

ANALYTICAL AND EXPERIMENTAL  
GEOCHEMISTRY OF VOLCANIC ROCKS  
FROM ISLAND ARCS

by

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Signed.....

Petr Jakeš.

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## CHAPTER 1

## INTRODUCTION

The notion that continents grow through geological time is not only a "non-catastrophic" and uniformitarian approach to the Earth's history but also a necessary consequence of chemical fractionation of the primitive Earth on a large scale. The processes of gradual continental growth associated with orogenic activity (c.f. review of Taylor, 1967) and accretion of younger orogenic belts to older cores, has been demonstrated e.g. for eastward growth of Asia (Gorai, 1968) or westward growth of North America (Hamilton, 1970). The actual mechanism of this growth i.e. the addition of primary but relatively highly fractionated sialic material which evolved from more primitive, probably chondritic upper mantle, has been attributed to andesitic volcanism (e.g. Wilson, 1952; Taylor & White, 1965, 1966; Taylor, 1967; Dickinson, 1968; Green & Ringwood, 1968; Ringwood, 1969; and others).

It has been suggested that island arcs and active continental margins both of which are areas of recent calc-alkaline volcanic activity are the loci of recent continental growth. Island arcs have, in general, been described as piles of monotonous andesites with some subordinate basalts

or dacites and sediments derived from them. Some recent authors have pointed out the chemical diversity of island arc lavas (e.g. Kuno, 1966; Sugimura, 1968; Donnelly et al., 1970) and correlated chemical features of island arc rocks, such as  $K_2O$  content, with the seismic evidence on island arc structure (e.g. Dickinson & Hatherton, 1967, 1968). Andesites were considered to be a demonstration of mantle fractionation but some authors have found difficulties in deriving the island arc andesites by a simple one stage process from the upper mantle, e.g. experimental evidence of Green and Ringwood (1968) and trace element abundances as interpreted by Taylor et al. (1969).

Petrological and experimental evidence suggests that derivation of island arc rocks has taken place in an environment containing substantial amounts of water, although most of these rocks appear on the Earth's surface devoid of volatiles. Only volumetrically insignificant amphibole- and biotite-bearing volcanic rocks (andesites and dacites) contain appreciable water; these have been considered by some authors (e.g. Kuno, 1952) to result from contamination of primitive basaltic melts by sialic crust.

The first part of this project was to establish possible chemical and petrological differences and similarities in major and trace element chemistry of amphibole-bearing

rocks and of other andesitic rocks in the circum-Pacific and continental orogenic areas.

The mineral chemistry of amphibole-bearing rocks has been studied in order to provide two lines of evidence:

(a) Distribution of trace elements between crystalline phases and host rocks, and distribution of trace elements between coexisting subsolidus phases, i.e. evidence bearing on trace element distribution between the possible phases of the residual assemblage and the derivative partial initial melts. This has been supplemented by experimental studies of trace element distribution.

(b) To compare conditions of crystallization of amphibole-bearing, and amphibole-free calc-alkaline volcanic rocks and to evaluate factors influencing the course of their crystallization or derivation.

Experimental studies made on wet andesites (5% H<sub>2</sub>O) are aimed at establishing differences between continental and island arc andesites and these also provide a comparison between naturally observed and experimentally determined crystallization sequences. These experiments were also intended to provide a basis for estimates of H<sub>2</sub>O content in andesitic melts.

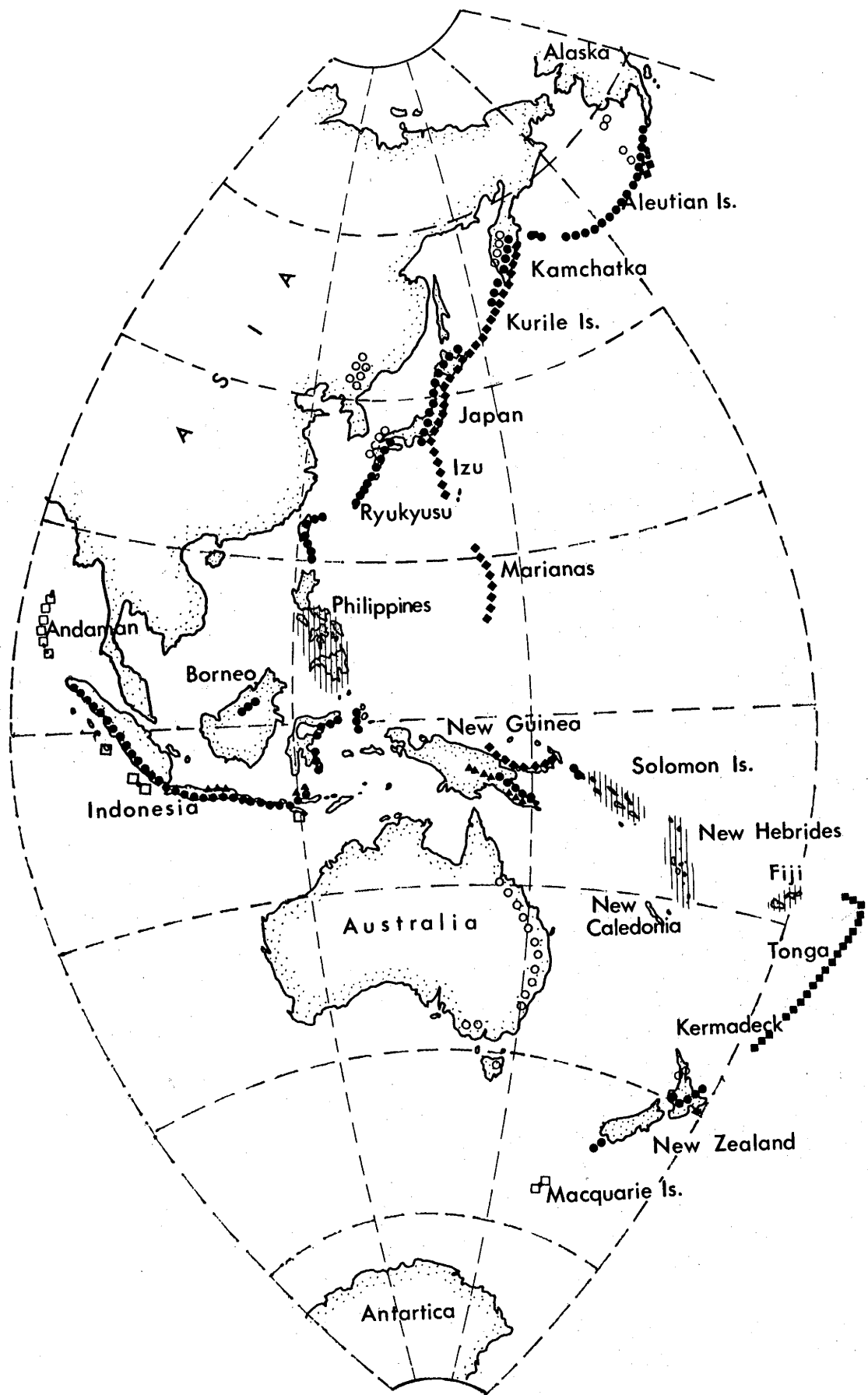
These geochemical studies led to an examination of the relation of calc-alkaline rocks to the other associations

of island arcs: tholeiites and shoshonites. Major and trace element analyses have been made on rocks of these three associations especially in those areas where the seismic zone is poorly developed (Melanesia) to ascertain the zonal arrangement of lavas. An attempt has been made to relate trace element abundances to mineralogy of likely source materials.

A model for island arc evolution based on the hypothesis of sea-floor spreading is proposed. This model replaces the "andesitic" model for continental accretion with the "tholeiite-andesite-shoshonite" model and also accounts for an island arc contribution to the continental crust. The areal and temporal variations in the geochemistry of island arc lavas provide the basis for this model. The model is believed to be applicable to older and probably oldest orogenic regions or areas of formation of continental crust (White, Jakes<sup>y</sup> and Christie, 1970) and offers a mechanism for the formation of highly fractionated layered continental crust from relatively primitive oceanic crust without the requirement of pre-existing sialic continents.

Figure 1.1: Island arcs of western Pacific area with Cenozoic volcanic provinces.

Open squares - "ophiolites" of non-volcanic arcs; full squares - island arc tholeiitic association; full circles - calc-alkaline association; triangles - shoshonitic association; empty circles - alkaline rocks; shaded areas - rock associations which do not show zonal arrangement.



## NOMENCLATURE

In island arc areas three volcanic rock associations can be recognized (Fig. 1.1); these are the tholeiitic association of island arcs, the calc-alkaline association and the shoshonitic association, all of which are related in space and time by transitional types. The association of alkaline rocks although geographically related to the island arc environment is not discussed.

Nomenclature used here corresponds in general to division proposed by Kuno (1960, 1966) and follows Taylor and White's (1966) suggestion to limit usage of the name andesite only to the calc-alkaline association. Principal division of rock associations is based on major element chemistry, particularly  $K_2O$  and total alkali contents,  $K_2O/Na_2O$  ratio, Fe/Mg ratio and "iron enrichment". In each association, however, rocks are named according to  $SiO_2$  content. In Table 1.1 analyses of characteristic rocks of island arcs are presented and in Table 1.2 rock names summarized. Figure 1.2 summarizes the  $K_2O/SiO_2$  relations of the three series, and Figure 1.3 shows AMF relations.

Tholeiitic association of island arcs. Most commonly the rocks are of basaltic composition, although a wide range of  $SiO_2$  values is typical. Rocks with low  $Al_2O_3$  (9-12%) and

Table 1.1.

Characteristic rocks of island arcs, examples from Melanesia

| Island<br>arc<br>tholeiites    | Calc-alkaline rocks |                    |                    | Low-K<br>andesite | Andesite | High-K<br>andesite | Dacite | Shoshonitic rocks |        | Abyssal<br>tholeiite |
|--------------------------------|---------------------|--------------------|--------------------|-------------------|----------|--------------------|--------|-------------------|--------|----------------------|
|                                | High-Al<br>basalt   | Low-Si<br>andesite | Low-Si<br>andesite |                   |          |                    |        | Shoshonite        | Latite |                      |
| 1                              | 2                   | 3                  | 4                  | 5                 | 6        | 7                  | 8      | 9                 | 10     |                      |
| SiO <sub>2</sub>               | 51.57               | 50.59              | 54.54              | 59.05             | 59.64    | 58.52              | 66.80  | 53.74             | 59.27  | 49.34                |
| TiO <sub>2</sub>               | .80                 | 1.05               | 1.13               | .69               | .67      | .76                | .23    | 1.05              | .56    | 1.49                 |
| Al <sub>2</sub> O <sub>3</sub> | 15.91               | 16.29              | 16.26              | 17.07             | 17.38    | 16.20              | 18.24  | 15.84             | 15.90  | 17.04                |
| Fe <sub>2</sub> O <sub>3</sub> | 2.74                | 3.66               | 2.31               | 3.90              | 2.54     | 2.93               | 1.25   | 3.25              | 2.22   | 1.99                 |
| FeO                            | 7.04                | 5.08               | 5.40               | 2.57              | 2.72     | 3.28               | 1.02   | 4.85              | 3.19   | 6.82                 |
| MnO                            | .17                 | .17                | .12                | .15               | .09      | .09                | .06    | .11               | .10    | .17                  |
| MgO                            | 6.73                | 8.96               | 6.97               | 3.25              | 3.95     | 4.14               | 1.50   | 6.36              | 5.45   | 7.19                 |
| CaO                            | 11.74               | 9.50               | 7.50               | 7.09              | 5.92     | 5.59               | 3.17   | 7.90              | 5.90   | 11.72                |
| Na <sub>2</sub> O              | 2.41                | 2.89               | 3.64               | 3.80              | 4.40     | 3.64               | 4.97   | 2.38              | 2.67   | 2.73                 |
| K <sub>2</sub> O               | .44                 | 1.07               | 1.49               | 1.27              | 2.04     | 2.67               | 1.92   | 2.57              | 2.68   | .16                  |
| P <sub>2</sub> O <sub>5</sub>  | .11                 | .21                | .23                | .20               | .28      | .25                | .09    | .54               | .41    | .16                  |
| H <sub>2</sub> O               | .45                 | .81                | 1.31               | .64               | 1.08     | 1.47               | .26    | 1.09              | 1.44   |                      |

1. Tholeiitic basalt, lake Dakataua, Talasea, New Britain (Lowder and Carmichael, 1970)
2. High-Al basalt, north slope of Mt. Trafalgar, Cape Nelson, East Papua (Jakeš and Smith, 1970)
3. Low-Si andesite, south slope of Mt. Trafalgar, Cape Nelson, East Papua (Jakeš and Smith, 1970)
4. Low-K andesite, Mau Quarry, Viti Levu, Fiji (present paper)
5. Andesite, lava dome of Mt. Lamington, East Papua (Jakeš and White, 1969)
6. High-K andesite, north-western slope of Mt. Trafalgar, Cape Nelson, East Papua (Jakeš and Smith, 1970)
7. Dacite, Savo volcano, Guadalcanal, Solomon Islands, (Jakeš and White, 1969)
8. Shoshonite, Gumnach river, Mt. Hagen, New Guinea Highlands (Jakeš and White, 1969)
9. Latite, Tambul, Mt. Giluwe, New Guinea Highlands (Jakeš and White, 1969)
10. Abyssal tholeiite, (Engel et al., 1965)

TABLE 1.2 Nomenclature of principal rocks from island arcs in the range 50-65% SiO<sub>2</sub> excepting the alkaline association\*.

| Rock Association   | I n c r e a s i n g    K <sub>2</sub> O / N a <sub>2</sub> O —<br>decreasing iron enrichment |                     |               |
|--------------------|----------------------------------------------------------------------------------------------|---------------------|---------------|
|                    | Tholeiitic                                                                                   | Calc-alkaline       | Shoshonitic   |
| SiO <sub>2</sub> % |                                                                                              |                     |               |
| 50                 | tholeiitic                                                                                   | high alumina basalt | absarokite    |
| 51                 | basalt                                                                                       |                     |               |
| 52                 | (tholeiite)                                                                                  |                     |               |
| 53                 |                                                                                              |                     |               |
| 54                 |                                                                                              |                     |               |
| 55                 | (low-Si icelandite)                                                                          |                     |               |
| 56                 |                                                                                              | low-Si andesite     | shoshonite    |
| 57                 |                                                                                              | (basaltic andesite) |               |
| 58                 | icelandite                                                                                   |                     |               |
| 59                 | (tholeiitic andesite)                                                                        |                     | banakite      |
| 60                 |                                                                                              | andesite            |               |
| 61                 |                                                                                              |                     | latite        |
| 62                 |                                                                                              |                     |               |
| 63                 |                                                                                              |                     |               |
| 64                 | tholeiitic                                                                                   |                     |               |
| 65                 | dacite                                                                                       | dacite              | quartz latite |

\* cf. Taylor (1968) for definition of mugearite, benmorite, hawaiite and tristanite i.e., andesitic equivalents within alkaline rock association.

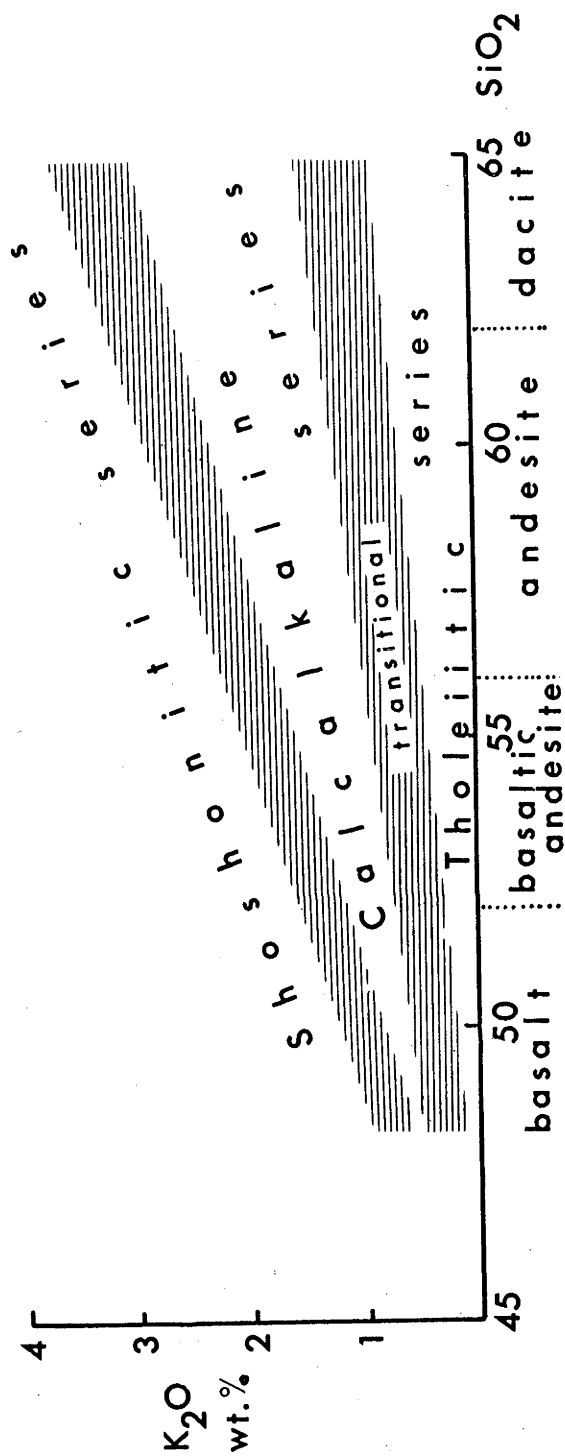


Fig. 1.2. Schematic diagram of  $K_2O$  vs.  $SiO_2$  relations of three rock series of island arcs (see also Jakes and Gill, 1970, fig.2). Names at the bottom of figure are relevant only to calc-alkaline series.

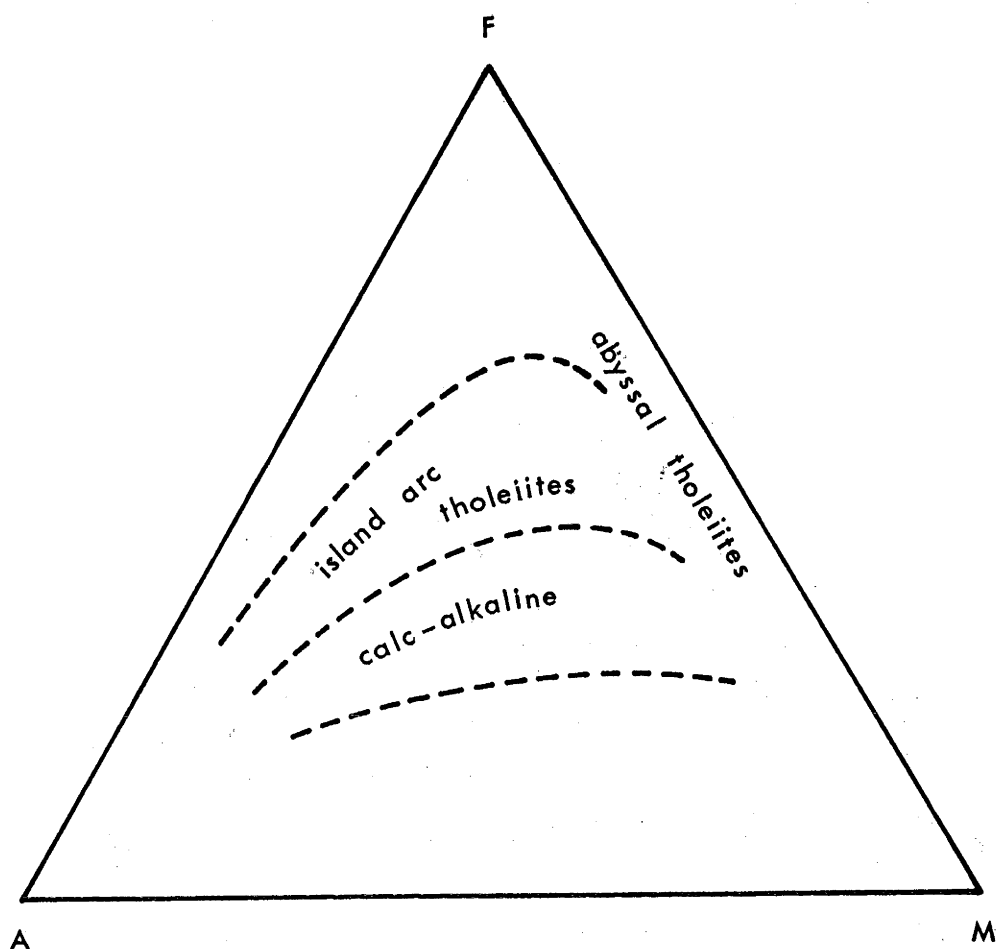


Fig.1.3. Schematic relations of AMF values ( $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{FeO} + .9\text{Fe}_2\text{O}_3 - \text{MgO}$ ) in the island arc tholeiitic association, abyssal tholeiites and calc-alkaline rocks.

relatively high in alkali content are extremely rare in island arcs whereas rocks with high  $\text{Al}_2\text{O}_3$  (14-17%) and less than 4% of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  are frequent.  $\text{K}_2\text{O}$  content is low and usually does not exceed 1.2% for  $\text{SiO}_2$ -rich rocks (58%). The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios are low, usually less than .35,  $\text{FeO}/\text{MgO}$  ratio varies widely and strong "iron enrichment" is characteristic. Most rocks are only slightly oxidised;  $\text{Fe}_2\text{O}_3/\text{FeO}$  does not exceed .5.

Calc-alkaline association. Andesites are the most widespread representatives of this association, although low-Si as well as high-Si rocks are common.  $\text{Al}_2\text{O}_3$  content is high (15-19%) although lower values occur in high  $\text{SiO}_2$  (<63%) rocks and wider variation in  $\text{Al}_2\text{O}_3$  content is characteristic of high-K rocks. Alkali content is high and increases smoothly with increasing  $\text{SiO}_2$ .  $\text{FeO}/\text{MgO}$  ratio is almost constant and AMF diagrams indicate little or no "iron enrichment". The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio varies between .35 to .75.  $\text{K}_2\text{O}$  varies from relatively low (1.0%) to high (3.0%) at 58%  $\text{SiO}_2$ .

Shoshonitic association. These rocks are poorly documented. Rocks with 54%  $\text{SiO}_2$  appear to be most frequent. The following features are characteristic;-a high, but very

variable  $\text{Al}_2\text{O}_3$  content (14.5-20.0%), a high content of alkali elements irrespective of  $\text{SiO}_2$  due to high  $\text{K}_2\text{O}$  content. The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio is high, fluctuating around unity. As in calc-alkaline associations the  $\text{FeO}/\text{MgO}$  ratio is almost constant and rocks do not show any apparent trends on AMF diagrams.  $\text{CaO}$  is relatively low.

## CHAPTER 2

## AMPHIBOLE-BEARING CALC-ALKALINE VOLCANIC ROCKS

Recent data on the structure of island arcs and variation of lava composition (e.g. Sugimura, 1968; Jakeš and White, 1969; Jakeš and Gill, 1970; Gill, 1970) cast some doubts on the exceptional significance of the andesitic contribution to the island arcs. The chemical composition of calc-alkaline rocks is transitional to both tholeiitic and shoshonitic rocks and rocks of calc-alkaline affinities form an important part of recently exposed island arcs. These rocks are believed to be formed by processes in which water played an important role (e.g. Osborn, 1959; Green and Ringwood, 1968; Yoder, 1969) although most of the lavas appear on the earth's surface devoid of volatiles and free of hydrous phases, this is probably due to loss of volatiles during eruption. However, amphibole- and biotite-bearing rocks occur infrequently in recent island arcs, but are more common in continental provinces (e.g. Andes) including intracontinental orogenic chains.

Major element composition

Amphibole- and biotite-bearing rocks of island arcs and older orogenic areas were analyzed using XRF and classical wet analytical techniques to determine their

major and trace element composition. The analytical methods used are described in Appendix 1 and chemical analyses of amphibole-bearing and some amphibole-free volcanic rocks are presented in Tables 2.1 to 2.6. Some of these analyses have been published in the accompanying papers by Jakes<sup>✓</sup> and White (1969) and Jakes<sup>✓</sup> and Smith (1970). Details of sample localities and petrographic features are contained in data in Appendix 2.

#### Eastern Papua

Analyses of Pliocene to Recent volcanic rocks from the Cape Nelson area (Mt Trafalgar and Mt Victory) and from Mt Lamington are presented in Table 2.1 to 2.3.

The Cape Nelson lavas are mainly andesitic with amphibole-bearing andesites forming more than 50% of all exposed rocks. From field observations and examination of 60 samples, the estimated volumes of erupted rocks are high-Al basalts (3%), low-Si andesites (39%), andesites (55%) and dacites (5%). Similar volume relationships are observed at Mt Lamington.

The  $\text{SiO}_2$  content (Fig. 2.1) of the rocks ranges from 50 to 65 wt%. Basalts and low-Si andesites are more common among the older units (Mt Trafalgar), whereas the  $\text{SiO}_2$ -rich lavas are more typical of later eruptions (Mt Victory).

TABLE 2.1. CHEMICAL ANALYSES OF VOLCANIC ROCKS FROM CAPE NELSON

|                                | 1      | 2      | 3      | 4     | 5     | 6     | 7     | 8      | 9     | 10    | 11     | 12    | 13    | 14     | 15    | 16    | 17    | 18     | 19    | 20    | 21     | 22     |
|--------------------------------|--------|--------|--------|-------|-------|-------|-------|--------|-------|-------|--------|-------|-------|--------|-------|-------|-------|--------|-------|-------|--------|--------|
| Field No.                      | 3544   | 6516   | 3528   | 3527  | 6514  | 3545  | 6513  | 3547   | 3548  | 3525A | 3543   | 3500B | 3501C | 3514   | 3500A | 3508  | 3530  | 3513   | 6518  | 3555  | 3536   | 3526B  |
| wt %                           |        |        |        |       |       |       |       |        |       |       |        |       |       |        |       |       |       |        |       |       |        |        |
| SiO <sub>2</sub>               | 50.59  | 53.85  | 54.54  | 55.33 | 55.68 | 55.97 | 56.43 | 56.76  | 58.52 | 58.99 | 59.03  | 59.69 | 60.85 | 61.75  | 61.8  | 62.08 | 62.14 | 62.50  | 62.64 | 62.98 | 63.04  | 64.12  |
| TiO <sub>2</sub>               | 1.05   | 1.51   | 1.13   | .97   | .84   | .93   | .93   | .88    | .76   | 1.01  | .99    | .67   | .69   | .72    | .70   | .26   | .93   | .70    | .67   | .64   | .71    | .61    |
| Al <sub>2</sub> O <sub>3</sub> | 16.29  | 15.60  | 16.26  | 14.69 | 14.29 | 16.20 | 16.00 | 16.50  | 16.20 | 18.20 | 17.43  | 16.01 | 16.69 | 16.00  | 16.4  | 17.00 | 16.72 | 16.21  | 16.48 | 16.26 | 16.48  | 16.80  |
| Fe <sub>2</sub> O <sub>3</sub> | 3.66   | 4.02   | 2.31   | 2.32  | 2.58  | 4.37  | 2.14  | 2.43   | 2.93  | 3.04  | 2.77   | 4.47  | 1.80  | 2.34   | 2.70  | 1.65  | 1.83  | 3.11   | 1.68  | 3.13  | 2.74   | 1.61   |
| FeO                            | 5.08   | 3.66   | 5.40   | 5.21  | 3.86  | 2.21  | 3.99  | 3.68   | 3.28  | 2.48  | 2.92   | .47   | 2.72  | 2.64   | 1.90  | 3.80  | 2.76  | .73    | 2.64  | 1.02  | 1.22   | 2.18   |
| MnO                            | .17    | .12    | .12    | .13   | .10   | .12   | .09   | .10    | .09   | .07   | .08    | .08   | .09   | .09    | .05   | .06   | .06   | .08    | .08   | .03   | .46    | .07    |
| MgO                            | 8.96   | 6.80   | 6.97   | 6.90  | 6.97  | 4.62  | 6.04  | 6.17   | 4.14  | 2.89  | 3.69   | 5.28  | 3.47  | 4.72   | 3.20  | 4.97  | 2.36  | 4.56   | 3.91  | 1.98  | 2.79   | 2.96   |
| CaO                            | 9.50   | 7.17   | 7.50   | 7.83  | 8.15  | 6.50  | 5.84  | 7.06   | 5.59  | 5.62  | 4.84   | 5.98  | 5.20  | 5.50   | 4.95  | 3.28  | 4.48  | 5.55   | 5.10  | 2.59  | 4.21   | 4.44   |
| Na <sub>2</sub> O              | 2.89   | 3.64   | 3.64   | 3.17  | 3.37  | 3.70  | 4.05  | 3.78   | 3.64  | 4.25  | 4.11   | 4.16  | 4.18  | 3.98   | 4.25  | 3.98  | 4.27  | 4.25   | 4.25  | 4.45  | 4.36   | 4.38   |
| K <sub>2</sub> O               | 1.07   | 1.56   | 1.49   | 1.53  | 2.54  | 2.15  | 1.92  | 1.87   | 2.67  | 2.16  | 2.37   | 2.00  | 2.57  | 2.31   | 2.60  | 1.64  | 3.51  | 2.27   | 1.06  | 3.80  | 3.35   | 2.41   |
| P <sub>2</sub> O <sub>5</sub>  | .21    | .45    | 0.23   | .26   | .49   | .28   | .31   | .29    | .25   | .36   | .34    | .24   | .27   | .30    | .27   | .03   | .34   | .28    | .26   | .35   | .25    | .41    |
| Loss                           | .81    | 1.66   | 1.31   | 1.10  | .31   | 2.52  | .99   | 1.11   | 1.47  | .85   | 1.51   | .76   | .76   | .92    | .96   | .32   | .32   | .36    | 1.05  | 2.76  | 1.41   | .32    |
| Total                          | 100.28 | 100.04 | 100.90 | 99.44 | 99.18 | 99.57 | 98.73 | 100.63 | 99.54 | 99.92 | 100.08 | 99.81 | 99.29 | 101.27 | 99.82 | 98.06 | 99.72 | 100.60 | 99.82 | 99.99 | 101.02 | 100.14 |

P.P.m.

|    | 52                                                                                             | 80*                                                      |
|----|------------------------------------------------------------------------------------------------|----------------------------------------------------------|
| Rb |                                                                                                |                                                          |
| Sr | 450 540 470 500 980 630 580 577*                                                               | 520 800 875 570 830 800 720 640 940 700 610 950 896* 680 |
| Ba | 400 550 600 640 1150 610 670 560 700 550 830 820 990 1000 920 740 1500 1000 1020 1230 1100 980 |                                                          |
| Sc | 31 22 25 22 24 20 19 20 16 14 18 21 16 16 16 17 13 16 14 11 22 19                              |                                                          |
| Ni | 150 200 125 540 54 46 150 46 37 10 23 44 22 35 32 32 23 35 27 29 27 28                         |                                                          |
| V  | 216 143 180 140 86 155 117 155 108 120 108 116 115 118 120 120 145 98 88 68 105 81             |                                                          |
| Cr | 360 450 350 850 300 160 320 280 160 51 130 220 140 280 220 250 170 - 120 115 150 135           |                                                          |
| Zr | 130 195 145 150 220 200 200 200 200 190 180 150 140 180 160 170 360 180 160 28 250 140         |                                                          |
| Cu | 34 33 17 59 80 18 67 21 17 11 15 23 15 13 23 32 36 20 12 12 11 14                              |                                                          |
| Th |                                                                                                | 12.8*                                                    |
| U  |                                                                                                | 1.9*                                                     |
| Gd |                                                                                                | 17 *                                                     |

Major elements were determined by XRF(author) except for FeO and Na<sub>2</sub>O which were determined at A.M.D.L. laboratories.

Trace elements have been determined by optical emission spectroscopy in the B.M.R. laboratory (analyst T.I. Slezak) except for those marked by an asterisk which were determined by XRF techniques at the Department of Geology A.N.U.

TABLE 2.2

## Chemical Analyses of Inclusions in Cape Nelson Volcanic Rocks

|                                    | 1      | 2      | 3     | 4      | 5      | 6      | 7     |
|------------------------------------|--------|--------|-------|--------|--------|--------|-------|
|                                    | 6503A  | 3512C  | 6505F | 3502B  | 6505C  | 3501B  | 3504  |
| wt %                               |        |        |       |        |        |        |       |
| SiO <sub>2</sub>                   | 48.07  | 50.54  | 53.87 | 54.26  | 54.34  | 56.80  | 57.26 |
| TiO <sub>2</sub>                   | 1.59   | .06    | .92   | 1.14   | 1.15   | .78    | .75   |
| Al <sub>2</sub> O <sub>3</sub>     | 16.55  | 16.76  | 15.63 | 16.13  | 15.64  | 15.21  | 15.60 |
| Fe <sub>2</sub> O <sub>3</sub>     | 1.99   | .39    | 3.68  | 3.14   | 3.58   | 4.72   | 2.31  |
| FeO                                | 3.99   | 2.86   | 3.34  | 3.72   | 3.32   | 1.75   | 3.52  |
| MnO                                | .11    | .09    | .12   | .11    | .10    | .11    | .09   |
| MgO                                | 10.94  | 9.88   | 6.95  | 6.55   | 7.23   | 6.96   | 6.36  |
| CaO                                | 15.04  | 18.84  | 8.21  | 8.01   | 8.12   | 8.12   | 7.32  |
| Na <sub>2</sub> O                  | 1.08   | 1.08   | 3.44  | 3.94   | 4.09   | 3.84   | 3.83  |
| K <sub>2</sub> O                   | .03    | .09    | 1.68  | 1.83   | 2.12   | 1.46   | 1.49  |
| P <sub>2</sub> O <sub>5</sub>      | .07    | .02    | .38   | .52    | .59    | .33    | .22   |
| H <sub>2</sub> O + CO <sub>2</sub> | .61    | .37    | .99   | .93    | .43    | .81    | .78   |
| TOTAL                              | 100.07 | 100.98 | 99.21 | 100.28 | 100.71 | 100.89 | 99.53 |
| p.p.m.                             |        |        |       |        |        |        |       |
| Rb                                 |        |        |       | 15*    |        |        | 42*   |
| Sr                                 | 48     | 31     | 900   | 1029*  | 750    | 540    | 713   |
| Ba                                 | 30     | < 30   | 840   | 920    | 1000   | 620    | 740   |
| Sc                                 | 34     | 40     | 24    | 24     | 21     | 28     | 27    |
| Ni                                 | 480    | 270    | 47    | 32     | 43     | 72     | 52    |
| V                                  | 76     | 105    | 190   | 190    | 150    | 168    | 185   |
| Cr                                 | 480    | 11000  | 380   | 210    | 205    | 370    | 250   |
| La                                 | < 40   | < 40   | 54    | 51     | 54     | < 40   | < 40  |
| Y                                  | < 20   | < 20   | 28    | 32*    | < 20   | 32     | 23    |
| Zr                                 | < 50   | < 50   | 185   | 250    | 200    | 155    | 125   |
| Cu                                 | < 7    | < 7    | 39    | 42     | 36     | 37     | 32    |
| Th                                 |        |        |       | 10.3*  |        |        | 5.8*  |
| U                                  |        |        |       | 6.0*   |        |        | 8.9 * |
| Gd                                 |        |        |       | 18.0*  |        |        | 15.0* |

Major elements were determined by XRF techniques at the Department of Geology A.N.U. except for FeO and Na<sub>2</sub>O which were determined at A.M.D.L. Laboratories.

Trace elements have been determined by optical emission spectroscopy in the B.M.R. Laboratory (analyst T.I. Slezak), except for those marked by an asterisk which were determined by XRF techniques at Department of Geology A.N.U.

Table 2.3.

Chemical analyses of volcanic rocks and their inclusions  
from Eastern Papua

|                                | 70     | 69    | 68     | 64     | 3547   | 3543   | 3500B  | 3536   | 3526B  | 65B   | 65A    | 3544   | 3502   | 6505C  | 75     | 3504  |
|--------------------------------|--------|-------|--------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|-------|
| SiO <sub>2</sub>               | 56.18  | 58.57 | 59.64  | 61.10  | 56.76  | 59.03  | 59.69  | 63.04  | 63.40  | 53.79 | 61.16  | 50.59  | 54.26  | 54.34  | 56.17  | 57.26 |
| TiO <sub>2</sub>               | .77    | .72   | .67    | .61    | .88    | .99    | .67    | .71    | .61    | .79   | .61    | 1.05   | 1.14   | 1.15   | .99    | .75   |
| Al <sub>2</sub> O <sub>3</sub> | 15.80  | 15.73 | 17.38  | 17.33  | 16.50  | 17.43  | 16.01  | 16.48  | 16.90  | 15.27 | 17.62  | 16.29  | 16.13  | 15.64  | 16.65  | 15.60 |
| Fe <sub>2</sub> O <sub>3</sub> | 2.77   | 2.26  | 2.54   | 2.65   | 2.43   | 2.77   | 4.47   | 2.74   | 2.14   | 5.52  | 4.44   | 3.66   | 3.14   | 3.58   | 3.53   | 2.31  |
| FeO                            | 3.90   | 4.13  | 2.72   | 2.12   | 3.68   | 2.92   | .47    | 1.22   | 1.83   | 3.50  | .74    | 5.08   | 3.72   | 3.32   | 3.14   | 3.52  |
| MnO                            | .12    | .11   | .09    | .09    | .10    | .08    | .08    | .46    | .07    | .19   | .09    | .17    | .11    | .10    | .11    | .09   |
| MgO                            | 7.59   | 5.79  | 3.95   | 3.68   | 6.17   | 3.69   | 5.28   | 2.79   | 3.27   | 7.07  | 3.65   | 8.96   | 6.55   | 7.23   | 6.46   | 6.36  |
| CaO                            | 7.65   | 7.31  | 5.92   | 5.65   | 7.06   | 4.84   | 5.98   | 4.21   | 4.67   | 8.32  | 5.84   | 9.50   | 8.01   | 8.12   | 7.90   | 7.32  |
| Na <sub>2</sub> O              | 3.81   | 2.63  | 4.40   | 4.50   | 3.78   | 4.11   | 4.16   | 4.36   | 4.59   | 3.97  | 3.36   | 2.89   | 3.94   | 4.09   | 2.84   | 3.83  |
| K <sub>2</sub> O               | 1.53   | 1.66  | 2.04   | 2.12   | 1.87   | 2.37   | 2.00   | 3.35   | 2.43   | 1.14  | 2.06   | 1.07   | 1.83   | 2.12   | 1.77   | 1.49  |
| P <sub>2</sub> O <sub>5</sub>  | .22    | .19   | .28    | .24    | .29    | .34    | .24    | .25    | .24    | .18   | .26    | .21    | .52    | .59    | .45    | .22   |
| loss (H <sub>2</sub> O)        | .57    | .21   | 1.08   | .34    | 1.11   | 1.51   | .76    | 1.41   | .05    | .24   | .20    | .81    | .93    | .43    | .78    | .78   |
| Total                          | 100.91 | 99.31 | 100.71 | 100.43 | 100.63 | 100.08 | 100.81 | 100.92 | 100.20 | 99.98 | 100.95 | 100.28 | 100.28 | 100.71 | 100.11 | 99.53 |
| Rb                             | 52     | 57    | 52     | 80     |        |        |        |        |        | 7     |        | 15     |        |        | 42     |       |
| Pb                             | 14     | 15    | 13     | 15     |        |        |        | 16     |        | 11    | 18     | 14     |        |        | 8      |       |
| Sr                             | 985    | 968   | 577    | 1227   |        |        |        | 895    |        | 32    | 1054   | 1029   |        |        | 713    |       |
| Y                              | 23     | 13    | 28     | 41     |        |        |        | 32     |        | 27    | 26     | 32     |        |        | 23     |       |
| Th                             | 4.3    | ---   | 7.1    | 12.8   |        |        |        | 14.1   |        | 4.4   | 8.0    | 10.3   |        |        | 5.8    |       |
| U                              | ---    | 2.0   | 1.9    | 1.7    |        |        |        | 4.2    |        | 2.9   | 1.8    | 6.0    |        |        | 8.9    |       |
| Ca                             | 18     | 18    | 17     | 22     |        |        |        | 20     |        | 21    | 19     | 18     |        |        | 15     |       |

Table 2.4. Chemical analyses of amphibole bearing rocks from orogenic areas

|                                | New Zealand |        |       |        | Fiji  |                  |       |       | Western United States |        |        |       | Argentina |
|--------------------------------|-------------|--------|-------|--------|-------|------------------|-------|-------|-----------------------|--------|--------|-------|-----------|
|                                | 47          | 48     | 50    | 46     | 52    | 2                | 6     | 18    | 53                    | 5      | 1      | 51    |           |
| SiO <sub>2</sub>               | 52.21       | 53.94  | 59.99 | 60.72  | 39.07 | 55.14            | 58.85 | 59.05 | 53.83                 | 64.75  | 66.49  | 63.74 |           |
| TiO <sub>2</sub>               | .95         | 1.10   | .56   | .53    | 2.00  | .70              | .66   | .69   | 1.11                  | .37    | .49    | .70   |           |
| Al <sub>2</sub> O <sub>3</sub> | 17.56       | 16.19  | 18.13 | 17.85  | 10.96 | 18.55            | 16.90 | 17.07 | 19.57                 | 17.41  | 16.46  | 16.19 |           |
| Fe <sub>2</sub> O <sub>3</sub> | 4.41        | 5.26   | 4.15  | 2.45   | 10.76 | 3.57             | 3.78  | 3.90  | 3.55                  | 1.34   | 1.80   | 1.36  |           |
| FeO                            | 3.81        | 4.06   | 1.76  | 1.79   | 9.78  | 3.93             | 2.57  | 2.57  | 3.17                  | 1.92   | 2.66   | 1.77  |           |
| MnO                            | .17         | .16    | .09   | .09    | .18   | .09              | .13   | .15   | .08                   | .07    | .09    | .06   |           |
| MgO                            | 3.65        | 4.83   | 2.04  | 2.32   | 11.15 | 4.52             | 3.40  | 3.25  | 8.94                  | 2.23   | 1.16   | 2.87  |           |
| CaO                            | 8.56        | 9.67   | 6.38  | 5.87   | 11.28 | 8.83             | 6.94  | 7.09  | 4.05                  | 5.35   | 2.46   | 4.50  |           |
| Na <sub>2</sub> O              | 5.28        | 2.65   | 2.53  | 3.99   | 1.35  | 2.93             | 3.92  | 3.80  | 2.93                  | 4.49   | 3.80   | 3.82  |           |
| K <sub>2</sub> O               | 1.62        | 1.20   | 1.02  | 2.09   | .16   | .34              | 1.36  | 1.27  | .70                   | .91    | 3.04   | 2.42  |           |
| P <sub>2</sub> O <sub>5</sub>  | .30         | .20    | .23   | .20    | .05   | .14              | .20   | .20   | .33                   | .12    | .24    | .22   |           |
| loss (H <sub>2</sub> O)        | .95         | .79    | 2.42  | 2.14   | 2.50  | 1.47             | .85   | .64   | 1.68                  | 1.20   | 1.32   | 2.07  |           |
| total                          | 99.47       | 100.05 | 99.30 | 100.04 | 99.27 | 99.21            | 99.56 | 99.68 | 99.94                 | 100.16 | 100.01 | 99.72 |           |
| Rb                             |             | 27.9   | 33.8  | 39.3   |       | 10.3             | 22.8  | 18.6  |                       | 21.0   | 48.9   |       |           |
| Ba                             | 950         | 641    | 456   | 1001   | 313   | 555              | 532   |       | 261                   | 1236   |        |       |           |
| Pb                             | 13          |        | 7     |        | 21    |                  | 10    |       | 4                     | 95     |        |       |           |
| Sr                             |             | 632    | 434   | 1047   | 58.6  | 510              | 501   |       | 298                   | 921.6  |        |       |           |
| La                             | 9.4         | 11.1   | 1.3   | 20.4   | 3.2   | 8.1              | 8.4   |       | 3.3                   | 45.1   |        |       |           |
| Ce                             | 38.1        | 34.4   | 23.9  | 63.9   | 10.9  | 26.9             | 25.9  |       | 13.9                  | 84.9   |        |       |           |
| Pr                             |             | 3.3    |       | 10.5   |       | 2.9              | 2.7   |       | 1.7                   | 6.0    |        |       |           |
| Nd                             | 15.9        | 14.0   | 7.2   | 19.1   | 4.5   | 7.4              | 10.4  |       | 4.4                   | 22.5   |        |       |           |
| Y                              | 19.9        | 21.7   | 19.1  | 17.8   | 74.4  | 17.6             | 17.9  |       | 15.6                  | 28.1   |        |       |           |
| Th                             | .9          |        | 4.6   |        | 4.8   | 1.8 <sup>+</sup> | 1.3   |       |                       | 8.3    |        |       |           |
| U                              | .7          |        |       |        | 1.1   | .75 <sup>+</sup> |       |       | 1.1                   | 4.3    |        |       |           |
| Zr                             | 144         | 111    | 119   | 134    |       |                  |       |       | 94.6                  | 317    |        |       |           |
| Nb                             | 4.7         | 4.1    | 4.4   | 12.3   |       |                  |       |       | 20.2                  | 44.8   |        |       |           |
| Cu                             | 88.5        | 47.2   | 25.2  | 25.3   | 34.7  | 41.0             | 28.6  |       | 15.3                  | 3.1    |        |       |           |
| Co                             |             |        |       |        |       |                  |       |       |                       |        |        |       |           |
| Ni                             | 7.6         | 26.5   | 3.0   | 7.5    | 15.0  | 8.6              | 9.2   |       | 11.6                  | 2.2    |        |       |           |
| V                              | 267         | 234    | 125   | 142    | 219   | 193              | 157   |       | 52.9                  | 8.6    |        |       |           |
| Cr                             | 59.4        | 74.5   | 43.2  | 46.4   | 35.5  | 45.2             | 42.1  |       | 12.1                  | 6.5    |        |       |           |
| Ga                             | 12.5        | 21.7   | 34.2  | 18.1   | 8.6   | 12.3             | 16.2  |       | 14.4                  | 16.5   |        |       |           |
| Zn                             | 85.2        | 60.7   | 59.9  | 39.8   | 37.2  | 58.0             | 57.5  |       | 45.2                  | 67.9   |        |       |           |

Table 2.5.

Chemical analyses of amphibole bearing rocks from Carpathians and Hunter River, N.S.W.

|                                | Carpathians (Europe) |       |       |                    |                    | Hunter River Valley, N.S.W. |                   |                   |                   |       |                   |                   |        |                   |                   |       |
|--------------------------------|----------------------|-------|-------|--------------------|--------------------|-----------------------------|-------------------|-------------------|-------------------|-------|-------------------|-------------------|--------|-------------------|-------------------|-------|
|                                | 34                   | 194   | 31    | 32                 | 33                 | 9                           | 10                | 7                 | 8                 | 15    | 13                | 14                | 12     | 17                | 11                | 16    |
| SiO <sub>2</sub>               | 56.56                | 59.76 | 61.29 | 62.04              | 62.54              | 62.44                       | 63.60             | 63.78             | 64.44             | 65.83 | 65.87             | 65.89             | 66.20  | 66.37             | 67.21             | 67.99 |
| TiO <sub>2</sub>               | .95                  | .49   | .68   | .52                | .65                | .75                         | .66               | .65               | .66               | .58   | .51               | .50               | .55    | .46               | .46               | .50   |
| Al <sub>2</sub> O <sub>3</sub> | 17.12                | 18.25 | 16.29 | 16.94              | 16.95              | 16.70                       | 15.33             | 15.03             | 15.30             | 15.82 | 15.20             | 15.84             | 16.39  | 15.17             | 14.94             | 14.70 |
| Fe <sub>2</sub> O <sub>3</sub> | 3.78                 | 1.87  | 2.85  | 2.27               | 3.76               | 1.94                        | 1.74              | 1.74              | 1.54              | 1.21  | 1.23              | 1.42              | 1.71   | 1.21              | .40               | 1.49  |
| FeO                            | 4.25                 | 2.55  | 1.99  | 2.68               | 1.18               | 3.00                        | 2.32              | 2.15              | 2.92              | 2.37  | 2.57              | 2.09              | 2.26   | 2.50              | 2.69              | 2.34  |
| MnO                            | .15                  | .12   | .10   | .10                | .06                | .09                         | .09               | .07               | .10               | .07   | .07               | .05               | .08    | .07               | .06               | .06   |
| MgO                            | 2.60                 | 1.81  | 2.22  | 1.99               | 1.19               | 2.37                        | 2.18              | 1.71              | 1.98              | 1.43  | 1.45              | 1.57              | 1.58   | 1.32              | 1.18              | 1.14  |
| CaO                            | 6.33                 | 6.67  | 4.73  | 5.30               | 4.67               | 4.46                        | 3.90              | 4.38              | 3.38              | 2.95  | 3.18              | 3.08              | 3.12   | 2.83              | 2.55              | 3.19  |
| Na <sub>2</sub> O              | 2.66                 | 4.06  | 3.19  | 3.19               | 3.80               | 3.80                        | 3.55              | 3.76              | 3.81              | 3.95  | 3.70              | 3.82              | 3.89   | 3.90              | 3.73              | 3.19  |
| K <sub>2</sub> O               | 1.94                 | 1.28  | 2.78  | 2.15               | 2.62               | 2.51                        | 2.68              | 1.70              | 2.96              | 3.27  | 3.48              | 3.41              | 3.10   | 3.52              | 4.03              | 3.72  |
| P <sub>2</sub> O <sub>5</sub>  | .19                  | .22   | .28   | .19                | .17                | .18                         | .18               | .15               | .15               | .14   | .13               | .12               | .13    | .12               | .18               | .12   |
| loss (H <sub>2</sub> O)        | 3.09                 | 1.87  | 2.85  | 2.45               | 2.35               | 1.74                        | 1.89              | 4.15              | 2.75              | 1.75  | 1.58              | 1.88              | 1.42   | 2.61              | 2.41              | 1.48  |
| total                          | 99.62                | 99.95 | 99.25 | 99.82              | 99.94              | 99.98                       | 99.74             | 99.27             | 99.99             | 99.37 | 98.97             | 99.67             | 100.43 | 100.08            | 99.84             | 99.92 |
| Rb                             | 82.9                 | 59.0  | 142   |                    | 113                |                             |                   |                   | 91.0              |       |                   | 156               | 160    |                   | 155               |       |
| Ba                             | 519                  |       | 817   | 636                | 892                | 633                         | 445               | 675               | 639               | 658   | 618               | 663               | 656    | 665               | 635               | 703   |
| Pb                             | 11                   | 9     |       | 10                 |                    |                             |                   | 7                 |                   |       |                   |                   | 16     |                   | 2                 |       |
| Sr                             | 287                  | 1345  | 425   | 337                | 298                |                             |                   |                   | 393               |       |                   | 319               | 422    |                   | 306               | 568   |
| La                             | 19.5                 |       | 27.9  | 23.2               | 24.5               | 22.3                        | 19.5              | 22.4              | 24.6              | 26.2  | 22.0              | 26.5              | 26.3   | 22.2              | 24.3              | 22.4  |
| Ce                             | 46.6                 |       | 67.6  | 57.5               | 57.7               | 48.8                        | 45.7              | 57.9              | 52.9              | 62.2  | 56.8              | 63.6              | 63.4   | 57.5              | 65.8              | 58.1  |
| Pr                             | 11.0                 |       | 13.6  | 8.8                | 10.5               | 7.6                         |                   | 7.7               | 7.0               | 16.1  | 8.7               | 8.7               | 3.6    | 9.6               | 6.2               | 11    |
| Na                             | 18.5                 |       | 18.1  | 13.1               | 18.3               | 18.6                        |                   | 19.5              | 19.5              | 26.3  | 18.0              | 18.7              | 21.8   | 23.4              | 15.2              | 25.0  |
| Y                              | 36.2                 | 34.6  | 35.4  | 30.7               | 38.3               |                             |                   | 8.5               | 35.9              |       |                   | 47.4              | 48.9   |                   | 50.3              |       |
| Th                             | 7.40 <sup>+</sup>    | 5.6   | 12.9  | 10.51 <sup>+</sup> | 13.22 <sup>+</sup> | 12.9 <sup>+</sup>           | 13.9 <sup>+</sup> | 13.7 <sup>+</sup> | 14.5 <sup>+</sup> | 16.8  | 17.1 <sup>+</sup> | 16.6 <sup>+</sup> | 15.0   | 17.4 <sup>+</sup> | 18.8 <sup>+</sup> | 14.8  |
| U                              | 2.11 <sup>+</sup>    | 1.2   | 3.77  | 2.83 <sup>+</sup>  | 2.57 <sup>+</sup>  | 3.6 <sup>+</sup>            | 3.9 <sup>+</sup>  | 3.9 <sup>+</sup>  | 4.1 <sup>+</sup>  | 4.2   | 4.1 <sup>+</sup>  | 4.2 <sup>+</sup>  | 4.6    | 4.0 <sup>+</sup>  | 4.6 <sup>+</sup>  | 4.1   |
| Zr                             | 153                  |       | 172   | 138                | 184                | 190                         | 180               | 177               | 195.6             | 221   | 225               | 217               | 227    | 216               | 213               | 203   |
| Nb                             | 20.9                 |       | 28.4  | 17.7               | 20.8               | 7.8                         | 8.5               | 24                | 8.4               | 9.8   | 8.4               | 9.5               | 8.4    | 7.3               | 8.5               | 7.7   |
| Cu                             | 21.0                 |       | 16.3  | 16.1               | 17.5               | 42.1                        | 19.3              | 11.2              | 17.4              | 29.3  | 17.5              | 18.3              | 28.4   | 20.8              | 20.8              | 23.7  |
| Co                             |                      |       |       |                    |                    |                             |                   |                   |                   |       |                   |                   |        |                   |                   |       |
| Ni                             | 5.6                  |       | 2.2   | 3.1                | 2.6                | 7.9                         | 4.6               | 7.2               | 5.1               | 3.7   | 6.0               | 3.6               | 9.4    | 4.7               | 2.8               | 4.5   |
| V                              | 194                  |       | 89.3  | 88.1               | 69.3               | 106                         | 91.1              | 86.7              | 89.0              | 87.8  | 62.9              | 60.3              | 67.5   | 59.2              | 53.9              | 52.3  |
| Cr                             | 15.2                 |       | 12.3  | 11.3               | 11.5               | 29.5                        | 28.3              | 26.5              | 14.5              | 18.0  | 23.4              | 10.2              | 25.6   | 21.5              | 19.1              | 23.5  |
| Ga                             | 17.7                 |       | 21.5  | 15.8               | 16.1               |                             | 19.3              | 20.1              |                   |       | 16.8              | 18.8              |        |                   | 4.3               | 48.1  |
| Zn                             | 82.4                 |       | 64.0  | 63.2               | 63.1               | 99.4                        | 57.4              | 61.1              | 35.5              | 70.4  | 61.8              | 63.5              | 74.1   | 68.3              | 63.4              |       |

Table 2.6. Chemical analyses of studied rocks from New Guinea Highlands

|                                | 107   | 102   | 105    | 109   | 108   | 99     | 101   | 95    |
|--------------------------------|-------|-------|--------|-------|-------|--------|-------|-------|
| SiO <sub>2</sub>               | 51.74 | 53.74 | 54.81  | 55.45 | 57.66 | 48.94  | 59.27 | 57.22 |
| TiO <sub>2</sub>               | 1.16  | 1.05  | 1.10   | .75   | .73   | .87    | .56   | .67   |
| Al <sub>2</sub> O <sub>3</sub> | 16.78 | 15.84 | 15.10  | 18.87 | 18.77 | 13.84  | 15.90 | 17.95 |
| Fe <sub>2</sub> O <sub>3</sub> | 3.32  | 3.25  | 2.59   | 2.60  | 4.44  | 2.53   | 2.22  | 2.23  |
| FeO                            | 5.23  | 4.85  | 6.28   | 3.60  | 1.84  | 6.52   | 3.19  | 4.70  |
| MnO                            | .13   | .11   | .15    | .13   | .13   | .15    | .10   | .13   |
| MgO                            | 6.39  | 6.36  | 6.14   | 4.26  | 3.92  | 12.66  | 5.45  | 3.74  |
| CaO                            | 8.81  | 7.90  | 8.62   | 5.19  | 4.86  | 7.17   | 5.90  | 6.70  |
| Na <sub>2</sub> O              | 2.46  | 2.38  | 2.26   | 2.55  | 2.50  | 2.29   | 2.67  | 2.50  |
| K <sub>2</sub> O               | 2.32  | 2.57  | 2.71   | 2.39  | 2.76  | 2.33   | 2.68  | 1.50  |
| P <sub>2</sub> O <sub>5</sub>  | .64   | .54   | .69    | .44   | .40   | .59    | .41   | .43   |
| Loss(ΣH <sub>2</sub> O)        | .75   | 1.11  | .26    | 3.32  | 1.35  | 2.40   | 1.46  | 1.96  |
| total                          | 99.73 | 99.70 | 100.45 | 99.55 | 99.36 | 100.29 | 99.81 | 99.75 |
| Rb                             | 60.2  |       | 98.3   |       | 76.1  | 60.0   | 111   |       |
| Pb                             | 4     |       | 8      |       | 14    | 7      | 16    |       |
| Sr                             | 592   |       | 611    |       | 603   | 530    | 840   |       |
| Y                              | 22.5  |       | 35.8   |       |       | 24.1   | 28.5  |       |
| Th                             | 1.6   |       | 1.3    |       | 4.5   | 1.8    | 2.7   |       |
| U                              |       |       | 3.2    |       | 2.1   | .4     | 1.3   |       |
| Ga                             | 14.8  |       | 18.2   |       | 20.8  | 16.3   | 14.3  |       |

Table 2.7. CHEMICAL ANALYSES OF STUDIED ROCKS FROM SOLOMON ISLANDS

|                                | 155    | 144    | 170    | 160   | 168    | 161    | 164   | 171   | 165   | 174    | 175    | 176   |
|--------------------------------|--------|--------|--------|-------|--------|--------|-------|-------|-------|--------|--------|-------|
| SiO <sub>2</sub>               | 57.02  | 56.08  | 59.95  | 66.80 | 67.96  | 42.15  | 42.27 | 44.45 | 44.61 | 45.17  | 46.93  | 52.68 |
| TiO <sub>2</sub>               | .56    | .53    | .86    | .23   | .22    | 1.32   | 1.28  | 1.23  | 1.20  | 1.16   | .63    | .72   |
| Al <sub>2</sub> O <sub>3</sub> | 18.89  | 19.04  | 16.03  | 18.24 | 18.76  | 11.72  | 10.64 | 10.45 | 12.29 | 15.75  | 5.26   | 17.27 |
| Fe <sub>2</sub> O <sub>3</sub> | 3.56   | 3.70   | 5.50   | 1.25  | 1.21   | 9.00   | 11.94 | 5.54  | 5.35  | 6.05   | 4.03   | 4.94  |
| FeO                            | 2.66   | 3.10   | .38    | 1.02  | 1.03   | 3.39   | 4.45  | 5.97  | 7.40  | 6.61   | 5.70   | 2.68  |
| MnO                            | .16    | .14    | .09    | .06   | .06    | .12    | .17   | .12   | .16   | .21    | .12    | .12   |
| MgO                            | 2.93   | 3.83   | 4.95   | 1.50  | 1.42   | 14.75  | 11.84 | 14.08 | 12.45 | 9.52   | 17.59  | 4.54  |
| CaO                            | 8.09   | 8.04   | 6.27   | 3.17  | 2.55   | 13.51  | 15.22 | 14.42 | 14.36 | 13.17  | 18.64  | 8.02  |
| Na <sub>2</sub> O              | 3.77   | 4.18   | 4.04   | 4.97  | 4.36   | 3.49   | 1.18  | 1.65  | 1.44  | 1.82   | .50    | 3.86  |
| K <sub>2</sub> O               | 1.60   | .88    | 2.08   | 1.92  | 2.08   | .42    | .22   | .48   | .30   | .38    | .05    | .84   |
| P <sub>2</sub> O <sub>5</sub>  | .27    | .16    | .33    | .09   | .08    | .01    | .04   | .02   | .03   | .08    | .01    | .20   |
| loss (ΣH <sub>2</sub> O)       | 1.35   | .82    | .16    | .26   | .36    | .16    | .58   | 1.10  | .12   | .31    | .68    | 2.46  |
| Total                          | 100.86 | 100.50 | 100.63 | 99.54 | 100.10 | 100.04 | 99.83 | 99.51 | 99.71 | 100.23 | 100.14 | 98.33 |
| Rb                             | 32     | 18     |        | 47    | 50     | 2      | 4     |       |       |        |        |       |
| Pb                             | 6      | 5      | 10     | 14    | 12     | 2      | 3     |       |       |        |        |       |
| Sr                             | 757    | 739    | 1245   | 1254  | 1339   | 257    | 379   |       |       |        |        |       |
| Y                              | 23     | 15     | ---    | 16    | 13     | 13     | 14    |       |       |        |        |       |
| Th                             | 2.2    | 1.3    | 2.7    | 1.6   | 3.3    | ---    | ---   |       |       |        |        |       |
| U                              | 1.9    | ---    | ---    | 1.1   | 0.8    | 2.6    | 4.8   |       |       |        |        |       |
| Ga                             | 17     | 19     | 28     | 23    | 25     | 15     | 17    |       |       |        |        |       |

TABLE 2.8

Hornblende andesites in the western circum-Pacific belt

| Arc                        | Depth to M-discontinuity in km | magma type occurring                     | inferred* and actual depth to Benioff zone | hornblende-bearing rocks             |
|----------------------------|--------------------------------|------------------------------------------|--------------------------------------------|--------------------------------------|
| Aleutians without Bogoslof |                                | calc-alkaline                            | 135*                                       | minor occurrences                    |
| Aleutians Bogoslof Is.     |                                | calc-alkaline with high-K                | 190*                                       | common                               |
| Eastern Kamchatka          |                                | tholeiitic, calc-alkaline                | 90-135                                     | minor occurrences (ghost amphiboles) |
| Central Kamchatka          |                                | calc-alkaline alkaline                   | 200                                        | numerous occurrences                 |
| Central Kuriles            | 9-20                           | tholeiitic                               | 100                                        | do not occur (ghost amphiboles)      |
| Northern Kuriles           | 25-30                          | tholeiitic calc-alkaline                 | 140                                        | minor occurrences                    |
| Southern Kuriles           | 15-20                          | tholeiitic                               | 100                                        | do not occur                         |
| Western Kuriles            | 30-35                          | calc-alkaline                            | 150                                        | common                               |
| Honshu (east)              | 15-20                          | tholeiitic calc-alkaline                 | 100 - 250                                  | common                               |
| Izu-Marianas               | 12-15                          | tholeiitic with calc-alkaline tendencies | 100                                        | do not occur (ghost amphiboles only) |

TABLE 2.8 (continued)

| Arc             | Depth to<br>M-dis-<br>contin-<br>uity in<br>km | magma type<br>occurring                    | inferred*<br>and actual<br>depth to<br>Benioff<br>zone | hornblende-<br>bearing rocks     |
|-----------------|------------------------------------------------|--------------------------------------------|--------------------------------------------------------|----------------------------------|
| New Guinea      | 15-25                                          | tholeiitic<br>calc-alkaline<br>shoshonitic | 100<br>150*<br>180                                     | do not occur<br>common<br>common |
| Solomons        | 12-15                                          | tholeiitic<br>calc-alkaline                | 150-165*                                               | do not occur<br>common           |
| New<br>Hebrides | 12-15                                          | tholeiitic<br>calc-alkaline                |                                                        | do not occur<br>do not occur     |
| Fiji            | 30                                             | calc-alkaline<br>shoshonitic               |                                                        | common<br>have not been<br>found |
| Tonga           | 10-15                                          | tholeiitic                                 | 100                                                    | do not occur                     |

that the oxidation state of most rocks is only slightly lower than the oxidation state of their cumulates whereas the  $\text{FeO}/\text{Fe}_2\text{O}_3$  ratio of accidental inclusions is substantially lower.

Amphibole is present in rocks of andesitic and dacitic composition more often than in low-Si andesites; in high-Al basalts in contrast to alkaline basaltic rocks of oceanic areas e.g. Tahiti (McBirney and Aoki, 1969), amphibole does not occur frequently and clinopyroxene and/or olivine occur instead. Biotite is usually confined to rocks with more than 60% of  $\text{SiO}_2$  but the occurrence of numerous amphibole and/or biotite-bearing cognate inclusions shows that both these phases may lie on the liquidus.

In the volcanic rocks studied from Eastern Papua, two groups of inclusions occur:

(a) Low-K, high-Ca inclusions usually consist of olivine + clinopyroxene + spinel sometimes with interstitial amphibole and plagioclase. These also have low  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents and low  $\text{FeO}/\text{Fe}_2\text{O}_3$  ratio.

(b) High-K inclusions are mostly amphibole + plagioclase + biotite with  $\text{SiO}_2$  content between 50 and 56%. These have most of the chemical features of their high-K calc-alkaline hosts.

### New Guinea Highlands

Analyzed samples of amphibole-bearing and amphibole-free rocks from the Cenozoic stratovolcanoes, Mt Hagen and Mt Giluwe are presented in Table 2.6 and Jakeš and White (1969, Table III). These rocks are shoshonitic and are chemically identical with those described from the Lesser Sunda Islands (Joplin, 1968) and similar in mineralogy and chemistry to rocks described by Dickinson et al. (1968) and Gill (1970) from Fiji. They are comparable to classical shoshonites from the Yellowstone area (Nicholls & Carmichael, 1969).

The  $\text{SiO}_2$  content ranges from 50-59% in 8 samples analysed; this is less than the range in typical calc-alkaline associations (Fig. 2.2). Furthermore field observations and chemical data suggest that low-Si members (averaging 54%) make up the bulk of the recent lavas and more siliceous rocks, commonly amphibole-bearing, are subordinate. The  $\text{Al}_2\text{O}_3$  content of rocks of this series varies widely, as in high-K andesites. The ratio of  $\text{K}_2\text{O}$  to  $\text{Na}_2\text{O}$  is close to 1.0 and this is a typical feature of shoshonites. The average CaO content is similar to that of high-Al basalts but is higher than for most shoshonites. It is apparent from  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  vs.  $\text{SiO}_2$  diagrams and from Harker variation diagrams (Fig. 2.3, 2.2) that there is only a

slight increase in alkali content with increase of  $\text{SiO}_2$ . There is no distinct trend in the AMF diagram (Fig.2 in Jakeš and White, 1969). Joplin (1968) also noted little iron enrichment in shoshonites compared to alkali basalts.

### Solomon Islands

Both sample areas, the Savo volcano and Mt Gallego on NE Guadalcanal, are Cenozoic calc-alkaline rocks in which pyroclastic types predominate. Amphibole-bearing rocks make up more than 60% of the recently exposed rocks. The five amphibole-bearing rocks analysed show all the characteristic features of the calc-alkaline association (Table 2.7, and Table 5 in Jakeš and White, 1969). They are relatively high in  $\text{Al}_2\text{O}_3$ , and are strongly oxidized and there is a preponderance of  $\text{Na}_2\text{O}$  over  $\text{K}_2\text{O}$ . Except for sample 144,  $\text{K}_2\text{O}$  content is similar to that of rocks from neighbouring Bougainville (Taylor et al., 1963). Total iron is relatively high, but still within the field of the calc-alkaline association (Fig.2 in Jakeš and White, 1969). In the Savo volcano, amphibole- and biotite-bearing silica-rich rocks ( $\approx 60\%$ ) predominate. The inclusions in these rocks (analyses in Table 2.7) can be divided into two groups:

- (a) accidental inclusions, with textural and mineralogical features suggesting that they are from

the neighbouring belt of ultramafic rocks (composed of clinopyroxene + olivine + spinel)

- (b) cognate inclusions, cumulative in origin and composed of amphibole, plagioclase, clinopyroxene and minor opaque phases.

#### New Zealand

The analyzed samples from New Zealand (Table 2.4, Nos 47, 48, 50) are from Mt Egmont where amphibole-bearing rocks prevail over amphibole-free rocks and where lavas are associated with large volumes of pyroclastic rocks (Gow, 1968). Sample 46, is an amphibole-bearing andesite from Solander Island. Samples from both localities can be classified as low- and medium-K andesites and have been described by Hatherton (1968) as examples of "miogeosynclinal" andesites. Analyses presented by Gow (1968) from Mt Egmont show a relatively small variation in  $\text{SiO}_2$  content and relatively high  $\text{Al}_2\text{O}_3$  content. Values for  $\text{Al}_2\text{O}_3$  and for  $\text{K}_2\text{O}$  presented here are lower than those given by Gow (1968). Comparison of analyses of the three amphibole-bearing andesites from Mt Egmont show that these rocks do not differ in any respect from calc-alkaline (amphibole-free) rocks of the same area.

### Fiji

Two of four analysed rocks (Table 2.4) are very close to the average circum-Pacific andesite of Taylor and White (1966), and are from the same locality as rock X-88 of Taylor et al. (1969). The sample from Vanua Levu (2) has several exceptional features: very low  $K_2O$  content, and relatively high  $CaO$  and  $Al_2O_3$ . The different age (Pliocene) and different geological setting of this rock can account for such peculiarities and also for slightly different composition of amphibole (c.f. Gill, 1970). Sample 52 is an amphibole cumulate from rock 6.

### Western United States

Two samples from the Cenozoic Cascades province have been analysed (Table 2.4). The lavas of Mt Shasta (5), according to Smith and Carmichael (1968) are characterized by a small range of  $SiO_2$  contents, relatively high  $Al_2O_3$  and a low content of  $FeO + Fe_2O_3$  and  $K_2O$ . Although the slight "iron enrichment" observed in the Shasta samples is characteristic of other amphibole-bearing rocks, low  $K_2O$  content is not a typical feature of Shasta rocks or amphibole-bearing rocks in general; the amphibole-bearing rocks, however, are relatively rare at Mt Shasta (Smith and Carmichael, 1968). A scoriaceous low-Si andesite (53) from Mt Mazama has all the features of the Cenozoic Southern Cascades lavas; high  $Al_2O_3$

and low alkalis, especially  $K_2O$ . The Mt Elden sample (1) from San Francisco Peaks (Arizona) has a higher content of alkali elements, very low total Fe and low  $CaO$ .

