# BASIC ALKALINE ROCKS

by

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Arguments and analyses presented in this thesis are my own, unless otherwise acknowledged

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TO DAD

WITH ALL MY LOVE

ABSTRACT

Rocks of the alkaline association occur in three tectonic settings. These are characterised by tensional failure of the crust and locally extensive partial melting (high heat flow, shallow seismic anomalies) in the underlying upper mantle.

Localised alkaline activity accompanies the formation of tholeiitic ocean crust along the mid-ocean ridges. The predominantly alkaline island chains in the ocean basins are added to the oceanic crust as the plate moves over a "hotspot" source in the low velocity channel. Alkaline volcanism also occurs along the continental rift systems, and in the neighbourhood of secondary spreading centres - interarc basins - in island arcs.

The "alkaline" rocks which are commonly believed to represent the final stage in the chemical zonation of magmas in island arcs, comprise two distinct associations. Firstly, there is the typical alkaline association. Secondly, there is the shoshonite association, distinguished by lower $TiO_2$ contents, and $K_2O/Na_2O$ ratios commonly near unity. Alkaline and shoshonitic activity in the island arc environment appears to be related to the disruption or cessation of steady state subduction.

Primary alkaline magmas are generated by partial melting processes in a hydrous, peridotitic upper mantle, in the absence of a fluid phase. The incompatable element geochemistry of primary alkaline rocks is not consistent with the simple partial melting model, and is attributed to a patchy distribution of accessory phases in the source regions. Heterogeneities of this kind eliminate the problem of magma segregation, and allow considerable latitude in both the volume and the incompatible element chemistry of the nephelinitic melt produced at the fluid absent solidus.

Primary magmas are represented in the typical alkaline association, the high-Ca alkaline association, the high-K alkaline association, kimberlites, and potassic lamproites. The typical alkaline association has a global distribution; the others appear to be restricted to continental occurrences.

New analytical data for the Tertiary Monaro volcanics, south-eastern NSW, Australia, illustrate the primary geochemical variations in the typical alkaline association in a continental (rift) environment.

The distinctive chemical features of the alkaline "sub-associations" are related to tectonic setting, and to the heterogeneous accessory mode in the upper mantle source regions.

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# CHAPTER 1 : INTRODUCTION

## 1.1 Thesis structure

This chapter discusses the layout of the thesis, and the terminology used therein. In Chapter 2, the global distribution of the alkaline association is examined from the viewpoint of plate tectonics. In oceanic regions, alkaline activity accompanies the formation of new ocean crust along the mid-ocean ridge spreading axes and at "point sources" within the ocean basins. Alkaline activity also occurs along continental rift systems, and in the neighbourhood of secondary spreading centres behind island arcs. The tensional failure of the crust in all the above environments is associated with high heat flow and shallow seismic anomalies, "diapirism", in the underlying upper mantle. Voluminous tholeiitic partial melts are commonly derived from this shallow, low velocity region; alkaline liquids originate at deeper levels, where the low velocity zone dips away from the spreading axis.

The mineralogies and composition of the peridotitic upper mantle source regions are examined in more detail in Chapter 3. A fluid phase need not coexist with the subsolidus mantle assemblages since all volatile components can be accommodated in crystalline phases eg. a carbonate polymorph, a pargasitic amphibole and/or a phlogopite-rich mica. In the absence of a fluid phase, the hydrous accessories break down at the solidus.

The atomic ratio 100Mg/Mg+Fe" ($Fe_2O_3$/FeO=0.25) provides a criterion for the identification of unmodified, upper mantle-derived partial melts. These primary (= primitive) magmas have 100Mg/Mg+Fe" ratios > 67.0.

Chapter 4 assesses several proposals for the origin of basic alkaline rocks. The preferred hypothesis - requiring small degrees of partial melting in a hydrous upper mantle - is consistent with experimental, geochemical and tectonic constraints.

Chemical variation within the alkaline association is discussed in Chapter 5. Five groups or "sub-associations"

can be recognised, and the diagnostic chemical features of each group are illustrated by its particular primary magma, or primary magma series. The sub-associations comprise:

1. the typical alkaline association
2. the high-Ca alkaline association
3. the high-K alkaline association
4. kimberlites
5. the potassic lamproites

Only the typical alkaline association has a global distribution; all other groups are apparently confined to continental environments.

New analytical data for Tertiary basic alkaline rocks from the Monaro district, southeastern NSW, are used to illustrate geochemical features of the typical alkaline association in a continental setting. The rocks have undergone only limited fractionation, so the initial fractionation trends are readily identified and thus provide indirect information on the chemical variations in the primitive parent liquids. Primary variations in the incompatable element chemistry of the Monaro volcanics show that the simple partial melting hypothesis requires further modification. The normalised concentration ranges of the various elements are not consistent with effectively linear dilution of a broadly coherent group. This conclusion likewise applies for a global compilation of analytical data for primitive alkaline rocks.

Chapter 6 briefly emphasises the distinction between the alkaline association and the shoshonite association and suggests that their mutual occurrence in an island arc environment is related to the disruption or cessation of steady state subduction. Shoshonite magmas may originate in the upper mantle above the foundering lithosphere, but presumably evolve at deeper levels, and in a different physical and chemical environment, than do alkaline liquids.

The introductory sections of Chapter 7 summarise the experimental and theoretical basis for many of the petrogenetic ideas introduced throughout the thesis. The primary geochemical variations in alkaline rocks are consistent with heterogeneous source regions, where the

heterogeneities simply involve the patchy distribution of hydrous accessory phases. Partial melting theory (Shaw, 1970) illustrates the consequences of a variable accessory mode on the trace element chemistry of the initial melts generated at the fluid absent solidus. A patchy distribution of hydrous accessory phases in a fluid absent paragenesis also overcomes the serious problem, with alkaline partial melts, of magma segregation.

Analytical data are tabulated in appendices.

## 1.2 Terminology

"The alkaline association" refers to a specific example of a rock association, which was defined by Bowen (1928) ... "to designate a group of rocks associated in the field and of the same age". Members of an igneous rock association have certain chemical and therefore mineralogical features in common, but do not necessarily have any direct genetic link. Brögger (1894) said that there was continuous compositional change in a rock series, thereby implying that the members of the series have a direct genetic link. Harker (1909) equated rock series with crystal fractionation series and the term is used in this sense in the thesis, unless explicitly stated otherwise - viz. partial melting series. A petrographic province (Judd, 1886) refers to a regional grouping of presumably related igneous rocks of similar age.

Classification of fine-grained or glassy rocks using modal parameters is unsatisfactory, so chemically oriented schemes have been introduced to name the members of volcanic associations. Alkali basalt, hawaiite, mugearite and benmoreite have been defined on the basis of both modal and normative plagioclase composition, normative nepheline content, $K_2O$:$Na_2O$ and differentiation index (Macdonald, 1960; Muir & Tilley, 1961; Macdonald & Katsura, 1964; Tilley & Muir, 1964); and Coombs & Wilkinson (1969) define the more undersaturated analogues in similar terms. The continuing emphasis on the C.I.P.W. normative nepheline content of alkaline rock types stems from Yoder & Tilley

(1962), who pointed out that most (basic) members of alkaline associations lie in the undersaturated volume of the normative system Fo-Di-Ne-Qz.

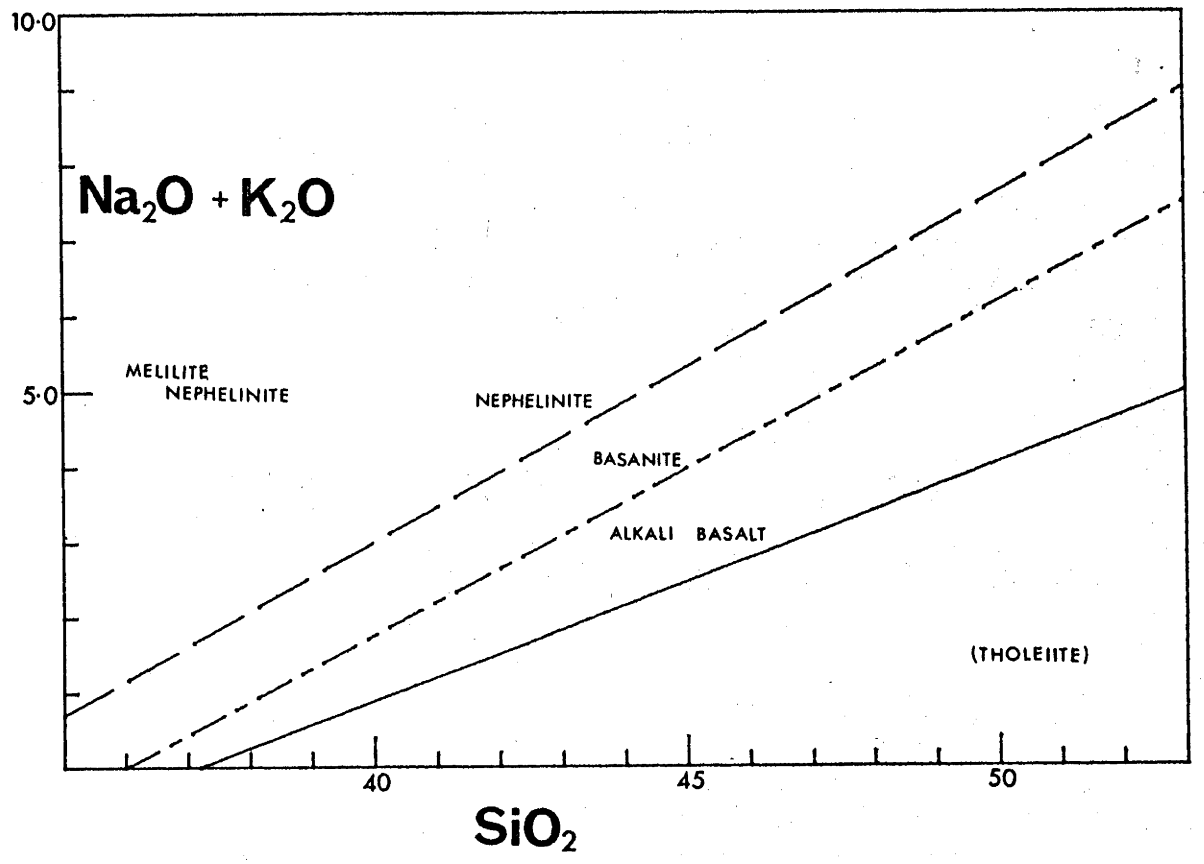
A norm calculation recasts the bulk rock chemistry in terms of ideal mineral compositions. A normative classification is generally most satisfactory when there is a fairly close correlation between the normative and observed mineralogies, so that chemical variation producing a change in the modal mineralogy is mirrored by a change in the normative mineralogy. In such a case eg. the granite mesonorm, the normative classification is convenient and meaningful. But some basic alkaline rocks are hypersthene normative. Macdonald & Katsura (1964) plotted weight $Na_2O+K_2O$ vs $SiO_2$ for Hawaiian basaltic rocks and placed an empirical linear boundary - corresponding approximately to a 10% normative hypersthene contour - between the tholeiitic and alkaline fields. The hypersthene normative rocks were assigned to tholeiitic or alkaline fields according to the presence or absence of a reaction relationship between olivine and Ca-poor pyroxene.

Although the reaction relationship is by no means an unequivocal indicator of tholeiitic affinity (Coombs & Wilkinson, 1969) it can generally be interpreted as an indication that some critical chemical (rather than physical) limit has been reached. This would seem to provide a logical and meaningful boundary position for a chemical classification, yet there is no change in the normative mineralogy at this point.

In this thesis <u>basic alkaline rocks</u> are compositions which typically have over 1.5% $TiO_2$, < 50% $SiO_2$ and lie above the $Na_2O+K_2O$ vs $SiO_2$ boundary drawn by Macdonald & Katsura (1964). Chayes and Velde (1965) showed that $TiO_2$ content is a very efficient discriminant between circumoceanic (ie. island arc) magmas and basic alkaline rocks from oceanic islands, so $TiO_2$ content can be used to distinguish the alkaline association from other non-tholeiitic compositions which plot above Macdonald & Katsura's boundary. $Na_2O+K_2O$ vs $SiO_2$ boundaries are also used to delineate alkali basalt from basanite (Strong, 1972)

Fig. 1.1

IDENTIFICATION OF BASIC ALKALINE ROCK TYPES




——————— Macdonald & Katsura (1964)

——·——·——·—— Strong (1972)

—— —— —— —— Saggerson & Williams (1964)

Table 1.1

Selected analyses of typical basic alkaline rocks

| ROCK TYPE | ALKALI BASALT | | BASANITE | | NEPHELINITE | | MELILITE NEPHELINITE | |
|---|---|---|---|---|---|---|---|---|
| LOCALITY | Hawaii | se. NSW | Comores Is. | se.NSW | New Zealand | se.NSW | Oahu | Tasmania |
| REFERENCE | 1 | 2 | 3 | 2 | 4 | 2 | 2 | 5 |
| $SiO_2$ | 46.53 | 46.88 | 42.44 | 44.13 | 41.1 | 41.72 | 35.95 | 36.93 |
| $TiO_2$ | 2.41 | 1.83 | 2.46 | 2.20 | 2.1 | 2.45 | 2.79 | 2.63 |
| $Al_2O_3$ | 14.91 | 14.41 | 11.88 | 14.36 | 11.4 | 13.81 | 10.13 | 9.21 |
| $Fe_2O_3$ | 3.69 | 2.47 | 4.45 | 3.12 | 4.2 | 2.72 | 7.02 | 4.14 |
| FeO | 9.09 | 8.69 | 8.75 | 7.60 | 7.7 | 8.96 | 9.63 | 8.96 |
| MnO | 0.19 | 0.18 | 0.23 | 0.15 | 0.19 | 0.18 | 0.24 | 0.24 |
| MgO | 8.69 | 8.99 | 11.69 | 9.73 | 11.4 | 8.62 | 11.46 | 15.90 |
| CaO | 9.86 | 9.50 | 12.12 | 9.54 | 12.9 | 10.11 | 12.61 | 12.80 |
| $Na_2O$ | 2.98 | 2.87 | 2.92 | 3.06 | 4.4 | 4.09 | 5.22 | 3.65 |
| $K_2O$ | 0.97 | 1.04 | 0.56 | 1.61 | 1.5 | 2.28 | 1.84 | 1.38 |
| $P_2O_5$ | 0.31 | 0.52 | 0.67 | 0.67 | 0.9 | 1.26 | 1.11 | 1.29 |
| LOI | | 1.96 | 1.86 | 3.29 | 1.15 | 3.24 | 1.12 | 1.9 |
| TOTAL | 99.63 | 99.34 | 100.04 | 99.46 | 98.94 | 99.47 | 99.11 | 99.03 |
| $100Mg/Mg+Fe"^6$ | 60.4 | 64.3 | 66.7 | 67.1 | 68.4 | 62.3 | 61.1 | 73.2 |

1 Helz (1972). This is the 1801 Hualalai alkali basalt, also used experimentally by Yoder & Tilley (1962), Nesbitt & Hamilton (1970), and Haygood *et al.* (1971).
2 this thesis: Alkali basalt K3; basanite K66; nephelinite K30; melilite nephelinite 2089.
3 Strong (1972). Basanite 23 ($Na_2O/K_2O$ is slightly high).
4 Black & Brothers (1965). Olivine nephelinite, Todd's Quarry, Arapohue, Northland, NZ.
5 Melilite nephelinite - D.H. Green, unpublished analysis.
6 $Fe_2O_3/FeO$ first recalculated to 0.25.

and basanite from nephelinite (Saggerson & Williams, 1964) and these divisions correspond approximately to 5% and 14% normative nepheline respectively. Fig. 1.1 illustrates this convenient and simple classification. Note that subsequent hydration effectively lowers the $SiO_2$ coordinate, but because the divisions between basic alkaline rock types are quite arbitrary, the classification of compositions close to field boundaries need not strictly conform to the proposed scheme. The problem of positioning meaningful and satisfactory boundaries in a chemical classification of the basic alkaline rocks can be side-stepped by simply illustrating the groupings by means of representative compositions, and this procedure has been adopted in this thesis (Table 1.1). Previous inconsistencies in nomenclature should mean that a subjectively selected example provides a more satisfactory typical composition than the mean, median or mode of a group of similarly labelled rock compositions.

Cluster and discriminant analysis demonstrates that basic alkaline rocks, continental (and Hawaiian) tholeiites and mid-ocean ridge tholeiites comprise chemically distinct groups (Bernotat, 1972). It is interesting to note that Bernotat's classification groups potassic alkaline provinces (ie. $K_2O/Na_2O$ ratios characteristically close to, or exceeding unity) with the typical alkaline association, whereas potassic series whose $TiO_2$ contents are characteristic of the shoshonite association (Kesson & Smith, 1972) form a separate group.

Continental and oceanic alkali basalt means (Bernotat, 1971) illustrate the characteristically higher $TiO_2$ content of the oceanic group (see also Manson (1967): Table 5). The higher $TiO_2$ in oceanic provinces is believed to be a primitive feature reflecting chemical and/or physical factors prevalent in, but not necessarily exclusive to, oceanic source regions.

## 1.3 Thermodynamic definitions

R gas constant

T temperature °K

$P_{load}$ load pressure

$\mu_i$ chemical potential of component i in phase m

$f_i$ fugacity of component i in phase m

$a_i$ activity of component i in phase m

$X_i$ mole fraction of component i in phase m

$\gamma$ activity coefficient; $\gamma_i = a_i/X_i$ and $\gamma_i = 1$ for ideal solutions and mixtures

fluid refers to a vapour phase, as distinct from a melt

$Pe_i$ is the equilibrium pressure of component i in phase m, where m is at a pressure $P_{load}$. This is the pressure of pure i which would be at equilibrium with component i in phase m through a membrane permeable only to component i (Greenwood, 1961).

$Pe_{H_2O}$ can be read from fugacity tables where $P_{load}$, T and fugacity or activity of $H_2O$ are known.

$^o$superscript refers to the standard state, here selected to be pure i in phase m at the temperature and pressure in question. However in silicate systems, solution of the condensed phases in the fluid phase can become significant at pressures higher than a few kilobars, so that even if only one volatile species is present, $a_i^{fluid} < 1$. To avoid this problem Holloway (1972) has modified the standard state definition so that $a_i^{fluid}$ and $X_i^{fluid}$ equal unity at $P_{load}$ and T when the only volatile component in the fluid phase <u>for that system</u> is component i.

For component i in phase m

$$\mu_i - \mu_i^o = RT \ln(f_i/f_i^o)$$

$$= RT \ln a_i$$

$$= RT (\ln X_i + \ln \gamma_i)$$

Equilibrium between phases m and n at constant temperature and load pressure requires that $\mu_i^m = \mu_i^n$ but does not necessarily imply that $\mu_i^{om} = \mu_i^{on}$ ie. $a_i^m = a_i^n$. However in specific silicate systems the same standard state applies for $H_2O$ in a hydrous phase, and in the melt and fluid phases, so at equilibrium, $a_{H_2O}^{solid} = a_{H_2O}^{melt} = a_{H_2O}^{fluid}$.

A fluid phase which coexists with hydrous phases and/or a $H_2O$-bearing magma must always contain a small quantity of $H_2O$.

# CHAPTER 2 : THE TECTONIC SETTING OF THE ALKALINE ASSOCIATION

## 2.1 Introduction

Plate theory has integrated earlier hypotheses of continental drift and sea floor spreading to produce a comprehensive kinetic model for global tectonics. Lithospheric plates 75-120 km thick are in relative motion above the low velocity channel in the upper mantle. The phenomena associated with the low velocity channel have been attributed to changes in mineralogy, composition or simply a high temperature gradient but the favoured interpretation of partial melting is most consistent with the low seismic velocities, high attenuation and heat flow and abrupt boundaries (Anderson & Sammis, 1970). In addition, this interpretation provides a low friction surface for plate movement and adds support to current ideas in petrology by providing a potential source region for basaltic magmas.

Lateral material transfer within the low velocity channel raises serious mechanical difficulties even when seismic continuity is correlated with physical continuity. With less than 6% interstitial melt not just the liquid but the complete melt-plus-residuum will be involved. McKenzie (1969), Green (1971) and McDougall (1971) favour "convection" within the low velocity channel, with the upper layers moving with the overlying plate, and return flow at depth. Indeed the uppermost layer will move with the overlying plate but this should involve a negligible proportion of the total thickness since from seismic evidence the transmission of shear stresses through this region is very low, and no doubt lower under the low strain rates related to the overriding plate. The mass balance required by the continuous displacement of lithosphere away from the mid-ocean rises can be met by the sector of mantle directly beneath the rise. There is no valid basis for assuming return flow at depth in the low velocity zone.

An interesting picture emerges when the global distribution of the alkaline association is examined from the viewpoint of plate theory.

(1) Alkaline activity commonly accompanies the production of oceanic crust (ocean ridge tholeiites) along the mid-ocean ridges, and may also accompany tensional failure of the plate away from the spreading axis.

(2) In the island arc environment, alkaline rocks typically occur when a secondary spreading axis has evolved behind the arc (interarc basin). The new spreading centre is preceded by rifting of either continental or oceanic crust.

(3) Alkaline activity characteristically occurs along major and minor continental rift systems. The final but not inevitable phase of a major rift system is the rupturing of the crust and the complete division of the continental plate by the formation or continuation of an oceanic axial spreading centre.

In all the above tectonic settings, contemporaneous tholeiitic activity is common. Since several of the rift systems, all ocean floors and recognisable interarc basins are late Mesozoic or younger, the geological column preserves only an incomplete record of alkaline activity before this time c.f. Engel et al., (1965).

## 2.2 The Alkaline Association in the Oceanic Environment

### Introduction

Mid-ocean ridges are physiographically and geophysically similar to the continental rift systems in having a median rift valley, high heat flow ($\sim$ 3 $\mu$cal/cm$^2$) and shallow seismicity (Langseth & von Herzen, 1970; Sclater *et al.*, 1971). The zone of partial fusion in the upper mantle beneath the ridge crests is defined by severe attenuation and low and laterally variable $P_n$ velocities, $\sim$ 7.5 km/sec (Shor & Raitt, 1969) and is believed to be the source region for the new basaltic ocean crust emplaced along the spreading axis (Green, 1971). Its upper boundary dips away from the ridge crests to delineate the low velocity zone at $\sim$ 80-100 km beneath the ocean basins (Anderson, 1970; Dziewonski, 1971).

Distribution of Alkaline Rocks

Igneous samples dredged from seamounts are commonly alkaline. The sharp topographic relief of seamounts is not consistent with the profile of an alkaline-capped tholeiitic shield. Seamounts are particularly common as chains along fracture zones and in the shallower waters on the flanks and crest of mid-ocean ridges, where they may be exposed as (alkaline) islands (Menard, 1969). Scarps produced by active transform faults at ridge crests are preserved on the inactive flanks and basin floors as fracture zones (Menard & Atwater, 1969). Excluding samples from seamounts and island chains, dredge hauls made away from the ridges have collected alkaline rocks only along the major fracture zones (van Andel et al., 1967; Melson et al., 1968; Bonatti et al., 1970).

Subaerial exposures of alkaline rocks include groups of islands along the mid-ocean rises, and island chains in the ocean basins. Active volcanism occurs in both settings.

Discussion

Green (1971) has considered ocean ridge tectonics in terms of a geophysically and petrologically satisfactory model requiring extensive diapirism and segregation of a large volume of basaltic liquid (ocean ridge tholeiite) at shallow levels. This takes place in the anomalous region of the upper mantle directly beneath the ridge crests whereas alkaline magmas are generated at deeper levels away from the central axial zone of diapirism.

McBirney & Gass (1967) correlated the degree of silica saturation of alkaline differentiates on oceanic islands with the geothermal gradient. Trachytic differentiates are most common near ridge crests where heat flux is high whereas phonolites are more abundant on islands on the flanks of the rise and in the ocean basins where heat flux is lower. This could suggest that at shallower depths beneath the ridge crests a larger degree of partial melting takes place and alkali basalt parent liquids, rather than nephelinitic liquids, are generated.

Island chains in the ocean basins have a brief history of alkaline ± tholeiitic volcanic activity (Johnson & Malahoff,

1971). In the Pacific basin the inactive Cook, Tuamoto, Society and Austral Islands lie on aseismic "ridges" i.e. volcanic piles, whereas shallow seismicity is recorded in the active Hawaiian chain (Wilson, 1970). There are weak velocity anomalies in the upper mantle beneath the Hawaiian ridge at $\sim$20 km (Furomoto et al., 1971).

Green (1971) and McDougall (1971) have discussed the evolution of island chains in some detail and conclude that local diapirism with subsequent segregation of melt within the lithosphere gives rise to tholeiitic liquids, whereas alkaline liquids are tapped directly from the low velocity zone. However age determinations (McDougall, 1971) show that the (tholeiitic) volcanic focus has migrated along the Hawaiian chain towards the East Pacific rise at more than twice the half plate spreading rate. Green (1971) and McDougall (1971) relate the propogation of a tensional fracture with consequent (sic) volcanism to the proposed return flow in the deeper levels of the low velocity channel.

Jackson et al. (1972) point out that although the chain as a whole is linear, individual volcanoes lie along short en echelon loci and there is a non-linear progression of volcanism along these loci. Their interpretation of the K-Ar ages is in accordance with the movement of the plate over a stationary "hotspot" source in the underlying upper mantle.

Summary

Minor alkaline activity accompanies the formation of new oceanic crust along the mid-ocean ridges with groups of alkaline islands and seamounts distributed along the spreading axis, and subsidence of islands and seamounts occurs as they are carried into deeper waters away from the rise. Alkaline liquids are tapped directly from the low velocity zone at depth beneath the ridge crests. The island chains in the ocean basins consist of alkaline magmas, sometimes accompanied by Hawaiian-type ("continental") tholeiites. These additions to the oceanic crust accompany tensional failure in the plate as it moves away from the mid-ocean spreading axis, and the source regions again lie in the low velocity zone.

## 2.3 The Alkaline Association in the Island Arc Environment

### Introduction

The chemical zonation of rock types across an island arc was first recognised by Kuno (1959, 1960) and correlated with depth to earthquake foci i.e. depth to dipping Benioff zone. Nearest the trench is the island arc tholeiitic series, followed by low-, medium- and high-K calcalkaline rocks (Jakeš & White, 1969). Kuno's suggestion that the final members of this progression are "alkaline rocks" has rarely been questioned (c.f. Jakeš & White, 1969). However more recent studies have shown that the superficially similar "alkaline" rocks in the island arc environment in fact can comprise two distinct associations - firstly the alkaline association, whose members also occur in other tectonic environments, and secondly the shoshonite association (Joplin, 1968) which is found in more evolved island arcs, and displays the characteristically low $TiO_2$ contents of island arc magmas ("circumoceanic basalts" of Chayes & Velde, 1965).

Interarc basins (Karig, 1971) or marginal seas (Packham & Falvey, 1971) are the regions behind an island arc where new oceanic crust is or was produced along an axial spreading centre. The mechanism producing rifting of the crust behind the arc is believed to be diapiric uprise in the underlying upper mantle (Oxburgh & Turcotte, 1970; Karig, 1971) which then also accounts for the high regional heat flow, and high attenuation and low seismic velocities in the underlying mantle. Karig (1971) has suggested that interarc spreading formed all the marginal basins (in the western Pacific) but admits that geophysical data are not yet sufficient to substantiate this hypothesis. Areas of controversy include basins behind the Izu-Bonin and Marianas arcs in the Philippine Sea plate, and behind the Aleutians; Jacob et al. (1972) report seismic retardation in the upper mantle beneath the Bering Sea behind the Aleutian arc.

### Discussion

In the island arc setting where an interarc basin has developed e.g. Sea of Japan, Sea of Okhotsk, and the Lau basin, the alkaline association typically occurs nearby. The

eruptive centres may be within the basin or on the adjacent continental and island arc landmasses. These areas are examined in more detail in the following paragraphs.

Sea of Japan and Sea of Okhotsk

Kanamori (1970) reported high heat flow, crustal thinning, and low velocity, high attenuation upper mantle beneath the Sea of Japan. $P_n$ retardation to 100 km (Vanek, 1969), high heat flow (Yasui et al., 1968) and crustal thinning (Kosminskaya et al., 1964) is found in the Sea of Okhotsk behind the Kurile-Kamchatka arc.

Analyses compiled by Ono (1962) reveal that the innermost "alkaline" series in the Japanese arc (Kuno, 1959, 1960) comprises two associations. In the northeast, generally within the 355 km earthquake foci isobath (Kanamori, 1970) are rocks of the shoshonite association. These can be unambiguously identified by their low $TiO_2$ contents (Kesson & Smith, 1972). In the south west, along the Izu lineament on the Pacific side, and continuing across Honshu into the Sea of Japan, are alkaline eruptive centres. These are part of the circum-Japan Sea province first recognised by Tomita (1935), which extends into Korea, Manchuria and Mongolia. Alkaline rocks in Sakhalin (Yagi, 1953) are either a part of this province, or are related to a similar tectonic environment in the Sea of Okhotsk. Rudich (1965) describes a Cenozoic silicic volcanic province on the Okhotsk coast.

Lau Basin

Mitrinovas and Isacks (1971) and Sclater et al. (1972) interpret the high heat flow and seismic attenuation in the Lau Basin, between the Lau ridge and the Tonga-Kermadec arc, in terms of axial spreading. Low velocity, high attenuation zones extending to depths of 120 km have been recorded behind the arc as far south as the Taupo acid volcanic province of North Island, New Zealand (Hatherton, 1970; Mooney, 1970) close to the Cenozoic Auckland alkaline province. The Fijian islands at the northern tip of the Lau ridge lie on a triangular plate bounded by two transform faults, both connecting the opposite-facing Tonga-Kermadec and New Hebrides arcs (Gill, 1970). Gill (1970) emphasises

the petrologic similarity between Viti Levu and currently active island arcs and suggests that the island was bordered by an active trench until 5-10 m.y. ago and has since drifted or rotated to its present position. On nearby Vanua Levu, and other smaller islands Recent lherzolite-bearing typical alkaline rocks overlie older island arc volcanics (Gill, 1972).

New Guinea

Alkaline volcanics and ignimbrites occur in the D'Entrecasteaux chain at the eastern tip of New Guinea (Davies & Smith, 1971). These islands lie in the Woodlark Basin, which Milsom (1970) has interpreted as a minor spreading centre.

Scotia Arc

Barker (1970) presents geophysical evidence for an active spreading centre behind the Scotia arc. Petrological studies of the Recent alkaline province at the tip of South America, which extends southwards into Antarctica, are summarised by Katsui (1972).

Summary

To date, the alkaline association has been recognised only in island arcs in which a secondary spreading axis has evolved behind the arc. Seismic and heat flow data are in accordance with the suggestion that interarc basins overlie a region of diapiric uprise in the upper mantle. Diapirism may simply be initiated by the oceanwards migration of the trench, however Oxburgh & Turcotte (1970) and Karig (1971) believe that diapiric uprise is triggered by the downgoing slab with the selective migration of a water-rich fluid phase into the overlying upper mantle. Gill (1972) argues that the mixing of lithosphere-derived and mantle-derived partial melts is an essential petrogenetic process in the derivation of island arc magma types. Hawkins & Nishimori (1971) and Sclater et al., (1972) report that basalts dredged from the spreading axis behind the Tonga-Kermadec arc have major and trace element compositions similar to ocean ridge tholeiites, so the lithospheric contribution to alkaline magmas in the same locality may be similarly negligible. The common occurrence

of very similar alkaline magmas in distinctly different tectonic environments suggests that this is so.

Experimentally derived constraints coupled with the mineralogies of the suite of ultrabasic xenoliths in alkaline rocks require that the source regions for the alkaline association lie at deeper levels (∿60-100 km) in or near the low velocity, high attenuation zone behind the arc. The new oceanic crust in the interarc basin consists of basaltic liquids segregated at shallow depths from the underlying seismically anomalous upper mantle. High heat flow may lead to partial fusion of thicker continental crust behind the arc, producing the highly silicic volcanics which commonly occur in these regions.

## 2.4 The Alkaline Association in Continental Rift Systems

### Introduction

Theoretical arguments favour a deep-seated, narrow, and ill-defined low velocity channel beneath ancient continental shield areas although seismic profiles are inconclusive.

Both tensional and compressional hypotheses have been advocated for the formation of the world rift systems (c.f. summary by Freund, 1965) but the concept of these structures as regions of tension and crustal thinning is now widely accepted. Negative Bouguer anomalies (Picard, 1970) and the available seismic and heat flow data suggest that there is a region of extensive partial melting in the upper mantle near the base of the crust beneath many rift systems with Cenozoic alkaline volcanics.

### Discussion

Surface heat flow measurements within the Rhine graben range from 2.2 to 4.0 $\mu cal/cm^2$ sec. contrasting with a mean of 1.7 $\mu cal/cm^2$ sec. in neighbouring areas (Hänel, 1970). In cross section there is a flattened elliptical zone between 30-40 km which is overlain by crustal strata ($P_n$ ∿ 7 km/sec) and underlain by upper mantle material with $P_n$ ∿ 8.2 km/sec (Ansorge *et al.*, 1970). $P_n$ velocities of 7.7 km/sec and S wave attenuation in this zone - the "rift cushion" of Ansorge *et al.*, (1970) - support the interpretation

that this is a region of partial melting in the upper mantle. Inferred P and S velocity profiles to 250 km show a weak low velocity channel to 220 km (Seidl et al., 1970). Little information is provided on the frequency and occurrence of deep focus earthquakes. Most documented seismic activity is shallow and is associated with a channel of attenuation and low velocity in the lower crust (St Müller, 1970).

Similarly most seismic activity is confined to crustal levels in the African rift system (Wohlenberg, 1970). Long & Sundaralingam (1970) suggest that P wave anomalies (at unspecified depths) in the upper mantle beneath the east African rift are due to partial fusion, and Wohlenberg (1970) has argued that there is a low velocity layer beneath the west African rift.

Crustal thinning occurs along the seismically active Baikal rift structure. Heat flow averaging 2.7 $\mu cal/cm^2$ sec. contrasts with a mean flux of 1.1 in surrounding areas (Liubimova, 1966; Zorin, 1966).

The Basin and Range province of the western United States lies in a tectonically complex region. Although the linear graben physiography is not strikingly apparent the geophysical similarities between this structure and other rift systems with Cenozoic alkaline volcanics are very pronounced.

The Basin and Range province lies between the Sierra-Cascades and the Rocky Mountains and is characterised by high heat flow, low Bouguer anomaly, thin crust, crustal extension and normal faulting, overlying anomalous high attenuation, low velocity upper mantle (Scholz et al., 1971).

Here crustal thicknesses averaging 30 km contrast with 40 km in adjacent regions (Prodehl, 1970) and heat flow $\sim$ 2.2 $\mu cal/cm^2$ sec. is high compared with 1.2 - 1.5 $\mu cal/cm^2$ sec. in neighbouring regions (Leeman & Rogers, 1970). Archambeau et al., (1969) showed that $P_n$ velocities of 7.7 km/sec and S wave attenuation define a low velocity zone in the upper mantle extending from the base of the crust to

150 - 175 km. This contrasts with the ill-defined, thinner and deeper low velocity zone beneath the Sierras and the Colorado Plateau between 100 - 175 km. Seismic activity is shallow and is restricted mainly to the eastern and western boundaries (Scholz et al., 1971).

Development of the rift systems

Ito & Kennedy (1970) believe that the zones with $7.4 < P_n < 7.9$ km/sec beneath the Rhine graben, Basin and Range province and mid-ocean ridges are a basal crustal layer of garnet granulite. Their model cannot account for the characteristically high attenuation in these regions, whereas a zone of partial fusion in the underlying upper mantle provides a satisfactory explanation for all the geophysical observations.

Bailey (1964) was the first to suggest that rapid pressure release by crustal rifting initiated partial melting in the underlying upper mantle due to adiabatic decompression. It is very difficult to imagine this type of unloading as an efficient process. An alternative hypothesis reverses cause and effect. The region of partial melting beneath the rift is interpreted in terms of diapiric uprise (Green, 1970), and this also produces the tensional stresses, crustal thinning and the dome-like uplift across the graben (Le Bas, 1971). The ultimate but not necessarily inevitable stage in the evolution of a rift system is the complete division of the continental plate and the formation or continuation of an axis of sea-floor spreading which can be either a mid-ocean ridge or a lesser spreading centre in an active interarc basin.

Scholz et al. (1971) conclude that the Basin and Range province is the precursor of a marginal sea,"an ensialic interarc basin", and the underlying zone of partial melting is an upper mantle diapir. They believe the diapir was generated when the collision of the east Pacific rise interrupted the descent of oceanic lithosphere along the western margin of the American plate. There is so far no way of determining whether this model is correct or whether the diapir simply developed through independent causes.

Summary

The shallow level, seismically anomalous region in the upper mantle beneath some recently active rift systems, is interpreted as a zone of partial melting and a potential source region for the voluminous "continental" tholeiites. Partial fusion of crustal material can result from the high geothermal gradient, producing the highly silicic volcanics which are not uncommon in rift systems (Leeman & Rogers, 1970). The source region of the alkaline rocks is believed to lie at greater depths in the ill-defined, seismically anomalous region of the upper mantle below the main zone of partial melting. This is consistent with experimental estimates of the P-T regime of the source region (Bultitude & Green, 1971).

## 2.5 The Tectonic Setting of the Alkaline Association in Eastern Australia

### Introduction

Cenozoic volcanism is confined to the eastern margin of the Australian continent away from the Precambrian shield, with the one exception of the Miocene leucite lamproites of the Fitzroy Basin, W.A. (Wellman, 1971). At a sufficient distance from the continental margin, the crustal thickness in both eastern Australia and in shield areas is 40 ± 5 km (Cleary, 1971). P wave station anomalies indicate a well developed low velocity zone under eastern Australia at a depth of approximately 100 - 200 km (Cleary, pers. comm.) but the low velocity zone is undetected under shield areas. The mean heatflow in southeastern Australia and Tasmania exceeds 2 $\mu cal/cm^2$ sec (Sass *et al.*, 1967). Although the crust in this region contains a large volume of granitic intrusives, the temperature at the M-discontinuity is estimated to be in the vicinity of 700°C. The upper mantle geothermal gradient is therefore unusually high, particularly below the Pliocene-Recent Newer Volcanics of western Victoria, where surface heat flow of 2.8 and 2.9 $\mu cal/cm^2$ sec has been recorded.

### Tectonic setting

The development of a spreading centre in the Tasman Sea at the end of the Cretaceous accompanied the separation

Figure 2·1 (a)

# MORPHOLOGICAL RECONSTRUCTION OF AUSTRALIAN-ANTARCTIC PLATE in LATE MESOZOIC

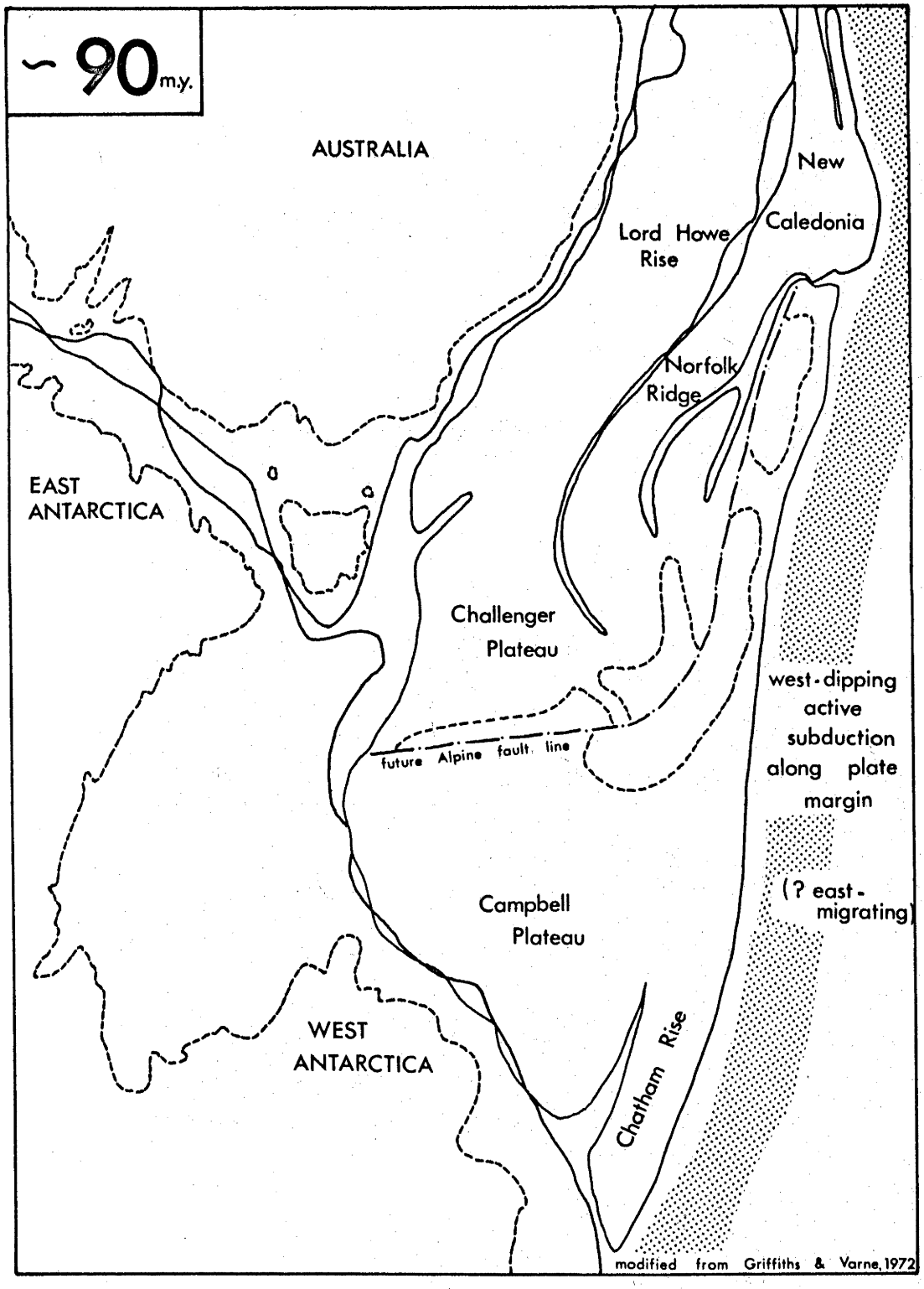
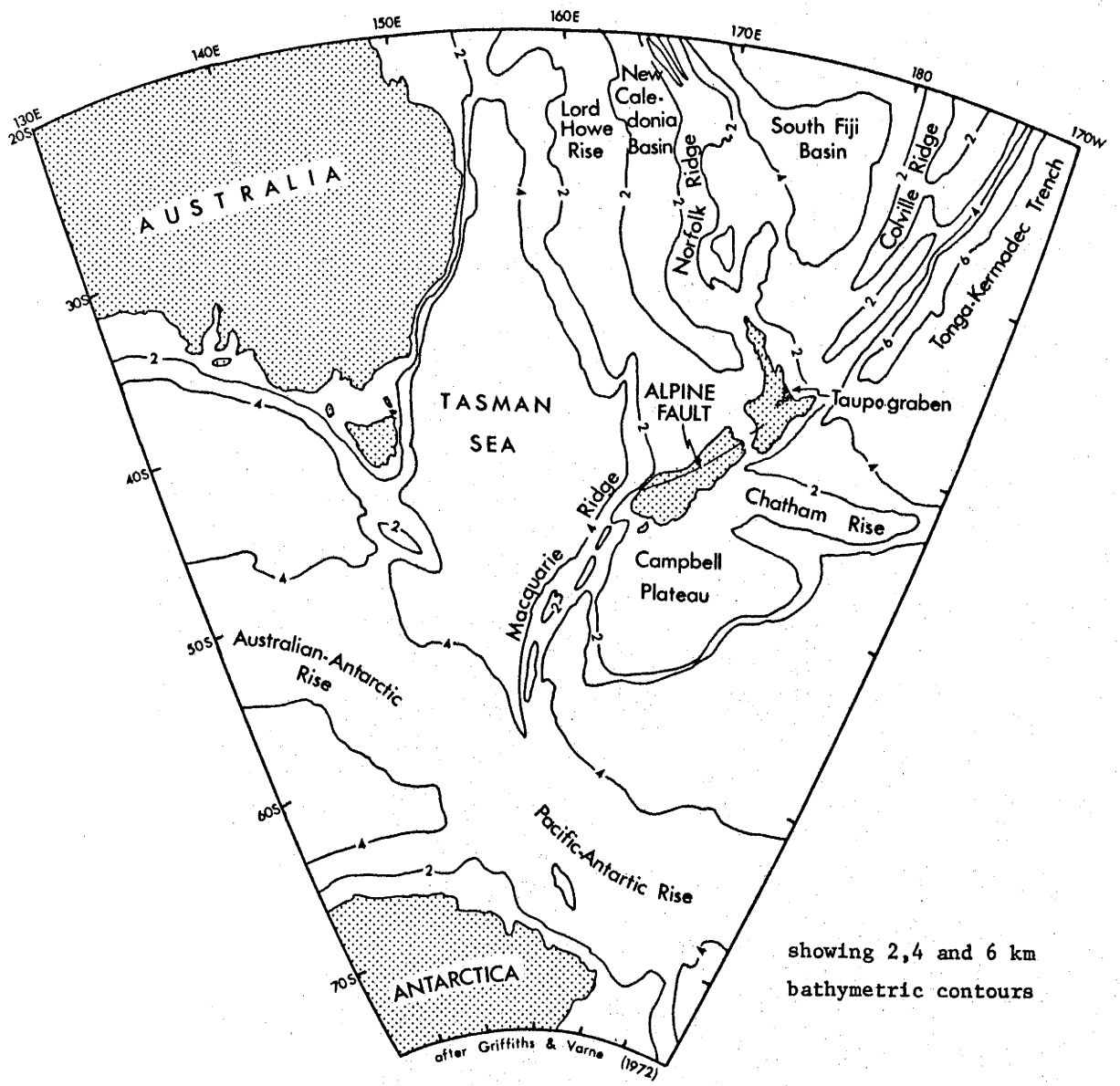


Figure 2·1(b)

# PRESENT DAY PHYSIOGRAPHY




showing 2,4 and 6 km bathymetric contours

and rotation of the Lord Howe rise and New Zealand away from Australia (Packham & Falvey, 1971). The northward movement of the Australian plate away from the Antarctic ridge is believed to have commenced at the close of the Palaeocene (Christoffel & Ross, 1970) or early Eocene (Weissel, 1971) which infers a mean half spreading rate of $\sim$ 3 cm/yr. The relative infrequency of magnetic reversals during the late Mesozoic (Helsley & Steiner, 1969; McElhinny, 1971) makes the precise dating of these events rather difficult.

A reconstruction of the southwest Pacific margin of the Mesozoic southern continent is given in Fig. 2.1 (after Griffiths & Varne, 1972). The opening of the Tasman Sea (80-60 m.y.) marked the commencement of alkaline volcanism in eastern Australia and overlaps with local shoshonitic activity in NSW. Alkaline rocks are also found on the Lord Howe rise (Game, 1970) which is the matching crustal fragment, 25 km. thick (Shor et al., 1971). The mid-Cretaceous 98 m.y. (Wellman, 1971) Port Cygnet alkaline complex in southern Tasmania may be related to the earliest phases of the rifting. The tectonic context of minor Jurassic tholeiitic and alkaline activity in NSW and northern Victoria, however, remains obscure.

Prior to the Palaeocene, the site of the nascent Antarctic ridge was probably delineated by a continental rift system. Mesozoic igneous rocks along the southern margin of the present Australian continent include the 100 m.y. Cretaceous Bunbury tholeiite at the southern tip of Western Australia and the 170 and 167 m.y. Jurassic tholeiites of Kangaroo Is. and Tasmania (ages from Wellman, 1971). If these are accepted as representatives of continental rift volcanism, then the eastern part of the rift structure is at least mid-Jurassic, and predates the formation of new ocean crust by a significant period. Except for the Jurassic dolerites bordering the Ross Sea, there are no igneous rocks of similar age exposed on the corresponding margin of Antarctica. Southeast of present day New Zealand the minimum age of the Antarctic ridge is Upper Cretaceous (Christoffel & Ross, 1970), which suggests that the new ocean floor spreading centre migrated westward with time.

Distribution of the Cenozoic Volcanics

Wellman (1971) presents a detailed chronology of the eastern Australian Cenozoic volcanics. There is no simple regional pattern. Cleary & Simpson (1971) believe that discontinuities in the rate of formation of lithosphere along the Antarctic ridge have produced regions of inhomogenous stress extending inwards from the margin of the continental plate. These regions are the major seismic zones, dividing Australia into four sub-plates. Although these lineaments may be new structures generated by the differential spreading, it is quite probable that pre-existing structural zones have been reactivated.

The Eocene-Miocene volcanic centres in Tasmania, eastern Victoria and New South Wales lie near the eastern sub-plate boundary along a belt of predominantly pre-Miocene uplift (Sutherland, 1971). The Oligocene-Pliocene volcanism in central and northern Queensland may be associated with pre-Miocene spreading in the Coral Sea and northward rotation of New Guinea and/or the collision between the leading edge of the north-moving Australian plate and the Indonesian arc in the Miocene (Hamilton, 1971). The Pliocene-Recent Newer Volcanics of western Victoria are associated with a series of northwest trending vertical faults within the sub-plate (Griffiths, 1971) which could suggest an anticlockwise rotation of Tasmania away from the main plate. The unusual potassic lamproite volcanics in the western Australia shield lie near the central sub-plate boundary. This tensional structure (Cleary & Simpson, 1971) may be the precursor of a continental rift system.

Summary

The late Cretaceous separation and rotation of the Lord Howe block away from the Australian-Antarctic continent is related to the initiation of spreading centres along the Antarctic-Pacific rise and in the Tasman Sea, with alkaline and minor tholeiitic activity in eastern Australia accompanying rifting and spreading in the Tasman. The Palaeocene-Eocene rifting and separation of Australia from Antarctica may have contributed to alkaline activity in southeastern Australia; volcanism related to this event is otherwise very restricted.

# CHAPTER 3 : THE UPPER MANTLE SOURCE REGIONS

## 3.1 Composition and Mineralogy

Convincing evidence for a peridotitic upper mantle with magnesian olivine and lesser orthopyroxene as major phases comes from the observed seismic velocities and anisotropy (Ringwood, 1969) and from natural occurrences (Green, 1970b). Basic alkaline rocks and kimberlites may contain natural examples of modified upper mantle material in the form of high density ultrabasic inclusions which commonly show evidence of chemical and isotopic disequilibrium with their hosts (Leggo & Hutchinson, 1968; Kleeman & Cooper, 1970; Paul, 1972). These inclusions are olivine-rich (Fo 89-92) spinel or garnet (pyrope >75%) lherzolites with high Ni and Cr contents, and are believed to be of a refractory nature, since their contents of Ti, K, P, Th, U, light REE etc. are generally too low for them to represent the parental source material from which basaltic liquids are generated (Jackson & Wright, 1970; Kuno & Aoki, 1970).

It is highly unlikely that unmodified, undepleted upper mantle assemblages are ever observed at the earth's surface. Even rapidly transported xenoliths must undergo partial equilibration either with the host liquid or with their own partial melt. Unusually high concentrations of U and REE have been reported in clinopyroxene and amphibole in certain upper mantle-derived lherzolites by Frey & Green (1971) and Varne & Graham (1971). Both publications note that the range of crystal-liquid distribution coefficients seems to preclude the possibility of previous equilibration with basaltic melt and suggest that the inclusions may represent the potential source material for alkaline magmas. However Frey & Green (1971 and in prep.) alternatively suggest that these assemblages are residual but also include a trapped melt component and thus do not represent unmodified upper mantle material.

Published estimates of the composition of the undepleted upper mantle are listed in Table 3.1. The experimentally

TABLE 3.1

Proposed Chemical Composition of Undepleted Upper Mantle on an anhydrous basis

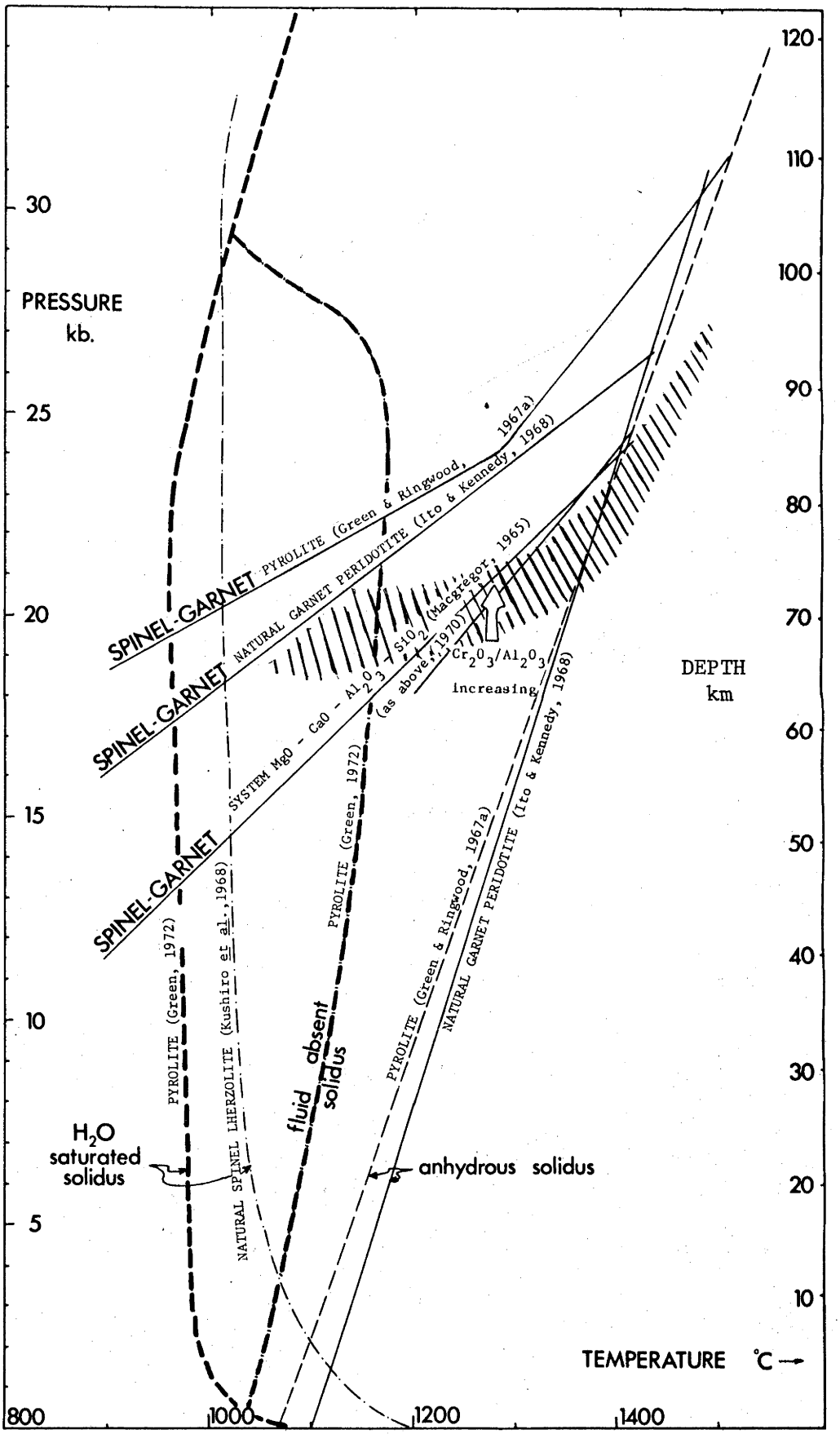
| | (1) | (2) | (3) |
|---|---|---|---|
| $SiO_2$ | 45.16 | 42.86 | 42.86 |
| $TiO_2$ | 0.71 | 0.5 | 0.33 |
| $Al_2O_3$ | 3.54 | 4.1 | 6.99 |
| $Cr_2O_3$ | 0.43 | 0.3 | 0.18 |
| $Fe_2O_3$ | 0.46 | 2.0 | 0.36 |
| FeO | 8.04 | 7.9 | 8.97 |
| MnO | 0.14 | 0.2 | 0.14 |
| NiO | 0.20 | 0.2 | 0.20 |
| MgO | 37.47 | 36.7 | 35.07 |
| CaO | 3.08 | 2.3 | 4.37 |
| $Na_2O$ | 0.57 | 0.6 | 0.45 |
| $K_2O$ | 0.13 | 0.02 | 0.003[1] |
| $P_2O_5$ | 0.06 | 0.1 | - |
| [2]100Mg/Mg+Fe" | 89.3 | 89.2 | 87.5 |
| [3]100Mg/Mg+Fe" | 88.8 | 87.1 | 87.1 |

(1) Ringwood (1966) "Pyrolite III"
(2) Nicholls (1967)
(3) Carter (1970)

[1]Low
[2]No adjustment of Fe oxide ratios
[3]Total iron expressed as FeO

Figure 3-1

HYDROUS and ANHYDROUS PERIDOTITE SOLIDI
AND
SPINEL PERIDOTITE - GARNET PERIDOTITE TRANSITION




shaded field = SPINEL-GARNET transition (O'Hara et al.,1971)

determined spinel peridotite-garnet peridotite transition and the solidi of several anhydrous peridotitic compositions are shown in Fig. 3.1 together with solidi determined under $H_2O$-saturated or $H_2O$-undersaturated conditions. Macgregor (1970) has emphasised that the spinel peridotite-garnet peridotite transition is particularly sensitive to the proportions of CaO, $Al_2O_3$, $Fe_2O_3$ and $Cr_2O_3$. The presence of small quantities of water and other volatiles in the upper mantle is indicated by fluid inclusions in basaltic olivine (Roedder, 1965), primary amphibole and mica in basaltic magmas and the volcanic gases from basaltic rocks. Confirming the predictions of Green & Ringwood (1963) and Oxburgh (1964), Green (1972) found that amphibole was present to 25-30 kb in the subsolidus assemblage of the pyrolite composition under hydrous conditions. Experiments by Yoder & Kushiro (1969) and Modreski & Boettcher (1970) indicate that phlogopite is a possible stable accessory to at least 40 kb in a peridotitic composition and Dawson et al. (1970) have argued that a natural phlogopite-bearing garnet lherzolite represents a primary assemblage.

## 3.2 Compositional heterogeneity in the upper mantle

Implicit in this discussion so far has been the assumption that the bulk composition of the upper mantle is approximately constant both laterally and radially. The uniformity amongst present day basalt types and the recurrence of these same basalt types throughout most of the geologic column points to overall chemical uniformity in the source regions for each basalt type. But the Sr and Pb isotope geochemistry of basaltic rocks, which is sensitive to small variations in the abundances of Rb, Sr, Pb, Th and U in the source regions implies both local and regional heterogeneities in the distribution of these elements (e.g. Hedge & Peterman, 1970; Oversby, 1971) and presumably a non-random distribution of accessory phases. Small local or regional variations in incompatable element abundances will be magnified during partial melting since these elements are strongly partitioned in the melt. Source heterogeneity provides a ready answer to all geochemical variations in

primitive basaltic magmas, but its importance is presently unknown since many other variables may also be involved.

