. Owing to their low abundances of Pb, Rb and Sr, dramatic changes in isotopic ratios can be effected with relatively low degrees of contamination.

7.2 INCORPORATION INTO MODELS FOR VOLCANISM IN EASTERN AUSTRALIA

In this section the findings of the previous chapters are compared with the models advanced by previous workers for volcanism in eastern Australia, which were summarised in Chapter 1.

The lava compositions and models for petrogenesis are clearly consistent with the four component model of Sun *et al.* (1980):

1. The plume component is recognised in the basalts of the 9-12 group which were generated by decompressional melting of anomalously hot (i.e. above 1280°C) asthenospheric material. Isotopic compositions overlap with other least-fractionated central volcano types which have been used to constrain the composition of the plume.
2. The component from the shallow asthenosphere is recognised in the basanites which appear to be slightly older than the plume-generated basalts, and overlap isotopically with lava field extrusives which show no consistent pattern in space and time, leading to the conclusion that they derive from the upper asthenosphere. The 12+ group appears to represent an unusual HIMU-type component from the shallow asthenosphere, which is plausibly a relic from Palaeozoic subduction in eastern Australia.
3. The lithospheric component is not readily recognised in the Buckland province. One sample from Springsure has anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ for its $^{143}\text{Nd}/^{144}\text{Nd}$ (0.703990 and 0.512899), overlapping the field of lavas from northern Queensland which have interacted with subduction-modified lithosphere. A lithospheric component has also been invoked to explain the isotopic characteristics (Sr-Nd-Pb) of mildly-saturated lavas from south Mitchell. These show similarities to isotope values shown by arc-related volcanics in the Tonga-Kermadec islands.
4. Most of the Buckland lavas, as well as those from Springsure and Mitchell, show clear geochemical and isotopic evidence for the effects of AFC in the crust. These processes are clearly polybaric, as demonstrated by the occurrence of both megacrysts and phenocrysts. Buckland lavas seem to have fractionated predominantly in the lower crust as phenocrysts are rare. Springsure lavas, by contrast, show more evidence of crystal-liquid fractionation in the upper crust where phenocrysts of olivine + plagioclase + clinopyroxene are more common.

Observations from the Buckland province show that it is typical of central-southeastern Queensland central volcano provinces whose characteristics were described and interpreted by Ewart *et al.* (1980). They provided evidence for considerable fractional crystallisation $\pm$ assimilation in the lower

crust where ascending plume-derived magmas ponded. The consequent underplating of basaltic material (deduced from seismic evidence and in xenolith assemblages) resulted in the uplift of the provinces, thus explaining their elevated topography.

7.3 FUTURE WORK

Clearly the conclusions which have been drawn about the petrogenesis of lavas in this study can be further investigated and substantiated with more analytical work. Further Pb-isotope work on the 12+ group could confirm their apparently HIMU-like isotopic composition. The comparison of the 9-12 group basalts with experimental melts could clearly be improved by using more lava samples, and REE studies to constrain degrees of melting. The AFC modelling of the evolved lavas requires substantiation with isotopic work, although this can be subject to error in the absence of exact compositions of the crust beneath the province, and because the crust is isotopically heterogeneous. The exact nature of the phase equilibria in the lower crustal magma chambers requires more constraint, perhaps using new experimental data or melting studies on Buckland lavas. More constraints on basanite formation await the publishing of experimental work on CO₂-bearing peridotites in the same detail as work on anhydrous samples.

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Appendix A: Sample localities

Localities of analysed samples are detailed below. Grid references are taken from the Australian 1:100,000 national topographic maps, where the initial four-figure number refers to the map sheet and the following six-figure number the position on the map. B, S, NM & SM refer to the province Buckland, Springsure or Mitchell (North and South) from which the sample was taken, and felsic, <9, 9-12 and 12+ the geochemically-defined group to which it belongs (see Chapter 2). At sections such as Battleship Spur, grid references are given for the ends of the section and heights (in metres a.s.l.) for each sample.

Sample	Province	Group	Reference		Location
1	B	<9	8547/153303	1069m	Battleship Spur
4	B	<9		1051m	“
6	B	<9	8547/176298		“
7	B	<9		1059m	“
8	B	<9		1035m	“
10	B	<9		1023m	“
11	B	<9		1016m	“
12	B	<9		986m	“
13	B	<9		966m	“
14	B	<9	8547/153300	945m	“
15	B	<9	8547/179301		Boowinda Creek
18	B	<9	8448/898440		Dooloogorah
19	B	<9	8447/981209		Mt Mcleay
20	B	12+	8447/906029		Mt. Ogilvie
21	B	12+	8447/906029		“
27	B	12+	8447/836009		Mt. Eddystone
35	B	<9	8448/668360		Mt. Emily
39	B	9-12	8447/661333		Bally Lethbridge
42	B	<9	8447/991270		Mt. Observatory
44	B	<9	8547/052281		Mt. Moffatt
50	B	<9	8547/052281		“
52	B	<9	8547/052281		“
54M	B	<9	8547/052281		“
59	B	<9	8448/952462		nr. Mt Sugarloaf
62	B	<9	8448/879515		“
63	B	<9	8448/888526		“
64	B	<9	8448/922532		“
73	B	<9	8448/757614		near Carnarvon
74	B	<9	8448/757614		“
77	B	<9	8448/802568		Rocky Crossing
78	B	<9	8448/851278	961m	Carnarvon section
79	B	<9		967m	“

Appendix A			Sample localities		
80	B	<9		970m	Carnarvon section
81	B	<9		970m	“
83	B	<9		948m	“
84	B	<9		954m	“
85	B	<9		990m	“
86	B	<9		1001m	“
87	B	<9		1012m	“
88	B	<9		1021m	“
89	B	<9		1028m	“
90	B	<9		1039m	“
91	B	<9		1044m	“
92	B	<9		1051m	“
97	B	<9		1095m	“
98	B	<9	8448/867586	1100m	“
99	B	9-12	8447/526110		Buradoo
100	B	9-12	8447/559126		Mt Tabor area
101	B	9-12	8447/559126		“
102	B	9-12	8347/490133		“
104	B	9-12	8347/500144		“
106	B	9-12	8347/500144		“
107	B	<9	8347/501143		“
108	B	9-12	8347/501143		“
110	B	<9	8447/535141		“
111	B	9-12	8447/535141		“
112	B	9-12	8447/535141		“
113	B	9-12	8447/535141		“
117	B	<9	8547/069324		near Mt Percy
118	B	<9	8547/070329		“
120	B	<9	8547/068327		“
121	B	<9	8547/168326		“
126	B	9-12	8547/109211		Mt Eden
127	SM	<9	8544/146655		Amby Quarry
129	SM	<9	8545/136695		New Quarry
131	SM	<9	8544/146655		Amby Quarry
135	SM	<9	8545/055752		The Peaks
138	SM	<9	8545/099828		The Gap
141	SM	<9	8545/037915		Westwood
142	S	<9	8549/225208		Rolleston Road
143	S	9-12	8549/211209		“
144	S	9-12	8549/211209		“
145	S	<9	8549/185215		“

Appendix A				Sample localities	
146	S	<9	8549/179219		Rolleston Road
148	S	<9	8549/152245		“
150	S	<9	8549/123303		“
152	S	<9	8449/985333		just off the Tambo Road
155	S	<9	8450/906470		Mt Walleroo
157	S	<9	8450/906470		“
161	S	<9	8450/906470		“
162	S	<9	8450/906470		“
164	S	<9	8450/913463		“
165	S	<9	8450/913459		“
167	S	9-12	8449/922299		Tambo Road
168	S	9-12	8449/948308		“
173	S	<9	8549/183999		Mt Catherine
174	S	<9	8549/183999		“
175	S	9-12	8549/181997		“
176	S	<9	8549/180996		“
177	S	<9	8549/181993		“
178	B	<9	8549/194005		“
181	B	<9	8448/909693		Vandyke
182	S	9-12	8549/072184		N of Heathfield
183	S	<9	8549/103253		near Rainworth Fort
184	S	felsic	8549/138380		Dilly Pinnacle
185	S	felsic	8549/138380		“
188	S	<9	8549/140378		near Dilly Pinnacle
189	S	felsic	8549/123395		near Level crossing
195	B	<9	8448/906705	919m	Vandyke
197	B	<9		944m	“
198	B	<9		936m	“
199	B	<9		926m	“
200	B	<9		912m	“
201	B	<9		906m	“
202	B	<9		898m	“
203	B	<9		885m	“
204	B	<9		880m	“
205	B	<9		874m	“
206	B	<9		866m	“
207	B	<9		858m	“
208	B	<9		858m	“
209	B	<9		851m	“
210	B	<9		846m	“
211	B	<9		841m	“

Appendix A				Sample localities	
212	B	<9		821m	Vandyke
213	B	<9		815m	“
214	B	<9		811m	“
215	B	<9		803m	“
216	B	<9		771m	“
217	B	<9		771m	“
218	B	<9	8448/893709	771m	“
219	S	felsic	8549/089359		Mt Zamia
220	S	felsic	8549/089359		“
221	S	felsic	8549/083362		“
224	S	<9	8549/142330		northeast of Springsure
226	S	felsic	8549/126447		Red Hill
228	S	<9	8549/326143		39 km west of Rolleston
232	B	9-12	8547/160300	887m	Battleship Spur
233	B	<9		897m	“
234	B	<9		907m	“
235	B	9-12		925m	“
236	B	9-12		945m	“
238	B	<9		966m	“
239	B	<9		986m	“
240	B	<9		1001m	“
241	B	<9		1021m	“
242	B	<9	8547/154301	1023m	“
246	B	<9	8448/007456		Mt Rugged
248	B	<9	8448/006457		“
252	B	<9	8448/006457		“
253	B	<9	8448/005458		“
255	B	<9	8448/005458		“
256	B	<9	8448/005458		“
261	S	<9	8449/958411		Bimbenang Peak
262	S	<9	8449/958411		“
R1	B	12+	8548/394381		Rewan
R2	B	12+	8548/394381		“
W1	NM	<9	8546/258423		Womblebank Gap
W2	NM	<9	8546/257424		“
W3	NM	<9	8546/256425		“
W4	NM	<9	8546/254425		“
W6	NM	<9	8546/254425		“
W7	NM	<9	8546/262454		“
W8	NM	<9	8546/262443		“

Appendix B: Whole-rock analyses

B.1 XRF MACHINE SPECIFICATION AND OPERATING CONDITIONS

Major and trace element analyses were performed on 153 samples using a Phillips PW1400 X-ray fluorescence wavelength-dispersive spectrometer at the Department of Earth Sciences, Oxford. X-rays were generated using an Rh tube, and diffracting crystals of LiF (220), LiF (200), PE and PX1 were used. Calibration was made using international geostandards. Major element corrections were made using De Jongh's formula within the Phillips X14 software package. 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.

B.2 SAMPLE PREPARATION

B.2.1 Major elements

Major elements were analysed using fused glass beads. Rock powder was heated to 110°C overnight to drive off non-structurally bound H₂O (e.g. atmospheric), and at 1000°C for a further night to remove structurally bound H₂O and other volatiles (e.g. from alteration). Weight loss on ignition (LOI) was calculated using the change in mass resulting from the two heatings. 1g of powder was mixed with 5g of the flux Spectroflux 100B (LiBO₄) in a zirconia-grained, Pt-5%Au alloy crucible, mixed and heated for seven and a half minutes at 1200°C. The mixture was swirled after two and a half and five minutes, and then again before pouring into a pre-warmed Pt-Au casting mould and quenching with a jet of cold air.

B.2.2 Trace elements

Trace element analysis was performed using pressed powder pellets. 10g of rock powder was mixed with 1ml of *moviol* glue (5% aqueous solution of poly-vinylacetate) using a pestle and mortar, placed in a hydraulic piston and subjected to 6 tonnes for 30 seconds. The resultant pellet was then dried at 60°C overnight.

B.3 ERRORS

Together with a full explanation of XRF analysis, Potts (1987) discusses potential errors. This section considers lower limits of detection, precision and accuracy.

B.3.1 Lower limits of detection

XRF measurements are based on the X-ray count rates at the relevant X-ray lines. The counting peak for a chosen element must be resolvable from the background radiation, which requires that the counting time be sufficiently long or the element concentration sufficiently high. The 'limit of

determination', as defined by Potts (1987), is the lowest concentration which can be quantitatively determined at the operating conditions of the machine, and is dependent on the count rate and rock composition. He provides limits of determination for a range of rock types (including basaltic rocks) at typical routine operating conditions. These are given below (Table B.1) as weight % for major elements (Bletcher, 1997) and ppm for trace elements.

Element/oxide	detection limit (wt. % or ppm)
SiO ₂	0.032
TiO ₂	0.001
Al ₂ O ₃	0.078
Fe ₂ O ₃ T	0.004
MnO	0.001
MgO	0.075
CaO	0.012
Na ₂ O	0.233
K ₂ O	0.021
P ₂ O ₅	0.031
Ga	6
Zn	9
Cu	6
Ni	6
Co	6
Cr	10
V	10
Ba	24
Rb	3
Sr	3
Y	3
Zr	6
Nb	6
Pb	6
Th	9
U	6

Table B.1 Detection limits for wavelength-dispersive XRF analyses from Potts (1997) with modifications by Bletcher (1997). Those for major elements (based on glass beads) are given in weight %, and those for trace elements (based on powder pellets) in ppm.

B.3.2 Precision

This refers to the reproducibility of an analysis, and is quantified by some measure of variation. Precision of XRF analysis is typically very good (Potts, 1987), and this has been shown to be the case for the instrument at Oxford by Bletcher (1997). Table B.2 (below) shows a mean analysis for a sample from Argent (1995), together with coefficients of variation (CV%=100 x standard deviation/mean analysis) calculated using ten replicate analyses.

Element/oxide	Mean analysis	CV%
SiO ₂	64.70	0.07
TiO ₂	0.65	0.34
Al ₂ O ₃	16.04	0.10
Fe ₂ O ₃ T	4.03	0.15
MnO	0.06	1.10
MgO	2.21	0.85
CaO	3.84	0.16
Na ₂ O	4.12	0.49
K ₂ O	3.19	0.14
P ₂ O ₅	0.16	1.15
Total	99.01	
Ga	20.6	1.5
Zn	62.3	1.2
Cu	21.1	3.8
Ni	36.2	1.7
Co	23.3	9.4
Cr	54.4	3.4
V	72.1	2.4
Ba	1138.3	0.6
Rb	62.7	0.6
Sr	715.7	0.3
Y	12.6	4.5
Zr	174.4	0.3
Nb	12.6	4.1
Pb	21.1	4.5
Th	6.4	4.8
U	b.l.d	

Table B.2 Precision of the Oxford XRF machine, showing coefficients of variation for data from a sample that was analysed ten times (unpublished data, Argent, 1995). b.l.d = below limit of detection.