#### Carpathians - Europe

The Tertiary calc-alkaline rocks from the Carpathians (Table 2.5) differ slightly from calc-alkaline andesites of Recent island arcs. According to data presented by Kuthan (1968) andesites and rhyolites occur frequently, intermediate rocks with  $\approx 66\% SiO_2$  are relatively rare and basaltic rocks are very rare. Kuthan's (1968) data indicate a wide range of  $Al_2O_3$  values, varied mineralogy, and numerous occurrences of garnet-bearing andesites. Analysed samples can be classified as medium to high-K andesites with a relatively high oxidation state and low  $CaO$  and  $MgO$  contents.

#### Hunter River area, N.S.W.

The dacites and rhyodacites of Carboniferous age show all the calc-alkaline tendencies (Table 2.5). A characteristic feature is a relatively uniform  $Na_2O$  content and steep positive gradient of  $K_2O$  vs.  $SiO_2$  (Fig. 2.5). The values of  $FeO/Fe_2O_3$  are low in comparison to recent amphibole-bearing rocks. Their exceptional feature is a high and uniform  $SiO_2$  content, over a geologically large area. Recent dacites in island arcs are not frequent and usually are confined to small

areas, but the geological setting and major element chemistry of the Hunter River lavas are more like those of the Andean andesitic and rhyolite association.

#### Amphibole-bearing vs amphibole-free rocks in island arcs

New analyses of amphibole-bearing rocks of recent island arcs and of older orogenic areas together with the compiled data show that these rocks do not differ substantially from amphibole-free rocks of similar  $K_2O$  content. Amphibole is a common ferromagnesian phase in andesitic or dacitic members of the calc-alkaline association and occurs in  $SiO_2$ -rich rocks of the shoshonite association (latites and banakites). Amphiboles do not occur commonly in rocks of the tholeiitic association in island arcs, although "ghost amphiboles" i.e. pseudomorphs of magnetite + plagioclase + pyroxene have been described (Schmidt, 1957). Hatherton (1968) has suggested that amphibole andesites are typical "miogeosynclinal andesites". If his suggestion is correct then the occurrence of amphibole-bearing andesites in older orogenic regions may have paleogeographical implications. In order to evaluate such a suggestion, chemical data on amphibole-bearing andesites have been compiled and plotted in the form of simple diagrams;  $K_2O$  vs.  $SiO_2$ ,  $Na_2O + K_2O$  vs.  $SiO_2$ ,  $Fe_2O_3$  vs.  $FeO$  and also AMF diagrams.

They show that the role of amphibole andesites is not as clear as is indicated by data on "miogeosynclinal volcanoes" of New Zealand (Mt Egmont and Solander Is.) by Hatherton (1968), and further that amphibole andesites do not form a specific and distinct group of single genetic importance. They are members of several chemically distinct rock series. Simple conclusions relating to the presence or absence of amphibole cannot be made on the basis of present data, but  $\text{SiO}_2$  content appears to be a major controlling factor (Figs 2.6, 2.7, 2.8, 2.9). Amphibole occurs almost exclusively in rocks with  $\text{SiO}_2$  contents higher than 55% in the calc-alkaline association, but it rarely occurs in rocks with lower  $\text{SiO}_2$  content. It is not common in island arc tholeiites. Amphiboles are more commonly found in rocks with higher  $\text{K}_2\text{O}$  contents within the calc-alkaline and shoshonitic associations, and since the absolute  $\text{K}_2\text{O}$  content is also related to the slopes of  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  correlation and total alkali content, similar relations can be found also for these parameters. The  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio, as shown in Figs 2.10, 2.11, can be correlated with the presence of amphibole as amphibole occurs only in the more oxidized rocks with ratios of  $\text{Fe}_2\text{O}_3/\text{FeO}$  .5 - 1.2. This upper limit may be slightly high, due to secondary surface oxidation. Also, AMF diagrams (Fig. 2.12) show that amphibole occurs in rocks with a very small degree of iron enrichment, a feature

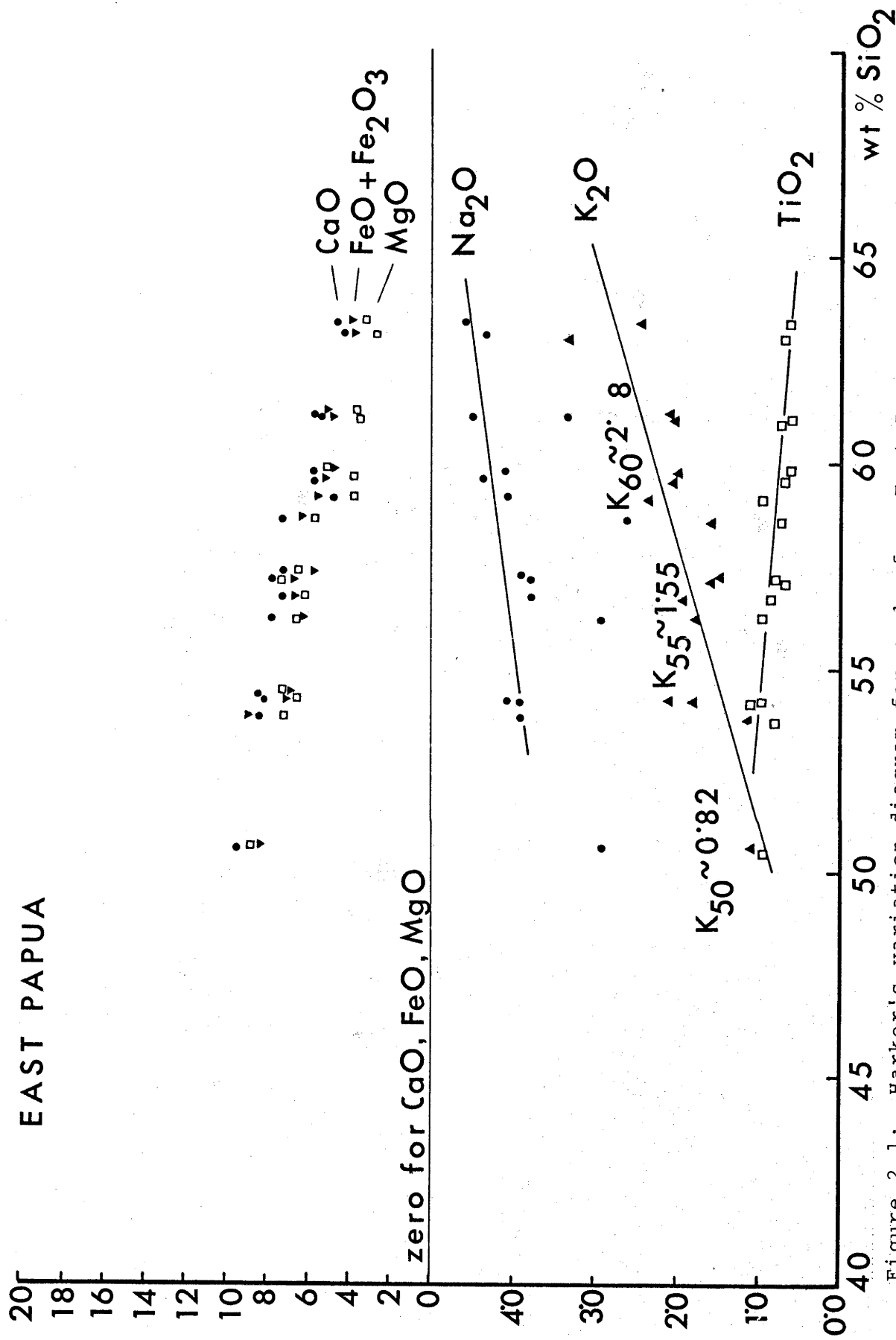


Figure 2.1: Harker's variation diagram for rocks from East Papua - Cape Nelson and Mt Lamington. Additional data in Jakes and Smith (1970) (Figs 3 and 5).

# NEW GUINEA HIGHLANDS

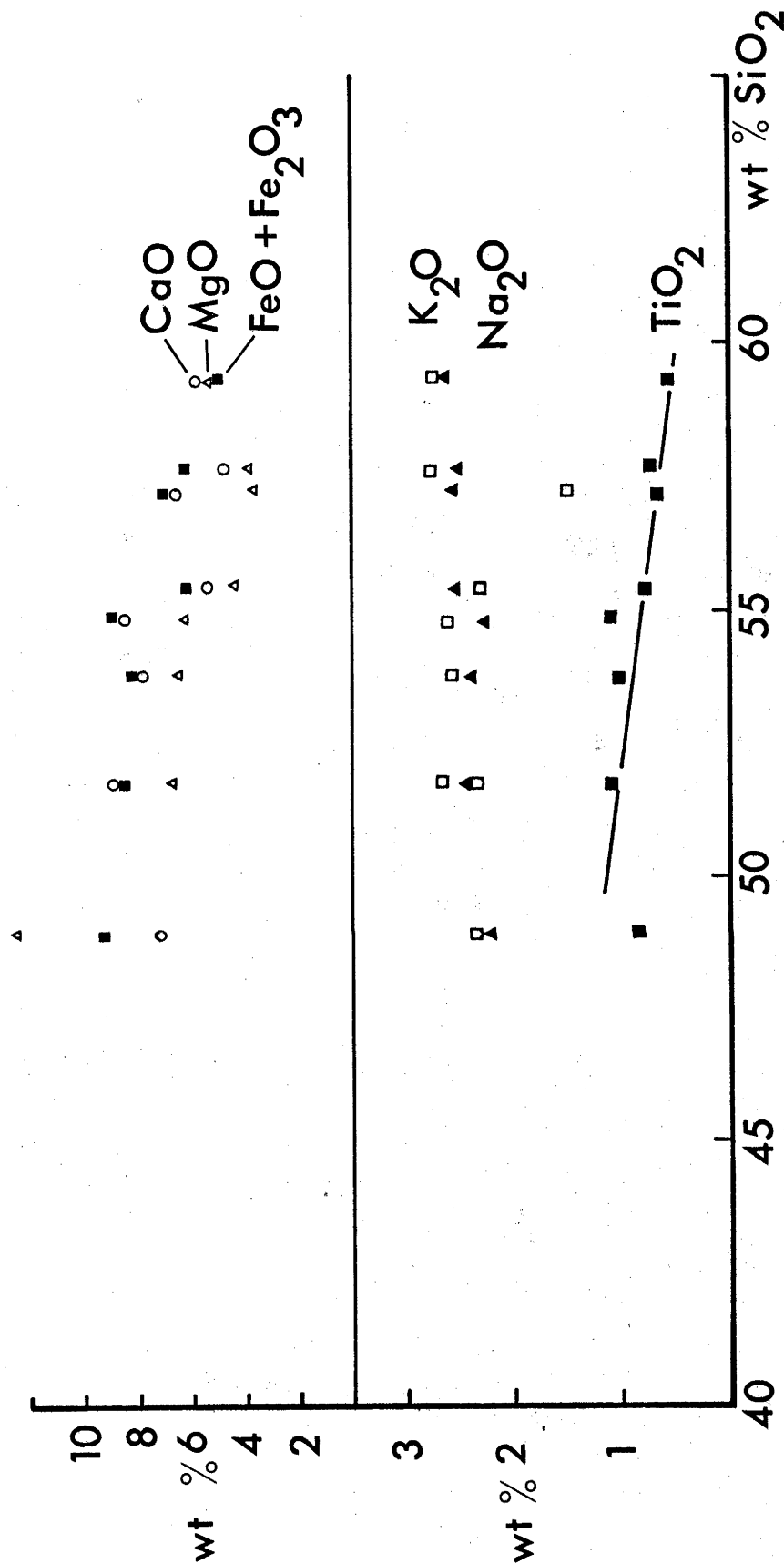


Figure 2.2: Harker's variation diagram for rocks from New Guinea Highlands.

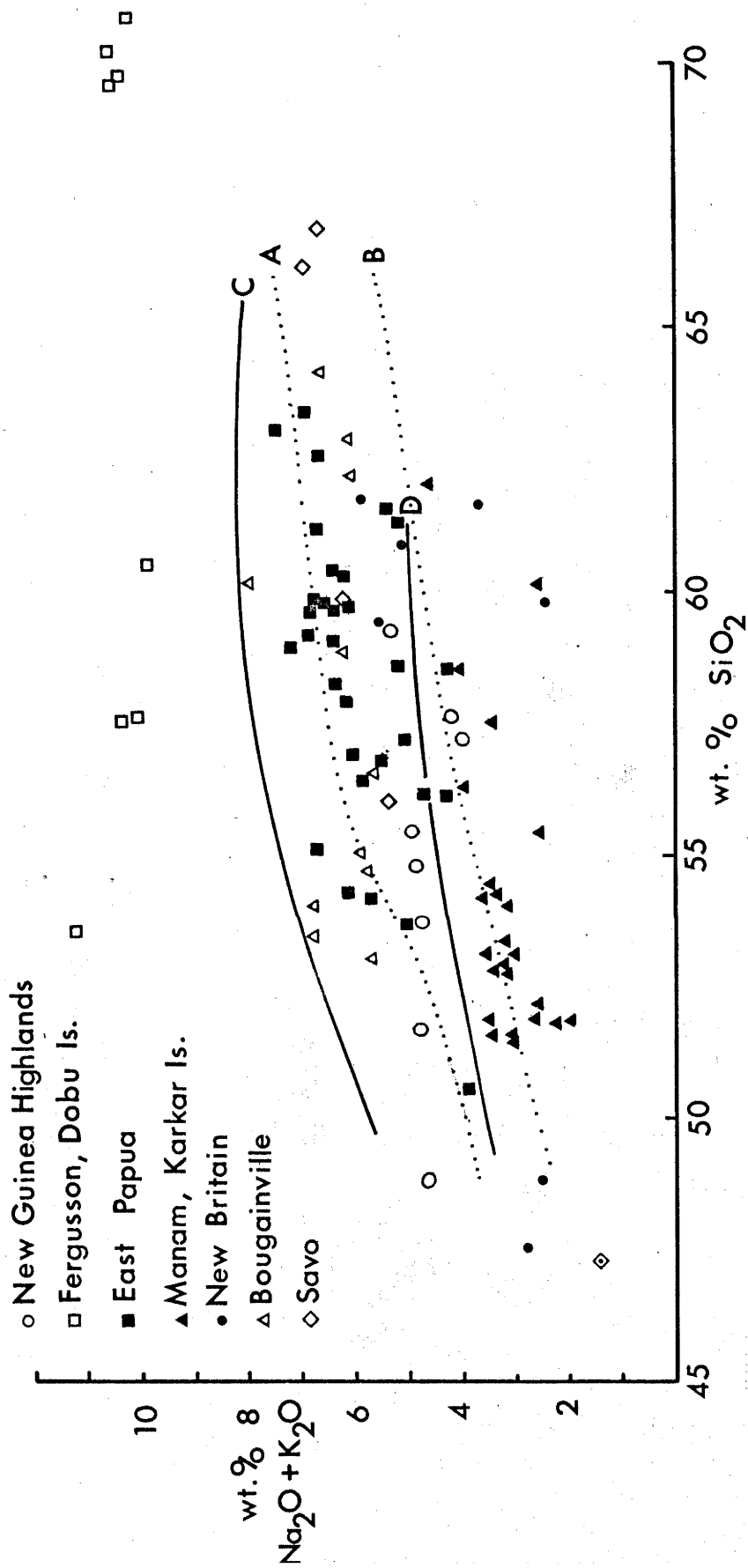


Figure 2.3: Variation diagram of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  of source rocks from Melanesia.

# SOLOMON ISLANDS

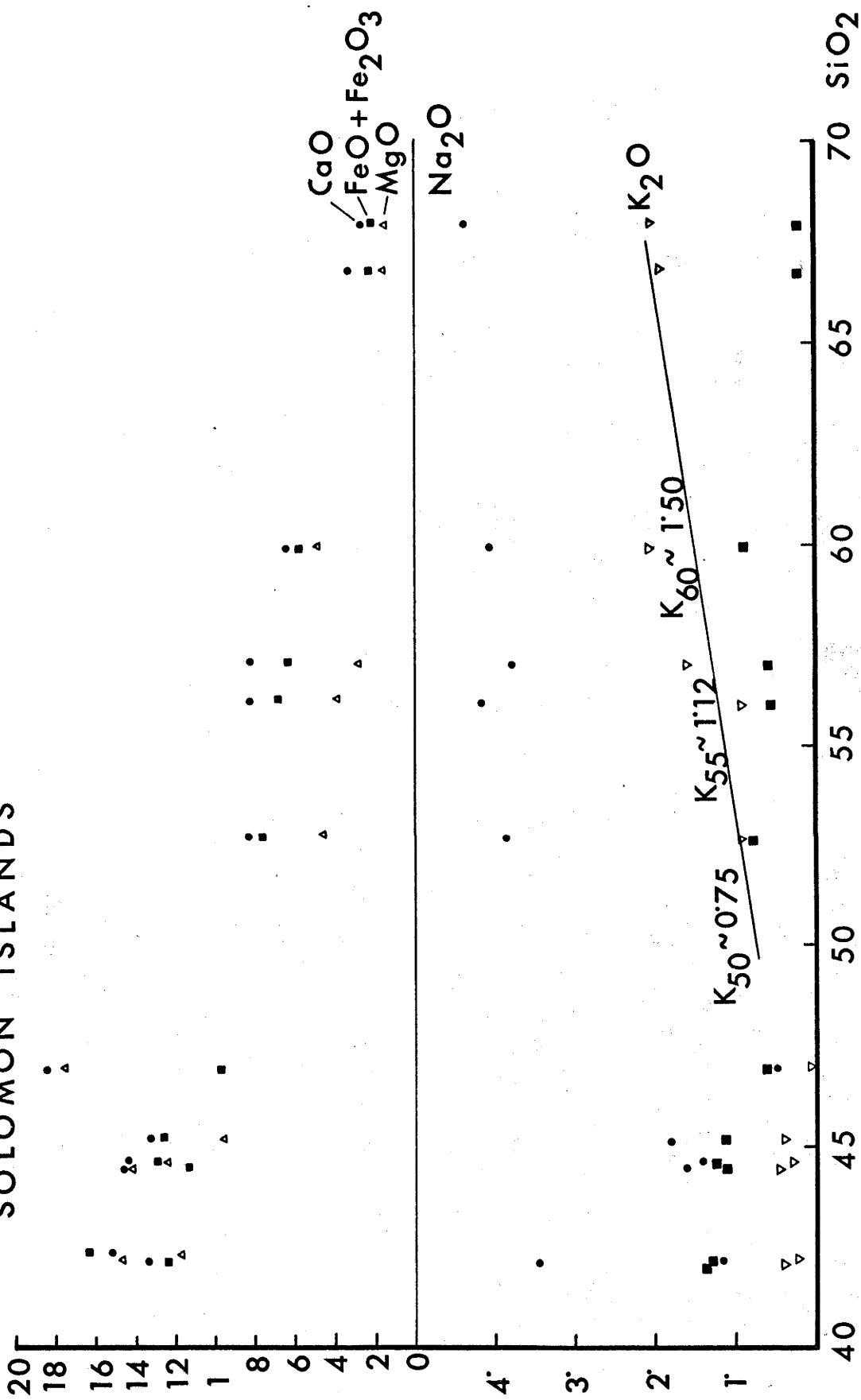
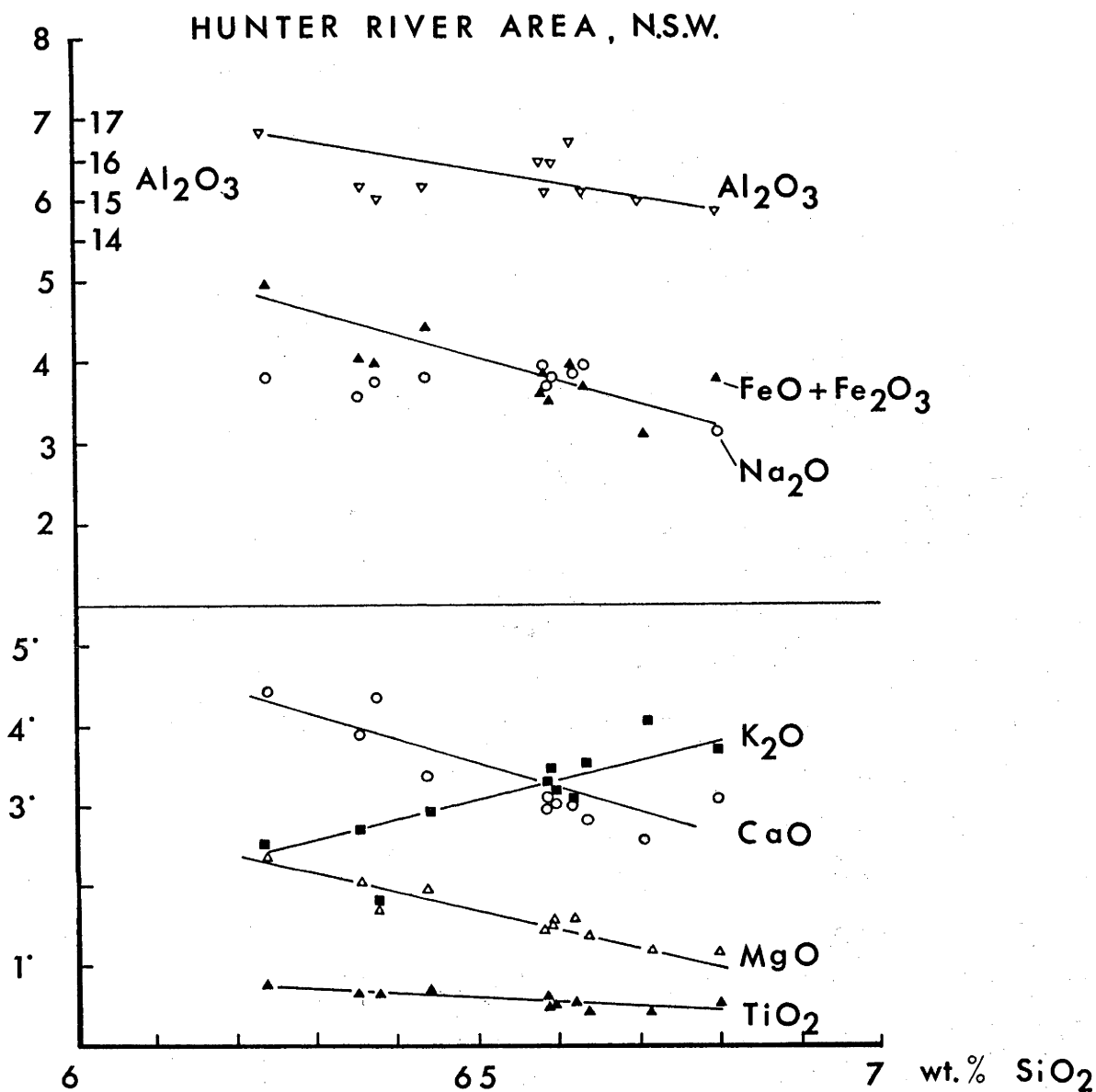


Figure 2.4: Harker's variation diagram for calc-alkaline rocks and their inclusions from Savo volcano and Isizu Point, Guadalcanal.



**Figure 2.5:** Harker's variation diagram for Carboniferous andesites and dacites of Hunter River area, N.S.W.

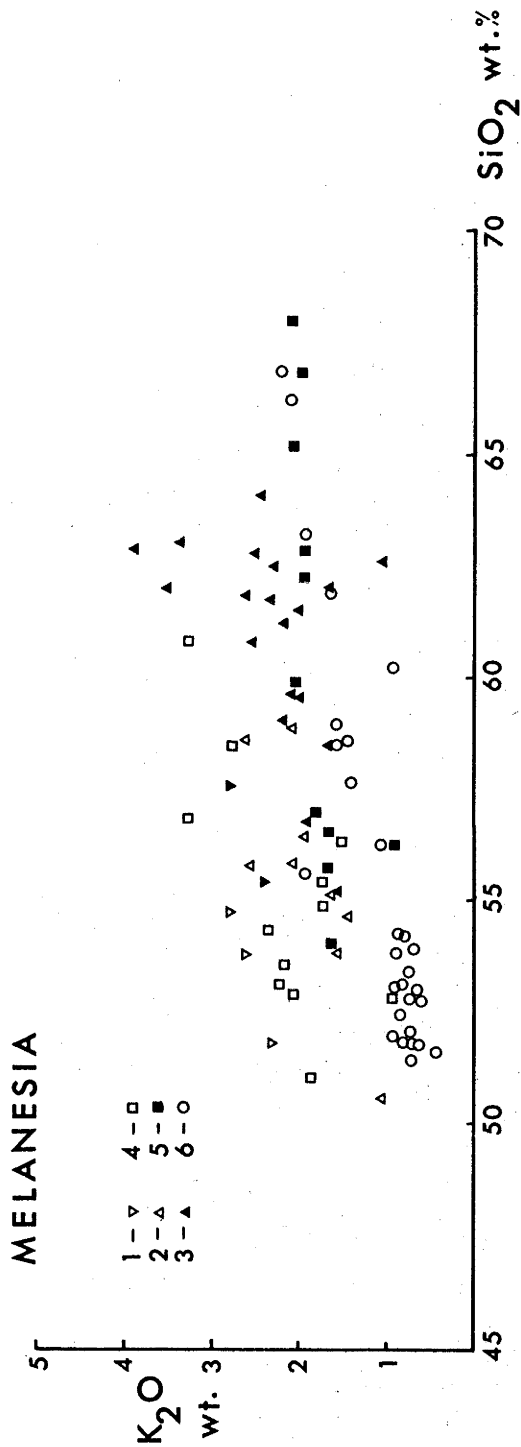


Fig. 2.6.  $K_2O$  vs.  $SiO_2$  plot for rocks from Melanesia. Empty symbols - amphibole-free rocks, filled symbols - amphibole bearing rocks. 1 - New Guinea Highlands, 2 and 3 Eastern Papua, 4 and 5 - Solomon Islands and Bougainville, 6 - New Britain and islands north of New Guinea.

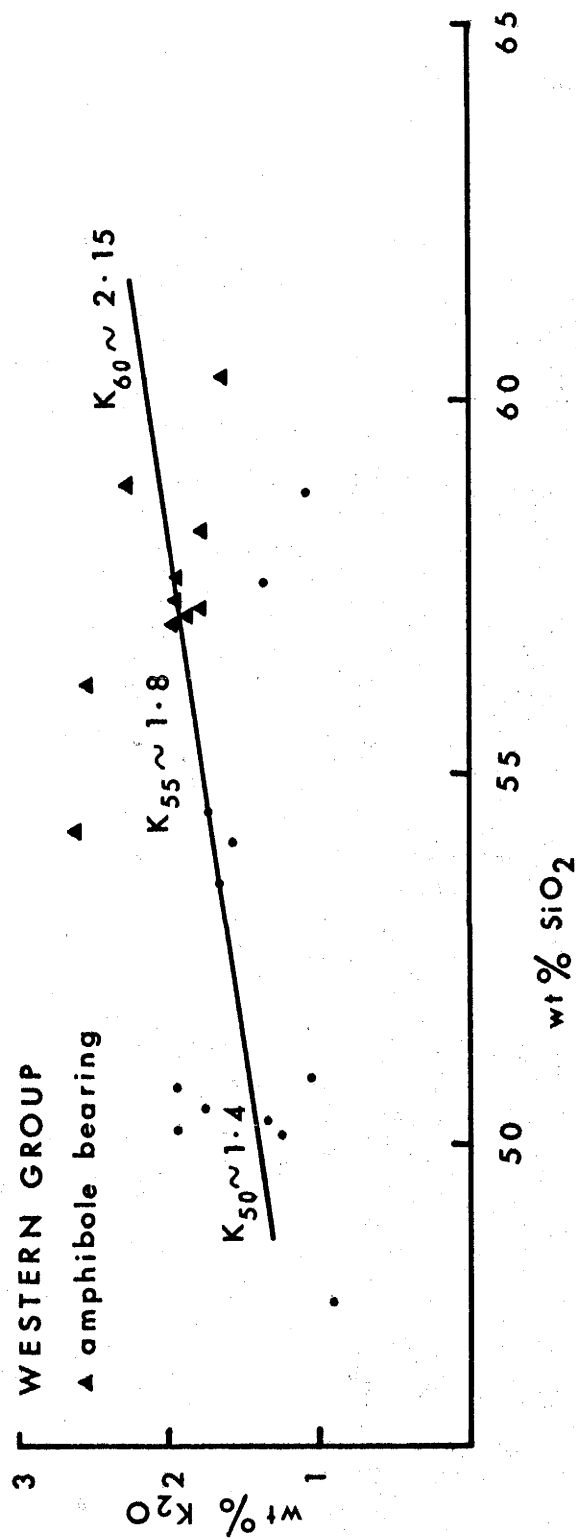


Fig. 2.7.  $K_2O$  vs.  $SiO_2$  for amphibole-bearing (triangles) and amphibole-free (dots) rocks of Western group of islands, Kurile Islands (data from Gorshkov, 1967).

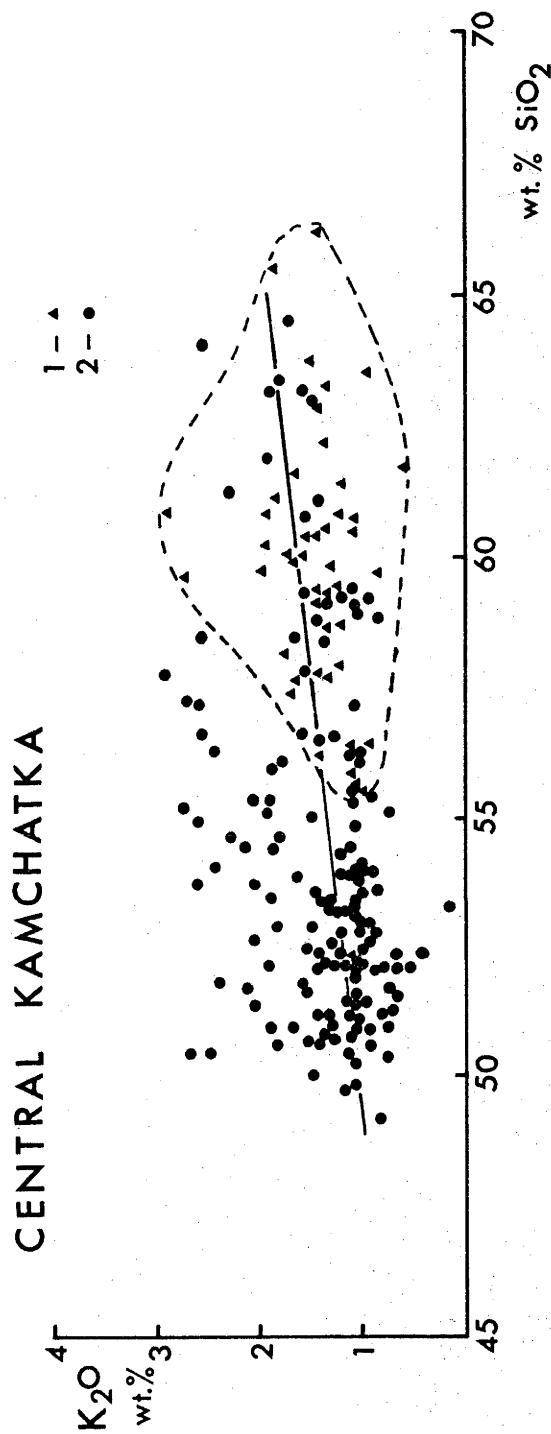


Fig. 2.8.  $K_2O$  vs.  $SiO_2$  plot for volcanic rocks from Central Kamchatka. Triangles amphibole-bearing rocks, dots- amphibole-free rocks. (Data from Ehrlich, 1968)

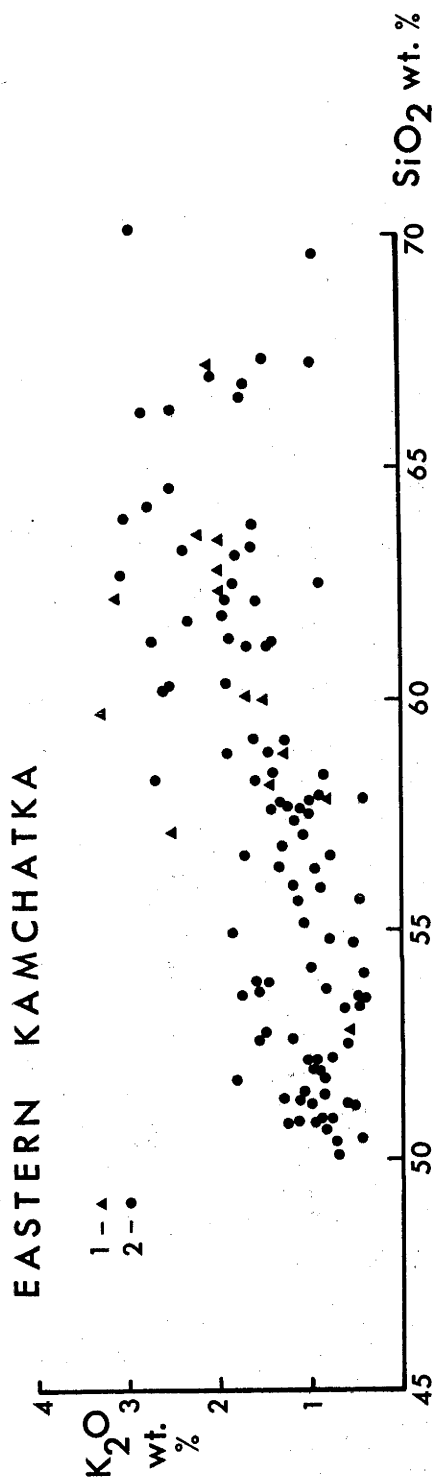


Fig. 2.9.  $K_2O$  vs.  $SiO_2$  plot for amphibole-bearing (triangles) and amphibole-free (dots) rocks from Eastern Kamchatka (data from Ehrlich, 1968).

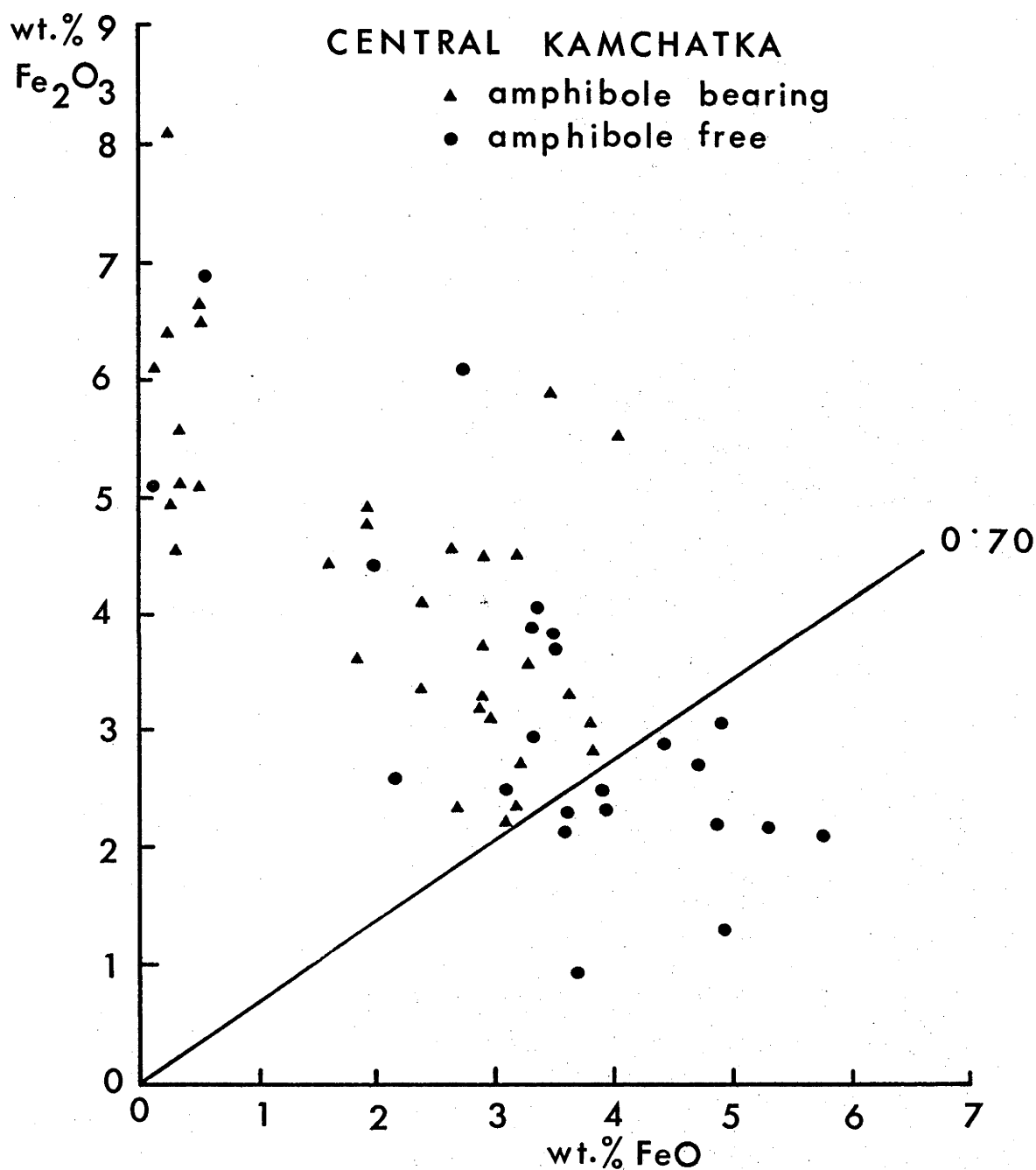


Figure 2.10:  $\text{Fe}_2\text{O}_3$  vs. FeO plot for amphibole-bearing and amphibole-free rocks from Central Kamchatka (data from Ehrlich, 1968).

# WESTERN GROUP KURILE ISLANDS

▲ amphibole bearing

--- free

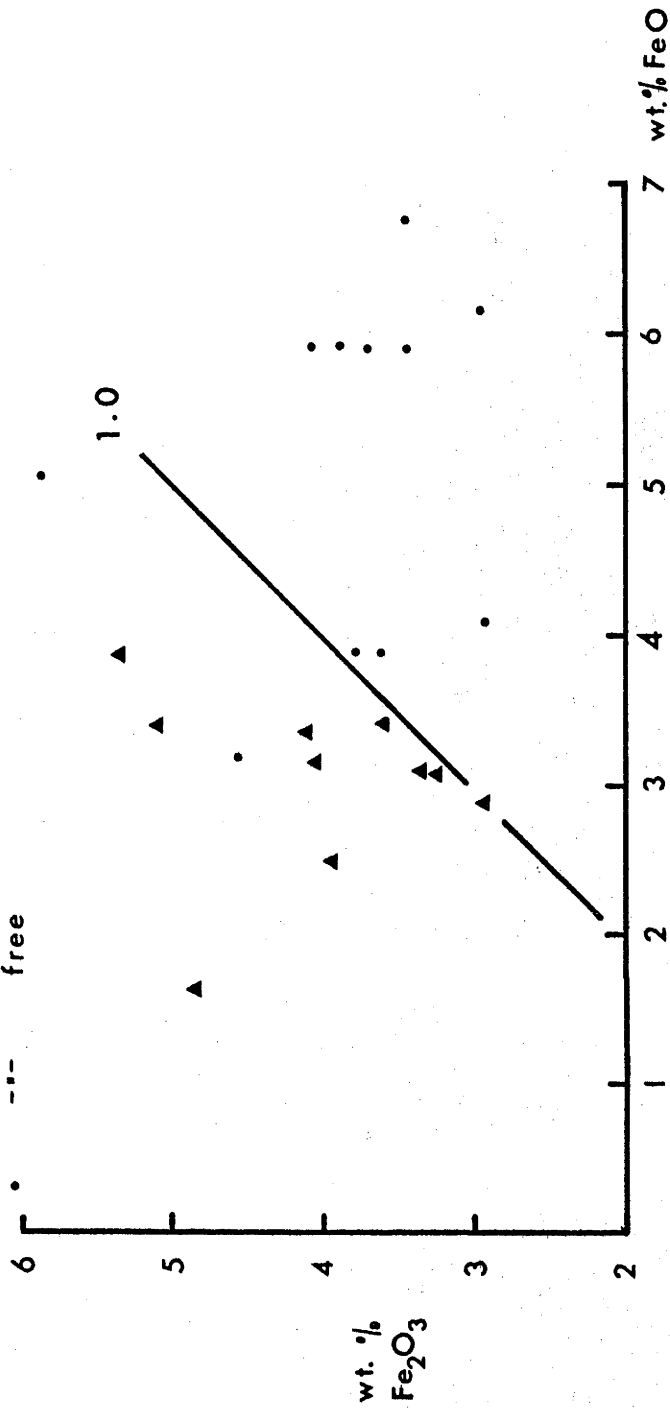
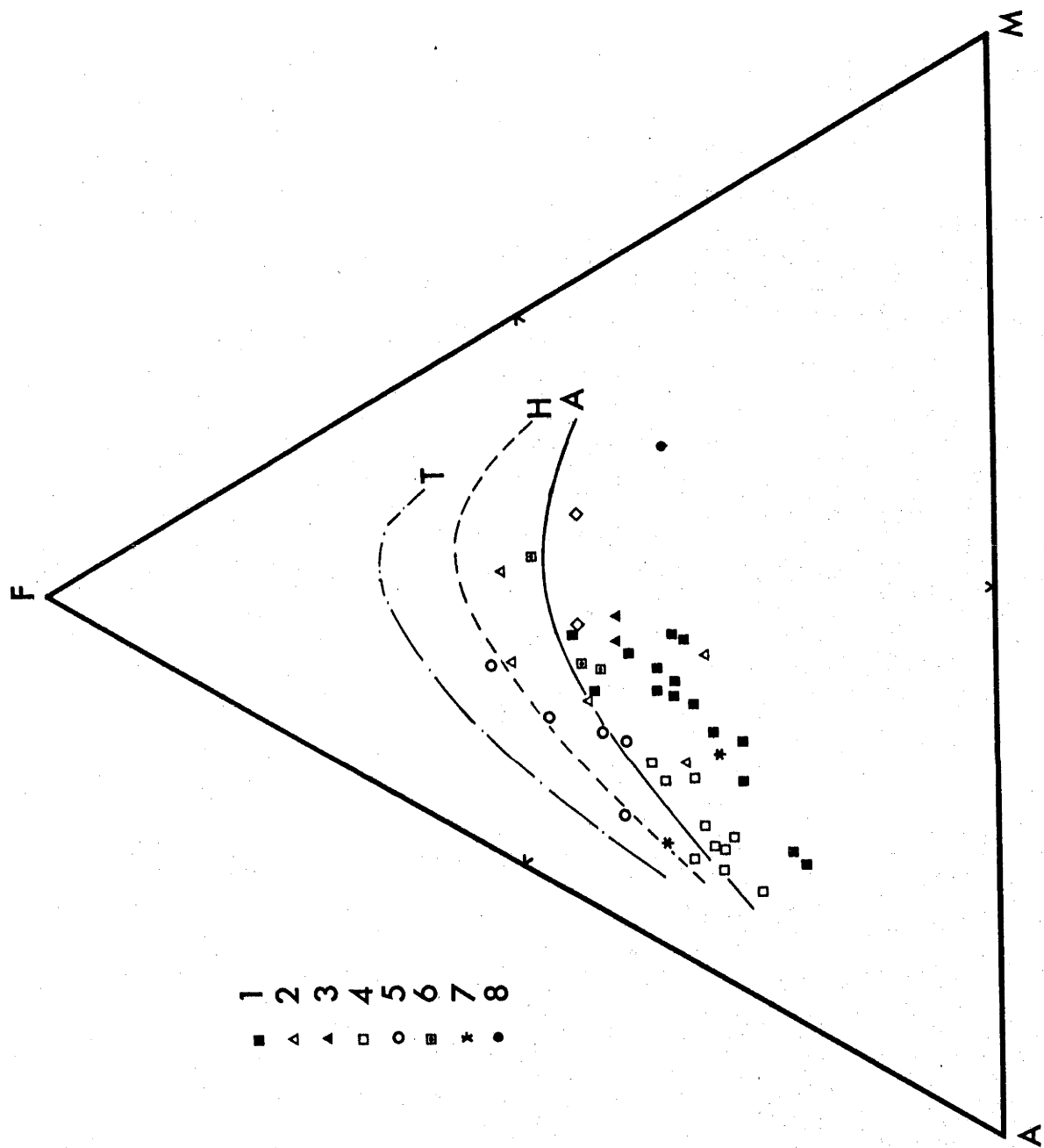


Fig. 2. 11.  $\text{Fe}_2\text{O}_3$  vs. FeO plot for amphibole-bearing (triangles) and amphibole-free (dots) rocks of Western group of islands, Kurile Islands (data from Gorshkov, 1967).

Figure 2.12: AMF diagram for new data on amphibole-bearing volcanic rocks of calc-alkaline provinces.

1 - Solomon Islands and East Papua; 2 - New Zealand; 3 - New Guinea Highlands; 4 - Hunter River area, N.S.W.; 5 - Carpathians (Europe); 6 - Fiji; 7 - Western United States; 8 - Argentine.



which is characteristic of medium-K or high-K calc-alkaline rocks or shoshonites.

Dickinson and Hatherton (1968) have found a relationship between the  $K_2O$  content at a given  $SiO_2$  value and the vertical distance to the inclined seismic zone. This relationship discriminates between various types of volcanic rocks in island arcs and therefore it has been applied to associations with amphibole-bearing rocks. Inferred and actual depths of the seismic zone are presented in Table 2.8. Data suggest that suites of volcanic rocks which contain amphibole in appreciable amounts originate at depths greater than 130 km. Correlation could also be made with the depth of the M-discontinuity beneath the island arcs; amphibole-bearing rocks are then confined to areas with a thicker crust.

Earlier authors (e.g. Kuno, 1952) considered the amphibole-bearing rocks of island arcs, because of their high volatile content, to be contaminated by a sialic crust. However, objections to this are listed below.

(a) There is no difference in major as well as trace element chemistry between amphibole-bearing and amphibole-free andesites in a particular area. Also Sr-isotope ratios do not differ (Puskar, 1968).

(b) Direct evidence of crustal contamination e.g. crustal xenoliths, are extremely rare in amphibole-bearing

as well as amphibole-free rocks. These are not more common in amphibole-bearing rocks.

(c) Amphibole-bearing rocks also occur in areas where "continental type of crust" is apparently absent (Solomon Islands or Kurile Islands).

(d) The amount of sialic material which can be assimilated by andesitic magma is limited because heat loss in assimilation of crustal rocks; the contribution of  $H_2O$  from crustal material (even assuming an extreme water content of 4.5% Poldervaart, 1955)) cannot lower the liquidus temperature to balance losses of heat required to completely melt crustal material.

The chemical similarities of amphibole-bearing and amphibole-free rocks of island arcs suggest that any medium- to high-K calc-alkaline magma with 55-65%  $SiO_2$  is potentially capable of crystallizing amphibole. Water is considered to play an important petrogenetic role, not only in amphibole-bearing andesites, but in most medium-K and high-K calc-alkaline rocks, and in shoshonites.

## CHAPTER 3

PETROGRAPHY AND MINERALOGY OF AMPHIBOLE-BEARING VOLCANIC  
ROCKS FROM SOME CALC-ALKALINE PROVINCES

Amphibole-bearing rocks are most commonly found in "highly developed" island arcs in which calc-alkaline rocks occur (e.g. Kamchatka, Japan, New Guinea, Solomon Islands). Amphibole-bearing rocks are rare in primitive island arcs in which low-K associations - especially arc tholeiites - are the only rocks present (e.g. South Sandwich Islands, Central Kurile Islands). Amphibole and biotite are the most common ferromagnesian silicates in andesites from the Andean province (Zeil and Pichler, 1968, 1969), and in rocks from intra-continental andesitic chains, e.g. Carpathians (Kuthan, 1968). Amphibole-bearing andesites in circum-Pacific areas are characteristically produced by calc-alkaline volcanoes with Pelean type explosive activity. Mt Lamington, Mt Victory and Trafalgar in Papua, Savo volcano in Solomon Islands, Mt Egmont - New Zealand and Bezemyanyi volcano - Kamchatka are examples of volcanoes with a preponderance of pyroclastic rocks which are mostly amphibole-bearing, and which have subordinate pyroxene or olivine-bearing lavas.

Published descriptions (e.g. Gow, 1968; Wise, 1969; Taylor, 1959) and field observations suggest that a proportion of amphibole-bearing rocks in a particular area is

related to the amount of explosive activity. This, however, does not imply that all pyroclastic rocks are amphibole-bearing and vice versa. The amphibole-bearing rocks may also form lava domes in recent volcanoes (e.g. East Papuan).

#### Textures of amphibole andesites

Porphyric or more frequently glomeroporphyric textures are most common. These clusters, are usually made up of clinopyroxene. Amphibole clusters are rare, but some rocks (e.g. Mt Victory, E. Papua) contain numerous cognate inclusions of amphibole gabbros, hornblendites or diorites.

Vitroclastic textures are characteristic of "continental" (Andean) amphibole andesites associated with more siliceous rocks (dacites and rhyolites). For example, the Hunter River andesites and dacites of Carboniferous age have typical fiamme structures which are characteristic of ignimbrites. Fiamme structures in other amphibole-bearing rocks of andesitic composition from circum-Pacific areas are extremely rare and smaller than those of typical ignimbrites and except for the Hunter River samples the use of "ignimbrite" would not be appropriate for the samples examined.

Ophitic, intersertal and hyalo-ophitic, sometimes vitroclastic textures are characteristic of rocks with a slightly crystallized groundmass.

Some degree of disequilibrium between amphiboles and the host rock is typical. The amphiboles show different degrees of resorption or recrystallization, suggesting that certain conditions must be maintained in order to preserve them. The necessary role of volatiles in the crystallization of amphiboles has long been recognized (e.g. Larsen, 1937; Bowen, 1929) but the retention of volatile content in late stages of magmatic crystallization is a necessary factor for the appearance of amphibole. Hazard (1895) described amphibole-bearing rocks from plugs, whereas amphiboles were absent in the associated extrusive comagmatic rocks. Gow (1968) described partially resorbed hornblendes in fine grained or glassy rocks, whereas strongly resorbed amphiboles were confined to holocrystalline rocks. Baker (1968) observed amphiboles in only the pyroclastic rocks and ejecta of recent eruptions of the Lesser Antilles.

### Amphiboles

Fifty-five new chemical analyses of amphiboles, primarily from andesites, are presented in Tables 3.1, 3.2, and 3.4. Analyses have been carried out using XRF and conventional wet chemical techniques on mineral separates, and to a lesser extent, using electron-microprobe techniques. Separation utilised electromagnetic and heavy liquid separation, followed by hand-picking. The counting of 500 grains

TABLE 3.1.

Major and trace element analyses of amphiboles from volcanic rocks

Calc-alkalines volcanic rocks

| analysed<br>coexisting<br>minerals | New Zealand |       |        |       | Fiji  |        | Western United States |        |       |       | Carpathians-Czechoslovakia |       |             |       | Hunter river area N.S.W. |       |       |        |
|------------------------------------|-------------|-------|--------|-------|-------|--------|-----------------------|--------|-------|-------|----------------------------|-------|-------------|-------|--------------------------|-------|-------|--------|
|                                    | 47          | 48    | 50     | 46    | 52    | 2      | 6                     | 18     | 53    | 5     | 1                          | 34    | 31          | 32    | 33                       | 9     | 10    | 7      |
|                                    | cpx         | cpx   |        | biot  |       |        | cpx                   |        |       |       |                            |       | biot<br>opx |       | biot<br>opx              |       |       |        |
| SiO <sub>2</sub>                   | 43.67       | 42.77 | 42.06  | 43.29 | 42.40 | 47.7*  | 44.42                 | 44.46  | 43.02 | 43.41 | 38.4*                      | 42.2* | 44.6*       | 44.30 | 43.64                    | 46.73 | 45.97 | 44.41  |
| TiO <sub>2</sub>                   | 2.09        | 1.80  | 2.57   | 1.39  | 1.75  | 1.4*   | 1.94                  | 1.99   | 2.96  | 1.62  | 5.1*                       | 1.9*  | 1.7*        | 1.73  | 1.97                     | 1.77  | 1.74  | 2.17   |
| Al <sub>2</sub> O <sub>3</sub>     | 10.77       | 13.08 | 13.49  | 10.30 | 12.47 | 4.0*   | 9.73                  | 9.75   | 11.22 | 10.40 | 14.5*                      | 16.1* | 9.8*        | 8.95  | 9.46                     | 7.53  | 7.39  | 8.13   |
| Fe <sub>2</sub> O <sub>3</sub>     | 7.43        | 5.22  | 6.28   | 5.71  | 5.46  | 12.1   | 5.56                  | 5.49   | 6.23  | 8.44  | 3.00                       | 4.8   | 3.62        | 4.84  | 15.32                    | 4.11  | 4.51  | 3.09   |
| FeO                                | 4.65        | 4.39  | 9.24   | 9.86  | 6.64  | 7.3    | 7.82                  | 7.93   | 4.96  | 2.79  | 9.8                        | 9.7   | 12.00       | 13.19 | 2.53                     | 9.92  | 9.88  | 12.31  |
| MnO                                | .28         | .33   | .01    | .42   | n.d.  | -      | .07                   | .06    | n.d.  | .14   | n.d.                       | -     | .4*         | .12   | .03                      | .25   | .25   | .01    |
| MgO                                | 13.18       | 13.02 | 12.60  | 11.03 | 14.00 | 14.4*  | 14.04                 | 13.60  | 14.24 | 15.21 | 11.6*                      | 11.7  | 11.3*       | 10.51 | 11.42                    | 13.89 | 13.26 | 14.59  |
| CaO                                | 13.18       | 12.55 | 11.34  | 12.20 | 11.84 | 9.3*   | 11.08                 | 11.63  | 11.10 | 10.78 | 11.0*                      | 10.1  | 10.1*       | 9.09  | 10.90                    | 11.44 | 12.10 | 11.06  |
| Na <sub>2</sub> O                  | 2.47        | 2.38  | 1.80   | 1.80  | 2.18  | 2.3*   | 3.80                  | 3.80   | 2.61  | 1.98  | 3.5*                       | 2.1   | 2.6*        | 2.28  | 1.51                     | 1.42  | 1.52  | 2.44   |
| K <sub>2</sub> O                   | .75         | .72   | .30    | .63   | .27   | .2*    | .18                   | .19    | .22   | .40   | .32*                       | .2    | .4*         | .79   | .68                      | .49   | .49   | .37    |
| P <sub>2</sub> O <sub>5</sub>      | n.d.        | .08   | .04    | .08   | .04   | n.d.   | n.d.                  | n.d.   | .09   | .04   | n.d.                       | -     | .4*         | .11   | .20                      | .32   | .08   | .09    |
| H <sub>2</sub> O <sup>+</sup>      | 1.21        | 1.48  | 1.07   | 1.80  | 1.71  | 1.08   | 1.84                  | 1.35   | 1.80  | 1.91  | 1.69                       | 1.8   | -           | 1.90  | .69                      | 1.87  | 1.74  | .30    |
| H <sub>2</sub> O <sup>-</sup>      | .20         | .83   | .14    | .15   | .20   | .20    | .16                   | .22    | .54   | .70   | .60                        | .30   | -           | 1.08  | .20                      | .20   | .14   | 1.53   |
| F                                  | .50         | .21   | .05    | .15   | n.d.  | .07    | .10                   | .09    | -     | .65   | .12                        | .005  | -           | .20   | .26                      | -     | .38   | .33    |
| Total                              | 100.38      | 98.66 | 100.99 | 98.81 | 98.96 | 100.05 | 100.74                | 100.56 | 98.99 | 98.47 | 99.63                      | 100.9 | 96.9        | 99.09 | 98.86                    | 99.94 | 99.45 | 100.83 |
| Rb                                 | 5.3         | 4.4   | 2.4    | 5.0   | -     | 3.7    | 1.3                   | 1.4    | -     | 1.7   | 1.7                        | 1.0   | 1.7         | -     | 3.4                      | 1.3   | 3.4   | 1.6    |
| Ba                                 | 225         | 239   | 45     | n.d.  | -     | 166    | 42.                   | -      | -     | 224   | 241                        | -     | -           | -     | -                        | -     | -     | 470    |
| Sr                                 | 245         | 276   | 114    | 154   | -     | 201    | 128                   | 135    | -     | 608   | 574                        | 153   | -           | -     | -                        | 80.   | 89.   | 94.    |
| La                                 | -           | -     | -      | 19.   | -     | -      | -                     | -      | -     | -     | -                          | -     | 27.         | 112   | 72                       | 31.   | 41.   | 30.    |
| Ce                                 | 34.         | 26.   | 8.3    | 90.   | -     | 9.     | 27.                   | 27.    | 10.7  | -     | 5.3                        | 127   | 134         | 164   | 141                      | 162.  | 136   | 136    |
| Pr                                 | 17.         | -     | 3.7    | 9.1   | -     | 16.    | 10.                   | 8.3    | 51.   | 28    | -                          | 11.   | -           | 44.   | 26.                      | 44.   | 36.   | 36.    |
| Nd                                 | 23.         | 8.6   | 18.    | 54    | -     | -      | 29.                   | 26     | 14.   | 4.4   | 4.6                        | 71.   | 78          | 111.  | 114                      | 114   | 110   | 110    |
| Y                                  | 46.         | 22.   | 27.    | 56.3  | -     | 21.    | 53.                   | 56     | 13.   | 25    | 23.                        | 8.1   | -           | 14.   | 167                      | 174   | 169   | 169    |
| Th                                 | 3.2         | -     | 2.     | n.d.  | -     | -      | 2.7                   | -      | -     | -     | -                          | .2    | -           | -     | -                        | -     | -     | n.d.   |
| U                                  | .5          | -     | n.d.   | n.d.  | -     | -      | n.d.                  | -      | 4.7   | -     | .7                         | -     | -           | -     | -                        | -     | -     | 1.3    |
| Cu                                 | 66.         | 23.   | 20.    | 12.   | -     | 27.    | 29.                   | 30.    | 198   | -     | 17.7                       | 23.   | 27.         | 8.8   | 11.                      | 2.5   | 5.7   | 5.7    |
| Co                                 | 48          | 61.   | 60     | 42.   | -     | 68     | 66                    | 61     | 73    | 77    | 74                         | 56.   | 55          | 89.   | 59.                      | 57.   | 58.   | 58.    |
| Ni                                 | 32.         | 97.   | 32.    | 38.   | -     | 136    | 28                    | 22     | 21    | 40    | 46                         | 25    | 58          | 19.   | 37.                      | 35.   | 35    | 35     |
| V                                  | 410         | 477   | 565    | 547   | -     | 693    | 425                   | 435    | 363   | 144   | 471                        | 386   | 403         | 535   | 385                      | 418   | 375   | 375    |
| Cr                                 | 43.         | 319.  | 154    | 86    | -     | 97.    | 62                    | 48     | 258   | 23    | 119                        | 30    | 30          | 42    | 86                       | 30    | 40    | 40     |
| Zn                                 | 102         | 76    | 107    | 152   | -     | 57     | 157                   | 147    | 138   | 101   | 92                         | 194   | 204         | 338   | 208                      | 198   | 197   | 197    |
| Pb                                 | .7          | n.d.  | 2.4    | -     | -     | -      | -                     | -      | -     | 6.7   | 6.9                        | -     | -           | -     | -                        | -     | -     | 8.0    |
| Ga                                 | 16.         | 15.   | 18.    | 22.   | -     | 15.    | 15.                   | 15.    | 15    | 14    | 10.                        | 22    | -           | 17.1  | 14.                      | -     | -     | 14.    |

\* electron microprobe determination

TABLE 3.1. (continued)

| Sample                         | 8      | 15  | 13    | 14    | 12                 | 17     | 11     | 16     | Other volcanic rocks |     |        |        |       |       |        |       |     |  |
|--------------------------------|--------|-----|-------|-------|--------------------|--------|--------|--------|----------------------|-----|--------|--------|-------|-------|--------|-------|-----|--|
|                                |        |     |       |       |                    |        |        |        | cpx                  |     | cpx    |        | cpx   |       | cpx    |       | cpx |  |
| Analyzed coexisting mineral    |        |     |       |       |                    |        |        |        |                      |     |        |        |       |       |        |       |     |  |
| SiO <sub>2</sub>               | 47.10  |     | 44.44 | 44.30 | 43.63              | 44.58  | 44.50  | 43.84  |                      |     | 42.81  | 39.32  | 40.82 | 38.72 | 40.00  | 39.03 |     |  |
| TiO <sub>2</sub>               | 1.72   |     | 2.01  | 2.00  | 1.85               | 2.38   | 2.00   | 1.88   |                      |     | 1.16   | 6.14   | 2.70  | 3.82  | 5.36   | 4.00  |     |  |
| Al <sub>2</sub> O <sub>3</sub> | 7.36   |     | 7.98  | 8.16  | 7.93               | 8.08   | 8.03   | 7.84   |                      |     | 10.67  | 14.51  | 11.96 | 13.50 | 14.27  | 12.91 |     |  |
| Fe <sub>2</sub> O <sub>3</sub> | 3.55   |     | 3.37  | 4.58  | 16.60 <sup>+</sup> | 6.72   | 4.39   | 5.08   |                      |     | 6.21   | 4.28   | 6.89  | 6.88  | 3.56   | 6.20  |     |  |
| FeO                            | 10.77  |     | 12.00 | 11.39 |                    | 9.42   | 11.64  | 11.76  |                      |     | 9.52   | 6.87   | 3.82  | 3.99  | 11.21  | 5.06  |     |  |
| MnO                            | .27    |     | .02   | .24   | .23                | .02    | .21    | .23    |                      |     | .27    | .10    | .14   | .10   | n.d.   | n.d.  |     |  |
| MgO                            | 13.41  |     | 12.88 | 12.27 | 12.46              | 12.71  | 12.36  | 12.68  |                      |     | 12.34  | 12.04  | 13.79 | 13.42 | 10.19  | 13.01 |     |  |
| CaO                            | 11.44  |     | 11.68 | 11.42 | 10.94              | 11.46  | 11.38  | 10.94  |                      |     | 12.73  | 10.87  | 11.98 | 11.24 | 9.77   | 14.68 |     |  |
| Na <sub>2</sub> O              | 2.50   |     | 2.33  | 2.06  | 1.53               | 2.30   | 2.71   | 1.55   |                      |     | 1.35   | 2.63   | 2.74  | 2.75  | 2.80   | 2.75  |     |  |
| K <sub>2</sub> O               | .49    |     | .70   | .69   | .84                | .73    | .69    | .87    |                      |     | .66    | 1.92   | 1.15  | 1.44  | 1.48   | .51   |     |  |
| P <sub>2</sub> O <sub>5</sub>  | .19    |     | .48   | .41   | .31                | .19    | .19    | .16    |                      |     | .14    | .06    | .31   | .52   | .06    | .11   |     |  |
| H <sub>2</sub> O <sup>+</sup>  | 1.23   |     | 1.48  | 1.78  | 2.04               | 1.85   | 1.91   | 2.02   |                      |     | 1.69   | 1.19   | 1.81  | 1.75  | 1.34   | .84   |     |  |
| H <sub>2</sub> O <sup>-</sup>  | .21    |     | .12   | .15   | .41                | .12    | .35    | .75    |                      |     | .93    | .18    | .29   | .40   | .39    | .19   |     |  |
| F                              | -      |     | .49   | .47   | .51                | .45    | .48    | .48    |                      |     | -      | .15    | .09   | .10   | .09    | n.d.  |     |  |
| Total                          | 100.34 |     | 99.98 | 99.92 | 99.28              | 101.01 | 100.84 | 100.08 |                      |     | 100.93 | 100.26 | 98.40 | 98.63 | 100.52 | 99.35 |     |  |
| Rb                             | 1.3    | 2.7 | 6.3   | 5.9   | -                  | 3.9    | 3.5    | 5.1    | 2.5                  | .7  | 13.    | -      | -     | 4.6   | 3.3    | 6.1   |     |  |
| Ba                             | -      | 309 | -     | -     | -                  | -      | -      | -      | 45                   | 123 | 729    | 1091   | -     | -     | 131    | 359   |     |  |
| Sr                             | 79.    | 88  | 89    | 93    | 109                | 84.    | 70     | 88     | 386                  | 277 | 622    | 542    | 727   | 610   | 1162   | -     |     |  |
| La                             | 27.    | 44. | 54    | 46    | 51                 | 53.    | 45     | 42     | -                    | -   | -      | -      | -     | -     | -      | -     |     |  |
| Ce                             | 138.   | 199 | 158   | 210   | 153                | 211    | 188    | 175    | 14                   | 9.5 | 28     | 25     | -     | -     | 22     | 67    |     |  |
| Tr                             | 26.    | 46  | 38    | 37    | 41                 | 14.    | 44     | 36     | 4.3                  | 2.1 | -      | -      | -     | -     | 5.8    | 16    |     |  |
| Nd                             | 102    | 172 | 165   | 153   | 167                | 170    | 169    | 154    | 10.                  | 5.6 | 21.    | 20     | -     | -     | 17.    | 48    |     |  |
| Y                              | 160    | 252 | 260   | 215   | 250                | 218    | 32     | 32     | 11.                  | 16  | 19.    | 21     | -     | -     | 19.    | 28    |     |  |
| Th                             | -      | -   | -     | -     | 5.4                | -      | -      | 6.9    | -                    | -   | -      | -      | -     | -     | -      | 1.4   |     |  |
| U                              | -      | -   | -     | -     | -                  | -      | -      | .9     | -                    | -   | -      | -      | -     | -     | -      | 1.4   |     |  |
| Cu                             | 5.0    | 23. | 13    | 10    | n.d.               | 72     | 20     | 3.2    | 145                  | 85  | 50     | 27     | -     | -     | 2.3    | 38    |     |  |
| Co                             | 35     | 57  | 60    | 56    | 62.                | 61.    | 57     | 58     | 72                   | 70  | 76     | 57     | -     | -     | 75     | 60    |     |  |
| Ni                             | 38.    | 38  | 42    | 38    | 37                 | 36     | 38     | 35     | 55                   | 55  | 20     | 177    | -     | -     | 12     | 58    |     |  |
| V                              | 376    | 452 | 440   | 436   | 439                | 447    | 446    | 437    | 413                  | 325 | 496    | 416    | 279   | 171   | 354    | -     |     |  |
| Cr                             | 95     | 49. | 81    | 49    | 48                 | 48     | 53     | 49     | 51                   | 169 | 363    | 410    | -     | -     | 35     | 65    |     |  |
| Zn                             | 216    | 214 | 225   | 221   | 218                | 225    | 220    | 226    | 153                  | 124 | 56     | 65     | -     | -     | 76     | 10    |     |  |
| Pb                             | -      | -   | -     | -     | 9.6                | -      | -      | 14.3   | -                    | -   | -      | -      | -     | -     | -      | -     |     |  |
| Ga                             | 13     | 15  | -     | 18    | -                  | 16     | 16     | 26     | 18                   | 10  | 14     | 12     | -     | -     | 14     | 12    |     |  |

+ total iron as Fe<sub>2</sub>O<sub>3</sub>

TABLE 3.2. Major and trace element analyses of amphiboles from other environments

| Inclusions in alkaline basalts (Kiana, N.S.W.) |        |       |        |         |        |        | Amphibolites and gabbros (Czechoslovakia) Granulites (Czechoslovakia) amphibolites |       |       |       |        |       |       |
|------------------------------------------------|--------|-------|--------|---------|--------|--------|------------------------------------------------------------------------------------|-------|-------|-------|--------|-------|-------|
| Sample                                         | 22     | 23    | 24     | 25      | 26     | 27     | 107                                                                                | 116   | 126   | 127   | 128    | 129   | 108   |
| analysed coex-<br>isting minerals cpx          |        |       | cpx    | bi, cpx | bi     | cpx    |                                                                                    |       |       |       |        |       |       |
| SiO <sub>2</sub>                               | 43.1*  | 38.25 | 40.20  | 39.2*   | 38.44  | 38.1*  | 45.28                                                                              | 46.14 | 47.01 | 43.64 | 43.78  | 42.52 | 47.89 |
| TiO <sub>2</sub>                               | 5.1*   | 5.87  | 6.40   | 4.5*    | 6.12   | 4.9*   | 1.68                                                                               | 1.80  | .51   | 1.08  | 1.15   | 1.55  | .34   |
| Al <sub>2</sub> O <sub>3</sub>                 | 13.7*  | 13.18 | 14.90  | 16.4*   | 13.21  | 16.3*  | 8.38                                                                               | 9.78  | 9.60  | 10.84 | 11.21  | 11.04 | 9.77  |
| Fe <sub>2</sub> O <sub>3</sub>                 | 1.52   | 1.85  | .53    | +       | 2.97   | .05    | .77                                                                                | 1.95  | 2.45  | 3.55  | 3.17   | 5.09  | 1.07  |
| FeO                                            | 7.89   | 9.89  | 9.96   | 10.7    | 7.78   | 10.85  | 13.28                                                                              | 12.60 | 8.56  | 12.28 | 12.56  | 13.08 | 8.04  |
| MnO                                            | n.d.   | .16   | n.d.   | n.d.    | .12    | n.d.   | .29                                                                                | .16   | .21   | .24   | .27    | .32   | .19   |
| MgO                                            | 10.91* | 10.27 | 10.4   | 10.3    | 11.59  | 10.2*  | 13.78                                                                              | 10.87 | 14.57 | 10.66 | 10.83  | 9.97  | 15.76 |
| CaO                                            | 10.2*  | 10.96 | 10.5   | 11.0*   | 11.77  | 11.6*  | 11.02                                                                              | 12.34 | 13.10 | 13.17 | 12.17  | 11.62 | 12.84 |
| Na <sub>2</sub> O                              | 3.87   | 5.25  | 5.6    | 5.7*    | 4.95   | 4.9*   | .96                                                                                | 1.20  | 1.15  | 1.19  | 1.21   | 1.24  | 1.36  |
| K <sub>2</sub> O                               | 1.10   | 1.97  | 1.2    | 1.2*    | 1.42   | 1.3    | .33                                                                                | .53   | .32   | .80   | .66    | .75   | .28   |
| P <sub>2</sub> O <sub>5</sub>                  | n.d.   | .23   | n.d.   | n.d.    | .09    | n.d.   | n.d.                                                                               | n.d.  | -     | -     | -      | -     | n.d.  |
| H <sub>2</sub> O <sup>+</sup>                  | 1.56   | 1.67  | 1.30   | -       | 1.58   | 1.73   | 1.98                                                                               | 2.13  | 2.13  | 1.79  | 2.58   | 2.20  | 2.23  |
| H <sub>2</sub> O <sup>-</sup>                  | .39    | .18   | .20    | -       | .15    | .31    | .24                                                                                | .20   | .06   | .32   | .49    | .25   | .07   |
| F                                              | .03    | .08   | .12    | -       | -      | n.d.   | .04                                                                                | .02   | .04   | .04   | .06    | .07   | -     |
| Total                                          | 99.37  | 99.81 | 101.31 | 99.00   | 100.19 | 100.24 | 98.03                                                                              | 99.72 | 99.71 | 99.60 | 100.14 | 99.70 | 99.84 |
| Rb                                             | 8.1    | 12.   | 11.    | 8.5     | 7.5    |        | 4.3                                                                                | 4.2   | 2.7   | 2.3   | 9.9    | 7.0   | 1.6   |
| Ba                                             | 1068   | 716   | 1178   | 607     | 350    |        | -                                                                                  | -     | 66.   | 107   | 62     | -     | -     |
| Sr                                             | 663    | 793   | 1176   | 1005    | 585    |        | 55.                                                                                | 68    | 87.   | 75.   | 95     | 75.   | 41    |
| La                                             | 7.5    | 32.   | -      | 10      | 30     |        | -                                                                                  | -     | -     | -     | 7.7    | 4.3   | -     |
| Ce                                             | 49     | 48    | 38     | 42      | 33     |        | 28                                                                                 | 17.   | 23    | 30.   | 62     | 95    | -     |
| Pr                                             | 27     | 14    | 20     | 21      | 15     |        | 4.5                                                                                | 2.1   | 9.    | 15.   | 14.    | 9.5   | -     |
| Nd                                             | 22     | 33    | 4.7    | 27      | 29     |        | 15.                                                                                | 12.5  | 12.   | 7.    | 47.    | 42.   | -     |
| Y                                              | 27     | 17    | 40.    | 22      | 22     |        | 39                                                                                 | 31    | 17.   | 28    | 43.    | 82    | 20    |
| Th                                             | 1.8    | -     | .8     | .9      | -      |        | -                                                                                  | -     | -     | -     | -      | -     | -     |
| U                                              | 2.2    | -     | 1.2    | 1.8     | -      |        | -                                                                                  | -     | -     | -     | -      | -     | -     |
| Cu                                             | 222    | 18    | 41     | 14      | 52     |        | 14                                                                                 | 14    | 24    | 31    | 32     | 25    | -     |
| Co                                             | 132    | 58    | 66     | 55      | 62     |        | 58                                                                                 | 66    | 67    | 56    | 54     | 40    | -     |
| Ni                                             | 223    | -     | 70     | 100     | 147    |        | 90                                                                                 | 145   | 96    | 76    | 73     | 9     | -     |
| V                                              | 463    | 377   | 382    | 370     | 364    |        | 422                                                                                | 471   | 259   | 551   | 502    | 352   | -     |
| Cr                                             | 48     | -     | 131    | 143     | -      |        | 516                                                                                | 457   | 368   | 161   | 154    | -     | -     |
| Zu                                             | 69     | 97    | 80     | 69      | 106    |        | 144                                                                                | 157   | 84    | 137   | 177    | 184   | -     |
| Pb                                             | -      | -     | 18     | 5.7     | -      |        | -                                                                                  | -     | -     | -     | -      | -     | -     |
| Ga                                             | 17.    | 17    | 18     | 14      | 17     |        | 13.                                                                                | 9.0   | 9.0   | 13.   | 17.    | 16    | -     |

\* electron microprobe determination  
+ total iron as FeO

TABLE 3.3.

