# SOME TRACE ELEMENTS IN LAVAS FROM THE LAU ISLANDS, TOFUA, TONGA, AND TUTUILA, AMERICAN SAMOA

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# ABSTRACT

Calc-alkaline and alkaline rocks from the Lau Islands and Tofua Island in the Tonga-Kermadec Island Arc, and from Tutuila, American Samoa have been analyzed for minor element abundances. Emission spectrography, atomic absorption, and X-ray spectrography were used to determine Ni, Co, Cr, V, Zr, Zn, Cu, Rb, Sr, and Ba.

The andesites and basaltic andesites of the Lau Islands and Tofua are depleted in Ni, Co, and Cr but are enriched in V. Alkalic rocks from the Lau Islands and Tofua are enriched in the transition elements, as are the alklalic rocks from Samoa.

Zr, Zn, and Cu values for all samples were close to previously reported values for calc-alkaline and alkaline rocks. These elements were generally not diagnostic with respect to source and degree of fractionation in the samples investigated.

The Lauan and Tofuan rocks are low in Rb, have low Rb/Sr ratios, and have high K/Rb ratios. Rb and Ba increase across the Tonga-Kermadec Arc toward the continent. The Samoan rocks have expected concentrations of Rb, Sr, and Ba.

Trace element abundances in the rocks investigated appear to indicate that the source of volcanic rocks in an island arc may not be coincident with a dipping seismic plane beneath the arc.

# INTRODUCTION

## A. Purpose of study

This study was initiated in order to investigate the abundance of certain trace metals in igneous rocks of the Lau Islands, Tutuila, American Samoa, and Tofua Island, Tonga. The elements studied are from two groups in the periodic table: (1) the alkali and alkaline-earth metals Rb, Sr, and Ba; and (2) the transitional metals Cr, Co, V, and Ni. In addition Zr, Cu, and Zn, which are often associated with the above elements, were also investigated.

It has become increasingly apparent that the circum-Pacific belt contains various rock suites whose chemical compositions seem to be related to the special tectonic conditions of island arc systems. The occurrence of andesitic rocks in the Tonga-Kermadec system and others has led to much speculation concerning the relationship between the geochemistry of andesites and the structure of the crust and upper mantle in these zones (Dickinson, 1968; Hatherton and Dickinson, 1969; Taylor, Capp, Graham, and Blake, 1969). In addition, trace element distributions provide limiting conditions on the possible history of the crust and upper mantle (Turekian, 1963), and therefore they are directly related to the evolution of the tectonically-active island arc system. However, a common aspect of many previous studies has been the selection of only certain samples representing the andesitic rock suites found in the circum-Pacific belt. These are often only the rocks which may be classified as andesites, although large volumes of other rocks of the calc-alkaline suite are present as well. Therefore, any limits placed on composition at depth from these restrictive suites must be somewhat questionable. Tectonic models based on the geochemistry of a single rock type are certain to be oversimplified as well. It is the aim of this study then, to provide data which are more representative of the actual trace-element distribution in various parts of the Tonga-Kermadec system, in rocks of various compositions, and to help establish compositional limits for deep source material which are meaningful in light of trace metal content in various volcanic settings.

## B. Geologic Setting

Tofua Island, in the Ha'apai Group, is one of a cluster of islands of the Tonga Archipelago. It is a small volcano five by six miles in diameter. The geology of Tofua has been described by Bauer (1970). The volcanic rocks consist of andesites and related rocks in four stratigraphic units (fig. 1). Sample T-4 is from the Hokula Froth Lava, an andesitic flow probably of Holocene age. T-68 is from an inclusion in the same flow. The most recent prehistoric flows issued from Lofia Cone, and T-17

HAMATUA FORMATION

h - basalt, pyroxene andesite pyroxene dacite lava flows

HOKULA FROTH LAVA

fl - Porphyritic andesite froth lava flow

KOLO FORMATION

ka - Consolidated lapilli-tuff breccia

kb - Unconsolidated tephra

kc - Andesite lava flow

LOFIA FORMATION

la - Consolidated lapilli-tuff, tuff, spotter, unconsolidated lapilli cinder, interbedded basalt to andesite lava flows

lap - Ponded lava flow

lb - Ash cone

lc - Large andesitic lava flow

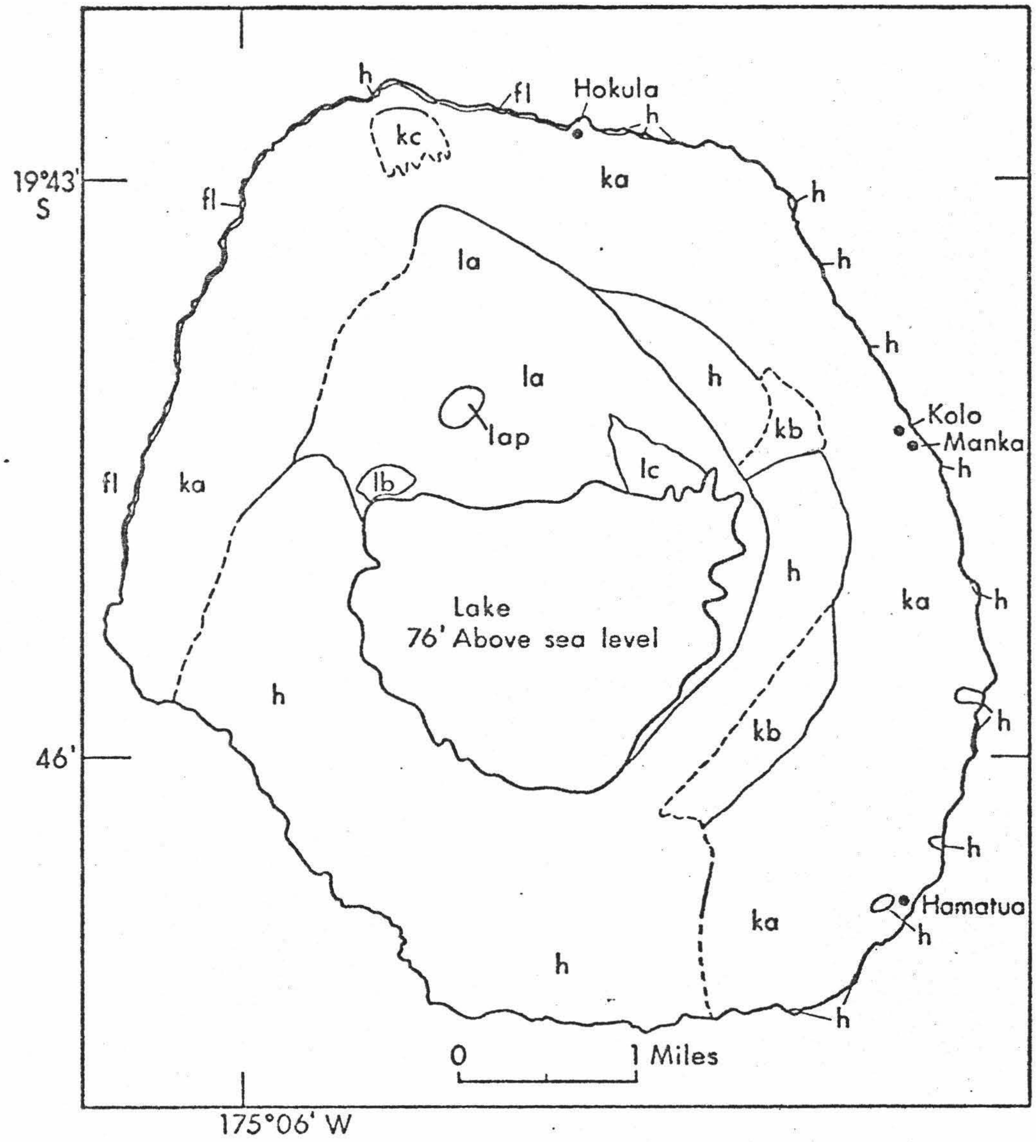

Fig. 1. Tofua Island, Tonga
(adapted from Bauer, 1970)

is from one of the small outpourings making up the cone. Samples T-32 and T-33 have been obtained from the Hamutua Formation, which is apparently the oldest of the four volcanic formations. T-50 is from a thick andesitic flow of the Kolo Formation on the northern slopes of the island.

The Fijiian Islands are divided into an eastern and a western group, the former being a north-south belt of about a hundred small islands known as the Lau Group. They are roughly parallel to the islands of the Tonga Archipelago, and together with the Tongan clusters form two concentric arcs convex to the eastern Pacific (fig. 2). Rock types and stratigraphic nomenclature for these islands are from Ladd and Hoffmeister (1945). Olivine tholeiites, alkali basalts, basaltic andesites, and andesites are found on the Lau Islands in two recognized volcanic groups, the Lower Miocene Lau Volcanics and the upper Miocene Koro Mbasanga Volanics.

Following is a brief description of the sample locations: Sample L-1 is from Kambara, which is a small subcircular island composed largely of limestone except for a large volcanic mass on the northwest coast, which contains alkali olivine basalts of which the sample is representative, and odinitic lamprophyres as well. Samples L-3 and L-36 were collected on Lakemba, the largest island of southern Lau. It contains rocks of the Lau Volcanics, from which the two samples were obtained. Sample L-11 is

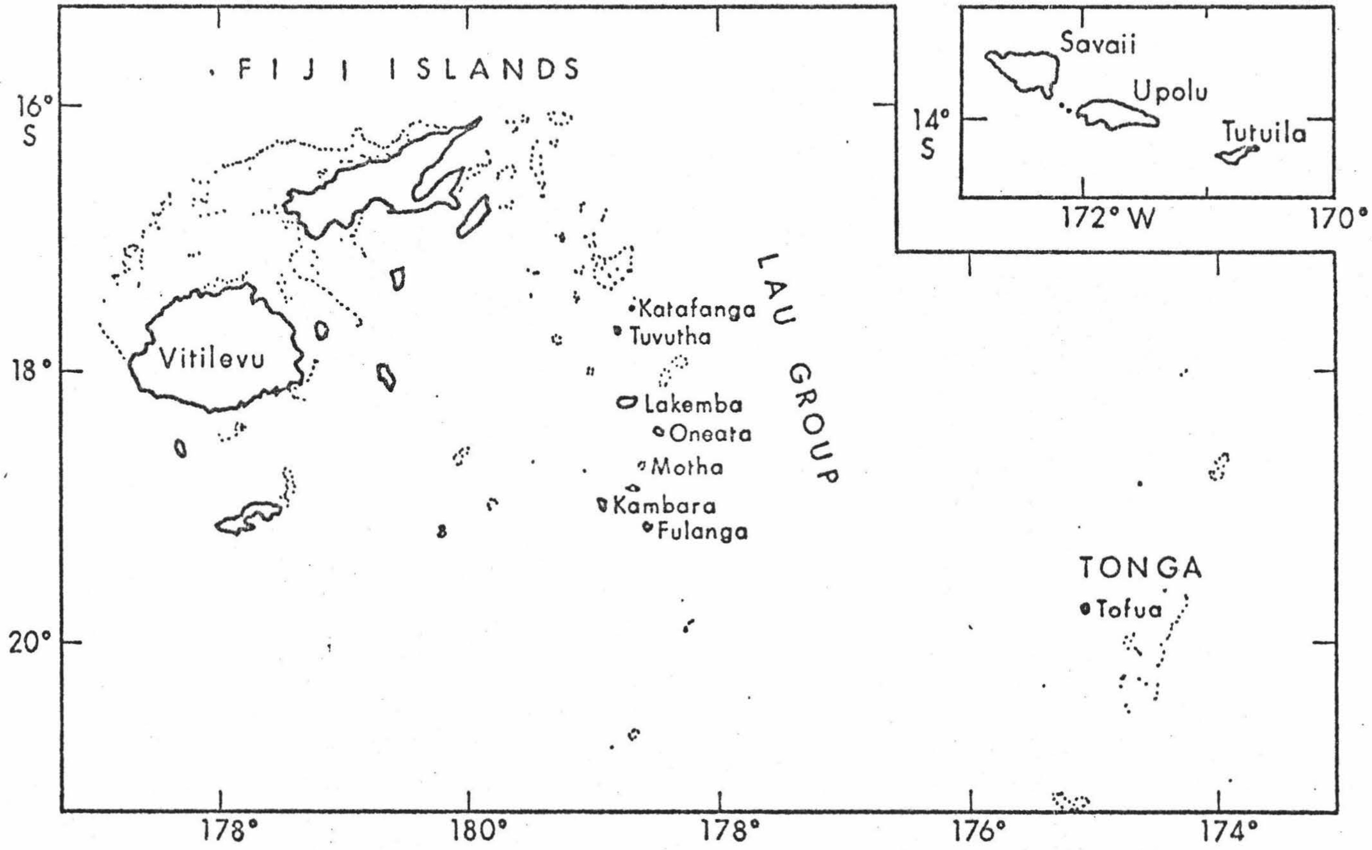

Fig. 2. Fiji Islands, the Lau Group, Tongan and Samoan Islands

from the small island of Thikombia-I-Lau on the eastern side of the lagoon of the Exploring Isles. The sample is from an andesitic agglomerate of the Lau Volcanics. L-18 was obtained from Munia, which is an elliptical island of only two and a half miles by one mile in diameter. The sample is from a member of the Koro Mbasanga Volcanics. Sample L-26 is from Vanua Mbalavu, the largest of the Exploring Isles. Both volcanic sequences appear on the island, and the sample is from the Lau Volcanics, as are samples L-30 and L-31. Sample L-34 is from the later volcanic sequence of the same island. Oneata, a small island in the Lau Group, is represented by L-45, but its source on the island is unknown. Samples L-62 and L-63 are from Mothe, another subcircular volcanic island whose volcanic history is not known. Sample L-76 is from Komo, an elongated island south of Lakemba. The sample is from an andesite dike which cuts through an agglomeratic andesite. Sample L-81 is from Olorua, which is a small island not described yet. Sample L-91 is from Naiau, which is an elliptical island. The sample is from an andesitic agglomerate, probably of the Lau Volcanics. Sample L-94 is from Tuvutha, an oval island containing a small volume of Lau Volcanics, from which the sample was collected. The island of Mango is circular and basin shaped in cross section. The sample L-109 is from the Lau Volcanics of the island, which contain lamprophyres as well. Sample L-120 is an alkali olivine basalt from Katafanga, a small rectangular island containing andesites of the Lau Volcanics in addition to the alkali basalts sampled. Specific locations for the Lau samples will be published at a later date.

Tutuila, American Samoa, is centrally located between the islands of Western Samoa (Savaii and Upolu), and the islands of the Manu'a Group. The island consists of five principal volcanic structures, all of which except one are considered to be of Pliocene or earliest Pleistocene age (Stearns, 1944). All rocks above sea level belong to the alkalic suite, and all samples analyzed are olivine basalts and hawaiites (Macdonald, 1968). These samples, then, are from a suite not characteristic of tectonically active island arc systems, but they have compositions characteristic of the later volcanism occurring in a number of oceanic islands. In addition, several samples from the Lau Islands have alkalic compositions, and thus are suitable for comparison.

Samples SM-1 and SM-2 are from the Taputapu Volcanics (fig. 3), which according to Macdonald (1968) form the youngest and least dissected of the major volcanoes of the island. SM-3 and SM-4 are from the earlier Alofau Volcanics near the eastern end of Tutuila. Next to oldest in the volcanic sequence is the Olomoana Volcanics, which form the eastern tip of the island, and are the

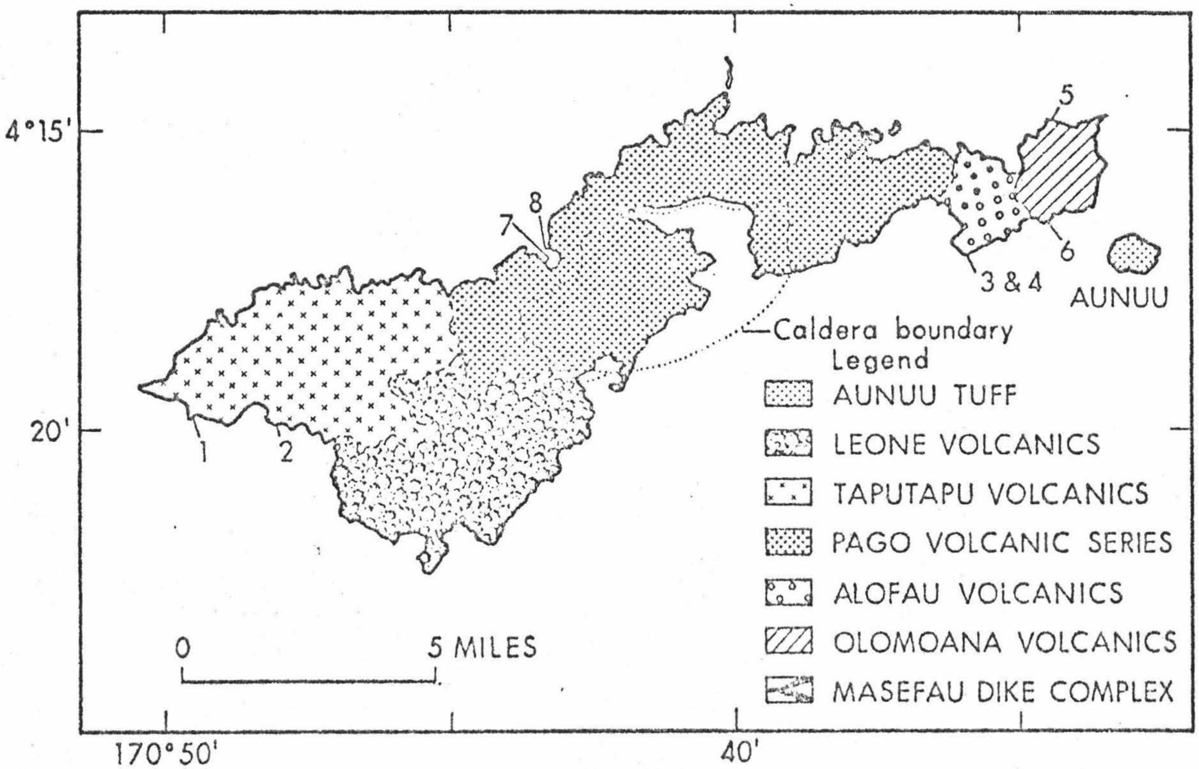

Fig. 3. Tutuila, American Samoa (From Macdonald, 1968)

source of SM-5 and SM-6. The Pago Volcanics form the largest of the volcanoes of Tutuila, and SM-7 and SM-8 are from this series. The Pago Volcanics are intermediate in age between the Alofau and Taputapu Volcanics.

### C. Analytical methods

Emission spectrographic analysis of trace elements was done on a Hilger three-meter, compact grating spectrograph with a reciprocal dispersion of about 2.8Å/mm in the second order. The power supply was a Hilger B.N.F.S. Spectrographic Source Unit operating as a D.C. unit. Samples were arced to completion for one hundred and five seconds at ten to eleven amperes. Anode excitation was used. The electrodes were National Carbon Co. preformed graphite electrodes L3942 (lower) and L3951 (upper). The slit opening was about .003 in.

