SOME TRACE ELEMENTS IN HAWAIIAN LAVAS

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Thesis

Doctor of Philosophy, Geosciences--Geology
University of Hawaii, 1967

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ABSTRACT

About 170 Hawaiian lavas have been newly analysed for Rb, Sr, and Zr, about 150 for Ni, and about 100 for Co and V. Twenty Samoan samples also have been analysed for Rb, Sr, Zr, and Ni. Eight HIG-USGS interlaboratory standards have been analysed for the above elements, and new independent Rb and Sr analyses have been made for the international rock standards W-1 and G-1.

The distribution of strontium in Hawaiian volcanoes is linked closely with that of phosphorus. Nickel and cobalt vary with magnesium, which is a function of the olivine content. The distribution of vanadium is more closely linked to that of titanium than to any other element. Zirconium varies with potassium in alkalic and post-erosional lavas but shows a weak covariance in Hawaiian tholeiites. Antarctic tholeiites, with higher potassium contents than Hawaiian tholeiites, show a K vs. Zr distribution that parallels that for Hawaiian alkalic lavas.

All element pairs investigated show clear to suggested differences between individual Hawaiian volcanoes. These differences presently show no definite correlation with other features. The covariation of any element pair is almost always smooth and indifferent to the tholeiite-alkalic distinction, indicating a common or closely interrelated origin for both suites. Lavas of the Honolulu and Koloa series, as well as similar lavas, are commonly distinct in their trace

element distributions but also show features that link them with other lavas of the same volcano.

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INTRODUCTION

Prior to this research little was known about trace element distributions in Hawaiian lavas. This is not to say that data did not exist but that it was limited, often of low precision and accuracy, and allowed few insights into the chemistry of Hawaiian volcanoes. This research has yielded detailed and extensive data on the distributions of four trace elements, Ni, Cr, Rb and Sr, in Hawaiian lavas and of two other trace elements, Co and V, in two Hawaiian volcanoes and two series of post-erosional lavas.

It was hoped that this research would shed some light on the tholeiitic-alkalic problem that has been the center of much controversy and research. This has been done in that previously unknown aspects of the problem have been outlined. For example, the close association of Sr and P was not only unknown, it was unexpected in Hawaiian lavas.

In presenting the results of this research I have emphasized similarities and differences in the data rather than the alkalic or tholeiitic classification of the samples. This emphasis was arrived at in analyzing the data.

MATERIALS, METHODS AND ANALYTICAL RESULTS

I. Samples used

The samples used in this study are mostly those for which Macdonald and Katsura (1964) have already published major element analyses. The second largest body of samples is from a similar study of the late lavas of the Hawaiian Islands by G. A. Macdonald. Major element analyses exist for these samples also. The Samoan samples are those used by G. Stice (unpublished University of Hawaii Ph.D. thesis) in a study of the geology and petrology of part of American Samoa. A set of eight 1955 Kilauean lavas was donated by H. A. Powers of the Volcano Observatory. Other data for these samples have been published by Macdonald and Eaton (1964).

While this research was in progress a set of eight Hawaiian lavas was assembled as Hawaii Institute of Geophysics-United States Geological Survey interlaboratory standards. They have been analyzed for the elements studied in this research.

II. Method and analytical results for Sr and Rb

The x-ray fluorescence method of Champion, Taylor and Whitten (1960) was used for both Sr and Rb. Aqueous standards for Rb and Sr were prepared from RbCl, $SrCl_2 \cdot 6H_2O$, and distilled water. Scattering factors relative to water were computed for each sample.

The scattering factors for all samples and standards were computed on an IBM 7040 computer using the S values given by Champion, Taylor and Whittem for individual elements and standard chemical analyses for each sample and standard. The program, co-authored by Ross Grunwald, is given in the appendix.

The liquid standards were used in ordinary inverted sample holders, into which a Saran Wrap liner and plastic retaining ring had been placed.

A Norelco Universal Vacuum X-Ray Spectrograph Type No. 52530 was used for all Rb and Sr analyses. The operating conditions were as follows: (1) a Tl activated NaI scintillation counter was operated at about 1.05 Kv; (2) a LiF crystal and fine collimator; (3) 50,000 counts were collected at the Sr K-alpha and Rb K-alpha 2 θ positions and background at +1.10 °2θ from the Rb K-alpha position; (4) the pulse-height analyser was set at about 15.0 v base and 13.0 v window, with the exact values determined daily.

On the following pages are tables showing the precision and accuracy of Rb and Sr data for Hawaiian lavas. The data are from the present report and from the literature. The new Rb and Sr analyses on W-1 and G-1 are also given. Following the tables is a discussion of the data presented in them.

TABLE I. PRECISION DATA FOR Rb IN NZC-USGS INTERLABORATORY STANDARDS, AND IN W-1 AND G-1

Sample	No. of runs	$\bar{X}$	2 sigma
NZC-1	8	9 ppm	2 ppm
NZC-2	3	8 ppm	2 ppm
NZC-3	8	244 ppm	4 ppm
NZC-4	3	7 ppm	2 ppm
NZC-5	8	35 ppm	4 ppm
NZC-6	7	9 ppm	1 ppm
NZC-7	3	120 ppm	1 ppm
NZC-8	6	33 ppm	2 ppm
G-1	3	216 ppm	2 ppm
W-1	3	22 ppm	1 ppm
Samoan	20	--	3 ppm
Hawaiian	13	--	4 ppm

Note: Samoan indicates 20 samples run in duplicate and Hawaiian 13 samples run in duplicate. All data given above are from the present research.

TABLE II. PRECISION DATA FOR Sr IN HIG-USGS INTERLABORATORY STANDARDS, AND IN W-1 AND G-1

Sample	No. of runs	$\bar{X}$	2 sigma
HIG-1	9	293 ppm	10 ppm
HIG-2	3	335 ppm	20 ppm
HIG-3	8	43 ppm	4 ppm
HIG-4	3	364 ppm	10 ppm
HIG-5	9	1,838 ppm	50 ppm
HIG-6	7	424 ppm	22 ppm
HIG-7	3	222 ppm	20 ppm
HIG-8	6	827 ppm	20 ppm
G-1	3	236 ppm	12 ppm
W-1	3	204 ppm	6 ppm
Samoan	20	--	15 ppm
Hawaiian I	7	--	10 ppm
Hawaiian II	4	--	35 ppm

Note: Samoan indicates 20 samples run in duplicate, Hawaiian I indicates 7 samples with less than 1,000 ppm Sr run in duplicate, and Hawaiian II indicates 4 samples with greater than 1,000 ppm Sr run in duplicate. All data given above are from the present research.

TABLE III. ACCURACY OF Rb AND Sr DATA FOR W-1 AND G-1

	Rb	Sr
W-1	22 ppm(1), 22 ppm(2)	194 ppm(1), 180 ppm(2)
G-1	216 ppm(1), 220 ppm(2)	236 ppm(1), 250 ppm(2)

(1) Present report. Norman Hubbard, analyst.

(2) Fleischer (1965).

TABLE IV. ACCURACY OF Rb DATA FOR HIG-USGS INTERLABORATORY STANDARDS

Sample	Rb ppm
HIG-1	9(1)
HIG-2	8(1)
HIG-3*	144(1), 124(2), 122(3), 300(4), 325(5)
HIG-4	7(1), 8(2)
HIG-5#	35(1), 25(2), 32(3)
HIG-6	9(1)
HIG-7	115(1)
HIG-8	33(1)

(1) Present report. Norman Hubbard, analyst.

(2) Hamilton (1965). Samples 1, 8, and 9.

(3) Lessing, Decker and Reynolds (1963).
Samples H-661, H-8-61g, 17, 18, and 62-99A.

(4) Wager and Mitchell (1953). Sample J.

(5) Nockolds and Allen (1956). Samples 15 and 16.

* These are five different samples from the same trachytic mass. The HIG sample is from Puu Waawaa while some of the other samples are from Puu Anahulu, a small hump on the trachytic flow from the cinder cone Puu Waawaa.

\# These are three different samples from the same flow.

TABLE V. ACCURACY OF Sr DATA FOR HIG-USGS INTERLABORATORY STANDARDS

Sample	Sr ppm
HIG-1	235(1), 250(2)
HIG-2	335(1), 340(2)
HIG-3	43(1), 46(2), 30(3), 35(6), 64(4), 100(5)
HIG-4	364(1), 400(2), 392(4)
HIG-5	1,830(1), 2,200(2), 1,736(4)
HIG-6	420(1), 380(2)
HIG-7	322(1), 360(2)
HIG-8	827(1), 680(2)

Note: Only the data of Hubbard and Neiman are on the HIG samples. All others are different samples from the same flow, quarry, hill, etc. so that there exists an unknown sampling error.

(1) Present report. Norman Hubbard, analyst.

(2) U.S.G.S. Harriet Neiman, analyst. See Appendix B for a copy of the report.

(3) Lessing and Catanzaro (1964). Samples H-S-61, H-S-61B, 17, and 18.

(4) Hamilton (1965). Samples 1, 8 and 9.

(5) Wager and Mitchell (1953). Sample J.

(6) Nockolds and Allen (1954). Samples 16 and 15.

TABLE VI. Sr DATA FOR 1955 EAST PUNA (KILAUEAN) LAVAS

Sample	Sr, PPM
1	690(1), 383(2)
2	740(1), 390(2)
3	720(1), 390(2)
4	670(1), 388(2)
6	700(1), 384(2)
8	720(1), 395(2)
9	760(1), 384(2)
10	760(1), 394(2)

(1) Sample numbers and data are from Macdonald and Eaton (1964). Paul Barnett, analyst.

(2) Present report. Norman Hubbard, analyst. These data are for samples collected at the same time and place so that sampling errors should be small.