Major and trace elements of biotites and pyroxenes coexisting with analyzed amphiboles

|                                | Biotites |       |        |       |       | Clinopyroxenes |       |       |       |       | Orthopyroxenes |       |       |       |       |        |       |        |       |        |       |       |
|--------------------------------|----------|-------|--------|-------|-------|----------------|-------|-------|-------|-------|----------------|-------|-------|-------|-------|--------|-------|--------|-------|--------|-------|-------|
|                                | 31       | 33    | 46     | 22    | 25    | 26             | 6     | 47    | 48    | 36    | 40             | 49    | 22    | 24    | 25    | 27     | 32    | 33     | 31    | 16     | 9     | 7     |
| SiO <sub>2</sub>               | 34.92    | 34.3* | 33.39  | 33.30 | 35.30 |                | 50.87 | 45.04 | 47.16 | 51.28 | 50.14          | 46.40 | 45.73 | 46.1* | 48.55 | 46.72  | 49.21 | 49.60  | 49.02 | 50.00  | 52.3* | 52.40 |
| TiO <sub>2</sub>               | 3.85     | 3.4*  | 6.81   | 5.88  |       |                | .41   | 1.61  | .76   | .30   | n.d.           | 1.56  | 2.57  | 1.9*  | 1.70  | 2.41   | .68   | .74    | .43   | .38    | .2*   | .67   |
| Al <sub>2</sub> O <sub>3</sub> | 16.03    | 16.8* | 13.96  | 15.20 |       |                | 2.50  | 4.07  | 4.43  | 4.34  | 3.56           | 5.36  | 8.29  | 8.2*  | 6.35  | 7.53   | 1.38  | 1.06   | 1.25  | 1.93   | .5    | 1.27  |
| Fe <sub>2</sub> O <sub>3</sub> | 5.88     | 11.5  | 5.24   | 2.83  |       |                | 2.40  | 10.46 | 6.99  | 1.62  | 1.55           | 4.62  | 2.02  | .20   | 1.86  | 1.94   | 1.83  |        | 5.71  |        |       | .40   |
| FeO                            | 12.72    | 6.0   | 14.24  | 11.46 |       |                | 7.17  | 8.87  | 5.12  | 5.71  | 7.88           | 3.52  | 7.01  | 7.5   | 6.98  | 6.82   | 4.51  | 27.59+ | 20.41 | 27.41+ | 24.3  | 22.60 |
| MnO                            | .14      | .2    | .84    | .40   |       |                | .50   | .47   | .18   | .27   | .25            | .06   | n.d.  | n.d.  | .18   | .15    | .84   | .77    | .96   | .70    | .5    | .22   |
| MgO                            | 12.59    | 14.1* | 13.03  | 13.91 |       |                | 14.28 | 9.79  | 13.85 | 14.09 | 14.28          | 13.72 | 11.87 | 12.0* | 11.68 | 11.97  | 18.91 | 16.59  | 18.79 | 16.63  | 21.5  | 19.10 |
| CaO                            | .50      | n.d.  | .44    | .88   |       |                | 19.89 | 18.07 | 20.49 | 20.64 | 19.95          | 22.75 | 20.51 | 22.9* | 20.95 | 21.23  | 1.09  | 1.33   | 2.12  | 1.50   | .9    | 1.58  |
| Na <sub>2</sub> O              | .20      | n.d.  | n.d.   | .40   |       |                | .60   | .50   | .55   | .16   | .33            | .44   | 1.64  | 1.4*  | 1.52  | 1.28   | n.d.  | n.d.   | n.d.  | n.d.   | n.d.  | .40   |
| K <sub>2</sub> O               | 8.85     | 9.1*  | 8.63   | 8.55  |       |                | .08   | .08   | n.d.  | n.d.  | n.d.           | n.d.  | n.d.  | n.d.  | .03   | n.d.   | n.d.  | .08    | .05   | n.d.   | n.d.  | n.d.  |
| P <sub>2</sub> O <sub>5</sub>  | .11      | -     | .68    | .43   |       |                | .12   | n.d.  | n.d.  | n.d.  | n.d.           | .08   | n.d.  | n.d.  | n.d.  | n.d.   | n.d.  | n.d.   | .26   | .21    | n.d.  | n.d.  |
| H <sub>2</sub> O <sup>+</sup>  | 3.03     | -     | 2.86   | 2.97  |       |                | -     | -     | -     | -     | -              | -     | -     | -     | -     | -      | -     | -      | -     | -      | -     | -     |
| H <sub>2</sub> O <sup>-</sup>  | .04      | -     | .36    | .81   |       |                | -     | -     | -     | -     | -              | -     | -     | -     | -     | -      | -     | -      | -     | -      | -     | -     |
| F                              | .05      | -     | n.d.   | .13   |       |                | -     | -     | -     | -     | -              | -     | -     | -     | -     | -      | -     | -      | -     | -      | -     | -     |
| Total                          | 99.27    | 95.4  | 100.48 | 99.15 |       |                | 98.82 | 98.96 | 99.53 | 98.41 | 98.04          | 99.01 | 99.64 | 100.2 | 99.80 | 100.05 | 98.45 | 97.76  | 99.04 | 98.81  | 100.1 | 98.64 |
| Rb                             | 422      | 244   | 155    | 229   | 161   | 511            | -     | 5.7   | 1.6   | -     | -              | -     | 1.5   | -     | 2.6   | -      | -     | -      | 3.8   | -      | -     | -     |
| Ba                             | 6410     | 6260  | 4228   | 4740  | 6892  | 3285           | 52    | 44    | 1194  | -     | -              | -     | 64    | -     | -     | -      | -     | -      | -     | -      | -     | -     |
| Sr                             | 50       | 33    | 220    | 346   | 266   | 617            | 44    | 75    | 71    | 20    | 33             | 183   | 147   | -     | 346   | 158    | -     | -      | 12    | 69     | 65    | 65    |
| La                             | -        | -     | -      | -     | -     | -              | 1.5   | -     | -     | -     | -              | -     | -     | -     | 12    | -      | 6.2   | 10.1   | -     | 6.1    | 20    | 20    |
| Ce                             | 12.4     | 62    | 33     | 26    | 34    | 43             | 11    | 27    | 30    | 4.6   | 6.9            | -     | 21    | -     | 37    | 20     | 19    | 24     | 37    | 20     | 20    | 20    |
| Pr                             | -        | 25    | 2.7    | -     | 25    | -              | -     | -     | -     | -     | -              | -     | -     | -     | -     | -      | 10.2  | 7      | 13    | 14     | 14    | 14    |
| Nd                             | -        | 22    | -      | 5.2   | -     | 8.3            | 5.7   | 16    | 20    | 2.1   | 6.2            | -     | 19    | -     | 18    | 11     | -     | -      | -     | -      | 3.9   | 3.9   |
| Y                              | 61       | 73    | 28     | 40    | 31    | -              | 31    | 33    | 26    | 10    | 13             | 22.   | -     | -     | 22    | 9      | -     | -      | 14    | 24     | 18    | 18    |
| Th                             | -        | -     | -      | 3.8   | -     | 2.8            | .2    | -     | -     | -     | -              | .3    | 4.2   | -     | -     | -      | -     | -      | 4.2   | 3.5    | 3.5   | 3.5   |
| U                              | -        | -     | -      | -     | -     | -              | 2.8   | -     | -     | -     | -              | -     | 1.3   | -     | -     | -      | -     | -      | .8    | -      | .7    | .7    |
| Cu                             | 2.7      | 22    | 18     | 19    | 14.2  | 33             | 208   | 29    | 14    | 180   | 24             | -     | 106   | -     | 18    | 21     | 13    | 2.8    | 7.1   | -      | -     | -     |
| Co                             | 71       | 98    | 59     | 67    | 53    | 86             | 35    | 48    | 30    | 42    | 57             | -     | 73.8  | -     | 32    | 39     | 86    | 85     | 29    | 151    | 151   | 151   |
| Ni                             | 17       | 45    | 57     | 12    | 30.5  | 87             | 26    | 22    | 44    | 65    | 67             | -     | 154   | -     | 102   | 89     | 17    | 13     | 32    | 32     | 2.0   | 2.0   |
| V                              | 370      | 493   | 505    | 118   | 244   | 295            | 154   | 551   | 249   | 142   | 269            | -     | 227   | -     | 216   | 262    | 111   | 127    | 152   | 152    | 90    | 90    |
| Cr                             | 24       | 36    | 67     | 49    | 192   | 81             | 369   | 48    | 315   | 818   | 579            | -     | 136   | -     | 495   | 533    | -     | -      | 15    | 15     | 33    | 33    |
| Zn                             | 211      | 261   | 177    | 178   | 128   | 162            | 111   | 149   | 82    | 78    | 72             | -     | 42    | -     | 57    | 46     | 305   | 307    | 417   | 417    | 95    | 95    |
| Pb                             | -        | -     | -      | 72    | -     | -              | -     | 3.9   | -     | -     | -              | -     | -     | -     | -     | -      | -     | -      | -     | -      | -     | -     |
| Ga                             | 18       | 18    | 26     | 19    | 17    | 18             | 6.2   | 12    | 11    | 6.6   | 3.7            | 9.3   | 13    | -     | 12    | 16     | 7.4   | 5.5    | 2.7   | 6.3    | 1.9   | 1.9   |

+ total iron as FeO

\* electron microprobe determination

Table 3.4.

Microprobe analyses of ferromagnesian minerals of volcanic rocks from Melanesia.

Eastern Papua

| sample                         | 63   |      | 61   |      | OOA  |      | 08   |       | 3513 |      |
|--------------------------------|------|------|------|------|------|------|------|-------|------|------|
| phase                          | amph | bi   | amph | bi   | amph | bi   | amph | oliv  | amph | bi   |
| SiO <sub>2</sub>               | 45.4 | 35.9 | 45.6 | 38.8 | 43.1 | 38.8 | 39.4 | 36.2  | 45.6 | 37.1 |
| TiO <sub>2</sub>               | 1.3  | 3.5  | 1.4  | 3.4  | 1.9  | 3.4  | 2.8  | -     | 1.1  | 1.0  |
| Al <sub>2</sub> O <sub>3</sub> | 10.1 | 16.8 | 8.9  | 16.6 | 11.0 | 16.6 | 12.2 | -     | 7.2  | 16.7 |
| FeO                            | 14.4 | 16.3 | 14.6 | 14.1 | 11.3 | 14.1 | 10.0 | 13.2  | 14.2 | 15.9 |
| MnO                            | .16  | .3   | -    | -    | -    | -    | .1   | .4    | .4   | .12  |
| MgO                            | 13.3 | 13.9 | 13.9 | 13.3 | 14.8 | 13.3 | 16.7 | 50.6  | 14.4 | 13.8 |
| CaO                            | 11.0 | .10  | 11.0 | -    | 10.6 | -    | 11.8 | -     | 10.8 | -    |
| Na <sub>2</sub> O              | 1.85 | .10  | 1.6  | .2   | 2.45 | .2   | 2.3  | -     | 1.8  | -    |
| K <sub>2</sub> O               | .70  | 9.0  | .5   | 8.8  | 1.9  | 8.8  | .69  | -     | .7   | 8.9  |
| Total                          | 98.2 | 95.9 | 97.5 | 95.2 | 97.0 | 95.2 | 96.0 | 100.4 | 96.2 | 95.7 |

Eastern Papua

| sample                         | 3555 |      | 3526 b |       | 3548  |       | 3528  |       | 3544 |      |
|--------------------------------|------|------|--------|-------|-------|-------|-------|-------|------|------|
| phase                          | amph | bi   | amph   | opx   | cpx   | opx   | cpx   | oliv  | cpx  | oliv |
| SiO <sub>2</sub>               | 43.4 | 37.6 | 43.5   | 53.4  | 53.0  | 53.4  | 53.1  | 35.3  | 50.8 | 36.5 |
| TiO <sub>2</sub>               | 2.4  | 4.1  | 2.1    | .2    | .2    | .2    | .2    | -     | .4   | -    |
| Al <sub>2</sub> O <sub>3</sub> | 10.0 | 17.4 | 10.1   | .7    | 2.7   | 16.6  | 1.6   | -     | 2.3  | 20.1 |
| FeO                            | 11.5 | 16.8 | 12.3   | .3    | 8.3   | 16.6  | 8.6   | 17.8  | 6.6  | .2   |
| MnO                            | .22  | .07  | -      | .3    | .1    | .3    | .1    | .2    | .1   | 43.1 |
| MgO                            | 15.2 | 12.3 | 15.3   | 28.2  | 17.5  | 28.2  | 17.1  | 46.9  | 17.8 | -    |
| CaO                            | 10.3 | -    | 10.9   | 1.2   | 20.1  | 1.2   | 20.6  | -     | 21.3 | -    |
| Na <sub>2</sub> O              | 2.3  | .54  | 2.2    | -     | -     | -     | -     | -     | -    | -    |
| K <sub>2</sub> O               | 1.25 | 8.6  | .7     | -     | -     | -     | .3    | -     | .36  | -    |
| Total                          | 96.5 | 97.4 | 97.1   | 100.6 | 101.9 | 100.6 | 101.6 | 100.2 | 99.6 | 99.9 |

SolomonsNew Guinea Highlands

| sample                         | 144  |       | 176   |       | 101  |       | RP   |      |
|--------------------------------|------|-------|-------|-------|------|-------|------|------|
| phase                          | amph | amph  | amph  | cpx   | amph | opx   | amph | amph |
| SiO <sub>2</sub>               | 42.8 | 45.4  | 45.4  | 53.9  | 41.4 | 48.8  | 39.8 | 39.8 |
| TiO <sub>2</sub>               | 1.5  | 1.9   | 1.9   | .2    | 2.3  | .5    | 2.2  | 2.2  |
| Al <sub>2</sub> O <sub>3</sub> | 12.3 | 12.2  | 12.2  | 1.9   | 10.8 | 3.8   | 13.7 | 13.7 |
| FeO                            | 13.4 | 9.9   | 9.9   | 8.1   | 12.4 | 9.6   | 11.5 | 11.5 |
| MnO                            | -    | -     | -     | -     | -    | -     | -    | -    |
| CaO                            | 11.2 | 11.1  | 11.1  | 20.9  | 11.0 | 1.0   | 12.7 | 12.7 |
| Na <sub>2</sub> O              | 2.8  | 2.25  | 2.25  | .3    | 2.3  | -     | 1.9  | 1.9  |
| K <sub>2</sub> O               | .28  | .48   | .48   | -     | 1.5  | .07   | .7   | .7   |
| Total                          | 98.7 | 96.13 | 96.13 | 100.6 | 96.6 | 100.7 | 97.2 | 97.2 |

Table 3.5. Chemical analyses of amphibole bearing inclusions from Kiama, N.S.W.

|                                | 28    | 23    | 26    | 24     | 22    | 27    | 25     |
|--------------------------------|-------|-------|-------|--------|-------|-------|--------|
| SiO <sub>2</sub>               | 40.53 | 33.10 | 35.00 | 38.11  | 38.89 | 39.95 | 40.47  |
| TiO <sub>2</sub>               | 3.82  | 5.93  | 7.00  | 5.12   | 5.05  | 3.34  | 2.75   |
| Al <sub>2</sub> O <sub>3</sub> | 12.00 | 10.62 | 11.97 | 11.68  | 9.26  | 8.57  | 9.40   |
| Fe <sub>2</sub> O <sub>3</sub> | 4.33  | 3.34  | 6.30  | 3.48   | 4.59  | 2.93  | 2.61   |
| FeO                            | 7.67  | 10.82 | 11.34 | 9.83   | 10.95 | 8.31  | 8.96   |
| MnO                            | .22   | .19   | .15   | .19    | .19   | .19   | .20    |
| MgO                            | 6.10  | 7.37  | 8.89  | 8.83   | 9.23  | 10.55 | 11.58  |
| CaO                            | 14.54 | 16.47 | 11.55 | 12.58  | 16.91 | 18.36 | 15.31  |
| Na <sub>2</sub> O              | 2.42  | 6.52  |       | 5.16   | 1.19  | 1.96  | 5.22   |
| K <sub>2</sub> O               | 2.01  | 1.35  | 1.73  | 1.46   | .32   | .54   | 1.85   |
| P <sub>2</sub> O <sub>5</sub>  | .07   | .28   | .48   | .19    | .21   | .36   | .17    |
| Loss (ΣH <sub>2</sub> O)       | 5.96  | 3.76  | 2.68  | 3.50   | 3.09  | 4.65  | 2.08   |
| total                          | 99.67 | 99.66 |       | 100.13 | 99.88 | 99.71 | 100.60 |
| Rb                             | 34.6  |       | 18.4  | 9.1    |       | 10.3  | 34.6   |
| Bg                             | 1336  | 238   | 678   | 1002   | 79.2  | 382   | 1336   |
| Pb                             | 6     |       | 3     | 1      |       |       | 6      |
| Sr                             | 1540  |       | 853   | 302    |       | 436   | 1540   |
| La                             | 59.8  | 35.4  | 5.7   |        |       | 15.7  | 59.8   |
| Ce                             | 166   | 130   | 63.5  | 53.9   | 29.1  | 66.9  | 166    |
| Pr                             | 27.5  | 41.0  | 35.1  | 33.0   | 25.7  | 26.4  | 27.5   |
| Na                             | 61.0  | 98.7  | 29.3  | 19.6   | 17.8  | 45.2  | 61     |
| Y                              | 38.7  |       | 25.7  | 18.9   |       | 23.9  | 38.7   |
| Th                             | 6.1   |       | 2.8   | 1.2    |       |       | 6.1    |
| U                              | 2.1   |       | .4    | 2.9    |       |       | 2.1    |
| Zr                             | 414   | 204   | 2.7   | 149    | 152   | 194   | 213    |
| Nb                             | 108   | 52.8  | 71.9  | 56.8   | 21.8  | 31.2  | 42.0   |
| Cu                             | 52.4  | 68.0  | 60.9  | 60.9   | 174   | 55.0  | 52.4   |
| Co                             |       |       |       |        |       |       |        |
| Ni                             | 133   | 19.0  | 94.4  | 91.1   | 234   | 142   | 133    |
| V                              | 200   | 379   | 475   | 386    | 728   | 342   | 200    |
| Cr                             | 222   | 12.2  | 272   | 222    | 142   | 608   | 222    |
| Ga                             | 16.6  |       | 19.7  | 19.3   |       | 13.4  | 16.6   |
| Zn                             | 120   | 128   | 136   | 77.9   | 95.7  | 76    | 120    |

in randomly selected concentrates indicates that purity of concentrates was better than 99% or in some cases better than 99.5%. Analyses of coexisting ferromagnesian phases and iron-titanium oxides are presented in Table 3.13.

Petrographic details of the host rocks are given in Appendix 2 and their major element chemistry is given in Tables 2.1 to 2.7. A brief summary of some relevant petrographic features is given below.

In most calc-alkaline volcanic rocks amphibole forms euhedral acicular or bladed phenocrysts. The presence of "opacite rims" consisting of a reaction corona of plagioclase, orthopyroxene and an abundance of a fine-grained opaque phase is characteristic. These rims are best developed in rocks with holocrystalline groundmass (e.g. Lewis, 1968). In some amphiboles there are two, three or more "buried" opacite rims observable in sections oriented perpendicular to "z".

Amphibole phenocrysts range from 0.8 to 5.0 mm (average 2.5 mm) in length. Polycrystalline aggregates are rare. The amount of amphibole varies, but in rocks with a glassy matrix the amphibole forms about 50% of the phenocrysts. Simple twins parallel to (100) are commonly observed. Distinct zoning is characterised by a deepening in colour and an increase in extinction angle. Electron

microprobe investigation of the zonal variation in major elements shows that for iron, magnesium and calcium oxides the variation does not exceed 2% by weight (Fig. 3.1).

Indices of refraction, extinction angles and optical axial angles of amphiboles are presented in Table 3.10. The immersion method has been used to measure refractive indices and a spindle stage was used to orient mineral grains. Measurements were carried out in sodium light but the low precision ( $\pm 0.004$  to  $0.006$ ) results from the compositional zonation. The measurement of extinction angles and optic axial angles were carried out on grain mounts and thin sections on a universal stage. The results presented are the average of at least three measurements and precision is believed to be better than  $\pm 5^\circ$ .

#### Composition of amphiboles and host rocks

It has been stated by several authors (e.g. Leake, 1965) that the composition of an amphibole reflects that of its host rock but their evidence is derived mainly from metamorphic rocks such as amphibolites in which amphibole is the sole ferromagnesian phase. In the crystallisation of igneous rocks Deer (1950) showed that there is preferential entry of Al into early formed amphiboles without change of Mg/Fe ratio during amphibole crystallization. In hypotheses of amphibole fractionation the fact that

amphiboles crystallizing at high pressures are low in  $\text{SiO}_2$  and highly aluminous but independent of rock composition, should be considered (e.g. data of Green and Ringwood, 1968; Takeshito and Oji, 1968; McBirney and Aoki, 1969).

New data on amphiboles and their host rocks are plotted in Figure 3.2 in terms of  $100\text{MgO}/\text{MgO} + \text{FeO} + 0.9 \text{Fe}_2\text{O}_3 + \text{MnO}$  to illustrate relationships between amphiboles and their host rocks. The diagram does suggest a general relationship between the composition of an amphibole and its host rock but there is also a strong tendency for a fairly constant iron-magnesium ratio in amphiboles from rocks with varied  $\text{Fe}/\text{Mg} + \text{Fe}$  ratio. Rocks with lower iron content contain amphiboles with lower  $\text{Fe}/\text{Mg} + \text{Fe}$  ratio but rocks with more iron have amphiboles where both ratios (in rocks and amphibole) approximate unity.

The  $\text{Fe}_2\text{O}_3/\text{FeO}$  plot (Fig. 3.3) shows a preferential entry of ferrous iron with respect to ferric iron into amphibole relative to clinopyroxenes and residual liquids (Aoki, 1963). Where  $\text{Fe}_2\text{O}_3/\text{FeO}$  of amphibole is higher than that of the total rocks it can be argued that amphibole has been oxidized under near surface conditions (Aoki, 1963).

The data on alkali contents is expressed as  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  wt %, and plotted in Figure 3.4. Except for amphiboles from basaltic alkaline rocks the ratio of  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  is higher in amphiboles than in their host lavas. The data on

alkaline rocks presented here are exceptional since other alkaline rocks and their amphiboles, e.g. those from Tahiti (McBirney and Aoki, 1969) show the same trends as calc-alkaline rocks (i.e. higher  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios in amphiboles). This implies that the early crystallization of amphibole could enrich the residual liquids in K relatively to Na.

Continental calc-alkaline andesites, where  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratio in more silicic rocks is close to 1.0 (shoshonitic ratio), usually have amphibole as a liquidus phase. The trace element chemistry (e.g. very low K/Rb ratio) also suggests that these rocks could have been derived from a source in which amphibole was a residual phase. Further evidence for this hypothesis comes from study of hornblende-gabbro inclusions in calc-alkaline andesites (e.g. Yamazaki *et al.*, 1966; Takeshito and Oji, 1968; and Jakes<sup>Y</sup> and Smith, 1970 - Tab. 2). These inclusions have  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios higher than their host rocks. More siliceous derivative liquids with lower  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios could be produced by the removal of such cognate accumulates and this mechanism may account for the shoshonitic rocks (latites) found in continental calc-alkaline provinces e.g. in the Andean region.

#### Composition of amphiboles

Numerous classifications for minerals of the amphibole group have been proposed (e.g. Hallimond, 1943; Sundius, 1946;

Deer et al., 1963). Leake (1968) presented a comprehensive compilation of calcic amphiboles and suggested a semi-descriptive classification using structural formula calculated on the basis of 24 (OH,F,O). This classification is used here, but calculation of structural formulae was based on 23 oxygens (water free), assuming the generalized formula  $A_{O-1}X_2Y_5Z_8O_{23}$ . 23 oxygens were used for the following reasons:

(a) Amphibole analyses done on an electron microprobe can be used, as can analyses of amphiboles where the amount of material was insufficient to determine the water content.

(b) Some amphiboles were found to be oxidized with the  $H_2O$  content below 1.80 wt %.

(c) Comparison with experimentally crystallized amphiboles can be made.

(d) There are only very small differences between formula calculated using 23 and 24 oxygens (Dodge et al., 1969).

Chemical analyses of amphiboles are presented in Tables 3.1, 3.2, 3.4 and structural formulae in Tables 3.6, 3.7, 3.8, 3.9.

Major element variations in amphibole composition include the differences in Si-Al relationship, oxidation state, nature of the divalent cations, Ti content and the Ca - (Na + K) relations. In all 55 analyses the content of

aluminium was sufficient to fill the Z group except for two (49, 2) where Ti has been added to Z group, although some authors (e.g. McBirney and Aoki, 1969) suggest that  $\text{Fe}^{3+}$  enters four-four co-ordination positions before Ti. However, there is no conclusive evidence supporting this (c.f. discussion by Leake, 1968; Phillips, 1963).

In most analyses the total number of cations in the Y position exceeds 5.00, but Leake (1968) claims a limit of 5.25 for superior analyses. There is, however, marked correlation between (OH + F) and total ions in the Y group. Because of the relatively low content of (OH + F) in amphiboles from volcanic rocks a satisfactory value for total ions in the Y group is 5.35.

The totals of A + X groups are in most samples well below the theoretical value of 3.00, except for two samples from inclusions in alkaline rocks. The other three samples from similar inclusions of the same locality are very close to 3.00. Because these amphiboles are relatively low in  $\Sigma Y$  (4.75) there is a possibility that Ca can enter the Y group.

The total aluminium contents vary from 1.4 to 3.2 and can be related to the geological setting of the host rock. Amphiboles with lowest  $\text{Al}^{\text{vi}} + \text{Al}^{\text{iv}}$  contents are from andesites of continental areas (Carpathians, Hunter River area). These amphiboles are very similar to those from

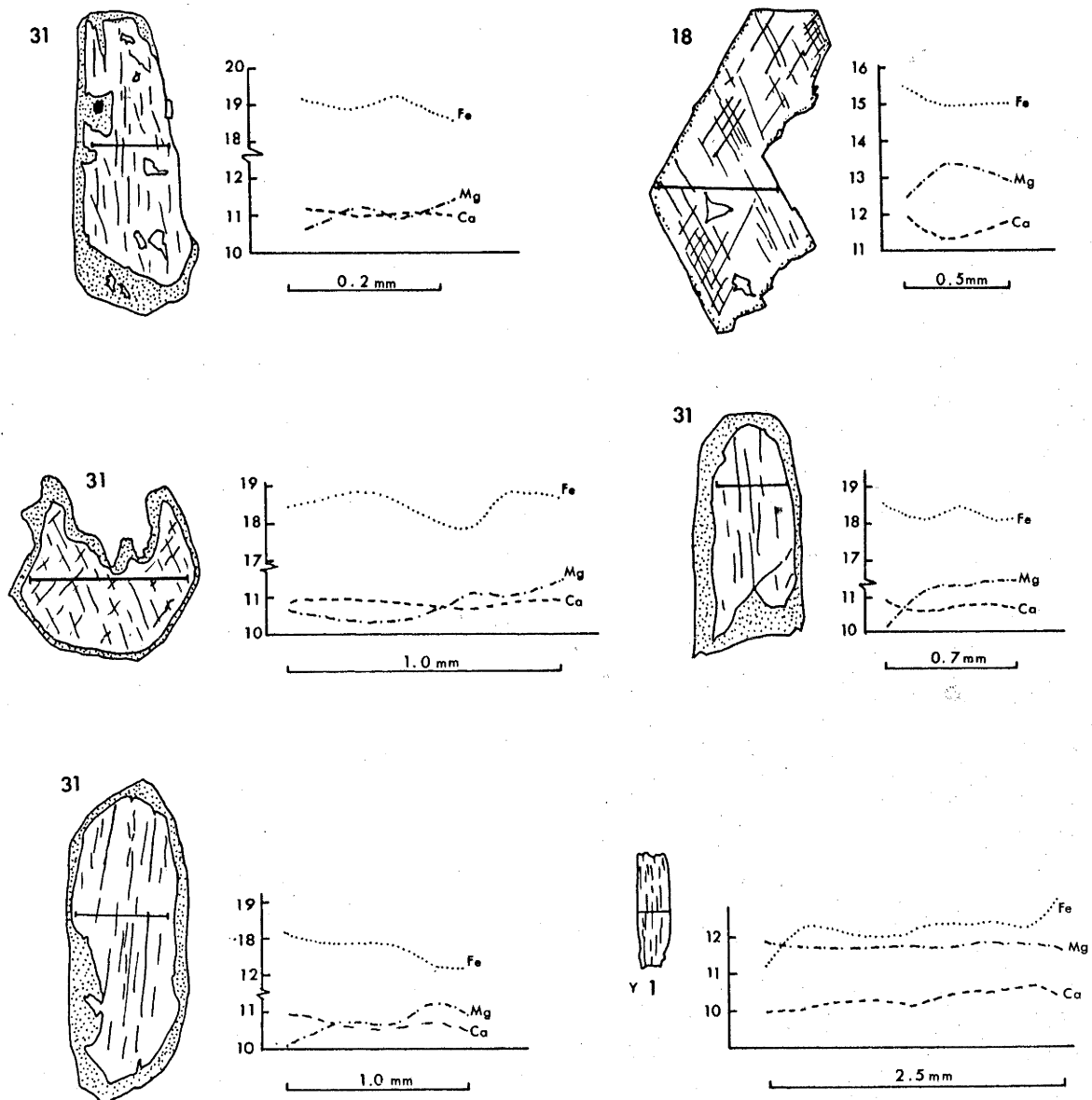


Figure 3.1: Electron microprobe data on optically strongly zoned amphiboles from calc-alkaline volcanic rocks, all data in weight %.

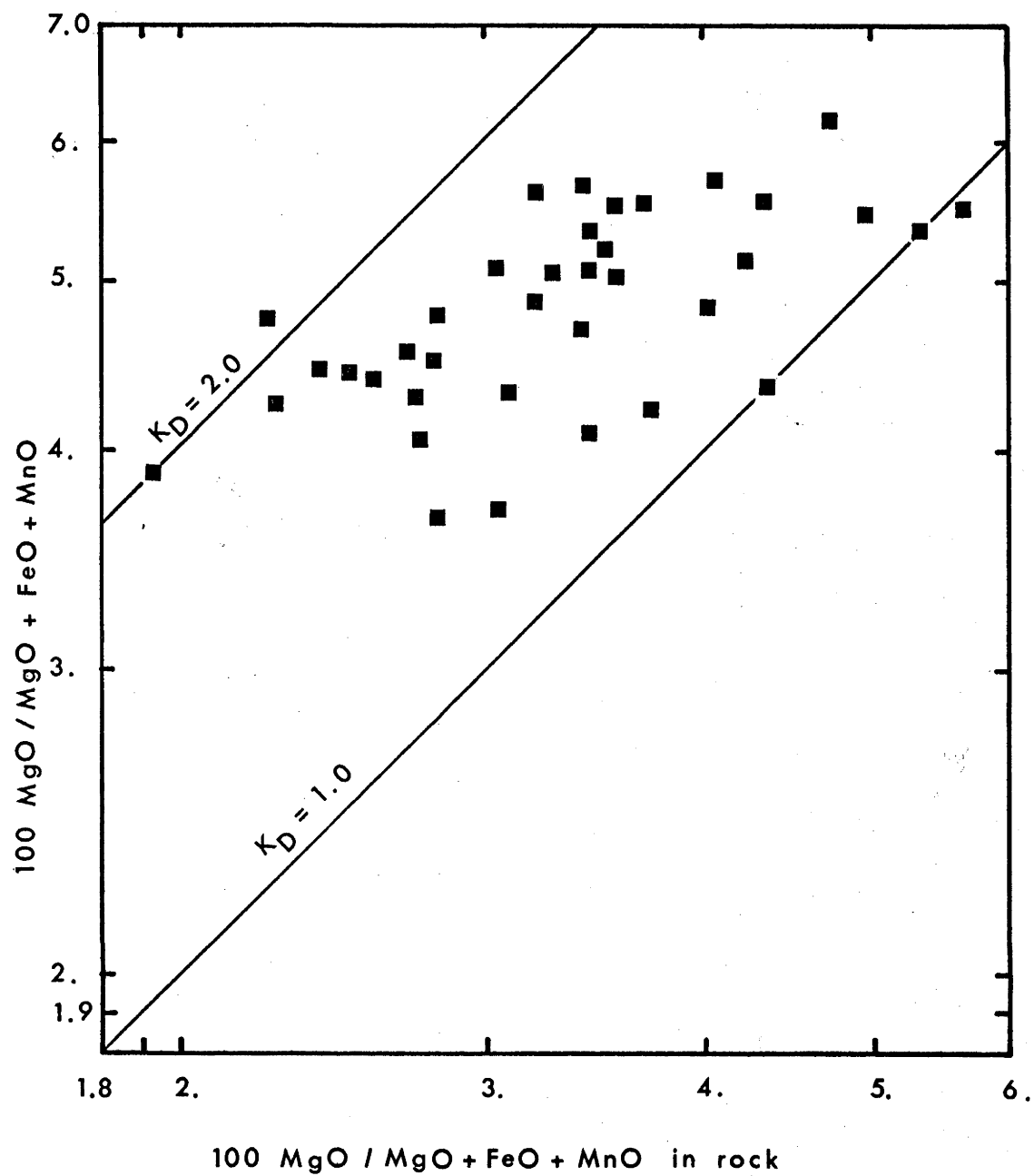


Fig. 3.2. New data on composition of amphiboles and their host rocks in terms of  $100 \text{ Mg} / \text{MgO} + \Sigma \text{FeO} + \text{MnO}$ . (See text).

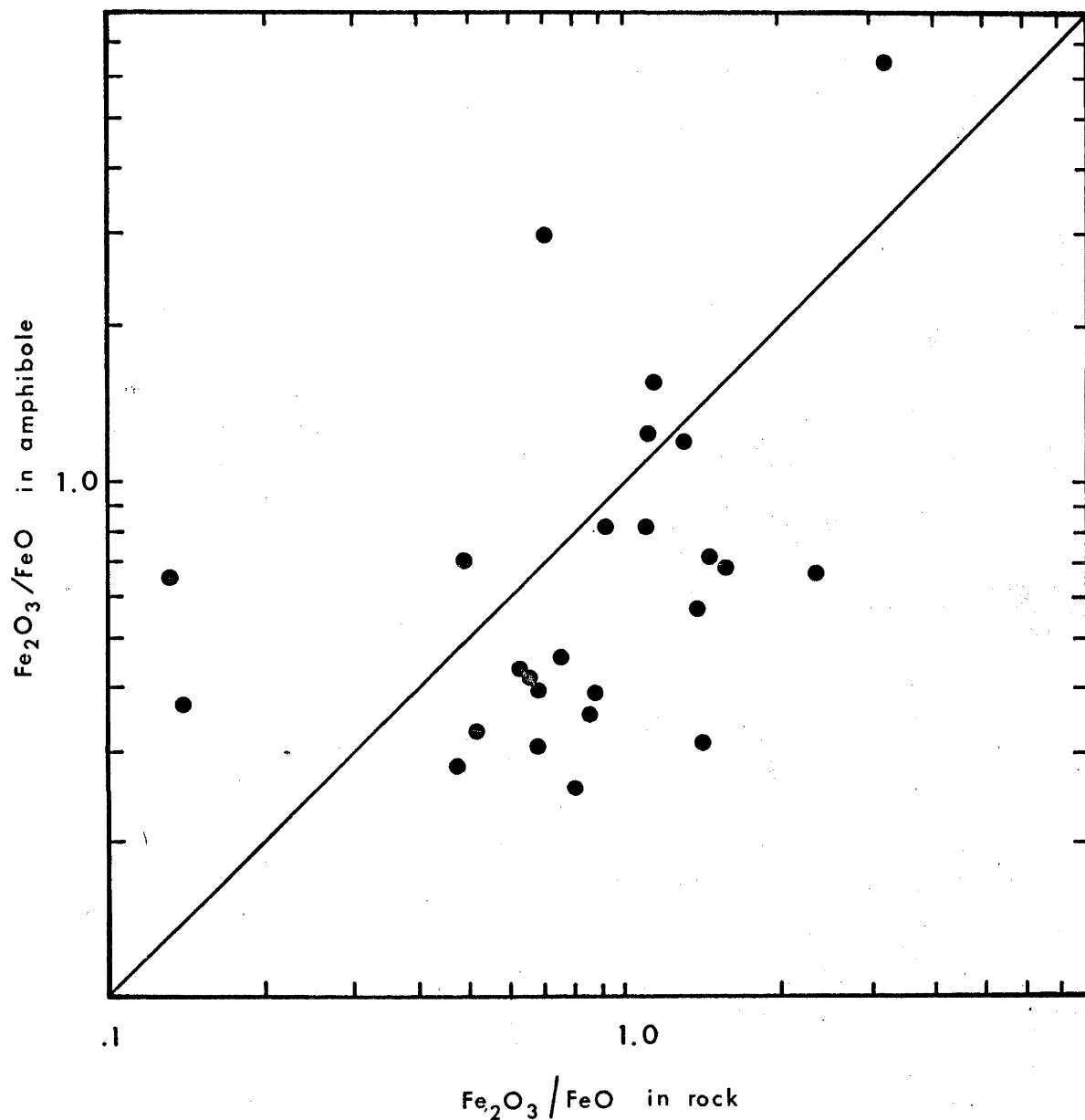


Figure 3.3: New data on Fe<sub>2</sub>O<sub>3</sub>/FeO relations of amphiboles and their host rocks. (See text)

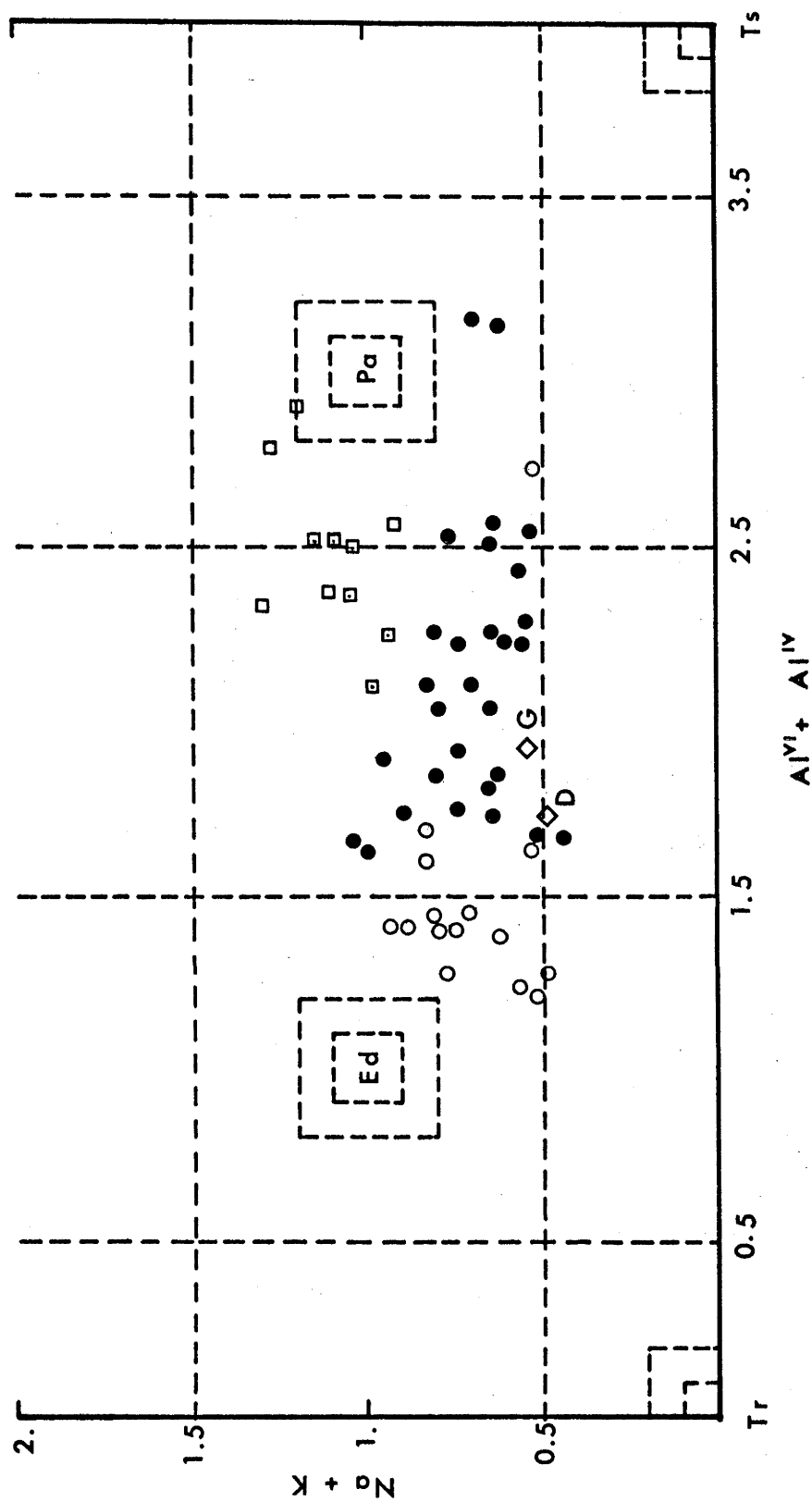
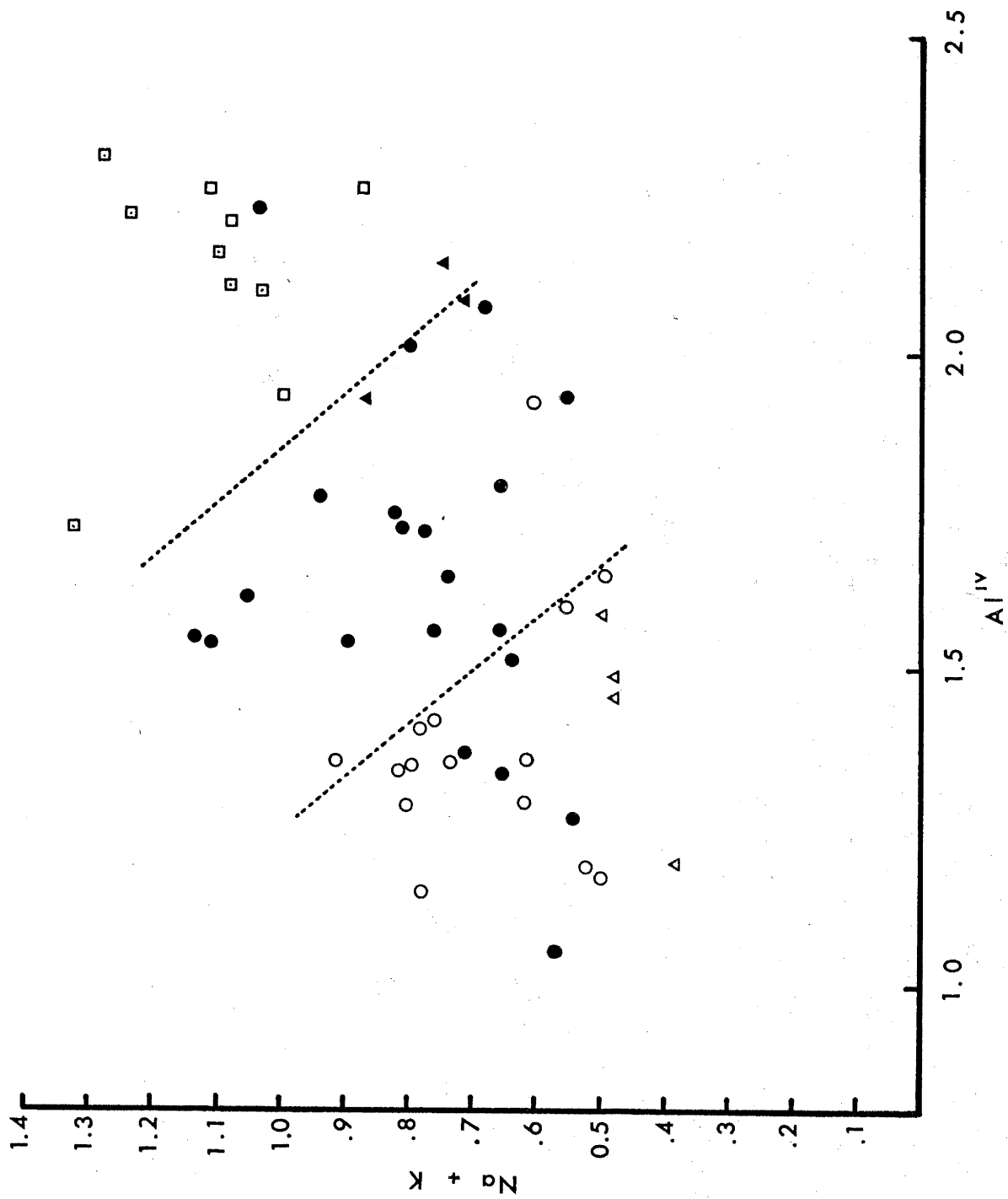


Fig. 3.4. Plot of  $Al^{iv} + Al^{vi}$  vs.  $Na + K$  for amphiboles from continental calc-alkaline volcanic rocks (open circles), andesites from island arcs (filled circles), alkaline basalts (open squares), and from inclusions in alkaline basalts (squares with dots). All new data except diamonds D - average amphibole from diorite, and G - average amphibole from gabbro, according to Kostyuk and Sobolev, 1969.

Figure 3.5: Plot of tetrahedral aluminium ( $\text{Al}^{\text{iv}}$ ) vs. Na + K of analysed amphiboles.

Open circles - amphiboles from andesites of continental areas; full circles - amphiboles from island arc areas; empty squares - amphibole xenocrysts from alkaline basalts; squares with dots - amphiboles from inclusions in alkaline basalts; empty triangles - amphiboles from gabbroic rocks; full triangles - amphiboles from ultramafic nodules.  
(Kuno and Aoki, 1970)



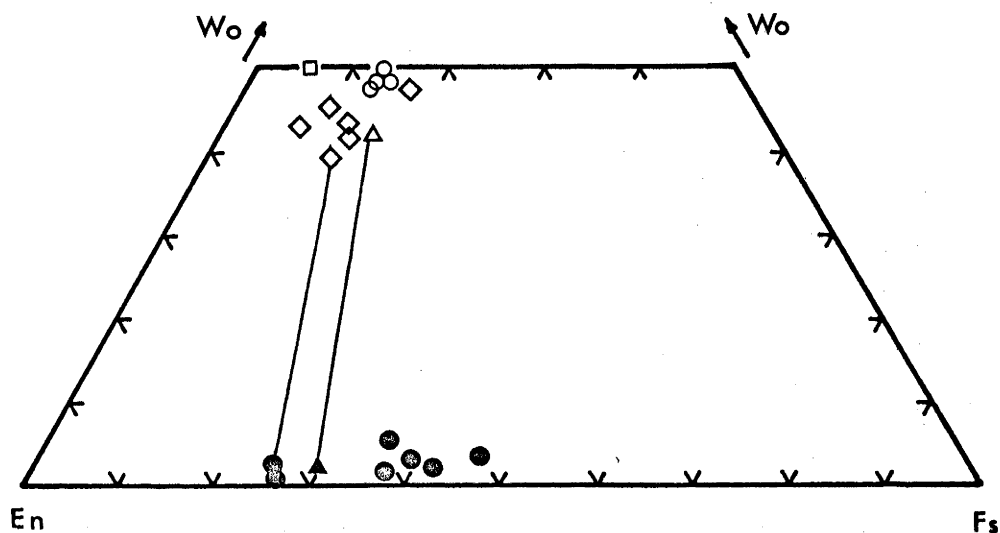


Fig. 3.6. New data on pyroxenes in triangular diagram  $\text{MgSiO}_3 - \text{FeSiO}_3 - \text{CaSiO}_3$ . Diamonds - clinopyroxenes from calc-alkaline rocks, empty triangle pyroxene from shoshonitic rock, empty circles clinopyroxenes from inclusions in alkaline basalts, square clinopyroxene from Etna. Filled circles - orthopyroxenes from calc-alkaline rocks, triangle-orthopyroxene from shoshonitic rock.

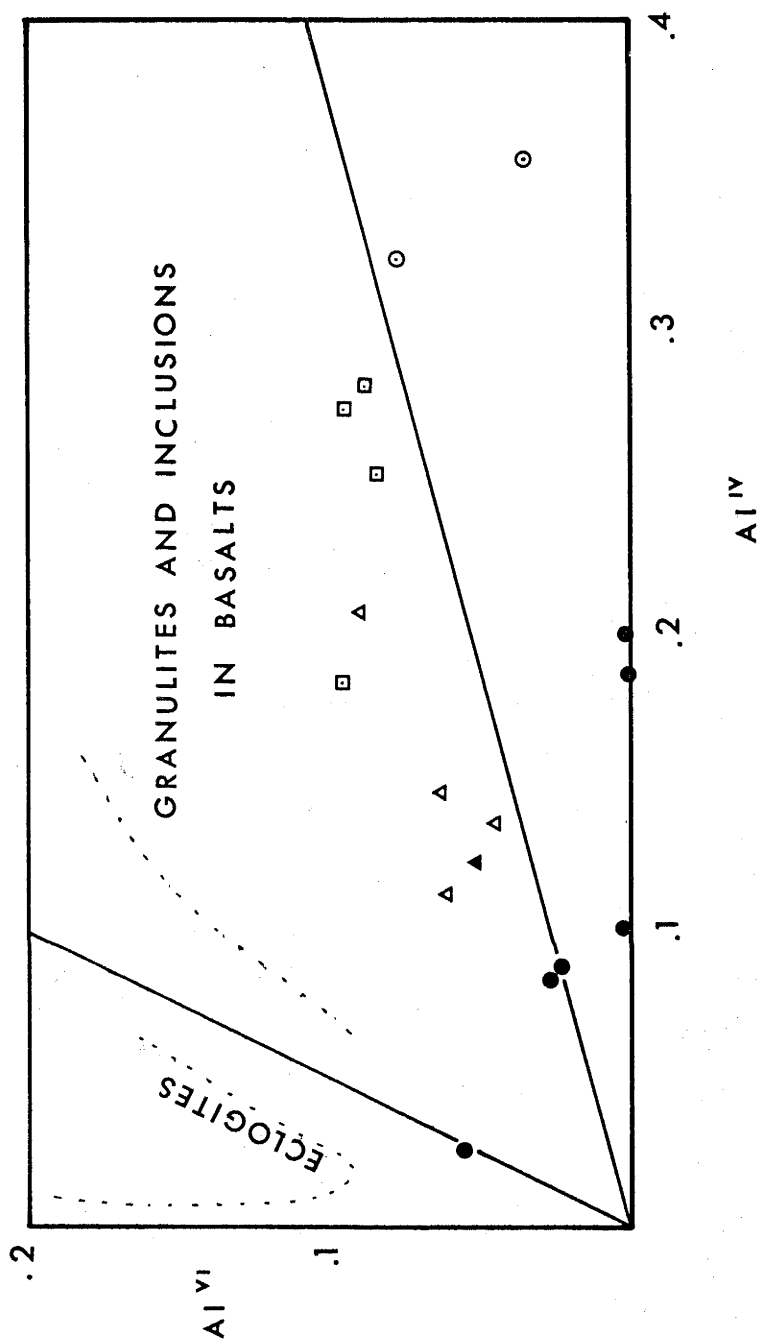


Fig. 3.7. New and selected data on the relationship of Al<sup>VI</sup> and Al<sup>IV</sup> of clinopyroxenes coexisting with amphiboles in calc-alkaline volcanic rocks (filled circles), inclusions in calc-alkaline basalts (squares), inclusions in calc-alkaline rocks (triangles) (data from Yamazaki et al., 1966; Kuno and Aoki, 1970) and plutonic inclusions from Tristan da Cunha (Le Maitre, 1969) (empty circles).

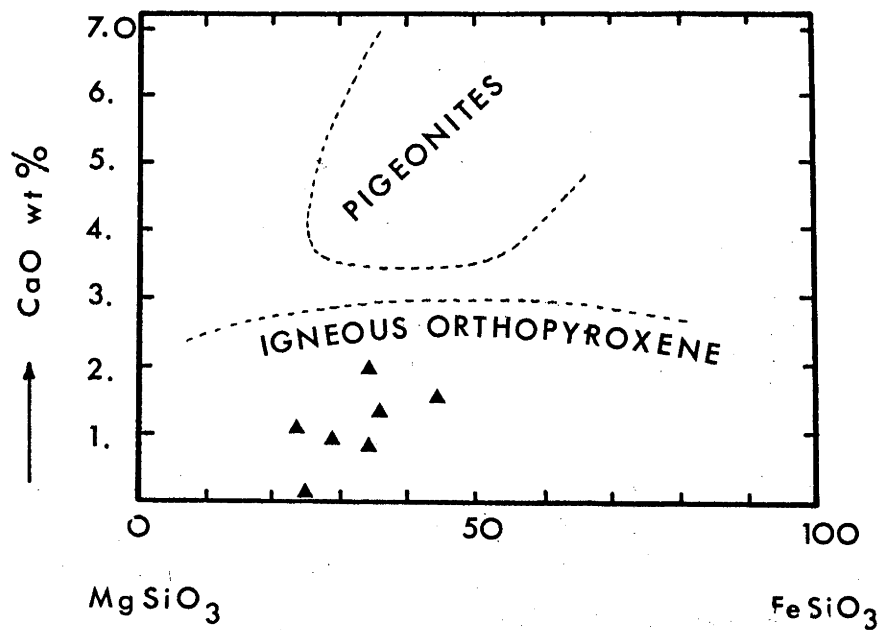


Fig. 3.8. Plot of CaO wt. % vs. En - Fs relations for orthopyroxenes from calc-alkaline volcanic rocks. According to Kuno, 1966. New data only.

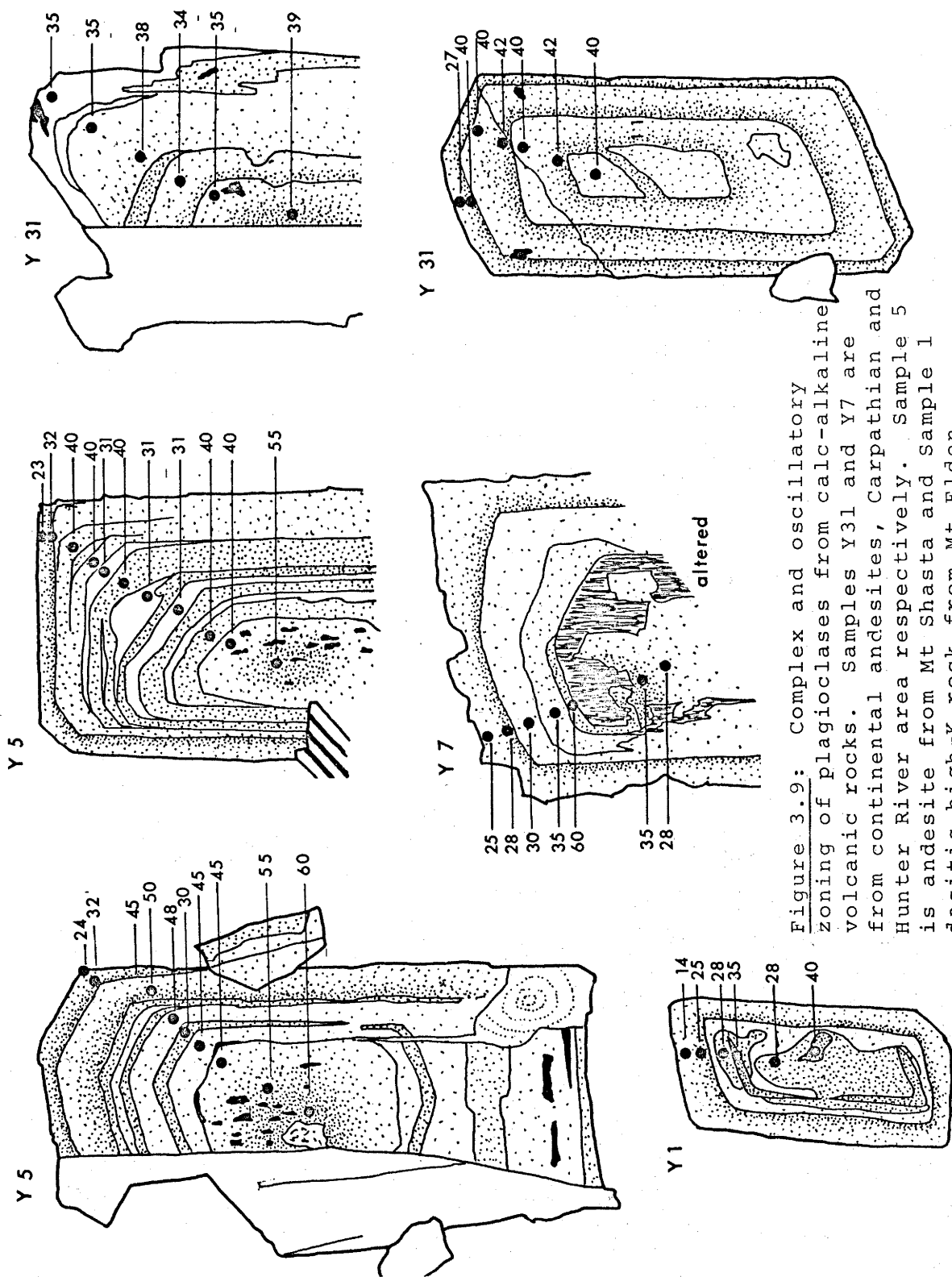


Figure 3.9: Complex and oscillatory zoning of plagioclases from calc-alkaline volcanic rocks. Samples Y31 and Y7 are from continental andesites, Carpathian and Hunter River area respectively. Sample 5 is andesite from Mt Shasta and Sample 1 dacitic high-K rock from Mt Elden.

rocks of granitic and granodioritic composition e.g. from Sierra Nevada batholith (Dodge et al., 1968) and are quite similar to amphiboles from diorites (e.g. Kostyuk and Sobolev, 1969). Amphiboles from andesites of island arcs have a higher total Al content; in some samples the Al content is as high as that of kaersutitic amphiboles from deep seated inclusions, however the alkali content is lower (Fig. 3.4).

The positive correlation between alkali content ( $\text{Na} + \text{K}$ ) and  $\text{Al}^{\text{iv}}$  (Fig. 3.5) indicates high edenite substitution. There is also a positive correlation between  $\text{Al}^{\text{iv}}$  and the sum of  $\text{Fe}^{3+} + \text{Al}^{\text{vi}} + \text{Ti}$  (cf. Dodge et al., 1968, Fig. 12). On the  $\text{Al}^{\text{iv}}$  vs.  $\text{Na} + \text{K}$  diagram (Fig. 3.4), amphiboles of different origins form separate groups. Low  $\text{Al}^{\text{iv}}$  and low  $\text{Na} + \text{K}$  is characteristic of amphiboles from continental andesites and from gabbroic rocks. Three of the four amphiboles from circum-Pacific andesites which fall within this field are from the high-K andesites of Eastern Papua; in the later rocks, the appearance of amphibole on the liquidus is a characteristic feature. The group of amphiboles from the circum-Pacific area contain higher  $\text{Al}^{\text{iv}}$  and  $\text{Na} + \text{K}$ . Amphiboles from inclusions in alkali basalts and "xenocrystic" amphiboles from alkali(?) basalts form the third group. Between the amphiboles of circum-Pacific andesites and the amphiboles from inclusions in alkaline rocks, there is a

grouping of amphiboles from garnet peridotites (Kuno and Aoki, 1970) and from inclusions in calc-alkaline rocks (Yamazaki et al., 1966).

The third group also includes hornblendes from alkali lavas from Tahiti (McBirney and Aoki, 1969), megacrysts from alkaline basalts (Binns, 1969), kaersutites from xenoliths from Tristan da Cunha (Le Maitre, 1969), as well as hornblendes from San Carlos (Mason, 1969, Prinz and Nehru, 1969) and those from Kakanui breccia (Mason, 1969).

The titanium content varies widely but is low in rocks of calc-alkaline parentage with the one exception of an amphibole from a high-K andesite. The different  $\text{TiO}_2$  contents of igneous and metamorphic amphiboles led Leake (1965) to suggest that increasing temperature produces an increase in Ti content. There is no systematic variation in the  $\text{TiO}_2$  content of amphiboles and their host rocks (continental and circum-Pacific andesites) which could be interpreted in terms of different temperatures but comparison of  $\text{TiO}_2$  content in parental rocks suggest a compositional control.

Fluorine has been determined in about half of the amphiboles; the amount of fluorine is generally very low, average .20%, except in samples from the Hunter River area with an average content of about .45%. With two exceptions, the amount of  $\text{H}_2\text{O}^+$  does not exceed 2%. In volcanic rocks,

Table 3.6.

Structural formulae of amphiboles from calc-alkaline volcanic rocks of island arcs

|                  | New Zealand |       |       |       | Fiji  |       |       |       | W. United States |       |       |
|------------------|-------------|-------|-------|-------|-------|-------|-------|-------|------------------|-------|-------|
|                  | 47          | 48    | 50    | 46    | 52    | 2     | 6     | 18    | 53               | 5     | 1     |
| Si               | 6.360       | 6.283 | 6.064 | 6.489 | 6.207 | 6.940 | 6.452 | 6.451 | 6.587            | 6.439 | 5.720 |
| Al <sup>iv</sup> | 1.640       | 1.717 | 1.936 | 1.511 | 1.793 | .687  | 1.548 | 1.548 | 1.713            | 1.561 | 2.280 |
| Ti               |             |       |       |       |       | .153  |       |       |                  |       |       |
| Al <sup>vi</sup> | .212        | .552  | .361  | .313  | .363  | -     | .121  | .122  | .224             | .260  | .279  |
| Ti               | .226        | .198  | .278  | .156  | .192  | -     | .211  | .217  | .325             | .180  | .571  |
| Fe <sup>3+</sup> | .814        | .577  | .681  | .644  | .602  | 1.325 | .607  | .599  | .685             | .942  | .337  |
| Fe <sup>2+</sup> | .566        | .539  | 1.114 | 1.236 | .812  | .888  | .950  | .963  | .606             | .346  | 1.222 |
| Mn               | .034        | .041  | .001  | .053  | -     | -     | .008  | .007  | -                | .017  | -     |
| Mg               | 2.862       | 2.852 | 2.709 | 2.466 | 3.056 | 3.124 | 3.041 | 2.943 | 3.103            | 3.364 | 2.579 |
| Ca               | 2.057       | 1.975 | 1.752 | 1.960 | 1.857 | 1.450 | 1.725 | 1.808 | 1.738            | 1.714 | 1.758 |
| Na               | .698        | .678  | .503  | .523  | .619  | .649  | 1.070 | 1.069 | .740             | .570  | 1.012 |
| K                | .139        | .135  | .055  | .120  | .050  | .037  | .033  | .035  | .041             | .076  | .061  |

|                  | Eastern Papua |       |       |       | Solomons |       |       |       | New Guinea |       |       |
|------------------|---------------|-------|-------|-------|----------|-------|-------|-------|------------|-------|-------|
|                  | 00A           | 008   | 3513  | 3555  | 3526B    | 63    | 61    | 144   | 176        | 101   | R.P.  |
| Si               | 6.398         | 5.911 | 6.942 | 6.453 | 6.437    | 6.663 | 6.736 | 6.261 | 6.643      | 6.225 | 5.920 |
| Al <sup>iv</sup> | 1.602         | 2.089 | 1.058 | 1.546 | 1.563    | 1.336 | 1.264 | 1.739 | 1.357      | 1.775 | 2.080 |
| Ti               |               |       |       |       |          |       |       |       |            |       |       |
| Al <sup>vi</sup> | .321          | .073  | .173  | .209  | .202     | .414  | .289  | .386  | .751       | .142  | .327  |
| Ti               | .211          | .316  | .112  | .268  | .233     | .143  | .155  | .165  | .209       | .259  | .246  |
| Fe <sup>3+</sup> | -             | -     | -     | -     | -        | -     | -     | -     | -          | -     | -     |
| Fe <sup>2+</sup> | 1.402         | 1.255 | 1.570 | 1.430 | 1.523    | 1.768 | 1.804 | 1.640 | 1.212      | 1.559 | 1.431 |
| Mn               | -             | .012  | .050  | .027  | -        | .020  | -     | -     | -          | -     | -     |
| Mg               | 3.274         | 3.736 | 3.376 | 3.370 | 3.376    | 2.911 | 3.062 | 3.141 | 2.815      | 3.341 | 3.261 |
| Ca               | 1.686         | 1.897 | 1.756 | 1.641 | 1.728    | 1.730 | 1.741 | 1.756 | 1.740      | 1.772 | 2.024 |
| Na               | .704          | .669  | .462  | .663  | .631     | .527  | .458  | .789  | .639       | .671  | .548  |
| K                | .358          | .132  | .114  | .237  | .132     | .131  | .094  | .054  | .089       | .288  | .133  |

Table 3.7.