Kodak Spectrum Analysis-1 plates were developed for two minutes and fifteen seconds at 23.5° C. in Kodak D-19 developer, rinsed for thirty seconds, and fixed in Kodak fixer for five minutes. Plates were then cured for one week before being read.

Primary standards for the determination of the three elements Ni, Zr, and V analyzed by this method were the U.S.G.S. Interlaboratory Standards 58-1 through 58-6. These synthetic standards are discussed in Bastron _et al_. (1960). The series contains successive dilutions of the trace metals in a matrix of quartz (60 parts), microcline (40 parts), and $Fe_2O_3$ (one part). The basalt standard, W-1, was also used routinely in conjunction with the synthetic standards.

Fe lines listed in Ahrens and Taylor (1961), and Bastron _et al_. (1960) were used for plate calibration. The standards used were ideal for plate calibration, exhibiting no self-absorption. Because arcing time, developing time, and temperature were rigidly controlled from day to day, only minor variations in the calibration curves were noted from plate to plate. A typical calibration curve is shown in fig. 4. This curve is the one used throughout the calibration period in which Kodak emulsion no. BIC 109B was used.

The model 2250 ARL microdensitometer was used with a Varian G-10 recorder to determine line intensity. Lines were scanned three times in succession. Background values adjacent to the lines were also read, and subtracted from the actual line intensity. Since electronic response was not linear, very dark lines could not be read accurately. Therefore, lines transmitting less than twenty percent of the light could not be read reliably. Consequently, accuracy in determining concentrations from these lines is poor, and will be noted as necessary.

Working curves for each element were constructed for each plate, although variations in standard compositions

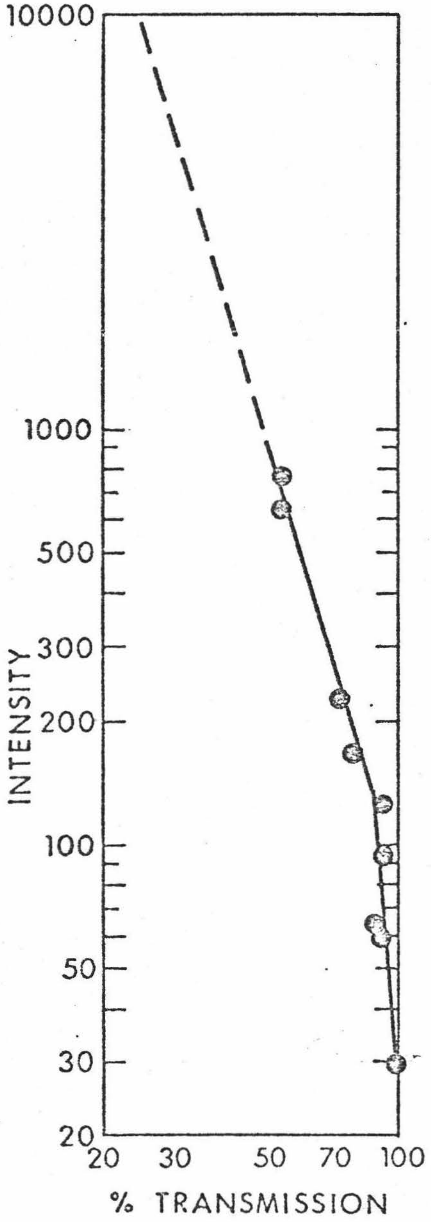

Fig. 4. Typical Plate Calibration Curve for Emission Spectrograph

due to working-curve fluctuations were always less than ten percent. Each element was plotted against line intensity, with the internal standards appearing at logarithmic intervals of concentration. The curve was then drawn through the six synthetic standard points. W-1 was then plotted, and its position noted. If additional matrix effects were present to the extent that the basalt standard did not plot with the synthetic standards, a curve parallel to the synthetic standard curve was drawn. The second curve was then used to determine values for the HIG rock powder standards, which are close in composition to the samples analyzed for this study.

Analysis of W-1 for five plates developed shows coefficients of variation of 9.8% for Zr, 30.2% for Ni, and 14.9% for V. Variance from the latest published averages for W-1 concentration of Zr is 25%, Ni 16.7%, and V is 0.3% (Fleischer, 1968).

Atomic absorption spectrophotometry was done with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Trace concentrations of Co, Cu, Cr, Zn, and Ni were determined. Elemental spectra were beamed through an air-acetylene flame to a photomultiplier system. Absorbance (in percent) was read from a counter controlling a null meter. Conversion to true absorbance was accomplished through the use of tables.

Samples were prepared by the acid digestion of about 200 mg. of coarsely ground rock powder taken from a 20 g. split. To decompose the sample, 10 ml. of HF was placed in a teflon cup with the rock powder. The cup was sealed to form a pressure bomb and heated for one hour at about 110°C. Boric acid was added to the rock solution to form a clear liquid which was diluted to 100 ml. Samples and rock standards were prepared the same way, in order to prevent variations in absorbance due to matrix additions or subtractions. A calibration blank containing HF, boric acid deionized water, and about one percent NaCl was made to form a solution of zero concentration.

Internal standards were of two different types. The first were simple solutions containing only water and varying amounts of the element to be determined. The absorbance of these synthetic standards was plotted against their concentration, and the resulting ideal curve was used to establish linearity in the concentration range, and to establish a slope for the U.S.G.S. rock powders BCR-1, GSP-1, AGV-1 and W-1. In addition the HIG standards were also used, although the two available analyses do not agree well.

Variance from the latest published averages for the four U.S.G.S. standards is about 5%. BCR-1 appears to be closest to the published values for all elements reported. The instrumental precision is generally within 2%, except for elements noted.

X-ray spectrographic analysis was used for detection of Ba, Rb, and Sr. A Norelco Universal Vacuum X-ray Spectrograph Type: No. 52530 was operated with tungsten tube at 50 mv and 45 ma. A LiF analyzing crystal was installed, and fine collimation was employed for analyses. For Rb and Sr, the NaI scintillation counter was set at 1040V with pulse height analyzer settings at 9V base and 11V width. Ba determinations required a voltage of 1595V, a 1.5V base, and a 4V window.

The K $\alpha$ peaks were used for Rb and Sr, while L $\beta$ peaks were necessary for Ba. Ba also required an Helium atmosphere for increased sensitivity. Background intensities were measured in the 2$\theta$ regions investigated, and where a slope was encountered, several background positions were chosen and an average value selected.

Working curves for Rb and Sr were constructed by plotting net intensity vs. concentration, as shown in figs. 5 and 6, which produced an acceptable line, although scatter due to matrix is evident. The working curve for Ba includes Ce, which could not be resolved due to its proximity to the Ba peak. However, Ce occurs in extremely minor amounts in basic igneous rocks, thereby introducing an error of no more than one or two percent.

Accuracy for Sr and Ba analyses was good, with variance from latest published values for W-1 of less than one percent. For Rb, determinations varied about 30% from the published values. Precision was not determined with these samples.

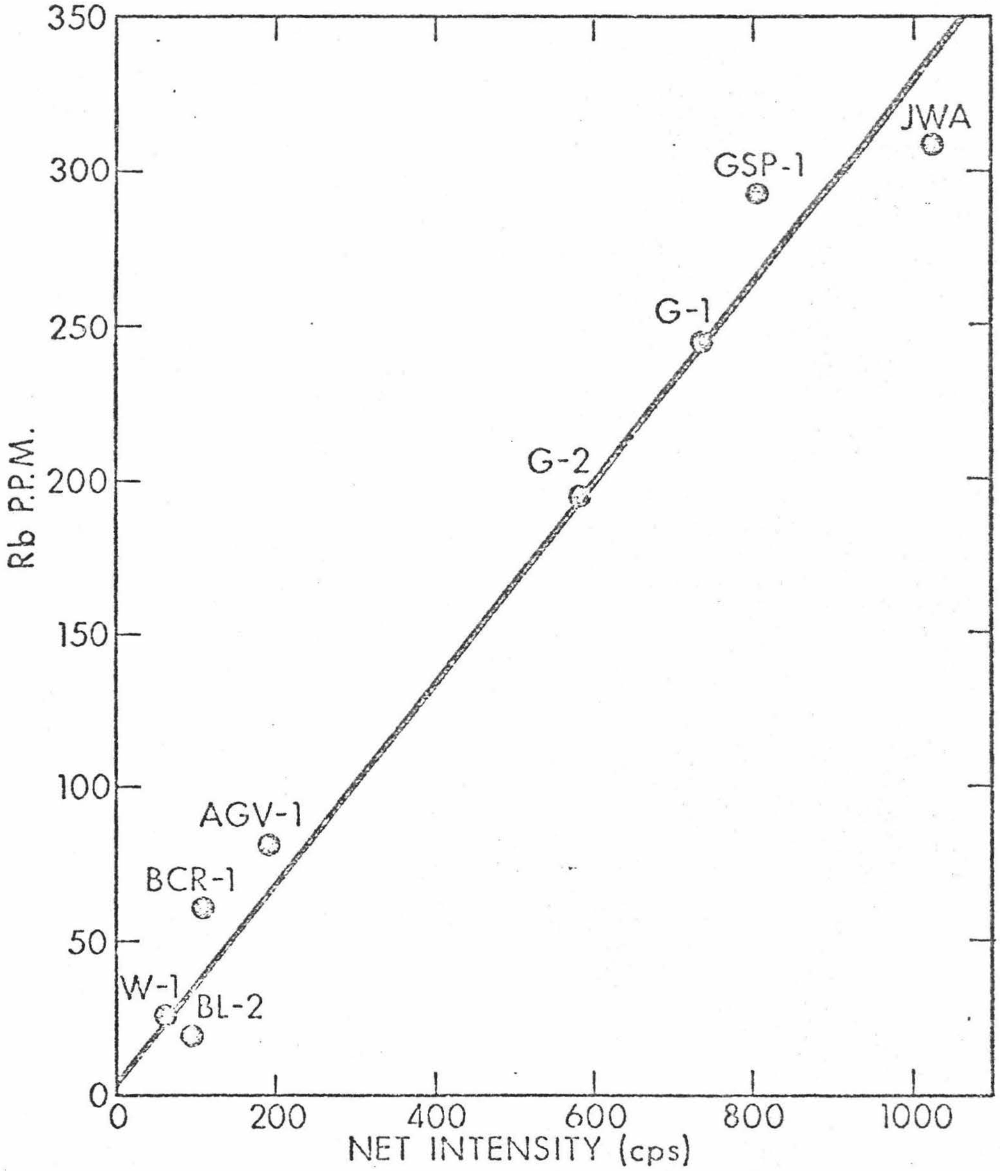

Fig. 5. Working Curve for X-ray Spectrographic Determination of Rb

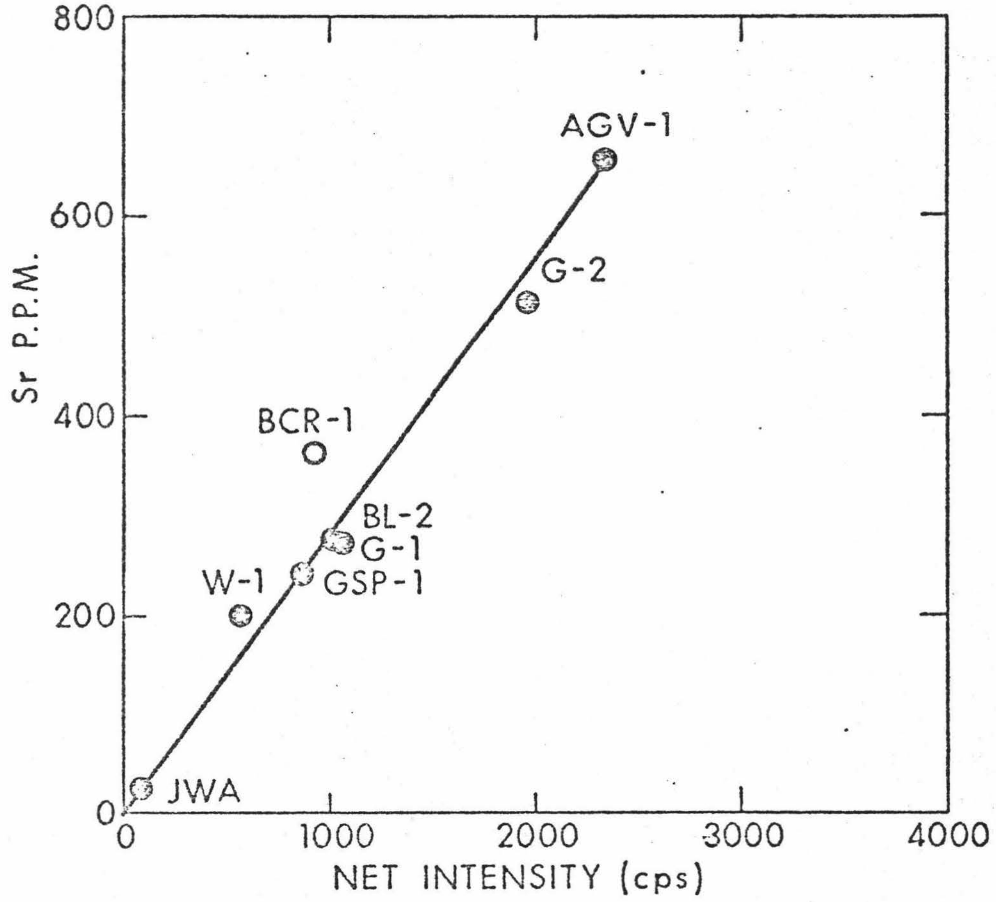

Fig. 6. Working Curve for X-ray Spectrographic Determination of Sr

# ELEMENTAL ABUNDANCES

Introduction. Calc-alkaline rocks of the western circum-Pacific have distinctive chemical characteristics, both in their major element compositions and minor element abundances. Four varieties of andesite have been reported in this region, based on significant differences in their major element geochemistry (Taylor, 1969). The terms low-Si andesite, low-K andesite, andesite, and high-K andesite are employed to classify these varieties in the various island arc systems of the region. Associated with these rock types are dacites, rhyolites, granodiorites, and high-Al basalts. The geographical distribution of these rock types within island arcs has been discussed by Kuno (1950); Dickinson and Hatherton (1967); Dickinson (1968); Taylor *et al*. (1969), and others. This distribution will be further related to trace element compositions of the Lauan, Samoan, and Tongan rocks in a later section of this study. Generally, elemental cation groups tend to vary with rock type and locality within an island arc, but trace element abundances are less variable with a varietal member of the calc-alkaline suite, even in widely separated occurrences.

The alkali olivine basalts and hawaiites of the Lau Islands and Tutuila, American Samoa, are classified as belonging to the alkalic suite based on the alkali-silica diagram (Macdonald and Katsura, 1964), in which a line is drawn through the region of low population that lies between the tholeiitic and alkalic suites (fig. 7). Normative analyses of the Samoan rocks contain hypersthene, which would classify them as undersaturated olivine tholeiite according to Yoder and Tilley (1962), but these rocks have a high ferric to ferrous ratio and high $TiO_2$ content, which result in high amounts of oxides in the norm, thereby releasing silica calculated as hypersthene (Macdonald, 1968). Other members of the alkalic suite are alkali basalt, basinite, basanitoid, ankaramite, and mugearite. Trace element data for these rocks are divided into Ne-normative, Ol-normative, and all alkali basalts, rather than by individual member as with andesites.

The results of the current study are presented in Table 1. Trace element abundances are given in parts per million. Abundances not reported were spuriously high due to contamination of bulk sample. Major element abundances for the rocks sampled are given in the Appendix.

## Nickel

Previous work. Calc-alkaline andesites from the western circum-Pacific typically contain a low abundance of Ni (Taylor *et al.*, 1969). The andesites with lower silica contain an average of 28 p.p.m. Ni, and the low-K and high-K varieties contain progressively less Ni. None of the andesite types found in New Zealand, Japan, Fiji, the Solomons, the Kuriles, Kamchatka, and the Aleutians contain

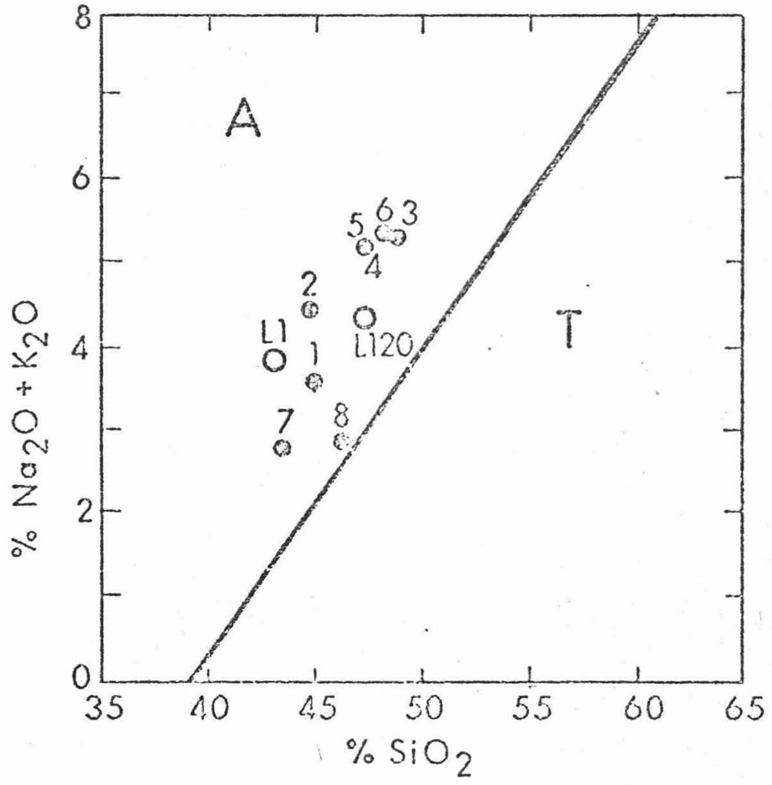

Fig. 7. Samoan and Lauan Samples Belonging to the Alkalic Suite

# Table 1

## TRACE ELEMENT ABUNDANCES

in p.p.m.