### 3.3 The incompatable elements

The "incompatable elements" (Ringwood, 1966) because of size, charge, electronegativity and crystal field effects, do not readily substitute in the major phases of the upper mantle but are preferentially accommodated in accessory phases. Loosely interpreted, this covers K, Rb, Sr, Ba, light rare earths, P, Ti, Zr, Nb, U, Th, Pb, C, F, Cl and H. The incompatable element abundances of basic alkaline rocks characteristically exceed those of tholeiitic basalts. In analysing partial melting processes, it is often convenient to treat these elements as dispersed trace elements (Gast, 1968; Greenland, 1970; Shaw, 1970) which is strictly true only when the host accessories are absent from the crystalline residuum, but apparently under natural conditions the host phases break down near the solidus and the incompatable elements are partitioned in the melt.

### 3.4 The Presence or Absence of a Fluid Phase in the Upper Mantle

Estimates of the amount of interstitial melt in the low velocity channel range from 1 to 6% (Birch, 1969; Anderson, 1970; Green, 1970b). Hill & Boettcher (1970) believe such a small volume of initial melt requires that $H_2O$ in the uppermost mantle is bound entirely in accessory phases in the subsolidus assemblages and does not exist as a $H_2O$-bearing fluid phase (cf. Wyllie, 1971), and this is consistent with Ringwood's (1969) estimate of the water content of the upper mantle, $\sim$ 0.1%. Geochemical arguments put forward by Oxburgh (1964) and Griffin & Murthy (1969) favour the predominance of amphibole over phlogopite to depths corresponding to the top of the low velocity zone, where the oceanic geotherm intersects the solidus of the amphibole-bearing peridotite. Within the low velocity zone all $H_2O$ previously contained in amphibole is dissolved in the $H_2O$-undersaturated melt; phlogopite may persist for a short interval above the solidus. Beneath the lower boundary

of the low velocity zone a liquid phase is no longer present. Lattice sites in dense phases such as titanclinohumite (McGetchin et al., 1970) or hydroxylated pyroxenes (Sclar et al., 1967; Ringwood & Major, 1967) may accommodate some or all $H_2O$, or an $H_2O$-rich fluid phase may be present at grain boundaries.

For fluid absent conditions to prevail to at least the base of the low velocity zone, not only water, but all other volatile components, must be entirely accommodated in melt or solid phases. Chlorine and fluorine are readily accepted into amphibole and mica lattices, and should be sufficiently soluble in silicate melts under upper mantle conditions. Sulphur is present as rare blebs of a complex liquid sulphide which coexist with S-saturated silicate melts at hypersolidus temperatures (MacLean, 1969). (O'Reilly (1972) reports chalcopyrite, pyrrhotite and pentlandite blebs within olivine and pyroxene in an upper mantle-derived spinel lherzolite.) Hill & Boettcher (1970) reported considerable solution of $CO_2$ in basaltic melts above $\sim$ 15 kb. Graphite or diamond suggests an obvious subsolidus site for carbon, but zonal growth structures in diamonds, the absence of graphite or diamond in upper mantle-derived peridotites (Mitchell & Crockett, 1971; Sobolev, 1971) and the appearance of graphite in the basalt-$H_2O$-$CO_2$ system at high pressures (Burnham, unpubl.) indicate that neither diamond nor graphite appears in any of the stable mineralogies of the undepleted upper mantle, but instead precipitates from a melt or fluid phase at high pressures. Although the high pressure stabilities of other carbonates are unknown, a calcium carbonate polymorph is stable to at least 45 kb and $\sim$ 1400°C (Wyllie & Boettcher, 1969) so there is no *a priori* reason for a fluid phase to coexist with either the subsolidus assemblage or with the melt. Independent evidence for the presence or absence of a fluid phase in the subsolidus assemblage should come from the relative electrical conductivities in the low velocity channel and in the upper mantle directly above - allowing for temperature dependence - but unfortunately the data are inconclusive.

The low geotherm of continental shield areas remains below the solidus to depths where amphibole is no longer stable and phlogopite is the only hydrous accessory. Only $\sim$ 0.05% $H_2O$ is required to saturate the pryolite composition under these conditions. Ringwood (1969) suggested an $H_2O$ content of $\sim$ 0.1% since the resulting activities in the experimental systems depress the pyrolite solidus by the required 200°C at 25 kb, but there are no similar constraints on estimates of the $H_2O$ content of the subsolidus assemblage outside the amphibole stability field. Much of the mantle underlying ancient shield areas has been depleted by previous partial melting episodes so arguments based on a pyrolite composition are not strictly correct. In any event, the subsolidus assemblage at pressures above $\sim$ 30 kb presents two alternatives: (1) with an excess of $H_2O$, a free C-O-H fluid phase coexists with an assemblage saturated with phlogopite and melting begins at the fluid saturated solidus. (2) All available $H_2O$ is contained in phlogopite so melting takes place under fluid absent conditions. The second alternative may require a radial variation in the $H_2O$ content of the upper mantle.

### 3.5 Evidence for crystal-liquid equilibrium during partial melting

Convincing but indirect evidence is provided by the comprehensive and internally consistent general model for basalt genesis which has been built up over the past ten years and which is based on experimental investigations clearly involving crystal-liquid equilibrium.

During disequilibrium partial melting a part of the subsolidus assemblage is converted to a liquid without equilibration between melt and residual phases. Disequilibrium partial melting generates liquids whose composition is a linear function of the compositions of major and accessory phases in the parent assemblage. The little information presently available on the phase chemistry of the undepleted upper mantle does not allow one to reach any definite conclusions using the above test, so throughout this thesis, it is assumed that there is equilibration between residual phases and primitive partial melts.

## 3.6 Primary and Derivative Magmas

Primary or primitive basaltic magmas are generated by partial melting processes in the earth's upper mantle.

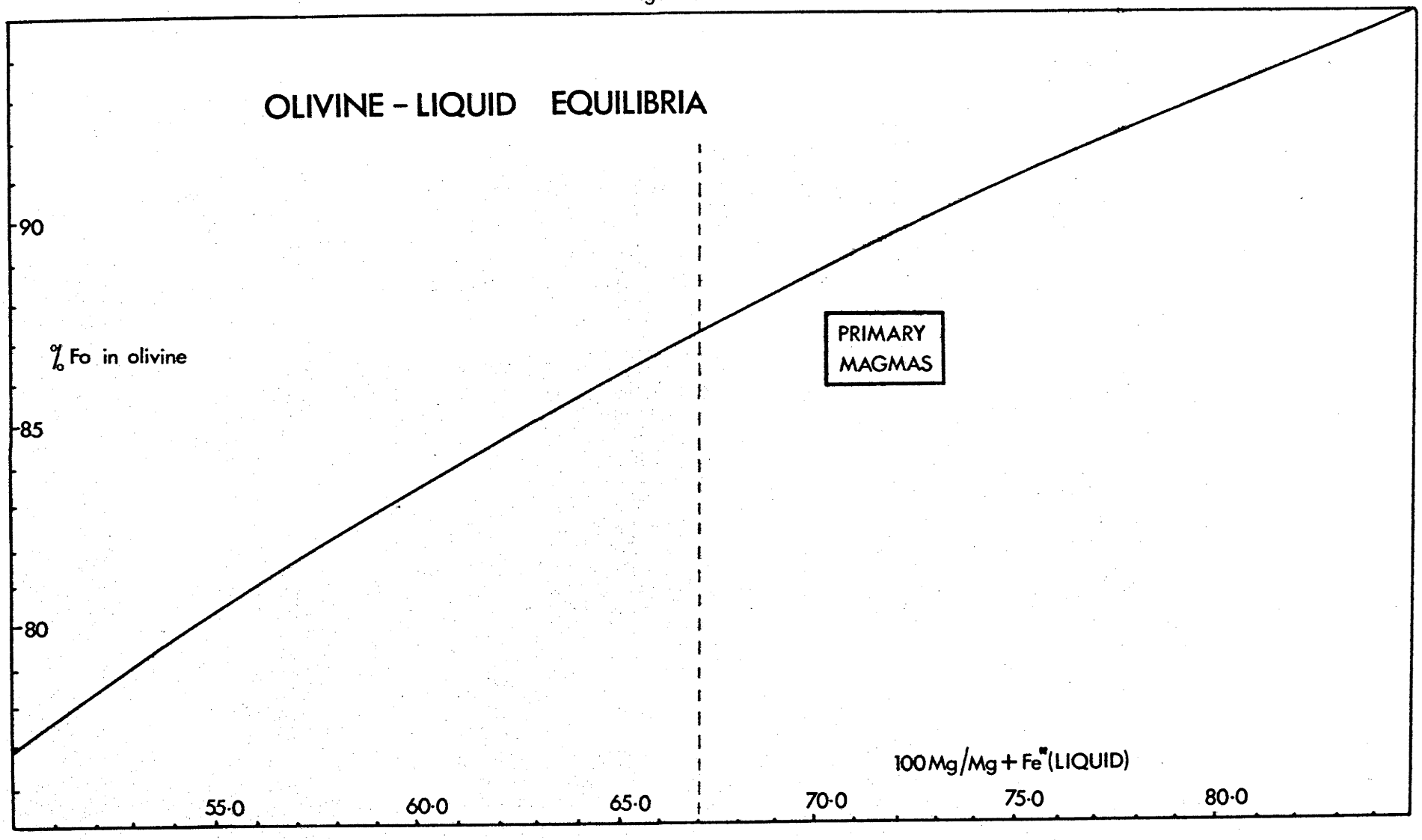
Roeder & Emslie (1970) found that $K_D = (Mg/Fe)_{liquid} \div (Mg/Fe)$ olivine = 0.3 and is effectively independent of temperature. Irving (1971) rearranged this expression to give $X_{Ol} = X_L/(X_L + K_D\ (100-X_L))$ where X = 100Mg/Mg+Fe" atoms and showed that experimental olivine-liquid equilibria to 30 kb for both terrestrial and lunar basalts plot close to this predicted curve (Fig. 3.2).

Estimates of the chemical composition of the undepleted upper mantle (Table 3.1) give 100Mg/Mg+Fe" ranging from 87.5 to 89.3, implying a similar range for upper mantle olivine. With data from refractory ultrabasic inclusions the complete compositional variation of upper mantle olivines is Fo 87.5 to $\sim$92. From the above curve, primary basaltic magmas in equilibrium with the upper mantle source regions must have 100Mg/Mg+Fe" from 68 to 77 (cf. Green, 1970b, 1971).

Unfortunately this ratio is affected by oxidation of ferrous iron in the melt prior to, during, or after eruption. This problem can be minimised by first recalculating $Fe_2O_3$/FeO ratios to 0.25. This usually lowers 100Mg/Mg+Fe" and has the advantage of bringing the values for highly undersaturated nephelinites (high $Fe_2O_3$/FeO) down to values comparable with other basic alkaline rocks. Throughout this thesis 100Mg/Mg+Fe" ratios ($Fe_2O_3$/FeO recalculated to 0.25) ranging from 67 to 77 are used as the criterion for the identification of primary magmas. Non-primitive compositions resulting from extreme ferromagnesian crystal accumulation fall in this group but can be recognised from field and chemical evidence. Other compositions which have undergone only limited crystal accumulation cannot be identified with certainty, but their classification with true primitive magmas should not seriously distort the geochemistry.

The presence of upper mantle peridotite xenoliths and certain other high density ultrabasic inclusions (Irving, 1971) means that the host rock has moved rapidly to the

Figure 3·2


OLIVINE – LIQUID EQUILIBRIA
90
85
80
% Fo in olivine
PRIMARY MAGMAS
55·0
60·0
65·0
70·0
75·0
80·0
100 Mg/Mg + Fe* (LIQUID)

surface from depths > 10 kb and has had little or no opportunity for crustal contamination or to undergo low pressure fractionation (Bultitude & Green, 1971). Many inclusion-bearing rocks have 100Mg/Mg+Fe" in the primitive range; those that do not have only been modified by high pressure fractionation. Note that the high 100Mg/Mg+Fe" ratios in some samples are in part due to xenocrystal fragments which could not be separated prior to analysis (Bultitude, 1968).

Derivative basaltic magmas are upper mantle-derived partial melts, whose compositions have subsequently been modified by crystal or liquid fractionation, or contamination.

# CHAPTER 4 : HYPOTHESES FOR THE ORIGIN OF BASIC ALKALINE ROCKS

## 4.1 Limestone syntexis

Daly (1914) suggested that the assimilation of limestone by basaltic (= tholeiitic) liquids produced melilite-bearing alkaline magmas. This idea was revived intermittently during the period of controversy over the magmatic origins of carbonatites (cf. Wyllie & Tuttle, 1960) but has since been clearly disproved by trace element and isotopic geochemistry. $Sr^{87}/Sr^{86}$ ratios of calcareous sediments are too high (Powell et al., 1966) and their abundances of Nb, REE, Y, Th, U and, generally, Sr and Ba are too low (Haskin et al., 1966; Thompson et al., 1970) to substantiate this hypothesis.

## 4.2 Fractional resorption of biotite and/or amphibole

The generation of alkaline liquids by this mechanism was first suggested by Bowen (1928), then revived by Tuthill (1968) who suggested that alkali basalt liquids could be derived by the resorption of kaersutite by olivine tholeiite.

The trace element chemistry of kaersutite has been summarised by Kesson & Price (1972). Griffin & Murthy (1969), Higuchi & Nagasawa (1969), Philpotts & Schnetzler (1970) and Schnetzler & Philpotts (1970) provide data for amphibole-liquid distribution coefficients which show that Sr, Ba, Rb and light REE are concentrated in the melt, so kaersutite precipitating from olivine tholeiites should have comparatively lower concentrations of these elements. For fractional resorption to produce the required increase in the concentrations of these elements, fairly extensive concomitant precipitation of liquidus phases such as olivine and pyroxene is required. However the similarity of Mg/Fe ratios in less fractionated tholeiites and alkali basalts places narrow limits on the extent of crystallisation and consequently on the viability of this mechanism. The resorption of biotite together with amphibole could produce satisfactory abundances of Rb and Ba, but the light REE and

Sr requirements are still not satisfied. Although Sr and light REE are concentrated in apatite the difference in the $P_2O_5$ contents of tholeiites and alkali basalts permits only an insignificant contribution from this phase.

## 4.3 Crystal Fractionation

### 4.3.1 High pressure fractionation of primitive tholeiitic parent liquids

Gast (1968) noted that the similarity in the Yb contents of alkaline and tholeiitic magmas placed severe limitations on the extent of garnet fractionation, and Bultitude & Green (1971) confirmed that high pressure fractionation processes involving garnet and clinopyroxene produce derivative liquids whose compositions bear little resemblance to natural rocks.

Green & Ringwood (1967a) and Ito & Kennedy (1968) suggested that high pressure fractionation processes involving essentially orthopyroxene could produce alkaline derivatives from primitive Mg-rich tholeiitic parents, but, as the former authors point out, nephelinitic members of the basic alkaline spectrum cannot be derived in this way. Within the limits imposed by MgO contents of primitive tholeiites and nephelinites, eg. 14% and 9% respectively, fractionation of the enstatite-rich liquidus orthopyroxene lowers the $SiO_2$ content of the differentiate to only $\sim$ 45%. Bultitude & Green (1968) emphasised the importance of orthopyroxene as a near-liquidus phase in nephelinite and melilite nephelinite compositions under high pressure hydrous conditions and proposed that these liquids could be derived from a parental olivine tholeiite if orthopyroxene fractionation took place in the presence of small amounts of water. But the above constraints on the MgO contents are still valid, so an alternative model is required for the genesis of Mg-rich nephelinitic magmas.

Since orthopyroxene fractionation cannot produce the complete spectrum of basic alkaline liquids, it is tempting to reject the hypothesis completely. Nonetheless some alkali basalt liquids might be produced in this way. Green & Ringwood (1967a), realising that fractionation alone could not be responsible for the incompatable element abundances

of typical alkali basalts, proposed an additional essential process of wall-rock reaction. However wall-rock reaction is by no means inevitable (see below) so the probability that this two stage process plays an important petrogenetic role must be very low.

4.32 Wall-rock reaction

Harris (1957) proposed that a progressive concentration of elements such as potassium in basaltic liquids was brought about by "solution stoping" in the upper mantle. The mechanism requires the solution of roof material in front of a rising magma column and the concomitant precipitation of phases in constant proportions at the base, while elements which do not readily substitute in the precipitated phases are concentrated in the melt, and the liquid composition is homogenised by convection. The specific heats of melt and solids are similar, the volume change in the liquid is required to be approximately zero or positive, and the latent heat of fusion is assumed to balance the latent heat of crystallisation. Harris compared "solution stoping" to zone refining but the latter, involving complete local melting in the system under consideration, provides a very poor analogy to any upper mantle process.

Using "solution stoping" as the basis for their ideas Green & Ringwood (1967a) suggested that "...near the depth of segregation of basaltic magmas there may be little temperature contrast between magma and mantle wall-rock". Wall-rock reaction under these conditions involves "...the solution of low melting components from the wall-rock and their incorporation into the magma, accompanied by precipitation of the liquidus phase of the basalt". Recognising the importance of water in the genesis of basic alkaline rocks, Green (1970a,b) added that if $Pe_{H_2O}$ (melt) < $Pe_{H_2O}$ (wall-rock), wall-rock reaction should result in the breakdown of hydrous accessory phases and the migration of a $H_2O$-rich fluid phase containing high concentrations of incompatable elements from wall-rock to melt.

Kushiro (1968) proposed a more realistic version of the "solution stoping" hypothesis in which partial melting preceded the rising magma column. He argued that the molten

of typical alkali basalts, proposed an additional essential process of wall-rock reaction. However wall-rock reaction is by no means inevitable (see below) so the probability that this two stage process plays an important petrogenetic role must be very low.

4.32 Wall-rock reaction

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Kushiro (1968) proposed a more realistic version of the "solution stoping" hypothesis in which partial melting preceded the rising magma column. He argued that the molten

zone would continue to have a near-eutectic composition while "partial zone melting" was responsible for its upward migration, although the composition of the eutectic melt component from the wall-rocks changed with depth.

Discussion

In essence, reaction between wall-rock and melt is the spontaneous attempt to reach chemical and thermal equilibrium The following discussion demonstrates that incompatable element contamination of the melt takes place only under a restricted set of circumstances, so the process cannot play an essential role in the genesis of alkaline magmas.

In some cases mantle wall-rocks comprise the refractory residue from previous partial melting episodes and are "inert" - in most cases liquidus phases precipitating at the melt/wall-rock interface eventually line the conduits so that any subsequent magma batches using the same path are isolated from the wall rocks. Quenching and precipitation of crystalline phases at the interface becomes more extensive as the temperature difference between melt and wall-rocks increases, and should effectively prevent contamination of the main body of magma in the higher levels of the upper mantle. Melt/wall-rock interaction requires the previous segregation of the melt from its crystalline residuum, and so the melt solidus is that of the magma, not that of its parent assemblage. The coexistence of melt with undepleted upper mantle assemblages is then possible at temperatures below the mantle solidus.

Wall-rock reaction in the sense envisaged by its advocates takes place when - and if - the heat budget between a unit volume of melt and the surface area of the interface results in an initial temperature at the interface which exceeds the solidus temperature of the wall-rock and produces a significant volume of contaminant melt. Since the process requires concomitant precipitation of liquidus phases, the extent to which chemical variation in primitive liquids could be due to wall-rock reaction is constrained by their range of 100Mg/Mg+Fe" ratios.

Lacking evidence to the contrary, it can only be assumed that when melting occurs in the wall-rocks apatite breaks

down and enters the liquid, adding $P_2O_5$ and corresponding amounts of REE, Y, Sr, Th, U and common and radiogenic Pb. If a fluid phase is present in the wall-rocks and amphibole and mica persist above the solidus, the contaminant melt should have relatively low concentrations of K, Ti, Rb and Ba and could produce only a selective enrichment in the incompatable element abundances. Should a free fluid phase exist in the wall-rock at the temperatures and pressures in question, it is not certain whether selective solution of fluid components in the melt would enhance or suppress the stabilities of the hydrous phases. There is considerable dissolved solute in the fluid phase, but its incompatable element chemistry is unknown.

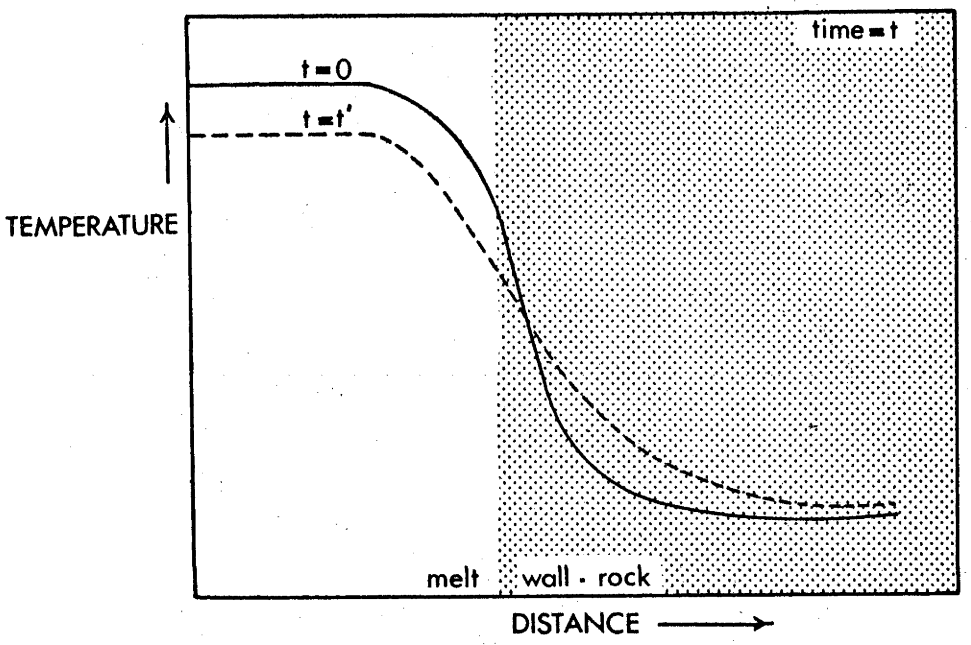
In the absence of a fluid phase, apatite, amphibole and mica break down at (and near) the solidus to produce a nephelinitic contaminant melt. But if this occurs near the depth of segregation of the reactant melt, the two liquids will be serially related and the composition of the mixture will differ very little from that of a melt resulting from a lesser degree of partial melting at the same depth without wall-rock reaction.

Comparison of $Pe_{H_2O}$, $\mu_{H_2O}$ or any similar parameter for the melt and the wall-rock must be made at the same temperature, namely the temperature at the interface. The thermal profile across a melt/wall-rock interface is illustrated schematically in Fig. 4.1. In the limiting situation where the temperature difference between melt at $T_m$ and wall-rocks at $T_r$ is small, the temperature at the interface $T_i = \frac{1}{2}(T_m+T_r)$.

If the temperature at the interface is below that of the wall-rock solidus, either of the situations illustrated in Fig. 4.2 may prevail. For simplicity only one crystalline hydrous phase, amphibole, is considered. Curve labelled (melt) refers to the reactant melt, curves labelled (amph) and (contaminant melt) relate to the wall-rocks, and their intersection corresponds to the fluid absent wall-rock solidus. In the unlikely event that a free fluid phase coexists with the subsolidus assemblage, the intersection corresponds to the hypersolidus breakdown of amphibole.

Fig. 4.1

Thermal profile across melt/wall-rock interface




adapted from Jaeger (1967)

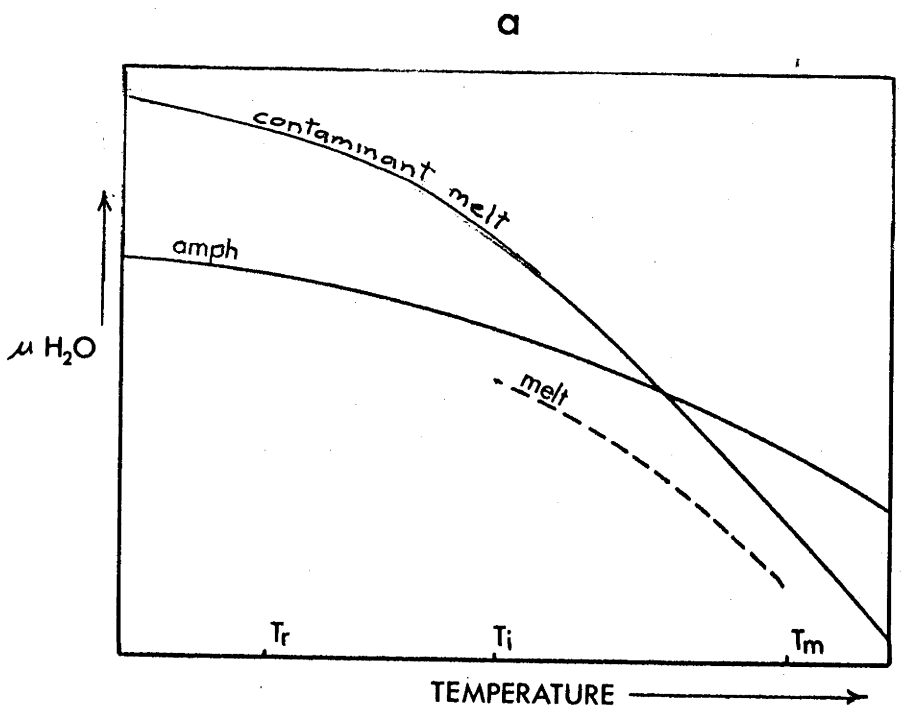
Figure 4.2

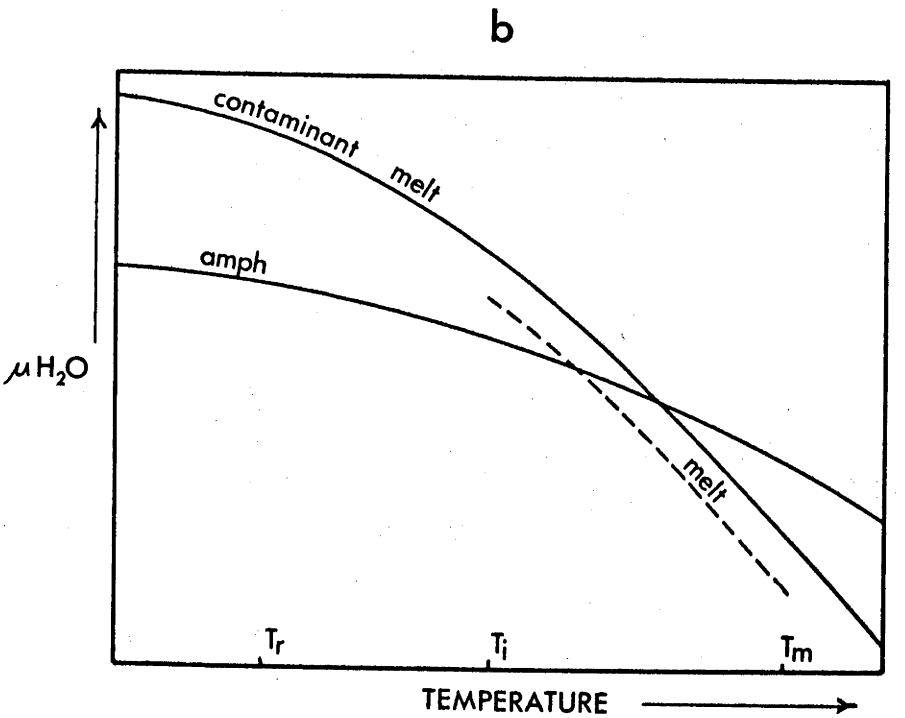
Illustrating interaction between wall-rock and melt when the temperature at the interface is below that of the wall-rock solidus

$T_m$ ... temperature of melt

$T_r$ ... temperature of wall-rocks

$T_i$ ... temperature at interface




$P_{Load}$, $X_{H_2O}$(melt), and $X_{H_2O}$(wall-rock system) are constant. The most stable configuration has the lowest $\mu_{H_2O}$. For further discussion, refer to text.

The value of $\mu_{H_2O}$ (reactant melt) at $T_m$ is lower than the value of $\mu_{H_2O}$ (amphibole-bearing wall-rock) at $T_r$, but at the interface at $T_i$. $\mu_{H_2O}$ (reactant melt) < $\mu_{H_2O}$ (amph)

...Fig. 4.2a

or

$\mu_{H_2O}$ (reactant melt) > $\mu_{H_2O}$ (amph)

...Fig. 4.2b

The former situation requires the subsolidus breakdown of amphibole i.e. dehydration. But alkaline magmas are relatively more saturated with $H_2O$ since they result from smaller degrees of partial melting, so that the geometry of the situation sketched in Fig. 4.2b is more likely to apply, with minor loss of $H_2O$ from melt to wall-rock.

While a temperature gradient is present, thermal diffusion requires the various species to migrate either up-gradient or down-gradient, diminishing or enhancing the mass transfer resulting from the concentration gradient.[1] Diffusion rates will be significant in melts and fluids and less important in solids. With small temperature differences and pronounced concentration gradients the resulting mass transfer in the incompatable elements is probably from melt to wall-rock. Once thermal equilibrium has been reached, isothermal diffusion processes can effect exchange between wall-rock and melt. But incompatable elements are enriched in the melt, so the nett concentration gradient and therefore the mass transfer is from melt to wall-rock, not from wall-rock to melt.

Summary

If the heat budget results in partial melting of the wall-rocks near the depth of segregation of the magma, the two liquid compositions are serially related, and the

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[1] Frey (1970) demonstrated that there was selective migration of the light REE from a pyroxene hornfels into the periphery of the Lizard peridotite. The controlling factor may be the concentration gradient from hornfels to peridotite, the temperature gradient (implying an up-gradient migration), or the combination of both.

consequences are trivial. In other circumstances material transfer from melt to wall-rock could take place; in many instances melt/wall-rock interaction is severely curtailed by precipitation of crystalline phases at the interface, so wall-rock reaction cannot play an essential role in the genesis of primitive alkaline magmas.

## 4.4 Partial melting of a hydrous upper mantle

### 4.4.1 Experimental constraints

Gast (1968) and Griffin & Murthy (1969) presented geochemical models to justify their proposal that the "parental" alkaline magma is a primitive liquid resulting from small degrees of partial melting in a hydrous upper mantle. Green (1969, 1970a & b) extended their proposal, suggesting that the complete basic spectrum of alkaline magmas - melilite nephelinites, nephelinites, basanites and alkali basalts - could be produced by varying degrees of partial melting under appropriate physical conditions. All authors agreed that tholeiitic magmas resulted from more extensive partial melting. These proposals accord with the relative volumes of tholeiitic and alkaline magmas erupted over a given period on a world-wide basis, and are also generally consistent with the relative concentrations of incompatable elements in peridotites, and tholeiitic and alkaline magmas.

However these same generalisations are also true for quartz-normative tholeiites and andesites. Kushiro et al. (1968) and Kushiro (1969) argued that in fact these compositions represented the initial partial melts of a hydrous peridotite. This alternative proposal was based on melting relationships in simple silicate systems in the presence of water - viz. En-$SiO_2$-$H_2O$; Fo-Di-$SiO_2$-$H_2O$; Fo-Di-Ne-$SiO_2$-$H_2O$ - but Green (1970b, p.46-49) defended his own interpretations and terminated the controversy with sound criticisms of Kushiro's interpretation of the relationships in the simple systems. Thereupon Dr I.A. Nicholls (pers. comm., 1972) demonstrated that Fo-rich olivine is the liquidus phase of an exactly $SiO_2$-saturated basalt to only 5 kb under anhydrous conditions, but persists to $\sim$ 17 kb in the presence of excess $H_2O$.

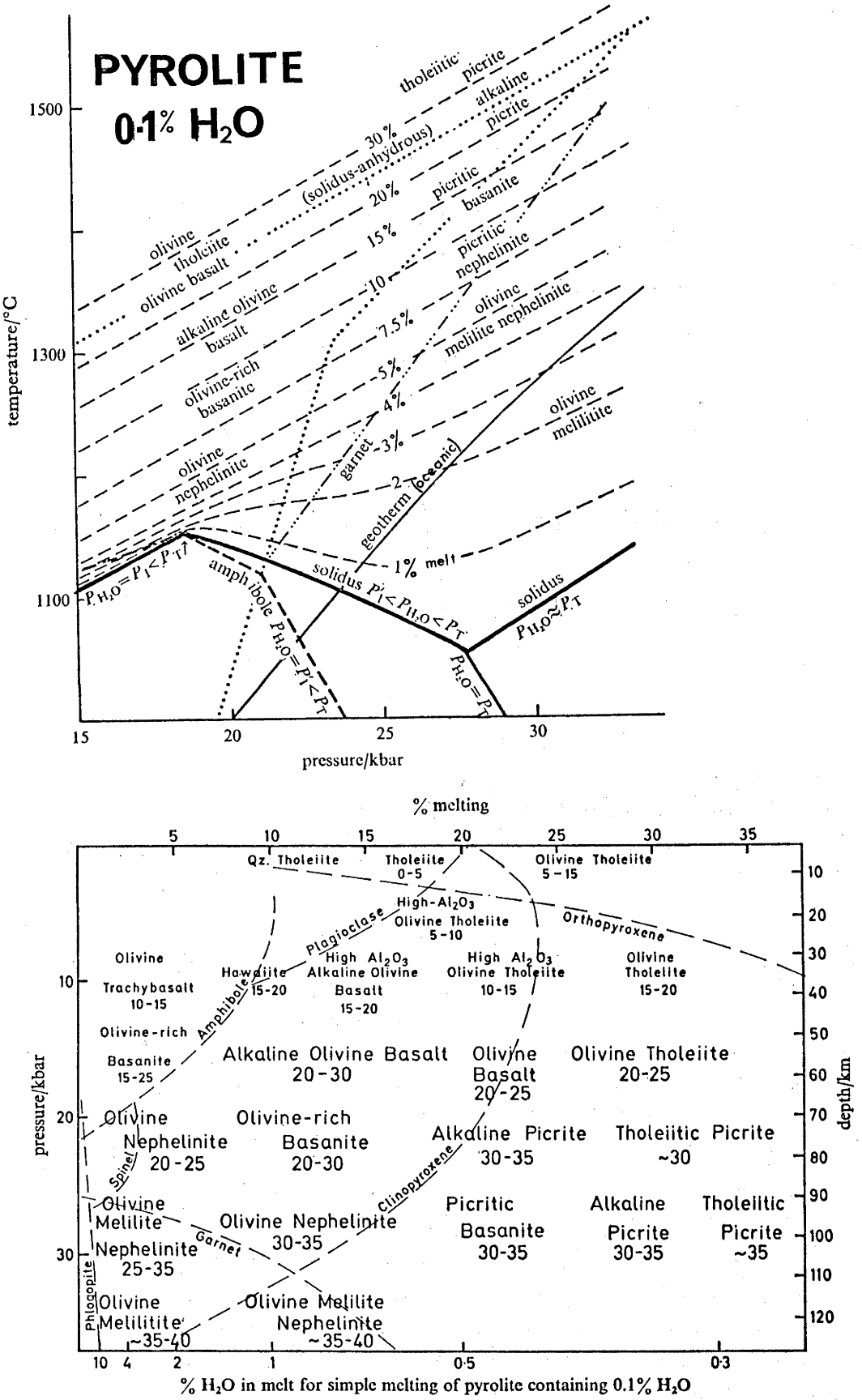
Nicholls' results are given precedence and are especially pertinent to the genesis of island arc magma series. The only probable place where partial melting in the upper mantle may occur with excess fluid is the wedge of upper mantle immediately above the subduced lithosphere and beneath the island arc volcanic ridge.

It is axiomatic that the liquidus phases of a primitive equilibrium partial melt must be identical with the residual phases of its peridotite parent when physical conditions correspond to those effective at the depth of magma segregation. Green (1971, 1972) has constructed a comprehensive petrogenetic grid for primary basaltic magmas based on experimentally derived crystal-liquid relationships and his model is reproduced in Fig. 4.3. The model illustrates the primitive magma types produced <u>if</u> partial melting occurs under the designated conditions and does not imply that all primitive compositions classified within a particular group are derived by partial melting in the manner outlined (Green, 1970b). Certain features of the model relevant to alkaline petrogenesis which are not apparent from the figures are summarised below without criticism.

1. At ∿ 20-30 kb and 1400-1500°C small degrees of partial melting of an anhydrous peridotite parent produce olivine-rich basanites and alkali picrites. The residual phases include olivine, aluminous orthopyroxene ± subcalcic aluminous clinopyroxene (∿ 10% CaO).
2. Hydrous peridotite (∿ 0.1% $H_2O$) melts near 1100°C 20-30 kb, producing olivine nephelinite, basanite and alkali basalt liquids and residual olivine, orthopyroxene ± clinopyroxene (16-20% CaO) ± spinel or garnet. Melilite nephelinites and olivine melilitites represent the initial liquid fraction at 25-35 kb with garnet as a residual phase.
3. With excess $H_2O$ melting begins at the $H_2O$-saturated solidus at ∿ 1050°C and primitive alkaline liquids are in equilibrium with olivine, low-$Al_2O_3$ orthopyroxene ± low-$Al_2O_3$ clinopyroxene (CaO > 20%) ± amphibole below ∿ 25 kb, or garnet above ∿ 25 kb.

Figure 4.3

Petrogenetic grid for primary basaltic magmas:
model proposed by GREEN (1970b, 1971)




A given phase is residual to the left of the dashed line bearing its label.

4. In all instances the residual olivines and orthopyroxenes have 100Mg/Mg+Fe" ratios in the range 88-92, whereas those of the residual clinopyroxenes and garnets are slightly lower.

5. The compositional variation in the residual pyroxenes mainly reflects the sensitivity of the pyroxene solid solution to temperature.

6. In general, tholeiitic liquids are in equilibrium with olivine and orthopyroxene only. The sequence of elimination of major phases in the peridotite parent is a complex function of its CaO, $Cr_2O_3$ and $Al_2O_3$ contents. The disappearance of spinel or garnet followed by clinopyroxene was noted by Green & Ringwood (1967a) and Kushiro, Syono & Akimoto (1968) whereas the reverse was observed by Ito & Kennedy (1968).

4.4.2 Geochemical constraints

The expressions governing the distribution of dispersed trace elements between solids and melt have been applied by Gast (1968), Griffin & Murthy (1969) and Kay (1972) to test the hypothesis that the initial liquids produced during partial melting have the trace element characteristics of alkaline magmas.

The unlikelihood of anhydrous upper mantle source regions is emphasised by these studies. The low abundances of Rb, Sr and Ba place severe constraints on the volume of basaltic partial melt which could be derived from such a source. Rb/Sr ratios would be too low to generate the $Sr^{87}/Sr^{86}$ ratios observed in recent basaltic magmas and K, U and Th are too low to satisfy heat flow requirements (Griffin & Murthy, 1969). Modal variations in the mineralogy of the anhydrous upper mantle model merely satisfy one geochemical parameter at the expense of others.

Alkali feldspar or plagioclase would accommodate K, Rb, Sr and Ba but felspar-liquid distributions for these elements, together with REE geochemistry (Eu-anomalies) suggest that felspar is not an important K-bearing mantle accessory (Philpotts & Schnetzler, 1970). A hydrous mantle containing accessory pargasitic amphibole and/or phlogopite proves more satisfactory, since melting can then occur at temperatures below the anhydrous solidus.

Most of the conclusions arising from partial melting models support the preferred partial melting hypothesis for the origin of alkaline magmas, which is reassuring. However large uncertainties in several parameters cast serious doubts on the validity of many quantitative results. Firstly, the absolute abundances of dispersed elements in the liquid depend on the absolute abundances in the source regions, and the latter are at best approximations based on a chondritic earth model (eg. REE) or modifications thereof (K, Rb, Sr, Ba). Other necessary approximations involve estimating both the modal mineralogy of the source, and the proportions in which the phases melt. For simplicity, the latter are assumed to remain constant throughout the melting interval!

Large uncertainties are associated with crystal-liquid distribution coefficients, and values for a set of elements are rarely correct relative to one another. Published values for some elements may range through orders of magnitude and the controlling factor is sample provenance. Solid-solid and solid-liquid distributions are estimated from xenolithic eclogite and peridotite assemblages in kimberlites or basic volcanics, from basic and ultrabasic assemblages in high grade metamorphic terrains, and from phenocryst-matrix relationships in volcanics. The implicit assumption that the distribution coefficients are independent of pressure, temperature and compositional parameters is certainly an oversimplification (eg. Nagasawa & Schnetzler, 1971). Phenocrysts are commonly zoned but despite the implications, the phenocryst-matrix concentration ratio is still assumed to correspond closely to the equilibrium crystal-liquid distribution. Estimated crystal-liquid distribution coefficients differing greatly from unity can be seriously in error if kinetic factors are ignored (Albarede & Bottinga, 1972). Kinetic effects in the upper mantle source regions are similarly assumed to be unimportant, but the lowest diffusion rates would be those of the large cation incompatable elements in the solid residuum, so the surface layers of the solid phases may not possess equilibrium concentrations of dispersed trace elements.

Gast (1968) and Griffin & Murthy (1969), recognising the potential importance of amphibole and mica in the upper mantle source regions, set up models in which the hydrous phases made substantial contributions to the melt. The liquid fractions with alkaline characteristics thus contain a considerable amphibole component but they are nonetheless required to equilibrate with hypersolidus residual amphibole ± phlogopite. One finds empirically that the results of these computations are most sensitive to the value of the liquid-accessory distribution coefficient, to the extent that a qualitative assessment of the melting relationships (see below) is probably more meaningful.

Amphibole and phlogopite together account for most of the K, Ti, Rb and Ba in the parent assemblage. The models proposed by Gast (1968) and Griffin & Murthy (1969) require the beginning of melting at the fluid saturated solidus. Holloway & Burnham (1972) established that in a fluid-saturated basaltic system, hypersolidus amphibole at first made little contribution to the melt, then broke down over a narrow temperature interval well above the solidus, causing the volume of liquid to increase by a factor of 2 or 3. In the upper mantle analogy, the smaller volumes of liquid coexisting with amphibole and phlogopite are most unlikely to have alkaline geochemistry. The breakdown of amphibole and phlogopite releases K, Ti, Rb and Ba into the melt, but with the consequent increase in volume "nephelinitic" concentrations are unlikely to result.

If melting takes place in the absence of a fluid phase, amphibole and phlogopite break down at the fluid absent solidus. This occurs over a narrow temperature interval with continuous Mg-Fe substitutions in reactants and products but the melting mode is constant. The maximum concentrations of incompatable elements occur in the initial melt fraction generated at the solidus, and subsequent dilution accompanies any further increase in temperature. Kay's (1972) REE computations are consistent with the fluid absent situation, but the liquids represent 0.1 - 2% partial melts, and their efficient segregation remains a serious problem.

Apatite is believed to be an accessory phase in the upper mantle (Kleeman et al., 1969). Published geochemical data are almost entirely confined to apatites from late stage igneous or carbonatitic parageneses and are thus not particularly pertinent to the upper mantle situation. However the geochemistry of apatite from a feldspar-free paragenesis, coexisting with melt, kaersutite, biotite, clinopyroxene and pseudomorphs after ?olivine/orthopyroxene, should be reasonably significant in this context (Appendix 3A). Significant concentrations of light REE, Y, Sr, Th, U, and Pb are found and presumably radiogenic Pb is high. Apatite is refractory during crustal anatexis but the $P_2O_5$ contents of upper mantle-derived basaltic magmas indicate that apatite enters the liquid in the initial stages of partial melting.

Green & Ringwood (1967a) suggested that ilmenite might also occur as an accessory phase. However there are no convincing examples of primary upper mantle-derived ilmenite (excluding exsolution) and there is no *a priori* requirement for its presence since all major and trace elements in ilmenite could be accommodated with equal facility in other stable phases.

# CHAPTER 5 : CHEMICAL VARIATION WITHIN THE ALKALINE ASSOCIATION

## 5.1 Introduction: Chemical variation and tectonic setting

Within the alkaline association several groups or "sub-associations" can be recognised. The diagnostic chemical features of each group are illustrated by its particular primary magma or, more commonly, by a series of primary magmas.

The typical alkaline association has a global distribution and encompasses the alkali basalt-basanite-nephelinite-melilite nephelinite spectrum with its intermediate and acid differentiates, together with the derivative "potassic alkaline lineages" of Coombs & Wilkinson (1969). Upper mantle-derived lherzolite xenoliths and high pressure (> 10 kb) phenocryst phases are particularly characteristic of the typical alkaline association. The Hawaiian alkaline province is conventionally selected as the type example but there are usually subtle chemical differences (mainly $TiO_2$ content) between the typical alkaline association in an oceanic environment, and the same in a continental environment. The basic alkaline rocks in the Monaro district of southeastern NSW provide a convenient example of the typical alkaline association in a continental setting.

Apart from one controversial occurrence, all other sub-associations are restricted to continental plates, where they occur along major lineaments and continental rift systems, or remnants thereof. However they are by no means exclusively confined to the low-geotherm shield areas. The high-Ca alkaline association comprises CaO-rich nephelinitic rock types (mainly sodic) and carbonatites. Primary magmas are uncommon, and upper mantle-derived xenoliths are rarely reported. The one documented occurrence of a carbonatite in an oceanic setting is that of the Cape Verde Is. (Assunacao et al., 1968; Barros, 1968) but these structurally complex islands can be interpreted as a remnant of the northeast-moving African continent or simply as a projection of the African plate,

as the bathymetry would suggest. The geochemical and tectonic implications of ankaratrites and alnoites (Allen & Deans, 1965) in the Solomons arc at the contact between the Australian and Pacific plates are uncertain.

The potassic alkaline association, identified by $K_2O/Na_2O$ ratios near unity and commonly higher, least merits group status since there appears to be some compositional overlap with nephelinitic primary magmas in both the typical alkaline association and the high-Ca alkaline association. However for the sake of clarity the subsequent discussion deals with these rocks as a separate category.

$K_2O/Na_2O$ ratios greater than unity are also characteristic of kimberlites and - for want of a better title - the potassic lamproites, but both rock types are represented by such distinctive and unique primary magmas that they must undoubtedly comprise separate and distinct sub-associations. Kimberlites show a close spatial and temporal correlation with high-Ca alkaline activity but there is no evidence for a direct genetic link. Amongst the abundant upper mantle-derived detritus in kimberlites is evidence that the kimberlite primary magma evolved at depths corresponding to 50-100 kb. The rare potassic lamproites usually accompany kimberlite activity but there is again no suggestion of a direct genetic link. Upper mantle-derived xenoliths have not yet been reported in these rocks, perhaps because of the reaction relationship olivine + liquid = phlogopite at low pressures.

Continental alkaline petrographic provinces normally contain representatives of several sub-associations whereas oceanic provinces involve only the typical alkaline association. For example:

With the inception of the mid-Atlantic ridge, the Appalachian-Ouachita belt, corresponding approximately to the Triassic margin of the eastern USA, became the locus of Mesozoic kimberlite activity (Watson, 1967) and alkaline-carbonatite intrusive complexes (Erickson & Blade, 1963). However Cretaceous spinel lherzolite-bearing nephelinites and melilite nephelinites on the Ouachita lineament in

Texas are strikingly similar in composition to their typical alkaline counterparts on Oahu, Hawaiian Is. (Spencer, 1969).

Relevant geochemical and petrological data for:

the typical alkaline association
the high-Ca alkaline association
the high-K alkaline association
kimberlites
the potassic lamproites

are summarised in this chapter in sections 5.2 - 5.6 inclusive. Although petrogenetic proposals are introduced in these summaries, a consideration of the fundamental link between the upper mantle source regions, and specific primary magma series is postponed to Chapter 7.

## 5.2 The Typical Alkaline Association

### 5.2.1 Crystal fractionation series

The gradational transitions between nephelinitic, basanitic, alkali basaltic and tholeiitic (continental- or Hawaiian-type) parent magmas are now well established in the extensive literature dealing with the geochemistry, mineralogy and taxonomy of the typical alkaline association. Each group contains examples of non-cumulative rocks with 100Mg/Mg+Fe" ratios in the primitive range, thereby refuting the possibility of a common genetic link involving crystal fractionation alone. Increasing degrees of $SiO_2$-undersaturation in the basic rocks are usually accompanied by an increase in the abundances of the incompatable elements.

In general, the degree of silica saturation of alkaline differentiates is inherited from their parent liquids (Coombs & Wilkinson, 1969; Wright, 1971) so that fractionation of nephelinitic and basanitic liquids produces phonolite, alkali basalt produces trachyte, and transitional basalts give rise to quartz trachyte. Evidence is provided by the in-situ compositional variation in intrusives and by the compositions of groundmass glass in lava flows, providing no quench phases have developed. This low pressure (near surface) derivation of the hawaiite/nepheline hawaiite - mugearite/nepheline mugearite - benmoreite/nepheline benmoreite -

trachyte/phonolite fractionation series from the alkali basalt/nephelinite spectrum of basic parent liquids has also been suggested by Baker (1969), Mackenzie & White (1970), Zielinsky & Frey (1970), Flower (1971) and Strong (1972). However the presence of spinel lherzolite inclusions in nepheline hawaiite and nepheline mugearite (Irving, 1971), nepheline benmoreite or basic phonolite (Price & Green, 1972) and trachyte (Wright, 1969) shows that fractionation at subcrustal levels can achieve similar results. Table 5.1 contains examples of typical phonolites with increasing degrees of $SiO_2$-undersaturation.

From near-surface conditions to at least 10 kb, fractionation in all members of the basic spectrum is initially controlled by olivine and clinopyroxene (Yoder & Tilley, 1962; Green & Ringwood, 1967a; Ito & Kennedy, 1968; Tuthill, 1968; Bultitude & Green, 1968, 1971) accompanied by early precipitation of Fe-Ti oxides under high $f_{O_2}$ (Hamilton *et al.*, 1964; Nesbitt & Hamilton, 1970). The stability field of plagioclase is suppressed under hydrous conditions, and kaersutitic amphibole and biotite can appear if $a_{H_2O}$ reaches the required levels (Irving, 1971). In addition, Irving (1971) demonstrated that at high presssures (15-20 kb) under hydrous conditions, crystal fractionation involving mainly amphibole (± biotite) produced nepheline hawaiites and nepheline mugearites from basanite parents, and hawaiites from alkali basalts, so trachytic and phonolitic bulk compositions may also be the end products of certain high pressure, hydrous fractionation series. Inconsistent europium anomalies in the REE distributions of both trachytes and phonolites (Fig. 5.1) show that fractionation has not always involved felspar(s), and this could perhaps illustrate the convergence of low pressure and high pressure fractionation trends. (Alternatively, Eu anomalies simply may not appear until fractionation effects a rapid drop in Sr concentrations).

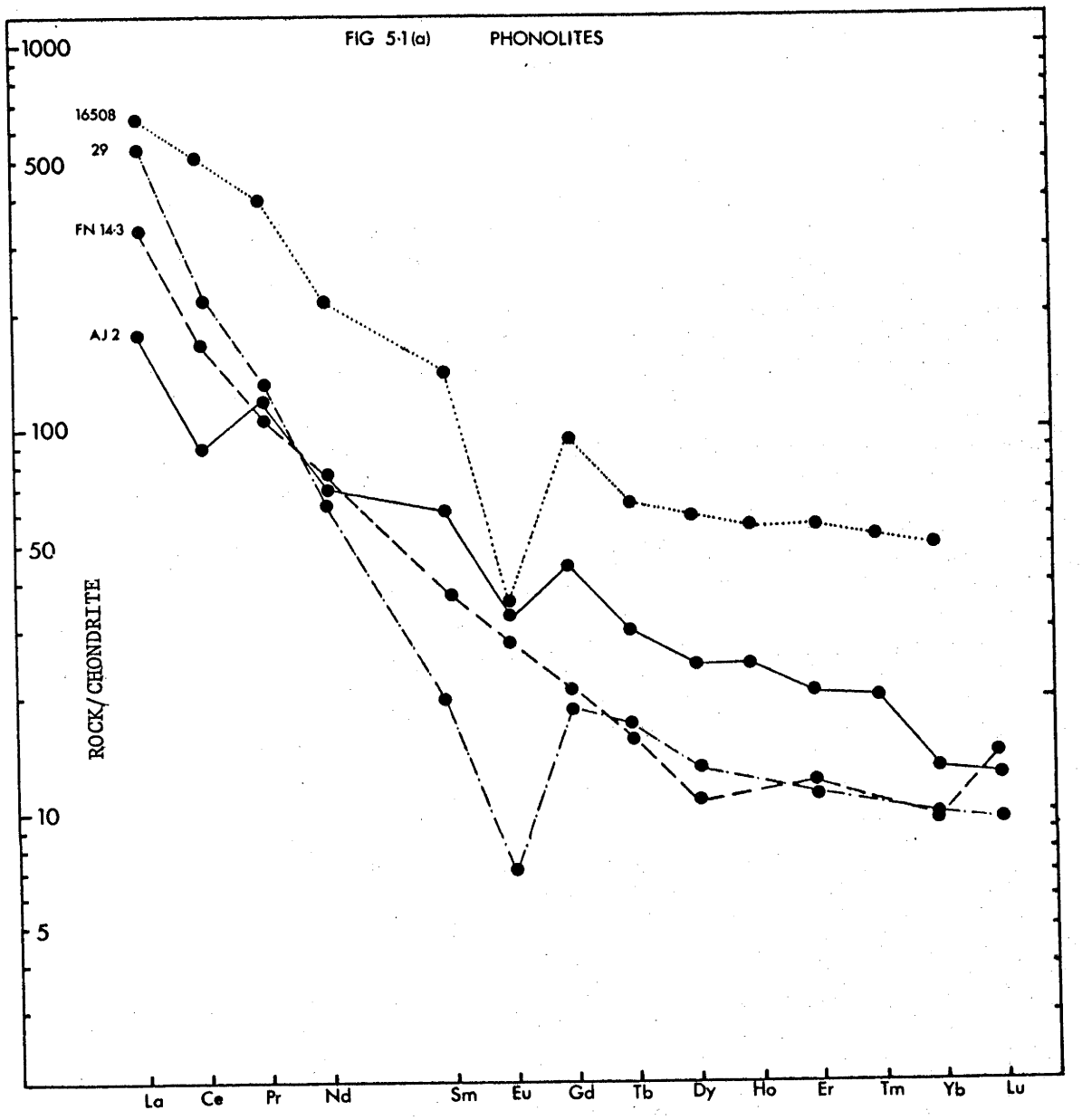
The fractionation series described above typically have $K_2O/Na_2O$ ratios near 0.5 and rarely exceeding 1.0 but there are some otherwise similar rock types with uncharacteristically high $K_2O/Na_2O$ ratios which correspond to members of

Table 5.1

The typical alkaline association: phonolites

| Rock no. | 16508[1] | NZ1[1] | 19679[1] |
|---|---|---|---|
| locality | Monaro district, NSW | Otago,NZ | Kosciusko, NSW |
| $SiO_2$ | 57.11 | 55.21 | 53.84 |
| $TiO_2$ | 0.07 | 0.09 | 0.03 |
| $Al_2O_3$ | 18.20 | 19.68 | 20.69 |
| $Fe_2O_3$ | 2.86 | 4.11 | 3.44 |
| FeO | 2.46 | 1.45 | 0.70 |
| MnO | 0.30 | 0.13 | 0.28 |
| MgO | 0.18 | 0.19 | 0.14 |
| CaO | 1.47 | 1.03 | 0.68 |
| $Na_2O$ | 7.22 | 9.48 | 10.38 |
| $K_2O$ | 5.21 | 5.36 | 4.82 |
| $P_2O_5$ | 0.03 | 0.01 | 0.06 |
| $H_2O\pm$ | 3.44 | 2.02 | 3.73 |
| $CO_2$ | 0.69 | n.d. | 0.07 |
| TOTAL | 99.19 | 98.76 | 98.66 |
| Na+K/Al | 1.00 | 1.10 | 1.07 |
| Rb | 277 | 212 | 367 |
| Ba | 35 | 24 | tr. |
| Sr | 143 | 66 | 10 |
| Pb | 26 | 25 | 27 |
| Th | 40 | 47 | 80 |
| U | 7 | 12 | 20 |
| Zr | 1750 | 1087 | 1781 |
| Nb | 274 | 269 | 379 |
| Y | 87 | 47 | 40 |
| La | 217 | 153 | 153 |
| Ce | 441 | 264 | 276 |
| V,Cr,Ni,Cu | tr. | tr. | tr. |
| Zn | 274 | 282 | 247 |
| Ga | 37 | 38 | 38 |

[1]this thesis




| PHONOLITE 16508 | | |
|---|---|---|
| | MS-7[1] | XRF |
| La | 209 | 217 |
| Ce | 414 | 441 |
| Pr | 49 | 45 |
| Nd | 154 | 129 |
| Sm | 27 | |
| Eu | 2.25 | |
| Gd | 24 | |
| Tb | 3.05 | |
| Dy | 36.43 | |
| Ho | 3.86 | |
| Er | 11.32 | |
| Yb | 9.53 | |

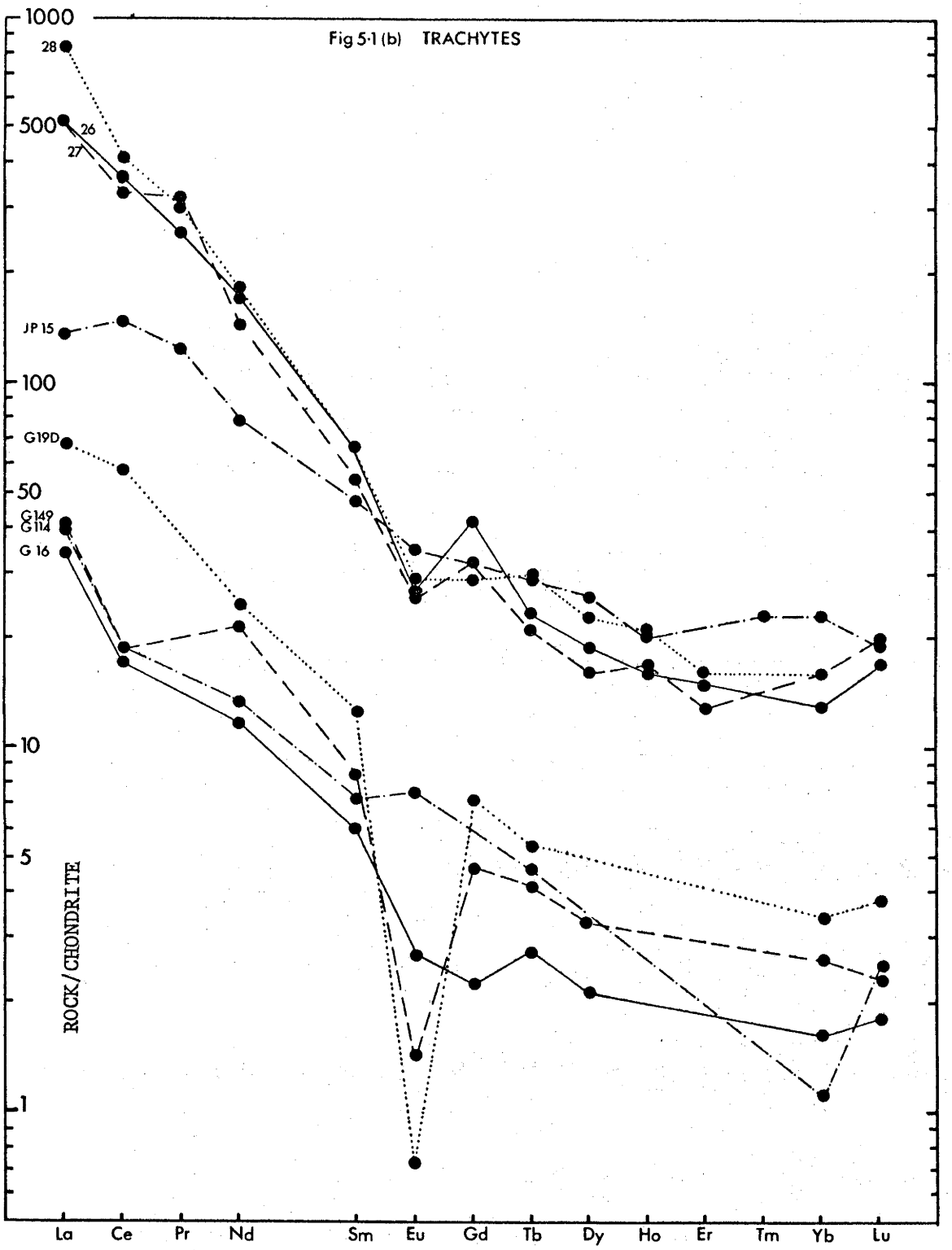
[1] spectrometric analysis
by courtesy of D.W.Haynes

16508, Monaro volcanics, this thesis

Westerwald, Germany (Herrmann, 1968)

FN14-3, Fernando Noronha, Atlantic ocean (Kay, 1972)

AJ2 Comores Archipelago, Indian ocean (Flower, 1971)




26,27,28, Rhine graben, Germany (Herrmann, 1968)
JP15, Hawaiian Is. (Schilling & Winchester, 1969)

G114,G16,G149,G19D Gough Is. Atlantic ocean (Zielinski & Frey, 1970)
NOTE: all values in this group reduced by a factor of 10

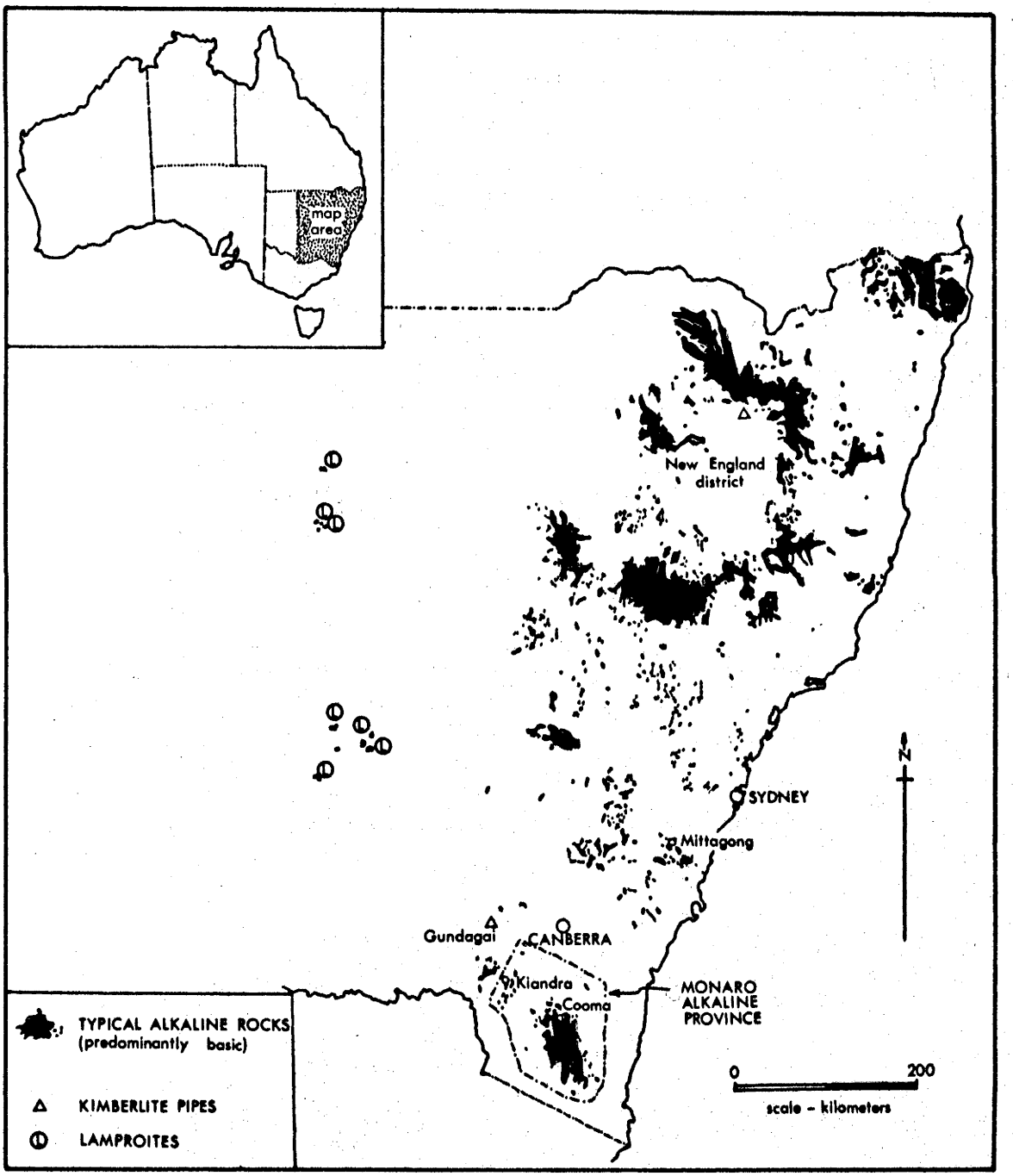
the "potassic lineages" recognised by Coombs & Wilkinson (1969). However the associated rocks in the provinces (eg. Gough Is, Tristan da Cunha) with 100Mg/Mg+Fe" ratios ($Fe_2O_3$/FeO recalculated to 0.25) in the primitive range have $K_2O$:$Na_2O$ ratios which do not exceed 0.60. This suggests that the higher $K_2O$:$Na_2O$ ratios are superimposed during fractionation, rather than inherited from a primitive potassic parent liquid, although mantle inhomogeneity on a local or regional scale, the nature of the partial melting process,or variation in P, T and $a_{H_2O}$ for partial melting may still account for minor chemical differences between partial melts.