TABLE VII. Sr DATA FOR OTHER KILAUEAN LAVAS

Sample	Sr ppm
HZO-1	200(2), 208(1)
HZO-2	340(2), 335(1)
Kilauea Iki*	
4	272(1)
5	254(1)
7	305(1)
8	330(1)
Other Kilauean samples	
1959 eruption	290(3)
1959 "	250(3)
1894 "	329(6)
1921(?) "	381(6)
recent flow	379(6)
1960 Kapoho	300(4)
date unknown	429, 392(5)

(1) Present report. Norman Hubbard, analyst.

(2) U.S.G.S. Harriet Neiman, analyst. See Appendix E for a copy of the report.

(3) Lessing and Catanzaro (1964).

(4) Hodge and Walthall (1962).

(5) Turekian and Kulp (1956).

(6) Faure and Hurley (1963).

* The sample numbers are from Macdonald and Katsura (1961). The samples are the powders used by Katsura.

As can be seen from Tables I and II the absolute precision of the Rb analyses for the HIG-USGS interlaboratory standards is good, but the relative precision (% 2 sigma) is poor at the lower concentrations. The precision for the Sr analyses is similar to that for Rb at similar concentrations. At Sr concentrations above 200 ppm the % 2 sigma is commonly under 7.0%.

Table III indicates that the accuracy of the analytical method has been high for Rb and Sr in W-1 and G-1. Table IV shows that three recent analyses of the Puu Anahulu-Puu Waawaa (HIG-3) trachyte are in rather good agreement. The absolute Rb values may reflect some sampling error as the K/Rb ratios from (1) and (3) are 291 and 291. Using the same criterion, the K/Rb ratios of HIG-5 and the two other samples of the Moiliili flow are 296(1), 632(2) and 400(3) while the K values are 1.65% (avg. of U.S.G.S. and Japan), 1.50%(2), and 1.47%(3). This indicates that the major error is in the Rb values, as a result of either analytical or sampling errors.

Agreement of the Sr data is generally good as shown by Table V. The poorest agreement is for HIG-5 and 8, where the U.S.G.S. values are lower.

One body of published Sr data is in very poor agreement with all other similar data. This is shown in Table VI along with new data from the present report. Table VII gives other published Sr data. It must be concluded that the Sr data published in Macdonald and Eaton (1964) are in serious disagreement with other data for Kilauea.

With the exception of the Sr values noted in the two above paragraphs, all Sr analyses made using W-1 and G-1 as standards are in excellent to essential agreement. On this basis the Sr data of Nockolds and Allen (1954) and Wager and Mitchell (1953) are no longer of much importance for Hawaiian lavas. The semi-quantitative nature of these two sets of older data also reduce their importance.

With the exception of the Rb values for the Moiliili flow (HIG-5), the few existing Rb analyses made using W-1 and G-1 are in good agreement.

There exists more data from more analysts for Sr than for any other trace element in Hawaiian lavas.

III. Method and analytical results for Ni

The basic method is the same as for Sr and Rb except that semi-synthetic rock standards and G-1 were used in place of aqueous standards. The standards were made by adding NiO to a tholeiitic basalt. The initial Ni content was determined by ordinary standard addition techniques. This series of standards was used to determine the Ni content of the HIG-USGS interlaboratory standards and W-1. G-1 was used as a 0 ppm Ni blank, although it contains about 2 ppm Ni or much less than the 10 ppm detection limits.

The S factors computed for Rb and Sr were also used for Ni. While these S factors are not the correct ones for the Ni K-alpha wavelength, they are an improvement over no corrections. While this is not the best practice, it causes an error of about ±2% in the extreme cases and about ±1% in about 80% of the samples. This accounts for about 1/10 of the total error of most Ni values. These S factors are second order corrections applied to the basic technique which uses scattered X-radiation as an internal standard. The maximum improvement in accuracy given by these corrections in the current body of data is about 20%. The maximum difference between S factors computed for Sr and S factors for Ni is also about 20%. Hence, the maximum error is 4% if the two extremes are compared with each other or ±2% if the extremes are compared with the average. Since there are few samples near the extremes, a better estimate is ±1% from the average. Data and equations used to estimate this error are in Champion, Taylor and Whittem (1966) and Compton and Allison (1935).

A Norelco X-ray Diffraction Unit Type No. 12045 with a X-ray Spectrograph Attachment Type No. 52260 was used for Ni. The Ni emission was recorded on a strip chart operated as a graphical averager.

Precision and accuracy were monitored by repeatedly interspersing the NZG-USGS standards and W-1, as well as by a number of duplicate determinations on actual samples. The NZG-USGS standards, W-1 and G-1 were also run on the instrument used for Sr and Rb in order to further check internal consistency. These results are given in Tables VIII and IX.

Above 500 ppm Ni duplicate runs often show spreads of 50 to 100 ppm, probably reflecting failure to completely homogenize the sample. As the Ni is almost entirely in the olivines, small failures to get a uniform and reproducible distribution of olivine on the surface of the sample can easily yield differences of 15% in the amount of Ni determined. MIC-6 has been particularly bad in this respect, as can be seen in Table VIII.

IV. Method and analytical results
for Co, V, and Zr

Only a brief description of the emission spectrographic methods will be given here. Details are given in Appendix D. The x-ray fluorescence method used for some Zr analyses is similar to those used for Rb, Sr and Ni; further information is also in Appendix D.

All the new V and Co data in this report are from emission spectrograms. The Zr data are from emission spectrograms and x-ray spectrograms.

Two emission spectrographs were used: a 1.5 meter Bausch and Lomb Littrow type with quartz optics and a 3-meter Hilger compact grating spectrograph. With both instruments D.C. arc sources were used. Powdered samples were mixed with Spectro-Pure (National Carbon Company) graphite and arced to completion in carbon electrodes; anode excitation was used.

TABLE VIII. PRECISION DATA FOR Ni ANALYSES

Sample	No. of runs	X̄	2 sigma
NSC-1	17	1,090 ppm	78 ppm
NSC-2	13	104 ppm	10 ppm
NSC-3	--	--	--
NSC-4	5	89 ppm	10 ppm
NSC-5	6	231 ppm	4 ppm
NSC-6	18	368 ppm	54 ppm
NSC-7	4	64 ppm	16 ppm
NSC-8	4	231 ppm	10 ppm
N-1	14	93 ppm	10 ppm
Hawaiian*	13	--	10 ppm

*These are 13 samples run in duplicate and with Ni less than 500 ppm.

TABLE IX. ACCURACY OF Ni DATA

Sample	Ni ppm
HZG-1	1,000(1), 1,200(2)
HZG-2	104(1), 100(2), 100(3)
HZG-3	-- , under 5(2), --
HZG-4	80(1), 100(2), 66(3)
HZG-5	231(1), 360(2), 227(3)
HZG-6	380(1), 400(2), 395(3)
HZG-7	64(1), 50(2), 55(3)
HZG-8	221(1), 230(2), 226(3)
W-1	93(1), -- , 66(3), 78(4)

(1) Present Report. Norman Hubbard, analyst. Data from instrument used for main body of data.

(2) U.S.G.S. Harriet Neiman, analyst. See Appendix E for a copy of the report.

(3) Present report. Norman Hubbard, analyst. Data from instrument used for main body of Sr and Rb data.

(4) Fleischer (1965).

All densitometry was with an Applied Research Laboratories Model 2250 microdensitometer and a Varian Model G-10 recorder. All plate calibration was by line intensity ratio methods. Iron was used as a variable internal standard for all three elements.

The standards were W-1, G-1 and the NIC-USGS interlaboratory standards 1 to 8. For V and Co W-1 was taken as the primary standard, while all standards were considered primary for Zr.

All emission spectrographic data, using an internal standard, have been internally normalized. The precision stated in Tables X, XI and XII refers to the maximum deviation from the reported average. Data on the precision and accuracy of the Co, V and Zr analyses are given in Tables X, XI and XII.

The U.S.G.S. analyses average about 15 ppm Zr lower than the average of all three sets of data, except for NIC-2 where their value is about 1/[illegible] that of Grunwald and Hubbard. Note that while the U.S.G.S. Zr values are generally lower than the average of all, they are still within or very close to their stated error of ±15% for all standards except NIC-3. Grunwald and Hubbard agree to well within their limits of error.

For Table XI the maximum deviation from the average is less than 11.0%, except for NIC-5 which is 30% and NIC-7 which is a single analysis. W-1 (42 ppm Co) was the primary standard. This value was chosen on the basis of recent Co analyses reported in Fleischer (1965). As can be seen, each set of values agrees with the average to well within the limits of error. HIG-5 has proven a difficult sample to get reproducible Co values for (see Appendix D, Table XIV). HIG-7 required a long extrapolation of the working curve, thus the reported value of 14 ppm is open to some question. The U.S.G.S. value of 5 ppm is near their detection limit of 2 ppm. From this viewpoint, the difference in the two cobalt values for HIG-7 is not presently serious.

There are currently few additional data allowing an independent comparison of the new V data. The few there are suggest that Hubbard's values are more nearly correct, but it is far from conclusive. The true V content of W-1 is also in so question (see Fleischer, 1965). The most pertinent additional set of V data for Hawaiian lavas is those given in Macdonald and Eaton (1964). These samples have been reanalyzed in the present work, and the new analyses are given in Appendix F along with the published values. The agreement between these two sets of analyses is much better than that for the HIG-USGS standards. The large variation of the differences given in Table XXI, column 6, indicates that the error is both systematic and highly random.

TABLE X. Zr DATA FOR HIG-USGS INTERLABORATORY STANDARDS, IN ppm Zr

Standard	1	2	3	4	5	6
HIG-1	134	100	131	122	-22	18.0%
HIG-2	163	120	149	144	-24	16.7%
HIG-3	1,120	340	1,100	--	--	--
HIG-4	115	90	125	110	-20	18.2%
HIG-5	191	190	198	193	+ 5	2.6%
HIG-6	192	160	180	177	-17	9.6%
HIG-7	170	190	172	177	+13	7.4%
HIG-8	250	240	248	246	- 6	2.4%

(1) Ross Grunwald, analyst. X-ray fluorescence.

