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**LA THÈSE A ÉTÉ
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THE GEOCHEMISTRY OF HAWAIIAN LAVAS

by

• John David Greenough

B.Sc. Acadia University

A thesis submitted to the Faculty of
Graduate Studies and Research in partial
fulfilment of the requirements for the
degree of Master of Science

Department of Geology

Carleton University

Ottawa, Ontario

1979

The undersigned recommend to the Faculty of Graduate
Studies and Research acceptance of the thesis

"The Geochemistry of Hawaiian Lavas"
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Abstract

The major element geochemistry, trace element geochemistry, and petrography were used to determine a possible petrogenesis for twenty-three lavas from the islands of Hawaii, Maui and Kauai. The modal and normative mineralogy revealed that nine of the lavas are tholeiitic basalts, eight are alkali basalts, one is a nephelinite, and six are differentiated lavas. Most of the trace elements are very similar in concentration from one island to another. However, Rb, Sr and the rare earth elements seem to vary between the islands. The concentrations of the rare earth elements, as well as Hf, Rb, Sr, Ba, Sc, Ti, Zr, Ga, V, Th, Pb and Zr in Hawaiian basalts are similar to those found in other oceanic island basalts. Cr, Co, Ni and Cu concentrations of Hawaiian basalts are higher and Nb concentrations lower than those abundances found in other oceanic island and ocean floor basalts.

The rare earth element distribution in the differentiated lavas was modelled using Gast's (1968) equation by assuming plagioclase, olivine and clinopyroxene are removed from an alkali basalt in the proportions of 2:3:5. The percentage of melting necessary to generate each undifferentiated lava was estimated by modelling the rare earth element distributions with the batch equation of Shaw (1970). The estimates suggest that the tholeiites represent 8 to 14 percent melting of the mantle, alkali basalts represent 2 to 8 percent melting and nephelinites represent 1 to 2 percent melting. Trace element modelling also suggest that the source for Hawaii lavas has high concentrations of K, Sr, Rb and the rare earth elements as well as lower concentrations of Sc, Ti, V, Cr, Co and Ni than the

sources for Kauai and Maui lavas. Rare earth element data from the literature for Oahu lavas suggest their source may be heterogeneous. These concentration differences may suggest the sources for Kauai, Maui, and some Oahu lavas have been "depleted" by previous melting events, more so than the sources for Hawaii lavas and other Oahu lavas.

THIS THESIS IS DEDICATED TO MY PARENTS
FOR AN INFINITE NUMBER OF REASONS.

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Chapter One Introduction

Stretched out along 3000 kilometers of the Pacific Ocean floor, and lying between $154^{\circ}40'W$, $18^{\circ}54'N$ and $171^{\circ}75'W$, $28^{\circ}15'N$ is the Hawaiian Archipelago. The islands in the north-west are small but there are eight major islands in the south-eastern most 640 kilometers of the chain. (Figure 1-1). These islands represent the tops of large volcanic mountains rising from the sea floor which is approximately 4500 meters below sea level. Their maximum height above sea level ranges from 385 meters for Paniau on the island of Niihau to 4200 meters for Mauna Kea on Hawaii (Table 1-1). The smallest of the south-eastern islands, Kahoolawe, covers 125 square kilometers whereas the largest, Hawaii, covers 11,194 square kilometers. Along with these distinctive geographical and topographic features are climatic extremes. The northeastern sides of the mountains tend to be wet and florally lush as a result of the moisture laden trade winds approaching from this direction. The leeward sides of the islands are usually arid to semiarid due to the trade winds having lost all their moisture on the windward side of the mountains (Stearns, 1966; Macdonald and Abbott, 1970).

Volcanic rocks from these islands have provided more information on the genesis of basaltic magmas than any other single petrologic province in the world. One of the reasons for this (aside from climatic ones) is the simplicity of the geological setting. The nearest continental rocks, over 3000 kilometers away, eliminate problems of contamination from sialic crust, and furthermore, the islands are located in the middle of a plate, away from

SOUTHEASTERN HAWAIIAN ISLANDS

Figure I-1. A map of the Southeastern Hawaiian Islands. Bathymetric contours are in meters below sea level.

Table 1-1 Geographical Data on the Southeastern Hawaiian Islands.

<u>Island</u>		<u>Area in Square</u>		<u>Altitude in meters</u>
		<u>Kilometers</u>	<u>Mountains</u>	<u>above sea level</u>
Hawaii	SE	10,154	Kilauea	1,247
			Mauna Loa	4,169
			Mauna Kea	4,205
			Hualalai	2,521
			Kohala	1,670
Maui		1,834	Haleakala	3,055
			Puu Kukui	1,764
Kahoolawe		113	Lua Makika	450
Lanai		355	Lanaikale	1,027
Malakai		655	Kamakou	1,515
			Puu Nana	421
Oahu		1,522	Puu Konahuanui	960
			Kaala	1,227
Kauai		1,398	Kawaikini	1,598
Niihau	NW	181	Paniau	390

spreading centers. Despite this geographic simplicity, the chemical complexity and variability of the lavas has been the basis for a great deal of debate.

Scope of Study

The major element oxides and the concentrations of La, Ce, Nd, Fm, Eu, Tb, Yb, Lu, Hf, Pb, Th, Zr, Nb, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, and Ba in 23 lavas from the islands of Hawaii, Maui, and Kauai in the Hawaiian Archipelago are reported and examined in this study. The modal and normative mineralogy of these samples are examined, and used to classify and name each of the rocks. The concentrations of all the elements are placed in perspective by reviewing the concentration data, published in the literature, from other oceanic island lavas as well as ocean floor basalts.

The primary objective of the thesis is to determine if there are any differences in the chemical composition of lavas among the islands in the Hawaiian Chain which can only be related to large scale mantle heterogeneity. Since the major element composition of a lava is relatively insensitive to the bulk composition of the source from which it is derived, it cannot be used to examine the mantle for heterogeneity. Trace elements behave in a different manner from the major elements. The concentration of a particular trace element in a lava reflects the concentration of that element in the mantle but is also sensitive to the percentage of the mantle which was melted to produce the lava. Methods are developed which account for the percentage of melting each lava

represents and make it possible to relate the concentrations of trace elements in the lavas to their concentrations in the mantle. The estimated mantle trace element concentrations are interpreted in terms of models for mantle evolution.

Previous Work

Mantle heterogeneity has been proposed by several authors (e.g. O'Nions and Pankhurst, 1974) to explain variations in trace element ratios and abundances as well as isotopic ratios in basaltic lavas. Such variations are picked up among oceanic islands, usually quite separate geographically, one from another (e.g. Azores and Canaries). There has not been, however, a lot of work done to determine the range of isotope and trace element variation within one island chain and the Hawaiian Islands represent an excellent locality for such a study.