| SAMPLE | Ni | Co | Cr | Cu | Zn | V | Zr | Rb | Sr | Ba |
|---|---|---|---|---|---|---|---|---|---|---|
| LAU-1 | 224 | 50 | 293 | 104 | 96 | 105 | 125 | 12 | 345 | 480 |
| LAU-3 | 26 | 37 | - | 212 | 96 | 155 | 100 | 10 | 300 | 700 |
| LAU-11 | 17 | 15 | - | 98 | 84 | 320 | 112 | 8 | 235 | 560 |
| LAU-18 | 18 | 13 | - | 84 | 95 | 155 | 112 | 4 | 278 | 560 |
| LAU-26 | 18 | 62 | - | 126 | 78 | 270 | 65 | 3 | 320 | 40 |
| LAU-30 | 39 | 32 | - | 99 | 83 | 105 | 120 | 4 | 310 | 590 |
| LAU-31 | 17 | 37 | - | 156 | 79 | 140 | 120 | 2 | 309 | - |
| LAU-34 | 17 | 12 | - | 85 | 83 | 58 | 65 | 18 | 400 | 580 |
| LAU-36 | 26 | 26 | - | 157 | 112 | 340 | 120 | 6 | 405 | 315 |
| LAU-45 | 25 | 25 | - | 106 | 126 | 200 | 100 | 8 | 253 | - |
| LAU-62 | 25 | 27 | 64 | 185 | 72 | 250 | 28 | 30 | 525 | 250 |
| LAU-63 | 25 | 32 | - | 136 | 83 | 270 | 34 | 28 | 515 | 160 |
| LAU-76 | 18 | 26 | - | 84 | 72 | 145 | 54 | 16 | 320 | - |
| LAU-91 | 25 | 33 | 111 | 130 | 74 | 155 | 44 | 14 | 270 | 510 |
| LAU-94 | 24 | 15 | 29 | 83 | 61 | 125 | 32 | 7 | 205 | 240 |
| LAU-109 | 40 | 30 | 136 | 87 | 108 | 44 | 40 | 8 | 260 | 140 |
| LAU-120 | 183 | 84 | 50 | 483 | 150 | 85 | 16 | 13 | 400 | 360 |
| T-4 | 26 | 33 | - | 103 | 72 | 420 | 95 | 6 | 160 | - |
| T-17 | 31 | 45 | 140 | 172 | 84 | 420 | 120 | 4 | 155 | 65 |
| T-32 | 26 | 33 | - | 194 | 99 | 300 | 120 | 4 | 180 | 95 |
| T-33 | 25 | 32 | 25 | 181 | 93 | 600 | 140 | 4 | 180 | 73 |
| T-50 | 25 | 32 | - | 171 | 83 | 300 | 85 | 2 | 180 | - |
| T-68 | 26 | 25 | - | 116 | 79 | 540 | 140 | 6 | 190 | - |

Table 1 (continued) TRACE ELEMENT ABUNDANCES

| SAMPLE | Ni | Co | Cr | Cu | Zn | V | Zr | Rb | Sr | Ba |
|---|---|---|---|---|---|---|---|---|---|---|
| SM-1 | 177 | 50 | 187 | 101 | 150 | 285 | 370 | 12 | 470 | 396 |
| SM-2 | 90 | 47 | 35 | 92 | 151 | 280 | 590 | 22 | 490 | 550 |
| SM-3 | 201 | 20 | 266 | 110 | 125 | 115 | * | 47 | 525 | 750 |
| SM-4 | 94 | 38 | 101 | 111 | 118 | 240 | 420 | 34 | 475 | 580 |
| SM-5 | 38 | 21 | - | 56 | 173 | 160 | 700 | 34 | 600 | 400 |
| SM-6 | 2 | 33 | - | * | * | 121 | 420 | 38 | 585 | 400 |
| SM-7 | 620 | 53 | 588 | 148 | 121 | 180 | 320 | 23 | 290 | 345 |
| SM-8 | 368 | 48 | 612 | 156 | 111 | 310 | 200 | 10 | 340 | 250 |

- not detected
* not reported

abundances approaching those of average alkalic and tholeiitic basalts. High-Al basalts and andesites from the island arcs of the Pacific are similar in Ni content, if all calc-alkaline andesite types are calculated together (Taylor, 1969).

The Ni is contained in early olivine, in which it is enriched, and to a lesser extent orthopyroxene (Vogt, 1923; Wager and Mitchell, 1951; Storm and Holland, 1957; Turekian, 1963). The octahedral lattice sites of these minerals, and especially olivine, are preferentially entered by Ni due to ligand field effects (Burns and Fyfe, 1964), and a removal of these early-formed minerals results in a depletion of the Ni content. In addition, differentiation also decreases Ni content. Therefore, orthopyroxene will contain more Ni than coexisting pigeonite (McDougall and Lovering, 1963). Excess olivine in alkali olivine basalts results in their having higher Ni contents than tholeiites or andesites, clearly demonstrating the major role of olivine in the distribution of Ni.

Turekian (1963) has found regional variations in Ni distribution, and he has suggested that this is caused by initial abundance variations of Ni. The linking of circum-Pacific andesite types by uniformly low Ni content seems to justify this possibility further.

Present work. This study has revealed that the andesites and basaltic andesites of the Lau Islands have expectedly low Ni values (Table 1), averaging about 25 p.p.m., which is close to the reported values for low-silica andesite (Table 2). Chemical analyses of major elements indicate that the Lau samples are, in fact, transitional between low-silica andesite and low-K andesite. This might account for Ni values slightly lower than the average low-silica andesite. Atomic absorption analyses of the Tofua rocks indicate Ni values similar to the Lau samples, although the Tofua samples are low-K andesites. Low-K andesites have reported averages of 3 p.p.m. for Ni (Taylor, 1968b). The average Ni content of 25 p.p.m. is also higher than values reported from elsewhere in Tonga (Bryan and Ewart, 1971). X-ray spectrometry values for the Tofua samples are closer to the lower concentrations of Ni in low-K andesites. However, the lower values do not fit the observed covariance between Ni and MgO. Therefore, the higher values are preferred.

The alkali basalts, both from the Lau Islands and Samoa, contain higher Ni contents than the andesites. The samples divide into two groups, widely separated in Ni content. The higher of these contains an average of about 340 p.p.m. Ni, and the lower about 56 p.p.m. The bimodal distribution of Ni in alkali basalts is evident in reported averages for Ne-normative and all alkali basalts (Prinz, 1968). The higher frequency of values at about 50 p.p.m.

## Table 2

### Nickel

| Rock Type | Ni (p.p.m.) | Source |
|---|---|---|
| Low-K andesite | 15 | Taylor (1968b) |
| Low-K andesite | 9 | Bryan and Ewart (1970) |
| Low-K andesite | 25 | This study |
| Low-Si andesite | 28 | Taylor *et al*. (1969a) |
| Low-Si andesite | 25 | This study |
| High-K andesite | 3 | Taylor *et al*. (1969a) |
| Alkali olivine basalt | 80 | Prinz (1968 |
| Alkali olivine basalt | 199 | This study |
| Alkali olivine basalt | 51 | Engel *et al*. (1965) |

and 300 p.p.m. in these rocks closely resembles the abundance pattern in Lauan and Samoan alkalic rocks. Covariance is shown between Ni and Mg in all samples analyzed (fig. 8). Ni is one of the ferromagnesian elements, which are those that enter silicates in six fold coordination (Taylor, 1969). These elements appear to be controlled to some extent by phenocryst content of olivine, since olivine contains many suitable lattice sites for ferromagnesian elements.

## Cobalt

Previous work. Co concentrations in calc-alkaline rocks of the circum-Pacific belt follow the same distribution patterns as Ni. Taylor (1969) has found Co in low-Si andesite > Co in andesite > Co in low-K andesite > Co in high-K andesite, but overall depletion is not as pronounced as with Ni. Average reported values for andesites of this region are between 13 and 28 p.p.m. Co. Ratios of Ni/Co for these rocks are usually < 1, which is similar to those of high-Al basalts.

Co enters the lattices of ferromagnesian minerals, as does Ni, but in lesser amounts and in more constant values (Prinz, 1968). Olivine and pyroxene contain Co, and both show a decrease of Co with differentiation (Carstens, 1958; McDougall and Lovering, 1963). Coherence of Co with Mg or Fe has been a source of discussion since

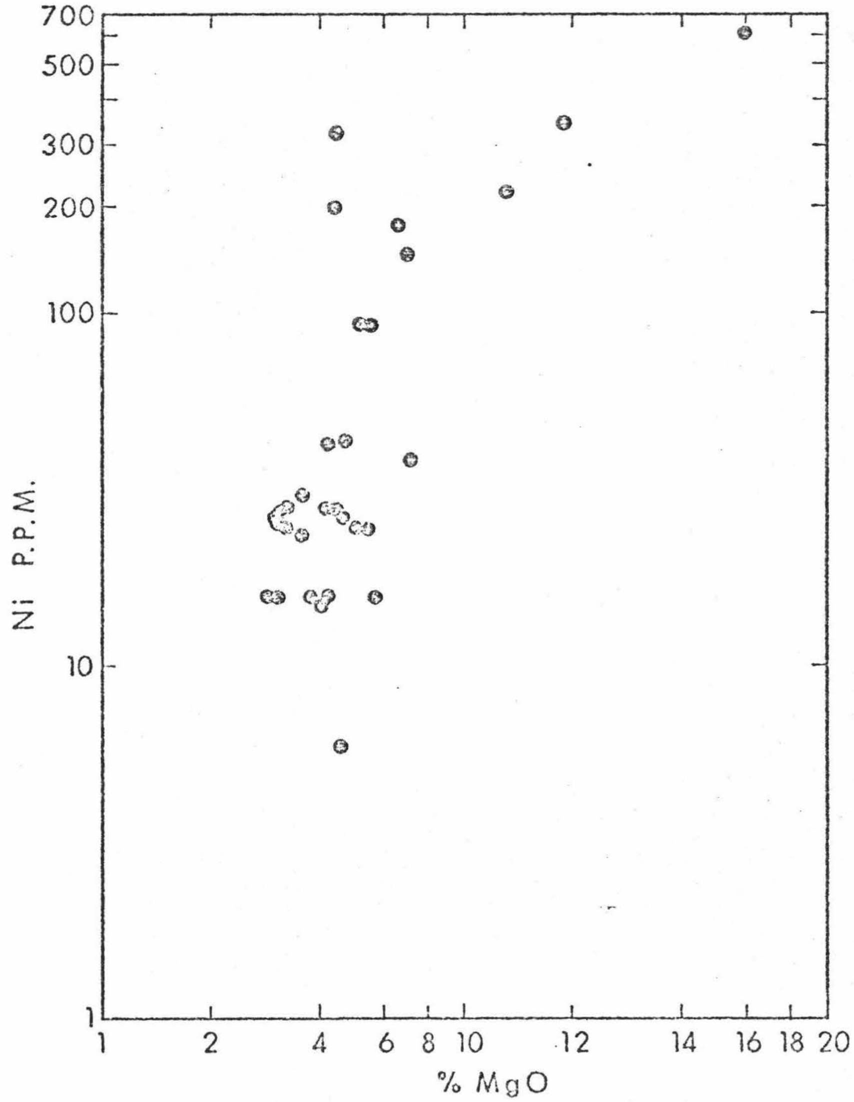

Fig. 8. Covariance of Ni and MgO in Lauan, Tofuan and Samoan lavas

Sandell and Goldich (1943) found that Co varied linearly with Mg for a series of unrelated rocks. Nockolds and Allen (1953, 1954) showed that both Co/Fe and Co/Mg were approximately constant for some alkali and calc-alkali assemblages. However, Wager and Mitchell (1957) indicated that in the Skaergaard intrusion Co follows Fe more closely than Mg. Carr and Turekian (1961) find that Co is dependent on the total number of Fe-Mg lattice sites, rather than the Fe/Mg ratio. Recently, Co concentrations have been related to octahedral "site preference energy" (Burns and Fyfe, 1964). Since this energy (in K cal mole$^{-1}$) for transition cation distribution is in the order Ni > Cu > Co > Fe > Mn > Ca-Zn, the Co will be taken up in solid crystals in that order of preference. Since Ni has the highest octahedral site preference energy, and a higher melting point-lower solubility than Mg, it is depleted in the melt more quickly than Co. Thus Ni/Co ratios decrease with fractionation.

Co in alkali basalts appears to be at the same concentration levels as in tholeiites (Prinz, 1968), with a frequency of distribution highest at about the same concentrations as other alkali basalts.

Present work. The andesites of the Lau Islands contain an average of 28 p.p.m. Co, which is the value established by Taylor (1969) for average Co content in low-Si andesites (Table 3). The Tofua andesites have slightly higher Co

## Table 3

## Cobalt

| Rock Type | Co (p.p.m.) | Ni/Co | Source |
|---|---|---|---|
| Low-K andesite | 20 | 0.75 | Taylor *et al*. (1969a) |
| Low-K andesite | 31 | 0.29 | Bryan and Ewart (1970) |
| Low-K andesite | 33 | 0.81 | This study |
| Low-Si andesite | 28 | 1.0 | Taylor *et al*. (1969a) |
| Low-Si andesite | 28 | 0.97 | This study |
| High-K andesite | 3 | 0.23 | Taylor *et al*. (1969a) |
| Alkali olivine basalt | 40 | 2.0 | Prinz (1968) |
| Alkali olivine basalt | 67 | 4.9 | This study |
| Alkali olivine basalt | 25 | 2.0 | Engel *et al*. (1965) |

values, averaging about 33 p.p.m. Co. This is about one third higher than values reported for low-K andesite in the island arcs of the circum-Pacific. The Samoan and Lauan alkali basalts have averages of 67 and 28 p.p.m. respectively, which are well within limits reported for these basalts.

All the lavas show that Co has coherence with both $Mg^{++}$ and $Fe^{++}$ (figs. 9 and 10). This has been reported in previous work, but it does not explain the behavior of Co with respect to Ni in basic rocks which have a fractionated character occurring within a limited geographical region. In the Lau samples, Ni/Co ratios are quite variable, with a range of 46 - 1.60. A majority of values are $> 1$. This is anomalous to reported ratios of $< 1$ for calc-alkaline andesites of this region (Taylor, 1969). However, the Tofua samples do have Ni/Co ratios of $< 1$. Since Tofua lavas appear to be fractionated to some extent, based on their iron enrichment on an A-F-M diagram (fig. 11), it would seem that an early depletion of Ni should lower the Ni/Co ratio as fractionation enriches the $Fe^{++}$ at the expense of $Mg^{++}$ and consequently enriches the relative proportion of Co as well. The Tofua samples show exactly the opposite of the expected result, with Ni/Co ratios increasing with fractionation (fig. 10). Considering the absence of normative olivine in these samples, it is possible that early-depleted Ni was redissolved in the