(2) U.S.G.S. Harriet Neiman, analyst. See Appendix E for a copy of the report.

(3) Norman Hubbard, analyst. The average of all individual emission spectrographic methods, except HIG-3 and 7 which are independent x-ray fluorescence determinations.

(4) The average of 1, 2 and 3.

(5) The maximum deviation from the average, with its sign.

(6) The percent maximum deviation from the average in 4.

TABLE XI. Co DATA FOR HIG-USGS INTERLABORATORY STANDARDS, IN ppm Co

Standard	1	2	3	4	5
HIG-1	71	80	76	5	6.6%
HIG-2	39	38	39	1	2.6%
HIG-3	l.t. 2	--	--	--	--
HIG-4	36	41	39	3	7.7%
HIG-5	100	62	81	19	23.5%
HIG-6	43	48	46	3	6.5%
HIG-7	5	14	10	5	50.0%
HIG-8	55	47	51	4	7.9%

(1) U.S.G.S. Harriet Neiman, analyst. See Appendix D for a copy of the report.

(2) Norman Hubbard, analyst. The average of all emission spectrographic analyses.

(3) The average of 1 and 2.

(4) The deviation from the average, in ppm Co.

(5) The percent deviation from the average.

TABLE XII. V DATA FOR HIG-USGS INTERLABORATORY STANDARDS, IN ppm V

Standard	1	2	3	4	5	6
HIG-1	340	260	253	257	5.4%	87
HIG-2	420	285	298	291	4.6%	122
HIG-3	10	--	--	--	--	--
HIG-4	330	207	239	223	14.4%	90
HIG-5	260	330	254	--	--	6
HIG-6	410	234	264	249	12.1%	36
HIG-7	60	--	38	--	--	22
HIG-8	420	254	253	254	0.8%	167

(1) U.S.G.S. Harriet Neiman, analyst. See Appendix E for a copy of the report.

(2) Norman Hubbard, analyst. These are average emission spectrographic data using absolute intensity ratios.

(3) Norman Hubbard, analyst. The average of all emission spectrographic analyses where an internal standard was used.

(4) The average of 2 and 3, except for HIG-5.

(5) The percentage differences between 2 and 3, computed on the average.

(6) The differences between 1 and 3.

V. Recommended values for Sr, Rb, Zr, Ni, Co, and V in HIG-USGS standards

The values given here are a personal choice based on the data given in this report. When there is good agreement the values from different analyst were averaged.

The Co values are an average of U.S.G.S. and the present report, as are the Ni, excepting the Ni value of HIG-5 which is Hubbard's. The Zr values are an average of Grunwald and Hubbard, except HIG-6 which is an average of U.S.G.S., Grunwald and Hubbard, and HIG-7 which is an average of Grunwald and an independent x-ray value by Hubbard. This has been done because Grunwald and Hubbard were trying for optimum results in these samples, while the U.S.G.S. values represent routine analyses. The Sr values are an average of U.S.G.S. and Hubbard or, where the difference was thought to be too great, Hubbard's alone. The V values are Hubbard's alone, representing a semiarbitrary choice. See Appendix F for more information on V values in Hawaiian lavas. The Rb values are Hubbard's alone, there being no others.

Values between 10 and 1,000 ppm are given to two places, with the third a zero. Below 10 ppm only one place is given: above 1,000 ppm three places are given, with a zero in the fourth. The recommended values are given in Table XIII.

TABLE XIII. RECOMMENDED VALUES FOR HZG-USGS INTERLABORATORY STANDARDS, IN ppm

Sample	Sr	Rb	Zr	Ni	Co	V
HZG-1	290	9	130	1,150	70	260
HZG-2	340	8	160	100	39	290
HZG-3	42	140	1,130	--	--	--
HZG-4	380	7	120	92	39	220
HZG-5	1,840	55	190	230	80	250
HZG-6	400	9	180	400	46	250
HZG-7	340	120	170	37	10	70
HZG-8	830	33	250	330	51	250

-- Denotes that the concentration is below 10 ppm.

GEOCHEMICAL RESULTS, DISCUSSION AND CONCLUSIONS

I. Discussion and presentation of geochemical results

A. Plan of presentation

Results for each element will first be discussed alone and then in light of results for previously discussed elements. Past research on the distribution of each element in situations bearing on the present results will be presented just before the discussion of present results. This scheme will be deviated from in presenting the results for the Honolulu and Koloa series. It is felt that a separate discussion of these two series is desirable in view of their geological and petrological differences.

B. Strontium

Past Research. The largest and most comprehensive body of Sr data for silicate rocks is that of Turekian and Kulp (1956). They have reported Sr and Ca data for 23 Hawaiian samples and for 21 other intra-Pacific basaltic samples. They found no correlation between Sr and Ca in basaltic rocks in general but for a given complex of basaltic rocks (Stillwater complex, Lebombo volcanics, for example), they found a marked negative correlation. Plagioclases from the Stillwater complex also show a negative correlation up to the least calcic member of the $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$ solid solution series analyzed, An 62.5. In granitic rocks they found a definite positive correlation between Sr and Ca. In Hawaiian samples the late stage lavas were found to contain much more Sr than the shield-building lavas. The late stage lavas show a general negative correlation between Sr and Ca while the shield-building lavas show no correlation between Sr and Ca.

Wager and Mitchell's (1951) data for the Skaergaard complex in East Greenland contain a second set of important Sr data. They found that Sr reached a maximum in andesine plagioclases and that the plagioclases contained about 20 to 100 times as much Sr as the pyroxenes. They found two apatites to contain roughly the same amount of Sr as the plagioclases. For the intrusion as a whole they found an initial increase in Sr content with differentiation, followed by an irregular fall in the most differentiated samples analyzed. Wager and Mitchell (1953) later reported Sr data for 10 Hawaiian samples. These data show a rise in Sr content until the mugearites, followed by a large decrease in the trachytes. This is the general pattern found by the present research.

The largest body of Sr data for the Hawaiian Islands prior to the present research was that of Nockolds and Allen (1954 and 1956). They found the same behavior as did Wager and Mitchell.

A small body of Sr data for a single eruption was published by Macdonald and Eaton (1964). These data have been discussed in the section dealing with the quality of all existing Sr data for the Hawaiian Islands. Lessing and [illegible] (1964), Hamilton (1965), and Faure and Hurley (1963) have all published total Sr data in conjunction with other data. Turekian (1963) has published some data for Sr in pyroxenes and garnets from Salt Lake Crater xenoliths. Tatsumoto, Hedge and Engel, and Engel, Engel and Havens (1965) have published data for Sr in some oceanic basalts. Gunn (1966) includes Sr data for some Antarctic tholeiitic intrusions, where the total Sr content is close to that of the low-K basalts of Engel, Engel and Havens but less than half the Sr content of Hawaiian tholeiitic basalts.

Nockolds and Mitchell (1948) included Sr in a study of the relationships of major and trace elements in some Caledonian plutonic rocks.

Present Research. The key to understanding the distribution of Sr in Hawaiian lavas is its relationship to P, as shown in Figure 1. Within the broad band of points shown in Figure 1 are more restricted areas occupied by the data for any one volcano. The trend lines for individual volcanoes are grouped together in Figure 2. Figures 3 through 9 show the distribution of Sr and P for individual volcanoes. The data for two volcanoes, East and West Maui, have been interpreted as falling along the two differing trend lines in the fashion indicated by the solid and dashed lines. The data for the Koloa series on Kauai have been interpreted as having a common origin with the other Kauai samples but showing two, quantitatively different, covariations of Sr and P. Data for both the Honolulu and Koloa series have been plotted on figure 9 together with the trend lines for Kauai. The interpretation is that Sr and P show the same distribution in the Honolulu series as in the Koloa series.

The close association of Sr and P in individual Hawaiian volcanoes indicates that apatite $(Ca,Sr,Mn)_5$ (F,Cl,OH) $(P,As,)_3O_{12}$ is responsible. Strontian hydroxylapatite has been made by Klement (1939) and strontian chlorapatite by Carobbi (1950). Larsen, Fletcher and Cisney (1952) have reported a Sr apatite containing 11.6% SrO. Cruft (1966) has published data showing that apatites from ultrabasic and alkalic rocks can be very high in Sr. Examples are: an apatite from alkalic rock, Kukisvumchoor, Khibina USSR, 7.35% Sr; from an ultrabasic rock, Snarum, Norway, 2.03%; from an omphacite-diopside-apatite vein in eclogite, Eriksundjosak, Norway, 2.61% Sr. Macdonald (personal communication) has reported 1-3% of large apatite crystals in Hawaiian mugearites, where both Sr and P reach their peaks. If all the Sr in mugearites (about 1,200 ppm) is assigned to these apatites, their Sr contents will range from 4-12%.

The density of common apatite is a little below 3.20 gm/cc, of a Sr apatite (11.6% SrO) 3.35, strontian fluorapatite 3.34, and of Sr hydroxylapatite 4.17 gm/cc. With the density of Hawaii basaltic magmas less than 2.90 gm/cc (Macdonald, 1968) and mugearitic magmas less iron rich and more volatile rich, hence less dense, gravitative settling of the large apatite crystals could easily occur.

Usual geochemical practice is to view the distribution of a trace element cation in relation to a chemically similar major element cation. For Hawaiian volcanoes this approach yields only a meager partial answer for Sr. The distribution of Sr relative to Ca is shown in Figures 10 and 11.

In the Waianae, Kohala and Kauai volcanoes, except the Koloa series, the covariance of Sr and P is very close, but not in all other volcanoes investigated. The close covariance of Sr and P in some volcanoes and not others indicates that either conditions or materials associated with some volcanoes are less uniform. That this close covariation exists in the Waianae and Kohala volcanoes and is indifferent to the distinction between tholeiitic and alkalic suites is evidence against mere magmatic differentiation being the cause of less uniformity but is evidence for one parent material, be it solid or liquid, for both alkalic and tholeiitic lavas of at least these volcanoes.

