THE GEOCHEMISTRY AND PETROLOGY OF THE KAROO ANDESITES AND ASSOCIATED BASALTS OF THE NORTH-EASTERN CAPE PROVINCE.

by

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DECLARATION

This is to certify that all the work in this thesis is the original work of the author except where specific acknowledgement is made to the work of others.

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CONTENTS

ABSTRACT

New geochemical data consisting of major and 15 trace element analyses are presented for 41 rocks from three andesitic and associated basaltic rock occurrences in the North Eastern Cape Province. These include the Pronksberg, Belmore and Roodehoek localities.

Field evidence suggests that the three andesites were emplaced during the early stages of Karoo volcanicity.

Geochemical variations within the Pronksberg and Roodehoek andesite are small, manifesting the undifferentiated nature of the magmas. Variations within the Belmore andesite are interpreted as representing fractionation of orthopyroxene, accompanied by only minor plagioclase fractionation. Differences in trace element concentrations and inter-element ratios between the andesites and associated basalts of the Pronksberg and Belmore volcanic suites precludes the possibility of the two rock types being genetically related. Geochemical differences constrain the possibility of the three andesites being cogenetic. Magmatic processes resulting in their formation are, however, thought to be similar.

The differences in chemistry between the Pronksberg Basalt (High K Type) and Pronksberg Basalt (Drumbo Type) are interpreted as representing the combined influence of weathering, the presence of amygdales and the within-flow variations of alkali elements on the Pronksberg Basalt (High K Type).

Similarities in petrography and chemistry justifies a correlation of the Pronksberg Basalt (Drumbo Type) with the Drumbo Basalt Member in the Barkly East area. Data for the Drumbo Basalt (This study) in the Barkly East area confirms and complements previously presented data.

Normative chemistry and strontium isotope data indicate a process involving crustal assimilation or melting of crustal rocks as being the most likely explanation for the genesis of the Karoo andesites.

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1. INTRODUCTION

The occurrence of andesites in the Karoo igneous province was first described by Du Toit (1904,1911), Gevers (1927) and Stockley (1947). No geochemical studies have, to date, been concerned with these andesites.

The aims of this dissertation are twofold. The first is to provide original major and trace element data for three occurrences of andesitic rocks. Data are also presented for basaltic rocks associated with the andesites. Secondly, it is intended to use these data, supplemented with strontium isotope data, to evaluate relationships between the associated volcanic rocks. It is hoped that interpretations regarding relationships between these rocks will lead to a fuller understanding of magmatic processes active during early Karoo volcanism.

New major and trace element analyses for 41 rocks are presented. Samples were collected from three localities in the north-eastern Cape Province. Sample localities include the farms Pronks Berg in the Dordrecht district, Moshesh's Ford in the Barkly East district and Roode Hoek in the Molteno district. For all three localities, both andesitic and associated basaltic lavas were sampled. Rock nomenclature is discussed in Chapter 4.

Strontium isotope data are presented for two samples. These are used in petrogenetic interpretations presented in Chapter 6.

While not an integral part of the International Geodynamics Programme, it is hoped that data and conclusions drawn from this study, will complement data from other areas of Karoo igneous activity currently being compiled by workers involved in the International Geodynamics Programme.

1.1 PREVIOUS WORK

The earliest description of intermediate lavas in the Karoo volcanic sequence is that of Du Toit (1904,1911). In his 1904 report on the geology of the Barkly East area, Du Toit describes the enstatite andesites crowning the Belmore 'Volcano', which takes its name from the old hotel which is located on the banks of the Bell river. Du Toit (1904) recognises the andesites as overlying an agglomerate containing inclusions of dolerite and basalt, which in turn overlies the Cave Sandstone. Du Toit (1904) recognises the agglomerate as being intrusive, grading into a siliceous breccia at the margin. This is contrary to the interpretations of Lock et al. (1974) who see the breccia as having been emplaced, separately from the agglomerate, as an ash-flow.

Du Toit (1911), in his geological report on part of the Stormberg, describes an enstatite andesite with petrographic characteristics as those at Belmore, capping the hill on the farm Pronks Berg, Dordrecht district. Du Toit describes the hill as being rudely T-shaped in plan, capped by 100-200 feet of vitreous enstatite andesites, breaking with conchoidal fracture, overlying the Cave Sandstone. He also describes an outlier of similar rocks, 8 km to the north, on the farm Leewe Spruit.

While Du Toit (1904) notes the presence of a volcanic field to the west of Jamestown, the major descriptive work on this area is that of Gevers (1927). Gevers recognises the occurrence of a 'highly compact, light andesitic type of basalt' on the farm Roode Hoek. Minor andesitic lavas in the Karoo sequence were also described by Stockley (1947) in his work on the geology of Lesotho. Stockley also identified enstatite as the pyroxene in the andesites. Due to inaccessibility, these andesites do not form part of the present study.

An early geochemical study of the Karoo volcanics was that of Walker and Poldervaart (1949) who noted the presence of bronzite basalts in the Barkly East area. Cox and Hornung (1966), on the basis of their analytical work, proposed a division of the Karoo basalts of Southern Africa into northern and southern provinces. Lock et al. (1974) present 4 major element analyses for basalts in the Barkly East area, although the major portion of their paper is devoted to a discussion of the stratigraphy of the area, as well as proposing the stratigraphic terminology for the Drakensberg Subgroup. Robey (1976) conducted a preliminary geochemical investigation of the basal volcanics in the Barkly East area as delineated by Lock et al. (op.cit.). The most recent study concerning the Karoo volcanics is that of Pemberton (1978) who analysed 61 basalt samples for major and trace elements, with over half of these analyses being of the basalts of the Lesotho Formation in the Naudes Nek section, Barkly East area. Geochemical differences between flows led to the confirmation of the stratigraphic units as proposed by Lock et al. (1974). Pemberton's study adds strength to the possibility that the Karoo basalts were derived from chemically heterogeneous mantle sources. Barree (1977) presents data for the Kraai River Basalt Formation, Barkly East area, which shows a bimodal potassium distribution within the sequence, thereby indicating the existence of two distinct tholeiite basalt sequences in the Kraai River Formation.

2. STRATIGRAPHY AND FIELD RELATIONSHIPS

2.1 STRATIGRAPHY

Lock et al. (1974) delineate several lithostratigraphic units within the Karoo sequence as follows:

Karoo Supergroup
- (Volcanic Group
  - Lebombo Subgroup
  - Drakensberg Subgroup
- (Stormberg Group
- (Beaufort Group
- (Ecca Group
- (Dwyka Group

On the basis of field relationships and stratigraphic height, Lock et al. (op.cit.) subdivide the Drakensberg Subgroup into three Formations. Subsequent unpublished field work by B.E. Lock and geochemical studies by Robey (1976) and Pemberton (1978) resulted in the identification of another formation, defined informally by Pemberton (op.cit.) as the Omega Formation. This unit had previously been grouped with the Kraai River Formation. The Drakensberg Subgroup may therefore be divided into:

4) Lesotho Formation
3) Kraai River Formation
2) Omega Formation
1) Moshesh's Ford Formation

The Moshesh's Ford Formation has been defined by Lock et al. as consisting of the following seven members:

7) Belmore Andesite Member
6) Bell River Andesite Breccia Member
5) The Dingle Tuffite Member
4) The Donnybrook Basalt Member
3) The Bell Kop Bedded Pyroclastics Member
2) The Jennerville Chaotic Pyroclastics Member
1) The Drumbo Basalt Member

Pemberton (op.cit.) recognises the Drumbo and Donnybrook Basalt Members as being petrographically and geochemically equivalent, although the two units are spatially separate. The basal volcanics, as defined, are used for correlation purposes with volcanics in the Dordrecht area, presented in this study.

2.2 FIELD RELATIONSHIPS

2.2.1. Pronksberg

Andesites and basaltic rocks are found on the hill known as the Pronksberg, which takes its name from the farm on which it is located. The Pronksberg ($31^{o}15,5'$ south: $26^{o}51'$ east) is situated 20km south of Jamestown (Figure 1).

At the Pronksberg, volcanic rocks overlie the Clarens Formation * (see map, Figure 2) and cover an area of approximately 1 sq. km. The volcanic sequence is 30-85 metres thick and comprises black vitreous andesites (30-60m) overlain by up to 5m of sandstone which is followed in turn by two distinct basalt flows. Fluxion banding is evident in the andesite, best observed on weathered surfaces, but evident in thin section as well. The andesite is thought to represent a single flow. The basalts include a vesicular basalt, greenish in colour, having a maximum thickness of 4m which underlies a basalt up to 20m thick, devoid of vesicles and resembling the Drumbo Basalt from the Barkly East area in both hand specimen and thin section. Outcrops of the basalt are restricted to the western limb of the outlier. Stratigraphic sections are presented in Figure 2.

Based on chemical characteristics of the basalts presented in Section 4, the massive basalt shall be termed, by definition, the Pronksberg Basalt (Drumbo Type), and the vesicular basalt the Pronksberg Basalt (High K Type).

A second andesite with petrographic characteristics identical to that at Pronksberg is located 8km to the north on the hill known as Dikkop, on the farm Leewe Spruit. This occurrence consists of approximately 30m of andesite overlying the Clarens Formation and shall be called the Dikkop Andesite. No basalts or interbedded sandstones are found at Dikkop, although a dolerite dyke intersects the andesite.

* Previously known as the Cave Sandstone.

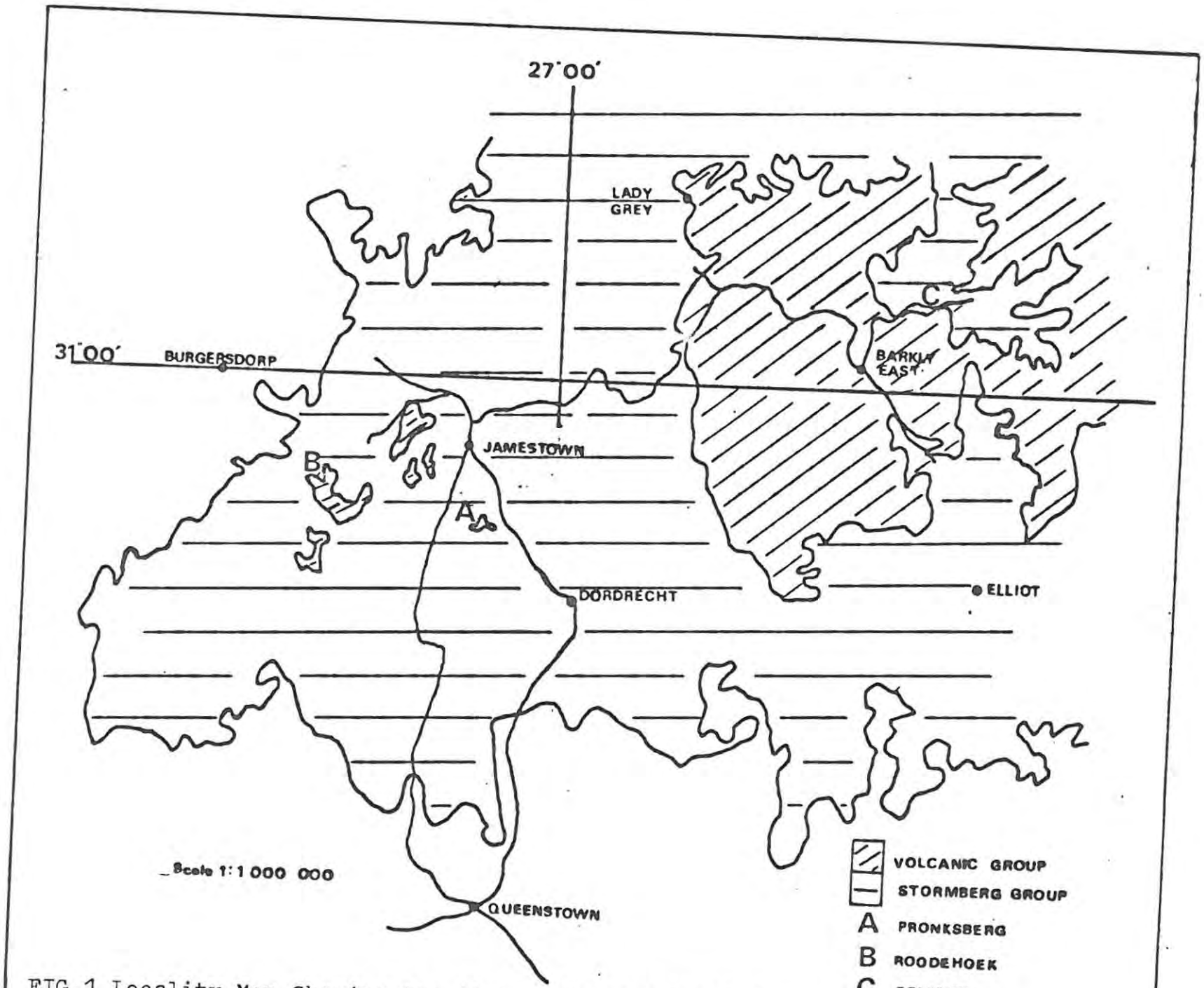
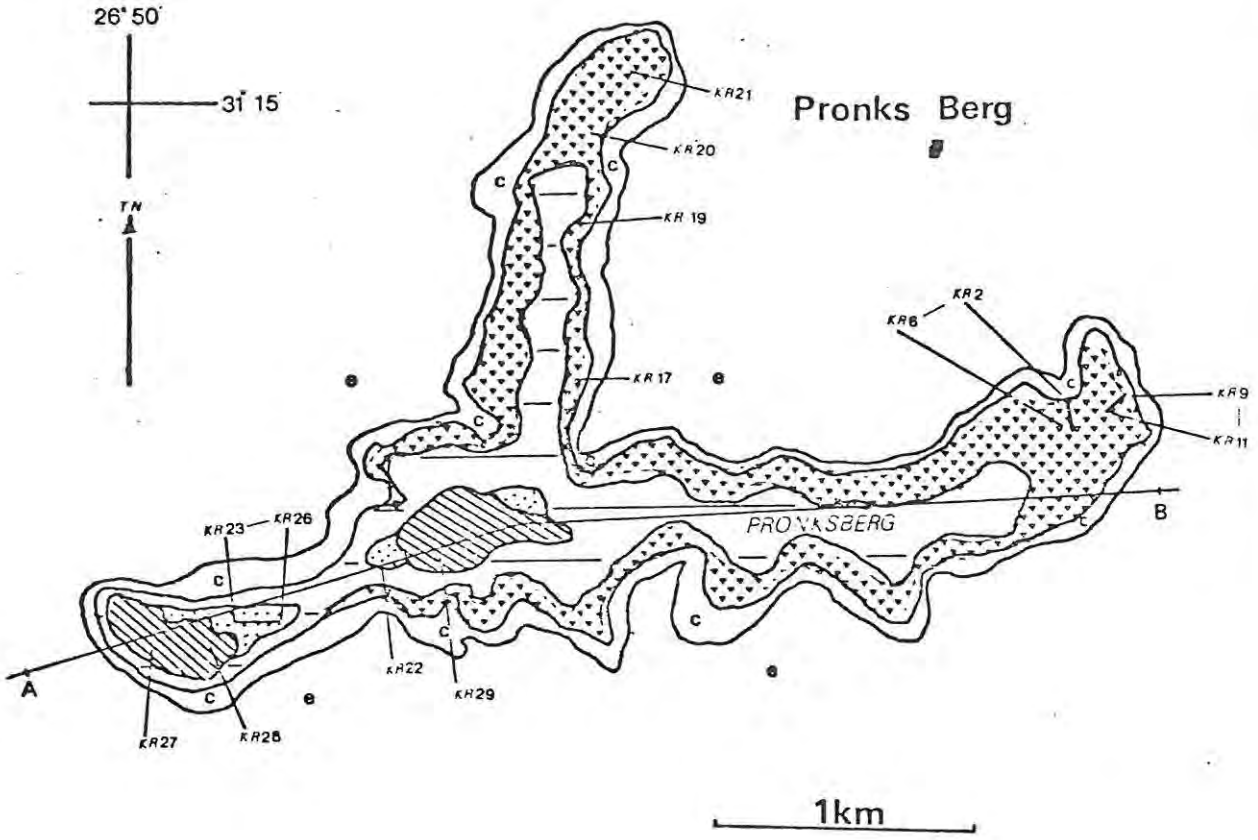
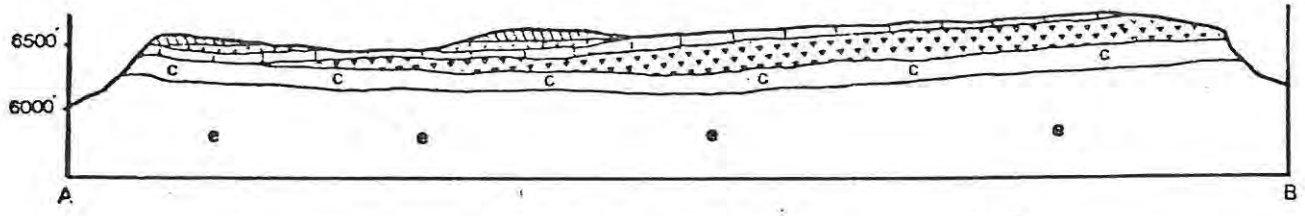


FIG.1 Locality Map Showing the three Outcrops Studied.

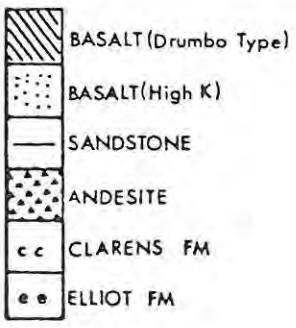
Fig 2 Diagram Showing the Geology of the Pronksberg.



GEOLOGICAL SECTION A–B



Thicknesses are not true to scale.



2.2.2. Belmore

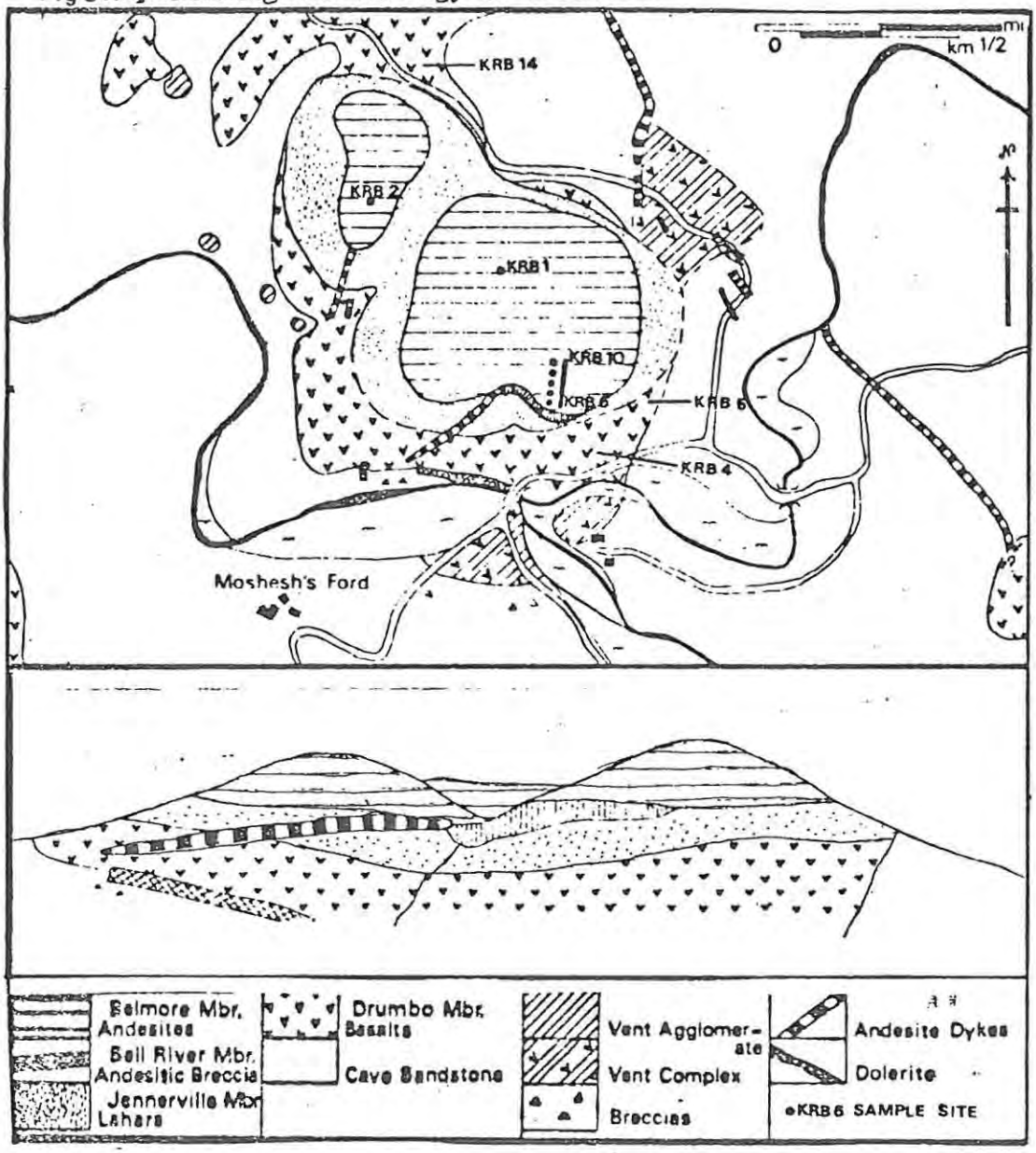
The hill locally referred to as the 'Belmore volcano' is found on the farm Moshesh's Ford (30° 50,8' south: 27° 46,7' east), some 29 km east of Barkly East.

The occurrence was first described by Du Toit (1904) and more recently by Lock et al. (1974). Mapping undertaken by the present author confirms the field relationships observed by Lock et al. (op.cit.). Field relationships are shown in Figure 3. The basal volcanics of the Moshesh's Ford Formation are underlain by the Clarens Formation. The contact between the Clarens Formation and basal lavas (Drumbo Basalt) of the Moshesh's Ford Formation is sharp on the eastern side of the hill, showing relatively steep dips (20-30°), while on the western side it is less steep (see geological section, Figure 3). The Jennerville Chaotic Pyroclastics Member, up to 30m thick, overlies the Drumbo Basalts. These pyroclastics are the result of emplacement by mass-flow rather than by air-fall and are believed to be lahars (Lock et al. 1974). Subsequently, Lock (1978) has confirmed that these pyroclastics accumulated from a series of ultrahigh-temperature lahars.

The pyroclastics are conformably overlain by the Bell River Andesite Breccia Member which occurs only on the Belmore volcano (Lock et al., op.cit.). In hand specimen the rock is a hard, black, glassy rock containing quartz particles, clastic fragments and volcanic andesite fragments embedded in andesitic glass (Plate 1). The breccia attains a maximum thickness of 39m and is believed to have been emplaced as an ash-flow. A detailed investigation of this member has not been undertaken by the author who has relied on the description of Lock et al. (1974).

The Belmore Andesite Member caps the Belmore volcano. In the region of 120m of andesite are seen in a vertical section through the hill (Figure 3).

Fig 3 Map Showing the Geology of Belmore.



From Lock et al.(1974).

On the basis of field and geochemical evidence, five separate flows forming the andesite pile have been defined. The petrography of the andesites is described in Section 3. The Belmore andesite forms the focus of the geochemical study at Belmore.

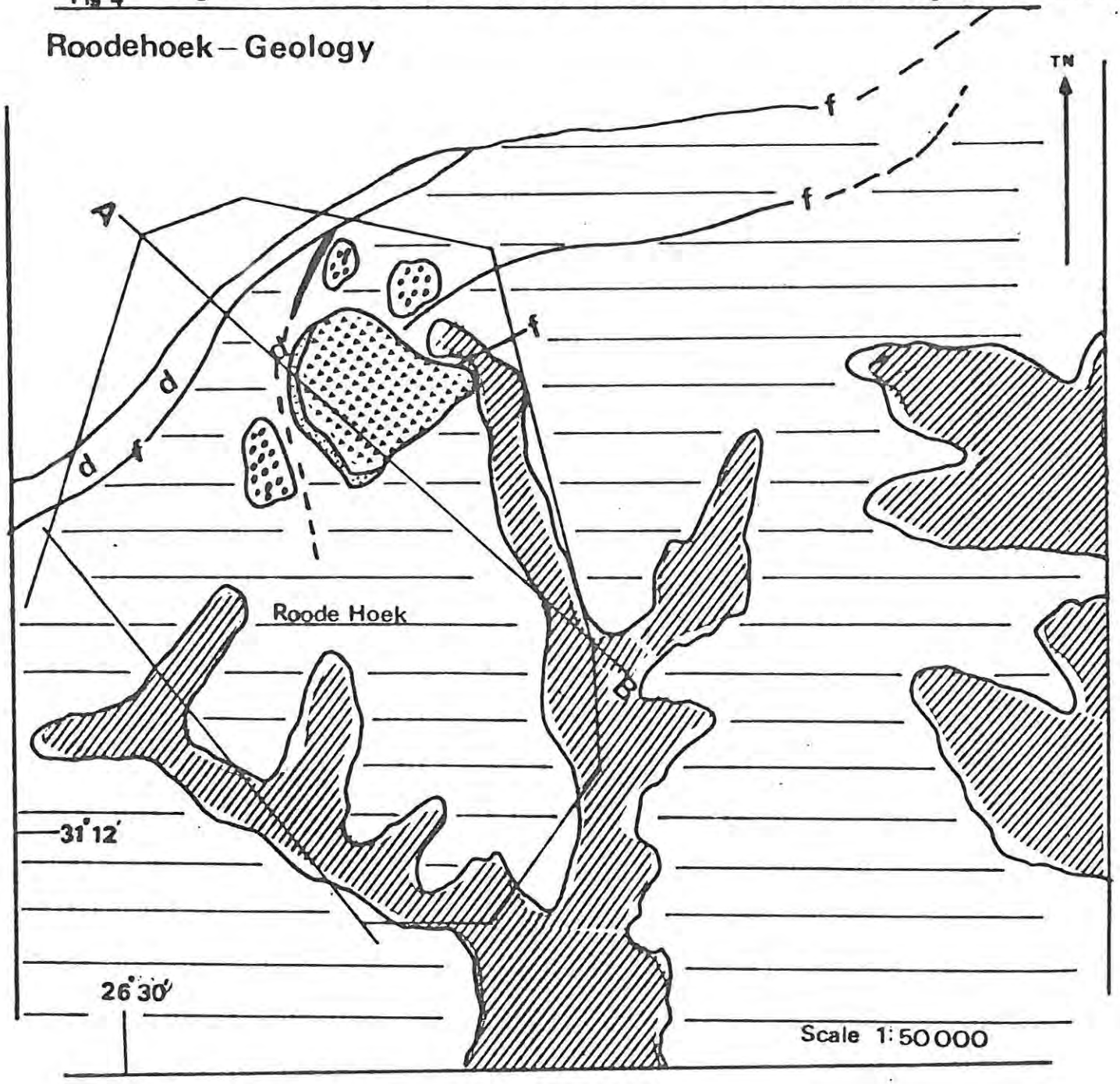
In summary, it would appear that the Belmore volcano had been the site of early Karoo-period phreatic volcanism, forming a maar-like structure, hence the Clarens Formation-Drumbo Basalt contact relationship previously described. A period of erosion and possibly subsidence followed. The basal lavas (Drumbo basalts) of the Moshesh's Ford Formation then covered the area, possibly erupted from the Belmore volcanic centre. After eruption of the basal lavas and lahars, subsidence took place in the vicinity of Belmore, and the Bell River Andesite Breccia, followed by Belmore andesites was emplaced. The andesites were probably erupted from a complex of dykes. The Lesotho Formation lavas were then erupted, covering over and burying the entire complex.

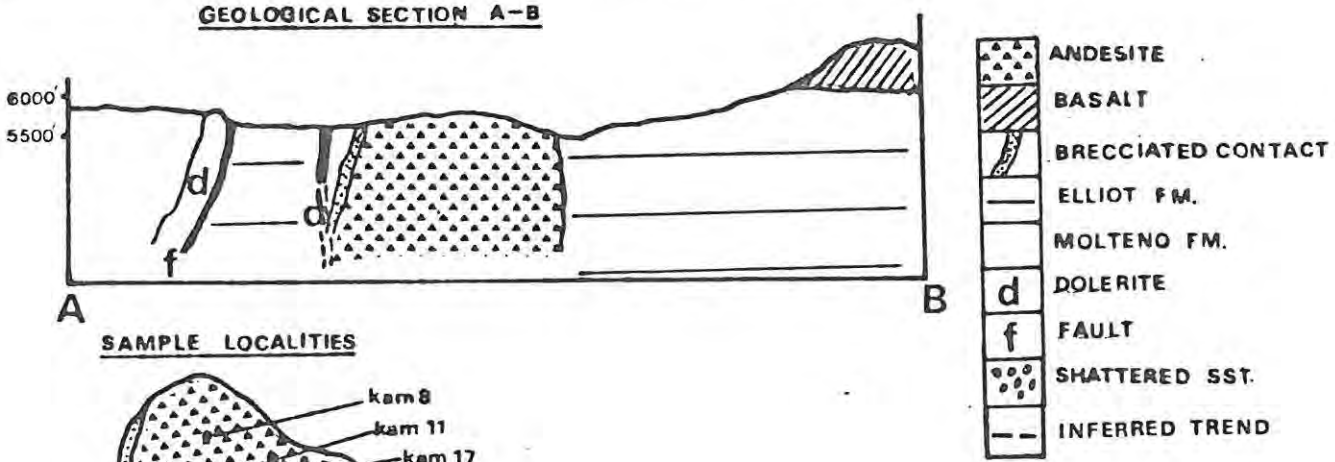
2.2.3 Roodehoek

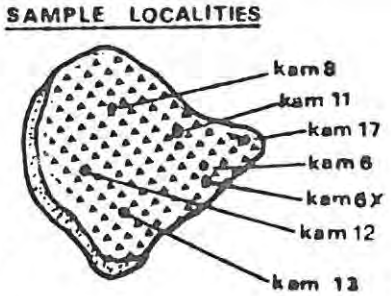
An andesite intrusion on the farm Roode Hoek, 29km north-east of Molteno, was first described by Gevers (1927). The geographical location of the intrusion is $31^{\circ}10,5'$ south and $26^{\circ}30,6'$ east.

In his description of the geology of the western Stormberg, Gevers (op.cit.) recognises in the region of 250 metres of volcanic material, mainly basalts, overlying the Clarens Formation. Gevers recognises the area in the vicinity of the farm Roode Hoek as being one of the major centres of eruption. Detailed mapping by the author and other members of the Department of Geology, Rhodes University, recognise the broad observations made by Gevers, but have made several minor refinements to his original map. The geological map of the area circumjacent to the andesite intrusion on the farm Roode Hoek appears as Figure 4 in the present text.

Fig 4 Diagram Showing the Geology of the Area Surrounding Roode Hoek.







The andesite is intruded into the Elliot Formation.* Contact relationships are illustrated in Figure 4. On the western flank of the intrusion, the andesite grades into brecciated andesite and finally into a brecciated agglomerate** with increasing distance from the centre of the intrusion. The agglomerate consists essentially of a light coloured sandstone, with minor andesitic inclusions. In the other areas surrounding the intrusion, the Elliot Formation is largely unaffected by the intrusion. Nowhere is the intrusion directly overlain by the volumetrically dominant basalts in the area. In addition to the andesite intrusion and basalts, other evidence for volcanic activity in the vicinity include shattered sandstones, tuffaceous sandstones and several dolerite dykes, all intrusive into the Elliot Formation.

A formal study of the stratigraphy of the area is at present being undertaken by Mr. A.A. Mitchell in the Department of Geology, Rhodes University, as is a study of the volcanic history and geochemistry of the basalts.

3. PETROGRAPHY AND MINERALOGY

The petrography of the Pronksberg and Belmore andesites is described briefly by Du Toit (1904,1911). Lock et al. (1974) include a brief discussion of the petrography of the Belmore andesite as well. No petrographic descriptions are included in Gevers' (1927) account of the volcanics of the Molteno district. Microprobe analyses of phenocryst phases for the Belmore and Pronksberg andesites are presented in the following section, as well as petrographic data for all three andesite occurrences. Petrographic descriptions of the Pronksberg basalts are presented as well.

3.1 PRONKSBERG ANDESITE

The Pronksberg andesite lavas are hypocrystalline, aphanitic and porphyritic to glomeroporphyritic. Phenocryst grain sizes vary from 0,1-0,8mm.

* Previously known as the Red Beds Formation.

** An agglomerate is defined as a pyroclastic rock that consists of volcanic fragments that are larger than 2mm in diameter and that may or may not have a matrix.

Both orthopyroxene (hypersthene) and zoned plagioclase occur as phenocryst and groundmass phases. Orthopyroxene shows limited compositional variations averaging Wo_1 En_{58} Fs_{41} and occurs as both phenocrysts and as part of groundmass. Microprobe analyses of unzoned plagioclase show limited variations from An_{68}-An_{73}. Average phenocryst compositions are given in Table 1. Plagioclase and orthopyroxene phenocrysts are subhedral and lathlike and are often sub-ophitically related. The Pronksberg lavas consist of approximately 50-60 percent of a clear glassy base. In the groundmass, plagioclase, orthopyroxene, Fe-Ti oxides and quartz occur as crystallites, while a microcrystalline hexagonal mineral has not as yet been identified. Vesicular infillings include chalcedony and quartz. A common alteration product occurring in the groundmass has been identified by X-ray diffraction methods as montmorillonite.

A marked banding observed on weathered surfaces in hand specimen is often not obvious in thin section. When it is observed microscopically, the banding is related to a fining-coarsening in grain size of groundmass. No mineralogical variations appear to be related to the banding. Typical Pronksberg andesites are shown in Plate 1.

3.1.2 Pronksberg Basalt (High K Type)

The Pronksberg Basalt (High K Type) is light grey-green in hand specimen, often exhibiting a speckled appearance due to alteration of mesostasis, as well as phenocryst phases, to chlorite.

The rock is hypocrystalline, aphanitic, microcrystalline with grain sizes up to 1mm in size. Subhedral crystals of plagioclase (An_{40}-An_{60}) and clinopyroxene (augite) are often ophitically related. Olivine is notably absent in all rocks studied. The rock consists of 40 percent of brown, glassy groundmass containing numerous Fe-Ti crystallites. Two pyroxenes, augite

TABLE 1

AVERAGE MICROPROBE ANALYSIS OF ORTHOPYROXENES AND PLAGIOCLASE - BELMORE AND PRONKSBERG ANDESITES.

	PRONKSBERG		BELMORE	
	OPX	PLAG	OPX	PLAG
SiO_2	49,83	51,67	54,14	51,57
TiO_2	0,36	-	0,11	-
Al_2O_3	3,14	31,23	1,36	31,23
FeO	0,23	-	0,23	-
MnO	0,23	-	0,23	-
MgO	18,82	-	28,35	-
CaO	0,53	13,90	1,70	13,89
Na_2O	-	3,43	-	2,92
	Cat. per 6 oxy.	cat. per 32 oxy.	cat. per 6 oxy.	cat. per 32 oxy.
	Si 1,936) 2,00 Al 0,064)	Si 9,353) 16,016 Al 6,663)	Si 1,967) 2,00 Al 0,033)	Si 9,373) 16,062 Al 6,689)
	Al 0,081) Ti 0,009) Fe^{2+} 0,773) 1,982 Mn 0,007) Mg 1,091) Ca 0,021)	Ca 2,696) 3,899 Na 1,203)	Al 0,024) Ti 0,002) Fe^{2+} 0,371) 2,002 Mn 0,006) Mg 1,534) Ca 0,065)	Ca 2,705) 3,734 Na 1,029)
	Wo 1,1 En 57,9 Fs 41,0	An 69,1 Ab 30,9	Wo 3,3 En 77,9 Fs 18,8	An 72,4 Ab 27,6

and pigeonite have been positively identified, occurring as discrete minerals. Alteration products include calcite and chlorite, while vesicular material includes calcite and zeolite.

3.1.3 Pronksberg Basalt (Drumbo Type)

The massive basalt completing the sequence preserved at Pronksberg closely resembles, both petrographically and chemically, the Drumbo Basalt in the Barkly East area, previously described by Lock et al. (1974), Robey (1976) and Pemberton (1978), and, as such, has been named accordingly.

A distinguishing feature of the Pronksberg Basalt (Drumbo Type) is the high percentage of glassy mesostasis, typically $\pm$ 10 percent in the Pronksberg occurrence. The basalt is hypocrystalline with intergranular to intersertal texture. Plagioclase (An_{40}-An_{60}) occurs as zoned subhedral laths, 0,5-1mm in length. Augite and pigeonite have been identified, occuring as discrete sub- to anhedral laths often ophitically related to the plagioclase. Olivine shows alteration to either iddingsite or bowlingite. Other alteration products are calcite and chlorite. Accessory minerals include Fe-Ti oxides, while K-feldspar has been tentatively identified. No directional textures are evident.

3.2 BELMORE ANDESITE

In hand specimen the Belmore Andesite resembles that of Pronksberg, but minor differences are evident in thin section.

The Belmore andesite is hypocrystalline, aphanitic and porphyritic to glomeroporphyritic. The phenocryst assemblage consists of plagioclase (An_{65}-An_{75}) and orthopyroxene (bronzite) with an average dimension of between 0,2 and 0,5mm but ranging up to 1,5mm in length. Microprobe analyses (Table 1) of the orthopyroxene (bronzite) show a slight range in composition,

from $Wo_3\ En_{78}Fs_{19}$ to $Wo_4\ En_{76}\ Fs_{20}$. Bronzite phenocrysts in Karoo lavas from the Barkly East area have previously been identified by Walker and Poldervaart (1949) and Pemberton (1978) in the Kraai River Formation, although no quantitative microprobe analyses were obtained.

The phenocrysts constitute about 20-30 percent of the rock. The mesostasis consists of lath-shaped plagioclase and pyroxene crystals up to 0,1mm in length in a brown glass matrix containing minute specks of opaque minerals.

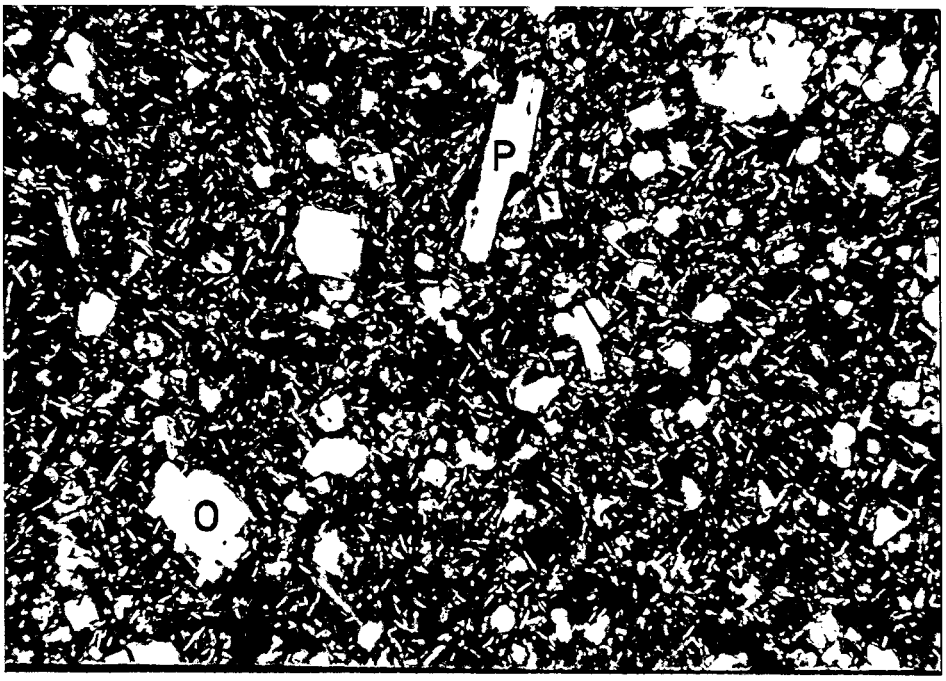
Several rocks include areas of up to 4mm in length consisting of a mosaic of small (20-100 micrometres), subhedral, equant to lath-shaped crystals of plagioclase and bronzite. These areas are reminiscent of spherulitic texture and are thought to be the result of either devitrification which has been nucleated by the presence of spherulites in the glass, or are xenolithic inclusions, the latter being the preferred hypothesis. The mosaics are composed of equal proportions of plagioclase and pyroxene (Plate 1).

No directional textures are evident in hand specimen or thin section.

3.3 ROODEHOEK ANDESITE

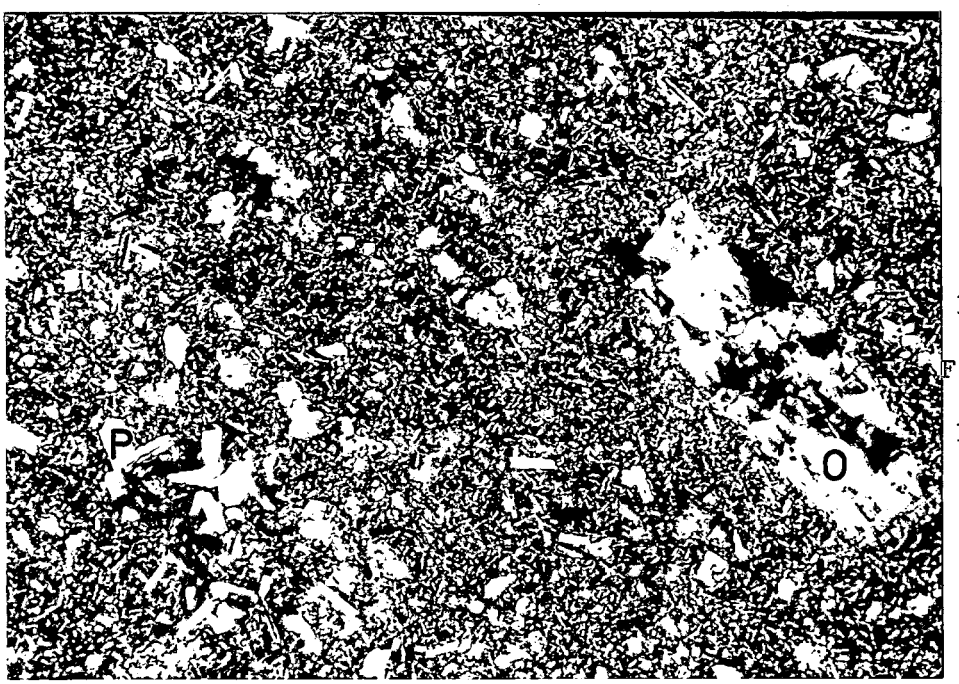
Thirteen samples from the Roodehoek intrusion have been examined microscopically. These include 3 contact-zone samples and 10 from the interior of the intrusion.

In thin section the rock is hypocrystalline, aphanitic-microcrystalline and displays a seriate texture. The groundmass shows intersertal texture, often including Fe-Ti oxide crystals. The dominant minerals are plagioclase (An_{40}-An_{60}), K-feldspar and quartz. No ferromagnesian minerals have been identified. The groundmass is vitrophyric and brown in colour and makes up 60 percent of the rock. The feldspars commonly exhibit myrmekitic inter-



PRONKSBERG
ANDESITE
Crossed Nicols (C.N.)
Field of view = 5 mm
o = orthopyroxene
P = plagioclase

Pronksberg andesite
plane polarised ligh
(p.p.l)
Field of view = 5 mm
o = orthopyroxene
P = plagioclase
U = unidentified
mineral.



Belmore Andesite
C.N.
Field of view = 4 mm
o = orthopyroxene
P = plagioclase

Plate 1 : Photomicrographs of Karoo basalts and andesites.

Pronksberg Basalt
(High K Type)

C.N.

