Chapter 2

TRACE ELEMENT GEOCHEMISTRY OF THE HONOLULU VOLCANIC SERIES, HAWAII

David A. Clague
Dept. of Geology
Middlebury College
Middlebury, Vermont 05753

and

Frederick A. Frey
Dept. of Earth and Planetary Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

INTRODUCTION

The Honolulu Volcanic Series consists of the eruptive products of 37 distinct vents or groups of vents on southeastern Oahu (Fig. 1.) The location of the vents from which the tuffs and flows of the Honolulu Volcanic Series were erupted are well known, having been mapped by Stearns and Vaksvik (1935), Stearns (1940), and Winchell (1947). The vents are arranged along rift zones perpendicular to the rift system of the underyling Koolau shield (Stearns and Vaksvik, 1935; Winchell, 1947; Jackson and Wright, 1970). The eruptive products include melilite-nepheline basalts (melilities), nepheline basalts (nephelinites), basanites, and alkali basalts (Winchell, 1947; Macdonald and Katsura, 1962, 1964; Macdonald, 1968; Jackson and Wright, 1970). The total volume of the Honolulu Volcanic Series is no more than a small fraction (<<1%) of that of the underlying 1.8 - 2.6 m.y. old Koolau shield (Doell and Dalrymple, 1973). Many of the flows fill valleys eroded into lavas of the older Koolau and Kailua Volcanic Series; the valley-filling nature of these flows indicates that they erupted after a prolonged period of erosion and gives rise to the usage of "post-erosional basalts" to describe these lavas. The earliest of the Honolulu Volcanic Series eruptions occurred in the vicinity of the Koolau caldera, whereas many of the most recent occurred on the Koko rift along the southeastern coast of Oahu. Tuffs and flows of 18 of the vents contain rare to abundant coarse grained inclusions of dunite, lherzolite, wherlite, and garnet peridotite (White, 1966; Jackson and Wright, 1970; Beeson and Jackson, 1970). The Honolulu Volcanic Series eruptions occurred between about 2 and 0.3 m.y. ago (Dalrymple and Lanphere, 1979).

Samples and Analytical Techniques

Thirty unaltered samples from the Honolulu Volcanic Series were analyzed for the rare earth elements and a wide array of other trace elements. The samples studied include nine samples described by Jackson and Wright (1970) and an additional 21 samples selected from 41 analyzed samples (E. D. Jackson and M. H. Beeson, unpub. data). From the additional 41 samples, only those having H_2O^+ less than 1% were analyzed for trace elements. A total of 23 of the 37 vents are represented in the subgroup of samples analyzed for this study.

The entire 30 samples were analyzed for the rare earth elements, Ba, Co, Cr. Hf, Ta, Th and Sc by instrumental neutron activation analysis (INAA), for Ni, Co, Cr, Cu, Sc and V by emission spectroscopy (ES), and for Ba, Rb, Sr, Zr, Y and Zn by X-ray fluorescence (XRF). Most of the nine samples having published major element analyses (Jackson and Wright, 1970) were analyzed by INAA in triplicate, twice at MIT and once at the U. S. Geological Survey laboratories. Results are within 4.5 - 8% for all elements. Clague et al. (1977) have briefly described some of the trace element data on these samples from the Honolulu Volcanic Series.

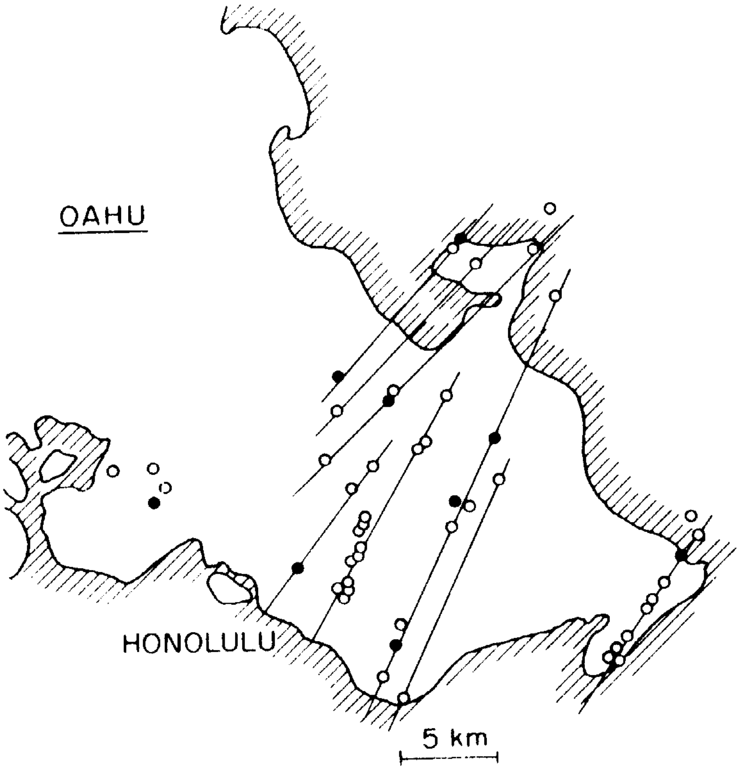

Figure 1. Location map showing the 37 vents and groups of vents of the Honolulu Volcanic Series on southeastern Oahu (after Winchell, 1947). The vents where the 9 samples described by Jackson and Wright (1970) and analyzed in this study were collected are shown by filled circles.