There are some important geological features of the Hawaiian Islands that require explanation in any model proposed for the evolution of the lavas. Each island, for example, shows a distinct sequence of lavas which show a marked change in chemical character with time (Stearns, 1966). The first step in the sequence involves a voluminous outpouring of tholeiitic basalt to form a huge shield volcano. An excellent example is Mauna Loa which represents $40,000 \text{ km}^3$ of basaltic lava (Carmichael et al., 1974). The shield lavas on Kauai, Oahu, West Maui and Mauna Loa and Kilauea on Hawaii are quartz normative tholeiites. Other shields such as Mauna Kea, Hualalai, and Haleakala are built mostly of olivine tholeiites which mineralogically resemble alkali basalts. These

lavas can contain xenoliths which are usually gabbroic in mineralogy and show cumulate textures. The shield building stage usually accounts for greater than 99 percent of all volcanism.

The shield building stage of volcanism is followed by a stage of declining activity in which periods of as much as 200,000 years may separate one volcanic event from another. The dominant lavas associated with this stage are mugearites and hawaiites; however, alkali basalts are also quite common (Macdonald, 1963). These lavas tend to be intercalated with tholeiitic flows on some volcanos. Trachytes, though rare, are also produced during this stage of volcanism on some volcanoes (e.g. Pau Kukuni on West Maui). Lavas from this stage tend to be more viscous than the earlier shield lavas and the resulting eruptions are often more explosive. Xenoliths are much more common in these rocks than in tholeiites but, like those from the tholeiites, they generally have cumulate textures.

The stage of declining activity is followed by a period of erosion and inactivity which lasts one to two million years (Carmichael et al., 1974; Stearns, 1966). In some islands, this period is followed by a stage of renewed activity which is characterized by strongly undersaturated alkali basalts and nephelinites. Lherzolite, or its mineral constituents can often be found in these lavas. They differ from the nodules in earlier lavas because they are strongly deformed. They are believed to be of mantle origin, unlike the cumulate origin proposed for the earlier stage nodules. Lavas from this rejuvenated stage occur on Kauai, Niihau, Oahu and Western Maui, and might be expected to occur on Hawaii at some time in the future.

There have been numerous schools of thought as to how and why the chemical characteristics of the lavas change through time. Macdonald (1949) first proposed that alkali basalt magma was generated from tholeiitic basalt by fractional crystallization. This hypothesis is supported by the higher melt temperatures of the tholeiites, the complete chemical gradation between the two types, and the fact that the alkali basalts always occur later than the tholeiites, supposedly due to the time required for differentiation. This hypothesis is not, however, supported by melting experiments. Yoder and Tilley (1962) and O'Hara (1968) have found that a model where high-pressure fractionation of a basalt, formed by partial melting in the mantle, gives rise to alkali olivine basalt, and lower pressure fractionation of the same basalt gives a tholeiitic magma, was consistent with their melting experiments. The hypothesis calls for various proportions of garnet and clinopyroxene precipitation to produce both rock types, but with the alkali basalt requiring more fractionation at higher pressure. This process also explains all of the previous observations.

Green and Ringwood (1967) showed that melting experiment results are consistent with a model where high pressure partial melting of the mantle produces alkali basalts, and lower pressure melting produces tholeiitic magmas. Gast (1968) found that trace element distributions in alkali basalts and tholeiites suggest that the former are produced by lower percentages of melting than the latter. Kay and Gast (1973) integrated the above two proposals on the basis of further trace element work. They suggested the copious

outpouring of basaltic lava increases the thickness of the lithosphere, which results in an increase in lithospheric pressure and a decrease in the percentage of melting in the mantle, thus explaining the later production of alkalic lavas.

A period of at least three million years is required to build a volcano, such as Mauna Loa, from the sea floor to the present size (Macdonald and Abbott, 1970). There is an amazing correlation between the geographic location of each island and when major volcanism ceased. On Kauai, major volcanic activity ceased 3.8 to 3.9 million years ago. Volcanism ended 2.2 to 2.5 million years ago on Oahu, which lies to the southeast of Kauai (See Figure 1-1). Volcanism ended on Maui 0.4 to 0.8 million years ago, and regular volcanic activity is still evident on the island of Hawaii (McDougall, 1964). These observations are consistent with the observations made by Dana (1849) that the more northwesterly islands are deeply eroded and hence, older than those islands to the southeast showing less erosion.

Several models have been proposed to explain the variation of ages along the Hawaiian Chain. A fixed "hot spot" in the mantle was originally envisaged by Wilson (1963). According to this model, lavas are generated in a stationary spot in the mantle. As the overlying lithospheric plate moves northwestward from the East Pacific Rise, it moves over the "hot spot" causing the zone of volcanism to migrate southeastward. Morgan (1971) elaborated on Wilson's hypothesis and suggested that the site of the volcanism overlies a place where the mantle is rising in a cylindrical

"plume". Lavas form in the "hot mantle plume" and are injected through the lithosphere which is moving northwestward. Since new mantle material is always rising above the plume, this theory suggests that the lavas have been generated from different portions of the mantle.

In trying to add some geophysical respectability to the mantle plume hypothesis, Parmentier et al. (1975) proposed that only the upper mantle is involved in the convection. Morgan (1971), on the other hand, suggested that the whole mantle was affected.

Shaw and Jackson (1973) proposed lava production is part of a cyclical process occurring in the mantle. After a lava is injected through the lithosphere the fluid-depleted mantle becomes coupled with the moving lithosphere. The dense residuum from melting sinks creating a "gravitational anchor", and new asthenosphere flows in to replace that volume lost as a result of producing the melt and from the sinking of residuum. The shear stresses from coupling produce renewed melting, and volcanism, and the cycle begins all over again.

Turcotte and Oxburgh (1973) argued that the Hawaiian Islands are produced by magma rising in cracks formed in the lithospheric plate. The cracks are supposedly extensional phenomena induced by cooling of the plate after production of an ocean ridge, or by movement of the lithosphere from an area of one sphericity to another.

Most of these hypotheses, with the exception of Wilson's (1963), proposed that the lavas erupted on each of the islands are

derived from different portions of the mantle. If this is correct, differences in the chemical composition of lavas on different islands might be expected to reflect the nature and composition of the underlying mantle. A heterogeneous mantle source for Hawaiian lavas was first proposed by Powell et al. (1965) and elaborated on by Powell and Delong (1966). Their observations were based on strontium isotopic studies.