Hawaiian volcanoes have been divided into two basic types, Haleakala and Kohala by Macdonald and Katsura (1964). The distinction is based on differences in late-stage eruptive history and shows no correlation with the distinction made in the above paragraph. The Waianae volcano is of Haleakala type but East Maui (Haleakala) does not show the same relationship of Sr to P. West Maui (Kohala type) shows a strong similarity to the Waianae and Kohala volcanoes in its distribution of Sr and I, but it also shows deviations that link it closely with East Maui. In the case of East and West Maui similar or identical paths of differentiation may have been the cause of these similarities. Figure 12 shows East and West Maui data plotted together. The lines drawn through the data are thought to represent the different trends in Sr and P covariation. The two concave downward lines are just analytically resolvable for Sr and less so for P at low concentrations but are easily resolved at high Sr values. The concave upwards line is easily resolvable from the other two. It should also be noted that the data for the Waianae, Kohala and Kauai, except Koloa, volcanoes all fall within narrow limits, approximating the analytical limits of error.

Different volcanoes show slightly different trend lines for distribution of Sr and P or, as East and West Maui, a different sign of curvature for one of the lines. Each Hawaiian volcano has its own maximum content of Sr and P, as can be seen in Figure 2. There is no relationship between the initial Sr/P ratio and the maximum content of Sr and P. There is little correlation between the initial content of Sr and P and the maximum. However, the latter is greatest in those volcanoes that produced mugearites or nephelinites.

It has been shown (Macdonald and Katsura, 1964) that different Hawaiian volcanoes have slightly different trends of differentiation in the major elements and that these differences are not related to the type of volcano. This is just what is found for the Sr and P data.

Macdonald (personal communication) has suggested that the upper magma chambers of different volcanoes were at different levels and, as low pressure differentiation is thought to produce mugearites from alkalic olivine basalts in these chambers, small pressure differences at this stage of magmatic differentiation may well have been an important variable in the alkalic series. For the present it is sufficient to know that different volcanoes followed slightly different paths of magmatic evolution and that the highest concentration of Sr and P obtainable in any one body of Hawaiian magma could be related to the detailed path of magmatic evolution.

In the East and West Maui volcanoes two different paths of differentiation seem to have operated in both volcanoes. The predominant path of one volcano seems to have been the secondary path of the other. If this interpretation of the data is the correct one, the factors controlling the differentiation paths of these Hawaiian volcanoes have been exterior to them, or alternatively, they had a common magma source which underwent a change in operating parameters, perhaps due to external influences.

O'Hara (1965) has outlined a scheme by which a wide range of magma types can be obtained. This scheme is based on the different types of fractional crystallization and partial melting that can occur at different pressures. By this scheme the composition of a magma erupted at the surface is a function of how long differentiation was allowed to proceed at different pressures. Present Sr and P data require that the following restriction be made, at least for some Hawaiian volcanoes. That is, that some volcanoes (Waianae, Kohala and Kauai) had one mean path of differentiation and that fluctuations around individual mean paths were small and independent of the distinction between alkalic and tholeiitic suites. In other words, O'Hara scheme must be able to operate with little or no interruption for the life of these volcanoes and to smoothly make the transition from production of tholeiitic magma to production of alkalic magma.

Green and Ringwood (1966) have recently pointed out that the Sr and P content of basalts from different regions show no correlation to major element chemistry. They find no way to account for this unless it is assumed that the Sr and P are in a minor mineral phase(s) in the upper mantle and that this phase(s) varies in concentration geographically. In addition, it is pointed out that the content of P in alkalic olivine basalts from Hawaii is greater than it would be if the alkalic olivine basalts were derived from olivine-rich tholeiitic basalts by the extraction of 10-20% of enstatite & subcalcic clinopyroxene. This is not entirely true. In Hawaiian alkalic olivine basalts of individual volcanoes P is about 20% to about 100% higher than in the tholeiites. Sr shows the same behavior. Note that the percentage range of solid phase removed overlaps the increase in Sr and P in

Hawaiian alkalic olivine basalts. Green and Ringwood propose that the great increase in Sr and P is due to selective enrichment of these elements from the wall-rock during slow ascent of magma at considerable depth within the mantle.

The basic scheme of Green and Ringwood is accepted as plausible but with an important modification. The revised version is: Alkalic olivine basalt magmas are derived from olivine-rich tholeiitic magmas by removal of 10-30% enstatite ± subcalcic clinopyroxene and the content of Sr and P, as well as certain other elements, may increase by this percentage; or it may increase by a greater percentage, possibly due to selective enrichment from the wall-rock while the magma is still at considerable depth within the mantle.

In summation, the distribution of Sr and P for any Hawaiian volcano is a function of the detailed path of magmatic evolution. This path may be determined by the length of time the magma is allowed to undergo differentiation in different pressure and temperature zones or, keeping temperature, pressure and time constant, differences in initial composition. Differentiation at any temperature and pressure, or combination of conditions, either with or without selective enrichment of Sr and P, must be able to produce smooth variations in both Sr and P and to do this without regard to the alkalic vs. tholeiitic distinction.

Figures 13 and 14 show that Sr also shows a close covariation with K. In addition, there is a good stratigraphic correlation in the Waianae volcano. The lower lavas have the lowest Sr content, the middle lavas have intermediate values, and the upper lavas the highest. One upper Waianae sample falls within the lower lavas. This may be due to an error in mapping (Macdonald, oral communication, 1966). In all volcanoes investigated, the alkalic basalts contain more Sr than the tholeiitic basalts. Tholeiitic basalts erupted late in a volcano's cycle of activity contain more Sr than earlier ones.

C. Rubidium

Past Research. The largest single body of pre-existing Rb data for Hawaiian lavas is that of Lessing, Decker and Reynolds, Jr. (1963). Their conclusion that the high-K alkalic lavas show a decrease in the K/Rb ratio is not substantiated by the present research. Hamilton (1965) has reported a small number of Rb data for Hawaiian lavas and concludes that there is little significant variation in the K/Rb ratio, except in the trachytes. He attributes the lower K/Rb ratios of the trachytes to extreme magmatic differentiation, not to contamination by marine material, as did Lessing, et al.

Both Faure and Hurley (1963) and Hedge and Walthall (1963) have published a very small number of Rb data for Hawaiian lavas in conjunction with Rb-Sr isotope studies.

Taubeneck (1965) considers the K/Rb ratio a good index to differentiation in most igneous rock suites and that the "normal" value of 240 has little meaning.

Gunn (1965) reports that forty-one samples of a differentiated Antarctic tholeiitic dolerite have a constant K/Rb ratio near 240. Two series of continental alkalic basalts from Antarctica and New Zealand have K/Rb ratios of [illegible] and show no change in the K/Rb ratio.

Gast (1965) has shown that lavas from Gough, Ascension and St. Helena Islands show an increase in K/Rb ratios with decrease in K concentration. The same is shown for some oceanic tholeiites.

Morse and Davis (1966) have shown a strongly increasing K/Rb ratio with increase in K for the Kiglapait layered intrusion, Labrador.

In light of the variety of results noted above, it appears that the only safe generalization that can be currently made about K/Rb ratios is that anything is possible.

Present Research. The distribution of Rb relative to K for the Hawaiian and Samoan Islands is shown in Figure 15. Data for the Waianae volcano are denoted with different symbols, showing the distribution of a single volcano in relation to the data for all Hawaiian volcanoes. Three Samoan lavas show K/Rb ratios of 800 to 1,500. These are not low-K tholeiitic basalts; they are alkalic lavas with 0.8 to 1.5% K. Other Samoan lavas show ratios within the range of Hawaiian lavas, or between 300 and 650.

Data for individual volcanoes are shown in Figures 16 to 21. Figure 22 shows data for the Koloa and Honolulu series together with that for the Hana and Kula series (East Maui).

In the Waianae volcano there is indication of a slight change in K/Rb ratio at about 1.3% K, with a definite change to 222 in the Mauna Kuwale rhyodacite. This is the only evidence found in this research of a systematic change in K/Rb ratio in a single volcano. The lower K/Rb ratio of the Mauna Kuwale rhyodacite is considered to be due to extreme low pressure differentiation.

East Maui (Haleakala) shows a spread of K/Rb values in the Kula series that is well outside the analytical limits of error (Figures 19 and 22). Figure 19 shows an interpretation of these data.

Kauai has a K/Rb ratio of around 450 for the shield-building lavas, as opposed to 300 for the Koloa series. Due to the special nature of the Koloa series this difference is considered due to a process such as that outlined by O'Hara (1965) for the generation of melilite basalt, nephelinites and leucite nephelinite.

In the following paragraphs the "constancy" of the K/Rb ratios will be discussed. Here "constancy" is used to mean that few, if any, of the data points fall more than two sigma (two standard deviations as computed from analytical data) off the mean K/Rb ratio for one volcano. Note that this allows for 10% of the points to fall outside these limits when the sample population is infinite and with the present limited populations, more than 10%.

The variation in the K/Rb ratio between individual volcanoes is often outside the limits of analytical uncertainty. The following computations are based only on samples with more than 10 ppm Rb and an average two sigma of ± 20% for the K/Rb ratio. The one basic assumption is that there exists only one K/Rb ratio for each volcano or group of lavas of interest. The equation (% uncertainty of an individual sample) $\sqrt{N-1}$ = (% uncertainty of the average), where N = number of samples, is used for computation. For Kohala with 5 samples the % uncertainty of the average is 10%; for the Waianae volcano with N=27 the uncertainty is 3.9%. Other volcanoes have intermediate uncertainties of the average K/Rb ratio.