Structural formulae of amphiboles from continental calc-alkaline volcanic rocks

|                  | Carpathians |       |       |       | Hunter river area N.S.W. |       |       |       |       |       |       |       |       |       |       |  |
|------------------|-------------|-------|-------|-------|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|
|                  | 34          | 31    | 32    | 33    | 9                        | 7     | 10    | 8     | 13    | 14    | 12    | 17    | 11    | 16    | 40    |  |
| Si               | 6.076       | 6.659 | 6.726 | 6.400 | 6.833                    | 6.548 | 6.814 | 6.852 | 6.655 | 6.650 | 6.703 | 6.582 | 6.643 | 6.628 | 6.342 |  |
| Al <sup>iv</sup> | 1.924       | 1.341 | 1.274 | 1.600 | 1.167                    | 1.416 | 1.186 | 1.148 | 1.345 | 1.350 | 1.297 | 1.408 | 1.357 | 1.372 | 1.658 |  |
| Ti               |             |       |       |       |                          |       |       |       |       |       |       | .010  |       |       |       |  |
|                  |             |       |       |       |                          |       |       |       |       |       |       |       |       |       |       |  |
| Al <sup>vi</sup> | .814        | .387  | .330  | .039  | .133                     |       | .107  | .117  | .067  | .096  | .141  |       | .059  | .028  | .209  |  |
| Ti               | .205        | .190  | .197  | .217  | .194                     | .204  | .194  | .118  | .226  | .225  | .214  | .254  | .224  | .214  | .129  |  |
| Fe <sup>3+</sup> | .520        | .407  | .553  | 1.707 | .452                     | .343  | .503  | .389  | .380  | .517  | -     | .747  | .493  | .578  | .692  |  |
| Fe <sup>2+</sup> | 1.168       | 1.499 | 1.675 | .310  | 1.213                    | 1.518 | 1.225 | 1.310 | 1.503 | 1.430 | 2.133 | 1.163 | 1.454 | 1.487 | 1.180 |  |
| Mn               | -           | .050  | .015  | .004  | .031                     | .001  | .031  | .033  | .003  | .030  | .029  | .003  | .026  | .029  | .034  |  |
| Mg               | 2.512       | 2.516 | 2.379 | 2.497 | 3.028                    | 3.208 | 2.940 | 2.909 | 2.876 | 2.746 | 2.854 | 2.789 | 2.751 | 2.859 | 2.726 |  |
| Ca               | 1.558       | 1.616 | 1.479 | 1.713 | 1.792                    | 1.747 | 1.922 | 1.784 | 1.874 | 1.837 | 1.801 | 1.813 | 1.820 | 1.772 | 2.020 |  |
| Na               | .586        | .753  | .671  | .429  | .402                     | .698  | .437  | .705  | .677  | .600  | .456  | .658  | .784  | .455  | .388  |  |
| K                | .037        | .076  | .153  | .127  | .091                     | .069  | .092  | .091  | .134  | .132  | .165  | .137  | .131  | .168  | .124  |  |

Table 3.8.  
Structural formulae of amphiboles from alkaline basalts

|                  | alkaline basalts "xenocrysts" |       |       |       |       | inclusions in alkaline basalts |       |       |       |       |       |  |
|------------------|-------------------------------|-------|-------|-------|-------|--------------------------------|-------|-------|-------|-------|-------|--|
|                  | 19                            | 41    | 42    | 44    | 49    | 22                             | 23    | 24    | 25    | 26    | 27    |  |
| Si               | 5.745                         | 6.071 | 5.791 | 5.899 | 5.739 | 6.271                          | 5.844 | 5.904 | 5.794 | 5.779 | 5.694 |  |
| Al <sup>iv</sup> | 2.255                         | 1.929 | 2.209 | 2.101 | 2.243 | 1.729                          | 2.156 | 2.096 | 2.206 | 2.221 | 2.306 |  |
| Ti               |                               |       |       |       | .018  |                                |       |       |       |       |       |  |
| Al <sup>vi</sup> | .249                          | .172  | .175  | .386  | -     | .625                           | .221  | .488  | .657  | .125  | .571  |  |
| Ti               | .674                          | .302  | .429  | .594  | .430  | .557                           | .674  | .706  | .499  | .691  | .550  |  |
| Fe <sup>3+</sup> | .470                          | .771  | .774  | .395  | .686  | .166                           | .212  | .058  | -     | .336  | .006  |  |
| Fe <sup>2+</sup> | .840                          | .475  | .499  | 1.383 | .622  | .960                           | 1.264 | 1.223 | 1.323 | .978  | 1.356 |  |
| Mn               | .012                          | .018  | .013  | -     | -     | -                              | .021  | -     | -     | .015  | -     |  |
| Mg               | 2.623                         | 3.058 | 2.993 | 2.241 | 2.853 | 2.370                          | 2.340 | 2.278 | 2.270 | 2.598 | 2.273 |  |
| Ca               | 1.702                         | 1.909 | 1.801 | 1.544 | 2.313 | 1.590                          | 1.958 | 1.827 | 1.885 | 1.924 | 1.915 |  |
| Na               | .745                          | .790  | .798  | .801  | .784  | 1.092                          | .604  | .653  | .860  | .618  | .841  |  |
| K                | .358                          | .218  | .275  | .278  | .095  | .204                           | .419  | .367  | .415  | .414  | .438  |  |

Table 3.9.

Structural formulae of amphiboles from plutonic and metamorphic environments

|                  | 126   | 127   | 128   | 129   | 107   | 108   | 116   |
|------------------|-------|-------|-------|-------|-------|-------|-------|
| Si               | 6.803 | 6.508 | 6.531 | 6.400 | 6.779 | 6.864 | 6.798 |
| Al <sup>iv</sup> | 1.197 | 1.491 | 1.468 | 1.600 | 1.221 | 1.136 | 1.202 |
| Al <sup>vi</sup> | .443  | .418  | .506  | .363  | .258  | .518  | .499  |
| Ti               | .055  | .121  | .129  | .175  | .188  | .036  | .199  |
| Fe <sup>3+</sup> | .267  | .398  | .356  | .577  | .080  | .115  | .216  |
| Fe <sup>2+</sup> | 1.036 | 1.532 | 1.567 | 1.647 | 1.663 | .964  | 1.553 |
| Mn               | .025  | .030  | .034  | .040  | .035  | .023  | .020  |
| Mg               | 3.144 | 2.371 | 2.409 | 2.238 | 3.075 | 3.368 | 2.388 |
| Ca               | 2.031 | 2.104 | 1.945 | 1.874 | 1.768 | 1.972 | 1.948 |
| Na               | .323  | .344  | .350  | .362  | .277  | .378  | .343  |
| K                | .059  | .152  | .125  | .144  | .063  | .051  | .099  |

Table 3.10.

Optical properties of selected analyzed amphiboles.

| sample           | 1     | 2     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\gamma$         | 1.700 | 1.680 | 1.705 | 1.693 | 1.695 | 1.673 | 1.679 | 1.674 | 1.676 | 1.681 | 1.680 | 1.680 |
| $\beta$          | 1.676 | 1.662 | -     | -     | 1.641 | 1.662 | 1.664 | 1.655 | 1.660 | 1.659 | 1.654 | -     |
| $\alpha$         | 1.674 | 1.660 | 1.668 | 1.668 | 1.631 | 1.653 | 1.648 | 1.642 | 1.645 | 1.646 | 1.643 | 1.641 |
| $\gamma/c^\circ$ | 9     | 16    | 5     | 13    | 9     | 14    | 13    | 10    | 13    | 12    | 16    | 10    |
| $2V\alpha^\circ$ | 58-64 | 88    | 85    | 79    | 83    | 81    | -     | 69    | -     | 72    | 88    | 52-56 |
| sample           | 16    | 17    | 18    | 19    | 22    | 23    | 24    | 25    | 26    | 27    | 31    | 32    |
| $\gamma$         | 1.680 | 1.684 | 1.681 | 1.710 | 1.702 | 1.708 | 1.699 | 1.702 | 1.688 | 1.701 | 1.672 | 1.692 |
| $\beta$          | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| $\alpha$         | 1.645 | 1.643 | 1.646 | 1.676 | 1.685 | 1.676 | 1.674 | 1.660 | 1.671 | 1.668 | 1.651 | 1.668 |
| $\gamma/c^\circ$ | 9     | 9     | 10    | 4     | 11    | 17    | 17    | 18    | 20    | 15    | 11    | 14    |
| $2V\alpha^\circ$ | 66    | 67    | 78    | -     | 75    | 63    | -     | 56    | 52    | 40    | 73    | 63    |
| sample           | 33    | 34    | 36    | 40    | 41    | 42    | 44    | 46    | 47    | 48    | 49    | 50    |
| $\gamma$         | 1.714 | 1.704 | 1.684 | 1.659 | 1.681 | 1.700 | 1.707 | 1.694 | 1.702 | 1.701 | 1.707 | 1.689 |
| $\beta$          | -     | -     | -     | -     | 1.674 | -     | -     | -     | -     | 1.689 | 1.699 | -     |
| $\alpha$         | 1.698 | 1.683 | 1.662 | 1.630 | 1.665 | 1.683 | 1.679 | 1.660 | 1.689 | 1.680 | 1.682 | 1.663 |
| $\gamma/c^\circ$ | 5     | 7     | 13    | 12    | 7     | 8     | 7     | 5     | 6     | 8     | 3     | 10    |
| $2V\alpha^\circ$ | -     | 74    | 79    | 46    | -     | -     | 81    | -     | -     | -     | -     | -     |

Table 3.11.

Structural formulae of clinopyroxenes

|                  | 47    | 48    | 6     | 3544  | 3548  | 176   | 101   | 36    | 40    | 49    | 22    | 24    | 25    | 27    |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Si               | 1.757 | 1.783 | 1.918 | 1.888 | 1.910 | 1.975 | 1.878 | 1.913 | 1.901 | 1.751 | 1.721 | 1.730 | 1.817 | 1.749 |
| Al <sup>iv</sup> | .187  | .197  | .082  | .100  | .089  | .025  | .121  | .087  | .099  | .249  | .279  | .270  | .183  | .251  |
| Al <sup>vi</sup> | -     | -     | .029  |       | .025  | .057  | .051  | .104  | .060  | .012  | .089  | .093  | .097  | .082  |
| Ti               | .047  | .022  | .012  | .011  | .005  | .005  | .014  | .008  | -     | .044  | .072  | .054  | .048  | .068  |
| Fe <sup>3+</sup> | .307  | .199  | .068  | .077  | .054  | -     | .063  | .045  | .047  | .131  | .057  | .005  | .052  | .055  |
| Fe <sup>2+</sup> | .289  | .162  | .226  | .126  | .196  | .248  | .245  | .178  | .250  | .111  | .220  | .235  | .218  | .214  |
| Mn               | .016  | .006  | .016  | .003  | .003  | -     | -     | .008  | .008  | .002  | -     | -     | .006  | .005  |
| Mg               | .569  | .780  | .803  | .979  | .940  | .836  | .797  | .784  | .807  | .772  | .666  | .671  | .651  | .668  |
| Ca               | .775  | .830  | .804  | .842  | .776  | .821  | .804  | .825  | .811  | .920  | .827  | .921  | .840  | .853  |
| Na               | .038  | .040  | .044  | -     | -     | .021  | .022  | .011  | .024  | .032  | .119  | .102  | .110  | .093  |
| K                | .004  | -     | .004  | .017  | -     | -     | .003  | -     | -     | -     | -     | -     | .001  | -     |

Table 3.12.

Structural formulae of orthopyroxenes

|                  | 31    | 32    | 9     | 7     | 16    | 101   | 3548  |
|------------------|-------|-------|-------|-------|-------|-------|-------|
| Si               | 1.890 | 1.911 | 1.967 | 1.988 | 1.949 | 1.955 | 1.929 |
| Al <sup>iv</sup> | .057  | .063  | .022  | .012  | .051  | .045  | .030  |
| Al <sup>vi</sup> | -     | -     | -     | .045  | .038  | .006  | -     |
| Ti               | .013  | .020  | .005  | .019  | .011  | .005  | .005  |
| Fe <sup>3+</sup> | .166  | .054  | .011  | .011  | -     | .028  | .019  |
| Fe <sup>2+</sup> | .658  | .796  | .752  | .717  | .893  | .562  | .483  |
| Mn               | .031  | .027  | .016  | .007  | .023  | -     | .092  |
| Mg               | 1.080 | 1.094 | 1.204 | 1.080 | .966  | 1.359 | 1.519 |
| Ca               | .088  | .045  | .036  | .064  | .063  | .039  | .046  |
| Na               | -     | -     | -     | .029  | -     | -     | -     |
| K                | .004  | -     | -     | -     | .002  | -     | -     |

# Electron-microprobe analyses of selected iron-titanium oxides

[illegible]

Table 3.14.

Structural formulae of biotites from calc-alkaline volcanic rocks.

|                  | 31     | 46     | 00A    | 3513   | 3555   | 63     |
|------------------|--------|--------|--------|--------|--------|--------|
| Si               | 5.295  | 5.545  | 6.226  | 6.006  | 5.990  | 5.846  |
| Al <sup>iv</sup> | 2.705  | 2.455  | 1.773  | 1.993  | 2.010  | 2.154  |
| Al <sup>vi</sup> | .216   | .752   | 1.372  | 1.199  | 1.263  | 1.077  |
| Ti               | .466   | .413   | .410   | .389   | .490   | .428   |
| Fe <sup>3+</sup> | .683   | 1.399  | -      | -      | -      | -      |
| Fe <sup>2+</sup> | 1.642  | .811   | 1.892  | 2.153  | 2.238  | 2.220  |
| Mn               | .018   | .027   | -      | .016   | .009   | .041   |
| Mg               | 2.896  | 3.399  | 3.182  | 3.331  | 2.922  | 3.375  |
| Ca               | .082   | -      | -      | -      | -      | .017   |
| Na               | .060   | -      | .062   | -      | .166   | .031   |
| K                | 1.742  | 1.877  | 1.801  | 1.838  | 1.748  | 1.870  |
| OH               | 3.119  | -      | -      | -      | -      | -      |
| F                | .024   | -      | -      | -      | -      | -      |
| O                | 20.856 | 24.000 | 24.000 | 24.000 | 24.000 | 24.000 |

Table 3.15

Chemical analyses of selected amphibole bearing rock

|                                | 19    | 41     | 42     | 44     | 49    | 40     | 36    |
|--------------------------------|-------|--------|--------|--------|-------|--------|-------|
| SiO <sub>2</sub>               | 46.67 | 44.49  | 42.42  | 46.31  | 59.29 | 49.83  | 51.42 |
| TiO <sub>2</sub>               | 2.52  | 2.43   | 6.73   | 1.28   | .70   | .65    | .74   |
| Al <sub>2</sub> O <sub>3</sub> | 13.49 | 15.60  | 15.92  | 15.36  | 17.00 | 13.49  | 17.12 |
| Fe <sub>2</sub> O <sub>3</sub> | .08   | 4.24   | 3.76   | 4.66   | .10   | 1.14   | 3.78  |
| FeO                            | 11.60 | 6.99   | 7.85   | 6.31   | 5.80  | 8.23   | 5.34  |
| MnO                            | .23   | .19    | .20    | .27    | .13   | .16    | .21   |
| MgO                            | 9.05  | 6.63   | 6.50   | 4.26   | 3.22  | 7.55   | 5.26  |
| CaO                            | 9.00  | 8.55   | 7.96   | 5.21   | 7.09  | 11.32  | 5.93  |
| Na <sub>2</sub> O              | 3.74  | 6.30   | 4.71   | 5.20   | 4.00  | 3.97   | 4.31  |
| K <sub>2</sub> O               | .84   | 1.83   | 1.55   | 3.41   | 1.24  | .64    | 2.01  |
| P <sub>2</sub> O <sub>5</sub>  | .13   | 1.34   | 1.47   | .92    | .21   | .40    | .36   |
| loss (ΣH <sub>2</sub> O)       | 2.13  | 1.78   | 1.44   | 7.36   | .76   | 3.34   | 2.86  |
| total                          | 99.49 | 100.37 | 100.51 | 100.55 | 99.54 | 100.72 | 99.34 |
| Rb                             |       |        |        |        | 30.2  |        |       |
| Ba                             | 1109  | 822    | 855    |        | 763   | 1012   | 355   |
| Pb                             |       |        |        |        | 5     |        |       |
| Sr                             |       |        |        |        | 2464  |        |       |
| La                             | 43.0  | 51.8   | 57.2   |        | 4.8   | 2.7    | 6.1   |
| Ce                             | 80.7  | 119    | 126    |        | 150   | 6.0    | 16.8  |
| Pr                             | 12.1  | 9.9    |        |        | 27.7  |        | 3.5   |
| Nd                             | 29.1  | 45.9   | 45.8   |        | 44.7  |        | 13.4  |
| Y                              |       |        |        |        | 27.8  |        |       |
| Th                             |       |        |        |        | 8.6   |        |       |
| U                              |       |        |        |        | 2.1   |        |       |
| Zr                             |       |        |        |        | 239   |        | 71.6  |
| Nb                             |       |        |        |        | 76.9  |        | 3.9   |
| Cu                             | 540   |        | 41.8   |        | 34.8  | 113    | 71.6  |
| Co                             |       |        |        |        |       |        |       |
| Ni                             | 133   | 62.4   | 67.9   |        | 6.4   | 34.9   | 16.1  |
| V                              | 162   | 142    | 142    |        | 272   | 246    | 244.7 |
| Cr                             | 173   | 106    |        |        | 13.1  | 256    | 66.9  |
| Ga                             |       |        |        |        | 18.2  | 3.7    |       |
| Zn                             | 107   | 106    | 112    |        | 86.4  | 90     | 93.5  |

water content of amphiboles is related to subsequent oxidation of Fe, and generally does not exceed 1.6%.

### Clinopyroxenes

Most amphibole-bearing volcanic calc-alkaline rocks usually contain euhedral, or partially resorbed, stumpy phenocrysts of clinopyroxene. Glomeroporphyritic aggregates associated with opaque phases are common. These clusters are often surrounded by a rim of plagioclase, amphibole and opaques.

The volume of clinopyroxene phenocrysts does not exceed 25% in these rocks in which clinopyroxene is an important liquidus phase; it is less than 10% in rocks in which amphibole is a predominant liquidus phase. The optical properties of both groundmass and phenocrystic clinopyroxene do not differ. The optical zonation is very weak, and so is the actual compositional zonation as detected by electron microprobe. Twinning is common.

Chemical analyses of clinopyroxenes from amphibole-bearing calc-alkaline volcanic rocks together with analyses of clinopyroxenes from inclusions in alkaline rocks are presented in Table 3.3, the structural formulae of these clinopyroxenes are presented in Table 3.11. All clinopyroxenes coexisting with amphiboles, including those from inclusions in alkaline basalts, show a very narrow range of

composition and can be classified as diopsides or augites. Calcium is high in all samples and the clinopyroxenes are entirely different from those rocks of the pigeonitic series of island arcs (c.f. Aoki, 1967). The clinopyroxenes which coexist with amphibole form a group similar to those described by Aoki and Kushiro (1968). Those from calc-alkaline rocks (except two doubtful samples from high Al basalts) (36 and 40) have relatively low  $Al^{vi}$ , whereas clinopyroxenes from amphibole-bearing inclusions in calc-alkaline rocks (Yamazaki et al., 1968) and inclusions in alkaline basalts (Kuno and Aoki, 1970) have slightly higher  $Al^{iv}$  and  $Al^{vi}$ . The clinopyroxenes from inclusions in alkali basalts from Kiama, N.S.W., have even higher  $Al^{iv}$  contents, similar to those of titan-augites from inclusions in alkali basalts from Tristan da Cunha (Le Maitre, 1969). See Figure 3.7.

The alkali content of clinopyroxenes coexisting with amphiboles in calc-alkaline volcanic rocks is similar to that of clinopyroxenes from non-amphibole bearing rocks and inclusions, e.g. websterite nodules (Kuno and Aoki, 1970), or clinopyroxenes from tholeiites (Aoki, 1967) or from amphibole-free inclusions in calc-alkaline rocks. The alkali content of amphiboles from inclusions in alkaline rocks is higher & of the same order as that of "high pressure megacrysts" reported by Binns et al. (1970).

The relatively low alkali and low  $\text{TiO}_2$  content of clinopyroxenes from calc-alkaline rocks, are features which are also observed in clinopyroxenes crystallized experimentally in andesitic compositions at pressures less than 10 kb.

### Orthopyroxenes

This mineral occurs as rare phenocrysts in amphibole-bearing calc-alkaline rocks and is generally confined to rocks with higher  $\text{SiO}_2$  content. It is common in the groundmass of some amphibole-bearing andesites. The rounded prisms are only weakly pleochroic. Augite lamellae are usually absent. Seven new analyses are presented in Table 3.3, with structural formulae in Table 3.12. The compositional range of these orthopyroxenes, from  $\text{Fs}_{24}$  to  $\text{Fs}_{45}$  (Figs 3.6, 3.8), is characteristic of the hypersthene series of Kuno (1968). The CaO content is low or moderate and analyses plot on the field where orthopyroxenes from igneous and metamorphic rocks overlap (Kuno, 1966) (Fig. 3.8). The low Ca content and absence of augite lamellae in orthopyroxenes suggests that the host rocks cooled rapidly from temperatures between 1190 and 980°C.

### Coexisting pyroxenes

It has been suggested that the distribution of  $\text{Fe}^{2+}$  and Mg between coexisting pyroxenes is temperature dependent

(Bartholomé, 1961; Kretz, 1961, Bunch et al., 1970).

Two orthopyroxene-clinopyroxene pairs have been analyzed (Fig. 3.6). Sample 3548 is a two-pyroxene-bearing andesite closely associated with amphibole-bearing lavas from Cape Nelson (Jakes<sup>v</sup> and Smith, 1970). The distribution coefficient ( $K_D = \frac{\text{Fe}^{2+}}{\text{Mg}} \text{ opx} / \frac{\text{Fe}^{2+}}{\text{Mg}} \text{ cpx}$ ) is 1.35. Using the diagram published by Bunch et al. (1970) which is based on McCallum's (1969) data the temperature of equilibration is about 1050<sup>o</sup>, and this estimate is in good agreement with experimentally determined liquidus temperatures of wet andesites (5% of water). Textural evidence for sample 101 from the New Guinea Highlands suggests that clinopyroxene and orthopyroxene were not coexistent liquidus phases. The distribution coefficient (1.15) also suggests unrealistic temperatures.

#### Iron-Titanium oxides

In most amphibole-bearing rocks, the opaque phases are represented by titaniferous magnetite in the groundmass. The experimental evidence of Osborn (1959, 1962) together with experiments reported herein, suggest that opaque minerals are the first minerals to crystallize from andesite but textural evidence from natural rocks (e.g. Smith and Carmichael, 1968) suggest that iron-titanium oxides are not

amongst the earliest phases to appear (or were not preserved?).

In Table 3.13 microprobe analyses of selected iron-titanium oxides are reported; only Si, Ti, Mn, Mg, Al and Fe were determined and therefore satisfactory totals are those over 96%. Analyses have been recalculated according to Carmichael (1967). Comparison of Ti-rich magnetites in the groundmass with those occurring as phenocrysts show that the phenocrystic magnetites are richer in Mg, Al and Si. This agrees with observations by Carmichael and Nicholls (1967) and Smith and Carmichael (1968). The crystallisation temperature, as deduced from the coexisting Fe-Ti oxides in sample 32 using Carmichael's (1967) recalculation and Buddington and Lindsley's (1964) graph is  $885^{\circ}\text{C}$  and  $\log f\text{O}_2$  is -13. This is comparable with the crystallization temperatures of Fe-Ti oxides of dacitic and andesitic lavas reported by Carmichael (1967) and Buddington and Lindsley (1964). These temperatures are probably those of the final stages of crystallization.

### Biotites

Biotite is rare in volcanic calc-alkaline rocks and the factors controlling the occurrence of amphiboles i.e. relatively high alkali content and retention of volatiles to late stages of crystallization, can be applied even more

strictly to biotite. Thus biotite rarely occurs as a liquidus phase. Biotite in the groundmass of some high-K andesites, i.e. in andesites from E. Papua (Jakes<sup>V</sup> and Smith, 1970) is also restricted, but is more common than amphibole. It is more common in continental andesites than from circum-Pacific andesites.

New chemical and microprobe analyses are presented in Tables 3.3, 3.4 and structural formulae in Table 3.14. Fe/Mg ratios of biotites are higher than those of coexisting amphiboles and/or clinopyroxenes.

### Plagioclases

Plagioclase is the dominant phenocryst phase of most calc-alkaline volcanic rocks. Grain sizes vary from .01 to 20 mm. Optical features (high-temperature optics - low temperature optics) vary from sample to sample. Strong zoning is characteristic and all kinds of zoning (e.g. reverse and oscillatory) can be found. Cores are commonly anorthite-rich (usually An 60, but may reach An 75-80). Lower anorthite contents characterise continental andesites (Fig. 3.9). In these rocks, the phenocryst cores very often have sharp boundaries against the remaining part of the grain or show evidence of resorption and sharp changes of composition between core and outer zones. Some of the examples of zoning are shown in Fig. 3.9.

## CHAPTER 4

AMPHIBOLE ANDESITES - COMPARISON OF NATURAL AND EXPERIMENTAL  
DATA ON LIQUIDUS AND NEAR LIQUIDUS PHASESCrystallization sequence in natural amphibole andesites

Textural criteria were used to evaluate the crystallization sequence in natural rocks. In amphibole andesites from Mau Quarry, Viti Levu, Fiji, clinopyroxene is a liquidus phase together with opaque minerals and minor plagioclase. Cores of clinopyroxene are enclosed in amphibole phenocrysts, but clinopyroxene is also found in the groundmass and as rims around amphibole, thus suggesting that crystallization of clinopyroxene has taken place in two stages. A crystallization sequence of clinopyroxene followed by amphibole followed by clinopyroxene may be characteristic of calc-alkaline rocks (Kuno, 1968). Opaque minerals enclosed in amphibole phenocrysts show reaction relationships to amphibole, and amphibole + opaques. Small grains of anorthite-rich plagioclases (An 70-80) are sometimes enclosed in amphiboles. These are similar to the strongly corroded "moth-eaten" plagioclases occurring in cores of some plagioclase phenocrysts. However, amphibole and plagioclase do not generally appear to have crystallized simultaneously.

The amphibole-bearing rock from Mt Shasta (U.S.A.), shows petrographic features similar to those of the Fijian samples except that orthopyroxene has crystallized after amphibole. The rare relict olivine, crystallized before clinopyroxene and plagioclase appeared. Plagioclase plus clinopyroxene clusters are often enclosed in the amphiboles and a reaction between clinopyroxene and plagioclase to produce amphibole, plagioclase and orthopyroxene can account for the disappearance of clinopyroxene in the later stages of crystallization. Amphiboles and clinopyroxenes are often found as the nuclei of orthopyroxene grains.

In petrographic data on the New Zealand andesites, olivine + magnetite clusters occur as cores of larger clinopyroxene crystals. These are rare in amphibole-bearing andesites, (Mt Egmont and Solander Island), but frequent in augite-bearing andesites (c.f. Gow, 1968). In amphibole-bearing andesites the earliest phases (together with minor olivine) are clinopyroxene and opaque minerals (mostly resorbed) and subsequently plagioclase also apparently resorbed. The appearance of clinopyroxene followed by amphibole followed by clinopyroxene is very common. There is no evidence that plagioclase or clinopyroxene + magnetite continue to crystallize during hornblende precipitation.

Rocks from Eastern Papua (Mt Lamington and Cape Nelson) and rocks from Savo volcano, Solomon Island, have a

different crystallization history. The liquidus phase is not clinopyroxene as in the above examples but amphibole. The amphibole is then followed by clinopyroxene and minor plagioclase and opaque phases appear with clinopyroxene. In some of the Cape Nelson rocks, biotite appears to crystallize first. Amphiboles from Eastern Papuan rocks are strongly zoned and have extensive reaction rims. The typical "xenocrystic" appearance of amphibole, with reaction rims of fine granular opaques, is a very common feature in these rocks as in most amphibole-bearing volcanic rocks; it is thought to occur late in the crystallization history of the melt.

The crystallization sequence of a few samples (intracontinental andesites) from the Carpathians area differs from that of circum-Pacific andesites. These rocks lack olivine, show a relatively "short period" of clinopyroxene and plagioclase crystallization, and have amphibole as a major liquidus phase and there is extensive late stage precipitation of biotite and orthopyroxene. As in the circum-Pacific andesites, opaque phases appear together with clinopyroxene. Similar relationships have been described in Andean andesites (Pichler and Ziel, 1969). Rocks from the Hunter River area, although older and slightly more siliceous than circum-Pacific andesites, are very similar to the Carpathian and Andean samples with small

amounts of early clinopyroxene, extensive crystallization of amphibole and small amounts of later opaque phases.

Amphibole-bearing rocks of the shoshonitic association of the New Guinea Highlands do not differ substantially from typical circum-Pacific andesites. The sequence clinopyroxene followed by amphibole followed by clinopyroxene is found. Opaque phases and plagioclase appear together with the later clinopyroxene. There is a reaction relationship between clinopyroxene and orthopyroxene and a time gap in their crystallization. The bulk of the opaques has been produced in the later stages, but textural evidence indicates that large opaque crystals have been resorbed during the period of amphibole crystallization.

In summary, petrographic observations define two distinct groups of amphibole-bearing calc-alkaline rocks:-

(a) Clinopyroxene + opaque minerals are the important liquidus phases of most circum-Pacific andesites. The later crystallization of amphibole is probably due to build up of water content (Brown and Schairer, 1968) during continued crystallization. This feature suggests that amphibole-bearing rocks of the island arcs were not in equilibrium with amphibole or amphibole-bearing residuum in their source regions.

(c) Amphibole appears as the primary liquidus phase and is followed by clinopyroxene. This is characteristic of

andesites of intracontinental chains and of Andean type of andesites and occurs rarely in high-K andesites from island areas (East Papua). This crystallization sequence indicates that these andesitic rocks may have been in equilibrium with an amphibole-bearing residuum suggesting higher water contents in the source region. Furthermore, a higher water content during crystallization would lower the liquidus temperatures to values similar to those obtained in experiments under hydrous conditions ( $950^{\circ}$  at 5Kb with 5 wt %  $H_2O$ ).

#### Crystallization sequence of andesite in experiments

Liquidus phases of "wet andesite" in the range 2.5 - 30 kb. Preliminary experiments by Green and Ringwood (1968, 1969) on calc-alkaline rocks under hydrous and anhydrous conditions led to two complementary hypotheses on the genesis of calc-alkaline rocks. The aim of the experiments recorded in this thesis is to determine the liquidus phases of "typical andesites" under hydrous conditions and to assess the petrogenetic significance of the results with respect to both circum-Pacific and continental areas. In all experiments 5% of water was sealed into the capsules.

Andesite "32", selected for experiments has a relatively high  $K_2O$  content and is similar in composition to amphibole-bearing andesite of intracontinental areas (including the Andean region). These ("group 2") lavas have

amphibole as the liquidus phase and can be distinguished both chemically and petrographically from the typical circum-Pacific andesites of "group 1".

Andesite "A" is a medium to low-K andesite similar to typical circum-Pacific andesite. The experiments with this composition were done to determine liquidus phases only.

The composition of both andesites is given in Table 4.1, and the methods of sample preparation and experimental techniques are given in Chapter 6.

Andesite "32" was prepared from natural rock which was crushed finely, pressed into a pellet and melted in an argon atmosphere, quenched, and the powdered glass used in the experiments; the oxidation state was determined by micro-chemical techniques. The absence of crystalline phases was confirmed by both petrographic and X-ray examination.

Experimental results are reported in Tables 4.2, 4.3 and Figures 4.1, 4.2. Experiments were carried out in the range 2.5 - 30 kb, using the piston cylinder apparatus and techniques described by Essene et al. (1970); a pressure correction of -10% has been applied (c.f. Green et al. 1968). The precision of pressure measurements is believed to be  $\pm 3\%$ .

#### Andesite "32"

The precision of pressure measurement in low pressure regions (2.3 kb) is less than reported above. At 2.3 kb the

crystallization sequence is similar to that at 4.5kb. Amphibole and minor plagioclase are near liquidus phases crystallizing at 975°C; and at lower temperatures, they are joined by abundant clinopyroxene.

Comparatively large amounts of opaque minerals crystallize near the liquidus at 975°C and 4.5kb together with small amounts of amphibole and lesser clinopyroxene. Plagioclase crystallizes at slightly lower temperatures, and this sequence occurs at 875°C also.

Only amphibole + minor amounts of opaque phase have been observed near the liquidus at 6.8kb and 975°C, at lower temperatures (925°C) amphibole is accompanied by both clinopyroxene and plagioclase.

Amphibole dominates liquidus and near-liquidus runs at 975°C, 950°C; at 925°C in the 9 to 11.4kb range, it is accompanied by minor amounts of clinopyroxene. Large amounts of clinopyroxene together with plagioclase appear in runs (9 - 11.4kb) at 875°C and 850°C.

Near-liquidus runs at 13.5kb (975°C - 925°C) are dominated by the crystallization of both amphibole and clinopyroxene in approximately equal proportions, but clinopyroxene is the major liquidus phase at 15.8kb in this temperature range and is accompanied by lesser quantities of opaques. Amphibole is absent on the liquidus at this pressure, appearing at 925°C and 875°C. Quartz has been

Table 4.1.

Composition of andesite mixes used in experimental work.

|                                | Andesite 32 | Andesite A | Andesite B                         | Andesite C                         |
|--------------------------------|-------------|------------|------------------------------------|------------------------------------|
| SiO <sub>2</sub>               | 60.50       | 60.50      | 60.30                              | 61.00                              |
| TiO <sub>2</sub>               | .75         | .75        | .75                                | .75                                |
| Al <sub>2</sub> O <sub>3</sub> | 16.94       | 17.50      | 17.40                              | 17.10                              |
| Fe <sub>2</sub> O <sub>3</sub> | 2.52        | .73+       | .75+                               | .75+                               |
| FeO                            | 2.68        | 3.92+      | 3.85+                              | 3.76+                              |
| MnO                            | .10*        | .10*       | .10*                               | .10*                               |
| MgO                            | 1.99        | 4.00       | 4.10                               | 4.00                               |
| CaO                            | 5.30        | 7.10       | 7.20                               | 7.10                               |
| Na <sub>2</sub> O              | 3.60        | 3.50       | 3.40                               | 3.40                               |
| K <sub>2</sub> O               | 2.14        | 1.40       | 1.40                               | 1.30                               |
| Σ H <sub>2</sub> O             | 1.60        |            |                                    |                                    |
|                                |             |            | Cr <sub>2</sub> O <sub>3</sub> .21 | La <sub>2</sub> O <sub>3</sub> .21 |
|                                |             |            | NiO .20                            | Yb <sub>2</sub> O <sub>3</sub> .22 |
|                                |             |            | V <sub>2</sub> O <sub>5</sub> .20  |                                    |
| Total                          | 99.41       | 99.50      | 99.86Δ                             | 99.69                              |

All data except for iron obtained by electron microprobe

+ microscale Fe<sup>2+</sup>/Fe<sup>3+</sup> determination according to Kiss, 1968

\* MnO not determined on electron microprobe

Δ includes 80 ppm Ni, 30 ppm Cr, 20 ppm V - determined by emission spectrograph by Mrs M. Kaye

Table 4.2. Results of experimental runs on andesite 32 + 5% H<sub>2</sub>O.

Conditions of run

| P kb | T °C | Time    | Phases present    |                      |
|------|------|---------|-------------------|----------------------|
| 2.3  | 925  | 3 hrs   | amph>plg,cpx,opq  |                      |
| 2.3  | 975  | 45 min  | amph>plg,(opq)    | cpx(?)               |
| 2.3  | 1000 | 45 min  | glass             | above liquidus       |
| 2.3  | 1050 | 45 min  | glass             | above liquidus       |
| 4.5  | 875  | 5 hrs   | amph>plg>cpx      | 20% of glass         |
| 4.5  | 925  | 45 min  | amph,cpx          |                      |
| 4.5  | 950  | 2.5 hrs | plg>>amph(opaque) | 95% glass            |
| 4.5  | 975  | 45 min  | opaque            | near liquidus run    |
| 4.5  | 1000 | 45 min  | glass             | quenched(?)          |
| 6.8  | 925  | 45 min  | amph,plg,cpx      |                      |
| 6.8  | 975  | 45 min  | amph(opaque)      |                      |
| 6.8  | 1000 | 45 min  | glass             |                      |
| 9.0  | 840  | 5 hrs   | amph,plg,cpx      | 50% of quench        |
| 9.0  | 875  | 20 hrs  | amph,plg,opx      | 50% of glass         |
| 9.0  | 925  | 45 min  | amph              | few primary crystals |
| 9.0  | 950  | 2 hrs   | amph              |                      |
| 9.0  | 975  | 45 min  | amph              | cpx(?) (<<1%)        |
| 9.0  | 1000 | 45 min  | glass             | quench amph          |
| 9.0  | 1050 | 2.5 hrs | glass             |                      |
| 11.4 | 925  | 45 min  | amph              | 70% fine grained     |
| 11.4 | 965  | 45 min  | amph>cpx          | 65% glass quench     |
| 11.4 | 985  | 45 min  | amph              |                      |
| 13.5 | 925  | 2.5 hrs | amph,cpx          |                      |
| 13.5 | 950  | 45 min  | cpx>plg           |                      |
| 13.5 | 975  | 45 min  | cpx               | amph (?)             |
| 13.5 | 1000 | 45 min  | glass             | quench amphibole     |
| 16.2 | 875  | 2 hrs   | amph              | amph only + quench   |
| 16.2 | 925  | 2 hrs   | cpx(amph?),ga?    |                      |
| 16.2 | 975  | 2 hrs   | cpx               |                      |
| 18.0 | 875  | 12 hrs  | cpx,qz,plg(?)     | doubtful qz          |
| 18.0 | 950  | 2 hrs   | cpx,ga            | 95% of glass         |
| 18.0 | 1050 | 3 hrs   | glass             | qz-lines in x-ray    |
| 22.5 | 875  | 10 hrs  | cpx,qz,ga         |                      |
| 22.5 | 950  | 15 hrs  | cpx,ga            |                      |

TABLE 4.3. Results of experimental runs on the andesite A + 5% H<sub>2</sub>O

| Conditions of the run |                  |            | Phases present                     | Comments                                                                                                                                                             |
|-----------------------|------------------|------------|------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pressure(Kb)          | Temperature (°C) | Time (hrs) |                                    |                                                                                                                                                                      |
| 5                     | 975              | 2          | amph > cpx plg (?)                 | large amount of quench material (≈ 50%)                                                                                                                              |
| 5                     | 1000             | 2          | amph (7%) cpx (2%) opaque (1%)     |                                                                                                                                                                      |
| 5                     | 1025             | 2          | amph (?) (opaque)                  | a few needle like grains at capsule bottom + clear glass with numerous bubbles                                                                                       |
| 5                     | 1050             | 2          | opaque phase (≈ 1%) (liquidus run) | weak lines of amphibole in X-ray pattern (quench?)<br>sporadic opaque phases + small amount of quench                                                                |
| 10                    | 975              | 2          | amph > cpx (plg?)                  | fine grained aggregate difficult to distinguish from quench                                                                                                          |
| 10                    | 1000             | 2          | amph ≈ cpx >> opaque (plg)         |                                                                                                                                                                      |
| 10                    | 1025             | 2          | amph >> cpx ≈ plg (opaque)         | large amount of quench, few large plg grains                                                                                                                         |
| 10                    | 1050             | 2          | opaque (?) (liquidus run)          | problematic opaque phase                                                                                                                                             |
| 15                    | 1050             | 2          | cpx >> amph ≈ opaque               | two types of cpx - tabular and needle-like, more than 85% glass                                                                                                      |
| 15                    | 1075             | 2          | cpx ≈ opaque (liquidus run)        | less than 1% crystallised                                                                                                                                            |
| 20                    | 950              | 2          | cpx >> amph > plg (?) opaque       | most of material crystallised (80%)                                                                                                                                  |
| 20                    | 1000             | 2          | cpx >> amph > opaque               | temperature and pressure slightly dropped before end of this run; large opaque crystals present, amphiboles shortly prismatic with almost straight extinction angles |
| 20                    | 1025             | 2          | cpx >> opaque                      | about 15% of material crystallised amph (?)                                                                                                                          |
| 20                    | 1050             | 2          | cpx >> opaque (amph?)              |                                                                                                                                                                      |
| 20                    | 1075             | 2          | cpx >> opaque                      | relatively small opaques, about 10% of clinopyroxene                                                                                                                 |
| 20                    | 1100             | 2          | above liquidus                     | clear glass with questionable opaque phase                                                                                                                           |
| 30                    | 1100             | 2          | cpx >> opaque                      | amphibole quench?                                                                                                                                                    |
| 30                    | 1150             | 2          | cpx >> opaque                      | about 10% crystallised, isolated small high R.I. grains (spinel?, garnet?) - as an accessory phase                                                                   |
| 30                    | 1175             | 2          | cpx                                | during first 20 minutes temperature at 1150 °C.                                                                                                                      |
| 30                    | 1200             | 2          | liquidus run                       | << 1% cpx and few grains of opaques                                                                                                                                  |

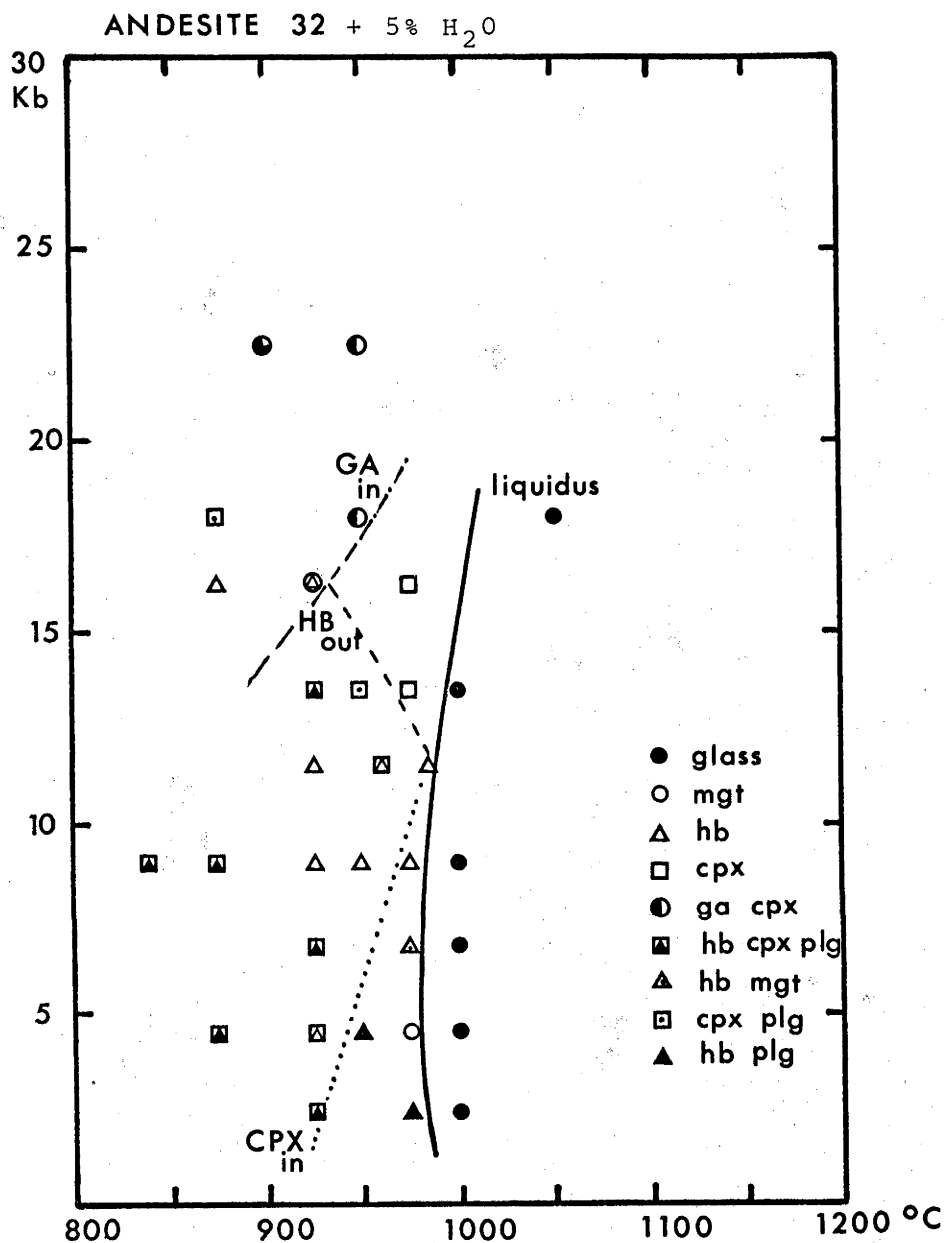


Fig. 4.1. Results of experimental runs on andesite 32 (see text).

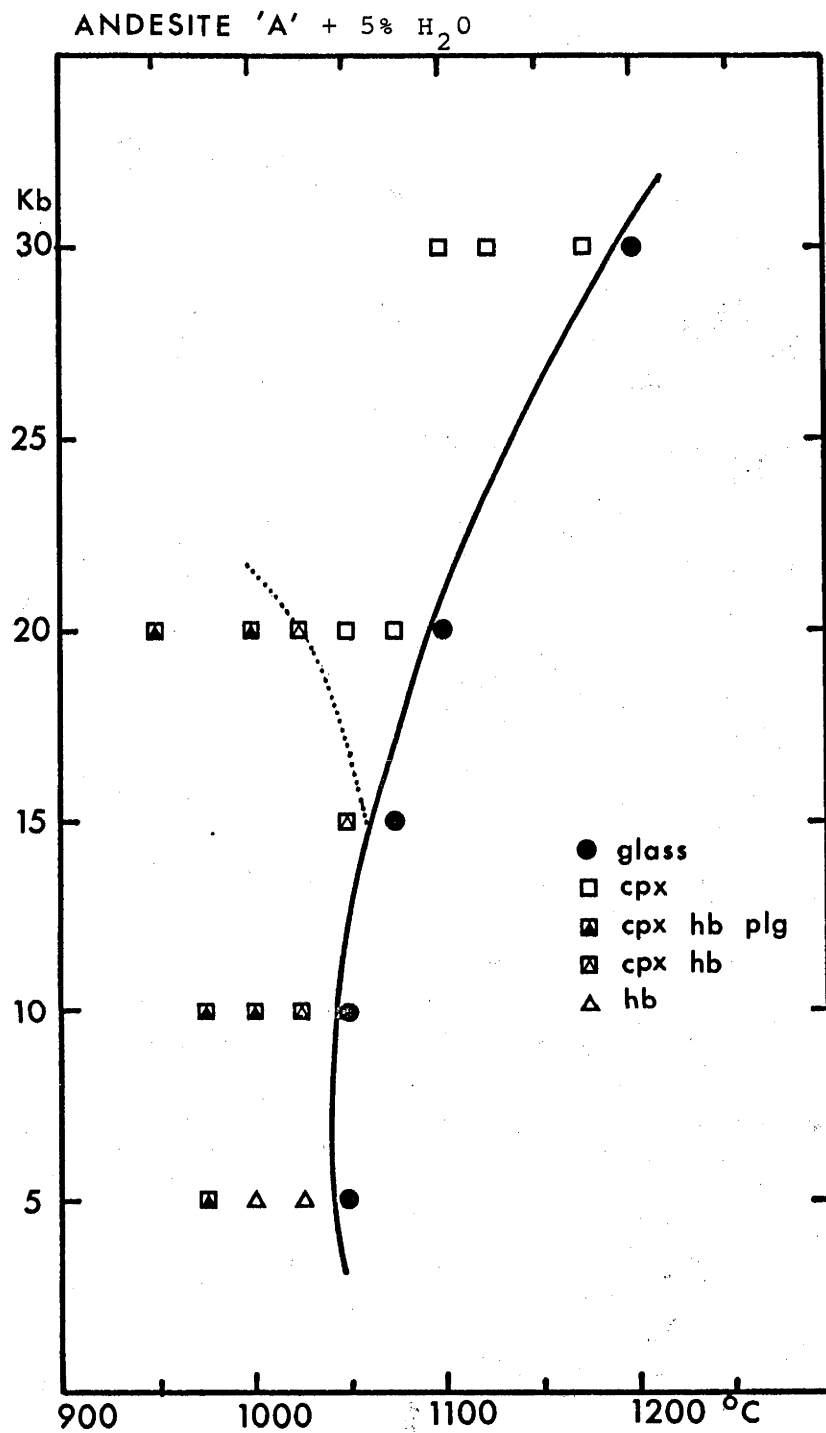


Fig. 4.2. Results of experimental runs on liquidus and near liquidus phases of andesite "A".

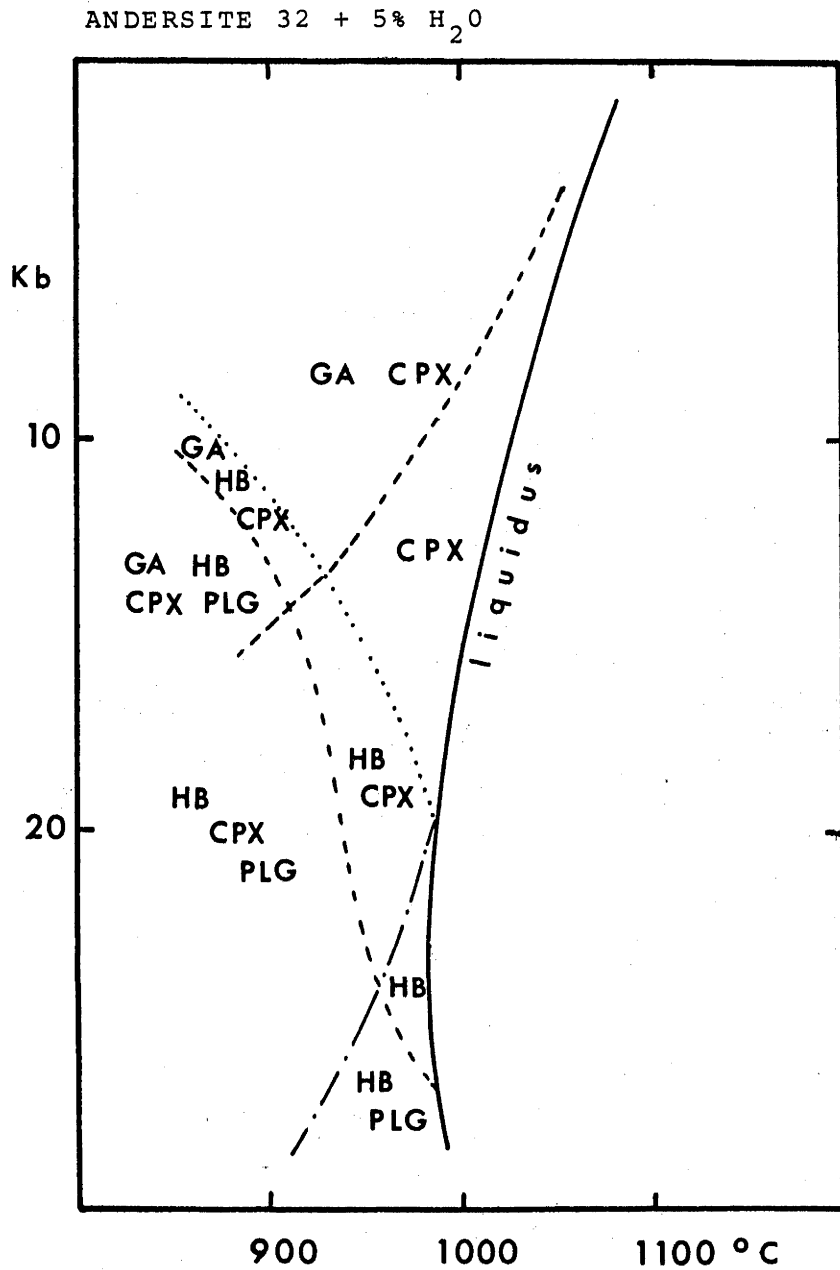


Fig. 4.3. Schematic representation of liquidus and near liquidus phases of andesite 32.

observed in low T runs.

Crystallization at 18kb and 22.5kb is dominated by clinopyroxene with minor quartz and plagioclase. At 22.5kb garnet appears at lower temperatures ( $950^{\circ}$  and  $875^{\circ}\text{C}$ ) together with clinopyroxene and quartz. Amphibole is absent in all runs above 18kb.

#### Andesite "A"

In the 5kb and 10kb pressure range, amphibole and clinopyroxene appear as liquidus phases and are accompanied by small amounts of opaque minerals. At 5kb and  $1000^{\circ}\text{C}$  amphibole is far more abundant than clinopyroxene, whereas at 10kb and  $1025^{\circ}\text{C}$  both occur in similar quantities. At 15kb clinopyroxene is a liquidus phase. Clinopyroxene is also the liquidus phase at 20kb where only small amounts of amphibole appear well below the liquidus and the amount of amphibole increases as near solidus temperatures are approached. In the 30kb region the liquidus temperature exceeds  $1150^{\circ}\text{C}$  and the liquidus phase is clinopyroxene  $\pm$  opaque phase.

In experimental work with andesite "A", garnet, previously reported by Green and Ringwood (1968) as a liquidus phase, has not been found, but in experiments carried out with andesite "32", garnet lies near the liquidus at  $950^{\circ}$

and 22.5kb. In runs at 30kb and 1150°C with andesite "A", very small high R.I. grains may be garnet but runs at 25kb although seeded with 2% of garnet (i.e. sufficient to appear in X-ray powder photographs) lack garnet after two hours at near liquidus temperatures; clinopyroxene appears instead. Similarly, dry runs with andesite "B" (andesite "A" + transition metal trace elements) at 30kb and 1350°C did not produce garnet. It seems that in andesite compositions, garnet is not a liquidus phase between 20 and 30kb, although experiments with andesite "32" suggest that garnet may crystallize about 30-50°C below the liquidus at these high pressures. Seeded runs clearly indicate that the problem does not lie in nucleation difficulties. In andesite "32", garnet appears at higher pressures (18kb) about 50°C below the liquidus. From a comparison of the experimental results obtained with andesite "A", andesite "32", and the andesite composition used by Green and Ringwood (1968, 1969), it appears that major element chemistry, particularly Fe/Mg and  $\text{SiO}_2$  may have a sensitive influence on the position of the curve for the incoming of garnet. The interpolated curve for incoming of garnet in andesite "32" is almost parallel to the liquidus at high pressures but could intersect the liquidus at pressures around 30kb. The intersection could lie at higher pressures in other andesite compositions.

### Liquidus temperatures

One of the most important feature of andesite is that its dry liquidus temperature at pressures near 30kb is the lowest of all the rocks of the calc-alkaline association (basalts, basaltic andesites or dacites) (Green and Ringwood, 1968, 1969). Green and Ringwood showed that the dry liquidus temperature at atmospheric pressure is only slightly lower than for a rock of the same composition at 30kb. Yoder (1969) demonstrated that the dry liquidus temperatures at atmospheric pressure depend on the iron-magnesium ratio ( $\text{FeO} + \text{Fe}_2\text{O}_3 / \text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3$ ) and that liquidus temperature is lower in continental calc-alkaline rocks than in island arc calc-alkaline rocks (Yoder, 1969, Fig. 1). The dry liquidus temperature generally decreases with increasing iron-magnesium ratio. Brown and Schairer (1968) and Tilley et al (1968) carried out experiments on dry liquids of calc-alkaline rocks at 1 atm and found that the first crystalline phases to appear in dry andesite (plagioclase) and in basalt (olivine) crystallize at temperatures in the range 1197-1227°C. Brown and Schairer (1968) studied rocks from the Solomon Islands and Lesser Antilles and reported plagioclase as a liquidus phase at 1180-1280°C. Similar liquidus temperatures of 1202 - 1232°C for andesites were reported by Fudali (1965) (1202 - 1232°C).

The  $\text{FeO} + \text{Fe}_2\text{O}_3 / \text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3$  ratio is .723 and .537 for andesite "32" and andesite "A" respectively which suggests dry liquidus temperatures of 1208 - 1210°C and 1220-1225°C respectively according to Yoder's (1969) curve for island arc calc-alkaline rocks.

Liquidus temperatures of both andesites were substantially lowered by adding 5%  $\text{H}_2\text{O}$  to experimental mixes. The difference in liquidus temperatures under the same P-T conditions is again explained by the slight compositional differences between the andesites i.e. in total iron/total iron + Mg ratios.

The reported liquidus temperatures are in good agreement with results of earlier experiments such as those of Green and Ringwood (1968) and Yoder (1969), but they lie between temperatures actually measured in calc-alkaline volcanoes (Paracutin) and temperatures determined from coexisting iron-titanium oxides (Buddington and Lindsley, 1964; Smith and Carmichael 1968; Carmichael, 1967 and new data presented here). The precision of temperature derivation from Fe-Ti oxides is relatively poor. Also, the textural evidence from amphibole-bearing rocks suggests that the opaque phases, present as microphenocrysts in the groundmass, are not liquidus phases. Therefore the temperatures deduced from the opaque phases could be about 100°C below the true liquidus temperatures. In contrast to

this Zies (1946) measured temperatures of  $1200^{\circ}\text{C}$  during the eruption of Paracutin and stated that this was "a close approximation to the temperature of the lava as it issues from the base of volcano." Unless Paracutin lavas were virtually anhydrous, or were erupted directly from their source region at 20 - 30kb, the temperatures reported by Zies seem high.

#### Liquidus mineralogy

There is some disagreement on the liquidus mineralogy of andesites. Yoder (1969) claims, by analogy with high-Al basalts, that olivine is a liquidus phase even in the presence of water, but data published by Green and Ringwood (1968) and data presented here suggest that olivine does not occur on the andesite liquidus. In the dry systems, plagioclase and orthopyroxene are liquidus phases at 1 atm and olivine is confined to lower temperatures in rocks of more basaltic compositions.

Under hydrous conditions, the low pressure (2 - 15kb) crystallization of andesite is dominated by amphibole. Clinopyroxene and plagioclase are also present. The amount of amphibole on the liquidus decreases above 10kb and at 15 - 18kb, amphibole is not a liquidus phase : clinopyroxene crystallizes instead. The amount of plagioclase also decreases with increasing pressure although substantial

amounts crystallize at lower temperatures and pressures. In wet compositions other than in the low pressure region (2.5kb) it does not appear near the liquidus.

In most runs carried out with wet andesite, magnetite appears as a liquidus phase over a very narrow temperature range. The quantity decreases sharply with the appearance of the first ferromagnesian silicate phase.

A comparison was made between the experimentally determined crystallization sequences of andesite + 5%  $H_2O$ , and the crystallization sequences of natural rocks. Only amphibole-bearing andesites from continental areas have a crystallization history similar to the sequence obtained experimentally. In most circum-Pacific andesites clinopyroxene crystallizes before amphibole. The low water contents of circum-Pacific andesites result in liquidus temperatures which are outside the stability field of amphibole. Although there are differences in the composition of amphiboles from both areas, the lack of variation in clinopyroxene compositions suggests that liquidus clinopyroxene has crystallized at lower pressures outside the stability field of amphibole.

It is most unlikely that water from external sources is introduced into the magma reservoirs, hence the crystallization of amphibole in island arc calc-alkaline rocks can only be attributed to "build up" of water pressure at lower

temperatures and advanced stage of crystallization as suggested by Brown and Schairer (1968). The absence of liquidus amphibole in andesites with rare exceptions (such as the East Papuan volcanoes) suggests that the melts did not co-exist with amphibole in circum-Pacific andesites. On the other hand, the amphibole-bearing andesites of continental or Andean areas may have been derived from an amphibole-bearing parent assemblage.

## CHAPTER 5

## VARIATION OF LAVA COMPOSITION IN ISLAND ARCS

Major elements - geographical relations in island arcs

A striking feature of the island arcs of the Western part of the Pacific (Fig. 1.1) is the relationship between the composition of Recent (Cenozoic) lavas and the position of their parent volcanoes in the island arc structure.

In most areas in which the seismic plane (Benioff zone) dips towards the continent, the following observations can be made: Tholeiites (i.e. island arc tholeiites) are erupted on the oceanic side (nearest the trench) of island arcs, and are followed by a series of calc-alkaline rocks whose K-content increases towards the continent. Shoshonites or alkali basalts may be present on the continental side of the high-K calc-alkaline rocks. The chemical variation across island arcs may be illustrated by simple comparison (weight per cent) of various oxides and there is no need to use more complex parameters such as "suite index"

$$= \sigma = \frac{(\text{Na}_2\text{O} + \text{K}_2\text{O})^2}{\text{SiO}_2 - 43} \quad \text{as suggested by Rittman (1953, 1958)}$$

and Sugimura (1968). Here most comparisons between rocks of the different associations are made at fixed  $\text{SiO}_2$  contents.

Rittman (1953) and Kuno (1959, 1966) have shown that there is a variation in the total alkali element content of island arc rocks. Dickinson and Hatherton (1968) showed that the  $K_2O$  content is primarily responsible for these variations and that  $K_2O$  contents (at a given  $SiO_2$  content) increases with distance from the trench and distance from the Benioff zone. In other words, in those island arcs where the seismic zone dips below the arc from the trench towards the continent, recent volcanics show an increase in  $K_2O$  content which is positively related to the distance of the volcanic centre from the trench. Dickinson and Hatherton (1968) state that rocks with low  $K_2O$  contents - i.e. those transitional between tholeiites and low-K calc-alkaline rocks, with  $K_2O$  contents of 0.8% at 55%  $SiO_2$  and of 1.2% at 60%  $SiO_2$  - can be correlated with a depth of 100 km or less to the underlying seismic zone. Associations with high- $K_2O$  contents (e.g. New Guinea Highlands with 2.2 and 2.4%  $K_2O$  at 55% and 60%  $SiO_2$  respectively) can be correlated with depths of about 200 km to the Benioff zone. This correlation between rock chemistry and the depth of the Benioff zone must be emphasised; the distance of the respective centres from the trench is not a critical feature, for this is simply related to the dip of the Benioff zone, which ranges from  $25^\circ$  for the Indonesian part of New Guinea

(Denham, 1969), through  $45^{\circ}$  in the Tonga-Kermadec region to vertical at Bougainville (Denham, 1969).

After Dickinson and Hatherton (1967) first pointed out the correlation between rock chemistry and the depth of the underlying seismic zone, similar observations were made in New Zealand by Hatherton (1969), in Melanesia by Jakeš and White (1969) and in most of the other arcs of the western part of the Pacific other than those with a vertically dipping or reversed seismic plane, e.g. Solomon Islands and New Hebrides respectively.

The slope of the  $K_2O$  vs.  $SiO_2$  plot also increases across an island arc towards the continent. This is supported by observations by Dickinson (1968) and Gill (1970) but there are exceptions. For example in the high-K calc-alkaline rocks described by Jakeš and Smith (1968) the gradient of  $K_2O$  vs.  $SiO_2$  is relatively low. Rocks of the shoshonite association may have very flat or even negative gradients (Joplin, 1968; Ruxton, 1966), but workers in classical shoshonite areas (Gill, pers. comm., and Gill, 1970) have also found extremely high gradients of  $K_2O$  vs.  $SiO_2$ .

$Na_2O$  contents do not change as much as  $K_2O$  contents in sections across island arcs and consequently the  $K_2O/Na_2O$  ratio increases with increasing  $K_2O$  from approximately 0.1 in the low-K rocks on the oceanic side of the arc,

to 1.0 in shoshonitic rocks. In some rocks of the shoshonitic association in central or western Kamchatka, the ratio of  $K_2O/Na_2O$  reaches 3 or 4, emphasising the strongly alkaline character of these rocks (c.f. Erlich, 1968).

Representatives of each of the three rock associations occurring in island arcs (i.e. tholeiitic, calc-alkaline, shoshonitic) show a wide range of  $SiO_2$  contents and this permits evaluation of Fe - Mg variations. This is demonstrated clearly in AMF diagrams. The trends shown by the island arc tholeiites are similar to those of tholeiites of continental and ocean ridge areas. The "iron enrichment" is less than that of true ocean ridge tholeiites (Fig.3, and Jakeš and Gill, 1970). However, it is more pronounced than most of the calc-alkaline and shoshonitic rocks on the continental side of island arcs. Thus the degree of "iron enrichment" decreases as the depth of the underlying Benioff zone increases. Rocks furthest from the oceanic side of the arc have virtually no "iron enrichment". The "iron enrichment" can be expressed using the ferro-femic index of Coates (1968): there is a positive correlation between the depth of the Benioff zone and the ferro-femic index.

The rocks of island arcs are generally high in  $Al_2O_3$ . The typical calc-alkaline, low and medium-K rocks have a fairly constant  $Al_2O_3$  content, usually not less than 16.0 and not more than 17.5% over most of the  $SiO_2$  range.

In island arc tholeiites  $\text{Al}_2\text{O}_3$  contents lie in the 14 - 17.5% range. In high-K rocks there is a fluctuation between low (14%) and extremely high values (19%). These extreme variations do not correlate with any major element.

In Kuno's (1959) scheme of variation of composition in Cenozoic island arc lavas, there is a substantial difference in  $\text{TiO}_2$  content between tholeiitic rocks (low values) and alkali basalts. Although there is a wide spread of values in calc-alkaline rocks, shoshonitic rocks appear to have higher titanium contents than rocks of tholeiitic and calc-alkaline associations, however new data of Gill (1970) do not confirm this scheme. MacGregor (1969) presented experimental evidence for differences of Ti content in tholeiites and alkaline rocks; assuming a homogeneous and compositionally similar source for all of these island arc associations, the  $\text{TiO}_2$  content should increase with increasing depth of derivation.

Although the ratio of ferrous to ferric iron is affected by near surface oxidation, it appears that the volume of more oxidized rocks increases away from the trench. It should also be noted, that in a very general sense, the amount of pyroclastic rocks increases from trench to inland areas. In shoshonitic rocks however, lavas are more prominent than pyroclastic deposits.

Field observations and descriptions of island arc areas show that the frequency of rocks having a particular  $\text{SiO}_2$  content are different for each association. This is shown schematically in Table 7.1. Basaltic rocks with less than 54% of  $\text{SiO}_2$  are the most frequent rocks of tholeiitic associations, basaltic andesites with about 56%  $\text{SiO}_2$  are very frequent in low-K calc-alkaline associations; frequency of types richer in  $\text{SiO}_2$  increases with increasing  $\text{K}_2\text{O}$ . Normal andesites (59%  $\text{SiO}_2$ ) are most abundant in normal and high-K calc-alkaline associations. However, in shoshonitic rocks, the more basic members with 54%  $\text{SiO}_2$  are again the most prominent.

#### Major elements - stratigraphical relations in island arcs

The complete variation in lava composition across island arcs, from tholeiitic to calc-alkaline and finally to shoshonitic associations, is a feature of island arcs of an advanced stage of evolution with a clearly definable seismic plane dipping towards the continent (e.g. Kamchatka, Japan, Sunda Island, New Guinea, New Zealand). Jakeš and White (1969) suggested that in regions where the seismic plane is not clearly developed or where it is vertical or dips towards the oceanic side (e.g. Solomon Islands, New Hebrides, Fiji) a similar compositional variation is shown in the stratigraphy of the volcanic pile. Thus tholeiitic

rocks are the earliest manifestation of island arc evolution (Baker, 1968) and are followed in time by calc-alkaline rocks and finally by shoshonites.

Aramaki (1963) has observed an increase in the total alkali content of the Asama lavas with increasing age. Gorshkov (1962) pointed out the similar evolutionary trends of Kurile-Kamchatka lavas. Data compiled by Erlich (1966) illustrates the increase of  $K_2O$  content and decrease of "iron enrichment" in these younger lavas. Jakes and Smith (1970) demonstrate that the increase of  $K_2O$  in calc-alkaline rocks of Cape Nelson correlates with decreasing age and also show that changes in  $K_2O$  vs.  $SiO_2$  in the most recent lavas resemble those of shoshonites.

Gill's (1970) account of the geochemical evolution of Fiji provides an excellent example of the parallel between the lateral and the stratigraphic progression of lava compositions. The increase of  $K_2O$  content, decrease of "iron enrichment", and change of  $K_2O$  vs.  $SiO_2$  slope correlate with the decreasing age of the volcanic rocks. Similar conclusions have been reached by Donnelly et al. (1970) who showed that the submarine tholeiitic volcanism of the Lesser Antilles gives way with time to subaerial calc-alkaline volcanism. Similarly Hackmann (1970 pers. comm.) has found a decrease in the "iron enrichment" in volcanic rocks of Guadalcanal (Solomon Islands) from Miocene to Recent lavas

(Fig. 5.1). Table 5.1 shows that island arcs in which only tholeiitic or low-K calc-alkaline rocks occur (e.g. Tonga-Kemadec, Izu - Marianas and Central Kurile Islands) are associated with younger sediments than are island arcs where tholeiitic, calc-alkaline and even shoshonitic rocks occur together. These island arcs contain pre-Miocene or even pre-Cretaceous sediments (e.g. Solomon Islands, New Hebrides, Aleutian Islands). When shoshonitic rocks occur (Kamchatka, Japan, Sunda Islands or New Guinea) the age of basement rocks and associated sediments is usually pre-Mesozoic. This variation infers that the basement of island arcs is formed from submarine arc tholeiites along with complementary ultramafic rocks and, in ideal cases, associated deep water sediments. This is overlain by calc-alkaline rocks and associated shallow water sediments derived essentially from the calc-alkaline rocks (c.f. greywackes of Chappell, 1969).