Rock Types and Distribution

Jackson and Wright (1970) modified the eruptive sequence of the 37 vents inferred by Winchell (1947). Available radiometric ages (Dalrymple and Lanphere, 1979) indicate that the sequence of eruptions inferred by Winchell is rough at best. There is no obvious relation between lava type and the sequence of eruption; nephelinites and melilitites were eruptive throughout the period of eruption of the Honolulu Volcanic Series.

Jackson and Wright (1970) noted that the distribution of both lava types and xenoliths are zonally arranged. Additional analyses (E. D. Jackson and M. H. Beeson, unpub. data) of lavas from other vents do not conform to the zonal arrangement proposed by Jackson and Wright (1970). It is still evident that the alkali olivine basalts erupted along the Koko rift are higher in SiO_2 than any of the lavas erupted nearer the caldera complex of the Koolau shield. Closer to the caldera complex, the distribution of nephelinites and melilitites (lavas containing 36-42% SiO_2) is random. In addition, nephelinite tuffs erupted in the vicinity of Salt Lake Crater are equally distant from the center of the Koolau shield, as are the alkali olivine basalts erupted along the Koko rift. The zonal distribution of the lavas is very rough, if it exists at all. On the other hand, the zonal distribution of xenolith types observed by Jackson and Wright (1970) is more compelling. The preponderance of xenoliths erupted near the Koolau caldera are dunites, while farther out lherzolite and finally garnet peridotites become more abundant (Jackson and Wright, 1970).

Previous Trace Element Studies

Abundant trace element and isotopic data exist for lavas from the Honolulu Volcanic Series, but only rarely for the same samples analyzed for major element chemistry. Schilling and Winchester (1968) published rare earth element data for six samples, Philpotts et al. (1972) for one more, and Kay and Gast (1974) for an additional three samples. Schilling and Winchester (1968) concluded that the melilitites and nephelinites probably were generated by variable degrees of partial melting or deep crystal fractionation dominated by orthopyroxene. Kay and Gast (1974) proposed that the nephelinites were generated by smaller degrees of partial melting than the alkalic basalts and that the mantle source for the nephelinites had a higher garnet/clinopyroxene ratio than the source for the alkali basalts.

Dalrymple and Lanphere (1979) analyzed 14 of the same samples used in this study for Sr isotopic ratios. Their results show that much of the $^{87}Sr/^{86}Sr$ variabilility of the earlier studies was due to poor analytical precision. The ratios they obtain are fairly uniform and range from 0.70324 ± 5 to 0.70358 ± 12. All these values are lower than the 0.70359 ± 15 to 0.70412 ± 22 ratios of the underlying Koolau shield (Lanphere et al., 1979).

Chemistry

All of the samples analyzed appear to be unmodified mantle partial melts except those from vent 32 which have undergone fairly extensive shallow crystal fractionation. All the other basalts have MgO > 10%, Mg-values > 65 (calculated with $Fe^{3+}/Fe^{3+} + Fe^{2+} = 0.16$), Ni greater than 180 ppm, and many contain high-pressure mantle xenoliths. The high Ni and MgO abundances demonstrate that these lavas are mantle partial melts that are relatively unmodified.

Figure 2 shows the chondrite-normalized rare earth elements for most of the nine samples with published major element analyses (Jackson and Wright, 1970) and the range of compositions for the entire 30 samples. All the samples have heavy REE depletion indicating residual garnet in the mantle source region. The wide variation in light REE abundances (La = 19 - 86 ppm) reflects a wide range of partial melting or an extremely heterogeneous mantle source. None of the basalts displays a Eu anomaly indicating partial melting at pressures higher than the stability range for plagioclase. There is a strong correlation between the degree of light rare earth enrichment (La/Yb ratio) and the amount of normative nepheline (Fig. 3). This correlation suggests that the more nepheline normative basalts are generated by smaller percentages of partial melting than the basalts with little normative nepheline.

Ratios of K/Rb (323-518) (Figure 4); K/Ba (9-22) and K/Sr (6-12) imply a mantle source lacking amphibole and with little or no phlogopite (Clague et al., 1977).

Abundances of strongly incompatible elements such as the light REE, P_2O_5, Th, Sr, and Ba are strongly correlated, indicating that these elements are not retained by residual phases. The P_2O_5/Ce ratio of all 30 samples is 79 ± 4.7 (Fig. 5) and the P_2O_5/Th ratio is 19 ± 2.2 (Fig. 6). The factor of 4 enrichment of each of these elements suggests that the alkalic basalts are generated by about 4x the percentage partial melting that generated the melilitites, assuming that the mantle source is homogeneous.

K_2O does not correlate well with the light REE, Th, P_2O_5, Sr or Ba (see Fig. 7). This suggests that K is either retained in a residual mantle phase such as phlogopite or that it is soluble in fluid phases or mobile during alteration (Frey et al., 1978). The basalts analyzed in this study are all unaltered; the K_2O variations are not due to alteration.

Hf, Zr and TiO_2 do not correlate with P_2O_5 or the light REE (Fig. 8), During the generation of the Honolulu Volcanic Series, these elements do not behave as strongly incompatible elements. The distribution of Zr relative to P_2O_5 suggests that Zr (and Hf and TiO_2) are retained in the source region and that more than one phase may be involved.