5.2.2 Liquid immiscibility

In all of the alkaline sub-associations a striking contrast to the observed fractionation series is provided by a number of reported occurrences of relatively leucocratic "spherulites" or "ocelli" in a wide range of ultrabasic, basic and intermediate host rocks (Mackenzie & White, 1970; Ferguson & Currie, 1971; Velde, 1971). This phenomenon is commonly held to represent liquid immiscibility. In the more $SiO_2$-undersaturated basic rocks these segregations have approximately phonolitic compositions. Immiscibility is an equilibrium phenomenon, with the criterion that both liquids are in equilibrium with identical phases during the course of crystallisation (Bowen, 1928). A given phase need only precipitate in one liquid, but if it were accidently incorporated into the other liquid, mutual equilibrium requires that no reaction takes place. Philpotts & Hodgson (1968); Ferguson & Currie (1971) and Philpotts (1971) have found sub-liquidus phases of identical composition common to both ocelli and host, and also instances of a single crystal straddling the liquid boundary with no evidence of reaction in either. A convincing experimental demonstration of immiscibility using natural alkaline rocks has yet to be provided. Presumably this reflects a narrow range of physical conditions for immiscibility, which would also account for the relatively infrequent occurrences in natural rocks. It has yet to be shown that sub-liquidus immiscibility is efficient, i.e. that there is complete segregation of the second liquid.

FIG 5·21

# DISTRIBUTION OF CENOZOIC ALKALINE ROCKS IN N.S.W.



### 5.2.3 The Typical Alkaline Association: Monaro district, southeastern NSW

In this section, new major and trace element analyses of Eocene-Miocene basic alkaline rocks from the Monaro district, southeastern NSW, are used to provide an example of the typical alkaline association in the continental environment. Appendix 2A contains the primary analytical data; Appendix 2B contains the analyses with totals (including trace elements) adjusted to 100% on a hydrous basis. Unless stated otherwise, all diagrams use values from Appendix 2B. The locality of the province is shown in Fig. 5.21.

#### 5.2.3.1 General petrographic features

This section aims to provide a summary of significant petrographic and mineralogical features but does not represent a detailed investigation. O'Reilly (1972) has made a comprehensive mineralogical study of the alkaline volcanics near Moss Vale and Mittagong, NSW, which are similar in age and composition to those of the Monaro district, and many of her conclusions should be valid for the entire eastern Australian province.

There is little systematic mineralogical variation between the alkali basalts, basanites and nephelinites other than the presence of nepheline in some basanites and all nephelinites; nephelinites K30, K71 and 4168 contain nepheline but no plagioclase. Ophitic, intergranular and fluidal textures are observed in all rock types, and olivine or olivine + clinopyroxene are the common pehnocryst phases, with plagioclase appearing as a third phenocryst phase in some alkali basalts and basanites. Euhedral microphenocrysts of titanomagnetite ± exsolved ilmenite lamellae, and also glomeroporphyritic aggregates of clinopyroxene or clinopyroxene + olivine, can be found in all rock types. Clinopyroxene and plagioclase phenocrysts may enclose stumpy prisms of apatite. Quite commonly individual or agglomerative clinopyroxene phenocrysts contain numerous small blebs of devitrified glass (?). Rare ragged and corroded plagioclase phenocrysts with narrow clear labradorite rims enclose numerous tiny grains of

clinopyroxene and/or a green or opaque spinel. Transparent anorthoclase and partially resorbed kaersutite megacrysts occur in K72. The significance of these latter phases is discussed by Irving (1971).

Olivine

Opaque euhedra in olivine are identified as chrome spinel by their lower reflectivity in comparison with titanomagnetite. Fluid inclusions in olivine may be visible under high magnification. Olivines are compositionally zoned, and the forsterite content of the core is generally consistent with the composition predicted from olivine-liquid equilibria (Roeder & Emslie, 1970) although the periphery is more fayalitic (Table 5.2).

Clinopyroxene

The clinopyroxene in all basic rock types is augite or titanaugite. Higher Fe and Ti and a deep pink or brick red colour are characteristic of groundmass clinopyroxenes and also of the border zones around more magnesian pink or neutral phenocryst cores (Table 5.2). O'Reilly (1972) noted that the poikilitic cores are slightly subcalcic (∿20% CaO) with $TiO_2$ contents typically ∿1.6% (implying crystallisation below 10kb) and showed that the bulk composition of the fine-grained mesostasis in the blebs corresponds quite closely to that of the host clinopyroxene.

Plagioclase

Large zoned phenocrysts may have cores as calcic as $An_{73}$; however most phenocrysts and groundmass laths range from $An_{50}$ to $An_{60}$ and clear narrow rims of calcic andesine are sometimes observed. The corroded poikilitic phenocrysts $An_{52}$ - $An_{65}$ enclosing granular spinels ± clinopyroxene (which do not correspond to the plagioclase - ferrian pleonaste intergrowths discussed by O'Reilly (1972)) may represent the exsolution products of a previously homogenous garnet or clinopyroxene solid solution once stable at higher pressures. Alternatively they may correspond to the breakdown products of amphibole below eg. 10 kb.

Alkali felspar

Sanidine (rarely anorthoclase) is normally the $K_2O$-rich phase in all basic rock types, including holocrystalline

Table 5.2

Microprobe analyses of phases from basic alkaline rocks, Monaro district, southeastern NSW

| PHASE | ol | ol | ol | ol | ol | ol | ol | ol | ol | ol | ol |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HOST | K9 | K9 | K60 | K60 | K69 | 19068 | 19068 | 4168 | 4168 | 4168 | 4168 |
| STATUS | phx core | phx rim | phx core | phx rim | ol-opx-sp inclusion | ol-cpx-phlog inclusion | phx core | phx | phx | phx core | phx rim |
| $SiO_2$ | 39.97 | 38.27 | 36.59 | 36.38 | 40.67 | 38.89 | 39.97 | 39.93 | 37.93 | 39.41 | 37.98 |
| tot.FeO | 15.50 | 20.95 | 29.31 | 34.87 | 9.19 | 14.86 | 12.53 | 14.98 | 24.18 | 14.98 | 24.22 |
| MnO | 0.33 | 0.33 | 0.55 | 0.61 | 0.10 | 0.17 | 0.17 | 0.22 | 1.44 | 0.33 | 0.50 |
| MgO | 43.69 | 39.25 | 35.06 | 27.62 | 48.17 | 44.55 | 46.89 | 43.65 | 35.22 | 43.69 | 35.13 |
| CaO | 0.32 | 0.31 | 0.55 | 0.63 | 0.01 | 0.26 | 0.22 | 0.22 | 0.56 | 0.22 | 0.56 |
| NiO | 0.08 | 0.07 | 0.05 | nd. | 0.35 | 0.15 | 0.19 | 0.15 | 0.13 | 0.11 | 0.04 |
| Total | 99.90 | 99.18 | 102.11 | 100.11 | 98.49 | 98.88 | 99.97 | 99.15 | 99.46 | 98.74 | 98.43 |
| $100Mg/Mg+Fe$ | 83.4 | 77.0 | 68.1 | 58.5 | 90.3 | 84.2 | 87.0 | 83.8 | 72.2 | 83.9 | 72.1 |

ABBREVIATIONS:

ol = olivine
cpx = clinopyroxene
opx = orthopyroxene
sp = spinel
mag = titanomagnetite
phlog = phlogopite
fhs = ferrohastingsite
phx = phenocryst
n.d. = not detected
n.a. = not analysed

TABLE 5·2(cont.)

| PHASE | cpx | cpx | cpx | cpx | cpx | cpx | cpx | cpx | cpx |
|---|---|---|---|---|---|---|---|---|---|
| HOST | K9 | K9 | K60 | K60 | 19068 | 19068 | 19068 | 19068 | 19068 |
| | | | | | ol-cpx-phlog inclusion | | | | |
| STATUS | phx core | phx rim | phx core | phx rim | core | rim | phx core | phx mid zone | phx rim |
| $SiO_2$ | 45.93 | 45.65 | 44.86 | 46.26 | 46.20 | 47.83 | 49.14 | 49.05 | 47.33 |
| $TiO_2$ | 1.58 | 1.81 | 1.96 | 2.35 | 1.33 | 1.57 | 0.47 | 1.18 | 2.21 |
| $Al_2O_3$ | 7.79 | 7.82 | 7.19 | 5.86 | 7.85 | 5.97 | 5.32 | 4.52 | 4.95 |
| tot.FeO | 7.93 | 7.94 | 8.44 | 8.56 | 6.50 | 8.47 | 12.07 | 6.97 | 7.56 |
| MnO | 0.09 | 0.09 | 0.13 | 0.14 | 0.09 | 0.16 | 0.32 | 0.08 | 0.16 |
| MgO | 13.54 | 13.53 | 12.62 | 12.42 | 13.76 | 12.53 | 9.64 | 14.92 | 14.09 |
| CaO | 22.13 | 21.69 | 22.91 | 22.82 | 22.40 | 20.77 | 19.85 | 22.41 | 23.24 |
| $Na_2O$ | 0.55 | 0.57 | 0.55 | 0.60 | 0.63 | 0.64 | 2.60 | 0.55 | 0.59 |
| TOTAL | 99.66 | 99.21 | 98.66 | 99.01 | 99.66 | 98.84 | 99.45 | 100.05 | 100.18 |
| 100Mg/Mg+Fe | 75.3 | 75.2 | 72.7 | 72.1 | 79.0 | 72.5 | 58.7 | 85.5 | 76.9 |
| Si | 1.732 | 1.728 | 1.721 | 1.765 | 1.744 | 1.824 | 1.881 | 1.833 | 1.779 |
| $Al^{IV}$ | 0.268 | 0.272 | 0.279 | 0.235 | 0.256 | 0.176 | 0.119 | 0.167 | 0.219 |
| $Al^{VI}$ | 0.078 | 0.077 | 0.046 | 0.029 | 0.093 | 0.092 | 0.117 | 0.032 | |
| Ti | 0.045 | 0.052 | 0.057 | 0.067 | 0.038 | 0.045 | 0.014 | 0.033 | 0.062 |
| Fe | 0.250 | 0.251 | 0.271 | 0.273 | 0.205 | 0.270 | 0.386 | 0.218 | 0.238 |
| Mn | 0.003 | 0.003 | 0.004 | 0.005 | 0.003 | 0.005 | 0.010 | 0.003 | 0.005 |
| Mg | 0.761 | 0.763 | 0.721 | 0.706 | 0.744 | 0.712 | 0.550 | 0.831 | 0.789 |
| Ca | 0.894 | 0.880 | 0.941 | 0.933 | 0.906 | 0.849 | 0.814 | 0.897 | 0.936 |
| Na | 0.040 | 0.042 | 0.041 | 0.044 | 0.046 | 0.047 | 0.193 | 0.040 | 0.043 |
| X+Y | 2.070 | 2.068 | 2.081 | 2.057 | 2.065 | 2.020 | 2.084 | 2.054 | 2.073 |
| Z | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.998 |

TABLE 5·2(cont.)

| PHASE | phlog[1] | fhs[2] | sp | sp | mag | mag |
|---|---|---|---|---|---|---|
| HOST | 19068 | 16508 | K69 | K69 | K60 | K60 |
| STATUS | ol-cpx-phlog inclusion | phx | ol-opx-sp inclusion | | micro-phenocrysts | |
| $SiO_2$ | 36.78 | 37.07 | nd. | nd. | nd. | nd. |
| $TiO_2$ | 5.01 | nd. | nd. | nd. | 25.90 | 24.41 |
| $Al_2O_3$ | 16.04 | 10.16 | 60.40 | 59.80 | 2.49 | 2.08 |
| tot.FeO | 9.96 | (3) | 11.14 | 10.79 | 67.10 | 66.50 |
| MnO | 0.03 | 1.44 | 0.08 | 0.08 | 0.64 | 0.70 |
| MgO | 18.89 | 0.14 | 22.45 | 22.07 | 1.04 | 1.55 |
| CaO | nd. | 9.41 | nd. | nd. | 0.10 | 0.07 |
| $Na_2O$ | 0.79 | 2.61 | na. | na. | na. | na. |
| $Cr_2O_3$ | na. | na. | 8.40 | 8.37 | 0.03 | 0.04 |
| TOTAL | 95.62 | 97.44 | 102.48 | 101.12 | 97.30 | 95.35 |
| 100Mg/Mg+Fe | 77.2 | | | | | |
| $Si_{iv}$ | 5.329 | 6.042 | | | | |
| $Al^{iv}$ | 2.671 | 1.952 | | | | |
| $Al^{vi}$ | 0.067 | | | | | |
| Ti | 0.546 | | | | | |
| Fe | 1.207 | (4) | | | | |
| Mn | 0.004 | 0.199 | | | | |
| Mg | 4.079 | 0.034 | | | | |
| Ca | | 1.644 | | | | |
| Na | 0.222 | 0.825 | | | | |
| K | 1.479 | 0.341 | | | | |
| X+Y | 7.606 | | | | | |
| Z | 8.000 | | | | | |

| PHASE | opx | opx |
|---|---|---|
| HOST | K69 | K69 |
| STATUS | ol-opx-sp inclusion | |
| $SiO_2$ | 55.06 | 54.55 |
| $Al_2O_3$ | 4.47 | 4.68 |
| tot.FeO | 6.42 | 6.23 |
| MnO | 0.09 | 0.09 |
| MgO | 33.89 | 33.18 |
| CaO | 0.64 | 0.64 |
| NiO | 0.02 | 0.02 |
| $Cr_2O_3$ | 0.25 | 0.25 |
| TOTAL | 100.84 | 99.64 |
| 100Mg/Mg+Fe | 90.4 | 90.5 |
| Si | 1.888 | 1.891 |
| $Al^{iv}$ | 0.112 | 0.109 |
| $Al^{vi}$ | 0.069 | 0.082 |
| Cr | 0.007 | 0.007 |
| Fe | 0.184 | 0.181 |
| Mn | 0.003 | 0.003 |
| Mg | 1.732 | 1.714 |
| Ni | 0.001 | 0.001 |
| Ca | 0.024 | 0.024 |
| X+Y | 2.020 | 2.012 |
| Z | 2.000 | 2.000 |

1 22 oxygens
2 23 oxygens
3 $Fe_2O_3$ = 15.94, FeO = 19.03
4 $Fe^{3+}$ = 1.955, $Fe^{2+}$ = 2.594

plagioclase-free nephelinites. Alkali felspars typically occur as feathery aggregates or on interstitial sites in the groundmass, although euhedral sanidine phenocrysts are the mineralogical expression of the high $K_2O/Na_2O$ ratio of K46. Leucite was not identified by X-ray or optical methods.

Other phases

Clinopyroxene, dendritic or granular opaque phases and less commonly olivine are the main mafic phases in the groundmass. Plagioclase laths and/or prismatic or interstitial nepheline are abundant and alkali felspar and rarely analcime may be observed. Accessory phases including acicular apatite, rare biotite, flakes of amphibole (? aenigmatite) and minute sulphide blebs together with a mesostasis of secondary zeolites, clays and carbonates comprise the remainder of the groundmass; K30 alone contains basaltic glass.

Inclusions

Cognate crystal accumulates are not uncommon. Rare quartzose xenoliths are surrounded by a corona of green or colourless clinopyroxene. The plagioclase-free nephelinite K71 contains limestone inclusions, presumably derived from the underlying Palaeozoic sequence, which are mantled by zones comprising several unidentified calc-silicate phases. Laths of melilite, and leucite (?) occur in the adjacent groundmass, but are clearly the direct consequence of local desilication of the melt. (Xenoliths were separated prior to analysis of the host.)

Partially disaggregated inclusions of upper mantle origin comprising olivine, orthopyroxene and chrome spinel (mineral analyses in Table 5.2) occur in K69 and a similar inclusion (not analysed) in K9 also contains patches of granular colourless clinopyroxene. Reaction occurs between orthopyroxene and the host rocks, and spinel and the hosts.

Subsolidus alteration

In many cases surface weathering is clearly responsible for the alteration of phenocryst and groundmass olivine to "iddingsite". Clays (including green saponite), a carbonate, and the zeolites phillipsite, levyne, chabazite, thompsonite, natrolite and analcime are secondary phases

which are produced during subsolidus alteration of the basaltic rocks. The alteration is least evident in the centres of massive flows, and most apparent in pyroclastic and brecciated units, where these phases occur as amygdale fillings, breccia cements, and within the rocks as pseudomorphs after glass or other primary crystalline phases.

Analcime is not a primary phase in most basic alkaline rocks. The stability field of analcime + melt ± fluid, delineated by Boettcher & Wyllie (1969) lies between 5 and 10 kb at temperatures below the $H_2O$-saturated basalt solidus (Hill & Boettcher, 1970; Haygood et al., 1971).

Specific petrographic features

K15 is an olivine and clinopyroxene-rich accumulate characterised by high 100Mg/Mg+Fe", Ni and Cr. Disaggregated lherzolite fragments are responsible for similar chemical features in K69, thus neither rock represents a primary magma.

The analcime dolerites K38A and K60, the most fractionated of the basic rocks, are the exposed central plugs of eroded volcanoes. The presence of numerous glomeroporphyritic aggregates of clinopyroxene with minor olivine, and also the composition of the olivine in K60 suggest that these rocks may comprise a mixture of an extensively fractionated melt and the liquidus precipitates of preceding magma batches.

"Phonolite globules" in basanite 19052 described in detail by Mackenzie & White (1970) are considered to result from liquid immiscibility.

Flows 19053 and 19063 are very similar in composition and may well represent the same magma.

Although 100Mg/Mg+Fe" ratio of the dyke 19068 lies in the primitive range, its atypical mineralogy shows that it does not represent a primitive magma. Evidence is provided by embayed pleochroic green cores in many clinopyroxene phenocrysts which were assumed to be Cr-rich (cf. Huckenholz, 1966). However microprobe analysis of the green core, neutral mid-zone and pink rims shows that the core is sodic and less magnesian than the peripheral zones. Furthermore,

although the composition of the euhedral olivine phenocrysts are consistent with theoretical predictions, a more fayalitic olivine occurs in glomeroporphyritic aggregates with phlogopite, kaersutite, an opaque phase and clinopyroxenes with reversed zonations (Table 5.2).

KPHI and K21-25 inclusive are samples taken from the one clinopyroxene-phyric dolerite flow, at separate localities. The variation in $K_2O$ and Rb is rather disturbing, and could be attributed to inadequate sample bulk or subsolidus alteration or, more probably, to a combination of both factors. However the geochemistry of the Monaro province compares favourably with published data for other typical alkaline provinces, so in most cases (in the samples selected for analysis) the subsolidus redistribution of elements operates on a scale much less than the sample size.

Phonolites

The outcrop of phonolite 16508 was never located. The rock consists of aegirine and ferrohastingsite microphenocrysts in a fluidal groundmass of sanidine laths, arborescent aenigmatite and nepheline. The phonolite dyke from Kosciusco, 19679, is thought to be coeval with the predominantly Cenozoic basic volcanics. Large equant nepheline euhedra, and rare plates of biotite and cloudy alkali felspar are contained in a fine-grained base of feathery sanidine and prismatic aegirine.

5.2.3.2 Geochemistry

There is an extensive volume of literature dealing with the chemical and mineralogical variations throughout low pressure fractionation series in the typical alkaline association but this style of investigation is inapplicable to the Monaro province since apart from 2 phonolites only a narrow range of basic compositions occur.

Of these basic rocks, 13 are considered to represent primary magmas whereas the remainder have been affected to a limited extent by low and/or high pressure fractionation processes. But if the fractionation trends are identified, the derivative compositions indirectly provide information on the chemical variations in primary parent magmas.

100Mg/Mg+Fe" ratios ($Fe_2O_3/FeO$ = 0.25) should provide a more efficient index of fractionation for this particular study than $SiO_2$ content, differentiation index or any of the other parameters in common usage.

The following summary together with Figs. 5.22(a) to (l), is primarily concerned with the early, and therefore linear, fractionation trends in the basic alkaline rocks, from 100Mg/Mg+Fe" = 67.0 to ∿60. Fractionation trends are not very obvious amongst the basanites because of their limited range of 100Mg/Mg+Fe" ratios.

$Al_2O_3$ and Ga

$Al_2O_3$ and Ga are remarkably constant in all rock types, although $Al_2O_3$ is slightly higher in the most fractionated basic rocks.

$TiO_2$, Zr and Nb

$TiO_2$ and Zr abundances in primary and derivative liquids, progressively decrease from nephelinites to basanites to alkali basalts, but increase with fractionation within each group (Fig. 5.22(a) and (b)). Nb shows a significant correlation with $TiO_2$ and Zr. The initial increase in $TiO_2$ indicates that fractionation processes do not involve Ti-rich phases, namely kaersutite, Ti-phlogopite, Fe-Ti oxides, or much low pressure clinopyroxene (cf. Yagi & Onuma, 1967).

Vanadium

The primary abundances of V in alkali basalts, basanites and nepelinites are similar (Fig. 5.22(c)). In the basanites and alkali basalts, V increases with fractionation and, coupled with the distribution of $TiO_2$, this demonstrates that the crystallisation history of the basanites and alkali basalts does not include the early precipitation of Fe-Ti oxides. The comparatively lower $TiO_2$ contents of the typical alkaline association in continental environments thus appears to be a primary feature.

However the increase in $TiO_2$ in fractionated nephelinites is accompanied by a definite decrease in V. Presumably an early oxide phase ($TiO_2$-poor) removes V from the melt with great efficiency.

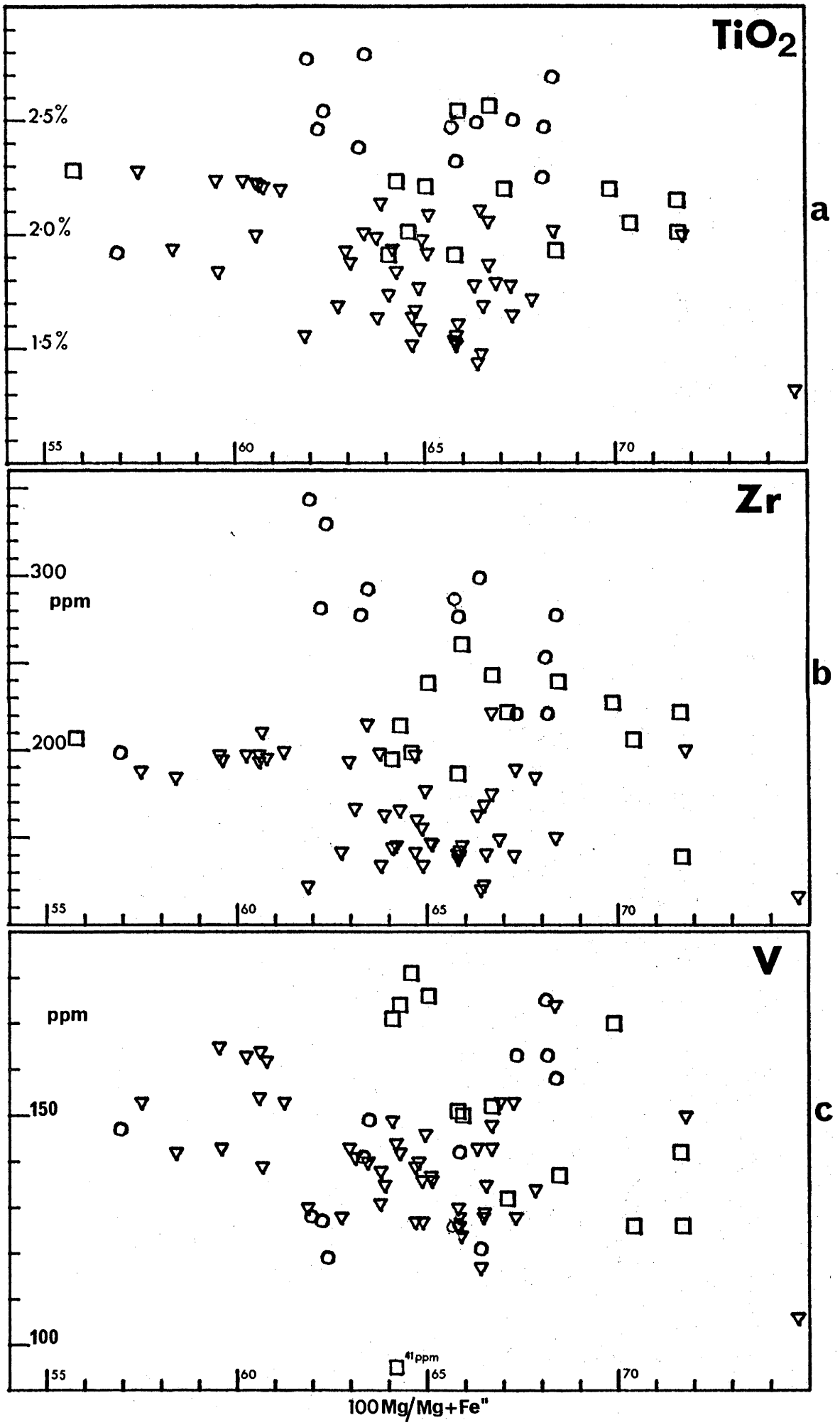
Figure 5.22

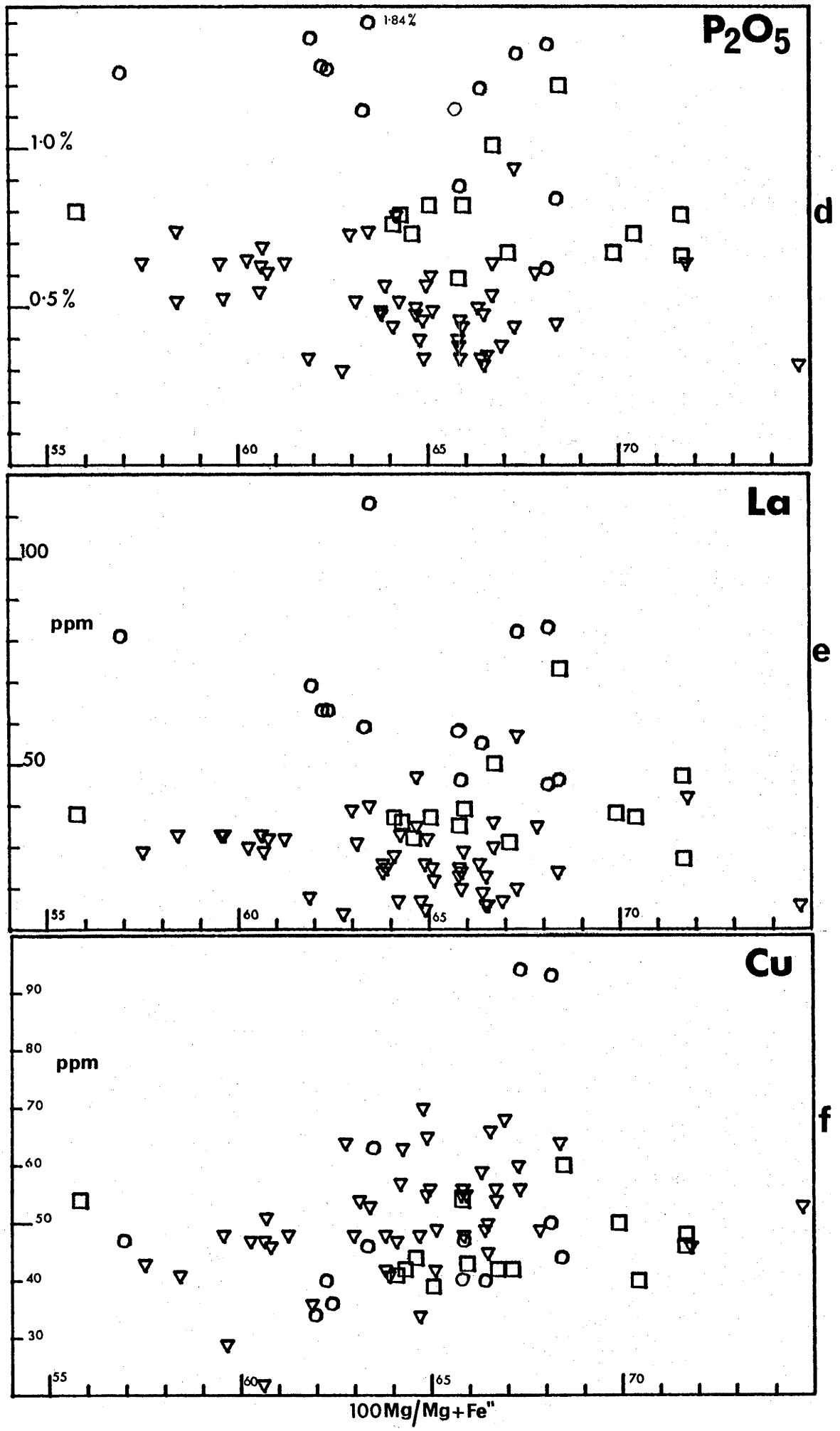
GEOCHEMICAL VARIATION IN THE MONARO VOLCANICS

KEY TO SYMBOLS:

- ▽ ALKALI BASALTS
- □ BASANITES
- ○ NEPHELINITES

| | | | |
|---|---|---|---|
| 100Mg/Mg+Fe" | vs. | $TiO_2$ | Fig.5.22(a) |
| " | | Zr | " (b) |
| " | | V | " (c) |
| " | | $P_2O_5$ | " (d) |
| " | | La | " (e) |
| " | | Cu | " (f) |
| " | | Sr | " (g) |
| " | | $K_2O$ | " (h) |
| " | | Ba | " (i) |
| " | | Ni | " (j) |
| " | | Cr | " (k) |
| " | | $SiO_2$ | " (l) |


TiO2
2·5%
2·0%
1·5%
a
55
60
65
70
Zr
300
ppm
200
b
V
ppm
150
100
c
41ppm
100 Mg/Mg+Fe"


P2O5
1·84%
1·0%
0·5%
d
55
60
65
70
La
100
ppm
50
e
55
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ppm
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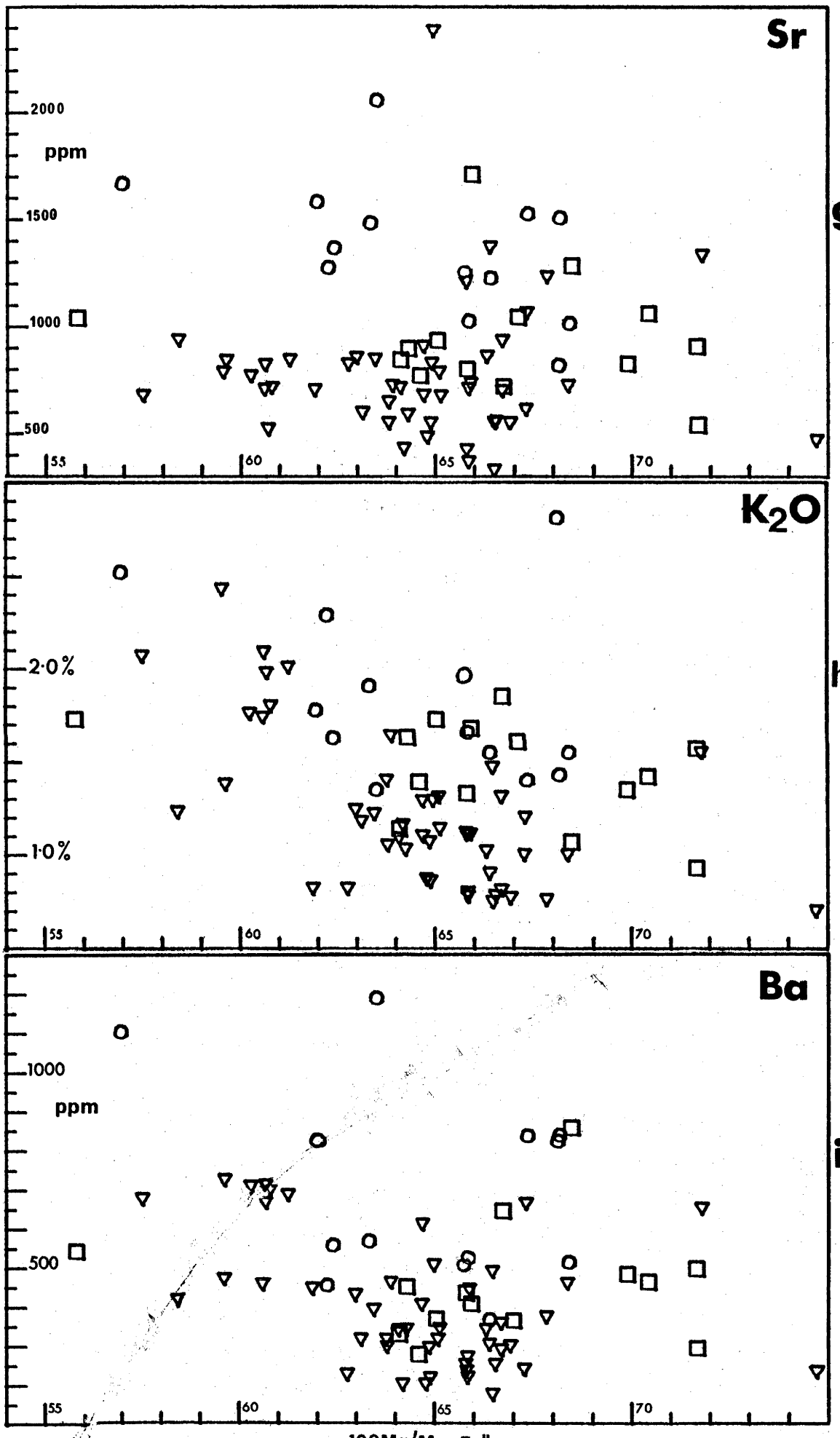
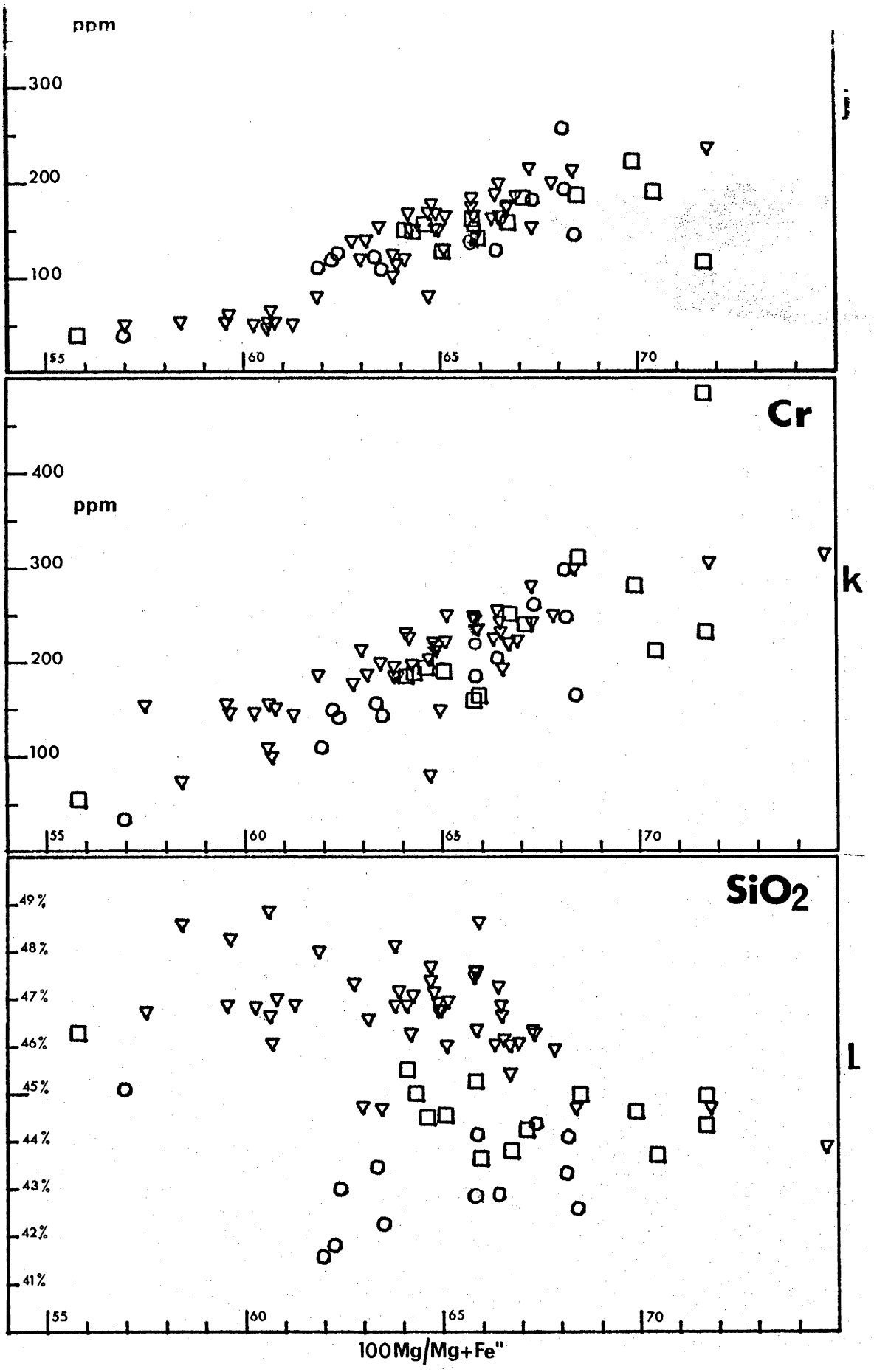
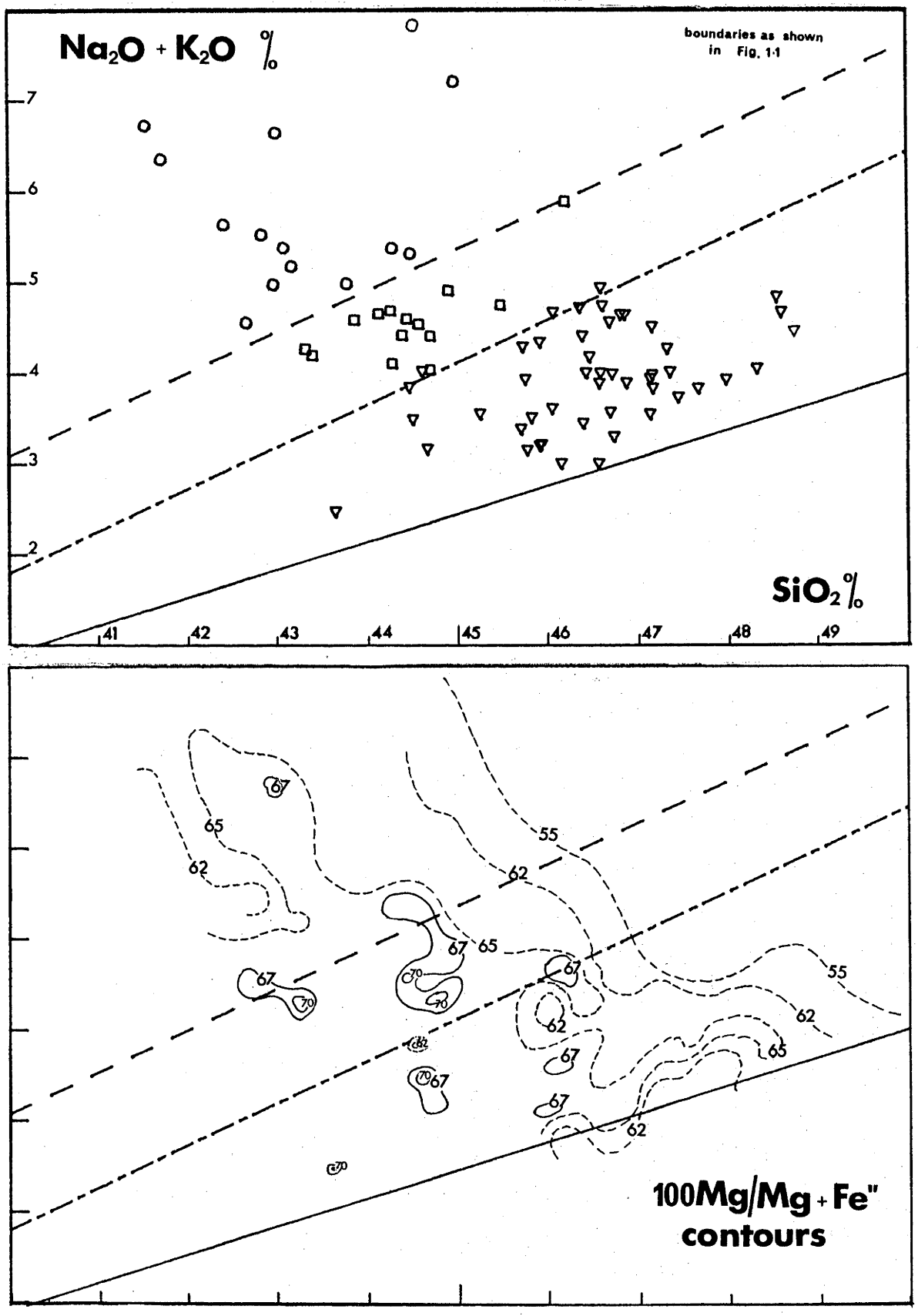
55
60
65
70
100Mg/Mg+Fe"


Sr
2000
ppm
1500
1000
500
55
60
65
70
g
$K_2O$
2·0%
1·0%
h
Ba
1000
ppm
500
i
100Mg/Mg+Fe"


ppm
300
200
100
55
60
65
70
j
Cr
400
ppm
300
200
100
55
60
65
70
k
SiO2
49%
48%
47%
46%
45%
44%
43%
42%
41%
55
60
65
70
l
100Mg/Mg+Fe"

# Figure 5·23

## MONARO VOLCANICS: distribution of analysed samples



$P_2O_5$ and light REE (La, Ce, Pr, Nd)

$P_2O_5$ contents decrease from nephelinites to basanites to alkali basalts. Since there is no obvious fractionation trend in basanites and alkali basalts, the $P_2O_5$ contents of the derivative liquids are similar to the primary abundances. The nephelinitic derivatives suggest a slight enrichment in $P_2O_5$. All rock types show a significant positive correlation between $P_2O_5$ and La, Ce, Pr and Nd, and the observations for the distribution of $P_2O_5$ are similarly true for the light REE (Figs. 5.22(d) and (e)).

Yttrium

The abundance of Y in the alkali basalts overlaps that of the basanites, however both rock types contain less Y than the nephelinites. Fractionation produces little change in Y abundances in alkali basalts and basanites whereas nephelinitic differentiates become slightly enriched. The rapid decrease in Y abundances which would accompany any fractionation process involving garnet (Gast, 1968) is not observed. Although Y provides an approximate measure of the abundances of the heavy REE (Taylor, 1965) it cannot indicate fractionation within the heavy REE group, so the characteristic depletion of the heaviest REE in nephelinitic rocks (Kay, 1972) is not recorded.

Pb and Th

Basanites and alkali basalts overlap in both the primary and derivative range, and contain slightly lower concentrations of these elements than do nephelinites. The scattered points show no obvious fractionation trend.

Zn and Cu

There is a complete overlap in the Zn contents of all rock types and no fractionation trends are apparent. The Cu contents of alkali basalts and basanites overlap, and are higher than those of the nephelinites; Fig. 5.22(f). There is some suggestion of a decrease with fractionation, which is consistent with the removal of Cu-bearing sulphides as inclusions in the early clinopyroxene.

$K_2O$, Rb and Sr

The concentration of Sr in both primary and derivative magmas, decreases from nephelinites to basanites to alkali

basalts; Fig. 5.22(g). The $K_2O$ contents of nephelinites and basanites overlap, and are higher than those of alkali basalts (Fig. 5.22(h)), and Rb shows very similar behaviour. Fractionation within each group is accompanied by an increase in $K_2O$, Rb and Sr. K/Rb ratios of alkali basalts and basanites overlap, whereas those of the nephelinites are slightly higher. In general, K/Rb ratios decrease with fractionation.

Barium

Despite considerable overlap in the Ba contents of all primary and derivative rock types, there is an indication of higher Ba in nephelinites; Fig. 5.22(i). Ba increases slightly with fractionation in nephelinites and alkali basalts, but appears to decrease in the basanite derivatives. If the latter trend were related to phlogopite fractionation there should be similar distributions for Rb and $K_2O$, and K/Rb should increase with fractionation. These are not observed so the apparent trend for Ba may simply reflect the inadequate sample population.

Ni and Cr

The excellent positive correlation between both Ni and Cr, and 100Mg/Mg+Fe" is related to the initial fractionation of Ni-rich, magnesian olivine together with Cr-rich spinel in the alkali basalt, basanite and nephelinite fractionation series. With reference to Fig. 5.22(j) and (k), Ni concentrations overlap in all rock types, in the primary field and in the derivative field. The same is true for Cr, except that nephelinitic derivatives have slightly lower concentrations than alkali basalt or basanite derivatives.

$SiO_2$

A positive correlation between 100Mg/Mg+Fe" and $SiO_2$ could point to high pressure fractionation of orthopyroxene. This is not a particularly sensitive indicator, because the $SiO_2$ contents of alkali basalts and aluminous Mg-rich orthopyroxenes are very similar. If small amounts of Mg-Cr spinel are also involved in fractionation, the trend towards lower $SiO_2$ contents in derivative melts may be camouflaged or even reversed.

The distribution of $Al_2O_3$ in the Monaro volcanics suggests that fractionation of aluminous spinel is unimportant, and Fig. 5.22(1) does not substantiate the derivation of basanites and nephelinites from alkali basalts by orthopyroxene fractionation alone (orthopyroxene control lines pass through 100Mg/Mg+Fe" ∿88; $SiO_2$ ∿48). A few nephelinite derivatives could result from orthopyroxene fractionation within the group, however the consequent enrichment in CaO is not evident.

Summary

The geochemical patterns observed in derivative alkali basalts, basanites and nephelinites in the Monaro province can be attributed to low pressure fractionation only. Petrographic examination demonstrates that low pressure fractionation involves olivine (+ minor Cr-rich spinel), then olivine + clinopyroxene, and the crystallisation of clinopyroxene overlaps with the crystallisation of Fe-Ti oxides and/or plagioclase. These observations are consistent with experimental studies.

The concentrations of $P_2O_5$, La, Ce, Pr, Nd, and Y in alkali basalt and basanite differentiates approximate primary values, whereas nephelinitic differentiates are enriched. Near-primary concentrations of Pb, Th, Cu, and Zn are observed in all groups of derivatives. $TiO_2$, Zr, (Nb), $K_2O$, Rb, Sr, and Ba are enriched in all derivative rock types, whereas Ni and Cr contents fall rapidly. Increasing concentrations of V in alkali basalt and basanite derivatives contrast with decreasing concentrations in nephelinitic derivatives.

A comparative study of the literature is not particularly rewarding. Most of the typical alkaline provinces for which major and trace element data are provided, contain very few non-cumulative rocks with 100Mg/Mg+Fe" ratios greater than ∿60, so the initial fractionation trends in this interval are generally difficult to identify. In rare instances eg. Stice (1968), and Hubbard (1971); Baker (1969), Gunn *et al.*, (1970); Strong (1972), low pressure fractionation trends similar to those in the Monaro volcanics, can be observed.

### 5.2.4 Primary geochemical variation in the typical alkaline association

#### 5.2.4.1 Introduction

Individual rock analyses which include trace element data, and which have 100Mg/Mg+Fe" ratios in the primitive range, were selectively compiled from the literature. High-K and high-Ca primary magmas with "typical alkaline" affinities are also included. Together with new data from this thesis, these analyses, recalculated to 100% on a loss-free basis, are tabulated in Appendix 4. Additional major element analyses provide extra information on the primary distribution of $TiO_2$, $K_2O$ and $P_2O_5$. These data are taken from Spencer (1969) - Texas, from Irving (1971) - Newer Basalts, Victoria; and from Bultitude's (1968) compilation of analyses of lherzolite-bearing alkaline rocks.

The aim of the following study is to examine the primary geochemical variations in alkaline rock types from the viewpoint of a partial melting model. (Note that recalculation of analytical data on an anhydrous basis may introduce a favourable bias.) The primary distributions of Ni and Cr provide independent justification for the use of 100Mg/Mg+Fe" ratios ($Fe_2O_3/FeO = 0.25$) as a criterion for the identification of primary magmas. Ideally, the excellent positive correlation between 100Mg/Mg+Fe" and both Ni and Cr, which is observed with derivative rocks, should be absent in primary magmas. Data are not available for the entire population, but the correlation is non-significant in the case of Cr ($r = 0.19$) and for Ni, geochemically meaningless ($r = 0.33$, statistically significant at only the 90% confidence level) - Cr, Ni shown in Fig. 5.24(b) and (a) respectively.