Trace element abundances in the volcanic rocks of island arcs

In the following discussion the trace element variation in the volcanic rocks of island arcs are presented in four geochemically distinct groups (Taylor, 1968):

1. The large cations of potassium-type (Rb, Ba, Sr, Pb)
2. The rare earth elements (La - Yb)

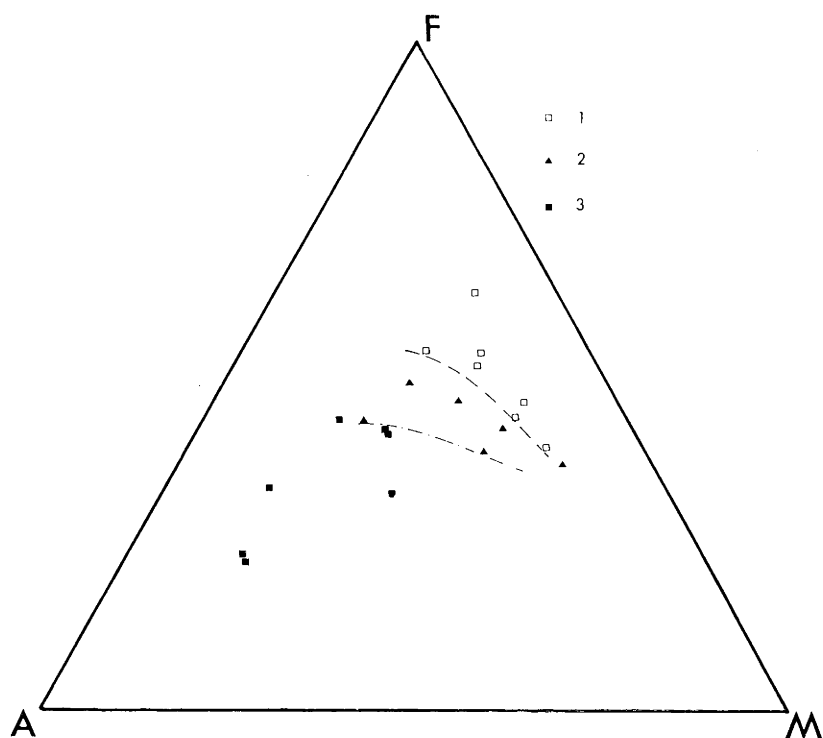


Fig. 5.1 Decreasing "iron enrichment" in volcanic rocks from Guadalcanal (Solomon Islands). 1 - pre-Miocene tholeiitic rocks, 2 - post-Miocene transitional tholeiitic and low-K calc-alkaline rocks, 3 - recent calc-alkaline rocks. Data of Hackman (pers. comm.) and new data included.

TABLE 5.1

Comparison of Cenozoic volcanism in island arcs and the age of basement sediments

| Arc                           | Cenozoic volcanism                                  | Age of sediments associated with basement |
|-------------------------------|-----------------------------------------------------|-------------------------------------------|
| Tonga - Kermadec              | tholeiitic                                          | Eocene                                    |
| Izu - Marianas                | tholeiitic + low K - calc-alkaline                  | Eocene                                    |
| South Sandwich Is.            | tholeiitic                                          | Pleistocene                               |
| Kurile Islands                | tholeiitic + calc-alkaline                          | Pliocene                                  |
| New Hebrides                  | tholeiitic - low K calc-alkaline                    | Miocene                                   |
| Solomons (incl. Bougainville) | tholeiitic + calc-alkaline                          | Upper Cretaceous                          |
| Lesser Antilles               | tholeiitic + calc-alkaline                          | Eocene                                    |
| Aleutian Island               | tholeiitic + calc-alkaline + alkaline               | Upper Cretaceous                          |
| Kamchatka                     | tholeiitic + calc-alkaline + shoshonitic + alkaline | Cretaceous                                |
| Fiji                          | tholeiitic - calc-alkaline - shoshonitic            | Lower Tertiary                            |
| Philippines                   | ? - calc-alkaline - alkaline                        | Palaeozoic                                |
| New Guinea                    | tholeiitic - calc-alkaline - shoshonitic + alkaline | Palaeozoic                                |
| New Zealand                   | ? calc-alkaline - alkaline                          | Lower Paleozoic (Precambrian)             |
| Honshu (Japan)                | tholeiitic - calc-alkaline - alkaline               | Palaeozoic                                |
| Indonesia                     | tholeiitic - calc-alkaline - shoshonitic            | Palaeozoic                                |

3. The large highly charged cations (Zr)
4. The ferromagnesian elements (Ni, V, Cr).

This section refers only to lavas (with 50-65%  $\text{SiO}_2$ ) from typical island arcs of the western Pacific. "Andean type" andesites (see below) together with those which appear in the intracontinental orogenic chains (Carpathians), and rhyolite-ignimbrite complexes (e.g. some of the New Zealand rocks) are not included.

Large cations of potassium-type; Rb, Ba, Sr, Pb

In a general sense, Rb, Ba, Sr and Pb in island arc rocks behave sympathetically to potassium in a geographical (from the oceanic to the continental side of an arc) and stratigraphical (from older to younger units) sense.

Each rock association in an island arc has certain characteristic abundances of these potassium-type trace elements. Because these large cations show a positive correlation with  $\text{SiO}_2$  content, comparison has again been made (where possible) between rocks of the same level of  $\text{SiO}_2$  content. This clearly illustrates that the abundance of these large cation trace elements increase from tholeiites through calc-alkaline rocks to shoshonites.

Extremely low Rb values (1 - 3 ppm) and high K/Rb values have been reported from oceanic tholeiites (e.g. Engel et al. 1965, Gast, 1965). The tholeiitic rocks of

island arcs also have low Rb values, ranging from 2 to 30 ppm over a range in  $\text{SiO}_2$  from 49 to 75%. Rocks with low  $\text{SiO}_2$ , more abundant in the tholeiitic series, have an average of 5 ppm of rubidium. Low-K calc-alkaline rocks (55%  $\text{SiO}_2$ ) have a higher Rb content (10 ppm) than rocks of the arc tholeiitic association with the same  $\text{SiO}_2$  content. The abundance of Rb increases through medium- to high-K calc-alkaline rocks. Taylor (1969) gives 31 ppm as an average value for andesite (59%  $\text{SiO}_2$ ) with 1.6%  $\text{K}_2\text{O}$ . In the shoshonitic association the content of Rb is high, with 80 ppm in rocks with 54%  $\text{SiO}_2$  (e.g. Nicholls and Carmichael, 1968; Jakes<sup>y</sup> and White, 1970). In more siliceous rocks the Rb content increases to values over 100 ppm.

Potassium-rubidium ratios have been discussed in detail by Jakes<sup>y</sup> and White (1970). They showed that K/Rb values decrease from 1000 in island arc tholeiites on the oceanic side to 250 in shoshonites on the continental side of island arcs. The paper is reproduced here (Appendix).

The complexity of Sr variation and its abundance in volcanic and plutonic rocks results from the strong fractionation of Sr by feldspar. Kolbe and Taylor (1966), Hall (1967), Rhodes (1969) and others found a decrease of Sr with increasing  $\text{SiO}_2$  in calc-alkaline plutonic rocks. Similar trends are observed in island arc rocks within the tholeiitic association, but in typical island arc calc-alkaline rocks,

such trends are not clear (c.f. Baker, 1968) and in high-K calc-alkaline rocks (e.g. Eastern Papua) the converse is found; Sr increases with increasing  $\text{SiO}_2$ .

There is only a twofold increase in the abundance of Sr in passing from the tholeiite association to the shoshonites in island arc environments. Kay et al. (1970) found a wide range in the Sr contents of oceanic tholeiites; an average of 110 ppm appears to be most frequent. There is also a wide range in the Sr abundances of island arc tholeiites but the data of Lowder and Carmichael (1970), Gill (1970) and Prinz (1968), suggest values of 200 - 250 ppm at 53%  $\text{SiO}_2$ . This is twice that of the oceanic tholeiites and hence Sr may be a very useful parameter in delineating island arc and oceanic tholeiites. In rocks transitional between arc tholeiites and calc-alkaline rocks, such as the low-K rocks of Izu islands, the New Zealand rocks (Taylor and White, 1966), and those from New Britain and New Hebrides (Ewart, 1970, pers. comm.) Sr abundances at 56 - 58%  $\text{SiO}_2$  are generally 350 - 450 ppm. In high-K calc-alkaline rocks and shoshonites, Sr contents are invariably high, even in rocks with lower  $\text{SiO}_2$  contents, and values of 800 ppm for the high-K calc-alkaline association and 1200 ppm for the shoshonitic association are characteristic.

Barium abundances show a positive correlation with potassium. Taylor (1969) has pointed out that some rocks

TABLE 5.2.

Abundances of Rb, Ba, Sr in some volcanic rock of island arcs in W. Pacific

|                                          | K <sub>2</sub> O%<br>at 55%<br>SiO <sub>2</sub> | K <sub>2</sub> O<br>at 60%<br>SiO <sub>2</sub> | SiO <sub>2</sub> |   | Rb     | Sr       | Ba               | Pb        | K/Rb              |
|------------------------------------------|-------------------------------------------------|------------------------------------------------|------------------|---|--------|----------|------------------|-----------|-------------------|
| Saipan <sup>1</sup>                      |                                                 |                                                |                  |   | 11     | 250      | 115              | 4         | 509               |
| Izu Peninsula <sup>2</sup>               | .45                                             | .60                                            | 53.8-56.8        | A | 9-17   | 326-400  | 170-220          | 3.5-715   | 430-510           |
|                                          |                                                 |                                                | 53.8             | B | 9      | 400      | 170              | 4         | 510               |
| New Britain <sup>3</sup>                 | 1.05                                            | 1.60                                           | 51.4-63.4        | A | 5-20   | 285-540  | 150-350          | 0-20      | 440-1160          |
|                                          |                                                 |                                                | 51.6             | B | 5      | 540      | 220              | 10        | 1100              |
| Fiji (1st period) <sup>4</sup>           |                                                 | .6                                             | 45.2-71.8        | A | 2-9    | 109-600  | 50-280           | 1-11      | 600-1700          |
|                                          |                                                 |                                                | 50.47            | B | 6      | 109      | 125              | 1.3       | 1700              |
| Japan Hakone<br>pigeonite <sup>5</sup>   | .5                                              | .75                                            |                  | B | 0      | 213      | 113              | -         | -                 |
| Japan Hakone <sup>5</sup><br>hypersthene | .5                                              | 1.0                                            |                  | B | 1      | 425      | 136              | -         | -                 |
| New Zealand <sup>2</sup>                 | .90                                             | 1.45                                           | 52.2-62.2        | A | 10-44  | 235-1000 | 140-1000         | 3.5-13.1  | 236-540           |
|                                          |                                                 |                                                | 56.5             | B | 10     | 345      | 280              | 5.4       | 540               |
| Japan Asama <sup>2</sup><br>volc.        | .75                                             | 1.15                                           | 57.3-61.7        | A | 17-32  | 214-362  | 250-340          | 8-13      | 332-400           |
|                                          |                                                 |                                                | 57.3             | B | 17     | 362      | 250              | 11        | 400               |
| Solomon Is. <sup>7</sup>                 | 1.12                                            | 1.50                                           | 56.0-67.9        | A | 18-50  | 739-1339 | -                | 5-14      | 335-420           |
|                                          |                                                 |                                                | 57.0             | B | 32     | 757      | -                | 6         | 420               |
| Bougainville <sup>1</sup>                | 1.55                                            | 1.80                                           | 54.0-60.8        | A | 24-88  | 550-810  | 180-400          | 1.7-7.2   | 297               |
|                                          |                                                 |                                                | 55.2             | B | 24     | 810      | 225              | 3.1       | 563               |
| Fiji II period <sup>4-7</sup>            |                                                 | 1.5                                            | 57.4-59.6        | A | 16-22  | 440-540  | 270-462          | 2.2-3.9   | 473-657           |
|                                          |                                                 |                                                | 59.3             | B | 16     | 480      | 460              | 3.9       | 510 <sup>10</sup> |
| Eastern Papua <sup>7</sup>               | 1.55                                            | 2.38                                           | 56.7-63.0        | A | 52-80  | 577-1227 | -                | 13.4-16.4 | 240-320           |
|                                          |                                                 |                                                | 59.6             | B | 52     | 985      | 560 <sup>8</sup> | 14.2      | 320               |
| New Guinea<br>Highlands <sup>7</sup>     | 2.40                                            | 2.60                                           | 51.7-59.3        | A | 60-111 | 530-840  | -                | 4.8-16.4  | 200-320           |
|                                          |                                                 |                                                | 51.7             | B | 60     | 592      | 540 <sup>9</sup> | 4.8       | 320               |

1. Taylor et al., 1969.
2. Taylor and White, 1966
3. Lowder and Carmichael, 1970
4. Gill, 1970
5. Prinz, 1968 (arithmetic means)
6. Aramaki, 1963
7. Present paper data
8. Jakes and Smith (1970)
9. Jakes and Gill (1970)
10. Jakes and White (1970)

from the calc-alkaline orogenic associations have low Ba contents. Oceanic tholeiites have an extremely low Ba content, usually not exceeding 50 ppm. Values between 50 and 100 ppm are characteristic of island arc tholeiites from the basement of Eastern Papua, Solomon Islands and Macquarie ridge (data of Jakeš and Gill, 1970). In recent island arc tholeiites and in rocks transitional to calc-alkaline rocks, low Ba values are typical and Ba contents of 120 - 320 ppm are found in samples with 54%  $\text{SiO}_2$ . In typical calc-alkaline rocks (andesites with 59%  $\text{SiO}_2$ ) the most common values lie between 220 and 800 ppm. In high-K calc-alkaline rocks, with 59%  $\text{SiO}_2$ , values around 800 ppm are common (Jakeš and Smith, 1970). In rocks with higher  $\text{SiO}_2$  ( $\approx 63\%$ ) Ba abundances of 1000 ppm are found. Shoshonitic rocks with low  $\text{SiO}_2$  contents have Ba contents near 600 ppm. More siliceous shoshonitic association rocks generally have Ba contents in excess of 1000 ppm (c.f. Nicholls and Carmichael, 1969). In some high-K rocks (e.g. Eastern Papua) the early crystallization of a mica phase distorts the pattern of Ba variation, and even a decrease of Ba with increasing  $\text{SiO}_2$  content can be observed.

The lead content of rocks with similar  $\text{SiO}_2$  contents increases from the tholeiites through to high-K calc-alkaline and shoshonitic rocks. Values near 4 ppm for low-K andesites and 10 - 15 ppm for high-K calc-alkaline andesites

are typical. Data on the Pb contents of shoshonitic rocks are limited but it would appear that they are similar to those of high-K andesites: a shoshonitic rock from the New Guinea Highlands has 16 ppm at 59%  $\text{SiO}_2$ . The "least fractionated" or more basic shoshonitic rocks have very low Pb values ( 3 - 5 ppm).

#### Rare earth elements

Abundances of rare earth elements (REE) in island arc rocks have been discussed by Jakes and Gill (1970). This paper is reproduced and appended together with new data in Appendix.

The total content of REE in island arc rocks is relatively low and usually does not exceed 100 ppm (Taylor, 1969). The most important fact emerging from the new data is that there are two types of distribution patterns in recently erupting island arc associations.

Chondritic or primitive REE patterns characterize tholeiitic rocks which lie on the oceanic side of an island arc and/or form the basement of the arcs. In Figure 3 and Table 3 of Jakes and Gill (1970) REE content and the pattern for tholeiitic rocks from a present-day volcano in New Britain (Ulawan) are shown, together with data on the basement rocks (basalts) in Eastern Papua, New Guinea. This

and new data on the basement rocks from the Solomon Islands (Fig. 4) and Macquarie Ridge (Fig. 5) and data from the literature (Japan - Masuda, 1966; Saipan - Taylor, 1968; and Fiji - Gill, 1970) together with unpublished data of Ewart and Graham (1970) on Tonga, clearly demonstrate that the production of tholeiitic rocks with this primitive REE pattern is not unique to mid-oceanic ridges, as inferred by some authors (e.g. Schilling, 1969). Thus genetic constraints, based on REE, applied to rocks of the mid-oceanic ridges should also be applied to rocks of the outer part of island arcs.

"Sedimentary-type" patterns (i.e. patterns strongly enriched in light REE), occur in calc-alkaline, shoshonitic and alkaline rocks of island arcs. Jakeš and Gill (1970) showed that within the groups of rocks with a "sedimentary type" of REE pattern, there is only a weak correlation between  $K_2O$  content and La/Yb ratio (Figs 7,8).

#### Large highly-charged cations (Zr, Th, U)

Data on abundances of zirconium in rocks from island arcs of the Western Pacific show a positive correlation between Zr and  $SiO_2$ . At a given  $SiO_2$  content, the Zr content of island arc tholeiites is less than that of calc-alkaline rocks. Gill (1970) found a decrease in Zr abundances in passing from calc-alkaline rocks to shoshonitic rocks,

whereas Nicholls and Carmichael (1969), found relatively high values for Zr in shoshonites, indicating the opposite trend. The tendency of Zr to concentrate in residual liquids (e.g. Ewart et al., 1968) and the different geochemical behaviour of Zr in plutonic and volcanic rocks (e.g. Rhodes, 1969; Gill, 1970) makes Zr an unreliable indicator of variation in parental magmas of island arcs. The Zr content of oceanic tholeiites is slightly higher than that of island arc tholeiites.

Donnelly et al. (1970), summarized available information on Th and U abundances and discussed the genetic implications. New data, and that given by Gill (1970) and Taylor (1969), suggest that the absolute abundances of both Th and U contents (although extremely variable) and Th/U ratios increase from tholeiites to shoshonites.

#### Ferromagnesian trace elements (Cr, Ni, V)

Ferromagnesian trace elements Cr and Ni are easily fractionated by early or liquidus phases such as opaque minerals, olivine, and clinopyroxene. For this reason the abundances of Cr, Ni and V show an inverse correlation with  $\text{SiO}_2$ . There is a wide range of absolute abundances even for one rock association within a particular region (Baker, 1968), but, in general ferromagnesian trace element concentrations in island arc rocks (except in a few rocks of cumulative

origin) are lower than those in rocks from either truly continental or truly oceanic areas.

In all rock associations the abundance of vanadium is inversely correlated with  $\text{SiO}_2$  over a very wide range of  $\text{SiO}_2$  values. In contrast Cr and Ni are strongly enriched in calc-alkaline and shoshonitic rocks with less than 54%  $\text{SiO}_2$ . In the island arc tholeiitic rocks, this enrichment is confined to rocks with less than 52%  $\text{SiO}_2$ . For example, low  $\text{SiO}_2$  rocks (53%) of the high-K calc-alkaline association have 500 ppm Cr and 200 ppm Ni (Eastern Papua, Jakes and Smith, 1970), whereas arc tholeiites with similar  $\text{SiO}_2$  contents are likely to have less than 40 ppm of Cr and less than 20 ppm of Ni (e.g. tholeiites from Fiji, Gill (1970), or pigeonitic series of Kuno in Prinz (1968)). A comparison of island arc tholeiites and tholeiites of oceanic areas reveals a lower Cr and Ni content in the rocks from island arcs.

Rocks which are transitional between island arc tholeiites and true calc-alkaline rocks e.g. those from Izu Peninsula (Taylor and White, 1966) have higher concentrations of the ferromagnesian trace elements than some rocks of the arc tholeiite association. Some typical high-K calc-alkaline rocks and shoshonites also have higher Ni, and the Cr varies from 0 - 400 and Ni from 0 - 100 ppm, whereas V contents are much the same in all three

associations and is 120 - 150 ppm at  $\text{SiO}_2$  58%.

#### Isotope studies

No isotopic studies were carried out in this project. Lead isotope data have been discussed in detail by Tatsumoto and Knight (1969) for the Japanese islands. They found that "the isotopic composition of lead in the primary basalts gradually decreases in radiogenic character from the Pacific Ocean side to the Japanese sea side, whereas the observed  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{232}\text{Th}/^{238}\text{U}$  ratios in the basalt increase in the same direction." Data on strontium isotopes, although numerous, do not show any significant variations and remain close to .704 or .705 (e.g. Gill, 1970).

#### Variation within given rock associations

It has been argued that rock associations of island arcs (e.g. low-K calc-alkaline) can be defined not only chemically but also using an independent variable such as distance from trench axis in regions with a normal seismic zone. It should be pointed out again, that each association usually includes rocks of wide  $\text{SiO}_2$  contents ranging from basalts to dacites or rhyolites in proportions typical for each association (Table 7.1). The relations of different members of a given association could be illustrated by:

a) stratigraphic relations of lavas within one volcano such as the successive appearance of basalt, andesite and dacite in one volcanic centre;

b) variations of  $\text{SiO}_2$  content of recently erupting lavas belonging to the same association in different volcanic centres at the same distance from the trench.

In island arc calc-alkaline associations (e.g. Eastern Papua; Asama Volcano, Japan) it appears that basaltic rocks give way in time to andesites and then to dacites. This relationship is difficult to explain by fractional crystallization of one parental magma which can produce rocks of different  $\text{SiO}_2$  content but fails to explain why basaltic rocks usually appear earlier than andesites and dacites. This could result from different degrees of partial melting caused by local temperature variations

#### Island arc and Andean andesites

The discussion of major and trace element abundances has so far been restricted to rocks from typical island arcs with 50-65%  $\text{SiO}_2$ , even though some areas of Cenozoic calc-alkaline volcanism which are associated with active continental margins, and rhyolitic rocks (with  $\text{SiO}_2 > 65\%$ ) represent an important fraction of the volcanic sequence (e.g. South American Andes). Similarly significant volumes of

andesites and rhyolite and only minor basic rocks are present in "intracontinental" orogenic chains (e.g. Carpathian Mts). Calc-alkaline volcanic rocks of island arcs and those of continental margins or intra-continental chains -- here termed "Andean" -- have a number of features in common, but they differ significantly in some respects. The differences can be summarized as follows:

(1) The island arc calc-alkaline association is an intermediate member of the orogenic association and grades into low-K rocks on the oceanic side, and into high-K rocks on the continental side of the arc. Andean calc-alkaline rocks invariably have high-K contents especially in the 62-65%  $\text{SiO}_2$  range. A spatial or stratigraphic variation of lava compositions does not occur in the Andean association, but in some andesites (e.g. Carpathians; Kuthan, 1968) there is a slight increase of K in a stratigraphical sense.

(2) In island arc calc-alkaline associations, high  $\text{SiO}_2$  rocks are extremely rare (< 10%) and rocks with less than 56%  $\text{SiO}_2$  are moderately abundant ( $\approx$  30% by volume). Andean calc-alkaline rocks are characterized by the association of andesites and rhyolites in approximately equal proportions. Low  $\text{SiO}_2$  rocks are extremely rare, and are generally absent (Northern Andes', Katsui, 1969; Alaskan volcanoes, Forbes et al., 1969). Andesites and rhyolites are separated by a time

hiatus, and over long periods of time there exist cycles of andesitic or rhyolitic activity.

(3) The major element chemistry of both Andean and island arc high-K calc-alkaline rocks is very similar (e.g. Forbes et al., 1969) but the available data suggest that Andean rocks have a more variable  $\text{Al}_2\text{O}_3$  content (14.0 - 20.5%, Radulescu, et al., 1964) and rocks of higher  $\text{SiO}_2$  content (over 63%) approach the shoshonitic ratio of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  (1 : 1) and there is a steeper gradient of  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  correlations.

(4) Phenocryst mineralogy is similar in both associations except for the frequent occurrence of garnet, some cordierite and "quartz phenocrysts" in andesites of the Andean association (in Carpathian andesites, Kuthan, 1968; Imramovský, 1962; Vasilescu, 1967). With the exception of garnet-bearing dacites in Japan, such phenocrysts do not occur in calc-alkaline island arc rocks. Olivine is rare in Andean type andesites.

(5) The abundances of trace elements of the potassium type (Ba, Rb, Sr), and Zr, Th, U, are substantially higher in Andean-type andesites when rocks with the same  $\text{SiO}_2$  content are compared. Vanadium, nickel and chromium abundances are highly variable in both associations but appear to be slightly lower in Andean andesites.

(6) The crystallization sequence of the major phenocryst phases also differs; in amphibole-bearing varieties, amphibole is rarely the liquidus phase in typical island arc andesites, whereas it commonly appears as the liquidus phase in the Andean andesites.

(7) In rock associations of continental areas, basic and ultra-basic inclusions such as lherzolite and websterite nodules have not been found, although they have been recorded in similar rocks from the island arcs (Japan, Solomon Islands).

(8) In continental areas such as the Western United States or Central America, both types of calc-alkaline rocks (island arc type and Andean type) probably occur. This is suggested by the two distinct patterns of strontium and lead isotopes found in these rocks (Doe et al., 1969). McBirney's (1969) "divergent" and "coherent" types also suggest the presence of both types.

(9) Andean calc-alkaline rocks have high contents of Pb, Zn and Cu, and "autometamorphic" or hydrothermal alteration (prophyllitization) is often observed : such a feature is rare in true island arc andesites.

Despite their differences both the Andean and island arc calc-alkaline associations are related to an orogenic environment.

The available data on major element chemistry and trace element abundances and their similarity to those of calc-alkaline plutonic associations, coupled with phenocryst mineralogy and experimental evidence, combine to suggest that the genesis of Andean calc-alkaline rocks is related to the later stages in the development of orogenic areas, when crustal thickness and thermal regimes permit partial melting of the lower crust. Ewart and Stipp (1968), have explained the petrogenesis of the acid volcanic rocks of Rotorua-Taupu volcanic province, New Zealand, by such a mechanism and they suggest that eugeosynclinal sediments are a possible source material.

The major and trace element chemistry of Andean calc-alkaline rocks -- namely high Ba, Rb, Sr, Th, U; low K/Rb, V, Cr, and Ni; and also high  $K_2O/Na_2O$  ratio -- is satisfactorily accounted for by a history of formation and fractionation in which amphibole is a liquidus phase.

## CHAPTER 6

DISCUSSION OF MINERALOGICAL LIMITATIONS OF TRACE ELEMENT  
DISTRIBUTION IN ISLAND ARC ROCKSIntroduction

If it is assumed that rocks of island arcs have their source at depths corresponding to that of the underlying Benioff zone as suggested by the correlation between  $K_2O$  contents and depth of the Benioff zone (Dickinson and Hatherton, 1967), then their source material is the upper mantle or the upper part of a down-going slab of lithosphere at depths ranging from 80 to 250 kms. Furthermore, if partial or fractional melting are principal petrogenetic processes, then the island arc rocks, at least those whose compositions are not seriously modified by high-level fractionation or crustal contamination should represent:

(a) Magmas which reached equilibrium with mineral phases stable at depths from which the magma was derived, or

(b) liquids corresponding at least in some respect to the composition of the low melting point phases or minerals which were no longer stable at the given conditions.

Some restrictions on hypotheses of evolution for island arc volcanic sequences have already been imposed by

major element chemistry. For example, assuming homogeneous source material, potassium abundances suggest that the amount of fractional or partial melting in the mantle in the downgoing slab material decreases with depth: 15-25% partial melting produces island arc tholeiites; 2-5% melting produces calc-alkaline rocks and lower percentages produce shoshonitic melts.

The use of distribution coefficients derived from phenocryst/matrix equilibria to calculate trace element abundances in the lavas and crystalline residuum is an appropriate way to deal with trace element abundances (c.f. Gast, 1968; Griffin and Murthy (1969) but there are reasons to believe that reliable distribution coefficients applicable to high-T and P processes have not yet been determined. Phenocryst/matrix partition coefficients only provide an approximation to the distribution of a given trace element between a partial melt and the crystalline residuum.

Distribution of Cr, V, Ni, La and Yb between melt and liquidus phases of wet andesite in 5-30 kb range

The problem of distribution coefficients clearly calls for elucidation by experiment, especially in cases where these parameters are not easily evaluated, such as distributions between the liquidus phases and the melt. The advantage of experimental work is that pressures, temperatures

and liquidus mineralogy are known precisely. However trace element concentrations must be raised to amounts detectable by the electron microprobe, so that experiments may give erroneous results because of concentration effects.

Preliminary experiments on Cr, V, Ni, La and Yb distribution have been carried out with an andesitic composition approximating that of a typical calc-alkaline andesite from the island arcs. It was prepared from oxides ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ), carbonates ( $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ), Al-sulphate and silicic acid in the appropriate proportions. These compounds were mixed in acetone and heated for 14 hours at  $1100^\circ\text{C}$ . The mix was then crushed and homogenized and metallic Fe added in the appropriate proportions to obtain the required oxidation ratio. After mixing in a tungsten carbide mixer, this was split into four parts:

A - "basic mix". This was used without further additions to determine liquidus phases at various pressures.

B - "transition metal mix". To the "basic mix" 0.2% of  $\text{NiO}$ , 0.2%  $\text{Cr}_2\text{O}_3$ , and 0.2%  $\text{V}_2\text{O}_5$  were added and ground under acetone for 45 mins. in an agate mortar.

C - "rare earth elements mix". To the "basic mix" 0.2% of both  $\text{Yb}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  were added and ground under acetone for 45 minutes in an agate mortar.

D - "spare basic mix" was used for preparation of glasses for calibration.

Mixes A, B and C were pelletized and melted ( $\approx 1450^{\circ}\text{C}$ ) in a high frequency heater in a dry nitrogen atmosphere, and the quenched glass was finely crushed and used in experimental runs. Mix D was split again into 5 parts, and to each portion known amounts of trace element oxides were added (3.04% NiO, 2.48%  $\text{V}_2\text{O}_5$ , 2.12%  $\text{Cr}_2\text{O}_3$ , 2.98%  $\text{La}_2\text{O}_3$  and 3.54%  $\text{Yb}_2\text{O}_3$ ). These were thoroughly mixed, pelletized and melted on an iridium strip (oxidation state was not controlled) and the glasses were used for calibration of the electron microprobe. The composition of glass fragments of prepared mixes A, B, C was checked using the electron microprobe and the oxidation state determined by microchemical techniques. The results are presented in Table 4.1. Only small losses of  $\text{K}_2\text{O}$  and consequently small increase of  $\text{SiO}_2$  were found. The basic mix was checked for any trace element contamination introduced by the added reagents using emission spectrographic techniques. The blank corrections thus determined are as follow: Ni = 80 ppm, V = 20 ppm and Cr = 30 ppm.

#### Experimental procedures

In order to determine the liquidus phases of the prepared andesite, charges of the basic andesite mix in the form of powdered glass with 5%  $\text{H}_2\text{O}$  were subjected to pressures ranging from 5-30 kb over a temperature range of  $950-1200^{\circ}\text{C}$ , in a piston-cylinder apparatus of the Boyd-

England type. The experimental techniques have been described elsewhere by other authors (e.g. Essene et al., 1970). In brief, 10-20 mg of sample was weighed into a Pt capsule and 5% water added using a microburette. The capsule was sealed and reweighed before and after the run to check for water loss. Results of runs in which water loss occurred were rejected. A talc furnace assembly was used and Pt - (Pt + Rh) thermocouples used for measurement and temperature control. In experiments with andesite mix (A) pressure was applied first and the assembly later brought to the required temperature. In experimental work with andesite enriched in trace elements (B and C) the pressure was applied first and temperature brought  $50^{\circ} - 70^{\circ}\text{C}$  above the liquidus in order to grow crystals of sufficient size to permit microprobe investigation. After 15 minutes at these temperatures, the cell was brought at approximately  $2^{\circ}\text{C}/\text{min.}$  to the desired temperature and held there for 1 to 2 hours. After quenching by cutting the power supply, the capsules were cleaned, reweighed and examined using powder mounts, X-ray powder photographs and the electron microprobe. The pressure applied was 10% higher than pressure required, to correct for friction (Green et al., 1967). Reported values are believed to be  $\pm 3\%$  P, and  $\pm 10^{\circ}\text{C}$ . A few unsuccessful runs in the low-P region were caused by extrusion of the thermocouple (5 kb at  $1000^{\circ} - 1075^{\circ}\text{C}$ ).

TABLE 6.1 Results of experimental runs on the Andesite C + 5% H<sub>2</sub>O

Andesite C

| Conditions of run |                     |             | Comments                                                   |
|-------------------|---------------------|-------------|------------------------------------------------------------|
| Pressure<br>(Kb)  | Temperature<br>T° C | Time<br>hrs |                                                            |
| 5                 | 1025                | 2           | no silicate phases present                                 |
| 10                | 1025                | 2           | quench present ( $\approx$ 20%) on bottom of capsule       |
| 15                | 1050                | 1           | about 10% of material crystallised<br>quench present       |
| 20                | 1075                | 1           | 10% of material crystallised,<br>relatively large crystals |
| 30                | 1175                | 1           | less than 5% crystallised large<br>cpx crystals            |

TABLE 6.2 Results of experimental runs on the andesite B + 5% H<sub>2</sub>O

Andesite B

| Conditions of run    |                  |          | Phases present and their estimated proportions | Comments                                                                                                                            |
|----------------------|------------------|----------|------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| Pressure K6          | Temperature T° C | Time hrs |                                                |                                                                                                                                     |
| 10                   | 1025°            | 2        | amph >> cpx (2%) > opaque                      | 15% of material crystallised                                                                                                        |
| 20                   | 1075°            | 2        | cpx >> amph (4%) >>> opaque                    | 10% of material crystallised                                                                                                        |
| 30                   | 1175°            | 2        | cpx = opaque (5%)                              | result slightly anisotropic high R.I. grains of unidentified mineral                                                                |
| 35                   | 1100°            | 2        | cpx                                            | drop in T (20° C) during first half an hour of experiment, most of run crystallised but x-ray photographs gives jd-pyroxene pattern |
| Andesite B - Dry run |                  |          |                                                |                                                                                                                                     |
| 30                   | 1350°            | 2        | qz, cpx, qa (?)                                | small isolated high R.I. grains                                                                                                     |

Table 6.3

Electron microprobe analyses of minerals and glasses from experimental runs.

| Andesite C                     |      |       |      |      |       |      |       |      |      |
|--------------------------------|------|-------|------|------|-------|------|-------|------|------|
| 2681                           |      |       |      |      | 2672  |      |       |      |      |
| run Nr.                        | cpx  | glass | opq  | cpx  | glass | opq  | glass | opq  | 2674 |
| phase                          |      |       |      |      |       |      |       |      | amph |
| SiO <sub>2</sub>               | 48.0 | 62.1  | .2   | 49.5 | 61.8  | .3   | 62.5  | 1.9  | 43.0 |
| TiO <sub>2</sub>               | .8   | .7    | .6   | .7   | .7    | .6   | .8    | .6   | .8   |
| Al <sub>2</sub> O <sub>3</sub> | 10.9 | 17.4  | 1.8  | 8.1  | 17.6  | .2   | 17.7  | .6   | 10.8 |
| FeO                            | 8.5  | 3.6   | 81.6 | 6.3  | 1.5   | 82.4 | 1.4   | 82.8 | 10.8 |
| MgO                            | 11.3 | 2.06  | .2   | 13.6 | 1.8   | 1.5  | 1.6   | .1   | 11.6 |
| CaO                            | 17.0 | 5.7   | .5   | 20.0 | 6.3   | .4   | 6.7   | .5   | 12.8 |
| Na <sub>2</sub> O              | 3.4  | 3.4   | -    | 1.1  | 3.4   | -    | 3.6   | -    | 2.9  |
| K <sub>2</sub> O               | -    | 1.4   | -    | .1   | 1.2   | -    | 1.2   | -    | .10  |
| La <sub>2</sub> O <sub>3</sub> | .18  | .23   | .31  | .16  | .21   | 1.3  | .20   | .34  | -    |
| Yb <sub>2</sub> O <sub>3</sub> | .30  | .14   | .90  | .43  | .15   | .9   | .19   | .85  | -    |
|                                |      |       |      |      |       |      |       |      | .16  |

## Andesite B

| 2676                           |      |      |       |      | 2677 |       |      |      |       |
|--------------------------------|------|------|-------|------|------|-------|------|------|-------|
| run Nr.                        | opq  | amph | glass | opq  | cpx  | glass | opq  | cpx  | glass |
| phase                          |      |      |       |      |      |       |      |      |       |
| SiO <sub>2</sub>               | .3   | 43.1 | 64.0  | .1   | 50.1 | 60.9  | -    | 48.5 | 61.5  |
| TiO <sub>2</sub>               | .9   | 1.3  | .7    | .6   | .7   | .6    | .7   | .6   | .65   |
| Al <sub>2</sub> O <sub>3</sub> | .2   | 12.0 | 18.0  | .1   | 9.0  | 17.6  | .2   | 10.6 | 18.1  |
| FeO                            | 72.2 | 10.5 | 1.2   | 73.0 | 8.8  | 1.4   | 69.8 | 6.7  | 1.0   |
| MgO                            | .1   | 12.3 | 2.4   | .1   | 11.3 | 1.5   | .1   | 10.4 | 1.8   |
| CaO                            | -    | 13.2 | 3.8   | -    | 19.1 | 3.8   | -    | 19.8 | 3.9   |
| Na <sub>2</sub> O              | -    | 2.6  | 3.6   | -    | .45  | 3.5   | -    | 1.9  | 3.5   |
| K <sub>2</sub> O               | -    | .3   | 1.9   | -    | -    | 1.5   | -    | 1.4  | 1.4   |
| Cr <sub>2</sub> O <sub>3</sub> | 1.8  | .82  | .06   | .98  | .90  | .10   | 3.6  | 1.66 | .06   |
| NiO                            | 16.2 | .1   | <.1   | 14.7 | <.1  | <.1   | 20.1 | -    | .11   |
| V <sub>2</sub> O <sub>5</sub>  | 1.6  | -    | .16   | .85  | .20  | .14   | .5   | .30  | .15   |

Conditions of runs 2681-30kb, 1175°C, 2673-15kb, 1050°C, 2672-10kb, 1025°C, 2674-20kb, 1075°C, 2676-10kb, 1025°C, 2677-20kb, 1075°C, 2679-30kb, 1175°C.

The analyses show that liquidus phase opaque grains are strongly zoned especially in Ni, Fe and Cr. Because of the size of mineral grains ( $5\ \mu$ ) and thus the possibility of interference from the surrounding glass, the probe analyses could only be carried out on the central parts of zoned grains. The distribution coefficients ( $C_{\text{solid}}/C_{\text{in residual glass}}$ ) do not represent true equilibrium distributions as this is confined only to the marginal parts of grains. Regardless of whether the distribution coefficients are calculated from abundances of trace elements in the total rock (starting mix) or from the amount determined in the residual glasses, there is a substantial variation from grain to grain. The use of increased amounts of trace element obviously introduces a serious error because of the concentration dependence of distribution coefficients. The experimental results for transition metal distributions in opaque phases are in poor agreement with natural data. For instance, Taylor and Duncan (1968) showed preferential concentration of V into magnetite; but the experimentally crystallized opaque phases from similar rock compositions as those studied by these authors showed only a 4-fold enrichment in V over the total rock, whereas Ni and Cr are enriched by a factor of 20.

The results of experiments on the partition of rare earth elements by opaque phases (with only one exception),

Table 6.3.

Experimentally determined distribution coefficients  
 ( $D = C_s/C_l$ ) in andesitic rocks.

---

| conditions of run | opq/melt | amph/melt | cpx/melt    |
|-------------------|----------|-----------|-------------|
| <b>Chromium</b>   |          |           |             |
| 10kb 1025°C       | 30.      | 14.       | -           |
| 20kb 1075°C       | 10.      | -         | .9          |
| 30kb 1175°C       | 60.      | -         | 28.         |
| <b>Nickel</b>     |          |           |             |
| 10kb 1025°C       | >162.    | 1.0       | -           |
| 20kb 1075°C       | >150.    | -         | low in both |
| 30kb 1175°C       | >200.    | -         | <1.0        |
| <b>Vanadium</b>   |          |           |             |
| 10kb 1025°C       | 10.      | <.9       | -           |
| 20kb 1075°C       | 6.       | -         | 1.4         |
| 30kb 1175°C       | 3.4      | -         | 2.0         |
| <b>Lanthanum</b>  |          |           |             |
| 10kb 1025°C       | 6.5      | -         | -           |
| 15kb 1050°C       | 1.5      | -         | .8          |
| 20kb 1075°C       | 1.7      | <.75      | -           |
| 30kb 1175°C       | -        | -         | .8          |
| <b>Ytterbium</b>  |          |           |             |
| 10kb 1025°C       | 4.8      | -         | -           |
| 15kb 1050°C       | 6.0      | -         | 2.8         |
| 20kb 1050°C       | 5.3      | <.9       | -           |
| 30kb 1050°C       | -        | -         | 2.1         |

are comparable with natural data. Experimentally derived distribution coefficients agree with the observations made by Balshov and Sobolev (1967). There is 1.5 - 2-fold enrichment of REE in magnetites and ilmenites relative to the total rock and preferential entry of heavy REE (Yb) relative to light REE (La).

Distribution of various elements between clinopyroxene and amphibole is in good agreement with that measured from phenocryst-matrix and phenocryst/total rock abundances. Preferential entry of Cr into clinopyroxene and almost equal partition of V and Ni between clinopyroxene/melt and amphibole/melt are in good agreement with data on natural phases. However the experimental values reported are averages of about 10-15 determinations for each run. Measurements for each run may vary by a factor 5 because of zonation of crystals.

La and Yb concentrations in amphibole are below detection limits, but these elements can be measured in clinopyroxenes. In accordance with observations made on natural clinopyroxenes, this phase was found to preferentially incorporate heavy REE.

#### Rare Earth Elements

It has been shown that the abundances and distribution patterns of rare earth elements divide the rocks of

island arc environments into two distinct groups:

- a. Island arc tholeiites which have primitive "chondritic" patterns.
- b. Calc-alkaline and shoshonitic rocks with "sedimentary" patterns.

Although large cations of the K-type show a gradational increase from rocks having "chondritic" patterns to those with "sedimentary" patterns i.e. from tholeiites to shoshonites, there is poor correlation between  $K_2O$  content and the degree of enrichment of light rare earth elements expressed as the La/Yb ratio (Fig. 8 in Jakeš and Gill, 1970). It has been suggested (Schilling and Winchester, 1966; Masuda, 1966) that rocks with "sedimentary" patterns (enriched in light REE) are produced by small degrees of partial melting (1-15%) or large degrees of fractionation of a homogeneous unfractionated source material, or could result from contamination of a primitive magma by crustal material. This hypothesis of crustal contamination would be supported by the observed continuous increase of K-type elements, but such a process would create not only a very broad spectrum of La/Yb ratios but also a more positive correlation between K and La/Yb ratios. Available data for island arc rocks (Fig. 6 of Jakeš and Gill, 1970) show that this correlation does not exist.

TABLE 6.5.

Rare earth element analyses of selected minerals

|    | 4523               |      |      | Granulite |      |
|----|--------------------|------|------|-----------|------|
|    | Eclogite - Kakanui |      |      |           |      |
|    | Cpx                | Amp  | Ga.  | Ga.       | Rock |
| La | 2.4                | 7.4  | .35  | 3.2       | 21.9 |
| Ce | 2.1                | 17.7 | 1.54 | 8.4       | 45.9 |
| Pr | n.d.               | 3.0  | .21  | .9        | 3.6  |
| Nd | 2.4                | 13.4 | .83  | 3.2       | 12.2 |
| Sm | 6.8                | 4.1  | .74  | 2.2       | 3.9  |
| Eu | 1.61               | 1.4  | .54  | .01       | .68  |
| Gd | 2.7                | 2.7  | 1.56 | 4.6       | 2.6  |
| Tb | .97                | .34  | .68  | 2.6       | .65  |
| Dy | 6.5                | 3.38 | 8.05 | 35.1      | 5.10 |
| Ho | 1.2                | .50  | 2.32 | 10.2      | 1.05 |
| Er | 2.14               | .96  | 5.88 | 22.9      | 2.6  |
| Tm | .80                | .15  | .71  | 2.4       | .42  |
| Yb | 3.41               | .69  | 7.25 | 23.5      | 2.90 |
| Ba | n.d.               | 263  | 2.5  | 13.8      | 585  |

Table 6.5. continued

Major element analyses of minerals and rock analysed  
for rare earth

|                                | Kakanui Eclogite 4523 |        |        | Granulite |          |
|--------------------------------|-----------------------|--------|--------|-----------|----------|
|                                | Cpx                   | Amp    | Ga.(1) | Ga.(2)    | Rock (3) |
| SiO <sub>2</sub>               | 49.91                 | 41.06  | 40.37  | 39.04     | 71.94    |
| TiO <sub>2</sub>               | 1.24                  | 4.87   | 0.33   | .086      | .32      |
| Al <sub>2</sub> O <sub>3</sub> | 8.19                  | 14.58  | 22.71  | 19.25     | 14.08    |
| Fe <sub>2</sub> O <sub>3</sub> | 2.63                  | 3.02   | 1.68   | 3.76      | .11      |
| FeO                            | 6.27                  | 8.12   | 15.03  | 26.62     | 2.31     |
| MnO                            | 0.14                  | 0.09   | 0.42   | .51       | .05      |
| MgO                            | 12.97                 | 13.16  | 14.38  | 7.11      | .60      |
| CaO                            | 16.97                 | 9.95   | 5.03   | 1.86      | 1.52     |
| Na <sub>2</sub> O              | 1.98                  | 2.86   | 0.03   | .09       | 3.07     |
| K <sub>2</sub> O               | 0.03                  | 1.55   | 0.04   | .08       | 4.40     |
| P <sub>2</sub> O <sub>5</sub>  | 0.05                  | 0.07   | 0.03   | .12       | .17      |
| H <sub>1</sub> O+              |                       | 1.13   |        | .48       | .31      |
| H <sub>2</sub> O-              |                       | -      |        | .02       | .19      |
| CO <sub>2</sub>                |                       | -      |        | -         | .16      |
|                                | 100.38                | 100.46 | 100.05 | 99.02     | 99.23    |

(1) White and Chappell, 1970, pers. comm.

(2) Kodym et al., 1969, analyst Huka, UUG-Prague

(3) Kodym et al., 1969, analyst Kucerova, UUG-Prague

The change of REE pattern suggests a change in the mineralogy of the source material rather than a decreasing degree of partial melting of a homogeneous source. The consistency of concentration of REE in the minerals of a given paragenesis, provides a means for evaluation of the mineralogy of the residuum. The distribution of REE between melt and the early precipitating phases and also some aspects of distribution of REE in subsolidus parageneses are therefore discussed in more detail. Complete REE patterns have been determined for 20 rocks and 4 mineral separates (in Jakes and Gill, 1970) and Table 6.5. Concentrations of the light REE elements (La, Ce, Pr, Nd) have been determined in most of the rocks and mineral concentrates using XRF techniques (Tables accompanying Chapters 1, 2 and 3).

### Olivine

The total abundances of REE in olivine are usually lower by at least two orders of magnitude than those of the total rock (Schnetzler and Philpotts, 1968, 1970; Frey, 1969). There is no characteristic enrichment of light or heavy REE in olivine in either meteorites or terrestrial rocks (Masuda, 1968), but some olivines are depleted in Sm, Eu and Gd. It is interesting to note, that slight enrichment of these elements appears in most island arc tholeiites, supporting the view of Jakes and Gill (1970), that extensive

fractionation of olivine and some pyroxene has taken place in the production of these rocks.

### Clinopyroxene

Data of Haskin et al. (1966), Schnetzler and Philpotts (1968), Frey (1969) and new data presented in this thesis show that REE patterns and abundances in clinopyroxene are determined by the coexisting phases. In volcanic and plutonic rocks where clinopyroxene coexists with amphibole and plagioclase, clinopyroxene is enriched in heavier REE (Frey, 1969) and clinopyroxene coexisting with melt also concentrates the heavy REE (Onuma et al., 1968; Schnetzler and Philpotts, 1968, 1970) although phenocryst/matrix distribution coefficients derived from their data may vary by an order of magnitude. The experimental data on the relative enrichment of La and Yb in melt and clinopyroxene agree with data on phenocryst/matrix distribution but distribution coefficients are higher by a factor of 2 than those of any natural rock. Recent reported experiments by Masuda and Kushiro (1970) confirm the preferential entry of heavy REE into clinopyroxene.

In eclogites, where clinopyroxene coexists with garnet (Haskin et al., 1966) the clinopyroxene is relatively enriched in light REE. In rocks such as the Kakanui "eclogite" (clinopyroxene + garnet + amphibole) (new data

in Table 6.5 and Fig. 6.1), clinopyroxene shows slight depletion in light REE, thus reflecting the enrichment of amphibole in light REE.

Clinopyroxene is a liquidus phase of andesite (5% H<sub>2</sub>O and dry) and probably shoshonite, over an extensive range of pressures above 15 kb. This suggests that if andesitic melts are derived from these depths then they were in equilibrium with residual clinopyroxene. This would account for enrichment in lighter REE.

#### Orthopyroxene

Frey et al. (1968), Onuma et al. (1969) and Frey (1969), show that orthopyroxene is invariably enriched in heavy REE relative to light REE, but the concentrations are lower by an order of magnitude than those measured in clinopyroxene. Four new analyses of the light REE in orthopyroxenes from calc-alkaline volcanic rocks show that there is an increase in the relative abundances with increasing atomic number thus inferring an enrichment in the heavier REE.

#### Garnet

Pronounced enrichment of heavy REE has been recorded in garnets (Haskin et al., 1966). This pattern is supported

by new data on "eclogite" assemblages from the Kakanui breccia (Table 6.5 and Fig. 6.1) and by data on garnet/whole rock REE distribution in garnet-bearing granulite. A strong enrichment in light REE and a low content of heavy REE can be expected in rocks from which an early separation of garnet has taken place or where garnet remains in the crystalline residuum after partial melting. REE fractionation patterns of calc-alkaline rocks has led to the suggestion that garnet remains in the crystalline residuum (Green and Ringwood, 1968). It should be noted that garnet is an important subsolidus phase in tholeiite compositions (e.g. Green, 1967) and oceanic tholeiite is believed to be the principal (although not the ultimate) source of calc-alkaline rocks. Garnet is also a high pressure phase of the upper mantle (pyrolite) composition (Green and Ringwood, 1970) and thus small amounts of melt derived directly from a garnet-bearing upper mantle assemblage would be enriched in light REE.

The two distinct REE patterns found in island arc volcanic rocks could reflect a progressive increase in the abundance of garnet and/or clinopyroxene in subsolidus parageneses of the source material, or, alternatively there may have been fractionation of garnet and/or clinopyroxene in a more primitive melt.

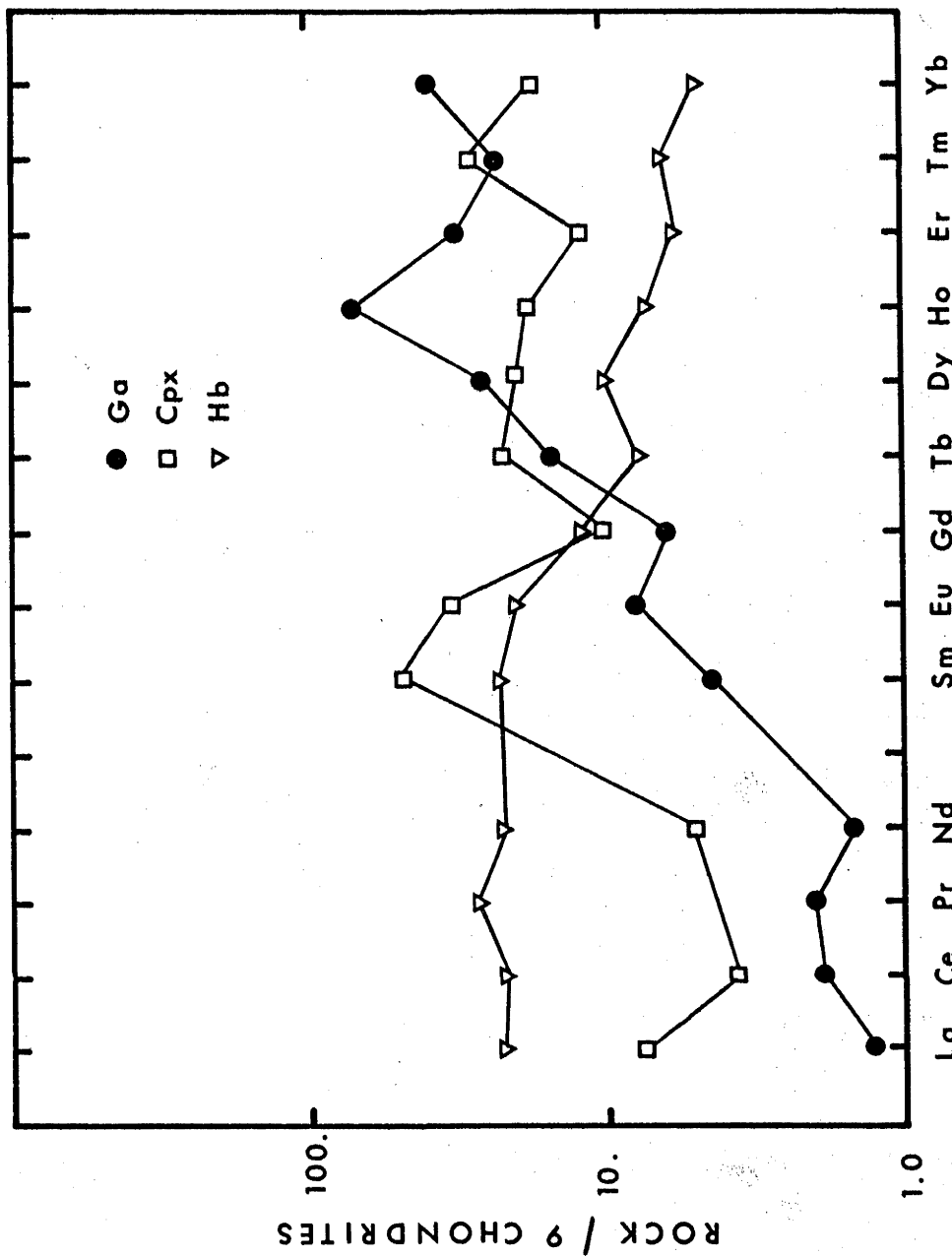


Figure 6.1: Rare earth elements in Kakanui eclogite minerals normalised to average of 9 chondrites. Ga - garnet, Cpx - clinopyroxene, Hb - amphibole.

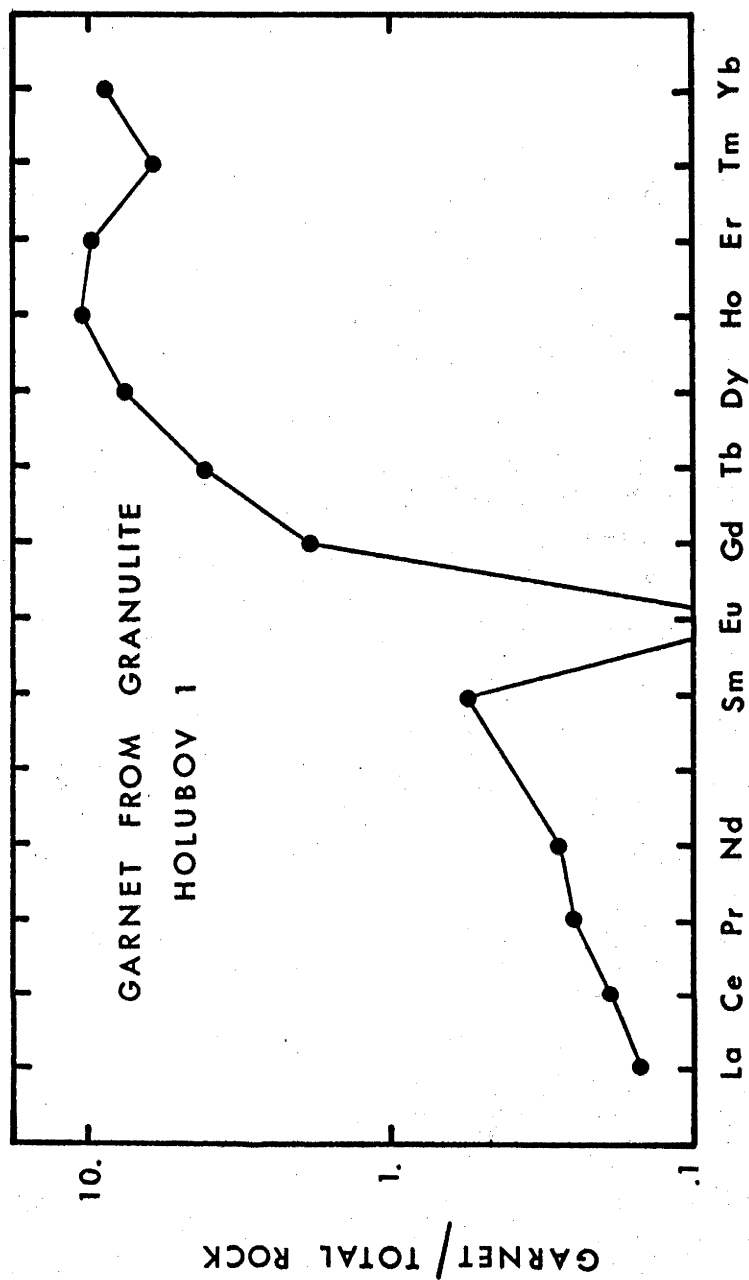


Figure 6.2: Rare earth elements in garnet from Ga-Ky granulite from Holubov, normalized to rare/earth elements of total rock.

### Amphibole

Data on the REE contents of amphiboles presented by Haskin et al. (1966), Schnetzler and Philpotts (1968) together with new data presented here suggest that there can be two enrichment patterns in amphiboles. These depend on the coexisting phases. Data on light REE contents of amphiboles crystallizing from andesites (Table 3.1, 3.2) and data on plutonic rocks (e.g. Rhodes, 1969) suggest that in all rocks where amphibole co-exists with plagioclase, or with melt, the concentration of REE increases with increasing atomic number from La to Nd, but Y contents suggest that there is no significant preferential uptake of REE heavier than Nd. This is also apparent from data for phenocryst/matrix distribution from Schnetzler and Philpotts (1970). Schnetzler and Philpotts (1970) also found that phenocrystic amphibole could be slightly enriched relative to the matrix in the Eu-Gd range but both ends of the pattern (La and Yb) are slightly depleted relative to the centre (Eu-Gd).

The second type of REE pattern in amphiboles is found in subsolidus parageneses which do not include a substantial amount of plagioclase. In the paragenesis amphibole + clinopyroxene ± biotite the light REE are preferentially incorporated in amphibole (e.g. inclusions in alkaline basalts, Table 3.2). Similar patterns also appear in

amphiboles of "eclogitic" parageneses, in which amphibole coexists with clinopyroxene and garnet (Table 6.5, Fig. 6.1).

### Micas

Data of Haskin et al. (1966) and Schnetzler and Philpotts (1970) and new data presented here show that the REE contents in mica are erratic. The absolute abundances of REE in micas are very low; one or two orders of magnitude lower than those of the parent rocks. Patterns showing enrichment in light, medium or heavy REE have all been documented, but in general it would appear that the heavy REE are preferentially incorporated (Higuchi and Nagasawa, 1969). New data (Appendix 3) for light REE suggest that these, particularly La, are very low in micas which coexists with feldspars and amphiboles.

### Opaque phases

Balashov and Sobolev (1967) found magnetites and ilmenites had concentrations of REE 1.5 - 2.0 times higher than those of their host rocks. Ilmenites concentrate more REE than do magnetites and heavy REE are preferentially incorporated in both. Experimental data show that partition coefficients for opaque phase and melt vary from 1.5 to 6.5 in favour of the opaque phase and it seems that Yb is preferred relative to La (Table 6.4).

Summary of petrogenetic limitations imposed by REE

The petrogenetic limitations imposed by REE abundances for island arc lavas can be summarized at this point.

1. Tholeiites of island arcs come from relatively primitive, unfractionated or little fractionated material. Fractional crystallization of olivine and minor pyroxene could have occurred but this will not change the overall pattern, and will account for slight enrichment in Eu, Gd.
2. There is no evidence for extensive fractionation of plagioclase in tholeiites but a slight increase in Eu in some samples could indicate fractional melting involving some plagioclase.
3. Fractional melting of amphibole from parageneses containing phases which do not substantially discriminate between light and heavy REE (olivine, orthopyroxene, spinel) could also create similar primitive patterns.
4. There is a relatively large spread in the absolute abundances of REE in arc tholeiites but these abundances are approximately the same as those in oceanic tholeiites. This indicates that unless complete melting of the oceanic tholeiite has taken place to produce arc tholeiites then an upper-mantle source for these rocks must be considered.
5. REE are strongly fractionated in calc-alkaline and shoshonitic rocks so these rocks may be derived from more primitive material by a very small degree of partial melting

or by more extensive melting of already fractionated material.

6. The source area (or residuum) of calc-alkaline and shoshonitic rocks must have contained minerals which strongly partition light REE in favour of melt. Garnet and clinopyroxene appear to be most effective.

7. There is no evidence of extensive fractionation of plagioclase in calc-alkaline or shoshonitic rocks.

#### Large cations

The increased abundances of large cation trace elements across the island arcs has been documented for the sequence from tholeiites to shoshonites. It should be pointed out again that trace element contents are compared in the rocks of the same silica content. The fact that andesite in the tholeiitic series has a different content of trace elements than andesite in the calc-alkaline series or in the shoshonitic series suggests that simple fractionation of one parent magma is not likely to produce these and other differences. Jakeš and White (1970) have also found difficulties in explaining the decrease of K/Rb ratios in island arcs by simple fractional crystallization of any mineral or partial melting of a homogeneous source material and have suggested that the melting involving an amphibole in shallower levels and mica phase in deeper levels may account for K/Rb ratios

in island arc rocks. Griffin and Murthy (1969) also advocated a fractional melting involving various hydrous phases to explain the geochemical characteristics of basaltic rocks.

In Table 6.6 available data on distribution coefficients of large K-type cations are compiled. The variation of distribution coefficients (derived from matrix/phenocrysts "equilibria") are so large that either disequilibrium, changes of P and T or concentration must be invoked to account for them.

If a melt was formed mainly from one mineral phase which contained a given element in large amounts compared with the other minerals present, the distribution coefficient between melt and residual phases is likely to be different from that between some other melt with lower contents of the given element and the same residual phase. This could be due to either equilibrium or the concentration effect. Assuming that island arc rocks come from the upper mantle or oceanic crustal material, the distribution coefficients and abundances of trace elements in island arc rocks indicate that island arc lavas could at some stage have been in equilibrium with olivine, clinopyroxene and garnet. But equilibrium of tholeiitic basalts with amphibole, because of the K/Rb ratio, tholeiites, andesites and shoshonites with biotite (because of Rb, Ba, K) or plagioclase (because of Sr) is unlikely. Instead, these minerals are believed

TABLE 6.6

Variations of  $K_D$  ( $C_{\text{solid}}/C_{\text{liquid}}$ ) for K type elements

|            | K           | Rb         | Ba         | Sr         |
|------------|-------------|------------|------------|------------|
| oliv /melt | .005 - .01  | .008 - .01 | .008 - .01 | .009 - .02 |
| cyst /melt | .0004 - .10 | .07        | .003 - .10 | .10 - .25  |
| ga /melt   | .02         | .01        | .02        | .02        |
| amph /melt | .2 - 1.5    | .04 - .50  | .09 - .5   | .18 - 1.0  |
| mica /melt | 2.2 - 6.0   | 2.0 - 3.0  | 9.0        | -          |
| plag /melt | .01 - .03   | .02 - .40  | .3         | .5 - 2.0   |

Data of Onuma et al., 1968; Higuchi and Nagasawa, 1968; Schnetzler and Philpotts, 1970; Gast, 1969 and new data were used.

to determine to some extent the geochemical characteristics of island arc rocks. Amphibole and mica are stable in some high-pressure high-temperature subsolidus parageneses under hydrous conditions but are low melting phases. The K/Rb ratios as interpreted by Jakeš and White (1970) suggest that more mica relative to amphibole is involved in partial melting with increasing depth.

The concentrations of barium support this suggestion. Ba abundances increases from tholeiites to shoshonites by a factor 8 - 10. Ba is chemically coherent with K and enters both amphibole and biotite but in a subsolidus paragenesis where both are present, the Ba concentration in mica is 6 - 8-fold higher compared with that of amphibole.

Strontium abundances also increase in the sequence across an island arc, but strontium increase is only 2-fold from tholeiites to shoshonites.

Mica phases in volcanic and metamorphic rocks have very low Sr abundances. There are not many data on deep-seated micas, but bitoties from inclusions in alkaline rocks have relatively high Sr concentrations (266-617 ppm). Even this concentration of Sr in micas however, fails to explain Sr abundances in shoshonites unless other high-Sr phases are involved in fractional melting.

Table 6.7.

Major element analyses of rocks analyzed for rare earth elements

|                                    | 7319 <sup>1</sup> | 2041 <sup>2</sup> | 2207 <sup>2</sup> | 3091 <sup>2</sup> | 23759 <sup>3</sup> | 23745 <sup>3</sup> | Zbecno <sup>5</sup> | 089NG <sup>6</sup> | 098NG <sup>6</sup> |
|------------------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|--------------------|---------------------|--------------------|--------------------|
| SiO <sub>2</sub>                   | 48.30             | 48.10             | 48.50             | 50.40             | 50.57              | 49.12              | 48.21               | 52.10              | 51.79              |
| TiO <sub>2</sub>                   | 1.45              | 1.29              | 1.41              | 1.28              | .91                | 1.05               | 1.16                | .75                | .74                |
| Al <sub>2</sub> O <sub>3</sub>     | 14.60             | 14.50             | 13.40             | 13.60             | 15.04              | 15.19              | 16.32               | 16.78              | 18.06              |
| Fe <sub>2</sub> O <sub>3</sub>     | 1.40              | 6.20              | 8.10              | 7.40              | 1.96               | 2.41               | 5.75                | 3.07               | 2.51               |
| FeO                                | 8.20              | 4.20              | 4.45              | 4.40              | 8.95               | 9.82               | 2.17                | 7.32               | 7.25               |
| MnO                                | .31               | .16               | .17               | .19               | .21                | .2                 | .21                 | .19                | .17                |
| MgO                                | 8.70              | 8.00              | 7.35              | 7.85              | 7.12               | 6.71               | 6.70                | 6.52               | 5.85               |
| CaO                                | 12.20             | 11.80             | 11.50             | 9.65              | 9.74               | 10.23              | 9.66                | 10.84              | 10.98              |
| Na <sub>2</sub> O                  | 2.60              | 2.75              | 2.25              | 3.20              | 2.97               | 2.05               | 3.20                | 2.19               | 2.19               |
| K <sub>2</sub> O                   | .05               | .07               | .07               | .39               | .33                | .59                | .27                 | .32                | .32                |
| P <sub>2</sub> O <sub>5</sub>      | .19               | .11               | .11               | .19               | .10                | .13                | .09                 | .09                | .09                |
| Σ H <sub>2</sub> O+CO <sub>2</sub> | 1.60              | 3.02              | 2.93              | 1.62              | 2.05               | 4.24               | 6.30                | .22                | .31                |

1 - Hackman, 1970, personal communication; 2 - Smith, 1970, personal communication, analyses by Australian Mineral Development Laboratories; 3-Christie, 1970 unpublished thesis, Dept. of Geology, A.N.U.; (see also White, Jakes<sup>✓</sup>, and Christie, 1970); 5 - White and Johnston, 1970, personal communication, analysts White and Wasik. Major element analyses of samples 144, 160, 105, and 101 in Jakes<sup>✓</sup> and White, 1969, sample 3514 in Jakes<sup>✓</sup> and Smith, 1970, analyses of 6640, 6719, 6785, 26 and 48 in progress.

## CHAPTER 7

## EVOLUTION OF ISLAND ARCS - DISCUSSION AND IMPLICATIONS

New geochemical, mineralogical and experimental evidence bearing on the origin of rocks occurring in island arcs, clearly indicates that the island arcs are not monotonous piles of andesitic rocks of one single origin from one ultimate source. Although data presented in this work and some of the inferred conclusions have been, or are to be, published (Jakeš and White, 1969; Jakeš and Smith, 1970; Jakeš and Gill, 1970; White, Jakeš and Christie, 1970) this chapter is a review of the features and evidence bearing on the concept of island arc evolution. The evolution of calc-alkaline volcanic rocks in continental areas is also discussed. The model presented here, builds upon the consequences of resorption of the oceanic crust beneath the island arcs (Isacks, Oliver and Sykes, 1968) and provides further evidence to support arguments of Raleigh and Lee (1969); McBirney (1969); Hamilton (1969, 1970).

Morphology, structure and general geology of island arcs

In general, an island arc consists of a deep-sea trench, bordered by a double chain of islands. Deep water invariably occurs on the outer or convex side of the trench

but either shallow or deep seas may occur on the concave, or continental side.

Although a double line of islands, either above sea level (e.g. Indonesia) or as submergent arc structures (e.g. Kamchatka) are characteristic, this feature does not appear in regions of large continental masses (New Zealand or Japan) and in regions with steep, diffuse or reversed seismic planes (Solomon Islands, New Hebrides). The outer arc (morphologically less distinct) is usually referred to as "non volcanic" but geological data suggest that the basement of these islands is an ophiolite series with predominantly tholeiitic submarine basalts and associated deep-water sediments. The ophiolites may be covered by later shallow-water sediments with subordinate lavas (Sunda Islands, Le Moine, 1959). Nicobar and Andaman Islands (Rodolfo, 1969) which are geophysically a direct continuation of the outer Sunda arc, are formed of ultrabasic rocks and submarine tholeiitic basalts (ophiolite suite). About twenty submarine volcanoes lie in the "outer arc structure" of the eastern Kamchatka coast and this passes directly into the Vitiaz ridge east of the Kurile Islands. Ultrabasic rocks together with tholeiitic basalts are also a characteristic feature of the basements of other circum-Pacific arcs (e.g. Eastern Papua, Solomon Islands, Phillipines) but elsewhere only submarine tholeiitic

rocks appear (Aleutians, Fiji). Jakes<sup>v</sup> and Gill (1970) using REE evidence provided by both old and recently erupted tholeiitic rocks in island arcs, argued that primitive tholeiites (island arc tholeiites) are autochthonous to island arcs and that all ophiolite suites do not necessarily originate in mid-oceanic ridges (c.f. Thayer, 1969).

The zonal variation of lava composition in island arcs provides indirect evidence on the composition of volcanoes off the Kamchatka coast, in the "outer arc structure" and suggests that volcanic rocks of "non volcanic ridges" of most arcs (Kurile Islands, Izu-Bonin, Kamchatka) represent "early" tholeiitic activity corresponding in composition to the low-K rocks of island arc basements, such as those recently exposed in Eastern Papua or the Solomon Islands.