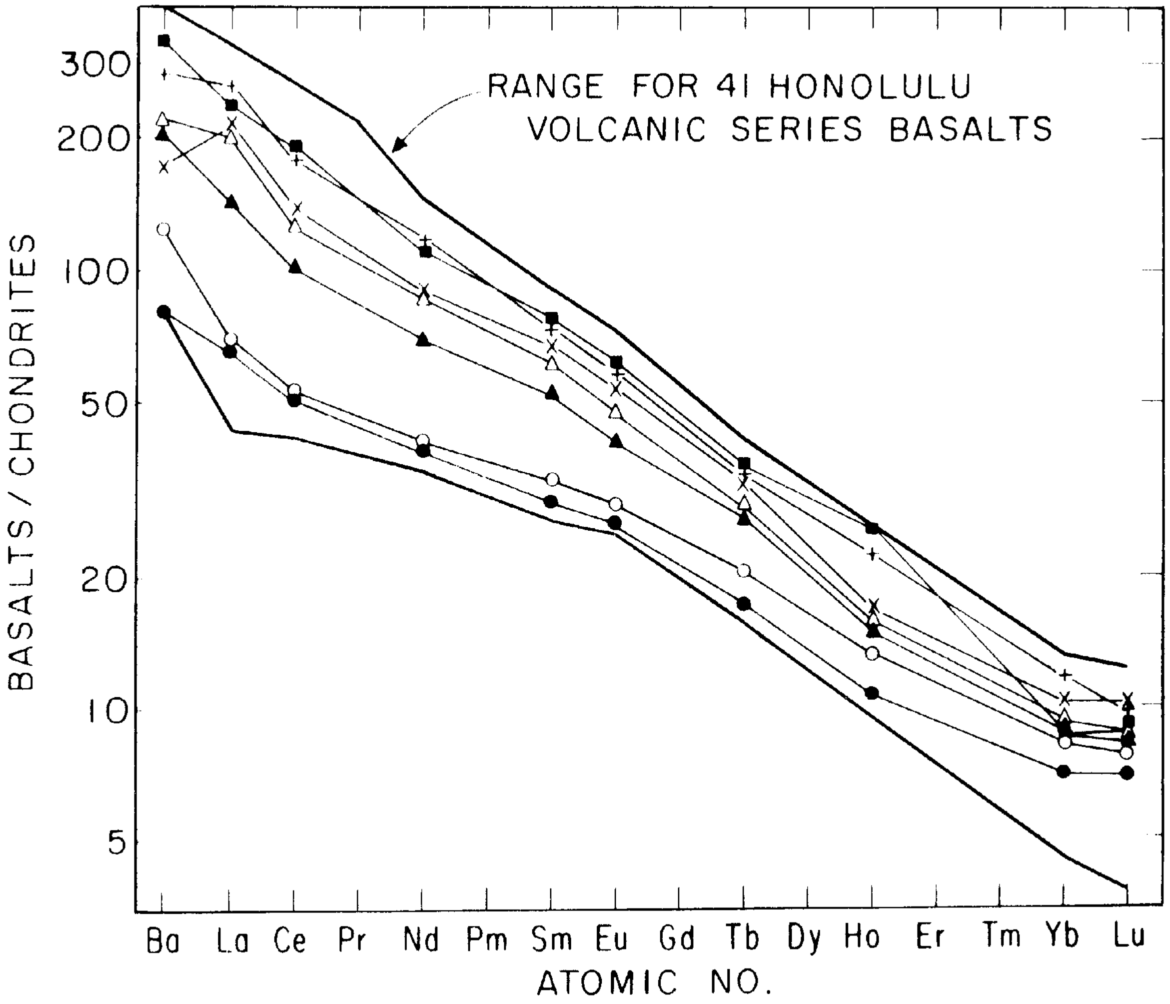

Figure 2. Chondrite normalized rare earth element plots for samples from the Honolulu Volcanic Series. The range of all 30 samples analyzed here, plus 11 previously published analyses, are shown. The samples shown are 65 AIN-1 (▲), 65 KPO-1 (O), 66 PY-1 (X), 68 KAU-1 (+), 68 TSV-1 (■), 68 PB-2 (△), and 68 FS-2 (●).