B.3.3 Accuracy

This is a measure of the closeness of analysis to its ‘true’ (i.e. international consensus) value. Since the consensus values for international rock standards are based on compilations from numerous laboratories, rather than the true values, the accuracy of results from a given source is only an estimate. A measure of the accuracy of the Oxford machine was made by Bletcher (1997) using analyses of a range of geostandards and comparing them with the consensus values of Gladney *et al.* (1983). The accuracy is given by the mean of relative deviation of an analysis from the consensus value, such that $RD\% = 100 \times (\text{measured} - \text{consensus}) / \text{consensus}$, and is shown in Table B.3. There is good comparison between the mean RD% of the Oxford spectrometer and the CV% of the data from Gladney *et al.* (op. cit.) indicating that they show similar amounts of uncertainty. The latter indicates the variation in the consensus composition of a widely used georeference which is used in turn to determine machine accuracy.

Element/oxide	Oxford XRF mean RD%	Gladney <i>et al.</i> AGV-1	CV%
SiO ₂	0.22	59.25	0.49
TiO ₂	2.08	1.06	2.40
Al ₂ O ₃	0.83	17.15	0.99
Fe ₂ O ₃ T	0.90	6.76	2.80
MnO	1.70	0.10	4.20
MgO	1.41	1.53	3.30
CaO	1.39	4.94	1.40
Na ₂ O	1.73	4.25	1.40
K ₂ O	1.18	2.90	1.70
P ₂ O ₅	2.51	0.48	3.10
Total		98.42	
Ga	1.41	20	7.5
Zn	2.43	88	1.1
Cu	15.12	60	5.0
Ni	3.10	17	12
Co	13.16	15	4.0
Cr	12.39	12	13
V	3.04	123	4.8
Ba	4.79	1221	0.7
Rb	3.06	67	0.7
Sr	2.63	662	0.7
Y	8.97	12	14
Zr	4.86	225	4
Nb	6.68	15	10
Pb	10.98	36	6.9
Th	2.14	6.5	2.8
U	b.l.d	1.9	6.6

Table B.3 Table illustrating the accuracy of the XRF technique. Mean RD% calculated for the Oxford spectrometer calculated by Bletcher (1997) from analyses of geostandards BHVO-1, BR, G-2, SiO₂, SY-2 (major elements) and AGV-1, BCR-1, DTS-1, G-1, G-2, W-1 (trace elements) using unpublished data from Parish (1995) and Haynes (1995). The data from Gladney *et al.* (1983) is a consensus value derived by compiling analyses of AGV-1 from different techniques and laboratories.

B.4 DATA

The full XRF analyses are presented in the following pages. Major element concentrations are expressed as weight %, and trace element concentrations as parts per million. Note that iron is given totally as Fe₂O₃.

	AJS 1	AJS 4	AJS 6	AJS 7	AJS 8	AJS 10	AJS 11	AJS 12	AJS 13	AJS 14	AJS 15	AJS 18	AJS 19	AJS 20	AJS 21	AJS27	AJS 35
SiO ₂	50.79	51.10	50.20	48.75	49.32	49.22	50.02	50.41	50.37	47.39	46.31	49.39	50.42	41.53	41.28	42.41	49.38
TiO ₂	2.11	1.70	2.79	2.13	2.43	2.59	2.55	2.45	2.63	1.76	1.98	2.57	2.22	2.36	2.40	2.31	3.04
Al ₂ O ₃	14.88	14.75	15.72	15.17	15.27	16.25	16.27	16.06	15.83	14.94	15.17	16.56	15.43	11.88	11.75	12.00	16.59
Cr ₂ O ₃	0.04	0.04	0.02	0.04	0.02	0.01	0.01	0.02	0.02	0.04	0.03	0.01	0.04	0.05	0.05	0.07	0.00
Fe ₂ O ₃ T	11.82	11.97	12.26	12.22	12.47	12.63	12.17	11.33	11.67	12.43	11.90	12.64	10.78	12.40	12.79	12.29	12.99
MnO	0.15	0.15	0.13	0.16	0.15	0.12	0.13	0.13	0.14	0.17	0.15	0.17	0.14	0.18	0.19	0.17	0.15
MgO	7.68	7.45	5.03	8.62	6.62	6.07	5.67	5.99	5.62	8.76	7.94	5.62	7.47	13.08	13.29	14.43	3.65
CaO	8.17	8.44	8.15	8.46	8.14	7.46	7.74	7.26	7.55	9.22	6.95	7.92	7.57	11.26	11.47	10.61	5.83
Na ₂ O	3.55	3.06	3.81	3.32	3.54	3.53	3.69	3.72	3.48	3.33	5.52	3.36	3.79	4.83	4.83	3.97	5.23
K ₂ O	1.11	0.86	1.32	0.71	1.20	1.28	1.40	1.74	1.61	1.35	2.54	1.27	2.10	1.55	1.52	1.13	2.41
P ₂ O ₅	0.39	0.25	0.61	0.33	0.49	0.49	0.52	0.51	0.60	0.47	0.95	0.44	0.61	0.92	0.93	0.80	0.88
Total	100.69	99.77	100.04	99.91	99.65	99.65	100.17	99.62	99.52	99.86	99.44	99.95	100.57	100.04	100.50	100.19	100.15
LOI	0.50	0.81	1.11	0.90	1.52	2.36	1.78	2.04	1.60	1.58	2.91	0.50	1.72	1.32	1.31	0.78	0.99
Ga	21.2	22.4	25.7	20.6	23.8	24.9	23.9	24.9	24.2	23.2	29.1	25.0	23.7	19.8	19.5	18.8	27.7
Zn	116.1	98.0	125.9	116.8	109.3	118.0	111.6	103.4	128.5	92.9	140.6	122.2	102.9	100.1	100.5	108.8	139.1
Cu	34.4	47.2	32.6	32.0	31.5	28.0	32.2	32.4	25.4	68.2	35.4	30.2	37.6	70.1	67.7	57.9	26.9
Ni	141.5	145.5	78.1	163.7	97.1	60.1	68.5	105.6	84.0	154.3	184.6	64.9	125.9	302.6	314.2	402.4	24.4
Co	45.8	45.3	52.7	53.6	44.7	42.1	49.8	43.6	44.9	48.6	47.7	41.1	43.9	64.2	65.0	73.5	40.7
Cr	232.7	227.8	88.5	270.4	119.1	22.0	31.4	96.4	123.1	197.8	178.1	33.9	177.2	319.8	331.5	451.9	8.7
V	150.2	157.7	139.0	104.6	147.2	138.6	134.9	119.6	120.1	127.9	86.5	143.6	128.2	187.8	190.5	171.4	108.0
Ba	193.3	172.2	295.1	183.7	236.3	236.0	263.7	312.2	279.2	254.3	249.3	222.1	426.1	397.4	396.6	398.1	477.9
Rb	20.5	25.7	26.3	8.3	22.5	22.7	22.9	30.9	27.7	24.4	16.8	22.4	39.6	15.8	16.8	23.1	38.5
Sr	465.7	346.0	462.1	458.3	460.3	484.5	544.3	605.8	645.2	655.2	1127.1	571.7	572.9	990.5	978.9	1254.3	615.5
Y	23.1	23.2	30.9	23.1	29.6	29.1	27.9	24.0	27.5	21.4	16.7	26.9	24.3	21.9	22.0	18.6	33.6
Zr	173.7	130.1	219.6	165.2	213.1	202.0	208.7	232.4	254.4	143.0	364.4	205.2	292.5	184.2	183.3	154.7	352.7
Nb	23.2	12.6	28.8	21.9	23.6	24.3	24.1	31.2	32.7	29.9	75.4	27.4	41.6	70.6	69.8	65.8	45.6
Pb	1.5	0.9	1.1	1.2	1.8	2.8	1.6	n.d.	1.4	1.5	4.1	2.7	2.1	3.4	3.1	3.1	5.9
Th	2.7	2.5	3.5	1.5	2.4	3.2	1.1	2.7	4.7	3.8	5.6	6.1	3.3	6.7	6.4	5.0	5.5
U	0.3	1.5	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	n.d.	1.4	2.6	0.7	0.8	n.d.	3.2	2.2	0.4
	AJS 39	AJS 42	AJS 44	AJS 50	AJS 52	AJS 54M	AJS 59	AJS 62	AJS 63	AJS 64	AJS 73	AJS 74	AJS 77	AJS 78	AJS 79	AJS 80	AJS 81
SiO ₂	44.09	51.38	51.14	51.88	51.22	49.91	50.06	48.01	49.39	48.99	50.47	50.38	49.10	47.89	47.95	50.49	50.29
TiO ₂	2.02	1.90	2.22	2.03	1.84	3.02	2.63	3.13	2.53	2.45	2.86	2.73	1.69	3.15	3.18	2.38	2.38
Al ₂ O ₃	13.00	15.42	15.97	15.89	15.00	15.85	16.17	15.84	16.23	15.32	16.43	15.84	15.17	15.95	15.98	15.99	15.99
Cr ₂ O ₃	0.05	0.03	0.04	0.04	0.05	0.01	0.02	0.00	0.01	0.03	0.01	0.02	0.04	0.00	0.00	0.02	0.02
Fe ₂ O ₃ T	13.28	11.36	11.59	11.72	11.91	13.27	12.76	14.34	11.98	12.14	12.59	12.82	11.55	14.09	14.06	11.79	11.46
MnO	0.20	0.15	0.14	0.12	0.14	0.13	0.13	0.17	0.13	0.15	0.13	0.15	0.15	0.16	0.16	0.14	0.13
MgO	10.28	7.05	5.47	5.23	7.20	3.76	4.59	4.53	6.68	7.31	4.41	4.51	8.67	5.15	5.25	6.29	5.86
CaO	9.16	7.74	8.39	8.90	9.00	7.19	8.51	7.48	7.52	7.73	6.93	8.07	8.60	7.28	7.03	7.75	7.88
Na ₂ O	4.70	3.64	3.86	3.51	3.35	4.18	3.74	3.99	3.41	3.50	4.03	3.76	3.36	3.78	3.75	3.77	3.77
K ₂ O	1.72	1.30	1.26	1.06	0.96	1.67	1.53	1.56	1.42	1.43	1.75	1.62	1.18	1.50	1.53	1.38	1.39
P ₂ O ₅	1.30	0.40	0.39	0.31	0.29	0.67	0.58	0.71	0.55	0.55	0.69	0.59	0.27	0.69	0.68	0.56	0.58
Total	99.80	100.37	100.47	100.69	100.96	99.66	100.72	99.76	99.85	99.60	100.30	100.49	99.78	99.64	99.57	100.56	99.75
LOI	1.38	0.85	1.02	2.12	1.80	0.66	3.66	0.86	4.13	1.81	0.60	3.11	2.29	2.05	2.35	2.75	2.41
Ga	22.5	23.8	23.3	22.5	20.9	26.4	23.3	25.2	23.1	23.2	26.8	23.3	20.5	25.5	26.1	22.5	23.2
Zn	135.7	105.8	100.8	98.9	103.0	136.1	130.4	128.7	106.5	104.2	122.9	121.4	90.0	129.7	127.6	112.8	111.6
Cu	44.6	34.4	35.4	21.3	31.3	27.6	25.7	30.6	24.9	17.1	33.3	24.9	58.9	58.3	22.5	27.5	21.5
Ni	250.9	127.3	79.9	76.3	158.3	40.7	95.4	41.5	73.7	110.7	67.9	69.4	157.4	43.2	42.9	92.7	89.5
Co	60.3	50.3	39.4	34.0	52.0	39.2	45.4	46.8	44.9	46.2	38.9	44.9	47.2	45.5	44.3	42.0	43.9
Cr	317.8	172.4	177.7	213.2	302.3	25.9	86.2	3.1	53.9	140.3	55.0	94.3	218.6	5.5	4.1	104.2	111.2
V	128.6	112.3	137.5	158.1	152.9	140.3	139.5	162.5	137.2	152.6	122.7	164.3	125.1	155.1	149.6	111.0	110.4
Ba	567.2	231.4	255.5	234.4	224.2	377.3	274.2	318.7	254.7	256.8	313.2	290.5	116.0	275.9	280.1	283.3	307.2
Rb	37.9	19.9	22.7	26.2	22.8	32.3	24.5	30.4	25.6	26.4	29.5	28.0	22.9	29.7	24.9	20	