Field of view = 4 mm

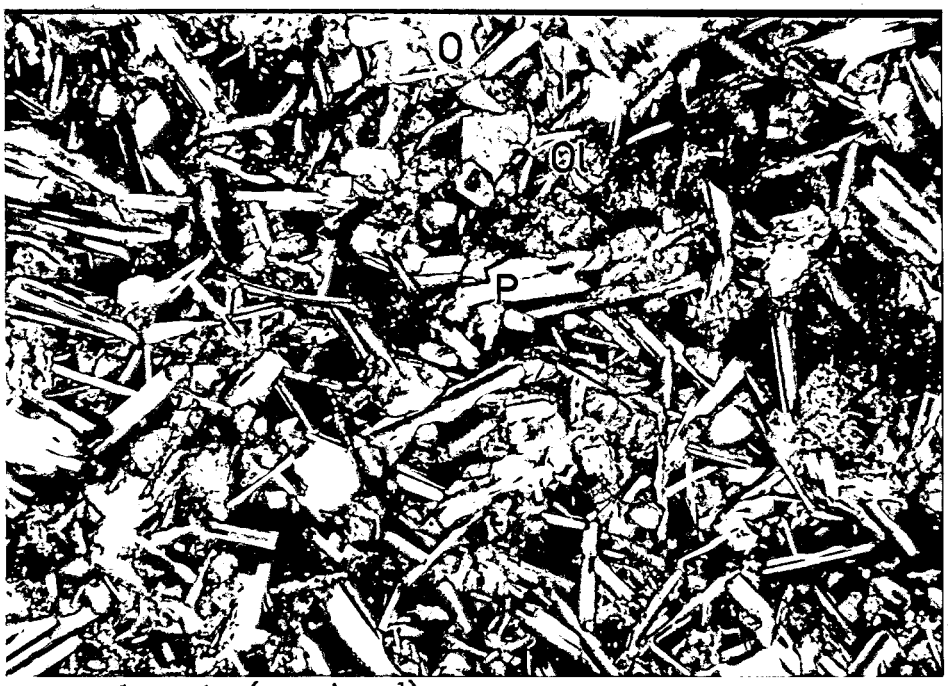
c = chlorite alteration
p = plagioclase
o = orthopyroxene

Pronksberg Basalt
(Drumbo Type)

C.N.

Field of view = 4 mm

ol = olivine
p = plagioclase
o = orthopyroxene



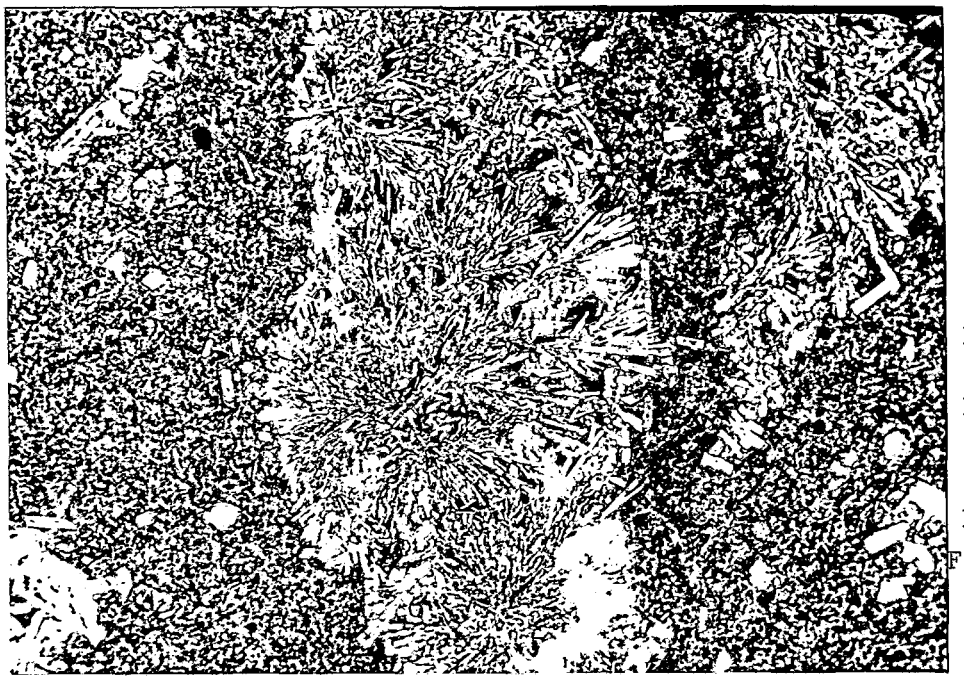
Drumbo Basalt
(Barkly East area)

C.N.

Field of view = 5 mm

ol = olivine
p = plagioclase
o = orthopyroxene

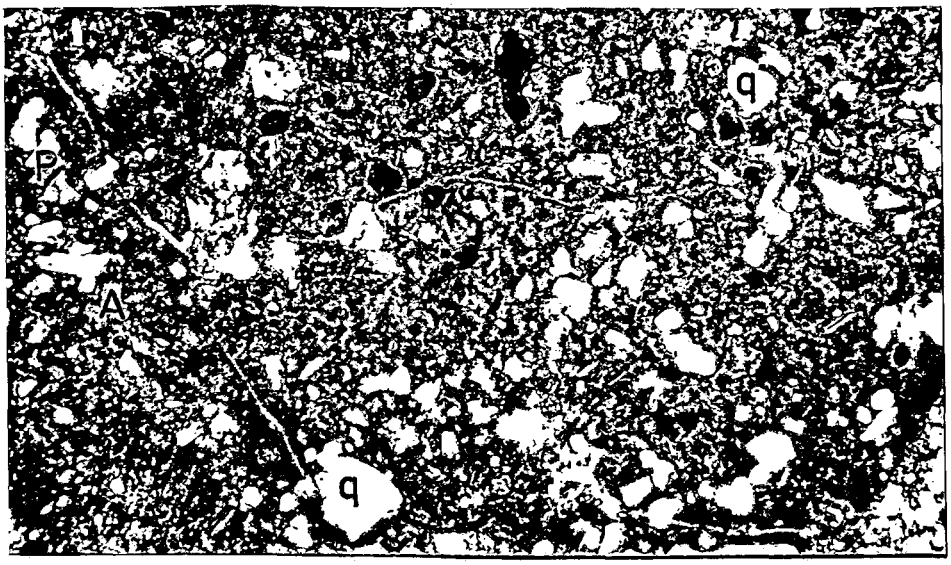
Plate 1 (continued)



Belmore Andesite showing mosaic of plagioclase and orthopyroxene

p.p.l.

Field of view = 4 mm

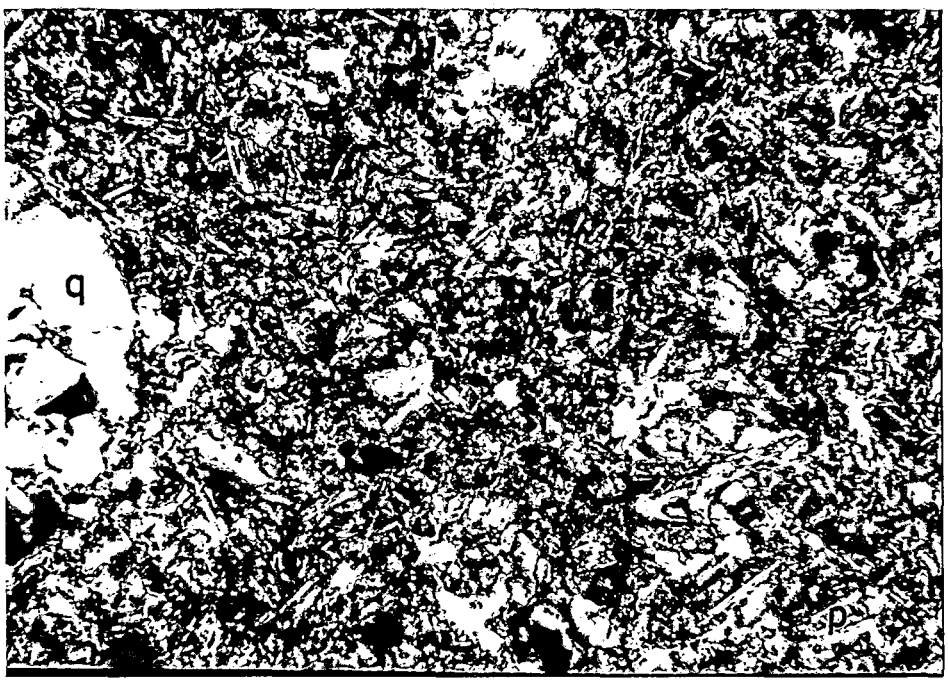


Bell River Andesite Breccia

C.N.

Field of view = 4 mm

q = quartz
p = plagioclase
a = andesitic glass



Roodehoek Andesite

C.N.

Field of view = 4 mm

q = quartz
p = plagioclase

Plate 1 (continued)

growths.

Contact-zone rocks are distinctly porphyritic to glomeroporphyritic with labradorite phenocrysts up to 1mm in length, with a groundmass consisting of brown glass, plagioclase, K-feldspar and quartz. One contact-zone rock consists of unaltered plagioclase phenocrysts set in a fine-grained mosaic of calcite which is thought to represent primary hydrothermal alteration at the time of intrusion. Non-contact andesites exhibit alteration of felsic constituents to calcite and chlorite. Several examples studied have quartz particles and lithic fragments welded and moulded upon one another, embedded in a glassy matrix. These probably represent wall-rock inclusions. A typical Roodehoek andesite is shown in Plate 1.

4. MAJOR ELEMENT GEOCHEMISTRY

4.1 INTRODUCTION

Major and trace element analyses are presented for 41 andesitic and associated basaltic rocks from the three occurrences under study. These include 24 from the Pronksberg and Dikkop locality, 10 from Belmore and 7 from Roodehoek. Analytical techniques and spectrometer settings used in this study are presented in Appendix 2.

The following section includes a discussion of the classification of the rock types being studied, and presents major element data for these rocks. Differences in chemical composition between andesitic and basaltic rocks are discussed, as well as variations through the Belmore and Pronksberg andesites with height. Major element variations are discussed with the aid of SiO_2 variation diagrams, AFM diagrams and normative chemistry.

All major element data quoted in the following section are given in the form of anhydrous values normalised to 100 percent and are listed in Appendix 1. All Fe was determined as Fe_2O_3.

TABLE 3 : MAJOR AND TRACE ELEMENT ANALYSES OF SAMPLES FROM PRONKSBERG, DIKKOP BELMORE AND ROODEHOEK.

PRONKSBERG ANDESITE

	KR2	KR3	KR4	KR5	KR6	KR8	KR9
SiO_2	63,15	62,95	63,99	62,08	63,18	64,01	63,50
TiO_2	0,77	0,75	0,78	0,74	0,75	0,76	0,77
Al_2O_3	16,44	16,49	16,56	16,19	16,66	16,79	16,65
Fe_2O_3	6,20	6,09	6,34	6,02	6,25	6,07	6,17
MnO	0,15	0,15	0,16	0,15	0,15	0,17	0,18
MgO	2,31	2,22	2,43	2,15	2,23	2,36	2,39
CaO	2,82	2,49	2,85	2,39	2,56	2,50	2,83
Na_2O	3,29	3,69	3,51	3,65	3,56	3,67	3,44
K_2O	1,46	1,17	1,27	1,28	1,15	1,25	1,29
P_2O_5	0;24	0,24	0,25	0,24	0,24	0,26	0,25
L.O.I.	3,25	2,75	2,36	2,52	2,87	2,52	2,61
H_2O^+	0,89	0,52	0,51	0,66	0,57	0,57	0,44
TOTAL	100,97	99,51	100,99	98,17	100,17	100,93	100,50
Ba	729	744	746	757	733	773	729
Sr	328	327	292	296	320	344	312
Rb	103	97	161	147	117	95	136
Y	30	31	32	31	31	31	30
Zr	196	194	197	201	198	196	198
Nb	12,9	12,5	13,9	12,9	12,9	14,9	12,0
Zn	91	91	97	96	93	98	93
Cu	27	25	28	26	24	28	26
Co	17,6	17,2	18,4	18,3	17,5	17,7	17,4
Ni	25	27	30	27	26	30	26
V	85	62	66	67	62	62	66
Cr	55	50	50	52	54	51	56
Ce	96	90	92	90	92	-	90
Nd	38	37	38	36	36	-	37
La	37	39	40	40	38	-	39

TABLE 3 (continued)

PRONKSBERG ANDESITE

	KR11	KR17	KR19	KR20	KR21
SiO_2	63,61	62,51	62,79	63,37	63,66
TiO_2	0,75	0,75	0,75	0,75	0,76
Al_2O_3	16,84	16,49	16,45	16,59	16,56
Fe_2O_3	6,18	6,08	6,12	6,15	6,02
MnO	0,15	0,17	0,16	0,17	0,17
MgO	2,15	2,31	2,30	2,29	2,26
CaO	2,57	2,86	2,84	2,77	2,66
Na_2O	3,28	3,52	3,20	3,27	3,33
K_2O	1,32	1,16	1,14	1,27	1,32
P_2O_5	0,24	0,24	0,25	0,24	0,25
L.O.I.	3,18	3,39	3,51	3,35	3,18
H_2O^+	0,69	0,30	0,36	0,41	0,31
TOTAL	100,91	100,29	99,86	100,65	100,48
Ba	751	713	724	712	717
Sr	312	310	299	313	300
Rb	157	162	166	173	181
Y	29	31	28	30	29
Zr	195	198	191	195	195
Nb	12,7	13,1	12,2	12,9	13,0
Zn	97	96	91	92	92
Cu	28	26	26	26	25
Co	17,4	18,5	19,0	17,8	17,8
Ni	28	27	26	28	27
V	64	65	65	64	63
Cr	55	53	49	51	49
Ce	95	93	91	92	90
Nd	37	36	36	37	35
La	37	36	38	33	38

TABLE 3 (continued)

PRONKSBERG BASALT (HIGH K)

	KR22	KR23	KR24	KR25	KR26
SiO_2	50,43	51,64	50,51	51,95	53,75
TiO_2	0,96	0,98	0,98	0,96	1,01
Al_2O_3	15,84	15,29	16,04	15,37	16,28
Fe_2O_3	9,75	9,81	9,84	9,65	10,10
MnO	0,23	0,25	0,27	0,25	0,25
MgO	6,39	5,95	6,62	6,01	6,47
CaO	6,58	6,40	6,88	6,31	6,59
Na_2O	3,21	3,31	2,92	3,12	3,49
K_2O	1,78	1,98	1,90	1,93	1,82
P_2O_5	0,24	0,24	0,23	0,22	0,25
L.O.I.	4,13	3,79	3,32	3,25	1,43
H_2O^+	0,35	0,37	0,30	0,23	0,24
TOTAL	99,89	100,01	99,81	99,25	101,67
Ba	708	559	778	681	588
Sr	473	506	484	443	451
Rb	37	45	40	37	41
Y	25	24	25	24	26
Zr	128	134	132	133	141
Nb	13,5	15,1	14,7	16,5	15,5
Zn	82	79	81	81	85
Cu	71	70	70	68	60
Co	38	36	37	38	38
Ni	69	67	67	66	72
V	143	146	149	164	159
Cr	224	208	225	224	238
Ce	41	42	41	37	42
Nd	18,2	19,0	19,5	19,6	21,2
La	14,6	16,1	15,7	15,7	17,3

TABLE 3 (continued)

	PRONKSBERG BASALT (DRUMBO TYPE)			DIKKOP ANDESITE			
	KR27	KR28	KR29	KRD1	KRD3	KRD4	KRD5
SiO_2	50,43	51,27	51,35	62,70	62,90	63,44	62,34
TiO_2	0,96	0,99	1,01	0,77	0,77	0,78	0,78
Al_2O_3	15,29	15,55	15,37	16,68	16,84	16,74	16,60
Fe_2O_3	9,93	10,20	10,28	6,31	6,27	6,43	6,33
MnO	0,24	0,24	0,27	0,17	0,16	0,18	0,16
MgO	6,28	6,20	6,14	2,27	2,29	2,27	2,29
CaO	9,96	9m94	9,98	2,54	2,52	2,56	3,11
Na_2O	2,60	2,44	2,73	2,59	2,54	2,62	2,82
K_2O	0,86	0,90	0,93	2,42	2,46	2,32	1,26
P_2O_5	0,24	0,25	0,24	0,25	0,25	0,25	0,25
L.O.I.	2,80	1,40	2,71	3,01	2,75	2,40	3,98
H_2O^+	0,44	0,15	0,28	0,43	0,45	0,30	0,61
TOTAL	100,03	99,54	101,28	100,14	100,19	100,29	100,53
Ba	262	233	299	735	738	749	828
Sr	298	297	322	290	296	289	313
Rb	20	21	20	147	155	152	93
Y	24	24	26	30	32	28	31
Zr	129	132	138	193	202	195	190
Nb	14,0	14,0	15	12,0	16,3	13,5	11,5
Zn	80	80	77	96	95	98	96
Cu	64	62	66	27	26	26	25
Co	35	37	35	17,7	17,8	17,5	18,0
Ni	70	67	69	27	26	26	26
V	134	135	174	64	68	67	67
Cr	241	214	216	46	47	50	46
Ce	40	45	38	96	89	95	93
Nd	16,7	20,5	15,6	39	36	36	35
La	16,4	20,4	15,7	39	38	38	39

TABLE 3 (continued)

BELMORE ANDESITE

	KRB1	KRB3	KRB6	KRB7	KRB8	KRB9	KRB10
SiO_2	63,81	61,55	61,26	61,93	61,69	62,17	62,52
TiO_2	0,73	0,77	0,80	0,79	0,79	0,78	0,79
Al_2O_3	15,74	15,41	15,59	15,61	15,48	15,73	15,66
Fe_2O_3	6,19	6,34	7,61	7,37	7,46	7,24	6,92
MnO	0,16	0,16	0,19	0,20	0,20	0,19	0,18
MgO	2,65	2,84	3,71	3,64	3,54	3,50	2,80
CaO	4,03	4,95	5,72	5,16	5,23	5,27	4,31
Na_2O	2,69	1,77	2,54	2,35	2,22	2,45	2,47
K_2O	1,57	2,16	1,71	2,40	2,49	2,10	2,30
P_2O_5	0,21	0,21	0,21	0,21	0,21	0,21	0,21
L.O.I.	2,73	3,41	1,25	0,38	0,43	0,93	1,64
H_2O^+	0,53	1,44	0,80	0,96	0,83	0,82	1,20
TOTAL	101,04	101,01	101,39	101,00	100,56	101,39	101,00
Ba	709	502	504	499	503	549	615
Sr	299	409	265	251	252	264	299
Rb	135	60	118	103	88	93	109
Y	34	30	28	29	30	30	31
Zr	214	197	192	193	191	197	210
Nb	11,4	10,5	9,8	10,6	9,0	10,8	11,2
Zn	79	80	87	84	85	84	85
Cu	31	33	41	-	44	42	34
Co	20	23	26	25	27	25	21
Ni	26	31	39	-	41	-	31
V	76	93	111	114	114	104	89
Cr	61	70	104	111	120	96	62
Ce	88	85	82	70	72	71	83
Nd	35	36	33	29	30	31	35
La	35	35	32	30	30	30	32

TABLE 3 (continued)

	DRUMBO BASALT			ROODEHOEK ANDESITE						
	KRB4	KRB5	KRB14	KAM6	KAM6X	KAM 8	KAM11	KAM12	KAM13	KAM17
SiO_2	48,93	51,04	52,28	63,71	63,83	62,39	63,82	63,88	63,89	64,95
TiO_2	1,05	1,06	1,11	0,76	0,76	0,74	0,76	0,76	0,75	0,73
Al_2O_3	15,76	15,70	16,30	15,55	15,48	15,03	15,56	15,29	15,39	15,42
Fe_2O_3	8,64	10,10	8,93	5,91	5,79	5,83	5,95	5,83	5,68	5,57
MnO	0,24	0,23	0,22	0,15	0,16	0,14	0,14	0,14	0,17	0,15
MgO	4,87	5,47	4,41	2,35	2,31	2,45	2,54	2,39	2,30	2,38
CaO	11,13	10,25	10,47	2,68	2,71	2,37	2,11	2,33	2,72	2,33
Na_2O	1,91	2,25	3,13	2,82	2,59	2,35	2,73	2,67	2,36	2,49
K_2O	0,79	0,90	0,98	2,53	2,62	2,75	2,90	2,66	2,62	2,87
P_2O_5	0,26	0,27	0,27	0,23	0,22	0,21	0,23	0,22	0,22	0,22
L.O.I.	5,19	2,36	1,37	4,05	4,38	7,25	2,39	2,54	2,35	1,81
H_2O^+	1,02	9,94	1,03	0,21	0,51	0,34	0,60	0,54	1,32	0,65
TOTAL	99,79	100,57	100,50	100,95	101,36	101,84	99,73	99,25	99,77	99,56
Ba	201	234	-	600	626	658	663	601	599	628
Sr	300	319	336	250	244	230	238	238	281	242
Rb	15,7	19,0	20,0	113	116	113	122	117	119	126
Y	25	27	28	30	31	28	29	30	-	29
Zr	135	150	152	216	224	213	216	218	222	221
Nb	15,0	17,0	17,3	9,3	11,4	10,6	10,5	10,6	11,1	10,9
Zn	82	77	-	85	87	82	77	87	85	81
Cu	67	72	-	20	20	25	20	21	20	23
Co	35	36	35	20	20	19	21	20	19	18
Ni	65	66	-	22	20	25	21	21	23	24
V	167	139	140	95	87	88	89	89	86	78
Cr	228	210	211	91	78	86	86	81	76	79
Ce	38	44	43	75	80	75	77	81	82	80
Nd	19	24	22	31	32	31	32	35	32	30
La	14	20	18	30	33	30	33	29	32	32

4.2 SAMPLING

A detailed sampling program was carried out during the course of three field trips to the study area in 1978. Of a total of 80 samples collected, 56 were selected for chemical analyses, of which 15 were rejected due to analytical problems. The sampling procedure was carried out on the basis of :

(a) Systematic sampling over as wide an area as possible for a particular outcrop.

(b) Sampling vertically through a flow e.g., Pronksberg andesite, or sequence of flows e.g., Belmore andesite, in order to determine inter- and and intraflow variations in chemistry.

(c) Sampling of over- and underlying rocks in order to investigate possible genetic links.

Sample localities are shown on Figures 2, 3 and 4 for Pronksberg, Belmore and Roodehoek respectively.

4.3 PRECISION OF THE DATA

When evaluating differences in chemical composition between a suite of lavas or variations within a particular lava, some measure is needed in deciding when a particular chemical variation is statistically significant or insignificant, especially where variations are slight.

The results of a study of analytical precision conducted by Kruger (1978) have been used in this investigation as an indication of the magnitude of chemical variation which may be expected to arise from method of sample preparation and analysis. Kruger (1978) separated 11 subsamples from a single Kimberlite sample during the crushing stage of sample preparation which were prepared for chemical analysis and analysed under exactly the same analytical conditions. The results of Kruger's study are listed in Table 2. It should be pointed out that Kruger's study was conducted

TABLE 2

STATISTICS OF THE L10 PRECISION RUN (KRUGER, 1978)

MAJOR ELEMENTS

	Range	X	s	$^{s}/_{X}\%$
SIO2	37,06 - 38,15	37,39	0,29	1.00
TIO2	1,58 - 1,64	1.60	0.02	1.09
AL203	5,16 - 5,30	5.20	0.05	0.98
FE203	9,72 - 10,16	9.86	0.12	1.18
MNO	0,14 - 0,16	0.15	0.01	4.61
MGO	24,58 - 25,28	24.81	0.20	0.82
CAO	7.05 - 7,31	7.16	0.08	1.10
NA20	0,39 - 0,42	0.40	0.01	2.61
K20	1,95 - 2,07	2.00	0.04	1.76
P205	0,51 - 0,53	0.52	0.01	1.22
L.O.I.	7,75 - 8,36	8.05	0.17	2.09
H20	2,55 - 2,87	2.71	0.10	3.79
TOTAL		99.85		

TRACE ELEMENTS

	Range	X	s	$^{s}/_{X}\%$	COUNTING PRECISION 1s PPM	L.L.D. PPM
SR	572 - 614	589	13	2.22	0.9	1.4
RB	67 - 72	69	1.2	0.03	0.5	1.3
Y	13 - 15	14	0.36	2.61	0.4	1.3
ZR	156 - 166	160	3	1.87	0.6	1.4
NB	88 - 92	90	1.1	1.22	0.5	1.4
ZN	67 - 70	68	1.1	1.64	0.6	1.4
CU	48 - 60	53	3.0	5.76	2.1	6.0
CO		83	-	-	0.8	3.0
NI	1146 - 1230	1172	24	2.03	1.7	1.4
V		139	-	-	1.1	3.9
CR		904	-	-	1.8	2.6
LA	43 - 46	45	0.9	2.10	1.5	5.0
CE	73 - 83	79	3.3	4.24	3.2	12.0
ND	31 - 36	33	1.7	5.07	1.7	6.0
TH		7	-	-	1.1	3.1

on a coarse-grained heterogeneous Kimberlite sample. Chemical variations listed by Kruger are specifically for particular concentration levels for each element. Chemical variations for a fine-grained andesite will differ from those found by Kruger, but his data are nevertheless significant in that chemical variations within a basalt or andesite, at comparable concentration levels, greater than those presented by Kruger will almost certainly represent real variations in chemistry.

The results and statistical analysis presented by Kruger (op.cit.) puts limits on the precision and accuracy that can be assumed from a single analysis. The results listed in Table 2 are therefore used in this study as a measure of what degree of chemical variation may be regarded as significant or whether the variation is a function of analytical precision.

4.4 CLASSIFICATION

4.4.1 Nomenclature

Coats (1967) and Irvine and Baragar (1971) have reviewed historical developments in methods to distinguish between basalts and andesites. Early definitions as proposed by Rosenbusch (1923), Harker (1923), Holmes (1929) and others, are based largely on variations in mineralogy, generally relying on the composition of plagioclase as the distinction between basalt and andesite, andesites being those rocks with the more sodic feldspar and basalts those containing labradorite and bytownite. Later workers such as Hatch et al. (1949) and Williams et al.(1954) adopted various classifications based on colour indices as well as normative plagioclase composition.

While modern classifications such as those of Irvine and Baragar (1971) Nicholls (1971), Peccerillo and Taylor (1976) and Le Maitre (1976) delineate the basalt-andesite boundary fairly precisely, it appears that the andesite-dacite division is less well established. Irvine and Baragar (op.cit.)

for example, state that the most arbitrary dividing line in their classification is between andesite and dacite, simply because this distinction is extremely vague in the literature.

The problem of nomenclature in this study is further complicated by the fact that many of the rocks being studied are located on the andesite-dacite transition, given by most authors as being in the region of 63-65 percent SiO_2 (Taylor, 1969). For this reason it was decided to use two different classifications in the present study, one using absolute oxide concentrations (Peccerillo and Taylor, 1976), and the other based on normative plagioclase and normative colour index (Irvine and Baragar, 1971). A comparison of results using both volatile-inclusive and volatile-free analyses was also undertaken. The results are plotted on Figures 5 and 6.

The classification of Peccerillo and Taylor (op.cit.) who use a K_2O vs. SiO_2 plot is relatively simple and therefore used fairly widely. Peccerillo and Taylor (op.cit.) do not indicate whether their classification is conceived using water-inclusive or water-free analyses. As their chemical analyses presented are water-free, one might assume that their classification has been derived using water-free analyses, which is logical. This study has, however, investigated the applicability of the Peccerillo and Taylor (op.cit.) classification using both volatile-inclusive and volatile-exclusive analyses. A major drawback of this classification, encountered in this study, is the fact that when using volatile-inclusive as opposed to volatile-free analyses, two different results are obtained. This problem is accentuated with analyses plotting on or near the andesite - dacite transition as is the case in this study. Volatile-inclusive analyses in the present study plot in the andesite field or on the andesite-dacite transition. Volatile-free analyses, however, plot further into the dacite

FIG.5 The Classification of the Karoo andesites (Following Peccerillo and Taylor, 1976).

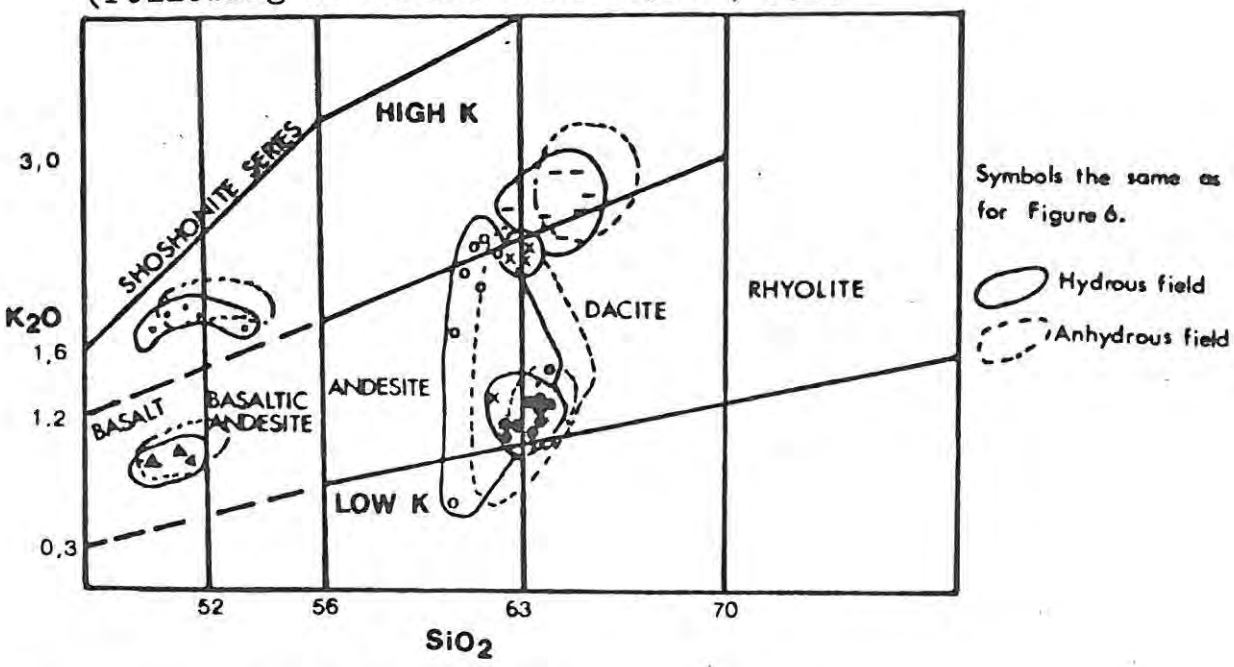
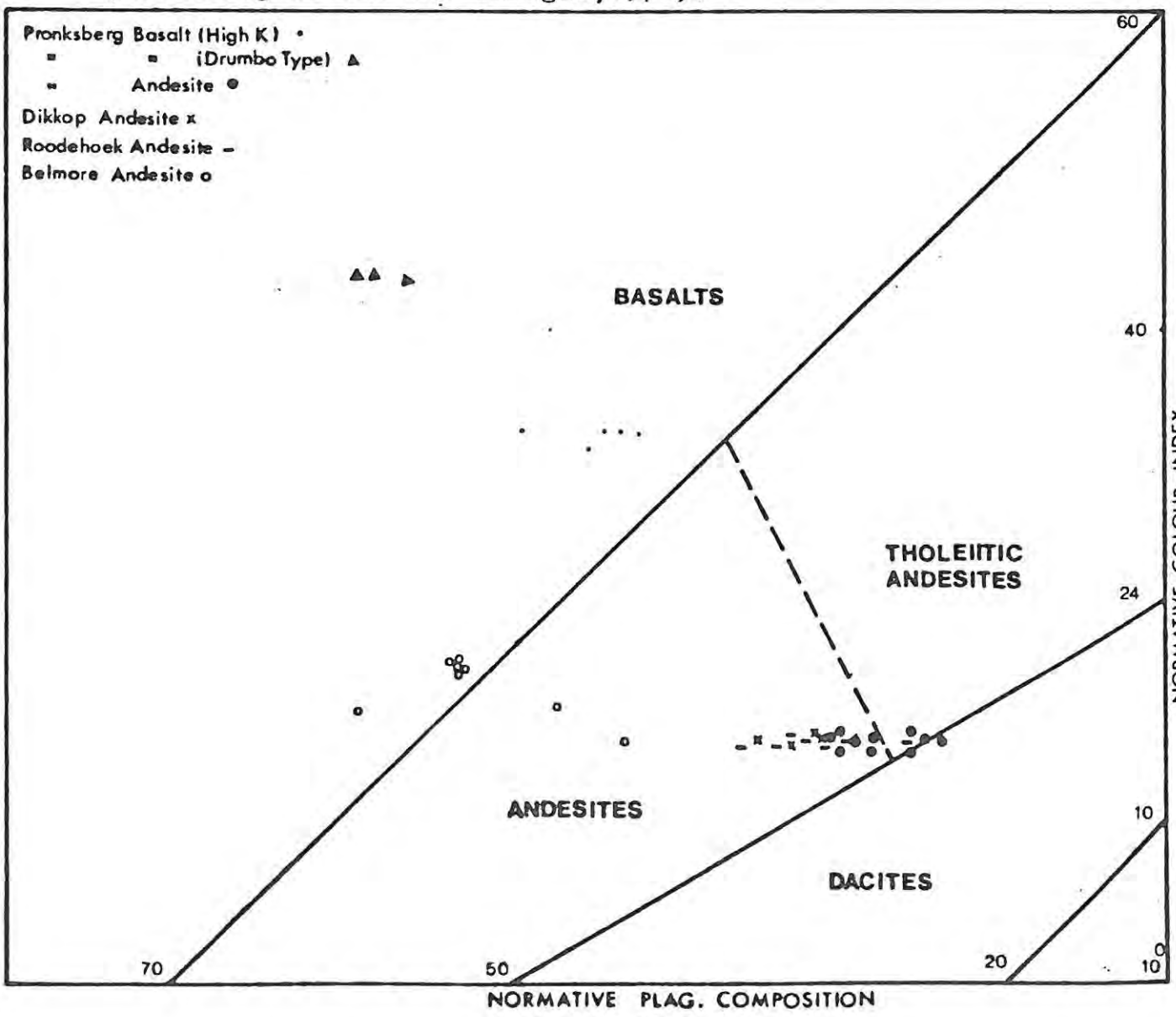


FIG.6 The Classification of the Karoo andesites (Following Irvine and Baragar, 1971).



field. A problem therefore arises as to which approach to adopt for classification purposes.

An advantage of the Peccerillo and Taylor (op.cit.) scheme is that the various fields are further categorised according to K_2O content. Suites of lava having substantial potassium differences may this be named accordingly.

The classification of Irvine and Baragar (1971) was devised using analyses normalised to 100 percent volatile-free. Irvine and Baragar (op.cit.) note that the classification should be applied without consideration of genetic or tectonic affiliations. Using the classification of Irvine and Baragar (op.cit.) in which normative plagioclase composition is plotted against normative colour index, consistent results are obtained irrespective of whether water-inclusive or water-exclusive analyses are used. Using this classification, the intermediate rocks studied plot largely in the andesite field, the exception being the Belmore andesite which plots in both the basalt and andesite field. On the basis of consistent results using volatile-inclusive and volatile-exclusive results, the Irvine and Baragar classification is preferred, and the intermediate rocks classified as andesites. The distinction based on differing K_2O contents of the Peccerillo and Taylor classification has, however, been recognised and the vesicular Pronksberg basalt has consequently been termed the Pronksberg Basalt (High K Type).

4.4.2 Calc-Alkali Trends

Robey (1976) and Pemberton (1978) confirm the tholeiitic character of the Drakensberg Subgroup. Robey (op.cit.) analysed one Belmore andesite and following the Irvine and Baragar (op.cit., Fig.2) classification, noted

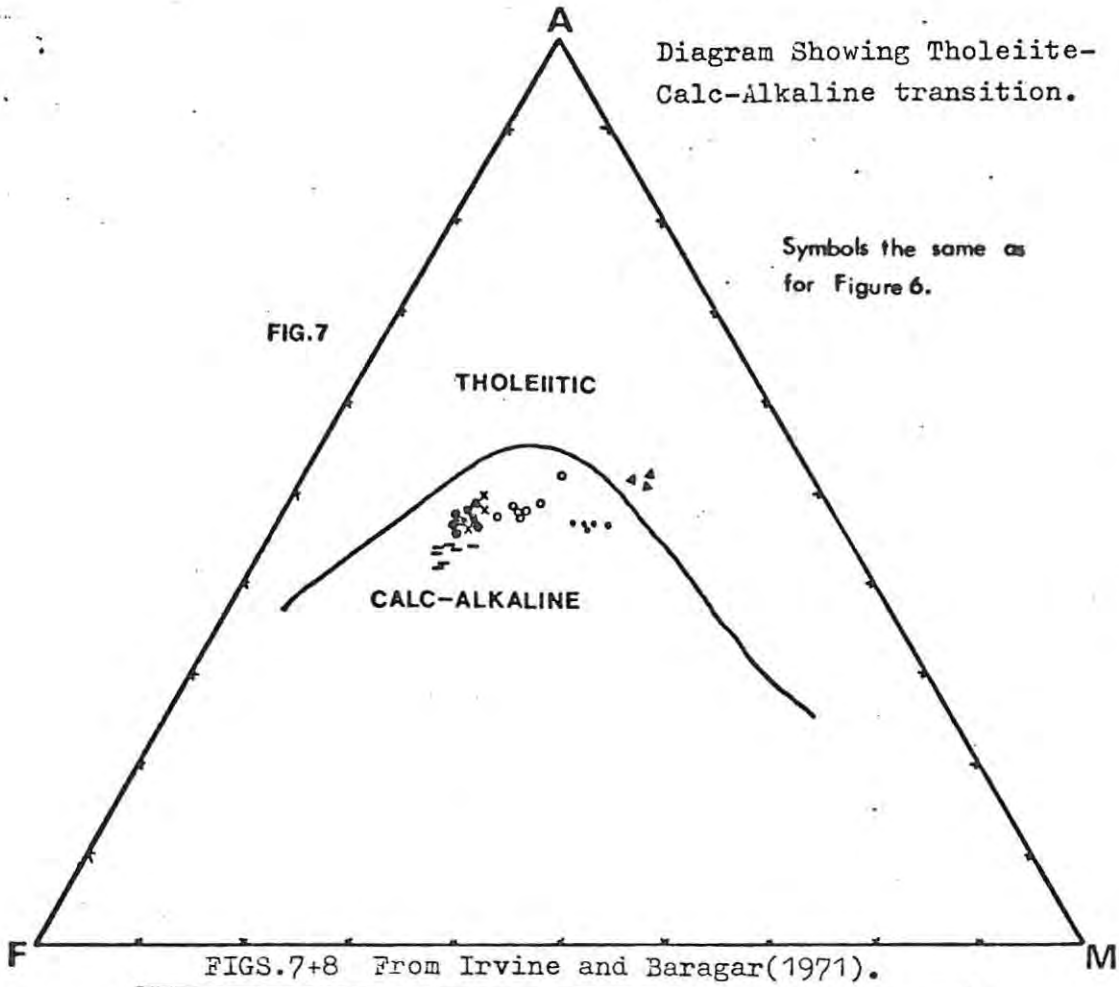


Diagram Showing Tholeiite-Calc-Alkaline transition.

Symbols the same as for Figure 6.

FIG.7

FIGS.7+8 From Irvine and Baragar(1971).

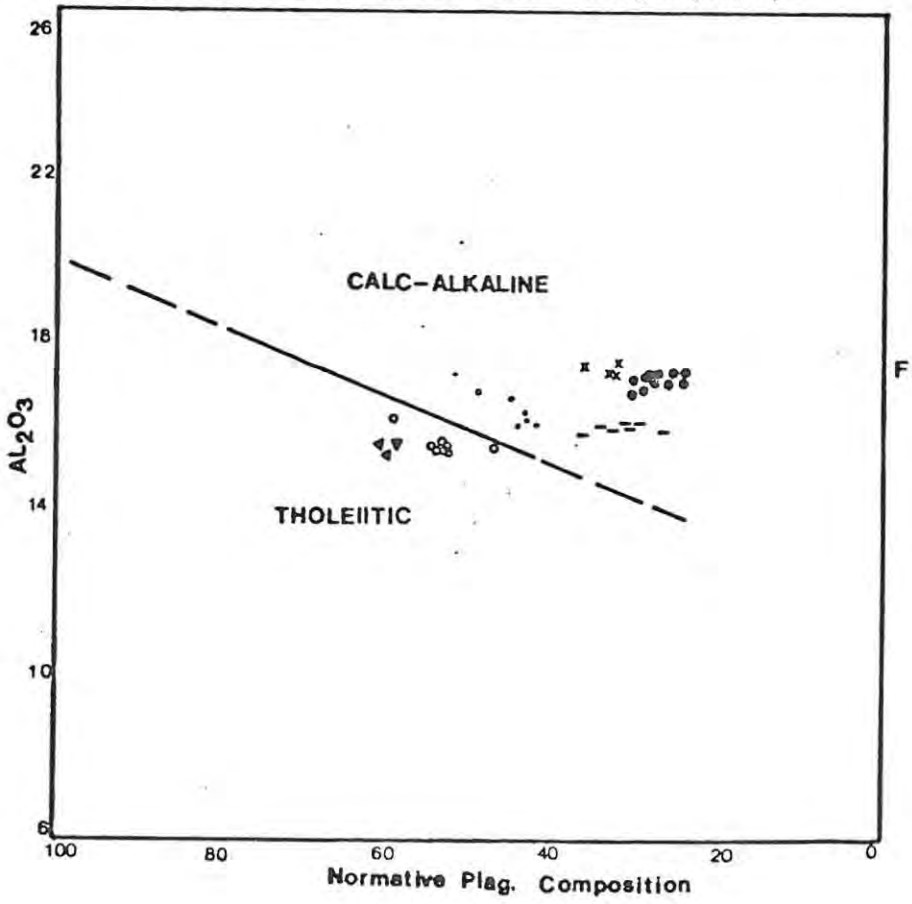


FIG. 8

that it plots near the boundary separating the tholeiite and calc-alkali fields. Robey (op.cit.) does, however, recognise that the andesite differs from normal calc-alkaline andesites in that it contains corundum in the norm. The significance of normative corundum is discussed in Section 4.6.

An AFM plot (Figure 7) illustrates the calc-alkaline affinities of the Karroo andesites and recognises the calc-alkaline tendencies of the Pronksberg Basalt (High K Type). All of the andesites are seen to plot well within the calc-alkaline field. Irvine and Baragar (op.cit.) use a plot of Al_2O_3 vs. normative plagioclase composition to separate the two fields. The calc-alkaline character of the Karroo andesites is confirmed using this plot, although several of the Belmore andesites plot on the calc-alkaline-tholeiite transition (Figure 8). Similar results are obtained using the classification of Green (1973). A detailed comparison of the Karroo andesites and typical calc-alkaline andesites is presented in Section 6.

4.5 MAJOR ELEMENT VARIATIONS

Major element data for rocks from the three localities under study are presented in Table 3. Differences in chemical composition between the various rock types for the three localities are discussed with the aid of SiO_2 variation diagrams (Figure 9a-h). Chemical variations with height for the Pronksberg and Belmore andesites are shown in Figures 10 and 11 respectively. A comparison is also drawn between the three andesite occurrences, and the Pronksberg basalts are compared with the Drumbo Basalt Member described by Pemberton (1978).

4.5.1 Pronksberg

4.5.1.1 Pronksberg and Dikkop Andesites

(Analyses KR 2-21, KRD 1,3,4 + 5 - Table 3)

Petrographic similarities and spatial proximity justify a combined discussion of the Pronksberg and Dikkop andesites.

The Pronksberg andesite shows only minor intraflow variations (Figure 10).