The inner arcs usually consist of subaerially erupting volcanoes with a composition varying from tholeiitic to calc-alkaline and shoshonitic as the continental side is approached. In older arcs, such as those associated with pre-Mesozoic basements, all three rock associations are represented (Japan, Kamchatka, New Guinea), but in younger arcs only tholeiitic and low-K calc-alkaline rocks are present (Kurile Islands, Izu-Marianas, Tonga-Kermadec).

The geophysical data on island arc structures have been discussed by numerous authors whose conclusions support the hypothesis of under-thrusting of oceanic crust beneath the island arcs (Isacks, Oliver and Sykes, 1968; Raleigh and Lee, 1969; Ringwood, 1969).

In island arcs in which the seismic plane dips towards the continent the pattern of gravity anomalies has a characteristic minima in the region of the deep sea trench (Umbgrove, 1949; Talwani et al., 1959). In areas with a disturbed or diffuse seismic plane, gravity minima occur on both sides of the island arc (e.g. Solomon Islands, Rose et al., 1968).

Seismic data (Sykes, 1966; Katsumuta and Sykes, 1969; Mitronovas et al., 1969; Isacks et al., 1968) has provided most of the evidence on island arc structure. Earthquake foci are concentrated in a seismic zone, inclined towards the continent. This zone is believed to be less than 20 km thick (Mitronovas et al., 1969) and usually dips at  $45^{\circ}$  but may also be vertical or reversed (e.g. Denham, 1969). First motion solutions support the idea of underthrusting of oceanic crust beneath the arcs (e.g. Katsumuta and Sykes, 1969). In island arc areas, the low velocity zone with  $V_p$  7.0-8.0 km/sec extends deep into the upper mantle (80 km, according to Fedotov, 1968) on the continental side of the seismic

plane and extends upwards to the base of crust (Thompson and Talwani, 1964; Drake and Kosminskaya, 1969). On the oceanic side of the seismic plane mantle material has a higher seismic velocity, and there is only a thin low velocity zone as in normal oceanic crust.

### Temperature distribution

Temperature distribution in the island arcs is based on heat flow data. The oceanic bottom adjacent to island arcs on the oceanic side is relatively cold and the heat flux is  $1.1 - 1.3 \mu\text{cal}/\text{cm}^2 \text{ sec}$  (c.f. compilation of Popova et al., 1969). The deep sea trenches have lowest heat flows, usually less than  $.9 \mu \text{ cal}/\text{cm}^2 \text{ sec}$  (McKenzie and Sclater, 1968), but continental margins and the volcanic islands have widely variable but high heat flows ( $2.0 \mu\text{cal}/\text{cm}^2 \text{ sec}$ ).

A simplified model compounded from Turcotte and Oxburgh's (1968) and Minear and Toksösz's (1970) models of island arc temperature distribution is shown in Figure 7.1. According to this model, the region of trenches and sedimentary piles is characterized by low heat flow, i.e. low geothermal gradients. This is where cold oceanic crust underthrusts the arc or continent. Low heat flow can also be anticipated on the continental side of the trench to about 40-70 km from trench. The region of the Benioff zone itself, which is probably less than 20 km in width (Mitronovas et al., 1969)

and which is probably at the junction of the upper part of the oceanic crust and the overlying mantle at depths greater than 80 km, is the source region of heat within the island arcs. This zone of elevated temperatures is thought to be the region in which island arc magmas are produced. In the upper mantle, overlying the Benioff zone, and below newly formed continental crust, heat is transferred not only by conduction but mostly by ascending newly generated magmas and probably by upward convection of the mantle itself. The thermal regime in this zone changes over geological time as the island arc evolves. In the initial stages of island arc evolution normal thermal gradients can be expected. As greater quantities of magma form along the Benioff zone, the geothermal gradient will increase and in the later stages of arc evolution it will be high.

This simplified model of thermal distribution during island arc development offers an explanation of such phenomena as polymetamorphism and formation of granitic magmas during the low pressure high temperature stages of metamorphism and the model can also be related to the concept of paired metamorphic belts introduced by Miyashiro (1961) (Dickinson, 1969).

A consequence of the thermal retardation of the under-thrust material is a relative increase in depths to which

hydrous phases in the slab are stable.

### Composition of oceanic crust

The concept of a layered structure in the oceanic crust is currently under review and the composition and metamorphic state of the geophysically definable layers (1, 2, 3) is still under discussion (e.g. Vine, 1966; Melson and van Andel, 1966; Miyashiro et al., 1970; Christensen, 1970). The relatively thin (0.4 km) upper layer is apparently composed of unconsolidated or semi-consolidated sediments and, despite some controversy, layer 2 is thought to be of basaltic composition (oceanic tholeiite). There is no doubt that abyssal tholeiites and their metamorphosed equivalents such as spilites (Cann, 1968), or greenstones or greenschist facies rocks (Aumento and Loncarevic, 1969; Miyashiro et al., 1970) form most of layer 2. Some alkaline basalts ( $\approx 1\%$ ) from deceased volcanic islands must also be expected in this layer. On the basis of seismic evidence, Christensen (1970) considered that layer 3 is of amphibolite or amphibole-gabbro composition, but the suggestion that this layer consists of serpentinitized peridotite (Hess, 1962, 1965), which is supported by numerous findings of serpentinites on the ocean floor (Cann, 1968; Cann and Vine, 1965; Van Andel and Bowin, 1968) has not yet been refuted (Miyashiro, et al., 1970).

Irrespective of which model for the composition of oceanic crust is chosen, the common feature of most models is that the rocks in the oceanic crust are partially hydrated. If partially hydrated oceanic crust is underthrust and resorbed beneath the island arcs (Isacks, Oliver and Sykes, 1968) it must undergo progressive metamorphism from greenschists through amphibolites and granulites to eclogite assemblages. Because of the relatively low temperature of the slab with respect to its surroundings metamorphic reactions are necessarily retarded relative to areas with normal continental or oceanic gradients, at least to depths of 60-80 km (c.f. Minear and Tokösz, 1970). Because of this, hydrous phases (amphibole and mica) are stable to greater depths in the slab than they would be in the surrounding mantle. Higher spreading rates will extend this depth. Amphibole decomposition is likely to take place at depths of 80-120 km.

The decomposition of hydrous phases in the slab produces water-rich melts and a denser crystalline residuum and finally eclogite with a density of 3.45 gms/cc (Ringwood and Green, 1966). This will be denser than the surrounding mantle. A sharp increase of slope apparent in the most well defined seismic planes could be interpreted as indirect evidence of this increase in density. The dip of the seismic zone steepens and may even become vertical between 100-200 km.

Island arc rock associations

The three rock associations occurring in island arc areas are closely related in space and time. These are tholeiitic, calc-alkaline and shoshonitic or alkaline. The associations can be defined on the basis of major element chemistry and also -- in regions with a well developed seismic plane -- by the distance of the volcano from the trench and by the depth to the Benioff zone beneath the volcano. Although each association has a typical major and trace element abundance, there are compositional gradations between them, and therefore all boundaries, if drawn at all, are artificial. In the sequence from tholeiites to calc-alkaline rocks to shoshonites the most important variations are the increase of  $K_2O$  content at given  $SiO_2$  content, the increase of  $K_2O/Na_2O$  ratio, the decrease of "iron enrichment", and the increase in the concentration of the potassium type and of other large cations (Zr, Th, U). The REE pattern changes from "primitive" in tholeiitic rocks to one of enrichment in light REE ("sedimentary-type") in calc-alkaline and shoshonitic rocks. Because of the transitional character of all associations in true island arc areas, any petrogenetic scheme is insufficient if it can only be applied to a single association or group of rocks : any valid hypothesis must account for spacial and temporal transitions for the lateral and stratigraphical gradations

in rock compositions.

The association of high-K calc-alkaline rocks with some high-Si shoshonitic types (Andean association) although related to continental orogenic environments and possibly present in some highly developed island arcs, is not considered in this discussion.

#### The model for the origin of island arc volcanic rock associations

Two possibilities for evolution of island arc rocks are presented, but both models (A and B) are considered to be complementary. Model A does not consider any extensive contribution from upper mantle material to the magmas appearing in the island arcs. The magmas are derived from the slab of hydrated oceanic crust underthrusting the island arc. In model B this underthrust oceanic crust provides "water" or more probably a water-rich siliceous melt. Variations in lava compositions reflect different degrees of partial melting, and fractionation of the magmas during their ascent.

If it is assumed that some material of the underthrust slab (oceanic crust) undergoes partial melting and is depleted in a low melting fraction during its descent, then the residual material cannot contribute to the production of further lavas. Melts produced at greater depths are believed to come from "undepleted" oceanic crust. The

amount of material in the productive upper part of the down-going slab is large enough to allow for this assumption. This also suggests that material with lower melting point than the melting point of hydrous oceanic tholeiite is more likely to contribute to melts produced along the upper part of the seismic plane. These materials could be alkaline rocks of decomposed seamounts or sediments dragged along the seismic zone.

#### Model A

This model has been proposed by Jakes<sup>V</sup> and White (1970) to account for K and K/Rb ratios of island arc rocks. All island arc rock types are partial melts produced from a more basic parent. This is the slab of oceanic crust which undergoes a progressive metamorphism through amphibole to eclogite assemblages during sinking.

Fractional melting takes place along the Benioff zone if the temperature exceeds the stability field of the hydrous phases. At the amphibole stage when tholeiites are produced melting involves decomposition of amphibole and it is very likely that the melt formed will inherit the character of both amphibole and oceanic tholeiite since the amount of melting will be high (50%). In the granulite facies stage of sinking the amount of amphibole decreases whereas mica (although in small amounts) can increase. Should garnet be included in the granulite assemblage and remain in the

crystalline residuum after partial melting, it would account for the observed REE trends in calc-alkaline and shoshonitic rocks. If the thermal regime is such that mica stability is exceeded, then melting takes place. These small volumes of melt inherit the geochemical characteristics of mica, including high  $K_2O$  contents, high trace element contents (e.g. Ba) as well as a relatively low  $SiO_2$  content. These are the characteristic features of shoshonitic rocks. The calc-alkaline rocks are then produced at intermediate depths from a combination of both these extremes:

a) extensive partial melting caused by decomposition of amphibole, and

b) small amounts of partial melting involving the decomposition of mica phase. The mica-bearing material from which high-K rocks are derived, was not necessarily oceanic tholeiite but could have been alkali-rich and similar to that found in some volcanic islands.

#### Model B

In this model low-melting point, hydrous silicate melt is formed in the region of the upper surface of the downgoing slab at depths from 80 to 250 km. This melt has dacitic or rhyolitic compositions in shallower regions and andesitic composition at greater depths. This water-rich melt is enriched in certain trace elements relative to the

parental oceanic crust. It rises into relatively hot and dry upper mantle above the down-going slab and causes melting. The extent of partial melting in the mantle is controlled by the water content of the melt but more significantly the difference in temperature between the cooler slab of oceanic crust and the hotter overlying mantle. More extensive melting is likely to occur in shallow regions (80-120 km) than in regions deeper than 200 km, but this will be dependent on the rate of descent of the slab (Minear and Toksözs, 1970).

The amount of melting induced in the overlying mantle will decrease from shallower to deeper levels (250 km) thus producing the respective island arc lavas, from tholeiites to calc-alkaline rocks and to shoshonites. Extensive partial melting of the upper mantle probably causes a diapiric rise and advection of the mantle (Green and Ringwood, 1967); fractional crystallization of olivine and minor pyroxenes in the 9-10 kb region can produce the arc tholeiites with their low ferromagnesian trace element contents such as Ni and Cr. Garnet is not a residual phase at this stage so the REE pattern of the melt is "primitive". It is likely that the cumulative residuum of olivine and pyroxene remains in the upper mantle but under favourable conditions, for example in the early stages of island arc evolution, this too, might be introduced into the overlying crust.

TABLE 7.1

Estimated volumes of rocks in island arc associations

|                        |                           | SiO <sub>2</sub> content |          |          |    | Ref. |
|------------------------|---------------------------|--------------------------|----------|----------|----|------|
|                        |                           | 50 - 55%                 | 55 - 60% | 60 - 65% | 65 |      |
| calc-alkaline<br>rocks | tholeiitic                | 50                       | 35       | 15       | <1 | 1    |
|                        | low-K (< 1.0) *           | 20                       | 50       | 25       | 5  | 5    |
|                        | medium K<br>(1.1 - 2.5) * | 15                       | 60       | 20       | 5  | 4    |
|                        | high-K (>2.5) *           | 5                        | 40       | 50       | 5  | 2    |
|                        | shoshonitic               | 50                       | 40       | 10       | <1 | 3    |

1. Kuno (1952) Hakone area (pigeonitic series).
2. Jakes and Smith (1970), Cape Nelson volcanic complex, East Papua.
3. Shoshonitic series of New Guinea Highlands (unpublished data).
4. Guess based on published analyses of Aleutian calc-alkaline rocks.
5. Guess based on published analyses of Izu - Marianas low-K rocks.

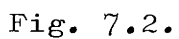
\* K<sub>2</sub>O values taken from K<sub>2</sub>O/SiO<sub>2</sub> correlation at 58% SiO.

According to this model calc-alkaline rocks result from a smaller degree of partial melting of a garnet-bearing parent assemblage at depths of 120-190 km. The amount of partial melting will correspondingly decrease from low-K to high-K calc-alkaline rocks continually limiting the contribution of mantle. To produce high-K calc-alkaline rocks and also shoshonites only the phases with the lowest melting temperatures in the mantle can be incorporated. These might include amphibole or the incipient melt probably present in the low velocity zone of shallow mantle regions, but at greater depths accessory mica may be included. Thus the contribution of mantle material necessary to produce shoshonite melt decreases to an extent where it can be called wall rock reaction (Green and Ringwood, 1967). The composition of island arc rocks, in this case, could also be correlated with the thickness of mantle material through which the magma must ascend.

Models A and B appear to be equally valid; it is believed that they are complementary and that the predominance of either depends on many factors, particularly the thermal regime of the down-going slab.

In Figures 7.1 and 7.2 these models for island arc evolution are illustrated. Some further implications are discussed below.

## Thermal regime of island arc area



A - early, tholeiitic stage

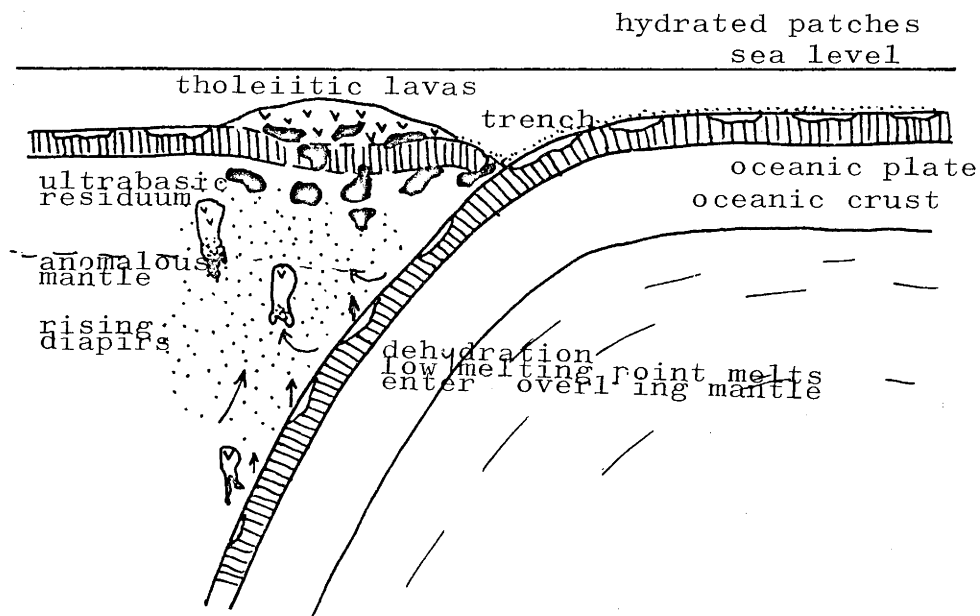
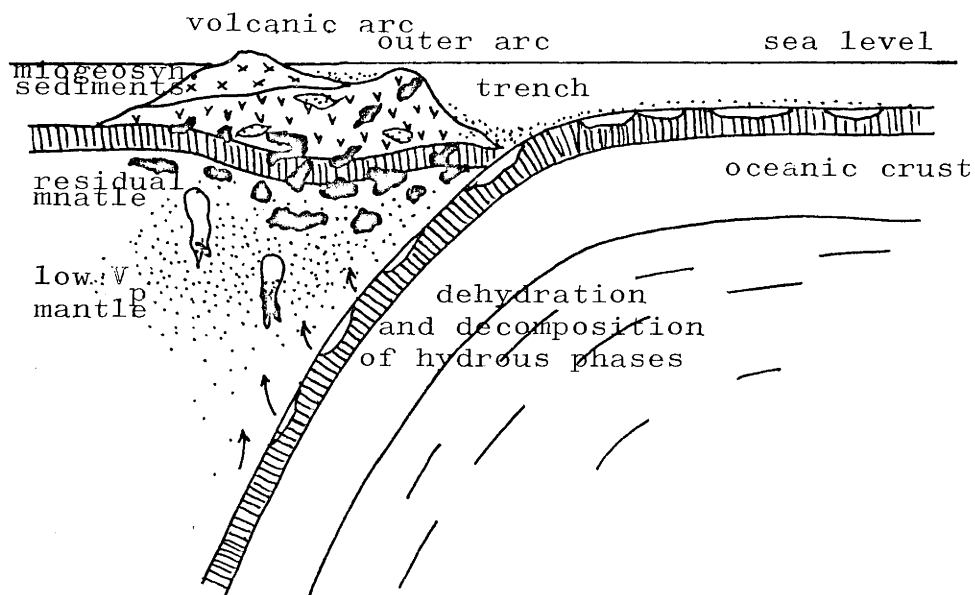
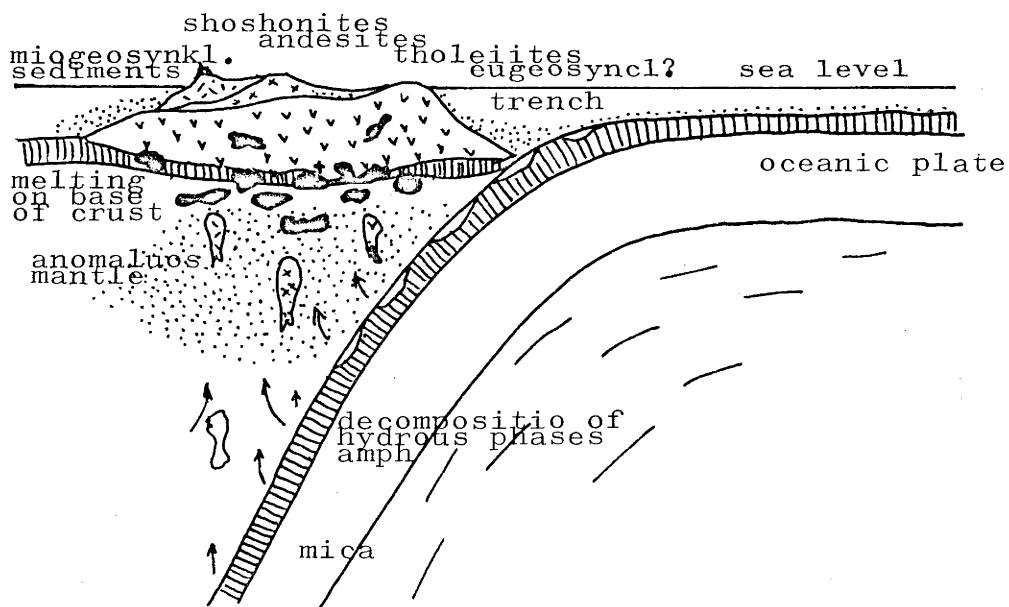


Fig. 7.2. continued

B - middle, tholeiitic-andesitic stage



C - late, tholeiite-andesite-shoshonite stage



### Ophiolites

Ophiolites are considered to be a polygenetic series of tholeiitic basalts and complementary ultrabasic rocks (Thayer, 1969; Maxwell, 1969; and others). It has been advocated by Jakeš and Gill (1970), that such an association may originate on the oceanic side of island arcs and thus represent the earliest stages of island arc development. The older orogenic areas, especially the Alpine-Hellenides, provide some geological observations on the nature of ophiolites, and consequently on the early evolution of island arcs. Auboin (1965), and later Reinhard (1969), pointed out that extrusive members of the ophiolite series have not erupted in the axes of furrows (trenches ?) but at their flanks, although some flows could have reached the slopes of furrows. The nature of sedimentation during the eruption of ophiolites points to the absence of emergent land in the near vicinity. This is consistent with the occurrence of embryonic island arcs in the midst of oceanic areas without any accompanying piles of thick sediments (c.f. Dewey, 1969).

There is a lack of extensive sedimentation in the basement of recent island arcs prior to onset of tholeiitic submarine volcanic activity (e.g. Eastern Papua, Smith, 1970; or the Solomons). Thus the mechanism of subduction of

horizontally moving plates has to be independent of the sedimentary pile for most circum-Pacific examples. One mechanism for this process was proposed by Ringwood and Green (1966). They suggested that cooling of a large pile of basalt in the oceanic crust, caused transition to eclogite in its base and that the density increase triggered subsidence. Other causes of subduction are the conversion of transform faults into trenches with change of the spreading vectors (McKenzie and Morgan, 1969) or interaction of two oceanic plates spreading in opposite direction (Jakeš and White, 1969).

#### Andean type of volcanism

It is assumed that volume relationships shown by the volcanic rocks in Japan are representative. If similar volumes have been consistently produced in the past, 80-100 m.y. are necessary to produce a volcanic pile about 10-15 km in thickness. The base of the island arc crust is thought to consist primarily of island arc tholeiites with lesser volumes of sediments, derived from the tholeiites as well as from subaerial calc-alkaline rocks, together with residual ultrabasic rocks. These are transformed to amphibolite facies assemblages. Under conditions when temperature gradients increase, mostly due to heat transfer

by magmas formed along the Benioff zone, partial melting of this basal crust takes place at about 5 kb). It is probable that wet sediments could melt at lower temperatures than amphibolites and residual phases will include amphibole and clinopyroxene, some calcic-plagioclase and probably garnet. If this melt undergoes extensive fractionation of amphibole with high  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios, more siliceous rocks with shoshonitic tendencies ( $\text{Na}_2\text{O} : \text{K}_2\text{O} = 1 : 1$ ) are produced. This is the characteristic  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratio of siliceous Andean association rocks.

This partial melting of metavolcanic rocks and associated sediments in earlier island arcs is believed to be the principal mechanism for the derivation of Andean type volcanic rocks. The geochemical characteristics of Andean lavas as well as the experimental data (Green and Ringwood, 1968; this work) lend support to this hypothesis. Isotope data (e.g. Doe et al., 1969) do not contradict this hypothesis if it is assumed that materials with low initial  $\text{Sr}^{87/86}$  ratios were remelted. Andean-type volcanic activity is believed to be related to the genesis of granite and granodiorite batholiths in orogenic areas (Hamilton, 1969, 1970).

Furthermore, the continental crust formed in an island arc shows primary stratification, with respect to

$K_2O$ ,  $SiO_2$ ,  $Na_2O/K_2O$ , large cation trace elements, and REE abundances. These all show an upward increase in the stratigraphic sequence from tholeiites to shoshonites. The upper mantle underlying highly developed island arcs is depleted in proportions complementary to the tholeiitic association of island arcs, and may also be depleted in any incipient melt that contributed to calc-alkaline and shoshonitic rocks.

The Andean type volcanism is believed to contribute substantially to a further stratification of the crust, causing the lower crust to become further depleted in a low melting fraction which includes large cations and light REE. It is proposed that the island arc mechanism produces stratified continental crust and Andean volcanism results in further fractionation.

The zonal arrangement of the Palaeozoic volcanic rocks in western Britain (Fitton and Hughes, 1970) the presence of island arc tholeiite-type rocks in the Czech pre-Cambrian and some zonal variations within tholeiites bordering eugeosynclinal and miogeosynclinal associations, suggest that the island mechanism is not confined to the present. Further support is lent to this suggestion by the chemistry of Archaean volcanic sequences, in particular by the presence of arc-type tholeiites in the Archaean

greenstone belts of the Western Australian Shield (White et al., 1970) and by the similarity of composition between Archaean volcanic sequences in Canada and island arc sequences. It is suggested that a layered crust of the island arc type formed in earliest Precambrian times. The REE evidence of Goles (1968) and certain geochemical features of granitic terranes may indicate that continental crust was produced by Andean type volcanism and fractionation of the island arc-type crust in the earliest stages of the geologic record.

Chemical composition of island arcs as a possible model composition of the continental crust.

The volume relationships of Quaternary volcanic rocks in Japan as presented by Sugimura (1968, p.555, fig.10) are considered to be representative of the volume relationships of highly developed island arcs. His data show that the bulk of the Japanese quaternary volcanic rocks are tholeiitic. For the formulation of a model crust composition, the volume relationships of lavas in Japan are preferred primarily because of the absence there of an outer arc of submarine volcanoes and because the arc is in such a state of development that all rock associations are present.

Baker (1968), Jakes<sup>V</sup> and White, (1969), Gill (1970) and this work show that lateral variations of lava composition

TABLE 7.2

Comparison of chemical composition of recent "highly developed" island arc with the composition of average volcanic rock from Canadian Archaean volcanic sequences and average composition of continental crust.

|                                | 1     | 2     | 3    | 4     |
|--------------------------------|-------|-------|------|-------|
| SiO <sub>2</sub>               | 58.88 | 56.00 | 59.4 | 63.1  |
| TiO <sub>2</sub>               | .82   | 1.00  | 1.2  |       |
| Al <sub>2</sub> O <sub>3</sub> | 15.70 | 15.58 | 15.6 | 15.2  |
| Fe <sub>2</sub> O <sub>3</sub> | 2.80  | 2.42  | 2.3  | 6.00* |
| FeO                            | 4.88  | 7.67  | 5.0  |       |
| MnO                            | .11   | .19   | -    |       |
| MgO                            | 4.48  | 5.22  | 4.2  | 3.1   |
| CaO                            | 7.83  | 7.74  | 6.6  | 4.1   |
| Na <sub>2</sub> O              | 3.45  | 2.99  | 3.1  | 3.4   |
| K <sub>2</sub> O               | .86   | .67   | 2.3  | 3.0   |
| P <sub>2</sub> O <sub>5</sub>  | .21   | .22   |      |       |

1. Highly developed island arc.
2. Average volcanic rock from Canadian shield Archaean, Barager and Goodwin (1969).
3. Poldervaart (1955) average continental crust.
4. Vinogradov (1962) two parts of felsic and one part of basic rocks.

\* As FeO.

across an island arc are also reproduced in the stratigraphical variations of the arc. Estimates can be made of the respective volumes of lavas in highly developed arcs and hence the chemical composition of the whole arc can be determined. The essential relationship for this calculation is that in the early arcs only tholeiitic rocks occur, followed in the next stage by tholeiitic rocks + low-K calc-alkaline, and later tholeiitic + low-K calc-alkaline + high-K calc-alkaline and in the final stage by tholeiitic + calc-alkaline + shoshonitic rocks. The contribution of the various rock associations is: 80.5% tholeiitic association, 19.0% of the calc-alkaline associations and .5% of the shoshonitic association.

In each association, however, different proportions of "basaltic", "andesitic" and "dacitic" rocks occur. From the data already given (Table 7.1) the approximate proportions of different rock members can be estimated for each association. The contribution of each to the overall composition of highly developed island arcs is as follows:

|               | "Basalt" | "Andesite" | "Dacite" |
|---------------|----------|------------|----------|
| Tholeiitic    | 40.25%   | 28.20%     | 12.05%   |
| Calc-alkaline | 2.5%     | 9.5%       | 7.0%     |
| Shoshonitic   | .25%     | .20%       | .05%     |

The rocks listed in the Table 1.1 and considered to be typical of island arc associations have been used to calculate

the model composition. These are all Melanesian examples except for a tholeiitic andesite from Fiji (Jakeš and Gill, 1970, Table 2) and a "tholeiitic dacite" from Saipan (Taylor et al., 1969).

The result of this calculation is presented in Table 7.2 together with the composition of average volcanic rocks from the Archaean volcanic sequences of the Canadian shield (Baragar and Goodwin, 1969) and with some estimates for element abundances in the continental crust.

There is a very good comparison between the island arc model composition and the average of volcanic rocks from the Canadian Archaean volcanic sequences, but differences include lower Si and Na slightly lower K and higher Fe in the Archaean volcanic rocks. This indicates a slightly more "tholeiitic" character than the model composition of recent island arcs. Although the selection of a typical arc tholeiitic composition must substantially influence the island arc model composition and perhaps provide better agreement with the Canadian Shield composition, it is believed that calc-alkaline rocks which are usually subaerial and stratigraphically above the tholeiites will be easily eroded and consequently contribute to sediment formation in larger proportions than tholeiites. This suggests that sampling in the Canadian Archaean volcanic sequences could have been biased towards tholeiites. Despite these differences, both

compositions show remarkable similarities.

The examples of zonal variation of lava composition in the British Palaeozoic and the pre-Cambrian of the Czech massive, the similarity of Archaean greenstones and island arc tholeiites, and the close similarity of recent island arc compositions with those of the Canadian shield and Archaean volcanic successions, suggests that similar or identical mechanisms for the production of continental crust from a primitive oceanic crust have been in operation for 3.5 b.y. In the latest stage of the development of the island arc, further petrogenetic mechanisms result in an upper crust of granite-granodiorite composition overlying a more basic layer.

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## Appendix 1. Preparation and analytical methods.

## APPENDIX 1

### Preparation

About 3 kg of sample collected from each locality was split to "nut" size. Where only small amounts of sample were available a slab 2 cm in thickness was cut with a diamond saw and split to "nuts". These were crushed in a tungsten carbide Siebtechnik swing mill and successively quartered to about 200 g. This amount was ground in agate mortar to pass -150 nylon mesh and used for major element analyses. The powder for trace element analyses was ground further in an agate mortar or tungsten carbide ball mill. Mineral analyses were carried out on minerals separated using electromagnetic, heavy liquid and hand picking techniques.

### Major element determinations

Si, Ti, Al, total Fe, Mn, Mg, Ca, K, P, were determined by X-ray spectroscopic analyses of fused glass discs. Corrections for "matrix effects" were applied using a computer program of Dr B.W. Chappell. The method used has been described in detail by Norrish and Chappell (1967) and Norrish and Hutton (1969).

Na was determined by flame photometry using the method described by Cooper (1963).

Ferrous iron was obtained by dissolving the sample in hydrofluoric acid in the presence of excess ammonium

## Appendix 1 (continued)

metavanadate. The excess vanadic ion was then titrated against standard B.H.D. ceric sulphate solution. When only small amounts of material were available the spectrophotometric method of Kiss (1968) was used to determine ferrous iron.

Combined  $H_2O$  and  $CO_2$  were determined by heating the sample in a tube furnace for two hours at  $1200^{\circ}C$  in a stream of dry nitrogen. Water and carbon dioxide driven off were collected in microabsorption tubes filled with phosphorous pentoxide and "carbosorb" soda asbestos.

Hygroscopic water was obtained by determining the loss in weight of a sample after heating for two hours at a temperature of  $110^{\circ}C$ .

Loss on ignition reported in some samples was obtained from a difference between weight of sample before and after heating for two hours at  $1200^{\circ}C$ .

Fluorine was determined using a modification of the colorimetric alizarine blue method of Hall and Walsh (1969). Where indicated major elements were determined using the ARL electron microprobe. Natural minerals of similar composition were used as standards but "matrix corrections" were applied using correction programme written by N.G. Ware.

## Appendix 1 (continued)

### Trace element determinations

Trace elements Ba, Rb, Sr, Pb, Zr, Nb, Y, La, Ce, Br, Nd, V, Cr, Co, Ni, Cu, Zn, and Ga were determined by X-ray spectroscopic analysis on pelletized powdered samples. Mass absorption coefficients for Rb, Sr, Zn, and Fe were measured directly. The equipment and method used corresponds to those recently described by Chappell et al. (1969) and Norrish and Hutton (1969). Lower detection limits were the same as presented by Rhodes (1969).

Thorium and uranium on some samples were carried out by Dr K.S. Heier using  $\gamma$ -ray spectrograph.

Rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tb, and Yb were measured using a solid source spark spectrograph according to the method described by Taylor (1965). Lutetium was used as an internal standard and values for W-1 and G-1 adopted by Gill (1970) used for calibration, except that the gadolinium value was doubled.

Appendix 2. List of analysed samples.

## APPENDIX 2

### LIST OF ANALYSED SAMPLES

1. Amphibole dacite (latite?), Mt Elden, SE from San Francisco Peak, Arizona, (Ph: plg, amph, minor bi, opaques, cpx, GM: plg, opx-microphenocrysts, glass, secondary actinolite)  
coll. A.J.R. White
2. Amphibole - low-Si andesite, Ndikilangi Creek, Nasavu Savu, Vanua Levu, Fiji, (Ph: plg, amph, opaques, residue of cpx, GM: plg (An58), amph, subordinate glass)  
coll. M.J. Rickard
4. Amphibole dacite, Martin's Creek Quarry, Hunter River Area, N.S.W., (Ph: plg (An35-40), amph, opx in relicts, GM: plg, amph, opaque, altered glass)  
from collection of Department of Geology, A.N.U.
5. Amphibole dacite, Mt Shosta, Cascades, California, U.S.A., (Ph: plg, amph, relicts of cpx, GM: plg, opaque, glass)  
coll. A.McBirney
6. Amphibole-clinopyroxene andesite, Mau Quarry, Viti Levu, Fiji, (Ph: plg, amph, rare cpx and opx, GM: relicts of amph, plg and large amount of glass)  
coll. R.S. Taylor
7. Amphibole dacite, Nelson Bay, Corlette, N.S.W., (Ph: amph, plg, opaque, GM: glass, plg, strongly altered)  
coll. A.J.R. White & author
8. Amphibole dacite, Nelson Bay, West Point, N.S.W. (Ph: amph, plg, opaque, GM: strongly altered glass)  
Coll. A.J.R. White & author
9. Amphibole andesite, Nelson Bay, Dutchies, N.S.W., (Ph: plg, opaque, relicts of amph, GM: some quartz in ground mass)  
coll. A.J.R. White & author
10. Amphibole dacite, Fingal Bay, Port Stephen, N.S.W., (Ph: plg, opaque, strongly resorbed amph)  
coll. A.J.R. White & author
11. Amphibole rhyolite, Camberwell, N.S.W. (Ph: relicts of amphibole + plg)  
coll. A.J.R. White & author
12. Amphibole - orthopyroxene dacite, Lambs Creek, Stanhope, N.S.W., (Ph: amph, opx, opaques)  
coll. A.J.R. White & author
13. Amphibole dacite, Glendonbrook, N.S.W., (Ph: large plg, slightly altered amph)  
coll. A.J.R. White & author

14. Amphibole dacite, Wallaroba, Hunter River Area, N.S.W.,  
(Ph: amph, plg, opaque, GM: glass, plg, some qz)  
coll. A.J.R. White & author
15. Amphibole dacite, Clarencetown, Williams River, N.S.W.,  
(Ph: amph, plg, relicts of opx) coll. A.J.R. White & author
16. Amphibole rhyolite, Martin's Creek Quarry, N.S.W.,  
(Ph: amph, plg, opaque) coll. A.J.R. White & author
17. Amphibole dacite, Martin's Creek, Quarry, N.S.W.,  
(Ph: plg, amph, opx (relicts), GM: glass, plg, strongly altered)  
coll. A.J.R. White & author
18. Amphibole andesite, Mau Quarry, Viti Levu, Fiji,  
(corresponds to Nr 6) Coll. Geol. Survey, Fiji
19. Alkali basalt, Yeoval, Dubbo District, N.S.W. (Ph: cpx, oliv, amph, GM: plg, cpx, opaque, glass)  
coll. B. Gulson
22. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: cpx, amph, opaques, mica)  
coll. author
23. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: amph, altered plg ?, opaques)  
coll. author
24. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: amph, mica, cpx, opaques)  
coll. author
25. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: amph, mica, cpx, opaques)  
coll. author
26. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: amph, cpx (altered glass?), opaques, mica)  
coll. author
27. Inclusion in alkali basalt, Bombo Quarry, Kiama, N.S.W.,  
(Ph: amph, cpx, plg ?, opaques)  
coll. author
28. Alkali basalt, Bombo Quarry, Kiama, N.S.W., (all above minerals could be present as phenocrysts (xenocryst) - ground more strongly altered)  
coll. author

31. Amphibole - biotite andesite, Kozelník, Stavnícké pohorie, Czechoslovakia, (Ph: plg, amph, bi, GM: plg, opaques, opx, glass)  
coll. E. Karolusová
32. Amphibole - orthopyroxene andesite, Dekys, Stavnícké pohorie, Czechoslovakia, (Ph: plg, amph, opx, GM: plg, glass, opaques, qz)  
coll. E. Karolusová
33. Amphibole - biotite andesite, Obyce, Pohronský Inovec, Czechoslovakia, (Ph: plg, amph, bi, opx, GM: plg, qz, glass, opaques)  
coll. E. Karolusová
34. Amphibole - orthopyroxene, low - Si andesite, Bábina-Sasa, Southern Slovakia, (Ph: plg, amph, opx, cpx, GM: plg, opx, opaque, minor glass, qz)  
coll. E. Karolusová
36. Amphibole - clinopyroxene, high-Al basalt, Wellington, N.S.W.  
(Ph: amph, plg, cpx, GM: completely altered, epidote, chlorite, sphene)  
coll. author
40. Amphibole bearing tholeiitic basalt, Jenolan Caves, N.S.W., (Ph: amph, plg, cpx, GM: plg, altered glass, relicts of cpx)  
coll. author
- 41-42. Alkaline basalt, Appin Road, Wollongong, N.S.W., (Ph: amph, cpx, oliv, spinel)  
coll. author
44. Alkaline basalt, Spring Mt, Glen Innes, N.S.W., Detailed description given by Wilkinson, 1962, (Ph: amph, bi, anorthoclase as phenocrysts)  
coll. E. Flood
46. Amphibole - biotite andesite, Solander Is, New Zealand, (Ph: plg, bi, amph, cpx, GM: plg, opaque, glass)  
coll. N.Z. Geol. Survey
47. Amphibole-clinopyroxene high-Al basalt, Waihi Beach, Mt Egmont, New Zealand, (Ph: amph, plg, cpx, opaque, GM: plg, glass, minor opaques)  
coll. N.Z. Geol. Survey
48. Clinopyroxene - amphibole low-Si andesite, Waihi Beach, Mt Egmont, New Zealand, (Ph: cpx, amph, plg, opaques, GM: plg, amph, minor glass and opaques)  
Coll. N.Z. Geol. Survey

49. Amphibole - clinopyroxene andesite, Mt Etna, Italy,  
(only mineral separates and powdered rock were available).  
Coll. J. Klerkx
50. Amphibole andesite, North Rd Quarry, Waitakaruru, New  
Zealand, (Ph: amph, plg, GM: plg, glass, opaques)  
Coll. N.Z. Geol.  
Survey
51. Amphibole andesite, Lago San Martin, Bahia d'l'Lanche,  
Argentina, (Ph: amph, plg)  
Coll. M.J. Rickard
52. Amphibole - minor plagioclase cumulate in amphibole  
andesite, Mau Quarry, Viti Levu, Fiji.  
Coll. R.S. Taylor
53. Amphibole bearing low-Si andesitic scoria, Sand Creek,  
Crater Lake National Park, Oregon, U.S., (Ph: amph, plg,  
cpx, opx, GM: glass)  
Coll. A.J.R. White
64. Biotite - amphibole - augite andesite, Mt Lamington,  
E. Papua.  
Coll. Author
- 65A. Amphibole - augite - plagioclase (diorite) inclusion in  
amphibole andesite, Mt Lamington, E. Papua  
Coll. Author
- 65B. Amphibole - plagioclase (diorite) inclusion in amphibole  
andesite, Mt Lamington, E. Papua  
Coll. Author
68. Amphibole andesite, Mt Lamington, E. Papua  
Coll. Author
69. Augite - amphibole andesite, Mt Lamington, E. Papua  
Coll. Author
70. Augite - amphibole andesite, Mt Lamington, E. Papua  
Coll. Author
75. Amphibole - plagioclase (diorite) inclusion in amphibole  
andesite, Mt Victory, E. Papua  
Coll. Author
95. Hypersthene - andesite, Ialibu Patrol Post, New Guinea  
Highlands  
Coll. Author

99. Olivine - augite absarokite, Tambul, Mt Giluwe, New Guinea Highlands  
Coll. Author
101. Amphibole - augite latite, Tambul, Mt Giluwe, New Guinea Highlands  
Coll. Author
102. Augite shoshonite, Gumnach River, Mt Hagen, New Guinea Highlands  
Coll. Author
105. Augite shoshonite, Kugogi, Mt Hagen, New Guinea Highlands  
Coll. Author
107. Augite - olivine shoshonite, Kugogi, Mt Hagen, New Guinea Highlands  
Coll. Author
108. Olivine - augite absarokite, Baiyer River, Mt Hagen, New Guinea Highlands  
Coll. Author
109. Amphibole - augite shoshonite, Baiyer River, Mt Hagen, New Guinea Highlands  
Coll. Author
144. Augite - amphibole andesite, Isisu Point, Guadalcanal  
Coll. Author
155. Augite - amphibole andesite, Vella Lavella, New Georgia  
Coll. Geol. Survey,  
B.S.I.P.
160. Amphibole dacite, Savo Volcano, Guadalcanal  
Coll. Author
161. Amphibole - clinopyroxene inclusion in amphibole dacite, Savo Volcano, Guadalcanal  
Coll. Author
164. Amphibole - clinopyroxene inclusion in amphibole dacite, Savo Volcano, Guadalcanal  
Coll. Author
165. Amphibole - clinopyroxene (minor plagioclase) inclusion in amphibole dacite, Savo Volcano, Guadalcanal  
Coll. Author
168. Biotite amphibole dacite, Savo Volcano, Guadalcanal  
Coll. Author

170. Amphibole andesite, Savo Volcano, Guadalcanal  
Coll. author
171. Amphibole - clinopyroxene (minor plagioclase) inclusion  
in amphibole dacite, Savo Volcano  
Coll. author
174. Amphibole - clinopyroxene inclusion in amphibole andesite,  
Savo Volcano, Guadalcanal  
Coll. author
175. Olivine - clinopyroxene - minor amphibole inclusion in  
amphibole - biotite dacite, Savo Volcano, Guadalcanal  
Coll. author
176. Amphibole - plagioclase (diorite) inclusion in amphibole  
andesite, Savo Volcano, Guadalcanal  
Coll. author
194. Amphibole andesite, Wzar Pieniny, Poland  
Coll. K. Birkenmajer
3544. Porphyritic-olivine-clinopyroxene basalt, northern slopes,  
Mt Trafalgar, Eastern Papua  
Coll. I.E. Smith and author
6516. Clinopyroxene-olivine, low-Si andesite, upper north-east  
slopes, Mt Victory, Eastern Papua  
Coll. I.E. Smith and author
3528. Porphyritic clinopyroxene-olivine, low-Si andesite, lower  
southern slopes Mt Trafalgar  
Coll. I.E. Smith and author
3527. Porphyritic olivine-clinopyroxene, low-Si andesite, lower  
southern slopes Mt Trafalgar  
Coll. I.E. Smith and author
6514. Fine grained clinopyroxene-olivine, low-Si andesite, upper  
south-east slopes Mt Victory  
Coll. I.E. Smith and author
3545. Porphyritic clinopyroxene-olivine-(minor orthopyroxene),  
low-Si andesite, lower northern slopes Mt Trafalgar  
Coll. I.E. Smith and author
6513. Porphyritic clinopyroxene-olivine-(minor hornblende),  
low-Si andesite, upper south-east slopes Mt Victory  
Coll. I.E. Smith and author

3547. Clinopyroxene-hornblende, low-Si andesite, lower north-west slopes Mt Trafalgar  
Coll. I.E. Smith and author
3548. Porphyritic orthopyroxene-clinopyroxene andesite, lower north-west slopes Mt Trafalgar  
Coll. I.E. Smith and author
- 3525A. Andesite, lower south-west slopes Mt Trafalgar  
Coll. I.E. Smith and author
3543. Hornblende-clinopyroxene andesite, lower northern slopes Mt Trafalgar  
Coll. I.E. Smith and author
- 3500B. Porphyritic hornblende-biotite-(minor clinopyroxene) andesite, upper south-west slopes Mt Victory  
Coll. I.E. Smith and author
- 3501C. Porphyritic hornblende-biotite andesite, upper south-west slopes Mt Victory  
Coll. I.E. Smith and author
3514. Hornblende-biotite-(minor orthoclase) andesite, north-west crater wall, Mt Victory  
Coll. I.E. Smith and author
- 3500A. Hornblende-biotite andesite, upper south-west slopes Mt Victory  
Coll. I.E. Smith and author
3508. Hornblende-biotite-(minor clinopyroxene) andesite, south-west slope, Mt Victory  
Coll. I.E. Smith and author
3530. Plagioclase hornblende-biotite andesite, lower south-west slopes, Mt Trafalgar  
Coll. I.E. Smith and author
3513. Hornblende-biotite andesite, northern crater wall, Mt Victory  
Coll. I.E. Smith and author
6518. Hornblende-(minor biotite) andesite, upper north-east slopes, Mt Victory  
Coll. I.E. Smith and author
3555. Hornblende-biotite andesite, small volcanic hill south-east of Mt Victory  
Coll. I.E. Smith and author
3536. Biotite (minor hornblende) dacite, lower north-east slopes Mt Trafalgar  
Coll. I.E. Smith and author

- 3526B. Biotite-opaques dacite, lower south-west slopes, Mt  
Trafalgar  
Coll. I.E. Smith and author
- 6503A. Amphibole-clinopyroxene-plagioclase, inclusion in  
porphyritic hornblende bearing andesite, upper north-east  
slopes Mt Victory  
Coll. I.E. Smith and author
3512. Clinopyroxene-plagioclase-olivine-tremolite-spinel,  
inclusion in porphyritic hornblende bearing andesites,  
upper north-east slopes Mt Victory  
Coll. I.E. Smith and author
- 6505F. Amphibole-clinopyroxene-plagioclase, inclusion in  
andesite, upper north-east slopes, Mt Victory  
Coll. I.E. Smith and author
- 3502B. Amphibole-plagioclase-(biotite), inclusion in andesite  
upper north-west slopes, Mt Victory  
Coll. I.E. Smith and author
- 6505C. Amphibole-biotite (minor plagioclase), inclusion in  
andesite upper north-east slopes, Mt Victory  
Coll. I.E. Smith and author
- 3501B. Amphibole-plagioclase (minor biotite), inclusion in  
andesite upper north-west slopes, Mt Victory  
Coll. I.E. Smith and author
3504. Amphibole-plagioclase (minor biotite), inclusion in  
andesite upper north-west slopes, Mt Victory  
Coll. I.E. Smith and author
- 51 NG 0089 Tholeiitic basalt, Ulawan Volcano, New Britain  
Coll. W. Johnson
- 51 NG 0098 Tholeiitic basalt, Ulawan Volcano, New Britain  
Coll. W. Johnson
- 7913 Spilitic pillow lava, Tetevasa River, E. Guadalcanal  
Coll. B. Hackman
- 6640 Spilitic pillow lava, Kandaho River, S.E. Guadalcanal  
Coll. B. Hackman
- 6719 Altered "basaltic andesite", Koloula River, S. Guadalcanal  
Coll. B. Hackman
- 6785 Chlorite actinolite schist (tholeiitic), Kolomoli River,  
S. Guadalcanal  
Coll. B. Hackman

- 2041 Altered tholeiitic basalt, Mussa valley, Eastern Papua  
Coll. I.E. Smith
- 2207 Altered tholeiitic basalt, Mussa Valley, Eastern Papua  
Coll. I.E. Smith
- 3091 Altered tholeiitic basalt, Mussa Valley, Eastern Papua  
Coll. I.E. Smith
- M.I.26 Dolerite, Macquarie Island  
Coll. Dept of Geol. ANU
- M.I.48 Spilitic basalt, Macquarie Island  
Coll. Dept of Geol. ANU
- 23759 Tholeiitic basalt (greenstone), Norseman, Western  
Australia  
Coll. D. Christie
- 23745 Tholeiitic basalt (greenstone), Norseman, Western  
Australia  
Coll. D. Christie
- ZBECNO Spilite (tholeiitic basalt), Zbečno-Křivoklát,  
Czechoslovakia  
Coll. E. Pivec
- 4523 Eclogite inclusion in breccia, Kakanui, New Zealand  
Coll. A.J.R. White
- H - 1 Garnet-kyanite granulite, Holubov Kremže,  
Czechoslovakia  
Coll. E. Fediuková

Explanations. plg - plagioclase,  
amph - amphibole,  
cpx - clinopyroxene,  
g.m. - groundmass,  
phen. - phenocryst,  
opx - orthopyroxene

Appendix 3. Major and trace element analyses of  
biotites and garnets from metamorphic  
environment.

## APPENDIX 3

TABLE 1.

Major and trace elements analyses of biotites from metamorphic and plutonic environment

|                                | Granulites - Czech Massiv |       |       |        |        |       | Gar-cord gneisses |       |       | Plutonic rocks |        |        |
|--------------------------------|---------------------------|-------|-------|--------|--------|-------|-------------------|-------|-------|----------------|--------|--------|
| Sample                         | 113                       | 121   | 114   | 106    | 122    | 105   | 111               | 103   | 109   | 115            | 101    | 112    |
| Coexisting Minerals and        |                           |       |       |        |        |       |                   |       |       |                |        |        |
| SiO <sub>2</sub>               | 36.71                     | 39.33 | 37.0* | 39.1*  | 39.46  | 38.32 | 36.1*             | 39.40 | 34.37 | 40.79          | 38.81  | 38.15  |
| TiO <sub>2</sub>               | 3.78                      | 2.46  | 3.7*  | 2.5*   | 2.52   | 2.42  | 3.7*              | 2.34  | 3.78  | 2.57           | 2.41   | 2.42   |
| Al <sub>2</sub> O <sub>3</sub> | 16.26                     | 15.65 | 18.9* | 16.1*  | 5.47   | 15.40 | 17.9*             | 17.42 | 19.02 | 16.32          | 15.41  | 13.95  |
| Fe <sub>2</sub> O <sub>3</sub> | 2.81                      | 1.41  | 2.79  | 10.85+ | 3.75   | 2.67  | 1.31              | 2.45  | 3.62  | 3.48           | 2.13   | 2.28   |
| FeO                            | 12.46                     | 12.25 | 17.58 |        | 10.49  | 12.20 | 17.29             | 11.59 | 17.90 | 11.03          | 14.82  | 14.81  |
| MnO                            | .11                       | .25   | .3*   | .25*   | .26    | .18   | .28*              | .17   | .18   | .26            | .25    | .18    |
| MgO                            | 12.69                     | 13.84 | 9.5*  | 18.4*  | 14.04  | 14.57 | 9.9*              | 12.24 | 6.58  | 11.36          | 14.11  | 14.62  |
| CaO                            | .31                       | .36   | .3*   | -      | .36    | .32   | .27*              | .42   | .19   | .37            | .34    | .33    |
| Na <sub>2</sub> O              | -                         | -     | -     | .66    | -      | -     | .27               | -     | .07   | .08            | -      | .10    |
| K <sub>2</sub> O               | 9.10                      | 9.67  | 9.73* | 9.42   | 9.78   | 9.71  | 9.50              | 9.46  | 8.08  | 10.00          | 9.58   | 9.38   |
| P <sub>2</sub> O <sub>5</sub>  | -                         | -     | -     |        |        |       |                   |       |       |                | .21    | .04    |
| H <sub>2</sub> O+              | 3.18                      | 2.54  | 4.72  | 3.07   | 2.98   | 2.42  | 2.73              | 2.48  | 4.68  | 3.01           | 2.02   | 3.04   |
| H <sub>2</sub> O-              | 1.15                      | .49   | 1.32  | .61    | .99    | .49   | .90               | .98   | 1.16  | .46            | .30    | .72    |
| F                              | -                         |       |       |        | .32    | .25   | .23               | .12   | .15   | .68            | -      | .38    |
| Total                          | 98.56                     | 98.25 | 99.90 | 100.96 | 100.42 | 98.95 | 100.38            | 99.07 | 99.78 | 100.38         | 100.41 | 100.40 |
| Rb                             | 882                       | 1320  | 946   | 1354   | 1320   | 1359  | 978               | 1125  | -     | 1410           | 1365   | 853    |
| Ba                             | 1172                      | -     | -     | 2535   | -      | 2413  | -                 | 1392  | 1208  | 2490           | 2463   | -      |
| Sr                             | 6.0                       | 9.5   | 7.1   | 6.6    | 9.6    | 8.4   | 6.1               | 14.   |       | 9.8            | 10.7   | 8.1    |
| Ga                             | 39.                       | 40.   | 37.   | 45.    | 40.    | 43.   | 42.               | 42.   |       | 42.            | 46.    | 33.    |
| La                             | -                         | -     | -     | -      |        | -     | 25.               | -     | -     | -              | -      | -      |
| Ce                             | 6.7                       | -     | 11.   | 31.    |        | 12.   | 73.               | 33.   | 13.   | 37.            | 26.    | 18.    |
| Pr                             | -                         | -     | 35.   | -      |        | 44.   | -                 | -     |       | 33.            | 38.    | 35.    |
| Nd                             | -                         | -     | 5.4   | 15.    |        | 3.3   | 22.               | 6.5   |       | 6.8            | -      | 22.    |
| Y                              | 132                       | 173   | 139   | 196    | 192    | 195   | 192               | -     |       | 144            | 198    | 122    |
| Cu                             | 13.4                      |       | 14.   | 12.    |        | 9.4   | 23.               | 25.   | 41    | 11.5           | 9.     | -      |
| Co                             | 39.                       |       | 38.   | 59.    |        | 57.   | 29.               | 49.   | 55.   | 58.            | 53.    | 55.    |
| Ni                             | 119                       |       | 53.   | 324    |        | 362   | 52.               | 228   | 98    | 315            | 362    | 180    |
| V                              | 572                       |       | 266   | 208    |        | 286.  | 316               | 233   | 775   | 194            | 282    | 197    |
| Cr                             | 491                       |       | 235   | 837    |        | 695   | 188               | 413   | 673   | 706            | 700    | 1159   |
| Zn                             | 359                       |       | 392   | 529    |        | 509   | 343               | 384   | 313   | 461            | 509    | 279    |

\* electron microprobe determination

+ total iron as FeO

## APPENDIX 3

TABLE 2.

Major and trace element analyses of garnets from metamorphic rocks

| sample<br>coexisting<br>mineral<br>analysed | Granulites |       |        |       | Gneisses |       |       |       |        |       |       |        | Migmatites (ga-cord-bi) |       |       |       |       |
|---------------------------------------------|------------|-------|--------|-------|----------|-------|-------|-------|--------|-------|-------|--------|-------------------------|-------|-------|-------|-------|
|                                             | 104        | 106   | 113    | 121   | 114      | 118   | 120   | 122   | 125    | 105   | 103   | 109    | 115                     | 131   | 133   | 134   | 135   |
|                                             |            | bi    | bi     | bi    | bi       |       |       | bi    |        | bi    | bi    | bi     | bi                      |       |       |       |       |
| SiO <sub>2</sub>                            | 37.0*      | 37.50 | 37.2*  | 39.4* | 37.46    | 36.94 | 38.79 | 38.1* | 38.16  | 38.44 | 36.08 | 37.8*  | 37.9*                   | 38.56 | 38.45 | 37.65 | 38.60 |
| TiO <sub>2</sub>                            | -          | .28   | .14*   | -     | 1.54     | .20   | .17   | .11   | 1.19   | .76   | .34   | -      | -                       | .18   | .08   | .08   | .09   |
| Al <sub>2</sub> O <sub>3</sub>              | 18.6*      | 21.41 | 19.8*  | 21.4* | 20.41    | 20.89 | 21.21 | 19.5* | 21.13  | 21.61 | 21.39 | 20.89* | 20.4*                   | 21.03 | 20.91 | 20.93 | 21.55 |
| Fe <sub>2</sub> O <sub>3</sub>              | 35.2 +     | 1.11  | 3.67   | 3.02  | 1.93     | 1.07  | .25   | 30.0* | 3.90   | 1.03  | .61   | 34.4   | 1.81                    | .65   | 2.53  | 2.24  | .25   |
| FeO                                         |            | 31.25 | 25.73  | 22.78 | 31.72    | 33.30 | 30.23 |       | 30.35  | 23.84 | 33.11 |        | 28.39                   | 33.63 | 29.53 | 29.52 | 30.40 |
| MnO                                         | 1.15*      | 1.29  | 1.09*  | .78*  | 2.13     | .84   | .78   | .80   | 1.56   | .46   | 1.12  | 3.0*   | 5.2*                    | .74   | .91   | .91   | .94   |
| MgO                                         | 6.4*       | 4.70  | 7.0*   | 9.0*  | 3.32     | 3.85  | 5.94  | 6.0   | 3.63   | 9.58  | 5.52  | 2.7*   | 3.6*                    | 2.48  | 6.54  | 6.04  | 6.22  |
| CaO                                         | .85*       | .59   | 5.8*   | 2.25* | .64      | 1.09  | 1.10  | 5.1   | .75    | 3.31  | 1.03  | 1.25*  | 2.7*                    | 2.51  | .99   | 1.01  | 1.04  |
| Na <sub>2</sub> O                           | .15*       | .09   | 20*    | -     |          | .20   | .15   |       |        |       | .18   |        | .15*                    |       |       |       |       |
| K <sub>2</sub> O                            | -          | -     | -      | -     | -        | -     | -     | -     | -      | -     | -     | -      | -                       | -     | -     | -     | -     |
| P <sub>2</sub> O <sub>5</sub>               | -          | -     | -      | -     | -        | -     | -     | -     | -      | -     | -     | -      | -                       | -     | -     | -     | -     |
| Total                                       | 99.35      | 98.22 | 100.63 | 98.63 | 99.15    | 98.18 | 98.67 | 99.76 | 100.67 | 99.03 | 99.38 | 100.04 | 100.15                  | 99.78 | 99.94 | 98.38 | 99.09 |
| Rb                                          |            | 6.0   |        | 2.9   | 4.9      |       |       | -     | 7.3    | 3.8   | 8.7   |        | 3.4                     |       | 7.5   |       | 3.3   |
| Ba                                          |            |       |        | -     |          |       |       | -     | -      | -     | -     |        | -                       |       |       |       | -     |
| Sr                                          |            |       |        | 9.5   | 1.4      |       |       | 9.2   | 2.6    | 6.1   | -     |        | 2.9                     |       | 2.1   |       | 2.2   |
| Ga                                          |            | 10.   |        | 8.4   | 8.2      |       |       | -     | 9.8    | 27.2  | 13.   |        | 4.5                     |       | -     |       | 7.0   |
| La                                          | 4.6        |       |        | 6.5   |          | 15.   | 5.8   |       | 11.0   | 7.3   | 2.7   |        | 4.9                     |       | 4.3   |       | 4.9   |
| Ce                                          | 9.4        | 4.8   |        | 13.3  |          | 42.   | 16.   | 7.8   | 22.    | 15.0  | 8.4   |        | 32.                     |       | -     | 7.3   | 11.0  |
| Pr                                          | 8.9        | 4.9   |        | 1.3   |          | 4.    | 4.6   | 2.1   | 2.8    | 2.0   | 9.2   |        | 5.6                     |       | -     |       |       |
| Nd                                          | 2.5        |       | 2.4    | 5.8   |          | 14.   | -     | 22.   | 6.8    | 4.5   | 21.   |        | 17.                     |       | 7.9   | 3.1   | 5.0   |
| Y                                           |            | 460   |        | 190   | 569      |       |       | 172   | 415    | 158   | 399   |        | 250                     | 230   | 465   |       | 358   |
| Ce                                          | 12.3       | 10.4  | 13.    | 19.   |          | 11.   | 6.6   | 18.   | 25.    | 8.1   | 10.   |        | 25.                     |       | 27.   | 13.   | 14.   |
| Co                                          | 30.        | 25.   | 16.    | 67.   |          | 32.   | 29.   | 25.   | 22.    | 26.   | 36.   |        | 46.                     |       | 43.   | 42.   | 30.   |
| Ni                                          | 4.3        | 11.   | 8.4    | -     |          | 1.4   | 2.9   | 2.8   | 2.4    | 13.   | -     |        | 13.                     |       | 8.5   | 4.7   | -     |
| V                                           | 138        | 91.   | 92.    | 109.  |          | 69.   | 125.  | 86.   | 40     | 125   | 132   |        | 72.                     |       | 49.   | 74.   | 98.   |
| Cr                                          | 409        | 208   | 546    | 86    |          | 209   | 244   | 654   | 764    | 109   | 813   |        | 418.                    |       | 126   | 112.  | 153.  |
| Zn                                          | 125        | 87    | 100    | 136   |          | 134   | 114   | 137   | 105    | 162   | 102   |        | 90.                     |       | 134   | 138   | 48    |

\* electron microprobe determination

+ total iron as FeO

Appendix 4. P. Jakes<sup>y</sup> and A.J.R. White  
Structure of the Melanesian arcs and  
correlation with distribution of magma  
types.

## STRUCTURE OF THE MELANESIAN ARCS AND CORRELATION WITH DISTRIBUTION OF MAGMA TYPES

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### SUMMARY

Chemical data on Cenozoic lavas (29 new analyses) from Melanesia indicate a zonal arrangement of lava types in the New Guinea–New Britain arc. Tholeiitic rocks occur on the oceanic side of New Guinea (Manam, Karkar), and north of New Britain. Calc-alkaline rocks occur on the East Papuan coast (Mt. Lamington, Mt. Victory). The shoshonitic rock association of the New Guinea highlands (Mt. Hagen, Mt. Giluwe) and East Papua probably represents the equivalent of the alkali-basalt association, or a further zone of magma variation across island arcs.

Zonation is not distinct within the Solomon Island Arc. Lavas of the New Georgia Group show tholeiitic as well as calc-alkaline affinities, and rocks from Bougainville and Guadalcanal are calc-alkaline. The equivalent of the alkali-basalt association has not been found in the Solomons.

Seismic data are reviewed. The position of the seismic zone may be correlated with the chemistry of the rocks and in the New Guinea Arc the plane dips towards the continent. In the Solomon Arc (Bougainville section) the seismic zone dips steeply towards the continent: in the southern section (New Georgia–Guadalcanal) it is almost vertical.

### INTRODUCTION

A relationship between the seismic zone (Benioff zone) and volcanic activity, and the chemical composition of Cenozoic lavas, has been demonstrated for a number of circum-Pacific island arcs (Sugimura, 1961; Gorshkov, 1962; Kuno, 1966; Sykes, 1966; Dickinson and Hatherton, 1967; Dickinson, 1968). The lack of chemical data on the composition of Cenozoic volcanic rocks from Papua–New Guinea and the Solomon Islands probably accounts for the fact that this area has not been discussed in this respect.

The strongly curved New Guinea–New Britain Arc and the almost straight Solomon Island–Bougainville Arc, both of which have their convex sides oriented towards continental Australia, are discussed in detail. A third important structure of the Melanesian region (New Hebrides Arc), is briefly discussed.

The region (Fig.1) is characterised by the presence of large islands in the vicinity of the arcs, by intermediate seismic activity (Miyamura, 1968),

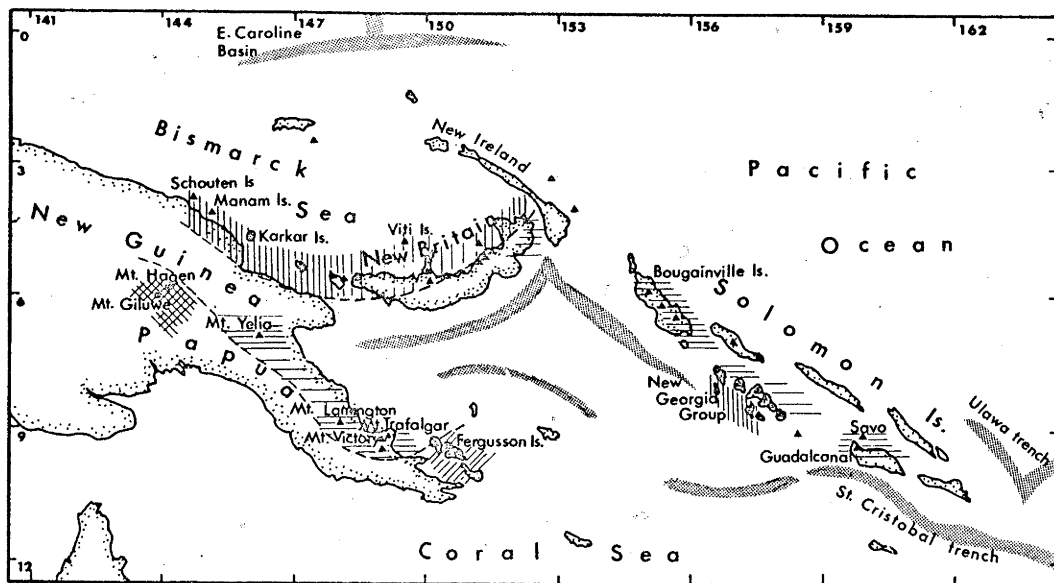


Fig.1. Studied area of two Melanesian arcs. Dotted areas – trenches deeper than 4,500 m. Vertical lines represent areas of Cenozoic tholeiitic volcanism, horizontal lines areas of calc-alkaline rocks, oblique lines alkaline rocks, cross shaded areas rocks of shoshonite association. Dense shading was used in the areas where analytical material is available, broad shading where analytical data not available.

and by the reversed position of deep-sea trenches. The Bougainville–New Britain trench and the trench southwest of Guadalcanal (San Cristobal–Torres Trench) are situated between the island arc and the continent. Trench-like structures on the oceanic side are not so distinct, although there are such features as the Uluwa Trench and its extension along the Pacific side of the Solomon Islands.

#### CENOZOIC VOLCANIC ROCKS OF THE NEW GUINEA–NEW BRITAIN ARC

The area discussed consists of the New Guinea mainland including Papua, the islands north of New Guinea, New Britain and the islands on the eastern edge of Papua (Fig.1). New Ireland, although geographically associated with the above group, is considered to be a direct continuation of the Solomon Islands–Bougainville structure (cf., Coleman, 1966). This view is supported by the existence of large magnetic anomalies between New Britain and New Ireland, reported by Rose et al. (1968), and by the presence of refraction seismic anomalies indicating a shallow depth to the M-discontinuity between the western coast of New Britain and Duke of York Island (Hart et al., 1969).

New chemical analyses (Tables I–III), together with published analyses (Miyake and Sugiura, 1953; Taylor, 1958; Morgan, 1966; Ruxton, 1966) bring

TABLE I

Chemical analyses of Cenozoic volcanic rocks from East Papua

|                                | Mt. Lamington |           |           |           | Mt. Trafalgar |             |             | Mt. Victory  |             |               |
|--------------------------------|---------------|-----------|-----------|-----------|---------------|-------------|-------------|--------------|-------------|---------------|
|                                | 1<br>(70)     | 2<br>(69) | 3<br>(68) | 4<br>(64) | 5<br>(3544)   | 6<br>(3547) | 7<br>(3543) | 8<br>(3500B) | 9<br>(3536) | 10<br>(3526B) |
| SiO <sub>2</sub>               | 56.18         | 58.57     | 59.64     | 61.10     | 50.59         | 56.76       | 59.03       | 59.69        | 63.04       | 63.40         |
| TiO <sub>2</sub>               | 0.77          | 0.72      | 0.67      | 0.61      | 1.05          | 0.88        | 0.99        | 0.67         | 0.71        | 0.61          |
| Al <sub>2</sub> O <sub>3</sub> | 15.80         | 15.73     | 17.38     | 17.33     | 16.29         | 16.50       | 17.43       | 16.01        | 16.48       | 16.90         |
| Fe <sub>2</sub> O <sub>3</sub> | 2.77          | 2.26      | 2.54      | 2.65      | 3.66          | 2.43        | 2.77        | 4.47         | 2.74        | 2.14          |
| FeO                            | 3.90          | 4.13      | 2.72      | 2.12      | 5.08          | 3.68        | 2.92        | 0.47         | 1.22        | 1.83          |
| MnO                            | 0.12          | 0.11      | 0.09      | 0.09      | 0.17          | 0.10        | 0.08        | 0.08         | 0.46        | 0.07          |
| MgO                            | 7.59          | 5.79      | 3.95      | 3.68      | 8.96          | 6.17        | 3.69        | 5.28         | 2.79        | 3.27          |
| CaO                            | 7.65          | 7.31      | 5.92      | 5.65      | 9.50          | 7.06        | 4.84        | 5.98         | 4.21        | 4.67          |
| Na <sub>2</sub> O              | 3.81          | 2.63      | 4.40      | 4.50      | 2.89          | 3.78        | 4.11        | 4.16         | 4.36        | 4.59          |
| K <sub>2</sub> O               | 1.53          | 1.66      | 2.04      | 2.12      | 1.07          | 1.87        | 2.37        | 2.00         | 3.35        | 2.43          |
| P <sub>2</sub> O <sub>5</sub>  | 0.22          | 0.19      | 0.28      | 0.24      | 0.21          | 0.29        | 0.34        | 0.24         | 0.25        | 0.24          |
| loss                           | 0.57          | 0.21      | 1.08      | 0.34      | 0.81          | 1.11        | 1.51        | 0.76         | 1.41        | 0.05          |
| Total                          | 100.91        | 99.31     | 100.71    | 100.43    | 100.28        | 100.63      | 100.08      | 100.81       | 100.92      | 100.20        |

1. Augite-amphibole andesite, Mt. Lamington, 148°12'E, 8°52'S. 2. Augite-amphibole andesite, Mt. Lamington, 148°12'E, 8°52'S. 3. Amphibole andesite, Mt. Lamington, 148°12'E, 8°52'S. 4. Biotite-amphibole-augite andesite, Mt. Lamington, 148°12'E, 8°52'S. 5. Pyroxene basalt, Mt. Trafalgar, 149°13'E, 9°07'S. 6. Augite andesite, Mt. Trafalgar, 149°13'E, 9°07'S. 7. Amphibole-biotite andesite, Mt. Trafalgar, 149°13'E, 9°07'S. 8. Amphibole-biotite andesite, Mt. Victory, 149°01'E, 9°12'S. 9. Amphibole-andesite, Mt. Victory, 149°01'E, 9°12'S. 10. Amphibole andesite, Mt. Victory, 149°01'E, 9°12'S.