	AJS 106	AJS 107	AJS 108	AJS 110	AJS 111	AJS 112	AJS 113	AJS 117	AJS 118	AJS 120	AJS 121	AJS 126	AJS 127	AJS 129	AJS 131	AJS 135	AJS 138
SiO ₂	43.46	47.26	44.13	47.35	42.62	42.95	42.46	51.44	51.67	51.15	50.87	45.57	52.05	51.78	55.86	53.47	53.54
TiO ₂	2.51	1.84	2.20	2.01	2.33	2.32	2.24	1.67	1.82	2.10	1.57	2.05	1.74	1.71	1.84	2.13	1.62
Al ₂ O ₃	13.66	14.93	13.73	17.68	12.21	12.86	12.59	15.37	15.31	14.02	14.94	14.70	14.55	14.79	16.39	14.76	14.48
Cr ₂ O ₃	0.05	0.04	0.04	0.02	0.06	0.05	0.05	0.03	0.05	0.06	0.05	0.03	0.03	0.03	0.03	0.03	0.04
Fe ₂ O ₃ T	13.18	12.62	12.93	10.43	14.08	13.71	13.85	11.69	11.94	12.19	11.59	12.33	12.36	12.80	9.94	11.50	11.54
MnO	0.19	0.17	0.20	0.15	0.21	0.20	0.21	0.15	0.13	0.14	0.16	0.16	0.16	0.16	0.11	0.16	0.15
MgO	10.72	8.88	9.33	5.31	11.94	10.80	10.94	7.47	6.48	8.04	8.42	9.19	6.77	7.02	3.55	5.27	7.11
CaO	9.89	8.72	9.14	10.43	9.82	9.96	9.46	7.87	8.81	8.81	8.61	7.75	9.13	9.41	9.12	8.52	9.18
Na ₂ O	4.28	3.64	4.34	3.66	3.80	4.04	4.64	3.46	3.41	2.98	3.09	4.79	2.91	2.86	3.13	3.02	2.74
K ₂ O	1.37	1.20	2.30	2.10	1.89	2.03	2.00	1.17	0.99	0.98	0.64	2.34	0.45	0.31	0.40	1.41	0.46
P ₂ O ₅	1.05	0.54	1.43	0.98	1.32	1.38	1.52	0.32	0.31	0.35	0.22	0.86	0.16	0.14	0.17	0.41	0.15
Total	100.36	99.84	99.77	100.12	100.28	100.30	99.96	100.64	100.92	100.82	100.16	99.77	100.31	100.99	100.54	100.68	100.99
LOI	2.01	1.06	3.11	2.51	2.42	2.40	1.47	1.65	1.18	2.36	0.90	1.46	0.55	1.78	3.09	1.33	0.42
Ga	19.4	22.2	23.7	24.4	22.9	23.0	23.9	21.1	20.7	20.3	20.0	24.5	21.4	20.5	21.1	23.6	21.3
Zn	107.7	108.0	136.2	94.8	128.5	127.8	136.5	100.1	100.1	103.9	95.4	125.5	112.0	108.2	109.1	120.7	108.1
Cu	48.3	56.2	34.6	60.0	34.7	38.3	38.4	58.3	44.9	18.6	41.0	51.8	61.5	59.9	64.3	46.9	66.6
Ni	225.3	173.3	198.1	66.8	287.4	239.9	252.0	164.8	169.0	178.0	208.4	220.1	110.0	111.8	80.4	98.2	150.6
Co	59.7	56.9	58.8	38.0	65.8	54.9	57.6	47.9	47.9	65.5	57.3	56.9	59.5	54.3	40.5	41.7	56.9
Cr	265.7	216.2	216.1	101.8	337.6	269.3	300.3	189.7	284.4	333.0	268.5	206.5	157.2	154.8	186.9	172.7	210.2
V	150.5	128.5	131.1	117.4	144.3	132.6	140.2	132.6	153.7	164.3	146.9	113.1	154.4	145.4	152.4	121.2	148.0
Ba	571.9	258.6	582.7	484.9	576.1	611.6	610.2	196.7	188.7	178.9	141.2	248.9	85.5	66.4	316.0	276.8	115.9
Rb	22.1	20.9	57.6	34.3	33.9	38.9	21.3	24.7	19.1	12.2	11.6	17.9	12.1	7.1	10.8	30.3	9.9
Sr	1104.1	868.0	1513.3	1176.1	1201.9	1361.6	1588.5	371.9	401.9	443.5	354.4	957.9	260.9	275.9	279.5	437.9	233.8
Y	27.3	21.0	30.9	26.6	28.4	30.3	30.6	24.0	24.5	21.3	21.5	16.8	22.4	21.5	53.2	23.8	23.1
Zr	301.5	187.6	459.8	276.9	388.5	391.9	376.1	175.2	137.9	153.7	123.5	294.0	90.0	87.4	89.8	190.7	91.5
Nb	82.9	42.0	113.0	69.2	97.8	99.7	98.6	18.1	17.4	18.7	13.1	61.0	9.9	9.0	11.0	26.8	10.6
Pb	3.0	2.1	4.6	4.5	7.2	6.1	4.3	2.3	4.7	1.0	2.2	4.0	2.2	n.d.	2.8	2.5	0.9
Th	8.0	5.6	11.5	8.9	10.7	11.5	11.4	2.5	2.6	2.1	1.9	4.3	1.8	1.0	1.7	4.2	1.3
U	2.0	n.d.	4.1	1.7	3.0	5.1	2.8	1.1	0.6	0.4	n.d.	0.8	1.3	n.d.	1.4	n.d.	0.7

	AJS 141	AJS 142	AJS 143	AJS 144	AJS 145	AJS 146	AJS 148	AJS 150	AJS 152	AJS 155	AJS 157	AJS 161	AJS 162	AJS 164	AJS 165	AJS 167	AJS 168
SiO ₂	52.44	50.76	48.37	48.34	51.41	52.15	47.98	49.65	51.04	51.99	53.56	49.48	51.18	47.17	48.75	48.56	46.88
TiO ₂	1.67	2.35	1.92	1.88	2.02	2.25	2.62	2.61	1.73	2.41	1.97	3.08	1.62	3.04	2.09	2.29	2.26
Al ₂ O ₃	14.91	16.67	14.89	14.87	16.61	16.56	15.28	14.83	15.09	15.31	15.27	16.33	14.88	14.92	14.60	14.38	13.58
Cr ₂ O ₃	0.03	0.00	0.04	0.04	0.00	0.00	0.03	0.04	0.03	0.03	0.03	0.01	0.04	0.03	0.01	0.04	0.06
Fe ₂ O ₃ T	12.34	12.74	12.36	12.31	12.05	12.19	12.39	12.22	12.14	11.36	9.94	11.93	12.24	13.28	16.11	12.25	13.26
MnO	0.16	0.16	0.17	0.16	0.15	0.19	0.17	0.14	0.20	0.10	0.08	0.12	0.14	0.19	0.27	0.16	0.17
MgO	6.58	3.73	9.08	9.40	2.78	2.92	8.05	7.11	6.82	6.48	5.47	5.86	7.51	7.59	3.94	9.47	11.31
CaO	9.47	5.77	8.85	8.52	5.71	5.49	8.92	8.46	9.56	7.21	7.70	7.39	8.55	8.74	6.76	8.32	8.80
Na ₂ O	2.85	4.12	2.91	2.98	4.52	4.44	3.20	3.39	3.13	3.57	3.82	3.88	3.18	2.92	3.60	2.96	2.40
K ₂ O	0.42	2.59	1.37	1.33	2.87	3.00	1.54	1.61	0.48	1.67	1.77	1.68	0.93	1.47	2.28	1.46	1.33
P ₂ O ₅	0.16	1.01	0.41	0.41	1.20	1.24	0.59	0.54	0.23	0.50	0.50	0.58	0.27	0.82	1.41	0.52	0.49
Total	100.99	99.90	100.37	100.24	99.32	100.43	100.77	100.60	100.45	100.63	100.11	100.34	100.54	100.17	99.82	100.41	100.54
LOI	0.66	3.17	1.93	1.51	2.26	1.93	1.60	2.20	1.24	2.24	3.21	1.96	2.18	2.13	1.19	1.94	2.42
Ga	20.4	25.9	20.0	19.9	28.4	28.6	21.9	23.0	19.8	25.0	24.1	24.1	22.3	21.3	24.5	20.9	19.6
Zn	103.7	142.5	96.4	94.0	158.0	151.6	105.5	108.9	99.3	121.7	122.8	11.2	108.5	107.2	154.2	109.7	105.4
Cu	64.5	8.7	34.0	52.3	6.3	3.7	34.2	33.3	70.0	24.7	41.4	13.5	63.9	34.8	31.3	45.7	60.0
Ni	116.8	2.3	191.9	173.6	3.0	1.4	138.3	157.6	149.0	117.0	147.8	91.3	161.4	125.3	47.0	185.7	235.7
Co	54.7	36.9	58.8	53.3	28.3	30.2	60.3	48.6	55.8	51.3	41.3	43.3	50.1	54.5	40.2	53.2	61.1
Cr	160.8	0.0	250.7	253.8	3.2	0.0	164.2	191.5	139.2	127.2	196.1	61.8	210.5	150.4	64.1	243.9	292.7
V	147.6	61.3	182.8	178.6	41.9	45.8	153.4	149.9	173.3	123.1	111.1	136.9	146.5	195.0	47.2	148.2	153.7
Ba	110.9	458.3	328.6	294.0	577.8	577.9	315.6	288.6	155.8	285.8	327.3	287.9	159.5	291.5	937.6	301.3	378.9
Rb	8.1	46.3	26.5	25.1	54.6	54.9	22.8	28.1	14.0	29.0	20.0	26.5	17.2	24.2	30.9	27.2	23.6
Sr	254.5	640.4	656.6	502.3	668.7	641.9	734.4	628.1	387.8	568.2	683.5	650.6	390.9	611.3	593.5	554.7	684.4
Y	21.7	42.7	23.7	23.9	49.6	49.7	26.5	26.5	22.6	22.0	19.4	23.8	21.9	28.5	53.9	22.9	19.5
Zr	85.4	367.2	193.1	186.6	430.6	416.7	249.9	243.8	138.8	250.8	281.4	261.8	146.9	214.1	334.1	218.5	191.7
Nb	10.8	54.7	27.4	26.8	60.9	61.3	35.7	35.2	16.5	30.2	33.1	35.9	16.4	32.4	41.4	37.0	36.4
Pb	0.8	6.2	4.2	0.9	6.3	4.4	3.4	2.6	2.4	4.2	0.9	5.3	2.6	5.0	5.8	1.0	4.8
Th	1.2	6.9	2.8	2.9	8.0	6.2	7.3	4.8	2.2	3.8	1.2	3.2	0.4	5.6	4.9	3.0	4.1
U	n.d.	1.3	0.5	n.d.	1.7	3.0	1.9	n.d.	n.d.	2.3	0.5	n.d.	0.8	n.d.	1.9	1.3	0.9

	AJS 173	AJS 174	AJS 175	AJS 176	AJS 177	AJS 178	AJS 181	AJS 182	AJS 183	AJS 184	AJS 185	AJS 188	AJS 189	AJS 195	AJS 197	AJS 198	AJS 199
SiO ₂	50.76	53.28	47.50	49.91	49.96	50.28	50.81	48.91	49.14	72.57	69.42	48.27	72.15	51.42	51.68	50.00	49.66
TiO ₂	2.54	1.64	1.91	2.17	2.32	2.26	1.91	1.96	2.44	0.13	0.16	3.10	0.13	1.97	2.44	2.26	2.38
Al ₂ O ₃	15.51	14.30	14.52	15.56	15.39	15.61	15.07	15.09	15.12	14.92	17.15	14.71	15.26	15.81	15.29	14.96	15.27
Cr ₂ O ₃	0.03	0.04	0.05	0.03	0.04	0.03	0.04	0.04	0.04	0.00	0.00	0.03	0.00	0.03	0.03	0.03	0.02
Fe ₂ O ₃ T	11.90	11.79	12.57	12.17	11.49	11.53	11.96	12.18	11.59	1.04	1.44	12.98	1.90	12.30	11.72	11.84	12.14
MnO	0.13	0.15	0.18	0.14	0.14	0.22	0.15	0.16	0.14	0.01	0.01	0.15	0.01	0.14	0.13	0.13	0.15
MgO	5.85	6.83	10.05	6.91	7.55	8.08	6.92	9.12	8.47	0.00	0.00	7.47	0.00	4.82	6.23	7.64	7.20
CaO	7.68	9.09	9.58	8.16	7.17	6.70	8.60	8.60	7.80	0.44	0.67	7.86	0.25	8.42	7.48	7.93	7.58
Na ₂ O	3.89	2.78	2.53	3.59	3.09	3.40	3.14	3.46	3.41	5.49	5.00	3.21	5.31	3.39	3.73	3.40	3.63
K ₂ O	1.47	0.55	1.12	1.26	1.72	1.78	0.78	1.04	1.79	5.29	6.02	1.96	5.14	1.03	1.40	1.22	

	AJS 200	AJS 201	AJS 202	AJS 203	AJS 204	AJS 205	AJS 206	AJS 207	AJS 208	AJS 209	AJS 210	AJS211	AJS 212	AJS 213	AJS 214	AJS 215	AJS 216
SiO ₂	51.64	50.36	50.53	50.75	50.77	50.25	49.38	49.51	49.27	49.94	50.04	49.61	49.20	49.92	49.56	49.14	50.04
TiO ₂	1.93	2.58	1.52	1.66	2.27	1.37	2.66	2.71	2.71	2.59	2.34	2.47	2.56	2.68	2.26	2.97	2.87
Al ₂ O ₃	15.48	16.23	15.08	15.13	15.00	15.41	16.05	16.02	16.04	16.54	15.34	16.54	16.50	16.40	16.23	16.32	16.46
Cr ₂ O ₃	0.04	0.01	0.04	0.04	0.04	0.06	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Fe ₂ O ₃ T	10.90	11.74	11.40	11.15	11.59	12.38	12.56	12.83	12.78	12.98	12.10	12.34	12.69	12.31	11.56	13.34	12.40
MnO	0.12	0.13	0.13	0.12	0.14	0.16	0.14	0.15	0.14	0.14	0.13	0.15	0.16	0.14	0.14	0.16	0.14
MgO	7.24	5.40	8.39	7.79	6.73	7.97	6.25	5.25	5.98	5.17	6.50	5.89	6.07	5.57	6.85	5.60	4.96
CaO	8.09	7.04	8.23	8.93	7.95	8.70	7.54	7.82	7.51	7.77	7.93	7.90	7.65	7.30	7.94	7.27	6.67
Na ₂ O	3.58	3.96	3.22	3.15	3.44	2.99	3.50	3.75	3.64	3.72	3.76	3.71	2.89	3.62	3.40	3.77	4.02
K ₂ O	1.42	1.79	1.00	0.82	1.28	0.54	1.27	1.33	1.32	1.24	1.22	1.19	1.25	1.43	1.20	1.47	1.68
P ₂ O ₅	0.37	0.59	0.25	0.31	0.44	0.21	0.52	0.55	0.53	0.48	0.44	0.48	0.49	0.49	0.46	0.62	0.60
Total	100.81	99.83	99.79	99.85	99.65	100.04	99.88	99.93	99.93	100.58	99.82	100.29	99.47	99.87	99.61	100.67	99.85
LOI	2.46	2.42	1.55	2.83	1.66	1.09	3.03	1.18	2.10	2.17	0.81	1.68	2.03	3.12	3.22	2.40	1.77

Ga	22.9	25.4	21.6	21.2	22.1	20.9	23.6	24.5	24.8	24.9	24.0	23.6	24.0	24.4	23.0	23.8	26.6
Zn	97.0	113.2	94.2	98.1	111.3	101.4	117.2	111.6	113.3	114.5	111.6	108.5	112.4	109.5	107.6	116.7	113.3
Cu	31.3	21.8	31.7	34.1	24.5	25.3	19.8	22.6	27.8	26.9	32.4	21.2	18.7	5.3	16.4	13.3	30.4
Ni	93.2	63.6	144.7	176.6	130.3	201.1	73.4	59.2	63.4	54.7	108.9	58.9	56.1	55.9	90.4	53.0	43.8
Co	43.6	39.7	46.0	49.9	43.5	53.1	43.5	45.9	43.9	41.6	44.4	45.2	46.8	39.4	42.8	45.7	42.6
Cr	218.4	49.3	232.8	246.9	211.0	324.7	46.2	23.1	20.2	20.0	143.3	17.3	15.9	19.8	59.6	22.2	14.2
V	126.4	105.9	126.7	125.5	141.3	145.3	138.3	147.7	141.1	148.2	143.3	138.0	148.4	118.3	132.5	145.3	104.7
Ba	261.4	324.7	182.1	199.4	241.0	153.8	231.7	272.0	237.7	213.0	248.0	221.8	232.2	237.4	210.0	256.3	323.2
Rb	31.7	30.4	26.8	11.3	20.6	13.7	20.3	24.3	23.8	19.5	21.2	21.7	21.2	24.2	19.4	25.5	29.1
Sr	466.5	516.4	354.7	444.6	505.4	350.7	448.2	522.6	487.3	503.7	530.5	495.1	505.4	492.2	472.9	492.9	588.8
Y	32.5	25.5	20.8	19.7	24.5	19.0	28.5	30.9	30.3	29.7	26.7	28.0	29.0	26.4	23.8	32.5	26.7
Zr	241.3	253.8	128.8	154.8	204.2	112.2	217.6	222.2	220.0	211.7	180.2	204.6	200.2	220.6	185.4	241.3	244.7
Nb	29.2	34.9	16.1	17.3	23.8	11.6	24.4	25.0	24.6	25.5	24.2	22.7	24.7	27.3	22.9	29.2	29.9
Pb	n.d.	4.2	2.7	2.4	3.3	0.5	0.9	1.3	n.d.	n.d.	1.8	1.6	2.6	2.8	3.6	n.d.	2.8
Th	5.4	5.6	3.6	3.7	2.6	3.4	3.0	4.0	5.5	3.0	2.8	2.9	3.9	3.5	3.4	5.4	3.6
U	0.2	n.d.	n.d.	1.6	0.4	n.d.	n.d.	2.2	n.d.	0.5	n.d.	n.d.	0.9	0.6	n.d.	0.2	0.6