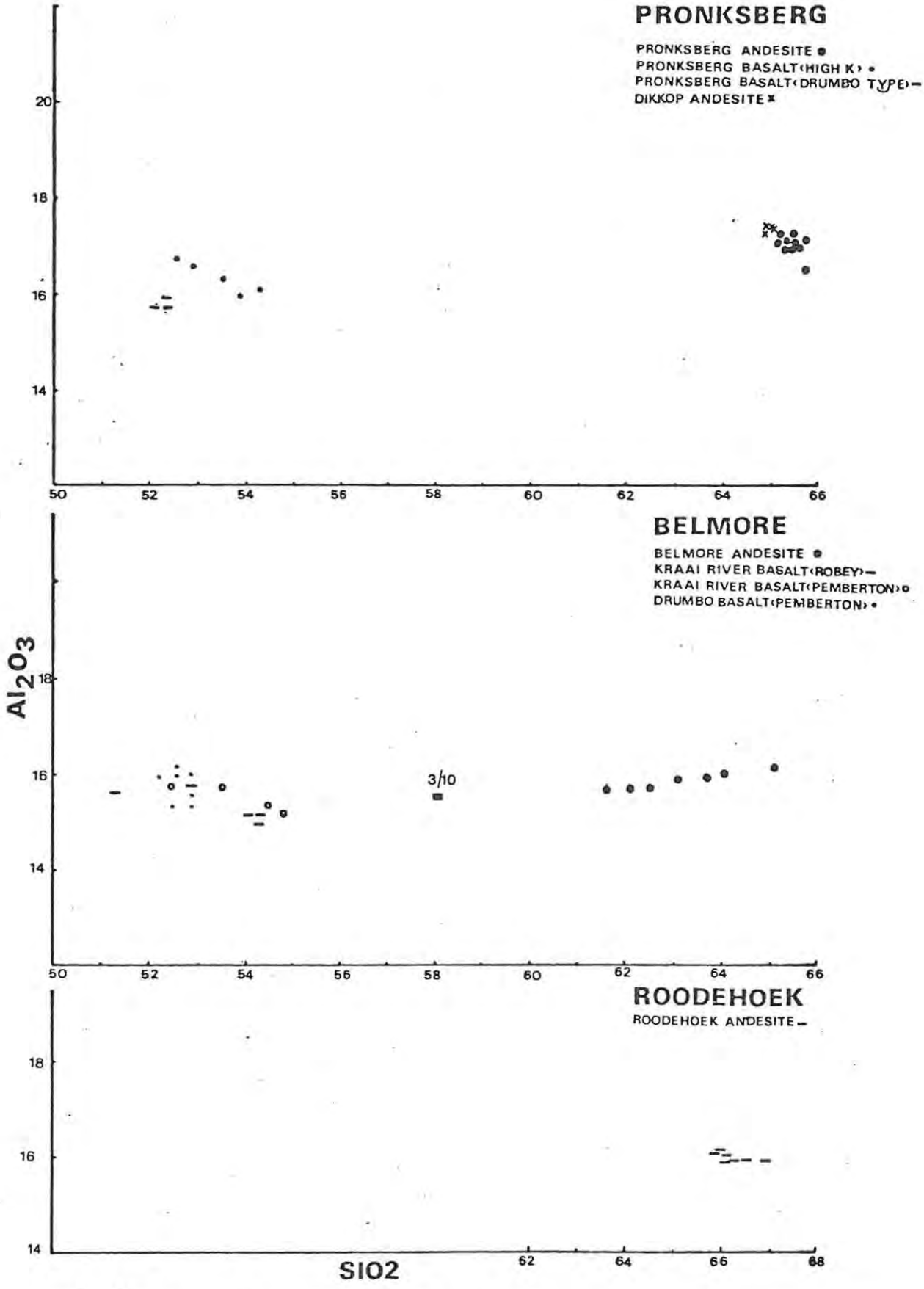


FIG.9 Major element data for the Karoo andesites and Basalts plotted against SiO_2.

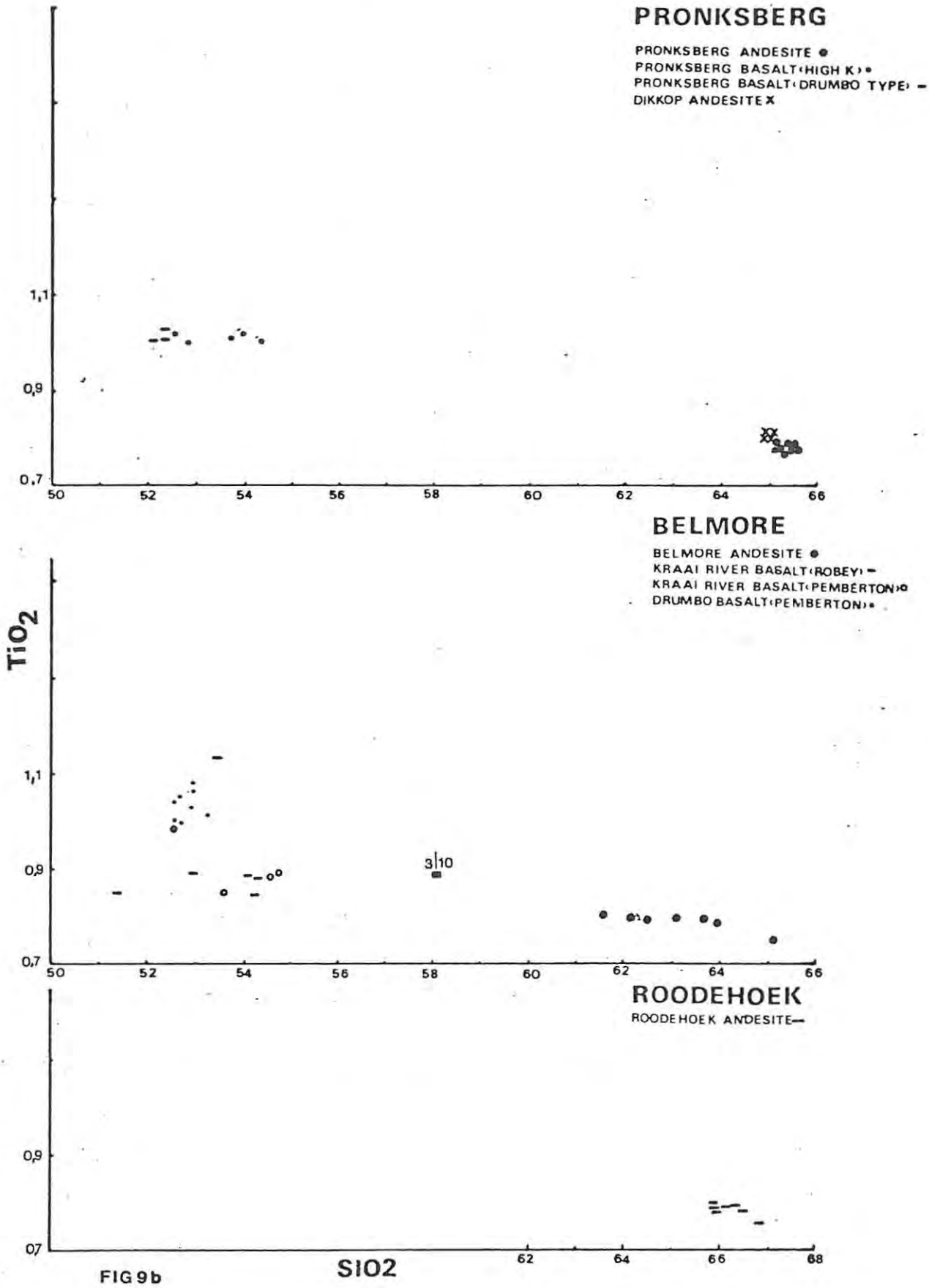

PRONKSBERG
PRONKSBERG ANDESITE
PRONKSBERG BASALT(HIGH K)
PRONKSBERG BASALT(DRUMBO TYPE)
DIKKOP ANDESITE
BELMORE
BELMORE ANDESITE
KRAAI RIVER BASALT(ROBEY)
KRAAI RIVER BASALT(PEMBERTON)
DRUMBO BASALT(PEMBERTON)
ROODEHOEK
ROODEHOEK ANDESITE
TiO2
SIO2
3|10
1,1
0,9
0,7
50
52
54
56
58
60
62
64
66
68

FIG 9b

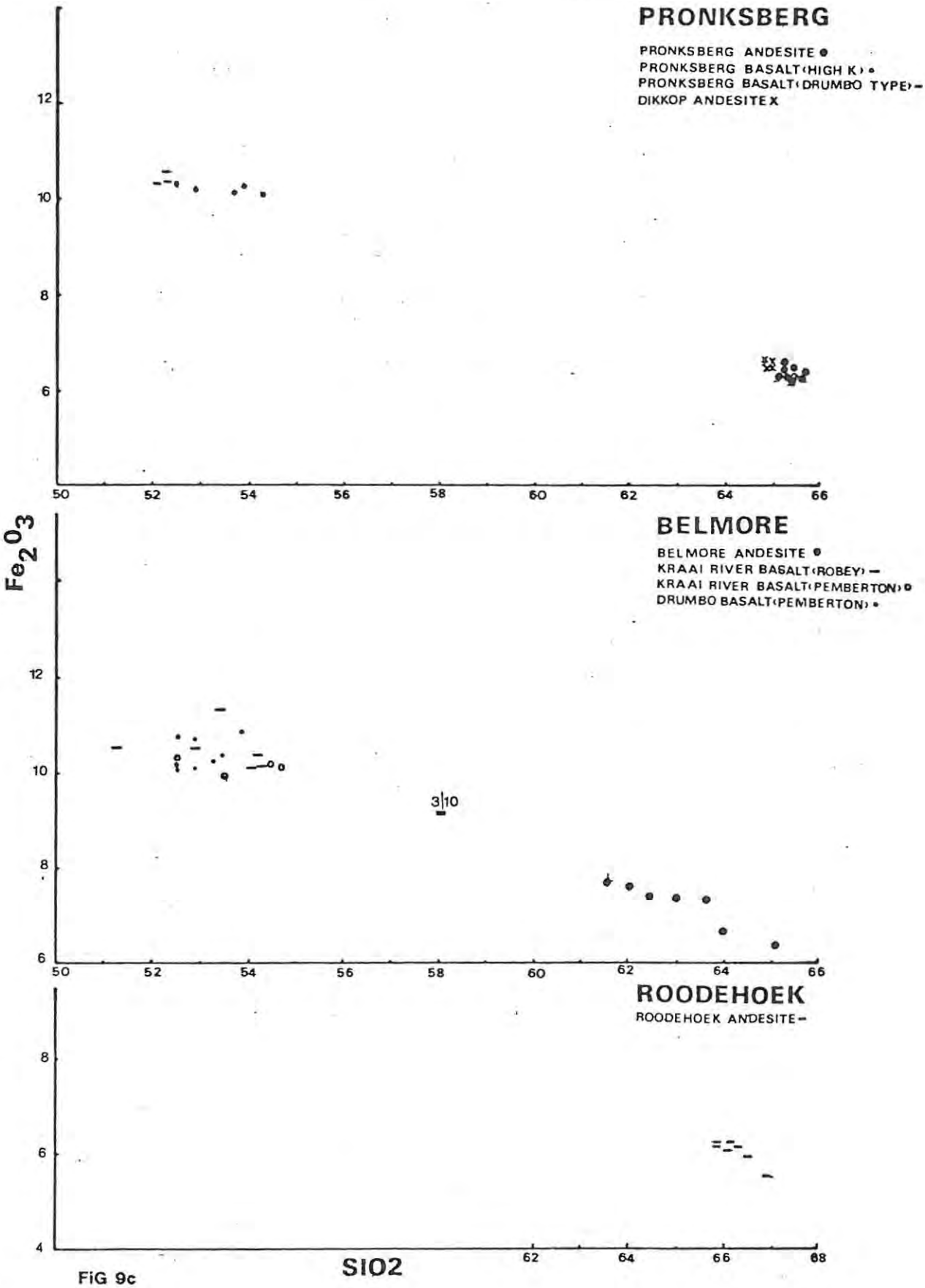

PRONKSBERG
PRONKSBERG ANDESITE
PRONKSBERG BASALT(HIGH K)
PRONKSBERG BASALT(DRUMBO TYPE)
DIKKOP ANDESITE
BELMORE
BELMORE ANDESITE
KRAAI RIVER BASALT(ROBEY)
KRAAI RIVER BASALT(PEMBERTON)
DRUMBO BASALT(PEMBERTON)
ROODEHOEK
ROODEHOEK ANDESITE
Fe2O3
SIO2
3/10
12
10
8
6
4
50
52
54
56
58
60
62
64
66
68

FiG 9c

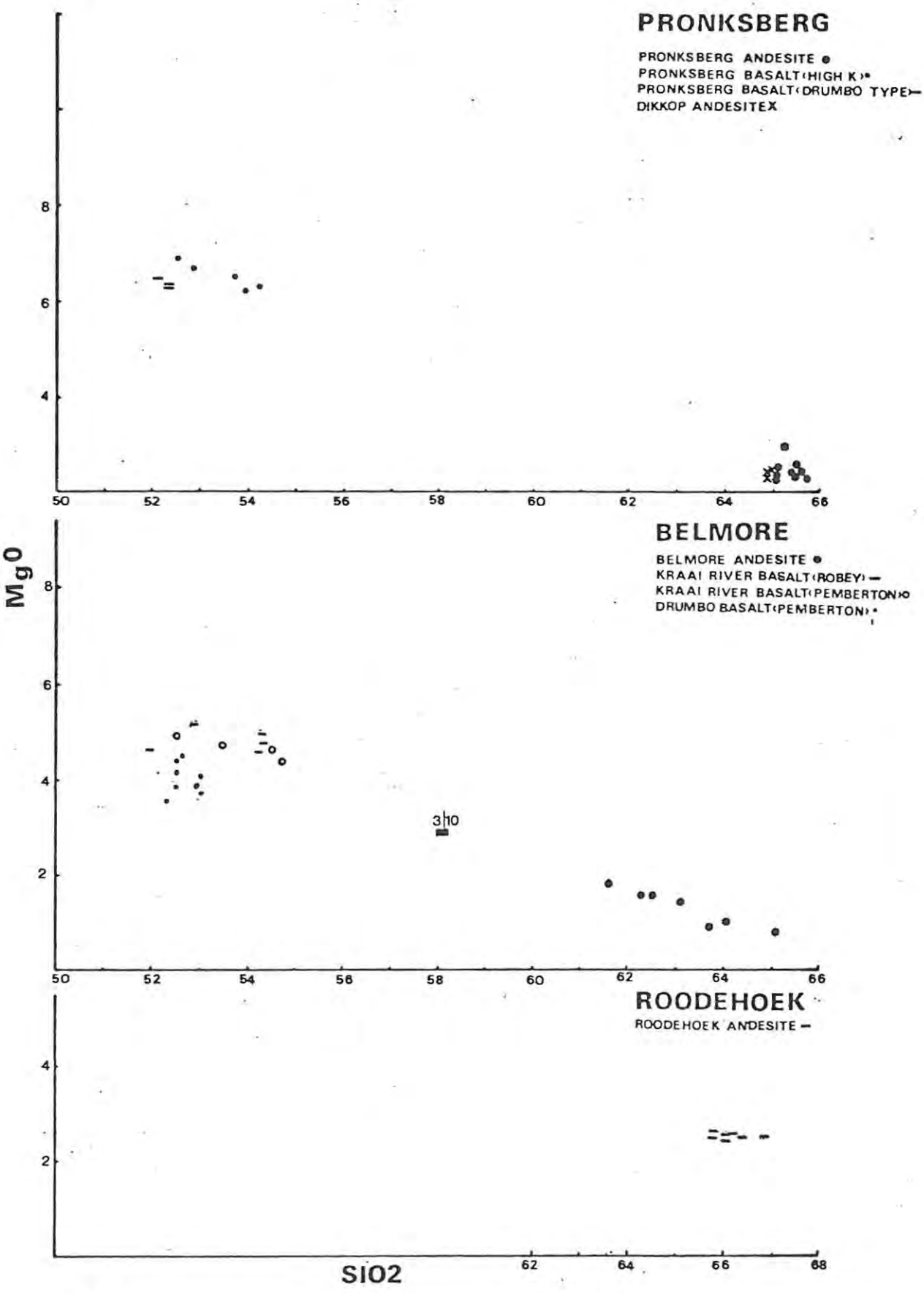

PRONKSBERG
PRONKSBERG ANDESITE
PRONKSBERG BASALT(HIGH K)
PRONKSBERG BASALT(DRUMBO TYPE)
DIKKOP ANDESITE
BELMORE
BELMORE ANDESITE
KRAAI RIVER BASALT(ROBEY)
KRAAI RIVER BASALT(PEMBERTON)
DRUMBO BASALT(PEMBERTON)
ROODEHOEK
ROODEHOEK ANDESITE
MgO
SiO2
8
6
4
2
50
52
54
56
58
60
62
64
66
68

Fig 9d

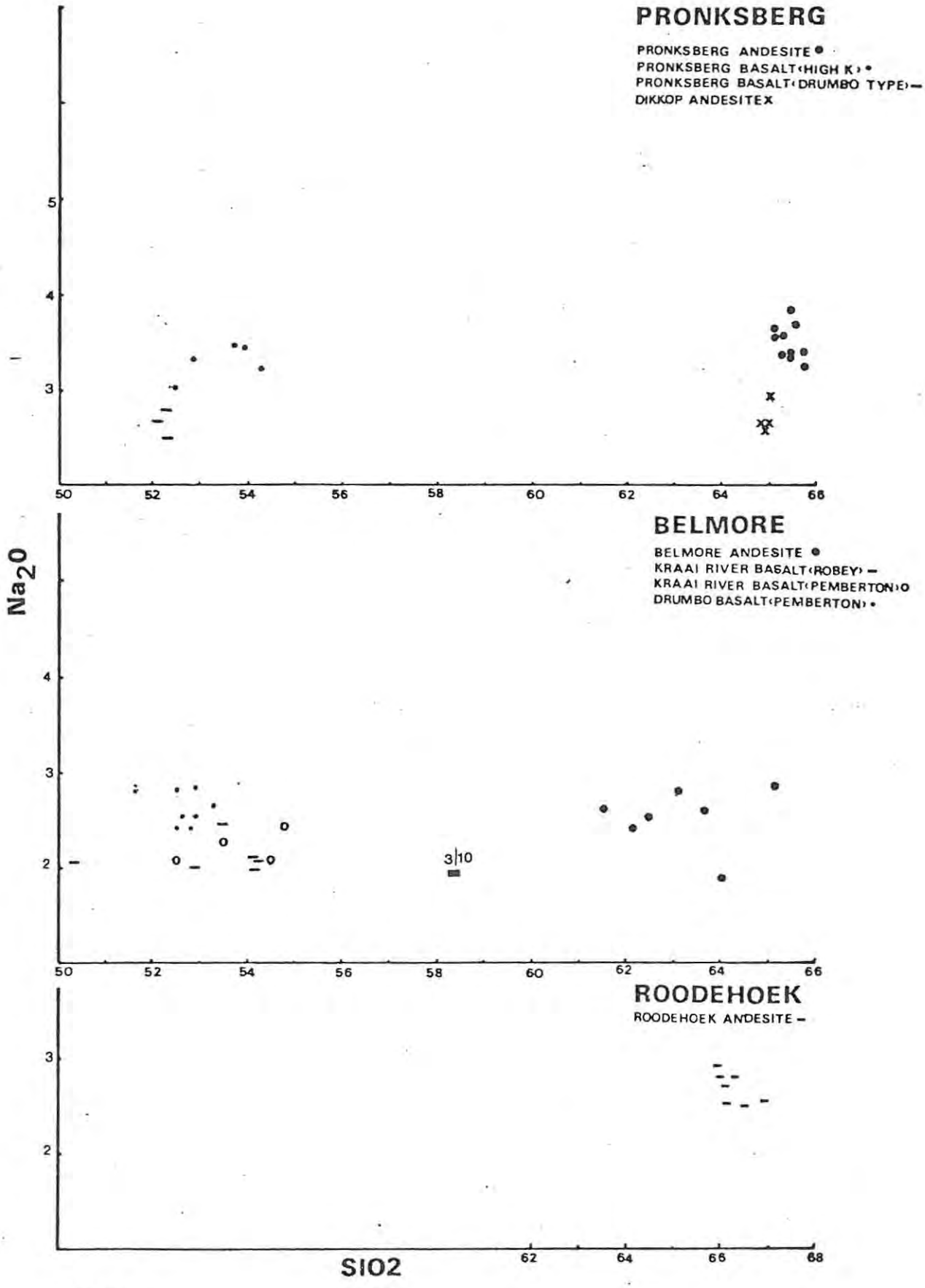

PRONKSBERG
PRONKSBERG ANDESITE ●
PRONKSBERG BASALT‹HIGH K› •
PRONKSBERG BASALT‹DRUMBO TYPE›—
DIKKOP ANDESITE X
BELMORE
BELMORE ANDESITE ●
KRAAI RIVER BASALT‹ROBEY› —
KRAAI RIVER BASALT‹PEMBERTON›O
DRUMBO BASALT‹PEMBERTON› •
ROODEHOEK
ROODEHOEK ANDESITE —
Na2O
SIO2
3|10
50
52
54
56
58
60
62
64
66
68
2
3
4
5

FiG 9 e

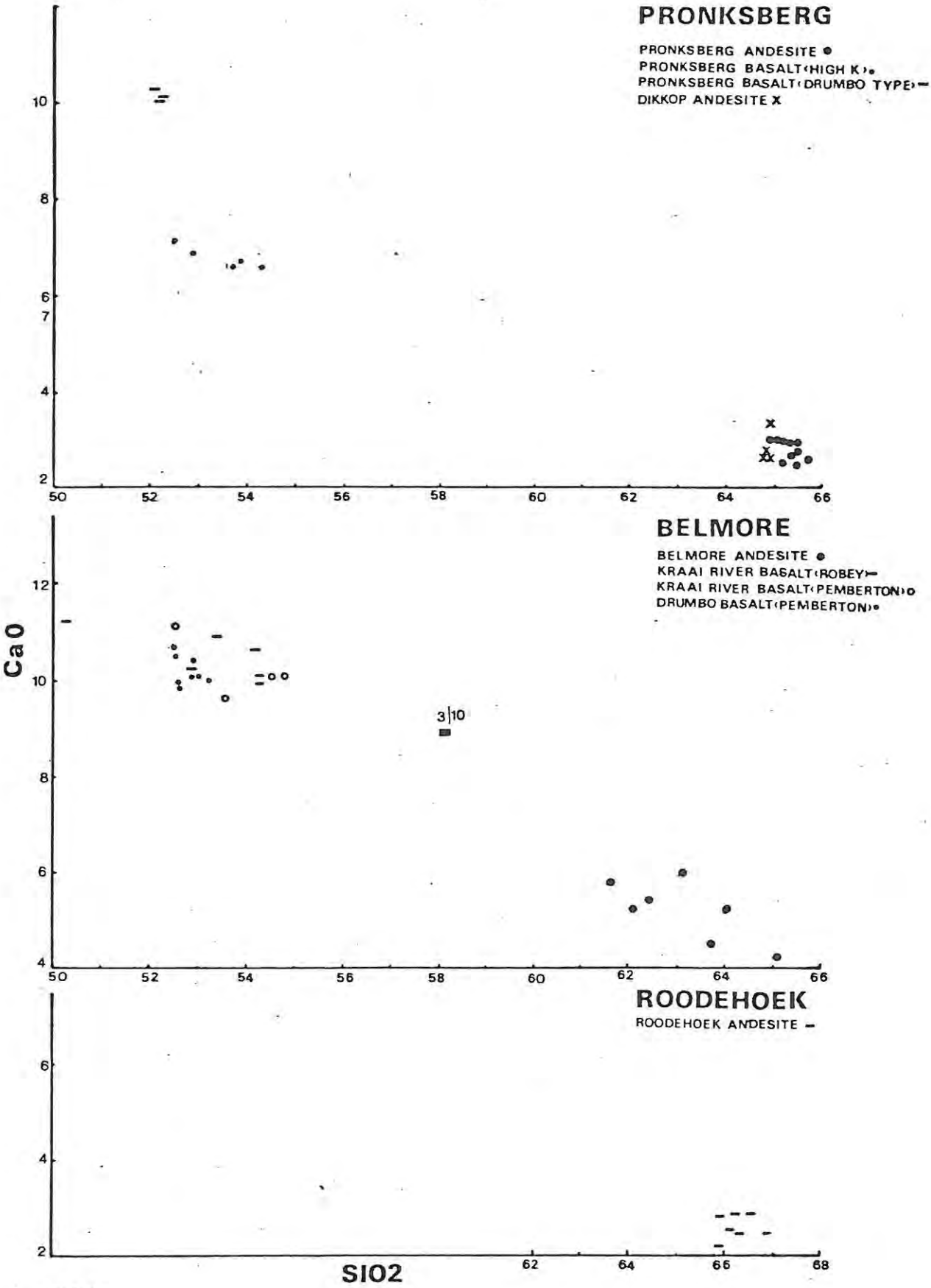

PRONKSBERG
PRONKSBERG ANDESITE
PRONKSBERG BASALT(HIGH K)
PRONKSBERG BASALT(DRUMBO TYPE)
DIKKOP ANDESITE X
BELMORE
BELMORE ANDESITE
KRAAI RIVER BASALT(ROBEY)
KRAAI RIVER BASALT(PEMBERTON)
DRUMBO BASALT(PEMBERTON)
3|10
ROODEHOEK
ROODEHOEK ANDESITE
CaO
SIO2
50
52
54
56
58
60
62
64
66
68
2
4
6
7
8
10
12

FIG 9 f

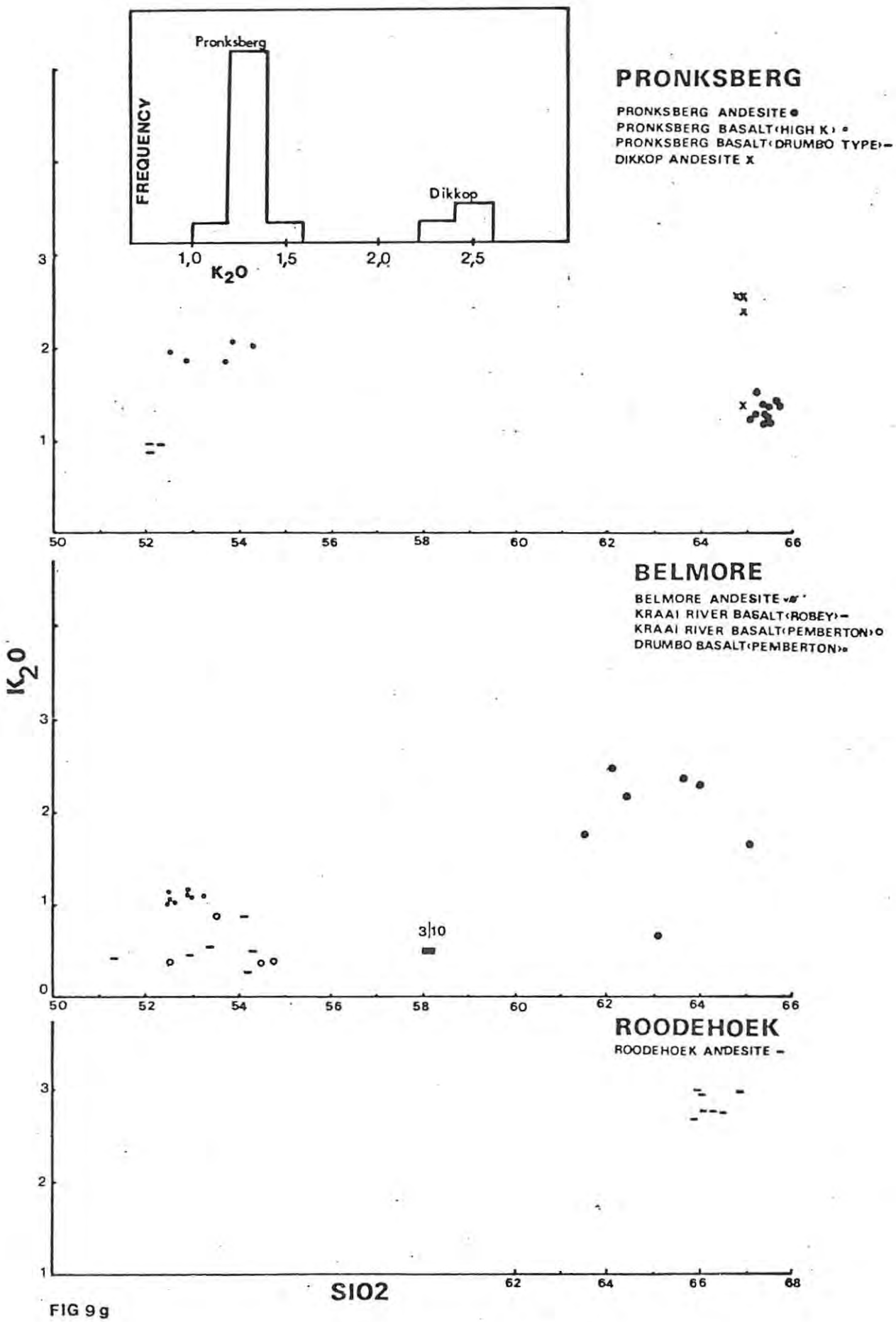

Pronksberg
FREQUENCY
Dikkop
1,0
1,5
2,0
2,5
K2O
PRONKSBERG
PRONKSBERG ANDESITE ●
PRONKSBERG BASALT (HIGH K) ◦
PRONKSBERG BASALT (DRUMBO TYPE) –
DIKKOP ANDESITE X
BELMORE
BELMORE ANDESITE
KRAAI RIVER BASALT (ROBEY) –
KRAAI RIVER BASALT (PEMBERTON) o
DRUMBO BASALT (PEMBERTON) »
3|10
ROODEHOEK
ROODEHOEK ANDESITE –
K2O
SIO2

FIG 9g

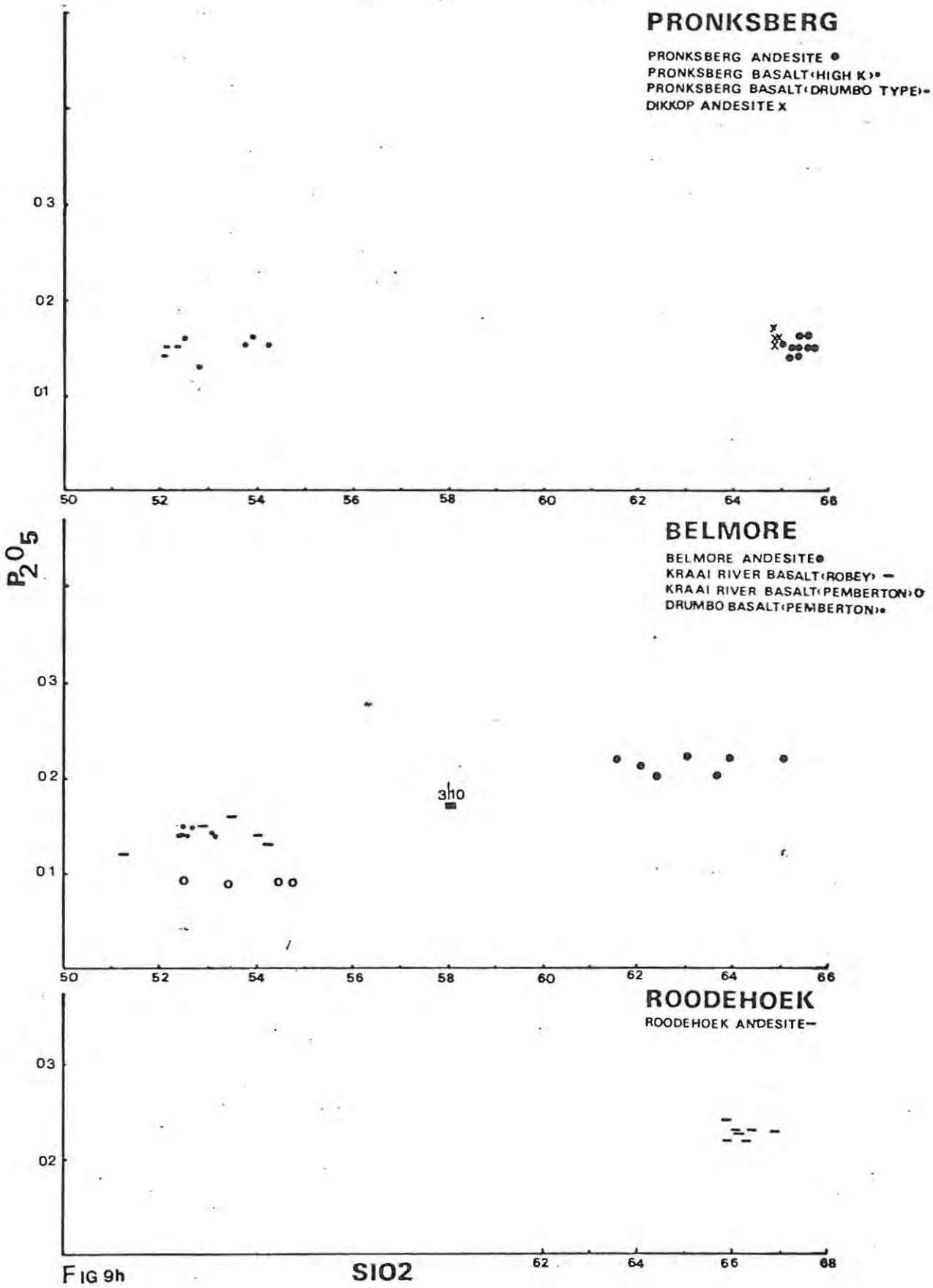

PRONKSBERG
PRONKSBERG ANDESITE ●
PRONKSBERG BASALT‹HIGH K›●
PRONKSBERG BASALT‹DRUMBO TYPE›–
DIKKOP ANDESITE x
BELMORE
BELMORE ANDESITE●
KRAAI RIVER BASALT‹ROBEY› –
KRAAI RIVER BASALT‹PEMBERTON›O
DRUMBO BASALT‹PEMBERTON›●
ROODEHOEK
ROODEHOEK ANDESITE–
P2O5
SIO2
0 3
0 2
0 1
50
52
54
56
58
60
62
64
66
68

FIG 9h

Differences in chemical composition between the Pronksberg and Dikkop andesites are, however, more pronounced. As illustrated by Figure 9, the Pronksberg and Dikkop andesites plot in a relatively tight chemical field, thereby manifesting the relatively undifferentiated, homogeneous nature of the andesites. Average analyses and range of chemical variation for the two andesites are listed in Table 4. A comparison between the Pronksberg and Dikkop andesites, shows the Pronksberg andesite to be:

(a) Enriched in Na_2O compared to the Dikkop andesite.

(b) Similar in SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO and P_2O_5 compared to the Dikkop andesite.

(c) Depleted in K_2O compared to the Dikkop andesite.

A single Dikkop sample (KRD5, Table 3) from near the base of the flow shows K_2O values similar to the average Pronksberg andesite, although it is slightly depleted in Na_2O relative to Pronksberg values. A histogram showing K_2O frequencies for the Pronksberg and Dikkop andesites is shown in Figure 9g. A distinct bimodal distribution is evident, the Dikkop andesite being significantly enriched. The lack of K_2O values intermediate between the two modes refute the likelihood of analytical or sampling errors, as well as weathering or deuteric effects. The lack of significant weathering in the andesites further substantiates this conclusion.

Differences in potassium content between the Dikkop and Pronksberg andesites are therefore thought to be significant, and probably represent a temporal variation in chemistry, hence the extrusion of an early Low K andesite, followed by a later high K episode, represented by the Dikkop andesite.

4.5.1.2 Major Element Variations with Height in the Pronksberg Andesite.

Variations in major element chemistry with height are shown in Figure 10. Sample heights are relative to the Clarens Formation (Cave Sandstone) contact

TABLE 4 : KAROO ANDESITES - CHEMICAL ANALYSES (AVERAGE AND RANGE)

	PRONKSBERG ANDESITE	DIKKOP ANDESITE (MINUS KRD5)	ROODEHOEK ANDESITE	BELMORE ANDESITE
SiO_2	65,21 65,08-65,75	64,89 64,83-65,00	66,26 65,92-66,90	63,02 61,60-65,16
TiO_2	0,79 0,78-0,79	0,80 0,79-0,80	0,77 0,75-0,79	0,79 0,75-0,80
Al_2O_3	17,19 16,88-17,40	17,26 17,15-17,36	16,00 15,89-16,12	15,81 15,59-16,10
Fe_2O_3	6,40 6,20-6,40	6,53 6,46-6,58	6,04 5,75-6,20	7,16 6,29-7,71
MnO	0,17 0,15-0,18	0,17 0,16-0,18	0,15 0,12-0,17	0,19 0,17-0,20
MgO	2,36 2,21-2,47	2,33 2,31-2,36	2,48 2,39-2,59	3,30 2,77-3,78
CaO	2,78 2,54-2,98	2,62 2,60-2,63	2,55 2,10-2,83	5,14 4,13-5,77
Na_2O	3,32 3,29-3,84	2,64 2,62-2,69	2,65 2,45-2,89	2,45 1,84-2,79
K_2O	1,53 1,18-1,50	2,48 2,38-2,54	2,81 2,65-2,97	1,94 1,61-2,51
P_2O_3	0,25 0,24-0,26	0,26 0,25-0,27	0,23 0,22-0,24	0,21 0,21-0,22

TABLE 4 : (continued) AVERAGES AND RANGES OF TRACE ELEMENTS

	PRONKSBERG ANDESITE	DIKKOP ANDESITE (MINUS KRD5)	ROODEHOEK ANDESITE	BELMORE ANDESITE
Ba	736 712-773	740 735-749	625 599-663	554 499-709
Sr	307 292-344	291 289-296	246 230-281	329 251-409
Rb	144 95-181	151 147-155	118 113-126	113 60-135
Y	30 28-32	30 28-32	29 28-31	30 28-34
Zr	196 191-201	197 193-202	218 213-224	199 191-214
Nb	13,2 12,0-14,9	13,9 12,0-16,3	10,6 9,3-11,4	10,4 9,9-11,4
Zn	94 91-97	96 95-98	83 77-87	84 79-87
Cu3	26 24-28	26 26-27	24 20-25	44 31-44
Co	17,9 17,2-19,0	17,6 17,5-17,8	19,6 18-21	24,0 20-27
Ni	27 25-30	26 26-27	22 21-25	35 26-41
V	66 62-85	66 64-68	87 78-95	100 76-111
Cr	52 49-56	48 46-50	82 76-91	104 61-120
La	38 33-40	38 38-39	31 29-33	33 30-35
Ce	92 90-96	93 89-96	79 75-82	79 70-88
Nd	37 35-38	37 36-39	32 30-35	33 29-36

at the base of the lava pile.

In the light of the analytical-precision data presented in Table 2, variations in MgO, CaO, Na_2O and K_2O are thought to be significant, while variations in SiO_2, TiO_2, Al_2O_3 and Fe_2O_3 are insignificant. Potassium shows general decrease with increasing height through the flow, while MgO and CaO increase sharply towards the middle of the flow. Na_2O shows a corresponding decrease in this region.

Although variations in SiO_2, TiO_2, Al_2O_3 and Fe_2O_3, with height through the flow are insignificant in the light of precision data presented in a previous section, several intriguing patterns are evident:

(a) Na correlates negatively with Ca but positively with Al and Si.

(b) Ca, Fe and Mg all exhibit a positive correlation with each other.

Considering the relatively insignificant variations in Al, Si, Ti and Fe, it may be argued that the patterns described above are in fact fortuitous. However, they are also suggestive of a process involving enrichment of a mafic phase towards the centre of the flow. Enrichment in orthopyroxene having a chemical composition similar to that presented in Table 1, would account for the observed Fe, Mg and Ti variations as well as the antipathetic behaviour of Si and Al. The sympathetic behaviour of Ca in relation to Fe and Mg is, however, more difficult to explain, unless accumulation of a Fe-Mg-Ca rich orthopyroxene occurred. Microprobe analyses do not support the presence of a Ca-rich orthopyroxene, and Ca enrichment would have to be explained by some other mechanism. The possibility of enrichment of a mafic phase towards the middle of the flow is further tested using trace element data.

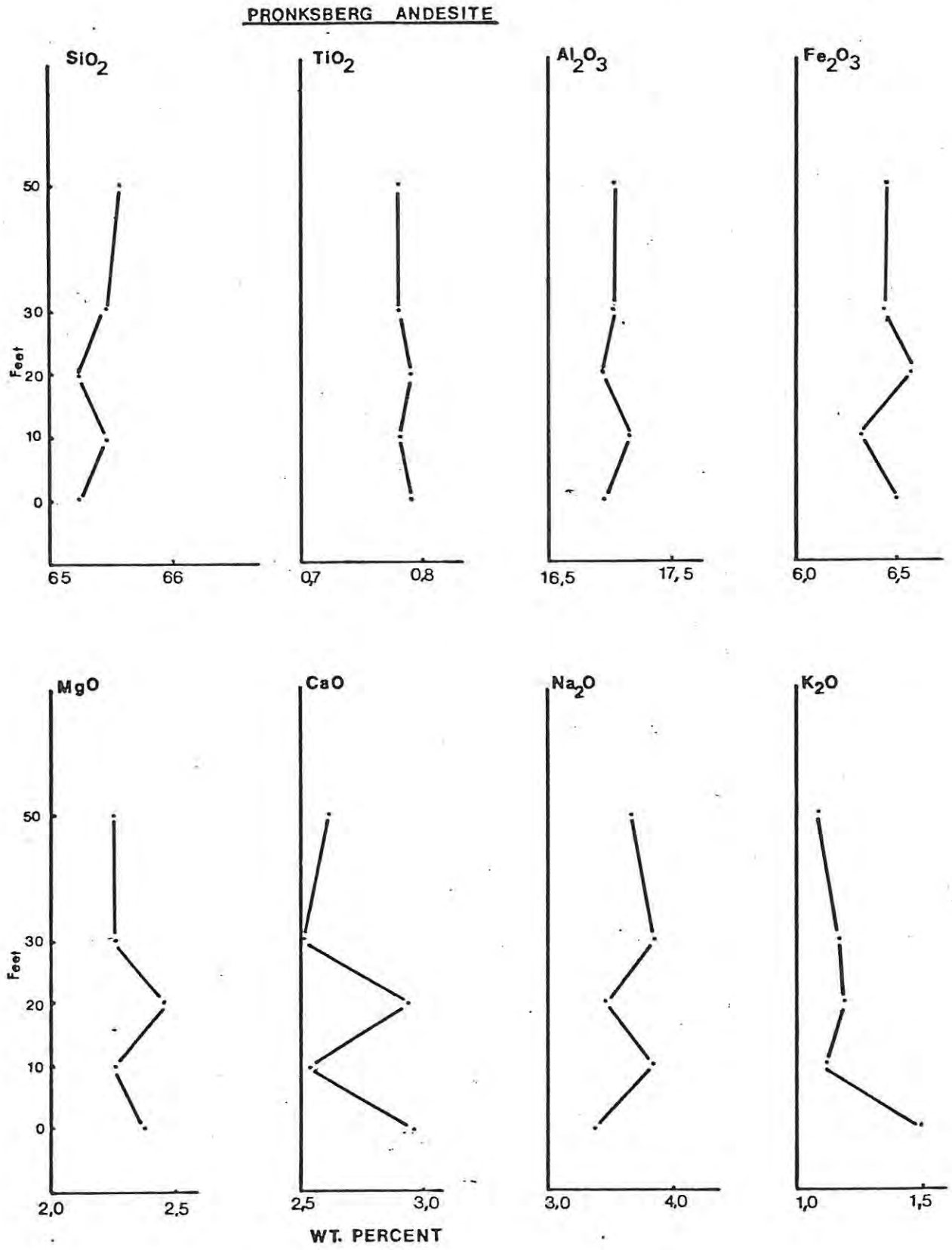


FIG.10 Major element data plotted against height-Pronksberg Andesite.