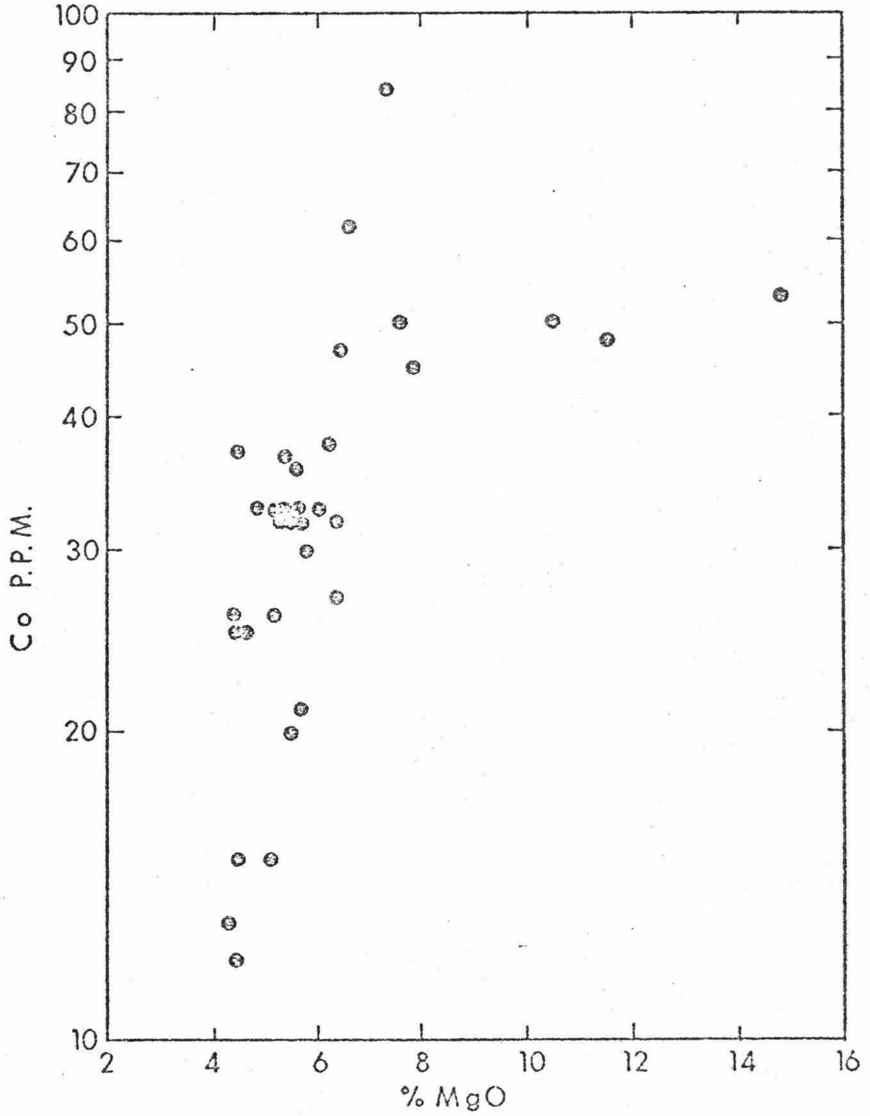

Fig. 9. Covariance of Co and MgO in Lauan, Tofuan, and Samoan Lavas

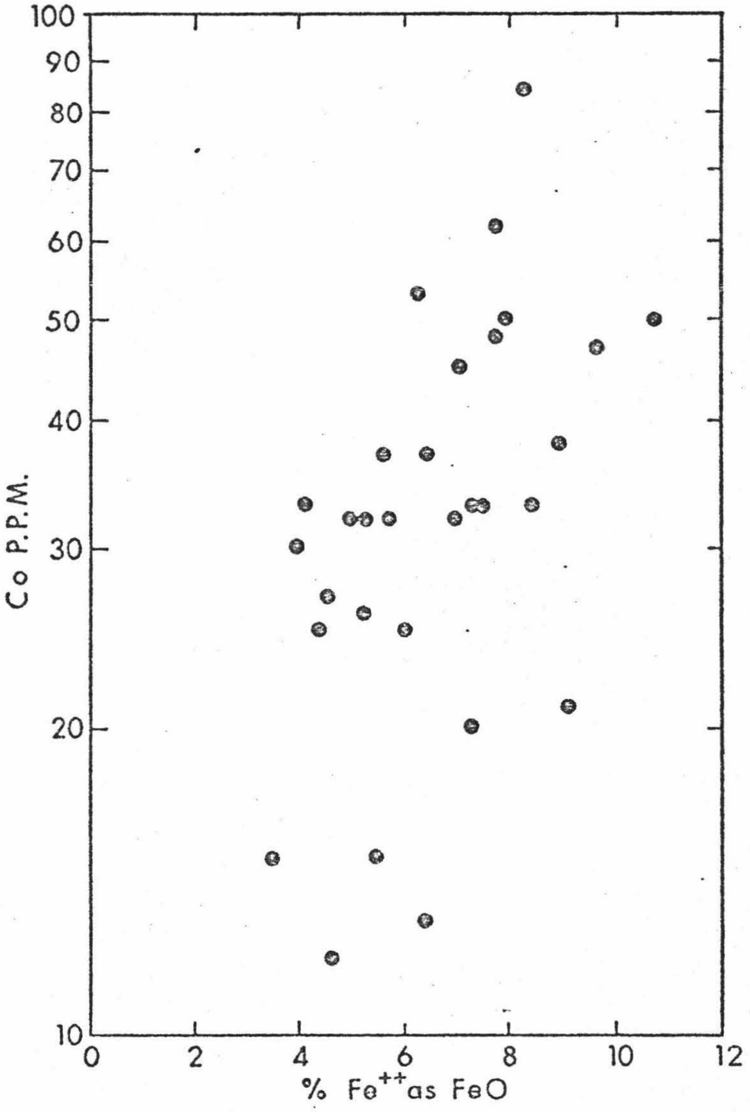

Fig. 10. Covariance of Co with $Fe^{++}$ in Lauan, Tofuan, and Samoan lavas

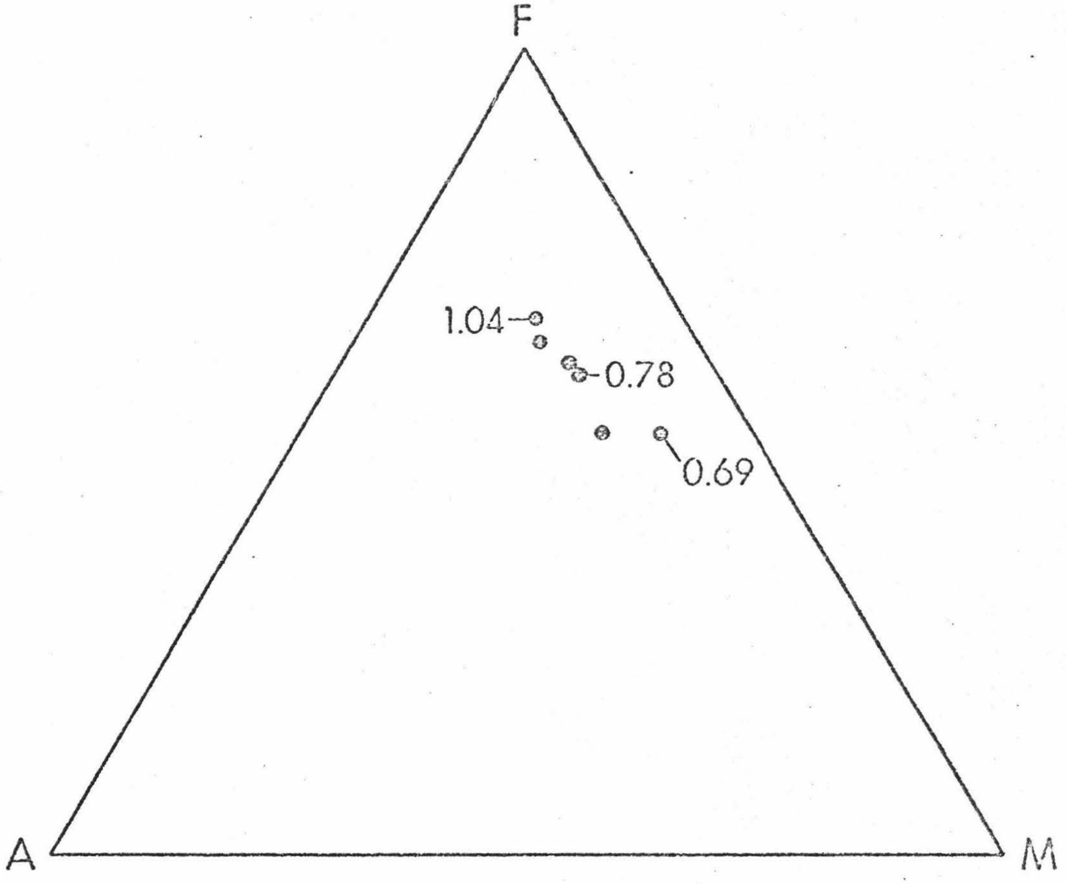

Fig. 11. Ni/Co ratios in Tofuan lavas plotted on an A-F-M diagram

melt and has entered orthopyroxenes and clinopyroxenes preferentially, due to a higher "site preference energy" than Co. This would be true for both Mg and Fe sites, therefore, Ni would not be effectively depleted until iron enrichment of the solid phase was complete.

In the Samoan alkali basalts, the more common case of early Ni depletion in olivine has apparently taken place. As fractionation continues, the Ni/Co ratios decrease (fig. 12), with one exception, toward the alkalic end-member. Co has been gradually depleted as well as Ni, but more slowly, as in most reported studies of differentiated complexes (Prinz, 1968).

In the Lau andesites, no distinct fractionation trend is evident, so little can be said about the behavior of Co with respect to Ni, except that in low-Si andesites, Ni/Co ratios are more variable than previously noted. Ratios of less than 1 are not, therefore, an invariable characteristic of calc-alkaline andesites.

## Chromium

Previous work. Cr, unlike Ni and Co, does not enter the olivine lattice (Turekian, 1963a). However, early pyroxene and magnetite prefer Cr, as shown by Wager and Mitchell (1951), Turekian (1963b), McDougall and Lovering (1963) and others. The "site preference energy" of Cr is the highest of $M^{+++}$ ions, including Mn, V, Ti, Fe and Sc, which accounts for Cr being first to be selectively taken

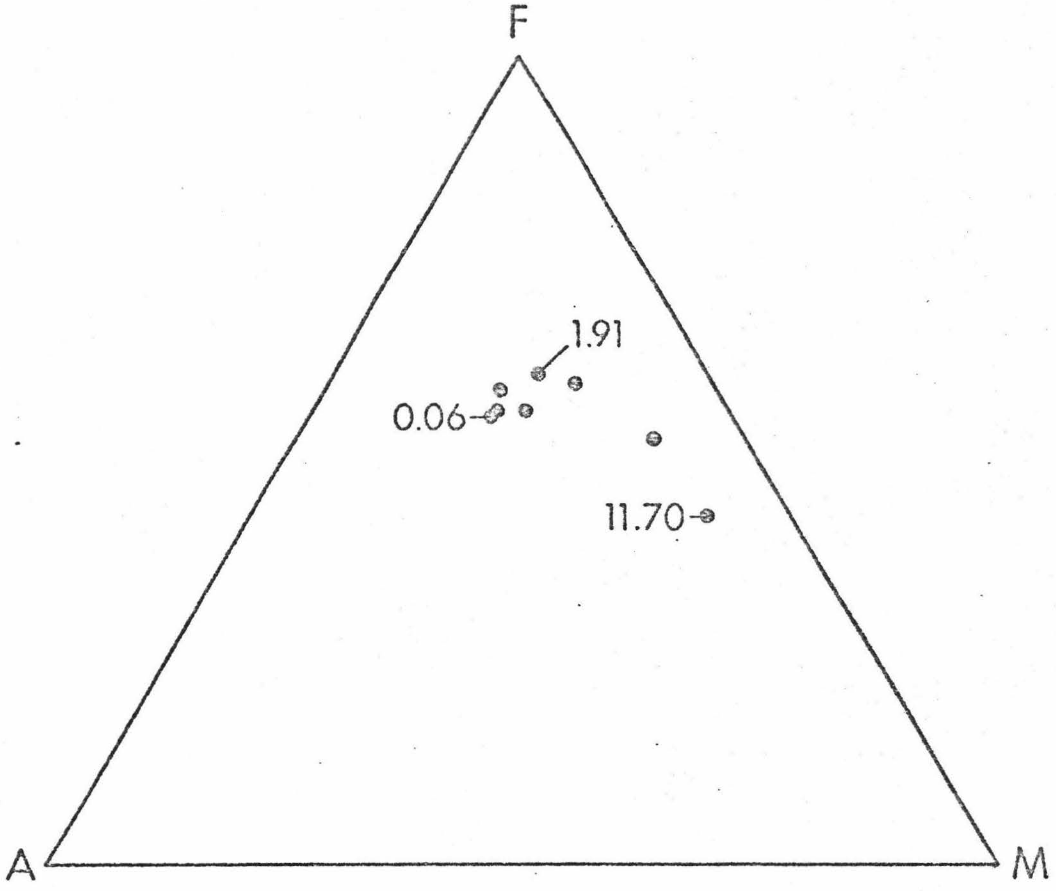

Fig. 12. Ni/Co ratios in Samoan lavas plotted on an A-F-M diagram

up in minerals (Burns and Fyfe, 1964). Cr, therefore, enters the chrome spinels, especially chromite and picotite. It is depleted in later pyroxenes, and appears to be strongly affected by fractionation. However, basalts in the same stage of fractionation from different areas show distinctly different Cr abundances, indicating a regional variation in initial abundance (Prinz, 1968).

Markhinin and Sapozhnikova (1962a) have reported values of Cr for volcanic rocks of Kamchatka and the Kurile Islands. The concentrations of Cr in these rocks are low, i.e., less than 100 p.p.m. This is in agreement with averages from New Zealand, Japan (Taylor and White, 1966), The Aleutians (Coats _et al_., 1961, and others) and Fiji and Bougainville (Taylor _et al_., 1969b). Taylor (1969) has plotted the frequency of distribution for circum-Pacific andesites, and has obtained a maximum between 50-100 p.p.m. Cr. Taylor _et al_. (1969a) report an average of 28 p.p.m. for low-Si andesite, 15 p.p.m. for low-K andesite, 18 p.p.m. for andesite, and 3 p.p.m. for high-K andesite. The depletion pattern, then, is the same as for Ni and Co.

In basalts, Turekian (1956) and Turekian and Carr (1960) have shown a marked covariance of Cr with Ni. Turekian (1963a) shows that the coherence is maintained during fractional crystallization in the Stillwater igneous complex, and suggests that the constant ratio is inherited from the mantle. Alkali basalts have a higher average Cr content than tholeiites, but the median value of 140 p.p.m. is about the same as for tholeiites (Prinz, 1968). Cr/Ni ratios of 2.05 are also the same for both basalt types.

Present work. The Lau and Tofuan andesites contain little Cr. Individual samples contain concentrations up to 140 p.p.m. Cr, but most values are below the detection limit. This is in agreement with other reported values for the region. The alkali basalts contain expected values of Cr, averaging close to reported concentrations. Samples which contain Cr are less fractionated than those which do not. Cr/Ni ratios are very variable, but Cr generally increases with Ni in both andesites and alkali basalts (fig. 13). Cr shows a slight covariance with total Fe in both rock types investigated (fig. 14), but the clearly fractionated Samoan basalts show a decrease of Cr with fractionation (fig. 15), which implies that an increase or decrease of total Fe sites does not control Cr distribution. The depletion of Cr, unlike Ni and Co, seems to be related to Cr removal from the magma more quickly than the loss of available lattice sites. This could be a function of the large difference in crystal field stabilization energy between Cr and Mn, which is the next preferred $M^{+++}$ transitional trace ion. Abundance of Cr in ultramafic rocks is generally agreed to between 1000-5000 p.p.m., which,

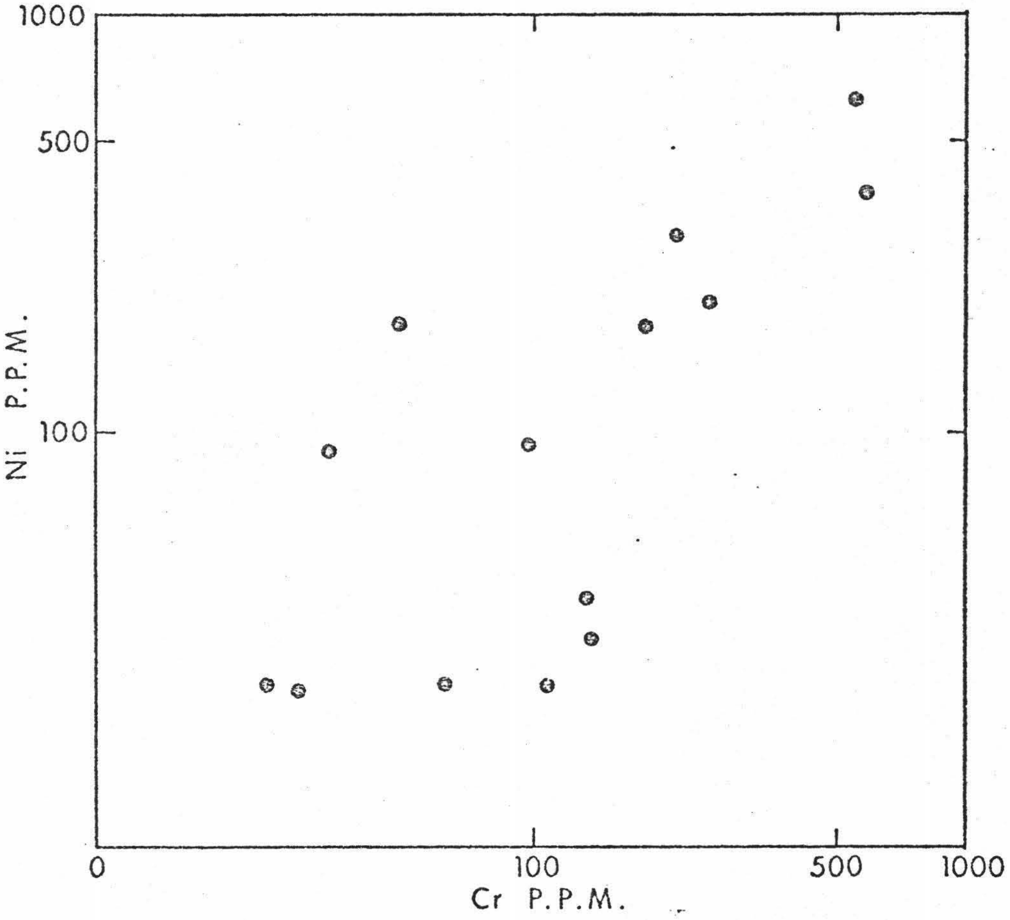

Fig. 13. Ni/Cr ratios in Lauan, Tofuan, and Samoan lavas

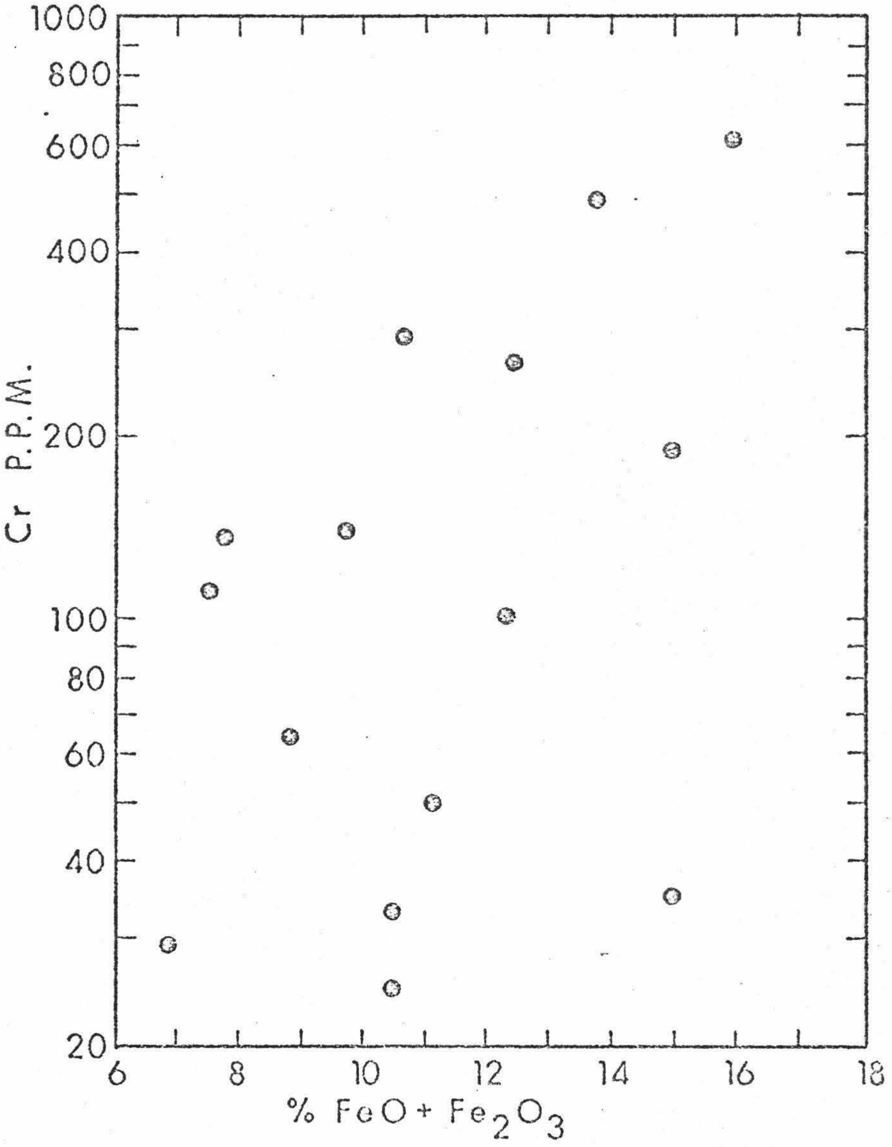

Fig. 14. Cr vs. total Fe in Lauan, Tofuan, and Samoan lavas

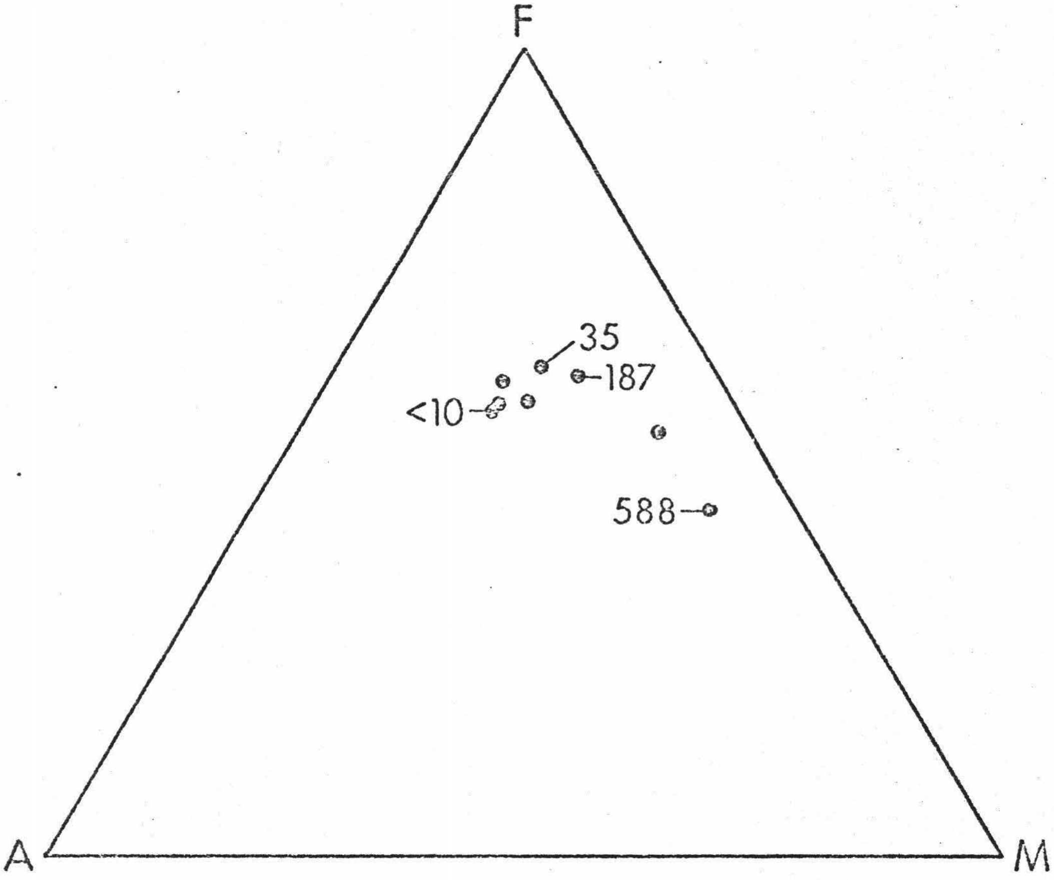

Fig. 15. Cr in Samoan lavas plotted on an A-F-M diagram

if considered to be a parental concentration for andesites and basalts, is high enough to require removal by incorporation into an early solid phase in large quantities in addition to removal by later fractionation. The Lauan and Tofuan samples may show the extent to which this early removal has been effective. Highly variable initial abundances of Cr have been mentioned above. The few large Cr concentrations, while appearing in less fractionated material, could be due to non-removal of most of the Cr in the first minerals to crystallize. Of the high initial abundance of Cr in these cases could be the underlying cause of the excess Cr.