	AJS 217	AJS 219	AJS 220	AJS 221	AJS 224	AJS 226	AJS 228	AJS 232	AJS233	AJS234	AJS 235	AJS 236	AJS 238	AJS 239	AJS 240	AJS 241	AJS 242
SiO ₂	50.01	68.00	66.90	69.54	49.44	72.37	51.58	45.89	46.44	46.10	45.25	47.42	50.54	50.80	47.28	50.70	48.35
TiO ₂	2.66	0.23	0.24	0.22	2.98	0.13	1.51	1.79	1.97	1.91	1.86	1.74	2.59	2.51	1.68	2.56	3.28
Al ₂ O ₃	16.28	15.81	17.34	16.45	16.05	14.66	14.81	14.81	15.23	15.04	14.79	14.89	15.77	16.17	15.10	15.91	16.09
Cr ₂ O ₃	0.01	0.00	0.00	0.00	0.01	0.00	0.05	0.04	0.03	0.03	0.04	0.04	0.03	0.02	0.04	0.02	0.00
Fe ₂ O ₃ T	11.89	3.21	3.88	1.36	12.00	1.34	12.04	13.54	12.05	11.90	13.79	12.47	11.85	11.43	12.76	12.58	14.31
MnO	0.13	0.02	0.02	0.01	0.12	0.01	0.14	0.19	0.15	0.16	0.19	0.17	0.12	0.12	0.17	0.13	0.15
MgO	5.79	0.19	0.18	0.00	6.03	0.00	8.25	9.92	7.60	7.95	9.99	9.01	6.32	5.94	8.90	5.41	5.52
CaO	7.47	0.42	0.30	0.36	7.11	0.10	8.82	9.44	7.30	7.11	9.03	9.25	8.02	7.50	8.90	7.59	6.67
Na ₂ O	3.62	5.49	4.77	5.80	3.80	5.34	2.93	3.26	5.55	5.81	3.80	3.12	3.60	3.93	3.30	3.60	3.74
K ₂ O	1.44	5.63	5.51	5.86	1.92	5.06	0.69	1.50	2.73	2.58	1.34	1.24	1.34	1.77	0.94	1.41	1.63
P ₂ O ₅	0.48	0.00	0.00	0.00	0.63	0.00	0.19	0.52	0.98	0.97	0.63	0.45	0.50	0.51	0.44	0.49	0.69
Total	99.78	99.00	99.14	99.60	100.09	99.01	100.99	100.90	100.03	99.56	100.71	99.80	100.68	100.70	99.51	100.40	100.43
LOI	2.81	1.60	3.18	0.44	2.52	0.65	1.27	1.89	2.68	2.06	1.38	1.68	2.22	1.96	1.16	2.42	2.39

Ga	24.2	34.1	35.2	37.8	25.6	39.6	21.0	21.8	27.6	28.6	22.8	21.9	23.6	22.6	22.7	23.7	25.9
Zn	118.3	194.8	184.6	110.8	118.7	285.5	97.7	101.0	133.1	134.8	111.7	93.3	118.7	100.1	102.7	119.3	122.8
Cu	15.7	1.6	1.1	3.1	22.9	4.4	54.0	62.4	35.4	38.1	56.4	64.8	28.5	24.5	64.9	39.7	10.5
Ni	79.8	1.9	2.3	3.1	79.6	2.7	183.8	175.5	168.2	172.6	176.0	157.6	101.6	101.0	167.6	84.6	39.8
Co	45.0	10.4	5.5	9.3	46.5	3.1	53.3	58.1	49.0	53.8	55.3	57.0	49.0	37.8	54.6	34.9	43.3
Cr	41.0	1.5	3.2	1.9	71.7	2.4	247.3	202.6	163.4	176.2	183.2	191.6	124.7	96.4	213.4	90.0	3.2
V	112.6	2.4	0.1	0.0	135.3	0.0	150.6	131.6	90.8	91.6	130.3	128.3	122.8	124.2	147.5	150.0	156.1
Ba	242.4	92.3	100.5	63.5	329.3	0.0	99.8	270.3	235.9	222.3	313.0	238.9	236.4	294.1	229.5	227.4	302.2
Rb	23.9	129.3	124.1	144.8	32.0	180.3	15.9	25.6	33.9	25.3	20.0	25.5	12.1	28.8	16.2	26.2	26.1
Sr	519.8	13.5	15.2	13.0	818.8	9.1	307.3	789.2	1108.1	1088.4	883.4	652.2	622.6	622.7	663.9	505.6	467.8
Y	24.7	67.5	88.9	72.6	21.2	53.4	20.1	20.8	16.3	16.1	23.3	19.9	22.5	23.5	20.7	29.9	35.2
Zr	213.4	881.8	899.9	861.4	267.4	494.5	110.2	176.3	348.2	362.4	200.0	138.1	222.0	234.5	138.8	203.1	267.1
Nb	27.0	116.3	114.3	132.7	40.4	153.0	11.3	39.8	74.9	75.0	46.2	28.7	29.4	31.8	30.6	25.2	32.7
Pb	1.1	18.0	12.9	10.3	0.9	13.5	n.d.	1.5	3.9	3.7	2.6	4.0	1.2	2.6	5.0	4.6	2.8
Th	3.3	15.2	15.9	18.0	5.3	16.2	6.0	5.9	5.6	7.2	4.7	4.4	3.5	2.2	4.1	4.5	4.6
U	n.d.	3.6	3.1	3.2	1.4	4.6	1.4	n.d.	2.1	0.8	1.5	1.1	n.d.	0.5	0.8	0.1	1.0

	AJS 246	AJS 248	AJS 252	AJS 253	AJS 255	AJS 256	AJS 261	AJS 262	AJS R1	AJS R2	AJS W1	AJS W2	AJS W3	AJS W4	AJS W6	AJS W7	AJS W8
SiO ₂	48.80	49.71	49.76	49.63	48.55	48.65	50.27	50.92	44.00	44.16	52.32	51.75	52.62	51.82	51.73	51.97	51.70
TiO ₂	3.28	2.53	2.56	2.63	3.20	3.23	2.56	1.83	2.07	2.07	2.48	2.43	1.63	2.46	2.43	2.57	2.53
Al ₂ O ₃	16.23	16.33	16.24	16.63	16.46	16.19	16.54	16.11	12.68	12.55	15.24	14.85	14.47	14.82	14.90	15.19	14.95
Cr ₂ O ₃	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.04	0.06	0.06	0.02	0.02	0.04	0.03	0.03	0.02	0.02
Fe ₂ O ₃ T	13.81	12.49	12.50	12.89	13.73	13.80	12.63	12.08	10.99	10.92	11.24	12.26	12.02	11.62	12.26	12.18	12.49
MnO	0.19	0.14	0.14	0.13	0.16	0.16	0.13	0.15	0.16	0.17	0.13	0.13	0.17	0.13	0.14	0.13	0.13
MgO	4.83	5.23	5.22	4.68	4.95	4.98	4.55	5.48	12.39	12.66	5.03	5.57	6.63	5.80	5.80	5.06	5.42
CaO	6.91	8.03	7.97	8.04	7.06	6.74	7.88	9.62	10.59	10.92	8.26	7.53	9.17	7.96	7.73	7.76	7.63
Na ₂ O	4.06	3.95	3.90	3.89	3.95	3.91	3.89	3.29	5.07	4.02	3.71	3.30	2.98	3.54	3.44	3.70	3.52
K ₂ O	1.73	1.29	1.27	1.32	1.60	1.70	1.35	0.70	1.27	1.78	1.61	1.73	0.63	1.75	1.62	1.64	1.53
P ₂ O ₅	0.71	0.50	0.51	0.52	0.68	0.69	0.48	0.31	1.01	1.03	0.56	0.56	0.19	0.56	0.56	0.58	0.57
Total	100.55	100.21	100.08	100.37	100.34	100.05	100.29	100.53	100.29	100.35	100.60	100.13	100.55	100.49	100.64	100.80	100.49
LOI	2.21	0.61	0.84	2.09	2.30	2.83	1.18	0.84	1.72	2.04	1.05	1.02	1.30	0.72	0.60	0.24	0.67

Appendix C: Microprobe analyses

C.1 MICROPROBE SPECIFICATION AND OPERATING CONDITIONS

Analysis was performed using 30µm thick polished thin sections, coated with a 20nm layer of carbon to prevent charge build-up. A Cambridge Instruments Microscan 9 electron microprobe at the Department of Earth Sciences, Oxford was used, which has two wavelength-dispersive spectrometers and is controlled by a Cambridge Instruments Microscan 9 software package. Calibration using standards was carried out before each session. A ZAF correction adjusts the results to account for the influence of atomic number (Z), X-ray absorption (A) and secondary fluorescence effects (F).

Standard operating conditions during analysis are: beam diameter 0.5µm, beam current 40 nA, accelerating potential 20 kV. The maximum diameter of the excitation volume of the target is 3µm. X-ray counting times vary between 10 and 30 seconds according to the element under analysis.

C.2 ERRORS

A comprehensive description of microprobe analysis, together with discussion of the problems of assessing errors in the analysis, are provided by Potts (1987). This section considers lower limits of detection, precision, accuracy and numerical estimation of uncertainties due to counting.

C.2.1 Lower limits of detection

Microprobe measurements are based on the X-ray count rates at the relevant X-ray lines, as is the case with XRF analysis, and consequently the definition of the ‘lower limit of detection’ described in section B.3.1 is applicable here also. Table C.1 provides limits of determination for a range of mineral standards obtained during typical operating conditions.

Element oxide	Lower limit of detection (wt.%)
SiO ₂	0.05
TiO ₂	0.05
Al ₂ O ₃	0.06
Fe ₂ O ₃ T	0.06
MnO	0.06
MgO	0.07
CaO	0.03
Na ₂ O	0.07
K ₂ O	0.04

Table C.1 Lower limits of detection for major element oxides (6σ) from Potts (1983) for the electron microprobe under typical operating conditions.

C.2.2 Precision

As discussed in section B.3.2, precision refers to the reproducibility of an analysis. Table C.2 provides the average of 54 replicate analyses performed by Potts (1983) on DSDP glass, with precision given in terms of coefficients of variation, such that $CV\% = 100 \times \text{standard deviation}/\text{mean analysis}$. This gives an indication of the precision of the technique, rather than the Oxford machine specifically. Values are generally low, with the exception of MnO and K₂O whose concentrations are close to detection limits and are thus unrepresentative.

Element oxide	Average (wt.%)	CV%
SiO ₂	51.53	0.47
TiO ₂	1.32	1.90
Al ₂ O ₃	15.01	0.65
FeO	9.05	0.74
MnO	0.18	7.20
MgO	7.96	1.00
CaO	11.15	0.68
Na ₂ O	2.76	1.60
K ₂ O	0.07	7.10

Table C.2 Estimates of precision made using 54 replicate analyses of a DSDP basaltic glass by Potts (1983).

C.2.3 Accuracy

As stated in section B3.3, accuracy is a measure of the closeness of an analysis to its ‘true’ value. This can be estimated for a machine by comparing analyses of standards with internationally recognised consensus analyses for those standards. This only provides an estimate of the accuracy since the consensus values are compiled from numerous laboratories and are thus not necessarily the true values for a given standard. An indication of the accuracy of the microprobe technique is provided in Table C.3 below (from Bletcher, 1997), where the consensus values for the DSDP glass referred to above are compared with the average of 54 replicate analyses performed by Potts (1983) and provided in Table C.2. The relative deviation ($RD\% = 100 \times (\text{measured}-\text{consensus})/\text{consensus}$) is low (<3%) except in the cases of MnO, Na₂O and K₂O whose concentrations approach their lower limits of detection.

Element oxide	Consensus value	RD%
SiO ₂	51.52	0.02
TiO ₂	1.30	1.54
Al ₂ O ₃	15.39	2.47
FeO	9.12	0.77
MnO	0.17	5.88
MgO	8.12	1.97
CaO	11.31	1.41
Na ₂ O	2.48	11.29
K ₂ O	0.09	22.22

Table C.3 Estimates of accuracy made by comparing the consensus values for a DSDP basaltic glass from Staudigal (1979) with the average of 54 replicate analyses of the glass by Potts (1983) given in Table C.2.

C.2.4 Uncertainties in the microprobe analysis

Since element concentrations are calculated from peak X-ray count rates, and X-ray emission is a random process, there will be some variation in count rate during analysis which gives rise to an uncertainty in the measurements. The print-out from the microprobe gives the 2σ variation of the count rate over the counting time for each element, and this serves as an estimate of the uncertainty of the measurements.

Bletcher (1997) noted that this 2σ variation, expressed in weight %, is generally <2% except where the oxide concentrations approach their lower limits of detection.

C.3 Data

Microprobe analyses are presented on the following pages, divided according to lava group (9-12, 12+ etc.). The key for crystal types is as follows:
M=Megacryst, (RX)=recrystallised, (R)=rim, R(OPX)=rimming orthopyroxene, M(AGG)=crystal within an aggregate, (SIEV)=sieved crystal, P=phenocryst, G=groundmass.