The pattern of K-depletion with height through the sequence is also difficult to explain. Associated trace elements Rb, Zr, Nb, La, Ce and Nd do not exhibit similar patterns and K variations cannot therefore be explained by fractionation processes. Jamieson and Clarke (1970) studying basaltic rocks, show that in general, potassium behaves almost independently of fractionation processes and should therefore be discounted as being a major indicator of intraflow variations. Pemberton (1978) examined intraflow variations with height through three basalt flows of the Lesotho Formation. In one instance, potassium increases with height. In a second flow, potassium behaves highly erratically, and in a third flow, potassium decreases towards the top of the flow. The unpredictable nature of potassium behaviour is therefore evident, and it may well be that a process such as that proposed by Hart et al. (1971) may be applied to explain potassium variations in the Pronksberg andesite. Hart et al. (op.cit.) show the behaviour of potassium to be dependent on migration of a late stage, alkali-rich residue.

Considering the chemical variations described above, it would appear that the Pronksberg andesite was extruded as a chemical, homogeneous flow, with chemical variations influenced by minor crystal settling after extrusion. These conclusions are further supported by trace element variations presented in Section 5.

4.5.1.3 The Pronksberg Basalt (High K Type).

(Analyses KR 22-26, Table 3)

Differences in major element chemistry between the Pronksberg Basalt (High K Type) and the underlying andesites are illustrated in Figure 9a-h. In relation to the andesites, the Pronksberg Basalt (High K Type) is:

(a) Depleted in SiO_2 and Al_2O_3.

(b) Similar to Na_2O and P_2O_5.

(c) Enriched in TiO_2, Fe_2O_3, MnO, CaO and K_2O (Table 3).

In comparison with the overlying Pronksberg Basalt (Drumbo Type), the Pronksberg Basalt (High K Type) is :

(a) Enriched in K_2O and Na_2O.

(b) Similar in SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MnO, MgO and P_2O_5.

(c) Depleted in CaO.

Compared to the previously mapped Drakensberg Subgroup lavas (Robey, 1976: Lock et al., 1974: Pemberton, 1978), the Pronksberg basalt (High K Type) is volumetrically insignificant yet chemically unique. Average analyses for the three dominant Drakensberg Subgroup basalt types (Lesotho Formation, Kraai River Formation and Drumbo Basalt Member) compared to the Pronksberg basalt (High K Type) are given in Table 5. With the exception of K-enrichment in the Drumbo Basalt, the Drakensberg Subgroup basalts in the Barkly East area may be regarded as relatively similar in major element chemistry. With respect to the Drakensberg Subgroup basalts in the Barkly East area, the Pronksberg Basalt (High K Type) is enriched in K_2O, P_2O_5 and Na_2O but depleted in CaO.

As will be shown in the following section, P_2O_5 variations between this and Pemberton's study are thought to represent systematic analytical differences, although the fact that they may be real cannot be discounted. Differences in K_2O, Na_2O and CaO between the Pronksberg Basalt (High K Type) on the one hand and the Pronksberg Basalt (Drumbo Type) and Drakensberg Subgroup basalts on the other are thought to represent the effect of weathering on the Pronksberg Basalt (High K Type). Differences between the two basalt groups mentioned may also be influenced by intraflow variations of alkalis. A detailed account of the influence of weathering and intraflow

TABLE 5 : KAROO BASALTS - CHEMICAL ANALYSES (AVERAGE + RANGE)

	A	B	C	D	E	F
SiO_2	53,44 52,51-54,24	52,22 52,1-52,32	52,71 52,57-53,23	52,37 52,30-52,45	54,43 52,52-54,76	58,11
TiO_2	1,01 1,01-1,02	1,01 0,99-1,03	1,03 0,98-1,07	1,11 1,08-1,13	0,88 0,84-0,98	0,89
Al_2O_3	16,31 15,95-16,67	15,74 15,64-15,87	15,80 15,28-16,24	16,53 16,15-16,83	15,42 15,05-15,73	15,43
Fe_2O_3	10,17 10,07-10,24	10,39 10,10-10,45	10,33 10,02-10,55	9,57 9,10-10,38	10,07 9,82-10,25	9,16
MnO	0,26 0,24-0,28	0,26 0,25-0,27	0,15 0,14-0,16	0,24 0,22-0,26	0,15 0,14-0,15	0,14
MgO	6,50 6,20-6,88	6,35 6,25-6,48	5,97 5,55-6,45	5,10 4,49-5,61	6,82 6,32-6,84	4,87
CaO	6,78 6,59-7,15	10,20 10,15-10,30	10,21 9,83-10,77	11,01 10,53-11,84	10,36 9,60-11,14	8,87
Na_2O	3,31 3,03-3,48	2,65 2,49-2,79	2,57 2,29-2,81	2,52 2,05-3,19	2,22 2,06-2,40	1,90
K_2O	1,94 1,82-2,06	0,92 0,89-0,95	1,03 1,00-1,13	0,92 0,85-1,00	0,49 0,34-0,87	0,48
P_2O_5	0,24 0,23-0,26	0,24 0,24-0,25	0,15 0,14-0,16	0,27 0,27-0,28	0,09 0,09	0,14

A = PRONKSBERG BASALT (HIGH K TYPE)
B = PRONKSBERG BASALT (DRUMBO TYPE)
C = DRUMBO BASALT (PEMBERTON, 1978)
D = DRUMBO BASALT (THIS STUDY)
E = KRAAI RIVER BASALT (PEMBERTON, 1978)
F = BASALT 3/10 (ROBEY, 1976)

TABLE 5 (continued)

	A	B	C	D	E	F
Ba	663 559-778	265 233-299	- -	217 201-234	- -	183
Sr	471 443-506	301 298-322	307 287-343	318 300-336	207 191-229	236
Rb	40 37-45	20 20-21	20,5 18-23	18,2 15,7-20	19,5 10-33	21
Y	25 24-26	24 24-26	26 24-27	27 25-28	27 26-28	29
Zr	134 128-141	133 129-138	149 138-156	147 135-152	113 110-116	158
Nb	15,1 13,5-16,5	14,4 14,0-15,0	15,7 14,7-16,6	16,5 15,0-17,3	4,7 4,2-4,6	8,0
Zn	82 79-85	79 77-80	83 76-93	80 77-82	81 74-85	83
Cu	68 60-71	64 62-66	74 58-78	70 67-72	61 54-68	47
Co	37 36-38	36 35-37	39 38-41	35 35-36	41 39-43	29
Ni	68 66-72	69 67-70	67 55-80	66 65-66	50 42-54	32
V	152 143-164	147 134-174	220 202-232	149 139-167	245 228-256	189
Cr	224 208-238	223 214-241	295 251-325	216 210-228	281 272-297	121
La	15,9 14,6-17,3	17,5 15,7-20,4	17,4 16-21	17,3 38-44	17,0 16-17	-
Ce	39 37-42	41 38-45	40 37-48	42 19-24	37 33-39	-
Nd	19,5 18,2-21,2	17,6 15,6-20,5	19,1 19-24	17,3 14,0-20,0	15,2 19-23	--

variations, considering both major and trace elements, is presented in Section 5. Enrichment levels of potassium and associated elements in tholeiitic basalts as argued by Jamieson and Clarke (1970) and Dickenson (1968) cannot, however, be ignored entirely.

4.5.1.4 The Pronksberg Basalt (Drumbo Type).

(Analyses KR 27,28,29 - Table 3)

Similarities in the petrography of the Pronksberg Basalt (Drumbo Type) and the Drumbo Basalt in the Barkly East area (Type area) have been discussed in an earlier section. Analyses of Drumbo basalts (average and range) presented by Pemberton (1978) are included in Table 5 for comparison with the Pronksberg Basalt (Drumbo Type). The major and trace element contents of the Pronksberg Basalt (Drumbo Type) compare well with those from the Barkly East area (Pemberton, 1978). With respect to the Drumbo Basalt (type area), the Pronksberg Basalt (Drumbo Type) is:

(a) Slightly enriched in MnO and P_2O_5

(b) Similar in the other major elements.

MnO and P_2O_5 differences are thought to represent systematic analytical differences in the work of the present author and that of Pemberton (op.cit.) although the possibility that they are real still exists. This is supported by the fact that analyses of Drumbo basalt presented in this study (analyses KRB 4,5 and 14, Table 3) sampled in the type area, exhibit similar enrichments in MnO and P_2O_5 with respect to analyses present by Robey (1976) and Pemberton (1978), although these differences may in fact, also be real. Trace element data and inter-element ratio data (Section 5) further illustrate similarities in chemistry between the Pronksberg Basalt (Drumbo Type) and Drumbo Basalt Member, which suggests that the two lavas are cogenetic.

4.5.2 Belmore

4.5.2.1 The Drumbo Basalt Member.

(Analyses KRB4,5,14 - Table 3)

Three analyses of the Drumbo Basalt underlying the Belmore andesite are presented for comparison with the data of Pemberton (1978).

Differences between Drumbo basalt analyses from the type area (this study) and those of Pemberton (op.cit.) are listed in Table 5. Analyses presented in this study conform fairly rigidly to trends established by Pemberton (op.cit.) in that they differ from basalts of the Lesotho Formation and Kraai River Formation. The Drumbo Basalts are enriched in K_2O, TiO_2 and Na_2O, but depleted in MgO relative to the other two basalt types. Similarities between the Drumbo basalt (this study) and that of Pemberton (op.cit.) are further emphasized by trace element data. As discussed in the previous section, apparent MnO and P_2O_5 enrichment reported in this study, which is revealed when comparisons are drawn with Pemberton's data, is thought to represent systematic analytical differences.

Differences in major element chemistry between the Belmore andesite and basalts of the Drakensberg Subgroup are discussed in the following Section.

4.5.2.2 The Belmore Andesite.

(Analyses KRB 1-10, Table 3).

Variations in major element chemistry between the Belmore andesite, Drumbo Basalt Member and Kraai River basalts (Pemberton, 1978) are illustrated in Figure 9a-h. Kraai River Basalt data (Robey, 1976) are included in Figure 9.

Robey (1976) analysed one Belmore andesite, six Kraai River basalts and two Drumbo basalt samples, and noted that with the exception of Na_2O and K_2O, the andesite plotted virtually on the extension of the Kraai River major element trends, although he recognised that this suite belonged to an earlier episode of volcanism. He also noted the similarities in the petrography of

the andesite and the Kraai River basalts, both containing orthopyroxene as phenocrysts. He therefore recognises the possibility that the andesite may represent an extreme differentiate from a magma source similar to that of the Kraai River basalt.

It would appear that Robey's conclusions regarding a fractionation link between the Belmore andesite and the Kraai River basalts are based largely on the nature of his analysis 3/10. Sample 3/10 (Table 5, this study) is largely atypical of Kraai River basalts (Pemberton, 1978) in that it is significantly enriched in SiO_2, but depleted in Fe_2O_3, MgO, CaO and Na_2O. Trace element data confirm the differences between 3/10 and typical Kraai River basalts. While the accuracy of Robey's analysis cannot be questioned, the validity of sample 3/10 must be viewed with some scepticism. Further field reconnaissance by members of the Department of Geology, Rhodes University, has been unsuccessful in relocating the sample site (Marsh, J.S., 1978, Pers. Comm.). Kraai River samples chemically resembling sample 3/10 were not encountered by Pemberton (1978) who conducted a more detailed investigation. Similarly, Barree (1977) studied the geochemistry of 14 Kraai River basalt samples in the Barkly East area, presenting analyses similar to those of Pemberton (op.cit.). None of Barree's samples approaches that of sample 3/10 in composition. Deviations of sample 3/10 from typical Kraai River basalts are supported by petrographic observations as well. While sample 3/10 contains only one pyroxene (bronzite), Pemberton (op.cit.) describes the Kraai River basalts as being typically two-pyroxene rocks.

It would therefore appear that analysis 3/10 is representative of a localised atypical Kraai River flow displaying unique chemical characteristics, possibly indicative of sediment contamination. This observation is supported by strontium isotope data. The fact that sample 3/10 plots on the extension of the Belmore andesite is not disputed. What is questioned, however, is the validity of classifying sample 3/10 as Kraai River basalt.

4.5.2.3 Major Element Variations with Height in the Belmore Andesite

While chemical variations within the Pronksberg and Roodehoek andesites are subdued, interflow variations at Belmore are more pronounced. SiO_2, Fe_2O_3 and MgO show pronounced variations with height, the latter two decreasing with height, while SiO_2 increases with height (Figure 11). Al_2O_3 shows a subdued increase with height, while CaO decreases although a slightly erratic pattern is evident. Potassium, although slightly erratic, exhibits two trends, first increasing to 2,51 percent and then decreasing to 1,61 percent at the top.

Oxide-oxide variation diagrams may be used to investigate the effect of one or more fractionating phases on the composition of residual liquid. A vector drawn from the composition of the fractionating phase to the initial liquid composition on the variation diagram, will indicate the direction of the resultant liquid composition as a result of extraction of that phase. In a situation where two phases fractionate, the liquid composition will be driven in the direction of the resultant of both vectors. This technique has been used in determining the fractionating phases influencing liquid compositions of the Belmore andesite. Vectors showing the resultant composition of a liquid involving fractionation of orthopyroxene and plagioclase, having the chemical compositions presented in Table 1, are shown in Figure 12. Simultaneous fractionation of similar proportions of orthopyroxene and plagioclase would drive the resulting liquid composition in the direction of point x (Figure 12), which approximates closely the Fe_2O_3 - SiO_2 and MgO-SiO_2 variations observed at Belmore. Plagioclase fractionation would also explain observed CaO-SiO_2 and Al_2O_3-SiO_2 variations. The Na_2O-SiO_2 and TiO_2-SiO_2 variations are, however, more difficult to explain and variations may be complicated by some other mechanism. If orthopyroxene

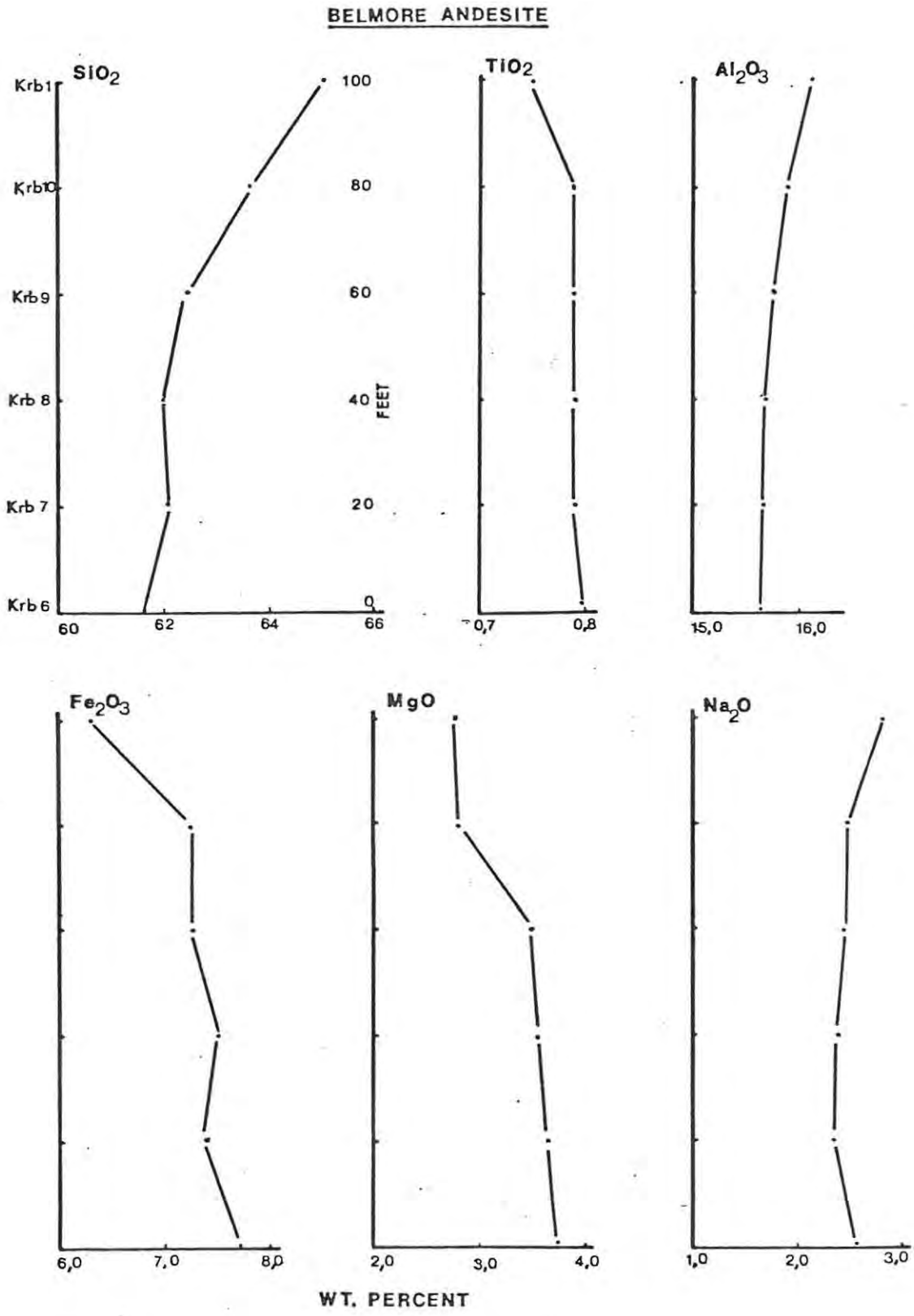
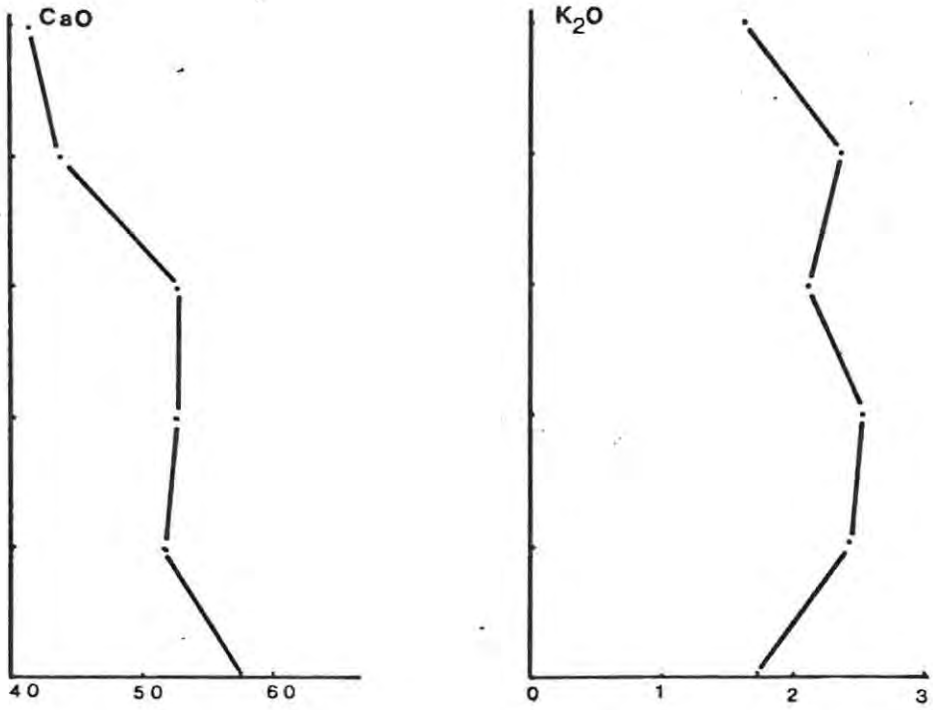


FIG.11 Major element data plotted against height-Belmore Andesite.

FIG. 11 (continued)



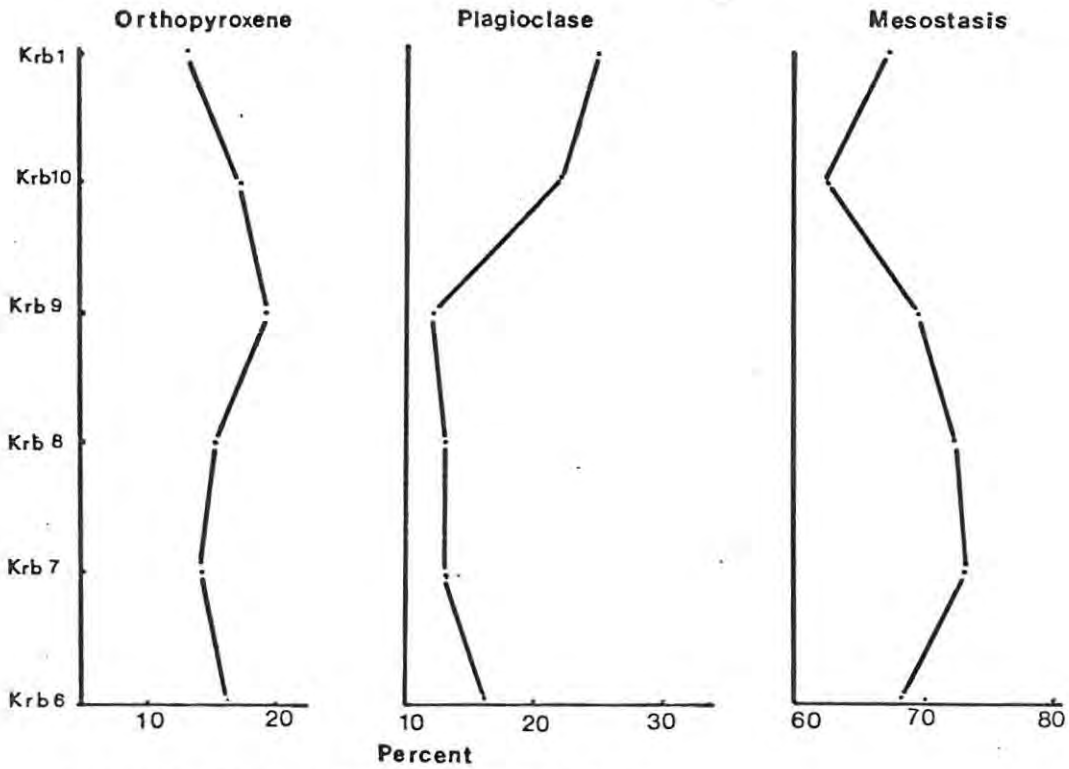


FIG. 13 Modal Analysis – Belmore Andesite

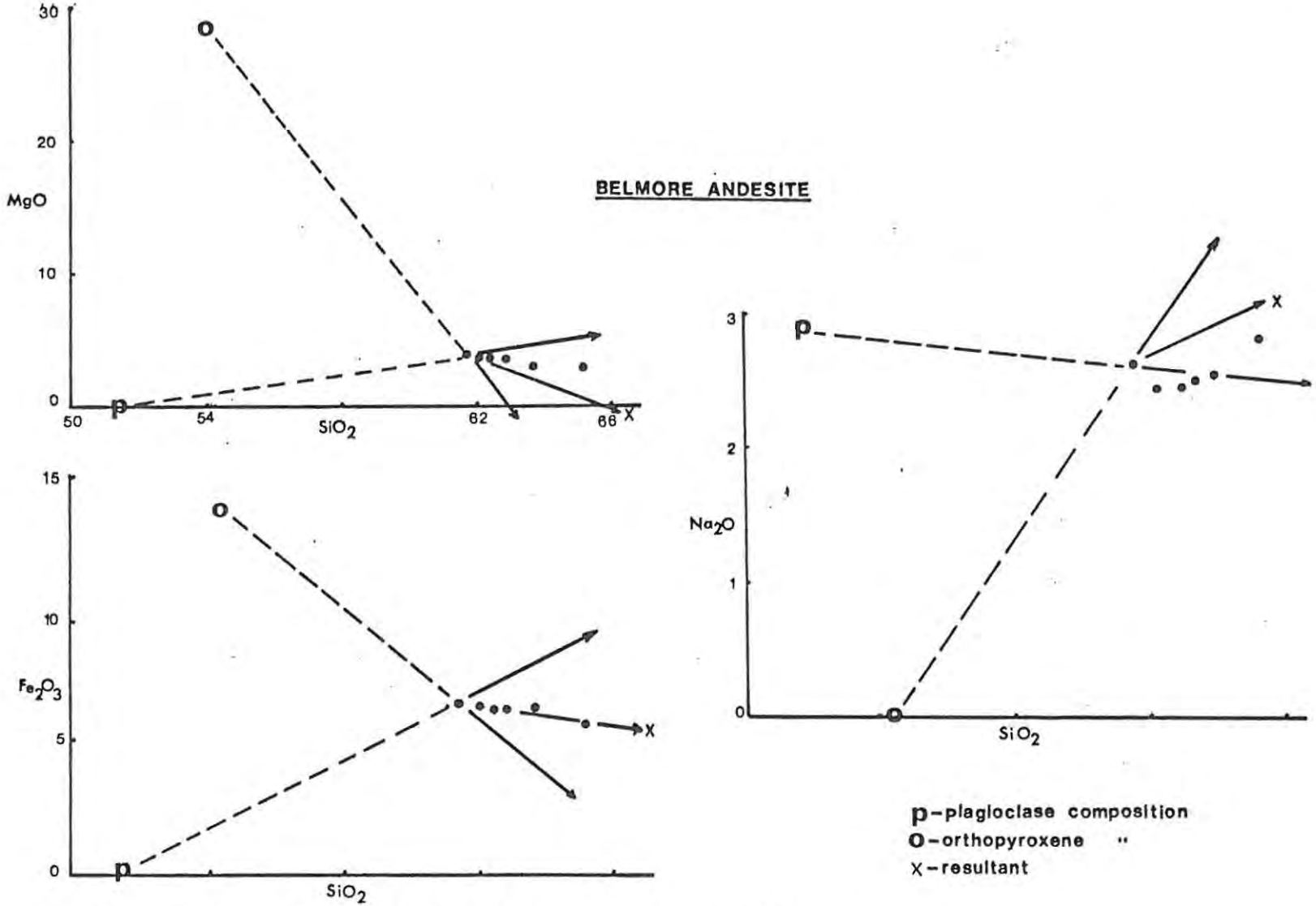
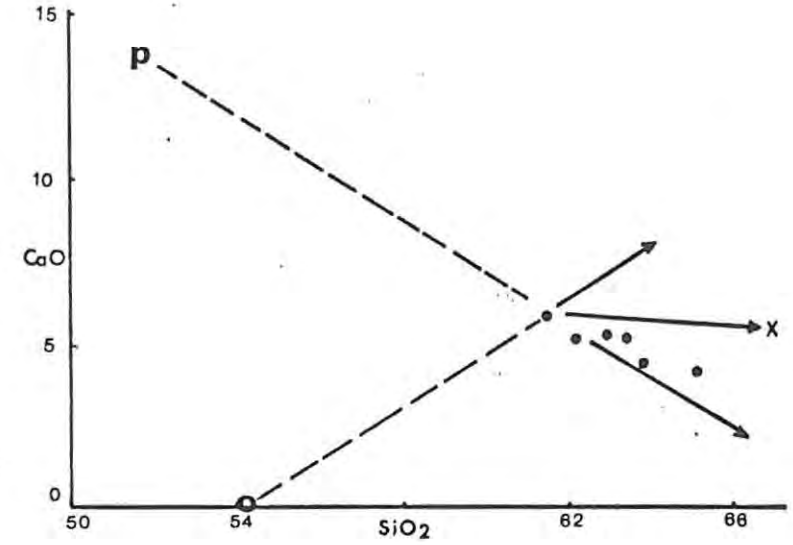
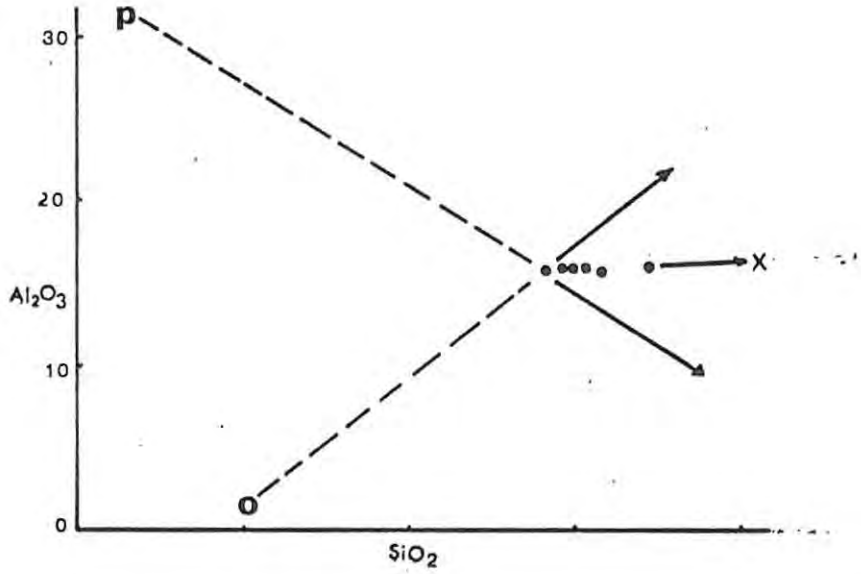


FIG 12 Major element data plotted against SiO_2-Belmore Andesite.





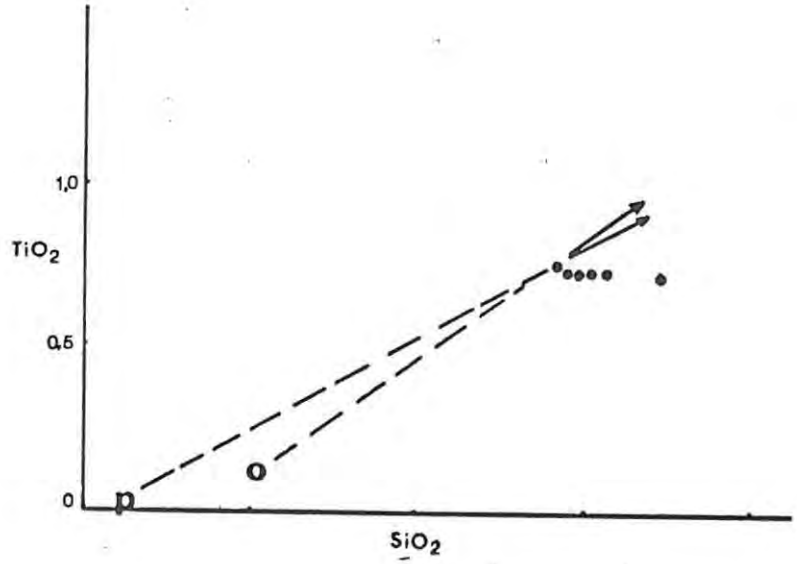


FIG.12(Continued).

and plagioclase were the only phases controlling chemical variations with height through the Belmore andesite sequence, TiO_2 would be expected to increase towards the top. As TiO_2 decreases slightly with height, it would appear as if variations in Ti may in fact be complicated by slight fractionation of a TiO_2-rich phase, possibly ilmenite or titaniferous spinel. Microprobe analyses of opaque phases present in the andesite were unfortunately not conducted and as such, the influence of ilmenite and/or magnetite fractionation cannot be tested.

The erratic regressive trend observed for K_2O is not thought to be significant. The trace elements (Rb, Zr, Nb, La, Ce, Nd) do not exhibit sympathetic variations, the majority of these increasing with height. Rb in particular shows a strong negative correlation with K. This feature is thought to represent strong evidence for K behaving independently of fractionation processes in the andesite suite under study. An interesting feature which may possibly explain K variation with height, through the andesite, is the variation of percentage of mesostasis in the andesite (see modal analysis, Figure 13). Potassium shows a remarkable positive correlation with the amount of mesostasis present. The variation of K with height may thus be a direct function of the amount of mesostasis, possibly implying migration of a late stage K and SiO_2 rich residue.

4.5.2.3 Comparison between the Belmore Andesite and other Karoo Andesites.

The range of chemical variation exhibited by the Belmore andesite is given in Table 4. A comparison of averages of the Pronksberg and Roodehoek andesites on the one hand and Belmore andesite on the other would be meaningless considering the differentiated nature of the latter. A comparison between the range of chemical variation for the Belmore andesite and the Pronksberg andesite shows:

(a) The Pronksberg is similar to, or plots within the Belmore andesite range for SiO_2, TiO_2, Fe_2O_3, MnO, K_2O and P_2O_5.

(b) The Pronksberg andesite is enriched in Al_2O_3 and Na_2O relative to the Belmore range.

(c) CaO and to a lesser extent MgO is enriched at Belmore relative to Pronksberg average compositions.

The Roodehoek andesite exhibits chemical compositions:

(a) Within or similar to the Belmore range for TiO_2, Al_2O_3, Fe_2O_3, MnO, P_2O_5, MgO and Na_2O,

(b) enriched in K_2O and SiO_2 relative to the Belmore range, and

(c) depleted in CaO relative to the Belmore range.

Differences in chemical composition (major and trace elements) are discussed further in Section 5, where reasons for the geochemical differences between the three andesites are discussed and evaluated. In summary, differences may be explained by:

(a) Varying degrees of fractionation from a common parent magma.

(b) Different parent materials with distinct chemistry.

4.5.3 The Roodehoek Andesite

(Analyses KAM 6-17, Table 3).

Variations within the Roodehoek andesite are subdued. Variations between the three andesite occurrences are more pronounced. Chemical compositions of seven Roodehoek andesite samples are shown in Figure 9a-h. Average chemical analyses and ranges are listed in Table 4.

Differences in major element concentrations between the Roodehoek and Belmore andesite have been discussed in the previous section.

In comparison to the Pronksberg andesite, the Roodehoek andesite is:

(a) enriched in SiO_2 and K_2O,

(b) depleted in Al_2O_3 and Na_2O, and

(c) similar in TiO_2, MnO, CaO, MgO, Fe_2O_3 and P_2O_5 contents.

Trace element data (Section 5) confirm the lack of any significant internal variations at Roodehoek, but similarly, confirm the differences in chemistry between the Roodehoek andesite on the one hand and the Pronksberg and Belmore andesites on the other.

Normative chemistry (Section 4.6) is suggestive of sediment contamination of mantle-derived magma, or of crustal melting modifying the andesite chemistry. The potassium enrichment shown by the Roodehoek andesite relative to the Pronksberg and Belmore andesites could be interpreted as being due to varying degrees of crustal contamination, the Roodehoek andesite being contaminated with more crustal potassium. Further possibilities for K enrichment include variations in parent magma or varying degrees of fractionation from an andesitic magma, although the latter is deemed unlikely in the light of trace element abundances presented in Section 5. The degree of weathering must also be considered as a possible influence on potassium variations. Altered trachytes analysed by Marsh, J.S. (1978, Personal Communication) show potassium contents up to 12 wt. percent, with K_2O/Na_2O ratios approaching infinity, i.e. having gained potassium relative to sodium, which is depleted. The fact that the Roodehoek andesite is more altered than either the Pronksberg or Belmore andesite suggests that weathering effects may in fact be important factors governing major element concentrations now prevailing at Roodehoek.

4.6 NORMATIVE CHEMISTRY

C.I.P.W. weight percent norms have been computed from water-free major element analyses, normalised to 100 percent, assuming an oxidation ratio of 0,2. Desilication and combination steps suggested by Kelsey (1965) have been used. The results are given in Table 6.

A striking feature of the norms is the presence of normative corundum in all but two of the andesite specimens. Robey (1976) reports the presence of corundum in the norm of a Belmore andesite. In the standard C.I.P.W. computation, corundum will occur only if salic $Na_2O+CaO+K_2O$ is less than molecular Al_2O_3. The occurrence of normative corundum is virtually unknown in extrusive rocks, only occasionally occurring in andesites (Chayes, 1970). According to Chayes (op.cit.), the presence of corundum in the norm is usually indicative of either a questionable analysis, or represents evidence for the assimilation of aluminous sediments or metamorphic rocks. The latter view is supported by the earlier work of Mountain (1960) who notes the occurrence of modal corundum in analyses of fused sediments associated with Karoo dolerites. Major element analyses in this study have been checked, and samples selected for analysis show only minor alteration.

The occurrence of corundum in the norm in the Karoo andesites is therefore thought to indicate crustal source-rocks for the andesite magmas or extensive contamination by Al-rich crustal rocks. These interpretations are substantiated by trace element and isotope data presented in a later section.

Fernandez et al. (1973) and Pichler and Zeil (1972) report petrographic observations, major and trace element chemistry as well as strontium isotope data which are indicative of a crustal origin for certain Andean andesites. Several chemical analyses from the aforementioned studies have been recalculated according to C.I.P.W. procedure in the present study. The occurrence of corundum in the norms of these analyses (Table 6) further substantiates the likelihood of crustal assimilation being an important factor in the genesis of these Karoo andesites.

TABLE 6 CIPW WEIGHT PERCENT NORMS FOR THE KAROO ANDESITES AND ASSOCIATED BASALTIC ROCKS.

SAMPLE	KR-2	KR-3	KR-4	KR-5	KR-6	KR-8	KR-9	KR-11	KR-17	KR-19	KR-20	KR-21
AP	0,57	0,62	0,59	0,59	0,62	0,62	0,59	0,59	0,59	0,62	0,59	0,59
IL	1,48	1,46	1,48	1,46	1,46	1,46	1,48	1,45	1,46	1,46	1,45	1,46
OR	8,86	7,27	7,62	7,98	7,03	7,56	7,80	7,98	7,09	6,97	7,74	7,98
AB	28,68	32,49	30,29	32,49	31,22	31,73	29,87	27,84	30,97	28,17	28,51	29,02
AN	12,87	11,10	12,75	10,82	11,40	11,00	12,80	10,97	13,15	12,99	12,56	12,01
C	5,05	5,45	4,92	5,32	5,54	5,58	5,15	6,51	5,02	5,63	5,55	5,57
MT	1,45	1,42	1,44	1,41	1,45	1,44	1,41	1,41	1,41	1,42	1,41	1,38
HYEN	5,93	5,63	6,15	5,63	5,65	6,00	6,10	5,50	5,95	5,98	5,88	5,80
HYFS	7,23	7,25	7,33	7,18	7,45	7,29	7,17	7,18	7,13	7,19	7,33	7,03
Q	27,36	26,95	26,92	26,63	27,84	27,05	27,13	30,15	26,71	29,06	28,51	28,66

Ap - Apatite Il - Ilmenite Or - Orthoclase ab - albite an - anorthite mt - magnetite Hyen) Hyfs) Hypersthene

Q - quartz Fo) Fa) olivine Dien) Difs) Diwo) diopside ru - rutile

Samples : Kr2 - Kr21 = Pronksberg andesite
Kr22-Kr26 = Pronksberg Basalt (High K)
Kr27- KR29 = Pronksberg Basalt (Drumbo Type)
KRD 1-5 = Dikkop andesite
KAM6 - KAM17 = Roodehoek Andesite
KRB1 - KRB10 = Belmore Andesite

Samples 1/6 - 1/19 = Central Andean Andesites (Fernandez et al.,1973).

TABLE 6 (continued)

SAMPLE	KR-22	KR-23	KR-24	KR-25	KR-26	KR-27	KR-28	KR-29	KRD-1	KRD-3	KRD-4	KRD-5
AP	0,54	0,62	0,62	0,59	0,59	0,57	0,59	0,57	0,64	0,59	0,62	0,59
IL	1,88	1,91	1,91	1,88	1,90	1,86	1,90	1,93	1,50	1,48	1,50	1,52
OR	10,99	12,17	11,64	11,88	10,75	5,26	2,48	5,61	14,83	15,01	14,06	7,74
AB	28,43	29,19	25,64	27,50	29,44	22,76	21,07	23,61	22,76	22,17	22,59	24,79
AN	24,70	21,96	26,07	23,27	23,43	28,19	30,89	27,35	11,28	11,27	11,30	14,34
C	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	5,98	6,17	6,04	5,80
MT	2,28	2,28	2,28	2,25	2,25	2,28	2,32	2,33	1,42	1,42	1,42	1,42
DIEN	1,87	2,15	1,81	1,78	1,77	4,90	4,05	4,83	0,00	0,00	0,00	0,00
DIFS	1,35	1,67	1,27	1,35	1,30	3,69	3,14	3,81	0,00	0,00	0,00	0,00
DIWO	3,35	3,96	3,22	3,25	3,19	8,91	7,45	8,95	0,00	0,00	0,00	0,00
HYEN	11,19	12,61	12,47	13,83	13,80	11,24	11,72	10,73	5,75	5,88	5,78	5,90
HYFS	8,06	9,81	8,76	10,47	10,13	8,47	9,09	8,46	7,07	7,31	7,29	7,09
Q	0,00	0,00	0,00	1,18	0,00	1,07	4,03	1,03	28,04	28,18	28,70	29,97
FO	2,52	0,48	2,00	0,00	0,38	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FA	2,00	0,41	1,55	0,00	0,31	0,00	0,00	0,00	0,00	0,00	0,00	0,00

TABLE 6 (continued)

SAMPLE	KRB-1	KRB-2	KRB-3	KRB-6	KRB-7	KRB-8	KRB-9	KRB-10	KAM-6	KAM-6X	KAM-8	KAM-11
AP	0,52	0,52	0,52	0,52	0,50	0,52	0,47	0,47	0,57	0,54	0,54	0,52
IL	1,41	1,48	1,50	1,50	1,48	1,48	1,48	1,48	1,48	1,48	1,48	1,46
OR	9,51	3,60	13,35	10,16	14,24	14,83	12,41	13,77	15,66	16,01	17,20	17,43
AB	23,61	23,18	15,57	21,66	19,97	20,05	20,81	21,24	24,45	22,68	21,07	23,35
AN	19,05	27,78	24,16	26,11	24,33	24,49	24,94	20,47	12,08	12,39	11,00	8,98
C	2,79	0,50	1,68	0,00	0,25	0,00	0,28	1,73	4,07	4,16	4,70	5,07
MT	1,41	1,61	1,46	1,71	1,65	1,68	1,61	1,62	1,35	1,35	1,38	1,38
DIEN	0,00	0,00	0,00	0,23	0,00	0,04	0,00	0,00	0,00	0,00	0,00	0,00
DIWO	0,00	0,00	0,00	0,45	0,00	0,09	0,00	0,00	0,00	0,00	0,00	0,00
HYEN	6,90	8,42	7,32	9,19	9,09	8,82	8,72	7,10	6,10	5,95	6,45	6,33
HYFS	7,16	8,37	7,50	8,75	8,57	8,64	8,39	8,40	6,74	6,80	6,94	6,90
Q	27,15	23,97	26,41	18,90	19,34	18,83	20,31	23,22	27,03	28,16	28,73	27,84

SAMPLE	KAM-12	KAM-13	KAM-17	1/11	1,17	1/19	1/6
AP	0,54	0,54	0,54	0,45	0,40	0,76	0,62
IL	1,48	1,46	1,41	1,60	0,34	1,45	1,93
OR	16,37	16,13	17,55	22,99	18,50	22,46	21,33
AB	23,44	20,73	21,32	18,19	22,42	16,92	19,29
AN	10,55	12,54	10,40	15,87	21,91	15,03	22,46
C	4,48	4,40	4,72	1,60	0,07	3,09	0,48
MT	1,36	1,32	1,28	0,50	0,00	3,65	1,91
HYEN	6,30	6,03	6,03	4,48	7,00	4,88	6,28
HYFS	6,79	6,66	6,42	0,00	0,00	2,83	4,49
Q	28,20	29,72	29,85	28,48	20,71	26,97	19,99
RU				0,00	0,38	0,00	0,00

5. TRACE ELEMENT GEOCHEMISTRY

Trace element data for the andesites from the three occurrences discussed in Section 4, as well as for the Pronksberg and Drumbo Basalts, are presented in Table 3. Forty one samples were analysed for fifteen trace elements by X-ray fluorescence spectrometry. Spectrometer settings and running conditions are listed in Appendix 2.

As discussed in Section 4.5, Robey (1976) finds that the Belmore andesite data plot on the extension of the Kraai River basalt major and trace element trends, with the exception of Na_2O, K_2O and Ba. Robey (op.cit.) therefore recognises the possibility of a fractionation link existing between the Kraai River basalts and Belmore andesite. This section will evaluate possible genetic links between the Belmore andesite and Drakensberg Subgroup basalts in the light of variations in trace elements. Differences between the three andesites will also be evaluated. Data are presented and discussed with the aid of SiO_2 variation diagrams (Figures 14, 16 and 18)*. Inter-element ratio data are presented in Table 9.