#### 5.2.4.2 Primary variation in the Monaro volcanics

In general, an element which is concentrated in a certain residual phase becomes progressively more abundant in larger melting fractions. If partial melting continues so that the phase in question disappears from the residuum, further melting then lowers the concentration of the particular element. The primary distribution of Cu illustrates its refractory behavior, and the maximum

Figures 5.24(a) to (k)

Geochemical variation in primary alkaline magmas

KEY TO SYMBOLS

Alkali basalts

- ▽ Monaro volcanics, NSW
- △ Newer Basalts, Vict.; Tasmania
- ▼ oceanic islands

Nephelinites

- ◯ Monaro volcanics, NSW
- ⊙ Murrumburrah, NSW
- ⊕ other continental provinces
- ⊗ high-K nephelinites
- Ⓣ Texas
- ● oceanic islands

Basanites

- □ Monaro volcanics, NSW
- ◇ Newer Basalts, Vict.; Cabramurra, NSW; 26918
- ⊕ other continental provinces
- Ⓣ Texas
- ■ oceanic islands
- ✡ tephritic basanites

Melilite nephelinites

- ✳ Oahu, Hawaii
- T Texas
- \+ other continental provinces
- ⊛ alnoitic rocks (Haast River, New Zealand)
- × high-K melilite nephelinites

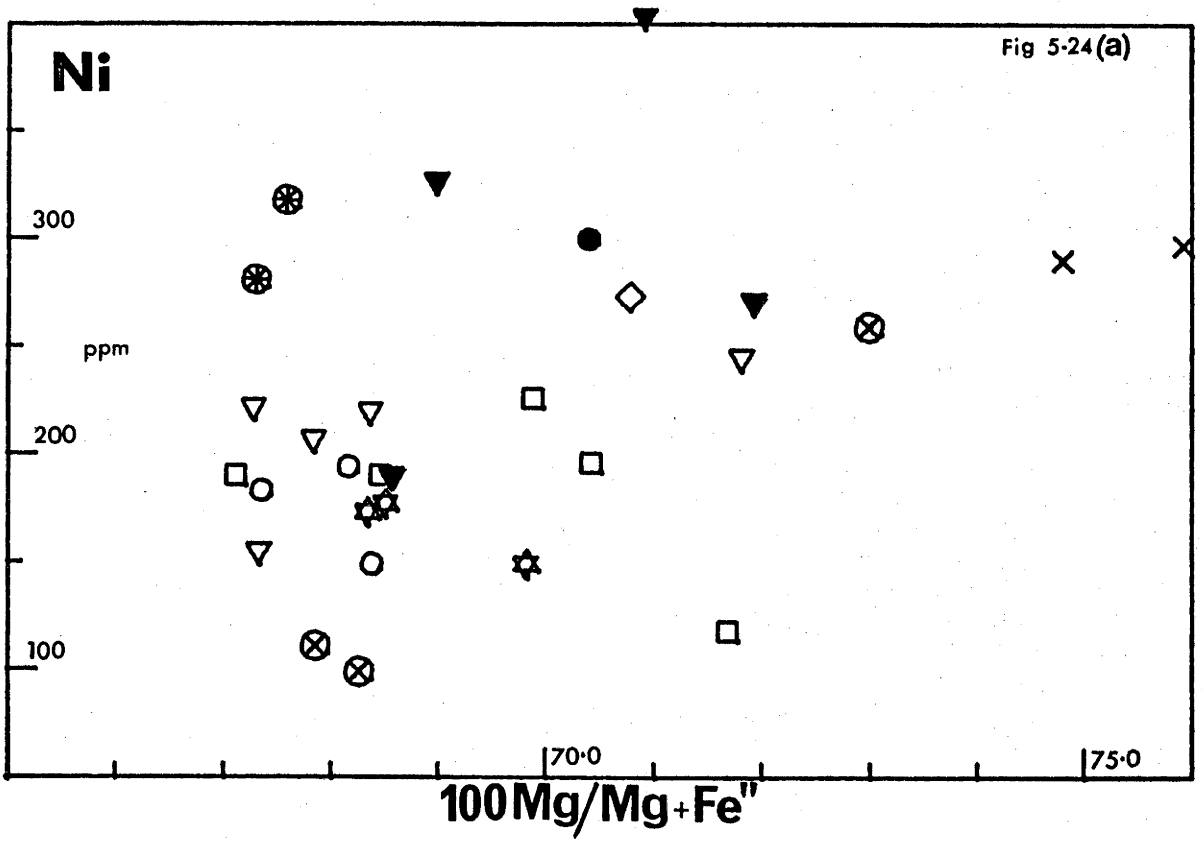
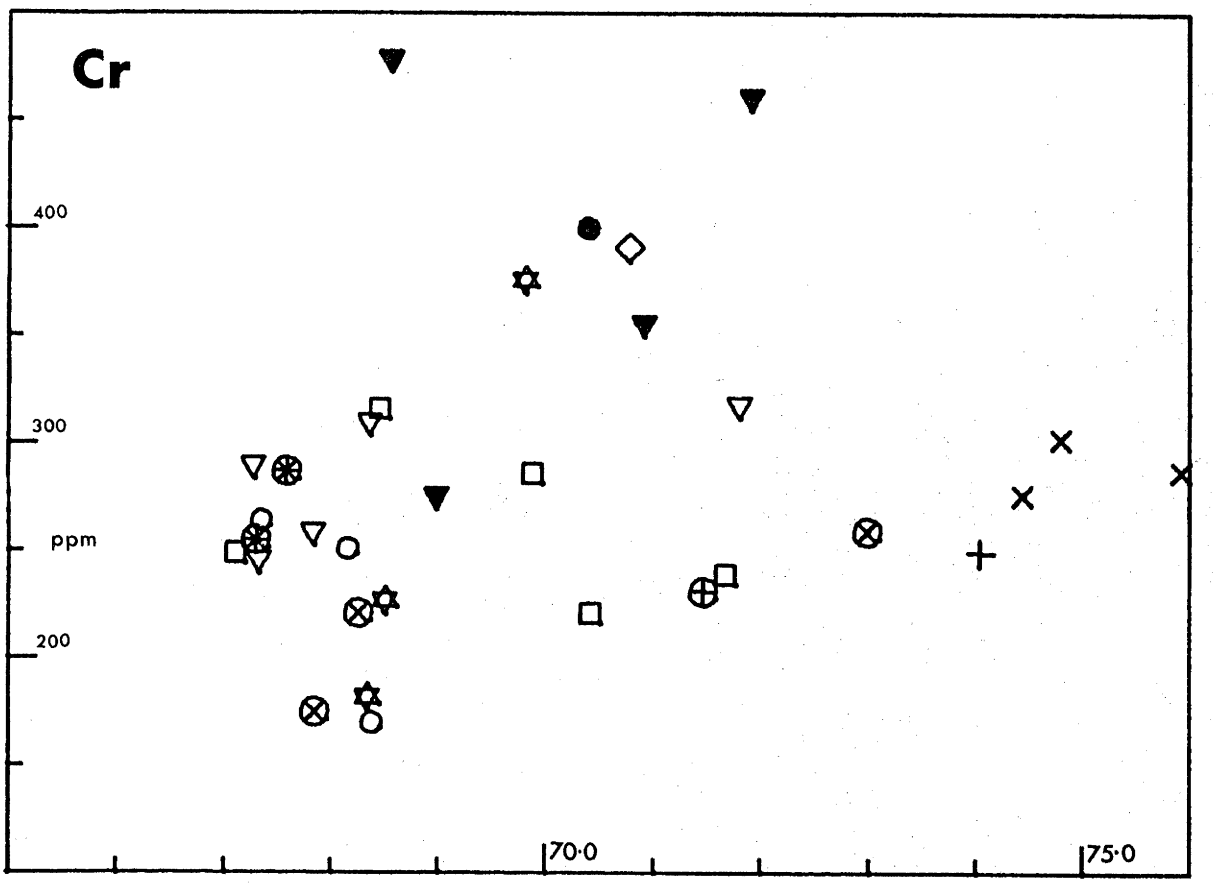


Fig 5·24(b) & (c)




100Mg/Mg+Fe"

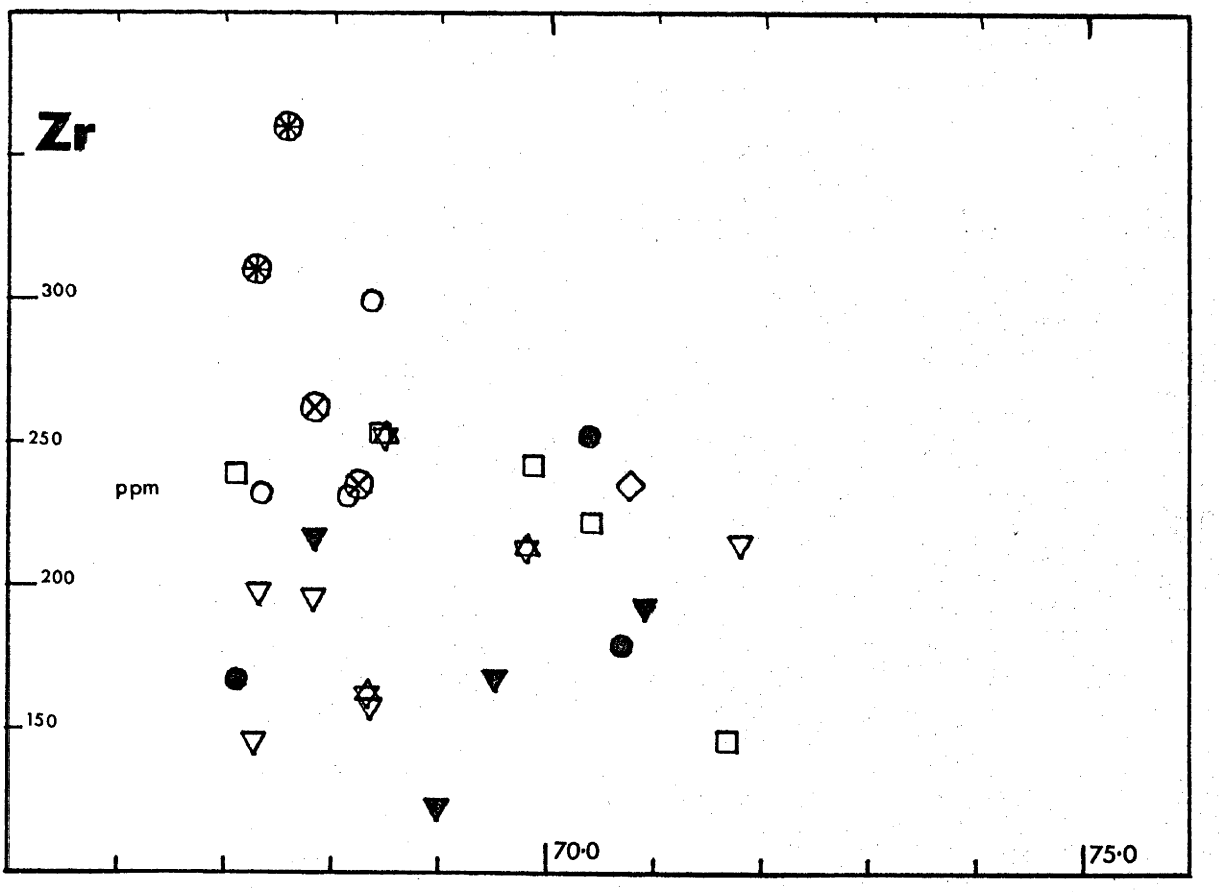


Fig 5·24(d)

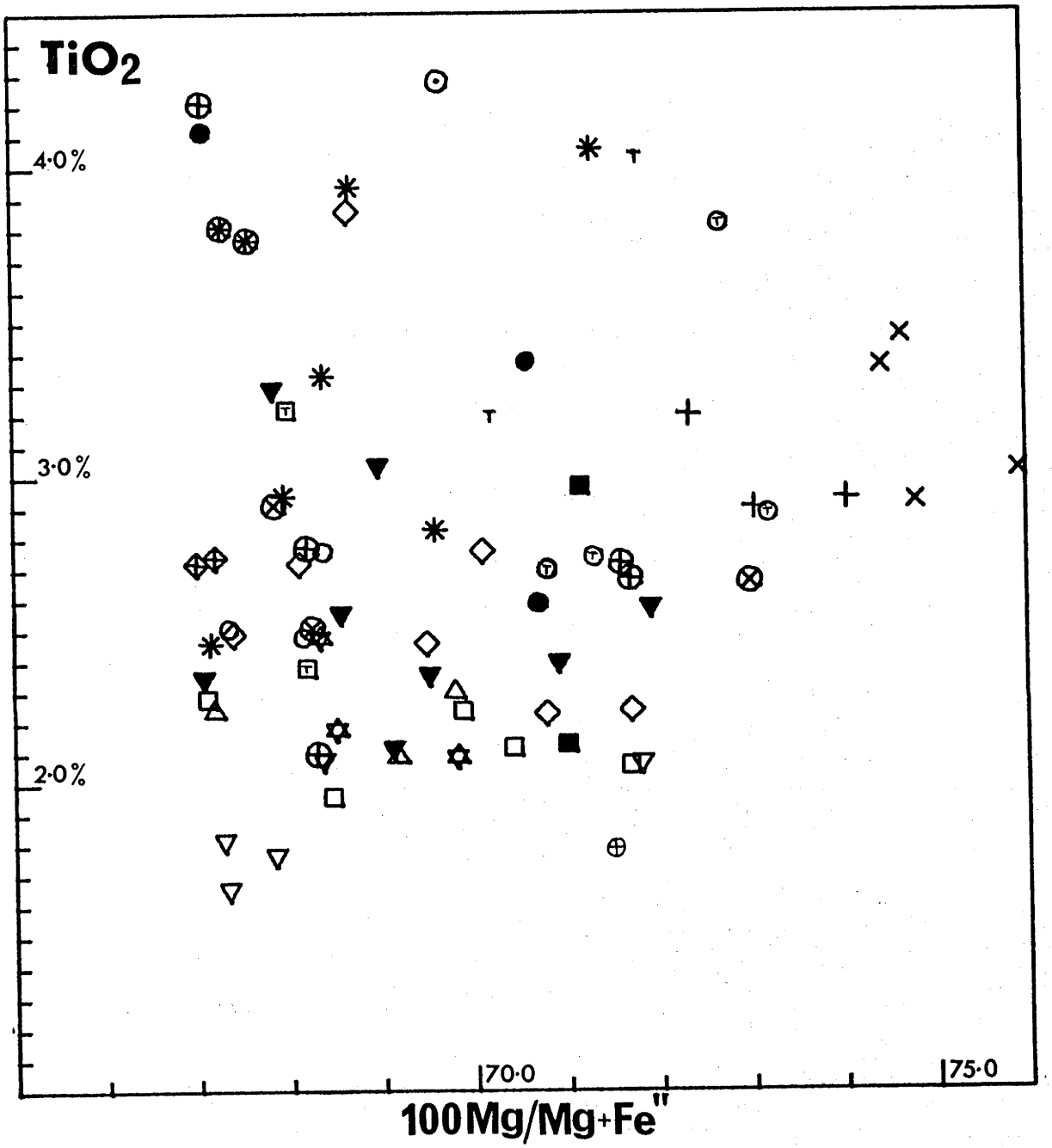


Fig 5·24(e)

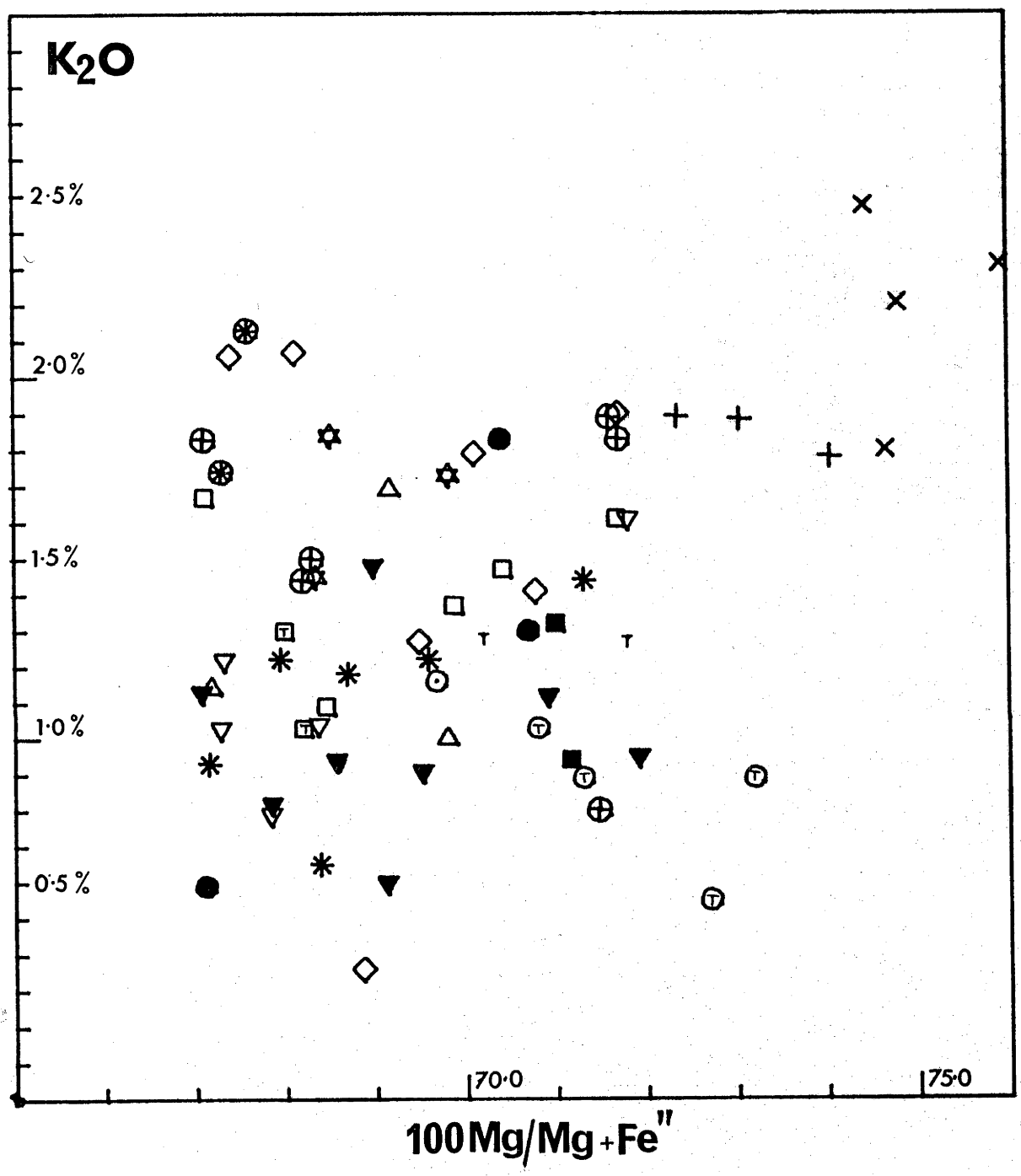


Fig 5·24(f)

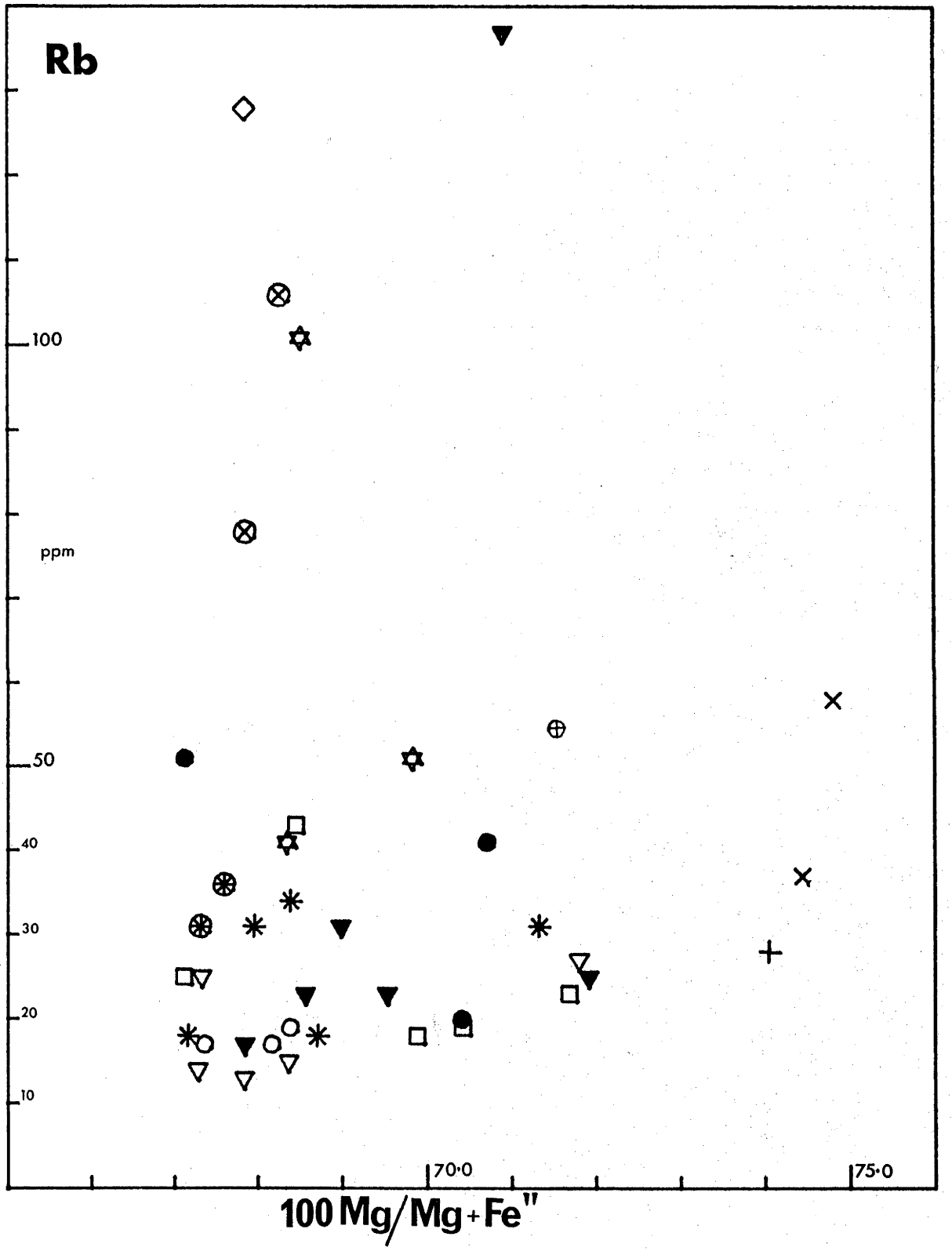
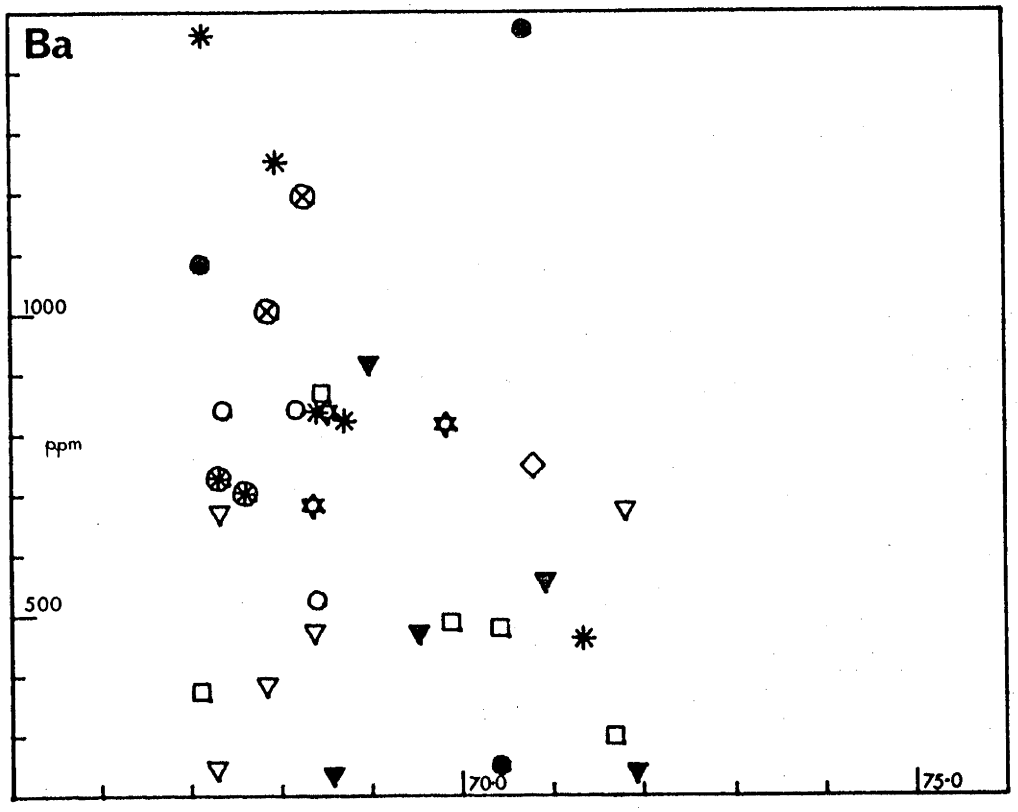


Fig 5·24(g) & (h)




100Mg/Mg+Fe$^{II}$

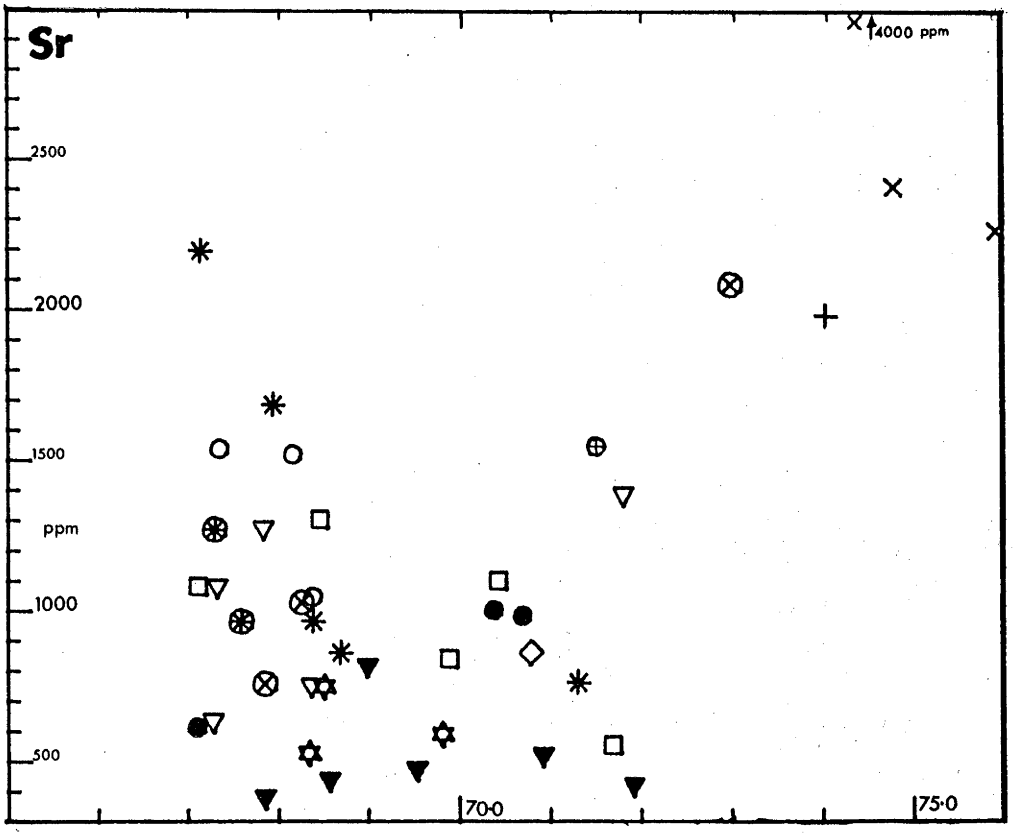


Fig 5·24(i)

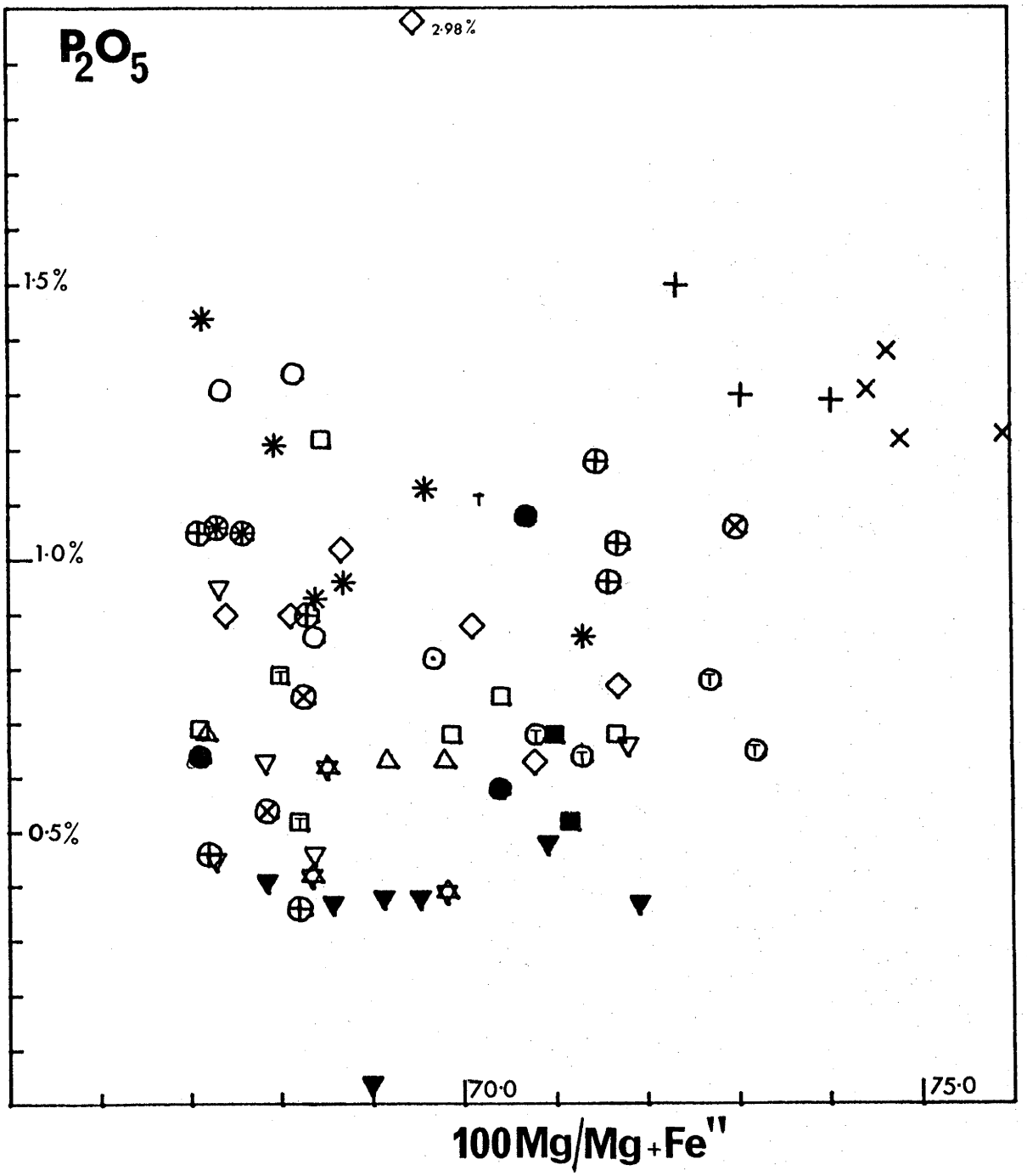
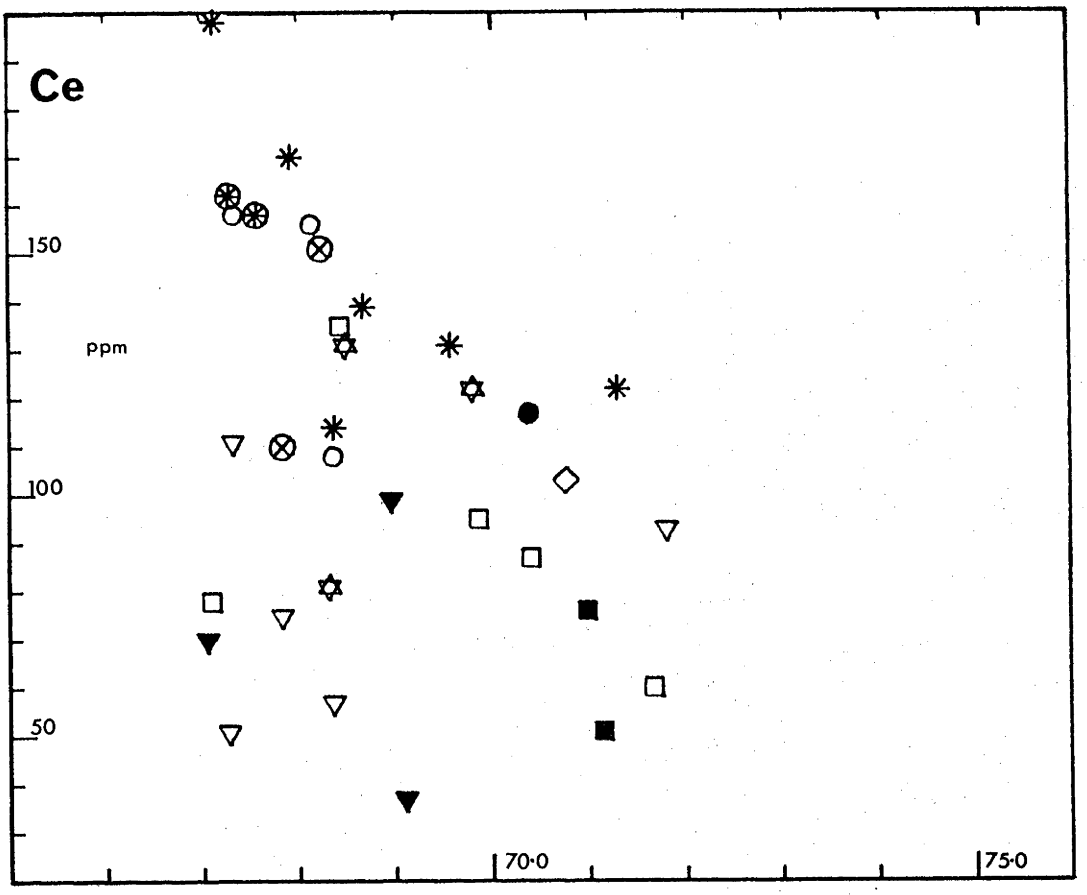
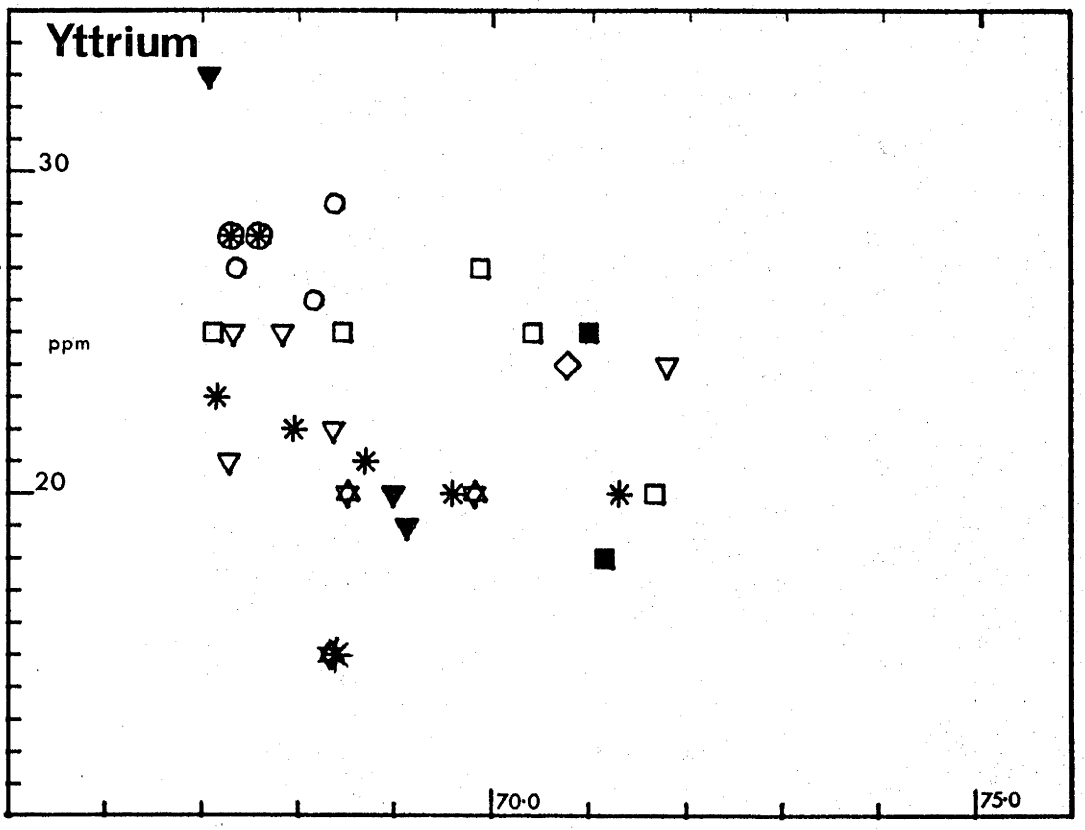


Fig 5·24(j) &(k)




100Mg/Mg+Fe"



concentration of Y in nephelinites may correspond to the elimination of a suitable host (garnet?) from the residuum. The absolute abundances of Ni and Cr in all primary basaltic magmas should be fairly similar, since these elements readily substitute in all major (and residual) phases in upper mantle assemblages.

The primary abundances of $TiO_2$, Zr, $P_2O_5$, La, Ce, Pr, Nd and Sr progressively decrease frm nephelinites to basanites to alkali basalts, and $K_2O$, Rb, Ba and Nb show similar, if less obvious behaviour. These distributions in general conform to a simple partial melting model, in which the concentration of any element that is strongly partitioned in the initial melt, is subsequently lowered as partial melting continues.

The measured primary abundances of incompatable elements in the various rock types, together with interpolations from initial fractionation trends, can be used to estimate relative concentration factors (Table 5.24). These values are obtained by normalising the maximum concentration of a given element to its minimum concentration (atypical data points are ignored). These values are then compared with the relative concentration factors predicted by a simple partial melting model ie. effectively linear dilution of incompatable elements in a partial melting series (Green, 1970b, 1971; this thesis, section 4.4).

The alkali basalts dramatically illustrate the diversity in the relative concentration factors for the supposedly coherent incompatable elements. Basanites, nephelinites and the entire primary magma population vary likewise, so for the Monaro province at least, the simple partial melting model requires further modification before it becomes an acceptable petrogenetic hypothesis.

5.2.4.3 Primary variation in the typical alkaline association

Conclusions arising from the following comparative study are valid only if the uncertainties introduced by different analytical methods and by different analysts are comparatively minor, and only if the sample population is representative.

Primary geochemical variations in the typical alkaline association on a global basis, are illustrated in

Table 5.24

Relative concentration factors : typical alkaline primary magmas

| | MONARO PROVINCE, NSW | | | | COMPREHENSIVE COMPILATION | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | alk. basalts | basanites | nephel-inites | all primary magmas | alk. basalts | basanites | nephel-inites | melilite nephelinites | all primary magmas |
| $TiO_2$ | 1.5 | 1.5 | 1.3 | 2 | 1.5 | 1.5 | 1.5-2 | | 2.5 |
| Zr | 1.5-2 | ~1.5 | 1.3 | 2.5 | 2 | 1.5 | 2 | 1.5 | 2.5 |
| Nb | 2.5 | 1.5 | 1.5 | 3 | | | | | |
| $K_2O$ | 2 | 2 | ~1 | 3 | 3 | 2 | 3.5 | 4 | 4-5 |
| Rb | 2.5 | 1.5 | ~1 | 3-4 | 2 | 3 | 3 | 2.5 | 4(-10) |
| Sr | 3-4 | 2.5 | 2 | 4 | 3 | 2.5 | 2 | 3 | 6 |
| Ba | 3 | 1.5 | ~2 | 3 | 4 | 2 | 3-4 | 3-4 | 6 |
| Th | 2 | 1.5 | 2 | 2 | | | | | |
| Pb | 2 | 2.5 | 2 | 3 | | | | | |
| $P_2O_5$ | 2.5 | 2 | 2.5 | 3-4 | 2 | 3 | 3 | 1.5 | 3-4 |
| La | 2 | 2 | 2 | 3-4 | | | | | |
| Ce | 3 | 1.5 | 1.3 | 4 | 2.5 | 2 | 1.5 | 1.5 | 3-4 |
| (K/Rb) | | | | 3 | | | | | 4 |
| (Y) | | | | 1.5 | | | | | 1.5-2 |
| predicted by simple partial melting model | 2 | 2 | 2 | 3 | 2 | 2 | 2-3 | 2-3 | 3-4 |

Table 5.31

High-Ca alkaline association: alnoitic rocks

| | Alnoite[1] | AC198[2] | AC59[2] | Alnoite[3] | BMR-152[4] | BMR-334[4] |
|---|---|---|---|---|---|---|
| $SiO_2$ | 38.00 | 37.00 | 38.40 | 35.41 | 36.0 | 36.2 |
| $TiO_2$ | 1.90 | 3.66 | 3.65 | 2.57 | 2.20 | 2.20 |
| $Al_2O_3$ | 10.69 | 9.45 | 9.67 | 11.25 | 9.45 | 9.50 |
| $Fe_2O_3$ | 7.34 | 6.79 | 6.66 | 6.27 | 2.95 | 2.20 |
| FeO | 4.52 | 7.28 | 7.39 | 5.07 | 7.65 | 8.35 |
| MnO | 0.21 | 0.21 | 0.21 | 0.24 | 0.18 | 0.20 |
| MgO | 10.12 | 12.63 | 12.79 | 13.29 | 14.5 | 14.7 |
| CaO | 14.76 | 13.59 | 12.99 | 18.42 | 16.1 | 15.6 |
| $Na_2O$ | 5.83 | 2.50 | 1.62 | 2.53 | 1.95 | 1.78 |
| $K_2O$ | 2.60 | 1.67 | 2.06 | 2.20 | 2.85 | 2.75 |
| $P_2O_5$ | 0.70 | 1.02 | 1.02 | 1.05 | 0.84 | 0.69 |
| $H_2O\pm$ | 1.80 | 1.97 | 1.81 | 1.21 | 3.87 | 4.61 |
| $CO_2$ | 1.50 | 1.85 | 1.16 | 0.24 | 1.40 | 1.20 |
| TOTAL | 99.97 | 99.62 | 99.43 | 98.70 | 99.94 | 99.98 |
| 100Mg/Mg+Fe" | 66.5 | 67.3 | 67.6 | 73.0 | 75.44 | 75.64 |
| $K_2O/Na_2O$ | 0.45 | 0.67 | 1.27 | 0.87 | 1.46 | 1.55 |
| Ba | | 700 | 680 | 2000 | | |
| Rb | | 30 | 35 | | | |
| Sr | | 1200 | 933 | 1000 | | |
| Zr | | 298 | 348 | | | |
| Nb | | 84 | 142 | | | |

[1]Egorov (1970): Maimecha-Kotui province, Siberia.

[2]Dr. A.F. Cooper (unpublished analyses): Haast River, South Westland, NZ.

[3]Gold (1967): Oka complex, Monteregian Hills, Quebec.

[4]Walker & Mond (1971): Radok Lake, Prince Charles Mtns., Antarctica.

Table 5.32

High-Ca alkaline association: phonolites

| | D2[1] phonolite | D3[1] phonolite | 18206[2] wollastonite phonolite | AC466[3] tinguite |
|---|---|---|---|---|
| $SiO_2$ | 53.35 | 49.15 | 50.24 | 52.69 |
| $TiO_2$ | 0.97 | 1.15 | 0.35 | 0.53 |
| $Al_2O_3$ | 19.96 | 18.53 | 18.67 | 19.27 |
| $Fe_2O_3$ | 3.29 | 6.07 | 2.36 | 3.28 |
| FeO | 2.37 | 0.84 | 1.44 | 1.11 |
| MnO | 0.42 | 0.22 | 0.28 | 0.17 |
| MgO | 3.12 | 3.64 | 0.39 | 0.56 |
| CaO | 0.79 | 0.27 | 7.93 | 1.93 |
| $Na_2O$ | 9.48 | 9.10 | 6.55 | 11.20 |
| $K_2O$ | 4.46 | 6.00 | 4.52 | 4.49 |
| $P_2O_5$ | 0.08 | 0.31 | 0.17 | 0.14 |
| $H_2O\pm$ | 1.58 | 1.62 | 5.91 | 2.96 |
| $CO_2$ | tr. | 0.63 | 0.08 | 1.23 |
| $SO_3$ | n.d. | n.d. | 0.23 | |
| Total | 99.87 | 100.21 | 99.12 | 99.61 |
| $K_2O/Na_2O$ | 0.47 | 0.66 | 0.69 | 0.40 |
| (Na+K)/Al | 1.02 | 1.20 | 0.87 | 1.18 |
| Ba | 10,000 | 10,000 | 2486 | 860 |
| Rb | 450 | 450 | 195 | 158 |
| Sr | 10,000 | 10,000 | 3626 | 1040 |
| Zr | > 450 | > 450 | 485 | 834 |
| Nb | 800 | 800 | 412 | 217 |

[1]Dawson (1966): Oldoinyo Lengai, Tanzania

[2]this thesis: Kaiserstuhl, Germany

[3]Dr. A.F. Cooper (unpublished analysis): Haast River, South Westland, NZ.

(peralkaline)[2] intrusives may also appear during the final phases of igneous activity in the region. There are no examples of in-situ differentiation to demonstrate a low-medium pressure fractionation relationship between miaskitic and agpaitic liquids, although Ferguson (pers. comm.) argues that this is so. Relative to phonolitic liquids of the typical alkaline association, the agpaitic rocks contain high concentrations of Cl, F, S, Li, Th, U, Zr, Nb, Ta and REE. Zr/Nb ratios are high, Th/U ratios are low (Gerasimovskii, 1968). $TiO_2$ contents typically 0.4-1.0% are high, and complex Ti-Zr silicates, rather than accessory zircon, appear in the mode. Peralkaline sodic "granites" which occur in some provinces (Hamilton, 1964; Kukharenko et al., 1965) have the geochemical characteristics of pantellerites, namely $SiO_2$ ~70%, $Al_2O_3$ ~10%, $Na_2O > K_2O$ and extreme concentrations of Zr, whilst Sr and Ba are low (eg. Gibson, 1970).

Many of the miaskitic nepheline syenites and phonolites of the high-Ca alkaline association display chemical features which immediately distinguish them from miaskitic nepheline syenites and phonolites of the typical alkaline association. Even after allowing for the introduction of CaO in secondary calcite, the phonolitic differentiates of the high-Ca association contain a small but finite CaO content, generally <3%, which in some cases may be expressed in the mode as wollastonite. The trace element characteristics include high Sr, Ba and Nb and low Zr/Nb (Table 5.32). The same features are common to miaskitic(?) tinguites and phonolites from the Kaiserstuhl, southern Germany (Wambeke, 1964 - note: no major element data. Unusually high concentrations of Ni, Cu and Pb in some of these German rocks are due to local sulphide mineralisation).

The validity of the diagnostic Zr/Nb ratio could be queried since it is identified using spectrographic determinations of limited accuracy. However Wambeke's data seem to be satisfactory since Zr, Nb and the Zr/Nb ratio of

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[2] agpaitic: atomic $(Na+K)/Al < 1.2$
peralkaline: molecular $(Na_2O+K_2O)/Al_2O_3 > 1.0$

a wollastonite phonolite compare favourably with the quantitative XRF analysis of the same rock type from the same locality (18206 - Table 5.32). Ferguson (1970) notes that Zr, Nb, Zr/Nb and $Na_2O/K_2O$ ratios increase with fractionation in agpaitic nepheline syenites so the characteristically low Zr/Nb ratios of miaskitic phonolites in high-Ca alkaline provinces may correlate with relatively low $Na_2O/K_2O$ ratios. The controversial Zr/Nb ratio in phonolite AC466 (quantitative XRF analysis) could be a function of its sodic, near-agpaitic composition.

Nockolds & Allen (1954), Baker (1969), Ridley (1970) and Strong (1972) demonstrate that the nephelinite (basanite) - phonolite fractionation series in the typical alkaline association shows a steady decrease in CaO, whilst Sr abundances reach a maximum at the nepheline mugearite stage of fractionation, and diminish rapidly thereafter. Ba fractionation trends are similar but may be complicated by alkali felspar accumulation in the late stage differentiates. One could argue that the high Sr, Ba and CaO which supposedly characterise phonolitic liquids in high-Ca alkaline provinces simply reflect less extensive fractionation. However the characteristically high Nb abundances and low Zr/Nb ratios of these particular rocks are not observed in the comparatively sodic nepheline mugearites and phonolites of the typical alkaline association.

Both field observations and major element trends clearly demonstrate that the miaskitic nepheline syenites and phonolites of the high-Ca alkaline association are unrelated to the melteigite-ijolite-urtite low pressure (<10 kb) fractionation series. Three possibilities remain. (1) They result from the high pressure (>10 kb) fractionation of the primitive magma which normally fractionates below 10 kb to give carbonatite, dunites and melteigite-ijolite derivatives. If $CO_2$ remains relatively insoluble in nepheline syenite liquids above $\sim$10 kb (cf. (Millhollen, 1971) both carbonatites and phonolites would be produced at subcrustal levels. (2) They are derived from the nephelinitic dyke magmas by liquid immiscibility

(Ferguson & Currie, 1971) or (3) by crystal fractionation processes to at least ∿10 kb. The final interpretation is preferred since it parallels the petrogenesis of phonolites in the typical alkaline association. The high concentrations of Sr, Ba and Nb, and low Zr/Nb ratios which are characteristic of many of the nepheline syenites and phonolites of the high-Ca alkaline association may be inherited from a primary parent liquid and/or superimposed during fractionation.

Carbonatites

After some controversy, the magmatic character of carbonatite was demonstrated experimentally in the system $CaO-H_2O-CO_2$ by Wyllie & Tuttle (1960) and subsequently verified in more complex systems (cf. summary by Wyllie, 1966), affording an explanation for the distinctive isotopic and trace element geochemistry of these rocks. Carbonatites are characterised by $Sr^{87}/Sr^{86}$ ratios consistent with an upper mantle origin (Powell et al., 1966) and by relatively high abundances of Sr, Ba, Nb, REE, Y, P, F, Th, U and sometimes V, Pb, Cu and Zn, and U > Th (eg. Gold, 1964; Wambeke, 1964; Loubet et al., 1972). Considerable chemical variation within individual carbonatites can be attributed to highly efficient crystal fractionation in the low viscosity carbonate melt (Wyllie & Boettcher, 1969). The natro-carbonatite lavas in the crater of an active volcano in Tanzania are generally accepted as the effusive equivalent of carbonatite (Dawson, 1966) despite low Nb and Y contents and abnormally high $Na_2O$ contents but Milton (1968) makes the more reasonable suggestion that these lavas result from local melting of troniferous secondary carbonates.

Carbonatite emplacement is characteristically accompanied by fenitization of the adjacent country rocks, in which typical nepheline syenite mineralogies are produced as the end products of reaction with the alkali-rich fluid (ie. vapour) phase lost from the carbonatite during solidification (Currie & Ferguson, 1971). Koster van Groos and Wyllie (1966) reported high dissolved solute

content and a sodic composition for the fluid phase in the system $Na_2O$-$Al_2O_3$-$SiO_2$-$CO_2$ at 1 kb. The highly improbable suggestion that some of the late stage discordant nepheline syenites and phonolites represent "remobilised" fenites is firmly entrenched in the literature, despite the fact that the necessarily near-complete anatexis of the fenitized country rocks, even in the presence of excess $H_2O$-rich fluid, would require temperatures well above 900°C at 0.5 kb, and 750°C at 5 kb (Millhollen, 1971). Currie & Ferguson (1971) estimate that fenitization occurs at temperatures ranging from 500° to 700°C at 0.5 kb.

5.3.2 The genesis of carbonatites and of the melteigite-ijolite series

Earlier hypotheses, summarised by Wyllie (1966), proposed that carbonatites represented the ultimate low pressure fractionation product of the melteigite-ijolite-urtite alkaline series with which they typically occur. However melting relationships in silicate-$H_2O$-$CO_2$ systems and silicate-carbonate-$H_2O$ systems are consistent with extremely limited solution of $CO_2$ in silicate melts below 10 kb cf. Koster van Groos & Piwinskii (1968), Millhollen (1971), Holloway & Burnham (1972). Watkinson & Wyllie (1971) report complete miscibility between silicate and carbonate liquids in the system $NaAlSiO_4$-$CaCO_3$-$H_2O$ at 1 kb but their seemingly contradictory results are invalid. Their charges contained a fixed weight of $H_2O$ and varying proportions of nepheline and $CaCO_3$ in the remainder. Thus $a^{fluid}_{H_2O}$ varies as some complex function of composition, and the boundaries presented as univariant on a T-X projection are in fact divariant. The same criticism applies to equilibria in the silicate-carbonate-$H_2O$ systems discussed by Wyllie (1966).

Above a critical pressure near 15 kb the previously negligible solubility of $CO_2$ in basaltic magmas increases considerably (Hill & Boettcher, 1970). However field evidence indicates that the critical pressure for basic alkaline magmas is closer to 10 kb, and this could relate to some feature of the chemistry of the melt or, alternatively, indicate a dissolved volatile component in which $X_{CO_2} >> X_{H_2O}$ (c.f. Holloway, 1972). As a $CO_2$ and

$H_2O$-bearing basic alkaline magma rises to levels corresponding to the critical pressure, it rapidly reaches $CO_2$ saturation and a separate $CO_2$ and $H_2O$-bearing fluid phase containing considerable dissolved solute is exsolved. This corresponds to the carbonatite, and at shallower levels in the crust and/or during solidifaction, it in turn reaches saturation and segregates to give a carbonate-precipitating melt, and the alkali-rich fluid which is responsible for fenitization.

An immediate and inevitable consequence of the loss of volatile components from solution in the silicate melt is the precipitation of liquidus phases. At the pressures in question the liquidus phase of nephelinitic melts under hydrous conditions is olivine (Bultitude & Green, 1968, 1971). The early dunite bodies ($Fo_{92-85}$) exposed in deep-seated alkaline complexes are attributed to the resulting fractionation, and the liquid which gives rise to the melteigite-ijolite-urtite series is correlated with the residual fractionated silicate melt remaining after the evolution of the carbonatite[1]. A less likely alternative, unsubstantiated in the field, is that the resulting fractionation is much more extensive and miaskitic nepheline syenites and phonolites are produced.

The segregation of the CaO, $P_2O_5$, REE, Nb, Sr and Ba-rich carbonatite, and fractionation of the originally $CO_2$-rich primary magma, are concurrent. Unfortunately there are no geochemical parameters which can be used to measure the mass balance involved in carbonatite segregation and which would thereby permit an estimate of the chemical composition of the primitive $CO_2$-bearing magma. Olivine-liquid equilibria require that the early magnesian olivine ($Fo_{92}$) in the dunite bodies coexists with a melt whose 100Mg/Mg+Fe" ratio is ∿77. The composition of the silicate

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[1] This hypothesis involves the assumption that the solubility of $CO_2$ in Ca-rich basic nephelinitic melts is negligible below ∿10 kb.[2] This is consistent with experiments using a wide range of rock compositions, but it would still be preferable to justify this assumption by direct experiment - at the <u>liquidus</u> rather than the solidus.

Table 5.33

Estimate of primary parent magma composition:

High-Ca alkaline association

| | melteigite[1] | [A] 80% melteigite +20% $Fo_{88}$ | [B] 70% melteigite + 30% $Fo_{88}$ |
|---|---|---|---|
| $SiO_2$ | 39.92 | 40.0 | 40.0 |
| $TiO_2$ | 3.21 | | |
| $Al_2O_3$ | 8.53 | 6.8 | 6.0 |
| Σ FeO | 15.38 | 14.6 | 14.3 |
| MgO | 9.93 | 17.6 | 21.4 |
| CaO | 16.42 | 13.1 | 11.5 |
| $Na_2O$ | 3.68 | 2.9 | 2.6 |
| $K_2O$ | 1.48 | 1.8 | 1.0 |
| 100Mg/Mg+Fe"[2] | 58.5 | 72.4 | 76.6 |
| | [C] typical carbonatite[2] | 90%[A] +10%[C] | 90%[B] +10%[C] |
| $SiO_2$ | 5.67 | 36.6 | 36.6 |
| $Al_2O_3$ | 1.77 | 6.3 | 5.6 |
| ΣFeO | 7.20 | 13.9 | 13.6 |
| MgO | 6.10 | 16.5 | 19.9 |
| CaO | 37.06 | 15.5 | 14.1 |
| $Na_2O$ | 1.09 | 2.7 | 2.5 |
| $K_2O$ | 0.87 | 1.7 | 1.0 |
| $CO_2$ | 32.16 | 3.2 | 3.2 |
| 100Mg/Mg+Fe" | 64.9 | 72.2 | 76.2 |

[1]King (1965)

[2]Gold (1964): This estimate does not allow for the solute component lost during fenitization.

melt prior to the separation of olivine should be similar to (A) or (B) in Table 5.33. These compositions are obtained by addition of the "average" olivine, $Fo_{88}$ to a natural melteigite. The latter was selected from the literature with considerable optimism as an example of the least fractionated and simultaneously least accumulative composition in the melteigite-ijolite series. To compensate for the compositional changes due to the segregation of the carbonatite fluid, a conservative 10% by weight of the typical carbonatite on an anhydrous basis (Gold, 1964) is added to 90% of (A) and (B) respectively. The solute lost during fenitization contains considerable $SiO_2$, $\Sigma FeO$, $Na_2O$ and $K_2O$ relative to the final carbonatite rock (Currie & Ferguson, 1971) so the typical carbonatite rock composition underestimates these oxide abundances when it is taken to approximate the initial carbonatite fluid. Despite the large uncertainties involved, this exercise illustrates the CaO-rich, $Al_2O_3$-poor, $SiO_2$-undersaturated compositions of the $CO_2$-bearing primary magmas which ultimately give rise to carbonatites and to the melteigite-ijolite series of the high-Ca alkaline association. One would not expect to find any natural examples of the unmodified primary magma, but in some cases, high-Ca provinces provide as possible candidates ($CO_2$ deficient), rare sodic monticellite peridotites (Janse, 1971, nos 4 & 5, Table 1) or, alternatively, primary sodic alnoitic melts.

5.3.3 The genesis of the alnoitic rocks

It seems very unlikely that the alnoitic dyke rocks are derived from a $CO_2$-rich primary magma. Their 100Mg/Mg+Fe" ratios indicate only minor fractionation, which is indirect evidence for comparatively lower values of $a_{CO_2}^{melt}$ at high pressures, and this may reflect major heterogeneities in the distribution of C in the upper mantle source regions. Another alternative would be a partial melting series, with highest concentrations of $CO_2$ in the "minimum melt" ie. the melteigite-ijolite parent whereas more extensive partial melting produces a primary alnoitic magma with lower concentrations of $CO_2$.

The $K_2O/Na_2O$ ratios of primitive and near-primitive alnoitic rocks vary considerably below and above unity and this is not simply a result of phlogopite accumulation. AC59 and AC198 (Table 5.31) are two very similar primitive alnoitic rocks, one sodic, the other potassic, and both have K/Rb ratios close to 470. The potassic nature of some primary nephelinitic liquids is discussed in more detail in section 5.4.

Like the typical alkaline association, it seems that the primary magmas of the high-Ca alkaline association involve various levels of $SiO_2$-undersaturation. Brown & Carmichael (1969, 1971) present chemical and mineralogical data for primary tephritic basanites in the African rift system. These plagioclase-bearing lavas are similar to basanites from the typical alkaline association, except for higher $Al_2O_3$ and CaO contents. This is a primary characteristic since unusually low K/Rb ratios (<300) preclude the possibility of plagioclase accumulation. Their intermediate differentiates, tephrites, are chemically equivalent to some of the intrusive rocks named "essexite".

## 5.4 The High-K Alkaline Association

### 5.4.1 Introduction

Primary alkaline magmas in this category have $K_2O/Na_2O$ ratios near unity or higher, a characteristic commonly inherited by their differentiates. Kimberlites and potassic lamproites satisfy the above criterion, but for simplicity are discussed elsewhere, in sections 5.5 and 5.6 respectively. The subjective recognition of a high-K alkaline association is accompanied by the problem of determining whether there is a unique primary magma series which is incidentally potassic, or whether "high-K" chemistry is sometimes superimposed on primary magmas of the typical alkaline association and the high-Ca alkaline association. In an attempt to resolve this question, two provinces in which high-K alkaline rocks are unusually abundant, are examined on the following pages.

5.4.2 High-K alkaline provinces

Southwest Uganda, west African rift

Tertiary-Recent alkaline volcanics in the western branch of the African rift system, in Uganda, are unusually rich in $TiO_2$ and also contain high concentrations of $P_2O_5$, Rb, Sr, Ba, Zr, and a relative enrichment in light rare earths (Higazy, 1954; Bell & Powell, 1969). Geochemical studies by these authors and also by Cundari & Le Maitre (1970) and Bell & Doyle (1971) refer to earlier publications on the geology of the province. Much of the petrological variety involves the more fractionated rock types. The igneous status of a few "carbonatitic" lavas is doubtful.

The similarity between some of these potassic African volcanics and the potassic lamproites (this thesis, section 5.6) is only superficial. 100Mg/Mg+Fe" ratios, $K_2O$, Sr, Zr and light REE are generally lower in the former; $TiO_2$, CaO and Ti/Zr are lower in the latter. Cundari & Le Maitre (1970) identified similar low pressure fractionation trends in the Roman province in the central Italian peninsular and suggested that the one parental magma type is common to both localities. But the low $TiO_2$, Zr and Nb contents (Savelli, 1967) of the lherzolite-bearing Italian volcanics (Kuno & Aoki, 1970) point to shoshonitic affinities (Kesson & Smith, 1972). In a tectonic context, the Italian province is related to the underthrust oceanic crust of the Mediterranean beneath Turkey, Greece and Italy (Aegean arc).