Analysis	Sample Type	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
Mg2.5-9 Megacryst-bearing Orthopyroxene														
1.A	120 M	54.01	0.18	3.28	10.45	0.23	28.71	2.11	0.13				99.10	83.0
1.B	120 M	54.80	0.18	3.37	10.51	0.24	28.57	2.17	0.08				99.92	82.9
1.C	120 M	54.20	0.26	3.45	10.56	0.18	28.48	2.17	0.13				99.43	82.8
1.D	120 M(RX)	54.32	0.40	1.14	13.33	0.27	27.50	2.03	0.03				99.02	78.6
1.E	120 M(RX)	54.73	0.42	1.17	13.72	0.28	27.41	2.01	0.05				99.79	78.1
1.Q	120 M	54.43	0.26	3.63	11.51	0.20	28.34	2.04	0.11				100.52	81.4
3.2	120 M(RX)	54.42	0.36	1.14	13.41	0.34	27.46	2.00	0.05				99.18	78.5
14.6	80 M	52.43	0.42	4.15	14.84	0.20	25.89	1.85	0.12		0.03	0.07	100.00	75.7
21.J	1 M	54.65	0.24	3.16	10.60	0.19	28.66	1.92	0.11			0.30	99.92	82.8
21.K	1 M	53.88	0.27	3.46	11.25	0.19	28.27	2.06	0.13			0.38	100.01	81.8
21.Q	92A M	53.58	0.27	3.46	13.98	0.19	26.59	1.88	0.13		0.11	0.16	100.35	77.2
21.R	92A M	52.76	0.33	3.78	13.82	0.20	26.39	1.80	0.13		0.05	0.23	99.49	77.3
21.U	92A M	54.02	0.25	3.09	12.46	0.23	27.68	1.67	0.14		0.11	0.45	100.10	79.8
21.V	92A M	53.90	0.29	3.48	12.49	0.19	27.46	1.79	0.14		0.09	0.30	100.13	79.7
22.A	81 M	52.46	0.54	3.52	16.43	0.28	24.89	1.92	0.10			0.13	100.27	73.0
22.B	81 M	52.78	0.52	3.15	16.21	0.27	25.25	1.88	0.08			0.10	100.24	73.5
22.G	81 M	53.27	0.42	3.22	14.41	0.27	26.41	2.00	0.08			0.12	100.20	76.6
22.H	81 M	53.15	0.38	3.22	14.41	0.19	26.28	1.88	0.08			0.18	99.77	76.5
22.AP	204 M	52.68	0.45	4.78	12.48	0.22	27.08	1.96	0.10			0.12	99.87	79.5
Clinopyroxene														
1.G	120 R(OPX)	52.87	0.73	1.40	8.35	0.22	17.43	17.84	0.31				99.15	78.8
1.I	120 R(OPX)	51.89	1.09	2.23	7.56	0.21	15.67	20.17	0.34				99.16	78.7
2.5	120 R(OPX)	52.24	0.73	1.69	7.78	0.19	16.96	18.68	0.32	0.05			98.64	79.5
3.V	120 M	50.93	0.56	5.90	7.57	0.15	17.16	15.71	0.64				98.62	80.2
3.X	120 M(R)	51.85	1.14	2.15	8.23	0.18	15.64	19.82	0.33				99.34	77.2
13.15	80 M?	50.88	0.95	4.37	10.77	0.16	15.22	16.55	0.62		0.02	0.02	99.56	71.6
13.18	80 M(R)	51.38	1.06	2.55	10.25	0.25	15.38	18.41	0.27				99.55	72.8
21.1	80 M	51.20	0.84	4.13	9.22	0.18	15.95	17.07	0.57		0.06	0.14	99.36	75.5
21.A	80 M	51.77	0.84	4.10	9.15	0.18	15.88	17.39	0.56			0.12	99.99	75.6
21.B	80 M	50.94	0.98	4.46	10.34	0.30	15.21	17.13	0.68			0.03	100.07	72.4
21.D	80 M	49.13	1.42	6.64	8.64	0.14	14.65	17.83	0.72			0.14	99.31	75.2
21.E	80 M	49.47	1.42	6.67	8.79	0.18	14.76	17.48	0.74			0.21	99.72	75.0
21.F	1 M	50.39	0.90	6.21	7.88	0.12	15.69	17.59	0.73			0.12	99.70	78.0
21.H	1 M	51.02	0.73	5.80	6.77	0.18	16.58	17.24	0.75			0.31	99.38	81.4
21.I	1 M	51.25	0.69	5.96	6.83	0.16	16.62	17.56	0.69			0.31	100.07	81.3
21.P	92A M	50.58	0.95	6.17	8.27	0.25	15.50	17.44	0.78		0.05	0.17	100.16	77.0
21.S	92A M	52.60	0.35	3.92	7.67	0.16	18.94	14.76	0.54		0.05	0.33	99.32	81.5
21.AA	92A M	51.36	0.75	5.24	8.43	0.25	16.65	16.14	0.78		0.03	0.29	99.92	77.9
21.AB	92A M	50.86	0.90	6.16	8.27	0.11	15.80	16.94	0.86		0.03	0.26	100.19	77.3
22.D	81 M	50.55	1.06	5.09	9.25	0.19	15.58	16.84	0.66			0.24	99.46	75.0
22.E	81 M	50.93	1.34	3.16	9.31	0.20	14.93	19.19	0.31			0.09	99.46	74.1
22.F	81 M	50.35	1.45	3.84	9.31	0.22	15.02	18.99	0.36			0.05	99.59	74.2
22.AJ	204 M	50.72	0.75	5.81	8.01	0.19	16.12	16.94	0.71			0	99.25	78.2
22.AK	204 M	50.70	0.77	5.85	7.76	0.16	16.55	16.62	0.74			0.31	99.46	79.2
22.AM	204 M	50.35	0.91	6.63	7.87	0.19	15.95	16.69	0.77			0.22	99.58	78.3
22.AN	204 M	51.18	0.69	4.98	7.87	0.18	17.09	16.41	0.66			0.34	99.40	79.5
22.AO	204 M	50.10	1.08	5.99	9.14	0.15	15.67	16.44	0.72			0	99.29	75.4
23.15	80 M(AGG)	49.27	1.36	6.35	8.64	0.22	14.63	17.38	0.74			0.19	98.78	75.1
23/20	80 M(AGG)	51.95	1.06	2.94	9.57	0.18	15.34	17.4	0.31		0.112		98.87	74.1
23.17	80 M(AGG)	52.72	0.68	3.44	12.01	0.27	18.99	11.61	0.51			0.12	100.35	73.8
23.18	80 M(AGG)	52.35	0.74	3.52	10.49	0.25	17.63	13.96	0.58			0.17	99.69	75.0
14.5	80 G	50.09	1.76	2.64	12.04	0.23	12.70	20.21	0.41				100.13	65.3
23.22	80 G	49.46	2.05	2.79	10.71	0.22	12.78	20.32	0.44			0.03	98.8	68.0
23.29	80 G	47.83	3.23	4.85	10.62	0.19	12.45	20.04	0.48			0.19	99.88	67.6
24.3	255 G	48.79	2.68	3.77	10.96		12.35	19.91	0.54				99	66.7
24.6	255 G	49.79	2.18	3.22	10.67		12.63	20.09	0.46				99.04	67.8
24.7	255 G	48.65	2.6	4.1	11.23		12.24	19.76	0.53				99.11	66.0
24.34	64 G	48.63	2.67	4.32	9.19		13.4	20.01	0.48				98.7	72.2
24.35	64 G	49.37	2.28	3.2	9.72		13.19	20.22	0.44				98.42	70.8
24.36	64 G	49.86	2.34	3.67	8.97		13.74	20.39	0.43				99.4	73.2
24/40	64 G	49.59	2.15	3.75	8.46		13.33	20.91	0.4				98.59	73.8
24.41	64 G	50.09	2.34	3.33	9.1		13.48	20.44	0.45				99.23	72.5
Plagioclase														
1.K	120 M	55.07	0.08	27.46	0.32	0.05		10.57	5.12	0.39			99.06	
1.L	120 M	55.34	0.06	27.36	0.39	0.01		10.49	5.16	0.41			99.22	
2.2	120 M(R)	54.26	0.13	27.64	0.74	0.01		11.18	4.80	0.38			99.14	
2.3	120 M(R)	53.24	0.11	28.33	0.67	0.00		11.85	4.46	0.34			99.00	
3.Z	120 M(SIEV)	53.32		28.01	0.67			11.58	4.56	0.33			98.47	
14.7	80 M	54.98		27.49	0.39			10.54	5.19	0.37			99.00	
21.M	92A M	55.97		27.21	0.27			10.31	5.53	0.39			99.68	
21.W	92A M	57.28		26.25	0.27			9.05	6.08	0.42			99.35	
21.X	92A M	55.59		27.47	0.26			10.46	5.43	0.29			99.50	
21.Y	92A M	55.67		27.50	0.22			10.26	5.48	0.31			99.44	
21.Z	92A M	55.17		27.71	0.26			10.62	5.25	0.31			99.32	
21.AD	92A M	56.83		26.72	0.23			9.75	5.80	0.40			99.73	
23.16	80 M(AGG)	55.56		26.99	0.36			10.12	5.43	0.43			98.89	

Analysis	Sample Type	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
24.1	255 M	56.96		27.24	0.35			9.93	5.58	0.51			100.57	
1.N	120 G	54.41	0.13	27.70	0.91	0.01		11.17	4.86	0.45			99.64	
3.AB	120 G	54.83		27.42	0.93			10.88	5.00	0.43			99.49	
23.24	80 G	53.89		28.16	0.52			11.48	4.74	0.32			99.11	
23.25	80 G	56.06		26.73	0.56			9.85	5.45	0.47			99.12	
23.27	80 G	56.07		26.91	0.42			9.83	5.37	0.47			99.07	
24.11	255 G	53.59		28.34	0.61			11.56	4.46	0.38			98.94	
24.12	255 G	54.75		28.08	0.55			11.02	4.81	0.39			99.6	
24.37	64 G	56.66		25.48	1.52			8.36	5.86	0.78			98.66	
24.38	64 G	57.28		25.98	0.65			8.87	5.74	0.62			99.14	
24.39	64 G	54.48		27.45	1.19			10.75	4.7	0.44			99.01	
Olivine														
1.J	120 G	36.77			31.92	0.40	31.51	0.19					100.79	63.8
1.U	120 G	36.17			35.02	0.46	28.82	0.18					100.65	59.5
3.4	120 G	36.04			34.43	0.49	29.30	0.19					100.45	60.3
23.23	80 G	38.56			23.47	0.24	37.96	0.21			0.22		100.66	74.2
23.26	80 G	37.89			27.39	0.37	34.91	0.21			0.12		100.89	69.4
23.28	80 G	38.14			25.27	0.35	36.32	0.21			0.16		100.45	71.9
24.4	255 G	35.69			40.43	0.72	24.14	0.38			0.04		101.4	51.6
24.8	255 G	36.44			36.65	0.57	27.48	0.34			0.06		101.54	57.2
24.9	255 G	35.41			42.08	0.8	22.96	0.4			0.01		101.66	49.3
24.27	64 G	37.87			27.49	0.47	33.28	0.31			0.06		99.48	68.3
24.29	64 G	38.08			28.37	0.33	33.98	0.27			0.13		101.16	68.1
24.31	64 G	37			33.16	0.48	30.03	0.33			0.12		101.12	61.7
Ilmenite														
10.1	120 G?	0.02	48.94	0.19	46.13	0.36	3.71					0.08	99.43	12.5
Mg2.5-9 olivine-phyric														
Olivine														
21.AE	200 P	39.63			18.04	0.22	42.77	0.20			0.17		101.03	80.9
21.AF	200 P	39.16			19.39	0.27	41.56	0.23			0.18		100.79	79.3
21.AG	200 P	39.44			18.16	0.22	42.71	0.24			0.08		100.85	80.7
21.AH	200 P	39.19			17.97	0.24	42.48	0.21			0.17		100.26	80.8
21.AI	200 P	39.35			18.82	0.22	41.86	0.24			0.11		100.60	79.9
21.AJ	200 P	39.20			18.91	0.32	42.20	0.21			0.17		101.01	79.9
21.AK	200 P	39.08			18.71	0.30	42.23	0.21			0.14		100.67	80.1
21.AM	200 P	39.43			18.59	0.16	42.02	0.24			0.14		100.58	80.1
21.AN	202 P	38.77			21.42	0.31	40.06	0.23			0.13		100.92	76.9
21.AP	202 P	39.06			20.85	0.25	40.37	0.18			0.24		100.95	77.5
21.AQ	202 P	39.10			19.66	0.26	41.26	0.24			0.21		100.73	78.9
22.P	91 P	39.02			19.57	0.24	41.37	0.25			0.15		100.60	79.0
22.Q	91 P	39.52			16.44	0.23	43.83	0.20			0.18		100.40	82.6
22.R	91 P	39.46			17.26	0.18	43.27	0.21			0.20		100.58	81.7
22.S	91 P	39.64			17.51	0.19	43.17	0.24			0.21		100.96	81.5
22.T	91 P	39.74			17.58	0.27	43.33	0.21			0.17		101.30	81.5
22.U	91 P	39.18			19.66	0.19	40.18	0.27			0.21		99.69	78.5
22.V	91 P	39.38			18.55	0.26	42.12	0.21			0.11		100.63	80.2
22.W	91 P	39.60			16.64	0.24	43.90	0.23			0.23		100.84	82.5
22.X	91 P	39.84			17.11	0.01	44.00	0.21			0.11		101.28	83.0
21.BF	202 G	36.85			32.89	0.54	30.65	0.29			0.13		101.35	62.4
21.BG	202 G	37.38			30.68	0.40	32.50	0.29			0.10		101.35	65.4
22.1	202 G	36.07			40.19	0.60	24.51	0.30			0.09		101.76	52.1
22.3	202 G	36.06			38.69	0.58	26.02	0.32			0.07		101.74	54.5
Clinopyroxene														
21.AU	202 G	52.76	0.79	1.41	8.60	0.23	15.65	20.42	0.26		0.02	0.15	100.29	76.4
21.BB	202 G	51.47	1.34	2.04	10.51	0.27	15.05	18.98	0.29		0.03	0.03	100.01	71.9
21.BC	202 G	51.80	1.01	2.17	8.50	0.16	15.33	19.36	0.31		0.06	0.31	99.01	76.3
21.BD	202 G	52.15	0.80	2.01	8.56	0.22	15.38	19.44	0.35		0.03	0.58	99.52	76.2
22.AB	91 G	51.62	1.08	2.40	8.43	0.23	15.29	19.83	0.25			0.26	99.39	76.4
22.AE	91 G	51.52	1.12	2.54	9.64	0.26	15.02	18.73	0.28			0.07	99.18	73.5
24.49	200 G	50.83	1.72	3.43	8.36		14.87	19.43	0.33				98.97	76.0
Plagioclase														
22.2	202 G	53.79		28.33	0.52			11.97	4.68	0.32			99.61	
22.M	202 M	55.38		27.30	0.33			10.23	5.41	0.41			99.06	
22.Z	91 G	53.08		28.72	0.39			12.53	4.19	0.23			99.14	
22.AA	91 G	53.17		28.54	0.49			12.07	4.45	0.21			98.93	
21.AV	202 G	53.55		28.45	0.51			12.43	4.49	0.27			99.70	
21.AX	202 G	53.54		28.38	0.54			11.84	4.61	0.32			99.23	
21.AY	202 G	51.96		29.51	0.45			13.30	3.75	0.17			99.14	
21.AZ	202 G	56.11		27.29	0.55			10.42	5.54	0.36			100.27	
24.42	200 G	54.54		28.01	0.45			11.35	4.7	0.36			99.41	
24.43	200 G	54.71		27.67	0.54			10.74	4.91	0.38			98.95	
24.45	200 G	53.9		28.15	0.52			11.84	4.5	0.3			99.21	
24.46	200 G	53.5		27.62	1.36			11.23	4.45	0.33			98.49	