## Vanadium

Previous work. V is abundant in magnetite, and to a lesser extent in pyroxene. Since $Cr^{+++}$ enters the early forming minerals, $V^{+++}$ is most abundant during the middle stage of fractionation. It decreases during the late fractionation stage (Wager and Mitchell, 1951; Wilkinson, 1959; Carstens, 1958). Most workers have found a diadochy between $V^{+++}$ and $Fe^{+++}$.

Osborn (1962) proposed that early crystallization and removal of magnetite would lead to the observed lack of iron enrichment in the calc-alkaline association, if this sequence of rocks is derived from a basic parent by fractionation. The V content of andesites is similar to that of basalts (Taylor, 1969), and Duncan and Taylor (1968) have shown that magnetite from New Zealand andesites contains an average of 0.60% V, which accounts for most of the V content of the samples. Removal of just 2% magnetite will deplete this magma in V by 120 p.p.m., but will not produce the observed iron deficiency. Osborn (1969) maintains that the magnetite is depleted in excess of 2%, and that in addition the V content is a function of the volatile content of these rocks, as discussed by Ringwood (1955).

Olivine-normative alkali basalts are rick in V because they represent the middle state of fractionation (Prinz, 1968). The median value is about 250 p.p.m. V, and somewhat less for alkali basalts in general. Nepheline-normative alkali basalts contain the lowest V content of the alkali basalts, possibly because they are from a late stage of fractionation.

Present work. V in Lau samples is consistent with previously established values (Taylor *et al*., 1969). The Tofua andesites have a much higher V content than any previously reported member of the calc-alkaline suite. V values for these rocks are, in fact, extraordinarily high for any igneous rock. Since other ferromagnesian trace elements in the Tofuan lavas are reasonable for the type of rock examined, it is likely that these V concentrations are spuriously high. The dark spectral lines involved in determining V have already been mentioned as a source of error.

The Samoan alkali basalts also show V concentrations close to reported values. V concentrations generally increase with total iron content. The lower V content of SM-3 and SM-5 is interesting in that these samples are more enriched in alkalis than the others, and thus more fractionated. It appears that within the fractionated sequence of Samoan alkalic rocks, the iron-enriched members are higher in V. Thus the middle stage of fractionation in rocks which are themselves representative of a middle stage of fractionation from a basic parent are most V rich. The Lau alkalic rocks are in an earlier stage in this process and are thus still V-poor with respect to other alkalic rocks.

In all samples, the covariance between V and total Fe (fig. 16) is clear. Although calc-alkaline rocks do not show as much iron-enrichment as tholeiitic or alkalic basalts, this study shows that V content is still dependent on Fe content, and locally iron enrichment increases V concentrations. Local fractionation toward iron enrichment, higher V concentrations, variable Ni, Co, and Cr concentrations, imply that andesitic ferromagnesian trace-element values can be derived from by a number of steps, including removal of magnetite, olivine, and chromite, and the crystallization of later minerals in their place. Partial completion of these steps is probably responsible for individually higher values of V, Cr, Co and Ni.

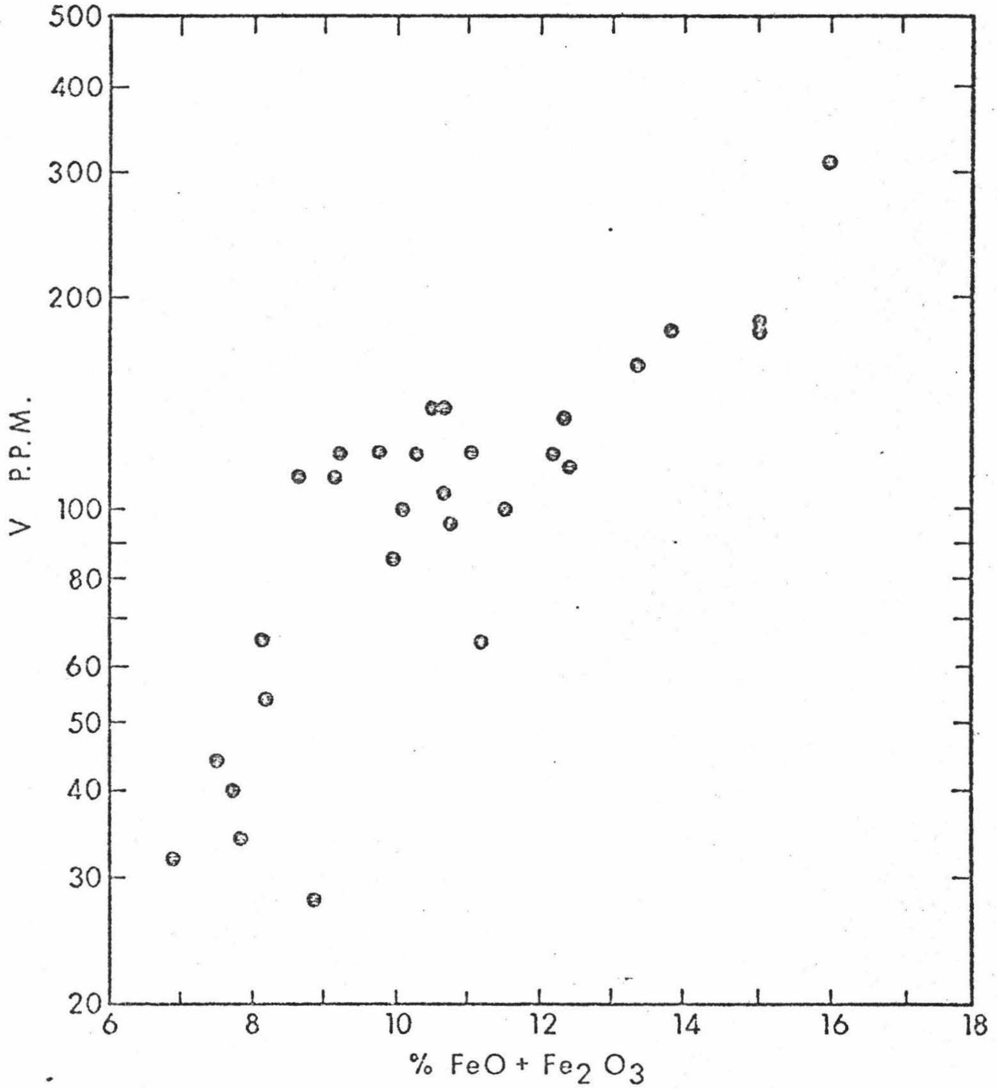

Fig. 16. Covariance of V and total Fe in Lauan, Tofuan and Samoan lavas

## Zirconium

Previous work. Zr is a large, highly charged cation which is concentrated in the pyroxene of the early and middle stages of crystallization (Wager and Mitchell, 1951; Cornwall and Rose, 1957; Wilkinson, 1959). Other minerals containing appreciable amounts of Zr and zircon are analcite (Wilkinson, 1959), the feldspathoids (Goldschmidt, 1954), and apatite. Chao and Fleischer (1960), report a regional variation in abundance of Zr. Based on large differences in regional averages, they conclude that an estimate of Zr in igneous rocks of any type would be of questionable value. Prinz (1968), concludes that initial abundance differences in the Zr content of basalts ". . . are too large to be solely due to petrographic type, fractionation stage, or inter-laboratory variation."

Zr in calc-alkaline rocks from the circum-Pacific has been determined by Markhinin and Sapozhnikova (1962b), for the Kuriles and Kamchatka, by Taylor *et al*. (1969) for Saipan, Bougainville and Fiji, and by Bryan and Ewart (1970) for Tonga (Table 4). Values for Zr are low as compared with those in most upper crustal materials, and are much like basalt values of about 100 p.p.m. High-K andesites are somewhat enriched in Zr, averaging about 170 p.p.m. Zr content appears to increase with K, along with other highly charged cations, perhaps in response to fractional crystallization or partial melting (Taylor *et al*., 1969).

## Table 4

## Zirconium

| Rock Type | Zr (p.p.m.) | Source |
|---|---|---|
| Low-Si andesite (Bougainville) | 98 | Taylor *et al.* (1969b) |
| Low-Si andesite | 76 | This study |
| Low-K andesite | 88 | Taylor *et al.* (1969b) |
| Low-K andesite | 40 | Bryan and Ewart (1970) |
| Low-K andesite | 117 | This study |
| High-K andesite | 170 | Taylor *et al.* (1969b) |
| Alkali olivine basalt | 125 | Prinz (1968) |
| Alkali olivine basalt | 378 | This study |
| Alkali olivine basalt | 333 | Engel *et al.* (1965) |

Chao and Fleischer (1960), report that alkalic rocks have higher Zr contents than tholeiites. They suggest that Zr is more soluble in alkalic magma. Nepheline-normative basalts are found to be especially rich in Zr. Values of about 100 p.p.m. for olivine-normative alkali basalts, 150 p.p.m. for nepheline-normative alkali basalts, and 125 p.p.m. for all alkali basalts are offered as guides to expected concentrations (Prinz, 1968).

Present work. Although Zr concentrations in the Lauan and Tofuan andesites are similar to previously reported averages for circum-Pacific andesites, no enrichment of Zr with increasing K is evident. The higher values of Zr in high-K andesites reported by Taylor *et al*. (1969) are not found in the present study, and it appears that any enrichment is restricted to high-K andesites. The influence of fractional crystallization or partial melting on the Zr content of the Lauan and Tofuan rocks is unclear, essentially because the only major element of those rocks which covaries with Zr is Fe. Fractionation, which in calc-alkaline rocks may lead to a removal of iron (Osborn, 1962) should permit a corresponding increase of Zr. This is not the case (fig. 17). Partial melting could successively enrich the melt in the large cations such as Zr, but it cannot be clearly shown to have occurred in these samples using the present data.

In the alkalic rocks, Zr is enriched in all but one of the samples. The concentrations covary with the K

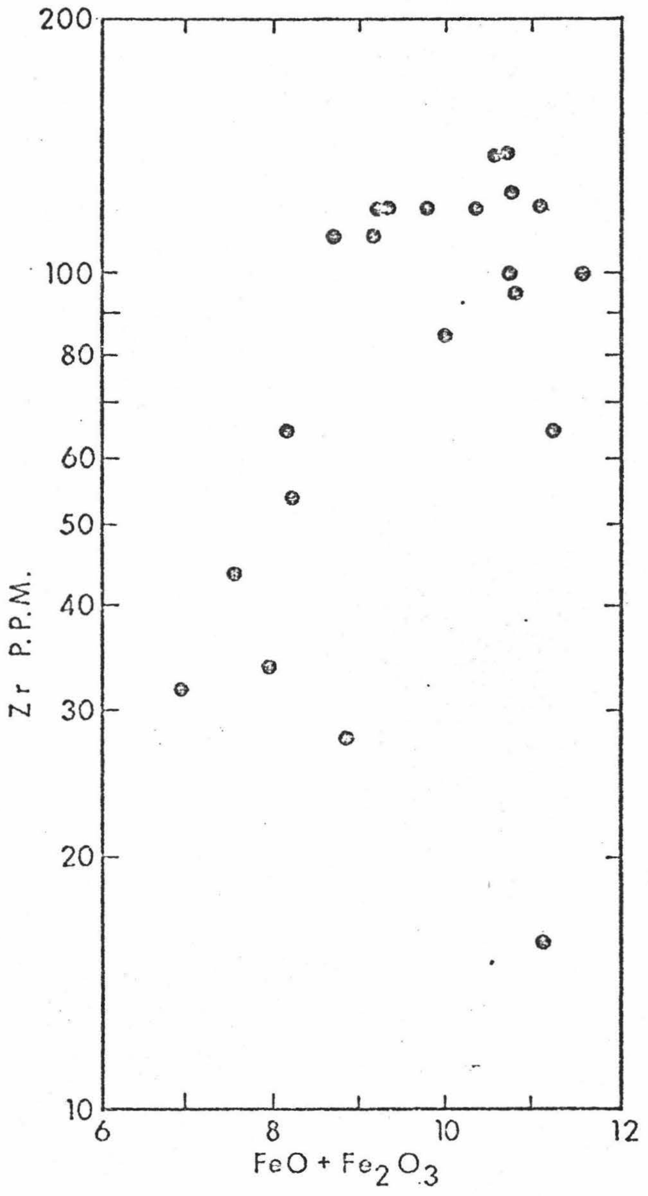

Fig. 17. Increase of Zr with increase of total Fe in Lauan, Tofuan and Samoan lavas

content, and in addition, Zr generally increases with fractionation (figs. 18 and 19). The enrichment of Zr in these rocks could be explained by a regional abundance variation, although more values are necessary to confirm this possibility.

## Zinc

Previous work. The similarity of radii between $Zn^{++}$, $Mg^{++}$, $Ni^{++}$, $Co^{++}$, $Fe^{++}$, and $Mn^{++}$ determines the geochemistry of Zn in crystal structures. The electron structure of its atoms tends to produce tetrahedral coordination in crystal structures (Goldschmidt, 1954), and therefore the "site preference energy" of Zn in octahedral lattice sites will be zero (Burns and Fyfe, 1964). Therefore, Zn enters the lattice after the transition elements Ni, Cu, and Co. It is probably less sensitive than these elements to differentiation processes, filling remaining available sites during crystallization.

Only a limited amount of data has been published recently on Zn concentrations in igneous rocks. Early averages of 100-130 p.p.m. for basic rocks and 60 p.p.m. for acidic rocks were reported (Goldschmidt, 1954). More recently, Rader *et al*. (1960) have shown that Zn in basalts and other basic volcanic rocks closely follows Fe content. No large-scale study of clac-alkaline Zn concentrations has been published, although Butler and Thompson (1967), have reported Zn in alkali acidic rocks

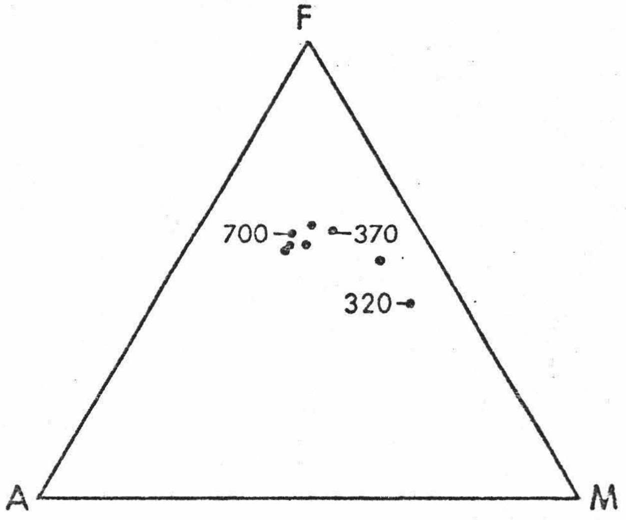

Fig. 18. Zr in Samoan lavas plotted on an A-F-M diagram

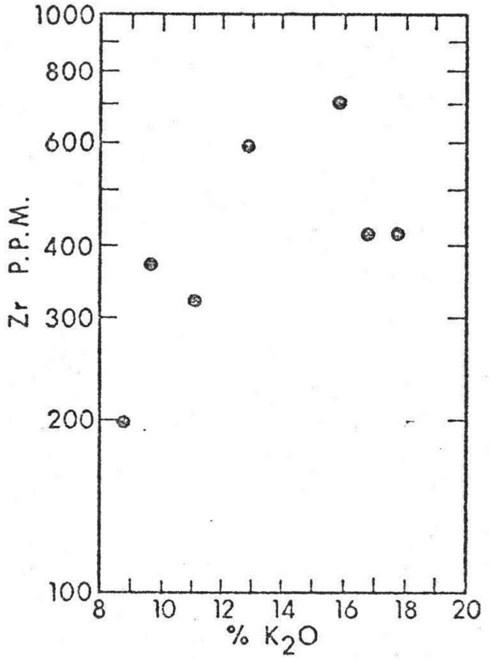

Fig. 19. General increase of Zr with increasing $K_2O$ in Samoan lavas

from Nigeria, and Ball and Filby (1965) have reported Zn contents of some standard rocks and reaffirmed the higher concentrations of Zn in basic rocks.

Present work. Zn concentrations for the Lauan, Tofuan and Samoan rocks appear to be close to reported values for basalts. The Samoan lavas and the Lauan alkali basalts are somewhat enriched in Zn, and this may be characteristic of alkali basalts, which are high in ferromagnesians. No compilation of Zn values for alkali rocks is yet available. Zn follows Fe (fig. 20), as expected. However, no covariance exists between Zn and other cations of similar radii in these samples. It is apparent, then, that Zn is not useful at this time as a diagnostic minor element for calc-alkaline rocks of the circum-Pacific or for oceanic alkali basalts.