Computed in the above fashion the results are as follows. The difference of 90 between the K/Rb ratios of Kohala and West Maui is greater than the combined uncertainty of 50. The difference of 60 between the Kohala and Waianae volcanoes is about equal to the combined uncertainty of 50. The Waianae and West Maui volcanoes differ by 30 in their K/Rb ratios, which is midway between the 95% and 67% limits of 42 and 21. For East Maui the inferred ratio of 650 differs by 320, or about twice the 95% limits, from the other ratio of 330 for the Hana series. Figure 22 shows an average K/Rb ratio of 300 ± 55, or 18%. This is very close to the above ± 20% for the analytical uncertainty. The 95% limits on the ratio are ± 4.3%, or 13. This is computed on the Honolulu and Koloa series lavas alone and separates them, as well as similar lavas, from all volcanoes except Kohala.

Note that the above computations include few tholeiitic basalts. Hawaiian tholeiitic basalts commonly have less than 10 ppm Rb so that the analytical uncertainty in the K/Rb ratio is much greater than 20%, and resolution of inter-volcano differences in the K/Rb ratios is impossible. However, judging from the symmetrical distribution of data points around the average K/Rb ratio, there is little change in the ratio at Rb concentrations of 10 to 2 ppm.

The constancy of the K/Rb ratio for individual Hawaiian volcanoes, but its variation between volcanoes, means that all comments of Green and Ringwood (1966) concerning the increase of K in the alkalic olivine basalts, with respect to olivine-rich tholeiites, also hold for Rb. This constancy and the inter-volcano variations also suggest that any phase, or phases, in the mantle under the Hawaiian Islands containing K and Rb must have a K/Rb ratio similar to that of the magma produced or, perhaps more important, be able to produce a constant, yet individual, K/Rb ratio in the magma of any one volcano. Note that these and following remarks do not apply to the Honolulu and Koloa series lavas, or to other post-erosional lavas. These lavas have a K/Rb ratio of 300

Ni data listed in Appendix A.

Of the above reports, only that by Turekian gives no Co data.

Notable sets of Ni and Co data for non-Hawaiian samples are those by Wager and Mitchell (1951) for the Skaergaard Intrusion, by Gunn (1966) for some Antarctic tholeiites, and by Engel and others (1965) for some submarine basalts. All sets of data show the usual increase of Ni with increase in MgO and olivine. Some of these data will be discussed along with the new data.

A short paper by Merlino (1965) is notable for his application of crystal field theory to some of Turekian's data. The data are Co and Ni concentrations in some Salt Lake garnets and pyroxenes separated from nodules. The basic conclusion is that the hypothesis of Yoder and Tilley (1962) that the alkalic and tholeiitic suites are derived by the fusion of varying proportions of garnet and alkali-rich pyroxene is in serious doubt.

<u>Present Results.</u> The Ni data for all Hawaiian lavas are plotted against MgO in Figure 23. The relationship is more or less semi-log above Ni concentrations of about 150 ppm and MgO concentrations of 7.0%. The Kohala and Waianae volcanoes, Figures 24 and 25, show good semi-log plots up to about 11.0% MgO. The three most deviate samples of the Waianae volcano, C-169, 134, and 52, are all hawaiites. They may represent the crystallization of olivines more iron-rich

than those of tholeiitic basalts. The graphs for West Maui, Mauna Kea and Kauai, Figures 26, 27 and 28, all show a gentle flexure at about 10% MgO, suggesting that the Kohala and Waianae volcanoes would also show this feature if samples of greater MgO content were analyzed.

Above 10-12% MgO the MgO and Ni contents seem due to settling of early-formed olivine crystals. This is suggested by the extrapolation of the upper part of the curve to near the Ni and MgO contents of Hawaiian olivines. Below this MgO concentration a more complex set of controls, involving extensive reactions of olivine with the melt, probably keep the melt and olivines in some semblance of equilibrium. Murata and Richter (1966) also suggest 10% MgO as the dividing line for olivine-enriched and olivine-depleted magmas.

The Koloa series show lower Ni concentrations for comparable MgO concentrations than do the non-Koloa samples of Kauai. This is consistent with O'Hara's scheme for the origin of melilite basalt, nephelinites and leucite nephelinites. This part of the scheme is based on unpublished data by O'Hara and Yoder, which show that the precipitation of olivine and spinel in this intermediate pressure regime, in place of garnet, selectively removes Cr, Ni, Co and V from the residual liquids. Co and V do not show this feature and will be discussed further later. Figure 29 shows that this difference in Ni concentration is valid in a general way for the Honolulu and Koloa series, as it is also for similar lavas from other Hawaiian volcanoes, in relation to data for all Hawaiian lavas.

O'Hara also points out that the precipitation of peridotite nodules containing clinopyroxenes such as those reported from peridotite nodules in basalts (Ross and others, 1954) must cause an increase in total alkalies in the residual liquid and a decrease in the K/Rb ratio. This decrease in the K/Rb ratio has been found for the Honolulu and Koloa series and similar lavas.

The distribution of Co is very closely linked with that of Mg, as can be seen in Figure 29. The interesting feature of this distribution is that the Honolulu and Koloa series samples plot along with the rest of the samples. The one exception is HIC-5, a Honolulu series sample which seems more related to C-124 and C-126. The latter two samples are alkalic basalts from the Honomanu series of East Maui. Figure 30 shows a comparison of data from Engel and others (1965) and from Gunn (1966) with Hawaiian data. With the possible exception of one or two samples, the data of Engel and others are consistent with the main body of Hawaiian data. The data for Antarctic tholeiites show two samples consistent with the main body of Hawaiian data, but three are more consistent with C-126, C-124 and HIC-5. This suggests that it is also possible to draw a second curve above the first one. This is not surprising as other data plots for Hawaiian volcanoes have also shown two different trends, in particular that for East Maui.

It is interesting that the Antarctic tholeiites show differences similar to those of at least one Hawaiian volcano. The Antarctic samples are from sills which were assumed to have differentiated in place.

The main distribution of Co and Mg, and the secondary one, may be explained if it is assumed that in the latter case either the olivines were more iron and/or cobalt rich or the melt was more cobalt rich. The factors presently known to yield more iron-rich olivines are lower temperatures of crystallization and higher ratios of Fe+2 to Mg and/or Fe+2 to Fe+3 in the melt. As more iron-rich olivines are also more Co rich, this would give more Co-rich olivines. If the samples falling along the implied secondary curve had higher ratios of Fe+3 to Fe+2 in their melts, this could have inhibited the formation of olivine, which in turn can result in cobalt not being removed from the melt. This nonremoval could have caused the higher cobalt concentrations found for some samples. This process is favored for reasons given in the following paragraph.

Tilley, Yoder, Jr. and Schairer (1964) have shown that the presence or absence of olivine on the liquidus of a Hawaiian sample is very dependent on the Fe+3/Fe+2 ratio, the greater the ratio the less the olivine. Samples C-124 and C-126 have higher Fe+3/Fe+2 ratios than the average alkalic basalt given by Macdonald and Katsura (1964). HZC-5 and C-43 have high Fe+3/Fe+2 ratios, as does C-31, and are the most iron-rich samples in the current study. The deviate samples from Gunn also show higher than normal Fe+3/Fe+2 ratios, except the one highest in Co, which is a hypersthene gabbro. Other samples also have high Fe+3/Fe+2 ratios but do not show the higher Co concentrations. Perhaps in these samples there was not time for the increased concentration of Fe+3 to alter the Co concentration.

It was mentioned earlier that Co does not show the lower concentrations in the Honolulu and Koloa series that O'Hara's scheme indicates. This may be due to the removal of all traces of this feature by a later reaction.

Figure 31 shows Co plotted against Fe and an interpretation of the paths of differentiation. The lines are drawn on the basis of the general behaviors of the samples on an AFM diagram. The short left line is drawn through data for tholeiitic samples that trend directly toward the A-F side of the AFM diagram. The right line is drawn through data for normal alkalic samples. The samples with 20-25 ppm Co are hawaiites. HZG-5 and C-43 may belong to a trend that joins the right one in the hawaiite region.

E. Vanadium

Past Research. Published vanadium data for Hawaiian lavas are limited to those in Wager and Mitchell (1953), in Nockolds and Allen (1954 and 1956) and in Macdonald and

Macon (1964).

Vanadium data are given by Gunn (1966) for some Antarctic tholeiites and by Engel and others (1965) for some submarine lavas. These data are plotted and discussed with the new data for Hawaiian lavas.

Present Research. Figure 32 shows that V and Ti are weakly covariant in Hawaiian basalts and the Honolulu and Koloa series. In the hawaiites they are strongly covariant. Note that the Honolulu and Koloa series have some of the highest V concentrations, the opposite of what O'Hara's scheme indicates. As for Co, this may be due to a later reaction having removed the V distribution features of the earlier one.

Figure 33 shows that the distribution of V and Ti in Antarctic tholeiites is an extension of that in submarine low-K tholeiites, with the exception of a pegmatoid. Alkalic basalts of the East Pacific Rise plot in the same region as HIG-8 and many other Hawaiian alkalic basalts.

The V and Ti data will be left for the present and discussed later along with the Zr and K data.

F. Zirconium

Past Research. Published zirconium data for Hawaiian lavas are limited to the same reports as the vanadium data. As with Co, Ni and V, the Zr data from Gunn and from Engel and others are compared with the new data.

Present Results. Zirconium and potassium have been plotted in Figure 34. One of the interesting results of this is that the East Pacific Rise alkalic basalts plot along with Hawaiian hawaiites. This is similar to the way these same samples plotted on the V vs. Ti graph. Samoan alkalic lavas, from picrite-basalt to hawaiite, plot nearby. Low-K tholeiites sometimes plot with Hawaiian tholeiites but more often show much lower Zr concentrations, similar to the Zr concentrations of some Antarctic tholeiites. The latter show K concentrations very similar to those of Hawaiian alkalic lavas but much lower Zr concentrations. Note that the tholeiitic nature of these samples has not altered the form of the Zr vs. K distribution.