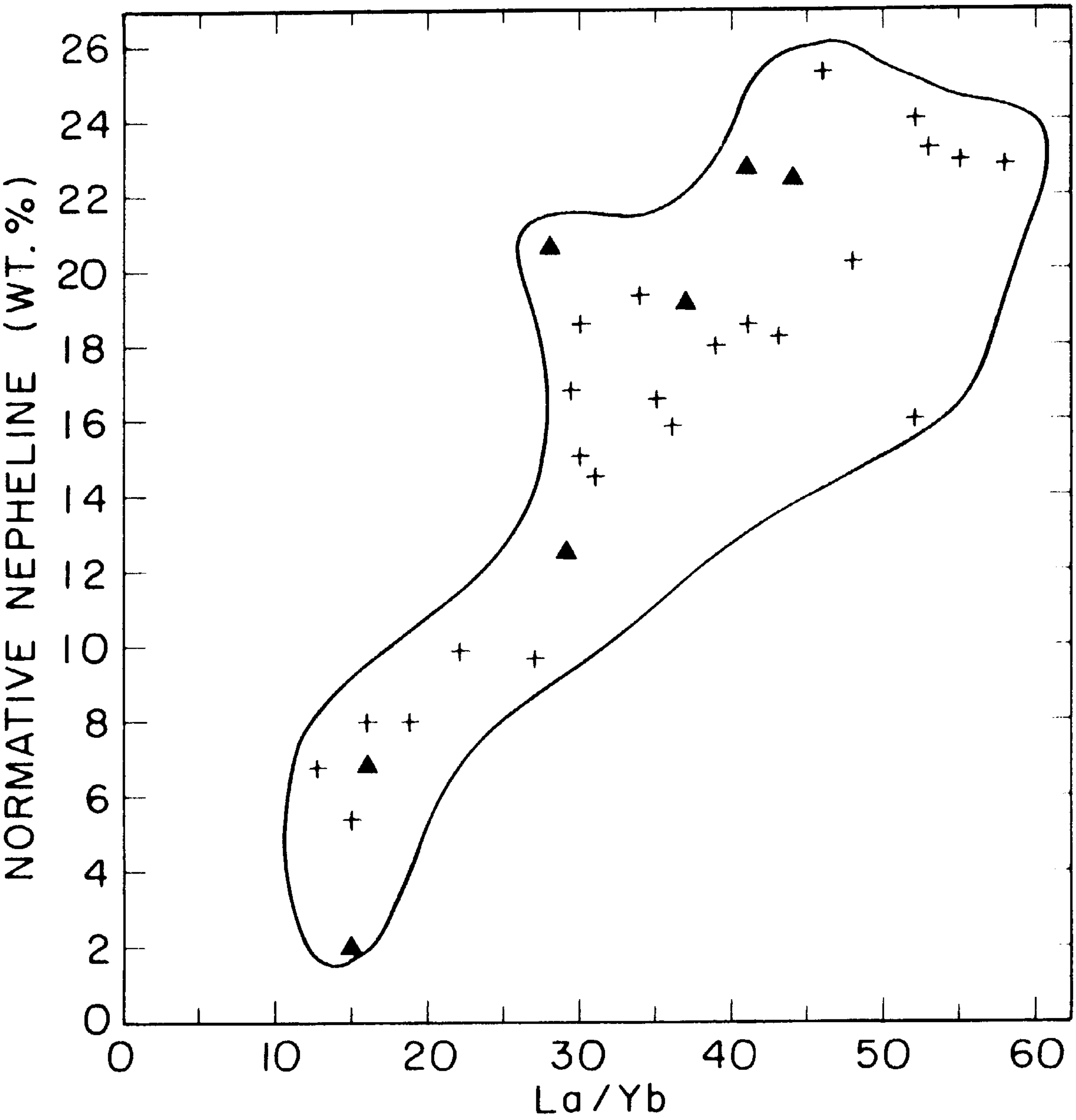

Figure 3. Normative nepheline plotted against the La/Yb ratio for 30 Honolulu Volcanic Series samples. The norm was calculated using Fe_2O_3/FeO 0.21. The filled triangles are average La/Yb for triplicate analyses of samples with published major element analyses (Jackson and Wright, 1970). The positive correlation indicates that the more nepheline normative basalts have greater light REE enrichment and were therefore generated by smaller degrees of partial melting.