To test the hypothesis that a heterogeneous mantle has produced lavas which are chemically distinct from one island in the archipelago to another, it is necessary to develop means of relating the chemical composition of a lava to its mantle source. The major elements cannot be used to do this, mainly because their concentration in a melt is fairly constant, as a result of the relatively small percentages of melting represented by basaltic rocks. As long as the phases present in the mantle are the same, and pressure is the same, a wide range of starting compositions will produce melts with identical initial starting compositions because melting begins at a common eutectic. Even though differences in the percentage of melting may produce some changes in the melt composition, significant differences in the starting material composition will still produce melts of similar major element composition (given equal percentages of melting), because the melt will, in most cases, never get away from a reaction or subtraction curve. This reasoning is substantiated by the relatively restricted major element composition of basaltic rocks (Yoder, 1976). To further complicate the problem, many of the changes in major element composition appear to be intimately related, not to the composition

of the starting material, but to the pressure of origin (O'Hara, 1968). A change in pressure can change the stable phase assemblages, and produce shifts in the eutectic starting composition.

The behaviour of minor elements is entirely different from that of the major elements. The concentration in a lava is controlled by the concentration of the element in the mantle, the percentage of melting, and a concentration ratio between mineral phases and melt which is dependent on the proportions and percentages of minerals present in the mantle (Gast, 1968). A cursory review of trace element concentrations in basaltic magmas shows that many elements vary in concentration by several orders of magnitude. This means that they are very sensitive to mantle melting processes and, as shown by Gast (1968), they can be modelled to obtain some insight into mantle processes. As a result of this modelling, mantle concentrations of some trace elements can be obtained.

Sample Information

Samples for this study were collected by Dr. Keith Bell during a visit to see the Hawaiian Islands in December, 1976. Samples were collected from Kauai, Maui and Hawaii, three islands in the southeastern portion of the archipelago (Figure 1-1). Sampling was done on a geographically random basis; however, some attempt was made to get a broad distribution of rock types. Accurate written descriptions of the sampling locations are given in Appendix I, and shown in Figures 1-2 to 1-4.

Seven samples (HW100, HW102, HW104, HW106, HW107 and HW109) are from the island of Kauai (Figure 1-2). Two samples, HW106 and HW107, are from the Waimea Canyon Series. Lavas from this series

Figure I-2. Map of Kauai showing sampling locations (x) as well as roads and towns referred to in Appendix I.

make up the bulk of the shield; all were produced before a period of inactivity, and are typically tholeiitic basalts and olivine tholeiites (Macdonald and Abbott, 1970). Five samples, (HW100, HW102, HW103, HW104 and HW109) are from the Koloa Series volcanics. Lavas from this series follow the stage of inactivity and thus overly an erosional unconformity. They are typically highly under-saturated basalts and nephelinites.

Five samples (HW115, HW116, HW117, HW118 and HW119) are from the island of Maui (Figure 1-3). Samples HW115 and HW116 are from Western Maui and belong to the Wailuku and Honolua Volcanic Series respectively. Wailuku volcanics are the oldest lavas on the island, and built the major shield volcano. These lavas consist predominantly of thin flows of tholeiitic and olivine tholeiitic basalt, but grade into alkali olivine basalt at the top of the series. Honolua volcanics form a thin discontinuous cap over Wailuku lavas and are made up of hawaiite, mugearite, and trachytic flows, domes and pyroclastic material. They were produced during the stage of declining volcanic activity (Macdonald and Abbott, 1970).

The remaining three samples (HW117, HW118 and HW119) come from Haleakala on East Maui. The Honomanu Series volcanics, which built the Haleakala shield, are nearly entirely buried by a thin veneer of Kula Volcanic Series lavas which are still being produced. The samples are from the Kula Series which is predominantly made up of alkali basalts and hawaiites.

Samples HW124, HW125 and HW126 come from Kohola mountain on the island of Hawaii (Figure 1-4). The first two samples

Figure I-3. Map of Maui showing sampling locations (x) and place names referred to in Appendix I.

were collected from the Pololu Series which is predominately tholeiitic and olivine tholeiitic basalts and makes up the oldest lavas on Kohala volcano. Sample HW126 belongs to the Hawi Volcanic Series which is predominantly made up of mugearite and overlies the Pololu Series Volcanics (Macdonald and Abbott, 1970).

Two samples HW127 and HW128 come from the Hamakua Volcanic Series on Mauna Kea Volcano (Figure 1-4). These lavas represent the early shield building stage of Mauna Kea activity which is made up predominately of tholeiitic and olivine tholeiitic basalts (Macdonald and Abbott, 1970). Sample HW133 is from the 1801 flow of Hualalai Volcano on the island of Hawaii (Figure 1-4). Most of the lavas from this volcano are alkali olivine basalts with a few flows of hawaiite composition.

The remaining samples (HW122, HW123, HW129, HW130 and HW131) come from Mauna Loa Volcano. Lavas from this active volcano are tholeiitic and olivine tholeiitic basalts.

Figure I-4. Map of Hawaii showing sampling locations (x) as well as roads and towns referred to in Appendix I.

Chapter Two Modal and Normative Mineralogy

The modal and normative mineralogy of samples from the Hawaiian Island rock suite are examined and compared in detail. The mineralogy, and an alkali silica plot, are used to place all lavas into either the alkalic, or tholeiitic basalt suites. As well, all samples are assigned a specific name on the basis of the normative and modal mineralogy.

Modal Mineralogy

All samples in the rock suite from the Hawaiian Islands may be divided into either the alkalic or tholeiitic categories on the basis of modal mineralogy. The following is a summary, from the literature, of the salient features of such a classification.

Tholeiitic basalts are characterized by the following criteria obtained from the literature (Tilley, 1950; Kuno, 1960; Macdonald and Katsura, 1964 and Hyndman, 1972):

1. Tholeiitic basalts generally have unzoned olivines, sometimes resorbed and mantled by orthopyroxene.
2. Pigeonite, or low-Ca clinopyroxene, occurs in the groundmass and orthopyroxene, commonly hypersthene, may occur as phenocrysts.
3. Plagioclase phenocrysts generally vary in composition from anorthite to bytownite; the groundmass plagioclase is usually bytownite to labradorite in composition.
4. Quartz can be present.
5. Peridotite or eclogite inclusions never occur in tholeiites.

Alkali basalts are characterized by the following criteria obtained from the literature (Tilley, 1950, Wilkinson, 1956, Macdonald and Katsura, 1964 and Hyndman, 1972):

1. Olivines are often zoned.
2. Clinopyroxene, usually titaniferous augite, is the only pyroxene.
3. Nepheline can be present.
4. Interstitial alkali feldspar is usually present.
5. Plagioclase composition ranges from labradorite to andesine in the phenocrysts, to andesine in the groundmass.
6. Quartz never occurs in these rocks.
7. Inclusions of peridotite or eclogite are not uncommon.