Run/letter	Sample	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
Mg2.5-9 Aphyric														
Olivine														
24.13	242	36.83			34.32	0.57	29.49	0.3			0.01		101.52	60.5
24.14	242	37.16			32.99	0.54	30.71	0.26			0.1		101.76	62.3
24.15	242	36.76			36.42	0.54	27.91	0.33			0.01		101.97	57.7
24.17	242	36.98			34.95	0.53	28.62	0.3			0.06		101.44	59.3
24.54	79	36.69			34.73	0.49	28.84	0.29			0.04		101.08	60.0
Clinopyroxene														
24.18	242	50.11	2.08	2.81	11.42		12.1	20.51	0.48				99.51	65.4
24.9	242	49.16	2.77	3.72	11.08		11.96	20.61	0.49				99.79	65.8
24.22	242	48.65	2.86	3.68	11.74		11.72	20.2	0.52				99.37	64.0
24.56	79	49.13	2.2	3.31	10.56		12.44	20.68	0.47				98.79	67.0
Plagioclase														
24.21	242	55.4		28	0.56			10.12	5.02	0.44			99.54	
24.23	242	56.16		26.15	0.98			9.54	5.45	0.55			98.83	
24.24	242	56.46		27.01	1.1			9.64	5.31	0.45			99.97	
24/50	79	55.13		27.89	0.46			11.08	4.95	0.38			99.89	
24.51		54.34		27.99	0.56			11.5	4.72	0.33			99.44	
Alkali Feldspar														
24.26	242	66.48		19.33	0.52			0.96	6.97	5.61			99.87	
Mg9-12														
Olivine														
16.Q	236 G	35.74			36.74	0.63	26.22	0.44			0.04		99.81	56.0
16	236 G	36.94			34.45	0.59	29.21	0.43			0.04		101.66	60.2
16S	236 G	37.34			31.00	0.42	31.88	0.38			0.09		101.11	64.7
18.A	236 G	37.87			29.21	0.50	33.63	0.36			0.13		101.70	67.2
16B	236 G	37.45			29.34	0.48	32.91	0.35			0.13		100.66	66.7
16C	236 G	36.67			35.69	0.54	28.32	0.44			0.09		101.75	58.6
16F	236 G	36.80			34.36	0.54	29.54	0.42			0.13		101.79	60.5
19.3	39 M?	40.11			14.05	0.15	44.42	0.10			0.27		99.10	84.9
19.5	39 P	39.93			18.09	0.30	42.57	0.03			0.27		101.19	80.8
19.8	39 P	38.91			22.39	0.36	39.02	0.21			0.24		101.13	75.7
19.9	39 P	38.29			24.84	0.45	36.83	0.46			0.13		101.00	72.6
19.11	39 P	38.48			24.84	0.56	36.92	0.48			0.16		101.44	72.6
19.13	39 P	28.52			25.01	0.47	36.76	0.46			0.09		101.31	72.4
17.W	112 G	37.82			28.91	0.68	33.73	0.61			0.13		101.88	67.5
17.Y	112 G	38.87			23.31	0.47	38.44	0.46			0.16		101.71	74.6
18.9	112 G	38.29			25.57	0.52	36.50	0.59			0.07		101.54	71.8
18.10	112 G	38.92			23.75	0.47	37.92	0.45			0.18		101.69	74.0
18.11	112 M	40.60			12.04	0.22	48.10	0.06			0.27		101.29	87.7
18.25	112 G	38.72			21.31	0.35	38.93	0.16			0.13		99.60	76.5
18.26	112 G	39.76			19.87	0.28	40.91	0.16			0.24		101.22	78.6
19.P	144 P	40.05			14.86	0.23	44.49	0.21			0.32		100.16	84.2
19Q	144 P	40.42			16.07	0.19	43.99	0.21			0.24		101.12	83.0
19R	144 P	39.88			18.28	0.28	42.6	0.24			0.18		101.46	80.6
19S	144 P	39.59			19.76	0.32	41.74	0.25			0.21		101.87	79.0
19T	144 P	39.90			16.94	0.19	43.34	0.20			0.23		100.80	82.0
19U	144 P	40.57			15.74	0.12	44.75	0.24			0.30		101.72	83.5
19V	144 P	39.57			19.24	0.23	42.29	0.18			0.30		101.81	79.7
19W	144 P	40.31			16.21	0.23	44.57	0			0.26		101.58	83.1
19Z	144 P	38.55			25.70	0.41	36.96	0.27			0.04		101.93	71.9
19AA	144 P	39.79			16.77	0.27	43.56	0.23			0.21		100.83	82.2
18.5	99 P	39.88			16.94	0.24	43.80	0.24			0.21		101.31	82.2
19.AB	182 G	40.05			14.86	0.23	44.49	0.21			0.32		100.16	84.2
19AC	182 G	40.42			16.07	0.19	43.99	0.21			0.24		101.85	76.7
19AD	182 G	39.57			20.19	0.30	41.17	0.25			0.14		101.62	78.4
19AE	182 G	39.59			18.33	0.13	42.25	0.26			0.20		100.76	80.4
19AF	182 G	39.84			18.40	0.24	42.62	0.24			0.17		101.51	80.5
13.K	236 G	36.02			35.56	0.54	28.40	0.40			0.07		100.99	58.7
Clinopyroxene														
16.K	236 G	48.46	3.07	4.29	8.62	0.18	12.42	21.79	0.58		0.01	0.03	99.45	72.0
16A	236 G	50.58	1.58	3.80	6.86	0.11	13.87	21.61	0.42		0.02	0.29	99.14	78.3
16C	236 G	50.15	1.63	4.10	6.61	0.15	13.88	21.86	0.46		0.03	0.86	99.73	78.9
16F	236 G	49.66	2.49	3.56	7.82	0.11	12.91	21.83	0.61		0.07	0.03	99.09	74.6
16G	236 G	50.03	2.72	3.55	8.11	0.18	12.30	21.74	0.78		0	0	99.41	73.0
16I	236 G	51.45	1.65	2.31	8.16	0.18	13.71	21.60	0.46		0.05	0.07	99.64	75.0
16J	236 G	50.04	2.05	3.99	7.40	0.08	13.59	21.75	0.46		0	0.17	99.53	76.6
16M	236 G	50.26	2.25	3.79	7.89	0.21	13.32	21.96	0.50		0.10	0.05	100.33	75.0
17.S	112 G	50.61	1.81	3.14	7.27	0.16	13.43	23.06	0.44			0.02	99.94	76.7
17.T	112 G	47.36	2.97	6.63	7.14	0.07	12.05	22.89	0.59			0.10	99.80	75.1
17.V	112 G	49.08	2.39	4.77	7.33	0.10	12.99	22.93	0.56			0.07	100.22	76.0
18.13	112 G	48.80	2.31	4.82	7.34	0.14	12.99	22.79	0.48			0.09	99.76	75.9
18.15	112 G	47.04	2.89	6.10	7.02	0.05	12.28	22.93	0.61			0.09	99.01	75.7
19X	144 P	51.59	0.86	3.67	6.90	0.18	15.61	20.13	0.40			0.55	99.89	80.1
19Y	144 P	49.51	1.27	5.64	7.11	0.08	14.15	20.76	0.46			0.83	99.81	78.0
19.E	182 G	50.33	1.84	4.00	7.71	0.16	13.72	21.48	0.43			0.41	100.08	76.0
19F	182 G	50.52	1.80	3.65	7.53	0.18	13.95	21.49	0.38			0.21	99.71	76.8

Analysis	Sample Type	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
19G	182 G	48.42	2.92	3.88	10.25	0.16	12.10	20.96	0.56			0.05	99.30	67.8
19H	182 G	49.31	2.34	4.05	8.48	0.22	13.31	21.06	0.43			0.31	99.51	73.7
19I	182 G	49.05	2.60	3.40	11.37	0.24	11.39	21.25	0.58			0.12	100.00	64.1
19K	182 G	47.81	3.73	4.83	11.34	0.20	11.66	20.41	0.62			0.03	100.63	64.7
19L	182 G	48.47	2.77	4.28	10.73	0.20	12.29	19.97	0.53			0	99.24	67.1
Plagioclase														
19.16	144 P	52.89		29.06	0.58			12.75	3.91	0.32			99.51	
19.17	144 P	51.77		29.32	0.59			13.10	3.73	0.28			98.79	
19.19	144 P	52.03		29.46	0.74			13.15	3.63	0.27			99.28	
18.1	99 P	51.45		29.14	0.82			12.89	3.53	0.52			98.35	
18.8	99 P	54.30		28.16	0.64			10.96	4.67	0.68			99.41	
19AI	182 G	53.88		28.51	0.59			11.67	4.48	0.31			99.44	
19AJ	182 G	55.81		27.43	0.54			10.62	5.06	0.37			99.83	
19AK	182 G	56.77		26.33	0.54			9.42	5.64	0.45			99.15	
19AM	182 G	58.30		25.18	0.77			8.07	6.16	8.07			99.15	
16.X	236 G	55.60		27.10	0.32			10.12	5.44	0.43			99.01	
Y	236 G	53.35		28.88	0.36			11.84	4.39	0.32			99.14	
AA	236 G	55.49		27.26	0.46			10.19	5.32	0.44			99.16	
AB	236 G	56.08		27.12	0.56			10.09	5.35	0.42			99.62	
AC	236 G	53.23		29.08	0.51			12.43	4.14	0.25			99.64	
AD	236 G	54.40		28.11	0.41			11.30	4.74	0.32			99.28	
AE	236 G	54.13		28.74	0.38			11.73	4.66	0.33			99.97	
13.10.	236 G	54.60		27.70	0.61			11.37	4.93	0.35			99.57	
Alkali Feldspar														
13.M	236 G	65.52		19.75	0.30			1.34	6.93	5.92			99.83	
17.AB	112 G	66.56		19.04	0.43			0.59	6.50	7.04			100.16	
18.17	112 G	65.84		18.76	0.36			1.13	5.06	9.06			100.21	
Nepheline														
18.20	112 G	47.86		31.48	0.61			0.52	15.27	3.42			99.16	
18.21	112 G	48.32		31.62	0.42			0.54	15.62	4.00			100.52	
18.22	112 G	47.28		32.20	0.56			0.28	16.33	3.75			100.40	
Ilmenite														
16.5	236 G	0	52.28	0.13	44.03	0.61	3.14						100.19	11.3
16.6	236 G	0	52.21	0.13	43.22	0.58	3.51						99.65	12.7
Ti-magnetite														
17.4	112 G	0.05	19.41	1.23	73.33	1.03	2.27	0				0.01	97.33	5.2
17.5	112 G	0.05	22.10	0.92	70.53	0.88	2.26	0.06				0.14	96.94	5.4
19.1	39 G	0.26	15.25	6.83	64.33	0.54	5.62	0.04				4.73	97.60	13.5
Ultramafic nodules														
Olivine														
4.AO	234	40.40			9.95	0.12	48.73	0.01					99.21	89.7
4.AP	234	40.33			10.02	0.15	48.66	0.01					99.17	89.6
4.AQ	234	40.97			10.17	0.15	48.92	0.01					100.22	89.6
4.G	234	40.33		0.05	9.85	0.07	48.75	0.01	0.02				99.08	89.8
4.H	234	40.42		0.03	9.83	0.16	48.70	0.03	0.03				99.20	89.8
4.L	234	40.92		0.03	10.13	0.16	49.13	0.01					100.40	89.6
4.X	234	40.57		0.03	10.05	0.12	49.00	0.04	0.02				99.83	89.7
4.AH	234	40.64		0.03	9.96	0.14	48.99	0.01	0.03				99.82	89.8
4.AI	234	40.53		0.03	9.89	0.15	48.92	0.01	0.02				99.57	89.8
6.G	234	41.02			9.35	0.10	49.17	0.06			0.41		100.11	90.3
6.H	234	41.13			9.42	0.12	49.02	0.06			0.38		100.13	90.3
12.F	15	40.69			10.92	0.11	48.69	0.03			0.35	0	100.79	88.8
12.L	15	40.69			10.72	0.19	48.34	0.03			0.35	0.03	100.34	88.9
23.AG	15	41.07			10.39	0.19	48.29	0.04					10.03	89.2
23.4	R2	41.17			9.72	0.12	48.95	0.01			0.35		100.32	90.0
23.5	R2	41.06		0.03	9.75	0.15	49.22	0.03	0.02		0.36	0	100.62	90.0
23.6	R2	41.34			9.9	0.15	49.29	0.01			0.45		101.14	89.9
23D	112	40.93			10.24	0.15	48.53	0.03			0.38		100.26	89.4
23E	112	41.14			10.42	0.15	48.64	0.03			0.38		100.76	89.3
23F	112	41.63			10.48	0.2	48.84	0.01			0.44		101.6	89.3
23K	112	41.04			10.51	0.08	48.43	0.03			0.36		100.45	89.1
23Z	39	41.3			10.17	0.15	48.62	0.11			0.27		100.62	89.5
23AA	39	41.63			10.54	0.15	49.02	0.04			0.42		101.8	89.2
23AC	39	41.47			10.43	0.14	48.72	0.03			0.36		101.15	89.3
30G	124N	40.57			9.99	0.11	48.63	0.03			0.36		99.69	89.7
30I	124N	41.17			9.72	0.16	49.21	0.03			0.32		100.61	90.0
30J	124N	41.03			9.84	0.16	49.12	0.04			0.42		100.61	89.9
30P REWAN2		40.94			10.44	0.12	48.6	0.06			0.44		100.6	89.3
30Q REWAN2		41.03			10.44	0.16	48.95	0.07			0.42		101.07	89.3
30V REWAN2		39.96			9.91	0.15	48.2	0.04			0.36		98.62	89.7
30X REWAN2		40.09			9.21	0.1	48.32	0.14			0.32		98.18	90.3
30Z REWAN2		40.55			11.03	0.16	48.45	0.06			0.41		100.66	88.7
30AF	114N	40.89			9.67	0.15	49.37				0.39		100.5	90.1