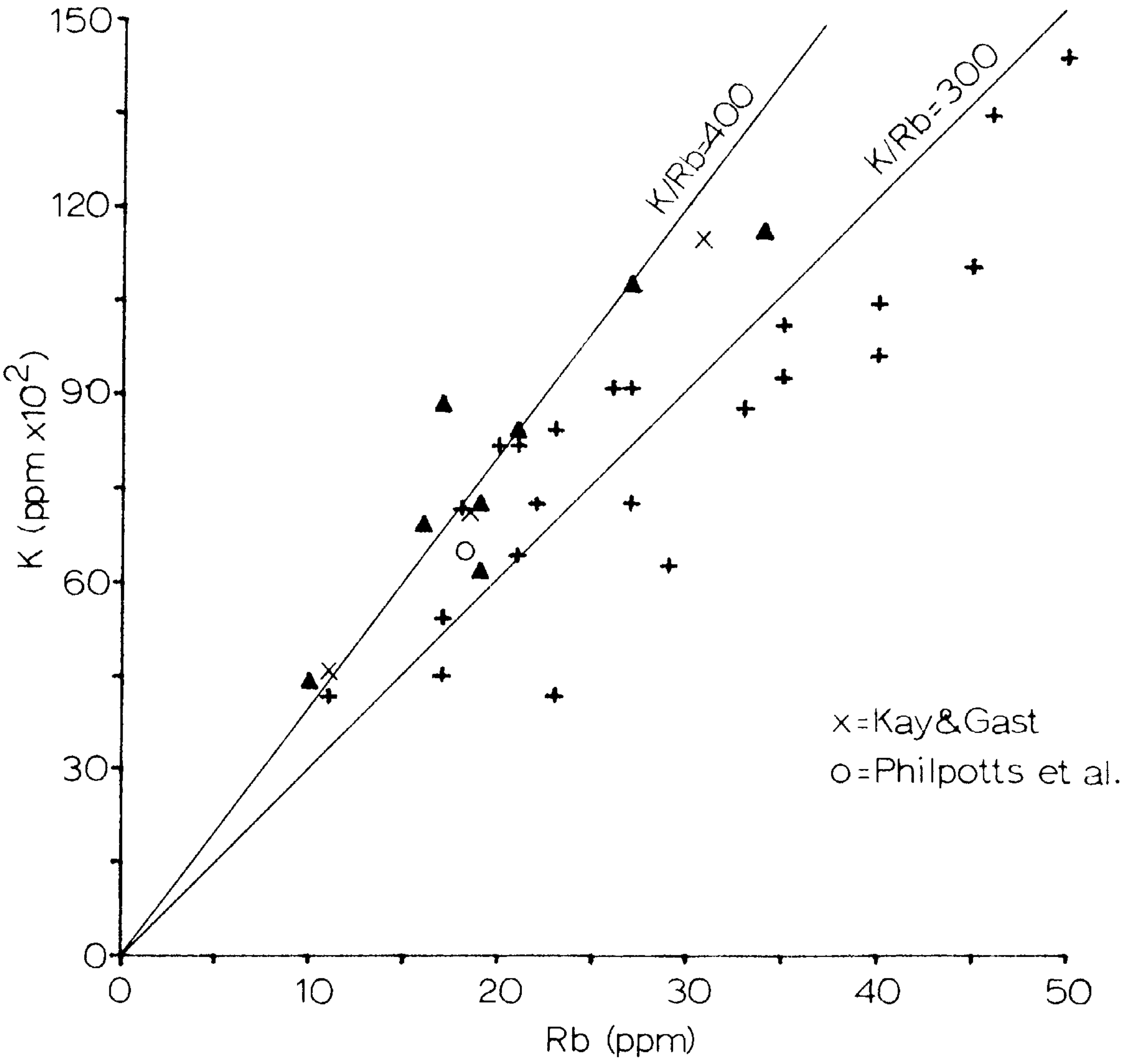

Figure 4. Plot of K against Rb for 30 new analyses of Honolulu Volcanic Series. Also shown are four analyses by isotope dilution published by Kay and Gast (1974) and Philpotts et al. (1972). The Honolulu Volcanic Series basalts have a wide range of K/Rb ratios, but average about K/Rb = 300. The highest quality Rb analyses are shown as filled triangles and give an average K/Rb = 300, in agreement with the Kay and Gast (1974) and Philpotts et al. (1972) data.

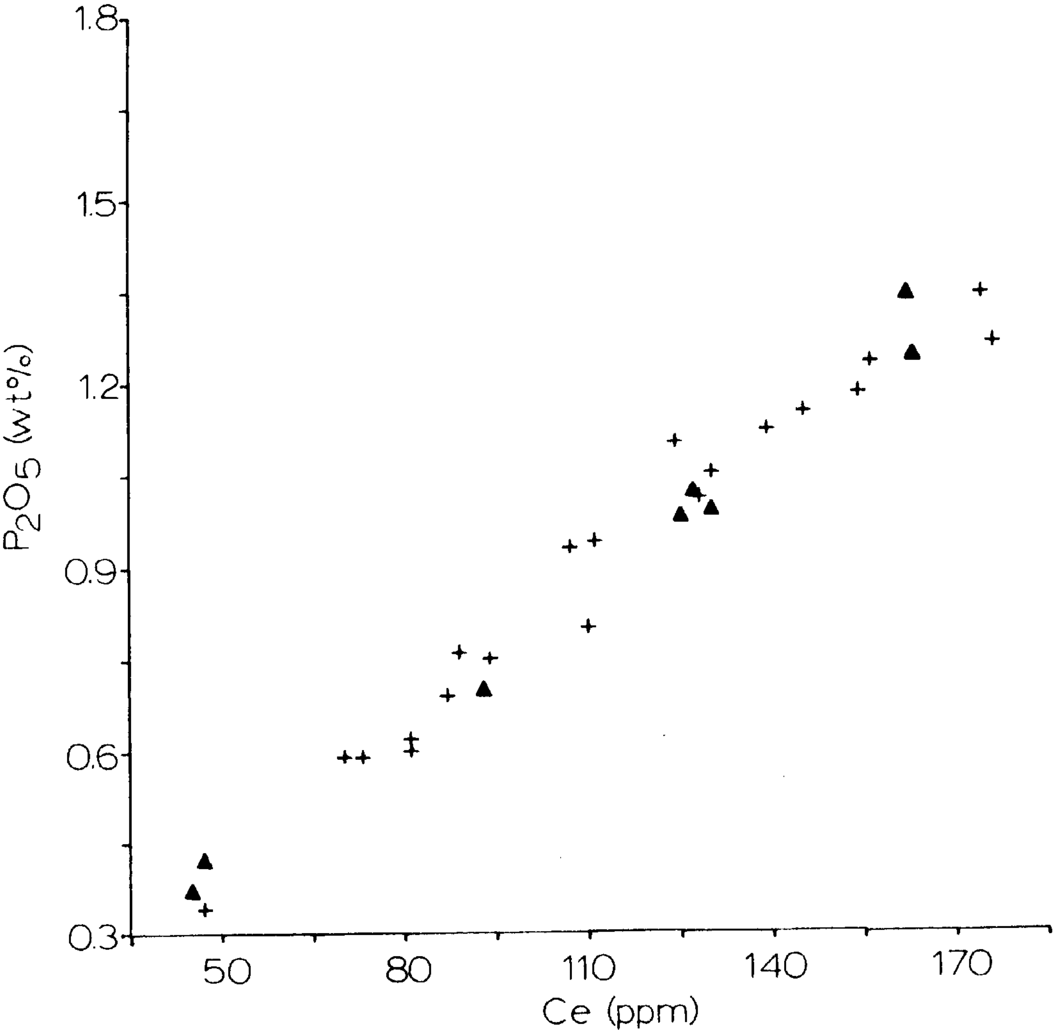

Figure 5. Plot of P_2O_5 against Ce showing the strong positive correlation of these elements. The average P_2O_5/Ce ratio is 79^{+}-4.7. The filled triangles are those samples that have REE analyzed in triplicate.