Using the criteria outlined above, the basalts were divided into either the tholeiitic or alkalic suite. Samples HW102, HW103 and HW109 are easily identified as alkalic basalts because all contain nepheline. Nepheline makes up about thirty percent of the total mineral abundance in HW109 and plagioclase is absent. This sample is a nephelinite. Samples HW102 and HW103 contain plagioclase but sample HW102 contains only about 2 percent. The presence of orthopyroxene (hypersthene) in HW107 positively identifies it as belonging to the tholeiitic suite.

The remainder of the samples from the Hawaiian Islands were more difficult to classify. Almost all have modal olivine which ranges in composition from Fe_{69} to Fe_{88} . Clinopyroxene is always present and when occurring in phenocryst form is augitic in composition. The fine-grained nature of the matrix made

it difficult to separate high and low Ca varieties of clinopyroxene by petrographic techniques. Plagioclase occurs in all of the samples (except HW109) and ranges in composition from An_{38} to An_{86} . These were very helpful in classifying the samples but unfortunately do not yield conclusive results.

The more obvious differences among the samples involved grain size variation and the modal mineral percentages. Matrix clinopyroxene, for example, varies from about 0.01 mm to 0.15 mm in size and makes up from 12 to 43 percent of the rock. Unfortunately, these characteristics are not helpful in classifying the samples.

Samples HW116, HW119, HW124, HW125, HW126 and HW128 do, however, have similar modal mineralogical characteristics. All have greater than 50 percent plagioclase (An_{50}). Clinopyroxene constitutes less than 25 percent of each sample, and all are generally rich in opaques. Hornblende occurs in sample HW119. Texturally these rocks are distinct, in that nearly all are pilotaxitic. Both the mineralogical and textural features suggest that these rocks may have undergone greater degrees of fractional crystallization than any of the other samples investigated. The high percentages of plagioclase and opaques, the presence of hornblende and pilotaxitic texture are typical features of differentiated lavas, particularly alkalic ones, (Macdonald and Katsura, 1964; Carmichael et al., 1974).

Normative Mineralogy

The normative mineralogy, differentiation index, and color index of each sample are given in Table 2-1. In addition, each sample has been given a name according to the scheme of Irvine and Baragar (1971).

The tholeiitic or alkalic nature of each sample is determined by plotting the normative composition of each sample on the Ne, Qtz, Ol face of the Yoder and Tilley (1962) basalt tetrahedron. The exact position of the dividing line which separates the samples into two groups was determined statistically using samples of known character (Irvine and Baragar, 1971). This dividing line is not exactly coincident with the olivine-plagioclase join, the "critical plane of undersaturation" in the Yoder and Tilley (1962) basalt tetrahedron. The rock name given each sample was then assigned using the color index and normative composition of the plagioclase feldspars after Irvine and Baragar (1971).

From the information given in Table 2-1, only one sample, HW109, is a nephelinite. This sample is characterized by having the highest percentage of normative Ne and the only sample with normative Lc and Ln. Two other samples from Kauai, HW102, and HW103, have modal nepheline but they also have modal plagioclase. Using Irvine and Baragar's classification these samples are called alkali basalts which is consistent with the modal mineralogy.

Two samples, HW124, and HW126 have En and Fs in the norm yet they are still considered alkalic in character. This is not uncommon, and reflects the fact that the equilibrium thermal divide is not precisely defined by the olivine-plagioclase-clinopyroxene plane (Irvine and Baragar, 1971). Normative nepheline

Table 2-1. Normative Mineralogy

Sample	Q	OR	AB	AN	LC	NE	DJ	HE	EN	FS	FO	FA	LN	MT	IL	AP	Diff. Index	Color Index	Name
HW100	0	1.74	16.49	20.74	0	0.51	23.96	5.98	0	0	12.17	3.84	0	7.10	6.31	1.70	18.74	59.35	Ankaramite (Alkaline)
HW102	0	3.48	7.55	13.97	0	11.11	26.28	6.90	0	0	14.29	4.74	0	5.83	4.69	1.15	22.15	62.74	Alkali Basalt
HW103	0	6.58	4.68	14.63	0	13.56	27.38	8.58	0	0	12.28	4.86	0	4.97	4.48	0.99	21.82	62.55	Alkali Basalt
HW104	0	6.08	10.90	19.04	0	4.22	25.20	5.71	0	0	13.55	3.89	0	5.88	4.78	0.78	21.20	59.03	Ankaramite (Alkaline)
HW106	0	2.18	16.35	21.49	0	0	15.37	3.55	22.49	5.96	2.02	0.59	0	5.35	4.22	0.43	18.53	59.55	Tholeiitic Basalt
HW107	0	0.37	13.43	23.54	0	0	10.98	2.48	23.37	6.07	7.98	2.28	0	5.22	3.90	0.38	13.79	62.28	Tholeiitic Basalt
HW109	0	0	0	8.30	5.38	17.71	31.76	7.26	0	0	11.83	3.42	0.82	6.42	5.48	1.62	23.09	66.17	Nephelinite
HW115	0	1.44	12.74	17.04	0	0	16.37	4.05	10.15	2.88	21.09	6.60	0	3.87	3.38	0.38	14.19	68.39	Tholeiitic Basalt
HW116	0	17.24	57.18	8.49	0	1.87	1.21	1.64	0	0	2.17	3.69	0	2.91	2.25	1.36	76.29	13.86	Benmorite (Alkaline)
HW117	0	5.53	7.72	18.96	0	7.79	21.74	8.99	0	0	12.55	6.56	0	3.80	5.67	0.68	21.04	59.32	Alkali Basalt
HW118	0	4.44	8.69	16.05	0	5.62	27.84	7.16	0	0	14.74	4.79	0	5.61	4.42	0.64	18.75	64.56	Alkali Basalt
HW119	0	16.04	31.63	8.91	0	14.36	7.28	7.80	0	0	2.78	3.76	0	3.03	3.16	1.28	62.02	27.80	Mugearite (Alkaline)

Table 2 -1 (Continued)