The chemical analyses for SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, total FeO, MnO, MgO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> have been carried out using X.R.F. techniques following the procedure described by Norrish and Chappell, 1966. Na<sub>2</sub>O has been determined by flame photometer. Ferrous iron has been determined by titration and microscale iron determination described by Kiss, 1967.

TABLE II

Chemical analyses of inclusions of volcanic rocks from East Papua

|                                | Mt. Lamington |            | Mt. Victory |              |           |             |
|--------------------------------|---------------|------------|-------------|--------------|-----------|-------------|
|                                | 1<br>(65B)    | 2<br>(65A) | 3<br>(3502) | 4<br>(6505C) | 5<br>(75) | 6<br>(3504) |
| SiO <sub>2</sub>               | 53.59         | 61.16      | 54.26       | 54.34        | 56.17     | 57.26       |
| TiO <sub>2</sub>               | 0.79          | 0.61       | 1.14        | 1.15         | 0.99      | 0.75        |
| Al <sub>2</sub> O <sub>3</sub> | 15.27         | 17.62      | 16.13       | 15.64        | 16.65     | 15.60       |
| Fe <sub>2</sub> O <sub>3</sub> | 5.52          | 4.44       | 3.14        | 3.58         | 3.53      | 2.31        |
| FeO                            | 3.50          | 0.74       | 3.72        | 3.32         | 3.14      | 3.52        |
| MnO                            | 0.19          | 0.09       | 0.11        | 0.10         | 0.11      | 0.09        |
| MgO                            | 7.07          | 3.65       | 6.55        | 7.23         | 6.46      | 6.36        |
| CaO                            | 8.32          | 5.84       | 8.01        | 8.12         | 7.90      | 7.32        |
| Na <sub>2</sub> O              | 3.97          | 3.36       | 3.94        | 4.09         | 2.94      | 3.83        |
| K <sub>2</sub> O               | 1.14          | 2.06       | 1.83        | 2.12         | 1.77      | 1.49        |
| P <sub>2</sub> O <sub>5</sub>  | 0.18          | 0.26       | 0.52        | 0.59         | 0.45      | 0.22        |
| Loss                           | 0.24          | 0.21       | 0.93        | 0.43         | n.d.      | 0.78        |
| Total                          | 99.98         | 100.95     | 100.28      | 100.71       | 100.11    | 99.53       |

1. Amphibole-plagioclase (gabbroic diorite) inclusion in amphibole andesite, Mt. Lamington. 2. Amphibole-augite-plagioclase (dioritic) inclusion in amphibole andesite, Mt. Lamington. 3. Amphibole-augite-plagioclase (gabbroic diorite) inclusion from amphibole andesite, Mt. Victory. 4. Amphibole-plagioclase (gabbroic diorite) inclusion from amphibole andesite, Mt. Victory. 5. Amphibole-plagioclase (dioritic) inclusion from amphibole andesite, Mt. Victory. 6. Amphibole-plagioclase (dioritic) inclusion from amphibole andesite, Mt. Victory.

TABLE III

Chemical analyses of Cenozoic volcanic rocks from New Guinea highlands

|                                | Mt. Hagen  |            |            |            |            | Mt. Giluwe |            | Mt. Ialibu |
|--------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|
|                                | 1<br>(107) | 2<br>(102) | 3<br>(105) | 4<br>(109) | 5<br>(108) | 6<br>(99)  | 7<br>(101) | 8<br>(95)  |
| SiO <sub>2</sub>               | 51.74      | 53.74      | 54.81      | 55.45      | 57.66      | 48.94      | 59.27      | 57.22      |
| TiO <sub>2</sub>               | 1.16       | 1.05       | 1.10       | 0.75       | 0.73       | 0.87       | 0.56       | 0.67       |
| Al <sub>2</sub> O <sub>3</sub> | 16.78      | 15.84      | 15.10      | 18.87      | 18.77      | 13.84      | 15.90      | 17.95      |
| Fe <sub>2</sub> O <sub>3</sub> | 3.32       | 3.25       | 2.59       | 2.60       | 4.44       | 2.53       | 2.22       | 2.23       |
| FeO                            | 5.23       | 4.85       | 6.28       | 3.60       | 1.84       | 6.52       | 3.19       | 4.70       |
| MnO                            | 0.13       | 0.11       | 0.15       | 0.13       | 0.13       | 0.15       | 0.10       | 0.13       |
| MgO                            | 6.39       | 6.36       | 6.14       | 4.26       | 3.92       | 12.66      | 5.45       | 3.74       |
| CaO                            | 8.81       | 7.90       | 8.62       | 5.19       | 4.86       | 7.17       | 5.90       | 6.70       |
| Na <sub>2</sub> O              | 2.46       | 2.38       | 2.26       | 2.55       | 2.50       | 2.29       | 2.67       | 2.52       |
| K <sub>2</sub> O               | 2.32       | 2.57       | 2.71       | 2.39       | 2.76       | 2.33       | 2.68       | 1.50       |
| P <sub>2</sub> O <sub>5</sub>  | 0.64       | 0.54       | 0.69       | 0.44       | 0.40       | 0.59       | 0.41       | 0.43       |
| Loss (H <sub>2</sub> O)        | 0.75       | 1.09       | 0.25       | 3.32       | 1.35       | 2.40       | 1.44       | 1.96       |
| CO <sub>2</sub>                | n.d.       | 0.02       | 0.01       | n.d.       | n.d.       | n.d.       | 0.02       | n.d.       |
| Total                          | 99.73      | 99.70      | 100.45     | 99.55      | 99.36      | 100.29     | 99.81      | 99.75      |

1. Augite-olivine shoshonite, Kugogi, Mt. Hagen, 144°10'E, 5°43'S.  
 2. Augite shoshonite, Gumanch River, Mt. Hagen, 144°12'E, 5°46'S. 3. Augite shoshonite, Kugogi, Mt. Hagen, 144°10'E, 5°45'S. 4. Amphibole-augite shoshonite, Baiyer River, Mt. Hagen, 144°10'E, 5°40'S. 5. Amphibole-augite banakite, Baiyer River, Mt. Hagen, 144°10'E, 5°40'S. 6. Olivine-augite absarokite, Tambul, Mt. Giluwe, 143°55'E, 5°55'S. 7. Amphibole-augite latite, Tambul, Mt. Giluwe, 143°53'E, 5°53'S. 8. Hypersthene andesite, Ialibu Patrol Post, Mt. Ialibu, 144°01'E, 6°15'S.

the total number of analyses for this region to 90. Taylor (1958) showed that the character of the Mt. Lamington lavas is calc-alkaline. Morgan (1966) pointed out that Karkar Island and Long Island have tholeiitic tendencies, whereas Mt. Lamington and Mt. Yelia are calc-alkaline and the lavas of Fergusson and Dobu Islands have alkaline affinities. It is suggested here, on the basis of additional material, that the chemical compositions of volcanic rocks from the New Guinea-New Britain arc show a regular lateral variation with respect to the position in the arc. This variation corresponds to the scheme given by Kuno (1966). From the oceanic side there are tholeiitic rocks, followed by calc-alkaline and finally by shoshonitic rocks. In the western part (New Guinea highlands) the alkali zone is probably replaced by shoshonitic rocks.

#### *Tholeiitic rocks*

These occur on the oceanic side of the New Guinea-New Britain Arc on the islands rimming the north coast of New Guinea. Analytical data are available from Blup Blup, Kadovar, Manam, Karkar and Long Island (Morgan, 1966). The tholeiitic zone probably follows the north side of New Britain. Analytical data available from the Rabaul area (northeastern New Britain) show that rocks from this region have tholeiitic affinities (data of Miyake and Sugiura, 1954). This is demonstrated by total alkali vs. silica relationships

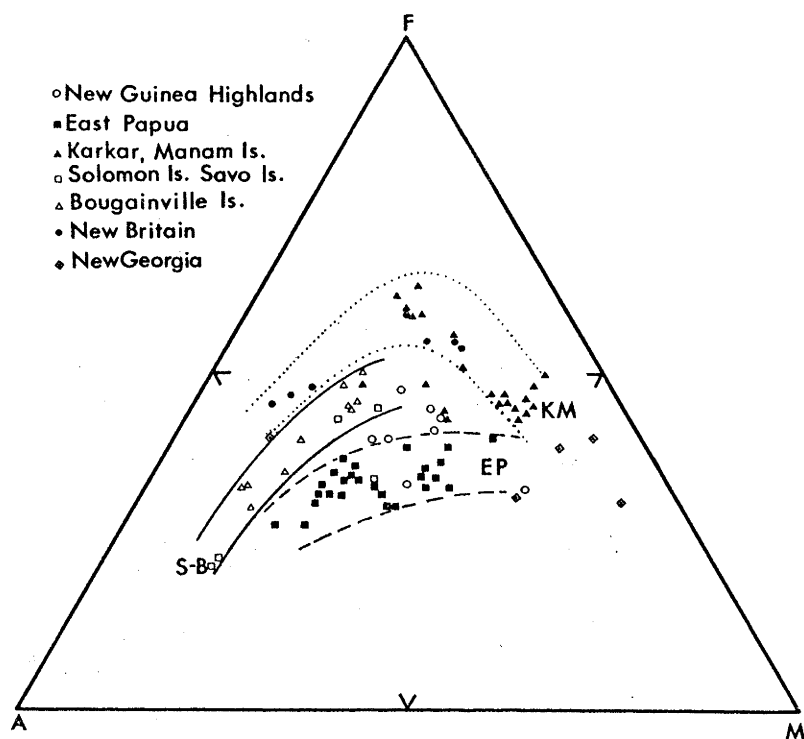


Fig.2. A.M.F. diagram for rocks of the Melanesian area. The tholeiitic trend (KM) represents the concave side of the New Guinea–New Britain arc (Karkar–Manam–northern New Britain Islands). The lower line of this trend coincides with the boundary of the pigeonitic and high-alumina series. It should be noted that three of four analyses (full triangles) from Manam and Blup Blup Islands which do not fall into the field of the trend have been carried out by a different laboratory (A.M.D.L.) than the thirteen analyses from the same area, which were analysed elsewhere (B.M.R.). Trend of calc-alkaline rocks (E.P.) represents rocks of the East Papuan coast. Analyses from Mt. Yelia, Mt. Lamington, Mt. Victory, and Mt. Trafalgar and their cognate inclusions are included. The trend S–B represents rocks from the Solomon Islands and from Bougainville. It is a calc-alkaline trend, although the iron enrichment is stronger than in the case of East Papua. (Without data for shoshonitic rocks of Ruxton, 1966).

TABLE IV

Ratio of  $K_2O/Na_2O$  (wt%) for rocks of Melanesia and Japan

| Zone          | Melanesia | Japan (Sugimura, 1961) |
|---------------|-----------|------------------------|
| Tholeiitic    | 0.30      | 0.15                   |
| Calc-alkaline | 0.50      | 0.25–0.39              |
| Alkaline      | 0.75      | 0.64                   |
| Shoshonitic   | 1.10      | not mentioned          |

along with the A.M.F. relationships (Fig.2). Low alkali contents, flat slope of the  $K_2O$  vs.  $SiO_2$ , and strong enrichment in iron during the middle stages of fractionation (Fig.2) are characteristic. Sugimura (1961) has shown that  $K_2O/Na_2O$  ratios of volcanoes along the front of the east Japan volcanic belt (tholeiitic) are smaller than those of any along the front of the west Japan volcanic belt. This fact applies to rocks of tholeiitic and other affinities in the New Guinea–New Britain Arc. Table IV shows average values of  $K_2O/Na_2O$  in tholeiitic rocks compared with Sugimura's data. In the tholeiitic zone of New Britain great variation of  $K_2O/Na_2O$  is shown in the older analyses of Miyake and Sugiura (1954).

#### *Calc-alkaline rocks*

These are represented in the New Guinea–New Britain Arc almost exclusively by amphibole andesites (Mt. Yelia, Mt. Lamington, Mt. Victory,

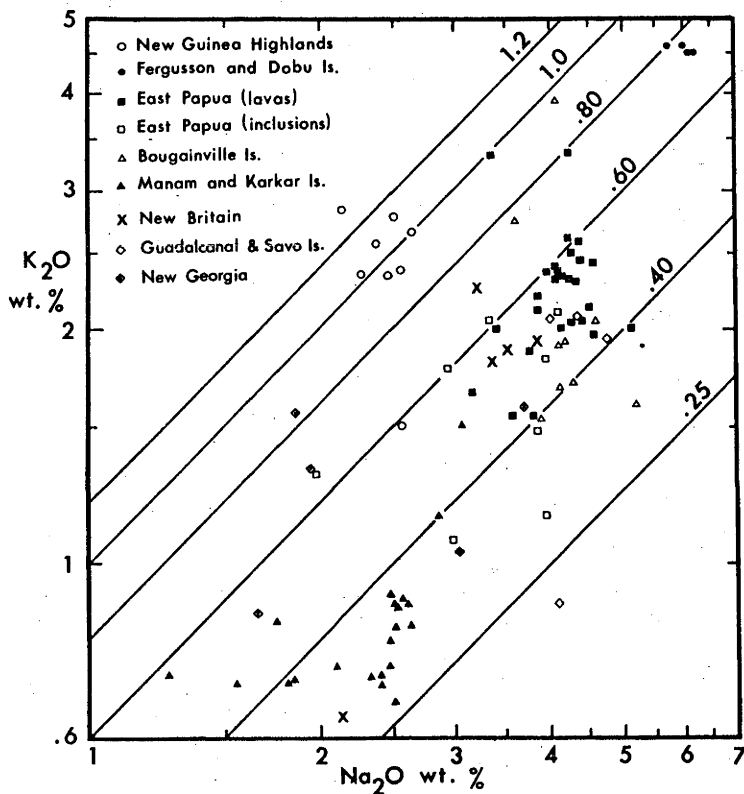


Fig.3. Logarithmic plot of  $K_2O/Na_2O$ . This shows that the ratio of  $K_2O/Na_2O$  increases from tholeiites (Manam and Karkar Islands) through calc-alkaline rock (East Papua, Bougainville, Solomons) to alkali rocks (Fergusson and Dobu Isls.) and further to the shoshonite association.

Mt. Trafalgar). Minor occurrences of high-Al pyroxene basalts and low-Si pyroxene andesites have been found in the older Mt. Trafalgar lavas. The chemical character is defined by relatively high alkali contents and small range of  $\text{SiO}_2$  variation even when cognate inclusions are included in variation diagrams. The ratio of  $\text{K}_2\text{O}$  to  $\text{Na}_2\text{O}$  varies from 0.4–0.6 and lies between those of tholeiitic and alkali rocks (Fig. 3, Table IV). On an A.M.F. diagram they are characterised by a flat trend indicating very little "iron enrichment", even compared with calc-alkaline rocks from the Aleutians or the Kurile Islands.

#### *Alkaline rocks*

Morgan (1966) suggested that the rocks of Fergusson and Dobu Islands are typical of alkali basalt-trachyte-comendite provinces (cf., Abbott, 1969). The  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio for these volcanic rocks shows only slight variation around 0.8. Also Ruxton (1966) suggested the alkaline character of some East Papuan rocks; they appear to be shoshonitic.

#### *Shoshonitic rocks*

Analysed rocks from the Cenozoic strato-volcanoes, Mt. Hagen and Mt. Giluwe in the New Guinea highlands, as well as "alkaline" rocks from East Papua described by Ruxton (1966), belong to the shoshonite rock association as defined by Joplin (1968). They are almost chemically identical with the rocks described from Java and the Lesser Sunda Islands (Joplin, 1968) and similar in mineralogy and chemistry to those described by Dickinson et al. (1968) from Fiji.

The ratio of  $\text{K}_2\text{O}$  to  $\text{Na}_2\text{O}$  is close to 1.0. The  $\text{SiO}_2$  and  $\text{CaO}$  contents are similar to those of basalt despite the high potassium content. It is apparent from  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  vs.  $\text{SiO}_2$  diagrams and from Harker variation diagrams that there is only a slight increase in alkali content with increase of  $\text{SiO}_2$ . There is no distinct group or trend in the A.M.F. diagram; Joplin (1968) noted little iron enrichment compared with alkali basalts.

In spite of the  $\text{K}_2\text{O}$  to  $\text{Na}_2\text{O}$  ratio, which is higher in shoshonites than in the alkali basalts, and in spite of the increase of this ratio across the island arc, it is suggested that the shoshonitic rocks in island-arc regions occupy the zone most remote from the oceanic side of the arc. This is in agreement with the current ideas that the shoshonite association is characteristic of newly stabilised or just consolidated orogenic regions (Joplin, 1968; Dickinson et al., 1968).

#### CENOZOIC VOLCANIC ROCKS OF THE SOLOMON ISLANDS

The Solomon Islands, including Bougainville, form a linear structure extending over 1,200 km. Morphology of the surrounding seas is complicated and the island arc is rimmed on both sides by a trench-like structure. Data on the chemical composition of the rocks are scanty. Blake and Miezeitis (1967) presented 10 analyses of rocks from Bougainville, Stanton and Bell will present some analyses, four of which appeared in Brown and Schairer (1968),

TABLE V

Chemical analyses of Cenozoic volcanic rocks from Solomon Islands

|                                | 1<br>(155) | 2<br>(144) | 3<br>(170) | 4<br>(160) | 5<br>(168) |
|--------------------------------|------------|------------|------------|------------|------------|
| SiO <sub>2</sub>               | 57.02      | 56.08      | 59.95      | 66.80      | 67.96      |
| TiO <sub>2</sub>               | 0.56       | 0.53       | 0.86       | 0.23       | 0.22       |
| Al <sub>2</sub> O <sub>3</sub> | 18.89      | 19.04      | 16.03      | 18.24      | 18.76      |
| Fe <sub>2</sub> O <sub>3</sub> | 3.56       | 3.70       | 5.50       | 1.25       | 1.21       |
| FeO                            | 2.66       | 3.10       | 0.38       | 1.02       | 1.03       |
| MnO                            | 0.16       | 0.14       | 0.09       | 0.06       | 0.06       |
| MgO                            | 2.93       | 3.83       | 4.95       | 1.50       | 1.42       |
| CaO                            | 8.09       | 8.04       | 6.27       | 3.17       | 2.55       |
| Na <sub>2</sub> O              | 3.77       | 4.18       | 4.04       | 4.97       | 4.36       |
| K <sub>2</sub> O               | 1.60       | 0.88       | 2.08       | 1.92       | 2.08       |
| P <sub>2</sub> O <sub>5</sub>  | 0.27       | 0.16       | 0.33       | 0.09       | 0.08       |
| Loss                           | 1.35       | 0.82       | 0.16       | 0.26       | 0.36       |
| Total                          | 100.86     | 100.50     | 100.63     | 99.54      | 100.10     |

1. Augite-amphibole andesite, Vella Lavella, New Georgia Group (Geol. Surv. B.S.I.P.). 2. Augite-amphibole andesite, Isisu Pt., Guadalcanal, 159°43'E, 9°15'S. 3. Amphibole-andesite, Savo Volcano, Guadalcanal, 159°50'E, 9°08'S. 4. Amphibole dacite, Savo Volcano, Guadalcanal, 159°50'E, 9°08'S. 5. Biotite-amphibole dacite, Savo Volcano, Guadalcanal, 159°50'E, 9°08'S.

and in this paper five new analyses are presented (Table V).

It appears that the picture of magma variation as seen in the New Guinea-New Britain Arc is not developed in the Solomons. The rocks of Bougainville and Guadalcanal (including Savo volcano) are calc-alkaline although the rocks of Bougainville tend to be potassium rich. The rocks from Guadalcanal are andesitic; at Savo volcano they are andesitic and dacitic and contain numerous basic and ultrabasic inclusions; the mineralogy of the inclusions corresponds to ultrabasic rocks occurring in N'gella group and St. Ysabel Island. In the A.M.F. diagram the andesites and dacites show a gently curved trend (Fig.2), relatively rich in iron but still in the calc-alkaline field. The characteristic feature is a high Al<sub>2</sub>O<sub>3</sub> content and preponderance of Na<sub>2</sub>O over K<sub>2</sub>O. The ratio K<sub>2</sub>O to Na<sub>2</sub>O is generally lower in rocks of Guadalcanal than in Bougainville but K<sub>2</sub>O increases rapidly with SiO<sub>2</sub>.

Rocks from the New Georgia Group between Bougainville and Guadalcanal appear to have tholeiitic as well as calc-alkaline affinities. Brown and Schairer (1968), using only the relationship of MgO to FeO + Fe<sub>2</sub>O<sub>3</sub>, maintained that they are calc-alkaline. Using conventional criteria such as Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O + Na<sub>2</sub>O or Na<sub>2</sub>O + K<sub>2</sub>O/SiO<sub>2</sub> as well as position in the A.M.F. diagram, it is suggested that three of their four analyses are tholeiitic basalts. For SiO<sub>2</sub> in the range 47-50% the content of Al<sub>2</sub>O<sub>3</sub> is 9.1%, 11.9%, 12.4% and of Na<sub>2</sub>O + K<sub>2</sub>O is 2.5%, 3.2% and 3.4%. Two other rocks from the region show calc-alkaline (high alumina) tendencies (Al<sub>2</sub>O<sub>3</sub> = 17.3%, and 18.86%, whereas Na<sub>2</sub>O + K<sub>2</sub>O = 5.0% and 5.3%).

The tholeiitic rocks present in the New Georgia Group appear to be unique because they are situated southwest of the island arc axis, i.e., on the continental side of the arc and because they are probably "mixed" with the calc-alkaline rock types. The islands on the northeast side of the axis do not show recent volcanic activity (St. Ysabel and Malaita).

## CENOZOIC VOLCANIC ROCKS OF THE NEW HEBRIDES

Mitchell (1966) and Warden (1967) compiled chemical analyses for the New Hebrides. Most of the rocks are calc-alkaline although tholeiitic types occur. Variation of magma type is similar to that of the New Georgia group.

### POSITION OF BENIOFF ZONE

Compilation of earthquake foci for the region (Brooks, 1965; Grover, 1955, 1958, 1960, 1965) is shown in Fig.4. Sections across the island arc show the position of the Benioff zone (Fig.5). Sections in the New Guinea-New Britain Arc are perpendicular to the tangent of curvature. In the Solomon-Bougainville Islands all sections are perpendicular to the arc axis. In section A, the Benioff zone dips gently southwest beneath the New Guinea mainland. The dip of the Benioff zone in section B (New Britain) is smaller but the plane dips to the southeast. The seismic zone in sections across the Solomon Arc (C, D, E) appears vertical although it may be argued that in section C (Bougainville Island) the seismic zone dips steeply towards the southwest. The area north and east of New Britain is not graphically presented; this is a junction of both arcs. The New Britain arc and its trenches are more strongly bent near the junction with the Solomon Arc than elsewhere. At the junction the tangent of the New Britain Arc is about  $60^\circ$  to the Solomons trend. This complex junction appears in the peculiar form of the deep-sea trenches

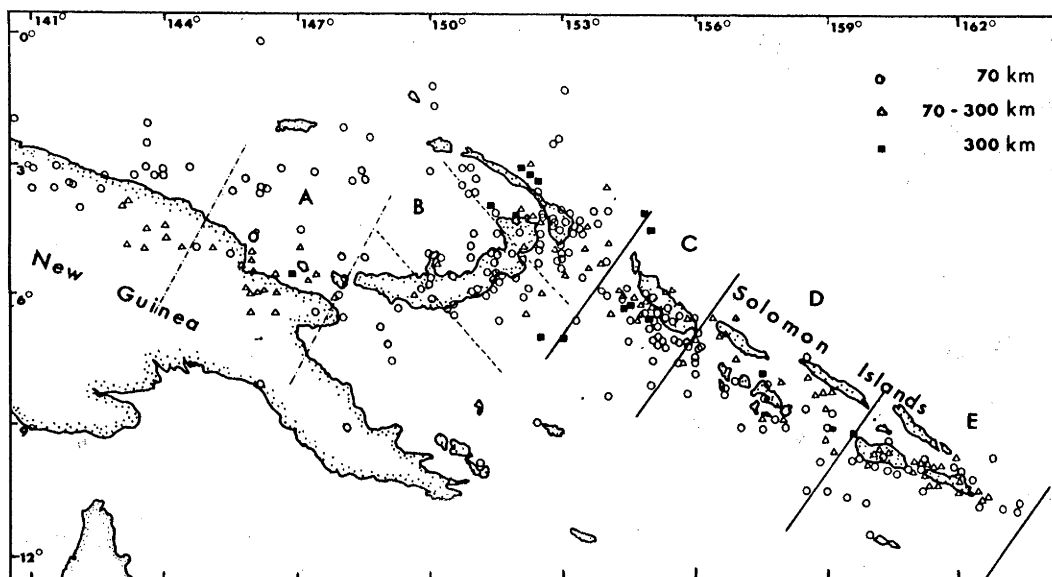


Fig.4. Earthquake foci for the Melanesian area compiled from Brooks (1965) and from Brit. Solomon Isls. Geol. Surv. Rept. and Mem.; compilation contains earthquake foci registered to 1962. A, B, C, D, E indicate the areas of sections oriented perpendicular to the arc structure plotted in Fig.5.

in this region. The area of the junction is extremely active seismically. Because of the lack of deep earthquake foci in the New Guinea structure and the existence of deep foci in the Solomon-Bougainville structure, it is suggested that deep foci occurring north of New Britain belong to the Solomon structure. Magnetic anomalies as well as seismic refraction anomalies (Rose et al., 1968; Hart et al., 1969) support this. Despite the small number of registered earthquake foci of known depth, an aseismic zone of the type described by

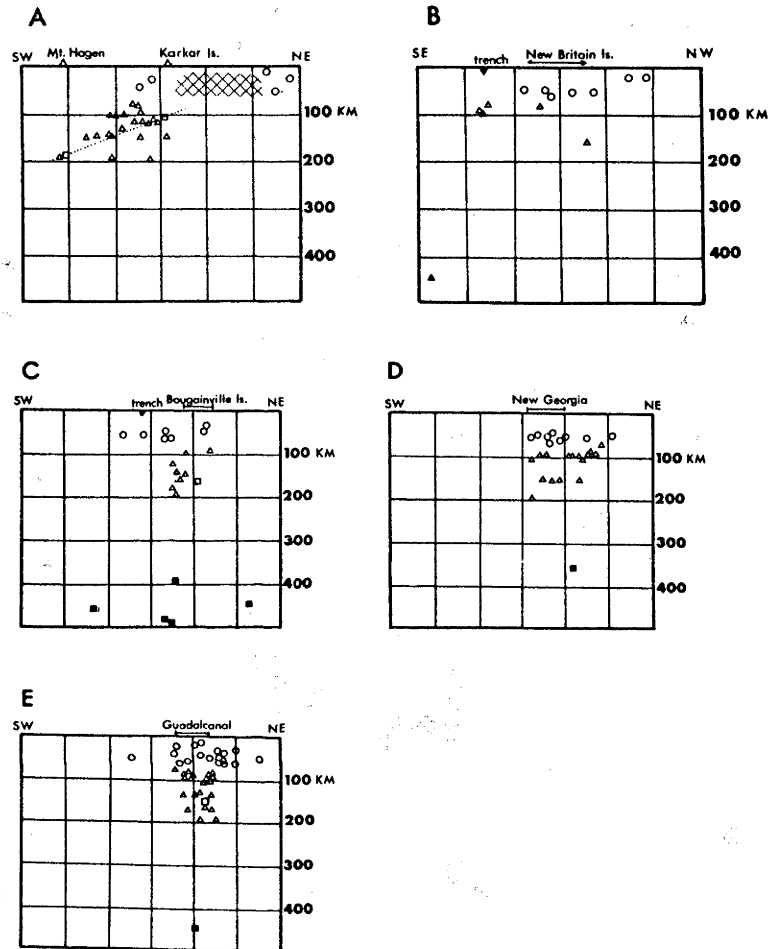


Fig.5. Earthquake foci of known depth plotted in sections perpendicular to the structure of island arcs. Circles are earthquakes to 70 km depth, triangles 70-300 km, full squares more than 300 km. The cross hatched area is of shallow earthquakes of unknown depth in the range 0-60 km. Note the good correlation of derived depth of seismic zone in section A, and inclination of A and B to the S.W. and S.E. respectively. No apparent inclination is seen in section C, D, E.

Miyamura (1968) probably exists, at a depth between 200–350 km (cf., Coleman, 1966).

In the New Hebrides region (not illustrated) the seismic zone, as indicated by data of Warden and Williams (1964) and Warden (1966), is vertical or dips towards the east.

#### COMPOSITION OF VOLCANIC ROCKS AND POSITION OF BENIOFF ZONE

It has been shown by Dickinson and Hatherton (1967), using circum-Pacific examples, that the  $K_2O$  content of volcanic rocks is related to the depth of the Benioff zone beneath the volcano. The absolute values of  $K_2O$  for the series of rocks are taken at 55 and 60%  $SiO_2$  from variation of  $K_2O/SiO_2$  (Harker's diagram) which is assumed to be linear. These values are correlated with depth to Benioff zone according to the diagrams presented

TABLE VI

Derived position of seismic plane according to Hatherton and Dickinson (1967) – based on correlation of  $K_2O$  and  $SiO_2$

| Rock type association  | Locality             | $K_2O$ (wt%) |             | Derived depth of seismic plane (km) | Actual depth of seismic plane (km) |
|------------------------|----------------------|--------------|-------------|-------------------------------------|------------------------------------|
|                        |                      | 55% $SiO_2$  | 60% $SiO_2$ |                                     |                                    |
| Tholeiitic association | Manam–Karkar Isls.   | 0.82         | 1.15        | ~ 105                               | 85–100                             |
| Tholeiitic association | New Britain          | 1.30         | 1.90        | ~ 135                               | 80–105                             |
| Calc-alkaline          | eastern Papua        | 1.55         | 2.28        | ~ 150                               | almost aseismic                    |
| Calc-alkaline          | Solomon Islands (SE) | 0.95         | 2.75        | ~ 150*                              | *                                  |
| Calc-alkaline          | Bougainville Isls.   | 1.60         | 1.84        | ~ 165                               | *                                  |
| Shoshonite             | New Guinea highlands | 2.20         | 2.40        | ~ 180                               | 170–200                            |

\*The position of seismic plane is vertical.

by Hatherton and Dickinson (1967). This method has been used here to derive the position of the Benioff zone. Results are given in Table VI and graphically shown in Fig.5. The correlation of derived depth with actual depth of earthquake epicentres shows good agreement for rocks of both the New Guinea–New Britain Arc, and the Solomon Islands. The area of calc-alkaline amphibole andesites from East Papua is not plotted; it appears to be aseismic.

#### COMPOSITION IN RELATION TO BENIOFF ZONE

The Melanesian example shows that lateral variation of magma composition is distinct in areas where the seismic zone dips gently towards the continental side, as is in the case of the New Guinea–New Britain Arc. Lateral variation is not realised in the Solomons–Bougainville structure. This region with a steep or vertically dipping seismic zone, consists of a mixture of tholeiitic and calc-alkaline rocks.

## MODEL FOR CHEMICAL DEVELOPMENT OF ISLAND ARCS

It has been pointed out that single volcanoes erupting over long periods of time, as well as whole island arcs, show a compositional evolution (Gorshkov, 1962; Baker, 1968). This evolution is characterised by increasing  $K_2O/Na_2O$  and increase of total alkalis for given  $SiO_2$  content, as well as by change of  $Al_2O_3$  content (cf., Asama volcano - Aramaki, 1963). It is, therefore, suggested that the chemical development of a single volcano, as well as of an island arc, is analogous to the lateral variation of magma composition across island arcs. Tholeiitic rocks with low  $K_2O/Na_2O$  are usually situated on the oceanic side of island arcs and are here considered to be the earliest manifestation of arc development (cf., Baker, 1968). There are several island arcs where only rocks with tholeiitic tendencies occur, while typical calc-alkaline rocks, especially high potassium andesites, do not appear. These include the Izu Islands (Isshiki, 1963), Tonga (Kuno, 1966) and South Sandwich Islands (Baker, 1968) and in part the Marianas and Kurile Islands. Arcs with tholeiites and transitional types to calc-alkaline rocks are perpendicularly oriented to recent compression vectors (Le Pichon, 1968).

Chemical evolution of island arcs, manifested by lateral variation of composition, shows an increase of  $K_2O$  relative to  $Na_2O$  as well as an increase of  $Al_2O_3$  relative to  $SiO_2$ , which are calc-alkaline features. The direction of island arcs having calc-alkaline rocks together with tholeiites is not strictly controlled by recent compression vectors (Aleutians, Bougainville-Solomons).

A further chemical development is the transition of calc-alkaline rocks to alkali association or to shoshonitic rocks. It should be stressed that alkali basalt associations are confined to continental margins and usually do not appear in recent island arcs, whereas shoshonitic volcanism appears to be confined to those island arcs close to large islands (Fiji, New Guinea, Sunda Islands) and to continental margins or newly stabilized areas (Joplin, 1968). Whereas arcs with tholeiitic volcanism have frequent as well as deep seismic activity, it appears that seismic activity is no longer a controlling factor in regions of shoshonitic or alkalic volcanism; some regions are almost aseismic. Recent structures associated with alkalic and shoshonitic rocks are not always perpendicular to present vectors of compression, and it is, therefore, suggested that these rocks mark the latest stages of island arc development.

It is suggested that the proposed model is consistent with the hypothesis of a mobile lithosphere with episodic opening of the sea floor (Ewing and Ewing, 1967; Le Pichon, 1968; Isacks et al., 1968) with change of direction of sea-floor spreading. Such spreading could create differently oriented island arcs with a progressive development of tholeiitic to alkali basalt or shoshonitic rocks. According to the sea-floor spreading hypothesis the reversed position of trenches or presence of trench-like structures on both sides of the Solomons arc could be explained by interaction of two lithosphere plates moving in opposite directions resulting in a vertical chimney-like type of seismic zone. Such interpretation is also consistent with Wright's (1966) suggestion of a convection cell in the Coral Sea region and with the observation of Rose et al. (1968) that "the Solomons appear to have little or no root and have essentially the same depth to the mantle as the oceanic area to the north". The proposed model suggests that tholeiitic volcanism is an earliest manifestation of island arc development, followed by calc-alkaline and by shoshonitic and/or alkalic

rocks. Thus the arc with rocks of only tholeiitic tendencies should have most recent sediments, while those with calc-alkaline and/or shoshonitic should have older sediments. This is generally true. However, it should be understood that the differential rate of spreading (e.g., recent rates of spreading differ by a factor of 10) in different parts of the world and in the different geological times could make such correlation inconsistent.

#### ACKNOWLEDGEMENT

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Appendix 5. P. Jakeš<sup>v</sup> and A.J.R. White  
K/Rb ratios of island arc rocks.

## K/Rb ratios of rocks from island arcs

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**Abstract**—The abundances of K and Rb have been determined in andesites and shoshonitic rocks from island arcs, inclusions from calc-alkaline rocks and alkali basalts, and in mineral separates from these rocks. It is suggested that the range of K/Rb values in a given magma series represents the degree of fractionation and/or contamination, whereas the highest K/Rb value results from processes of magma derivation. Across island arcs there is an increase of  $K_2O$  content with decrease of K/Rb ratio from tholeiites to low-K calc-alkaline rocks, calc-alkaline rocks, high-K calc-alkaline rocks and finally to shoshonites. This is explained by the different K/Rb ratios of amphibole and biotite and different mutual proportions of these minerals involved in fractional melting (decomposition) of a sinking slab of oceanic crust undergoing transformation from amphibolite to eclogite.

### INTRODUCTION

LATERAL variation in the composition of volcanic rocks across island arcs and their correlation with depth to the Benioff Zone has been established by a number of workers (e.g. KUNO, 1966; DICKINSON and HATHERTON, 1967; SUGIMURA, 1968). Tholeiites occur on the oceanic sides of island arcs, followed towards the continent by low-, medium- and high-potassium calc-alkaline rocks, and finally by shoshonites (JAKEŠ and WHITE, 1969) and/or alkaline rocks. This sequence is valid only for regions with a seismic zone dipping towards the continent.

In this paper new data are presented for K and Rb in andesites and shoshonites from island arcs, amphibole-bearing inclusions from andesites and alkali basalts, and amphiboles, biotites and clinopyroxenes separated from these rocks. New data on amphiboles, biotites, clinopyroxenes and garnets from metamorphic and plutonic environments are also presented. Rubidium was determined by X-ray spectrometry using the same equipment and methods as used and described by CHAPPELL *et al.* (1969) so that detection limits are between 0.3 and 0.9 ppm. These and other published data are used to correlate K/Rb ratios with varying magma composition across island arcs and also with the mineralogy of likely magma source materials.

### K/Rb RATIOS OF DIFFERENT ROCK ASSOCIATIONS

#### *Tholeiitic rocks*

The K/Rb ratios of tholeiitic rocks vary with geological setting. Oceanic tholeiites (ENGEL *et al.* 1965; GAST, 1965; TATSUMOTO *et al.* 1965) have extremely high K/Rb values (800–2000). The Hawaiian tholeiites and the accompanying suite of alkaline rocks have relatively constant K/Rb values of around 500 (LESSING *et al.*, 1963; TAUBENECK, 1965), and other tholeiitic-alkaline associations of oceanic areas (e.g. McDougall and Compston, 1965) are similar in this respect. Continental

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# GALLEY W AA-32

K/Rb ratios of rocks from island arcs

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Table 1. K, Rb and K/Rb ratios in calc-alkaline and related rocks from island arcs

|                                    | K %  | Rb ppm | K/Rb |
|------------------------------------|------|--------|------|
| <b>Fiji</b>                        |      |        |      |
| hornblende-andesite (2)*           | 0.32 | 10.3   | 310  |
| hornblende-andesite (6)*           | 1.16 | 22.8   | 510  |
| hornblende-andesite (18)*          | 1.05 | 18.6   | 555  |
| <b>New Zealand</b>                 |      |        |      |
| hornblende-andesite (48)*          | 1.00 | 27.9   | 360  |
| hornblende-andesite (50)*          | 0.85 | 33.8   | 250  |
| hornblende-andesite (46)*          | 1.73 | 39.3   | 470  |
| <b>Western United States</b>       |      |        |      |
| hornblende-dacite (5)*             | 0.76 | 21.0   | 360  |
| hornblende-dacite (1)*             | 2.52 | 48.9   | 525  |
| <b>Solomon Islands</b>             |      |        |      |
| hornblende-andesite (155)          | 1.33 | 31.6   | 420  |
| hornblende-andesite (144)          | 0.73 | 17.7   | 410  |
| hornblende-dacite (160)            | 1.59 | 47.3   | 335  |
| hornblende-dacite (168)            | 1.73 | 49.6   | 350  |
| <b>East Papua</b>                  |      |        |      |
| pyroxene-andesite (3547)           | 1.55 | 52.05  | 300  |
| hornblende-biotite andesite (3543) | 1.97 | 80.0   | 245  |
| hornblende-andesite (68)           | 1.69 | 52.0   | 325  |
| hornblende-andesite (64)           | 1.76 | 56.8   | 310  |
| <b>New Guinea</b>                  |      |        |      |
| olivine-pyroxene absarokite (99)   | 1.94 | 60.0   | 320  |
| hornblende-latitude (101)          | 2.22 | 111.0  | 200  |
| pyroxene-shoshonite (105)          | 2.25 | 98.3   | 230  |
| olivine-pyroxene shoshonite (107)  | 1.93 | 60.2   | 320  |
| pyroxene-banakitite (108)          | 2.29 | 76.1   | 300  |

\* Hornblendes from these rocks have been analysed.

Clinopyroxenes from Nos. 47 and 48 and biotite from No. 46 have been analysed (See Table 3).

## EFFECTS OF FRACTIONATION AND CONTAMINATION ON K/Rb RATIOS

It has been shown (e.g. HEIER and ADAMS, 1964; ABBOTT, 1967; BARBIERI *et al.*, 1968; SHAW, 1968) that fractionation or differentiation usually leads to a decrease in K/Rb ratio. Few exceptions in which K/Rb increases during the evolution of rocks involve mica fractionation (in migmatites described by WHITE, 1966), fractionation of olivine and clinopyroxene (GRIFFIN and MURTHY, 1969) and of garnet (GRIFFIN and MURTHY, 1968), although it can be argued in the case of olivine, clinopyroxene and garnet that large quantities would have to be removed to significantly raise the K/Rb ratio of the residual melt.

COMPSTON *et al.* (1968), discussing the contamination of continental tholeiites suggested a process of "selective enrichment" whereas GREEN and RINGWOOD (1967) explained the variation of trace element chemistry in basalts in terms of "wall rock reaction" and selective enrichment of magma in "incompatible elements" including Rb. Unless contamination involves material of high K/Rb (e.g. lower continental crust; LAMBERT and HEIER, 1969), it is apparent that contamination by crustal material (of low K/Rb) decreases the K/Rb value of the original magma.

Table 1. K, Rb and K/Rb ratios in calc-alkaline and related rocks from island arcs

|                                    | K %  | Rb ppm | K/Rb |
|------------------------------------|------|--------|------|
| Fiji                               |      |        |      |
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It is considered that contamination of island arc rocks is negligible (DICKINSON, 1968; HEDGE, 1966 and others) so that the range of K/Rb values of a given magma series probably represents the various degrees of later fractionation whereas the highest value of K/Rb for a given series of volcanic rocks (e.g. low-K calc-alkaline rocks) probably approaches the "initial" K/Rb value least affected by later, high level processes. Such "initial" values (compiled in Table 2 and Fig. 1) show a decrease from tholeiitic to shoshonitic rocks across island arcs.

Table 2. Maximum reported K/Rb ratios in rock associations from various regions (Fiji tholeiite value is an average)

| Rock association     | Region                | K/Rb | Reference                    |
|----------------------|-----------------------|------|------------------------------|
| tholeiitic           | New Britain—          | 1000 | LOWDER and CARMICHAEL (1969) |
|                      | New Guinea            |      |                              |
|                      | Fiji                  | 1070 | GILL (1970)                  |
|                      | Saipan                | 590  | TAYLOR (1968)                |
| low-K calc-alkaline  | Izu Peninsula         | 510  | TAYLOR and WHITE (1966)      |
|                      | Bougainville          | 560  | TAYLOR <i>et al.</i> (1969)  |
| calc-alkaline        | Fiji                  | 565  | present paper                |
|                      | New Zealand           | 540  | TAYLOR and WHITE (1966)      |
|                      |                       |      | present paper                |
| high-K calc-alkaline | Western United States | 525  | present paper                |
|                      | Asama, Japan          | 400  | TAYLOR and WHITE (1966)      |
|                      | Solomon Islands—      | 420  | TAYLOR <i>et al.</i> (1969)  |
|                      | Bougainville          |      | and present paper            |
|                      | East Papua            | 325  | present paper                |
| shoshonitic          | New Guinea Highlands  | 320  | present paper                |

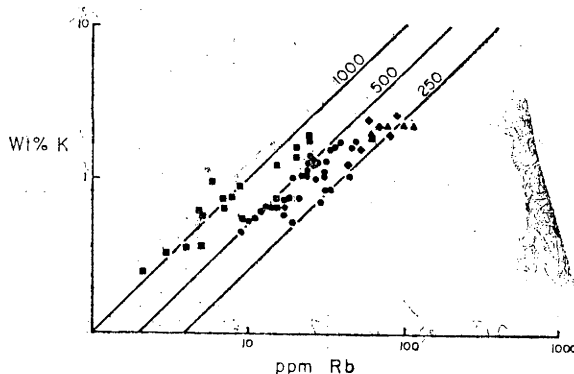


Fig. 1. K/Rb ratios of rocks from island arcs.

Squares—tholeiitic rocks from New Britain (LOWDER and CARMICHAEL, 1970) and from Fiji (GILL, 1970); Circles—calc-alkaline rocks from New Zealand and Japan (TAYLOR and WHITE 1966); Saipan, Bougainville and Fiji (TAYLOR *et al.* 1969) and Fiji, Solomon Islands, New Zealand and W. United States (present paper); Diamonds—high-K calc-alkaline rocks from Bougainville (TAYLOR *et al.* 1969) and Eastern Papua (present paper); Triangles—shoshonitic rocks from New Guinea (present paper).

#### K AND Rb DISTRIBUTION IN AMPHIBOLES AND MICAS

If the magmas of island arcs are derived from the upper mantle or a sinking slab of wet oceanic crust,  $K_2O$  is most likely contained in the hydrous phases amphibole and biotite (e.g. RINGWOOD 1969). The tendency of micas to concentrate Rb is well

established (AHRENS *et al.*, 1952; HEIER and ADAMS, 1964; ALDRICH *et al.*, 1965). SHAW (1968) has suggested that most obvious control of K/Rb in ordinary igneous rocks is the modal proportion of biotite and amphibole. Our data demonstrate that the absolute amounts of Rb (e.g. in biotites) are controlled by the amount of Rb in the parental rock. Biotites from andesites and from inclusions in alkali basalts have relatively low Rb values (Table 3), implying relatively high K/Rb values (200). In metamorphic biotites, however, Rb values are about 1000 ppm. and K/Rb ratios about 70 (Table 3; see also HEIER and ADAMS, 1964).

Table 3. K/Rb values of minerals

|                                                        | No.                         | K %   | Rb ppm | K/Rb |                                                                | No.                                          | K %   | Rb ppm | K/Rb |
|--------------------------------------------------------|-----------------------------|-------|--------|------|----------------------------------------------------------------|----------------------------------------------|-------|--------|------|
| Andesites, Fiji                                        |                             |       |        |      | Inclusions in alkali basalts, Kiama, N.S.W., Australia         |                                              |       |        |      |
| amphibole                                              | 2                           | 0.17  | 3.7    | 460  | amphibole                                                      | 22                                           | 0.91  | 8.1    | 1120 |
|                                                        | 6                           | 0.15  | 1.3    | 1150 | biotite                                                        | —                                            | 7.16  | 229    | 312  |
|                                                        | 18                          | 0.16  | 1.4    | 1140 | amphibole                                                      | 23                                           | 1.63  | 12.6   | 1290 |
| Andesites, Western United States                       |                             |       |        |      | biotite                                                        | 25                                           | 7.05  | 161    | 438  |
| amphibole                                              | 1                           | 0.27  | 1.7    | 1580 | amphibole                                                      | 24                                           | 1.00  | 11.3   | 880  |
|                                                        | 5                           | 0.33  | 1.7    | 1940 | amphibole                                                      | 26                                           | 1.18  | 8.5    | 1390 |
| Andesites, New Zealand                                 |                             |       |        |      | amphibole                                                      | 27                                           | 1.08  | 7.5    | 1440 |
| amphibole                                              | 46                          | 0.52  | 5.0    | 1040 | Gabbroic rocks, Bohemian Massif, Europe                        |                                              |       |        |      |
|                                                        | 46                          | 6.22  | 155    | 40   | amphibole                                                      | 126                                          | 0.27  | 2.7    | 1000 |
|                                                        | 47                          | 0.62  | 5.3    | 1170 |                                                                | 127                                          | 0.61  | 2.3    | 2650 |
|                                                        | 47                          | 0.07  | 57     | 122  |                                                                | 128                                          | 0.55  | 0.9    | 550  |
|                                                        | 48                          | 0.60  | 4.4    | 1360 |                                                                | 129                                          | 0.62  | 7.0    | 885  |
|                                                        | 48                          | <0.02 | 1.6    | >125 | Amphibolites, Bohemian Massif, Europe                          |                                              |       |        |      |
|                                                        | 50                          | 0.25  | 2.4    | 1040 | amphibole                                                      | 107                                          | 0.27  | 4.3    | 630  |
| Andesites, Carpathians, Czechoslovakia                 |                             |       |        |      |                                                                | 116                                          | 0.44  | 4.2    | 1670 |
| 31                                                     | 0.33                        | 1.7   | 1940   | 108  |                                                                | 0.23                                         | 1.6   | 1440   |      |
| biotite                                                | 31                          | 6.80  | 422    | 161  | Garnet-kyanite granulites with minor biotite (Bohemian Massif) |                                              |       |        |      |
| amphibole                                              | 33                          | 0.55  | 3.4    | 1620 | biotite                                                        | 113                                          | 7.55  | 882    | 85   |
| biotite                                                | 33                          | 7.30  | 244    | 299  |                                                                | 121                                          | 8.02  | 1320   | 60   |
| Andesites and dacites, Hunter River, N.S.W., Australia |                             |       |        |      |                                                                | 121                                          | <0.02 | 2.9    |      |
| amphibole                                              | 4                           | 0.31  | 4.5    | 690  |                                                                | 114                                          | 8.06  | 946    | 85   |
|                                                        | 7                           | 0.40  | 1.6    | 2500 |                                                                | 114                                          | <0.02 | 4.0    |      |
|                                                        | 8                           | 0.41  | 1.3    | 3150 |                                                                | 108                                          | 7.80  | 1354   | 57   |
|                                                        | 9                           | 0.41  | 1.3    | 3150 |                                                                | 106                                          | <0.02 | 6.0    |      |
|                                                        | 10                          | 0.41  | 3.4    | 1200 |                                                                | 122                                          | 8.12  | 1320   | 61   |
|                                                        | 11                          | 0.57  | 3.5    | 1630 |                                                                | 105                                          | 8.06  | 1359   | 59   |
|                                                        | 13                          | 0.58  | 6.3    | 920  |                                                                | 105                                          | <0.02 | 3.8    |      |
|                                                        | 14                          | 0.57  | 5.9    | 970  |                                                                | 111                                          | 7.89  | 978    | 80   |
|                                                        | 17                          | 0.60  | 3.9    | 1540 |                                                                | 125                                          | <0.02 | 7.3    |      |
|                                                        | Andesitic rock from Mt Etna |       |        |      |                                                                | Garnet-cordierite gneisses (Bohemian Massif) |       |        |      |
| amphibole                                              | 49                          | 0.42  | 6.1    | 690  | biotite                                                        | 103                                          | 7.95  | 1125   | 70   |
| High-Al basalts—N.S.W., Australia                      |                             |       |        |      | garnet                                                         | 103                                          | <0.02 | 8.7    |      |
| amphibole                                              | 36                          | 0.37  | 2.5    | 1480 | biotite                                                        | 115                                          | 8.30  | 1410   | 58   |
| amphibole                                              | 40                          | 0.37  | 1.7    | 2175 | garnet                                                         | 115                                          | <0.02 | 3.4    |      |
| Alkali basalts, N.S.W., Australia                      |                             |       |        |      | Garnet-bearing migmatites (Bohemian Massif)                    |                                              |       |        |      |
| amphibole                                              | 19                          | 1.59  | 13.1   | 1210 | garnet                                                         | 133                                          | <0.02 | 7.5    |      |
|                                                        | 44                          | 1.23  | 3.3    | 3720 | garnet                                                         | 135                                          | <0.02 | 3.3    |      |
|                                                        | 42                          | 0.61  | 4.6    | 1326 |                                                                |                                              |       |        |      |

HART and ALDRICH (1967) and GRIFFIN *et al.* (1967) gave high K/Rb values for amphiboles, mostly within the range 400–1400 (extreme values being 2800). New data (Table 3) for 38 hornblendes range from 460 to 3720. In amphibole-bearing inclusions which are apparently cognate (e.g. East Papua, Table 4) K/Rb ratios are proportionally related to the modal content of amphibole. Gabbroic rocks with more than 50% of amphibole have K/Rb around 1000 whereas a dioritic rock with less than 15 per cent of modal amphibole has a low K/Rb value (295). Values lower by a factor of two to four have been found in coexisting pyroxenes and plagioclases and lower by a factor of ten for coexisting biotites. Very similar distribution relationships have been found by GRIFFIN and MURTHY (1968) in minerals of eclogites. New data presented in Table 3 indicate extremely high K/Rb values, almost without exception, for amphiboles and low values for clinopyroxenes and garnets. According to GILL and MURTHY (1969) plagioclase from anorthosites also has a very high K/Rb ratio.

GRIFFIN and MURTHY (1968) showed that for coexisting pyroxenes and garnets, K/Rb values are lower for garnets. In the garnets from granulite facies rocks studied here, the  $K_2O$  contents were found to be lower than the detection limit (0.025  $K_2O$ ), but measurable amounts of Rb were found (Table 3), implying low K/Rb ratios of granulite facies garnets.

## DISCUSSION

If fractional melting of basic material gives rise to island arc rocks and if this basic material is a slab of underthrust oceanic crust, then the composition of the lavas produced and their lateral variation can be correlated with the mineralogy of the slab and crystal-liquid equilibria during fractional melting. Variation of K/Rb in island arc rocks can be also explained using these assumptions.

A sinking slab of partly hydrated oceanic crust, consisting mainly of oceanic tholeiite, undergoes progressive subsolidus dehydration from greenschist to amphibolite to pyroxene granulite and finally to eclogite as it moves down the Benioff zone. Reactions take place at deeper levels than normal because of thermal retardation of the slab this extends the depth at which hydrous phases may be stable. In the granulite and eclogite stages of this metamorphism all of the potassium (although small) can no longer be accommodated in amphibole so that mica (phlogopite) occurs as a separate although minor (<1%) phase. Thus during metamorphism of the slab the relative proportions of K and Rb-bearing phases vary with depth; amphibole with high K/Rb decreases but phlogopite with low K/Rb increases because of the relative stability of these phases.

Study of andesitic liquids (GREEN and RINGWOOD, 1968), JAKŠ (in progress) as well as models for temperature regimes of the down-going slab (TURCOTTE and OXBURG, 1969) indicate that fractional melting must take place in a hydrous environment. Comparison of the volumes of the hydrated upper layer of the oceanic slab with the volumes of lavas produced, suggests that fractional melting is also a localized phenomena. Fractional melting of parts of the slab at the amphibolite stage involves decomposition of hornblende so that the trace element chemistry of the melt will in part reflect that of amphibole. Although all the K and Rb of the amphibolite will presumably go into the melt rather than into residual phases, the amount of melt

relative to residue is likely to be large at this stage so that the K/Rb of the resultant melt will also reflect that of the original rock (oceanic tholeiite).

If the thermal regime is such that the solidus temperature of some part of the slab, not previously affected by partial melting, is exceeded at the pyroxene granulite or eclogite stage, then this temperature will be above the phlogopite stability and the decomposition of this phase will strongly influence the chemistry of the melts (high K and low K/Rb). Phlogopite-bearing rocks were not necessarily oceanic tholeiites, but could have been alkali-rich basalts similar to those found in some oceanic islands. The amount of magma produced relative to residual phases (pyroxene and garnet) is very low at this stage.

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Appendix 6. P. Jakes<sup>v</sup> and J.B. Gill  
Rare earth elements and island arc  
tholeiitic series.

# RARE EARTH ELEMENTS AND THE ISLAND ARC THOLEIITIC SERIES

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## Abstract

It is chemically inappropriate to call many of the rocks in island arcs calc-alkaline and we suggest they be known as the "island arc tholeiitic series". They differ from calc-alkaline rocks by having a lower silica mode, more iron-enrichment, higher  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios, less K and associated trace elements,  $\text{K/Rb} \sim 1000$ ,  $\text{Th} \sim 1-2$ , and chondritic REE patterns with  $\text{La/Yb} = 1-2$ . When erupting concurrently, rocks with these characteristics occur above shallower earthquake foci on the trenchward side of island arcs than do the calc-alkaline. They and not rocks of the traditional calc-alkaline series are the most dominant in many western Pacific and Atlantic Island arcs and represent the earliest stages in arc evolution.

Although sharing some tholeiitic features, they differ from normal tholeiitic series by having a higher percentage of intermediate and acid members and too little normative olivine, for example, to have been in equilibrium with peridotite. In such distinctive features as REE, Th, and U contents and  $\text{La/Yb}$ ,

Th/U, and K/Rb ratios, they are more like mid-ocean ridge tholeiites than any other terrestrial rocks, but they differ from them in silica mode, alkali content and isotopic composition, and MgO, FeO, Ni, and Cr contents. Some of their spatial, temporal, and chemical characteristics may be explained by mixing of the partial melting products of resorbed lithosphere and overlying upper mantle.

We report REE data for 19 samples, chosen to highlight the different patterns found in modern and ancient island arcs.

## I. INTRODUCTION

It is important to understand the petrochemistry of island arc volcanism, not only because it is volumetrically more significant than any other subaerial volcanism at present, but also because in the idea of plate tectonics it is associated with sites where lithosphere is thought to be resorbed (1). Thus, island arcs provide further tests for plate tectonics, form a critical link between plate tectonics and theories of orogenesis, and may have significance in the development and maintenance of continents.

It is a truism of modern geology that the typical volcanic rocks of island arcs or orogenic zones are andesites and subordinate amounts of closely related basalts, dacites, and rhyolites. This association is commonly called the calc-alkaline rock series. It is traditionally distinguished from the alkali basalt series by high alkali-lime indices (2) and from the tholeiitic series because it lacks iron enrichment and is characterized by more intermediate than basic members. Trace element contents of calc-alkaline rocks have been summarized by Nockolds and Allen (3) and Taylor (4). As a result of this truism, island arcs are often treated as featureless piles of calc-alkaline volcanics eagerly awaiting accretion to the nearest continent.

It is difficult to reconcile this view with the spatial zonation that has been recognized in Japan for nearly four decades (5) and more recently in other circum-Pacific arcs

(6,7). Fundamental to the idea of zonation is recognition that all rocks in island arcs are not calc-alkaline and that rocks of the tholeiitic series occur closest to the trench while alkali basalts or shoshonites occur furthest from the trench. Recently a temporal variation in island arcs has also been emphasized (7,8,9,10) in which tholeiitic rocks occur prior to eruption of the calc-alkaline, and alkali basalts or shoshonites afterwards.

Although this occurrence of tholeiitic rocks in island arcs was long emphasized by Kuno (11) and recognized by Tilley (12), it seems to have been largely ignored or thought volumetrically insignificant - at most, one parent from which a calc-alkaline series might have differentiated. We contend, however, not only that there is a complete and separate "island arc tholeiitic magma series" which can be distinguished chemically, spatially, and temporally from the "calc-alkaline magma series", but also that it is at least as if not more common than the calc-alkaline series in Tertiary circum-Pacific island arcs. In this paper we summarize evidence for this contention and present rare earth element data for some Recent and older island arc tholeiites. Using these data we emphasize the differences between rocks of the island arc tholeiitic and calc-alkaline series, re-emphasize that abyssal tholeiites are not the only terrestrial rocks with chondritic rare earth abundance patterns, and argue that the ophiolite complexes of island arcs and orogenic areas need

not be considered fossil remnants of ocean crust.

## II. COMPARISON BETWEEN THE CALC-ALKALINE AND ISLAND ARC THOLEIITIC SERIES

The distinctive rocks of island arcs and orogenic zones are an association which on petrographic criteria would be called basalt, andesite, dacite, and rhyolite, in which intermediate members are more common than basic. Such an association is usually called the "calc-alkaline series". It is both possible and useful, however, to distinguish between two different rock series in many island arcs both having these general petrographic characteristics. (A third and alkaline series also occurs but will not be considered here.) Failure to make this distinction has led to confusion about the nature of island arc magmatism and added unnecessary complexity to the "andesite problem".

Petrographically the "typical" calc-alkaline series is principally characterized by large plagioclase phenocrysts with complex oscillatory zoning, moth-eaten appearance, and calcic cores, and by groundmass pyroxene which is more likely to be hypersthene than pigeonite. Chemically its most distinguishing features are a silica mode of 58-59%, lack of iron enrichment (Fig. 1), and moderate concentrations and enrichment of  $K_2O$  (Fig. 2); other useful chemical features are summarized in Table 1.

Also in Table 1 are data for many rocks occurring in island arcs which it is chemically inappropriate to call calc-alkaline. Although they have a similar silica range, the mode is 53-54%. They have varying degrees of iron enrichment (Fig. 1), less  $K_2O$  (Fig. 2) and Rb, Ba, Cs, Pb, and Sr, higher  $Na_2O/K_2O$  and K/Rb ratios, lower Th and U contents and Th/U ratios, low Ni (0-30 ppm) and Cr (0-50 ppm), and REE concentrations as discussed later. Analyses of samples with intermediate silica content from each series are contrasted in Table 2. Spatially these rocks occur closer to the trench (i.e., above shallower earthquake foci) than do the calc-alkaline. Temporally they represent the earliest volcanism in oceanic island arc history and often form an extensive basement upon which subsequent calc-alkaline volcanism develops. Their phenocryst mineralogy is similar to that of calc-alkaline rocks but phenocrysts are less abundant, there are more opaques, and the groundmass pyroxene is more likely to be pigeonite than hypersthene. These can be distinguished from calc-alkaline rocks in many Tertiary (7,8), Paleozoic (14) and even Archean orogenic zones (15).

Because these rocks are not calc-alkaline as traditionally understood, and because they persistently differ in chemistry, space, and time from those which are calc-alkaline, we propose to emphasize these differences by using a name other than calc-alkaline to describe them. Because they are less potassic, more iron-enriched, more likely to have groundmass pigeonite

in their basic members, and were considered tholeiitic by Tilley (12), we suggest that they be called the "island arc tholeiitic series". "Tholeiitic" is thus used to describe rocks with silica contents ranging between 45-75%. As in any empirical classification the criteria employed are relative and the classes are end members of a continuum between which there is considerable overlap. Although in any one area (i.e., Fiji, the Lesser Antilles) there be no overlap, some of these criteria and particularly the amount of iron enrichment may vary independently thereby blurring the distinction.

### III. ANALYTICAL METHODS

REE data were obtained using spark-source mass spectrographic methods similar to those of Taylor (16). Lu 175 was used as an internal standard and the W-1 and G-1 concentrations adopted by Gill (8) were used for calibration except for Gd where his values were doubled. Samples were analyzed in duplicate or triplicate. Precision, expressed as relative deviation ( $1\sigma$ ) and measured by replicate analyses, is  $\pm 10\%$  for all elements except Gd which is  $\pm 15\%$ .

### IV. RESULTS

Flat rare earth abundance patterns parallel but enriched relative to those of chondrites are thought by some (17) to unambiguously characterise abyssal basalts of mid-ocean ridges

Such patterns have been known in rocks of island arcs for some time (18, 19), but, as with the tholeiitic volcanics in which they occur, they have been largely ignored.

Rare earth data for nineteen samples are listed in Table 3 and presented relative to the average of nine chondrites (19) in Figures 3-5. These samples were chosen to represent the variety of rocks occurring in several southwest Pacific island arcs from which we had specimens. "Chondritic" patterns are shown in each figure characterizing samples from recent volcanism in New Britain, basement complexes of Eastern Papua, New Guinea, the Solomon islands, and Macquarie Ridge, two Archean and one Proterozoic site. These flat rare earth patterns are characteristic of rocks of the island arc tholeiitic series. They have been described in rocks of this series from Japan (18), Saipan (20), Fiji (8), and Tonga (21).

Figure 6 summarizes published island arc REE data (54 analyses from 9 western Pacific arcs) and compares them with data for mid-ocean tholeiites (22). Rare earth abundance patterns in abyssal and arc tholeiitic series are almost identical and no more characteristic of one than the other. Whatever genetic constraints are implied by such patterns, they apply equally to both. No significant positive or negative Eu anomalies occur in our tholeiitic samples (although Gd precision is poor) which suggests that their  $\text{Al}_2\text{O}_3$  contents are primary and not the accidental result of plagioclase accumulation, and that plagioclase crystallization has not been sufficient

to affect the REE distribution as is argued for abyssal tholeiites (23).

From Figures 3-6 it is clear that rocks of the calc-alkaline and island arc tholeiitic series have different rare earth abundance patterns, a difference that is maintained even at  $\text{SiO}_2 = 70-75\%$  (8, 20). In contrast to the chondritic patterns of island arc tholeiitic rocks, calc-alkaline samples have patterns enriched in the lighter elements (La-Sm) with concentrations similar to those of Hawaiian tholeiites (24). They have La/Yb ratios of 5-20, clustering around 6-8, whereas those of the island arc tholeiitic series are less than 3 and usually 1-2. Calc-alkaline and more  $\text{K}_2\text{O}$ -rich rocks having these inflected REE patterns and higher La/Yb ratios have also been reported from Japan (18, 25), Bougainville (20), Fiji (8, 20), and New Zealand (25).

There is a weak correlation between  $\text{K}_2\text{O}$  and La (Figure 7 and 20) and between  $\text{K}_2\text{O}$  and La/Yb ratios (Figure 8) in island arcs. This may be significant in light of the apparent depth dependence on  $\text{K}_2\text{O}$  in such samples (26). However, in contrast to Japanese alkali basalts, most New Guinea and Fiji shoshonites have neither the high La nor correspondingly high La/Yb ratios expected in high-K rocks.

It is of fundamental importance to realize that volcanic rocks with chondritic REE patterns are characteristic of the early tholeiitic stages in island arc evolution. The recent eruption of such rocks in Japan, New Britain, and Tonga and

their occurrence in the mid-Tertiary basement complexes of Saipan and several Melanesian arcs make it unnecessary to assume that such similar rocks as the Mesozoic ophiolites of Papua or those of Macquarie Ridge were derived from a mid-ocean ridge or pre-arc environment.

#### V. SIGNIFICANCE OF THE ISLAND ARC THOLEIITIC SERIES

Rocks of the island arc tholeiitic series are at least as and perhaps more common than those of the calc-alkaline series in Tertiary oceanic island arcs. These arcs are characterized either by Quaternary volcanism which is principally or entirely tholeiitic (i.e., Japan (13), New Britain, the southern Kurile and South Sandwich islands), by an extensive mid-Tertiary or older tholeiitic basement on which more recent calc-alkaline  $\pm$  shoshonitic volcanism may have developed (i.e., Saipan-Guam, Fiji, the Solomon and Aleutian islands, and the Antilles), or both (Tonga). Only the abundance of Quaternary calc-alkaline volcanism in the Americas and Lesser Antilles lured petrologists into believing it was the dominant rock type of island arcs.

Although island arc basement volcanics are not well studied, they often bear evidence of submarine volcanism (pillow lavas associated with radiolarian cherts, pelagic limestones, and turbidites) and have an abundance of spilites, keratophyres, or entire ophiolite sequences including alpine ultramafics. As already stressed, an important corollary of

of recognising the integral importance of non-calcalkaline volcanism in island arcs is that the tholeiitic/ophiolitic rocks of island arc basements or other orogenic belts could have originated where they now are, i.e., at sites where lithosphere is consumed, not created. While it may yet prove correct, it is at least unnecessary to assume (27) that alpine ultramafic or ophiolite complexes originated at mid-ocean ridges and were moved to their present location by sea-floor spreading.

The volumetric significance of this volcanic basement is difficult to assess but is likely to equal or exceed that of its calc-alkaline successors. For example, the so-called "non-volcanic ridges" of Indonesia (28) and Tonga (29), are known to include rocks of more tholeiitic than calc-alkaline affinities.

Where occurring alone, the spilites and keratophyres of this association are indistinguishable from rocks of the island arc tholeiitic series (8,9). The mafic lavas of ophiolite complexes are usually tholeiitic (30), but whether any particular such rocks can be designated as mid-ocean ridge or island arc tholeiites depends on our ability to distinguish between these two.

## VI. COMPARISON BETWEEN THE MID-OCEAN AND ISLAND ARC THOLEIITIC SERIES

Salient chemical features of island arc and abyssal tholeiites are summarized in Table 1. In such distinctive

aspects as Th, U, and REE contents and K/Rb, La/Yb, and Th/U ratios, they resemble each other more than any other terrestrial rock type. Rocks of both series have lower concentrations of K and related trace elements than do those of calc-alkaline or continental and Hawaiian tholeiitic series, but this is more pronounced in abyssal tholeiites.

It is important, however, to emphasize this and other differences. Although similar in  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  ranges, rocks of the island arc tholeiitic series have a greater silica range and many more rocks with  $\text{SiO}_2 > 52\%$ . At any silica content they have less FeO, MgO, Ni, and Cr but more K, Rb, Ba, Cs, Pb, and Sr and these differences appear critical. The contrast in iron enrichment pattern during fractionation is marked and illustrated in Figure 2.

Not only do island arc tholeiitic rocks have higher concentrations of alkali elements, these also have a somewhat more radiogenic character. When normalized to 0.7080 for the MIT Sr standard, initial Sr 87/86 ratios of Pacific abyssal tholeiites average 0.7024 (31), whereas those of arc tholeiites average 0.7034 in Japan (32), 0.7038 in Saipan (33), 0.7035 in New Britain (34), 0.7041 in Fiji (8), and 0.7042 in the Antilles (9). Hawaiian tholeiites have ratios of 0.703-0.704 (35). Whether this variation reflects genetically significant differences or just lateral upper mantle inhomogeneities is not clear.

Both Japanese and Antillean tholeiites are slightly richer in  $\text{Pb}^{207}$  than their abyssal counterparts when corrected for instrumental mass fractionation (8, 32, 36, 37, 38). In addition, Japanese differ from abyssal tholeiites in having an inverse rather than positive correlation between  $\text{Pb } 206/204$  and  $\text{U}238/\text{Pb}204$  (37). Thus, although neither Sr nor Pb isotopic compositions unambiguously delimit genetically significant differences between the two tholeiitic series, they may suggest a somewhat greater radiogenic component in the geochemical reservoir from which the arc variety came.

#### VII. GENESIS OF THE ISLAND ARC THOLEIITIC SERIES

Island arc tholeiites are chemically analagous to, but nevertheless different from, both calc-alkaline and abyssal tholeiitic rocks. Whatever is said about their genesis depends in part on which analogy is emphasized.