5.1 THEORETICAL BACKGROUND

The historical background to the developments in trace element geochemistry has recently been reviewed by Allégre and Minster (1978), who discuss the systematic approach to geochemistry initiated by workers such as Wager and Mitchell (1951) and Nockolds and Allen (1953, 1954), which eventually led to the use of partition coefficients and their application in the partial melting and fractional crystallisation models of Schilling and Winchester (1967), Gast (1968) and Shaw (1970). Equations describing the theoretical models of trace element behaviour during magmatic processes have been reviewed by Arth (1976) and Allégre and Minster (1978). Arth

* Lines joining andesite and basalt compositions are an aid in illustrating possible fractionation trends and not actual paths of variation.

(op.cit.) summarises theoretical models for partial melting and fractionation. Allégre and Minster (op.cit.), in addition to partial melting and fractionation models, evaluate contamination and mixing models, as well as present mathematical expressions for complex models.

(a) FRACTIONAL CRYSTALLISATION

Allégre and Minster (op.cit.) present the following equation for simple fractional crystallisation, which is based on the Rayleigh distillation law:

$$C_\ell^i = C_{O,1}^i F^{\bar{D}^i - 1} \quad \ldots\ldots\ldots (1)$$

where $\bar{D}^i$ = the bulk partition coefficient:

$$\bar{D}^i = \sum D_{\alpha/1}^i X_\alpha \quad \text{and:}$$

X_α = weight fraction of crystallising mineral α .

$D_{\alpha/1}^i$ = Partition coefficient for element i between mineral α and liquid

F = weight proportion of residual magma.

C_ℓ^i = concentration of element i in the derived melt.

$C_{O,1}^i$ = concentration of element i in the parent magma.

Different equations for the bulk partition coefficient, deviating from that for sample fractional crystallisation, are presented by Allégre and Minster (op.cit.) for multisequence fractional crystallisation, fractional crystallisation with a simultaneous escape of a fluid phase, fractional crystallisation in a convecting magma chamber and for trapped liquids in a cumulate.

(b) PARTIAL MELTING

Allégre and Minster (op.cit.) present the following equation to describe the behaviour of trace elements during equilibrium partial melting (batch partial melting):

$$C_{\ell}^{i} = \frac{C_{O,5}^{i}}{\bar{D}_{o}^{i} + F(1-\bar{P}^{i})} \qquad \ldots\ldots\ldots\ldots (2)$$

where C_{ℓ}^{i} = concentration of trace element in residual liquid.

$C_{O,5}^{i}$ = concentration of element i in the initial solid.

F = degree of partial melting.

D_{o}^{i} = bulk partition coefficient for the initial assemblage.

$\bar{P}^{i}$ = bulk partition coefficient for the minerals entering into the liquid $P^{a} K^{a/1} + P^{b} K^{b/1}$ ...etc., where P^{a} and P^{b} are the fraction of liquid contributed by phases a,b ...etc., during melting and $K^{a/1}$, $K^{b/1}$ etc., = solid-liquid partition coefficients for a,b ... etc.

This equation may be applied in situations where thermodynamic equilibrium is attained between the melt and the solid, and is thought to be the model that applies to most cases of partial melting. Allégre and Minster (op.cit.) also present equations describing disequilibrium partial melting and partial melting involving distillation processes.

During modal melting (when proportions of each phase in the solid assemblage remain constant), $P = D$ and therefore:

$$C_{\ell}^{i} = \frac{C_{O,5}^{i}}{\bar{D}_{o}^{i} + F(1-\bar{D}_{o}^{i})} \qquad \ldots\ldots\ldots\ldots (3)$$

(c) CONTAMINATION AND MIXING MODELS (following Allégre and Minster, (op.cit.))

During sample mixing of trace elements from two differing sources, the relationship may be expressed as follows:

$$C_{\ell}^{i} = C_{1}^{i}\alpha + C_{2}^{i}(1 - \alpha)$$

where; C_{ℓ}^{i} = concentration in contaminated magma.

C_{1}^{i} = concentration of element i in uncontaminated magma.

C_{2}^{i} = concentration of element i in contaminant.

α = weight proportion of contaminated magma.

When the bulk partition coefficient approaches zero, the equations for both partial melting and fractional crystallisation may be reduced to

$$\frac{C_{\ell}^{i}}{C_{0,5}^{i}} \approx \frac{1}{F} \qquad \ldots\ldots\ldots(4)$$

For partial melting and fractional crystallisation therefore, the concentration of an element with a very small partition coefficient in the residual liquid will depend almost entirely on the extent of partial melting or degree of crystallisation (Arth, 1976). This has important consequences, in that for two elements with small partition coefficients, the ratio of these elements in the residual liquid will remain the same in the parent and may therefore be used as an indicator of consanguinity. For elements with large partition coefficients, however, small differences in the degree of partial melting and fractional crystallisation will change the inter-element ratios considerably.

When F approaches zero, or is much smaller than $\bar{D}_O^i$, the equation for partial melting reduces to:

$$\frac{C_\ell^i}{C_O^i} \approx \frac{1}{\bar{D}_O^i} \quad \ldots\ldots\ldots\ldots (5)$$

and the behaviour of the trace elements will depend on the magnitude of the partition coefficient. For an element with a partition coefficient much less than unity, most of that element will concentrate in the first melt that forms, and even for extremely small degrees of partial melting, the source is strongly depleted. For partition coefficients greater than unity, concentrations of a trace element in the melt vary significantly only after about 50 percent partial melting, and the concentration in the residue remains constant for low degrees of partial melting.

During fractional crystallisation, if the bulk partition coefficient is very large for a particular element, that element is rapidly depleted in the residual melt. For partition coefficients approaching unity, the concentration of an element may be expected to remain relatively constant for all stages of fractionation (and partial melting). For an element with a partition coefficient less than unity, concentrations will only vary significantly after about 50 percent of the crystals have fractionated out.

These equations stress the importance of the magnitude of the partition coefficient and relative degrees of partial melting and fractional crystallisation in determining the behaviour of trace elements during magmatic processes. The expressions presented above have been used by the present writer in evaluating the possible roles of fractional crystallisation, partial melting and crustal contamination in the light of observed trace element abundances for the andesites and associated basaltic rocks under consideration.

5.2 PARTITION COEFFICIENTS

By definition, the partition coefficient of a (trace) element between two phases is the ratio of the concentration in these two phases i.e. the ratio of the concentration of element x in the crystal to the concentration of element x in the coexisting liquid in equilibrium. Albarede and Bottinga (1972), however, present data to show that a state of disequilibrium often exists between phenocrysts and host lava, due to limitations imposed by the rate of crystal growth and trace element diffusion in the lava and in the crystal lattice, and this results in deviations from the normally accepted definition for the partition coefficient. Allégre and Minster (1978) include modified mathematical expressions of trace element behaviour for disequilibrium partial melting.

Partition coefficients have been shown to vary with temperature, pressure, composition of the host magma and the presence of a gaseous phase. The effects of these factors have, however, only been experimentally confirmed for only a few elements in a few minerals and only over a very limited range of temperature, pressure and composition (Arth, 1976).

Sun et al. (1974) investigated variations in partition coefficients for plagioclase-liquid and clinopyroxene-liquid pairs, showing the plagioclase partition coefficient for strontium to decrease from 2,213 to 1,525 with a temperature increase from 1130°C to 1190°C. Clinopyroxene partition coefficients for Sr decrease from 0,278 at 1142°C to 0,167 at 1162°C. Similar results were obtained by Philpotts and Schnetzler (1970) and Korringa and Noble (1971).

The effect of varying composition of the crystallising phase on partition coefficients has been examined by Ewart et al. (1973), who calculated partition coefficients for clinopyroxene -liquid and orthopyroxene -liquid pairs, showing partition coefficients for Ni, Co and Sc for clino- and orthopyroxenes to increase with increasing Fe/Mg ratio of the pyroxene.

Irving (1978) shows Ni partition coefficients for olivine to vary systematically with MgO content of the liquid, D_{Ni}^{ol} decreasing from 36 at 2 wt. percent MgO to 5 at 24 wt. percent MgO. There is also evidence that H_2O, Cl_2 and other volatiles may reduce partition coefficients by modifying the structure of the melt (Irving, 1978).

Shimizu (1974) presents data showing the influence of pressure on the partition coefficients of some elements for clinopyroxene - liquid pairs. Rb and Ba show a steady decrease with increasing pressure from 15-30 Kb at constant temperature. Partition coefficients of Sr for clinopyroxene remain relatively constant with increasing pressure. Banno and Matsui (1973) show partition coefficients of Ba and Sr for plagioclase to vary depending on the composition of the host magma. Both Ba and Sr partition coefficient for plagioclase increase from andesitic host magma to basalt host magma. Allégre et al. (1977a) present equations describing the influence of a gas phase on partition coefficients, while Drake (1974) discusses the influence of oxygen fugacity on europium partition coefficients for plagioclase.

The factors influencing partition coefficients are important and cannot be ignored when published data are used for trace element modelling. In order to obtain an accurate estimate of partition coefficients for a specific mineral, all of the above factors should be taken into consideration. This is often difficult due to the lack of data indicating the influence of these factors on partition coefficients, and as such, inaccurate values may be selected for trace element modelling, thereby yielding unrealistic results.

The behaviour of trace elements during magmatic processes have been described from various standpoints. Taylor (1965), reviews the behaviour of individual elements considering ionic radii, electronegativities, ionic and ionization potentials.

Goodman (1972) recognises further factors specifically influencing the behaviour of potassium and rubidium. He postulates the random absorption of potassium and rubidium into crystals. The reason for this, Goodman propounds, is that large rubidium cations occur as 'trapped' inclusions between successive growth layers of crystals and would therefore occur as minute inclusions, randomly distributed throughout the individual phenocryst. Jensen (1973), studied the variation of partition coefficients with ionic radii, concluding that there is a pattern of partition coefficient behaviour determined by the sizes of the various cation sites in the mineral structure and the 'elasticity' of the structure, thereby confirming the importance of ion size as emphasised by Taylor (1965).

The behaviour of the transition elements, often deviating from Goldschmidt's empirical rules, have been treated by Burns and Fyfe (1964), Dale and Henderson (1972) and Burns (1973) in terms of crystal field theory applied to the melt and crystals. Burns and Fyfe (op.cit.) point out that the transition elements preferentially enter available octahedral rather than tetrahedral sites. The difference in crystal field stabilisation energies between the tetrahedral and octahedral sites in silicate minerals is expressed as the octahedral site preference energy (O.S.P.E., Table 7).

TABLE 7 O.S.P.E. FOR TRANSITION ELEMENTS

Cr^{3+}	37,7 K. Cal. $Mole^{-1}$
Ni^{2+}	20,6 K. Cal. $Mole^{-1}$
Co^{2+}	7,4 K. Cal. $Mole^{-1}$
Cu^{2+}	15,6 K. Cal. $Mole^{-1}$
V^{3+}	12,8 K. Cal. $Mole^{-1}$
Zn	0,0 K. Cal. $Mole^{-1}$

Burns and Fyfe (op.cit.) predict the following order of uptake into the crystallising phases, according to O.S.P.E. :

Ni > Cu > Co > Fe > Mg > Zn for M'' ions.

Cr > Mn > V > Ti > Fe > Sc for M''' ions.

These observations are confirmed by Dale and Henderson (op.cit.) who examined the partitioning of certain transition elements between olivines, pyroxenes and groundmass and obtained a linear correlation between the logarithm of the partition coefficient and the O.S.P.E., thereby confirming the importance of O.S.P.E. as emphasised by Burns and Fyfe (op.cit.). The linear correlation is questioned by Leeman and Scheiddegger (1976) who find a strong correlation between logarithm D and ionic radius. Leeman and Scheiddegger (op.cit.) thus conclude that the sum of various factors (ionic size, O.S.P.E.) may be important in influencing the behaviour of trace elements.

Previous theses presented in the Department of Geology, Rhodes University by Robey (1976) and Pemberton (1978) have concentrated on the basaltic rocks of the Drakensberg Subgroup. These authors have reviewed in detail the theoretical considerations of trace element behaviour. Rather than duplicate information presented in these two studies, a summary of trace element behaviour relevant to this study is presented. Partition coefficients used in this study are listed in Table 8.

5.3. TRACE ELEMENT BEHAVIOUR

(a) Barium

According to the classical Goldschmidt rules and modifications, reviewed by Taylor (1965), Ba should readily substitute into K positions in K feldspar and biotite. Ba shows only limited substitution in plagioclase, clinopyroxene, orthopyroxene and olivine. This is confirmed by

partition coefficient data presented in Table 8(a).

Considering the partition coefficient data presented, Ba will be enriched in the residual melt until K-feldspar separation takes place. Similarly, Ba/K ratios should remain fairly constant until K-feldspar fractionation occurs. As K-feldspar has only been identified as a groundmass constituent in the rocks under consideration, Ba/K ratios should remain constant for all degrees of fractionation in the basalt-andesite system under study.

(b) Strontium

The behaviour of Sr is influenced by its ionic size and electronegativity, which is intermediate between Ca and K (Taylor, 1965), and should therefore be readily accepted by plagioclase and K-feldspar. Sr does not readily enter the Ca positions of pyroxenes, and very little Sr enters the olivine lattice. Partition coefficient data for olivine, orthopyroxene and clinopyroxene (Table 8(a)) indicate a value very much less than unity. Partition coefficients for plagioclase and K-feldspar are greater than unity for Sr, thereby indicating preferential enrichment of Sr into the lattice of these phases. Significant plagioclase fractionation, in association with pyroxene fractionation, would tend to bring the bulk partition coefficient close to unity and therefore subdue Sr enrichment in the residual melt. Extreme plagioclase crystallisation would increase the bulk partition coefficient to greater than unity, a situation which would result in Sr depletion in the residual melt.

(c) Rubidium

Rb behaves similarly to K due to comparable ionic size, similar ionic potentials and electronegativities. Following the classical rules of

TABLE 8(a)

PARTITION COEFFICIENTS FOR INCOMPATIBLE ELEMENTS

	Rb	Zr	Y	Nb	Ba	La	Ce	Nd	Sr
Plagioclase	0,026[2]	0,01[12]	0,01[3]	0,01[12]	0,20[8]	0,10[4]	0,11[5]	0,17[5]	1,66-13[8]
Olivine	0,0002[2]	0,01[3]	0,002[11]	0,01[3]	0,010[1]	0,01[9]	0,01[6]	0,01[7]	0,0004[8]
Clinopyroxene	0,002[2]	0,05-0,22[12]	0,20[11]	0,01-0,03[12]	0,040[1]	0,10[4]	0,15[5]	0,35[5]	0,10[8]
Orthopyroxene	0,01[1]	0,2[3]	0,009[11]	0,2[3]	0,013[1]	0,03[4]	0,031[1]	0,034[1]	0,0004[8]
Magnetite						0,015[7]	0,016[7]	0,026[7]	0,0

References:

(1) Philpotts + Schnetzler (1970)
(2) Hart + Brooks (1974)
(3) Le Roux + Reid (1978)
(4) Allégre et al. (1977)
(5) Sun + Hanson (1976)
(6) Shimizu + Arculus (1975)
(7) Paster et al. (1970)
(8) Korringa + Noble (1971)
(9) Arth (1976)
(10) Lopez-Escobar et al. (1977)
(11) Frey et al. (1978)
(12) Mcullum + Charette (1978)

TABLE 8(b) PARTITION COEFFICIENTS FOR TRANSITION (FERROMAGNESIAN) ELEMENTS

	Zn	Cu	Ni	Co	Cr	V
PLAGIOCLASE		0,08-0,32(3)	0,26(7) 0,01(8)	0,1(7) 0,06(8)	0,06(8)	
OLIVINE	0,95(1) 0,73-1,1(2)	0,37-1,05(2)	8,3-23,5(6) 13,5-15,9(9) 3,6-12(2)	3,6-6,3(4) 1,3-6,5(5)	1,5-5,2(1) 3,1-10(2)	0,02-0,09(4)
ORTHOPYROXENE		0,16-1,2(3)	6,6(7)	2,0(5) 3,4-9,2(3)	0,65-23(3) 1,0(8)	0,5-2,3(3)
CLINOPYROXENE		0,12-0,87(3)	4,0(7)	1,2(5) 1,7-4,7(3) 6,2-11(3)	0,75-33(3) 8-36(2) 30(8)	0,94-4,1(3) 0,22-2,31(4)
MAGNETITE		1,3-2,3(3)	12(7)		27-58(3)	24-63(3)

References :

(1) Gunn (1971)
(2) Flower (1973)
(3) Ewart et al. (1973)
(4) Duke (1976)
(5) Frey et al. (1978)
(6) Leeman + Scheiddegger(1976)
(7) Allégre et al. (1977)
(8) Lopez - Escobar et al. (1977)
(9) Häkli and Wright (1967)

Goldschmidt and modifications (Taylor, 1965), Rb is accepted into the crystal lattice of K-feldspars and micas, but rejected by plagioclase, clinopyroxene, orthopyroxene and olivine. Considering the partition coefficient data presented in Table 8(a), a steady increase in Rb content could be predicted for a process involving separation of any phenocryst phase in the andesite-basalt system under study.

(d) Niobium and Zirconium

A lack of partition coefficient data exists for Nb and Zr. The characteristic ionic size of Zr results in the formation of a separate phase (Zircon), rather than its substitution for any other cations in minerals. Zr has, however, been known to enter early pyroxenes and late apatites, but does not enter plagioclase and olivine (Taylor, 1965). Zr may be expected to substitute to some extent for Ti. Nb, on the basis of ionic radii, may substitute for Ti, Sn, Zr, Mo and W. Taylor (op.cit.) recognises that the bulk of Nb may exist as a $(NbO_4)^{3-}$ complex and because of the large size of this complex in comparison to $(SiO_4)^{4-}$, will concentrate in the residual melt.

Although there is a lack of partition coefficient data for Nb and Zr, they are however, recognised as incompatible elements. Robey (1976) reports an increase in Zr from 67ppm to 357ppm with increasing fractionation in the Stapelbergkloof section, Birds River, with a corresponding Nb enrichment from 9,3 to 34,5 ppm. Similarly, Erlank and Kable (1976), Eales and Robey (1976) and Flower (1973) note the incompatible behaviour of Nb and Zr in basalt systems. Partition coefficients for plagioclase and orthopyroxene determined experimentally by McCallum and Charette (1978) for Zr and Nb in lunar basalts are all well below unity, further confirming their incompatible nature.

(e) Yttrium

Y is intermediate in size and valency between Fe^{2+} and Ca, but is closest in size to Ca. Trivalent Y can thus be expected to substitute for Ca. However, due to the more covalent character of the Y-O bond compared to the Ca-O bond, Y concentrates in later-forming apatites and titanites (Taylor, 1965).

The geochemistry of Y in the Drakensberg Subgroup has previously been discussed by Robey (1976) and Pemberton (1978) in terms of the behaviour predicted by Lambert and Holland (1974). Lambert and Holland (op.cit.) recognise Y-accepting minerals as being K-feldspar and apatite, while Y-rejecting minerals include clinopyroxene, orthopyroxene and plagioclase.

The incompatible behaviour of Y is recognised by Robey (op.cit.) who reports an increase from 20ppm to 86ppm with increasing fractionation in the Stapelbergkloof Section, Birds River, an increase by a factor of nearly 4,5. Similarly, Pemberton (op.cit.) investigated enrichment of the incompatible elements for the Lesotho Formation, with stratigraphic height, in the Naudes Nek section. Pemberton (op.cit.) reports an enrichment factor for Y of 1,29 through the sequence, which is similar to factors calculated for TiO_2, Zr, Rb, Ce and Nd which are elements that he considers to behave incompatibly.

In summary, Y will be rejected by clino- and orthopyroxene, olivine and plagioclase, but will be accepted by minerals such as K-feldspar, apatite, garnet and hornblende. Considering the data presented above, Y would be expected to be enriched in residual melts during fractionation of phases in the basalt-andesite system under study.

(f) Lanthanum, Cerium and Neodymium

The Rare Earth elements (REE) have become important petrogenetic indicators in igneous petrology. The lanthanide group show similar electronegativities and ionization potentials, but there is a steady decrease in ionic radii with increasing atomic number. Under conditions of extreme fractionation, the differences in ionic radii become important, resulting in preferential entry of the smaller REE into crystallising phases, with subsequent enrichment of the larger cations (La, Ce and Nd) into the residual melt (Taylor, 1965). Similarly, the larger cations would be preferentially enriched in the early melt phase relative to the smaller cations.

Arth (1976) has summarised partition coefficients for the REE. Partition coefficient data for La, Ce and Nd are well below unity, indicating their incompatible behaviour on fractionation or melting for minerals in the basalt-andesite system. Partition coefficients show a general increase from La to Lu in the REE series. REE partition coefficient data presented by Arth (1976) are large for apatite and the REE would therefore behave compatibly in the rhyolite system. However, as apatite has not been identified as a fractionating phase in the basalt-andesite system, La, Ce and Nd would be expected to behave incompatibly in all but very late stages of fractionation.

(g) Zinc

Zn is similar in ionic size to Fe^{2+}, but has a more covalent bond to O than Fe^{2+}. This results in Zn being preferentially enriched in the residual liquid relative to Fe^{2+}. Partition coefficient data for Zn are limited, although Gunn (1971) and Flower (1973) report values between 0,73 and 1,1 (Table 8(b))for olivine. The behaviour of zinc is largely unpredictable, a fact which is supported by its O.S.P.E. which is zero (Flower, 1973).

Robey (1976) presents data in verification of partition coefficients for Zn being less than unity for olivine and pyroxene. In the Stapelbergkloof section, Birds River, Zn is enriched from 61ppm to 150ppm with increasing fractionation.

(h) Copper

Cu^{2+} substitutes for Fe^{2+} due to similarities in ionic radii, as will Cu^{+} for Na^{+}. Copper will enter plagioclase and apatite, substituting for Na^{+} and Ca^{2+}, and will enter minerals containing Fe^{2+} (Taylor, 1965). Cu is thus likely to substitute into most common rock forming minerals. The characteristic trend shown by Cu in many fractionation sequences is one showing a steady increase from early to relatively late stages of fractionation. Continued fractionation results in rapid depletion of Cu by separation of Cu sulphides or by its entry into minerals such as magnetite which can accept substantial amounts of Cu into the lattice. These trends are emphasised by data presented by Wager and Brown (1968) and Robey (1976). This pattern may be explained by crystal field theory. The transition metal ions Cr^{2+}, Mn^{3+}, Cu^{2+} and Ni^{3+} are influenced by large Jahn-Teller distortions in coordinating octahedral polyhedra in oxide structures, resulting in compounds of these ions being distorted from type structures (Burns and Fyfe, 1967: Curtis, 1964) until a late stage of fractionation where Cu-rich minerals separate.

In general, Cu is rejected by plagioclase, clinopyroxene and olivine, but may to a small extent enter the lattice of orthopyroxene and more extensively into magnetite. Partition coefficients for Cu (Table 8(b)) support these conclusions.

(i) Nickel

Ni behaves 'compatibly' in that it is depleted from the magma and incorporated into the structure of early crystallising olivine, pyroxene and iron oxides. Ni and Co are similar in size and intermediate in size between Fe^{2+} and Mg^{2+}, substituting for these elements in the crystal lattice of mafic minerals.

According to crystal field theory, Ni is rapidly depleted in the melt due to its high O.S.P.E. and incorporated into the structure of olivine, ortho- and clinopyroxene. As previously mentioned, these observations are supported by Dale and Henderson (1972) and Leeman and Scheiddegger (1976) although the latter authors see factors other than just O.S.P.E. and ionic radius as being important in predicting the incorporation of Ni into the olivine lattice. In summary, Ni is concentrated into the lattice of orthopyroxene, clinopyroxene, olivine and magnetite. This is supported by partition coefficient data presented in Table 8(b).

(j) Cobalt

Co behaves similarly to Ni due to the fact that both are similar in size and intermediate in ionic radius between Fe^{2+} and Mg^{2+}, although Co is slightly larger in size compared to Ni. The latter fact results in Co entering the Mg positions in minerals to a lesser extent than Ni. Co may also substitute for Fe^{2+} but also to a lesser extent than Ni.

Co exhibits a lower O.S.P.E. (Table 7) than Ni and Cr and as such shows relatively subdued entry into olivine and pyroxene compared to Ni and Cr. For olivine, Ni and Co preferentially enter M_1 sites, while in ortho- and clinopyroxenes, Ni preferentially enters the M_1 sites and Co the M_2 sites (Burns, 1970).

The fact that Co enters the orthopyroxene, clinopyroxene and olivine structures will result in depletion of this element in the residual melt on

fractionation. These observations are supported by Co partition coefficient data for these minerals, which are all greater than unity. The opposite holds for plagioclase which excludes Co from its lattice, hence the partition coefficient is less than 1. Significant plagioclase fractionation, in association with olivine and for pyroxene fractionation, would tend to reduce the bulk partition coefficient and therefore subdue Co depletion in the residual melt, a situation which has been described by Robey (1976) for the Birds River intrusive complex.

(k) Chromium

Cr has an ionic radius almost identical to Fe^{3+}, but due to a more ionic bond to oxygen than to Fe^{3+}, preferentially enters Fe^{3+} positions, resulting in depletion of chromium at an early stage of fractionation (Taylor, 1965).

Cr has a higher O.S.P.E. than Ni (Table 7) and as such is rapidly depleted in the residual melt. Burns (1970) describes the enrichment of Cr^{2+} ions into the M_2 site in clinopyroxene (augite), while in orthopyroxene Cr^{3+} substitutes in the M_1 site with Cr^{2+} in the M_2 site. Partition coefficient data confirm the fact that Cr readily enters into magnetite, clino- and orthopyroxene and to a lesser extent olivine, thereby depleting the residual liquid in Cr, but it is excluded by plagioclase, crystallisation of which would tend to enrich the melt in Cr. Significant plagioclase fractionation would tend to reduce the bulk partition coefficient, resulting in subdued Cr depletion in the residual melt.

(l) Vanadium

Vanadium (V^{3+}) is similar in ionic potential and electronegativity to Cr^{3+}, but is larger in size than Cr^{3+}. Cr^{3+} thereby enters available Fe^{3+},

Fe^{2+} and Ti^{4+} sites earlier than V^{3+} (Taylor, 1965).

Duke (1976) recognises the variability in V distribution within a silicate liquid, although he notices the preferential concentration of V into clinopyroxene rather than olivine. These observations support those of Walker (1970) who finds V uptake in the order magnetite-clinopyroxene-orthopyroxene, with no olivine or plagioclase accepting V^{3+} ions.

From the partition coefficient data presented in Table 8 the strong preference of V for magnetite is evident. Taylor (1969) predicts a decrease of up to 60ppm in V content for calc-alkali magmas per 1 percent magnetite fractionation. The geochemical behaviour of V in any basalt-andesite system, therefore depends on the relative amounts of - and stage at which fractionation commences for magnetite, orthopyroxene, clinopyroxene, plagioclase and olivine.

5.4 TRACE ELEMENT VARIATIONS

The systematic use of trace elements is widely accepted in modern geochemistry for deciphering the petrogenesis of different rock types. For example in the Karoo volcanic province, Pemberton (1978), attributes major and trace element differences between basaltic members of the Drakensberg Subgroup to a chemically heterogeneous mantle, while Robey (1976) recognises the possibility of a fractionation sequence existing between the Kraai River Basalt Formation and the Belmore Andesite. From a consideration of differences in trace element content between the andesites and basalts under study, it is intended to evaluate possible magmatic processes operative during early Karoo volcanism.

Possibilities for the origin of the Karoo andesites are:

(1) Fractional crystallisation from basaltic magmas.

(2) One or more stages of partial melting of the upper mantle.

(3) Anatexis of lithosphere in subduction zones.

(4) Contamination of basic magmas by assimilation of crustal material or anatexis of sialic crust.

A systematic discussion of the incompatible elements Ba, Rb, Sr, Zr, Y, La, Ce and Nd followed by a discussion of the transition elements Ni, Co, Cr, V, Cu and Zn (although the latter two are not strictly transition elements) are presented in this section. Trace element variations are complemented with inter-element ratio data for each of the occurrences studied. Although the behaviour of potassium has been discussed under major element variations, a discussion of ratios including potassium is included in this section.

5.4.1 Pronksberg

Differences in trace element abundances between the Pronksberg Andesite, the Dikkop Andesite and the Pronksberg Basalts are illustrated in Figure 14. Averages and ranges of trace element abundances are listed in Tables 4 and 5, while inter-element ratio data are given in Table 9.

5.4.1.1 The Pronksberg and Dikkop Andesites

From a consideration of trace element averages and ranges (Table 4), it is evident that the Dikkop andesites have compositions within the range of the Pronksberg andesite. A single Dikkop andesite analysis (KRD5, Table 3) is enriched in Ba (828ppm) and depleted in Rb (93ppm) relative to the range for the other three Dikkop andesite analyses. The Rb content of sample KRD5 is, however, within the range for the Pronksberg andesite. All of the other trace element abundances are similar for the Pronksberg and Dikkop (including KRD5) andesites.

Inter-element ratios (averages and ranges) for the Pronksberg and Dikkop andesites are listed in Table 9. The high potassium content of the Dikkop andesite (excluding KRD5) in relation to the Pronksberg andesite has been discussed in Section 4.5. These high potassium values are reflected in increased potassium-inclusive ratios at Dikkop compared with the Pronksberg andesite, e.g., K/Zr, K/Rb and K/Y. Potassium-inclusive ratios for flow KRD5 are within the range for the Pronksberg andesite and this flow has therefore been correlated with the Pronksberg andesite. Although the potassium-inclusive ratios vary considerably, the other inter-element ratios (Zr/Nb, Zr/Y, Ti/Zr, Ba/Sr, Ba/Zr, Cr/V and Ni/Co) show only slight differences between the Dikkop and Pronksberg andesites.

Any theory of petrogenesis for the Pronksberg and Dikkop andesites would have to take cognisance of the relative potassium enrichment of the Dikkop

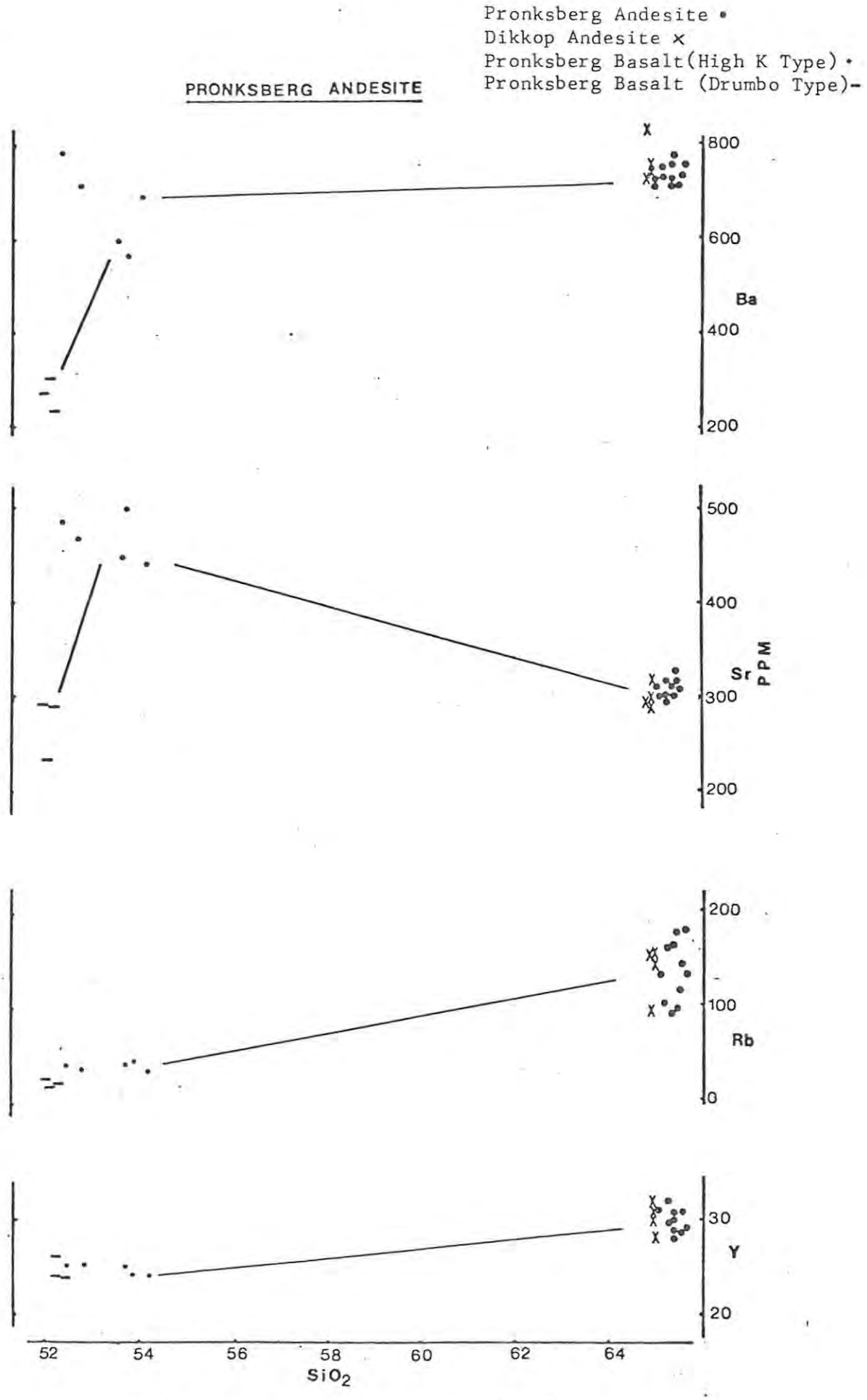


FIG.14 Trace element data for the Pronksberg Andesite and Basalts vs. SiO_2

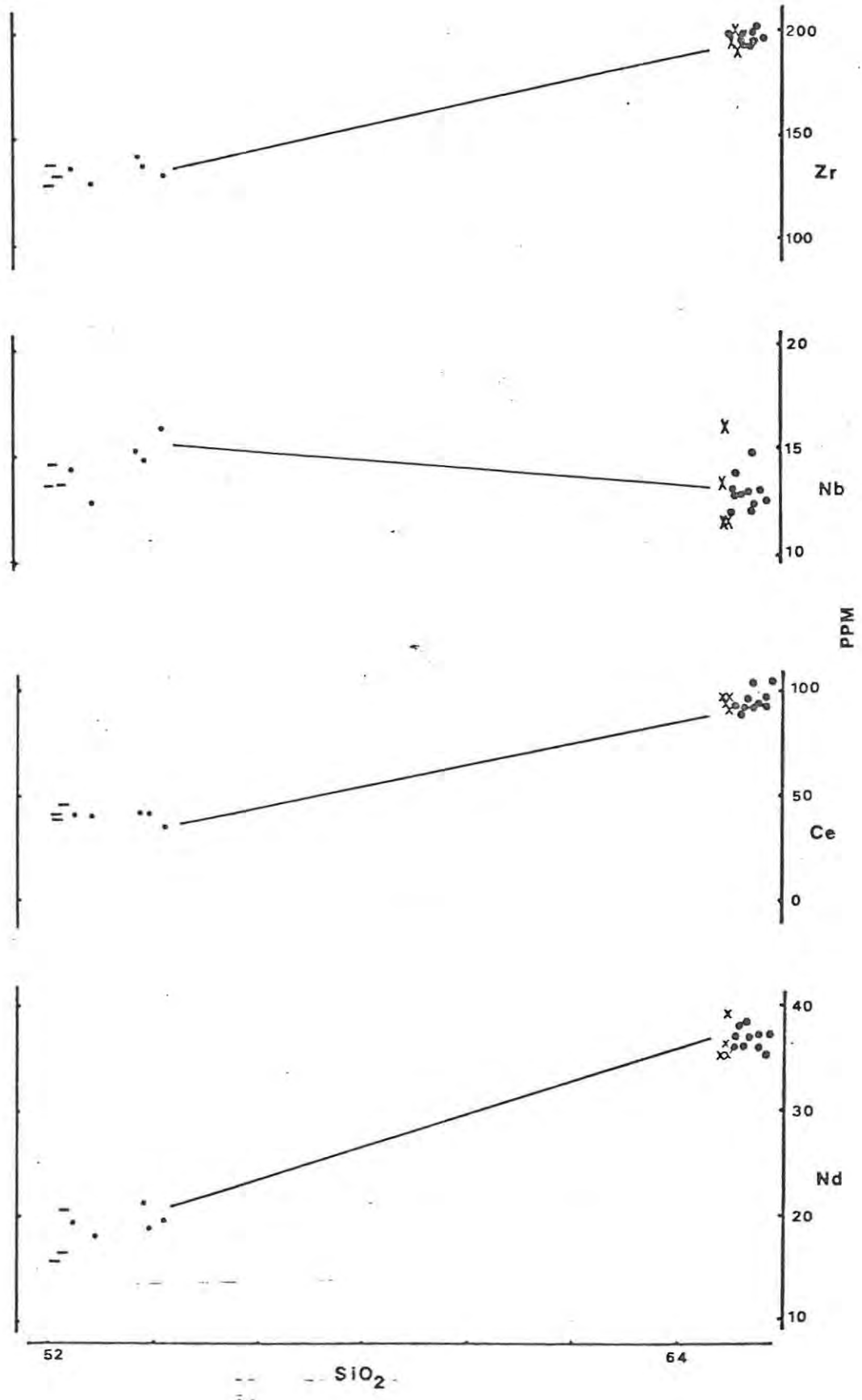


FIG.14(Cont.)

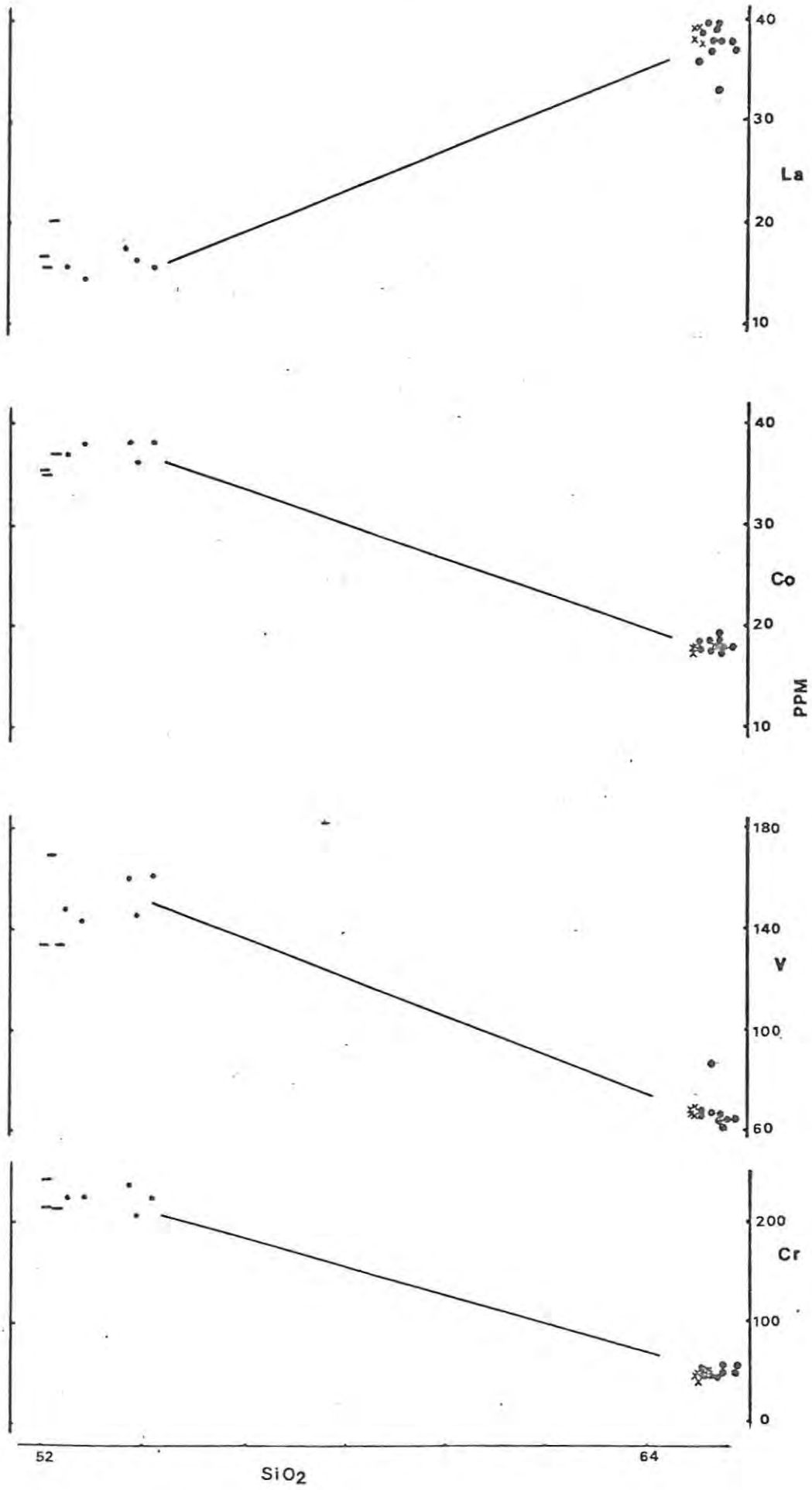

40
30
La
20
10
40
30
Co
20
PPM
10
180
140
V
100
60
200
Cr
100
0
52
64
SiO2

FIG.14(Cont.)

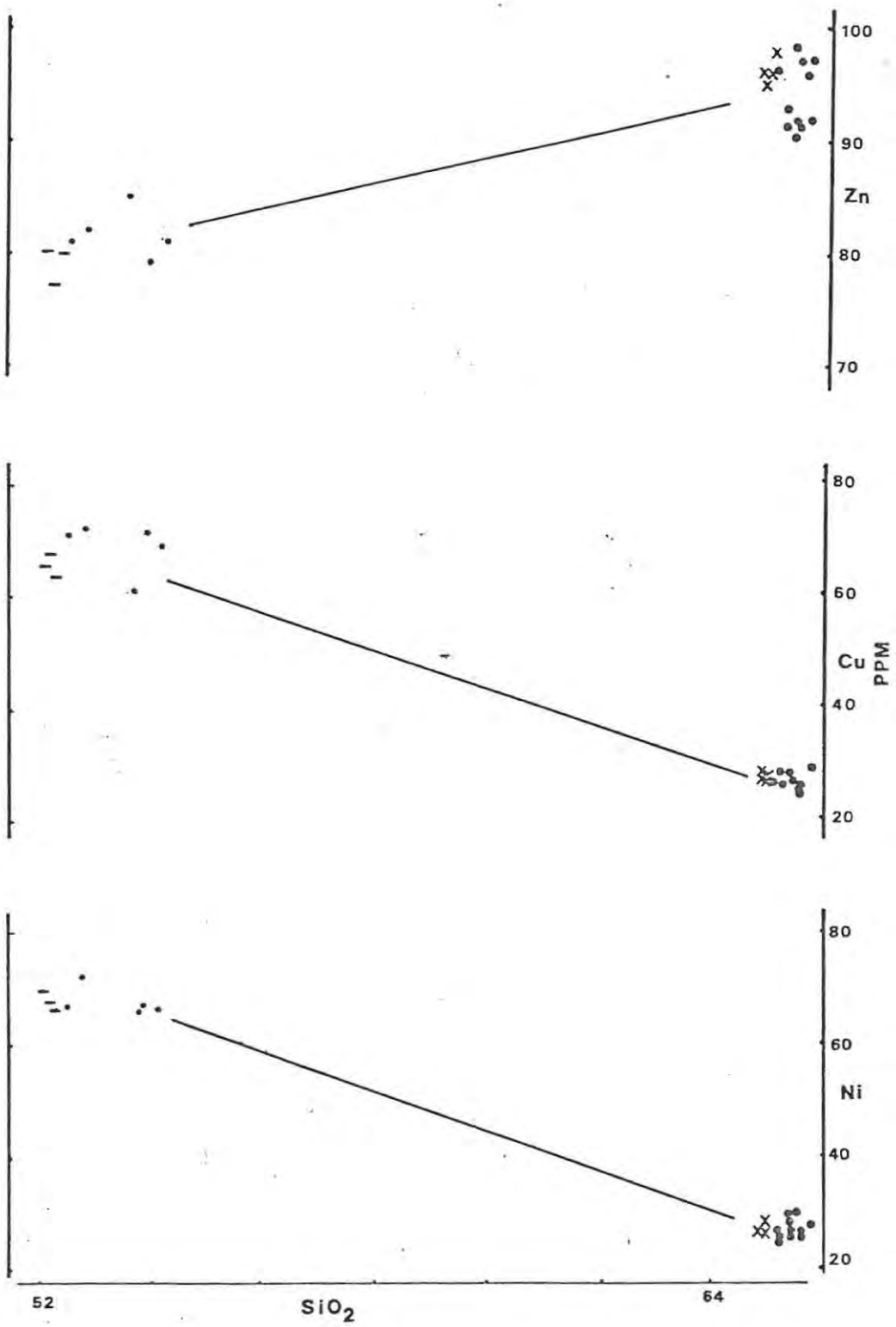


FIG.14(Cont.)