Sample	Q	OR	AB	AN	LC	NE	DI	HE	EN	FS	FO	FA	LN	MT	IL	AP	Diff. Index	Color Index	Name
HW122	0	2.41	16.97	22.63	0	0	15.34	6.82	16.20	8.26	3.17	1.78	0	1.68	4.35	0.40	19.38	57.59	Tholeiitic Basalt
HW123	3.43	2.07	21.93	24.06	0	0	15.28	6.30	12.45	5.89	0	0	0	4.16	3.93	0.49	27.43	48.02	Tholeiitic Basalt
HW124	0	4.92	24.96	25.91	0	0	14.89	7.84	0.70	0.42	5.57	3.71	0	4.17	5.97	0.94	29.88	43.28	Alkalic Basalt
HW125	2.77	6.12	27.74	25.16	0	0	11.84	3.48	6.39	2.16	0	0	0	6.92	6.17	1.25	36.64	36.96	Tholeiitic Basalt
HW126	0	8.66	24.40	20.56	0	0	12.94	4.49	3.12	1.24	4.98	2.18	0	6.23	5.27	0.94	38.06	40.44	Hawaiite (Alkalic)
HW127	0	3.92	27.79	22.11	0	0	21.41	6.33	3.23	1.10	10.77	4.02	0	4.52	4.64	0.57	21.31	56.01	Tholeiitic Basalt
HW128	0	11.56	39.44	18.20	0	1.64	6.09	2.70	0	0	4.54	2.55	0	5.83	5.38	2.08	52.64	27.09	Hawaiite (Alkalic)
HW129	5.07	2.16	19.48	25.57	0	0	14.03	6.27	12.54	6.42	0	0	0	4.23	3.81	0.47	26.67	47.28	Tholeiitic Basalt
HW130	0	1.32	13.66	17.17	0	0	13.88	3.64	21.04	6.34	12.39	4.11	0	3.09	3.05	0.31	14.98	67.55	Tholeiitic Basalt
HW131	5.43	2.42	19.66	25.20	0	0	13.86	7.44	11.34	6.98	0	0	0	2.92	4.22	0.52	27.51	46.76	Tholeiitic Basalt
HW133	0	6.10	24.74	23.66	0	0.59	12.94	5.74	0	0	9.97	5.58	0	5.61	4.44	0.62	31.44	44.28	Alkalic Basalt

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occurs in eleven of the samples and illustrates their alkalic nature. All four samples with normative quartz are considered tholeiitic. On the basis of the normative mineralogy ten of the samples are tholeiitic and thirteen are alkalic (Table 2-1).

Two parameters useful in summarizing the normative mineralogical aspects of the Hawaiian suite of rocks are the Thornton and Tuttle (1960) differentiation index, and the normative color index (Irvine and Baragar, 1971). The former is the sum of normative quartz, orthoclase, albite, nepheline, kalsilite, and leucite. The latter is the sum of normative olivine, orthopyroxene, magnetite, ilmenite, and hematite.

Sample HW115 has the lowest differentiation index (14.19) and highest color index (68.39) of all the samples. According to Irvine and Baragar this rock would be a tholeiitic picrite (Table 2-1). This name is essentially consistent with the mode. Samples HW100 and HW104 are considered ankaramites (Table 2-1), rocks similar to picrites but with lower abundances of the mafic minerals.

Samples with high differentiation indices and low color indices correspond to those samples considered "more differentiated" on the basis of the modal mineralogy. These samples (HW116, HW119, HW124, HW125, HW126, and HW128) have a color index less than 50 and a differentiation index greater than 30. Samples HW124 and HW125 are still thought to be "basalts" (Irvine and Baragar, 1971) but the remainder represent highly differentiated rock types that fall outside the basalt field.

Samples HW126 and HW128 are considered hawaiites, rocks with moderate to high color index as well as normative and modal feldspar of andesine composition. Usually the soda:potash ratio is greater than 2:0, (Macdonald and Katsura, 1964). On the basis of the norm, sample HW119 is a mugearite, a rock with oligoclase plagioclase composition. The modal plagioclase composition is somewhat low (An_{49}) to classify this rock as a mugearite, but given the uncertainties in the petrographic determination of plagioclase composition, the name can be considered consistent with the mode. Sample HW116 is a benmorite on the basis of the normative mineralogy. A benmorite is a rock with sanidine or anorthoclase as a dominant feldspar (Carmichael et al., 1974). The modal mineralogy does not agree with this name because the dominant feldspar is a sodic plagioclase feldspar. The important fact remains; this sample is highly differentiated.

Alkali vs. Silica Plot

Perhaps the simplest method of distinguishing alkalic from tholeiitic basalts was given by Macdonald and Katsura (1964). In this plot, $Na_2O + K_2O$ is plotted against SiO_2 content and a line divides the samples into the two groups. The position of this line has been determined statistically using samples of known chemical character (Figure 2-1). Those samples plotting above the line are considered alkalic and those below are considered tholeiitic.

This plot not only separates the samples into two groups but also illustrates their broad range of chemical compositions and illustrates the approximately even split between alkalic and

Figure 2-1. Alkali-silica diagram. Points above the line are alkalic, and those below are tholeiitic.

tholeiitic rock types (Figure 2-1). Samples HW116, HW119, and HW128 are not shown in Figure 2-1 because of their high total alkali enrichment (6.8 - 10.0 percent). Their SiO_2 contents range from 50 to 58 percent. On the basis of such SiO_2 and total alkalis content, these samples are considered alkalic in nature.

Discussion

The three methods for determining the alkalic versus tholeiitic nature of the rock samples for the most part agree very well. The Irvine and Baragar (1971) normative Ne, Qtz, and OL plot agrees with the alkali-silica plot in all cases except sample HW124. Since the modal mineralogy supports the division based on the Irvine and Baragar (1971) plot, the rock is assumed to be tholeiitic in character. A comparison of the rock names in Table 2-1 with those based on the modal mineralogy in Appendix I shows the very good agreement between the two.

Chapter Three Analytical Data

Introduction

It was noted in the previous chapter that the volcanic suite from the Hawaiian Islands contains a wide range of rock types.

This point is re-emphasized by comparing both major and minor element compositions of the samples. Several other workers (eg. O'Nions and Pankhurst, 1974, and Macdonald and Katsura, 1964) have shown that volcanic rocks from the Hawaiian Islands and other oceanic islands are extremely variable. No one, as yet, had compared the major and minor elements from one island to another within the Hawaiian Chain.

Analytical Information

The major element oxides and important trace element compositions of each sample are given in Tables 3-1 to 3-3. The major elements as well as Nb, Zr, Pb, Ga, Zn, Ni, Cu, Ba, V, and Cr (Tables 3-1 and 3-2) were determined by X-ray fluorescence at the Department of Geology, Memorial University, Newfoundland. Rb and Sr (Table 3-2) were determined by X-ray fluorescence at Carleton University, Ottawa. Hf, Sc, Co, and Th (Table 3-2) as well as La, Ce, Nd, Sm, Tb, Yb, and Lu (Table 3-3) were determined by instrumental neutron activation analysis at the University of Toronto. Further details on analytical procedures as well as precision are given in Appendix II.

Table 3-1. Major Element Composition of Samples.