Analytical data for rocks from the southwest Uganda province with 100Mg/Mg+Fe" ratios greater than 67.0 are compiled in Table 5.41. Obviously accumulative rocks are excluded, so the tabulated compositions should correspond quite closely to primitive liquids. The first group, analyses HA-HJ inclusive, is characterised by low $SiO_2$ and $Al_2O_3$, and high CaO, with CaO > MgO. On a loss-free basis, the second group, namely BP30 (? accumulative olivine), BP25 and BP43 have comparatively higher $SiO_2$ and $Al_2O_3$, and lower CaO. Even though the grouping corresponds to the two published sources used in the compilation, it must still reflect a real difference in major element chemistry. But unfortunately comparison of trace element abundances between

Table 5.42

High-K alkaline association: Rhine graben

| | (26918)[1] basanite | 26922[1] leucite basanite | 18285[1] leucite neph. | L3[2] melilite neph. | L5[2] melilite neph. | L12[2] melilite neph. |
|---|---|---|---|---|---|---|
| $SiO_2$ | 44.29 | 43.07 | 43.61 | 38.1 | 38.2 | 37.0 |
| $TiO_2$ | 2.19 | 2.89 | 2.49 | 2.78 | 3.18 | 3.29 |
| $Al_2O_3$ | 12.69 | 13.65 | 12.68 | 10.1 | 11.1 | 11.6 |
| $Fe_2O_3$ | 4.42 | 5.20 | 7.20 | 4.66 | 4.10 | 3.75 |
| FeO | 6.53 | 5.31 | 2.36 | 6.13 | 7.12 | 7.34 |
| MnO | 0.20 | 0.19 | 0.18 | 0.21 | 0.20 | 0.17 |
| MgO | 11.66 | 9.66 | 8.71 | 14.9 | 14.7 | 14.3 |
| CaO | 10.56 | 12.60 | 13.75 | 13.5 | 12.4 | 13.0 |
| $Na_2O$ | 3.20 | 2.84 | 3.52 | 3.03 | 3.07 | 3.36 |
| $K_2O$ | 1.38 | 3.11 | 3.76 | 2.28 | 2.12 | 2.43 |
| $P_2O_5$ | 0.62 | 0.54 | 0.75 | 1.47 | 1.17 | 1.28 |
| $H_2O^{\pm}$ | 1.76 | 0.48 | 0.45 | 2.17 | 2.04 | 1.59 |
| $CO_2$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| TOTAL | 99.50 | 99.54 | 99.50 | 99.34 | 99.49 | 99.11 |
| 100Mg/Mg+Fe" | 70.7 | 67.7 | 68.1 | 75.90 | 74.80 | 74.44 |
| $K_2O/Na_2O$ | 0.44 | 1.10 | 1.07 | 0.75 | 0.69 | 0.72 |
| K/Rb | 92 | 335 | 297 | 592 | 320 | 560 |
| Rb | 125 | 77 | 105 | 32 | 55 | 36 |
| Sr | 843 | 752 | 1020 | 1800 | 2300 | 4000 |
| Ba | 734 | 998 | 1187 | - | - | - |
| Ni | 268 | 110 | 98 | 330 | 210 | - |
| Cr | 383 | 174 | 220 | 250 | 290 | 270 |

[1] This thesis

[2] Lohmann, (1964)

TABLE 5.41

THE HIGH-K ALKALINE ASSOCIATION : SOUTHWEST UGANDA, AFRICAN RIFT SYSTEM

| | HA[1] | HB | HC | HE | HF | HG | HJ | BP30[2] | BP25 | BP43 |
|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 35.51 | 37.93 | 33.89 | 33.22 | 33.52 | 35.37 | 38.94 | 39.28 | 43.37 | 46.70 |
| $TiO_2$ | 4.88 | 4.12 | 4.43 | 6.08 | 6.04 | 3.87 | 3.88 | 4.29 | 4.44 | 2.45 |
| $Al_2O_3$ | 6.83 | 6.59 | 8.27 | 9.71 | 8.04 | 6.50 | 6.92 | 7.90 | 10.34 | 10.86 |
| $Fe_2O_3$ | 9.68 | 6.81 | 7.03 | 6.68 | 5.88 | 7.23 | 5.27 | 4.88 | 4.02 | 3.34 |
| FeO | 2.70 | 4.37 | 5.21 | 5.30 | 5.50 | 5.00 | 5.09 | 5.23 | 5.54 | 8.67 |
| MnO | 0.22 | 0.18 | 0.26 | 0.52 | 0.15 | 0.24 | 0.23 | 0.27 | 0.17 | 0.16 |
| MgO | 11.67 | 14.54 | 10.93 | 12.12 | 13.54 | 14.08 | 11.58 | 17.58 | 11.60 | 13.00 |
| CaO | 16.00 | 15.23 | 16.98 | 15.64 | 15.22 | 16.79 | 15.95 | 11.03 | 14.16 | 9.76 |
| $Na_2O$ | 1.56 | 0.88 | 1.42 | 1.51 | 1.42 | 1.32 | 1.01 | 1.05 | 1.77 | 0.96 |
| $K_2O$ | 3.3 | 2.65 | 3.65 | 3.54 | 4.26 | 4.09 | 3.96 | 4.98 | 3.55 | 1.56 |
| $P_2O_5$ | 1.18 | 1.03 | 0.97 | 1.12 | 0.82 | 0.74 | 0.91 | 0.36 | 1.17 | 0.79 |
| $H_2O^{\pm}$ | 4.42 | 4.80 | 3.27 | 4.08 | 4.02 | 3.93 | 3.46 | 2.76 | 0.56 | 0.90 |
| $CO_2$ | 1.47 | 0.50 | 3.27 | 0.42 | 0.96 | 0.96 | 2.12 | 0.14 | n.d. | tr. |
| TOTAL | 100.30 | 100.44 | 100.29 | 100.21 | 99.96 | 100.12 | 99.96 | 100.56 | 100.10 | 99.80 |
| 100Mg/Mg+Fe" | 69.1 | 75.1 | 67.4 | 70.1 | 73.3 | 72.8 | 72.0 | 80.0 | 73.4 | 70.8 |
| K/Rb | 137 | 147 | 126 | 196 | 93 | 170 | 329 | 248 | 168 | 144 |
| Rb | 200 | 150 | 240 | 150 | 380 | 200 | 100 | 167 | 175 | 90 |
| Sr | 7500 | 3800 | > 1% | 4000 | 9500 | 4500 | 2500 | 2004 | 824 | 764 |
| Ba | 2800 | 2600 | 7000 | 1800 | 4500 | 2900 | 1700 | | | |
| Zr | 800 | 1100 | 1100 | 1200 | 800 | 1200 | 1200 | 613 | 276 | 282 |
| Nb | | | | | | | | 205 | 101 | 99 |
| La | 30 | < 30 | 100 | 30 | 70 | 40 | < 30 | | | |
| Ni | 230 | 140 | 100 | 160 | 180 | 270 | 250 | 628 | n.d. | 393 |
| Cr | 700 | 800 | 290 | 500 | 1200 | 900 | 550 | 616 | n.d. | 1095 |

[1]Analyses HA-HJ from Higazy (1954): semiquantitative spectrographic trace element determination

[2]Analyses BP25-30-43 from compilation in Bell & Powell (1969), Table 3.

these groups may be meaningless since Bell & Powell (1969) obtained substantially lower Rb, Sr and Zr values than did Higazy (1954) for similar rock types. The overlap in the range of 100Mg/Mg+Fe" ratios of the two groups effectively precludes any crystal fractionation relationship, and this, together with the major and trace element variation (eg. in BP30, BP25 and BP43) is consistent with a partial melting series.

Primary alnoitic melts (Table 5.31) are commonly potassic, so one might try to equate the primary magmas in the Uganda volcanics with an alnoitic partial melting series. The primary geochemical variation in the high-Ca alkaline association is presently so ill-defined that any such comparison cannot be meaningful, although it suggests that the Uganda volcanics are unique, with no known counterparts.

Petrogenetic hypotheses involving assimilation or crystal fractionation are not substantiated by trace element and isotopic studies (cf. Bell & Powell, 1969). A partial melting model probably requires modification in terms of source heterogeneities and/or unusual physical conditions. In the absence of upper mantle-derived xenoliths, no minimum value can be placed on the depth of segregation of the partial melts. Note that the P-T conditions estimated by Nicholls et al. (1971) lie below the $H_2O$-saturated pyrolite solidus (Fig. 3.1).

The Rhine graben

The Tertiary-Recent petrotectonic history of Europe includes rifting and alkaline activity. Local volcanic centres are scattered from France to Czechoslovakia, but most of the activity was localised along the Y-shaped, longitudinal, Rhine graben system. High-K alkaline rocks occur near the rift triple junction (von Frechen, 1962).

Rocks with 100Mg/Mg+Fe" ratios in the primitive range have $K_2O/Na_2O$ ratios which rarely exceed unity (Table 5.42). Their increasing levels of $SiO_2$-undersaturation and increasing $P_2O_5$, (light REE), and Sr contents are consistent with a partial melting series. However the distribution of Rb is inconsistent. Rb is abnormally high in 26922 and 18285, and is present in ∿10 times normal

concentrations in the primary typical basanite 26918. Amongst the primary melilite nephelinites, many of which contain upper mantle-derived spinel lherzolite xenoliths, the rock with one of the lowest $K_2O/Na_2O$ ratios contains one of the highest concentrations of Rb (Lohmann, 1964). There is an overlap in the primary K/Rb ratios of sodic and potassic melilite nephelinites, and, were it not for their diagnostic $K_2O/Na_2O$ ratios, high-K melilite nephelinites would be indistinguishable from their typical alkaline contemporaries.

5.4.3 Summary

In many instances, primary magmas of the high-K alkaline association are the potassic counterparts of primary magmas of the high-Ca alkaline association, or of the typical alkaline association. "High-K" chemistry does not consistently involve higher Rb contents and lower K/Rb ratios, so it cannot always be explained in terms of the relative abundance of accessory phlogopite in the upper mantle source regions.

In addition, it seems quite possible that the $TiO_2$-rich, strongly $SiO_2$-undersaturated Cenozoic volcanics in southwest Uganda comprise a unique high-K partial melting series, rather than a potassic variant of the high-Ca alkaline association.

## 5.5 Kimberlites

The geology and petrology of kimberlites has been reviewed by Wyllie (1967), Frantsesson (1970) and Mitchell (1970). Most kimberlites are extensively altered and contain abundant mantle and crustal-derived xenoliths and crystal fragments, factors which seriously complicate the assessment of published analytical data. Nonetheless compositional averages are presented in Table 5.5 to illustrate the characteristically high abundances of $TiO_2$, $K_2O$, $P_2O_5$, Rb, Sr, Ba, Zr and light REE (Fig. 5.5) in these ultrabasic rocks. Analytical data for one of the rare kimberlite sills are also contained in Table 5.5. Berg & Allsopp (in prep.) find its $Sr^{87}/Sr^{86}$ ratios range from 0.7045 to 0.7055. Usually isotopic contamination is common;

Table 5.5

Selected analyses of POTASSIC LAMPROITES and KIMBERLITES

| | LH10[3] | LH16[3] | LH12[3] | average[5] "basaltic kimberlite" | average[6] "micaceous kimberlite" | Benfon-[7] tein sill |
|---|---|---|---|---|---|---|
| $SiO_2$ | 53.07 | 43.56 | 55.14 | 35.2 | 36.33 | 25.19 |
| $TiO_2$ | 2.41 | 2.31 | 2.58 | 2.32 | 1.86 | 1.89 |
| $Al_2O_3$ | 8.96 | 7.85 | 10.35 | 4.4 | 5.09 | 2.27 |
| $Fe_2O_3$ | 3.86 | 5.57 | 3.27 | | 7.43 | 3.72 |
| FeO | 0.91 | 0.85 | 0.62 | 9.8 | 3.40 | 6.72 |
| MnO | 0.08 | 0.15 | 0.16 | 0.11 | 0.10 | 0.22 |
| MgO | 11.17 | 11.03 | 6.41 | 27.9 | 26.63 | 29.69 |
| CaO | 3.56 | 11.89 | 3.45 | 7.6 | 6.78 | 13.59 |
| $Na_2O$ | 1.15 | 0.74 | 1.21 | 0.32 | 0.37 | 0.01 |
| $K_2O$ | 10.72 | 7.19 | 11.77 | 0.98 | 2.43 | 0.15 |
| $P_2O_5$ | 1.24 | 1.50 | 1.40 | 0.72 | 0.66 | 2.20 |
| $H_2O\pm$ | 1.56 | 4.98 | 2.04 | 7.4 | 7.25 | 1.15 |
| $CO_2$ | n.a. | n.a. | n.a. | 3.3 | 1.64 | 12.83 |
| $SO_3$ | 0.16 | 0.52 | 0.40 | | | |
| TOTAL | 99.80 | 99.51 | 99.79 | 100.05 | 99.97 | 99.62 |
| [1] 100Mg/Mg+Fe" | 84.8 | 80.4 | 79.7 | 86.4 | 85.2 | 86.5 |
| [2] 100Mg/Mg+Fe" | 82.0 | 77.0 | 76.2 | 83.5 | 82.5 | 84.0 |
| K/Rb | 310 | 295 | 320 | range of averaged abundances[5] | | |
| Rb | 290 | 205[4] | 310 | 11-250 | | 8-12[8] |
| Sr | 2285 | 3400[4] | 2200 | 200-1140 | | 1200-1400[8] |
| Ba | 3050 | 11010[4] | 4660 | 740-1000 | | |
| Zr | 1925 | 2000 | 2000 | 97-455 | | |
| Ni | | | | 450-1200 | | |
| Cr | 550 | 275 | 275 | 1000-1500 | | |

[1] $Fe_2O_3/FeO$ ratios recalculated to 0.25

[2] Total iron expressed as FeO

[3] Major and trace element analyses from Carmichael (1967): Leucite Hills, Wyoming.

[4] Kay (1972)

[5] Dawson (1967)

[6] Nockolds (1954)

[7] Dawson & Hawthorne (1968)

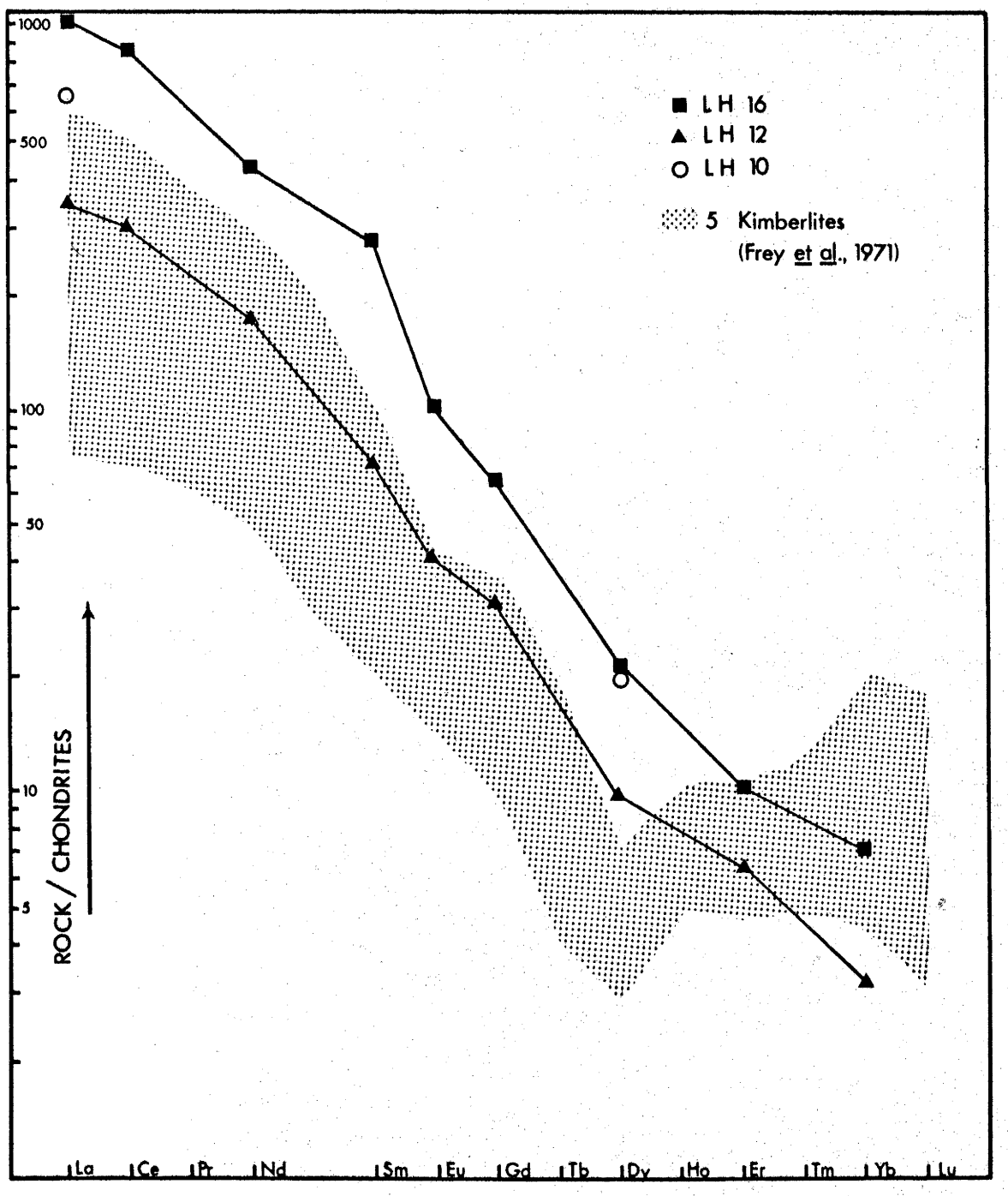
[8] Berg & Allsopp (in prep.)

Figure 5.5

Rare earth relative abundance patterns

for

KIMBERLITES and POTASSIC LAMPROITES



ratios ranging from 0.706 to 0.716 were reported in kimberlites analysed by Mitchell & Crocket (1971). Meimechites and mica peridotites are compositionally equivalent; the wide range in CaO content can be attributed to redistribution of carbonates.

The range in the 100Mg/Mg+Fe" ratios (total iron expressed as FeO) for kimberlites are close to those of the estimated undepleted upper mantle (Table 3.1) so hypotheses deriving kimberlites from primitive partial melts by crystal fractionation (eg. O'Hara, 1968) are highly improbable. A high pressure origin for kimberlites is favoured by the following mineralogical evidence: kimberlites contain diamond-bearing eclogite xenoliths and diamond xenocrysts. The experimentally determined diamond-graphite transition (Bundy et al., 1961) has a positive slope and is intersected by the shield geotherm of Ringwood et al. (1964) at ∿50 kb and by higher geothermal gradients at higher pressures. Secondly, xenolithic pyroxene-ilmenite intergrowths in kimberlite have been interpreted by Ringwood & Lovering (1970) as the exsolution products of a previously homogenous garnet solid solution. Synthesis of this garnet is only possible above 100 kb, ie. at pressures near the olivine-spinel transition on the continental geotherm.

The explosively eruptive nature of kimberlites and the extensive development of secondary phases point to high initial contents of $H_2O$ and $CO_2$. The isothermal solubility of $H_2O$ in basaltic melts increases with increasing pressure, and $CO_2$ is soluble above ∿15 kb (Hill & Boettcher, 1970). The partial molar volume of $H_2O$ in the fluid phase is approximately equal to that in silicate melts above 15 kb (Burnham, unpubl.) so at higher pressures the mutual solubility between $H_2O$ and a silicate melt is relatively insensitive to pressures. But solubility measurements in simple systems (in Clark, 1966) indicate a more rapid convergence of liquid and fluid compositions in $SiO_2$-undersaturated bulk compositions, and this extrapolated closure of the miscibility gap between melt and fluid phases occurs at pressures of ∿50 kb. Kimberlites, representing small volumes of melt produced at great depths in the upper

mantle, may be generated in the supercritical region. Their characteristically high 100Mg/Mg+Fe" ratios could be ascribed to pressure dependence of the Mg/Fe olivine-liquid distribution coefficient.

## 5.6 The Potassic Lamproites

Potassic volcanics similar to the quartz normative, leucite-bearing lavas of the Kimberley area, Western Australia, also occur in the Ivory Coast, Africa (Mitchell, 1970), Murcia, Spain (Borley, 1967), Corsica (Velde, 1967) and the Leucite Hills, Wyoming (Carmichael, 1967). Mid-Miocene volcanics (Wellman, 1971) from central western NSW are petrographically similar (cf. Joplin, 1968; ANU collection 6620-22 incl.).

The chemical characteristics of the lamproites (Table 5.5 and Fig. 5.5) include extremely high Rb, Ba, Sr, $K_2O$, $K_2O/Na_2O$, Mg/Fe, Cr, Zr, $P_2O_5$, La/Yb and light REE whereas $FeO/Fe_2O_3$, $Al_2O_3$, K/Rb, Ti/Zr and heavy REE are low. 100Mg/Mg+Fe" (total iron expressed as FeO) range from 72-83; with $Fe_2O_3/FeO$ recalculated to 0.25 the ratio ranges from 76-85. Minettes are a widespread variety of lamprophyre (Métais & Chayes, 1963) and many of the compositions described as minettes display the above chemical characteristics in a similar or lesser degree eg. Navajo province, Arizona (Nicholls, 1969). The strontium isotope geochemistry seems to be primarily a geographic feature. Bell & Powell (1970) found that $Sr^{87}/Sr^{86}$ ratios range from 0.7125 - 0.7215 in Spain and Western Australia and from 0.7052 to 0.7099 in the Leucite Hills and Navajo provinces.

The high 100Mg/Mg+Fe" ratios are a primary feature since these rocks are not cumulative, and there is no evidence for the early precipitation of an Fe-rich oxide phase. Phlogopite resorption in a nephelinitic melt might explain some, but not all, of the observed geochemical features. $Sr^{87}/Sr^{86}$ ratios do not preclude the possibility of crustal contamination but the anatectic contaminant responsible for the geochemical peculiarities of these rocks would be required to have extremely high $K_2O/Na_2O$ ratios and an improbable $K_2O$ content. The lower rare earth abundances

in the more acid compositions eg. LH10 and LH12 led Kay (1972) to suggest that they are related to the more basic rocks eg. LH16 by processes involving liquid immiscibility. Velde (1971) attributed the spherical structures found in many minettes to liquid immiscibility but the analytical data she provides do not support Kay's hypothesis since the phenomenon is normally observed only in the more acid rock types, and there is little compositional difference between the globules and the matrix. Crystal fractionation may play a limited role eg. fractionation of Fo-rich olivine could derive L12 from a composition similar to LH10 but there is no obvious way to derive compositions such as LH16.

Carmichael (1967) suggested that this group of unusual potassic alkaline magmas resulted from eclogite fractionation in kimberlites, but the overlap in 100Mg/Mg+Fe" ratios and heavy REE abundances of the two groups restricts the extent of fractionation and does not justify this hypothesis. Nicholls et al. (1971) estimate that the Leucite Hills lavas formed at pressures near 37 kb, but this is not consistent with the reported occurrence of diamond in leucite lamproite dykes (Dawson, 1967).

Summary

Lamproites and many minettes comprise a unique group of potassic alkaline magmas characterised by $K_2O >> Na_2O$ and very high concentrations of the light REE, Ba, Rb, Sr and Zr. The genetic relationships between rock types are uncertain, and may reflect liquid immiscibility, crystal fractionation or varying degrees of partial melting. The most likely candidates for the primitive parental magma(s) are compositions with $SiO_2$ contents typically ~52% since these generally have the highest 100Mg/Mg+Fe" ratios. The high 100Mg/Mg+Fe" ratios of the group as a whole, indicate that crystal fractionation processes are most unlikely to be involved in the petrogenetic evolution of the parental liquids. Disequilibrium partial melting could account for the high 100Mg/Mg+Fe" ratios but is unlikely to provide the observed trace element abundances. Although no upper mantle-derived xenoliths have been reported so far, the most reasonable hypothesis attributes a unique primitive

potassic alkaline magma series to partial melting deep in the upper mantle. As with kimberlites, the discrepancy between the observed 100Mg/Mg+Fe" ratios and those predicted from olivine-liquid equilibria (Fig. 3.2) could be related to pressure dependence of the Mg/Fe olivine-liquid distribution coefficient.

# CHAPTER 6 : CHEMICAL VARIATION AND ISLAND ARC TECTONICS: THE ALKALINE AND SHOSHONITE ASSOCIATIONS

The following conclusion is perhaps premature but in the island arc environment, the eruption of alkaline and shoshonitic rocks and the inception of spreading behind the arc appear to follow the interruption or cessation of steady state subduction. Several examples follow.

The late Mesozoic-Cenozoic petrotectonic history of Japan involves the congruent development (ie. constant polarity), migration and interaction of two contemporary arc-trench systems. The Oligocene-Miocene genesis of the Japan Sea behind the arcs was accompanied or followed by the eruption of lherzolite-bearing volcanics with typical alkaline composition (alkali basalts through to melilite nephelinites) south of the arc junction, and by shoshonitic activity above the Benioff zone in the north (Dickinson, 1972).

Fiji, the New Hebrides and (?) the Solomons formed a continuous ridge in Eocene-Miocene times on the Australian side of a west-dipping, east-migrating subduction zone marking the Australian/Pacific plate boundary (Gill & Gorton, 1972). Subsequent tectonic events contemporaneous with the overthrusting of oceanic crust onto New Guinea (I.E. Smith, pers. comm.) led to fragmentation of this formerly continuous volcanic ridge (Gill & Gorton, 1972) and a reversal in the polarity of the New Hebrides and Solomons arcs (Karig & Mammerickx, 1972), and coincide with the intrusion of spinel lherzolite-bearing alnoites and ankaratrites in the Solomons (Allen & Deans, 1965). The high MgO contents of the alnoites and ankaratrites are related to disaggregated lherzolitic and eclogitic material but their high $K_2O$ contents and $K_2O/Na_2O$ ratios are primary characteristics which contrast with the chemical compositions of melilite nephelinites of the typical alkaline association. There is no seismically delineated Benioff zone beneach present day Fiji and mainland New Guinea, and shoshonites and typical alkaline volcanics occur in both areas (Davies & Smith, 1971; Gill, 1972).

The Montana-Wyoming basin to the east of the Rocky Mountains, physiographically defined by en echelon normal faulting, is the focus of contemporaneous shoshonitic and alkaline activity. The Cenozoic evolution of the western margin of the American plate includes the termination of active subduction (eg. Shor et al., 1971) so that there is now no seismic Benioff zone beneath the region. It is suggested that the Montana province, home of the type shoshonite, is in some way related to this event. The basic shoshonites can be identified by their higher $K_2O/Na_2O$ ratios and low $TiO_2$ contents. The chemical diagnostics of phonolites of shoshonite parentage, relative to phonolites of the typical alkaline association, include $K_2O/Na_2O$ ratios near unity or higher, low Zr and Nb but Zr > Nb, low Zn, Th and U, high Cu, and commonly, extreme Ba contents. The $SiO_2$-undersaturated potassic Shonkin Sag intrusion is the subject of an extensive geochemical study by Nash & Wilkinson (1970, 1971) who point out that the chemical variation throughout its crystallisation history is not directly comparable to that reported in many alkaline intrusions and volcanic provinces. Their conclusions are hardly surprising since the Shonkin Sag provides a typical example of the undersaturated shoshonite association. The alkaline rocks are mainly basic dykes with typical alkaline chemistry but a few potassic monticellite peridotites and alnoites also occur (Larsen et al., 1941).

Petrogenesis: a discussion

100Mg/Mg+Fe" ratios in both alkaline magmas and shoshonitic magmas are consistent with equilibration between the liquid and upper mantle olivine, and imply that both primary alkaline magmas and primary shoshonitic magmas originate in the upper mantle above the foundering lithosphere. Physical conditions apparently enable typical alkaline liquids to evolve; unknown factors are responsible for the potassic alnoites and monticellite peridotes. Gill (1972) attributes the chemical diagnostics of basic shoshonites (low $TiO_2$, Zr, Nb, Th and U relative to primary alkaline magmas) to the imprint of residual sphene or perovskite, and low $Na_2O/K_2O$ ratios and K/Rb ratios may imply a

deep-seated parent assemblage in which phlogopite alone is the stable hydrous accessory (Jakeš & White, 1969). Gill (1972) suggests that a lithosphere-derived siliceous(?) "minimum melt" is subsequently responsible for partial melting in the overlying mantle, and produces shoshonitic hybrids whilst atypical physical conditions stabilise perovskite in the mantle residuum.

# CHAPTER 7 : THE GENESIS OF PRIMARY ALKALINE MAGMAS

## 7.1 Introduction: Theoretical and experimental background

The introductory section of this chapter summarises the theoretical and experimental basis for the petrogenetic interpretations presented in this thesis.

### 7.1.1 The stability of pargasite and phlogopite in the upper mantle

The bulk composition and P-T regime of the upper mantle require that the accessory amphibole and mica contain a considerable pargasite or phlogopite component respectively. This is petrogenetically significant because above ∿1 kb the temperature-sensitive breakdown reactions bounding the stability fields of pargasite and phlogopite involve incongruent melting, not dehydration (Boyd, 1959; Luth, 1967). Phlogopite melts to pressures of at least 40 kb (Yoder & Kushiro, 1969), and possibly to ∿100 kb (Kushiro et al., 1968) - although it has not been reported as inclusions in diamond (Sobolev, pers. comm.). Since amphibole stability is limited to pressures below ∿30 kb (eg. Essene et al., 1970) the incongruent melting of pargasite occurs only within this range (Gilbert, 1968; Holloway, 1972).

Pargasite stability

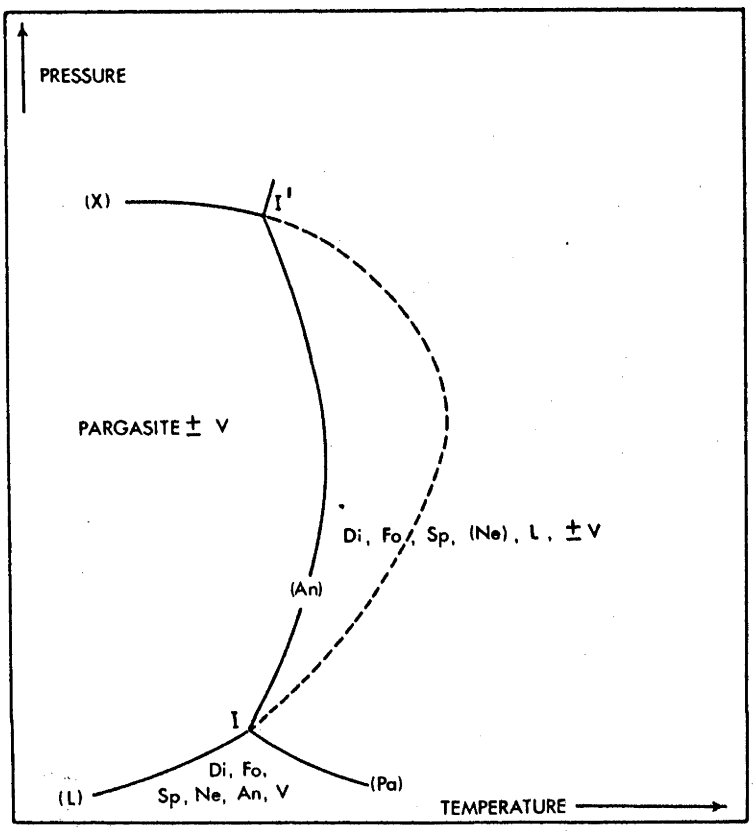
Thermodynamic calculations demonstrate that dehydration curves develop negative slopes at high pressures due to the high compressibility of $H_2O$. Should denser phases appear in the breakdown products at high pressures, the resultant increase in $\Delta V$ also contributes to the change in slope (Essene et al., 1970). These factors affect the metastable extension of the low pressure dehydration curve in the system pargasite-$H_2O$, and the high pressure intersection between this metastable projection, and the melting curve, marks the beginning of the pressure-sensitive subsolidus dehydration bounding the stability field at high pressures (see Fig. 7.10).

The addition of any inert volatile component to silicate-$H_2O$ systems causes dehydration reactions to

Figure 7.10

**Schematic illustration of pargasite stability in the system**

PARGASITE - $H_2O$




Pa ... pargasite
Di ... diopside
Fo ... forsterite
An ... anorthite
Ne ... nepheline
Sp ... spinel
V ... fluid ($H_2O$)
L ... melt[1]

Bracketed phases identifying each reaction are absent from that reaction
Reactions and invariant points related to the appearance of garnet at high pressures are not shown

(L) Low pressure subsolidus dehydration: Pa = Di + Fo + Sp + An + Ne + V (Boyd, 1959). Dashed curve is the metastable projection of this reaction.

(Pa) An + Ne + V = L (Boyd, 1959)

(X) High pressure subsolidus dehydration. Using natural pargasitic amphiboles, biotite may appear as a product of this reaction (Gilbert, 1968)

(An) Melting curve: Pa = Di + Fo + Sp (± Ne) + L + V
at a critical pressure above I, this reaction becomes
Pa + V = Di + Fo + Sp (± Ne) + L (Holloway, 1972)

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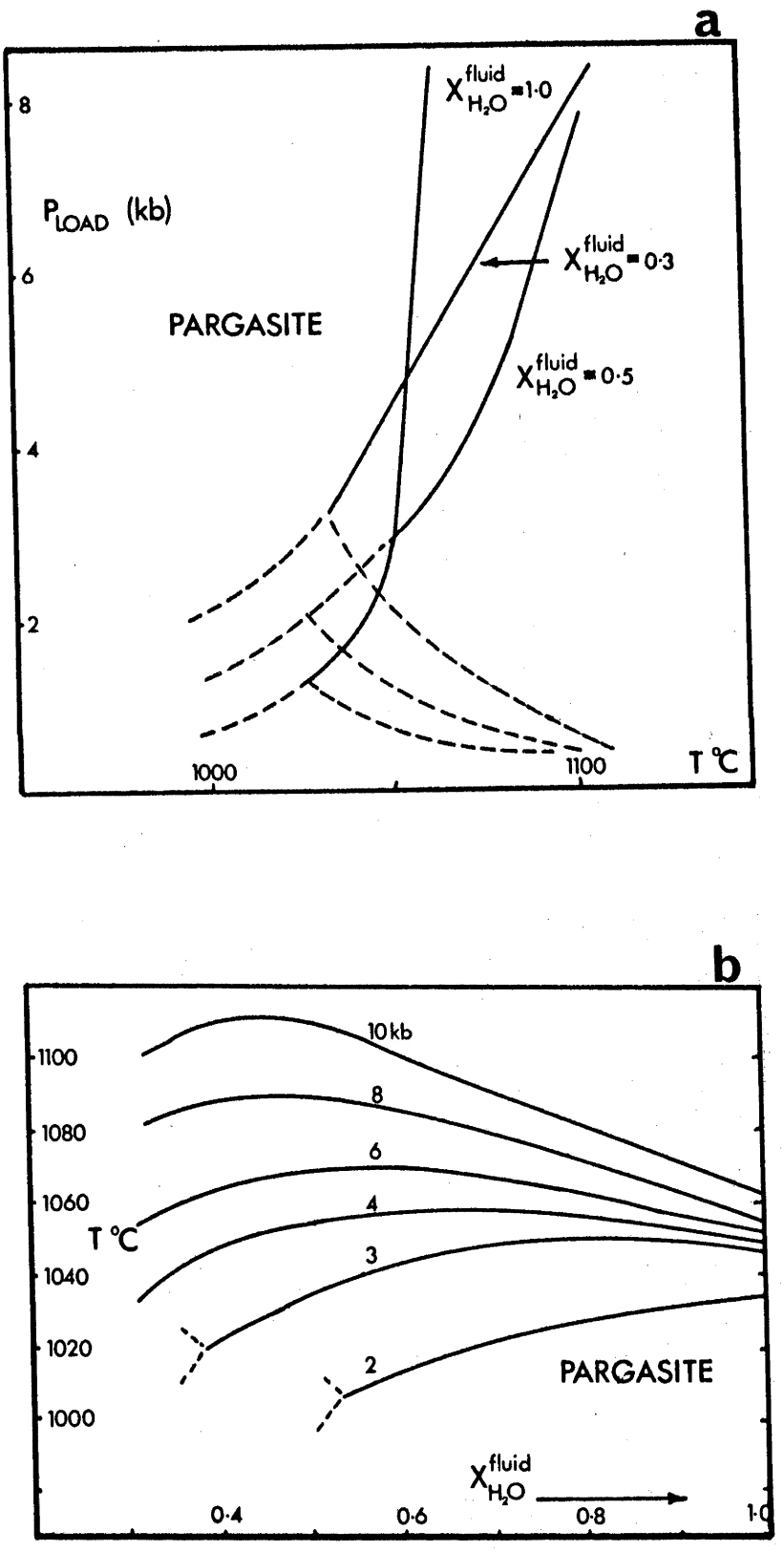
[1]Liquid compositions vary along univariant curves; the unique composition common to intersecting reactions occurs only at the invariant point.

Figure 7.11

PARGASITE - $H_2O$ - $CO_2$




from Holloway(1972)
with permission

migrate to lower temperatures (Greenwood, 1961) whereas melting now begins at temperatures above those of the $H_2O$-saturated solidus (Wyllie & Tuttle, 1960). The suppression of amphibole dehydration curves has been discussed by Bryhni et al., (1970) and Essene et al., (1970), and Holloway (1972) verified that the addition of $CO_2$ to the fluid phase below 10 kb, enhanced the stability of pargasite in the melting range, but in a rather complicated manner. Above ∿4 kb the pargasite stability field expands to higher temperatures as $X_{H_2O}^{fluid}$ is progressively diminished, reaching a maximum at some value of $X_{H_2O}^{fluid}$ which depends on $P_{load}$, and then shifts to lower temperatures with further decrease in $X_{H_2O}^{fluid}$; see Fig. 7.11(a).

Such behaviour could suggest that $CO_2$ is no longer inert at high fluid concentrations although melting relationships in other silicate-$H_2O$-$CO_2$ systems are consistent with extremely limited solubility of $CO_2$ in silicate melts below 10 kb (eg. Wyllie & Tuttle, 1960; Millhollen, 1971; Holloway & Burnham, 1972). Holloway (1972) also points out that the pargasite stability field is independent of $f_{O_2}$, unlike the stability fields of natural Fe-bearing amphiboles (cf. Allen & Boettcher, 1971), and relates the position of the pargasite melting curves to the solubility of $H_2O$ in the melt at the $P_{load}$ and $X_{H_2O}^{fluid}$ in question. In the immediate vicinity of the low pressure invariant point I (cf. Fig. 7.10), the melting reaction is

$$\text{pargasite} = Fo + Di + Sp + L + H_2O \qquad ..(A)$$

so that an isobaric decrease in $X_{H_2O}^{fluid}$ causes reaction (A) to shift to lower temperatures. As $P_{load}$ increases, the solubility of $H_2O$ in the melt increases, and at some critical $P_{load}$ (itself a function of $X_{H_2O}^{fluid}$) all $H_2O$ previously accommodated in pargasite can dissolve in the melt, and the melting reaction becomes

$$\text{pargasite} + H_2O = Fo + Di + Sp + L \qquad ..(B)$$

which shifts to higher temperatures as $X_{H_2O}^{fluid}$ decreases isobarically. The singular point marking the change from reaction (A) to reaction (B) corresponds to the maximum on an isobaric T-X projection; Fig. 7.11(b). The P-T projection of these maxima (ie. the locus of the singular points) defines the maximum stability of pargasite, namely the fluid absent melting reaction

$$\text{pargasite} = Fo + Di + Sp \pm ? + L$$

$a_{H_2O}$ and $Pe_{H_2O}$ vary with $P_{load}$ and T along this curve as controlled by the amphibole. Another phase (presumably crystalline) is permitted to appear in the products of this univariant reaction, so the composition of the initial liquid produced under fluid absent conditions may differ markedly from that produced when a fluid phase is present in the system. Fluid absent melting equilibria for hydrous assemblages cannot be realised when any fluid (vapour) phase - regardless of composition - is present. Their investigation poses experimental problems because with no buffer in use, $H_2$ diffusion is unrestricted and $a_{H_2O}$ in the system is no longer strictly controlled by the hydrous phase.

The solution of $CO_2$ in (basic) silicate melts above $\sim$15 kb (Hill & Boettcher, 1970) implies that the pargasite melting curves with $a_{H_2O}^{fluid} < 1$ will converge towards the $H_2O$-saturated melting curve at higher pressures. Preliminary studies indicate that $\gamma_{H_2O}$ in $H_2O$-$CO_2$ mixtures may be considerably greater than unity at high pressures (Burnham, unpubl.) so $f_{H_2O}$ in mixtures with $X_{H_2O}$ close to unity may be greater than $f^{o}_{H_2O}$ under the same conditions. This would cause a depression of corresponding melting curves to temperatures below those of the $H_2O$-saturated solidus, whereas dehydration curves would shift to higher temperatures (cf. Hill & Boettcher, 1970). In other words, the effect of a small mole fraction of $CO_2$ in the fluid phase at high pressures may be precisely the reverse of that observed at low pressures.

Fluoramphiboles are more stable than their hydroxy analogues when breakdown involves dehydration at low

interpretation provides a satisfactory alternative, and implies that phlogopite equilibria are precisely analagous to those of pargasite, with the fluid absent melting curve defining the maximum stability of phlogopite (cf. Yoder & Kushiro, 1969; Modreski & Boettcher, 1970).

The low pressure dehydration of fluorphlogopite takes place at temperatures above that of hydroxyphlogopite (Munoz & Eugster, 1969) so presumably their relative stabilities are reversed in the melting range, at least at low pressures. The effects of chlorine substitution are uncertain.

7.1.2 Melting relationships in the upper mantle

The position of the fluid saturated solidus is determined by $a_{H_2O}^{fluid}$ and is independent of the $H_2O$ content of the system in question (Millhollen, 1971; Holloway & Burnham, 1972). The disappearance of the fluid phase above the solidus requires that all volatile species are soluble in the melt and there is insufficient fluid to saturate the final volume of melt. Hydrous phases can persist above the fluid saturated solidus, and break down when $a_{H_2O}^{hydrous\ phase} > a_{H_2O}^{melt} = a_{H_2O}^{fluid}$. Amphibole persists above the fluid saturated pyrolite solidus with $a_{H_2O}^{fluid} = 1.0$ (Green, 1972). With $a_{H_2O}^{fluid} < 1.0$ the fluid saturated peridotite solidus may lie inside or outside the stability field of pargasite-rich amphibole, and this can be determined by superimposing the fluid saturated solidus curves on the appropriate amphibole melting curves.[1] Fig. 7.13 illustrates this relationship schematically with $a_{H_2O}^{fluid}$ = constant; an analagous situation applies if $Pe_{H_2O}^{fluid}$ = constant. The locus of the intersection of the two sets of curves in either case, is the fluid absent solidus, ie. the beginning of melting when all $H_2O$ is tied up in amphibole.

The fluid absent solidus, also, is independent of the $H_2O$ content of the system (eg. Green, 1972, Fig. 3). The relative stabilities of pargasite and phlogopite with

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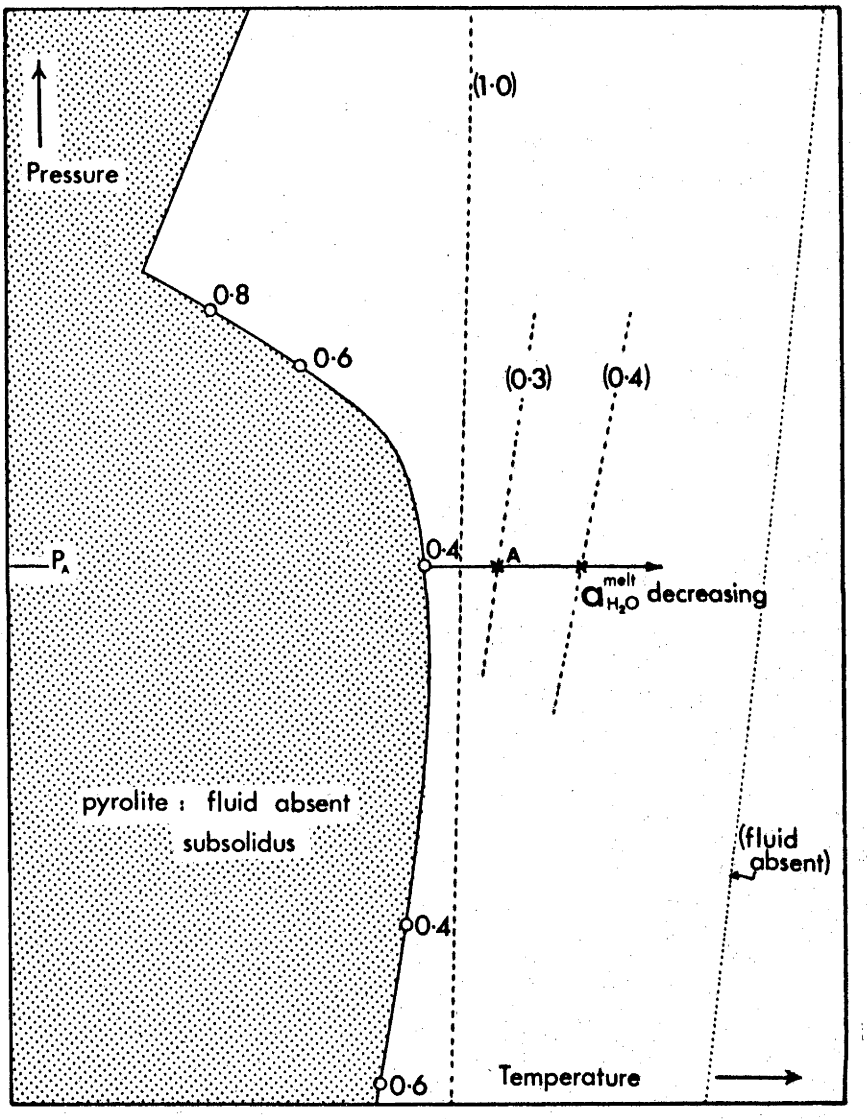
[1] Values of $a_{H_2O}^{fluid}$ are meaningful only for the specific systems in question so any superposition of this kind is invalid unless the standard state for $H_2O$ is common to both systems. Since Figs. 7.12 and 7.13 are merely schematic illustrations, the necessary corrections have not been made.

Figure 7·12

Relative stabilities of pargasite and phlogopite
in the upper mantle, under fluid absent conditions

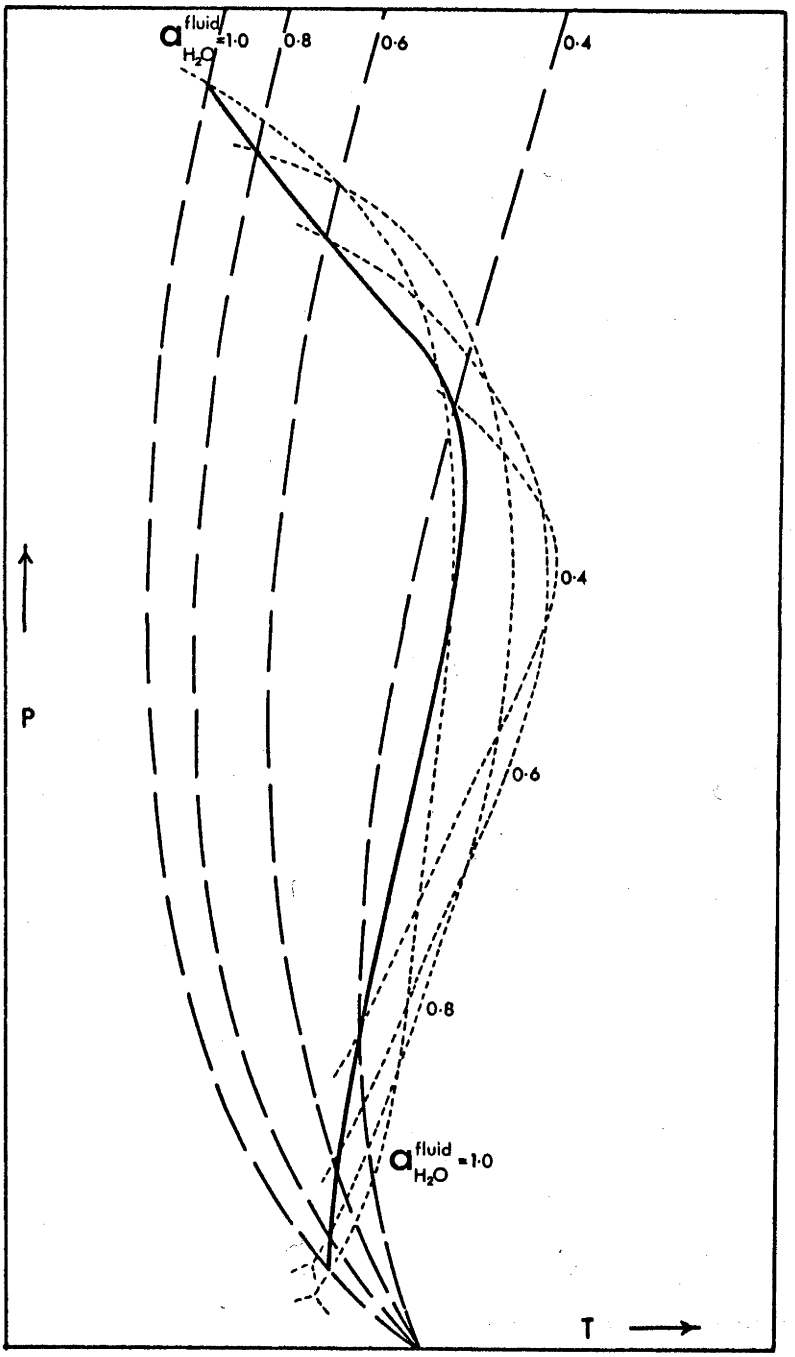



Numerical values are arbitrary, and represent $a^{melt}_{H_2O}$ = hydrous phase
Dotted curves and bracketed terms relate to the melting of phlogopite alone.

On an isobaric section at $P_A$, the initial melt coexists with phlogopite, but as melting continues and $a^{melt}_{H_2O}$ decreases, the stability of phlogopite is consequently lowered, so that phlogopite breaks down at A.

Figure 7·13

Construction of fluid absent solidus
for pargasite-bearing peridotite (schematic)




——— peridotite melting curves: $a_{H_2O}^{fluid}$ = constant

..... pargasite melting curves: " "

——— fluid absent peridotite solidus

$a^{fluid}_{H_2O}$ = 1.0, indicate that the fluid absent peridotite solidus involves melting of pargasite-rich amphibole in the assemblage in question, whereas phlogopite-rich mica, whilst reacting with the melt, persists through the solidus melting interval, to break down almost immediately above. The complex geometrical relationships on which this conclusion is based are illustrated schematically in Fig. 7.12.

Holloway & Burnham (1972) observed that a marked increase in the volume of melt accompanies the hypersolidus breakdown of amphibole in fluid saturated basaltic systems. The isobaric maximum stability of amphibole coexisting with fluid saturated melt occurs at some value of $a^{fluid}_{H_2O}$ below unity (Eggler, 1972; Holloway, 1972). However isobaric, fluid saturated solidus temperatures rise increasingly rapidly as inert components dilute the fluid phase, so the temperature interval between the solidus and the breakdown of amphibole is not necessarily a maximum when $a^{fluid}_{H_2O} = a^{melt}_{H_2O} = 1.0$. This relationship adds extra weight to the geochemical arguments presented in section 4.4.2, against the existence of a free fluid phase in the upper mantle.

The presence or absence of a fluid phase during partial melting in the upper mantle may be a fundamentally significant factor in the petrogenesis of primary magmas. If n crystalline phases coexist with melt and fluid at the fluid saturated solidus, the phase rule permits - but does not necessarily require - the coexistence of n+1 solid phases with melt at the fluid absent solidus. Thus in a given system at P and T, the composition of the initial melt can still depend on the presence or absence of a fluid phase at the solidus. For these reasons alone, experimental investigation of fluid saturated systems may not be very relevant to upper mantle petrogenesis. In any event, the interpretation of fluid saturated high pressure relationships is ambiguous, due to the incongruent solution of reactants in the fluid phase.

The "position" of the minimum melt in a multicomponent system determines the order in which crystalline phases are

subsequently eliminated as melting continues. Thus the liquidus mineralogies of isobaric partial melts are also related to the presence or absence of a fluid phase in the parent assemblage. In a peridotitic upper mantle, this is most likely to affect clinopyroxene, and garnet and/or spinel.

7.1.3 The nature of the partial melting process

Disequilibrium partial melting ideally involves the conversion of crystalline phases to melt, in the proportions specified by the melting mode, with no opportunity for equilibration of any kind between crystals and melt. However partial melting (= partial fusion) is generally interpreted as an equilibrium process which operates between two hypothetical extremes (Presnall, 1969).

1. Equilibrium fusion: the liquid continually reacts and reequilibrates with the crystalline residuum.

2. Fractional fusion: there is momentary surface equilibrium between liquid and residual phases but the liquid is thereafter isolated. The aggregate liquid is said to result from "batch melting".

Following Gast (1968), Shaw (1970) derived more flexible expressions for the relative concentration of a dispersed trace element in the liquid and in the residuum. The expressions are valid between limits corresponding to the successive elimination of phases from the residuum.

For equilibrium fusion $C^L/C_o = 1/(D_o + F(1 - Q))$

For fractional fusion $C^\ell/C_o = (1/D_o)(1 - QF/D_o)^{(1/Q-1)}$

and this applies when each fraction of melt is separated continuously from preceding liquids. The concentration in the aggregate liquid is $\bar{c}^\ell$ and is given by

$$\bar{c}^\ell/C_o = 1/F(1 - (1 - QF/D_o)^{1/Q})$$

The concentration of the given element in the crystalline residuum is given by $DC^L$ and $D\bar{c}^\ell$ respectively.

$C^L$, $C^\ell$ are the concentration of the element in the melt

$C_o$ is the initial concentration in the subsolidus assemblage

phlogopite, in the upper mantle source regions, and melting occurs in the absence of a fluid phase i.e. these accessories break down at the solidus.

Relative to the homogenous upper mantle model, a larger volume of initial melt is generated in accessory-rich source regions. At P and T, phases still melt in the same eutectic proportions, but the larger initial melt fraction will "involve" more olivine, and thus equilibrate with a comparatively Fo-rich olivine. By similar logic, this liquid is also required to equilibrate with a comparatively Ni and Cr-rich residuum. However the magnitude of this effect, in terms of the residual olivine and corresponding 100Mg/Mg+Fe" ratios in the melt, is unlikely to exceed the normal consequences of extensive partial melting in a homogenous source.

A patchy distribution of accessory phases should have little effect on the major element chemistry of the source regions, but there will be considerable heterogeneity in the distribution of incompatable elements. The concentration of a particular incompatable element is <u>not</u> directly proportional to the accessory mode in the source regions.

$a^{melt}_{H_2O}$ in the liquid generated at the fluid absent solidus is independent of the modal abundance of hydrous accessories in the parent assemblage, and its bulk composition is approximately constant, but its incompatable element chemistry varies in a subtle and complex manner. This is illustrated below with reference to the trace element relationships summarised in section 7.1.3.

7.2.2 <u>Partial melting in a heterogenous upper mantle</u>

Consider a heterogeneous upper mantle at P and T, in which subsolidus assemblages (A), (B) and (C) respectively contain eg. 1%, 5% and 10% accessories. For the time being, it is assumed that the modal abundances of individual accessory phases do not vary with respect to one another. The relative proportions of the anhydrous phases are assumed to remain constant, and Table 7.1 lists the initial mode in each case.

At the solidus, the phases melt as specified by the melting mode. The selected melting mode emphasises the role

of the accessory phases in the evolution of primary alkaline magmas. In reality, the contribution from the accessories may not be so important, but this possibility does not alter any of the conclusions which follow. At the fluid absent solidus, the accessories break down and enter the melt, and do not persist as residual phases. The volume of melt generated (F) is directly proportional to the subsolidus accessory mode.

The relationships summarised in section 7.1.3 were used to calculate the relative concentrations in the initial melts. The values of the liquid-crystal distribution coefficients for the anhydrous phases (Table 7.1) are fairly typical for all the incompatable elements, and are found to have very little effect on the results once they are very much greater than unity. The computations are most sensitive to the value of $K^{\ell/acc}$, so this is permitted to vary from 0.3 to 3.0.

The dispersed element concentration in the initial melts resulting from disequilibrium, equilibrium, and batch melting of assemblages (A), (B) and (C), are plotted in Fig. 7.20, as a function of $K^{\ell/acc}$. Concentration is measured relative to unit concentration in subsolidus assemblage (A). The parameters derived during the computations are tabulated in Table 7.1.

The concentration of a particular dispersed element in the liquids produced from source regions (A), (B) and (C), can be read from Fig. 7.20 at the appropriate value of $K^{\ell/acc}$. For example: if the accessory phase is phlogopite, $K_{Rb}^{\ell/phlog} < 1$, and the lowest concentration of Rb is found in melt (A). However this liquid contains the highest concentrations of Sr, since $K_{Sr}^{\ell/phlog} >> 1$. Although the primitive liquids (A), (B) and (C) have comparable bulk chemistry, <u>their concentrations of a particular incompatable element will differ, and the concentrations of the incompatable elements with respect to one another, can vary from (A) to (B) to (C)</u>.

An important corollary of the above argument is that <u>element ratios which are constant in the various parent assemblages, may differ in the respective partial melts</u>.