TABLE 9 : AVERAGES AND RANGES FOR INTER-ELEMENT RATIOS - KAROO ANDESITES AND BASALTS

	K/Zr	K/Rb	K/Y	Zr/Nb	Zr/Y	Ti/Zr
PRONKSBERG ANDESITE	53 48-62	78 57-118	346 308-404	15,2 13,1-16,5	6,5 6,2-6,8	23,2 22,1-24,
SAMPLE KRD5	55	112	337	15,8	6,1	24,5
DIKKOP ANDESITE	101 95-106	132 124-137	670 602-738	14,2 12,6-16,0	6,5 6,3-6,9	23,7 23,3-24,
PRONKSBERG BASALT (HIGH K TYPE)	117 107-123	392 365-433	631 581-685	8,5 7,8-8,9	5,4 5,1-5,6	43,8 42,8-44,
PRONKSBERG BASALT (DRUMBO TYPE)	55 54-56	362 348-386	298 290-308	9,3 9,2-9,4	5,4 5,3-5,4	44,4 43,8-45,
BELMORE ANDESITE	88 61-108	186 96-299	580 383-689	19,0 17,6-21,2	6,7 6,3-6,8	23,5 20,5-25,0
ROODEHOEK ANDESITE	103 97-111	191 183-202	761 700-830	20,5 19,4-24,0	7,4 7,2-7,6	20,6 19,8-21,
3/10 (ROBEY)	22	166	120	19,7	5,5	32,2
KRAAI RIVER FORMATION (PEMBERTON)	35 24-65	241 86-317	149 103-270	25,8 24-28	4,2 4,2-4,3	75,0 73-76
KRAAI RIVER (ROBEY)	38 21-62	250 122-322	153 89-270	21,2 19-26	4,5 4,4-5,5	46,3 -
DRUMBO BASALT (PEMBERTON)		417 380-433		9,4 9-10,2	5,7 5,5-5,9	68 65-71

TABLE 9 (continued)

	Rb/Sr	Cr/V	Ni/Co	Ba/Zr	Ba/Sr
PRONKSBERG ANDESITE	0,46 0,28-0,6	0,73 0,65-0,86	1,46 1,37-1,69	3,76 3,60-3,94	2,36 2,22-2,56
SAMPLE KRD5	0,30	0,69	1,52	4,36	2,64
DIKKOP ANDESITE	0,52 0,51-0,53	0,72 0,69-0,75	1,49 1,46-1,52	3,77 3,70-3,85	2,54 2,49-2,60
PRONKSBERG BASALT (HIGH K TYPE)	0,08 0,08-0,09	1,51 1,31-1,82	1,85 1,81-1,89	4,74 4,1-5,5	1,41 1,11-1,60
PRONKSBERG BASALT (DRUMBO TYPE)	0,07 0,06-0,07	1,54 1,24-1,80	1,93 1,81-2,0	1,98 1,76-2,32	0,86 ,79-,93
BELMORE ANDESITE	0,35 0,15-0,45	0,87 0,75-1,05	1,43 1,30-1,52	2,79 2,58-3,31	1,94 1,23-2,37
ROODEHOEK ANDESITE	0,48 0,42-0,51	0,94 0,88-1,01	1,14 1,0-1,32	2,85 2,70-3,09	2,54 2,13-2,86
3/10 (ROBEY)	0,09	0,64	1,13	1,16	0,78
KRAAI RIVER FORMATION (PEMBERTON)	0,10 0,04-0,17	1,14 1,08-1,18	1,10 1,00-1,40	- -	- -
KRAAI RIVER (ROBEY)	0,07 0,06-0,10	1,0 0,98-1,09	1,30 1,14-1,54	1,36 1,19-1,57	0,75 0,70-0,80
DRUMBO BASALT (PEMBERTON)	0,06 0,06-0,08	1,37 1,24-1,52	1,67 1,3-1,95	- -	- -

andesite. However, due to the similarity of the potassium-exclusive ratios of the Pronksberg and Dikkop andesites, it would appear as if the two are genetically related, with the Dikkop andesite being preferentially enriched in potassium by some mechanism. The fact that the Dikkop andesite represents a later episode of volcanism (i.e. overlies a correlate of the Pronksberg andesite - flow KRD5) suggests a relationship between the time of eruption and potassium-enrichment. The potassium enrichment could perhaps be explained by extensive wall-rock reaction, contamination by a potassium-rich source or variations in depth of melting (Dickenson, 1968).

K/Rb ratios for the Pronksberg and Dikkop andesites are significantly lower by a factor of almost three compared to volcanic rocks of mantle origin (Gast, 1965). The K/Rb ratios for the Pronksberg andesite are, however, lower than typical crustal values quoted by Gast (op.cit.) which average in the region of 200, but according to Jakes and White (1970), variable K/Rb ratios may result from variable degrees of crustal contamination.

5.4.1.2 Variation in trace element content with height - Pronksberg Andesite.

Variation of trace element concentrations with height through the Pronksberg andesite (which is thought to represent a single flow) is shown in Figure 15. Although trace element variations are generally subdued, several interesting patterns of variation are observed, which do not entirely support interpretations regarding major element variations with height at Pronksberg.

Considering the analytical precision of the data presented in Section 4.4.1, the variations with height of Ba, Y, Zr, Nb, La, Ce, Nd, Co and Cr are considered to be insignificant. Significant variations are displayed by Sr, which decreases markedly towards the centre of the flow, Rb, Zn, Ni

and Cu which increase towards the centre and V which decreases towards the base of the flow.

Variations in inter-element ratios with height through the andesite are shown in Figure 15(b). Ratios with potassium vary fairly widely, while the ratios Ti/Zr, Zr/Nb, Zr/Y, Ba/Sr, Cr/V and Ni/Co remain constant through the flow.

Pemberton (1978) sampled three individual basalt flows in the Naudes Nek section at various heights through the flows and reports positive correlations between Fe-Ti, Al-Ca and K-Rb as well as between Zr, Nb and Y. Pemberton's data also indicate a strong negative correlation between Rb and Sr. Inter-element ratio variations within the same flow showed TiO_2/Zr to be constant through a single flow, with Zr/Y, Zr/Nb and Cr/V fairly constant. The K-inclusive ratios determined by Pemberton are erratic due to the erratic variation of K within flows. Most of the intraflow variations are attributed to the non-random distribution of plagioclase and olivine phenocrysts, with alkali variations attributed in part to laminar flows (Watkins et al., 1970).

The variations in major element concentrations with height discussed in Section 4.4.2 may be interpreted as representing the concentration of a mafic phase, probably orthopyroxene, towards the centre of the flow. This should be accompanied by an increase in the concentrations of the transition elements Cr, Ni, V and Co, with a corresponding decrease in concentration of the incompatible elements. Considering the partition coefficient data presented in Table 8, Zn and Cu would be expected to remain relatively constant on concentration of orthopyroxene. As the incompatible elements remain essentially constant with height and the transition elements Zn and Cu increase in similar proportions to Ni towards the centre of the flow, it would appear that the variations described above do not represent entrichment of a mafic phase towards the centre of the flow and intraflow variations would

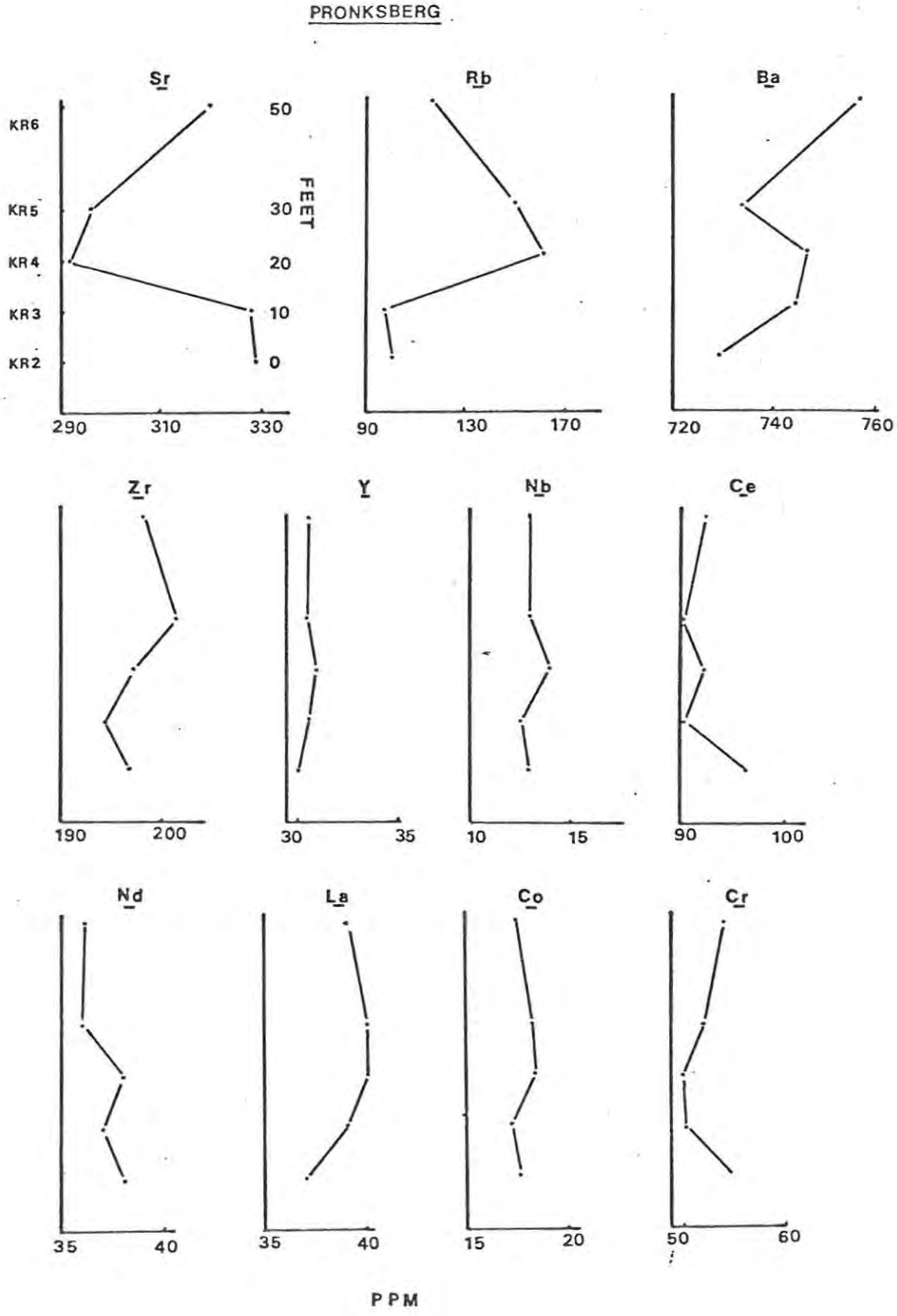
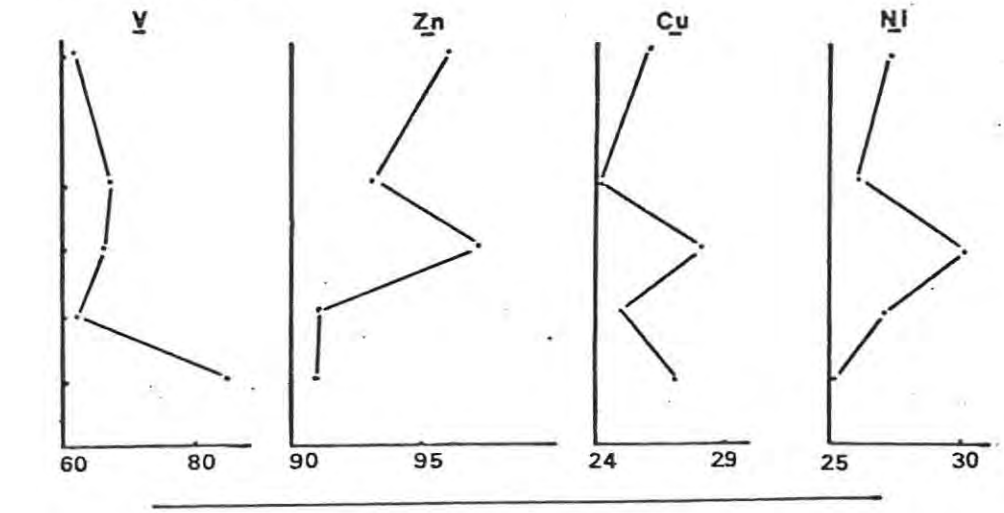


FIG.15(a) Trace element data vs. height-Pronksberg Andesite.

FIG 15(a) cont.



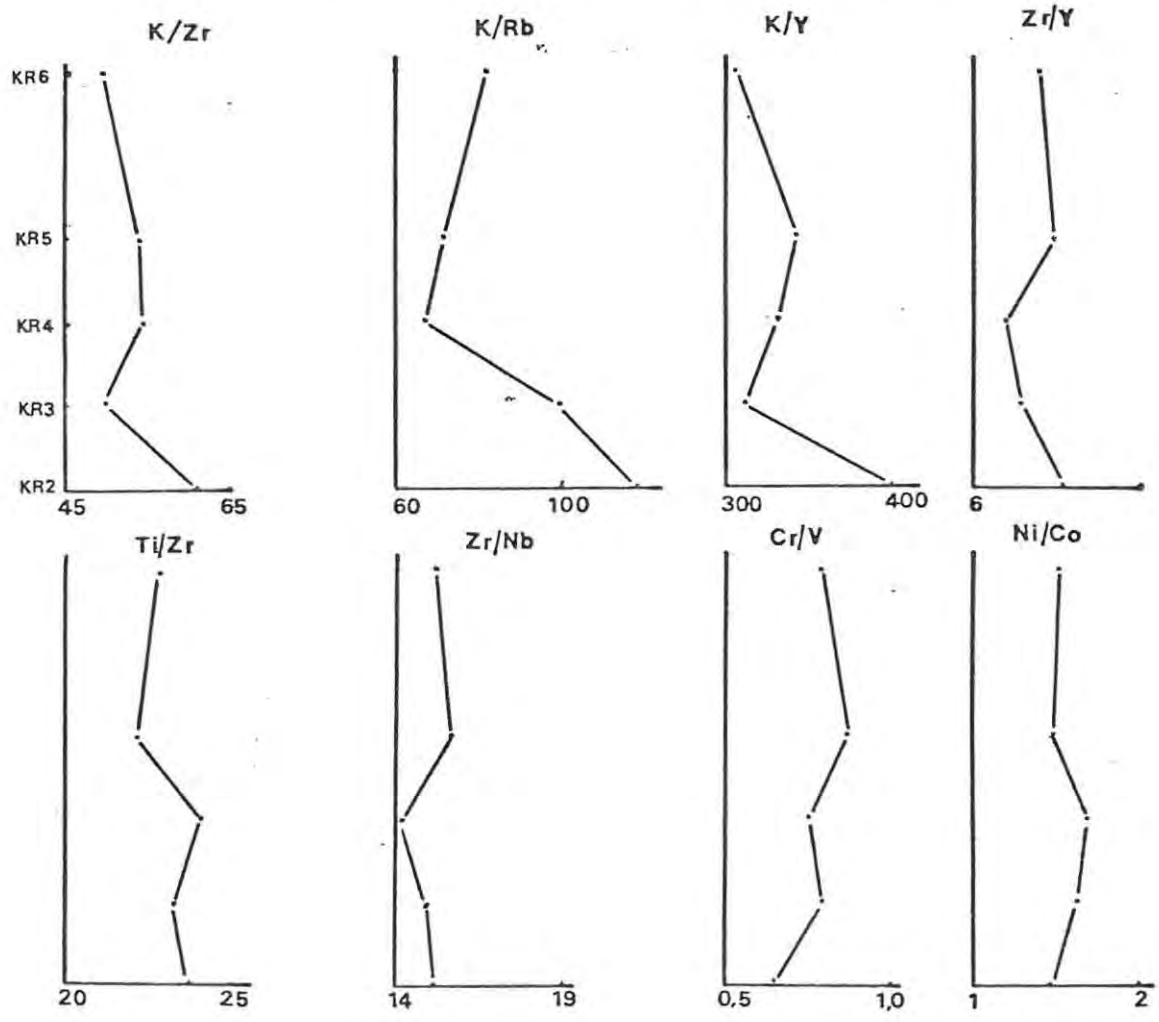


FIG.15(b) Inter-element ratios vs. height-Pronksberg Andesite.

have to be explained by some other mechanism influencing chemical variations within the andesite.

5.4.1.3 The Pronksberg Basalts.

Differences in major and trace element concentrations (averages and range, Table 5) between the Pronksberg Basalt (High K Type) and Pronksberg Basalt (Drumbo Type) are as follows:

(1) The Pronksberg Basalt (High K Type) is enriched in Ba, Rb, Sr, K_2O and Na_2O relative to the Pronksberg Basalt (Drumbo Type).

(2) The Pronksberg Basalt (High K Type) is depleted in CaO compared to the Pronksberg Basalt (Drumbo Type).

Incompatible element ratios (averages and range) do not reflect gross differences between the Pronksberg Basalt (High K Type) and the Pronksberg Basalt (Drumbo Type), with the exception of K/Zr, K/Y and Ba/Zr which are higher by a factor of 2 in the Pronksberg Basalt (High K Type). Significantly similar ratios include Zr/Nb, Zr/Y, Ti/Zr, Rb/Sr, Cr/V and Ni/Co.

The Pronksberg Basalt (High K Type) is a relatively highly weathered amygdaloidal basalt by comparison with the Pronksberg Basalt (Drumbo Type), which is only slightly altered and contains no amygdaloidal material. Cann (1970) examined fresh and altered ocean floor basalts for Rb, Sr, Y, Zr, Ti, K and Nb. The dominant conclusion to emerge from this study is that Zr, Y, Nb and Ti are unaffected by alteration, whereas K, Rb and to a lesser extent Sr show marked variations, all increasing with increasing degree of alteration. Similar observations have been recorded by Nicholls and Islam (1971), while Baragar et. al. (1977) record an increase in Ba content in basalts due to ocean floor weathering.

These studies illustrate the mobility of elements such as K, Sr, Rb and Ba, which are all influenced considerably by ocean-floor alteration. The less mobile elements Ti, Zr, Y, Nb and the REE are therefore widely used for genetic interpretations, regardless of weathering, spilitization and low-grade metamorphism (Floyd and Winchester, 1975: Pearce and Cann, 1973). The fact that the studies of Cann (1970) and Baragar et. al. (1977) are concerned with ocean-floor weathering is recognised, and the influence of weathering under conditions prevalent on continents may therefore differ from ocean-floor weathering. However, the fact that elements such as K, Rb, Sr and Ba are mobile is significant to weathering on continents in that it is these elements which will also be influenced to a greater extent than the less mobile elements. Ratios of Y, Zr, Nb and Ti are therefore particularly useful for comagmatic comparisons. Pemberton (1978) investigated chemical variations due to the presence of amygdales in basaltic rocks and concludes that the presence of amygdales leads to increases in K, Ca, Mn, Al, Rb and Sr, but with the exception of Sr which in one instance increases from 127ppm-214ppm, differences are slight.

Watkins et. al. (1970) examined chemical variations through a single Icelandic lava and report intraflow variations of between 2-7 percent for most of the major elements, excluding SiO_2. Particularly high variations are shown by the elements Na, K and Rb. Hart et al. (1971) confirm these conclusions. The Pronksberg Basalt (High K Type) shows fairly extensive alteration, particularly of plagioclase. Variations of Ca, K, Rb, Ba and Sr would thus be influenced substantially by weathering, and may be further affected by the presence of amygdales and by intralava variations. Useful comagmatic indicators would therefore be Ti, Zr, Y and Nb and in particular, inter-element ratios of these elements. As the Pronksberg Basalt (High K Type) and Pronksberg Basalt (Drumbo Type) show similar trace element contents for Y, Nb, Zr and Ti as well as similar Zr/Nb, Zr/Y and Ti/Zr ratios, it

would appear that these two basalts are possibly genetically related.

The Pronksberg basaltic rocks exhibit K/Rb ratios of between 300-400, which are similar to those presented by Gast (1965) for typical basaltic rocks. The K/Rb ratios for the Pronksberg Basalts are similar to values presented by Engel et al. (1965) for the Hawaiian basalts and fall within the range for the Drakensberg Subgroup rocks presented by Pemberton (1978), although the Kraai River basalts exhibit ratios markedly lower than those of the Lesotho Formation and Drumbo Basalt Member.

The similarity in petrographic and major element characteristics of the Pronksberg Basalt (Drumbo Type) and Drumbo Basalt in the type area have been discussed in a previous section. Trace element concentrations and inter-element ratios further illustrate the similarity between these two basalts. Cr and V are the only trace elements which differ significantly between the basalts from the two areas, both elements being depleted in the Pronksberg Basalt (Drumbo Type) in comparison with Drumbo Basalt averages and ranges from the Barkly East area (Table 5). The similar inter-element ratios (Zr/Nb, Ti/Zr, Zr/Y, Table 9) of the Pronksberg Basalt (Drumbo Type) and Drumbo Basalts from the type area further justifies a correlation of the two.

5.4.1.4 Pronksberg Andesite - Basalt Variations.

SiO_2 variation diagrams (Figure 14) are used to illustrate differences in trace element content between the basaltic and andesitic lavas at Pronksberg. Compared to the Pronksberg basalts, the Pronksberg andesite is enriched in Rb, Y, Zr, La, Ce, Nd, Ba and Zn. It is also enriched in Sr compared to the Pronksberg Basalt (Drumbo Type), but depleted in Sr relative to the Pronksberg Basalt (High K Type). The Pronksberg andesite is depleted in Nb relative to the Pronksberg basalts and also depleted in the transition elements Co, Cr, V, Cu and Ni.

If one assumes a genetic link to exist between the Pronksberg andesite and basalts, the most likely processes that could explain observed trace element differences between the basaltic and andesitic rocks are fractional crystallisation and/or varying degrees of partial melting from a common parent which is assumed to have the composition of a garnet lherzolite. The fact that the Pronksberg basalts contain clinopyroxene, olivine and plagioclase compared to the Pronksberg andesite which contains orthopyroxene and plagioclase suggests that the two rock types are not genetically related.

Using the equations for fractional crystallisation (equation 1) and bulk partition coefficient (equation 2) presented in Section 5.1, it is possible to model, from trace element data, approximate proportions of phases involved in fractional crystallisation, as well as obtain estimates of partition coefficients for these phases. By calculating enrichment factors $(\frac{C_{\ell}^{i}}{C_{O}^{i}})$ for the incompatible elements, it is possible to estimate F from the approximation given in equation 4 in Section 5.1. The following enrichment factors were calculated for the incompatible element:

		Enrichment Factor	F
Rb	=	3,60	.28
Zr	=	1,20	.83
Y	=	1,46	.68
Nb	=	0,87	-
La	=	2,40	.42
Ce	=	2,40	.42
Nd	=	1,90	.53
av.	=	1,97	

The fact that the enrichment factors vary widely for the incompatible elements suggests that a simple fractionation link does not relate the andesitic and basaltic composition at Pronksberg.

The average enrichment factor is 1,97 which gives F = 50 percent, assuming the initial liquid to have the average Pronksberg Basalt composition and the final liquid to have the average andesite composition. Sr and Ba were not included in the calculations as they are thought to have been influenced by weathering in the Pronksberg Basalt (High K Type). By substituting analytical data for a particular element, it is possible to calculate the bulk partition coefficient for that element. From the bulk partition coefficient and knowledge of published individual mineral partition coefficients, it is possible to estimate proportions of the phases involved in the fractionation.

An immediate constraint on fractional crystallisation linking the two rock types is the relative enrichment of Nb in the Pronksberg Basalts compared to the andesite. By substituting analytical data into equation 1, a bulk partition coefficient for Nb of greater than unity is obtained, which is unrealistic and cannot be explained by fractionation processes.

If the Sr enrichment in the Pronksberg Basalt (High K Type) is not due to weathering, the enrichment could be explained by strong plagioclase fractionation which would however not explain the depletion of the transition elements in the andesite relative to the basalts.

The equation for partial melting and approximation (equation 4) may be applied in a similar manner as for fractional crystallisation. From the enrichment factors for the incompatible elements (page 101), and approximation (equation 4) of the partial melting equation, it is possible to estimate that the average enrichment would be explained by 50 percent partial melting of that responsible for the generation of the Pronksberg Basalts. Calculations using this estimate, analytical data and the equation for partial melting (equation 3), assuming modal melting, again indicate Nb to have a partition coefficient greater than unity, which is unrealistic.

Further evidence for non-consanguinity between the Pronksberg Basalts and andesite are the differences in inter-element ratios. During magmatic processes such as partial melting or fractional crystallisation, the ratio of two elements with very small partition coefficients remains essentially the same in successive residual fractions as in the parent magma. Ratios such as Zr/Nb, Ti/Zr, Zr/Y and Ba/Zr are thus widely used as indicators of cogenetic magmas (Erlank and Kable, 1976: Robey, 1976). Inter-element ratios (average and range) for the Pronksberg basalts and andesites are listed in Table 9. It is evident from these data that all the inter-element ratios of the andesite differ significantly from the basaltic types, and it would therefore appear that they are genetically unrelated.

5.4.1.5 Conclusions.

Similarities in trace element content of the Pronksberg and Dikkop andesites are suggestive of consanguinity, the exception being that K and Rb are enriched in the Dikkop andesite. Inter-element ratios involving K and Rb express the K enrichment, but ratios such as Zr/Nb, Ti/Zr, Zr/Y and Rb/Sr and others are identical for the two andesites, thereby supporting a cogenetic origin.

Differences in inter-element ratios, petrography and trace element abundances as well as semi-quantitative trace element modelling deem the possibility of a fractionation link between basaltic and andesitic compositions at Pronksberg as unlikely.

Differences in major and trace element abundances, as well as inter-element ratios between the Pronksberg Basalt (High K Type) and Pronksberg Basalt (Drumbo Type) constrain the possibility of a fractionation link between the two lava types. Inter-element ratios are suggestive of a cogenetic link between the two. The enrichment in the incompatible elements Ba, Rb and Sr, with a corresponding enrichment in K_2O and Na_2O, as well as

CaO depletion in the Pronksberg Basalt (High K Type) relative to the Pronksberg Basalt (Drumbo Type) may be explained by weathering and intra-flow variations, although the possibility of crustal assimilation, wall-rock reaction and melting of a source enriched in K, Na, Rb, Sr and Ba cannot entirely be discounted.

Similarities in trace element content of the Pronksberg Basalt (Drumbo Type) and Drumbo Basalt in the Barkly East area justifies the correlation between the two, although V is slightly depleted in the former.

5.4.2 Belmore

Trace element variations confirm the differentiated nature of the Belmore andesite suggested by major element variations. Differences in incompatible and transition element concentrations for the Belmore andesite and associated basaltic rocks in the Barkly East area are illustrated in Figure 16. Inter-element ratios are listed in Table 9. Variations in trace element content with height through the andesite sequence are shown in Figure 17.

5.4.2.1 Variations in Trace Element Content with Height - Belmore Andesite.

The variation of trace elements with height through the andesite sequence exhibit two distinct trends. As discussed in Section 4.5.2, the major element variations are subdued, with only K_2O and Na_2O showing the two trends.

The incompatible elements show distinct changes in abundance in the vicinity of flow KRB8. Rb, La, Ce and Nd decrease with height up to sample KRB8, thereafter increasing steadily to the top of the sequence. Zr and Y increase in a regular fashion from base to top of sequence. Nb behaves rather erratically although it does generally increase towards the top of

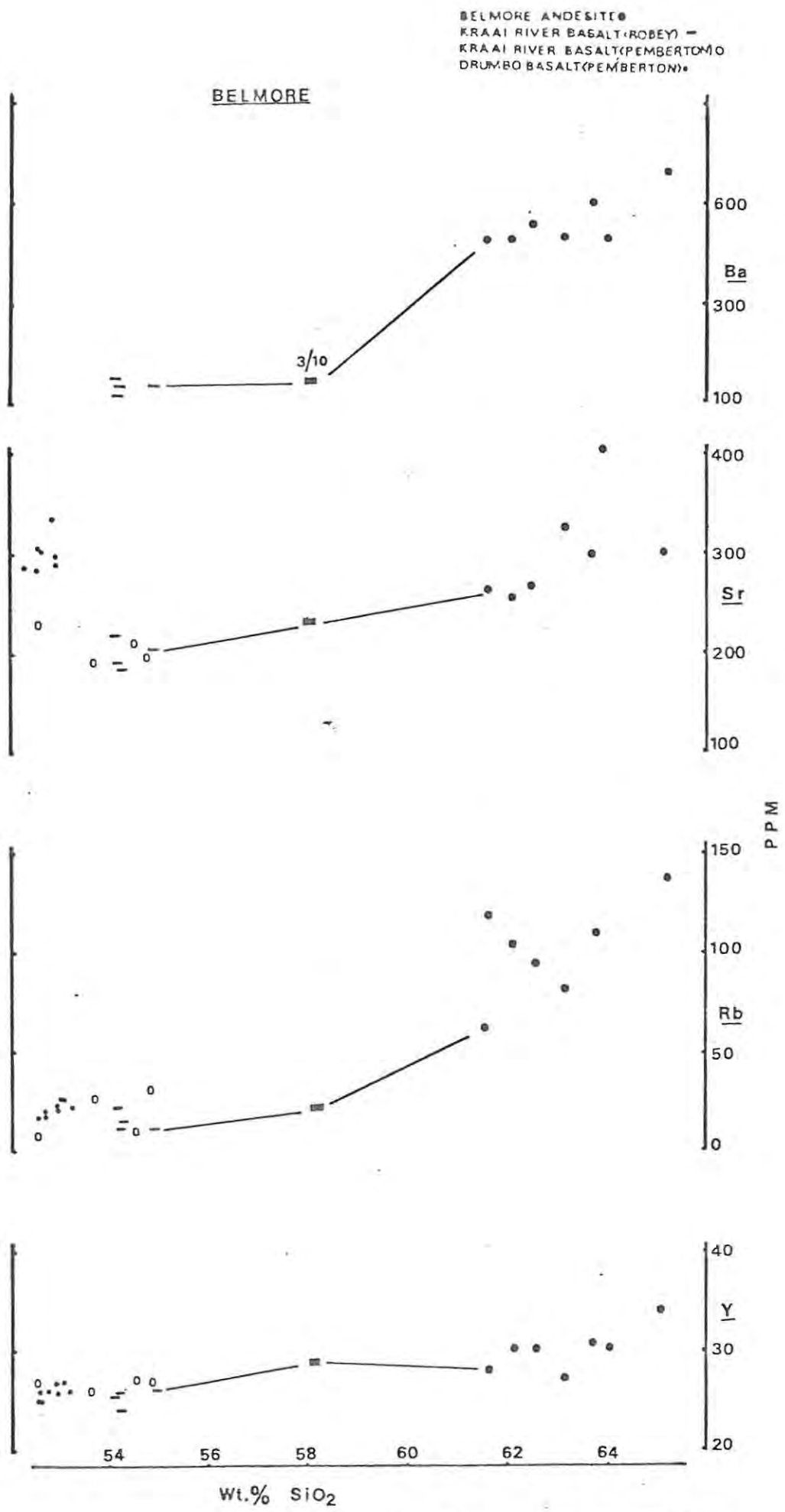


FIG.16 Trace element data for the Belmore andesite and Drakensberg Subgroup basalts plotted against SiO_2.

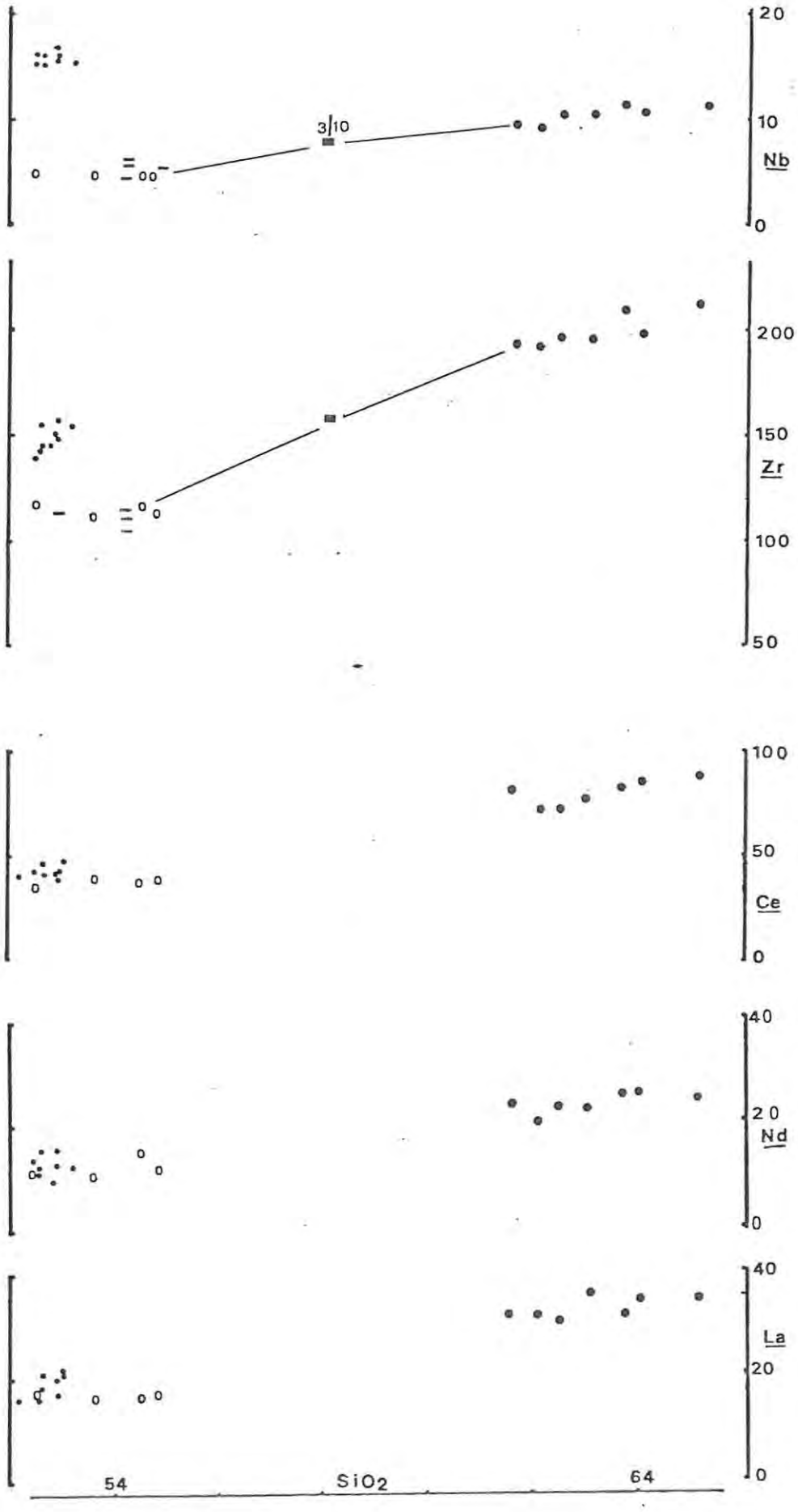

20
10
Nb
0
3/10
200
150
Zr
100
50
100
50
Ce
0
40
20
Nd
0
40
La
20
0
54
SiO2
64

FIG.16(Cont.)

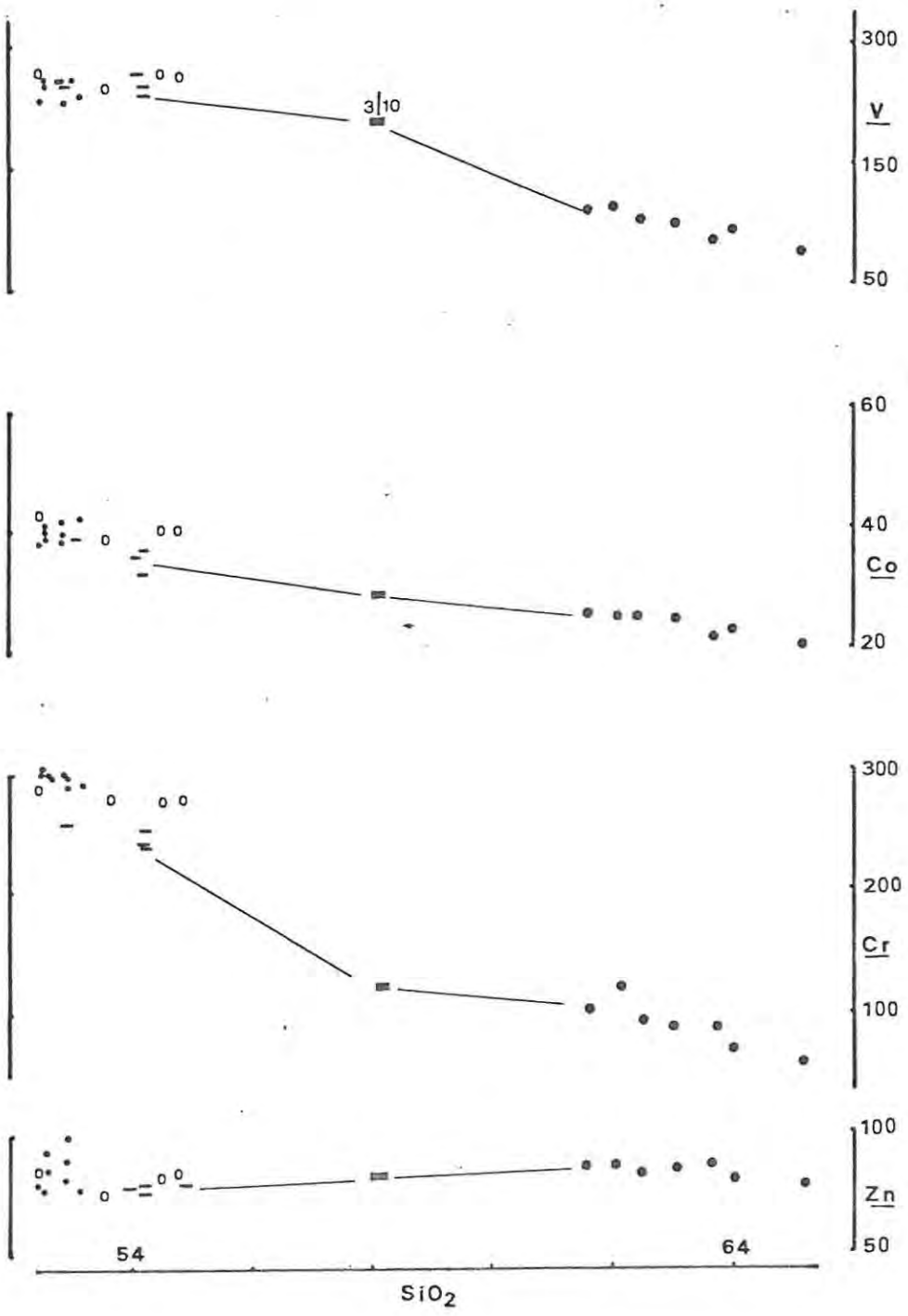


FIG.16(Cont.)

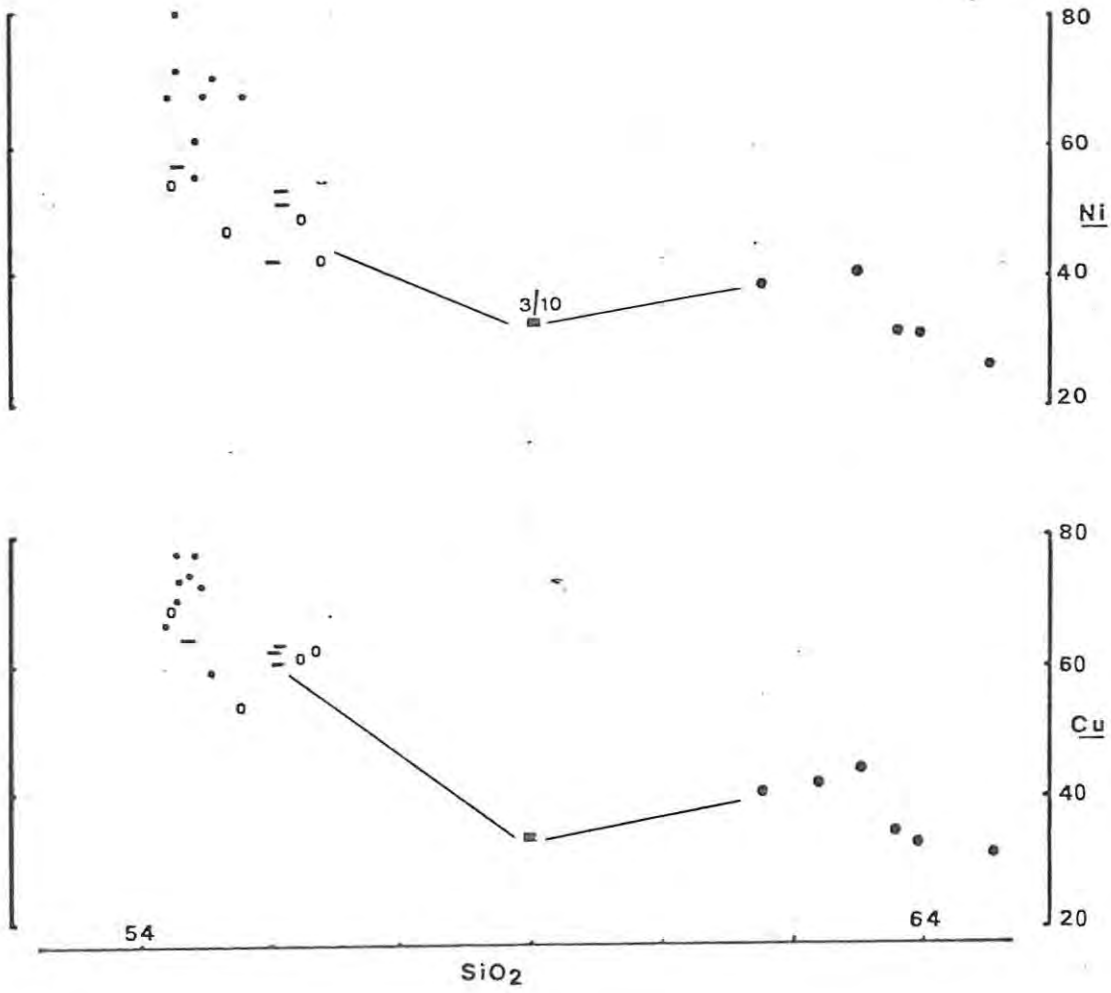


FIG.16(Cont.)