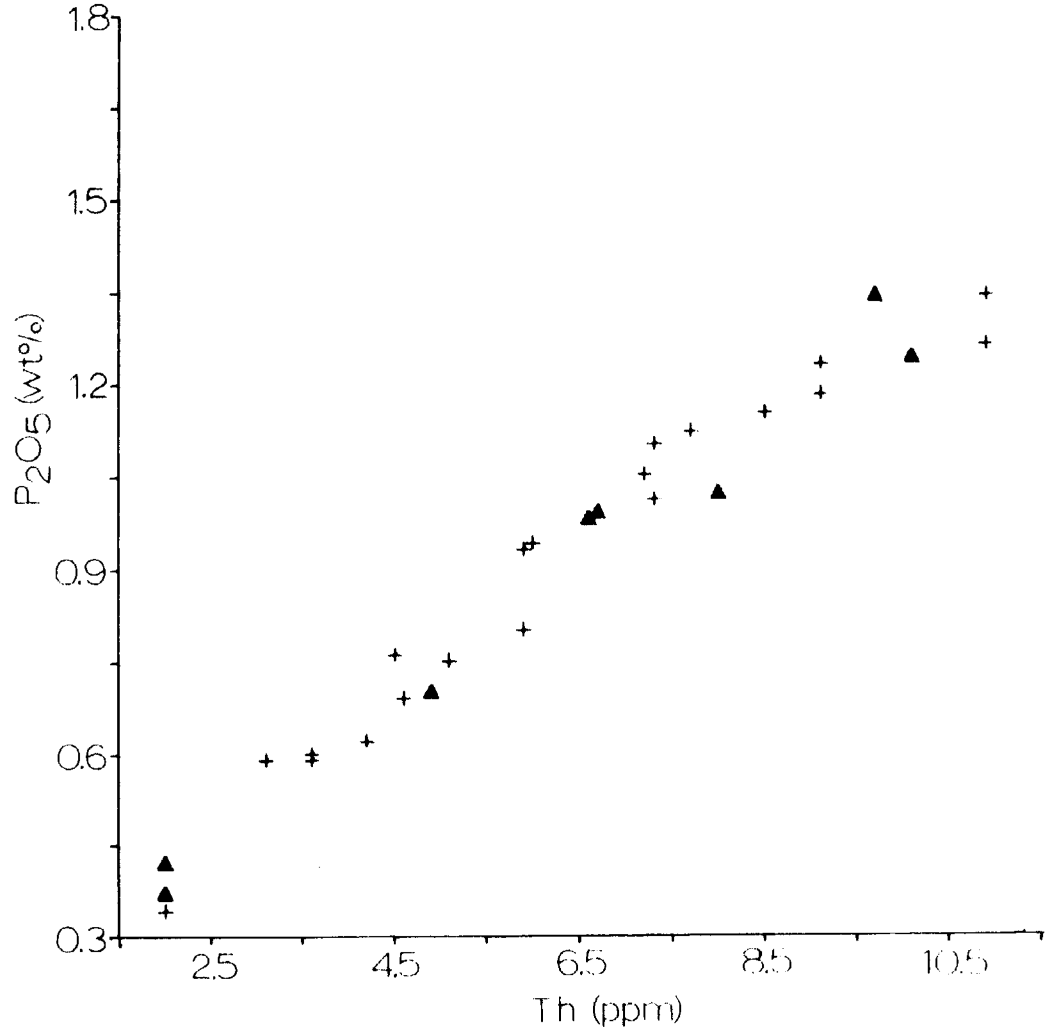

Figure 6. Plot of P_2O_5 against Th showing the strong positive correlation of these elements. The average P_2O_5/Th ratio is $19^+-2.2$ The filled triangles are those samples that have REE analyzed in triplicate. The strong correlation suggests that P_2O_5, Ce, and Th are not retained by any residual mantle phases and that the mantle source has uniform ratios of these elements. The factor of 4 variation in elemental abundances indicates that the percent partial melting required to generate these magmas from a homogeneous source varies by a factor of 4.