## Copper

Previous work. Cu is distributed in all minerals of basalts and andesites, but the formation of sulfide dominates the geochemistry of Cu. The distribution of Cu in non-sulfide minerals such as olivine, pyroxene, plagioclase, and iron ores, may be due at least partially to sulfide inclusions, and not to incorporation into the lattice of these minerals. Wager et al. (1957) studied sulfide and silicate partition of Cu in the rocks of Skaergaard. They found that Cu entered basaltic minerals before an immiscible sulfide

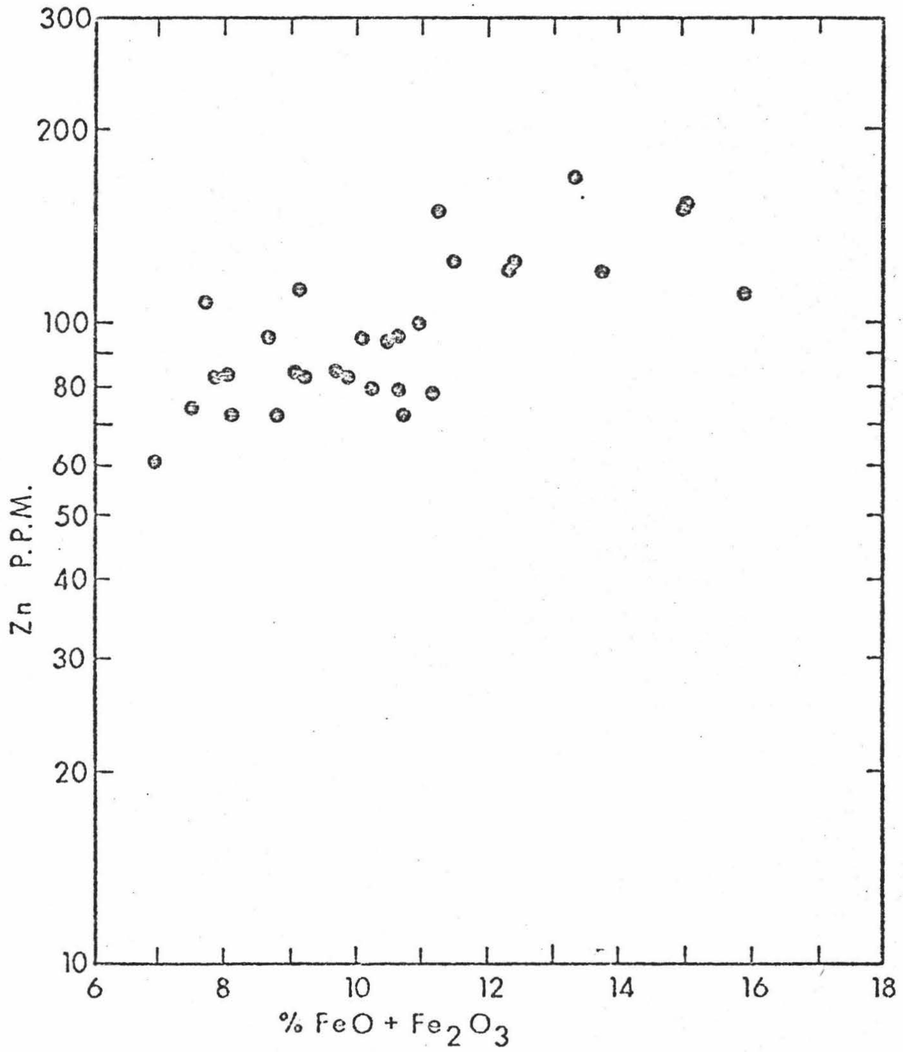

Fig. 20. Covariance of Zn with total Fe in Lauan, Tofuan and Samoan lavas

liquid accumulated by gravity. As differentiation progressed, the partition ratio between silicate liquid and sulfide liquid increased, progressively enriching the silicate liquid fraction until unity is reached in the acid-granophyre stage. Wager and Mitchell (1951); Cornwall and Rose (1957); Tiller (1959); and McDougall and Lovering (1963) show that Cu content in some nonsulfide minerals increases with fractionation. The relationship of Cu to sulfide and non-sulfide minerals in various magmas other than that of Skaergaard is still unknown, and the distribution of Cu therefore, cannot be used with assurance to explain magmatic processes.

The average value for Cu in alkalic basalts is 108 p.p.m. which is significantly different from that of tholeiites (127 p.p.m.). Taylor et al. (1969) report an average of 54 p.p.m. for andesites from Saipan, Bougainville, and Fiji. No distinctions in concentration can be made for the various members of the circum-Pacific suite.

Present work. The Lauan and Tofuan andesites have higher Cu concentrations than the average values for basalt in about half the samples. The high Cu values are not unknown in andesites of the region, with values of 150 p.p.m. reported for a high-K andesite from Bougainville (Taylor et al. 1969), and 215 p.p.m. for andesite from Late, Tonga (Bryan and Ewart, 1970). It is interesting to note that Cu in dacites from the two areas above is depleted to about 10 p.p.m. (Table 5). This is in contrast to previously described increases with fractionation (Prinz, 1968).

The Cu concentration of the Samoan alkali basalts is about average for this rock type. The concentrations of Cu do not correlate well with any major element in these rocks, or the andesites. The lack of diadochic replacement between Cu and the ferromagnesian ions of similar charge is of course partially due to the very different atomic radii of Cu, but Cu has a "site preference energy" for octahedral coordination that is only slightly less than that of Ni, and thus some preferential replacement of major cations should occur. The partition of Cu into the sulfide liquid during magmatic evolution must be responsible to some degree for the absence of covarient trends noted in this study.

## Rubidium

Previous work. The geochemistry of the rare alkali metal Rb is very closely related to that of K. Ionic radii of the two metals are very similar permitting Rb to replace K in ionic lattices. A weaker electrostatic bond force in Rb tends to concentrate it in the later K minerals, thereby concentrating Rb in the more acidic rocks, and hence in the upper parts of the lithosphere (Goldschmidt, 1954).

## Table 5

## Copper

| Rock Type | Cu (p.p.m.) | Source |
|---|---|---|
| Low-Si andesite (Bougainville) | 52 | Taylor *et al*. (1969b) |
| Low-Si andesite | 122 | This Study |
| Low-K andesite | 215 | Bryan and Ewart (1970) |
| Low-K andesite | 156 | This study |
| High-K andesite (Bougainville) | 150 | Taylor *et al*. (1969b) |
| Dacite (Bougainville) | 22 | Taylor *et al*. (1969b) |
| Dacite (Fonualei) | 28 | Bryan and Ewart (1970) |
| Alkali olivine basalt | 108 | Prinz (1968) |
| Alkali olivine basalt | 97 | This study |
| Alkali olivine basalt | 36 | Engel *et al*. (1965) |

Rb appears to be present only in feldspars and feldspathoids. It prefers K feldspar to plagioclase (Heier, 1962), where it substitutes for K positions. It is not known whether Rb replaces Ca or Na in plagioclase.

Ahrens _et al_. (1952) first noted the uniformity of K/Rb ratios in meteorites and terrestrial rocks. Much data have since accumulated to establish ratios for rocks in various geologic settings. Oceanic tholeiites, considered by some workers to be primitive basalts, have high K/Rb ratios of 800-2000 (Engel _et al_., 1965; Gast, 1965; Tatsumoto _et al_., 1965). Tholeiitic-alkaline associations, such as in Hawaii and other oceanic areas, have K/Rb ratios of about 500 (Lessing _et al_., 1963; Taubeneck, 1965). Tholeiites associated with calc-alkaline rocks in island arcs have high K/Rb values (Lowder and Carmichael, 1970).

Of the calc-alkaline rocks in island arcs, the low-K andesites have medium to high K/Rb values of 236-540 (Taylor and White, 1966; Taylor _et al_., 1969). High-K andesites have relatively low K/Rb ratios. Jakes and White (1970) show that the K/Rb ratios reflect the zonal arrangement of these rocks across island arcs, with values decreasing from tholeiites to calc-alkaline rocks to alkaline basalts.

As discussed above, alkaline rocks of oceanic areas have K/Rb ratios of about 500. Continental alkaline rocks have values closer to 400 (Gunn, 1965; Abbott, 1967; and others), which may reflect higher K/Rb ratios in the oceanic mantle (Lessing, *et al.*, 1963). Chayes (1964) has found that the K content in oceanic and circum-oceanic basalts is similar, and suggested that if oceanic areas have higher K/Rb ratios, Rb must be depleted in the oceanic mantle. Recent studies are divided on the question of regional Rb depletion (Heier, 1964; Prinz, 1968).

Seismic data have been interpreted by some writers to suggest that the origin of alkaline rocks is not directly related to the Benioff zone (Jakes and White, 1970), in which case the K/Rb ratios of these rocks would not reflect their position within an island arc along the Benioff zone. However, Kuno (1966) suggests that alkaline rocks represent the last stage of island arc formation. The medium K/Rb values of oceanic alkaline basalts would then indirectly place them between the high K/Rb values of tholeiites from island arcs and the low values of calc-alkaline rocks. This would not correlate with other evidence for a deep origin of alkali basalts (Juno, 1966, 1968, and others). Testing of the suggestion of Jakes and White (1970) that alkali basalts are not directly related to the origin of island arcs based on seismic evidence requires more data on the K/Rb ratio of alkalic basalts from island arc areas, which may differ from oceanic alkalic basalt in much the same way oceanic tholeiites differ in K/Rb ratio from those associated with island arcs (up to 2000 for oceanic tholeiites, and up to 1000 for island arc tholeiites).

It has been shown that fractionation or differentiation usually leads to a decrease in the K/Rb ratio (Heier and Adams, 1964; Abott, 1967; Barbieri et al., 1968; Shaw, 1968). Since it is considered that contamination is negligible in island arc rocks (Dickinson, 1968; Hedge, 1966, and others), the K/Rb values in a given volcanic series could represent the various degrees of fractionation (Jakes and White, 1970). Highest values in a series would be closest to initial K/Rb values of the magma, if these represent rocks least affected by later processes. The role of fractionation in island arc calc-alkaline rocks, then may be shown to some extent by K/Rb ratios across the arc.

Present work. Values for Rb covary closely with K in all rocks studied (fig. 21). The concentrations of Rb for all three volcanic sequences are considered to be accurate, at least relative to each other, on the basis of the K and Rb covariance. A problem is presented by K/Rb ratios in the Lauan and Tofuan rocks. The Lau andesites, which are chemically similar to the low-Si andesites of Bougainville (Taylor et al., 1969), have K/Rb ratios much like the tholeiites associated with island arcs (Table 6). The geographic location of the Lau samples in the island arc

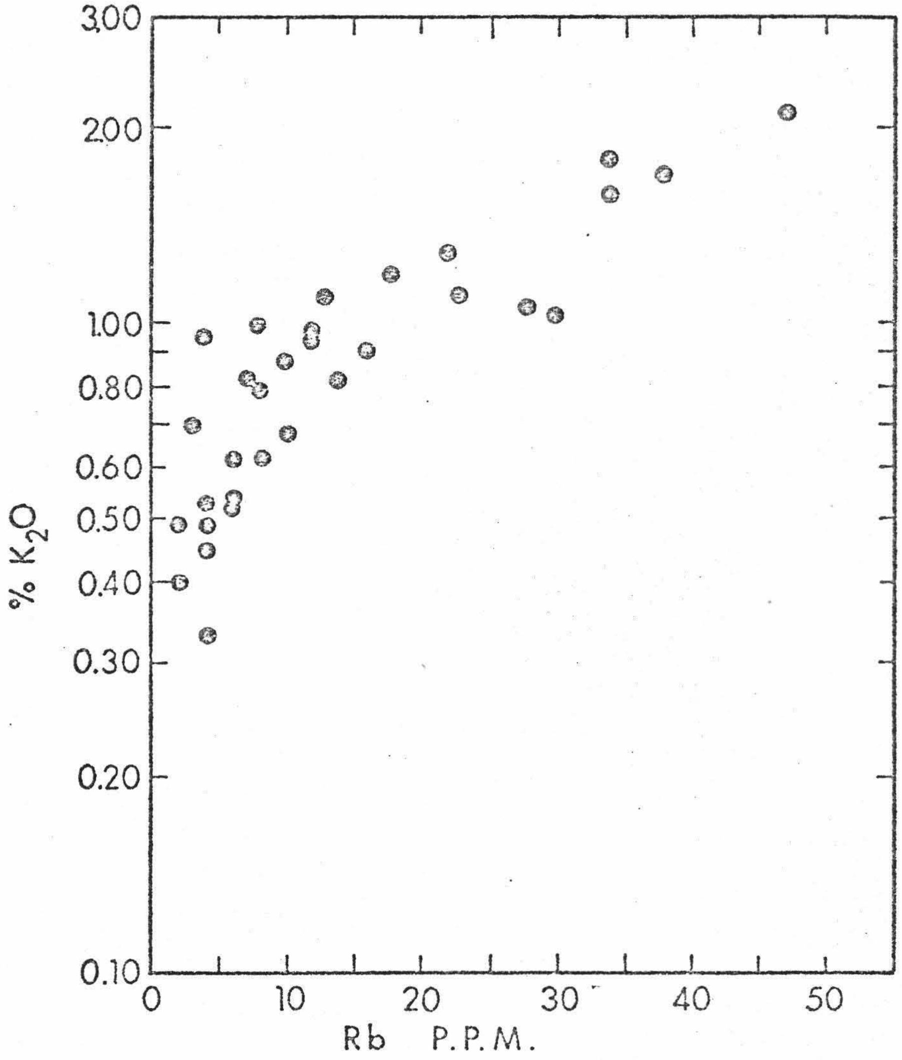

Fig. 21. Covariance of Rb and $K_2O$ in Lauan, Tofuan and Samoan lavas

## Table 6

### K/Rb RATIOS ACROSS ISLAND ARC STRUCTURE

| VOLCANIC SEQUENCE | K/Rb | SOURCE |
|---|---|---|
| Island arc tholeiite | 1070 | Gill (1970) |
| Island arc tholeiite | 440-1160 | Lowder and Carmicheal (1970) |
| Low K andesites | 236-540 | Taylor and White (1966) |
| Low K andesites | 590 | Taylor *et al*. (1969) |
| Low K andesites | 515-563 | Taylor *et al*. (1969) |
| Low K andesites | 1190 | This study |
| High K andesite | 297-330 | Taylor *et al*. (1969) |

### K/Rb RATIOS FOR OCEANIC ALKALI BASALT

| | | |
|---|---|---|
| Oceanic alkali basalt | 500 | Lessing *et al*. (1963) |
| Oceanic alkali basalt | 580 | This study |

would seem to require them to be in the medium K/Rb range, as are the low-Si andesites of Bougainville, assuming the zonal arrangement of Jakes and White (1970) to be correct. Moreover, the Lauan values should be less than the Tofuan K/Rb ratios, if low-K andesites on the oceanic side of island arcs have higher K/Rb values than low-Si andesites further from the oceanic crust, as suggested by the zonal arrangement of K/Rb ratios. In fact, the Tofuan lavas have the same K/Rb ratio as the Lau rocks. In this instance then, the zonal decrease in K/Rb does not seem to be valid. One possible reason for the absence of a K/Rb decrease across the arc and high K/Rb values in these rocks is a Rb depletion. As mentioned above, Heier (1964)suggested that Rb-depleted areas may exist. In addition, the Rb values for the Lauan samples are about half the concentrations in the Bougainville rocks (Table 6), and the Tofuan values are about half the reported Rb values for low-K andesites from Saipan. A second possibility is that with the extremely low abundance of Rb in these rocks, relative to K, a small increase or decrease of Rb detected vastly changes the ratio of K/Rb. In many cases 3 or 4 p.p.m. Rb more than detected will change the ratio to within previously reported values. However, reported values are subject to the same difficulties.

The Samoan samples display a K/Rb ratio which is very close to reported values for oceanic alkali basalts (Table 6).

The accuracy of the Samoan K/Rb ratios and the distinct covariance of K and Rb seems to indicate that the unusually high values described for the andesites are also accurate, and actually different from previously described ratios. In view of this, there is one additional factor which could affect the K/Rb ratio of volcanic sequence and that is the degree of fractionation it has undergone. The Lauan and Tofuan andesites do not show strong fractionation when K/Rb is plotted against K (fig. 22). The previously reported island arc samples do show a fractionated character, (Taylor *et al.*, 1969) which would in effect lower the average K/Rb ratio. Also, Taylor (1965) has shown that K/Rb ratios may be used as petrogenetic indicators. Low K/Rb can be attributed to fractional crystallization. The high values of K/Rb in addition to the absence of a trend in the K/Rb vs. K diagram indicates little fractionation in the Lauan and Tofuan rocks.

## Strontium

*Previous work*. Sr is distributed in Ca-rich minerals such as plagioclase, clinopyroxene and apatite. It is also found in high-temperature K-bearing minerals such as K feldspar and feldspathoids. In plagioclase, it is the oligoclase through labradorite members which contain the most Sr (Heier, 1962), although no direct correlation is shown between Ca and Sr content.

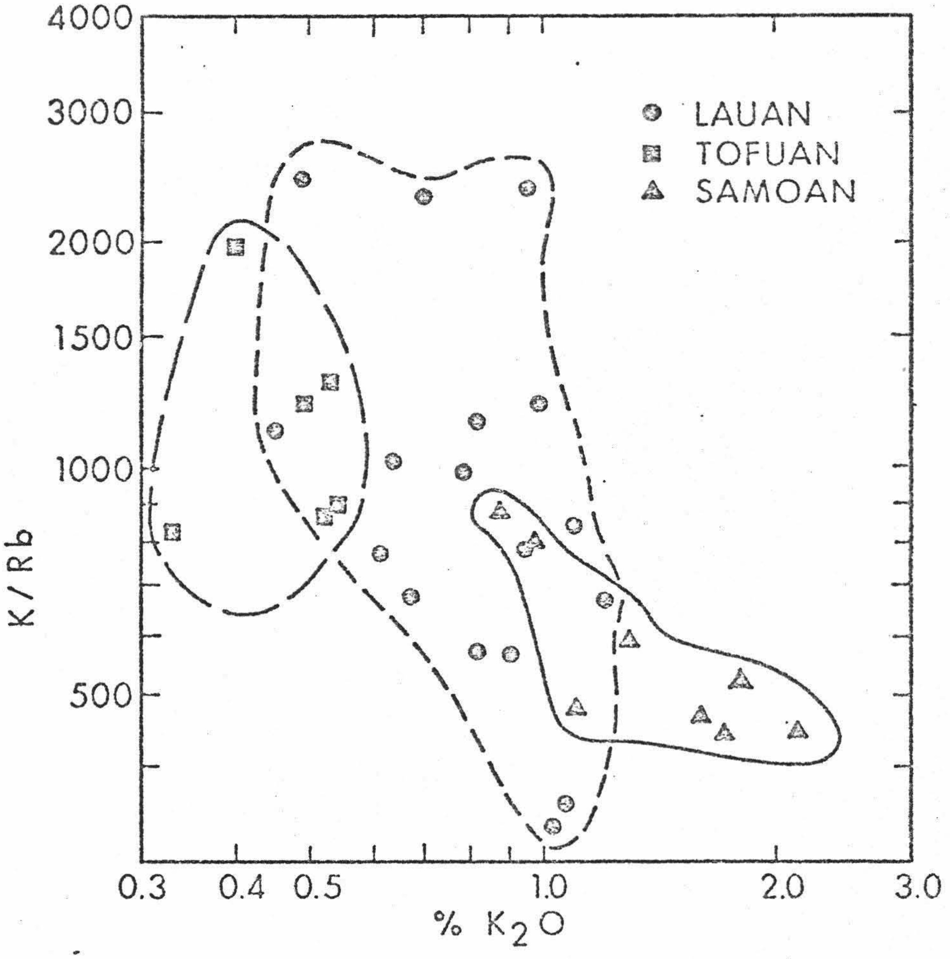

Fig. 22. K/Rb vs $K_2O$ in Lauan, Tofuan and Samoan lavas

Turekian and Kulp (1956) found no marked covariance between Ca and Sr in plutonic and extrusive rocks. They attribute this to regional variation of Sr and local fractionation stage. Wager and Mitchell (1951) reported that Sr increases in residual magma until about 60% solidification, and then drops off.