If they are but a variation on the traditional calc-alkaline theme, one must modify theories of calc-alkaline genesis to explain the chemical differences. They cannot be explained by fractionation under lower and less constant  $p\text{O}_2$  from the same basaltic parent which under other conditions produced a calc-alkaline series because: (1) this explains neither the difference in  $\text{SiO}_2$  mode nor the differences in alkali element, REE, Th, or U concentrations which are persistent throughout the series and seem to include the basaltic members; (2) the abundance of intermediate and acidic rocks

in both series makes fractionation of basaltic magma alone seem inadequate; and (3) it fails to explain the consistent temporal and spatial relationships between rocks of the two series. Calc-alkaline magmatism (s.s.) in oceanic island arcs may alternatively result from partial melting of amphibolite or quartz eclogite either at the base of an arc or in lithosphere thrust beneath it (39), or from the incongruent melting of enstatite in the upper mantle under high  $\text{pH}_2\text{O}$  (40). Neither process is well enough understood to see how it could be modified to also consistently yield rocks of the island arc tholeiitic series at the right time and place.

If, instead, the similarities with abyssal tholeiites are emphasized, the residual differences might be explained by adding small amounts of radiogenic alkalis and oxygen to a tholeiitic magma or magma source. One possible source for both is the lithosphere thought to be thrust beneath island arcs (1), particularly if that lithosphere includes minor alkali basalts or has retained some portion of its sedimentary component and free water.

Oceanic sediments are rich in K, Rb, Ba, Cs, Pb, and Sr (41), and their Sr and Pb are enriched in radiogenic isotopes (42). One would expect some fraction of these volatile elements together with  $\text{H}_2\text{O}$  to be lost either through dehydration of sinking lithosphere (the upper portion of which is likely to move from greenschist to amphibolite or eclogite facies assemblages) or upon its initial melting. The low-melting

fraction fraction of this hydrated and dominantly mafic upper surface of lithosphere would be andesitic to dacitic in composition (39). The depth at which this would be expected is dependent on the angle and rate of underthrusting and the composition of the slab. Using isotherms calculated by Minear and Toksoz (43), any such melt would rise into even hotter overlying upper mantle, probably resulting in its partial fusion and/or hydration. Such a process might yield olivine tholeiitic magma either near the surface or underthrusting or at depths of 15-35 fm in a rising diapir of previously depleted but partially molten and/or hydrous peridotite (44).

Magma evolution in more oxygen-rich environments will result in less iron enrichment during fractionation (45). Rocks of the island arc tholeiitic series seem to have had access to more oxygen than those of the abyssal tholeiitic series (Fig. 2). If  $\text{Cr}^{+2}$  as well as  $\text{Fe}^{+2}$  is oxidized under such conditions and precipitated as chromite, this could account for both the order of magnitude lower Cr contents in island arc tholeiitic basalts and the concentrations of podiform chromite deposits in island arcs (46). Absence of inflection of negative Eu anomalies in island arc tholeiitic REE patterns suggests that olivine more than plagioclase has dominated early fractionation history and the low Ni contents agree. This is also consistent with the presence of increased

$\text{pO}_2$  (47). All island arc tholeiitic basalts reported in the literature have too little MgO, Ni, and Cr to have been in equilibrium with peridotite. Therefore, they either represent fusion products from a mafic rather than ultramafic source (as discussed above), or have lost considerable olivine by crystal settling. The range of rock types and characteristic plagioclase phenocrysts of both the island arc tholeiitic and calc-alkaline series suggest that both have undergone extensive and probably near-surface fractionation.

If island arc tholeiitic rocks do result from mixing the early melting fraction of descending lithosphere with that of the upper mantle overlying it (37), this could explain both the continuity between the island arc tholeiitic and calc-alkaline series and the intimate association of tholeiitic and alpine ultramafic rocks in island arcs and other orogenic zones.

#### VIII. CONCLUSIONS

It is possible and important to distinguish between calc-alkaline and tholeiitic rock series in island arcs and to recognize the volumetric significance of the latter. We have attempted to facilitate this distinction by delineating the general geochemical characteristics of the island arc tholeiitic series and its REE features in particular. There are similarities between abyssal and arc tholeiites but also significant differences.

The current eruption of such tholeiites in island arcs demonstrates conclusively that rocks which occur in arc basements and have similar chemical characteristics could have originated in an arc environment and need not be rinds of oceanic crust. This is not to say that some ophiolite complexes or their purely eruptive equivalents in island arcs or orogenic zones could not be the original oceanic crust upon which the arc developed or pieces of allochthonous crust moved into place by sea floor spreading. It merely argues that this is not necessarily so, as is often assumed. Whether any particular tholeiite or ophiolite complex now in an island arc or Alpine belt did in fact originate above descending lithosphere is a matter for debate, the resolution for which depends on our ability to distinguish between arc and abyssal tholeiites.

Whether one explain the genesis of the island arc tholeiitic series by reference to a mafic or ultramafic source depends on whether its similarities to the calc-alkaline or tholeiitic series are emphasized. It may be possible to explain their distinguishing chemical features by envisioning an imprecise mixture of partial melts from descending lithosphere, enriched in alkalis and water, and overlying upper mantle. Such a process may yield both the continuum between the calc-alkaline and island arc tholeiitic series and the association of the latter with alpine ultramafic rocks in island arcs.

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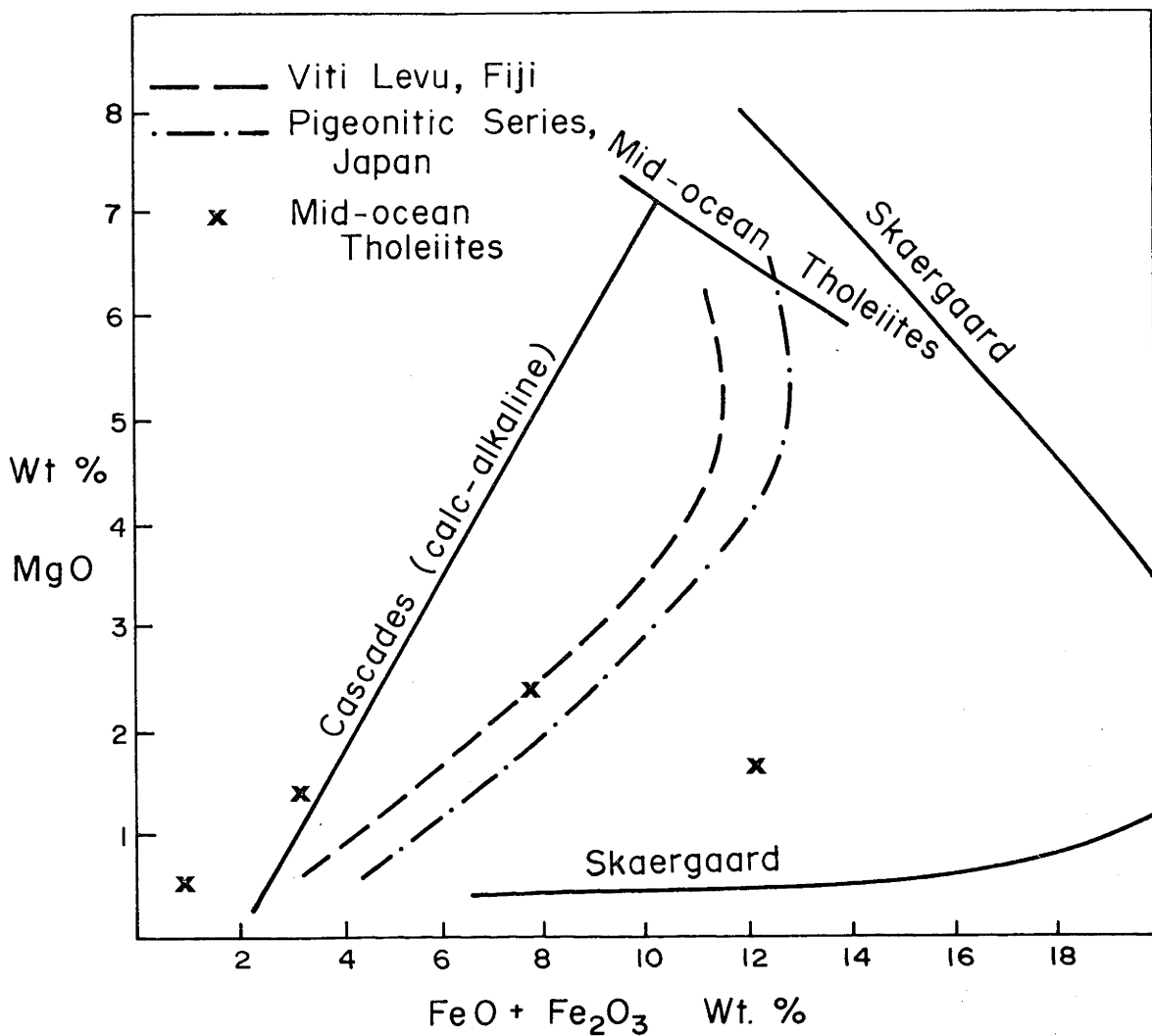


Figure 1.

Generalized MgO-FeO+Fe<sub>2</sub>O<sub>3</sub> relationships in selected igneous provinces. Data for the Cascades are from (54), Fiji (8), pigeonitic series of Japan (11), mid-ocean tholeiites (23), and the Skaergaard (55).

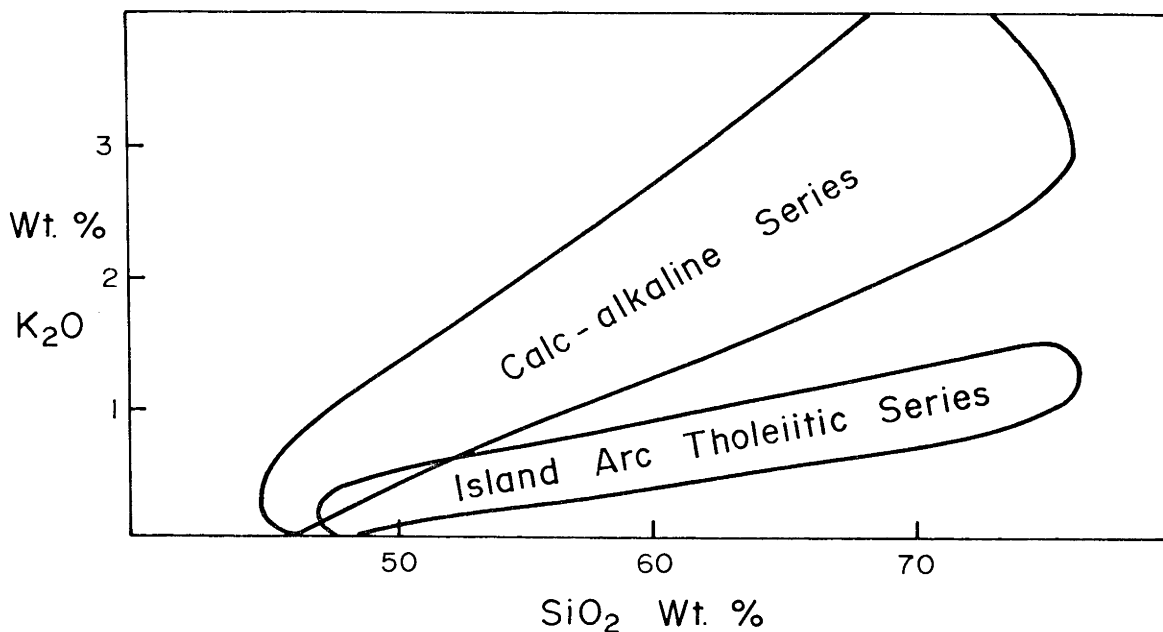
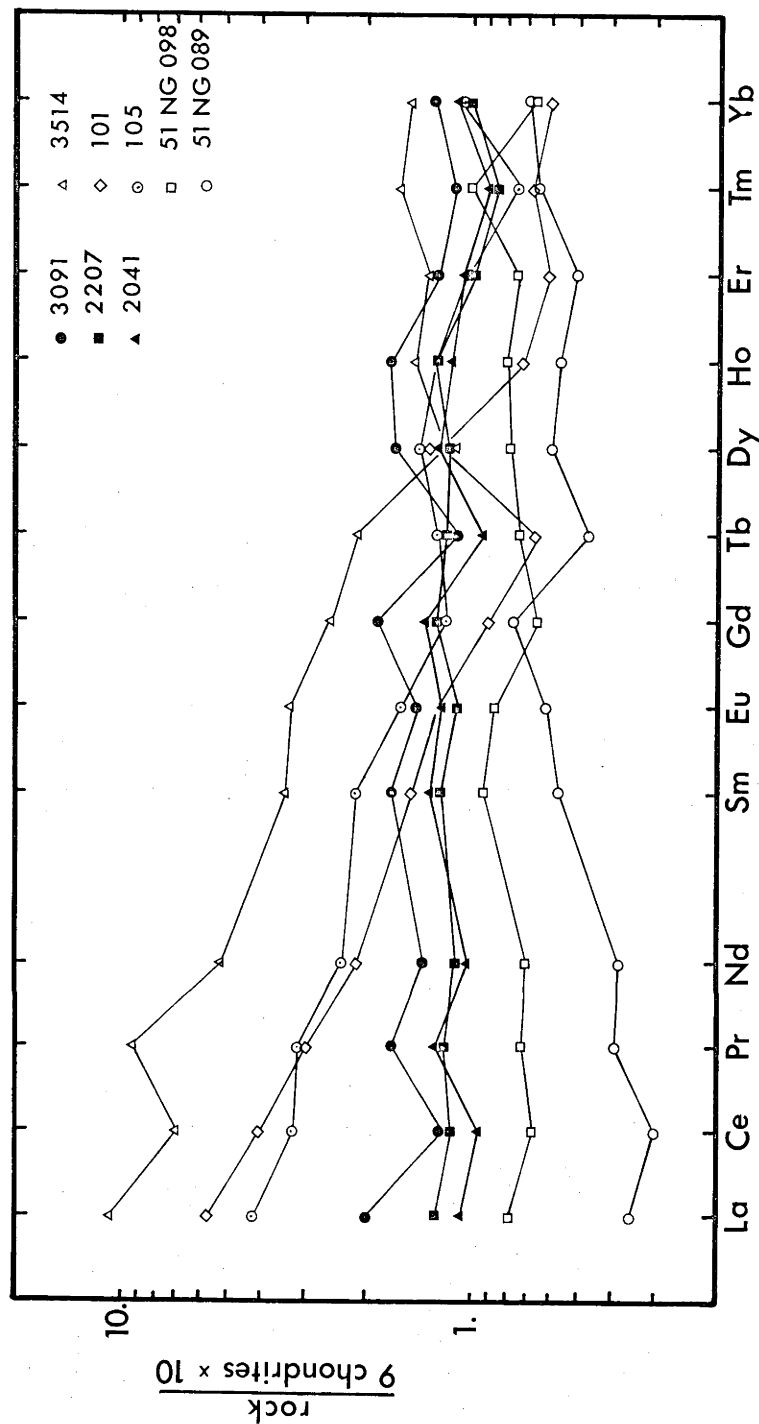


Figure 2

Generalized K<sub>2</sub>O-SiO<sub>2</sub> relationships in selected island arcs. Data from Gill (8) Fig. 8). Analyses from Tonga, Fiji, S. Kurile and S. Sandwich islands, Saipan-Guam, and the pigeonitic series of Japan and the Izu-N. Mariana islands all fall within the island arc tholeiitic series field. Analyses from the Aleutian and N. Kurile islands, central New Guinea, Bougainville, the New Hebrides, and central Viti Levu, Fiji fall within the calc-alkaline series field. Note that analyses from St. Kitts, Lesser Antilles also plot within the island arc tholeiitic field but have no iron-enrichment. Similarly, those from northern New Guinea and New Britain have characteristic iron enrichment but nevertheless plot within the calc-alkaline field.



**Figure 3**

Relative rare earth element patterns for rocks from Papua-New Guinea. Empty symbols Recent lavas : 3514 - Andesite from Mt. Victory, Cape Nelson-East Papua, 101 and 105 latite and shoshonite from New Guinea Highlands, Mt. Giluwe and Mt. Hagen respectively, 51 NG 098 and 51 NG 089 island are tholeiites from Uluwatu volcano New Britain. Full symbols basement tholeiitic lavas from Eastern Papua (samples by courtesy of I. Smith).

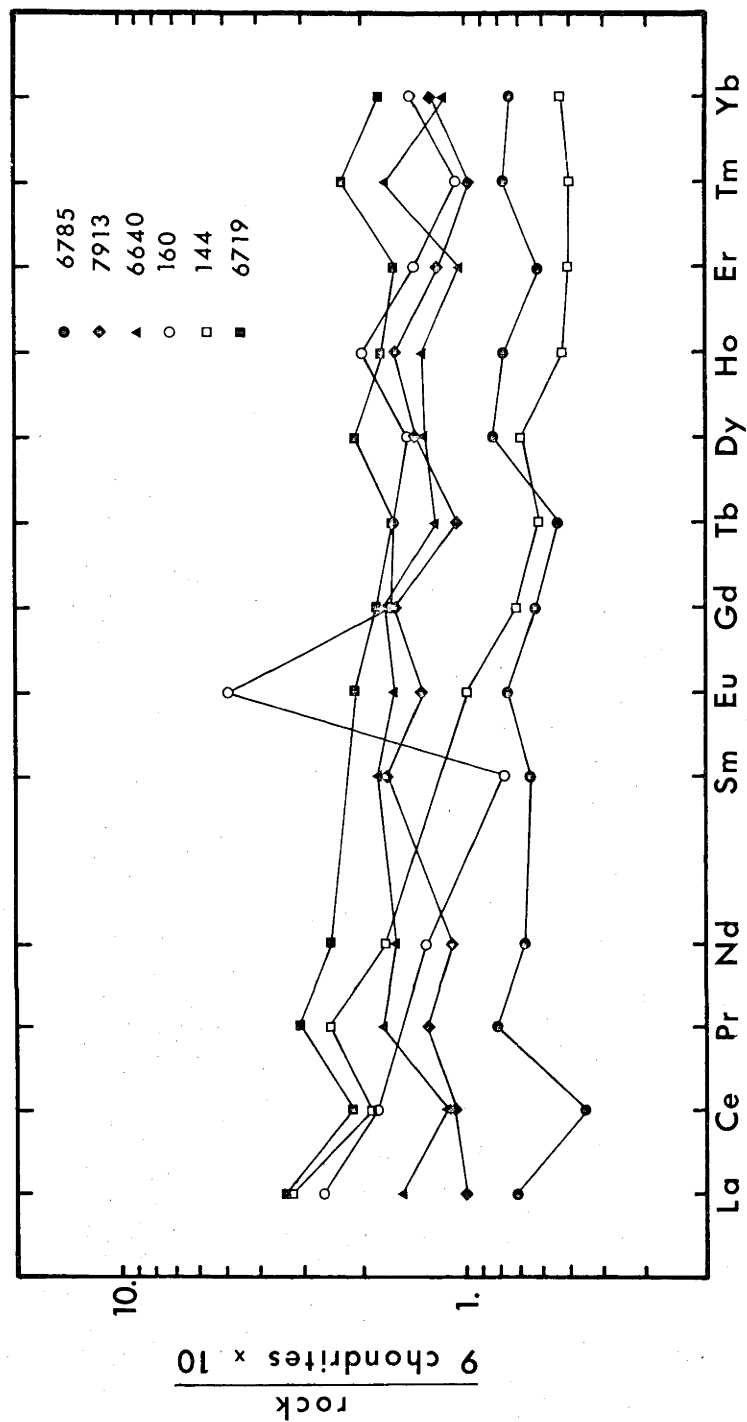


Figure 4

Relative rare earth element patterns for rocks from Solomon Islands. Empty symbols Recent lavas from Savo (160) and Guadalcanal (144). Full symbols Tertiary lavas of Guadalcanal basement (samples by courtesy of Dr. B. Hackman).

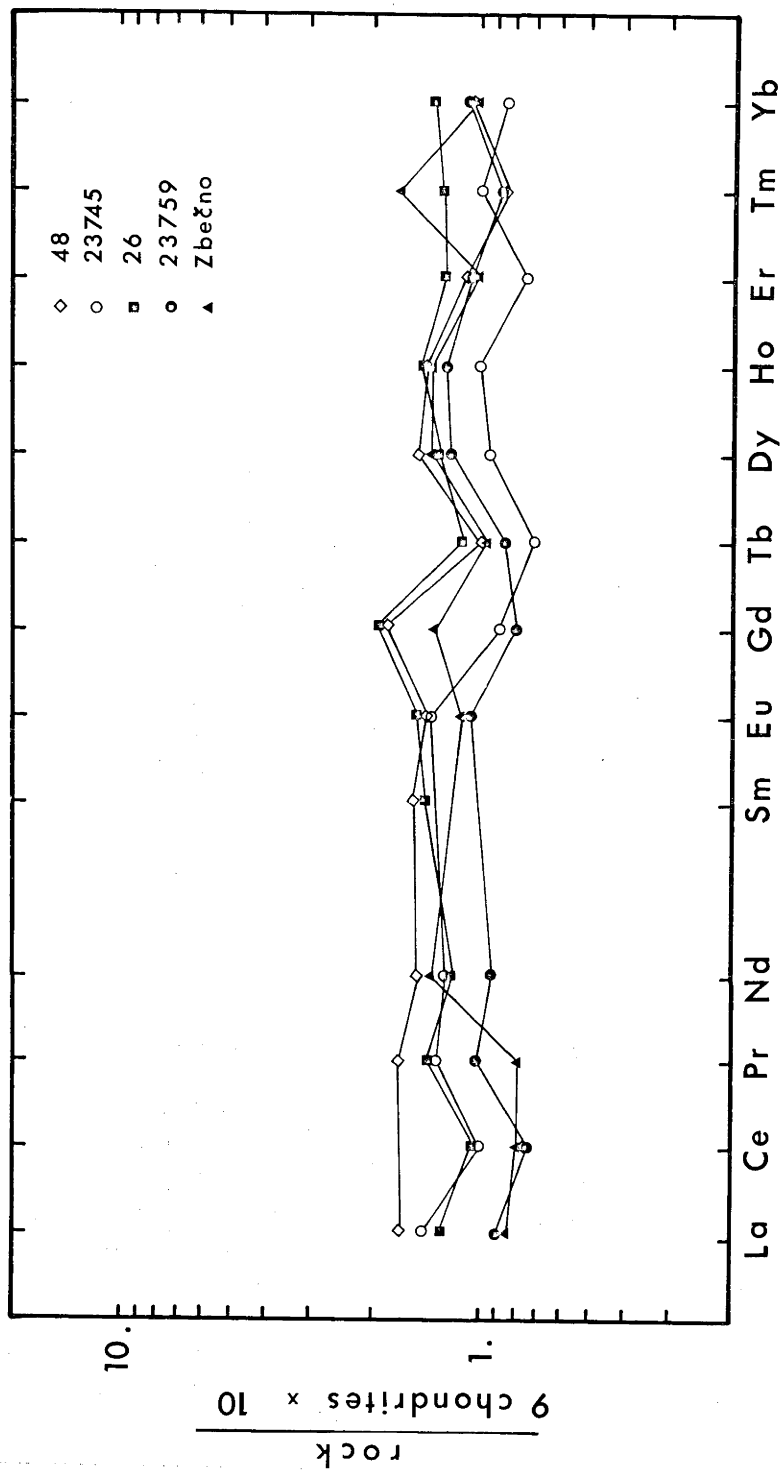
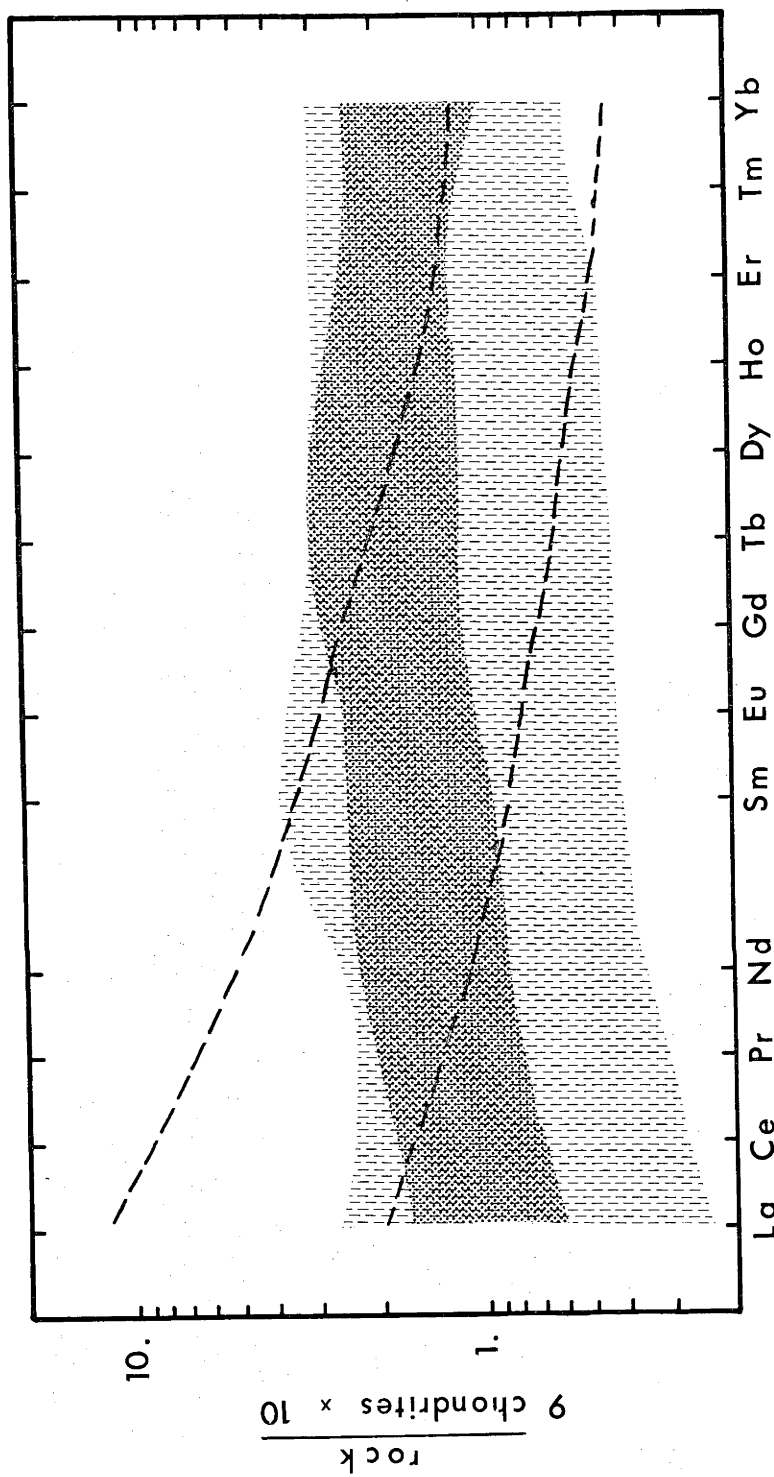


Figure 5

Relative rare earth element patterns for rock from Macquarie Island (48, 26), spilite from Upper Proterozoic of Czech Massif (Zbečno), and meta-tholeiites from Archaean greenstone belt - Norseman Western Australia.



**Figure 6**

Relative rare earth element patterns of published and new data on island arc tholeiites (vertical stiples), compared with patterns on mid-ocean tholeiites (22) and published and new data on calc-alkaline, shoshonitic and alkaline rocks of island arcs (between dashed lines).

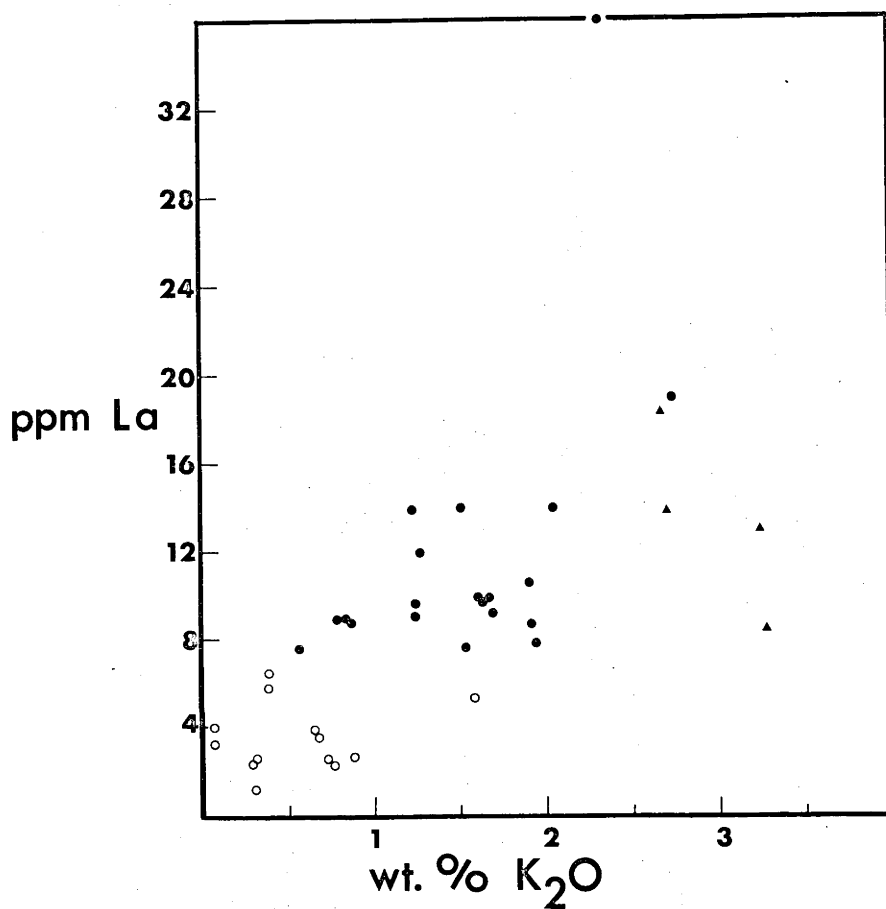


Figure 7

Correlation of  $K_2O$  and La content for island arc rocks including published and new data. Open circles - island arc tholeiites; full circles - calc-alkaline rocks; triangles, shoshonitic rocks from island arcs.

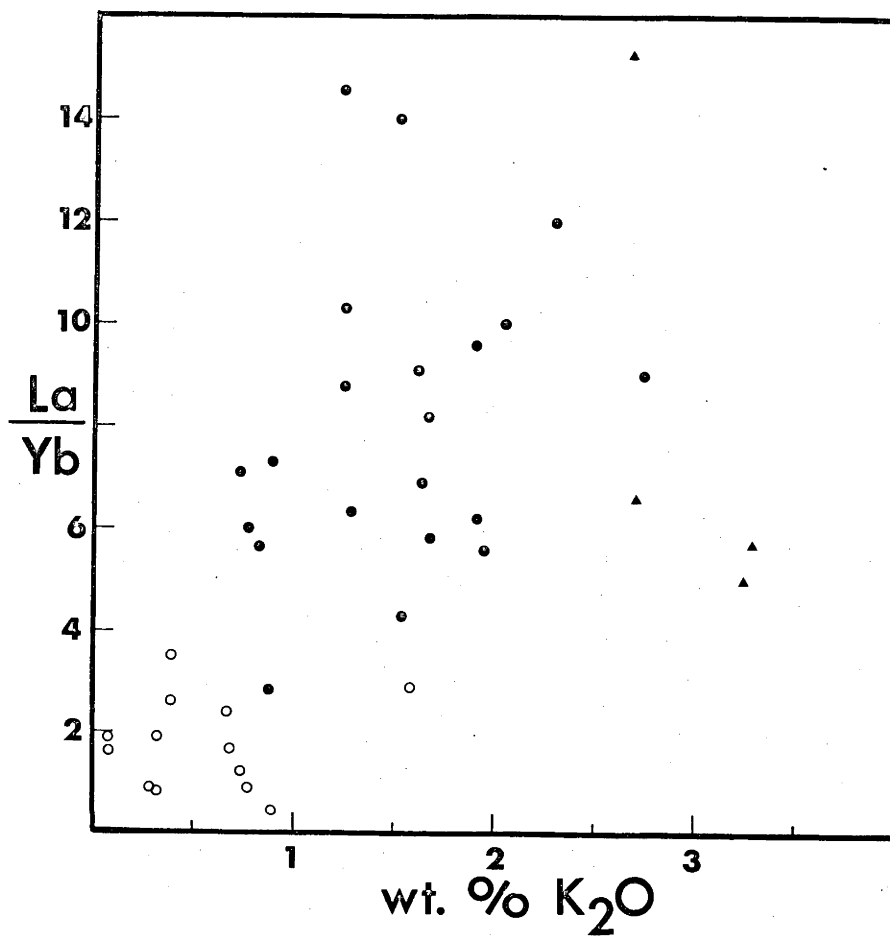


Figure 8

Correlation of K<sub>2</sub>O content and La/Yb ratio. Symbols as in Figure 7.

Table 1.

Comparison of means and ranges for selected  
chemical features of three rock series

|                                    | <u>Calc-alkaline</u><br><u>Series</u> | <u>Island Arc</u><br><u>Tholeiitic</u><br><u>Series</u> | <u>Abyssal</u><br><u>Tholeiitic</u><br><u>Series</u> |
|------------------------------------|---------------------------------------|---------------------------------------------------------|------------------------------------------------------|
| SiO <sub>2</sub> Range             | 53-70%                                | 45-75%                                                  | 47-62%                                               |
| mode                               | 59%                                   | 53%                                                     | 49%                                                  |
| TiO <sub>2</sub>                   | 0.5-1.2%                              | 0.5-1.5%                                                | 1.0-2.5%                                             |
| Al <sub>2</sub> O <sub>3</sub>     | 16-19%                                | 14-19%                                                  | 14-19%                                               |
| Na <sub>2</sub> O/K <sub>2</sub> O | 2-3                                   | 4-6                                                     | 10-15                                                |
| Rb                                 | 30 ppm                                | 3-10 ppm                                                | 0.2-5.0 ppm                                          |
| Sr                                 | 380 "                                 | 100-200 "                                               | 70-150 "                                             |
| Ba                                 | 270 "                                 | 50-150 "                                                | 6-30 "                                               |
| Pb                                 | 3-7 "                                 | 2-4 "                                                   | 0.5 "                                                |
| Cs                                 | 0.5-1.0 ppm                           | 0.1 "                                                   | .05 "                                                |
| K/Rb                               | 400-500                               | 1000                                                    | 1000                                                 |
| Rb/Sr                              | .05-.10                               | .01-.05                                                 | .02                                                  |
| Th                                 | 2 ppm                                 | 0.5 ppm                                                 | .15 ppm                                              |
| U                                  | 0.7 "                                 | 0.3 "                                                   | .10 "                                                |
| Th/U                               | 3-4                                   | 1-2                                                     | 1-2                                                  |
| Ni                                 | 18 "                                  | 0-30 "                                                  | 30-200 ppm                                           |
| Cr                                 | 56 "                                  | 0-50 "                                                  | 200-400 "                                            |
| La                                 | 12 "                                  | 1-6 "                                                   | 2-8 "                                                |
| La/Yb                              | 6-8                                   | 1-2                                                     | 1-2                                                  |

Table 1 (cont)

Data for the calc-alkaline series are compiled principally from this paper, Nockolds and Allen (3), Taylor (4), Chayes (48) and Taylor et al. (20); data for the island arc tholeiitic series are from this paper, Nockolds and Allen (8), Hier and Rogers (49), Masuda (18), Tatsumoto (37), Gill (8), Donnelly et al. (9), Ewart (unpublished) and Gill (unpublished); data for the abyssal tholeiitic series are from Engel et al. (50), Frey et al. (19), Tatsumoto (37), Philpotts et al. (51), Hart (52), Aumento (53) and Kay et al. (23).

Table 2 (cont)

|          | <u>Calc-alkaline</u> | <u>Island Arc</u> |
|----------|----------------------|-------------------|
|          | <u>Series</u> *      | <u>Tholeiitic</u> |
|          |                      | <u>Series**</u>   |
| Th       | 1.4                  | 0.31              |
| U        | 0.29                 | 0.34              |
| Th/U     | 4.8                  | 0.9               |
| La       | 9.1                  | 2.4               |
| La/Yb    | 10.3                 | 1.0               |
| Ni       | 8                    | nd                |
| Cr       | 36                   | 2                 |
| Sr 87/86 | 0.7040               | 0.7037            |

nd = not detectable; - = not measured

\* Data from Taylor et al. (20); Table 2, sample X-96 except Ni and Cr data from sample X-88 and Sr 87/86 for X-88 (Gill, unpublished).

\*\* Data from Gill (8); Table 1, sample 68-55 except for Cs, La and Yb data from sample 68-60.

TABLE 3

New data on rare earth elements in island arc  
rocks and older orogenic areas

|    | Solomon Islands<br>tholeiites |      |       | Eastern Papua<br>tholeiites |      |      | Macquarie<br>Island |      | Norseman, West<br>Australia<br>Greenstones | Upper Proterozoic of Czech<br>Massive spilit |       |        |
|----|-------------------------------|------|-------|-----------------------------|------|------|---------------------|------|--------------------------------------------|----------------------------------------------|-------|--------|
|    | 7913                          | 6640 | 6719  | 6785                        | 2041 | 2207 | 3091                | 26   | 48                                         | 23759                                        | 23745 | ZBECNO |
| La | 3.3                           | 5.2  | 10.8  | 2.3                         | 3.50 | 4.0  | 6.6                 | 4.2  | 5.3                                        | 2.9                                          | 4.8   | 2.8    |
| Ce | 9.8                           | 9.9  | 19.2  | 4.0                         | 8.4  | 10.0 | 10.5                | 9.1  | 6.7                                        | 6.5                                          | 8.8   | 6.9    |
| Pr | 1.4                           | 1.9  | 3.5   | .92                         | 1.4  | 1.4  | 1.9                 | 1.6  | 1.9                                        | 1.2                                          | 1.5   | .90    |
| Nd | 6.6                           | 9.6  | 14.9  | 4.2                         | 6.2  | 6.4  | 8.1                 | 7.3  | 9.1                                        | 5.6                                          | 7.5   | 8.30   |
| Sm | 3.1                           | 3.2  | n.d   | 1.2                         | 2.4  | 2.4  | 3.1                 | 2.7  | 2.8                                        | n.d                                          | n.d   | n.d    |
| Eu | .91                           | 1.1  | 1.4   | .53                         | .84  | .76  | .99                 | 1.0  | .95                                        | .73                                          | .95   | .78    |
| Gd | 4.1                           | 4.2  | 4.0   | 1.6                         | 3.4  | 3.2  | 4.6                 | 4.8  | 3.8                                        | 1.5                                          | 2.2   | 3.4    |
| Tb | .5                            | .58  | .75   | .26                         | .42  | .46  | .51                 | .48  | .45                                        | .41                                          | .34   | .45    |
| Dy | 4.5                           | 4.3  | 6.7   | 2.7                         | 3.8  | 3.8  | 5.3                 | 4.5  | 4.7                                        | 3.8                                          | 3.0   | 4.4    |
| Ho | 1.1                           | .91  | 1.3   | .55                         | .80  | .87  | 1.2                 | 1.0  | .98                                        | .80                                          | .70   | .95    |
| Er | 2.4                           | 2.0  | 3.2   | 1.25                        | 2.1  | 2.0  | 2.5                 | 2.5  | 2.3                                        | 2.1                                          | 1.5   | 2.1    |
| Tm | .29                           | .54  | .70   | .24                         | .27  | .25  | .33                 | .40  | .26                                        | .26                                          | .30   | .56    |
| Yb | 2.5                           | 2.2  | 3.6   | 1.5                         | 2.2  | 2.1  | 2.6                 | 2.7  | 2.3                                        | 2.1                                          | 1.7   | 2.1    |
| Ba | 6.3                           | 31.6 | 360.0 | 48.4                        | 16.4 | 23.1 | 24.5                | 38.2 | 25.3                                       | 85.0                                         | 92.0  | 44.5   |

TABLE 3 continued

|    | New Britain |                        | Guadalcanal      |        | Eastern Papua |                    | New Guinea Highlands |  |
|----|-------------|------------------------|------------------|--------|---------------|--------------------|----------------------|--|
|    | 51NG0089    | tholeiites<br>51NG0098 | andesites<br>144 | 160    | 3514B         | shoshonites<br>105 | 101                  |  |
| La | 1.1         | 2.5                    | 8.8              | 10.6   | 36.1          | 13.8               | 18.4                 |  |
| Ce | 2.6         | 5.8                    | 15.9             | 15.8   | 61.5          | 28.6               | 34.8                 |  |
| Pr | .44         | .81                    | n.d              | 2.8    | 10.3          | 3.40               | 3.3                  |  |
| Nd | 2.3         | 4.2                    | 8.0              | 10.1   | 31.1          | 13.8               | 12.6                 |  |
| Sm | 1.0         | 1.6                    | 1.4              | n.d    | 6.1           | 3.9                | 2.6                  |  |
| Eu | .43         | .59                    | 3.4              | .66    | 2.3           | 1.0                | .85                  |  |
| Gd | 1.9         | 1.6                    | 4.1              | 1.7    | 6.3           | 6.0                | 2.2                  |  |
| Tb | .22         | .34                    | .80              | .30    | 1.0           | .56                | .30                  |  |
| Dy | 1.9         | 2.5                    | 4.3              | 2.2    | 3.6           | 4.3                | 4.1                  |  |
| Ho | .40         | .55                    | 1.58             | .36    | 1.1           | .89                | .50                  |  |
| Er | 1.0         | 1.5                    | 2.6              | .98    | 2.4           | 2.0                | 1.2                  |  |
| Tm | .20         | .31                    | .30              | .15    | .5            | .24                | .2                   |  |
| Yb | 1.4         | 1.3                    | 3.1              | 1.0    | 3.0           | 2.1                | 1.2                  |  |
| Ba | 62.1        | 96.0                   | 300.0            | 1330.0 | 630.0         | 482.0              | 543.0                |  |

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Appendix 7. P. Jakeš and I.E. Smith  
High-K calc-alkaline rocks from  
Cape Nelson - East Papua.

**High potassium calc-alkaline rocks  
from Cape Nelson, Eastern Papua**

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**Abstract:** High-K calc-alkaline rocks from Cape Nelson, eastern Papua are dominated by andesites containing numerous basic inclusions. High-Al basalts and dacites are subordinate. The slight iron enrichment, variable  $Al_2O_3$  content and a systematic variation in  $K_2O/SiO_2$  correlation observed in these rocks suggests a relationship to the rocks of the shoshonite association. The chemical composition of the inclusions illustrates the trends of major and minor element evolution and contradicts the idea of complementarity of high-K calc-alkaline rocks and alpine ultramafic rocks. The chemical character of the lavas, (high Rb and Ba as well as high Cr and Ni) can be explained by a fractional melting which involves a mica phase.

## INTRODUCTION

The Cape Nelson volcanic complex on the north-eastern coast of Papua (Fig.1) consists of two Quaternary stratovolcanoes, Mount Victory (1925 metres) and Mount Trafalgar (1720 metres), and several small flank cones. The complex is composed of high-K calc-alkaline rocks, ranging from high-Al basalts to dacites.

FISHER (1957) gave a brief account of the location, form, structure and eruptive history of the Cape Nelson volcanoes. MORGAN (1966) presented one chemical analysis and described two specimens and JAKES and WHITE (1969) presented four chemical analyses from Mount Victory. Material for the present study was collected during a visit to the volcanoes in September 1968. In this paper new chemical data are presented and the origin of high-K calc-alkaline rocks and their relation to shoshonites are discussed.

## REGIONAL GEOLOGY

North-eastern Papua is made up of three south-easterly trending structural units (Fig.2).

a. the Owen Stanley metamorphic belt, composed of greenschist with minor amphibolite facies rocks of probable Cretaceous age.

b. the Papuan ultramafic belt.

c. the Cape Vogel geosyncline dating from the middle Miocene containing mainly shallow water terrigenous sediments and a

belt of Pliocene to Recent volcanoes of calc-alkaline and shoshonitic affinities (Fig.2). It contains the basaltic Sessara volcano (SMITH and GREEN, 1961) of mid-Pliocene age; the Pleistocene to Recent "trachybasalt to rhyodacite" associations on the Managlas Plateau (RUXTON, 1966) referred to here as shoshonitic association; Hydrographers Range representing the remnant of a Pleistocene calc-alkaline volcano; Mount Lamington, an active calc-alkaline stratovolcano well known since the catastrophic eruption of 1951 (TAYLOR, 1958) Waiowa volcano, active in 1943 - 1944 (BAKER, 1946) the most recent in a series of small volcanic cones to the south of Cape Nelson, and the two Cape Nelson volcanoes described here.

#### CAPE NELSON VOLCANIC COMPLEX

Mount Trafalgar is the remnant of one or possibly two Pleistocene volcanoes. Mount Victory is active, the latest phase of activity commenced during the 1890s with the eruption of nuée ardentes followed by a period of dome building. Four small flank cones are preserved on the south-western slopes of Mount Victory and a further two flank cones occur in the saddle between Mount Victory and Mount Trafalgar.

The rock nomenclature adopted here follows that of TAYLOR and WHITE (1966) and of TAYLOR et al. (1969). The lavas of the Cape Nelson volcanoes are mainly andesitic in composition with amphibole andesites forming more than 50% of all exposed rocks. From examination of 60 samples the estimated volume of erupted rocks forming the Cape Nelson complex is summarised as follows in Table 1:

Table 1

|                      | high-Al basalts | low-Si andesites | andesites | dacites |
|----------------------|-----------------|------------------|-----------|---------|
| SiO <sub>2</sub> wt% | < 53%           | 53-57%           | 57-63%    | < 63%   |
| estimated vol.       | 3%              | 37%              | 55%       | 5%      |

### PETROGRAPHY

Basalts (Table 2, analysis 1) These are porphyritic rocks with phenocrysts of plagioclase (3.5 mm), clinopyroxene and olivine set in a fine grained groundmass consisting of plagioclase, clinopyroxene, minor olivine, opaques and a small amount of glass. The plagioclase phenocrysts (An<sub>65-75</sub>) show normal zoning and, to a lesser extent, oscillatory zoning within a narrow range of composition. A zone of fine-inclusions between core and margin is common. The olivine phenocrysts (2.0 mm) are rounded with wide iddingsitic rims. Clinopyroxene (less than 2.0 mm) commonly with simple twins is subhedral; larger crystals contain inclusions of olivine and plagioclase.

Low-Si Andesites (Table 2, analyses 2-7) These are either moderately porphyritic or fine even-grained rocks. In the porphyritic varieties, plagioclase forms the dominant phenocryst (3.0 mm) accompanied by smaller phenocrysts of clinopyroxene, orthopyroxene, opaques, olivine and, rarely, amphibole and biotite. The groundmass consists of devitrified glass with plagioclase, clinopyroxene, orthopyroxene and opaques. Plagioclase phenocrysts (An<sub>35-63</sub>) exhibit normal and oscillatory zoning. Amphibole and biotite, when present, are surrounded by rims of opaque oxides. The non-porphyritic

varieties consist of clinopyroxene, altered olivine, flow-oriented plagioclase, opaques and rare orthopyroxene.

Andesites and dacites (Table 2, analyses 8-22) These are strongly porphyritic. Plagioclase and amphibole are common phenocrysts, whereas biotite, clinopyroxene, opaques and, rarely, alkali feldspar are less abundant. The fine-grained groundmass consists of abundant glass with crystals of plagioclase, amphibole, biotite, opaques and minor clinopyroxene. Plagioclase phenocrysts (5.0 mm) are strongly zoned and range in composition from andesine to labradorite. The amphibole is the common brown variety but deep red brown "oxyhornblende" or green amphibole occur in some specimens. Opaque oxide rims are common; sometimes several opaque zones may occur in one crystal alternating with zones of unaltered amphibole. Clinopyroxene occurs in aggregates often surrounded by a rim of fine-grained amphibole, or less commonly, biotite. Alkali feldspars occur as small (0.5 mm) phenocrysts in some specimens.

Inclusions (Table 3) Inclusions (up to 30 cms) are common in all rocks although they occur more commonly in the amphibole andesites. The following mineral assemblages have been observed:

1. Clinopyroxene + plagioclase + olivine  
± spinel + tremolite (secondary);
2. olivine + clinopyroxene + plagioclase ± opaques;
3. amphibole + biotite ± plagioclase;
4. amphibole + plagioclase + opaques;
5. plagioclase + clinopyroxene + olivine ± amphibole.

### PETROCHEMISTRY

The  $\text{SiO}_2$  content of the Cape Nelson rocks varies from 50 to 65 wt %. Basalts and low-Si andesites occur more frequently among the older units (Mount Trafalgar), whereas the  $\text{SiO}_2$ -rich lavas are more typical of later eruptions (Mount Victory).

The  $\text{Al}_2\text{O}_3$  content varies widely compared to other calc-alkaline associations ( $\text{Al}_2\text{O}_3$  14.20 - 18.20 %). The most common value is 16.2 % which is 1% lower <sup>than</sup> /in most calc-alkaline rocks (TAYLOR 1969). Data on other high-K calc-alkaline rocks suggest that large variations in  $\text{Al}_2\text{O}_3$  content are characteristic of these rocks, contrasting with the uniform values found in low-K calc-alkaline rocks. This observation can be extended to the shoshonite association<sup>1</sup>, where  $\text{Al}_2\text{O}_3$  values fluctuate by more than 5 % (c.f. JOPLIN, 1968; NICHOLLS and CARMICHAEL, 1969; JAKES and WHITE, 1969).

$\text{TiO}_2$ , CaO, MgO and  $\text{FeO} + \text{Fe}_2\text{O}_3$  show a negative correlation with  $\text{SiO}_2$ . On an AFM diagram (Fig.3) the Cape Nelson rocks show a comparatively flat trend; the "iron enrichment" characteristic of low-K rocks is indistinct. This is consistent with other high-K provinces including shoshonite provinces and with the observation that in island arc environment iron enrichment decreases with increasing  $\text{K}_2\text{O}$ .

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<sup>1</sup> The term "shoshonite association" is used arbitrarily for rocks termed by NICHOLLS and CARMICHAEL (1969) as the Absarokite-shoshonite-banakitite series.

The weight percent of alkali elements increases with increasing  $\text{SiO}_2$ ; the slope of the  $\text{K}_2\text{O}/\text{SiO}_2$  correlation is steep for the early lavas and flatter for the later lavas (Fig.4).

The ratio  $\text{FeO}/\text{Fe}_2\text{O}_3$  varies widely. The  $\text{SiO}_2$ -poor rocks are generally less oxidised than  $\text{SiO}_2$ -rich rocks. Comparison of  $\text{FeO}/\text{Fe}_2\text{O}_3$  of two different types of inclusions, (cumulative and accidental) and their host lavas indicates that the oxidation stage of most rocks is only slightly lower than the oxidation state of their cumulates whereas the  $\text{FeO}/\text{Fe}_2\text{O}_3$  ratio of accidental inclusions is substantially lower.

#### Minor elements

Ba, Sr, Rb, Cr, Ni, V, Sc, Y abundances correlate with major elements ( $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ) and with mineralogical variations in the samples. Ba and Sr generally increase with increasing  $\text{SiO}_2$  content, whereas Cr, Ni, Sc, Y and V decrease.

Barium is higher (400 ppm - 1500 ppm) than values given by TAYLOR (1969) for high-K andesites (400 ppm). EWART et al.'s (1968) data indicate that Ba concentrates into residual liquids; data on our rocks in which biotite is an early precipitating phase show that residual liquids can be Ba-poor.

Strontium (450 ppm - 950 ppm) increases with increase of  $\text{SiO}_2$  and consequently with  $\text{K}_2\text{O}$  (Fig.5). EWART et al. (1968) have shown that residual glasses of andesites are depleted in Sr relative to the whole rock. Since the feldspars are not major early crystallizing phases in some Cape Nelson rocks, strontium concentrates in the residual liquids causing a positive correlation of  $\text{Sr}/\text{K}_2\text{O}$  not found

in plutonic-calc-alkaline rocks (c.f. HALL, 1967).

Rubidium has been determined in two rocks and two inclusions; it varies with  $K_2O$  content. K/Rb ratios are very relatively low (245-300) compared with low-K calc-alkaline rocks (JAKES and WHITE, 1970).

The content of ferromagnesian trace elements (Ni, Cr, V) decreases with increasing  $SiO_2$  content. Ni values vary from 10 to 540 ppm and Cr values from 51 to 850 ppm (Fig.6). Relatively high Ni and Cr in the  $SiO_2$ -poor rocks is considered to result from olivine and clinopyroxene accumulation, although this is complicated by biotite accumulation. Specimen 6514 from Mount Victory, for example, has apparently been formed by accumulation of biotite; it has a high Ba content (1150 ppm), relatively low Ni and V content (54 and 86 ppm respectively) and moderately high Cr (300 ppm). On the other hand a rock from Mount Trafalgar (3527) with a similar  $SiO_2$  content appears to be the result of clinopyroxene and olivine cumulation and Ni and Cr values are very high (540 ppm and 850 ppm respectively), whereas Ba is lower by a factor of two.

#### INCLUSIONS

Two groups of inclusions occur:

1. Low-K, high-Ca inclusions usually of olivine-clinopyroxene + spinel mineralogy (sometimes with rims of amphibole and plagioclase) have low  $SiO_2$ , low  $Al_2O_3$  and low  $FeO/Fe_2O_3$  content.

2. High-K inclusions, mostly amphibole + plagioclase + biotite with a  $SiO_2$  content between 50 and 56%, have most of the chemical

features of the host high-K calc-alkaline rocks.

Low-K inclusions are characterised by high Cr and Ni abundances whereas the high-K inclusions have higher abundances of Ba, Sr, Rb, and La. Low-K inclusions petrographically correspond to the rocks of the nearby Papuan ultrabasic belt (SMITH and GREEN, 1961; DAVIES, 1968) whereas the high-K inclusions are considered to be early cumulates of the Cape Nelson lavas.

### DISCUSSION

The Cape Nelson volcanic rocks and their cognate inclusions illustrate two possible "high-level fractionation trends" of  $K_2O$ -rich calc-alkaline rocks. Microscopic criteria show that olivine + clinopyroxene + plagioclase on the one hand, and amphibole + biotite (+ minor plagioclase) on the other hand, can be liquidus or near liquidus phases. Early separation of olivine and clinopyroxene is not common, whereas cumulates of amphibole + biotite often occur. Chemical data on the Cape Nelson rock association suggest that the "cumulates" also occur as an independent rock type (lava flows). The correlation of  $K_2O/SiO_2$  and correlation of potassium-like minor elements with  $SiO_2$  shows the effect of amphibole and biotite fractionation. High  $K_2O$  and Ba values together with low Ni values in the  $SiO_2$ -poor rocks are typical geochemical features of biotite (Fig.6).

The biotite crystallization and separation is also apparent among  $SiO_2$ -rich rocks where  $K_2O$  poor rocks occur (Fig.4). This indicates that a residual liquid poor in  $K_2O$  and potassium-like

trace elements can be formed. It complicates the interpretation of  $K_2O/SiO_2$  correlations in high-K rocks and their slopes. In extreme cases where a large amount of biotite crystallizes in early stages, rock series formed by fractional crystallization can have negative correlation of  $K_2O/SiO_2$ . This is also valid for fractional melting that involves biotite.

Amphibole-gabbroic inclusions also occur frequently in the neighbouring lavas, e.g. Mount Lamington and Savo Volcano in the Solomons.

The occurrence of this type of inclusion in calc-alkaline lavas has led several authors (e.g. TAKESHITO and OJI, 1968) to suggest that the host lavas have been derived from high-Al basaltic parents by fractionation, but the volume of basic rocks with relatively high  $K_2O$  in orogenic regions is too small to allow this. OSBORNE (1969) has suggested the ultrabasic belts represent the complimentary accumulates but in Eastern Papua and the Solomon Islands, no andesites (s.s.) or sediments bearing andesitic detritus comparable in age to the ultrabasic rocks are known. This observation together with the observation of relatively high-K content of hornblende gabbroic inclusions suggest that there is not a complementary relationship between the high-K calc-alkaline volcanics and the alpine ultrabasics in Eastern Papua or the Solomon Islands (cf. OSBORNE, 1969).

#### $K_2O/SiO_2$ correlation

DICKINSON and HATHERTON (1967) have correlated the  $K_2O$  content of volcanic rocks at given  $SiO_2$  with the depth from the volcanic centre

to the Benioff zone. DICKINSON (1968) suggested that the slope of the curves should be steeper for magmas derived from greater depths and has shown that the slope of  $K_2O/SiO_2$  correlations increases from the tholeiitic rocks of island arcs to low-K calc-alkaline to medium-K calc-alkaline rocks.

It has been suggested (JAKES and WHITE, 1969) that the rocks of the shoshonitic association generally follow in time and space the high-K calc-alkaline rocks in some island arcs. In Eastern Papua, high-K calc-alkaline rocks and shoshonitic rocks are closely associated, although it is not clear how they are related in time. If this is true, there should be a further systematic change of the slopes of  $K_2O/SiO_2$  correlation. Our data show that the slopes of  $K_2O/SiO_2$  correlation of high-K calc-alkaline rocks tend to become flatter with increased age (Fig.4). The slopes of the  $K_2O/SiO_2$  correlation in shoshonitic rocks are also very flat (JOPLIN, 1968). Data on shoshonitic rocks from the New Guinea Highlands, data for high-K calc-alkaline rocks of Cape Nelson (present paper), and shoshonites (RUXTON, 1966) from East Papua show that the slope flattens from medium-K to high-K calc-alkaline rock and finally to shoshonites. The flat and even negative slopes of  $K_2O/SiO_2$  correlation of some shoshonites do not contradict the ideas of transition and relationship of high-K calc-alkaline rocks and shoshonites and can be explained by early crystallization or fractional melting of biotite.

Further evidence for the relationship of high-K calc-alkaline rocks to shoshonites is:-

- (a) Variable content of  $Al_2O_3$  characteristic for high-K

calc-alkaline rocks (14 - 18.50%  $\text{Al}_2\text{O}_3$ ) and for shoshonites (13.5 - 19.5%  $\text{Al}_2\text{O}_3$ ).

(b) Flat trends in AFM diagrams for high-K calc-alkaline rocks are very similar to those for shoshonites.

(c) A spatial relationship in the island arcs where high-K calc-alkaline and shoshonitic rocks occur on the continental side.

Features which apparently negate a petrogenetic relation of high-K calc-alkaline rock and shoshonites are high Ni and Cr contents characteristic of shoshonites contrasting with low abundance of Ni and Cr in some high-K calc-alkaline rocks (e.g. Bouganville TAYLOR et al., 1969). There is a common occurrence of silica-poor (50 - 56%  $\text{SiO}_2$ ) members in the shoshonitic association whereas the high-K calc-alkaline rocks are mostly silica-rich (57 - 64%).

To explain the decreasing K/Rb ratio across the island arcs, JAKES and WHITE (1969) suggested on the basis of GREEN and RINGWOOD's (1968) and RINGWOOD's (1969) model of sinking eclogite the increasing role of the mica phase in fractional melting of amphibole- and mica-bearing "eclogite". The source material of high-K calc-alkaline rocks and shoshonites probably contains a mica phase. This accounts for the high contents of the large cations such as K, Ba and Rb as well as the relatively high Cr and Ni.

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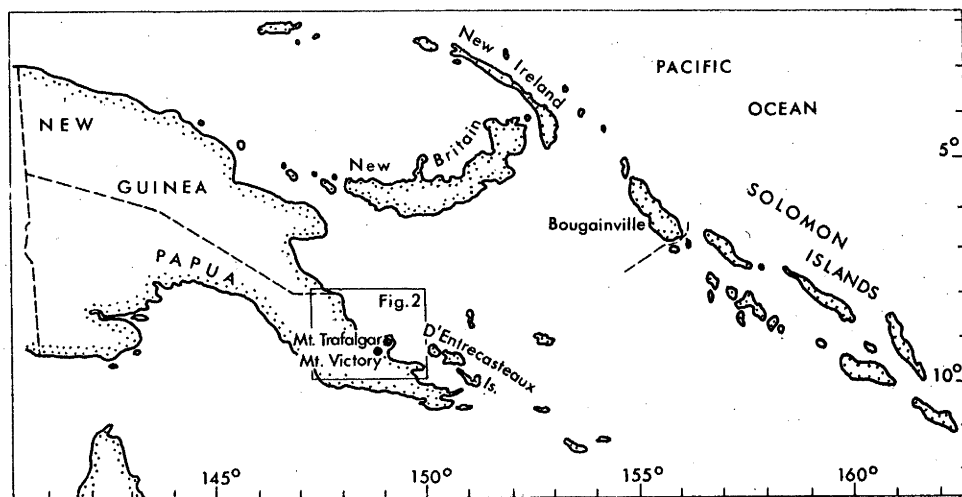


Fig.1 New Guinea and Solomon Island area with location of Cape Nelson volcanoes Mount Victory and Mount Trafalgar.

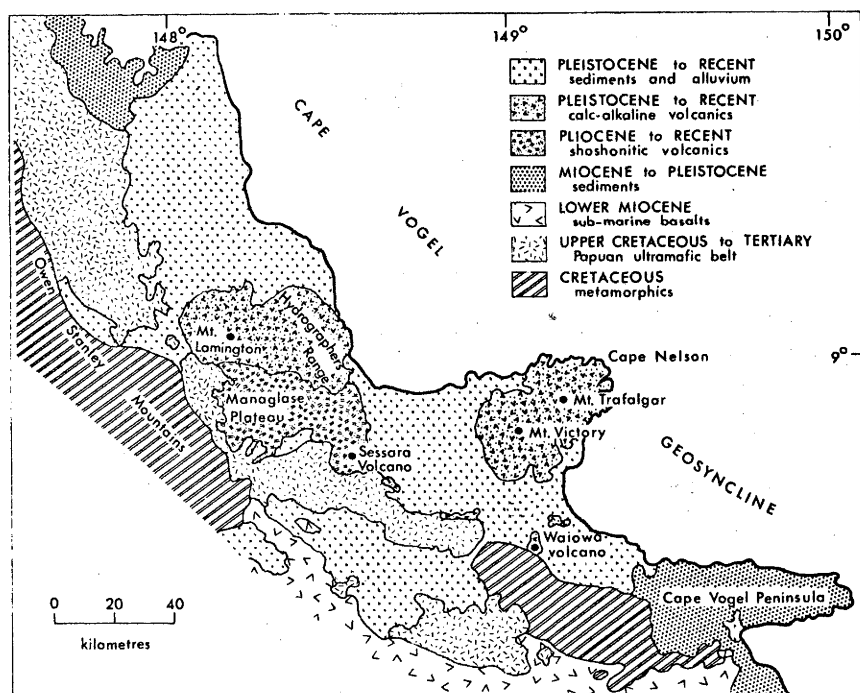


Fig.2 Generalised geological map of North-eastern Papua with Cape Nelson volcanic complex.

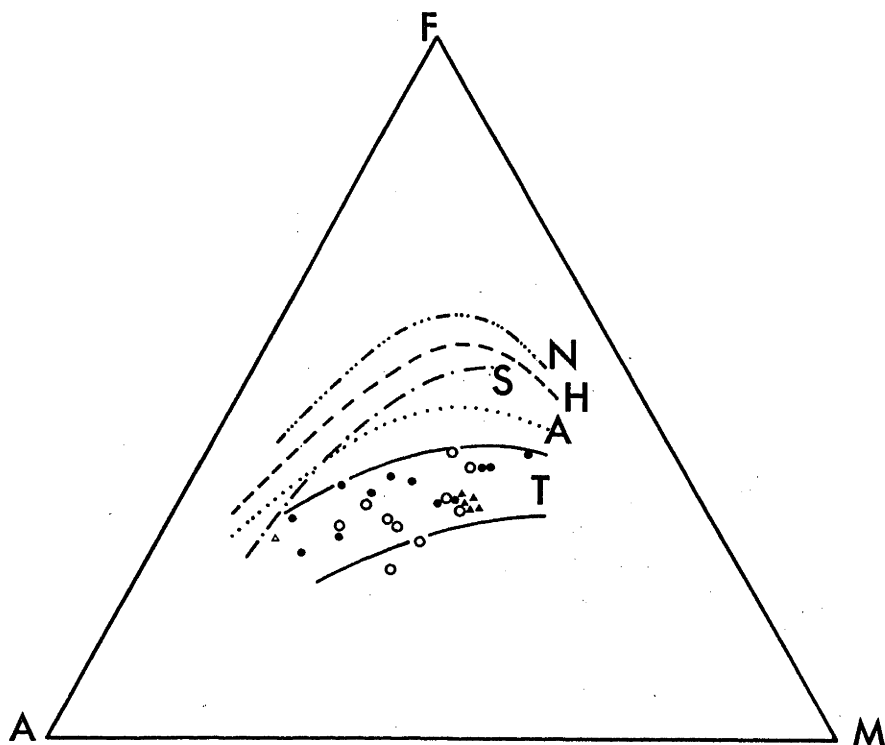


Fig.3 AMF diagram for analysed rocks from Cape Nelson (T); full triangles-inclusions, open circles Mount Victory, full circles Mt Trafalgar, open triangle Waiowa volcano; for comparison the trend of calc-alkaline rocks from the Aleution Islands (A), Solomon Islands and Bougainville (S), and tholeiitic rocks from Hakone (H) and New Guinea (N) are given.

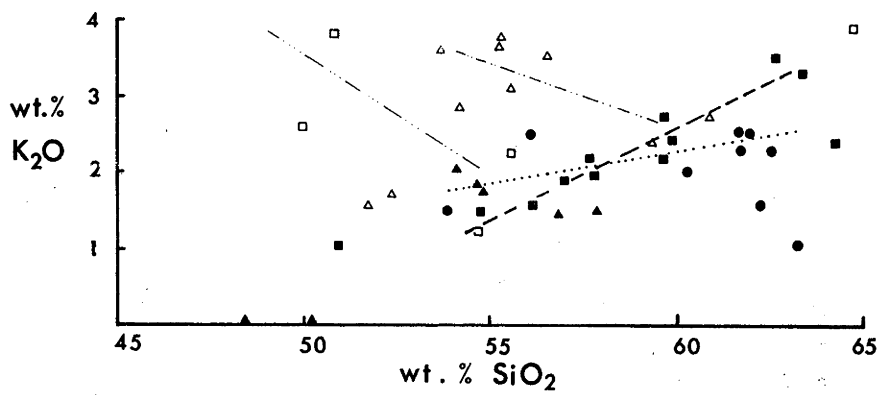


Fig.4  $\text{K}_2\text{O}/\text{SiO}_2$  correlation. Analyses recalculated on a 100% full anhydrous basis. Older lavas (Mount Trafalgar - squares) show steeper correlation than rocks of later lavas (full circles - Mount Victory).

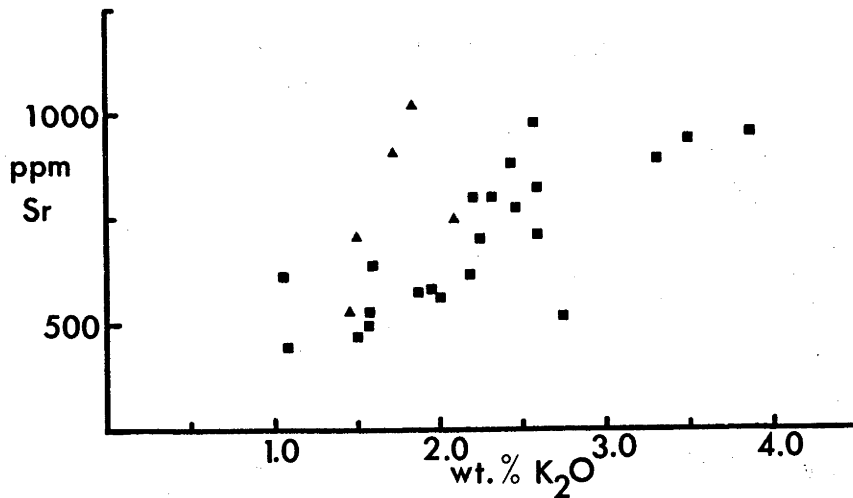


Fig.5 Plot of Sr vs.  $\text{K}_2\text{O}$  showing the positive  $\text{Sr}/\text{K}_2\text{O}$  correlation (squares lavas, triangles - inclusions).

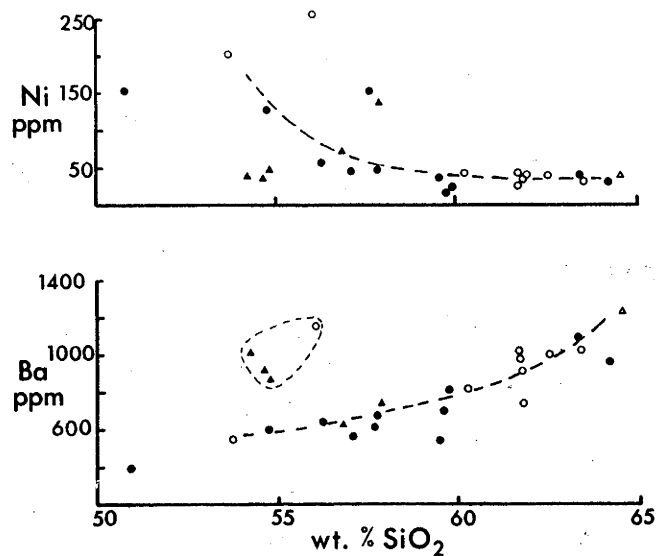


Fig.6 Plot of Ni + Ba vs. SiO<sub>2</sub>. The rocks with enrichment in Ba correspond to those with high K<sub>2</sub>O and low Ni values. Note that in the region of SiO<sub>2</sub> = 60 wt. % both elements are linearly correlated with SiO<sub>2</sub>; full triangles inclusions, open circles Mount Victory, full circles Mount Trafalgar, open triangle Waiowa volcano.