Table 7.1

Partial melting in a heterogeneous upper mantle : Figures 7-20 & 7-21

| | | olivine | opx | cpx | garnet | accessories | INITIAL MELT (F) |
|---|---|---|---|---|---|---|---|
| INITIAL MODE | A: | 0.594 | 0.167 | 0.104 | 0.125 | 0.01 | 0.0111 |
| | B: | 0.570 | 0.160 | 0.100 | 0.120 | 0.05 | 0.0556 |
| | C: | 0.540 | 0.152 | 0.095 | 0.114 | 0.10 | 0.1111 |
| MELTING MODE | : | 0.005 | 0.015 | 0.04 | 0.04 | 0.90 | |
| $K^{\ell/acc}$ | : | 1000 | 200 | 20 | 40 | k | |

ASSUME $C_o(A)$ = unity (Fig 7-20)

$C_m = C_n(K^{\ell/n}/K^{\ell/m})$

$C_{acc} = (D_o(A).K^{\ell/acc}) - 1$

$C_o(B) = D_o(B)/D_o(A)$

$C_o(C) = D_o(C)/D_o(A)$

conc. in disequilibrium melt $= Q/D_o(A)$

$D_o(A) = 0.00976 + 0.01/k$

$D_o(B) = 0.00937 + 0.05/k$

$D_o(C) = 0.00888 + 0.10/k$

$Q = 0.00308 + 0.90/k$

| k | $D_o(A)$ | $D_o(B)$ | $D_o(C)$ | Q | $C_o(B)$ | $C_o(C)$ |
|---|---|---|---|---|---|---|
| 0.3 | 0.0431 | 0.1760 | 0.3422 | 3.3003 | 4.085 | 7.938 |
| 0.5 | 0.0298 | 0.1094 | 0.2089 | 1.8031 | 3.675 | 7.018 |
| 0.7 | 0.0241 | 0.0808 | 0.1517 | 1.2888 | 3.360 | 6.309 |
| 1.0 | 0.0198 | 0.0594 | 0.1089 | 0.9031 | 3.004 | 5.509 |
| 1.5 | 0.0164 | 0.0428 | 0.0755 | 0.6031 | 2.599 | 4.597 |
| 3.0 | 0.0131 | 0.0261 | 0.0422 | 0.3031 | 1.988 | 3.223 |

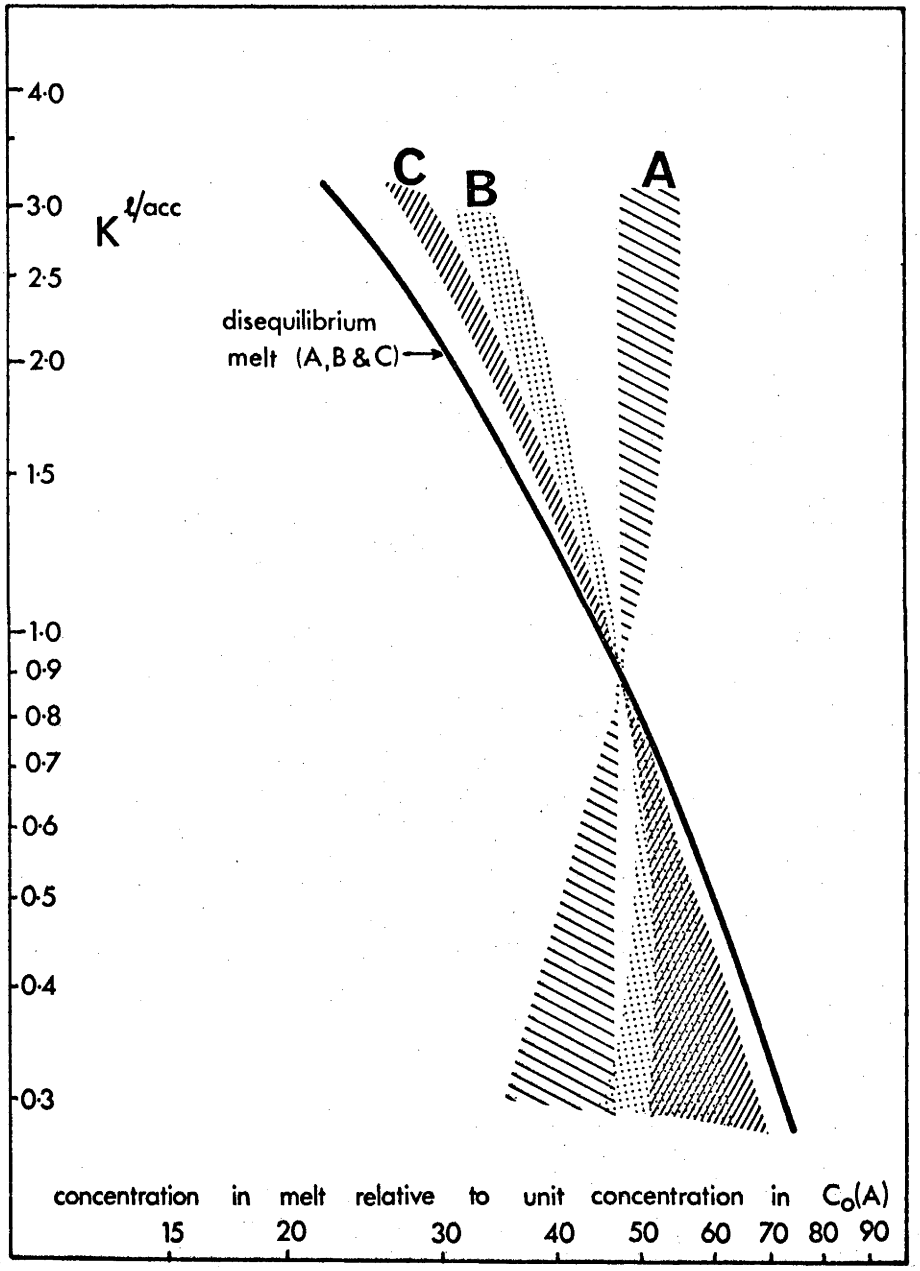
ASSUME unit concentration in accessories (Fig 7-21)

$C_o(A,..) = K^{\ell/acc}.D_o(A,..)$

disequm. melt conc. $= K^{\ell/acc}.Q$

Figure 7.20

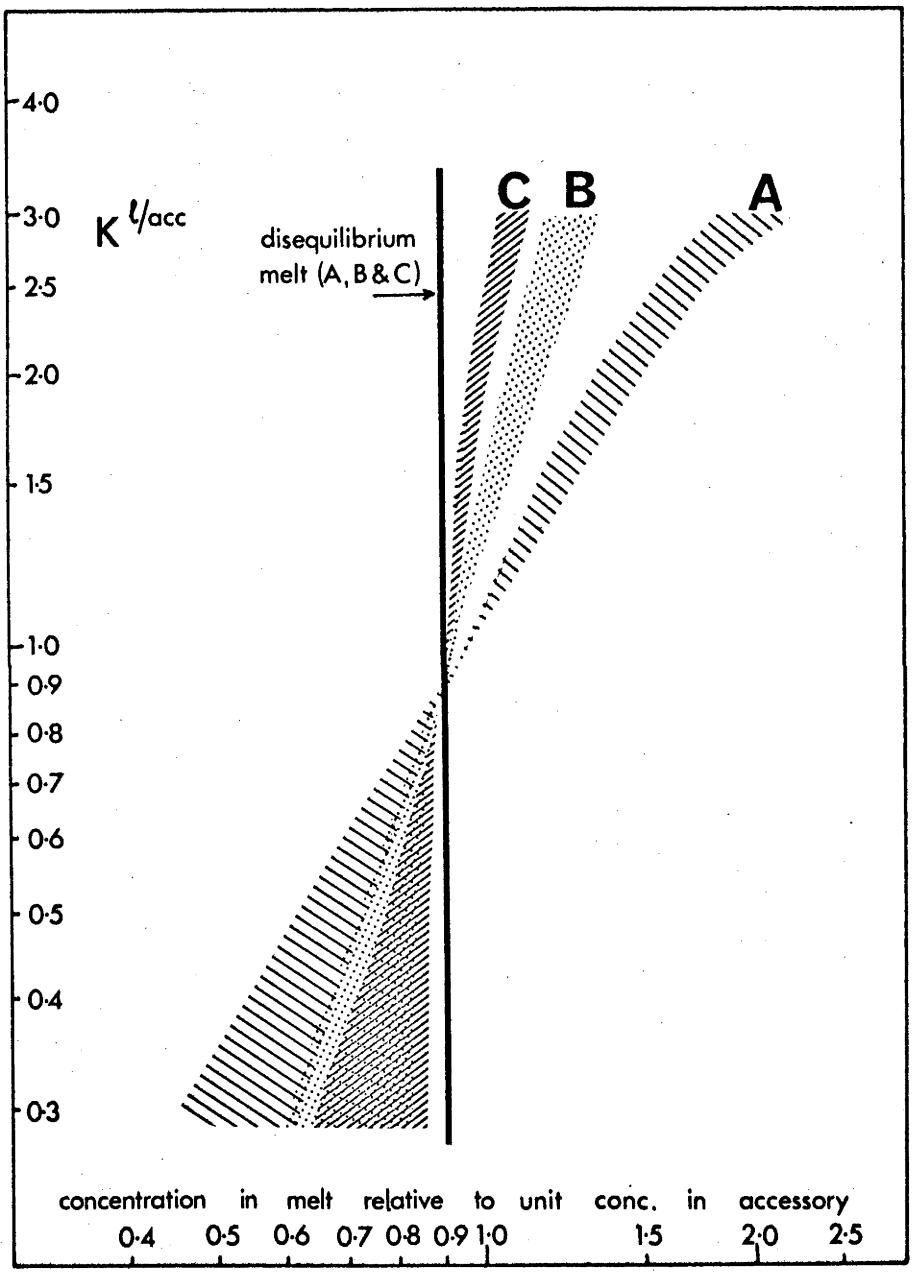
Partial melting in a heterogeneous upper mantle, illustrating concentration range in initial liquids




right hand boundaries of concentration fields correspond to batch melting for upper sectors, equilibrium melting for lower sectors

Figure 7.21

Partial melting in a heterogeneous upper mantle, illustrating concentration range in initial liquids




right hand boundaries of concentration fields correspond to batch melting for upper sectors, equilibrium melting for lower sectors

of garnet or clinopyroxene at the solidus, the bulk composition of the initial melt would change, presumably towards alkali basalt compositions as more orthopyroxene entered the liquid.

The primary distribution of $P_2O_5$ in alkaline rock types - Fig. 5.24(i) - suggests that the bulk chemical variation is best explained in terms of an isobaric partial melting series. For the sake of illustration, assume that the minimum liquid volume which can segregate efficiently, is ∿10%. With reference to Fig. 7.20, the nephelinitic liquid (C) may reach the surface, but in the case of liquid (B), melting must continue above the solidus to generate 10% volume with e.g. basanite composition, and one half the initial $P_2O_5$ content. The partial melt from source (A) would erupt as e.g. transitional basalt, following the necessary tenfold dilution. The concentrations of incompatable elements in the 10% volume liquids produced from sources (A) and (B) are respectively 1/10 and 1/2 of those shown in Fig. 7.20. The flexibility in the relative concentration factors is preserved.

Summary

A heterogeneous accessory mode in the upper mantle source regions allows considerable latitude in both the incompatable element geochemistry and the volume of the nephelinitic liquid produced at the fluid absent solidus. Presumably there is a critical lower limit to the volume of liquid which can segregate efficiently and therefore eventually reach the earth's surface. The bulk chemical variation in the primitive alkaline spectrum (melilite nephelinite through to alkali basalt) is attributed to partial melting extending above the solidus; this is consistent with the observed primary distribution of $P_2O_5$. The flexibility in the relative concentration factors for the incompatable elements, which results from source heterogeneity, is preserved as melting continues above the solidus. This model satisfactorily accounts for most of the primary geochemical variation observed in the typical alkaline association.

7.2.3 The evolution of the alkaline "sub-associations"

Geochemical variation in the typical alkaline association has been discussed in the preceding section. A heterogeneous accessory mode can also account for compositions in which high-K chemistry is superimposed on otherwise normal primary magmas with high-Ca or typical alkaline affinities. High-K chemistry could also be attributed to higher abundances of phlogopite relative to amphibole in the source regions. However, for kimberlites, potassic lamproites and some alnoites, which all have $K_2O >> Na_2O$, alternative explanations are required.

Clinopyroxene solid solutions melt to give comparatively sodic liquids (Bell & Davis, 1965), so liquids which are both Ca-rich and potassic are probably derived from a peridotitic source in which phlogopite is the only stable hydrous accessory, ie. a continental paragenesis.

The low shield geotherm intersects the pyroxene-garnet transition, then the olivine-spinel transition (Ringwood, 1970) at comparatively shallow levels ($\sim$100 kb). As the pyroxene-garnet miscibility gap narrows, the remaining clinopyroxene presumably becomes increasingly jadeitic. If this clinopyroxene is essentially residual, the initial partial melts (? kimberlites) will be potassic. The chemical features of the potassic lamproites provoke endless speculation, but few definite conclusions.

The feasibility of an accessory Ca- or CaMg-carbonate (with the potential to accommodate significant concentrations of Nb, Sr and Ba), down to at least the top of the low velocity zone, is favoured by the $CaCO_3$ stability field outlined by Bell & England (1964) and Wyllie & Boettcher (1969). A stable carbonate permits the possibility of fluid absent conditions in the upper mantle. The breakdown of the carbonate involves congruent melting and its stability is enhanced in the absence of $CO_2$ fluid (Wyllie & Boettcher, 1969). This relationship suggests a situation analagous to that described by Holloway (1972) for pargasite, but with $CO_2$ as the active volatile species.

Since $CO_2$ is soluble in basaltic melts at upper mantle pressures (Hill & Boettcher, 1970) the peridotite solidus

with $a_{CO_2}^{fluid} = 1.0$ does not coincide with the anhydrous solidus at these depths. In the absence of a fluid phase the isobaric beginning of melting of a peridotite containing accessory carbonate should occur at a unique temperature between the solidus with $a_{CO_2}^{fluid} = 1.0$ and the anhydrous solidus, and this theoretical beginning of melting curve could be constructed in the manner outlined in section 7.12 and Fig. 7.13, if the melting curves for the peridotite and the carbonate in question were known for values of $a_{CO_2}^{fluid}$. The relative positions of the pyrolite and $CaCO_3$ melting curves indicate that the fluid absent melting of carbonate-bearing peridotite could only occur at pressures above 25-35 kb or greater; carbonate could persist above the solidus at lower pressures.

The natural subsolidus upper mantle assemblage contains accessory phlogopite. Burnham's unpublished observations for basalt-$H_2O$-$CO_2$ near 30 kb can be interpreted in terms of higher solubilities for $H_2O$-$CO_2$ mixtures in basaltic melts than for either volatile species alone. If this is the case, the fluid absent solidus of a phlogopite + carbonate-bearing peridotite assemblage would lie below the fluid absent solidi of the assemblages containing either phlogopite or carbonate alone. The ill-defined low velocity channel at $\sim$150 km beneath ancient shield areas corresponds quite closely to the extrapolated intersection of the geotherm and melting curves for phlogopite (Yoder & Kushiro, 1969) and pyrolite (Green, 1972) ie. to the intersection of the shield geotherm with the fluid absent solidus of a phlogopite-bearing peridotite. Note that this fluid absent solidus does not exist below $\sim$45 kb.

The above discussion, admittedly highly speculative, may be relevant to continental regions where the mantle geotherm remains below the solidus beyond the stability field of amphibole. Geothermal gradients locally higher than average may intersect the fluid absent solidus of a carbonate and phlogopite-bearing peridotite at pressures above e.g. 30 kb. It is proposed that these conditions may occur at some stage in the history of a continental rift system, at depth in the upper mantle flanking the rift

axis. Nephelinitic $H_2O$- and $CO_2$- undersaturated magmas are produced, and these ultimately give rise to the carbonatites and associated rock types of the high-Ca alkaline association.

## 7.3 Source heterogeneity: its petrogenetic implications

Some of the arguments presented in this thesis may have a wider application. Analytical methods are now sufficiently sensitive to determine whether source region heterogeneities are likewise involved in the genesis of continental and ocean ridge tholeiites.

In island arcs, the (eclogitic) crustal layers of the downgoing slab are very likely to have a variable accessory mode. The thermal regime of the slab (Minear & Tuksöz 1970) suggests that the stability fields of the accessory amphibole and biotite are bounded by melting reactions. The presence or absence of a free fluid phase is an open question, but in either case $H_2O$ is probably transferred to the overlying upper mantle in solution in a silicate melt. These points are relevant to the impending controversy over the role of the underthrust lithosphere in the evolution of island arc magma types.

## LIST OF APPENDICES

## APPENDIX 1 : ANALYTICAL METHODS

Surface weathering of the basalts is extensive. Fresh samples were obtained from the more massive flows from quarries and cuttings where possible. The extensive subsolidus alteration did not permit the sampling of fractured or clastic basaltic units. This may account for the apparent scarcity of inclusion-bearing rocks and nephelinitic compositions in the samples collected, since these rock types are commonly explosively eruptive.

Sawn rock slabs, 1-2 cm thick, were ground clean with carborundum then split into rough cubes with a hydraulic rock splitter. 0.5 - 1 kg of fragments of fresh material was reduced to a fine powder in a Siebtechnic mill and its bulk was reduced by quartering. The rock powder was then stored in screwtopped glass jars. Since crushing in tungsten carbide introduced cobalt and tungsten as contaminants, these elements were excluded from analysis.

### X-ray fluorescence spectrometry

Major and trace element abundances were determined using an automated Philips PW1220 spectrometer with 2kW generator. Operating conditions are summarised in Table A1.1. Precision and detection limits were determined from counting statistics (Norrish & Chappell, 1967). The accuracy of the method used in major element analysis has been discussed in detail by Norrish & Hutton (1969). Accuracy in trace element analysis was estimated by comparison of the measured trace element abundances in known natural standards with preferred values obtained by a variety of analytical methods (Table A1.2). The measured standard abundances in this series of analyses compare favourably in this respect, and are also in good agreement with previous determinations made in this laboratory.

### Trace Element Analysis

All samples have been analysed in duplicate. Samples and standard mixes were prepared as discs of pelletised powders with boric acid sides and base. All intensities have been automatically corrected for detector dead time,

and instrument drift was monitored against an internal standard. The analytical line and operating conditions are selected so that inter-element interferences are minimised while intensities are as high as possible. Background positions, distributed symmetrically about the preferred analytical line, were selected so that interference is minimal, and peak and total background times were equal. Following Norrish & Chappell (1967) a further empirical correction for inter-element interferences is applied to the measured intensities. The background profile is also corrected for non-linearity, including the effects of tube contamination. In silicate analysis the background profile for most elements is measured on one or more of the following: Spec pure $Al_2O_3$, Spec pure $SiO_2$ and "Herasil" (silica glass supplied by Heraeus GmbH., Hanau, W. Germany). Ni blanks are measured on NBS 165 (glass sand).

Calculation of trace element abundances

The concentration (p) of a trace element is related to the intensity of the characteristic radiation emitted (C) by the relationship.

$$p = \frac{A\ C}{K}$$

where K is a constant
A is the mass absorption coefficient for the radiation being analysed.

The values of K for each element were determined by analysing synthetic standards whose A and p are known, under the conditions given in Table A1.1.

Mass absorption coefficients for samples and standards were measured for shorter wavelengths ($Sr_{K\alpha}$ and $Rb_{K\alpha}$) using the following method: approximately 300 mg samples were pressed into a 1.27 cm. diameter hole in a Perspex holder. The attenuation ($I_o/I$) of the desired wavelength was measured, and A calculated from the relationship

$$A = \frac{1}{\rho x} \ln(I_o/I) \quad \text{where } \rho x = \text{mass cm}^{-2}$$

For measurements at longer wavelengths ($Zn_{K\alpha}$ and $Fe_{K\alpha}$) the samples were first diluted with an approximately equal known mass of cellulose to prevent extreme attenuation.

Major element analysis

The major element oxides of Fe (as $Fe_2O_3$), Mn, Ti, Ca, K, P, Si, Al and Mg - have been determined in duplicate on glass discs following the fusion method of Norrish & Hutton (1969). Background interference in the analysis of Mg is largely due to crystal fluorescence so this was minimised by setting the pulse height selector window symmetrically below the $Mg_{K\alpha}$ peak, and also by applying an empirical correction (Norrish & Hutton, 1969).

The following wet chemical techniques have been carried out in duplicate. $Na_2O$ was determined on a double beam photometer with a propane-air flame, using Li as an internal standard; the method is similar to that described by Cooper (1963) for potassium.

The determination of FeO involved the dissolution of the sample in HF in the presence of an excess of ammonium metavanadate. The excess vanadic ion was then titrated against a ferrous ammonium sulphate solution which had been previously standardised against BDH standard ceric sulphate. Ferric iron was calculated by difference.

$H_2O^-$ is the percentage weight loss of a sample after 90 mins. at 110°C.

$H_2O^+$ and $CO_2$ were determined by heating a sample for 90 mins. in a tube furnace at 1000-1050°C in a stream of dry, $CO_2$-free nitrogen. The $H_2O$ and $CO_2$ lost from the sample are collected in microabsorption tubes containing a mixture of $P_2O_5$ and pumice, and "carbosorb" soda asbestos.

Other techniques

Mineral separation was carried out using a combination of magnetic and heavy liquid techniques.

Where necessary, mineral identification was confirmed by X-ray diffraction.

Microprobe Analysis

A limited number of mineral analyses were made using a 3-spectrometer ARL-EMX microprobe. Standards and samples were carbon coated simultaneously. Accelerating voltages of 12kV were used for all elements except Ni (16kV) and a specimen current of 0.35 μamps/sec was employed. Counts were accumulated over 40 sec. intervals.

Peak and background intensities were measured and corrected for detector dead time. Beam current drift was monitored by the variation in specimen current on a single standard during each analytical run. The correction for matrix effects included an absorption correction, a fluorescence correction and an atomic number correction and the calculations used a Fortran program written by N.G. Ware. Standards were provided by N.G. Ware of Dept. Geophysics and Geochemistry, ANU.

Stain tests

Felspathoid staining is wholly unsatisfactory, since the stain is taken up by "iddingsite" and by clays in the mesostasis and along grain boundaries. Cobaltinitrate staining is similarly ambiguous and gives very poor results with sanidine.

TABLE A1.1 SUMMARY OF ANALYTICAL CONDITIONS FOR X-RAY SPECTROMETRY

| ELEMENT | ANALYTICAL LINE | X-RAY TUBE | ANALYSING CRYSTAL | COLLIMATOR | DETECTOR | ABSORPTION COEFF. | % RELATIVE STD DEVIATION on BCR-1 | on W-1 | DETECTION LIMIT 3σ |
|---|---|---|---|---|---|---|---|---|---|
| oxide percentages | | | | | | | | | |
| $SiO_2$ | Kα | Cr | PE | Coarse | F.C | | 0.134 | | 0.032 |
| $TiO_2$ | Kα | Cr | LiF(200) | Coarse | F.C | | 0.121 | | 0.003 |
| $Al_2O_3$ | Kα | Cr | PE | Coarse | F.C | | 0.240 | | 0.021 |
| $Fe_2O_3$(total) | Kα | W | LiF(200) | Coarse | F.C | | 0.067 | | 0.003 |
| MnO | Kα | W | LiF(200) | Coarse | F.C | | 0.450 | | 0.004 |
| MgO | Kα | Cr | ADP | Coarse | F.C | | 0.931 | | 0.078 |
| CaO | Kα | Cr | LiF(200) | Coarse | F.C | | 0.096 | | 0.001 |
| $K_2O$ | Kα | Cr | LiF(200) | Coarse | F.C | | 0.172 | | 0.001 |
| $P_2O_5$ | Kα | Cr | Ge | Coarse | F.C | | 0.194 | | 0.003 |
| parts per million | | | | | | | | | |
| Ba | $Lβ_1$ | W | LiF(220) | Coarse | F.C | Fe | 0.29 | 0.75 | 2 |
| Rb | Kα | Mo | LiF(200) | Fine | S.C | Rb | 0.63 | 1.18 | 1 |
| Sr | Kα | Mo | LiF(200) | Coarse | S.C | Sr | 0.18 | 0.23 | 1 |
| Pb | $Lβ_1$ | Mo | LiF(200) | Fine | S.C | Rb | 1.19 | 2.11 | 0.5 |
| Th | $Lα_1$ | Mo | LiF(200) | Fine | S.C | Rb | 7.70 | 14.93 | 1 |
| U | $Lα_1$ | Mo | LiF(220) | Fine | S.C | Rb | | | 2 |
| Zr | Kα | W | LiF(200) | Coarse | S.C | Sr | 0.49 | 0.86 | 2 |
| Nb | Kα | W | LiF(200) | Fine | S.C | Sr | 4.95 | 8.78 | 2 |
| Y | Kα | Mo | LiF(200) | Coarse | S.C | Sr | 0.55 | 0.84 | 0.5 |
| La | $Lα_1$ | W | LiF(220) | Coarse | F.C | Fe | 1.65 | 3.88 | 1 |
| Ce | $Lβ_1$ | W | LiF(200) | Fine | F.C | Fe | 3.09 | 7.98 | 4 |
| Pr | $Lα_1$ | W | LiF(220) | Coarse | F.C | Fe | 5.48 | 14.77 | 1 |
| Nd | $Lβ_1$ | W | LiF(220) | Coarse | F.C | Fe | 4.14 | 8.27 | 3 |
| V | Kα | W | LiF(220) | Fine | F.C | Fe | 0.35 | 0.43 | 1 |
| Cr | Kα | W | LiF(200) | Fine | F.C | Fe | 2.29 | 0.72 | 1 |
| Ni | Kα | Au | LiF(200) | Coarse | S.C | Zn | 11.10 | 0.99 | 1 |
| Cu | Kα | Au | LiF(200) | Coarse | S.C | Zn | 3.48 | 0.56 | 1 |
| Zn | Kα | Au | LiF(200) | Coarse | S.C | Zn | 0.46 | 0.45 | 1 |
| Ga | Kα | Mo | LiF(200) | Coarse | S.C | Zn | 2.27 | 2.74 | 1 |

Coarse collimator = 480 μ F.C = Flow Counter

Fine collimator = 160 μ S.C = Scintillation Counter

Table A1.2

Comparison of Measured Trace Element Abundances in Natural Standards with Preferred Values

| | BCR-1 | | W-1 | | PCC-1 | |
|---|---|---|---|---|---|---|
| Ba | 697 | *700* | 160 | *165* | | |
| Rb | 46.6 | *47.5* | 21.1 | *21.6* | | |
| Sr | 330 | *335* | 189 | *185* | | |
| Pb | 19 | *15* | 10 | *8* | | |
| Th | 6 | *6* | 3 | *2.3* | | |
| U | | *1.8* | | *0.55* | | |
| Zr | 188 | *180* | 92 | *94* | | |
| Nb | 11 | *13* | 6 | *9* | | |
| Y | 33 | *40* | 20 | *26* | | |
| La | 27 | *24* | 10 | *10* | | |
| Ce | 52 | *52* | 19 | *23* | | |
| Pr | 7.1 | *7* | 2.6 | *3.6* | | |
| Nd | 24 | *29* | 12 | *15* | | |
| V | 362 | *360* | 234 | *245* | | |
| Cr | 12 | *14* | 91 | *115* | | |
| Ni | 5 | *10* | 66 | *75* | 2415 | *2500* |
| Cu | 11 | *16* | 102 | *115* | 4 | *8* |
| Zn | 126 | *120* | 90 | *83* | 44 | *42* |
| Ga | 21 | *21* | 17 | *17* | | |

Italicised abundances are preferred values taken from compilations of superior analytical data.

## 2A ALKALI BASALTS

| | K1 | K2 | K3 | K4 | K5 | K7 | K9 | K10 | K11 | K12 |
|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 45.76 | 48.22 | 46.88 | 48.22 | 44.61 | 47.45 | 47.16 | 46.43 | 45.71 | 45.25 |
| TIO2 | 1.92 | 1.84 | 1.83 | 1.93 | 2.00 | 1.52 | 1.63 | 1.96 | 1.77 | 2.05 |
| AL203 | 14.65 | 15.26 | 14.41 | 16.17 | 14.57 | 14.81 | 15.25 | 14.37 | 14.38 | 14.52 |
| FE203 | 2.98 | 3.34 | 2.47 | 3.78 | 3.76 | 2.78 | 2.86 | 3.54 | 3.09 | 2.55 |
| FEO | 8.18 | 6.82 | 8.69 | 6.28 | 8.10 | 8.16 | 6.98 | 6.97 | 7.78 | 8.03 |
| MNO | .15 | .14 | .18 | .13 | .17 | .15 | .14 | .14 | .15 | .15 |
| MGO | 8.92 | 6.65 | 8.99 | 6.23 | 9.14 | 9.42 | 8.02 | 8.63 | 9.53 | 9.48 |
| CAO | 9.32 | 9.17 | 9.50 | 9.05 | 9.82 | 8.05 | 9.54 | 9.50 | 9.50 | 9.85 |
| NA20 | 2.79 | 3.08 | 2.87 | 3.42 | 2.81 | 2.74 | 2.90 | 2.73 | 2.38 | 2.26 |
| K20 | 1.16 | 1.39 | 1.04 | 1.23 | 1.23 | .81 | 1.10 | 1.29 | 1.02 | 1.31 |
| P205 | .78 | .53 | .52 | .52 | .74 | .34 | .48 | .57 | .50 | .64 |
| H20- | 1.00 | .98 | .52 | .80 | .69 | .59 | .79 | .87 | .80 | .79 |
| H20+ | .85 | 2.01 | 1.20 | 1.19 | 1.83 | 2.42 | 2.27 | 1.64 | 2.21 | 2.23 |
| C02 | .24 | .19 | .24 | .06 | .03 | .30 | .11 | .19 | .17 | .20 |
| TOTAL | 98.86 | 99.85 | 99.54 | 99.23 | 99.74 | 99.70 | 99.48 | 99.23 | 99.22 | 99.56 |
| MG NO. | 64.19 | 59.63 | 64.26 | 58.41 | 63.46 | 65.85 | 64.69 | 64.97 | 66.32 | 66.71 |
| RB | 13. | 33. | 20. | 29. | 27. | 14. | 24. | 29. | 17. | 22. |
| SR | 435. | 848. | 594. | 938. | 853. | 375. | 910. | 2376. | 862. | 938. |
| Y | 22. | 25. | 23. | 23. | 24. | 21. | 25. | 22. | 22. | 25. |
| TH | 4. | 8. | 6. | 7. | 7. | 5. | 9. | 6. | 5. | 7. |
| ZR | 147. | 202. | 170. | 190. | 223. | 143. | 204. | 182. | 167. | 230. |
| NB | 46. | 74. | 63. | 76. | 98. | 44. | 89. | 72. | 63. | 79. |
| PB | 4. | 6. | 6. | 7. | 6. | 6. | 9. | 6. | 5. | 6. |
| GA | 16. | 16. | 18. | 17. | 14. | 16. | 15. | 16. | 14. | 17. |
| V | 142. | 143. | 141. | 141. | 140. | 128. | 138. | 145. | 142. | 142. |
| CR | 225. | 148. | 198. | 74. | 200. | 235. | 82. | 150. | 225. | 221. |
| NI | 167. | 63. | 151. | 56. | 155. | 167. | 82. | 151. | 163. | 176. |
| CU | 56. | 29. | 63. | 41. | 53. | 56. | 34. | 56. | 59. | 54. |
| ZN | 85. | 79. | 95. | 79. | 83. | 95. | 81. | 85. | 88. | 79. |
| BA | 202. | 472. | 342. | 420. | 393. | 221. | 610. | 505. | 341. | 358. |
| LA | 22. | 38. | 38. | 38. | 45. | 25. | 52. | 37. | 31. | 41. |
| CE | 43. | 72. | 69. | 74. | 92. | 48. | 102. | 75. | 61. | 82. |
| PR | 6. | 9. | 7. | 7. | 9. | 5. | 9. | 8. | 6. | 10. |
| ND | 15. | 27. | 23. | 24. | 24. | 15. | 30. | 30. | 26. | 30. |

## 2A ALKALI BASALTS (cont.)

| | BB22 | K15 | K16 | K17 | K18 | KPH1 | K21 | K22 | K23 | K24 |
|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 47.17 | 43.65 | 44.67 | 45.78 | 45.94 | 46.69 | 46.86 | 46.61 | 46.36 | 46.81 |
| TIO2 | 1.67 | 1.31 | 2.02 | 1.68 | 1.78 | 2.23 | 2.20 | 2.23 | 2.26 | 2.20 |
| AL203 | 14.94 | 10.02 | 14.28 | 14.59 | 14.89 | 15.57 | 15.53 | 15.52 | 15.13 | 15.51 |
| FE203 | 2.70 | 3.87 | 3.33 | 3.16 | 3.03 | 2.89 | 2.95 | 3.01 | 3.44 | 2.43 |
| FEO | 8.72 | 9.96 | 8.11 | 8.16 | 8.10 | 6.97 | 6.84 | 6.77 | 6.54 | 7.38 |
| MNO | .18 | .22 | .18 | .15 | .19 | .17 | .16 | .16 | .13 | .16 |
| MGO | 9.40 | 18.19 | 11.00 | 10.03 | 10.04 | 6.65 | 6.88 | 6.69 | 5.97 | 6.80 |
| CAO | 9.17 | 6.19 | 9.74 | 9.23 | 9.04 | 10.22 | 10.22 | 10.37 | 10.31 | 10.53 |
| NA20 | 2.97 | 1.78 | 2.17 | 2.39 | 2.45 | 2.82 | 2.64 | 2.66 | 2.68 | 2.86 |
| K20 | .88 | .71 | 1.01 | .78 | .78 | 1.76 | 2.02 | 2.10 | 2.06 | 1.80 |
| P205 | .40 | .32 | .45 | .35 | .38 | .65 | .64 | .63 | .63 | .61 |
| H20- | .46 | .82 | .94 | 1.01 | .93 | .80 | .81 | .78 | .99 | .78 |
| H20+ | 1.10 | 1.92 | 1.52 | 1.55 | 1.88 | 1.96 | 1.88 | 1.99 | 2.24 | 1.42 |
| C02 | .06 | .21 | .19 | .09 | .02 | .00 | .01 | .10 | .17 | .00 |
| TOTAL | 100.00 | 99.38 | 99.85 | 99.13 | 99.64 | 99.63 | 99.89 | 99.88 | 99.14 | 99.53 |
| MG NO. | 64.79 | 74.70 | 68.37 | 66.55 | 66.93 | 60.26 | 61.26 | 60.63 | 57.49 | 60.80 |
| RB | 17. | 11. | 15. | 11. | 10. | 31. | 37. | 41. | 29. | 59. |
| SR | 492. | 476. | 732. | 562. | 556. | 776. | 851. | 829. | 681. | 721. |
| Y | 23. | 16. | 21. | 20. | 20. | 23. | 21. | 22. | 21. | 21. |
| TH | 4. | 3. | 4. | 4. | 4. | 4. | 5. | 5. | 5. | 5. |
| ZR | 165. | 117. | 154. | 143. | 152. | 204. | 207. | 205. | 193. | 202. |
| NB | 33. | 37. | 50. | 47. | 45. | 73. | 73. | 73. | 71. | 72. |
| PB | 6. | 5. | 5. | 7. | 5. | 3. | 7. | 6. | 5. | 5. |
| GA | 17. | 13. | 16. | 15. | 18. | 17. | 16. | 16. | 17. | 16. |
| V | 140. | 105. | 174. | 134. | 152. | 162. | 153. | 164. | 152. | 161. |
| CR | 223. | 315. | 301. | 193. | 224. | 147. | 146. | 157. | 155. | 152. |
| NI | 179. | 490. | 214. | 159. | 186. | 53. | 53. | 55. | 53. | 55. |
| CU | 70. | 53. | 64. | 65. | 68. | 47. | 48. | 47. | 43. | 46. |
| ZN | 101. | 108. | 95. | 87. | 107. | 79. | 88. | 90. | 74. | 89. |
| BA | 205. | 236. | 462. | 253. | 302. | 711. | 686. | 716. | 676. | 698. |
| LA | 22. | 21. | 29. | 21. | 22. | 35. | 37. | 38. | 34. | 37. |
| CE | 44. | 34. | 55. | 44. | 43. | 85. | 71. | 76. | 72. | 74. |
| PR | 4. | 4. | 5. | 6. | 5. | 8. | 8. | 9. | 7. | 7. |
| ND | 17. | 18. | 23. | 15. | 15. | 31. | 28. | 27. | 24. | 27. |

## 2A ALKALI BASALTS (cont.)

| | K25 | K26 | K28 | K29 | K31 | K32 | K33 | K34 | K42 | K44 |
|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 46.59 | 46.72 | 45.73 | 46.59 | 47.14 | 46.39 | 47.16 | 45.92 | 47.36 | 46.74 |
| TIO2 | 2.23 | 2.08 | 1.91 | 1.98 | 1.53 | 2.10 | 2.14 | 2.21 | 1.52 | 1.42 |
| AL203 | 15.34 | 14.41 | 14.39 | 14.77 | 14.43 | 14.17 | 14.85 | 15.34 | 14.20 | 14.15 |
| FE203 | 2.43 | 2.62 | 2.19 | 2.56 | 2.59 | 2.42 | 3.11 | 3.15 | 2.80 | 3.25 |
| FEO | 7.42 | 8.27 | 9.00 | 8.02 | 8.16 | 8.30 | 7.25 | 7.22 | 8.11 | 7.56 |
| MNO | .15 | .15 | .15 | .14 | .14 | .14 | .14 | .15 | .15 | .15 |
| MGO | 6.48 | 9.10 | 9.38 | 8.33 | 9.25 | 9.52 | 8.15 | 7.11 | 9.38 | 9.50 |
| CAO | 10.20 | 9.46 | 9.68 | 9.40 | 8.76 | 8.70 | 9.34 | 10.19 | 8.03 | 9.27 |
| NA20 | 2.54 | 2.87 | 3.00 | 2.62 | 2.84 | 2.96 | 2.88 | 2.38 | 2.92 | 2.42 |
| K20 | 2.42 | 1.14 | 1.31 | 1.40 | 1.12 | 1.47 | 1.65 | 1.98 | 1.11 | .90 |
| P205 | .64 | .49 | .60 | .49 | .40 | .48 | .57 | .69 | .38 | .34 |
| H20- | .70 | .81 | .78 | .98 | .58 | .64 | .76 | 1.06 | 1.06 | 1.00 |
| H20+ | 1.76 | .86 | .95 | 1.54 | 1.89 | 1.80 | 1.62 | 1.94 | 2.10 | 1.68 |
| C02 | .21 | .25 | .02 | .34 | .19 | .08 | .09 | .08 | .17 | .19 |
| TOTAL | 99.37 | 99.44 | 99.30 | 99.36 | 99.27 | 99.38 | 99.93 | 99.64 | 99.46 | 98.84 |
| MG NO. | 59.55 | 65.14 | 65.11 | 63.78 | 65.80 | 66.48 | 63.90 | 60.68 | 65.82 | 66.41 |
| RB | 47. | 20. | 19. | 24. | 26. | 31. | 28. | 43. | 21. | 19. |
| SR | 791. | 681. | 791. | 652. | 1206. | 558. | 731. | 527. | 430. | 1364. |
| Y | 21. | 19. | 20. | 22. | 21. | 20. | 20. | 24. | 21. | 19. |
| TH | 5. | 5. | 5. | 6. | 6. | 5. | 6. | 7. | 6. | 6. |
| ZR | 204. | 149. | 150. | 205. | 143. | 173. | 168. | 218. | 140. | 121. |
| NB | 73. | 62. | 53. | 68. | 46. | 60. | 60. | 89. | 49. | 37. |
| PB | 5. | 5. | 5. | 4. | 7. | 6. | 6. | 6. | 7. | 4. |
| GA | 16. | 14. | 15. | 13. | 16. | 16. | 15. | 13. | 15. | 13. |
| V | 164. | 135. | 136. | 130. | 125. | 127. | 135. | 138. | 129. | 116. |
| CR | 156. | 251. | 222. | 196. | 249. | 233. | 187. | 101. | 247. | 254. |
| NI | 55. | 165. | 130. | 125. | 175. | 165. | 116. | 67. | 184. | 187. |
| CU | 48. | 49. | 42. | 42. | 55. | 45. | 41. | 51. | 56. | 48. |
| ZN | 90. | 93. | 84. | 83. | 86. | 89. | 80. | 84. | 98. | 86. |
| BA | 726. | 344. | 317. | 316. | 253. | 490. | 465. | 665. | 237. | 303. |
| LA | 38. | 27. | 30. | 31. | 30. | 28. | 30. | 34. | 28. | 24. |
| CE | 76. | 50. | 59. | 64. | 55. | 57. | 61. | 70. | 53. | 49. |
| PR | 8. | 6. | 7. | 7. | 6. | 7. | 7. | 7. | 4. | 4. |
| ND | 30. | 21. | 25. | 21. | 19. | 22. | 24. | 27. | 2. | 12. |

## 2A ALKALI BASALTS (cont.)

| | K46 | K49 | K50 | K51 | K52 | K54 | K55 | K56 | K58 | K61 |
|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 44.51 | 45.83 | 47.98 | 48.32 | 47.67 | 46.40 | 47.33 | 47.16 | 48.54 | 46.57 |
| TIO2 | 1.99 | 1.86 | 1.63 | 1.60 | 1.55 | 1.58 | 1.51 | 1.68 | 1.99 | 1.47 |
| AL203 | 13.86 | 14.80 | 15.54 | 14.75 | 15.35 | 14.87 | 14.18 | 15.23 | 15.60 | 13.99 |
| FE203 | 3.52 | 2.92 | 3.44 | 2.16 | 4.12 | 3.16 | 3.06 | 4.35 | 3.49 | 3.43 |
| FEO | 6.64 | 7.90 | 6.28 | 7.84 | 6.70 | 7.88 | 7.18 | 7.18 | 6.28 | 7.62 |
| MNO | .14 | .15 | .11 | .14 | .15 | .15 | .14 | .15 | .15 | .16 |
| MGO | 11.45 | 9.66 | 7.57 | 8.67 | 7.74 | 9.09 | 8.34 | 8.57 | 6.64 | 9.73 |
| CAO | 9.75 | 9.62 | 9.88 | 9.27 | 9.16 | 8.52 | 9.24 | 8.99 | 8.33 | 7.75 |
| NA20 | 1.96 | 2.71 | 2.89 | 2.96 | 3.03 | 2.51 | 3.00 | 2.74 | 3.12 | 2.27 |
| K20 | 1.55 | .82 | 1.06 | 1.11 | .82 | .86 | 1.29 | .83 | 1.74 | .75 |
| P205 | .64 | .54 | .48 | .44 | .34 | .34 | .50 | .30 | .55 | .32 |
| H20- | 1.31 | .86 | .80 | .66 | 1.01 | 1.39 | .92 | .76 | 1.09 | .97 |
| H20+ | 1.74 | 1.43 | 1.56 | 1.02 | 1.38 | 2.17 | 1.16 | 1.32 | 1.57 | 4.02 |
| C02 | .09 | .19 | .25 | .17 | .04 | .07 | 1.13 | .14 | .00 | .12 |
| TOTAL | 99.48 | 99.50 | 99.65 | 99.33 | 99.26 | 99.19 | 99.20 | 99.60 | 99.30 | 99.32 |
| MG NO. | 71.81 | 66.69 | 63.80 | 65.92 | 61.88 | 64.91 | 64.69 | 62.77 | 60.60 | 66.48 |
| RB | 26. | 13. | 17. | 22. | 14. | 20. | 29. | 18. | 44. | 13. |
| SR | 1334. | 705. | 558. | 738. | 708. | 830. | 682. | 831. | 711. | 337. |
| Y | 23. | 24. | 21. | 22. | 20. | 21. | 22. | 21. | 25. | 19. |
| TH | 8. | 8. | 7. | 6. | 4. | 4. | 8. | 4. | 8. | 4. |
| ZR | 207. | 180. | 137. | 148. | 123. | 136. | 144. | 144. | 200. | 124. |
| NB | 83. | 66. | 60. | 54. | 43. | 41. | 64. | 34. | 65. | 35. |
| PB | 6. | 6. | 10. | 8. | 5. | 5. | 7. | 4. | 9. | 4. |
| GA | 15. | 14. | 14. | 15. | 16. | 14. | 14. | 14. | 17. | 15. |
| V | 149. | 147. | 138. | 123. | 129. | 126. | 126. | 127. | 153. | 128. |
| CR | 306. | 221. | 186. | 235. | 187. | 217. | 203. | 178. | 110. | 243. |
| NI | 236. | 174. | 103. | 144. | 81. | 168. | 169. | 139. | 49. | 199. |
| CU | 46. | 56. | 48. | 55. | 36. | 64. | 48. | 64. | 22. | 50. |
| ZN | 77. | 83. | 74. | 75. | 84. | 88. | 85. | 80. | 83. | 96. |
| BA | 652. | 292. | 299. | 443. | 445. | 218. | 405. | 228. | 455. | 177. |
| LA | 47. | 35. | 29. | 34. | 23. | 20. | 40. | 19. | 38. | 21. |
| CE | 90. | 63. | 54. | 51. | 47. | 43. | 75. | 36. | 78. | 38. |
| PR | 10. | 7. | 5. | 5. | 5. | 5. | 7. | 4. | 9. | 4. |
| ND | 33. | 23. | 19. | 19. | 18. | 19. | 23. | 14. | 28. | 11. |

## 2A ALKALI BASALTS (cont.)

| | K62 | K63 | K64 | K65 | K67 | K68 | 1906S[1] | K70 |
|---|---|---|---|---|---|---|---|---|
| SIO2 | 46.16 | 44.47 | 46.58 | 46.47 | 45.92 | 46.70 | 46.07 | 46.06 |
| TIO2 | 1.55 | 1.92 | 1.76 | 1.88 | 1.72 | 1.73 | 1.64 | 1.77 |
| AL203 | 14.49 | 14.62 | 14.40 | 14.33 | 14.13 | 15.02 | 14.63 | 14.39 |
| FE203 | 2.64 | 3.75 | 2.50 | 2.30 | 2.46 | 3.52 | 2.28 | 2.32 |
| FEO | 8.07 | 7.31 | 8.69 | 9.16 | 8.39 | 7.27 | 8.25 | 8.96 |
| MNO | .17 | .15 | .15 | .16 | .18 | .15 | .18 | .17 |
| MGO | 9.23 | 8.33 | 9.26 | 8.81 | 10.25 | 8.54 | 9.73 | 10.41 |
| CAO | 9.70 | 11.10 | 9.43 | 9.54 | 10.15 | 9.87 | 9.93 | 8.67 |
| NA20 | 2.23 | 2.63 | 2.84 | 3.01 | 2.45 | 2.49 | 3.49 | 2.63 |
| K20 | .79 | 1.24 | 1.07 | 1.19 | .77 | 1.10 | 1.20 | 1.00 |
| P205 | .46 | .73 | .46 | .52 | .61 | .44 | .94 | .44 |
| H20- | .95 | .94 | .50 | .89 | .98 | 1.03 | .45 | .73 |
| H20+ | 2.60 | .85 | 1.17 | 1.49 | 1.25 | 1.48 | .42 | .70 |
| C02 | .28 | 1.07 | .21 | .20 | .35 | .05 | .01 | .89 |
| TOTAL | 99.52 | 99.35 | 99.21 | 100.15 | 99.89 | 99.60 | 99.52 | 99.34 |
| MG NO. | 65.85 | 62.98 | 64.88 | 63.13 | 67.84 | 64.10 | 67.33 | 67.28 |
| RB | 14. | 20. | 20. | 22. | 13. | 18. | 25. | 14. |
| SR | 717. | 858. | 555. | 607. | 1241. | 722. | 1068. | 617. |
| Y | 20. | 22. | 22. | 22. | 24. | 22. | 25. | 20. |
| TH | 5. | 7. | 7. | 6. | 7. | 6. | 12. | 6. |
| ZR | 145. | 200. | 159. | 172. | 191. | 147. | 195. | 142. |
| NB | 60. | 77. | 64. | 70. | 64. | 54. | 79. | 36. |
| PB | 5. | 7. | 6. | 6. | 8. | 6. | 8. | 5. |
| GA | 12. | 17. | 16. | 15. | 15. | 16. | 15. | 17. |
| V | 126. | 143. | 136. | 141. | 134. | 149. | 128. | 153. |
| CR | 246. | 214. | 212. | 189. | 252. | 232. | 243. | 281. |
| NI | 145. | 120. | 152. | 141. | 201. | 121. | 153. | 215. |
| CU | 48. | 48. | 55. | 54. | 49. | 47. | 56. | 60. |
| ZN | 85. | 88. | 91. | 87. | 98. | 86. | 74. | 88. |
| BA | 273. | 429. | 296. | 319. | 377. | 342. | 664. | 241. |
| LA | 29. | 44. | 31. | 36. | 40. | 33. | 62. | 25. |
| CE | 54. | 84. | 55. | 70. | 73. | 65. | 109. | 49. |
| PR | 6. | 10. | 6. | 6. | 7. | 6. | 10. | 4. |
| ND | 18. | 30. | 20. | 23. | 27. | 24. | 35. | 16. |

## PHONOLITES

| 16508 | 19679 |
|---|---|
| 57.10 | 53.84 |
| .02 | .03 |
| 18.20 | 20.69 |
| 2.86 | 3.44 |
| 2.46 | .70 |
| .30 | .28 |
| .18 | .14 |
| 1.47 | .68 |
| 7.22 | 10.38 |
| 5.21 | 4.82 |
| .03 | .06 |
| .72 | .31 |
| 2.72 | 3.42 |
| .69 | .07 |
| 99.56 | 99.21 |
| 7.24 | 7.45 |
| 277. | 367. |
| 143. | 10. |
| 87. | 40. |
| 40. | 80. |
| 1750. | 1781. |
| 274. | 379. |
| 26. | 27. |
| 37. | 38. |
| 0. | 0. |
| 0. | 1. |
| 3. | 3. |
| 0. | 0. |
| 274. | 247. |
| 35. | 0. |
| 217. | 153. |
| 441. | 276. |
| 45. | 26. |
| 129. | 56. |

[1]FeO, $Na_2O$, and ignition loss determined by Mackenzie & White (1970)

## 2A BASANITES

| | K6 | K19 | K27 | K35 | K36 | K37 | K38A | K38C | K39 | K45 |
|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 44.70 | 44.39 | 43.86 | 44.57 | 44.28 | 43.40 | 46.20 | 45.48 | 44.26 | 43.32 |
| TIO2 | 2.00 | 2.19 | 2.56 | 2.21 | 2.00 | 2.53 | 2.28 | 1.91 | 2.20 | 2.03 |
| AL203 | 13.95 | 14.36 | 13.71 | 14.52 | 14.48 | 14.52 | 17.15 | 14.53 | 14.73 | 13.87 |
| FE203 | 2.42 | 2.33 | 3.41 | 3.13 | 3.08 | 2.81 | 2.44 | 5.83 | 3.01 | 3.50 |
| FEO | 7.55 | 8.24 | 7.53 | 7.78 | 8.14 | 8.10 | 7.46 | 5.60 | 7.95 | 6.78 |
| MNO | .15 | .20 | .16 | .15 | .16 | .15 | .14 | .15 | .17 | .15 |
| MGO | 11.28 | 10.99 | 9.74 | 8.75 | 9.12 | 9.43 | 5.58 | 8.87 | 9.09 | 10.83 |
| CAO | 9.80 | 9.92 | 10.00 | 9.65 | 9.94 | 9.98 | 9.82 | 9.26 | 10.05 | 9.93 |
| NA20 | 2.86 | 3.09 | 2.75 | 2.94 | 2.74 | 2.54 | 4.17 | 3.62 | 2.98 | 2.87 |
| K20 | 1.56 | 1.34 | 1.85 | 1.61 | 1.38 | 1.67 | 1.73 | 1.14 | 1.72 | 1.41 |
| P205 | .66 | .67 | 1.01 | .78 | .73 | .82 | .80 | .76 | .81 | .72 |
| H20- | .57 | .79 | .97 | .69 | .71 | 1.03 | .92 | .95 | .91 | 1.05 |
| H20+ | 1.62 | .65 | 2.30 | 1.56 | 2.43 | 2.08 | .83 | 1.45 | 1.11 | 2.10 |
| C02 | .09 | .01 | .00 | .41 | .08 | .04 | .05 | .14 | .10 | .26 |
| TOTAL | 99.39 | 99.44 | 00.12 | 99.00 | 99.49 | 99.43 | 99.81 | 99.92 | 99.34 | 99.09 |
| MG NO. | 71.68 | 69.88 | 66.73 | 64.31 | 64.59 | 65.94 | 55.78 | 64.09 | 65.05 | 70.42 |
| RB | 22. | 18. | 28. | 30. | 19. | 28. | 28. | 26. | 22. | 18. |
| SR | 538. | 822. | 721. | 890. | 768. | 1702. | 1038. | 845. | 931. | 1052. |
| Y | 19. | 26. | 22. | 22. | 23. | 26. | 22. | 22. | 23. | 24. |
| TH | 5. | 6. | 8. | 6. | 7. | 7. | 6. | 7. | 6. | 7. |
| ZR | 142. | 237. | 254. | 221. | 205. | 271. | 215. | 202. | 247. | 212. |
| NB | 56. | 77. | 102. | 83. | 67. | 92. | 108. | 75. | 87. | 83. |
| PB | 6. | 7. | 6. | 6. | 6. | 6. | 6. | 6. | 5. | 9. |
| GA | 15. | 14. | 16. | 16. | 16. | 13. | 16. | 16. | 14. | 14. |
| V | 125. | 169. | 152. | 172. | 180. | 149. | 41. | 171. | 175. | 125. |
| CR | 232. | 280. | 252. | 187. | 194. | 164. | 55. | 186. | 190. | 211. |
| NI | 115. | 221. | 158. | 148. | 155. | 141. | 41. | 150. | 127. | 188. |
| CU | 48. | 50. | 42. | 42. | 44. | 43. | 54. | 41. | 39. | 40. |
| ZN | 77. | 82. | 92. | 87. | 82. | 84. | 72. | 91. | 82. | 67. |
| BA | 291. | 479. | 644. | 445. | 275. | 404. | 542. | 328. | 365. | 458. |
| LA | 32. | 43. | 55. | 41. | 37. | 44. | 43. | 42. | 42. | 42. |
| CE | 58. | 93. | 104. | 79. | 71. | 83. | 85. | 79. | 84. | 83. |
| PR | 7. | 9. | 10. | 8. | 7. | 9. | 9. | 8. | 10. | 10. |
| ND | 26. | 30. | 31. | 27. | 28. | 29. | 29. | 29. | 30. | 28. |

| | BASANITES (cont.) | | | | 2A NEPHELINITES | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | K57 | K66 | K69 | 19052[1] | K8 | K14 | K20 | K30 | K47 | K59 |
| SIO2 | 44.70 | 44.13 | 44.44 | 44.90 | 42.84 | 42.67 | 42.97 | 41.72 | 43.17 | 43.78 |
| TIO2 | 1.89 | 2.20 | 2.15 | 1.93 | 2.53 | 2.69 | 2.49 | 2.45 | 2.36 | 2.30 |
| AL203 | 14.35 | 14.36 | 11.77 | 14.20 | 14.43 | 14.30 | 14.36 | 13.81 | 14.15 | 14.58 |
| FE203 | 3.73 | 3.12 | 3.41 | 3.45 | 4.30 | 2.81 | 3.56 | 2.72 | 3.65 | 4.46 |
| FEO | 7.19 | 7.60 | 8.02 | 7.04 | 6.86 | 8.22 | 7.46 | 8.96 | 7.48 | 6.22 |
| MNO | .15 | .15 | .16 | .18 | .17 | .19 | .19 | .18 | .17 | .17 |
| MGO | 9.30 | 9.73 | 12.85 | 10.09 | 8.16 | 10.65 | 9.65 | 8.62 | 8.52 | 9.04 |
| CAO | 9.39 | 9.54 | 8.84 | 10.05 | 9.49 | 10.23 | 9.60 | 10.11 | 10.31 | 9.61 |
| NA20 | 2.74 | 3.06 | 3.68 | 3.85 | 3.92 | 3.02 | 3.44 | 4.09 | 3.29 | 3.35 |
| K20 | 1.31 | 1.61 | .93 | 1.07 | 1.62 | 1.55 | 1.55 | 2.28 | 1.90 | 1.65 |
| P205 | .58 | .67 | .79 | 1.20 | 1.25 | .84 | 1.19 | 1.26 | 1.11 | .87 |
| H20- | 1.20 | .86 | 1.25 | .59 | .91 | .83 | .90 | .70 | 1.11 | .84 |
| H20+ | 1.97 | 2.40 | 1.39 | .86 | 2.53 | 1.83 | 2.39 | 2.43 | 1.70 | 1.84 |
| CO2 | .00 | .03 | .20 | .01 | .28 | .05 | .10 | .14 | .06 | .17 |
| TOTAL | 98.73 | 99.72 | 100.20 | 99.79 | 99.61 | 100.16 | 100.14 | 99.77 | 99.31 | 99.16 |
| MG NO. | 65.81 | 67.11 | 71.66 | 68.46 | 62.40 | 68.38 | 66.39 | 62.25 | 63.33 | 65.85 |
| RB | 24. | 24. | 18. | 42. | 36. | 19. | 19. | 23. | 26. | 20. |
| SR | 792. | 1042. | 911. | 1281. | 1363. | 1018. | 1229. | 1273. | 1474. | 1018. |
| Y | 22. | 24. | 21. | 25. | 28. | 28. | 26. | 28. | 29. | 27. |
| TH | 6. | 6. | 7. | 14. | 11. | 6. | 9. | 9. | 8. | 7. |
| ZR | 191. | 230. | 231. | 249. | 346. | 291. | 314. | 294. | 289. | 288. |
| NB | 78. | 80. | 76. | 118. | 122. | 108. | 114. | 113. | 105. | 97. |
| PB | 6. | 5. | 6. | 12. | 9. | 4. | 8. | 6. | 6. | 6. |
| GA | 16. | 14. | 15. | 16. | 17. | 14. | 17. | 14. | 16. | 15. |
| V | 149. | 132. | 142. | 137. | 119. | 158. | 121. | 127. | 140. | 141. |
| CR | 158. | 240. | 486. | 311. | 141. | 166. | 205. | 150. | 156. | 184. |
| NI | 160. | 183. | 425. | 187. | 126. | 145. | 129. | 119. | 121. | 152. |
| CU | 53. | 42. | 46. | 60. | 36. | 44. | 40. | 40. | 46. | 47. |
| ZN | 88. | 68. | 116. | 82. | 85. | 79. | 86. | 98. | 88. | 85. |
| BA | 428. | 362. | 497. | 854. | 552. | 513. | 366. | 451. | 561. | 518. |
| LA | 39. | 36. | 52. | 78. | 68. | 51. | 60. | 68. | 64. | 51. |
| CE | 80. | 75. | 104. | 133. | 129. | 105. | 123. | 127. | 121. | 96. |
| PR | 9. | 9. | 11. | 13. | 13. | 11. | 11. | 12. | 13. | 11. |
| ND | 27. | 25. | 36. | 40. | 44. | 39. | 37. | 44. | 49. | 33. |

[1] FeO, $Na_2O$, and ignition loss determined by Mackenzie & White (1970)