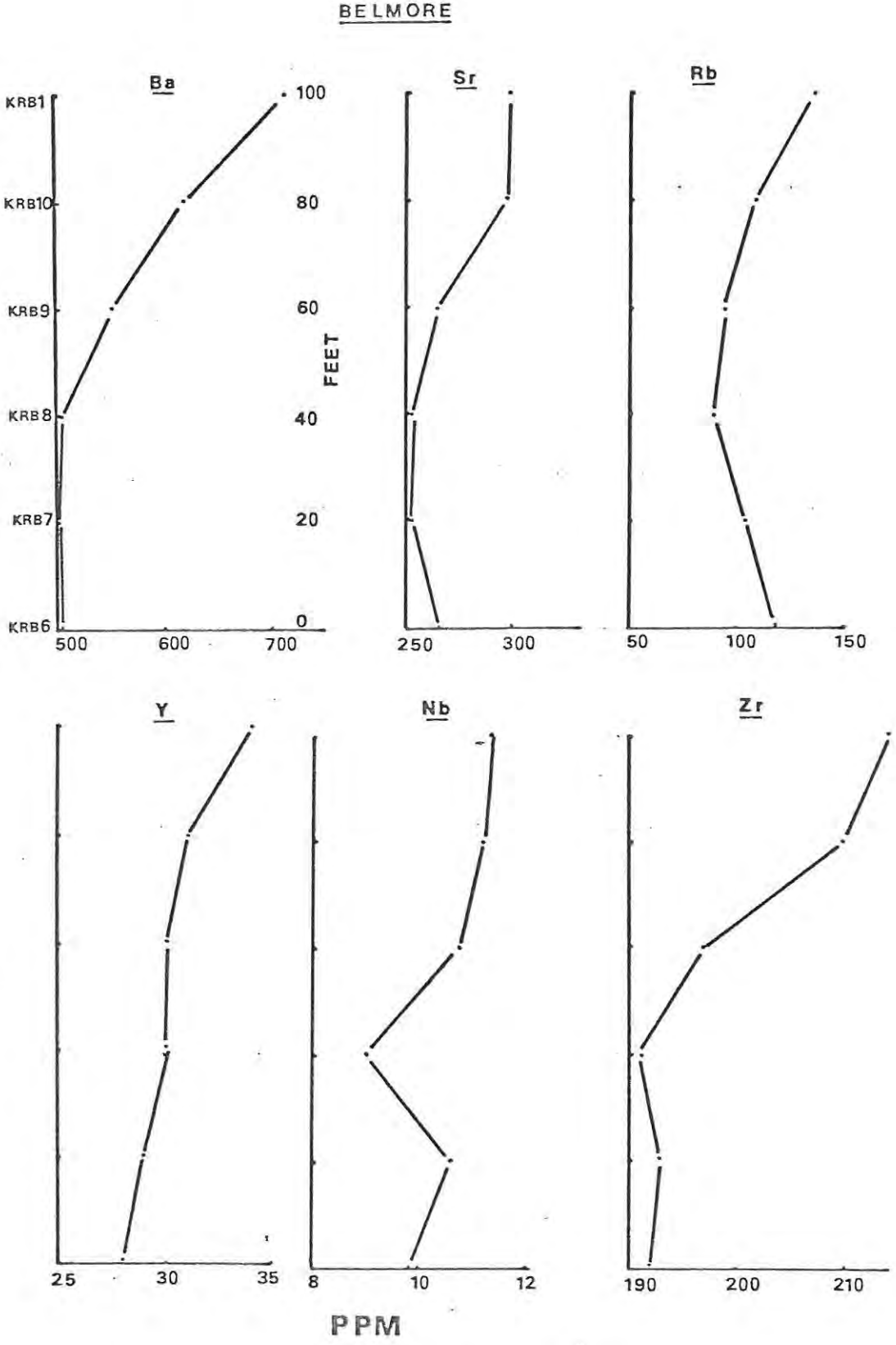


FIG.17 Trace element data vs. Height - Belmore Andesite.

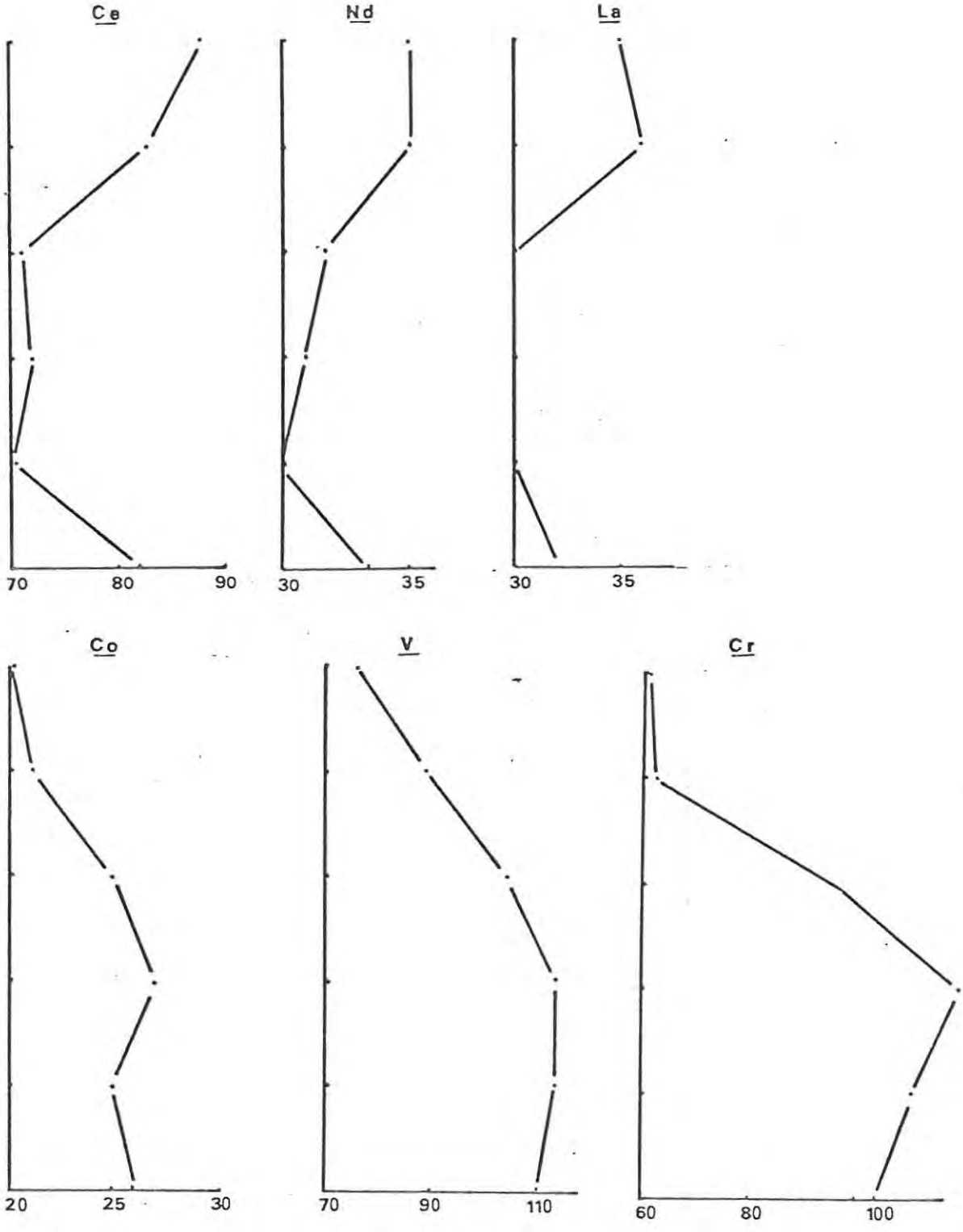


FIG.17(Cont.)

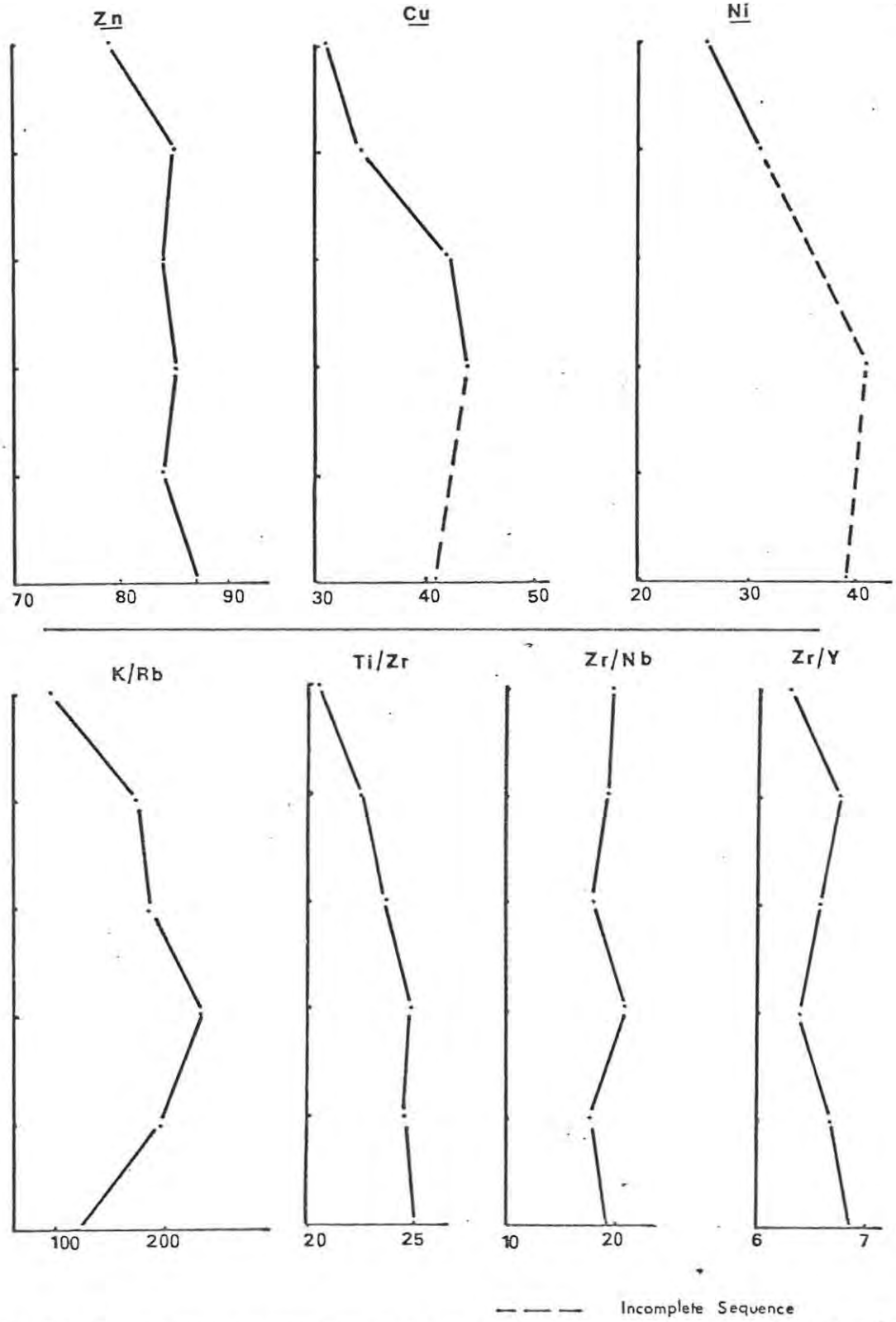


FIG.17(b) Inter-element ratios vs. Height-Belmore Andesite.

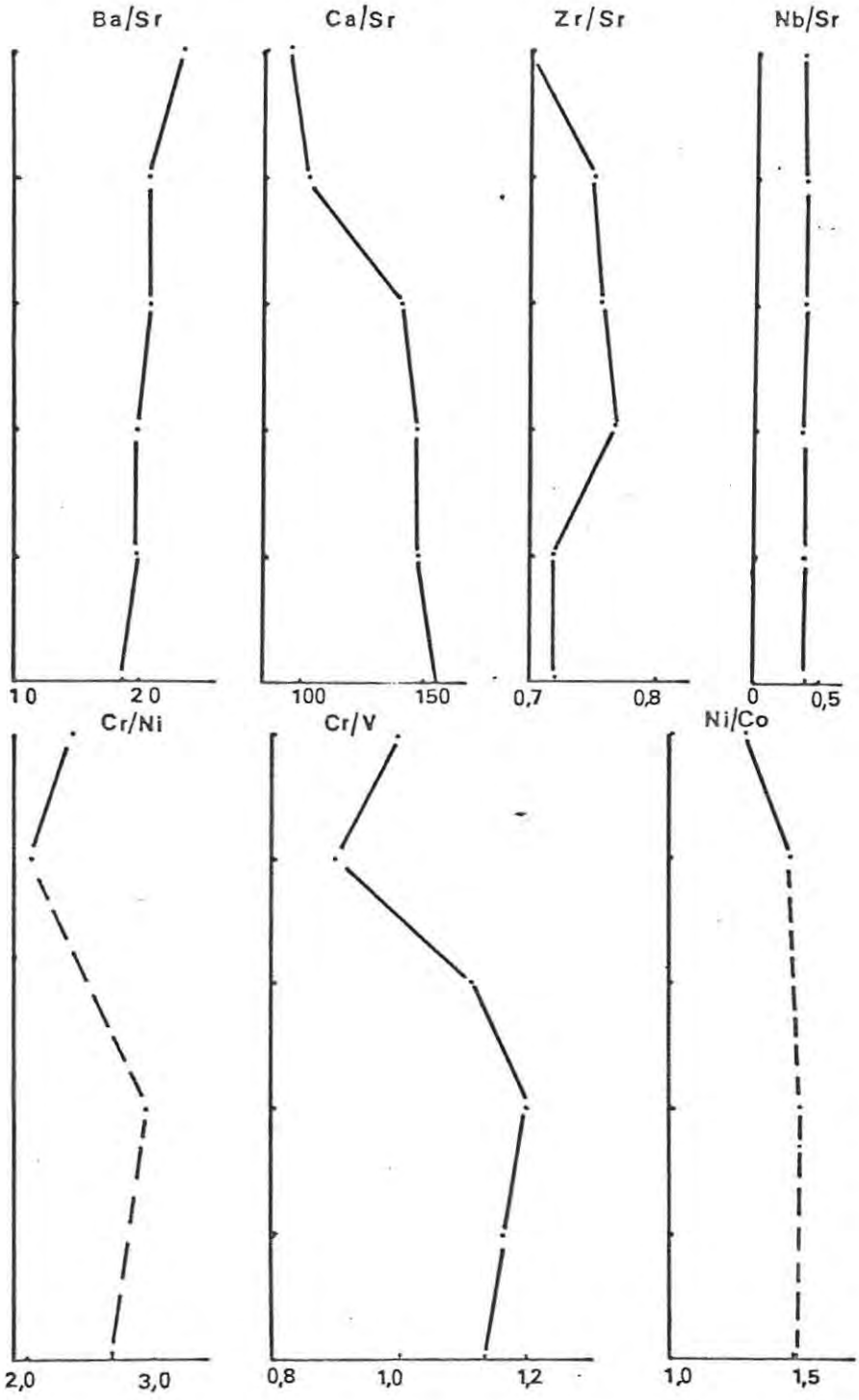

Ba/Sr
10
20
Ca/Sr
100
150
Zr/Sr
0,7
0,8
Nb/Sr
0
0,5
Cr/Ni
2,0
3,0
Cr/V
0,8
1,0
1,2
Ni/Co
1,0
1,5

FIG.17(b) Cont.

the sequence. Ba is constant up to flow KRB8, after which it shows strong enrichment, increasing by over 200ppm to the top of the sequence.

The transition elements manifest the two different trends, generally remaining constant up to flow KRB8, after which they decrease in content towards the top of the sequence. Only Cr show any substantial increase in content up to flow KRB8. Of the other transition elements Co, V, Cu and Ni remain constant up to flow KRB8, after which they decrease markedly towards the top of the sequence. Zn remains constant through the andesite, only decreasing slightly at the top.

Inter-element ratios plotted against height are included in Figure 17(b). K/Rb ratios reflect the two trends, first increasing with height to flow KRB8 and then decreasing from this point to the top of the sequence. Zr/Sr and Nb/Sr remain essentially constant through the sequence as do Zr/Nb, Zr/Y and Ti/Zr. Ba/Sr increases slightly at the top of the sequence. Following Lambert and Holland (1974), the Belmore andesite plots on the Ca/Y variation trend matching that of the 'standard series , indicating a constant relationship between Y-accepting (e.g. apatite) and Y-rejecting (e.g. plagioclase) minerals. The Ni/Co ratio remains constant through the sequence only decreasing slightly towards the top. The Cr/V and Cr/Ni ratios display a similar pattern, remaining constant up to flow KRB8, then decreasing markedly to flow KRB10, after which the ratios increase slightly to the top of the sequence.

In summary, with the exception of Nb which increases erratically and Y which increases regularly from base to top of sequence, the incompatible elements exhibit two distinct trends, both increasing or remaining constant down the sequence from flow KRB8 and increasing upwards from this point. The transition elements behave in a similar but opposite mode, decreasing in the upper half of the sequence. The behaviour of the trace elements in

manner aforementioned is suggestive of fractionation processes becoming important only after extrusion of flow KRB8. Fractionation of orthopyroxene would be able to explain the observed trends of the incompatible and transition elements, as well as inter-element ratios. As Sr shows an increase towards the top of the sequence, significant plagioclase fractionation may be discounted. This observation is supported by Ba/Sr, Zr/Sr and Nb/Sr ratios which should increase with increasing plagioclase fractionation. These ratios, however, remain essentially constant and therefore discount plagioclase as being an important fractionating phase. Orthopyroxene fractionation would explain the depletion of the transition elements in the sequence above flow KRB8. According to Gunn (1971), more Cr than Ni is accepted by pyroxenes, which is confirmed by partition coefficients presented in Table 8. Thus the Cr/Ni ratio should decrease with increasing pyroxene-controlled fractionation, which is observed for flows above KRB8. Similarly, more Cr enters Fe lattice positions than V, due to smaller Cr ion size, and the Cr/V ratio should therefore decrease with increasing fractionation, (Taylor, 1965), a pattern which is observed at Belmore. The effect of orthopyroxene fractionation is evident petrographically, although variations are relatively slight. Modal analyses (Figure 13) shows the effect of orthopyroxene fractionation, in that the presence of orthopyroxene decreases in the upper half of the andesite sequence, where plagioclase becomes the dominant phenocryst. Magnetite variations remain insignificant (less than 1 percent) through the sequence. An interesting feature of the modal analyses is the pattern of variation of the mesostasis, which although slight, approximates the pattern of variation for K_2O relatively closely. K_2O variations may thus correlate with variations of K-feldspar or another K-rich phase within the mesostasis.

The observed pattern of trace element variation with height through the Belmore andesite could be explained by a two-phase sequence of eruption.

The first phase involves extrusion of a number of undifferentiated flows. The second phase follows igneous differentiation (possibly due to cooling) within the magma chamber which results in separation of orthopyroxene, and subsequent extrusion of a plagioclase rich andesite forming the upper half of the sequence.

A similar technique as described in Section 5.4.1 may be used to model, from trace element data, approximate proportions of phases involved in fractional crystallisation, as well as to obtain estimates of partition coefficients for these phases. By calculating enrichment factors for the incompatible elements (Table 10), it is possible to estimate F from the approximation for fractional crystallisation given in equation 4, Section 5.1. The average enrichment factor is 1,24 which indicates that approximately 20 percent crystallisation took place (F = 0,8), assuming the initial liquid to be flow KRB8 and the final liquid to be flow KRB1. By substituting analytical data for a particular element it is possible to calculate the bulk partition coefficient for that element. From the bulk partition coefficient and knowledge of published individual mineral partition coefficients, it is possible to estimate proportions of the phases involved in the fractionation.

As partition coefficients for Sr have probably been studied in the greatest detail, accurate estimates of Sr partition coefficients for plagioclase and orthopyroxene could therefore be obtained and the proportion of phases fractionating could be modelled. From equation 1, a bulk partition coefficient of 0,19 for Sr was calculated. By substituting a Sr partition coefficient of 1,8 (An_{74}) for plagioclase (Philpotts and Schnetzler, 1970) and 0,01 for orthopyroxene (Arth, 1976), the bulk partition coefficient for Sr can be modelled by fractionation of about 20 percent of the initial liquid (KRB8) in the proportion 10 percent plagioclase and 90 percent orthopyroxene.

TABLE 10 : ENRICHMENT FACTORS FOR THE INCOMPATIBLE ELEMENTS, BELMORE ANDESITE.

	Enrichment Factor	F
Ba	1,41	0,71
Sr	1,19	0,84
Rb	1,53	0,65
Y	1,13	0,88
Zr	1,12	0,89
Nb	1,26	0,78
Ca	1,22	0,81
Ce	1,16	0,85
Nd	1,16	0,85
	1,24	

In a similar manner, the following bulk partition coefficients for the transition elements were calculated from equation 1 :

$$D^{Zn}_{Bulk} = 1,35$$

$$D^{Cu}_{Bulk} = 2,66$$

$$D^{Ni}_{Bulk} = 3,16$$

$$D^{Cr}_{Bulk} = 4,21$$

$$D^{Co}_{Bulk} = 2,42$$

$$D^{V}_{Bulk} = 2,92$$

By substituting the proportion of plagioclase and orthopyroxene in the ratio 10 : 90, and by using published values of Sr partition coefficients for plagioclase (Table 8(a)), the following orthopyroxene partition coefficients have been calculated for the transition elements :

	D^{plag}	$D^{opx.}$
Zn	0,01	1,5
Cu	0,19	2,9
Ni	0,01	3,5
Cr	0,04	4,7
Co	0,01	2,7
V	0,01	3,2

The calculated orthopyroxene partition coefficients, with the exception of Cu are similar to or within the range for documented partition coefficients (Table 8b). In the light of accuracy of the present calculations, the small differences between calculated (this study) and documented partition coefficients for V and Co are not considered unreasonable. The significantly higher partition coefficient for Cu is difficult to explain. Significant magnetite fractionation which would increase the bulk partition co-

efficient to higher levels, would however, increase the bulk partition coefficient for the other transition elements beyond acceptable limits and must therefore be discounted as being a significant fractionating phase. Considering, in general, the agreement between calculated and documented partition coefficients, the figure of 20 percent fractional crystallisation in the proportion of 10 percent plagioclase and 90 percent orthopyroxene is thought to represent a reasonable estimate of fractionation in the upper half of the Belmore andesite sequence.

5.4.2.2. Kraai River Basalt - Belmore Andesite Variations.

As previously mentioned, Robey (1976) analysed one Belmore andesite and six Kraai River Formation basalts. Robey's major and trace element data plot on an almost smooth trend of variation from Kraai River basalt, flow 3/10 to the Belmore andesite. This trend implies that a process of fractionation may link the basaltic and andesitic compositions. Exceptions to a smooth variation trend between basalt and andesite lavas are Ba which shows marked enrichment and Y which shows subdued enrichment in the andesite relative to basalt compositions (Robey, 1976).

The atypical nature of analysis 3/10 relative to normal Kraai River analyses presented by Robey (1976), Pemberton (1978) and Barree (1977) as well as the uncertain stratigraphic position of sample 3/10 has been discussed previously. Different mineral assemblages between sample 3/10 and typical Kraai River basalts further constrain a fractionation hypothesis. The writer doubts the validity of classifying sample 3/10 as Kraai River basalt.

Data presented in this study (Figure 16) confirm the observations recorded by Robey (op.cit.). With the exception of Ba, Y and Ni, trace element analyses for sample 3/10 plot on the Belmore andesite - Kraai River basalt trend. REE analyses for sample 3/10 are unfortunately unavailable.

Ba is enriched in the Belmore andesite relative to flow 3/10 and typical Kraai River basalt analyses, while Ni is depleted in flow 3/10 in relation to the Belmore andesite - Kraai River trend. Y enrichment is subdued in the Belmore andesite relative to Kraai River basalt compositions.

A comparison of inter-element ratios may be used to illustrate the differences between typical Kraai River basalts and flow 3/10. Inter-element ratios for flow 3/10 that are similar to or within the range for the remainder of Robey's Kraai River samples (Table 9) include K/Rb, K/Y, Zr/Nb, Rb/Sr and Ni/Co, while Ba/Zr, Zr/Y and Ti/Zr are significantly different. Inter-element ratios of flow 3/10 that are similar to ranges for the Kraai River basalts determined by Pemberton (1978) are K/Zr, K/Rb, K/Y, Rb/Sr and Ni/Co. Ratios that are significantly different for flow 3/10 and Kraai River basalts (Pemberton, 1978) include Zr/Nb, Zr/Y, Ti/Zr and Cr/V.

There is a marked difference in the inter-element ratios between flow 3/10 and the Belmore andesite. Only K/Rb and Zr/Nb are similar for both rock types. K/Rb ratios for the Belmore andesite and Kraai River basalts are in the range for crustal material presented by Gast (1965), although the Kraai River basalt ratios are generally higher than those of the Belmore andesite.

In the light of:(a) Differences in inter-element ratios of flow 3/10 compared to the Belmore andesite, and

(b) the atypical nature of sample 3/10 compared to typical Kraai River basalts, it would appear that a process involving orthopyroxene and plagioclase fractionation does not relate the Belmore andesite and Kraai River basalt. These conclusions are supported by semi-quantitative modelling of observed trace element abundances, which are modelled in a similar manner as described for the Pronksberg and Belmore andesites. Enrichment factors calculated from incompatible element data

could be explained by approximately 20 percent crystallisation (F = .8), assuming 3/10 to represent the initial liquid composition and sample KRB6 the final. By substituting a figure of $F \simeq 0,8$ in the equation for fractional crystallisation, a bulk partition coefficient of less than 1 is obtained for Ni, compared to the other transition elements which have bulk partition coefficient greater than 1. The bulk partition coefficient for Y is greater than unity, which cannot be explained by fractionation of a combination of any phases in the basalt - andesite system under study. Similarly, the extreme Ba enrichment in the andesite cannot be explained by fractionation of plagioclase or orthopyroxene in the same proportions as that explaining enrichment of the other incompatible elements.

Strontium isotope data (Section 6) further constrains the possibility of flow 3/10 and the Belmore andesite being genetically related.

5.4.2.3 Comparison between the Belmore Andesite and other Karoo Andesites.

Differences in the major element compositions of the Belmore, Roodehoek and Pronksberg andesites have been presented in Section 4.5. A comparison of trace element concentrations is listed in Table 4. In comparison with the Pronksberg andesite, the Belmore andesite is :

(a) enriched in Co, Cr and V,

(b) depleted in Rb, Ba, Nb and Ce, and

(c) similar in Ca, Y, Zr, La, Nd, Ni, Cu and Zn.

In comparison with the Roodehoek andesite, the Belmore andesite is :

(a) enriched in Cu, Ni and Cr,

(b) slightly depleted in Zr, and

(c) similar in Ba, Sr, Y, Nb, La, Ce, Nd, Zn,V and Co.

A comparison of inter-element ratios (Table 9) of the Karoo andesites further illustrates the differences between the three occurrences. The Belmore and Pronksberg andesites show similar Ti/Zr, Zr/Y and Rb/Sr ratios. The same ratios vary widely between the Belmore and Pronksberg andesites on the one hand, and Roodehoek andesite on the other, with the exception of the Rb/Sr ratio which is similar for all three occurrences. Zr/Nb and Ba/Zr ratios are similar for the Belmore and Roodehoek andesites, but differ from Pronksberg ratios. Similarly, Cr/V ratios for the Belmore and Roodehoek andesites are alike, but differ from Pronksberg ratios. Ratios involving potassium vary widely between all three occurrences.

A consideration of inter-element ratios and major and trace element concentrations of the three andesite occurrences under study suggest that they are non-consanguineous, although broad similarities in petrography, geological setting as well as normative, major and trace element chemistry suggest that similar magmatic processes initiated their formation. Evidence pertaining to a possible petrogenetic process for the three andesites is presented in Section 6.

5.4.2.4 Conclusions.

Patterns of trace element variation with height through the Belmore andesite sequence reflect two distinct trends, which are thought to represent a two phase sequence of eruption. A relatively undifferentiated series of flows appears to have preceded an extrusive phase which has had its chemistry modified by orthopyroxene fractionation. These observations are supported by trace element modelling which suggests the chemical variations in the upper half of the andesite sequence could be modified by fractionation of about 20 percent of the initial liquid in the proportion 10 percent plagioclase and 90 percent orthopyroxene.

Trace element abundances, inter-element ratios and trace element modelling constrain the possibility of the andesitic composition at Belmore being derived by fractionation from a Kraai River basalt source.

Differences in major and trace element concentrations and inter-element ratios between the three Karoo andesite occurrences suggests that they are not genetically related.

5.4.3. Roodehoek.

The limited chemical variation of the Roodehoek andesite evident from major element data are confirmed by trace element data. Incompatible and transition element data plotted against SiO_2 are illustrated in Figure 18. Inter-element ratio data (average and range) are listed in Table 9.

No pattern of chemical variation is apparent for the incompatible elements, with the exception of Rb which shows a general increase with increasing SiO_2, and therefore exhibits a positive co-variance with potassium. Certain of the transition elements show a general decrease with increasing SiO_2. This is particularly evident for V and Co, while the behaviour of Cr is more erratic. The behaviour of Zn, Cu, and Ni is erratic, although the magnitude of the variations is slight. Considering the lack of significant chemical variation within the intrusion, it would appear that the andesite was intruded as a relatively homogeneous magma.

Inter-element ratios for the Roodehoek andesite are relatively constant, the exception being K/Y ratios. As indicated by the range in values in Table 9, K/Zr, Zr/Nb, Zr/Y, Ba/Zr, Rb/Sr, Ni/Co and Cr/V show only slight variations. The K/Rb ratios are typical of ratios presented by Gast (1965) for crustal material (granites and granodiorites). A preliminary investigation of trace element ratios precludes the possibility of cogenetic links between the andesite and overlying basaltic rocks in the vicinity of Roodehoek (A.A. Mitchell, 1978, Personal Communication).

ROODEHOEK ANDESITE

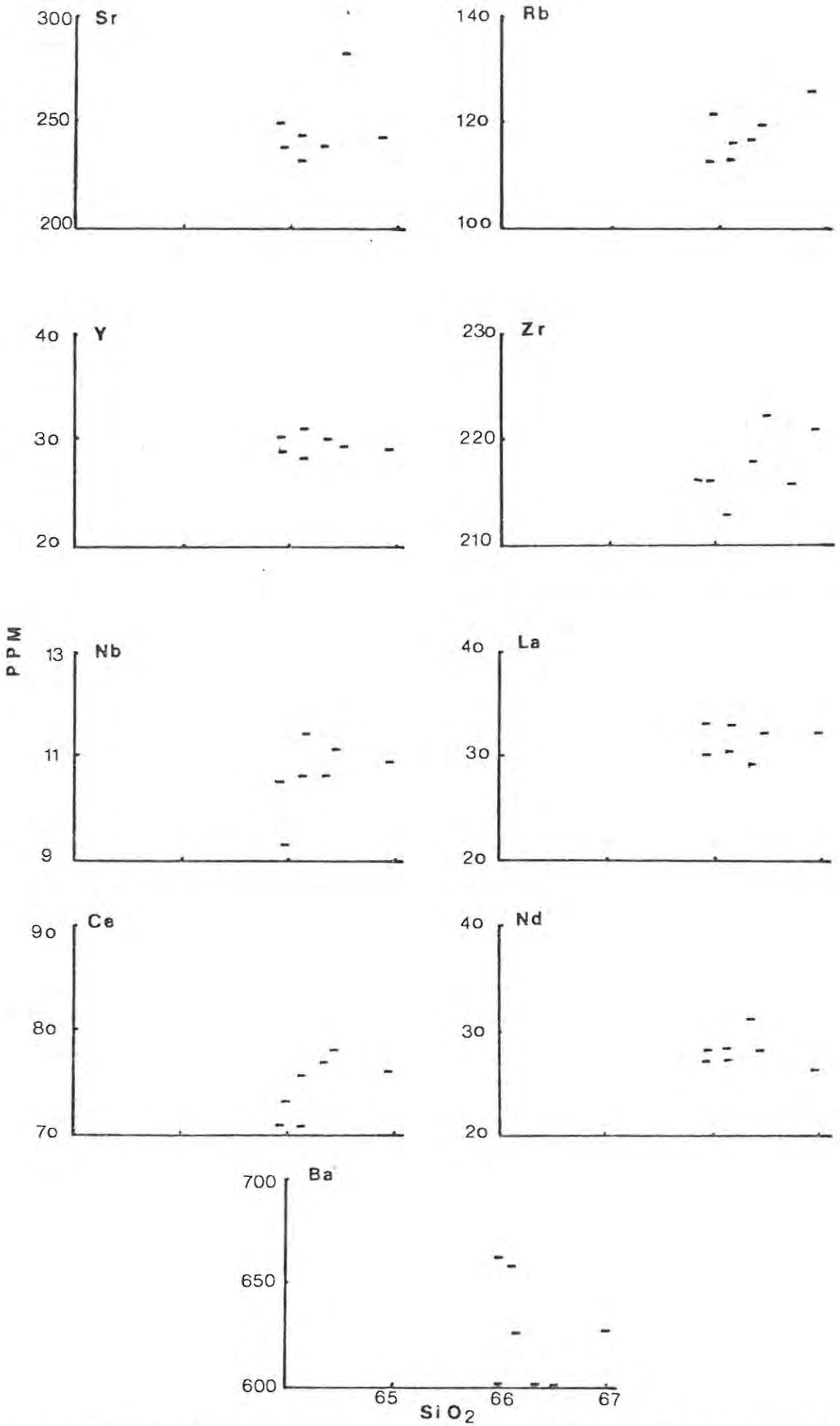


FIG.18 Trace element data plotted against SiO_2-Roodehoek Andesite.

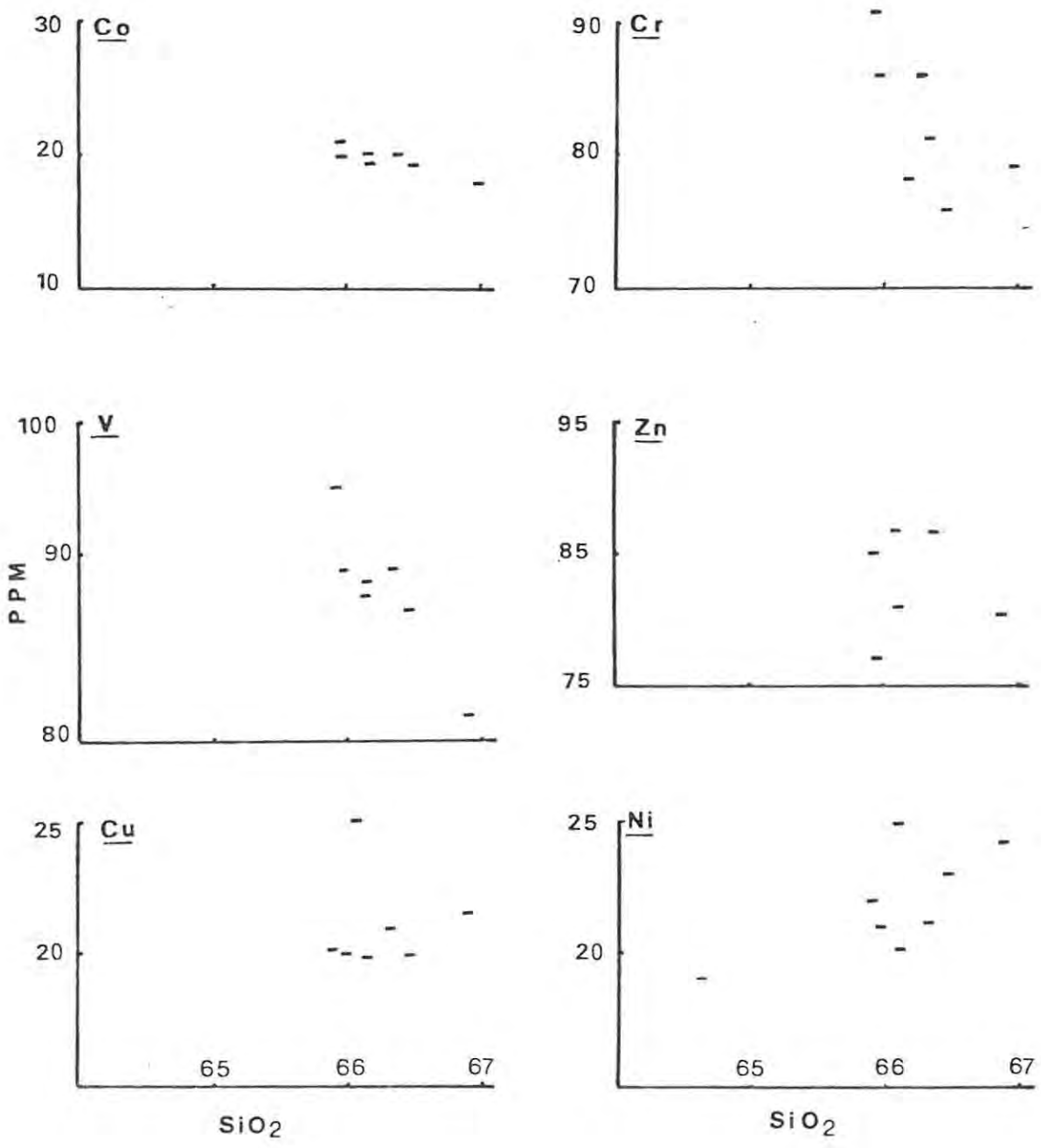


Fig. 18 (continued)

A comparison between the Roodehoek and Pronksberg andesites shows the Roodehoek andesite to be :

(a) enriched in Zr and Cr,

(b) depleted in Ba, Sr, Nb and Ce, and

(c) similar in Rb, Y, La, Nd, Cu, Co, Ni, and V.

Differences between the Roodehoek and Belmore andesites have been discussed in the previous section. A comparison of inter-element ratios (Table 9) of the three andesites substantiates these differences. Specific differences have been discussed in the previous section. In general, ratios are different for the three andesites, suggesting non-consanguinity, but the magmatic processes resulting in their formation are thought to be similar. Possible models for andesite genesis are presented and discussed in the next section, considering data presented so far.

6. PETROGENESIS

6.1 INTRODUCTION

The origin of andesite is currently one of the more controversial problems in igneous petrology, for which numerous models have been proposed. Models for the genesis of andesites have been reviewed by Wyllie (1971), T.H. Green and Ringwood (1968), Boettcher (1973) and Ringwood (1975). These include :

(1) One or more stages of partial melting of the upper mantle.

(2) Anatexis of lithosphere in subuuction zones.

(3) Fractional crystallisation of basaltic magmas.

(4) Contamination of basic magmas by assimilation of crustal material or anatexis of sialic crust.

The hypotheses proposed above, have been tested from various standpoints. These include major and trace element chemistry, experimental petrology, field relationships and a limited amount of isotope petrology.

The major proportion of the literature dealing with andesite genesis have been concerned with the orogenic andesites, i.e. those found along continental margins or island arc environments, and associated with subduction zones (e.g., Taylor and White, 1965 : Pichler and Zeil, 1972 : Ewart et al., 1973 and Taylor, 1969). Modern chemical data concerning continental interior andesites has been presented by Zelinski and Lipman (1976), Fernandez et al. (1973), Doe et al. (1969) and others.

The following section will present the theoretical considerations for each of the models of andesite genesis presented previously, comparing and evaluating the Karoo andesites in the light of this data.

6.2 ONE OR MORE STAGES OF PARTIAL MELTING OF THE UPPER MANTLE.

6.2.1 Experimental Evidence.

Numerous experimental studies in recent years have done little to resolve the controversy of whether partial melting of a 'wet' peridotite produces andesitic or basaltic magmas. The following section will present and evaluate experimental data concerning the relevance of melting of the mantle to andesite genesis.

The existence of a 'hydrous' mantle is generally well accepted and preferred over an anhydrous mantle (Mysen and Boettcher, 1975 : Eggler, 1973). Volatile components can occur dissolved in silicate and carbonate liquids, bond in minerals (e.g., amphibole, phlogopite, titanclinohumite) or they may occur as a separate vapour phase. In general, melting of a 'hydrous' peridotite occurs at temperatures several hundred degrees lower than for 'dry' peridotite. Researchers have favoured two approaches in

examining stability fields of mantle phases. These include studying the resulting composition of partial melting of mantle peridotite (and in some cases eclogite) on the one hand, and by examining crystallisation products at mantle temperatures and pressures of source compositions thought to have a mantle origin, on the other. Developments in experimental studies concerning the 'hydrous' melting of the mantle have led to a conflict of views. D.H. Green, T.H. Green, A.E. Ringwood and co-workers favour the generation of silica-undersaturated magmas (basaltic) as a result of partial melting of the mantle, but do recognise the fact that silica-saturated and -oversaturated magmas can be generated under conditions of unrealistically low pressure (Nicholls and Ringwood, 1972). I. Kushiro, H.S. Yoder, B.O. Mysen and A.L.Boettcher and co-workers recognise the fact that basalts may be generated in the mantle, but also obtain data which suggests that silica-saturated and -oversaturated magmas (andesites, dacites and rhyolites) may be generated under conditions of high P_{H_2O} (Kushiro, 1972, 1974) at pressures prevailing in the Upper Mantle.

D.H. Green and Ringwood (1967) report experimental results of fractional crystallisation of natural basaltic compositions under varying high temperatures and pressures. The results of Green and Ringwood (op.cit.) favour the generation of a range in basaltic compositions varying from alkali olivine basalts to olivine tholeiites, depending on the depth of basalt-liquid separation from the peridotite mantle and degree of partial melting. They cite the occurrence of chemically distinctive magma provinces, e.g., Jurrassic Ferrar dolerites and Karoo dolerites as being evidence for different genetic conditions resulting in chemically different mantle-derived rock types.

Opposition to the views of Green and Ringwood (1967) were put forward by Kushiro et al. (1968) who suggest that andesitic liquids may be generated from partial melting of mantle peridotite.

Kushiro et al. (op.cit.) studied the composition of the system enstatite-water at vapour pressures between 5 and 30 kilobar. They noted that the melting remained incongruent (enstatite + vapour = forsterite + liquid) in contrast to the anhydrous melting of enstatite which is congruent (enstatite-liquid) at pressures greater than 5 kilobar. These experiments indicated that for at least some 'hydrous' compositions, a quartz normative liquid can coexist with forsterite or forsterite + enstatite. Kushiro et al. (op.cit.) thus infer that silica saturated liquids could result by partial melting of 'hydrous' peridotite.

Bultitude and Green (1968) and D.H. Green (1970) draw conclusions which conflict with those of Kushiro et al. (1968). Bultitude and Green (op.cit.) experimented on the role of water in depressing the liquidus of undersaturated magmas (olivine nephelinite) and reported a major role for orthopyroxene as a near liquidus phase at 20-30 Kb. Bultitude and Green thus infer that highly undersaturated rocks such as melilites, nephelinites and olivine rich basanite magmas could be formed by partially melting a peridotite mantle with P_{H_2O} less than P_{total} at pressures of 20-30 Kb. They infer that parental olivine tholeiite could fractionate to these silica poor magmas in the presence of small water contents. Their data were, however, criticized by Kushiro (1969), as their experiments were conducted in open capsules with no control on water activity. Green (1970) repeated the experiments using sealed platinum crucibles and known water content. In addition, Green (1970) conducted experiments on water-saturated and water-undersaturated quartz tholeiites at 22,5 Kb and found that olivine did not occur as a liquidus or near liquidus phase. He therefore inferred that silica saturated compositions could not coexist with 'wet' mantle peridotite.

Numerous re-investigations and further refined experimental techniques have been adopted in an attempt to verify their initial conclusions. Experimental research by Nicholls and Ringwood (1972), D.H. Green (1973), Nicholls (1974) and Brey and Green (1976) all arrive at similar conclusions

to those arrived at initially by D.H. Green and Ringwood (1967) and Bultitude and Green (1968) in that experimental results favour the genesis of silica undersaturated melts or small degrees of partial melting of a 'wet' mantle peridotite with generation of silica-saturated and -oversaturated melts only at low pressures by large degrees of partial melting.