Analysis	Sample	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
30AK	114N	40.51			9.49	0.16	49.24	0.03			0.42		99.85	90.2
30AM	114N	40.51			9.64	0.1	49.18	0.04			0.42		99.89	90.1
30AN	114N	40.33			9.22	0.15	49.13	0.01			0.42		99.26	90.5
31A	112N	41.35			9.83	0.1	49.91	0.04			0.45		101.68	90.1
31B	112N	40.13			9.44	0.23	49.07	0.03			0.39		99.29	90.3
31F	112N	40.42			9.74	0.18	49.18	0.03			0.38		99.93	90.0
31J	112N	40.46			9.63	0.1	49.47	0.03			0.35		100.04	90.2
31K	112N	40.75			9.89	0.16	49.44	0.04			0.3		100.58	89.9
29M	105N	40.74			10.3	0.16	49.01	0.03			0.38		100.62	89.5
29N	105N	41			10.34	0.14	48.87	0.03			0.35		100.73	89.4
29P	105N	40.81			10.07	0.12	48.69	0.03			0.35		100.07	89.6
29W	15N	40.73			10.47	0.1	48.65	0.01			0.39		100.35	89.2
29X	15N	40.51			10.27	0.19	48.17	0.03			0.36		99.53	89.3
29AA	15N	40.71			10.46	0.15	48.29	0.01			0.3		99.92	89.2
29AG	113A	41.16			8.71	0.14	49.65	0.03			0.41		100.1	91.0
29AH	113A	40.97			8.32	0.12	50.03	0.04			0.39		99.87	91.5
29AI	113A	41.18			8.38	0.12	49.91	0.03			0.38		100	91.4
21AK	113A	41.15			8.24	0.11	50.33	0.04			0.42		100.29	91.6
21AP	113A	40.91			8.04	0.08	50.18	0.12			0.41		99.74	91.8
21AQ	113A	40.78			8.37	0.14	50.31	0.03			0.39		100.02	91.5
21AR	113A	41.06			8.22	0.12	50.45	0.12			0.41		100.29	91.6
28.33	124B	41.11			10.42	0.14	48.77	0.04			0.45		100.93	89.3
28.34	124B	41.08			10.1	0.15	49	0.06			0.39		100.78	89.6
28.36	124B	40.85			10.66	0.18	48.1	0.14			0.27		100.2	88.9
28.37	124B	41.05			9.96	0.15	49.06	0.04			0.38		100.64	89.8
28L	124B	41.4			10.06	0.12	49.16	0.03			0.36		101.13	89.7
28M	124B	41.17			9.86	0.1	49.07	0.04			0.36		100.6	89.9
28.53	28N	40.97			10.68	0.11	48.53	0.01			0.42		100.72	89.0
28S	28N	41.24			10.78	0.12	48.4	0.07			0.41		101.02	88.9
28W	28N	41.08			10.83	0.18	48.5	0.03			0.39		101.01	88.9
28X	28N	40.96			10.64	0.11	48.72	0.03			0.38		100.84	89.1
28A REWAN2		40.63			10.07	0.14	48.87	0.04			0.36		100.11	89.6
28B REWAN2		40.83			10.08	0.12	48.82	0.01			0.41		100.27	89.6
28C REWAN2		41.1			10.13	0.12	48.73	0.03			0.42		100.53	89.6
Clinopyroxene														
4.B	234	52.13	0.57	6.87	2.35	0.11	14.13	20.25	2.02				98.43	91.5
4.D	234	52.13	0.61	6.22	2.51	0.08	14.37	20.19	1.98				98.09	91.1
4.Q	234	52.11	0.59	6.24	2.46	0.08	14.32	20.31	1.91				98.02	91.2
4.R	234	52.10	0.61	6.67	2.38	0.08	14.17	20.27	1.96				98.24	91.4
4.Y	234	52.47	0.55	5.91	2.48	0.12	14.60	20.53	1.88				98.54	91.3
4.Z	234	52.49	0.57	6.12	2.45	0.12	14.35	20.39	1.87				98.36	91.3
4.AF	234	52.00	0.66	6.59	2.53	0.10	14.21	20.25	1.98				98.32	90.9
6.E	234	52.83	0.59	6.29	2.48	0.04	14.45	20.42	1.96		0.03	0.55	99.91	91.2
11.P	15	53.07	0.15	6.87	3.01	0.15	13.54	19.12	2.54		0.06	0.87	99.38	88.9
12.21	15	51.33	0.68	5.05	4.09	0.15	14.32	23.28	0.79		0	0.91	100.60	86.2
23.AI	15	53.34	0.17	6.9	2.79	0.05	14.02	18.79	2.61			0.98	99.65	89.9
23AJ	15	53.69	0.23	6.72	2.79	0.03	14.03	18.89	2.67			1.03	100.08	89.9
23AK	15	52.48	0.26	4.42	2.8	0.11	16.34	20.98	0.87			0.94	99.2	91.2
23AM	15	53.17	0.15	6.94	2.78	0.08	14.04	18.76	2.63			0.86	99.41	90.0
23.7	R2	52.97	0.45	5.97	2.35	0.18	14.27	21.08	1.81		0.05	1.03	100.16	91.6
23G	112	46.07	3.1	7.03	6.72	0.12	11.98	22.66	0.58			0.22	98.48	76.1
23.9	112	52.55	0.49	3.15	2.65	0.07	16.13	22.74	0.5			0.81	99.09	91.6
30M REWAN2		51.01	0.81	5.78	2.78		13.82	21.01	1.2			0.77	97.18	89.9
30AA REWAN2		51.66	0.64	4.19	2.74		15.19	22.86	0.55			0.86	98.69	90.8
30AH	114N	52.87	0.17	5.1	2.3		14.38	20.3	1.8			1.4	98.32	91.8
30AI	114N	51.53	0.19	3.96	2.54		16.15	21.61	0.51			1.28	97.77	91.9
31G	112N	53.06	0.25	2.48	2.81		16.51	22.26	0.58			1.38	99.33	91.3
31H	112N	52.18	0.21	3.91	2.3		15.75							
29D	105N	54.12	0.32	5.02	4.55		22.58	10.8	1			0.45	98.84	89.8
29F	105N	52.63	0.51	6.81	2.49		13.93	20.19	2.04			0.86	99.46	90.9
29G	105N	52.3	0.53	6.57	2.49		14.04	20.53	2.03			0.82	99.31	91.0
29J	105N	53.04	0.51	6.38	2.48		14.34	20.21	2.22			0.8	99.98	91.1
29U	15N	52.56	0.49	6.61	2.51		14.23	20.35	1.96			0.75	99.46	91.0
29V	15N	52.54	0.57	6.3	2.35		14.24	20.53	1.88			0.68	99.09	91.5
28Q	28N	52.69	0.66	6.38	2.52		14.01	20.85	1.92			0.68	99.71	90.8
28R	28N	52.82	0.65	4.2	2.52		15.99	22.85	0.68			0.88	100.59	91.9
28V	28N	52.17	0.66	4.46	2.52		15.73	23.23	0.59			0.89	100.25	91.8
28G REWAN2		51.84	0.53	6.68	2.39		14.14	20.8	1.87			0.87	99.12	91.3
Orthopyroxene														
4.E	234	55.10	0.13	3.76	6.33	0.20	32.95	0.42	0.09				98.98	90.3
4.I	234	54.55	0.11	4.53	6.38	0.11	32.32	0.55	0.10				98.65	90.0
4.J	234	55.39	0.09	3.56	6.28	0.15	32.98	0.43	0.09				98.97	90.4
4.N	234	55.27	0.11	3.80	6.30	0.11	32.83	0.42	0.10				98.94	90.3
4.S	234	54.78	0.15	4.60	6.32	0.16	32.20	0.77	0.13				99.11	90.1
4.T	234	55.37	0.11	4.12	6.25	0.20	32.65	0.56	0.09				99.35	90.3
4.U	234	54.64	0.15	4.92	6.33	0.12	32.01	1.01	0.15				99.33	90.0
4.V	234	55.71	0.09	3.54	6.41	0.16	33.11	0.42	0.10				99.54	90.2
4.AN	234	55.46	0.11	3.44	6.35	0.15	33.07	0.42	0.10				99.10	90.3

Analysis	Sample	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
6.D	234	54.79	0.15	5.09	6.30	0.12	31.77	0.92	0.15		0.12	0.49	99.90	90.0
23.8	R2	56.16	0.07	3.56	6.26	0.22	32.92	0.45	0.09		0.06	0.31	100.1	90.4
23U	39	56.26		3.83	6.51	0.2	32.92	0.46	0.1				100.58	90.0
23W	39	55.59		4.36	6.51	0.14	32.15	0.98	0.15				99.88	89.8
23X	39	56.01		3.82	6.48	0.11	32.76	0.39	0.1				99.67	90.0
23AB	39	55.48		4.51	6.63	0.12	32.49	0.56	0.12				99.91	89.7
30H	124N	54.97	0.07	3.54	6.13		33.12	0.52	0.12			0.38	98.85	9.1
30K	124N	55.28	0.13	3.72	6.02		32.49	0.49	0.13			0.46	98.72	90.6
30L	124N	55.76	0.11	3.86	6.22		33.15	0.48	0.1			0.43	100.11	90.5
23.1	112	57.87	0.07	0.22	6.14	0.18	33.5	1.55	0.1			0.26	99.89	90.7
30AJ	114N	55.98	0.04	3.78	6.12		32.94	0.46	0.1			0.51	99.93	90.6
29K	105N	56.11	0.11	3.27	6.39	0.16	33.12	0.4	0.07			0.22	99.85	90.2
29S	15N	55.13	0.13	4.76	6.58	0.18	32.33	0.42	0.07			0.37	99.97	89.8
29T	15N	55.05	0.11	4.1	6.59	0.18	32.77	0.4	0.04			0.31	99.55	89.9
21AM	113A	57.46	0.02	1.29	5.16	0.14	34.52	0.42	0.06			0.38	99.45	92.3
21AN	113A	57.76	0.02	1.17	5.12	0.11	34.69	0.39	0.04			0.33	99.63	92.4
21AO	113A	57.6	0	1.19	5.06	0.15	34.68	0.41	0.03			0.38	99.5	92.4
28.35	124B	55.85		3.82	6.18		32.34	0.55				0.38	98.82	90.3
28K	124B	56.22	0.09	3.53	6.25		32.99	0.51				0.38	99.97	90.4
28N	124B	55.76	0.11	3.85	6.26		32.78	0.49				0.46	99.71	90.3
28P	28N	54.69	0.11	4.85	6.75		31.94	0.49				0.41	99.3	89.4
28.56	28N	55.19		4.46	6.73		32.27	0.65	0.12			0.32	99.87	89.5
28D	REWAN2	54.9	0.13	5.07	6.42		32.15	0.55				0.48	99.79	89.9
28.11	REWAN2	55.17	0.13	6.39	6.39		32.38	0.45				0.49	100.05	90.0
Spinel														
29Y	15N		0.11	58.95	10.71		20.43				0.37	8.75	99.32	77.3
29Z	15N		0.09	59.04	10.7		20.38				0.4	8.58	99.19	77.3
29AB	15N		0.09	58.99	10.68		20.49				0.4	8.58	99.23	77.4
29AD	113A		0.08	21.49	15.25		14.72				0.16	48.84	100.54	63.2
29AE	113A		0.06	21.45	15.73		14.71				0.16	48.26	100.37	62.5
29AF	113A		0.06	21.57	15.28		14.58				0.07	48.61	100.17	63.0
29AJ	113A		0.08	21.59	14.81		15.28				0.19	48.61	100.56	64.8
28.31	124B		0.09	51.46	11.74		19.56				0.3	16.77	99.92	74.8
28H	124B		0	52	11.24		19.57				0.37	16.67	99.85	75.6
28J	124B		0.12	52.21	11.33		19.6				0.39	16.41	100.06	75.5
28.19	REWAN1		0.11	58.2	10.96		20.45				0.4	9.64	99.76	76.9
28.21	REWAN2		0.09	58.19	10.79		20.5				0.4	9.76	99.73	77.2
29A	105N		0.11	57.44	11.06		20.26				0.43	9.93	99.23	76.6
29B	105N		0.12	57.63	11.04		20.27				0.42	9.96	99.44	76.6
29C	105N		0.11	57.61	11.21		20.39				0.36	9.97	99.65	76.4
29Q	105N		0.09	57.79	10.87		20.7				0.36	9.32	99.13	77.3
6.A	234	0.06	0.12	58.21	10.95	0.12	20.40	0.00			0.45	9.47	99.93	76.9
6.B	234	0.03	0.11	58.45	11.03	0.11	20.21	0.01			0.40	9.31	99.72	76.6
23.1	R2	0.06	0.09	53.78	11.49	0.17	19.68	0			0.27	13.1	98.64	75.3
23.2	R2			54.26	11.46	0.17	19.86				0.3	12.18	98.23	75.5
23.3	R2			53.93	11.4	0.16	19.78				0.39	13.06	98.72	75.6
23A	112			57.55	10.51	0.12	21.09				0.4	8.47	98.14	78.1
23C	112			58.14	10.55	0.11	20.75				0.3	8.54	98.39	77.8
23H	112			56.2	15.44	0.2	18.39				0.37	8.43	99.03	68.0
23I	112			56.66	14.78	0.19	18.67				0.33	8.44	99.07	69.2
23J	112			57.72	11.23	0.13	20.2				0.42	8.66	98.36	76.2
23L	112			57.98	10.93	0.16	20.58				0.37	8.59	98.61	77.0
23.11	39			58.44	10.29	0.13	20.73				0.39	8.97	98.95	78.2
23.M	39			58.51	10.54	0.12	20.51				0.37	9.03	99.08	77.6
23N	39			57.85	10.25	0.15	20.83				0.39	9.02	98.49	78.4
23P	39			58.17	10.32	0.13	20.9				0.31	8.87	98.7	78.3
23Q	39			58.59	10.58	0.13	20.64				0.33	9.08	99.35	77.7
23R	39			58.12	10.43	0.17	20.95				0.34	9.02	99.03	78.2
23S	39			58.65	10.6	0.09	20.7				0.34	8.88	99.26	77.7
23T	39			58.58	10.57	0.13	20.62				0.34	8.98	99.22	77.7
30A	124N	0.06	0.09	50.31	15.91		16.77				0.37	15.94	99.45	65.3
30B	124N	0.06	0.18	47.26	23.88		12.78				0.25	15.26	99.67	48.8
30C	124N	14.76	12.11	13.05	40.85		2.79				0.1	8.74	92.4	10.8
30D	124N	0.03	0.12	52.34	11.04		19.85				0.36	16.41	100.15	76.2
30E	124N	0.12	0.09	51.99	10.13		20.01				0.22	16.25	98.81	77.9
30F	124N	0.06	0.09	52.83	10.25		20.37				0.36	15.74	99.7	78.0
30R	REWAN2	0.09	0.18	57.42	11.13		20.63				0.4	9.8	99.65	76.8
30S	REWAN2	0.09	0.12	57.28	10.77		20.72				0.39	9.7	99.07	77.4
30T	REWAN2	13.5	0.68	31.6	13.35		22.51				0.24	10.13	92.01	75.0
30U	REWAN2	0.09	nd	57.36	11.31		20.66				0.4	9.58	99.4	76.5
30AC	114N	0.06	0.05	48.78	11.17		19.03				0.33	19.59	99.01	75.2
30AD	114N	0.06	0.07	49.1	11.1		18.94				0.33	19.71	99.31	75.2
31C	112N		0.1	48.44	11.34		19.21				0.28	20.36	99.73	75.1
31D	112N		0.07	48.26	11.41		19.37				0.25	20.09	99.45	75.2
31L	112N		0.05	48.47	10.98		19.45				0.27	20.17	99.39	75.9