## 2A NEPHELINITES (cont.)

| | K60 | KX | 4168 | 19050[2] | 19053[1] | 19063[2] | 19068 | K71 | K72 |
|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 44.97 | 43.10 | 41.54 | 42.42 | 44.28 | 44.48 | 43.00 | 39.02 | 44.66 |
| TIO2 | 1.91 | 2.48 | 2.77 | 2.79 | 2.47 | 2.50 | 2.25 | 2.29 | 2.00 |
| AL203 | 17.00 | 14.15 | 13.80 | 13.60 | 14.07 | 14.12 | 12.64 | 11.41 | 15.11 |
| FE203 | 2.43 | 3.77 | 4.86 | 4.73 | 3.38 | 2.90 | 3.74 | 4.25 | 3.86 |
| FEO | 6.74 | 7.36 | 6.92 | 6.70 | 7.48 | 7.94 | 6.58 | 6.84 | 6.42 |
| MNO | .15 | .17 | .22 | .19 | .18 | .18 | .18 | .20 | .23 |
| MGO | 5.41 | 9.46 | 8.43 | 8.73 | 10.32 | 9.97 | 9.74 | 12.33 | 6.23 |
| CAO | 9.92 | 10.32 | 10.26 | 11.07 | 10.50 | 10.42 | 8.69 | 14.44 | 8.33 |
| NA2O | 4.71 | 3.42 | 4.96 | 4.30 | 3.95 | 3.93 | 3.67 | 3.53 | 6.01 |
| K2O | 2.51 | 1.97 | 1.78 | 1.35 | 1.44 | 1.40 | 2.79 | 1.59 | 1.85 |
| P2O5 | 1.24 | 1.13 | 1.35 | 1.85 | 1.34 | 1.30 | .62 | 1.35 | 1.34 |
| H2O- | .50 | .74 | .90 | .97 | .29 | .32 | 1.21 | .70 | .84 |
| H2O+ | 1.57 | 1.98 | 1.79 | 1.15 | .30 | .35 | 3.34 | .90 | 1.25 |
| CO2 | .26 | .15 | .02 | .03 | .02 | .02 | .46 | .83 | .80 |
| TOTAL | 99.70 | 100.51 | 99.98 | 100.36 | 100.41 | 100.22 | 99.23 | 99.91 | 98.93 |
| MG NO. | 56.94 | 65.75 | 61.96 | 63.49 | 68.16 | 67.35 | 68.12 | 71.62 | 57.88 |
| RB | 37. | 29. | 30. | 20. | 17. | 17. | 77. | 41. | 0. |
| SR | 1663. | 1254. | 1583. | 2067. | 1514. | 1529. | 814. | 1953. | 0. |
| Y | 26. | 26. | 32. | 30. | 26. | 27. | 22. | 11. | 0. |
| Th | 15. | 9. | 11. | 17. | 12. | 12. | 11. | 0. | 0. |
| ZR | 205. | 302. | 362. | 308. | 231. | 231. | 263. | 203. | 0. |
| NB | 146. | 111. | 151. | 158. | 102. | 98. | 71. | 119. | 0. |
| PB | 14. | 8. | 11. | 15. | 12. | 11. | 7. | 0. | 0. |
| GA | 13. | 14. | 14. | 15. | 15. | 15. | 17. | 0. | 0. |
| V | 147. | 127. | 128. | 150. | 164. | 163. | 174. | 0. | 0. |
| CR | 34. | 219. | 110. | 145. | 250. | 263. | 297. | 0. | 0. |
| NI | 40. | 132. | 111. | 109. | 194. | 182. | 255. | 0. | 0. |
| CU | 47. | 40. | 34. | 63. | 93. | 94. | 50. | 0. | 0. |
| ZN | 69. | 90. | 92. | 95. | 91. | 89. | 96. | 0. | 0. |
| BA | 1101. | 508. | 827. | 1194. | 840. | 837. | 816. | 0. | 0. |
| LA | 86. | 63. | 74. | 118. | 88. | 87. | 50. | 0. | 0. |
| CE | 150. | 118. | 146. | 210. | 156. | 157. | 97. | 0. | 0. |
| PR | 15. | 12. | 15. | 21. | 15. | 17. | 8. | 0. | 0. |
| ND | 40. | 37. | 51. | 61. | 44. | 50. | 32. | 0. | 0. |

[1]FeO, $Na_2O$, and ignition loss determined by Mackenzie & White (1970)

[2]Major element analysis by Mackenzie & White (1970)

2B ALKALI BASALTS

| | K1 | K2 | K3 | K4 | K5 | K7 | K9 | K10 | K11 | K12 | 8822 | K15 | K16 | K17 | K18 | KPH1 | K21 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 46.29 | 48.29 | 47.10 | 48.59 | 44.72 | 47.59 | 47.41 | 46.79 | 46.07 | 45.45 | 47.17 | 43.92 | 44.74 | 46.18 | 46.10 | 46.86 | 46.91 |
| TIO2 | 1.94 | 1.84 | 1.84 | 1.94 | 2.01 | 1.52 | 1.64 | 1.98 | 1.78 | 2.06 | 1.67 | 1.32 | 2.02 | 1.69 | 1.79 | 2.24 | 2.20 |
| AL203 | 14.82 | 15.28 | 14.48 | 16.29 | 14.61 | 14.85 | 15.33 | 14.48 | 14.49 | 14.58 | 14.94 | 10.08 | 14.30 | 14.72 | 14.94 | 15.63 | 15.55 |
| FE203 | 3.01 | 3.35 | 2.48 | 3.81 | 3.77 | 2.79 | 2.87 | 3.57 | 3.11 | 2.56 | 2.70 | 3.89 | 3.33 | 3.19 | 3.04 | 2.90 | 2.95 |
| FEO | 8.27 | 6.83 | 8.73 | 6.33 | 8.12 | 8.18 | 7.02 | 7.02 | 7.84 | 8.07 | 8.72 | 10.02 | 8.12 | 8.23 | 8.13 | 7.00 | 6.85 |
| MNO | .15 | .14 | .18 | .13 | .17 | .15 | .14 | .14 | .15 | .15 | .18 | .22 | .18 | .15 | .19 | .17 | .16 |
| MGO | 9.02 | 6.66 | 9.03 | 6.28 | 9.16 | 9.45 | 8.06 | 8.70 | 9.60 | 9.52 | 9.40 | 18.30 | 11.02 | 10.12 | 10.08 | 6.67 | 6.89 |
| CAO | 9.43 | 9.18 | 9.54 | 9.12 | 9.85 | 8.07 | 9.59 | 9.57 | 9.57 | 9.89 | 9.17 | 6.23 | 9.75 | 9.31 | 9.07 | 10.26 | 10.23 |
| NA20 | 2.82 | 3.08 | 2.88 | 3.45 | 2.82 | 2.75 | 2.92 | 2.75 | 2.40 | 2.27 | 2.97 | 1.79 | 2.17 | 2.41 | 2.46 | 2.83 | 2.64 |
| K20 | 1.17 | 1.39 | 1.04 | 1.24 | 1.23 | .81 | 1.11 | 1.30 | 1.03 | 1.32 | .88 | .71 | 1.01 | .79 | .78 | 1.77 | 2.02 |
| P205 | .79 | .53 | .52 | .52 | .74 | .34 | .48 | .57 | .50 | .64 | .40 | .32 | .45 | .35 | .38 | .65 | .64 |
| RB | 13. | 33. | 20. | 29. | 27. | 14. | 24. | 29. | 17. | 22. | 17. | 11. | 15. | 11. | 10. | 31. | 37. |
| SR | 440. | 849. | 597. | 945. | 855. | 376. | 915. | 2395. | 869. | 942. | 492. | 479. | 733. | 567. | 558. | 779. | 852. |
| Y | 22. | 25. | 23. | 23. | 24. | 21. | 25. | 22. | 22. | 25. | 23. | 16. | 21. | 20. | 20. | 23. | 21. |
| TH | 4. | 8. | 6. | 7. | 7. | 5. | 9. | 6. | 5. | 7. | 4. | 3. | 4. | 4. | 4. | 4. | 5. |
| ZR | 149. | 202. | 171. | 191. | 224. | 143. | 205. | 183. | 168. | 231. | 165. | 118. | 154. | 144. | 153. | 205. | 207. |
| NB | 47. | 74. | 63. | 77. | 98. | 44. | 89. | 73. | 63. | 79. | 33. | 37. | 50. | 47. | 45. | 73. | 73. |
| PB | 4. | 6. | 6. | 7. | 6. | 6. | 9. | 6. | 5. | 6. | 6. | 5. | 5. | 7. | 5. | 3. | 7. |
| GA | 16. | 16. | 18. | 17. | 19. | 16. | 15. | 16. | 14. | 17. | 17. | 13. | 16. | 15. | 18. | 17. | 16. |
| V | 144. | 143. | 142. | 142. | 140. | 128. | 139. | 146. | 143. | 143. | 140. | 106. | 174. | 135. | 153. | 163. | 153. |
| CR | 228. | 148. | 199. | 75. | 201. | 236. | 82. | 151. | 227. | 222. | 223. | 317. | 301. | 195. | 225. | 148. | 146. |
| NI | 169. | 63. | 152. | 56. | 155. | 167. | 82. | 152. | 164. | 177. | 179. | 493. | 214. | 160. | 187. | 53. | 53. |
| CU | 57. | 29. | 63. | 41. | 53. | 56. | 34. | 56. | 59. | 54. | 70. | 53. | 64. | 66. | 68. | 47. | 48. |
| ZN | 86. | 79. | 95. | 80. | 83. | 95. | 81. | 86. | 89. | 79. | 101. | 109. | 95. | 88. | 107. | 79. | 88. |
| BA | 204. | 473. | 344. | 423. | 394. | 222. | 613. | 509. | 344. | 360. | 205. | 237. | 463. | 255. | 303. | 714. | 687. |
| LA | 22. | 38. | 38. | 38. | 45. | 25. | 52. | 37. | 31. | 41. | 22. | 21. | 29. | 21. | 22. | 35. | 37. |
| CE | 43. | 72. | 69. | 75. | 92. | 48. | 103. | 76. | 61. | 82. | 44. | 34. | 55. | 44. | 43. | 85. | 71. |
| PR | 6. | 9. | 7. | 7. | 9. | 5. | 9. | 8. | 6. | 10. | 4. | 4. | 5. | 6. | 5. | 8. | 8. |
| ND | 15. | 27. | 23. | 24. | 24. | 15. | 30. | 30. | 26. | 30. | 17. | 18. | 23. | 15. | 15. | 31. | 28. |
| K/RB | 741. | 350. | 432. | 352. | 378. | 480. | 380. | 369. | 498. | 494. | 430. | 536. | 559. | 589. | 648. | 471. | 453. |
| K/NA | .42 | .45 | .36 | .36 | .44 | .30 | .38 | .47 | .43 | .58 | .30 | .40 | .47 | .33 | .32 | .62 | .77 |
| ZR/NB | 3.20 | 2.73 | 2.70 | 2.50 | 2.28 | 3.25 | 2.29 | 2.53 | 2.65 | 2.91 | 5.00 | 3.16 | 3.08 | 3.04 | 3.38 | 2.79 | 2.84 |
| MG NO. | 64.19 | 59.63 | 64.26 | 58.41 | 63.46 | 65.85 | 64.69 | 64.97 | 66.32 | 66.71 | 64.79 | 74.70 | 68.37 | 66.55 | 66.93 | 60.26 | 61.26 |

ALKALI BASALTS (cont.)

| | K22 | K23 | K24 | K25 | K26 | K28 | K29 | K31 | K32 | K33 | K34 | K42 | K44 | K46 | K49 | K50 | K51 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 46.67 | 46.76 | 47.03 | 46.89 | 46.98 | 46.05 | 46.89 | 47.49 | 46.68 | 47.19 | 46.09 | 47.62 | 47.29 | 44.74 | 46.06 | 48.15 | 48.65 |
| TIO2 | 2.23 | 2.28 | 2.21 | 2.24 | 2.09 | 1.92 | 1.99 | 1.54 | 2.11 | 2.14 | 2.22 | 1.53 | 1.44 | 2.00 | 1.87 | 1.64 | 1.61 |
| AL203 | 15.54 | 15.26 | 15.58 | 15.44 | 14.49 | 14.49 | 14.87 | 14.54 | 14.26 | 14.66 | 15.40 | 14.28 | 14.32 | 13.93 | 14.87 | 15.59 | 14.85 |
| FE203 | 3.01 | 3.47 | 2.44 | 2.45 | 2.63 | 2.21 | 2.58 | 2.61 | 2.44 | 3.11 | 3.16 | 2.82 | 3.29 | 3.54 | 2.93 | 3.45 | 2.17 |
| FEO | 6.78 | 6.60 | 7.41 | 7.47 | 8.32 | 9.06 | 8.07 | 8.22 | 8.35 | 7.26 | 7.25 | 8.15 | 7.65 | 6.67 | 7.94 | 6.30 | 7.89 |
| MNO | .16 | .13 | .16 | .15 | .15 | .15 | .14 | .14 | .14 | .14 | .15 | .15 | .15 | .14 | .15 | .11 | .14 |
| MGO | 6.70 | 6.02 | 6.83 | 6.52 | 9.15 | 9.45 | 8.38 | 9.32 | 9.58 | 8.16 | 7.14 | 9.43 | 9.61 | 11.51 | 9.71 | 7.60 | 8.73 |
| CAO | 10.38 | 10.40 | 10.58 | 10.27 | 9.51 | 9.75 | 9.46 | 8.82 | 8.75 | 9.35 | 10.23 | 8.07 | 9.38 | 9.80 | 9.67 | 9.91 | 9.33 |
| NA20 | 2.66 | 2.70 | 2.87 | 2.56 | 2.89 | 3.02 | 2.64 | 2.86 | 2.98 | 2.88 | 2.39 | 2.94 | 2.45 | 1.97 | 2.72 | 2.90 | 2.98 |
| K20 | 2.10 | 2.08 | 1.81 | 2.44 | 1.15 | 1.32 | 1.41 | 1.13 | 1.48 | 1.65 | 1.99 | 1.12 | .91 | 1.56 | .82 | 1.06 | 1.12 |
| P205 | .63 | .64 | .61 | .64 | .49 | .60 | .49 | .40 | .48 | .57 | .69 | .38 | .34 | .64 | .54 | .48 | .44 |
| RB | 41. | 29. | 59. | 47. | 20. | 19. | 24. | 26. | 31. | 28. | 43. | 21. | 19. | 26. | 13. | 17. | 22. |
| SR | 830. | 687. | 724. | 796. | 685. | 797. | 656. | 1215. | 561. | 732. | 529. | 432. | 1380. | 1341. | 709. | 560. | 743. |
| Y | 22. | 21. | 21. | 21. | 19. | 20. | 22. | 21. | 20. | 20. | 24. | 21. | 19. | 23. | 24. | 21. | 22. |
| TH | 5. | 5. | 5. | 5. | 5. | 5. | 6. | 6. | 5. | 6. | 7. | 6. | 6. | 8. | 8. | 7. | 6. |
| ZR | 205. | 195. | 203. | 205. | 150. | 151. | 206. | 144. | 174. | 168. | 219. | 141. | 122. | 208. | 181. | 137. | 149. |
| NB | 73. | 72. | 72. | 73. | 62. | 53. | 68. | 46. | 60. | 60. | 89. | 49. | 37. | 83. | 66. | 60. | 54. |
| PB | 6. | 5. | 5. | 5. | 5. | 5. | 4. | 7. | 6. | 6. | 6. | 7. | 4. | 6. | 6. | 10. | 8. |
| GA | 16. | 17. | 16. | 16. | 14. | 15. | 13. | 16. | 16. | 15. | 13. | 15. | 13. | 15. | 14. | 14. | 15. |
| V | 164. | 153. | 162. | 165. | 136. | 137. | 131. | 126. | 128. | 135. | 139. | 130. | 117. | 150. | 148. | 138. | 124. |
| CR | 157. | 156. | 153. | 157. | 252. | 224. | 197. | 251. | 234. | 187. | 101. | 248. | 257. | 308. | 222. | 187. | 237. |
| NI | 55. | 53. | 55. | 55. | 166. | 131. | 126. | 176. | 166. | 116. | 67. | 185. | 189. | 237. | 175. | 103. | 145. |
| CU | 47. | 43. | 46. | 48. | 49. | 42. | 42. | 55. | 45. | 41. | 51. | 56. | 49. | 46. | 56. | 48. | 55. |
| ZN | 90. | 75. | 89. | 91. | 94. | 85. | 84. | 87. | 90. | 80. | 84. | 99. | 87. | 77. | 83. | 74. | 76. |
| BA | 717. | 682. | 701. | 731. | 346. | 319. | 318. | 255. | 493. | 465. | 667. | 238. | 307. | 655. | 293. | 300. | 446. |
| LA | 38. | 34. | 37. | 38. | 27. | 30. | 31. | 30. | 28. | 30. | 34. | 28. | 24. | 47. | 35. | 29. | 34. |
| CE | 76. | 73. | 74. | 76. | 50. | 59. | 64. | 55. | 57. | 61. | 70. | 53. | 50. | 90. | 63. | 54. | 51. |
| PR | 9. | 7. | 7. | 8. | 6. | 7. | 7. | 6. | 7. | 7. | 7. | 4. | 4. | 10. | 7. | 5. | 5. |
| ND | 27. | 24. | 27. | 30. | 21. | 25. | 21. | 19. | 22. | 24. | 27. | 2. | 12. | 33. | 23. | 19. | 19. |
| K/RB | 425. | 590. | 253. | 427. | 473. | 572. | 484. | 358. | 394. | 489. | 382. | 439. | 393. | 495. | 524. | 518. | 419. |
| K/NA | .79 | .77 | .63 | .95 | .40 | .44 | .53 | .39 | .50 | .57 | .83 | .38 | .37 | .79 | .30 | .37 | .37 |
| ZR/NB | 2.81 | 2.72 | 2.81 | 2.79 | 2.40 | 2.83 | 3.01 | 3.11 | 2.88 | 2.80 | 2.45 | 2.86 | 3.27 | 2.49 | 2.73 | 2.28 | 2.74 |
| MG NO. | 60.63 | 57.49 | 60.80 | 59.55 | 55.14 | 65.11 | 63.78 | 65.80 | 66.48 | 63.90 | 60.68 | 65.82 | 66.41 | 71.61 | 66.69 | 63.80 | 65.92 |

## 2B ALKALI BASALTS (cont.)

| | K52 | K54 | K55 | K56 | K58 | K61 | K62 | K63 | K64 | K65 | K67 | K68 | 19065 | K70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 48.03 | 46.78 | 47.71 | 47.35 | 48.88 | 46.89 | 46.38 | 44.76 | 46.95 | 46.40 | 45.97 | 46.89 | 46.29 | 46.37 |
| TIO2 | 1.56 | 1.59 | 1.52 | 1.69 | 2.00 | 1.48 | 1.56 | 1.93 | 1.77 | 1.88 | 1.72 | 1.74 | 1.65 | 1.78 |
| AL203 | 15.46 | 14.99 | 14.30 | 15.29 | 15.71 | 14.09 | 14.56 | 14.72 | 14.51 | 14.31 | 14.15 | 15.08 | 14.70 | 14.49 |
| FE203 | 4.15 | 3.19 | 3.08 | 4.37 | 3.51 | 3.45 | 2.65 | 3.77 | 2.52 | 2.30 | 2.46 | 3.53 | 2.29 | 2.34 |
| FEO | 6.75 | 7.94 | 7.24 | 7.21 | 6.32 | 7.67 | 8.11 | 7.36 | 8.76 | 9.15 | 8.40 | 7.30 | 8.29 | 9.02 |
| MNO | .15 | .15 | .14 | .15 | .15 | .16 | .17 | .15 | .15 | .16 | .18 | .15 | .18 | .17 |
| MGO | 7.80 | 9.16 | 8.41 | 8.60 | 6.69 | 9.80 | 9.27 | 8.36 | 9.33 | 8.80 | 10.26 | 8.57 | 9.78 | 10.48 |
| CAO | 9.23 | 8.59 | 9.31 | 9.03 | 8.39 | 7.80 | 9.75 | 11.17 | 9.51 | 9.53 | 10.16 | 9.91 | 9.98 | 8.73 |
| NA20 | 3.05 | 2.53 | 3.02 | 2.75 | 3.14 | 2.29 | 2.24 | 2.65 | 2.86 | 3.01 | 2.45 | 2.50 | 3.51 | 2.65 |
| K20 | .83 | .87 | 1.30 | .83 | 1.75 | .76 | .79 | 1.25 | 1.08 | 1.19 | .77 | 1.10 | 1.21 | 1.01 |
| P205 | .34 | .34 | .50 | .30 | .55 | .32 | .46 | .73 | .46 | .52 | .61 | .44 | .94 | .44 |
| RB | 14. | 20. | 29. | 18. | 44. | 13. | 14. | 20. | 20. | 22. | 13. | 18. | 25. | 14. |
| SR | 713. | 837. | 688. | 834. | 716. | 339. | 720. | 864. | 559. | 606. | 1242. | 725. | 1073. | 621. |
| Y | 20. | 21. | 22. | 21. | 25. | 19. | 20. | 22. | 22. | 22. | 24. | 22. | 25. | 20. |
| TH | 4. | 4. | 8. | 4. | 8. | 4. | 5. | 7. | 7. | 6. | 7. | 6. | 12. | 6. |
| ZR | 124. | 137. | 145. | 145. | 201. | 125. | 146. | 201. | 160. | 172. | 191. | 148. | 196. | 143. |
| NB | 43. | 41. | 65. | 34. | 65. | 35. | 60. | 78. | 65. | 70. | 64. | 54. | 79. | 36. |
| PB | 5. | 5. | 7. | 4. | 9. | 4. | 5. | 7. | 6. | 6. | 8. | 6. | 8. | 5. |
| GA | 16. | 14. | 14. | 14. | 17. | 15. | 12. | 17. | 16. | 15. | 15. | 16. | 15. | 17. |
| V | 130. | 127. | 127. | 128. | 154. | 129. | 127. | 144. | 137. | 141. | 134. | 150. | 129. | 154. |
| CR | 188. | 219. | 205. | 179. | 111. | 245. | 247. | 215. | 214. | 189. | 252. | 233. | 244. | 283. |
| NI | 82. | 169. | 170. | 140. | 49. | 200. | 146. | 121. | 153. | 141. | 201. | 121. | 154. | 216. |
| CU | 36. | 65. | 48. | 64. | 22. | 50. | 48. | 48. | 55. | 54. | 49. | 47. | 56. | 60. |
| ZN | 85. | 89. | 86. | 80. | 84. | 97. | 85. | 89. | 92. | 87. | 98. | 86. | 74. | 89. |
| BA | 448. | 220. | 408. | 229. | 458. | 178. | 274. | 432. | 298. | 319. | 377. | 343. | 667. | 243. |
| LA | 23. | 20. | 40. | 19. | 38. | 21. | 29. | 44. | 31. | 36. | 40. | 33. | 62. | 25. |
| CE | 47. | 43. | 76. | 36. | 79. | 38. | 54. | 85. | 55. | 70. | 73. | 65. | 110. | 49. |
| PR | 5. | 5. | 7. | 4. | 9. | 4. | 6. | 10. | 6. | 6. | 7. | 6. | 10. | 4. |
| ND | 18. | 19. | 23. | 14. | 28. | 11. | 18. | 30. | 20. | 23. | 27. | 24. | 35. | 16. |
| K/RB | 486. | 357. | 369. | 383. | 328. | 479. | 468. | 515. | 444. | 449. | 492. | 507. | 398. | 593. |
| K/NA | .27 | .34 | .43 | .30 | .56 | .33 | .35 | .47 | .38 | .40 | .31 | .44 | .34 | .38 |
| ZR/NB | 2.86 | 3.32 | 2.25 | 4.24 | 3.08 | 3.54 | 2.42 | 2.60 | 2.48 | 2.46 | 2.98 | 2.72 | 2.47 | 3.94 |
| MG NO. | 61.88 | 64.91 | 64.69 | 62.77 | 60.60 | 66.48 | 65.85 | 62.98 | 64.88 | 63.13 | 67.84 | 64.10 | 67.33 | 67.28 |

## 2B BASANITES

| | K6 | K19 | K27 | K35 | K36 | K37 | K38A | K38C | K39 | K45 | K57 | K66 | K69 | 19052 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 44.97 | 44.64 | 43.81 | 45.02 | 44.51 | 43.65 | 46.29 | 45.52 | 44.56 | 43.72 | 45.27 | 44.25 | 44.35 | 45.00 |
| TIO2 | 2.01 | 2.20 | 2.58 | 2.23 | 2.01 | 2.54 | 2.28 | 1.91 | 2.21 | 2.05 | 1.91 | 2.21 | 2.15 | 1.93 |
| AL203 | 14.04 | 14.44 | 13.69 | 14.67 | 14.55 | 14.60 | 17.18 | 14.54 | 14.83 | 14.00 | 14.53 | 14.40 | 11.75 | 14.23 |
| FE203 | 2.43 | 2.34 | 3.41 | 3.16 | 3.10 | 2.83 | 2.44 | 5.83 | 3.03 | 3.53 | 3.78 | 3.13 | 3.40 | 3.46 |
| FEO | 7.60 | 8.29 | 7.52 | 7.86 | 8.18 | 8.15 | 7.47 | 5.60 | 8.00 | 6.84 | 7.28 | 7.62 | 8.00 | 7.06 |
| MNO | .15 | .20 | .16 | .15 | .16 | .15 | .14 | .15 | .17 | .15 | .15 | .15 | .16 | .18 |
| MGO | 11.35 | 11.05 | 9.73 | 8.84 | 9.17 | 9.48 | 5.59 | 8.88 | 9.15 | 10.93 | 9.42 | 9.76 | 12.82 | 10.11 |
| CAO | 9.86 | 9.98 | 9.99 | 9.75 | 9.99 | 10.04 | 9.84 | 9.27 | 10.12 | 10.02 | 9.51 | 9.57 | 8.82 | 10.07 |
| NA20 | 2.88 | 3.11 | 2.75 | 2.97 | 2.75 | 2.55 | 4.18 | 3.62 | 3.00 | 2.90 | 2.78 | 3.07 | 3.67 | 3.86 |
| K20 | 1.57 | 1.35 | 1.85 | 1.63 | 1.39 | 1.68 | 1.73 | 1.14 | 1.73 | 1.42 | 1.33 | 1.61 | .93 | 1.07 |
| P205 | .66 | .67 | 1.01 | .79 | .73 | .82 | .80 | .76 | .82 | .73 | .59 | .67 | .79 | 1.20 |
| RB | 22. | 18. | 28. | 30. | 19. | 28. | 28. | 26. | 22. | 18. | 24. | 24. | 18. | 42. |
| SR | 541. | 827. | 720. | 899. | 772. | 1712. | 1040. | 846. | 937. | 1062. | 802. | 1045. | 909. | 1284. |
| Y | 19. | 26. | 22. | 22. | 23. | 26. | 22. | 22. | 23. | 24. | 22. | 24. | 21. | 25. |
| TH | 5. | 6. | 8. | 6. | 7. | 7. | 6. | 7. | 6. | 7. | 6. | 6. | 7. | 14. |
| ZR | 143. | 238. | 254. | 223. | 206. | 273. | 215. | 202. | 249. | 214. | 193. | 231. | 231. | 250. |
| NB | 56. | 77. | 102. | 84. | 67. | 93. | 108. | 75. | 88. | 84. | 79. | 80. | 76. | 116. |
| PB | 6. | 7. | 6. | 6. | 6. | 6. | 6. | 6. | 5. | 9. | 6. | 5. | 6. | 12. |
| GA | 15. | 14. | 16. | 16. | 16. | 13. | 16. | 16. | 14. | 14. | 16. | 14. | 15. | 16. |
| V | 126. | 170. | 152. | 174. | 181. | 150. | 41. | 171. | 176. | 126. | 151. | 132. | 142. | 137. |
| CR | 233. | 282. | 252. | 189. | 195. | 165. | 55. | 186. | 191. | 213. | 160. | 241. | 485. | 312. |
| NI | 116. | 222. | 158. | 149. | 156. | 142. | 41. | 150. | 128. | 190. | 162. | 164. | 424. | 187. |
| CU | 48. | 50. | 42. | 42. | 44. | 43. | 54. | 41. | 39. | 40. | 54. | 42. | 46. | 60. |
| ZN | 77. | 82. | 92. | 88. | 82. | 84. | 72. | 91. | 83. | 68. | 89. | 68. | 116. | 82. |
| BA | 293. | 482. | 643. | 449. | 276. | 406. | 543. | 328. | 367. | 462. | 433. | 363. | 496. | 856. |
| LA | 32. | 43. | 55. | 41. | 37. | 44. | 43. | 42. | 42. | 42. | 40. | 36. | 52. | 78. |
| CE | 58. | 94. | 104. | 80. | 71. | 83. | 85. | 79. | 85. | 84. | 81. | 75. | 104. | 133. |
| PR | 7. | 9. | 10. | 8. | 7. | 9. | 9. | 8. | 10. | 10. | 9. | 9. | 11. | 13. |
| ND | 26. | 30. | 31. | 27. | 28. | 29. | 29. | 29. | 30. | 28. | 27. | 25. | 36. | 40. |
| K/RB | 589. | 618. | 548. | 446. | 603. | 495. | 513. | 364. | 649. | 650. | 453. | 557. | 429. | 211. |
| K/NA | .55 | .43 | .67 | .55 | .50 | .66 | .41 | .31 | .58 | .49 | .48 | .53 | .25 | .28 |
| ZR/NB | 2.54 | 3.08 | 2.49 | 2.66 | 3.06 | 2.95 | 1.99 | 2.69 | 2.64 | 2.55 | 2.45 | 2.87 | 3.04 | 2.11 |
| MG NO. | 71.68 | 69.88 | 66.73 | 64.31 | 64.59 | 65.94 | 55.78 | 64.09 | 65.05 | 70.42 | 65.81 | 67.11 | 71.66 | 66.46 |

| | 2B NEPHELINITES | | | | | | | | | | | | | | | PHONOLITES | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | K8 | K14 | K20 | K30 | K47 | K59 | K60 | KX | 4168 | 19050 | 19053 | 19063 | 19068 | K71 | K72 | 16508 | 19679 |
| SIO2 | 43.01 | 42.60 | 42.91 | 41.82 | 43.47 | 44.15 | 45.10 | 42.88 | 41.55 | 42.27 | 44.10 | 44.38 | 43.34 | 39.05 | 45.14 | 57.35 | 54.27 |
| TIO2 | 2.54 | 2.69 | 2.49 | 2.46 | 2.38 | 2.32 | 1.92 | 2.47 | 2.77 | 2.78 | 2.46 | 2.49 | 2.27 | 2.29 | 2.02 | .02 | .03 |
| AL203 | 14.49 | 14.28 | 14.34 | 13.84 | 14.25 | 14.70 | 17.05 | 14.08 | 13.80 | 13.55 | 14.01 | 14.09 | 12.74 | 11.42 | 15.27 | 18.28 | 20.86 |
| FE203 | 4.32 | 2.81 | 3.55 | 2.73 | 3.68 | 4.50 | 2.44 | 3.75 | 4.86 | 4.71 | 3.37 | 2.89 | 3.77 | 4.25 | 3.90 | 2.87 | 3.47 |
| FEO | 6.89 | 8.21 | 7.45 | 8.98 | 7.53 | 6.27 | 6.76 | 7.32 | 6.92 | 6.68 | 7.45 | 7.92 | 6.63 | 6.85 | 6.49 | 2.47 | .71 |
| MNO | .17 | .19 | .19 | .18 | .17 | .17 | .15 | .17 | .22 | .19 | .18 | .18 | .18 | .20 | .23 | .30 | .28 |
| MGO | 8.19 | 10.63 | 9.64 | 8.64 | 8.58 | 9.12 | 5.43 | 9.41 | 8.43 | 8.70 | 10.28 | 9.95 | 9.82 | 12.34 | 6.30 | .18 | .14 |
| CAO | 9.53 | 10.21 | 9.59 | 10.13 | 10.38 | 9.69 | 9.95 | 10.27 | 10.26 | 11.03 | 10.46 | 10.40 | 8.76 | 14.45 | 8.42 | 1.48 | .69 |
| NA20 | 3.94 | 3.02 | 3.44 | 4.10 | 3.31 | 3.38 | 4.72 | 3.40 | 4.96 | 4.28 | 3.93 | 3.92 | 3.70 | 3.53 | 6.08 | 7.25 | 10.46 |
| K20 | 1.63 | 1.55 | 1.55 | 2.29 | 1.91 | 1.66 | 2.52 | 1.96 | 1.78 | 1.35 | 1.43 | 1.40 | 2.81 | 1.59 | 1.87 | 5.23 | 4.86 |
| P205 | 1.25 | .84 | 1.19 | 1.26 | 1.12 | .88 | 1.24 | 1.12 | 1.36 | 1.84 | 1.33 | 1.30 | .62 | 1.35 | 1.35 | .03 | .06 |
| RB | 36. | 19. | 19. | 23. | 26. | 20. | 37. | 29. | 30. | 20. | 17. | 17. | 78. | 41. | 0. | 278. | 370. |
| SR | 1368. | 1016. | 1227. | 1276. | 1484. | 1027. | 1668. | 1248. | 1583. | 2060. | 1508. | 1526. | 820. | 1955. | 0. | 144. | 10. |
| Y | 28. | 28. | 26. | 28. | 29. | 27. | 26. | 26. | 32. | 30. | 26. | 27. | 22. | 11. | 0. | 87. | 40. |
| TH | 11. | 6. | 9. | 9. | 8. | 7. | 15. | 9. | 11. | 17. | 12. | 12. | 11. | 0. | 0. | 40. | 81. |
| ZR | 347. | 291. | 314. | 295. | 291. | 290. | 206. | 300. | 362. | 307. | 230. | 230. | 265. | 203. | 0. | 1758. | 1795. |
| NB | 122. | 108. | 114. | 113. | 106. | 98. | 146. | 110. | 151. | 157. | 102. | 98. | 72. | 119. | 0. | 275. | 382. |
| PB | 9. | 4. | 8. | 6. | 6. | 6. | 14. | 8. | 11. | 15. | 12. | 11. | 7. | 0. | 0. | 26. | 27. |
| GA | 17. | 14. | 17. | 14. | 16. | 15. | 13. | 14. | 14. | 15. | 15. | 15. | 17. | 0. | 0. | 37. | 38. |
| V | 119. | 158. | 121. | 127. | 141. | 142. | 147. | 126. | 128. | 149. | 163. | 163. | 175. | 0. | 0. | 0. | 0. |
| CR | 142. | 166. | 205. | 150. | 157. | 186. | 34. | 218. | 110. | 144. | 249. | 262. | 299. | 0. | 0. | 0. | 1. |
| NI | 126. | 145. | 129. | 119. | 122. | 153. | 40. | 131. | 111. | 109. | 193. | 182. | 257. | 0. | 0. | 3. | 3. |
| CU | 36. | 44. | 40. | 40. | 46. | 47. | 47. | 40. | 34. | 63. | 93. | 94. | 50. | 0. | 0. | 0. | 0. |
| ZN | 85. | 79. | 86. | 98. | 89. | 86. | 69. | 90. | 92. | 95. | 91. | 89. | 97. | 0. | 0. | 275. | 249. |
| BA | 554. | 512. | 365. | 452. | 565. | 522. | 1104. | 505. | 827. | 1190. | 837. | 835. | 822. | 0. | 0. | 35. | 0. |
| LA | 68. | 51. | 60. | 68. | 64. | 51. | 86. | 63. | 74. | 118. | 88. | 87. | 50. | 0. | 0. | 218. | 154. |
| CE | 129. | 105. | 123. | 127. | 122. | 97. | 150. | 117. | 146. | 209. | 155. | 157. | 98. | 0. | 0. | 443. | 278. |
| PR | 13. | 11. | 11. | 12. | 13. | 11. | 15. | 12. | 15. | 21. | 15. | 17. | 8. | 0. | 0. | 45. | 26. |
| ND | 44. | 39. | 37. | 44. | 49. | 33. | 40. | 37. | 51. | 61. | 44. | 50. | 32. | 0. | 0. | 130. | 56. |
| K/RB | 374. | 477. | 677. | 823. | 607. | 685. | 563. | 564. | 493. | 560. | 703. | 684. | 301. | 322. | 0. | 156. | 109. |
| K/NA | .41 | .51 | .45 | .56 | .58 | .49 | .53 | .58 | .36 | .31 | .36 | .36 | .76 | .45 | .31 | .72 | .46 |
| ZR/NB | 2.84 | 2.69 | 2.75 | 2.60 | 2.75 | 2.97 | 1.40 | 2.72 | 2.40 | 1.95 | 2.26 | 2.36 | 3.70 | 1.71 | .00 | 6.39 | 4.70 |
| MG NO. | 62.40 | 68.38 | 66.39 | 62.25 | 63.33 | 65.85 | 56.94 | 65.75 | 61.96 | 63.49 | 68.16 | 67.35 | 68.12 | 71.62 | 57.88 | 7.24 | 7.45 |

APPENDIX 2C

C.I.P.W. NORMS, WEIGHT PERCENT (ANHYDROUS BASIS) $Fe_2O_3/FeO=0.25$

ALKALI BASALTS

| | K1 | K2 | K3 | K4 | K5 | K7 | K9 | K10 | K11 | K12 | 8822 | K15 | K16 | K17 | K18 | KPH1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Q-CLASE | 7.10 | 8.53 | 6.31 | 7.51 | 7.50 | 4.98 | 6.77 | 7.94 | 6.30 | 8.06 | 5.30 | 4.36 | 6.16 | 4.79 | 4.77 | 10.77 |
| ALBITE | 24.20 | 27.05 | 24.94 | 29.89 | 18.23 | 24.10 | 25.56 | 24.06 | 21.03 | 19.90 | 25.60 | 15.67 | 18.43 | 21.02 | 21.47 | 21.90 |
| ANORTH | 24.88 | 24.61 | 23.99 | 25.97 | 24.27 | 26.74 | 26.40 | 24.11 | 26.68 | 26.65 | 25.29 | 17.95 | 27.09 | 27.83 | 28.30 | 25.50 |
| NEPHEL | 0.13 | 0.0 | 0.0 | 0.0 | 3.43 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.28 | 0.0 | 0.0 | 1.53 |
| DIOPSIDE | 14.37 | 15.50 | 16.96 | 13.78 | 17.07 | 19.10 | 15.91 | 17.08 | 15.48 | 16.93 | 14.91 | 9.49 | 15.93 | 14.06 | 12.59 | 18.37 |
| HYPERSTH | 0.0 | 5.76 | 0.45 | 2.12 | 0.0 | 13.89 | 2.69 | 0.84 | 4.90 | 1.37 | 0.45 | 8.22 | 0.0 | 6.28 | 6.95 | 0.0 |
| OLIVINE | 20.31 | 10.60 | 19.20 | 12.71 | 20.26 | 13.07 | 15.31 | 17.57 | 17.60 | 19.18 | 20.90 | 36.80 | 23.66 | 18.46 | 18.16 | 13.02 |
| FE304 | 3.33 | 3.02 | 3.32 | 2.96 | 3.51 | 3.28 | 2.94 | 3.13 | 3.26 | 3.18 | 3.36 | 4.14 | 3.39 | 3.38 | 3.32 | 2.93 |
| ILMENITE | 3.78 | 3.63 | 3.57 | 3.79 | 3.92 | 3.00 | 3.22 | 3.88 | 3.51 | 4.05 | 3.23 | 2.59 | 3.96 | 3.32 | 3.50 | 4.39 |
| APATITE | 1.91 | 1.30 | 1.26 | 1.27 | 1.81 | 0.84 | 1.18 | 1.41 | 1.24 | 1.58 | 0.96 | 0.79 | 1.10 | 0.86 | 0.93 | 1.59 |

| | K21 | K22 | K23 | K24 | K25 | K26 | K28 | K29 | K31 | K32 | K33 | K34 | K42 | K44 | K49 | K46 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Q-CLASE | 12.32 | 12.84 | 12.76 | 10.96 | 14.83 | 6.92 | 7.95 | 8.59 | 6.87 | 8.99 | 10.03 | 12.15 | 6.84 | 5.56 | 5.01 | 9.55 |
| ALBITE | 20.37 | 18.92 | 20.51 | 20.07 | 17.84 | 24.34 | 15.24 | 23.03 | 24.94 | 23.14 | 23.87 | 19.27 | 25.76 | 21.42 | 23.70 | 15.95 |
| ANORTH | 25.35 | 25.04 | 24.29 | 24.89 | 24.17 | 23.71 | 22.52 | 25.35 | 24.20 | 21.77 | 23.38 | 26.31 | 23.31 | 26.24 | 26.66 | 25.49 |
| NEPHEL | 1.46 | 2.36 | 1.16 | 2.63 | 2.41 | 0.34 | 3.70 | 0.0 | 0.0 | 1.50 | 0.65 | 0.90 | 0.0 | 0.0 | C.0 | 0.73 |
| DIOPSIDE | 18.40 | 19.42 | 20.39 | 20.15 | 19.49 | 17.18 | 18.44 | 16.01 | 14.74 | 15.86 | 16.57 | 17.49 | 12.66 | 15.82 | 15.37 | 16.52 |
| HYPERSTH | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | C.0 | 2.40 | 3.88 | 0.0 | 0.0 | 0.0 | 7.23 | 9.67 | C.27 | 0.0 |
| OLIVINE | 13.32 | 12.59 | 11.23 | 12.59 | 12.34 | 19.02 | 15.64 | 16.33 | 18.14 | 20.23 | 16.85 | 14.74 | 16.97 | 14.38 | 20.81 | 23.21 |
| FE304 | 2.90 | 2.90 | 2.99 | 2.92 | 2.95 | 3.23 | 3.33 | 3.17 | 3.22 | 3.21 | 3.06 | 3.09 | 3.28 | 3.24 | 3.22 | 3.03 |
| ILMENITE | 4.31 | 4.38 | 4.50 | 4.30 | 4.39 | 4.06 | 3.73 | 3.91 | 3.02 | 4.13 | 4.18 | 4.36 | 3.01 | 2.82 | 3.65 | 3.94 |
| APATITE | 1.56 | 1.54 | 1.56 | 1.49 | 1.57 | 1.19 | 1.46 | 1.21 | 0.98 | 1.18 | 1.39 | 1.70 | 0.94 | 0.84 | 1.32 | 1.58 |

| | K50 | K51 | K52 | K54 | K55 | K56 | K58 | K61 | K62 | K63 | K64 | K65 | K67 | K68 | K7C | 19065 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Q-CLASE | 5.48 | 6.74 | 5.02 | 5.33 | 7.97 | 5.06 | 10.68 | 4.72 | 4.89 | 7.62 | 6.51 | 7.22 | 4.69 | 6.72 | 6.10 | 7.21 |
| ALBITE | 25.28 | 25.75 | 26.58 | 22.29 | 26.53 | 25.91 | 27.41 | 20.44 | 19.77 | 15.68 | 23.93 | 22.71 | 21.36 | 21.79 | 22.98 | 19.24 |
| ANORTH | 27.19 | 24.35 | 26.81 | 28.09 | 22.38 | 27.64 | 24.32 | 27.43 | 26.49 | 25.41 | 24.07 | 22.66 | 26.06 | 27.46 | 25.31 | 21.05 |
| NEPHEL | 0.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.05 | 0.44 | 1.86 | 0.0 | 0.0 | C.0 | 5.84 |
| DIOPSIDE | 16.41 | 16.17 | 14.65 | 11.30 | 17.93 | 13.27 | 12.08 | 9.12 | 15.21 | 21.85 | 17.01 | 18.22 | 17.55 | 16.38 | 13.04 | 18.41 |
| HYPERSTH | 5.63 | 5.40 | 6.51 | 12.05 | 0.47 | 8.15 | 7.08 | 22.90 | 11.73 | 0.0 | 0.0 | 0.0 | 2.57 | 4.78 | 2.89 | 0.10 |
| OLIVINE | 11.77 | 14.42 | 13.34 | 13.61 | 17.43 | 14.58 | 10.25 | 8.24 | 12.46 | 16.52 | 20.14 | 18.98 | 19.69 | 15.21 | 21.75 | 19.72 |
| FE304 | 2.87 | 2.98 | 3.19 | 3.33 | 3.07 | 3.38 | 2.85 | 3.37 | 3.24 | 3.29 | 3.33 | 3.41 | 3.23 | 3.19 | 3.38 | 3.10 |
| ILMENITE | 3.20 | 3.12 | 3.05 | 3.15 | 3.00 | 3.29 | 3.92 | 2.97 | 3.08 | 3.79 | 3.44 | 3.67 | 3.37 | 3.40 | 3.47 | 3.17 |
| APATITE | 1.18 | 1.07 | 0.83 | 0.85 | 1.24 | 0.73 | 1.35 | 0.81 | 1.14 | 1.80 | 1.12 | 1.26 | 1.49 | 1.08 | 1.08 | 2.26 |

BASANITES

| | K6 | K19 | K27 | K35 | K36 | K37 | K38A | K38C | K39 | K45 | K57 | K66 | K69 | 19052 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Q-CLASE | 9.51 | 8.10 | 11.33 | 9.91 | 8.49 | 10.29 | 10.46 | 6.96 | 10.49 | 8.74 | 8.13 | 9.90 | 5.67 | 6.46 |
| ALBITE | 13.37 | 13.08 | 13.17 | 17.15 | 16.68 | 13.43 | 15.28 | 21.23 | 13.21 | 12.13 | 19.60 | 14.18 | 17.16 | 17.41 |
| ANORTH | 21.27 | 21.85 | 20.31 | 22.56 | 24.10 | 24.27 | 23.49 | 20.69 | 22.42 | 21.82 | 24.15 | 21.53 | 13.25 | 18.70 |
| NEPHEL | 6.28 | 7.41 | 5.93 | 4.74 | 4.05 | 4.86 | 9.11 | 5.64 | 6.94 | 7.23 | 2.58 | 6.91 | 8.10 | 8.60 |
| DIOPSIDE | 19.61 | 19.32 | 19.55 | 17.79 | 18.06 | 17.55 | 17.15 | 17.53 | 19.05 | 20.04 | 16.83 | 18.68 | 21.39 | 19.53 |
| OLIVINE | 21.45 | 21.24 | 18.55 | 18.29 | 19.50 | 19.59 | 17.23 | 19.04 | 18.35 | 21.11 | 20.23 | 19.59 | 24.90 | 19.59 |
| FE304 | 2.97 | 3.13 | 3.25 | 3.27 | 3.36 | 3.28 | 2.92 | 3.31 | 3.25 | 3.08 | 3.28 | 3.20 | 3.38 | 3.07 |
| ILMENITE | 3.92 | 4.26 | 5.04 | 4.37 | 3.96 | 5.01 | 4.43 | 3.75 | 4.31 | 4.05 | 3.77 | 4.35 | 3.21 | 3.74 |
| APATITE | 1.61 | 1.62 | 2.48 | 1.92 | 1.80 | 2.02 | 1.94 | 1.86 | 1.98 | 1.79 | 1.44 | 1.65 | 1.93 | 2.90 |

NEPHELINITES

| | K8 | K14 |
|---|---|---|
| Q-CLASE | 10.03 | 9.43 |
| ALBITE | 14.05 | 8.31 |
| ANORTH | 17.81 | 21.50 |
| NEPHEL | 11.22 | 9.75 |
| DIOPSIDE | 18.61 | 20.18 |
| OLIVINE | 16.81 | 20.26 |
| FE304 | 3.33 | 3.27 |
| ILMENITE | 5.04 | 5.26 |
| APATITE | 3.10 | 2.05 |

| | K20 | K30 | K47 | K59 | K60 | KX | 4168 | 19050 |
|---|---|---|---|---|---|---|---|---|
| Q-CLASE | 9.50 | 14.00 | 11.69 | 10.17 | 15.29 | 11.97 | 10.88 | 8.18 |
| ALBITE | 13.18 | 2.47 | 10.31 | 14.06 | 11.04 | 7.64 | 3.68 | 10.49 |
| ANORTH | 19.88 | 13.08 | 18.99 | 20.74 | 18.38 | 17.94 | 10.48 | 14.16 |
| NEPHEL | 9.22 | 18.15 | 10.12 | 8.40 | 16.28 | 11.98 | 21.52 | 14.52 |
| DIOPSIDE | 17.31 | 24.73 | 21.65 | 18.63 | 19.60 | 21.90 | 26.77 | 24.04 |
| OLIVINE | 19.80 | 16.13 | 16.52 | 18.12 | 9.91 | 17.70 | 14.48 | 15.37 |
| FE304 | 3.27 | 3.51 | 3.32 | 3.16 | 2.72 | 3.27 | 3.46 | 3.32 |
| ILMENITE | 4.91 | 4.84 | 4.97 | 4.56 | 3.74 | 4.84 | 5.44 | 5.43 |
| APATITE | 2.92 | 3.10 | 2.74 | 2.15 | 3.03 | 2.75 | 3.31 | 4.49 |

NEPHELINITES (cont.)

| | 19052 | 19053 | 19063 | 19065 | 19068 | K72 |
|---|---|---|---|---|---|---|
| Q-CLASE | 6.46 | 8.56 | 8.35 | 7.21 | 17.58 | 11.38 |
| ALBITE | 17.41 | 11.58 | 13.07 | 19.24 | 4.64 | 16.90 |
| ANORTH | 18.70 | 16.51 | 16.90 | 21.05 | 16.43 | 9.15 |
| NEPHEL | 8.60 | 11.95 | 11.09 | 5.84 | 15.43 | 19.53 |
| DIOPSIDE | 19.53 | 21.81 | 21.49 | 18.41 | 25.15 | 20.22 |
| OLIVINE | 19.59 | 18.53 | 18.06 | 19.72 | 17.51 | 12.40 |
| FE304 | 3.07 | 3.13 | 3.15 | 3.10 | 3.14 | 3.05 |
| ILMENITE | 3.74 | 4.72 | 4.70 | 3.17 | 4.56 | 3.96 |
| APATITE | 2.90 | 3.19 | 3.11 | 2.26 | 1.57 | 3.30 |

| | K71 |
|---|---|
| ANORTH | 10.89 |
| LEUCITE | 7.58 |
| NEPHEL | 16.64 |
| DIOPSIDE | 23.91 |
| OLIVINE | 22.44 |
| CA2SI04 | 7.40 |
| FE304 | 3.25 |
| ILMENITE | 4.47 |
| APATITE | 3.29 |

PHONOLITES

| | 16508 | 79679 |
|---|---|---|
| Q-CLASE | 32.45 | 30.05 |
| ALBITE | 43.48 | 29.61 |
| ANORTH | 1.97 | 0.0 |
| NEPHEL | 11.36 | 29.44 |
| ACMITE | 0.0 | 2.36 |
| NA2SIO3 | 0.0 | 1.40 |
| DIOPSIDE | 4.87 | 2.78 |
| OLIVINE | 4.24 | 4.15 |
| FE304 | 1.57 | 0.0 |
| ILMENITE | 0.04 | 0.06 |
| APATITE | 0.07 | 0.15 |

| | alkali dolerite | basanite | tephrite | leucite basanite | leucitophyre | leucitophyre | haüyne melilitite | wollastonite phonolite | melilite nephelinite | leucite nephelinite |
|---|---|---|---|---|---|---|---|---|---|---|
| | 26917 | 26918 | 26921 | 26922 | 26926 | 26927 | 18157 | 18206 | 18283 | 18285 |
| SIO2 | 48.98 | 44.29 | 47.97 | 43.07 | 48.16 | 47.86 | 34.01 | 50.24 | 39.32 | 43.63 |
| TIO2 | 2.26 | 2.19 | 2.07 | 2.89 | 1.04 | .72 | 1.83 | .35 | 3.16 | 2.49 |
| AL203 | 15.81 | 12.69 | 16.67 | 13.65 | 18.78 | 22.27 | 14.01 | 18.67 | 11.77 | 12.68 |
| FE203 | 3.23 | 4.42 | 6.40 | 5.20 | 4.29 | 2.66 | 5.22 | 2.36 | 6.93 | 7.20 |
| FEO | 5.47 | 6.53 | 1.90 | 5.31 | 2.22 | 1.43 | 5.10 | 1.44 | 4.83 | 2.36 |
| MNO | .17 | .20 | .19 | .19 | .34 | .21 | .42 | .28 | .25 | .18 |
| MGO | 5.74 | 11.66 | 4.40 | 9.66 | 1.44 | .82 | 3.41 | .39 | 9.30 | 8.71 |
| CAO | 8.27 | 10.56 | 8.90 | 12.60 | 6.42 | 2.92 | 18.06 | 7.93 | 16.03 | 13.75 |
| NA20 | 4.83 | 3.20 | 5.00 | 2.84 | 7.50 | 7.99 | 4.02 | 6.55 | 3.68 | 3.52 |
| K20 | 2.61 | 1.38 | 4.42 | 3.11 | 5.97 | 8.80 | 1.26 | 4.52 | 2.69 | 3.76 |
| P205 | .71 | .62 | .56 | .54 | .56 | .11 | 1.10 | .17 | .95 | .75 |
| H20- | .17 | .34 | .14 | .16 | .77 | 1.15 | 1.78 | 1.06 | .30 | .20 |
| H20+ | .73 | 1.42 | .45 | .32 | 1.29 | 1.76 | 4.88 | 4.85 | .35 | .25 |
| C02 | .00 | .00 | .09 | .00 | .02 | .00 | 2.72 | .08 | .00 | .00 |
| TOTAL | 99.31 | 99.83 | 99.67 | 99.85 | 99.28 | 99.18 | 98.75 | 99.73 | 99.94 | 99.86 |
| MG NO. | 59.93 | 70.78 | 55.63 | 67.85 | 34.07 | 31.88 | 43.17 | 19.28 | 64.72 | 68.26 |
| RB | 65. | 125. | 115. | 77. | 169. | 162. | 53. | 195. | 63. | 105. |
| SR | 1028. | 843. | 1679. | 752. | 1556. | 1690. | 4830. | 3626. | 1072. | 1020. |
| Y | 23. | 24. | 27. | 22. | 33. | 20. | 59. | 16. | 26. | 21. |
| TH | 15. | 9. | 14. | 7. | 41. | 24. | 34. | 56. | 10. | 14. |
| ZR | 401. | 230. | 355. | 260. | 607. | 385. | 415. | 485. | 307. | 233. |
| NB | 87. | 76. | 128. | 66. | 263. | 176. | 346. | 412. | 120. | 86. |
| PB | 12. | 5. | 15. | 5. | 25. | 17. | 18. | 38. | 8. | 7. |
| GA | 21. | 16. | 19. | 15. | 25. | 22. | 16. | 23. | 15. | 15. |
| V | 165. | 215. | 199. | 301. | 169. | 157. | 456. | 50. | 413. | 304. |
| CR | 117. | 383. | 24. | 174. | 3. | 3. | 3. | 0. | 149. | 220. |
| NI | 62. | 268. | 22. | 110. | 3. | 0. | 2. | 1. | 77. | 98. |
| CU | 41. | 54. | 25. | 61. | 5. | 5. | 64. | 6. | 119. | 108. |
| ZN | 91. | 98. | 356. | 75. | 197. | 130. | 170. | 240. | 83. | 61. |
| BA | 839. | 734. | 1755. | 998. | 1239. | 1706. | 2212. | 2486. | 1047. | 1187. |
| LA | 78. | 54. | 98. | 54. | 144. | 101. | 220. | 267. | 91. | 81. |
| CE | 146. | 101. | 180. | 109. | 264. | 161. | 302. | 408. | 160. | 150. |
| PR | 14. | 10. | 17. | 10. | 24. | 13. | 21. | 28. | 14. | 13. |
| ND | 46. | 36. | 53. | 37. | 74. | 35. | 93. | 85. | 60. | 47. |
| LOCALITY: | Laachersee | | | | | | Kaiserstuhl | Kaiserstuhl | Württemburg | Eifel |

| | melanephelinite | melilite nephelinite | phonolite | melilite nephelinite | | KAERSUTITES | | | | APATITE |
|---|---|---|---|---|---|---|---|---|---|---|
| | 7110 | 2089 | NZ1 | 2927 G[1] | 2854 G[1] | 25139 | 25140 | 25141 | 25142 | |
| SIO2 | 45.72 | 35.95 | 55.21 | 36.93 | 38.77 | 38.85 | 38.86 | 38.67 | 39.98 | .83 |
| TIO2 | 1.86 | 2.79 | .09 | 2.63 | 3.22 | 6.02 | 5.71 | 5.71 | 5.68 | .00 |
| AL203 | 14.27 | 10.13 | 19.68 | 9.21 | 9.21 | 14.83 | 13.33 | 13.31 | 14.17 | .06 |
| FE203 | 7.69 | 7.02 | 4.11 | 4.14 | 5.00 | .86 | .64 | 3.88 | 10.02 | .32 |
| FEO | 4.50 | 9.63 | 1.45 | 8.96 | 10.51 | 12.48 | 11.32 | 9.91 | 4.01 | .00 |
| MNO | .22 | .24 | .13 | .24 | .20 | .18 | .12 | .15 | .13 | .05 |
| MGO | 4.15 | 11.46 | .19 | 15.90 | 13.69 | 10.72 | 11.14 | 10.15 | 10.45 | .29 |
| CAO | 8.40 | 12.61 | 1.03 | 12.80 | 11.03 | 10.29 | 11.86 | 11.56 | 9.62 | 53.71 |
| NA20 | 5.78 | 5.22 | 9.48 | 3.65 | 2.93 | 2.71 | 2.13 | 2.20 | 3.49 | .00 |
| K20 | 3.23 | 1.84 | 5.36 | 1.38 | 1.51 | 1.03 | 1.99 | 2.03 | 1.52 | .00 |
| P205 | .49 | 1.11 | .01 | 1.29 | 2.27 | .04 | .05 | .05 | .02 | 40.52 |
| H20- | 1.42 | .50 | 1.26 | .00 | .00 | .00 | .00 | .00 | .00 | .00 |
| H20+ | 1.29 | .45 | .76 | 1.60 | .17 | 2.05 | 2.08 | 2.10 | .99 | (5.00) |
| C02 | .39 | .17 | .00 | .30 | .00 | .00 | .00 | .00 | .00 | .00 |
| TOTAL | 99.81 | 99.55 | 99.02 | 99.23 | 98.70 | 100.24 | 99.52 | 100.00 | 100.40 | 101.45 |
| MG NO. | 44.23 | 61.06 | 7.45 | 73.23 | 66.56 | 63.83 | 67.14 | 62.30 | 63.65 | 68.73 |
| RB | 73. | 43. | 212. | 32. | 11. | 2. | 9. | 9. | 5. | 0. |
| SR | 1299. | 1679. | 66. | 1600. | 1379. | 698. | 798. | 879. | 855. | 3732. |
| Y | 24. | 21. | 47. | 16. | 21. | 28. | 18. | 15. | 19. | 192. |
| TH | 10. | 8. | 47. | 0. | 0. | 0. | 0. | 0. | 0. | 16. |
| ZR | 181. | 232. | 1087. | 245. | 349. | 60. | 110. | 135. | 116. | 0. |
| NB | 68. | 71. | 269. | 99. | 97. | 26. | 36. | 48. | 36. | 0. |
| PB | 14. | 7. | 25. | 0. | 0. | 19. | 18. | 25. | 1. | 7. |
| GA | 19. | 21. | 38. | 0. | 0. | 9. | 17. | 16. | 19. | 0. |
| V | 200. | 239. | 1. | 0. | 0. | 398. | 422. | 373. | 203. | 7. |
| CR | 2. | 235. | 0. | 0. | 0. | 6. | 75. | 81. | 99. | 8. |
| NI | 15. | 202. | 0. | 0. | 0. | 7. | 55. | 70. | 195. | 0. |
| CU | 136. | 65. | 3. | 0. | 0. | 280. | 560. | 240. | 60. | 0. |
| ZN | 130. | 190. | 282. | 0. | 0. | 96. | 77. | 86. | 1297. | 0. |
| BA | 1629. | 984. | 24. | 0. | 0. | 181. | 653. | 701. | 264. | 4. |
| LA | 64. | 73. | 153. | 0. | 0. | 5. | 15. | 19. | 11. | 596. |
| CE | 117. | 151. | 264. | 0. | 0. | 15. | 39. | 48. | 34. | 1337. |
| PR | 11. | 18. | 24. | 0. | 0. | 1. | 1. | 5. | 1. | 154. |
| ND | 36. | 60. | 68. | 0. | 0. | 14. | 24. | 33. | 27. | 630. |