Sample	Conc. of Element/oxide in sample												Total
	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	
HW100	42.05	3.16	10.76	7.67	6.14	0.16	10.88	11.80	1.96	0.28	0.48	3.76	99.07
HW102	42.20	2.79	10.85	5.10	8.10	0.18	12.66	11.45	3.21	0.57	0.48	1.89	99.08
HW103	43.40	2.31	11.04	9.22	3.36	0.16	11.89	12.29	2.80	1.09	0.42	1.32	99.30
HW104	43.91	2.45	11.41	7.89	4.18	0.16	12.13	11.75	2.15	1.00	0.31	1.23	98.58
HW106	48.30	2.17	11.20	8.01	3.61	0.15	12.76	9.15	1.89	0.36	0.18	0.58	98.36
HW107	46.35	1.99	10.97	7.98	4.25	0.16	15.53	8.12	1.54	0.06	0.16	1.72	98.83
HW109	40.41	2.81	10.37	4.68	8.76	0.17	12.35	12.64	3.76	1.13	0.68	0.98	98.74
HW115	45.63	1.75	8.83	9.86	2.62	0.16	18.87	8.65	1.48	0.24	0.16	0.41	98.66
HW116	57.71	1.17	17.84	4.77	1.98	0.21	1.45	3.13	7.08	2.88	0.58	0.44	99.24
HW117	43.38	2.94	12.06	10.74	2.53	0.18	11.06	11.68	2.57	0.92	0.29	0.59	98.99
HW118	43.53	2.26	10.11	8.58	4.07	0.16	13.25	12.08	2.19	0.73	0.27	0.77	98.00
HW119	51.17	1.63	17.17	6.99	2.05	0.21	2.89	6.05	6.74	2.66	0.54	0.57	98.67

Table 3-1 (Continued)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
HW122	49.26	2.25	11.82	9.97	1.14	0.15	10.98	10.12	1.97	0.40	0.17	0.20	98.43
HW123	51.87	2.07	13.45	8.03	2.87	0.15	7.84	10.50	2.59	0.35	0.21	0.30	100.23
HW124	47.03	3.10	15.04	8.97	2.84	0.14	6.16	11.23	2.91	0.82	0.40	0.49	99.13
HW125	49.00	3.20	15.50	6.10	5.70	0.14	4.70	9.49	3.23	1.02	0.53	0.0	98.61
HW126	48.47	2.73	14.60	7.43	4.49	0.15	6.41	8.90	3.42	1.44	0.40	0.33	98.73
HW127	46.04	2.38	11.90	8.49	3.04	0.15	11.17	11.46	2.05	0.58	.24	0.42	98.28
HW128	49.64	2.78	16.74	6.63	3.95	0.18	3.67	6.91	4.93	1.92	0.88	0.52	98.76
HW129	51.48	1.98	13.38	8.16	2.88	0.16	7.55	10.34	2.27	0.36	0.20	0.38	99.14
HW130	48.37	1.58	9.05	9.50	2.10	0.16	17.86	7.93	1.59	0.22	0.13	0.39	99.48
HW131	51.44	2.17	13.19	8.51	1.97	0.14	6.97	10.40	2.27	0.40	0.22	0.45	98.13
HW133	46.30	2.29	14.50	8.37	4.36	0.16	7.95	9.56	2.99	1.01	0.26	0.30	98.25

Table 3-2. Minor Elements in Hawaiian Lavas.

Sample	Rb	Sr	Ba	Sc	Ti	Zr	Hf	V	Nb	Cr	Co	Ni	Cu	Zn	Ga	Pb	Th
HM100	7	675	690	24	18900	189	4.5	362	38	432	107	347	93	114	24	1	4.0
HM102	8	700	503	23	14300	174	3.6	341	35	577	126	485	97	114	23	6	4.0
HM103	23	601	496	23	13800	144	3.4	302	27	423	119	298	97	101	23	2	3.6
HM104	21	542	1473	25	14700	164	3.4	267	33	322	123	303	102	106	26	2	3.1
HM106	5	259	86	26	13000	129	3.4	272	11	520	98	470	109	102	20	6	0.9
HM107	1	232	76	25	11900	119	2.8	270	10	631	93	759	108	109	24	N.D.	0.6
HM109	23	951	777	21	16800	210	4.8	316	47	315	91	316	97	116	22	N.D.	5.9
HM115	3	268	75	25	10500	119	2.7	227	8	850	144	807	107	102	17	N.D.	0.4
HM116	77	1605	734	4	7010	635	17.4	27	62	3	25	3	28	119	26	N.D.	6.1
HM117	21	510	428	28	17600	169	3.8	364	26	386	157	271	118	113	27	10	2.1
HM118	17	437	411	32	13500	156	3.4	302	21	564	106	304	78	92	26	N.D.	1.8
HM119	63	816	1034	5	9770	360	18.2	89	61	64	59	42	34	124	28	8	8.2

Table 3-2 (Continued)

Sample	Rb	Sr	Ba	Sc	Ti	Zr	Hf	V	Nb	Cr	Co	Ni	Cu	Zn	Ga	Pb	Th
HW122	6	270	122	29	13500	145	3.6	290	11	497	105	297	126	99	22	N.D.	1.0
HW123	6	296	96	29	12400	131	3.2	274	9	230	82	123	130	96	23	N.D.	0.6
HW124	14	578	270	29	18600	222	5.5	313	17	131	63	77	97	100	27	2	1.7
HW125	12	537	355	22	19200	285	6.9	304	23	116	77	65	70	97	26	N.D.	1.9
HW126	27	530	374	24	16400	327	8.0	294	30	160	77	126	77	113	28	N.D.	2.6
HW127	11	448	199	32	14300	169	3.9	281	16	464	102	301	89	95	21	N.D.	1.3
HW128	35	1221	612	10	16700	409	10.7	146	44	5	43	4	28	112	28	6	3.9
HW129	6	304	102	29	11900	130	3.3	279	11	283	91	128	133	102	26	N.D.	0.9
HW130	5	225	59	23	9470	102	2.3	236	11	674	123	857	110	98	20	N.D.	0.6
HW131	8	336	110	24	13000	145	2.9	285	9	225	56	113	134	104	24	N.D.	0.5
HW133	27	535	338	20	13700	109	3.1	333	24	236	92	152	96	95	25	3	1.7

Table 3-3. Rare Earth Element Concentrations (PPM) in Hawaiian Lavas.