Further research conducted by Kushiro (1972), Yoder (1969), Kushiro (1974) and Mysen and Boettcher (1975 a,b) still favour the generation of silica-saturated magmas at mantle pressures and temperatures. Mysen and Boettcher (1975 a,b) conducted research on natural peridotite of varying compositions under controlled activities of water, carbon dioxide and hydrogen, and conclude that it would appear as if almost any liquid composition from andesite to olivine nephelinite could be obtained, provided that the correct peridotite composition, temperature, pressure and oxygen, hydrogen and CO_2 fugacities were selected. Because the andesitic and basaltic rocks, in general, have similar Sr_{87}/Sr_{86} ratios, have low trace element concentrations and are closely associated in space and time, Mysen and Boettcher do not favour fractional crystallisation as relating them. Their data indicates that initial melting of peridotite yields andesitic magmas, and with lowering of the water activity, for example by increasing the degree of melting, generation of basaltic melts. Variations in K would be related to some other mechanism subsequent to partial melting of peridotite.

In conclusion, conditions in the experimental field are best summed up by Mysen and Boettcher (1975b) who state : "It thus seems that researchers involved in the debate over phase relations of mantle peridotite have data that generally agree. However, there are disagreements in the interpretations".

6.2.2 Additional evidence for partial melting of the mantle.

Over and above the experimental data discussed in the preceding section, several other lines of geological evidence point to the possibility of the

calc-alkali andesite being a 'primary' magma of mantle origin. These are :

(1) The occurrence of andesites in areas of thin crust, such as island arcs.

(2) Andesites generally have low initial Sr_{87}/Sr_{86} ratios typical of mantle values. Initial Sr_{87}/Sr_{86} values (.7046-.7067) from the Taupo region, North Island, New Zealand are consistent with derivation from a primary mantle magma (Ewart and Stipp, 1968). Taylor and White (1965) also present trace element data consistent with a primary origin for andesites.

(3) The large volumes of lavas of similar chemistry erupted in areas of differing crustal chemistry and thickness (Taylor, 1969).

(4) Major and trace element chemistry. Rocks generated along orogenic zones should exhibit distinct geochemical characteristics to those in intra-oceanic or shield areas. Major element differences between continental and island arc volcanics are discussed by Forbes et al. (1969). Island arc andesites differ from continental andesites in that they are enriched in Fe and Ca and depleted in K, although Forbes et al. (op.cit.) reconise the probability of crustal contamination as being an important factor modifying the chemistry of continental andesite.

Taylor and White (1965) list critical features of andesite chemistry which would have to satisfy a mantle origin. These include :

(a) Low concentrations of the large cations. Slightly higher Sr contents resulting in low Ba/Sr and Rb/Sr ratios. K/Rb ratios are variable.

(b) Rare Earth Element concentrations are low. Total Rare Earth concentrations generally total less than 100.

(c) The highly charged cations, e.g. Zr, Nb, U, Th etc, are low in abundance in andesites.

(d) The transition elements, Ni and Co in particular are low in abundance. Vanadium and scandium are present in high concentrations and Cr is low but variable.

Taylor (1969) presents a two stage model of mantle origin for the derivation of the calc-alkali suite. The first stage proposed by Taylor (op.cit.) involves partial melting of primitive mantle. Ni, Co and Cr remain behind in the refractory phases (e.g. orthopyroxene, chromite and olivine). The larger cations and the highly charged cations (Rb, Sr, Ba, Zr, Nb) are concentrated by melting of minor phases (e.g. phlogopite). Since the distribution of these minor phases is probably sporadic, Taylor (op.cit.) suggests that variations in concentrations of these phases would result. Variable Rb/Sr and K/Rb ratios will thus result. This material forms part of the anomalous upper mantle zone with low P wave velocities found in orogenic areas.

The second stage involves partial melting of this (first stage) material at depths less than 70 km in this zone of low P wave velocity. Eruption of the calc-alkali rocks follows partial melting. Depending on the time interval between stages one and two, variations in Sr_{87}/Sr_{86} ratios

may occur. The eruptive rocks will show variable concentrations of the large cations, Rare Earths and the large highly charged cations, thus reflecting the details of the two stage process.

6.2.3 North-Eastern Cape Andesites

Major and trace element data for the average cenozoic andesite and dacite thought to have been generated in the mantle (Taylor, 1969) are presented for comparison with the average Karoo andesite (Table 11). The average Karoo andesite is compared with Taylor's (op.cit.) average calc-alkaline data in the light of the criteria presented by Taylor and White (1965). The present writer feels that the average calc-alkali dacite (Taylor, 1969) is perhaps more comparable with the average Karoo andesite than Taylor's average calc-alkaline andesite.

A comparison of the average Karoo andesite with the average calc-alkaline dacite and andesite (Taylor, 1969) reveals :

(a) The Karoo andesites are enriched in the large highly charged cations (Zr, Nb) by a factor of two relative to Taylor's average calc-alkali dacite and andesite.

(b) Three fold enrichment of Rb in the Karoo andesites, with comparable concentrations of Ba and slightly depleted Sr. K/Rb and Rb/Sr ratios are within the range presented by Gast (1965) and Compston et al. (1968) for granites, granodiorites and for basalts having undergone crustal assimilation. Ratios presented by Taylor for the average andesite and dacite are typically mantle.

TABLE 11 : TABLE SHOWING AVERAGE CALC-ALKALINE ANDESITE AND DACITE (TAYLOR, 1969) AND AVERAGE KAROO ANDESITE.

		DACITE (A)	ANDESITE (B)	KAROO ANDESITE (C)
	SiO_2	65,1	59,5	64,8
	Al_2O_3	16,5	17,2	16,6
	FeO	3,86	6,10	6,50 *
	MgO	1,48	3,42	2,60
	CaO	4,75	7,03	3,30
	Na_2O	4,60	3,68	2,80
	K_2O	2,05	1,60	2,20
	TiO_2	0,51	0,70	0,79
LARGE	Rb	44	31	131
CATIONS	Sr	460	385	293
	Ba	520	270	663
RARE	Y	20	21	30
EARTH	La	14	12	35
ELEMENTS	Ce	19	24	86
	Nd	16	13	35
LARGE	Zr	100	110	202
HIGHLY CHARGED CATIONS	Nb	6,0	4,3	12,0
	Cu	54	22	30
	Co	9	24	20
TRANSITION	Ni	5	18	28
ELEMENTS	V	68	175	84
	Cr	13	56	71
K/Rb		386	430	145
Ba/Sr		1,13	0,70	2,40
Rb/Sr		0,096	0,08	0,44
Zr/Nb		16,6	25,6	17,3

* as Fe_2O_3

(A) - TAYLOR (1969) AV. CALC-ALKALINE DACITE.
(B) - TAYLOR (1969) AV. ANDESITE.
(C) - AV. KAROO ANDESITE.

(c) Taylor and White (1965) recognise total REE concentrations for orogenic andesites as being low, generally totalling less than 100ppm. Total REE in the Karoo andesites exceed 100ppm, with La+Ce+Nd totalling over 150ppm. Compared to averages presented by Taylor (1969), La, Ce and Nd are enriched by a factor of 3 in the Karoo andesites.

(d) The transition elements Co and V are present in the Karoo andesites in similar contents to average calc-alkaline data (Taylor, 1969). Cr and Ni are enriched relative to the average calc-alkali dacite and andesite, while Cu is depleted relative to Taylor's average dacite but similar to the average andesite.

Considering the systematic differences to average calc-alkali trace element data (Taylor, op.cit.) presented above, it would appear that a mantle origin for the Karoo andesites may be regarded as unlikely. Strontium isotope data presented in a later section further substantiates these conclusions.

6.3 ANATEXIS OF LITHOSPHERE IN SUBDUCTION ZONES

The development of modern plate tectonic theories has initiated a viable mechanism for the generation of the calc-alkali suite. Geological evidence and experimental petrology lend weight to the concept of anatexis in subduction zones. Subduction zones for example, provide a ready explanation as to why voluminous andesites are absent in oceanic basins, but occur in abundance at continental margins and island arcs. The lack of conventional evidence for subduction along the Southern Africa continental margin severely constrains a model for the Karoo andesites which assumes

marginal subduction. Recently, however, Cox (1978) has hypothesised the possibility of subduction being active during Karoo volcanism. Cox (op.cit.) recognises the fact that tensional tectonics prevailed in the Karoo (as manifested by the Zambesi and Limpopo orogenic belts, normal faulting and the intrusion of numerous dykes) at the same time as compressional forces were responsible for the formation of the Cape Fold Belt. These features are suggestive of the existence of a zone of subduction to the south of the fold belt, with extension, widespread basalt volcanism and subsidence being typical features of a back-arc environment. Cox (op.cit.), while recognising the speculative nature of these ideas, extrapolates them to other areas of Gondwanaland, in particular to the Panjal Trap volcanics (Kashmir), Sylhet Traps and Arbor volcanics (India), Siberian Traps and Columbia River Plateau volcanics.

An early model for the genesis of andesite in subduction zones is that of T.H. Green and Ringwood (1968) whose data suggests that the calc-alkali suite may be generated by a two stage igneous process involving fractionation of basaltic magmas (formed by melting of subducted lithosphere) to form quartz normative basaltic compositions which may transform to eclogite in the mantle. Partial melting of the eclogite will result in rocks of the calc-alkaline suite.

Nicholls and Ringwood (1972) propose a model involving production of tholeiitic magmas close to silica-saturated compositions by partial melting of the 'hydrous' mantle wedge overlying downgoing oceanic lithosphere. Depths at which the oceanic tholeiites are produced are between 80-120 km, with a mean temperature of less than 600^{o}C (Oxburgh and Turcotte, 1970), so that dehydration occurs below the basalt-amphibolite-eclogite solidus and partial melting does not occur. Water may therefore escape into the overlying mantle, causing a reduction in viscosity and increased mobility. Diapirs of 'hydrous' peridotite may thus rise, undergoing partial melting to form silica-saturated tholeiite magmas. Fractionation of these magmas will result

in the production of basaltic andesites, andesites and dacites.

Further support for the genesis of andesites due to lithosphere subduction are presented by Marsh (1976), Thorpe et al. (1976) and Lopez-Escobar et al. (1977).

6.3.1 North-Eastern Cape Andesites.

Partial melting of subducted lithosphere (converted to eclogite) could possibly explain the trace element abundances observed in the Karoo andesite. Rare Earth Element data would add considerable strength in evaluating the probability of the Karoo andesites being initiated by melting of subducted lithosphere.

Severe constraints on a hypothesis involving partial melting of eclogitic material are Sr_{87}/Sr_{86} ratios presented in Section 6, which are suggestive of a crustal process being important in the genesis of the Karoo andesites. As previously mentioned, the lack of documented continental margin subduction along the Southern African coast further constrains this hypothesis, although Cox (1978) has speculated at the possibility of subduction being an active process during Karoo volcanism.

6.4 FRACTIONAL CRYSTALLISATION OF BASALTIC MAGMAS

A preceding section of this study has shown that 'wet' partial melting of the mantle is believed to be capable of generating basaltic liquids (Green and Ringwood, 1967: Nicholls and Ringwood, 1972 and Mysen and Boettcher, 1975 a,b). Magnetite and amphibole fractionation are recognised as the two dominant processes generating andesitic liquids from basaltic magmas.

6.4.1 Magnetite Fractionation

Osborne (1962) following the ideas of Muan and Osborne (1956), examined phase equilibria data for the system $MgO-CaO-FeO-Fe_2O_3-SiO_2$, and recognised that basaltic liquids followed two different trends of differentiation depending on the prevailing oxygen fugacity at low pressure. In the first trend, where oxygen fugacities remain high during fractionation of a basaltic liquid, magnetite co-precipitates with silicates such as plagioclase, olivine and pyroxene resulting in a silica enriched melt, and suppression of iron-enrichment, characteristic of the calc-alkaline trend. In the second trend, where oxygen fugacities are much lower, Mg-silicates fractionate rather than magnetite and the residual liquid displays an iron-enrichment or tholeiitic trend. In order to maintain the high oxygen fugacity during fractionation, Osborne (1969) recognises the need for O_2 to be added to the magma. He envisages a system whereby H_2O is inhaled by the magma and H_2 exhaled. This maintains the required metabolism for the magma in developing andesitic liquids during fractional crystallisation.

While the data of Osborne present a useful model for the generation of andesitic liquids from basaltic magmas, his ideas have not gone uncriticised. Work on iron-titanium oxides in calc-alkaline rocks by Carmichael (1967), however, indicate that oxygen fugacity does not remain constant during fractionation in the calc-alkaline series. Taylor et al. (1969) contest the views of Osborne (1962) and show that crystallisation and removal of magnetite with vanadium contents of up to 0,8 percent would strongly deplete the magma in vanadium. Taylor et al. (op.cit.) cite the similarity in vanadium contents of basalts and andesites as placing severe restrictions on the amount of removal of magnetite by fractionation. Osborne (1969), however, maintains that fractionation of at least 3,3 wt. percent could still permit trace element abundances presented by Taylor et al. (1969). A further refutation of

Osborne's model is presented by Eggler and Burnham (1973) who investigated phase relations of a Mount Hood andesite at varying H_2O fugacities. They note that at high fluid pressures (H_2O, and H_2O+CO_2), Fe-Ti oxides were not stable at temperatures of the silicate liquidus, and would only be stable if the oxygen fugacity rose above unrealistic limits. Therefore, because differentiation of basalt to form andesite must involve subtraction of an iron-rich phase, these authors do not recognise magnetite fractionation as being a likely explanation for production of andesitic liquids.

6.4.2 Amphibole Fractionation

Amphibole fractionation is a second process whereby calc-alkali liquid compositions may be produced. T.H. Green and Ringwood (1968) recognise the formation of subsilicic amphibole (40-41% SiO_2), clino- and orthopyroxene as the liquidus phase at 1040°C for basaltic compositions. At lower temperatures (940°C) amphibole is the dominant phase, while plagioclase appears at 920°C. A similar sequence of crystallisation occurs for basaltic-andesite compositions. Green and Ringwood (op.cit.) interpret these results as strongly supporting the hypothesis for the origin of the calc-alkaline sequence by either partial melting of hydrous mantle peridotite or by fractionation of amphibole from a basaltic parent magma. The large field of crystallisation of the subsilicic amphibole together with minor clinopyroxene, orthopyroxene and calcic plagioclase are interpreted by Green and Ringwood as providing an efficient mechanism for silica and alkali enrichment, with suppression of iron-enrichment.

These results are also in concert with those of Allen et al. (1972) who recognise the separation of a low silica (39-41 percent) amphibole from basaltic compositions by fractional crystallisation in the presence of water, a process which provide efficient silica enrichment.

A refutation of this theory is provided by Eggler and Burnham (1973) who recognise the presence of amphibole as a liquidus phase at pressures above 8 Kb under H_2O saturated conditions. Amphibole has a maximum stability temperature of $\pm$ 940°C for conditions of < 4,4 wt. percent H_2O in the melt. For melts with > 4,4 wt. percent H_2O in the melt, the liquidus temperature will be lowered. Eggler and Burnham (op.cit.), therefore see these low melting temperatures, relative to other silicate phases, as precluding andesite generation by basalt fractionation involving amphibole at pressures characteristic of upper mantle conditions.

6.4.3 Additional Evidence for Fractional Crystallisation.

Taylor (1969) presents average data for 45 elements for the calc-alkaline suite. This data does not support fractionation from basaltic magmas as being a likely process for andesite generation, for the following reasons :

(a) Elements normally concentrated by fractionation (Cs, Rb, Ba, Th, U, Zr etc.) are in low abundance and generally resemble concentrations found in basaltic rocks.

(b) K/Rb, K/Cs and Ba/Rb ratios are high, while Rb/Sr and Ba/Sr are low. These ratios are therefore opposite to what one would expect as a result of fractional crystallisation.

(c) Similar Ni contents and Ni/Co ratios of andesites and High alumina basalts preclude fractionation. Nickel should be depleted in the residual magma.

While the data of Taylor (op.cit.) precludes the fractional crystallisation hypothesis, various other geochemical studies present data supporting this theory. Ewart et al. (1973) interpret basaltic andesites as the

product of direct mantle peridotite melting, subsequently modified by olivine fractionation to form andesites and dacites. The conclusions of Ewart et al. (op.cit.) are substantiated by strontium isotope data analyses ranging from high alumina basalts, andesites to dacites, presented by Dostal et al. (1977) for volcanic rocks from N.W. Sardinia. Geochemical data and least squares numerical modelling favour a crystal-liquid fractionation process relating basaltic and andesitic rock types, following generation of the basalts by partial melting of peridotite in the upper mantle. Strontium isotope data of andesites and associated basalts further suggest that the two rock types may be genetically related (Hedge and Lewis, 1971), as do oxygen isotope ratios (H.P. Taylor, 1968).

6.4.4 North-Eastern Cape Andesites.

The possibility of a fractionation process relating the Karoo basalts and andesites has largely been evaluated and discussed in the previous section concerned with trace element variations of the Karoo andesites and associated basaltic rocks. In summary, the main conclusions are :

(1) The Pronksberg volcanic suite has a lack of rock types intermediate between andesitic and basaltic compositons. The incompatible element Nb is depleted in the andesite relative to the overlying basalts, whereas all the other incompatible elements are enriched. Strontium is also depleted in the andesite relative to the overlying Pronksberg basalt (High K Type) which may be interpreted as indicating strong plagioclase fractionation. Plagioclase fractionation would, however, be incapable of pro-

ducing the observed trace element contents of the transition elements in the andesite.

The fact that amphibole is absent in all of the Drakensberg Subgroup basalts precludes the possibility of amphibole fractionation as being an active silica-enrichment process.

The diagnostic trace element ratios Ti/Zr, Zr/Nb, Ba/Zr and Zr/Y are markedly different in the basalts compared to the andesites and this feature also suggests non-consanguinity.

(2) The same rationale may be applied in examining possible cogenetic links between the Belmore andesite and Kraai River basalts. Ba is markedly enriched and Y slightly enriched in the andesite relative to the Kraai River basalts, although the composition of the anomalous sample 3/10 suggests that it may be related to the Belmore andesite by crystal fractionation. Ni, however, shows only subdued enrichment in flow 3/10 relative to the Belmore andesite. Semi-quantitative modelling of these trends constrains the possibility of crystal fractionation relating the basalt and andesite compositions. Similarly, inter-element ratios and Sr isotope ratios are significantly different between andesites and basalts. Sr isotope ratios for the Belmore andesites and flow 3/10 suggest modification by crustal contamination.

6.5 CONTAMINATION OF BASIC MAGMAS BY CRUSTAL MATERIAL OR ANATEXIS OF SIALIC CRUST.

As many arguments relevant to a theory of crustal contamination are relevant to crustal melting as well, a combined discussion of these two processes is justified.

6.5.1 (a) Contamination of Basic magmas by Crustal Material

Trace element and isotope data are widely used as indicators of crustal contamination. While most data concerned with the orogenic andesites lend no support to crustal contamination, several studies have indicated that contamination is a viable mechanism for andesite genesis.

A major constraint on the contamination thesis is the geographic distribution of the orogenic andesites. The theory fails in that it cannot explain the development of the calc-alkaline series in island arcs which have formed in the absence of continental crust.

Taylor (1969) shows that the mixing of average granodiorite to average continental basalt in the ratio 60:40 results in the concentrations of numerous trace elements (Rb, La, Ce, Nd, Cr, Th, Ni, Li and others) varying by greater than a factor of two from average andesite compositions. Similar results are obtained for a 50:50 granite-basalt mix. Low nickel contents further restrict a mixing hypothesis to about 20-30 percent basalt. Vanadium contents initiate similar difficulties.

Isotope studies present data both for and against a crustal assimilation theory for andesite genesis. Ratios for orogenic andesites are generally within the range 0.7030-0.7050. These are substantially less than would be expected from crustal material (Ewart and Stipp, 1968). Ewart et al. (op.cit.) use similarities in Sr isotope data for between the Tongan Island

volcanics (basaltic andesites-acid andesites-dacites) as an indicator of consanguinity. Similarly Doe et al. (1969) and Lipman et al. (1978) use strontium and lead isotopes to distinguish between rocks of mantle origin and those having undergone crustal assimilation.

Many continental felsic volcanics are significantly enriched in radiogenic strontium. Data presented by Hedge (1966) for oceanic basalts, continental basalts and continental andesites show marked enrichment in radiogenic Sr in the andesites, which suggests that some continental felsic volcanics are derived within the crust or are partially assimilated. Similarly, Hurley et al. (1965) report Sr_{87}/Sr_{86} ratios of 0.7073 for quartz diorites which are higher than for associated basaltic material, but much lower than average ratios for the sialic crust (0.71-0.73). Hurley et al. (op.cit.) thus interpret the quartz dioritic ratios as representing a mixture of oceanic basalt and crustal sial. Andesitic and rhyodacitic rocks from North Island, New Zealand, exhibit a range in Sr isotope values from 0.7046-0.7067, compared to associated basaltic ratios of 0.7041-0.7044. These differences have been interpreted by Ewart and Stipp (1968) as being most consistent with hybridisation of basalt with crustal material, or possibly representing primary andesitic magma.

6.5.2 Anatexis of Sialic Crust.

Partial or complete melting of deep crustal material of appropriate composition may be considered as a possible origin for the origin of the calc-alkaline suite.

Boettcher (1973) argues that liquidus temperatures in the region of 1200°C determined by Fudali (1965) for basaltic and andesitic rocks are too high for anatexis of the crust to be a viable mechanism for andesite

genesis. Boettcher's arguments are perhaps irrelevant when one considers that liquidus temperatures determined by Green and Ringwood (1968), Kushiro et al. (1968) and other researchers for basaltic and andesitic compositions under 'hydrous' conditions are in the region of 1000°C, which is realistic when applied to crustal melting. Similarly, Turner and Verhoogen (1960, p.287) maintain that "thickening of the crust with its high radioactivite content could conceivably raise locally, the temperature at the base of the root to the point of partial or complete fusion".

Substantial support for a crustal fusion theory for andesite genesis include studies by Pichler and Zeil (1969, 1972) and Fernandez et al., (1973). Trace element data (Ba, Sr, Rb and Ni) presented by Pichler and Zeil (1969) for the 'Andesite Formation' of the Chilean Andes are consistently closer to averages of crustal chemistry than to those of basaltic rocks. Further diagnostic features include an alumina surplus in the acidic rocks, a feature which is manifested in the formation of cordierite in the Rittman norm, as well as aggregates of quartz xenocrysts and the absence of true basalts. Similar observations concerning the same formation are returned by Pichler and Zeil (1972). Strontium isotope ratios for the andesites are consistently higher than typical basaltic ratios. Pichler and Zeil (op.cit.) therefore recognise that partial fusion of crustal rocks or extensive assimilation of crustal material by material of mantle origin are the most likely genetic processes for the generation of the andesites. Partial melting of crustal rocks is suggested for volcanic rocks from S.W. Bolivia (Fernandez et al., 1973). Evidence includes an alumina surplus, quartz and plagioclase xenocrysts and unusually high Zn contents.

6.5.3 North-Eastern Cape Andesites

6.5.3.1 Strontium Isotope Data.

Strontium isotope ratios (Sr_{87}/Sr_{86}) are widely used as petrogenetic

indicators, providing information about source of origin and processes influencing chemical and isotopic compositions (Faure, 1977). In this section, a brief resumé of the theoretical considerations of Sr isotope data concerning the Karoo igneous province will be presented and evaluated.

Strontium isotope data from oceanic islands, ocean ridges and ultramafic xenoliths (in kimberlites, etc.,) show typical average mantle Sr_{87}/Sr_{86} ratios to be in the region of $0.704 \pm .002$. Evidence for systematic differences in Sr_{87}/Sr_{86} ratios for volcanic rocks formed in different mantle environments is, however, increasing, thereby strengthening the concept that the mantle is chemically heterogeneous (Compston et al., 1968; Erlank and Duncan, 1976; Faure, 1977). The lowest Sr_{87}/Sr_{86} ratios (0.7028) occur in the oceanic tholeiites extruded along mid-ocean ridges, with continental volcanics having consistently higher ratios in the region of 0.70577 (Faure, 1977). Products of partial melting of crustal material generally show higher ratios in the range beyond 0.710, while contaminated mantle rocks show isotopic ratios intermediate between typical crustal ratios and those of continental basaltic volcanics (Heier et al., 1965).

Strontium isotope data for the Karoo volcanics have been presented by Macdougall (1963) and Compston et al. (1968). Manton (1968) presented data for the Lebombo rhyolites and associated rocks. Recent unpublished Sr isotope data for the Karoo volcanics have been presented by the National Geodynamics Programme. In this section, two new Sr isotope ratios are presented. These are for the Belmore andesite (sample JR31) and the Kraai River Basalt (?) sample 3/10, analysed by Robey (1976). These data were obtained from A.J. Erlank (personal communication), the isotope analyses being carried out at Oxford University. Isotope ratios have been initialled to 185 million years (Table 12). Isotope analyses for

TABLE 12 Sr ISOTOPE DATA

SAMPLE	Rb/Sr	Initial Sr 87/86
GA 461[A]	0,076	0,7065
GA 466[A]	0,100	0,7050
GA 468[A]	0,060	0,7045
GA 508[A]	0,035	0,7065
GA 508[A]	0,460	0,7066
GA 510[A]	0,022	0,7050
3/10[B]	0,089	.70878
JR31[B]	0,40	.70981

source : A Macdougall et al., 1968
B This study.

JR31 = Belmore andesite
3/10 = Kraai River Basalt.

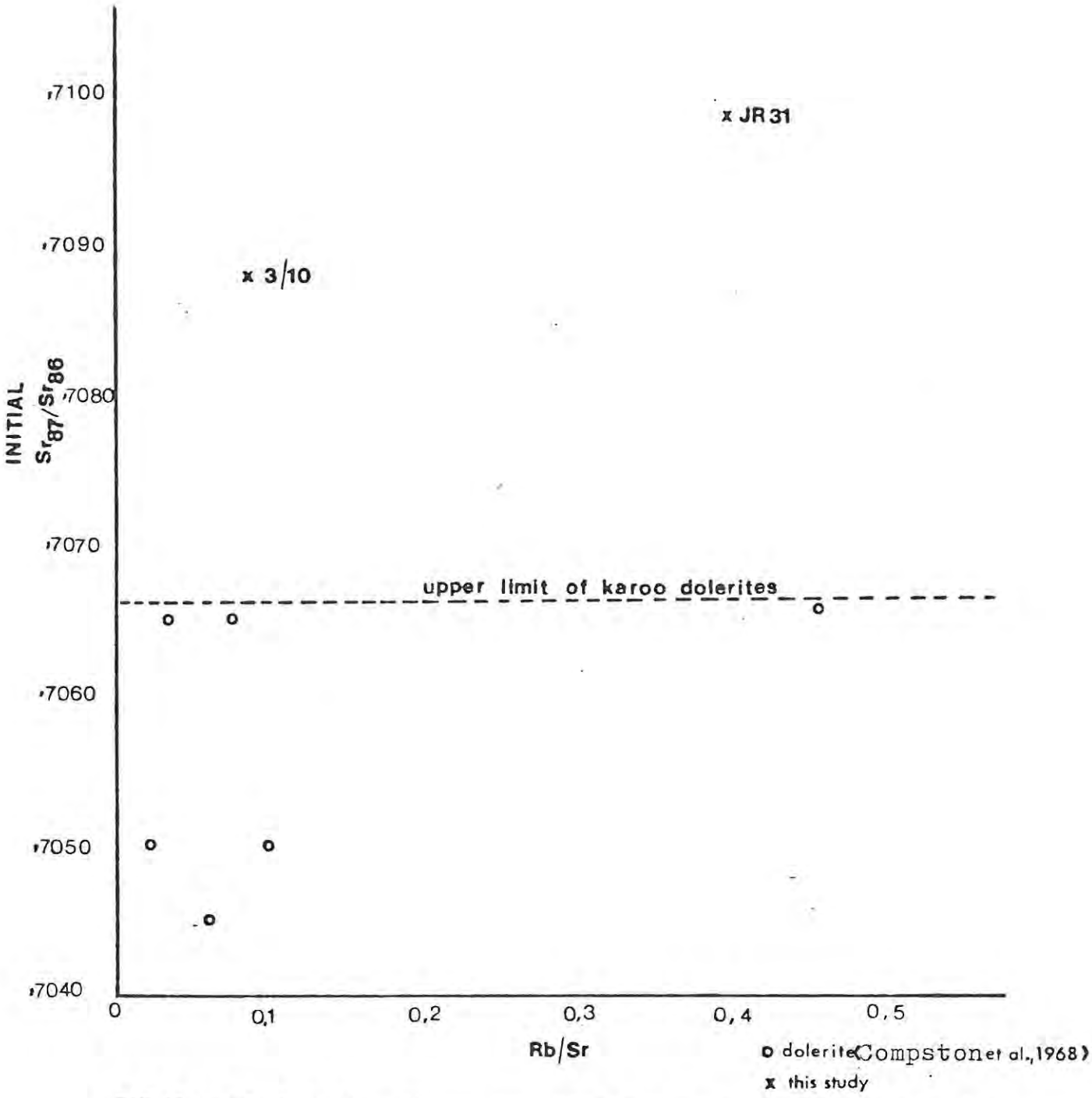


FIG 19 Initial Sr_{87}/Sr_{86} vs. Rb/Sr for the Karoo Dolerites and Andesites.

the Pronksberg volcanic suite, Dikkop andesite and Belmore andesite are at present being conducted at the Bernard Price Institute, University of the Witwatersrand. These results were unfortunately unavailable at the time of writing.

Compston et al. (1968) investigated Sr isotope ratios for the Karoo dolerites, Ferrar dolerites of Antarctica, Sierra Gerral dolerites and the Tasmanian dolerites. The Karoo and Sierra Gerral analyses show identical mean Sr_{87}/Sr_{86} (av = 0.7057) ratios which are slightly higher than the upper limit for oceanic basalts, but are within the range for continental basalts. Compston et al. (op.cit.) interpret these ratios as being indicative of a primary mantle source. The Antarctica and Tasmanian dolerites show initial ratios in the range 0.7090-0.7143 which Compston et al. (op.cit.) interpret as being indicative of crustal contamination.

The initial Sr_{87}/Sr_{86} ratios for the Kraai River basalt sample 3/10 are substantially higher than the ratios for Karoo dolerites obtained by Compston et al. (1968) and other typical Karoo basaltic ratios (Marsh, J.S., personal communication). Differences in initial Sr isotope ratios between typical Karoo lavas and sample 3/10 and the Belmore andesite are shown in Figure 19. The initial Sr isotope ratios for samples 3/10 and JR31 are intermediate in the range generally quoted for crustal ratios (0.710+) and for continental basalts (0.70577) and are therefore interpreted as representing either crustal contamination of a basaltic magma or a primary product of crustal melting.

Similarities in petrography, major and trace element chemistry, normative chemistry and geological setting suggest that similar processes were operative in the genesis of the Pronksberg and Roodehoek andesites. Further isotope data are, however, needed for the Pronksberg and Roodehoek andesites in order to validate these opinions.

CONCLUSIONS

In addition to the conclusions drawn in Sections 5.4.1 and 5.4.2 concerning the geochemistry of the Pronksberg volcanic suite and the Belmore andesite and associated basalts, the following conclusions may be drawn from the petrographic and geochemical study of the Karoo andesites and associated basalts:

(a) Field relationships indicate that the Pronksberg andesite is the result of early Karoo-period volcanic activity. The Belmore andesite succeeds the initial volcanic activity in Barkly East area which resulted in the extrusion of the Drumbo basalts, while the age relationships of the Roodehoek andesite and overlying basalts is uncertain.

(b) Geochemical classifications are used to confirm the andesite label proposed by the early authors, namely Du Toit (1904, 1911) and Gevers (1927), while the calc-alkaline character of the Karoo andesites is recognised. The Pronksberg basaltic rocks display tholeiitic affinities.

(c) The Pronksberg andesite and one Dikkop andesite (sample KRD5) have similar chemical characteristics and are thought to represent a single volcanic episode. Three samples from a flow overlying flow KRD5 found on Dikkop are enriched in K_2O, and this difference is thought to represent a temporal variation in chemistry possibly due to variations in depth of melting, wall-rock reaction or contamination by a K-rich source.

Differences in major and trace element chemistry between the Pronksberg Basalt (High K Type) and Pronksberg Basalt (Drumbo Type) are restricted to K_2O, Na_2O, Sr and Ba enrichment and CaO depletion in the Pronksberg Basalt (High K Type).
The inter-element ratios Zr/Nb, Ti/Zr, Zr/Y and Rb/Sr are similar for the two Pronksberg basalts. Differences in chemistry may possibly reflect the combined influence of the greater degree of weathering, the presence of amygdales and intralava variations on the Pronksberg Basalt (High K Type).
The similarity of the Pronksberg Basalt (Drumbo Type) and Drumbo Basalt in the Barkly East area, as suggested by their petrography, are confirmed by geochemical similarities between the two basalt types, the only significant difference between the two being V and Cr depletion in the Pronksberg basalt (Drumbo Type).
Trace element modelling precludes the possibility of the Pronksberg andesites and basalts being genetically related.

(d) The Belmore andesite is not genetically related to the Kraai River basalts as proposed by Robey (1976). The inter-element ratios Ti/Zr, Zr/Y, K/Y, Ba/Zr, Ba/Sr and Ni/Co are substantially different between the two rock types. The Belmore andesite is enriched in Ba, Ni and Cu, but shows subdued enrichment relative to the Kraai River - 3/10 trend. These trends cannot be explained by crystal fractionation or varying degrees of partial melting.
The fact that the incompatible elements increase in concentration from flow KRB8 to the top of the sequence, while the transition elements show a corresponding decrease to the top of the sequence suggests that trace element variations are controlled by crystal

fractionation. Trace element modelling by applying the equations presented in Section 5.1 indicate that trace element variations in the upper half of the Belmore andesite sequence have been modified by 20 percent crystallisation in the proportion 10 percent plagioclase and 90 percent orthopyroxene. The lower half of the sequence is thought to represent a series of undifferentiated flows. Major and trace element analyses for the Drumbo Basalt Member in the Barkly East area confirm the geochemical character of this member previously described by Robey (1976) and Pemberton (1978). MnO and P_2O_5 differences between data from this study and those previously presented, are thought to represent systematic analytical differences.

(e) The Roodehoek andesite is significantly enriched in K_2O compared to the Pronksberg and Belmore andesites, but displays only minor chemical variations within the intrusion. The potassium enrichment is thought to represent a parent material with distinct chemistry.

(f) Differences in major and trace element concentrations and inter-element ratios precludes the possibility of the three Karoo andesite occurrences being genetically related. Broad similarities in chemistry (in particular normative chemistry) suggest that magmatic processes initiating their formation may, however, be similar.

(g) A Sr isotope analysis for a single Belmore andesite sample yields Sr_{87}/Sr_{86} ratios of 0,7098 (initialled to 185 million years) which are in the range commonly quoted for crustal contamination or crustal melting. Normative chemistry of the three andesite occurrences further indicate that either crustal assimilation

or melting of crustal material has been the dominant magmatic process in their formation. Strontium isotope analyses currently being conducted at the Bernard Price Institute, University of the Witwatersrand may substantiate these observations.

APPENDIX 1 MAJOR ELEMENTS - NORMALISED TO 100% H_2O and L.O.I. FREE.

	KR2	KR3	KR4	KR5	KR6	KR8	KR9	KR11	KR17	KR19	KR20	KR21
SiO_2	65,22	65,46	65,21	65,44	65,56	65,43	65,16	65,75	65,08	65,41,	65,40	65,64
TiO_2	0,79	0,78	0,79	0,78	0,78	0,78	0,79	0,77	0,78	0,78	0,77	0,78
Al_2O_3	16,97	17,17	16,88	17,06	17,07	17,17	17,08	17,40	17,16	17,14	17,11	17,07
Fe_2O_3	6,40	6,26	6,46	6,35	6,37	6,20	6,33	6,28	6,32	6,37	6,27	6,20
MnO	0,16	0,16	0,16	0,16	0,17	0,17	0,18	0,15	0,17	0,16	0,17	0,18
MgO	2,38	2,26	2,47	2,26	2,27	2,41	2,45	2,21	2,39	2,40	2,36	2,33
CaO	2,90	2,58	2,90	2,51	2,64	2,56	2,91	2,54	2,98	2,96	2,86	2,75
Na_2O	3,38	3,84	3,58	3,84	3,69	3,75	3,53	3,29	3,66	3,33	3,37	3,43
K_2O	1,50	1,23	1,29	1,35	1,19	1,28	1,32	1,35	1,20	1,18	1,31	1,35
P_2O_5	0,24	0,26	0,25	0,25	0,26	0,26	0,25	0,25	0,25	0,26	0,25	0,25

	KR22	KR23	KR24	KR25	KR26	KR27	KR28	KR29	KRD1	KRD3	KRD4
SiO_2	52,83	53,87	52,51	54,24	53,75	52,10	52,32	52,24	64,83	64,85	65,00
TiO_2	1,00	1,02	1,02	1,00	1,01	0,99	1,01	1,03	0,80	0,79	0,80
Al_2O_3	16,59	15,95	16,67	16,05	16,28	15,72	15,87	15,64	17,26	17,36	17,15
Fe_2O_3	10,20	10,24	10,23	10,07	10,10	10,30	10,41	10,45	6,54	6,46	6,58
MnO	0,24	0,26	0,28	0,26	0,25	0,26	0,25	0,27	0,16	0,16	0,18
MgO	6,69	6,20	6,88	6,27	6,47	6,48	6,33	6,25	2,31	2,36	2,32
CaO	6,90	6,68	7,15	6,59	6,59	10,30	10,15	10,15	2,63	2,60	2,62
Na_2O	3,36	3,45	3,03	3,25	3,48	2,69	2,49	2,79	2,69	2,62	2,67
K_2O	1,86	2,06	1,97	2,01	1,82	0,89	0,92	0,95	2,51	2,54	2,38
P_2O_5	0,23	0,26	0,26	0,25	0,25	0,24	0,25	0,24	0,27	0,25	0,26

Symbols the same as for Table 3.

APPENDIX 1 (continued)

	KRD5	KRD2	KRD6	KRD7	KRB1	KRB3	KRB6	KRB7	KRB8	KRB9	KRB10
SiO_2	64,98	51,47	51,15	51,37	65,16	64,00	61,60	62,14	62,09	62,46	63,65
TiO_2	0,81	0,92	0,95	0,94	0,75	0,80	0,80	0,79	0,79	0,79	0,79
Al_2O_3	17,29	15,34	15,41	15,34	16,10	16,01	15,64	15,66	15,59	15,74	15,88
Fe_2O_3	6,58	11,06	11,28	11,15	6,29	6,60	7,71	7,39	7,51	7,25	7,29
MnO	0,16	0,25	0,26	0,27	0,17	0,17	0,19	0,20	0,20	0,20	0,18
MgO	2,37	7,26	7,10	7,21	2,77	2,94	3,78	3,65	3,56	3,50	2,85
CaO	3,22	10,70	10,76	10,66	4,13	5,16	5,77	5,18	5,27	5,29	4,39
Na_2O	2,93	2,36	2,63	2,41	2,79	1,84	2,56	2,36	2,37	2,46	2,51
K_2O	1,31	0,40	0,23	0,43	1,61	2,26	1,72	2,41	2,51	2,10	2,33
P_2O_5	0,25	0,22	0,23	0,22	0,22	0,22	0,22	0,21	0,22	0,20	0,20

	KRB4	KRB5	KRB14	KAM6	KAM6X	KAM8	KAM11	KAM12	KAM13	KAM17
SiO_2	52,36	52,45	52,30	65,92	66,13	66,12	65,99	66,33	66,47	66,90
TiO_2	1,12	1,08	1,13	0,79	0,79	0,79	0,78	0,79	0,78	0,75
Al_2O_3	16,83	16,15	16,62	16,12	16,04	15,98	16,09	15,90	15,98	15,89
Fe_2O_3	9,23	10,38	9,10	6,04	6,07	6,20	6,17	6,12	5,93	5,75
MnO	0,26	0,24	0,22	0,15	0,16	0,15	0,14	0,12	0,17	0,15
MgO	5,20	5,61	4,49	2,45	2,39	2,59	2,54	2,53	2,42	2,42
CaO	11,84	10,53	10,67	2,75	2,80	2,52	2,10	2,43	2,83	2,40
Na_2O	2,05	2,31	3,19	2,89	2,68	2,49	2,76	2,77	2,45	2,52
K_2O	0,85	0,92	1,00	2,65	2,71	2,91	2,95	2,77	2,73	2,97
P_2O_5	0,28	0,27	0,27	0,24	0,23	0,23	0,22	0,23	0,23	0,23

APPENDIX 2 : X-RAY FLUORESCENCE SPECTROMETRY

All major and trace element analyses were conducted in the Department of Geology, Rhodes University, using the semi-automatic Phillips PW 1410 spectrometre by x-ray fluorescence techniques. X-ray fluorescence procedures were set up under the supervision of Dr. J.S. Marsh. Data reduction was done by computer.

MAJOR ELEMENTS

Major element analyses, with the exception of Sodium were determined in duplicate on fusion discs, prepared by the method of Norrish and Hutton (1969). Sodium was determined separately on a pressed powder briquette.

Corrections were made for dead-time, background and instrumental drift.

Analytical conditions were as follows:

	Fe	Mn	Ti	Ca	K	P	Si	Al	Mg	Na
Tube	Cr	———	———	———	———	———	———	———	———	———
Kv	55	———	———	———	———	———	———	———	———	———
mA	40	———	———	———	———	———	———	———	———	———
Counter	Flow	———	———	———	———	———	———	———	———	———
Collinator	Fine	coarse	fine	———	———	———	coarse	———	fine	———
Crystal	LIF 200	———	———	———	———	Ge	PET	———	TLAP	———
Counting time on peak (sec)	20	40	10	10	10	20	40	40	200	100

Pulse height descrimination was also used.

H_2O^- was determined gravimetrically by heating the samples at 110°C for 6 hours. In a similar manner L.O.I. was determined by igniting the sample for 8 hours at 950°C. All Fe is stated as Fe_2O_3.

TRACE ELEMENTS

All of the trace elements were determined on pressed powder briquettes. Full corrections for background, spectral line interferences, dead-time and instrumental drift were applied. Corrections for Mass absorption coefficients,

calculated from major element analyses using Heinrich's values, were also applied. The working curves were calculated using international rock standards (AGV-1, GSP-1, BCR-1, G-2, NIM-N, NIM-P. NIM-G and NIM-D).

	Ba	Sr	Rb	Zr	Y	Nb	La	Ce	Nd
Tube	Cr	W							
kV	55								
mA	40								
Counter	Flow	Scintillation							
Collinator	Fine								
Crystal	LiF(220)								

	Zn	Cu	Ni	Co	Cr	V
Tube	Mo			W		
kV	55					
mA	40					
Counter	Flow + Scintillation			FLOW		
Collinator	Fine					
Crystal	LiF(220)					

ELECTRON MICROPROBE ANALYSIS

Partial chemical analyses were conducted on polished sections, coated to a maximum thickness of 25nM with carbon. Analyses were performed using the Cambridge Scientific instruments Microscan V, X-ray Micro-analyser, using pulse height discrimination.

The instrumental conditions were as follows:

	Si	Na	Al	Mg	Fe	Ti	Mn	K
Crystal	KAP							
	LiF							
	Quartz							
	Eht 20 Kv							
	30 Na							
Counter	Flow							

Counting time 10 secs on all peaks.

Date reduction was performed by the Rhodes University, Geology Department S.W.T.P 6800 computer, using the H.V.E. Mark I program. The following Rhodes University, Geology Department in-house standards were used for calibration :

Si	=	Wollastonite
Ti	=	Rutile
Mg,Fe	=	St. Johns Island olivine
Al	=	Jadeiite, Corundum
Na	=	Orthoclase (J.V.P.L.), Jadeiite
K	=	Orthoclase (J.V.P.L.)
Mn	=	Rhodonite

AVERAGE LOWER LIMITS OF DETERMINATION (L.L.D.) AND ERRORS OF DETERMINATION

TRACE ELEMENTS

	av. L.L.D.	av. Absolute Error
Ba	13,5	6,2
Sr	1,27	0,50
Rb	1,27	0,71
Y	1,20	0,39
Zr	1,32	0,54
Nb	1,37	0,39
La	2,19	0,54
Ce	4,52	1,11
Nd	1,89	0,49
Zn	2,07	0,88
Cu	2,28	0,85
Ni	3,13	1,16
Co	0,20	0,05
Cr	0,20	0,07
V	0,24	0,07

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