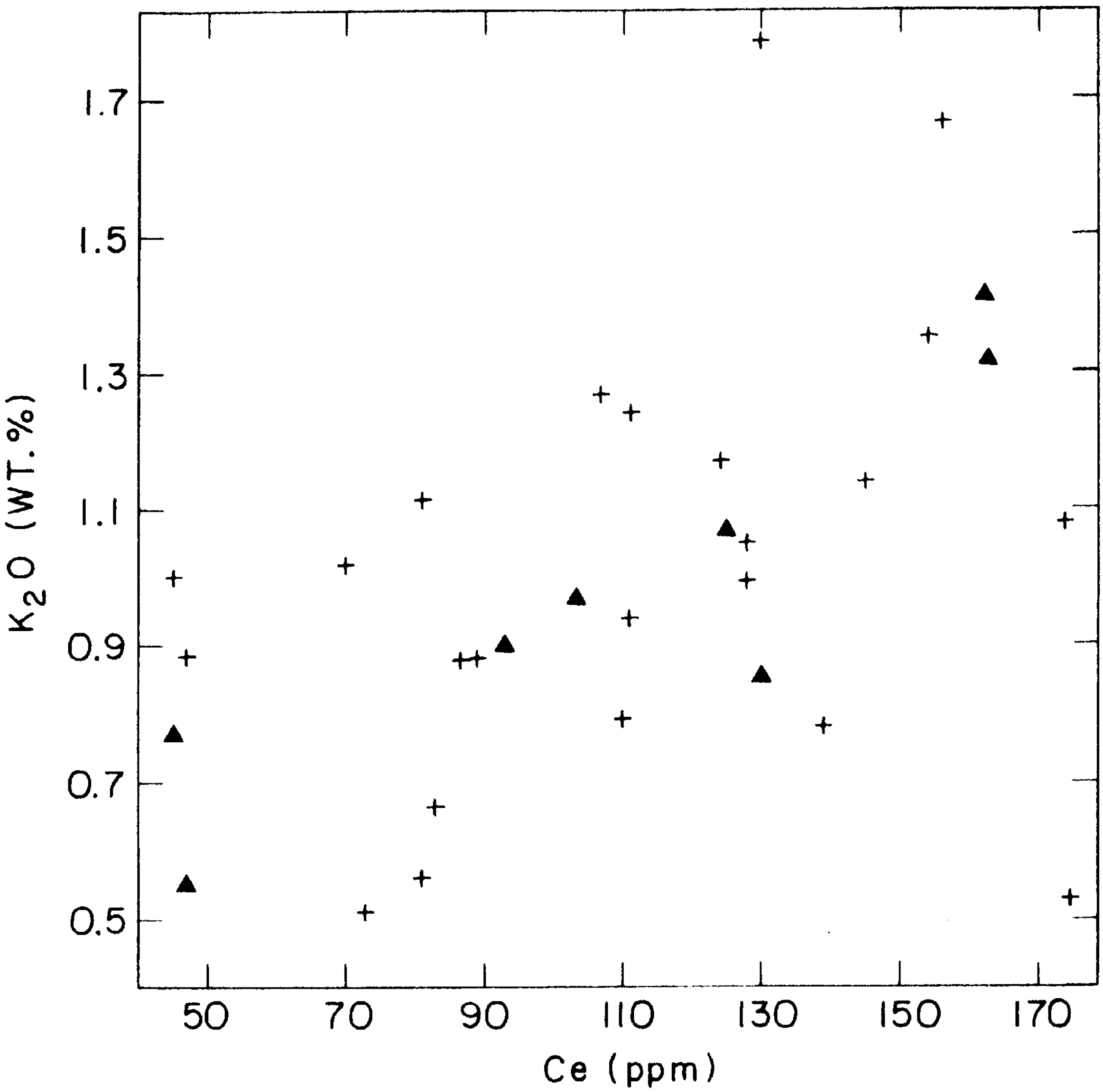

Figure 7. Plot of K_2O against Ce showing the poor correlation between these elements. K_2O does not behave as an incompatible trace element during generation of these magmas. Since all the analyzed samples are relatively unaltered, this variability is probably due to the presence of a K-bearing phase such as phlogopite in the mantle residuum or to mobility of K in fluid phases.