[1] major element data: unpublished analyses - D.H. Green

| LOCALITY: | Mosonik, Tanzania | Oahu, Hawaiian Is. | Dunedin, New Zealand | Tasmania, Aust. | Kelly's Pt. NSW. | ← Kiama, NSW → | Anakies, Vict. | Kiama NSW. |
|---|---|---|---|---|---|---|---|---|

ALKALI BASALTS

| | K16 | K46 | K67 | K70 | 19065 | 836 | 1013 | 2122 | 4868 | 671 | 221 | CE21 | CE32 | 2 | 7 | C32 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 45.96 | 46.20 | 47.19 | 47.48 | 46.71 | 43.60 | 48.23 | 47.85 | 49.26 | 47.06 | 46.82 | 45.20 | 46.73 | 44.95 | 46.02 | 43.39 |
| TIO2 | 2.08 | 2.07 | 1.77 | 1.82 | 1.66 | 2.30 | 2.24 | 2.08 | 2.35 | 3.04 | 3.29 | 2.58 | 2.56 | 2.40 | 2.36 | 2.12 |
| AL203 | 14.49 | 14.39 | 14.52 | 14.83 | 14.83 | 13.80 | 13.83 | 12.63 | 13.05 | 14.47 | 10.12 | 11.22 | 12.15 | 10.25 | 10.13 | 13.44 |
| FE203 | 3.43 | 3.65 | 2.53 | 2.39 | 2.31 | 4.20 | 3.80 | 1.97 | 2.15 | 2.59 | 2.94 | 2.85 | 2.08 | 3.52 | 3.91 | 2.47 |
| FEO | 8.34 | 6.89 | 8.62 | 9.24 | 8.36 | 8.10 | 7.63 | 9.26 | 9.05 | 8.41 | 10.18 | 8.90 | 9.57 | 9.00 | 8.80 | 10.59 |
| MNO | .19 | .15 | .18 | .18 | .18 | .17 | .17 | .17 | .24 | .12 | .16 | .16 | .16 | .19 | .19 | .19 |
| MGO | 11.32 | 11.68 | 10.53 | 10.73 | 9.86 | 12.60 | 10.36 | 11.34 | 10.25 | 10.95 | 12.41 | 13.45 | 11.43 | 12.59 | 12.88 | 13.15 |
| CAO | 10.02 | 10.12 | 10.43 | 8.94 | 10.07 | 11.40 | 7.65 | 8.86 | 9.88 | 9.08 | 10.72 | 11.98 | 11.72 | 12.43 | 12.22 | 11.09 |
| NA2O | 2.23 | 2.03 | 2.52 | 2.71 | 3.54 | 2.20 | 4.26 | 3.53 | 2.61 | 2.51 | 2.07 | 2.21 | 2.16 | 1.86 | 2.08 | 2.57 |
| K2O | 1.04 | 1.61 | .79 | 1.03 | 1.22 | 1.00 | 1.14 | 1.68 | 1.13 | 1.48 | .82 | .95 | .94 | 1.12 | .91 | .60 |
| P2O5 | .46 | .66 | .63 | .45 | .95 | .63 | .69 | .63 | .00 | .04 | .41 | .37 | .37 | .48 | .38 | .38 |
| RB | 15. | 27. | 13. | 14. | 25. | 0. | 0. | 0. | 0. | 31. | 17. | 25. | 23. | 137. | 23. | 0. |
| SR | 753. | 1385. | 1275. | 636. | 1083. | 0. | 0. | 0. | 0. | 818. | 383. | 429. | 441. | 523. | 474. | 0. |
| Y | 22. | 24. | 25. | 21. | 25. | 0. | 0. | 0. | 33. | 20. | 0. | 0. | 0. | 0. | 0. | 19. |
| TH | 4. | 8. | 7. | 6. | 12. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZR | 158. | 215. | 196. | 146. | 198. | 0. | 0. | 0. | 0. | 123. | 217. | 0. | 0. | 193. | 168. | 0. |
| NB | 51. | 86. | 66. | 37. | 80. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| PB | 5. | 6. | 8. | 5. | 8. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| GA | 14. | 15. | 15. | 18. | 15. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| V | 179. | 155. | 138. | 158. | 130. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CR | 310. | 318. | 259. | 290. | 246. | 0. | 0. | 0. | 0. | 276. | 0. | 461. | 479. | 356. | 0. | 0. |
| NI | 220. | 245. | 207. | 222. | 155. | 0. | 0. | 0. | 0. | 327. | 0. | 271. | 190. | 404. | 0. | 0. |
| CU | 66. | 48. | 50. | 62. | 57. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZN | 98. | 80. | 101. | 91. | 75. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| BA | 475. | 677. | 387. | 248. | 673. | 0. | 0. | 0. | 0. | 920. | 0. | 242. | 238. | 559. | 473. | 0. |
| LA | 30. | 49. | 41. | 26. | 43. | 0. | 0. | 0. | 39. | 41. | 0. | 0. | 0. | 0. | 0. | 19. |
| CE | 57. | 93. | 75. | 51. | 111. | 0. | 0. | 0. | 70. | 0. | 0. | 0. | 0. | 0. | 0. | 37. |
| PR | 5. | 10. | 7. | 4. | 10. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ND | 24. | 34. | 28. | 16. | 35. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/RB | 559. | 495. | 492. | 593. | 398. | 0. | 0. | 0. | 69. | 401. | 396. | 315. | 339. | 68. | 325. | 37. |
| K/NA | .47 | .79 | .31 | .38 | .34 | .45 | .27 | .48 | .43 | .59 | .40 | .43 | .44 | .60 | .43 | .24 |
| ZR/NB | 3.08 | 2.49 | 2.98 | 3.94 | 2.47 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 |
| MG NO. | 68.37 | 71.81 | 67.84 | 67.28 | 67.33 | 69.83 | 67.18 | 69.17 | 67.08 | 68.99 | 67.85 | 71.92 | 68.57 | 70.92 | 69.53 | 69.13 |
| OCCURRENCE: | | | MONARO VOLCANICS, NSW. | | | TASMANIA | NEWER BASALTS, VICT. | | DREDGE HAUL INDIAN OCEAN | GOUGH IS. ATLANTIC | SAMOA PACIFIC | | CROZET IS. INDIAN OCEAN | | COMORES IS. INDIAN OCEAN | CANARY IS. ATLANTIC |
| REFERENCE: | | | 1 | | | 2 | 3 | | 4 | 5 | 6 | | 7 | | 8 | 9 |

BASANITES

| | K6 | K19 | K45 | K66 | 19052 | 837 | 2194 | 026 | 2679 | 2127 | 71008 | 818 | 826 | TEX 10 | TEX 11 | 26918 | 9982 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 46.03 | 45.30 | 45.28 | 45.76 | 45.66 | 43.08 | 47.06 | 45.35 | 44.99 | 46.32 | 43.99 | 45.59 | 44.36 | 46.08 | 45.62 | 45.18 | 43.25 |
| TIO2 | 2.06 | 2.24 | 2.12 | 2.28 | 1.96 | 3.46 | 2.24 | 2.72 | 2.77 | 2.50 | 3.86 | 2.72 | 3.20 | 2.74 | 2.37 | 2.23 | 2.97 |
| AL203 | 14.36 | 14.66 | 14.50 | 14.89 | 14.44 | 13.57 | 11.90 | 12.62 | 12.68 | 12.51 | 10.54 | 15.97 | 12.70 | 12.07 | 12.58 | 12.95 | 11.57 |
| FE203 | 2.49 | 2.38 | 3.66 | 3.24 | 3.51 | 4.33 | 2.15 | 3.02 | 2.97 | 3.27 | 4.65 | 3.83 | 4.74 | 2.39 | 2.70 | 4.51 | 3.37 |
| FEO | 7.77 | 8.41 | 7.09 | 7.88 | 7.16 | 6.81 | 9.25 | 9.11 | 9.00 | 8.92 | 7.66 | 7.35 | 7.45 | 9.12 | 9.47 | 6.66 | 9.11 |
| MNO | .15 | .20 | .16 | .16 | .18 | .15 | .17 | .17 | .16 | .17 | .18 | .19 | .18 | .16 | .22 | .20 | .13 |
| MGO | 11.42 | 11.22 | 11.32 | 10.09 | 10.26 | 11.19 | 12.99 | 11.58 | 12.54 | 11.24 | 12.00 | 10.02 | 10.99 | 10.98 | 11.69 | 11.90 | 13.74 |
| CAO | 10.09 | 10.12 | 10.38 | 9189 | 10.22 | 10.63 | 7.93 | 8.32 | 8.75 | 8.34 | 11.85 | 8.97 | 12.50 | 10.91 | 10.73 | 10.77 | 11.34 |
| NA2O | 2.95 | 3.15 | 3.00 | 3.17 | 3.92 | 3.54 | 3.62 | 4.12 | 3.48 | 3.75 | 3.89 | 3.37 | 2.61 | 3.18 | 3.08 | 3.26 | 3.05 |
| K2O | 1.61 | 1.37 | 1.47 | 1.67 | 1.09 | 1.27 | 1.90 | 2.08 | 1.79 | 2.07 | .36 | 2.00 | 1.28 | 1.29 | 1.02 | 1.41 | .94 |
| P2O5 | .68 | .68 | .75 | .69 | 1.22 | 2.98 | .77 | .90 | .88 | .90 | 1.02 | .00 | .46 | .62 | .52 | .63 | .52 |
| RB | 23. | 18. | 19. | 25. | 43. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 128. | 0. |
| SR | 554. | 839. | 1100. | 1081. | 1303. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 860. | 0. |
| Y | 20. | 27. | 25. | 25. | 25. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 24. | 18. |
| TH | 5. | 6. | 7. | 6. | 14. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZR | 146. | 242. | 224. | 239. | 253. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 235. | 0. |
| NB | 58. | 79. | 87. | 83. | 120. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 78. | 0. |
| PB | 6. | 7. | 9. | 5. | 12. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| GA | 15. | 14. | 15. | 15. | 16. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| V | 139. | 172. | 131. | 137. | 139. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CR | 239. | 286. | 221. | 249. | 316. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 391. | 0. |
| NI | 118. | 226. | 196. | 190. | 190. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 273. | 0. |
| CU | 49. | 51. | 42. | 44. | 61. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZN | 79. | 84. | 70. | 71. | 83. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| BA | 300. | 489. | 479. | 375. | 869. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 749. | 0. |
| LA | 33. | 44. | 44. | 37. | 79. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 55. | 18. |
| CE | 60. | 95. | 87. | 78. | 135. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 103. | 51. |
| PR | 7. | 9. | 10. | 9. | 13. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ND | 27. | 31. | 29. | 26. | 41. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 92. | 51. |
| K/RB | 589. | 618. | 650. | 557. | 211. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/NA | .55 | .43 | .49 | .53 | .28 | .36 | .53 | .50 | .51 | .55 | .09 | .59 | .49 | .41 | .33 | .43 | .31 |
| ZR/NB | 2.54 | 3.08 | 2.55 | 2.87 | 2.11 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | 3.03 | .00 |
| MG NO. | 71.68 | 69.88 | 70.42 | 67.11 | 68.46 | 69.52 | 71.70 | 68.12 | 70.11 | 67.40 | 68.86 | 66.95 | 67.18 | 68.01 | 68.20 | 70.78 | 71.16 |
| OCCURRENCE: | | | MONARO VOLCANICS | | | CABRAMURRA, NSW. | | NEWER BASALTS, VICT. | | | | LUDLOW, CALIF | SW. JAPAN | BALCONES PROVINCE, TEXAS | | RHINE GRABEN, GERMANY | OAHU, HAWAIIAN IS. |
| REFERENCE: | | | 1 | | | 2 | | 3 | | | | 2 | 2 | 10 | | 1 | 15 |

| | tephritic basanites | | | | NEPHELINITES | | | | | NEPHELINITES | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GC9 | 8K | 18K | 10K | K19 | 19053 | 19063 | M83 | 838 | 839 | 843 | 853 | 857 | TEX 14 | TEX 16 | TEX 17 | TEX 18 |
| SIO2 | 43.39 | 44.07 | 45.78 | 44.97 | 43.79 | 44.37 | 44.69 | 41.99 | 43.09 | 42.90 | 42.32 | 42.08 | 40.55 | 44.50 | 43.65 | 44.64 | 41.08 |
| TIO2 | 2.13 | 2.48 | 2.09 | 2.18 | 2.76 | 2.48 | 2.51 | 4.29 | 2.72 | 2.67 | 4.21 | 2.10 | 2.77 | 2.74 | 2.88 | 2.70 | 3.82 |
| AL2O3 | 12.63 | 15.96 | 15.57 | 15.65 | 14.67 | 14.10 | 14.19 | 10.97 | 11.21 | 10.96 | 15.82 | 11.62 | 14.16 | 12.31 | 10.82 | 12.43 | 10.86 |
| FE2O3 | 2.06 | 2.86 | 3.72 | 4.67 | 2.88 | 3.39 | 2.91 | 4.21 | 8.01 | 4.65 | 2.13 | 4.31 | 5.74 | 2.53 | 3.80 | 2.61 | 4.02 |
| FEO | 9.43 | 7.23 | 5.52 | 5.03 | 8.44 | 7.50 | 7.98 | 8.71 | 4.80 | 8.15 | 8.70 | 7.92 | 8.82 | 8.66 | 7.94 | 8.44 | 8.02 |
| MNO | .23 | .16 | .17 | .19 | .19 | .18 | .18 | .19 | .16 | .17 | .18 | .20 | .00 | .19 | .18 | .19 | .17 |
| MGO | 12.65 | 9.69 | 9.40 | 9.21 | 10.93 | 10.34 | 10.02 | 13.18 | 13.88 | 14.38 | 9.92 | 11.62 | 11.04 | 12.47 | 14.21 | 11.98 | 14.18 |
| CAO | 12.41 | 12.43 | 11.78 | 11.25 | 10.50 | 10.52 | 10.47 | 10.70 | 9.60 | 9.97 | 10.24 | 13.23 | 11.78 | 11.14 | 11.17 | 11.11 | 13.11 |
| NA2O | 3.07 | 3.06 | 3.59 | 4.12 | 3.10 | 3.96 | 3.95 | 3.78 | 3.72 | 3.78 | 3.61 | 4.51 | 3.32 | 3.99 | 3.79 | 4.20 | 3.41 |
| K2O | 1.32 | 1.45 | 1.73 | 1.84 | 1.59 | 1.44 | 1.41 | 1.17 | 1.89 | 1.83 | 1.83 | 1.50 | 1.44 | .89 | .89 | 1.03 | .55 |
| P2O5 | .68 | .42 | .39 | .62 | .86 | 1.34 | 1.31 | .82 | .96 | 1.03 | 1.05 | .90 | .34 | .64 | .65 | .68 | .78 |
| RB | 0. | 41. | 51. | 101. | 19. | 17. | 17. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| SR | 0. | 527. | 589. | 747. | 1045. | 1517. | 1536. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| Y | 25. | 15. | 20. | 20. | 29. | 26. | 27. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| TH | 0. | 0. | 0. | 0. | 6. | 12. | 12. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZR | 0. | 162. | 213. | 252. | 299. | 231. | 232. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| NB | 0. | 111. | 132. | 172. | 111. | 102. | 98. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| PB | 0. | 0. | 0. | 0. | 4. | 12. | 11. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| GA | 0. | 0. | 0. | 0. | 14. | 15. | 15. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| V | 0. | 0. | 0. | 0. | 162. | 164. | 164. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CR | 0. | 182. | 376. | 227. | 170. | 251. | 264. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| NI | 0. | 122. | 173. | 177. | 149. | 194. | 183. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CU | 0. | 0. | 0. | 0. | 45. | 93. | 94. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZN | 0. | 0. | 0. | 0. | 81. | 91. | 89. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| BA | 0. | 683. | 817. | 838. | 526. | 842. | 841. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| LA | 48. | 81. | 91. | 91. | 52. | 88. | 87. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CE | 76. | 81. | 122. | 131. | 108. | 156. | 158. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| PR | 0. | 0. | 0. | 0. | 11. | 15. | 17. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ND | 0. | 0. | 0. | 0. | 40. | 44. | 50. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/RB | 76. | 297. | 282. | 151. | 677. | 703. | 684. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/NA | .43 | .47 | .48 | .45 | .51 | .36 | .36 | .00 | .51 | .48 | .51 | .33 | .43 | .23 | .23 | .25 | .16 |
| ZR/NB | .00 | 1.45 | 1.62 | 1.47 | 2.69 | 2.26 | 2.36 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 |
| MG NO. | 71.00 | 68.39 | 69.82 | 68.81 | 68.38 | 68.16 | 67.35 | 69.69 | 71.61 | 71.79 | 67.10 | 68.26 | 63.27 | 71.35 | 73.18 | 70.80 | 72.66 |
| OCCURRENCE: | COMORES IS., INDIAN OCEAN | | ETHIOPIA | | MONARO VOLCANICS, NSW. | | MURRUMBURRAH NSW. | PRINDLE VOLCANO, ALASKA | | ROSS IS., ANTARCTICA | | ARAPAHOE, NEW ZEALAND | CZECHOSLOVAKIA | | | | BALCONES PROVINCE, TEXAS |
| REFERENCE: | 8 | | 11 | | 1 | | 3 | 2 | | 2 | | 2 | 2 | | | | 10 |

| | NEPHELINITES | | | | | | | MELILITE NEPHELINITES | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | L1A | L2 | 26922 | 18285 | R2 | 21 | 29 | TEX 25 | TEX 28 | L4 | L6 | L11 | L13 |
| SIO2 | 43.19 | 42.55 | 43.36 | 43.92 | 42.57 | 43.08 | 41.14 | 38.80 | 39.02 | 40.53 | 39.57 | 40.87 | 38.49 |
| TIO2 | 2.61 | 2.66 | 2.91 | 2.51 | 3.36 | 4.12 | 2.59 | 3.16 | 4.04 | 2.90 | 3.44 | 3.20 | 2.93 |
| AL2O3 | 13.74 | 13.08 | 13.74 | 12.76 | 12.83 | 10.97 | 10.17 | 11.77 | 10.75 | 12.14 | 11.34 | 12.37 | 12.66 |
| FE2O3 | 5.59 | 3.82 | 5.24 | 7.25 | 3.46 | 3.99 | 5.69 | 3.64 | 5.16 | 4.76 | 4.65 | 6.41 | 4.64 |
| FEO | 5.32 | 6.95 | 5.35 | 2.38 | 8.99 | 9.08 | 7.07 | 8.42 | 8.07 | 6.56 | 6.97 | 4.81 | 6.78 |
| MNO | .21 | .19 | .19 | .18 | .19 | .20 | .22 | .19 | .22 | .19 | .21 | .22 | .20 |
| MGO | 11.88 | 12.87 | 9.73 | 8.77 | 13.19 | 11.84 | 13.48 | 12.66 | 14.84 | 13.48 | 13.48 | 12.69 | 14.32 |
| CAO | 11.78 | 11.21 | 12.69 | 13.84 | 8.94 | 12.02 | 13.85 | 15.81 | 12.99 | 12.65 | 13.29 | 12.58 | 13.90 |
| NA2O | 3.78 | 2.78 | 2.86 | 3.54 | 3.82 | 3.28 | 3.13 | 3.17 | 3.64 | 3.65 | 2.57 | 3.69 | 2.79 |
| K2O | .76 | 2.57 | 3.13 | 3.78 | 1.83 | .59 | 1.30 | 1.27 | 1.28 | 1.88 | 1.78 | 1.89 | 1.78 |
| P2O5 | 1.14 | 1.06 | .54 | .75 | .58 | .64 | 1.08 | 1.10 | .00 | 1.26 | 1.34 | 1.27 | 1.29 |
| RB | 0. | 0. | 78. | 104. | 20. | 51. | 41. | 0. | 0. | 0. | 0. | 0. | 28. |
| SR | 0. | 2076. | 757. | 1027. | 1000. | 612. | 982. | 0. | 0. | 0. | 0. | 0. | 1971. |
| Y | 0. | 0. | 22. | 21. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| TH | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZR | 0. | 0. | 262. | 235. | 350. | 167. | 179. | 0. | 0. | 0. | 0. | 0. | 0. |
| NB | 0. | 0. | 66. | 87. | 70. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| PB | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| GA | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| V | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CR | 0. | 259. | 175. | 221. | 400. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 249. |
| NI | 0. | 259. | 111. | 99. | 300. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CU | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZN | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| BA | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| LA | 0. | 0. | 1005. | 1195. | 250. | 1083. | 1472. | 0. | 0. | 0. | 0. | 0. | 0. |
| CE | 0. | 0. | 54. | 82. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| PR | 0. | 0. | 110. | 151. | 117. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ND | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/RB | 0. | 0. | 335. | 297. | 760. | 96. | 264. | 0. | 0. | 0. | 0. | 0. | 529. |
| K/NA | .20 | .93 | 1.10 | 1.07 | .48 | .18 | .42 | .40 | .35 | .62 | .69 | .51 | .44 |
| ZR/NB | .00 | .00 | 3.94 | 2.71 | 5.00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 |
| MG NO. | 71.97 | 72.99 | 67.85 | 68.26 | 70.40 | 67.11 | 70.70 | 70.25 | 71.82 | 73.05 | 74.66 | 72.35 | 74.05 |
| OCCURRENCE: | RHINE GRABEN, GERMANY | | | CANARY IS., ATLANTIC | | COMORES IS., INDIAN OCEAN | | BALCONES PROVINCE TEXAS | | | RHINE GRABEN, GERMANY | | |
| REFERENCE: | 11 | 11 | 1 | 1 | 9 | 8 | | 10 | | | 11 | | |

CONTINUED ON FOLLOWING PAGE

MELILITE NEPHELINITES(cont.)

| | L5 | L10 | L12 | AC59 | AC198 | 23K | VV3 | FN8 | 023 | 035 | 9961 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO2 | 39.12 | 39.91 | 37.78 | 39.69 | 38.50 | 38.91 | 38.92 | 39.77 | 37.59 | 37.47 | 39.10 |
| TIO2 | 3.26 | 3.02 | 3.36 | 3.77 | 3.81 | 3.33 | 4.06 | 3.94 | 2.94 | 2.46 | 2.83 |
| AL203 | 11.37 | 12.18 | 11.89 | 9.99 | 9.83 | 9.46 | 10.95 | 10.50 | 11.27 | 12.22 | 11.87 |
| FE203 | 4.20 | 4.53 | 3.83 | 6.88 | 7.06 | 5.80 | 13.02 | 14.39 | 6.62 | 6.17 | 5.28 |
| FEO | 7.29 | 6.33 | 7.49 | 7.64 | 7.57 | 9.14 | .00 | .00 | 7.41 | 7.60 | 7.89 |
| MNO | .20 | .20 | .17 | .22 | .22 | .16 | .19 | .19 | .09 | .08 | .11 |
| MGO | 15.05 | 15.09 | 14.60 | 13.22 | 13.14 | 14.24 | 13.35 | 13.02 | 12.98 | 12.32 | 13.26 |
| CAO | 12.70 | 12.07 | 13.27 | 13.43 | 14.14 | 14.37 | 13.77 | 13.14 | 13.74 | 14.08 | 13.02 |
| NA2O | 3.14 | 2.89 | 3.43 | 1.67 | 2.60 | 2.79 | 3.29 | 2.70 | 4.62 | 4.84 | 4.28 |
| K2O | 2.17 | 2.31 | 2.47 | 2.13 | 1.74 | .65 | 1.44 | 1.18 | 1.22 | .93 | 1.22 |
| P2O5 | 1.20 | 1.23 | 1.31 | 1.05 | 1.06 | .93 | .86 | .96 | 1.21 | 1.44 | 1.13 |
| RB | 56. | 0. | 37. | 36. | 31. | 34. | 31. | 18. | 31. | 18. | 0. |
| SR | 2355. | 2251. | 4084. | 964. | 1269. | 965. | 760. | 859. | 1682. | 2192. | 0. |
| Y | 0. | 0. | 0. | 28. | 28. | 15. | 20. | 21. | 22. | 23. | 20. |
| TH | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZR | 0. | 0. | 0. | 360. | 310. | 0. | 0. | 0. | 0. | 0. | 0. |
| NB | 0. | 0. | 0. | 147. | 87. | 0. | 0. | 0. | 0. | 0. | 0. |
| PB | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| GA | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| V | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| CR | 297. | 287. | 276. | 287. | 255. | 0. | 0. | 0. | 0. | 0. | 0. |
| NI | 215. | 297. | 0. | 318. | 281. | 0. | 0. | 0. | 0. | 0. | 0. |
| CU | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ZN | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| BA | 0. | 0. | 0. | 703. | 728. | 838. | 461. | 823. | 1252. | 1962. | 0. |
| LA | 0. | 0. | 0. | 91. | 84. | 58. | 40. | 68. | 90. | 109. | 53. |
| CE | 0. | 0. | 0. | 158. | 162. | 114. | 122. | 139. | 170. | 198. | 131. |
| PR | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| ND | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| K/RB | 320. | 0. | 558. | 489. | 462. | 158. | 386. | 544. | 321. | 420. | 129. |
| K/NA | .69 | .80 | .72 | 1.27 | .67 | .23 | .44 | .44 | .26 | .19 | .28 |
| ZR/NB | .00 | .00 | .00 | 2.45 | 3.55 | .00 | .00 | .00 | .00 | .00 | .00 |
| MG NO. | 74.80 | 75.92 | 74.49 | 67.59 | 67.30 | 68.39 | 71.32 | 68.70 | 67.95 | 67.15 | 69.60 |

| | | | |
|---|---|---|---|
| OCCURRENCE: | RHINE GRABEN, GERMANY | HAAST R., NEW ZEALAND | OAHU, HAWAIIAN IS. |
| REFERENCE: | 11 | 13 | 14 |

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3 IRVING (1971)
4 BALASHOV et al., (1970)
5 LE MAITRE (1962)
6 STICE (1968); HUBBARD (1971)
7 GUNN et al., (1970)
8 STRONG (1972)
9 RIDLEY (1970
10 SPENCER (1969)
11 BROWN & CARMICHAEL (1969)
12 LOHMANN (1964)
13 A.F. COOPER (unpublished analyses)
14 KAY (1972)
15 SCHILLING & WINCHESTER (1969)

## APPENDIX 5 : SAMPLE NUMBERS AND LOCALITIES

| SAMPLE NO. | ANU Collection No. | LOCALITY or REFERENCE |
|---|---|---|
| ALKALI BASALTS | | |
| K1 | 27415 | 36°34'S 149°17'E |
| K2 | " 16 | " 38' " 17' |
| K3 | " 17 | " 52' " 16' |
| K4 | " 18 | " 57.5' " 14' |
| K5 | " 19 | " 45.5' " 15.5' |
| K7 | " 20 | " 20' " 12' |
| K9 | " 21 | " 31' " 16' |
| K10 | " 22 | " 31.5' " 15.5' |
| K11 | " 23 | " 31' " 12' |
| K12 | " 24 | " 31' " 8.5' |
| BB22 | " 25 | " 32' 148°58.5' |
| K15 | " 26 | " 31.5' 149° 7' |
| K16 | " 27 | " 36' " 4' |
| K17 | " 28 | " 38' " 3' |
| K18 | " 29 | " 38.5' " 3' |
| KPHI | " 30 | " 12.5' 148°55.5' |
| K21 | " 31 | " 12' " 55.5' |
| K22 | " 32 | " 12' " 55.5' |
| K23 | " 33 | " 12' " 55' |
| K24 | " 34 | " 12' " 55' |
| K25 | " 35 | " 11.5' " 55.5' |
| K26 | " 36 | " 10' " 52.5' |
| K28 | " 37 | " 12.5' " 46.5' |
| K29 | " 38 | " 18.5' " 48' |
| K31 | " 39 | " 10.5' " 45.5' |
| K32 | " 40 | " 10' " 45' |
| K33 | " 41 | " 13' " 58.5' |
| K34 | " 42 | " 15' " 56.5' |
| K42 | " 43 | " 15' 149° 1.5' |
| K44 | " 44 | " 15' 9' |
| K46 | " 45 | " 15.5' " 10.5' |
| K49 | " 46 | " 16' " 12' |
| K50 | " 47 | " 22' " 17.5' |
| K51 | " 48 | " 21.5' " 15.5' |
| K52 | " 49 | " 25.5' " 13' |
| K54 | " 50 | " 27' " 11' |
| K55 | " 51 | " 26' " 12' |
| K56 | " 52 | " 27' " 11' |
| K58 | " 53 | " 27' " 10.5' |
| K61 | " 54 | " 36' " 21.5' |
| K62 | " 55 | " 36' " 21' |
| K63 | " 56 | " 51' " 16' |
| K64 | " 57 | " 52' " 16' |
| K65 | " 58 | " 51.5' " 16.5' |
| K67 | " 59 | " 17' " 8' |
| K68 | " 60 | " 19.5' " 8.5' |
| K70 | " 61 | 35°07' 148°24' |

| SAMPLE NO. | ANU Collection No. | LOCALITY or REFERENCE | |
|---|---|---|---|
| **BASANITES** | | | |
| K6 | 27462 | 36°34' | 149°17' |
| K19 | " 63 | " 35.5' | " 4' |
| K27 | " 64 | " 12.5' | " 47' |
| K35 | 29292 | " 15' | 148°56' |
| K36 | " 93 | " 14.5' | " 53' |
| K37 | " 94 | " 21.5' | " 51.5' |
| K38A | " 95 | " 20' | " 59' |
| K38C | " 96 | " 20' | " 59' |
| K39 | " 97 | " 21' | " 58' |
| K45 | " 98 | " 15.5' | 149°10.5' |
| K57 | " 99 | " 27' | " 11' |
| K66 | " 300 | " 21.5' | " 16' |
| K69 | 301 | " 33' | 148°44' |
| **NEPHELINITES** | | | |
| K8 | " 02 | 30°26.5'S | 149°14.5'E |
| K14 | " 03 | " 29' | " 7' |
| K20 | " 04 | " 14.5' | 148°58' |
| K30 | " 05 | " 10.5' | " 45.5' |
| K47 | " 06 | " 18' | 149°14' |
| K59 | " 07 | " 27' | " 10' |
| K60 | " 08 | " 26.5' | " 10' |
| KX | " 09 | " 12.5' | " 10.5' |
| K71 | " 10 | 34°55.5' | 148°45' |
| K72 | " 11 | Macpherson's Swamp Creek, 8.8 km WNW of Wee Jasper, NSW | |
| **MINERALS** | | | |
| Kaersutite | 25139 | sample localities and sources documented in Kesson & Price (1972) | |
| " | 25140 | | |
| " | 25141 | | |
| " | 25142 | | |
| APATITE | | from kaers-cpx-bi- ?ol/opx inclusion, basic alkaline dyke, Kiama, NSW. | |

Dept Geophysics and Geochemistry, ANU

| | |
|---|---|
| 2854 | Scottsdale quarry, northeast Tasmania |
| 2927 | south of Lyell highway, St Clair sheet, Tasmania |

| A.N.U. No. | ROCK TYPE | LOCALITY or REFERENCE |
|---|---|---|
| 19679 | phonolite | dyke at Blue Lake, Mt Kosciusko, NSW |
| 16508 | " | specimens from Eucumbene and Kiandra, NSW |
| 4168 | nephelinite | locality details provided by Mackenzie (1967) |
| 19050 | " | |
| 19052 | basanite | |
| 19053 | nephelinite | |
| 19063 | " | |
| 19068 | " | |
| 26917 | alk. dolerite | Laachersee, Rhine graben, Germany, ANU |
| 26918 | basanite | collection provides locality details. |
| 26921 | tephrite | Many samples were collected from |
| 26922 | leucite basanite | localities described by von Frechen (1962) |
| 26926 | leucitophyre | |
| 26927 | " | |
| 18157 | haüyne melilitite | Kaiserstuhl, Germany (included in ANU collection |
| 18206 | wollastonite phonolite | " " ; initially provided by Kranz' collection) |
| 18283 | melilite nephelinite | Würtemburg, Schwabia, Germany |
| 18285 | leucite nephelinite | Eifel district, Germany |
| 7110 | melanephelinite | Mosonik, Tanzania |

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# The Major and Trace Element Chemistry of Kaersutite and Its Bearing on the Petrogenesis of Alkaline Rocks

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*Abstract.* New major and trace element analyses are presented for 7 kaersutites from basic alkaline rocks. K/Rb ratios lie between 1209 and 4276. Rb is low, averaging 6 ppm. Sr ranges from 532 to 1060 ppm and Ba from 181 to 701 ppm. Zr averages 109 ppm, Nb 44 ppm and V 390 ppm. There is a moderate enrichment in light REE. Zn correlates with $FeO + Fe_2O_3$ but the concentrations of Ni, Co, Cr, Cu and Pb are variable. Large variations in trace element concentration in kaersutites reflect only small variations in the melt when the distribution coefficient for a given element strongly favours the amphibole.

Kaersutite is significant in the petrogenesis of alkaline rocks as a possible accessory phase in the upper mantle source regions, and as an important phase in the fractionation of basic alkaline liquids over a wide range of pressures.

## Introduction

The aluminous amphiboles pargasite and kaersutite commonly occur as megacrysts or xenocrysts in basic alkaline dykes and volcanics. They are also found as a primary phase in some basic and ultrabasic inclusions in alkaline rocks. Experimental studies of basic alkaline compositions in the presence of water have shown that amphibole may be stable to pressures of 25–30 Kb, both in subsolidus assemblages and coexisting with melt. The near-liquidus amphibole is a titaniferous pargasite or kaersutite (Tuthill, 1968; Irving, 1971). Kaersutite is therefore significant in the petrogenesis of alkaline rocks—initially as a possible accessory phase in the upper mantle source regions, and subsequently during fractionation. The major element and, more importantly, the trace element composition of kaersutite can provide constraints on petrogenetic hypotheses.

This paper presents new major and trace element analyses of 7 kaersutites from alkaline rocks.

## Chemical Composition

### *Major Elements*

The new data for 7 kaersutites are presented in Table 1, together with comparative data from published and unpublished sources for kaersutites with trace element analyses.

Wilkinson (1961) has stated that kaersutites should be considered as Mg-rich members of the pargasite-ferropargasite series with high Ti (0.5 atoms or more per formula unit) and some substitution of K for Na. Many structural formulae

have $Na + K > 1$ which suggests that Na, as well as sharing the vacant site with K, also shares the site normally occupied by Ca. One formula unit commonly contains slightly more than 2 atoms of Al in four-fold coordination. The magnesio-hastingsite—ferrohastingsite series is derived by the complete substitution of $Fe^{3+}$ for $Al^{VI}$ in the ideal end-members of the pargasite series. Substitution of this kind is limited in kaersutites. But oxidation during eruption replaces $Fe^{2+}(OH, F)^-$ by $Fe^{3+}O^{2-}$ and is largely responsible for the ferric iron content. Almost completely oxidised yet undissociated kaersutite has been described by Aoki (1963).

Table 1

| | 25139 | 25140 | 25141 | 25142 | 15308 | 15380 | 21341 | 1001 | 1002 | 1003 | 1004 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 38.85 | 38.86 | 38.67 | 39.98 | 38.20 | 38.67 | 39.44 | 39.31 | 37.4 | 39.51 | 39.32 |
| $TiO_3$ | 6.02 | 5.71 | 5.71 | 5.68 | 6.23 | 5.90 | 5.16 | 4.14 | 6.0 | 5.64 | 6.14 |
| $Al_2O_3$ | 14.83 | 13.33 | 13.31 | 14.17 | 13.81 | 13.50 | 13.84 | 15.37 | 15.7 | 14.26 | 14.51 |
| $Fe_2O_3$ | 0.86 | 0.64 | 3.88 | 10.02 | 5.23 | 11.32 | 4.16 | 4.71 | 12.4 | 1.75 | 4.28 |
| FeO | 12.48 | 11.32 | 9.91 | 4.01 | 7.04 | 4.30 | 6.67 | 4.66 | 1.1 | 10.92 | 6.87 |
| MnO | 0.18 | 0.12 | 0.15 | 0.13 | 0.17 | 0.19 | 0.08 | 0.10 | 0.2 | 0.09 | 0.10 |
| MgO | 10.72 | 11.14 | 10.15 | 10.45 | 11.29 | 9.55 | 12.99 | 13.89 | 11.4 | 11.36 | 12.04 |
| CaO | 10.29 | 11.86 | 11.56 | 9.62 | 12.13 | 11.88 | 11.57 | 12.54 | 11.9 | 10.12 | 10.87 |
| $Na_2O$ | 2.71 | 2.13 | 2.20 | 3.49 | 2.46 | 2.55 | 2.18 | 2.36 | 2.3 | 2.80 | 2.63 |
| $K_2O$ | 1.03 | 1.99 | 2.03 | 1.52 | 0.85 | 1.05 | 2.04 | 1.36 | 1.5 | 1.59 | 1.92 |
| $P_2O_5$ | 0.04 | 0.05 | 0.05 | 0.02 | 0.12 | 0.17 | 0.05 | 0.04 | | | 0.06 |
| $H_2O-$ | | | 0.01 | | 0.07 | 0.02 | 0.01 | | 0.1 | | 0.18 |
| $H_2O+$ | 2.05 | 2.08 | 2.09 | 0.99 | 1.34 | 0.50 | 1.19 | 1.38 | 0.1 | 1.68 | 1.19 |
| Cl | | | | | | | | | 0.9 | | |
| F | | | | 0.142 | | | | | 0.4 | | 0.15 |
| (corrected) Total | 100.06 | 99.23 | 99.72 | 100.16 | 99.03 | 99.65 | 99.46 | 99.78 | 101.0 | 99.81 | 100.26 |
| *Structural formulae*[a] | | | | | | | | | | | |
| Z Si | 5.771 | 5.849 | 5.085 | 5.807 | 5.673 | 5.675 | 5.792 | 5.700 | 5.395 | 5.847 | 5.748 |
| $Al^{iv}$ | 2.229 | 2.151 | 2.195 | 2.193 | 2.327 | 2.325 | 2.208 | 2.300 | 2.605 | 2.153 | 2.252 |
| Y $Al^{iv}$ | 0.368 | 0.199 | 0.161 | 0.233 | 0.091 | 0.011 | 0.188 | 0.327 | 0.065 | 0.335 | 0.059 |
| Ti | 0.673 | 0.646 | 0.645 | 0.620 | 0.696 | 0.651 | 0.570 | 0.451 | 0.651 | 0.628 | 0.675 |
| $Fe^{3+}$ | 0.096 | 0.072 | 0.438 | 1.095 | 0.584 | 1.250 | 0.460 | 0.514 | 1.346 | 0.195 | 0.471 |
| $Fe^{2+}$ | 1.550 | 1.425 | 1.244 | 0.487 | 0.874 | 0.528 | 0.819 | 0.565 | 0.133 | 1.352 | 0.840 |
| Mn | 0.023 | 0.015 | 0.019 | 0.016 | 0.021 | 0.024 | 0.010 | 0.012 | 0.024 | 0.011 | 0.012 |
| Mg | 2.373 | 2.499 | 2.271 | 2.262 | 2.499 | 2.689 | 2.843 | 3.002 | 2.451 | 2.506 | 2.623 |
| X Ca | 1.638 | 1.913 | 1.860 | 1.497 | 1.930 | 1.686 | 1.820 | 1.948 | 1.839 | 1.605 | 1.703 |
| Na | 0.781 | 0.622 | 0.640 | 0.983 | 0.708 | 0.726 | 0.621 | 0.664 | 0.643 | 0.804 | 0.746 |
| K | 0.195 | 0.382 | 0.389 | 0.282 | 0.161 | 0.197 | 0.382 | 0.252 | 0.276 | 0.300 | 0.358 |
| OH | 2.031 | 2.088 | 2.093 | 0.959 | 1.327 | 0.489 | 1.166 | 1.335 | 0.096 | 1.659 | 1.161 |
| F | | | | 0.065 | | | | | 0.183 | | 0.069 |
| Cl | | | | | | | | | 0.220 | | |
| Z | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |
| Y | 5.083 | 4.856 | 4.778 | 4.713 | 4.765 | 4.553 | 4.890 | 4.871 | 4.670 | 5.027 | 4.680 |
| X | 2.614 | 2.917 | 2.889 | 2.762 | 2.799 | 2.791 | 2.823 | 2.864 | 2.864 | 2.756 | 2.709 |
| ~~X~~ | ~~2.614~~ | ~~2.917~~ | ~~2.889~~ | ~~2.762~~ | ~~2.799~~ | ~~2.791~~ | ~~2.823~~ | ~~2.864~~ | ~~2.756~~ | ~~2.709~~ | ~~2.807~~ |
| 100 $Mg/Mg + Fe^{2+} + Fe^{3+} + Mn$ | 59 | 62 | 57 | 59 | 63 | 54 | 69 | 73 | 62 | 62 | 66 |

[a] Calculated on the basis of 23 oxygens.

Table 1 (Continued)

| | 25139 | 25140 | 25142 | 25142 | 15308 | 15380 | 21341 | 1001 | 1002 | 1003 | 1004 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| K/Rb | 4275 | 1836 | 1872 | 2524 | 1411 | 1453 | 1210 | 1129 | | 4400 | 1226 |
| Rb | 2 | 9 | 9 | 5 | 5 | 6 | 14 | 10 | | 3 | 13 |
| Sr | 698 | 798 | 879 | 855 | 890 | 1060 | 532 | 500 | 30 | 610 | 622 |
| Ba | 181 | 653 | 701 | 264 | 410 | 492 | 289 | 555 | | 131 | 729 |
| Pb | 19 | 18 | 25 | 1 | 3 | 19 | 4 | <10 | 4 | | |
| U | <1 | <1 | <1 | n.d. | 1 | 1 | 1 | | | | |
| Zr | 60 | 110 | 135 | 116 | 93 | 179 | 67 | 90 | 120 | 45 | |
| Nb | 26 | 36 | 48 | 36 | 18 | 57 | 88 | 60 | 15 | | |
| Y | 28 | 18 | 15 | 19 | 27 | 27 | 13 | 10 | 20 | 19 | 19 |
| La | 5 | 15 | 19 | 11 | | | | 40 | | | |
| Ce | 15 | 39 | 49 | 34 | | | | 30 | | 22 | 28 |
| Pr | 1 | 1 | 5 | <1 | | | | 5 | | 6 | |
| Nd | 14 | 24 | 33 | 27 | | | | 20 | | 17 | 21 |
| V | 398 | 422 | 373 | 203 | 410 | 492 | 289 | 570 | 350 | 131 | 496 |
| Cr | 6 | 75 | 81 | 99 | 15 | 2 | 107 | 3 | <10 | | 363 |
| Ni | 7 | 55 | 70 | 195 | 4 | 49 | 199 | 155 | 22 | 12 | 20 |
| Co | | | | | 250 | 87 | 108 | | 35 | 75 | 76 |
| Cu | 28 | 56 | 24 | 6 | 27 | 10 | 28 | 55 | | 2 | 50 |
| Zn | 96 | 77 | 86 | 1297 | 112 | 125 | 69 | 30 | | 76 | 56 |
| Ga | 9 | 17 | 16 | 19 | 12 | 18 | 17 | 10 | 16 | 14 | 14 |
| Sc | | | | | | | | | 50 | | |

*Sample Localities*

25139 Kaersutite xenocryst from basic alkaline dyke, Kelly's Pt. NSW., Australia
25140 Kaersutite from basic inclusion in basic alkaline dyke, Kiama, NSW., Australia
25141 As above
25142 Kaersutite xenocryst from nephelinitic breccia, Anakies, Vict., Australia
15308 Kaersutite xenocryst from "Kaiwekite", Purakanui, Dunedin, New Zealand
15380 Kaersutite from amphibolite inclusion, "Kaiwekite", Long Beach, Dunedin, New Zealand
21341 Kaersutite xenocryst from Camptonite dyke, Mt Cameron, North West Otago, New Zealand
1001 Titaniferous pargasite megacryst from tephrite, Ethiopia (Brown & Carmichael, 1969)
1002 Kaersutite from xenolith in tuff. Tristan da Cunha. (Le Maitre, 1969)
1003 Kaersutite megacrysts from alkali basalt, Spring Mtn, NSW., Australia (Wilkinson, 1962). Trace element analysis from Jakes (1970)
1004 Kaersutite megacryst from alkali basalt dyke near Yeoval, NSW., Australia. (Jakes, 1970)

The first 4 numbers refer to specimens in the collection of the Geol. Dept., ANU, Canberra. The next 3 refer to the collection of the Geol. Dept., University of Otago.

*Analytical Techniques*

Major and trace element abundances were determined by means of an automated Philips PW1220 XRF spectrometer with 2Kw generator. Major elements were determined using the fusion method of Norrish and Hutton (1969). $Na_3O$ was measured on a dual channel flame photometer with Li as an internal standard. FeO was obtained by volumetric methods.

The major element chemistry and structural formulae of all amphiboles in Taable 1 are typical of kaersutites al though the less titaniferous kaersutites 1001 and 21341 are unusually magnesian with $100\ Mg/Mg + Fe^2 + Fe^3 + Mn = 73$ and 69 respectively.

the distribution of Zr and Nb between kaersutite and liquid. Zr is found to be enriched in the melt, whereas Nb is partitioned equally.

*Ferromagnesian Trace Elements*

The concentrations of V, Cr, Ni and Co in kaersutites are all very variable and show no significant correlation with any other chemical parameter. The concentrations of these elements in basic alkaline liquids are modified by fractionation of the liquidus phase, since Ni and Co can be partitioned in olivine, Cr can be concentrated in magnesian clinopyroxene and spinel, and the precipitation of an opaque phase efficiently removes V from the melt. The partition of V between kaersutite and liquid does not favour either phase very strongly, since the range in the V content of kaersutites (131 to 570 ppm) is similar to the range in basic alkaline rocks (Ridley, 1970). Gast (1968) has indicated that the amphiboleliquid distribution coefficient is less than unity for both Ni and Cr.

The abundance of Cu in the kaersutite ranges from 2 to 56 ppm. The concentrations of both Cu and Ni are low if the paragenesis of the kaersutite includes a sulphide phase, as does 25139. Zn ranges from 30 to 1297 ppm and shows a significant correlation with the total iron content of the kaersutites.

## Discussion

*Kaersutite and Alkaline Fractionation Series*

Phases other than kaersutite are involved in the fractionation of basic alkaline liquids, but kaersutite can be important over a wide pressure range when $P_{e_{H_2O}}$ is high. Kaersutite fractionation reduces MgO, $TiO_2$ and K/Rb while concentrating Rb, Sr, Ba, REE and Zr in the residual liquid.

*Kaersutite as an Accessory Phase in the Upper Mantle*

The small amount of water in the upper mantle is bound entirely in accessory phases in the subsolidus assemblages. Convincing geochemical arguments have been put forward by Oxburgh (1964) and Griffin and Murthy (1969), suggesting that amphibole predominates over phlogopite to depths corresponding to the top of the low velocity zone, where the geotherm intersects the solidus of the amphibole-bearing peridotite. Green (1970) has suggested that increasing degrees of partial melting in this region produce basaltic liquids whose compositions pass gradationally from nephelinite through basanite and alkali basalt to tholeiite. The composition of the nephelinitic "minimum melt" is very close to that of kaersutite.

The residual crystalline phases in equilibrium with a partial melt must also appear on the liquidus under the same physical conditions. Phases intially present in the subsolidus assemblage which have since been entirely incorporated in the melt, appear below the liquidus. The occurrence of kaersutite as the near-liquidus amphibole in both alkaline and tholeiitic compositions (Tuthill, 1968; Holloway & Burnham, 1970) is significant in this context, implying that kaersutite, or at least a pargasitic amphibole, is an accessory phase in the uppermost mantle.

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*Alkali and Alkaline Earth Elements*

Hart and Aldrich (1967) have shown that amphiboles preferentially concentrate K with respect to Rb. The kaersutites (Table 1) have Rb contents ranging from 2 to 14 ppm and K/Rb ratios as high as 4400. The measured abundances of Ba are spread between 130 and 730 ppm. Apart from an unusually low concentration of 30 ppm in 1002, the Sr content of the kaersutites ranges from 500 to 1060 ppm.

Many kaersutites are xenocrysts and their chemical composition therefore cannot be directly equated with that of their host. Griffin and Murthy (1969) and Philpotts and Schnetzler (1970) provide data on amphibole-liquid coefficients which show that Sr, Ba and Rb are concentrated in the melt whereas K/Rb, K/Ba, and K/Sr ratios are higher in amphibole. The Ba content of an amphibole correlates with the abundance of Ba in the liquid from which it crystallises. Should the initial Ba content of an alkaline melt be depleted by early fractionation of biotite, then Ba is low in the later phases, which often include kaersutite.

Since the equilibrium distribution of Sr between amphibole and liquid is less than unity (Philpotts and Schnetzler, 1970), the Sr-rich kaersutites have crystallised from liquids with relatively high Sr contents. The Sr content of alkaline rock series reaches a peak at the hawaiite-mugearite stage of fractionation. There can also be an initial variation in the concentration of Sr in basic parent liquids, with higher Sr occurring in more nephelinitic compositions.

*Rare Earth Elements, Yttrium*

The generalised configuration of a chondrite normalised rare earth pattern can be obtained by comparison of normalised light REE abundances with normalised yttrium, since the geochemical behaviour of yttrium parallels that of the heavy REE (Taylor, 1965). In agreement with Higuchi and Nagasawa (1969) and Jakes (1970), we find that kaersutites from basic alkaline rocks are slightly enriched in the light REE. The garnet structure readily accommodates heavy REE so the coexisting phases in a garnet-bearing assemblage commonly show a complementary enrichment in light REE. White *et al.* (1972) have shown that this is the case for kaersutite in an eclogite accumulate from Kakanui, New Zealand.

The equilibrium distribution of REE between amphibole and liquid partitions the heavy REE equally between crystals and liquid, and preferentially ceoncentrates light REE in the melt (Higuchi and Nagasawa, 1969; Schnetzler and Philpotts, 1970).

*Lead, Thorium and Uranium*

Th and U contents are less than 1 ppm (detection limit). Pb is very variable, ranging from 1 to 25 ppm.

*Zirconium and Niobium*

The measured concentrations of Zr are remarkably consistent, averaging 102 ppm. This suggests that Zr is accommodated in the kaersutite lattice, rather than contained in zircon inclusions. Comparison of the measured abundances of Zr and Nb in kaersutites with the average concentrations of these elements in basic alkaline rocks (Le Maitre, 1962; Baker, 1969; Ridley, 1970) gives an estimate of

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# $TiO_2$ Content and the Shoshonite and Alkaline Associations

THERE are two distinct genetically unrelated "alkaline" magma series. First, there is the alkaline association proper which occurs on oceanic islands, continental margins and continental rift systems. Second, there is the characteristically potassic shoshonite association[1], which typically appears in the later stages of island arc evolution[2]. Basaltic members lie in the alkaline field on the diagram of $Na_2O+K_2O$ against $SiO_2$, above the Macdonald–Katsura line, but are rarely strongly nepheline normative.

A comparison of the chemical composition of typical basic rocks (< 50% $SiO_2$) in the two associations reveals characteristic chemical differences. Alkali oxides provide a useful discriminant function in most cases. Contrasted with the alkaline association, shoshonites typically have higher $K_2O$ contents and $K_2O/Na_2O$ ratios close to unity, but some overlap—the potassic alkaline lineages[3], for example—has been recognized. A more efficient discriminant is $TiO_2$, which invariably makes up less than 1.3% of members of the shoshonite association, whereas a range of 2 to 3% is characteristic of basic alkaline rocks. Chayes and Velde[4] recognized the importance of $TiO_2$ in discriminating between the alkaline association on oceanic islands and the circumoceanic (island arc) magma series. The low $TiO_2$ contents and certain trace element ratios of shoshonites support their affinity with the calcalkaline rocks of island arcs[2,5]. Thus although potassic rocks may occur in either the alkaline or the shoshonite association, lower $TiO_2$ contents readily identify shoshonites.

By way of illustration we present new analyses of basic alkaline lavas from south-eastern Australia, potassic alkaline rocks from the Laachersee, Rhine Graben, and basic shoshonitic lavas from eastern Papua (Table 1). Although the higher $K_2O$ contents and $K_2O/Na_2O$ ratios of some of the rocks from the Rhine Graben are comparable with those of the shoshonites from Papua, their higher $TiO_2$ contents clearly indicate their alkaline affinities.

Samples 27465 to 27473 were analysed by standard wet chemical techniques; all other samples were analysed by X-ray fluorescence spectrometry[7]. Rock numbers refer to specimens in the collection of the Australian National University.

**Table 1** Analysis of Rock Samples

| | Hawaii | | Alkaline association | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Alkaline basalt (mean of 28)[6] | Hawaiite (mean of 33)[6] | Monaro district, south-eastern New South Wales | | | | | | | | | |
| Rock No. | | | 27415 | 27416 | 27417 | 27418 | 27419 | 27420 | 27421 | 27422 | 27423 | 27424 |
| $SiO_2$ | 46.46 | 48.60 | 42.84 | 42.67 | 42.97 | 46.65 | 46.39 | 47.16 | 45.92 | 46.20 | 44.26 | 43.10 |
| $TiO_2$ | 3.01 | 3.16 | 2.53 | 2.69 | 2.49 | 2.22 | 2.10 | 2.14 | 2.21 | 2.28 | 2.20 | 2.48 |
| $Al_2O_3$ | 14.64 | 16.49 | 14.43 | 14.30 | 14.36 | 15.43 | 14.17 | 14.85 | 15.34 | 17.15 | 14.73 | 14.15 |
| $Fe_2O_3$ | 3.27 | 4.19 | 4.30 | 2.81 | 3.56 | 2.86 | 2.42 | 3.11 | 3.15 | 2.44 | 3.01 | 3.77 |
| FeO | 9.11 | 7.40 | 6.86 | 8.22 | 7.46 | 6.99 | 8.30 | 7.25 | 7.22 | 7.46 | 7.95 | 3.36 |
| MnO | 0.14 | 0.18 | 0.17 | 0.15 | 0.19 | 0.16 | 0.14 | 0.14 | 0.15 | 0.14 | 0.17 | 0.17 |
| MgO | 8.19 | 4.70 | 8.16 | 10.65 | 9.65 | 6.58 | 9.52 | 8.15 | 7.11 | 5.58 | 9.09 | 9.46 |
| CaO | 10.33 | 7.79 | 9.49 | 10.23 | 9.60 | 10.31 | 8.70 | 9.34 | 10.19 | 9.82 | 10.05 | 10.32 |
| $Na_2O$ | 2.92 | 4.43 | 3.92 | 3.02 | 3.44 | 2.68 | 2.96 | 2.88 | 2.38 | 4.17 | 2.98 | 3.24 |
| $K_2O$ | 0.84 | 1.60 | 1.62 | 1.55 | 1.55 | 2.06 | 1.47 | 1.65 | 1.98 | 1.73 | 1.72 | 1.97 |
| $P_2O_5$ | 0.37 | 0.69 | 1.25 | 0.84 | 1.19 | 0.63 | 0.48 | 0.57 | 0.69 | 0.80 | 0.81 | 1.13 |
| $H_2O^-$ | | | 0.91 | 0.83 | 0.90 | 0.79 | 0.64 | 0.76 | 1.06 | 0.92 | 0.91 | 0.74 |
| $H_2O^+$ | | | 2.53 | 1.83 | 2.39 | 1.88 | 1.80 | 1.62 | 1.94 | 0.83 | 1.11 | 1.98 |
| $CO_2$ | | | 0.28 | 0.05 | 0.10 | 0.07 | 0.08 | 0.09 | 0.08 | 0.05 | 0.10 | 0.15 |
| Total | | | 99.3 | 99.9 | 99.8 | 99.3 | 99.2 | 99.7 | 99.4 | 99.6 | 99.1 | 100.0 |

| | Alkaline association Laachersee, Rhine Graben | | | | Shoshonite association Eastern Papua | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rock No. | 26917 | 26918 | 26921 | 26922 | 27465 | 27466 | 27468 | 27469 | 27470 | 27471 | 27472 | 27473 |
| $SiO_2$ | 48.98 | 44.29 | 47.97 | 43.07 | 47.20 | 47.30 | 47.90 | 48.20 | 48.60 | 49.00 | 50.30 | 51.50 |
| $TiO_2$ | 2.26 | 2.19 | 2.07 | 2.89 | 1.01 | 0.78 | 0.73 | 0.75 | 0.88 | 0.54 | 1.17 | 0.65 |
| $Al_2O_3$ | 15.81 | 12.69 | 16.67 | 13.65 | 13.2 | 11.3 | 13.6 | 17.2 | 17.4 | 15.9 | 17.8 | 16.0 |
| $Fe_2O_3$ | 3.23 | 4.42 | 6.40 | 5.20 | 4.60 | 7.05 | 5.55 | 7.15 | 5.80 | 3.15 | 7.95 | 4.1 |
| FeO | 5.47 | 6.53 | 1.90 | 5.31 | 4.65 | 5.90 | 5.05 | 1.81 | 4.10 | 4.30 | 7.33 | 4.5 |
| MnO | 0.17 | 0.20 | 0.19 | 0.19 | 0.16 | 0.20 | 0.18 | 0.17 | 0.18 | 0.14 | 0.15 | 0.16 |
| MgO | 5.74 | 11.66 | 4.40 | 9.66 | 8.15 | 11.80 | 7.15 | 9.35 | 3.80 | 8.95 | 3.70 | 5.55 |
| CaO | 8.27 | 10.56 | 8.90 | 12.60 | 10.10 | 8.00 | 11.80 | 3.95 | 9.35 | 6.45 | 8.35 | 7.45 |
| $Na_2O$ | 4.83 | 3.20 | 5.00 | 2.84 | 2.10 | 1.50 | 2.05 | 2.55 | 3.05 | 3.05 | 3.65 | 4.05 |
| $K_2O$ | 2.61 | 1.38 | 4.42 | 3.11 | 3.85 | 4.05 | 3.15 | 2.60 | 2.55 | 3.05 | 2.70 | 3.15 |
| $P_2O_5$ | 0.71 | 0.62 | 0.56 | 0.54 | 0.82 | 0.68 | 0.31 | 0.49 | 0.32 | 0.40 | 0.60 | 0.52 |
| $H_2O^-$ | 0.17 | 0.34 | 0.14 | 0.16 | 1.13 | 0.24 | 0.20 | 1.71 | 0.73 | 1.92 | 0.97 | 0.28 |
| $H_2O^+$ | 0.73 | 1.42 | 0.45 | 0.32 | 2.75 | 1.05 | 1.88 | 4.05 | 2.30 | 2.90 | 0.95 | 2.00 |
| $CO_2$ | | | 0.09 | | 0.11 | | 0.60 | 0.40 | 1.20 | 0.40 | 0.13 | 0.20 |
| Total | 99.0 | 99.5 | 99.1 | 99.5 | 99.8 | 99.9 | 100.2 | 100.3 | 100.3 | 100.4 | 99.8 | 100.1 |

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