The Honolulu, Koloa, Lahaina and Hana series lavas have Zr values intermediate between those of the Antarctic tholeiites and most Hawaiian lavas. East and West Molokai lavas, as well as some other Hawaiian samples and some East Pacific Rise lavas, plot along with the Honolulu and Koloa series. It is possible to draw a second curved line through these samples. The Zr concentrations along this undrawn line are about one half those of samples along the drawn line. While these lines can be drawn it is perhaps more correct to describe the covariance of Zr and K by a family of curves similar to the drawn one and differing only in their Zr concentrations.

Both O'Hara and Green and Ringwood have developed schemes showing how it may be possible to get a wide range of magma types by varying either the conditions of initial generation or subsequent differentiation. Except for one low-pressure thermal barrier, both schemes can give a continuous spectrum of magma types or element distributions. The Zr vs. K distributions shown in Figure 34 may be an indication that such schemes are basically correct.

Figure 34 may be an indication of large variations in Zr concentrations in magmatic source materials. This idea is particularly well illustrated in the Hawaiian data, where two source materials may exist. Alternatively, the two parallel lines that can be drawn through the Hawaiian Zr and K data may indicate two predominant paths of differentiation, one for normal tholeiitic and alkalic basalts and one for the post-erosional lavas and some otherwise apparently normal alkalic and tholeiitic lavas.

On an earlier page it was pointed out that some East Maui samples mapped as Kula resemble the Hana lavas in K/Rb ratio. These same samples plot along with Hana lavas on the Zr vs. K graph. The samples are: C-135, C-141, C-143, C-146 and C-147.

Figure 35 is similar to Figure 13 except that a middle member hawaiite plots with the upper member samples, which are also hawaiites. The one upper member tholeiitic basalt again plots along with the lower member. The most important feature of this graph is the smooth covariation of Zr and K in the Waianae volcano. This feature is common for all Hawaiian volcanoes and all elements studied and is perhaps the most important single result of this research.

C. Post-erosional Lavas

These lavas have been discussed at various points in preceding parts of this report. Here salient features will be collected and restated.

The close similarities of these lavas are perhaps their most important feature and indicates a common mode of origin.

Perhaps the second most important feature of this group of lavas is that the distribution pattern of any element pair is very similar to that for tholeiitic and alkalic lavas in general. This indicates that many of the chemical reactions associated with these lavas are only quantitatively different from those associated with tholeiitic and alkalic basalts.

The Koloa series of Kauai is clearly linked by its Sr and P distributions to the other lavas of that volcano in the same manner that the tholeiitic and alkalic lavas of any one Hawaiian volcano are related (see Figure 5). For East and West Maui volcanoes, the Hana and Lahaina series lavas plot along with the other lavas and are not separately noted on the Sr vs. P graphs of these volcanoes. This indicates that the genesis of these lavas is closely linked to that of the other lavas of these volcanoes.

Figure 10 shows that the Sr vs. CaO distribution of these lavas overlaps Hawaiian and Samoan alkalic lavas extensively and Hawaiian tholeiites slightly.

In conclusion, the post-erosional lavas are commonly distinct from, but related to, the other lavas of the volcano on which they occur. Post-erosional lavas of Hawaiian volcanoes are often more similar chemically to one another than to other Hawaiian lavas.

XI. Conclusions

Perhaps the most potentially fruitful conclusion is that the similarities and differences of Hawaiian lavas are more important in understanding their origins than are their alkalic or tholeiitic classifications.

The most significant feature of the data presented in this report is the repeated occurrence of smooth covariations of such element pairs as Sr-P, Zr-K and Ni-Mg in individual Hawaiian volcanoes and the indifference of these covariations to the alkalic or tholeiitic classification of the complex. Even the post-erosional lavas show more similarities than differences when compared with other lavas. From this I conclude that the lavas of any one Hawaiian volcano have closely interrelated origins.

Not surprisingly, each Hawaiian volcano is somewhat different from all others. This is not a new conclusion, but we now have data on the existence and extent of some more differences. At present little correlation is known between the chemical and physical features of Hawaiian volcanoes. Further study could give correlations or could show that the two aspects are basically unrelated in individual volcanoes.

Some Hawaiian volcanoes, for example Waianae and Kohala, have been uni-modal in their chemical variations, and hence in the way they operated. Others such as East and West Maui have been either less consistent or multi-modal. The Sr-P data for East and West Maui volcanoes suggest that factors external to either volcano were important in controlling at least the Sr-P covariations.

The distributions of some trace elements, for example Sr, Ni and Co, are a function of the concentration of single mineral phases.

The behavior of Zr and K indicates that the distribution of Zr in the rocks studied is in some presently obscure way related to the K concentration.

The Co-Mg data indicate that oxidation of the iron can occur early enough to alter the "normal" Co-Mg distribution. This seems to take place before extensive olivine crystallization.

There are significant variations in the K/Rb ratio between individual Hawaiian volcanoes. This may indicate heterogeneity of one or both of these elements in the source region of Hawaiian magmas or variations of the conditions under which Hawaiian magmas were generated. However, the constancy of the K/Rb ratio in the post-erosional lavas may indicate the opposite for these lavas.

The concentrations of Sr, Rb and K are usually a function of the period in a volcano's eruptive cycle when the lavas are erupted. Zirconium and vanadium are functions of rock type while Co and Ni are so associated with olivine that this relationship may have wiped out other possible features, excepting oxidation of iron.

The last conclusion is that the Hawaiian petrogenesis problem is still very much in the definition stage.

APPENDIX A

In this appendix are the raw data from the emission spectrographs and x-ray spectrometers. Eighty to ninety percent of the x-ray fluorescence values are single analyses, with the rest duplicates. Duplicate analyses are not noted.

The precision for the Sr values is two sigma = ± 5%. For the Zr and Ni values two sigma = ± 10%, except above 500 ppm Ni where ± 15% is a better estimate. All emission spectrographic values have two sigma ± 15%. Precision is variable for Rb (see method).

The x-ray fluorescence Zr values are enclosed in parentheses: the emission spectrographic ones are not. Dashed lines denote no analysis. Asterisks denote that the element was below the detection limits. The detection limits are: 10 ppm Ni, 2 ppm Rb, 5 ppm Co and 25 ppm V. The detection limits for Co and V may be high and have not been carefully checked.

APPENDIX A. RAW DATA

Waianae Volcano, Island of Oahu

Lower Member

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-1	4	398	--	43	263	135
C-2	3	332	--	49	312	134
C-3	8	374	210	37	247	161
C-4	--	359	235	45	350	158
C-5	5	373	245	42	291	179
C-6	4	399	767	--	--	--
C-7	4	361	--	50	262	133
C-8	2	386	--	41	250	122
C-9	4	376	--	45	294	146
C-10	8	405	--	42	251	149
C-11	6	409	292	45	266	165
C-12	4	360	142	45	290	194
C-13	4	365	--	--	--	--
C-14	6	345	188	--	--	--
C-15	5	391	--	47	255	128
C-16	8	425	138	--	--	--
C-17	7	362	--	--	303	--
C-18	7	398	--	44	--	195
C-19	6	350	185	49	267	142
C-20	5	375	--	39	293	197
C-21	3	316	190	47	256	156
C-22	4	404	150	50	270	155
C-23	6	425	188	--	--	--
C-24	0	405	208	39	282	200
C-25	6	305				
C-26	6	301	142	--	--	--
C-27	11	356	142	42	--	140
C-28	2	383	--	46	267	205
C-29	--	--	--	47	294	139
C-30	6	303	135	--	--	--
C-34	7	363	109	44	327	145
C-35	7	365	170	49	291	163
C-36	8	374	134	43	286	160

Waianae Volcano, Island of Oahu (continued)

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-37	11	368	183	35	327	169
C-38	6	316	--	--	--	--
C-39	9	390	138	--	--	--
C-40	8	360	142	30	333	161
C-41	6	345	132	41	259	(160),139
C-46	13	432	152	--	330	(165)
			Middle Member			
C-47	16	665	165	51	302	(233),210
C-48	14	575	74	--	--	(220)
C-49	10	475	314	--	--	(142)
C-50	8	528	521	55	240	(215),184
C-51	11	415	212	42	--	(127),139
C-52	21	690	339	45	--	(273),380
			Upper Member			
C-30	33	627	231	50	275	261
C-31	21	985	52	46	274	(230),236
C-42	26	700	66	--	--	(245)
C-43	--	--	--	47	469	280
C-134	26	780	355	43	352	(305)
C-169	23	725	723	51	266	(250)
C-170	26	960	**	28	265	(300)
C-171	25	936	**	25	230	(315)
C-172	25	934	--	28	260	(265)
C-173	27	975	**	27	247	(313)
C-174	33	900	**	29	245	(325)
C-175	31	872	**	29	273	(335)
C-176	28	800	**	28	282	(340)
C-177	27	863	**	26	249	(382)
C-178	44	915	**	17	162	(370)
C-179	41	855	**	20	180	(390)
C-180	40	935	**	27	220	(322)
C-181	43	894	**	18	196	(410)
C-182	45	895	**	22	227	(368)
C-198	10	402	207	47	236	(135),159

Kohala Volcano, Island of Hawaii

Pololu Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-53	6	308	137	--	--	(200)
C-54	4	274	180	--	--	(145)
C-55		265	317	--	--	(125)
C-56		300	165	--	--	(138)
C-57		338	95	--	--	(167)
C-58		248	265	--	--	(125)
C-59	2	309	192	--	--	(138)
C-60		270	142	--	--	(118)
C-61	2	279	170	--	--	(142)
C-62		304	113	--	--	(153)
C-63	6	302	152	--	--	(240)
C-64	3	280	125	--	--	(120)
C-65	3	365	93	--	--	(203)
C-66	8	303	167	--	--	(242)