Sample	La	Ce	Nd	Sm	Eu	Lb	Yb	Lu
HW100	34	85	21	7.5	2.58	0.93	1.3	0.21
HW102	33	77	19	7.1	2.19	0.96	1.5	0.17
HW103	31	63	19	6.1	2.09	0.87	1.4	0.21
KAUAI HW104	21	50	22	5.1	1.92	0.73	1.5	0.15
KAUAI HW106	9	24	10	4.4	1.66	0.67	1.3	0.22
KAUAI HW107	10	23	15	4.2	1.49	0.65	1.6	0.23
KAUAI HW109	47	109	26	9.5	3.20	1.02	1.1	0.19
HW115	8	23	12	3.8	1.40	0.68	1.4	0.20
HW116	67	184	72	15.2	4.86	1.91	4.2	0.66
MAUI HW117	23	58	17	6.0	2.08	0.80	1.5	0.24
MAUI HW118	20	47	20	5.2	1.74	0.68	1.3	0.18
MAUI HW119	64	165	37	9.7	3.20	1.24	2.7	0.40
HW122	12	34	27	5.2	1.85	0.78	2.8	0.26
HW123	9	26	13	4.7	1.69	0.82	2.1	0.32
HW124	22	62	26	7.4	2.60	0.96	2.5	0.37
HW125	32	81	32	11.0	3.14	1.30	3.0	0.42
HW126	33	91	38	9.4	3.04	1.39	3.0	0.42
HAWAII HW127	18	48	23	5.8	2.03	0.84	2.0	0.29
HAWAII HW128	54	156	67	15.3	5.07	1.83	3.9	0.53
HAWAII HW129	10	29	17	4.7	1.77	0.89	2.2	0.31
HW130	7	20	8	3.4	1.15	0.58	1.8	0.25
HW131	11	25	28	5.1	1.41	0.71	2.5	0.29
HW133	20	40	26	5.3	1.47	0.57	2.1	0.30

Table 3-3 (Continued)

Sample	La	Ce	Nd	Sm	Eu	Lb	Yb	Lu
BCR-I	27	61	18	6.5	2.03	1.07	3.5	0.54
JB-I	40	82	19	5.0	1.50	0.86	2.2	0.32
Chond- rites	0.329	0.865	0.630	0.203	0.077	0.052	0.220	0.0339

Schilling and Winchester (1969) and Kay and Gast (1973) analyzed for some elements not listed above. The chondritic concentrations of these elements are:

Gd = 0.276; Dy = 0.343;
Er = 0.225 and Tm = 0.034.

Sources for chondritic normalizing values are: Smewing and Potts (1976) and Nakamura (1974).

The Major Elements

In the broadest sense of the word, all the samples in the suite from the Hawaiian Islands may be classified as "basalts" on a mineralogical basis. Each sample has been classified as alkalic or tholeiitic on the basis of the modal and normative mineralogy. Those samples which do not fall into the basalt category under Irvine and Barager's (1971) normative classification scheme were noted as also having distinct mineralogical and textural characteristics suggesting they are "differentiated", (Chapter Two).

A ternary plot of Na_2O , K_2O , and CaO has been used successfully by a number of authors (eg. McBirney and Aoki, 1968 and Baker, 1969) to illustrate the differentiation of oceanic island lava suites (Figure 3-1a). An undifferentiated basalt would plot at about 80% CaO , and 15% Na_2O , and 5% K_2O on this diagram. In general, the lower the CaO content, the greater the likelihood a lava has been affected by differentiation. Undifferentiated samples do not all plot at exactly the same location because the percentage of partial melting in the mantle, which generated each sample in the first place, varies, and this is reflected as variation in the percentages of Na_2O , K_2O , and CaO . The CaO content decreases as the amount of differentiation increases because the minerals which precipitate from a basaltic magma, such as augite and plagioclase, remove CaO from the melt while enriching the remaining lavas in Na_2O and K_2O .

Lavas, such as trachytes, thought to be highly differentiated (eg. Macdonald and Katsura, 1964), have very low CaO .

Figure 3-1. (a) A ternary plot of Na_2O , K_2O , and CaO (wt.%) of samples in the Hawaiian suite. Tholeiites are shown as dots and alkalic lavas as triangles. Sample numbers are also shown. (b) A ternary plot of $\text{Na}_2\text{O} + \text{K}_2\text{O}$, FeO , and MgO (wt.%) with all iron shown as FeO . Symbols are the same as in the above.

contents and plot toward the $K_2O - Na_2O$ side of the ternary diagram. Benmorites (HW116) mugearites (HW119) and hawaiites (HW128 and HW126), which are progressively less differentiated, have higher percentages of CaO , and lower percentages of K_2O and Na_2O .

It is impossible to draw a line on Figure 3-Ib which clearly separates differentiated from undifferentiated samples; however, the modal and normative mineralogy suggest samples HW116, HW119, HW124, HW125, HW126, and HW128 are "differentiated". With the exception of HW124, all of these samples have lower CaO , and higher Na_2O and K_2O concentrations than the other samples in the suite, as shown in Figure 3-Ia, and this supports the mineralogical conclusions that these samples are differentiated.

Another useful plot for comparing the major element geochemistry of oceanic island volcanics is the AFM ternary plot, in which $Na_2O + K_2O$, FeO , and MgO are plotted. McBirney and Aoki (1968) and Baker (1969) found that highly differentiated lavas plot closest to the $Na_2O + K_2O$ corner of the ternary plot and undifferentiated lavas have much lower concentrations of $Na_2O + K_2O$. A suite of lavas representing highly differentiated to undifferentiated rock types defines a curved differentiation trend (Figure 3-Ib). A curved trend is produced because the early minerals precipitating from a basaltic liquid, such as olivine and augite, are very rich in Mg and their removal depletes the lava in MgO and enriches it in FeO and the alkalis. As differentiation proceeds, the Fe content of olivine and the pyroxenes increase and both Fe and Mg are depleted in the lava, while Na_2O and K_2O continue to be enriched in the remaining liquid. Phenocrysts of olivine and augite

may be concentrated in part of a lava by crystal setting or flowage differentiation (Bahatbacharji, 1967). The high MgO content of these minerals, especially in the early stages of differentiation will cause this portion of the lava to plot close to the MgO apex of the AFM diagram.

As with the Na_2O , K_2O , CaO diagram, it is difficult to draw a line on the AMF diagram which separates differentiated from undifferentiated samples. However, all samples which the modal and normative mineralogy suggest are differentiated (HW116, HW119, HW124, HW125, HW126, and HW128) have higher concentrations of $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and therefore plot farther along the differentiated trend than all the other samples. Sample HW116, a benmorite, has the highest concentration of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ which suggests it is the most differentiated sample. Mugearite (HW119) and hawaiites (HW128 and HW126) have not had as much Na_2O and K_2O enrichment as sample HW116, and so plot close to the undifferentiated samples. Sample HW115, on the basis of the normative and modal mineralogy, is a picrite; which means it has a high concentration of mafic minerals. This sample, along with sample HW130 (a basalt), plot closest to the MgO corner of the AFM suggesting they may be affected by some crystal accumulation.