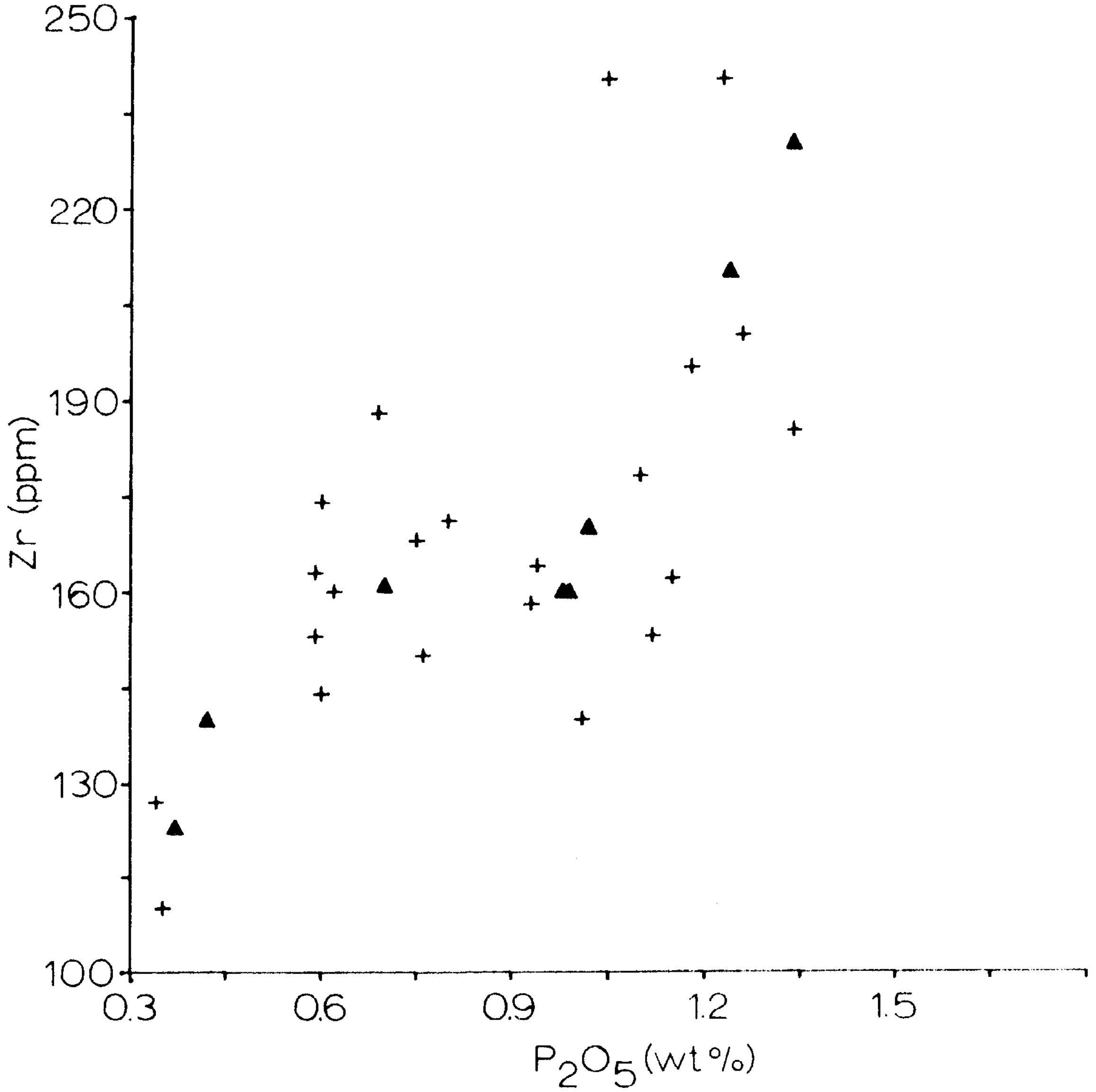

Figure 8. Plot of Zr against P2O5 showing the poor correlation of these two elements. There is some indication that there are two groups of basalts, those with high Zr/P_2O_5 (between 57 and 73) and those with low Zr/P_2O_5 (between 27 and 52). The factor of 2 increase in Zr while P_2O_5, Th and Ce increase by a factor of 4, indicates that Zr is retained in a residual mantle phase during partial melting (as are TiO_2 and Hf). The two groups of basalts identified suggest that more than one phase may control Zr abundance in the magmas.

DISCUSSION

Nd isotopic data for two Honolulu Volcanic Series samples (DePaolo and Wasserburg, 1976; O'Nions et al., 1977) indicate that at least some of the Honolulu Volcanic Series samples were derived from a time-averaged light REE depleted source. Using 3x chondritic abundances for the heavy REE and the Nd isotopic data we estimate that Ce in the mantle is 1.4x chondrites. Derivation of the Honolulu Volcanic Series basalts from such a source region by simple partial melting requires <1% partial melting of a garnet peridotite source.

Another alternative to the above model would be generation from a light REE source region followed by a process of zone-refining as the magma moved to the surface. Zone-refining models can be construed to yield trace element pattens similar to those observed (Clague et al., 1977). This alternative offers no explanation of how the magmas still contain high pressure mantle xenoliths.

The Nd-isotopic data are insensitive to relatively recent enrichment events. As an alternative to the very small percentages of partial melting indicated above, it is possible that the mantle source region underwent a recent enrichment in light REE and other incompatible elements. In this case, the recent enrichment event would be followed by the generation of the Honolulu Volcanic Series basalts from a light REE enriched source by considerably larger percentages of partial melting.

REFERENCES

Beeson, M. H., and Jackson, E. D., 1970, Origin of the garnet pyroxenite xenoliths at Salt Lake Crater, Oahu, Mineral. Soc. Am. Spec. Paper 3, p. 95-112.

Clague, D. A., Frey, F. A., and Natland, J. H., 1977, Petrogenesis of the Honolulu Volcanic Series: Constraints based on trace element data, Am. Geophys. Union Trans. 58, p. 533.

Dalyrmple, G. B., and Lanphere, M. A., 1979, Age and Sr-isotopic composition of the Honolulu Volcanic Series, Hawaii, American Jour. Sci. (Jackson volume) in press.

Doell, R. R., and Dalrymple, G. B., 1973, Potassium-argon ages and plageomagnetism of the Waianae and Koolau Volcanic Series, Oahu, Hawaii. Geol. Soc. Am. Bull., 84, p. 1217-1242.

Frey, A. A., Green, D. H., and Roy, S. D., 1978, Integrated models of basalt petrogenesis: A study of Quartz tholeiites to olivine melilitites from South Eastern Australia utilizing geochemical and experimental petrologic data, Jour. Petrol. 19, p. 463-513.

Jackson, E. D., and Wright, T. L., 1970, Xenoliths in the Honolulu Volcanic Series, Hawaii, Jour. Petrol., 11, p. 405-430.

Lanphere, M. A., Dalrymple, G. B., and Clague, D. A., 1979, Rb-Sr systematics of basalts from the Hawaiian-Emperor Volcanic chain, In Jackson, E. D., Koizumi, I., et al., Initial Reports of the Deep Sea Drilling Project, V. 55, Washington (U. S. Government Printing Office), in press.

Kay, R. and Gast, P. W., 1974, The rare earth content and origin of alkali-rich basalts, J. Geol., 81, p. 653-682.

Macdonald, G. A., 1968, Composition and origin of Hawaiian lavas, Mem. Geol. Soc. Am., 116, p. 477-522.

Macdonald, G. A., and Katsura, T., 1962, Relationships of petrographic suites in Hawaii, Monogr. Am. Geophys. Union, 6, p. 187-195.

Macdonald, G. A., and Katsura, T., 1964, Chemical composition of Hawaiian lavas, Jour. Petrol., 5, p. 82-133.

Philpotts, T. A., Schmetzler, C. C., and Thomas, H. H., 1972, Petrogenetic implications of some new geochemical data on eclogitic and ultrabasic inclusions. Geochem. cosmochem. Acta, 36, p. 1131-1166.

Schilling, J. -G., and Winchester, 1969, Rare earth contribution to the origin of Hawaiian lavas, Contrib. Mineral. Petrol., 23, p. 22-37.

Stearns, H. T., 1940, Supplement to the geology and groundwater resources of the island of Oahu, Hawaii, Bull. Hawaii Div. Hydrogr., 5, p. 1-164.

Stearns, H. T., and Vaksvik, K. N., 1935, Geology and groundwater resources of the island of Oahu, Hawaii. Bull. Hawaii Div. Hydrogr. 1, p. 1-479.

White, R. W., 1966, Ultramafic inclusions in basaltic rocks of Hawaii, Cont. Miner. Petrol., 12, p. 245-314.

Winchell, H., 1947, Honolulu series, Oahu, Hawaii, Bull. Geol. Soc. Am. Bull., 58, p. 1-48.