Hawi Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-70	32	540	215	--	--	(348)
C-69	17	506	95	--	--	(250)
C-68	58	1,294	**	--	--	(485)
C-210	48	1,670	**	--	--	(370)
C-211	--	--	--	--	--	(355)
C-212	47	1,700	**	--	--	(333)

Mauna Kea Volcano, Island of Hawaii

Hamakua Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-77	12	400	215	--	--	(240)
C-70	11	223	302	--	--	(205)
C-76	7	354	502	--	--	(152)
C-75	11	468	270	--	--	(215)
C-74	3	454	75	--	--	(200)
C-71	13	461	350	--	--	(172)
C-67	13	479	435	--	--	(165)

Laupahoehoe Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-72	46	1,260	**	--	--	(455)
C-73	51	1,170	**	--	--	(535)
C-79	43	1,294	**	--	--	(445)
C-201	37	1,245		--	--	(447)
C-202	17	975		--	--	(315)
C-203		404	113	--	--	(175)
C-204	40	1,243	**	--	--	(437)
C-205	12	970	62	--	--	(220)
C-206	43	1,210	**	--	--	(520)
C-207	23	608	74	--	--	(260)
C-208	60	970	**	--	--	(1,310)
C-209	8	385	798	--	--	(120)

Kauai Volcano, Island of Kauai

Waimea Canyon Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-80	4	304	173	--	--	(159)
C-81	5	202	190	--	--	(150)
C-82	7	209	143	--	--	(152)
C-83	9	294	135	--	--	(130)
C-84		177	1,440	--	--	
C-85	9	327	85	--	--	(169)
C-86	5	333	176	--	--	(155)
C-87	8	262	1,240	--	--	(207)
C-88	11	403	692	--	--	(130)
C-89	7	255	519	--	--	(103)

Koloa Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-90	14	522	672	--	--	--
C-91	27	477	342	--	--	(140)
C-183	60	1,470	--	26	144	(350),325
C-184	25	550	645	70	323	(120)
C-185	34	668	207	46	322	(148),162
C-186	41	695	400	66	340	(168)
C-187	30	650	425	56	293	(138),224
C-188	23	610	305	52	325	(115),154
C-189	36	752	357	58	350	(165),160
C-190	14	628	462	64	351	(162),174
C-191	42	785	460	51	284	(250),166
C-192	59	1,340	112	39	329	(260),244
C-193	23	551	380	56	306	(117)

West Maui Volcano, Island of Maui

Wailuku Series

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-93	5	322	162	50	295	195
C-94	3	352	275	59	200	158
C-95	8	355	173	50	291	140
C-96	6	309	295	46	264	155
C-97	--	265	--	58	251	159
C-98	5	325	229	49	273	131
C-99	5	332	120	46	275	127
C-100	8	310	262	56	271	--
C-101	--	--	--	39	296	164
C-102	2	338	230	51	257	134
C-103	2	271	312	59	257	138
C-104	2	293	206	--	291	--
C-105	3	270	840	68	223	122
C-106	2	327	193	50	252	136
C-107		370	166	48	256	--
C-108	2	260	672	69	230	129
C-109	10	479	90	40	293	247
C-110	9	378	159	44	274	157
C-111	7	355	79	42	247	203
C-112	5	428	522	61	275	175
C-113	5	410	202	43	286	159
C-116	6	575	90	40	242	(208),208
C-117	9	404	525	68	255	147
C-118		262	972	76	245	118
C-119	10	584	52	48	310	207
C-120	5	355	318	65	280	118

Honolua Series

C-92	58	1,090	**	**	**	(748)
C-116	72	416	**	**	**	--
C-128	68	528	**	**	**	(950)
C-149	57	1,126	**	**	**	(725)
C-150	50	1,163	**	**	**	(705)
C-151	54	1,060	**	**	**	(805)

West Maui Volcano, Island of Maui (continued)

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-152	56	1,056	**	**	**	(722)
C-153	9	422	62	34	245	(280)
C-154	58	41?	**	**	**	(820)
C-155	51	1,227	**	**	**	(677)
			Lahaina Series			
C-115	46	795	295	57	262	189
C-120	14	207	321	65	304	(104),109

East Maui (Haleakala) Volcano, Island of Maui

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
			Honomanu Series			
C-123	1	308	1,210	60	300	(143),152
C-122	9	258	700	70	243	(100),102
C-124	5	490	68	59	326	(239),178
C-125	--	--	--	--	--	--
C-126	5	378	340	90	250	(165),160
C-121	2	330	285	53	318	(310),204
			Kula Series			
C-127	34	949	**	26	158	(310)
C-135	42	505	--	--	--	(365)
C-137	--	--	--	--	--	(330)
C-140	26	575	--	--	--	(260)
C-141	71	770	**	--	--	(450)
C-143	41	1,085	**	--	--	(250)
C-144	31	940	**	--	--	(317)
C-145	23	1,095	**	--	--	(263)
C-146	49	1,065	**	--	--	(270)
C-147	40	980	13	--	--	(235)
			Hana Series			
C-129	27	505	352	64	360	(257),263
C-136	--	--	--	--	--	(290)
C-130	--	--	--	--	--	(210)
C-139	41	680	--	--	--	(212)
C-142	34	770	43	--	--	(202)
C-160	--	--	--	--	--	(195)

East Molokai Volcano, Island of Molokai

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-158	55	1,300	**	--	--	(400)
C-159	46	2,775	**	--	--	(272)
C-160	43	1,315	**	--	--	(350)
C-161	70	1,155	**	--	--	(505)

West Molokai Volcano, Island of Molokai

C-44	24	873	15	--	--	(140)
C-45	30	914	--	--	--	
C-162	9	322	128	--	--	(175)

Honolulu Series, Island of Oahu

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zr ppm
C-98	22	555	302	66	207	133
C-103	10	649	475	55	201	(165),144
C-104	21	509	357	54	266	(115),93
C-105	29	1,205	305	58	309	(162),146
C-194	10	473	267	41	205	(160),178
C-195	42	1,210	374	56	280	(109),138
C-196	18	723	107	48	295	(130),100
C-197	52	1,010	290	--	--	(242)
HKCC-5	55	1,320	291	69	259	190

Koolau Volcano, Island of Oahu

C-200	10	390	135	--	--	(149)

Kilauea Volcano, Island of Hawaii

Sample No.	Rb ppm	Sr ppm	Ni ppm	Co ppm	V ppm	Zn ppm
KI-4	10	261	1,070	--	--	--
KI-6	10	263	1,740	--	--	--
KI-7	8	320	800	--	--	--
KI-8	17	340	325	--	--	--
1955-9	19	391	91	--	--	--
1955-10	17	376	146	--	--	--
1955 Puna						
1	20	395	95	--	377	(245)
2	21	390	85	--	359	(240)
3	18	390	110	--	352	(260)
4	17	380	91	--	302	(240)
5	16	384	125	--	295	(223)
6	17	395	147	--	307	(203)
7	14	384	146	--	293	(203)
8	17	394	135	--	312	(220)

APPENDIX B. IBM 7040 COMPUTER PROGRAM FOR COMPUTATION OF X-RAY SCATTERING FACTORS

```
$IBFTC XSCAF
      2 FORMAT (1H1)
      4 FORMAT (48X,25H X-RAY SCATTERING FACTORS)
      1 WRITE (6,2)
        WRITE (6,4)
        LINE=1
      6 READ (5,5) ID,SIO,TIO,ALO,FE30,FE20,EMNO,
        EMGO,ECAO,ENAO,EKO,PO
      5 FORMAT (I6,11F6.4)
      3 FORMAT (10X,I6,5H S = ,F9.3)
        SSIO=SIO*1.10
        STIO=TIO*1.58
        SALO=ALO*1.03
        SFE30=FE30*1.79
        SFE20=FE20*1.87
```

APPENDIX B. (Continued) IBM 7040 COMPUTER PROGRAM FOR COMPUTATION OF X-RAY SCATTERING FACTORS

```
  SMNO=HMNO*1.81
  SMGO=HMGO*1.02
  SCAO=CAO*1.76
  SNAO=HNAO*0.97
  SKO=HKO*1.80
  SPO=PO*1.13
  STOTAL=SSIO+STIO+SALO+SFE3O+SFE2O+SMNO+SMGO+
  1SCAO+SNAO+SKO+SPO
  WRITE (6,3) ID,STOTAL
  LINE=LINE+1
8 IF (ID) 7,7,9
9 IF (LINE-54) 6,6,1
7 STOP
  END
```

APPENDIX D. (Continued) IBM 7040 COMPUTER PROGRAM FOR COMPUTATION OF X-RAY SCATTERING FACTORS

ID = sample number

SIO = %SiO_2

TIO = %TiO_2

ALO = %Al_2O_3

FE3O = %Fe_2O_3

FE2O = %FeO

MMNO = %MnO

MMgO = %MgO

CAO = %CaO

MNAO = %Na_2O

MKO = %K_2O

PO = %P_2O_5

SSIO, etc. are the partial scattering factors due to individual oxides. The number to the right of the asterisk is from Champion, Taylor and Whittem, 1966.