Faure and Hurley (1963) suggested that the source region for basaltic magmas has a very narrow range of Rb/Sr ratios. Roe (1964) showed that Rb and Sr in these rocks is from their source material in the mantle. He suggested that shallow regions of the upper mantle have higher Rb/Sr ratios than deeper regions. Tholeiitic rocks have a higher Rb/Sr ratio than alkalic rocks. This would indicate a deeper origin for alkalic basalt, as suggested by petrologic evidence.

Sr in calc-alkaline rocks of the circum-Pacific has been reported by several workers. Ewart and Stipp (1968) have shown considerable variation in Sr content throughout the volcanic sequence studied. The Rb/Sr is generally high, with a ratio of about 1 for most rocks in the series, except the andesites, which range from 0.25-0.05. Taylor et al. (1969) have found high Sr values ( >500) in most andesites from Saipan, Bougainville and Fiji. Rb/Sr ratios are typically low (0.03-0.04) except in high-K andesite, which has a high Rb/Sr ratio. The high Sr was attributed to high Ca content of these rocks. Bryan and

Ewart (1970) reported relatively low Sr (225 p.p.m.) in andesite from Late Island, Tonga. The Ca content of this andesite is also relatively high, however, and the Sr depletion is probably a reflection of regional source differences.

Nockolds and Allen (1954) reported very high values of Sr for the middle members of the Polynesian alkali basalts based on the function [(1/3 Si + K) - (Ca + Mg)], and complete depletion in the end stage members of the sequence. Turekian and Kulp (1956) reported one value of 495 p.p.m. for Sr in basalt from Tutuila, Samoa. Other oceanic basalts showed a range of 43-1367 p.p.m. The average value for all alkali basalt is 700 p.p.m. (Prinz, 1968).

Present work. Sr in Lauan, Tofuan and Samoan lavas does not show a covariance with Ca (fig. 23), due to the factors mentioned above. However, increasing K content in these rocks is paralleled by increasing Sr values (fig. 24). As shown in Table 7, the Tofuan andesites, which are lower in K than the Lauan rocks, have less Sr. The Tofuan lavas are sufficiently depleted in Sr (average value of 174 p.p.m.) with respect to the Lauan rocks (327 p.p.m.) to suggest a zonal or regional variation across the Tonga Island Arc. The average value of 585 p.p.m. for high-K andesites found by Taylor et al. (1969) would represent a further progression of Sr values across an island arc.

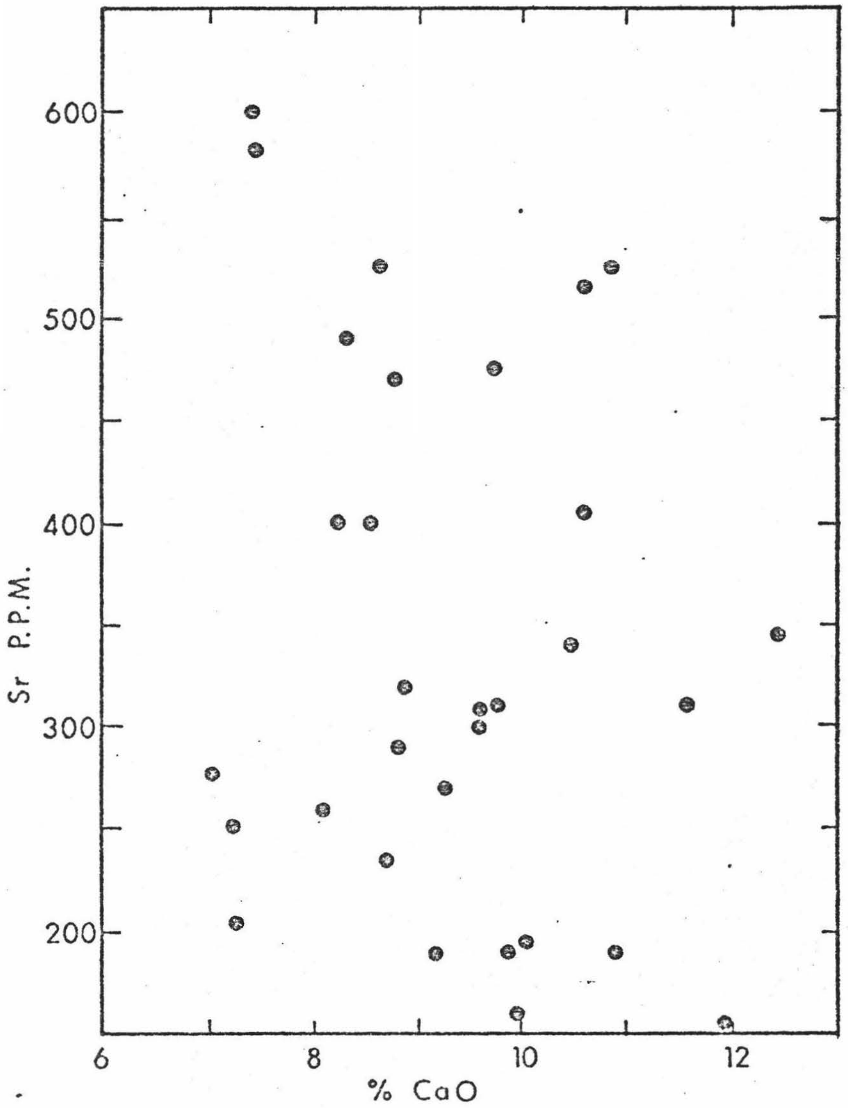

Fig. 23. Sr vs. CaO in Lauan, Tofuan and Samoan lavas

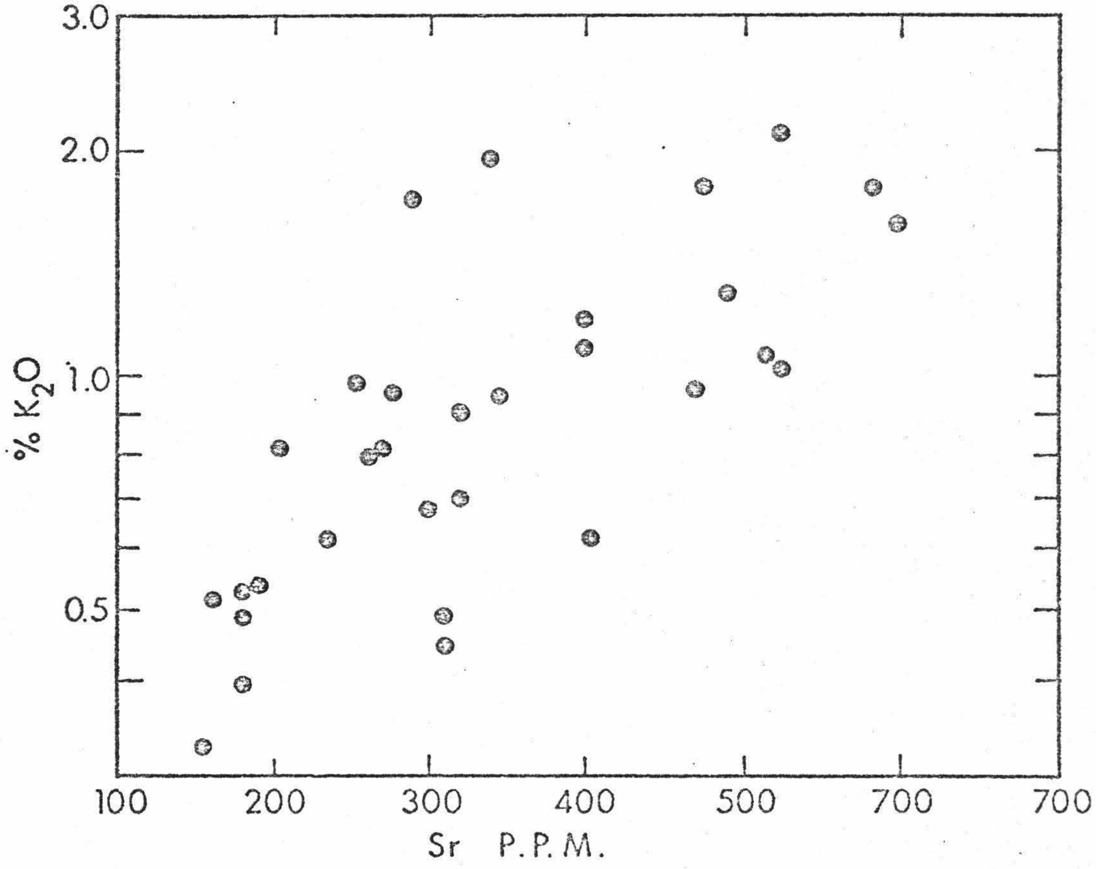

Fig. 24. Covariance of Sr and $K_2O$ in Lauan, Tofuan and Samoan lavas

## Table 7

## Strontium

| Rock Type | Sr (p.p.m.) | Rb/Sr | Source |
|---|---|---|---|
| Low-Si andesite | 327 | 0.03 | This study |
| Low-Si andesite (Bougainville) | 792 | 0.03 | Taylor *et al.* (1969b) |
| Low-K andesite | 225 | 0.04 | Bryan and Ewart (1970) |
| Low-K andesite | 174 | 0.03 | This study |
| High-K andesite (Bougainville) | 585 | 0.13 | Taylor *et al.* (1969b) |
| Alkali basalts | 472 | 0.05 | This study |
| Alkali basalts | 700 | 0.04 | Prinz (1968) |
| Alkali basalts | 815 | Not Reported | Engel *et al.* (1965) |

Rb/Sr values for the Lau samples are uniformly low, averaging .03. This is coincident with other calc-alkaline Rb/Sr values for island arcs of the circum-Pacific. The ratio is about the same for the Tofuan rocks as well. All samples studies show some covariance between Rb and Sr (fig. 25), which accounts for the uniformity of Rb/Sr ratios. Since both are covarient with K, the relationship between Rb and Sr is most likely an indirect one.

The Samoan alkali basalts contain an average of 472 p.p.m. Sr, which is very close to the one previously reported value from Tutuila. The average value of 0.05 for Rb/Sr in these samples is very much like that for average alkali basalt reported by Prinz (1968), although individual ratios vary from 0.02-0.08. If previous studies are correct, a deep source of origin for these rocks is indicated.

In all the rocks studied, there is a close association of Sr and P (fig. 26). The apatite which contains Sr appears to control the overall Sr content to some extent. Although many authors have published data showing high Sr content in apatite from various rocks (Larsen _et al_., 1952; Cruft, 1966), no evaluations of the effect of apatite on the Sr content in calc-alkaline and alkalic source material have been made. The higher Sr values away from the oceanic side of an island arc could be due, at least in part, to inclusion of more apatite in these rocks. Because of the

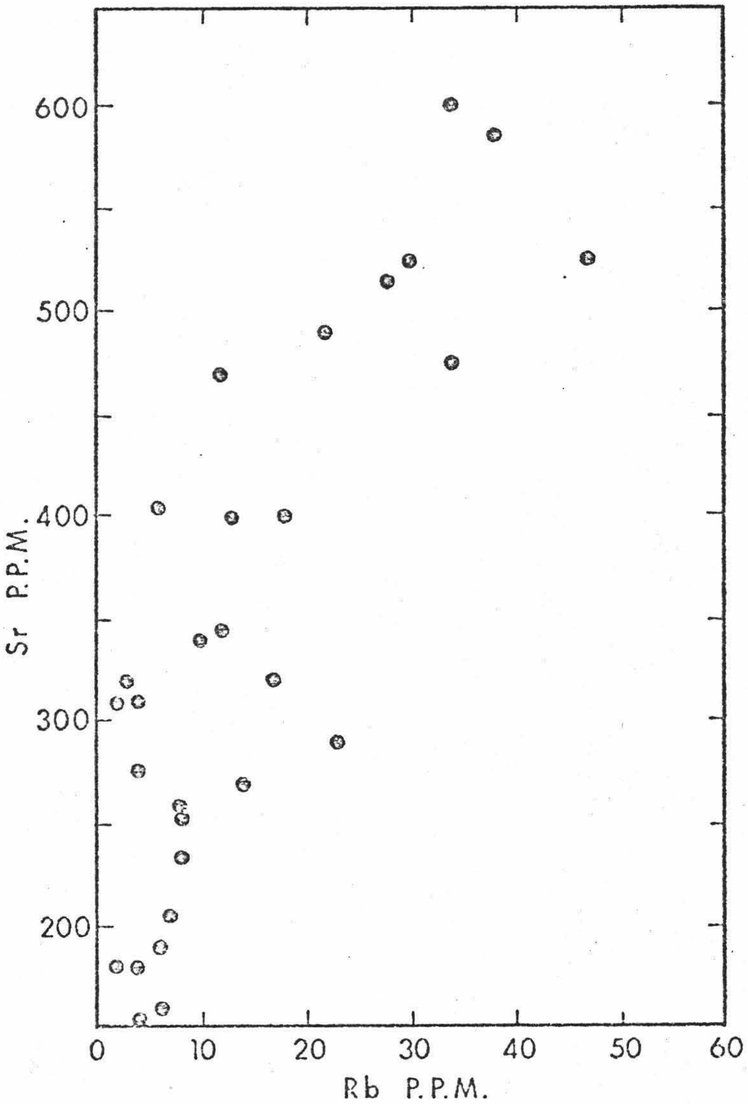

Fig. 25. Covariance of Sr and Rb in Lauan, Tofuan and Samoan lavas

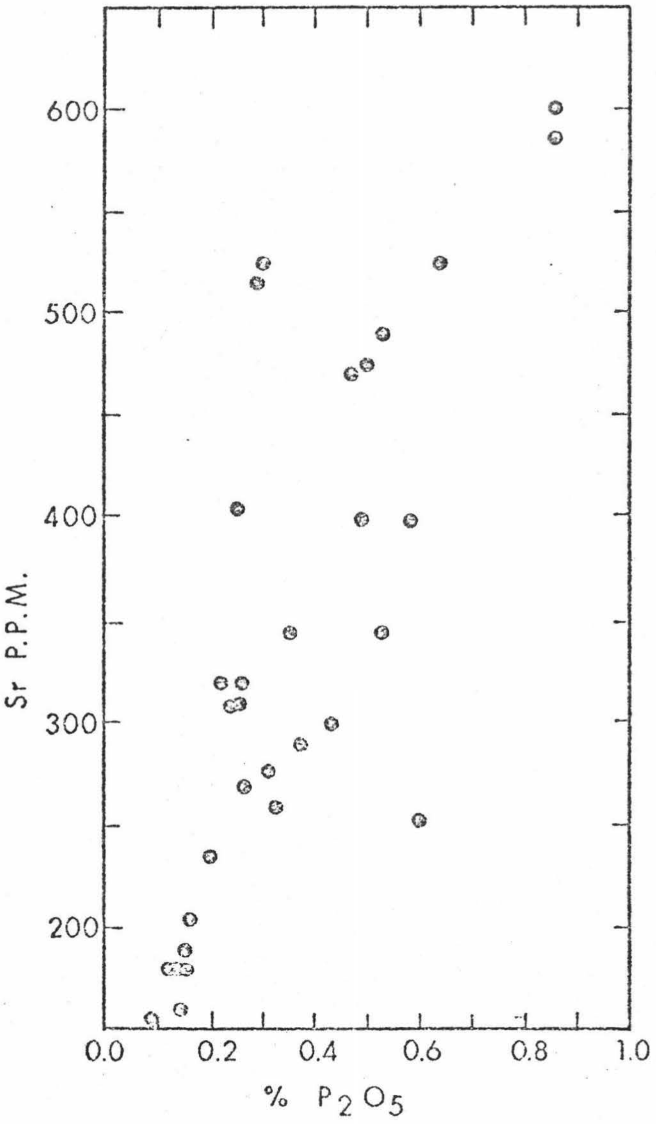

Fig. 26. Covariance of Sr and $P_2O_5$ in Lauan, Tofuan and Samoan lavas

nature of apatite in igneous melts, volatiles and magmatic density could be important factors in the Sr distribution of calc-alkaline rocks. The removal of accumulation of apatite in alkali basalts whose density as a melt favors gravitative setting of apatite would enrich or deplete Sr in these rocks and tend to obscure the initial abundance of Sr. Rb/Sr ratios based on a fractionated Sr content would be incorrect in such cases. More investigation of the effect of apatite phases on calc-alkaline and alkalic source material is necessary.

## Barium

Previous work. The geochemistry of Ba is characterized by its relationship to K. The ionic radii of divalent Ba and univalent K are similar, and capture of Ba occurs in the crystal lattice of K-bearing minerals (Goldschmidt, 1954).

Ba is found mainly in feldspars, feldsparthoids, and apatite. Clinopyroxene and chlorite are also known to contain Ba. In plagioclase, oligoclase through labradorite have the most abundant Ba (Heier, 1962). K feldspars are rich in Ba (2000-3000 p.p.m.) because of the K-Ba coherence.

Goldschmidt (1954) and Nockolds and Allen (1953) showed that the K/Ba ratio remains constant or increases slowly as crystallization proceeds. Wager and Mitchell (1951) showed that Ba is enriched in residual liquids.

Thus the Ba content of magma changes with fractionation, and probably increases.

Large differences in Ba content within a basaltic province and within petrographic types cannot be explained except by initial abundance variations (Prinz, 1968).

Ba in calc-alkaline rocks from the circum-Pacific has been studied by Markhinin (1964) for Kamchatka and the Kuriles, Taylor *et al*. (1969) for Fiji, Bougainville and Saipan, and Taylor (1969) for average circum-Pacific andesites. The Ba content of andesites from these areas is generally low, averaging about 300 p.p.m. Bryan and Ewart (1970) reported very low values of Ba from Tonga, corresponding to low-K contents. However, no significant difference in Ba content was noted between high-K andesites and low-Si andesites. As shown below, covariance between K and Ba in andesites is most effective below 1% K.

Alkali basalts contain about twice the Ba content of tholeiites. Nepheline-normative alkali basalts contain more Ba than olivine-normative alkali basalts without nepheline, because of the Ba rich feldspathoids in the former. The generally high average value of Ba in alkali basalts (400 p.p.m.) is probably due to the increase of alkalies. Nockolds and Allen (1954) have reported a range of 50-1100 p.p.m. Ba in Polynesian alkali basalt, with average values close to the reported average for all alkali basalts (Prinz, 1968).

Present work. Ba in Tofuan andesites is extremely depleted, averaging only 38 p.p.m. The K content is very low in these rocks, therefore, the low abundance of Ba is not unusual. The Lau andesites and alkali basalts have Ba distributions very much like those of other areas in the circum-Pacific, with an average of 310, which is close to that reported for andesites by Taylor (1969).