Analysis	Sample Type	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Ni	Cr	Total	Mg#
Mg12+														
Olivine														
20B	AJS R1 M	41.34			9.79	0.19	49.28	0.10			0.36		101.06	90.0
20C	AJS R1 P	40.52			13.47	0.20	46.17	0.21			0.23		100.80	85.9
20E	AJS R1 P	40.76			13.06	0.19	46.97	0.21			0.27		101.46	86.5
20F	AJS R1 M	40.89			11.33	0.20	47.91	0.07			0.38		100.78	88.3
20G	AJS R1 P	40.85			13.11	0.22	46.57	0.23			0.29		101.27	86.5
20H	AJS R1 P	40.70			13.97	0.20	45.69	0.17			0.24		100.97	85.4
20I	AJS R1 M	41.36			10.47	0.08	49.06	0.06			0.38		101.41	89.3
20J	AJS R1 P	40.73			12.67	0.18	47.33	0.20			0.30		101.41	86.9
20L	AJS R1 M	41.20			9.62	0.12	49.46	0.10			0.41		100.91	90.2
20N	AJS R1 P	40.41			13.86	0.19	45.72	0.23			0.20		100.61	85.5
20P	AJS R1 P	40.57			13.50	0.23	45.60	0.20			0.17		100.27	85.8
20R	AJS R1 P	40.40			13.11	0.22	46.46	0.19			0.23		100.61	86.3
20T	AJS R1 P(R)	39.14			16.87	0.32	42.73	0.38			0.12		99.56	81.9
20U	AJS 27 M	41.57			10.54	0.11	48.86	0.03			0.38		101.49	89.2
20V	AJS 27 M	40.99			10.65	0.16	48.72	0.04			0.44		101.00	89.1
20W	AJS 27 M(R)	40.33			13.03	0.16	46.04	0.33			0.18		100.07	86.3
20Y	AJS 27 M	41.06			10.25	0.18	48.97	0.03			0.39		100.88	89.5
20AA	AJS 27 P	40.69			12.41	0.19	46.62	0.24			0.18		100.33	87.0
20AB	AJS 27 P	40.59			13.14	0.20	46.14	0.24			0.23		100.54	86.2
20AC	AJS 27 P	40.69			13.43	0.14	46.27	0.21			0.18		100.92	86.0
20AD	AJS 27 P	40.70			13.18	0.16	46.39	0.23			0.27		100.93	86.3
20AE	AJS 27 M	41.27			8.86	0.15	50.08	0.04			0.44		100.84	91.0
20AF	AJS 27 P	40.62			14.48	0.20	45.73	0.17			0.24		101.44	84.9
20AG	AJS 27 M?	41.30			10.30	0.10	49.32	0.04			0.33		101.39	89.5
20AF	AJS 27 P	40.35			13.83	0.19	45.78	0.19			0.26		100.60	85.5
20AJ	AJS 20 P	40.11			17.44	0.34	42.84	0.36			0.17		101.26	81.4
20AO	AJS 20 P	39.72			18.14	0.46	41.97	0.67			0.14		101.10	80.5
20AP	AJS 20 M?	41.12			12.49	0.19	47.32	0.07			0.30		101.49	87.1
20AQ	AJS 20 M	40.82			13.78	0.22	46.29	0.06			0.33		101.50	85.7
20AU	AJS R2 P	39.19			19.54	0.39	40.00	0.42			0.11		99.65	78.5
20AV	AJS R2 P	39.94			17.56	0.26	42.76	0.33			0.12		100.97	81.3
20AZ	AJS R2 P	39.70			17.86	0.36	42.86	0.34			0.17		101.23	81.1
Nepheline														
20.1	AJS 20	44.04		33.16	1.17			0.13	15.54	5.32			99.36	
20.2	AJS 20	43.52		32.71	1.21			0.26	16.68	5.21			99.59	

Appendix D: Isotopic analysis

A total of 26 samples were analysed: 10 for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ at Géosciences, Rennes in 1996, and a further 16 for $^{87}\text{Sr}/^{86}\text{Sr}$ at Oxford in 1997. Preparative methods are given below and are followed by the data.

D.1 ELEMENT CONCENTRATIONS

Whole-rock XRF analyses were used for Rb and Sr abundances, while isotope dilution was used to calculate concentrations of Sm and Nd.

D.2 ANALYTICAL PROCEDURE FOR Rb-Sr AND Sm-Nd AT RENNES

Approximately 0.05 g of each sample was weighed out into a closeable teflon beaker, and a quantity of concentrated Nd-Sm spike ($0.2124295 \mu\text{g/g } ^{150}\text{Nd}$; $0.5894866 \mu\text{g/g } ^{149}\text{Sm}$) was added such that $^{144}\text{Nd}/^{150}\text{Nd}$ would be ~ 0.5 (the concentration of Nd, as then unknown, was estimated using the known concentration of Zr). The mixture was then dissolved in HF (~ 5 ml) and HNO_3 (~ 12 drops), and dried on a hotplate. 1 ml of 2M HCl was added to each, and the drying procedure repeated, to purify the residue. A blank was also prepared using 0.06286 g of dilute Nd spike ($0.01416502 \mu\text{g/g } ^{150}\text{Nd}$; $0.1155202 \mu\text{g/g } ^{149}\text{Sm}$) and 0.03902 g of Sr spike ($0.036424 \mu\text{g/g } ^{84}\text{Sr}$). One of the rock samples (AJS182) was run twice for both isotope systems to observe errors.

Sr and the REE were then separated using the first set of columns. The mixture was taken up in 1 ml of 2M HCl, and dropped into prepared columns containing Bio-Rad AG 50W-X8 200-400 mesh resin. After elution with 11 ml of 2M HCl, the Sr fraction was collected using 10 ml of 2M HCl, and the REE fraction with 10 ml of 6M HCl. The fractions were evaporated on the hotplate.

Refining of strontium was carried out in own-made 100 μl teflon columns, filled with 100-150 μ resin, conditioned with 3M HNO_3 . The samples were taken up in 200 μl aliquots of 3M HNO_3 and dropped into the columns. After elution with 1300 μl of 3M HNO_3 , the Sr was collected with 2 ml of H_2O , and dried on the hotplate.

Neodymium and samarium were separated from the REE fraction using a reverse chromatographic method. 50 ml columns with 0.5 cm diameter quartz tubing were employed, with a fill of teflon powder (10 g) and 1 g of HDEHP powder [Bis-(2-ethylhexyl) hydrogen phosphate]. These were washed using 50 ml 6M HCl and then conditioned with 14 ml 0.15M HCl. The samples were taken up in 0.2 ml 0.15M HCl and dropped into the column. According to the calibration carried out beforehand, 17 ml 0.15M HCl were eluted, then the Nd was collected with 10 ml 0.15M HCl; after elution with 4 ml 0.30M HCl, the Sm fraction was collected with 5 ml 0.30M HCl.

Both sets of liquid were evaporated overnight, and then purified with a drop of concentrated HNO_3 before drying again.

The samples were run on a Finnigan MAT 262 mass spectrometer equipped with 7 collectors, between the 4th and 11th December 1996. Strontium was loaded onto tungsten filaments, using 0.5M HNO₃ with a little TaF₅ added to prevent excessively rapid vaporisation, and was run with the collectors in static mode. Neodymium was loaded onto rhenium filaments with 0.5M HNO₃, and was run as Nd⁺ in static and semi-dynamic modes (the latter being used additionally due to wear on the Faraday collecting cups).

The mean ⁸⁷Sr/⁸⁶Sr value of the NBS987 standard during the period of analysis was 0.710257±7 (2σ) and the ¹⁴³Nd/¹⁴⁴Nd value of the AMES standard was 0.511962±5 (2σ).

The blanks were 220 pg (Sr), 33 pg (Sm) and 86 pg (Nd).

D.3 ANALYTICAL PROCEDURE FOR RB-SR AT OXFORD

Approximately 0.2 g of powdered rock sample was weighed into an FEP beaker, and dissolved using 5 ml HF and 2-3 drops of 16M HNO₃. This was evaporated to dryness in a PTFE evaporator (with a supply of filtered air) under infra-red lamps. 5 ml of 6M HCl was then added and evaporated to incipient dryness. The sample was then taken up in 4 ml of 3M HCl and centrifuged at 2000 rpm for 10 minutes, before 2 ml of the solution was loaded onto a prepared cation exchange column.

Separation was conducted in 0.7 cm quartz columns with 8.5 cm of AG50W X-12 200-400 mesh resin (Bio-Rad - batch 41722A). Before sample addition the columns were equilibrated with 5 ml 3M HCl. After loading, the columns were washed with 3M HCl in batches of 2 x 1 ml, 1 x 2 ml and 1 x 15 ml before the Sr was collected in 8 ml of acid of the same strength, according to the calibration. After collection, the columns were washed with 6M HCl and then water before equilibration with 3M HCl for the next separation.

The samples were then evaporated to ~10 % of their original volume and poured into quartz phials in which evaporation to dryness was completed. A few drops of Aqua Rega (HCl/HNO₃) were added to remove any organic impurities; drying was then completed.

The samples were loaded onto tantalum filaments using H₃PO₄, and were out-gassed before running on a fully automated VG-Isomass 54E mass spectrometer at the Department of Earth Sciences in Oxford between 27th and 30th June, 1997. The average value of the NBS987 standard was 0.710274±20.

D.4 DATA

The results of the analyses are given below, in both their raw and age-corrected form. Correction was carried out to 25 Ma, an average age for the rocks on the basis of published data (e.g. Griffin *et al.*, 1987), using the equation:

$$(^{87}\text{Sr}/^{86}\text{Sr})_0 = (^{87}\text{Sr}/^{86}\text{Sr})_m - ^{87}\text{Rb}/^{86}\text{Sr} \cdot (e^{\lambda t} - 1)$$

and its equivalent for the Sm-Nd system, where the suffixes o and m represent age-corrected and measured ratios respectively.

$\lambda(^{87}\text{Sr}/^{86}\text{Sr}) = 1.42 \times 10^{-11}$

$\lambda(^{143}\text{Nd}/^{144}\text{Nd}) = 6.54 \times 10^{-12}$

abundances: ⁸⁷Rb = 0.278346 of natural Rb
 ⁸⁶Sr = 0.098600757 of natural Sr

Sample	Type	(⁸⁷ Sr/ ⁸⁶ Sr) _m	analytical error ±	Rb ppm	Sr ppm	⁸⁷ Rb/ ⁸⁶ Sr	(⁸⁷ Sr/ ⁸⁶ Sr) _o
27	basanite	0.702996	0.000007	23.1	1254.3	0.0520	0.702997
101	basanite	0.703302	0.000007	26.2	1230.9	0.0601	0.703281
102	basalt	0.703773	0.000007	23.8	556.8	0.1207	0.703730
104	basanite	0.703531	0.000007	37.2	1142.6	0.0919	0.703498
108	basanite	0.703568	0.000007	57.6	1513.3	0.1074	0.703530
113	basanite	0.703488	0.000006	21.3	1588.5	0.0379	0.703475
144	basalt	0.703888	0.000007	25.1	502.3	0.1411	0.703838
182I	basalt	0.704007	0.000007	12.4	696.1	0.0503	0.703990
182II	basalt	0.704007	0.000007	12.4	696.1	0.0503	0.703990
235	basalt	0.703456	0.000007	20	883.4	0.0639	0.703434
236	basalt	0.703716	0.000006	25.5	652.2	0.1104	0.703677

Table D.1 Measured and age-corrected Sr-isotope ratios for the samples analysed at Rennes. Rb and Sr concentrations from XRF analysis were used (Table B.1).

Sample	Type	(⁸⁷ Sr/ ⁸⁶ Sr) _m	analytical error ±	Rb ppm	Sr ppm	⁸⁷ Rb/ ⁸⁶ Sr	(⁸⁷ Sr/ ⁸⁶ Sr) _o
20	basanite	0.70282	0.000020	15.8	990.5	0.045031	0.702804
21	basanite	0.702802	0.000020	16.8	978.9	0.048448	0.702785
39	basanite	0.703613	0.000024	37.9	1433.0	0.074662	0.703586
99	basanite	0.703761	0.000015	40.0	983.9	0.114766	0.703720
100	basanite	0.703278	0.000020	28.2	1297.5	0.061355	0.703256
106	basanite	0.703485	0.000021	22.1	1104.0	0.056510	0.703465
111	basanite	0.703552	0.000020	33.9	1201.9	0.079623	0.703524
112	basanite	0.703547	0.000021	38.9	1361.6	0.080650	0.703518
126	basanite	0.703087	0.000019	17.9	957.9	0.052752	0.703068
143	basalt	0.703938	0.000021	26.5	656.6	0.113933	0.703898
167	basalt	0.703912	0.000023	27.2	554.7	0.138425	0.703863
168	basalt	0.703903	0.000021	23.6	684.4	0.097343	0.703868
175	basalt	0.703931	0.000014	20.6	850.3	0.068391	0.703907
232	basalt	0.703584	0.000020	25.6	789.2	0.091571	0.703551
R1	basanite	0.703027	0.000020	19.2	1161.0	0.046685	0.703010
R2	basanite	0.703036	0.000020	17.4	1212.5	0.040511	0.703022

Table D.2 Measured and age-corrected Sr-isotope ratios for the samples analysed at Oxford. Rb and Sr concentrations from XRF analysis were used (Table B.1).

Sample	Type	$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{m}}$	analytical error $\pm$	Sm ppm	Nd ppm	$^{147}\text{Sm}/^{144}\text{Nd}$	$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{o}}$
27	basanite	0.513023	0.000008	6.31	30.74	0.1241	0.513003
101	basanite	0.512888	0.000005	11.01	57.69	0.1154	0.512869
102	basalt	0.512800	0.000005	4.91	22.76	0.1305	0.512779
104	basanite	0.512816	0.000005	10.13	56.18	0.1090	0.512798
108	basanite	0.512822	0.000006	13.27	73.63	0.1090	0.512804
113	basanite	0.512843	0.000006	13.11	74.29	0.1067	0.512826
144	basalt	0.512788	0.000004	5.65	26.17	0.1306	0.512767
182I	basalt	0.512924	0.000006	5.70	22.42	0.1538	0.512899
182I	basalt	0.512914	0.000006	4.40	17.3	0.1537	0.512889
235	basalt	0.512892	0.000006	6.63	32.16	0.1247	0.512872
236	basalt	0.512854	0.000006	4.96	22.16	0.1352	0.512832

Table D.3 Measured and age-corrected Nd-isotope ratios for the analysed samples. Concentrations of Sm and Nd were established by isotope dilution.