APPENDIX C. IBM 7040 COMPUTER PROGRAM FOR RUBIDIUM ANALYSES

```
$IBFTC RB
   11 WRITE (6,12)
        LINE=1
   12 FORMAT (1H1)
        WRITE (6,13)
   13 FORMAT (40X,12H RB ANALYSES)
    1 READ (5,2) N,ID,BG,RB,S
    2 FORMAT (I3,I6,2F6.2,7X,F3.2)
        HBG=50000./BG
        HRB=50000./RB
        Y=((HRB/HBG)-1.)*S
        CEPT=0.205
        SLOPE=1.00
        CRB=((Y-CEPT)/SLOPE)*(145./95.)*100.
        LINE=LINE+1
        WRITE (6,3) N,ID,Y,S,CRB
     3 FORMAT (10X,I3,3X,3H C-,I3,3X,5H Y = ,F5.3,3X,
        15H S = ,F4.2,3XF4.0,7H PPM RB)
        IF (N) 5,5,4
     4 IF (LINE-54) 1,1,11
     5 STOP
        END
```

BG = time for 50,000 counts at the background position

RB = time for 50,000 counts at the Rb K-alpha position

APPENDIX C. (Continued) IBM 7040 COMPUTER PROGRAM FOR RUBIDIUM ANALYSES

B = scattering factor

CEPT = intercept of the standard curve for that day's analyses

SLOPE = slope of the standard curve

APPENDIX D. DETAILED EMISSION SPECTROGRAPHIC METHODS

Three groups of samples were run on the Bausch and Lomb spectrograph and three on the Hilger spectrograph. Below are given the operating conditions and techniques used with each group. Following this is a section about the internal normalization of the six groups of analyses. The average emission spectrographic values for Zr, V, and Co in the MIT-USGS interlab standards are given along with the normalized values from each group.

Group 1. The S Series

Spectrograph: 1.5 meter Bausch and Lomb with quartz optics.

Power supply: A Mellophone Corp. rectifier, type E10AP, full wave, 230 DC volts at a maximum current of 10 amperes.

Arcing conditions: Samples were arced to completion at 6.2 amperes. Anode excitation was used. The electrodes were National Carbon Co. preformed graphite electrodes L3951 ACKSP (upper) and L4036 ACKSP (lower). Each sample was arced twice on the same plate.

Photography: Kodak Spectrum Analysis -1 plates were developed for 3 minutes 15 seconds at 26.0°C in Kodak D-19 developer, fixed for 5 minutes at 26.0°C in Kodak Fixer, and washed for 30 minutes at the same temperature. Plate calibration was by a line intensity ratio method using Fe lines. This method differs from that given in the USGS Bulletin

APPENDIX D. (Continued) DETAILED EMISSION SPECTROGRAPHIC METHODS

1084-G, pp. 177-178, in that different Fe lines were used. The Fe lines used are those given in Ahrens and Taylor, 1961, p. 153. Line densities were measured by an Applied Research Laboratories Model 2250 Projection Comparator Densitometer, with a Varian recorder replacing the galvanometer.

Lines: Co 3453.505 Å
Zr 3438.230 Å
Fe 3450.33 Å - the internal standard line for Zr and Co.
V 3102.3 Å
Fe 3205.3 Å - the internal standard line for V.

Slit: About 250 microns. The accuracy of the slit adjustment is open to question. This very wide slit was unintentional and was reduced in a later group. It seems to have had little effect on either the precision or accuracy of the data.

Standards: W-1 was the primary standard for all three elements. The AEC-USGS interlab standards did not yet exist. Standards and samples were on separate plates, a practice that was abandoned for all subsequent groups. This practice required a normalization of the S series to the C series. This was done by rearcing samples from the S series in the C series and then plotting the values from the S series vs. those from the C series. The results for V are shown in

Figure 36. There were three plates in the S series that contained two or three samples shared in the series, while others contained only one. These data were used to plot Figure 36. The conclusion is obvious; there were serious interplate errors. The errors cannot be photographic; the lines drawn through the points parallel the line of no systematic error. Using this information, each plate was normalized to the C series for V, Co, and Zr.

Precision: Only data for V will be given here; overall precision for the other elements will be given later. Thirty-two samples in duplicate give 2 sigma = 22.6 ppm V. This is about 10%. Twenty-two runs of W-1 on 5 different plates give % 2 sigma = 21.0%, indicating large interplate differences. Duplicates are on the same plates.

Group 2. The C Series

Everything is as for the S series except that HEC-2, 4, and 5 were used as secondary standards for Co and as primary standards for Zr. Standards and samples were intermixed on the plates.

Precision: Fifteen samples in duplicate give 2 sigma = 30 ppm V, or about 12%. Eleven runs of W-1 on 5 different plates give % 2 sigma = 12.6%, indicating small interplate differences.

Group 3. The B and L Series

Basically the techniques are the same as for the S and

C series. The slit was reduced to about 25 microns, and the entire HIG-USGS interlab series was used as secondary standards for Co and as primary standards for Zr.

Precision: Twenty-six samples in duplicate give 2 sigma = 20.4 ppm V, or about 11%. Seventeen runs of W-1 on 5 different plates give % 2 sigma = 15.4%, indicating moderate interplate differences. Four runs of W-1 on one plate and six runs on a second plate give % 2 sigma = 11.0%, supporting the indicated interplate differences.

Groups 4 through 6. The Hilger Series

There are only minor changes in operating conditions for these three groups. It was sometimes necessary to use separate working curves for the different groups, hence the separation into three groups. The cause of the differing working curves is unknown but thought to reflect unconscious daily variations by the operator. Whatever the cause, it often affected the integrated intensity of emission lines to varying extents.

The operating conditions for these groups are given below.

The features in common for these three groups will be given first.

Spectrograph: A Hilger 3 meter compact grating spectrograph with a reciprocal dispersion of about 2.8 Å/mm in the second order was used.

Power supply: A Hilger - D.N.F.S. Spectrographic Source

Unit was operated as a DC unit.

Photography: Kodak Spectrum Analysis #1 plates were developed in Kodak D-19, fixed for 5 minutes in Kodak Fixer, and washed for 30 minutes. The developing times were determined by the temperature. A time vs. temperature plot was made from 2 plates having the same gamma but which were developed at different times and temperatures. Line densities were measured as before.

Plate calibration was by the Na 3302 doublet.

This method uses Na lines in the sample spectra and requires previously calibrated plates.

Step 1. Determine the intensity ratio of the Na doublet in similar samples on previously calibrated plates.

Step 2. Read the Na doublet in samples on the plates to be calibrated.

Step 3. Use the data from steps 1 and 2 to construct a plate calibration curve for the new plates.

This method suffers from all the limitations inherent to such a method. Of special importance are errors due to self-absorption and variations in the intensity ratio due to matrix changes or changes in arcing conditions.

The calibration of the plates exposed on the Hilger spectrograph seems to contain an error due to a change in the arcing conditions: the Na intensity ratio was taken from plates exposed on the Bausch and Lomb. The effect of this error is included in the Zr, Co, and V values given in

Tables X, XI, and XII for the Hilger series.

Lines: Co 3453.505 Å

Zr 3438.230 Å - for lower concentrations.
Almost all analyses were with
this line.

Zr 3430.53 Å - for higher Zr concentrations.

Fe 3450.33 Å - the internal standard line for
Zr and Co.

V 3102.3 Å

Fe 3160.66 - the internal standard line for V.

Slit: 0.020 mm.

Standards: W-1 was primary for Zr, V, and Co. The HIC-USGS interlaboratory standards were secondary for Co and primary for Zr.

Arcing conditions: Samples were arced to completion at 10.5 amperes.

The overall precision for all groups of analyses from both spectrographs and for all three elements is set at 2 sigma = ± 15%.

TABLE XIV. INTER-SERIES ACCURACY FOR VANADIUM.
(W-1 V=250 PPM WAS THE PRIMARY STANDARD)

				Hilger plates		
Std.	Avg.	C	D and E	7	10	11, 12, 20-22
HZG-1	253	--	250	259	237	264
HZG-2	298	297	293	285	315	--
HZG-3	--	--	--	--	--	--
HZG-4	239	233	242	239	245	230
HZG-5	254	287	253	238	245	247
HZG-6	264	--	--	262	250	268
HZG-7	82	--	82	--	--	--
HZG-8	253	--	270	240	247	255

--Denotes no analysis.

TABLE XV. INTER-SERIES ACCURACY FOR COBALT.
(W-1 CO=42 PPM WAS THE PRIMARY STANDARD)

Std.	Avg.	C	D and E	Hilger plates 10-12	 20-23
HZC-1	80	70	75	80	--
HZC-2	38	39	41	34	--
HZC-3	--	--	--	--	--
HZC-4	41	42	43	41	40
HZC-5	62	72	64	--	49
HZC-6	48	--	48	47	--
HZC-7	14	--	14	--	--
HZC-8	47	--	47	47	46

--Denotes no analysis.

TABLE XVI. INTER-SERIES ACCURACY FOR ZIRCONIUM.
(W-1, 100 PPM, AND G-1, 220 PPM WERE OTHER PRIMARY STANDARDS)

Std.	Avg.	C	B and L	Hilger plates 7 and 8	 10-12
HZC-1	131	136	139	124	124
HZC-2	155	163	158	148	153
HZC-3	--	--	--	--	--
HZC-4	125	123	128	116	132
HZC-5	198	190	189	215	198
HZC-6	180	--	163	177	200
HZC-7	--	--	--	--	--
HZC-8	248	--	250	250	245

--Denotes no analysis.

APPENDIX F.

TABLE XVII. VANADIUM DATA FOR LAVAS OF THE 1955 PUNA ERUPTION, IN PPM V

Sample	1	2	3	4	5	6
1	400	377	--	22	5.8%	--
2	400	359	--	41	11.4%	--
3	390	352	370	38	10.8%	5.4%
4	400	302	--	98	32.4%	--
6	370	295	--	75	25.4%	--
8	340	307	350	33	10.4%	2.9%
9	340	293	--	47	16.0%	--
10	350	312	--	38	12.2%	--

1. USGS. Paul Barnett, analyst. Data from Hawaiian Volcanoes During 1955, USGS Bull. 1171, p. 87.
2. Norman Hubbard, analyst. Data from Bausch and Lomb C series: average of two runs.
3. Norman Hubbard, analyst. Data from Bausch and Lomb D and E series: average of six runs.
4. Difference between 1 and 2.
5. Percent difference between 1 and 2, computed on 2.
6. Percent difference between 1 and 3, computed on 3.

APPENDIX G

The diagrams on the two following pages have been included to provide the reader ready reference to them. One is from Green and Ringwood (1966) and the other from O'Hara (1965).

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