The Ba content of the Samoan basalts averages 396 p.p.m., which is almost the average for all alkali basalts.

Although a number of authors have related Ba to K in igneous rocks, the relationship is not as strong as expected in the rocks studied. The best covariance for K and Ba occurs at less than 1% K for all rocks (fig. 27). The underlying reason for lack of covariance in the Lau samples could be initial abundance variation. The similar K contents, regional proximity, and lithologic similarities of the Lau samples suggest that Ba variations are not due to mineralogic or petrologic differences, but are based on local initial abundance variations such as those reported in the literature.

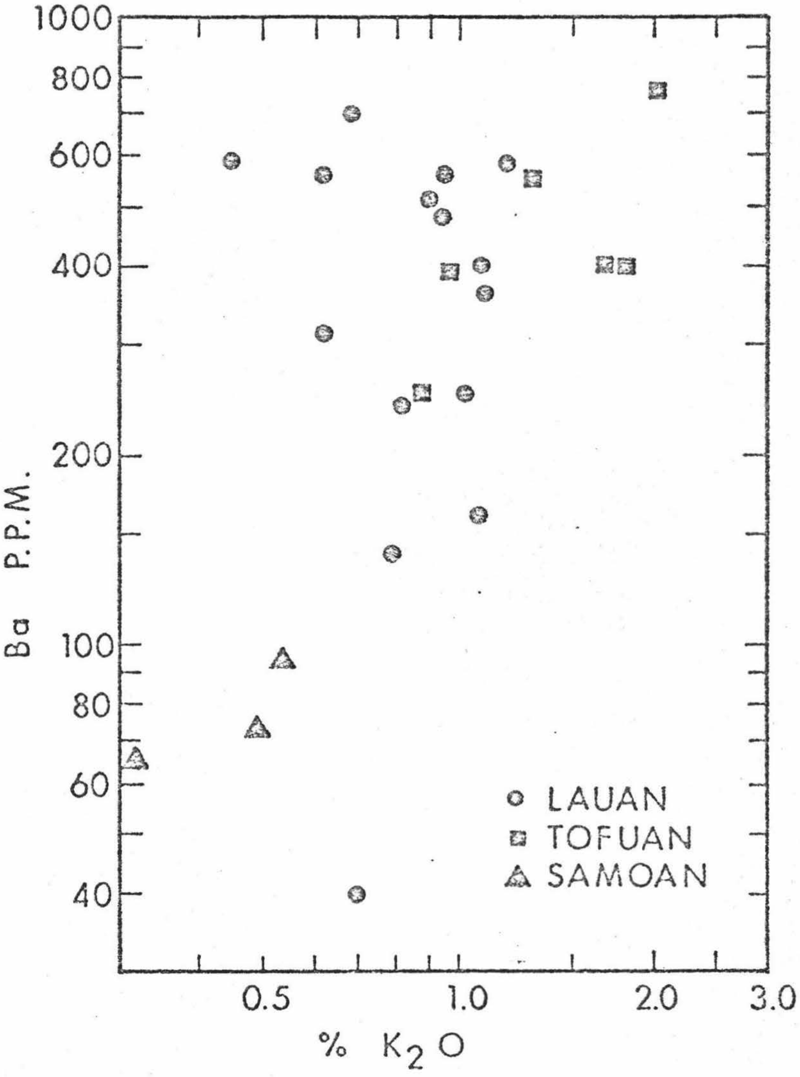

Fig. 27. Ba vs $K_2O$ in Lauan, Tofuan and Samoan lavas

# DISCUSSION AND CONCLUSIONS

Chemical variations within rocks of the calc-alkaline suite have been attributed to a number of causes. The differentiation of a parent basalt magma under high oxygen partial pressures has been suggested as a source of variation in andesites (Osborn, 1959). Earlier, the concept of contamination of mantle-derived basalt by hydrous crustal matter was introduced to explain the geochemistry of andesites (Waters, 1955). More recently, Hamilton (1964) has proposed that partial melting of the mantle or crust is responsible for various andesitic compositions.

Geochemical and geophysical evidence have led to the hypothesis that andesites are derived directly from the mantle, and are not influenced by crustal materials or processes. The lack of thick crust or contaminating sial beneath island arcs (Gorshkov 1962, 1965) has convinced a number of authors that primary andesite magmas are the means by which sialic crust is segregated from the mantle (White 1965; Taylor 1967). However, there is no currently accepted quantitative geochemical model for deriving andesites by the partial melting of any of the suspected mantle compositions. Several qualitative models which support experimental data have been suggested. Yoder and Tilley (1962) presented arguments the formation of andesite from feldspathic mantle rock. Green and Ringwood (1966) gave experimental data which indicated that initial liquids formed by partial melting of eclogite within the mantle will likely have the composition of andesite. None of the experimental data preclude the subsequent evolution of magmas by subcrustal fractionation, such as that suggested by O'Hara (1965) for basalt magmas. However, large scale fractionation of basalt to produce andesite is seen as unlikely in view of the immense volume of crystal accumulates that must be separated to form andesites (Green and Ringwood, 1966).

Since it appears that crustal structure in island arcs is not a primary influence on the variability of andesitiic magma, numerous authors have directed attention to subcrustal structure, especially the inclined seismic zones dipping beneath island arcs. Since Benioff (1954) suggested these zones as probable loci of magma generation, evidence relating chemical composition and depth to a seismic zone has accumulated. Kuno (1959, 1960) noted the relationship between tholeiitic, high-Al, and alkalic olivine basalt volcanoes and vertical depth to the inclined seismic zone. Taneda (1963) and Sugimura (1966) demonstrated that alkalinity of andesitic rocks can be related to depth to the seismic zone. Dickinson (1968) determined that there is a close correlation between potash content in a given andesite suite and vertical depth to the seismic zone dipping beneath a volcanic arc. Taylor (1969) and Taylor *et al.* (1969) suggested that calc-alkaline rocks with their characteristic trace element distributions in island arcs reflect varying degrees of partial melting along the seismic zone. The incorporation of higher crustal material transported down the dipping seismic plane is considered unimportant by these authors, based on the high values of Mn, Pb, Ba, Ni etc. which would be added by the sediments. These are not seen in the andesites above the seismic zone. Jakes and White (1970) proposed a zonal arrangement of the calc-alkaline rocks with respect to trace element abundances based on fractional crystalization of a sinking slab of oceanic crust.

The current study supports some of the previously established concepts explaining the genesis of andesitic magma. However, several questions are raised concerning the effects on trace element distribution of processes not directly related to the tectonic mechanisms which operate on island arc structure.

It is readily apparent that the andesites and basaltic andesites of the Tonga-Kermadec Arc where investigated are depleted in ferromagnesian trace elements. Alkali basalts from the same region are not (Lau 1 and Lau 120). The low abundance of ferromagnesian elements in andesites is consistent with data from elsewhere in the circum-Pacific. Since ultramafic rocks contain high values for these elements, removal from the mantle parent of andesites seems inevitable. The depletion of ferromagnesian elements from various possible mantle materials has been discussed by many authors (O'Hara 1965; Green and Ringwood 1966; Gast 1968). It is only clear that such possible parents as high-Al basalts cannot explain the unusually low abundances of Ni, Co, Cr, etc. In such a case, minerals containing these elements would be removed during fractionation, thereby depleting the residual fluids in these elements. Other possible mantle rocks, such as eclogite or pyrolite may be depleted in ferromagnesians to produce an andesitic composition.

Other trace element patterns do not seem to limit the origin of andesites to one parent or process. K/Rb ratios are high, which does not favor fractional crystallization, but the large highly charged cations Ba and Zr are not significantly depleted, which does imply a certain degree of fractional crystallization. The regional zonation of major and minor elements in the andesites of Lau and Tofua is strong enough to merit comparison with similarly zoned island arcs of the circum-Pacific. K, Ba, Rb, and Sr clearly increase while V decreases away from the oceanic side of the island arc structure. Whether this zonation applies to rocks not appearing on the highest parts of the volcanic platform making up the island arc is not known. Recently, for example, Karig (1970) has found rocks of tholeiitic composition between the Lau Islands and Tofua. Jakes and

White (1970) maintain that tholeiites associated with calc-alkaline rocks of island arcs have variable K/Rb ratios, but most are high. This would tend to place these rocks out of the zonation sequence. The alkalic basalts from the Lau Islands in this study also have high K/Rb values. These rocks do not fit any zonation scheme involving compositional variation either. It would appear then, that only calc-alkaline rocks which represent a relatively late stage in the development of the island arc can clearly be shown to be chemically variable across an arc. These calc-alkaline rocks could be related to the seismic zone, whereas the associated lavas of different petrologic suites do not require an origin at the dipping seismic plane.

The alkali olivine basalts of American Samoa and the Lau Islands provide a geochemical contrast to the andesites of the Lau Islands and Tofua. It is interesting to note that alkalic rocks from Samoa and the Lau Islands have very similar trace element geochemistry, although they are separated by the trench and arc structure of the Tonga-Kermadec System. Basalts from both areas are high in Ni, Co, Cr, and Sr, and in addition they contain expected abundances of other trace elements. Following Kuno (1957) and others, alkalic basalt may be derived from an independent parent magma. Several schemes for accomplishing the necessary fractionation have been proposed

(O'Hara 1965; Green and Ringwood 1966). None of the models inferred reliance on partial melting along a dipping seismic plane to produce alkalic basalts. Kuno (1966) did relate the appearance of alkali basalts to depth of melting along the Benioff zone. It appears therefore, that more than one subcrustal structure is suitable for the evolution of alkali basalts. In view of this, the trace element content reported in this study does not behave as an indicator of the subcrustal structure, and the minor elements only establish qualitative limits on the composition of the source from which the basalts came.

In summary, the following conclusions can be offered:

1. The andesites and basaltic andesites of the Lau Islands and Tofua are depleted in ferromagnesian trace elements except V.
2. These rocks are low in Rb, have low Rb/Sr ratios, but have unusually high K/Rb ratios.
3. Rb and Ba increase across the arc toward the continental side, while V decreases.
4. In a fractionated sequence of the andesites, Ni/Co ratios display an enrichment opposite to the expected trend.
5. Alkali basalts from the Lau Islands and Samoa contain high ferromagnesian contents and expected values of other trace elements.

6. Although in agreement with past data for other circum-Pacific island arcs, the present study does not conclusively limit the source of island arc volcanic rocks to depths coincident with the dipping seismic plane beneath the arc.

# APPENDIX A

## CHEMICAL ANALYSES OF LAUAN ROCKS

### Results of Chemical Analyses

| | L-1C | L-3C | L-11C | L-18C |
|---|---|---|---|---|
| $SiO_2$ | 43.02 | 51.89 | 54.85 | 56.86 |
| $TiO_2$ | 2.18 | 1.38 | 0.90 | 1.17 |
| $Al_2O_3$ | 14.05 | 18.34 | 17.62 | 17.32 |
| $FeO$ | 7.92 | 6.43 | 5.52 | 6.40 |
| $Fe_2O_3$ | 2.78 | 3.69 | 3.63 | 2.26 |
| $CaO$ | 12.46 | 9.58 | 8.58 | 7.02 |
| $MgO$ | 10.63 | 3.19 | 3.88 | 2.93 |
| $MnO$ | 0.16 | 0.18 | 0.18 | 0.21 |
| $Na_2O$ | 2.89 | 3.00 | 2.75 | 3.47 |
| $K_2O$ | 0.95 | 0.68 | 0.62 | 0.96 |
| $H_2O(+)$ | 1.72 | 1.01 | 0.93 | 1.45 |
| $H_2O(-)$ | 0.56 | 0.50 | 0.67 | 0.27 |
| $P_2O_5$ | 0.53 | 0.43 | 0.20 | 0.31 |

## Results of Chemical Analyses

Unit : %

| | L-26c | L-30c | L-31c | L-34c | L-36c | L-45c | L-62c |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 47.50 | 50.40 | 50.99 | 56.03 | 50.52 | 54.10 | 50.13 |
| $TiO_2$ | 0.94 | 0.73 | 0.77 | 0.72 | 1.18 | 1.73 | 0.76 |
| $Al_2O_3$ | 19.00 | 19.54 | 19.63 | 18.12 | 20.32 | 15.04 | 19.54 |
| $Fe_2O_3$ | 3.63 | 4.52 | 4.68 | 3.38 | 3.91 | 5.47 | 4.24 |
| FeO | 7.57 | 5.74 | 5.65 | 4.73 | 5.28 | 6.09 | 4.59 |
| MnO | 0.17 | 0.21 | 0.18 | 0.21 | 0.17 | 0.22 | 0.13 |
| MgO | 5.78 | 4.29 | 4.25 | 3.09 | 3.05 | 3.31 | 5.49 |
| CaO | 11.57 | 9.76 | 9.60 | 8.24 | 10.58 | 7.23 | 10.84 |
| $Na_2O$ | 1.90 | 2.62 | 2.34 | 3.33 | 2.70 | 3.81 | 2.03 |
| $K_2O$ | 0.70 | 0.45 | 0.49 | 1.20 | 0.62 | 0.99 | 1.03 |
| $H_2O(+)$ | 0.38 | 0.92 | 0.89 | 0.91 | 0.97 | 0.80 | 1.08 |
| $H_2O(-)$ | 1.32 | 0.89 | 0.91 | 0.35 | 0.77 | 0.67 | 0.72 |
| $P_2O_5$ | 0.22 | 0.25 | 0.24 | 0.49 | 0.25 | 0.60 | 0.30 |
| Total | 100.68 | 100.32 | 100.62 | 100.80 | 100.23 | 100.06 | 100.77 |

| | L-63c | L-76c | L-91c | L-94c | L-109c | L-120c |
|---|---|---|---|---|---|---|
| $SiO_2$ | 50.40 | 55.39 | 55.25 | 58.76 | 54.57 | 47.22 |
| $TiO_2$ | 0.72 | 0.75 | 0.81 | 0.81 | 1.07 | 2.51 |
| $Al_2O_3$ | 19.76 | 17.83 | 16.56 | 17.26 | 17.86 | 16.64 |
| $Fe_2O_3$ | 2.91 | 4.42 | 3.43 | 3.35 | 3.80 | 2.87 |
| FeO | 5.03 | 3.77 | 4.11 | 3.58 | 3.99 | 8.26 |
| MnO | 0.14 | 0.15 | 0.15 | 0.14 | 0.18 | 0.17 |
| MgO | 5.49 | 4.01 | 5.13 | 3.60 | 4.78 | 6.70 |
| CaO | 10.60 | 8.87 | 9.26 | 7.26 | 8.08 | 8.55 |
| $Na_2O$ | 1.92 | 2.61 | 2.79 | 3.06 | 3.21 | 3.29 |
| $K_2O$ | 1.07 | 0.91 | 0.82 | 0.82 | 0.79 | 1.10 |
| $H_2O(+)$ | 1.24 | 0.65 | 0.71 | 0.87 | 0.77 | 1.35 |
| $H_2O(-)$ | 0.70 | 0.74 | 0.66 | 0.69 | 0.67 | 0.73 |
| $P_2O_5$ | 0.29 | 0.26 | 0.26 | 0.16 | 0.32 | 0.58 |
| Total | 100.27 | 100.36 | 99.94 | 100.36 | 100.09 | 99.97 |

## APPENDIX B

### Chemical Analysis of Tofuan Rocks

Unit : %

| | Tofua 4 | Tofua 17 | Tofua 32 | Tofua 33 | Tofua 50 | Tofua 68 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 56.03 | 53.80 | 57.13 | 56.04 | 54.42 | 55.93 |
| $Al_2O_3$ | 15.83 | 14.47 | 14.59 | 15.38 | 16.56 | 16.59 |
| $Fe_2O_3$ | 3.47 | 2.71 | 2.58 | 3.63 | 4.65 | 6.25 |
| FeO | 7.32 | 7.07 | 8.43 | 6.92 | 5.32 | 4.41 |
| $TiO_2$ | 0.77 | 0.49 | 0.74 | 0.71 | 0.64 | 0.73 |
| CaO | 9.95 | 11.92 | 9.17 | 9.86 | 10.89 | 10.03 |
| MgO | 3.61 | 7.34 | 4.22 | 4.46 | 4.71 | 3.15 |
| $Na_2O$ | 2.29 | 1.48 | 2.23 | 2.07 | 2.00 | 1.98 |
| $K_2O$ | 0.52 | 0.33 | 0.53 | 0.49 | 0.40 | 0.54 |
| MnO | 0.16 | 0.17 | 0.18 | 0.17 | 0.16 | 0.16 |
| $H_2O(+)$ | 0.48 | 0.51 | 0.62 | 0.61 | 0.64 | 0.50 |
| $H_2O(-)$ | 0.15 | 0.29 | 0.24 | 0.27 | 0.25 | 0.21 |
| $P_2O_5$ | 0.14 | 0.09 | 0.15 | 0.14 | 0.12 | 0.15 |
| Total | 100.72 | 100.67 | 100.81 | 100.75 | 100.76 | 100.63 |

# APPENDIX C

## Chemical Analyses of Tutuilan Rocks

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 45.09 | 45.08 | 48.95 | 48.02 | 47.94 | 48.33 | 43.88 | 46.22 |
| $Al_2O_3$ | 13.70 | 14.87 | 14.03 | 13.75 | 14.81 | 16.16 | 8.88 | 10.63 |
| $Fe_2O_3$ | 4.29 | 5.34 | 5.15 | 3.37 | 4.22 | 4.77 | 7.57 | 5.41 |
| $FeO$ | 10.71 | 9.67 | 7.28 | 8.99 | 9.16 | 7.43 | 6.23 | 7.72 |
| $CaO$ | 8.79 | 8.31 | 8.63 | 9.74 | 7.40 | 7.45 | 8.80 | 10.48 |
| $MgO$ | 7.01 | 5.64 | 4.47 | 5.28 | 4.61 | 4.56 | 16.00 | 11.94 |
| $Na_2O$ | 2.66 | 3.19 | 3.23 | 2.89 | 3.65 | 3.76 | 1.73 | 1.96 |
| $K_2O$ | 0.97 | 1.29 | 2.11 | 1.78 | 1.59 | 1.68 | 1.11 | 0.88 |
| $H_2O(+)$ | 0.74 | 0.81 | 0.90 | 0.71 | 0.99 | 1.31 | 1.05 | 0.87 |
| $H_2O$ | 0.54 | 0.50 | 0.76 | 0.48 | 0.72 | 0.91 | 0.96 | 0.78 |
| $TiO_2$ | 5.26 | 5.29 | 3.95 | 4.06 | 3.69 | 3.00 | 3.06 | 3.13 |
| $MnO$ | 0.15 | 0.15 | 0.15 | 0.16 | 0.17 | 0.16 | 0.16 | 0.15 |
| $P_2O_5$ | 0.47 | 0.53 | 0.64 | 0.50 | 0.86 | 0.86 | 0.37 | 0.35 |
| Total | 100.38 | 100.67 | 100.25 | 99.73 | 99.81 | 100.38 | 99.80 | 100.52 |

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