Both diagrams shown in Figure 3-1 can be used to separate alkalic from tholeiitic lavas. In Figures 3-1a, tholeiites tend to define a trend line with lower K_2O content than the alkalic lavas. In the AFM diagram, Figure 3-1b, alkalic lavas define a differentiation trend which tends to have lower FeO content than the tholeiitic trend line.

The Rare Earth Elements

The concentrations of La, Ce, Nd, Sm, Eu, Tb, Yb and Lu in Hawaiian lavas are given in Table 3-3. A standard presentation of the rare earth elements is given in which the concentrations are normalized to those in chondritic meteorites, (Figures 3-2 to 3-5). The normalizing values are from Nakamura (1974) and Smewing and Potts (1976) and are average concentrations from a variety of chondritic meteorites. These average concentrations are very similar to the rare earth element concentrations in the Leedey meteorite. Table 3-3 gives the values used in normalizing both the new data from the Hawaiian Islands as well as data from Schilling and Winchester (1969) and Kay and Gast (1973).

Each of the rare earth elements falls on the X axis of the normalization plot (Figures 3-2 to 3-5), with the light rare earth elements (eg. La and Ce) closest to the Y axis and the heavy rare earth elements (eg. Yb and Lu) farthest from the Y axis. The Y axis gives the concentration of each rare earth element in a lava divided by the concentration in chondrites. A trend line is produced by joining the normalized concentrations of all the rare earth elements from a sample.

Careful evaluation of Figures 3-1 to 3-5 indicates that each of the rare earth trends can be described in terms of the slope of the line and the normalized concentration of the heavy rare earth elements. The slope of the trend line is, for most samples, controlled by the concentration of light rare earth elements as the heavy rare earth elements show limited concentration variability. Tholeiitic samples show the lowest concentrations of light rare earth

Figure 3-2. Normalized concentrations of the rare earth elements in lavas from the island of Hawaii. Dots represent tholeiites, triangles alkali basalts, and squares represent "differentiated" lavas. Samples beginning with HW are new data, all others are from Schilling and Winchester 1969.

Figure 3-3. Normalized concentrations of REE in lavas from Maui. Dots represent tholeiites, triangles alkali basalts and squares represent "differentiated" lavas. Samples beginning with HW are new data, all others are from Schilling and Winchester 1969.

Figure 3-4. Normalized concentrations of the rare earth elements in lavas from Oahu. Dots represent tholeiites, triangles represent alkali basalts, and inverted triangles are nephelinites. Samples 035, 023, and 04 are from Kay and Gast (1973). All other samples are from Schilling and Winchester (1969).

Figure 3-5. Normalized concentrations of the rare earth elements in lavas from Kauai. Dots represent tholeiites, triangles alkali basalts and inverted triangles are nephelinites. Samples beginning with HW are new data, and all others are from Kay and Gast (1973).

elements and thus produce trends which have relatively low negative slopes (Figures 3-1 to 3-4). Tholeiitic basalts grade into alkali basalts which show more light rare earth element enrichment. Alkali basalts grade into nephelinites which have the highest light rare earth element concentrations and the greatest slopes.

It is very interesting that there is very little spread in the Yb and Lu concentrations in Kauai lavas (Figure 3-4) in spite of the fact that all three rock types are represented. This illustrates the fact that the main difference between these rock types, in terms of the rare earth elements, is in the concentrations of the light rare earth elements. Lavas from Maui and Hawaii (Figures 3-1 and 3-2) also show these relationships, but of importance is the observation that Hawaii lavas have higher Yb and Lu concentrations than Maui and Kauai lavas if the "differentiated" lavas are ignored. The mean normalized concentration of Lu in Hawaii lavas is about 9 whereas it is about 6 for Maui and Kauai lavas (ignoring differentiated samples). These differences are far outside analytical uncertainties which are between 1 and 5 percent for Yb and Lu. Oahu lavas (Figure 3-3) show normalized concentrations ranging from 5 to 10 with one lava (JP16) at about 3.

Invariably the differentiated lavas shown in Figures 3-1 to 3-4 have higher concentrations of the heavy rare earth elements than the other lavas. This is particularly well shown in the samples from Maui (Figure 3-2). Despite the fact these samples are distinct in terms of their heavy rare earth element concentrations, their slopes are very similar to those of the alkali basalt samples.

Those samples which were analyzed by Schilling and Winchester (1969) and Kay and Gast (1973) were subdivided into the

four groups, tholeiites, alkali basalts, nephelinites, and differentiated lavas, using mineralogical and chemical criteria outlined in chapter two and the major element geochemistry section of this chapter. On this basis, samples JP15, JP10, 1104, 1102, and 1106 were placed into the differentiated group. Their heavy rare earth element data, shown in Figures 3-1 and 3-2, support this conclusion.

A comparison of these rare earth element trends with those in other oceanic islands and ocean ridge basalts shows some interesting similarities and differences. Lo and Gales (1976) studied the rare earth element concentrations in Tavas from Formosa, an oceanic island in the Pacific. Sun and Hanson (1975a) examined the rare earth element concentrations in alkali basalts from Ross Island. Since analyses by these workers were done by neutron activation, or mass spectrometry, accuracy of their data is comparable or better than the accuracy for the Hawaiian Islands lavas reported here (e.g. $\pm 5\%$ for La and Yb). Since La and Yb are good indicators of the relative concentrations of light and heavy rare earth element concentrations respectively, these will be used in the discussion.

The range of Yb concentrations in undifferentiated Maui and Kauai basalts is 1.1 ppm to 1.6 ppm with a mean of 1.4 ppm. The range of Yb concentrations in Hawaii lavas is 1.8 to 2.8 ppm with a mean of 2.2 ppm. There is no significant difference between the mean Yb concentrations in tholeiites, alkali basalts and nephelinites in Maui, Kauai and Hawaii lavas, as long as the lavas being compared are from the same island.

Yb concentrations range from 1.0 to 1.8 ppm with a mean of 1.4 ppm in Formosan tholeiites. These concentrations are the same as those in all Kauai and Maui basalts. The Yb concentrations

in alkali basalts from Formosa are higher than those in the tholeiites and show a range of 1.5 to 2.8 ppm with a mean of 2.0 ppm. These concentrations are very similar to the Yb concentrations in all Hawaii basalts. Yb concentrations in alkali basalts from Ross Island vary from 2.0 to 2.7 ppm with a mean of 2.3 which is comparable with the concentrations in Hawaii basalts in general.

The total range of La concentrations in Hawaiian Islands tholeiites is 7 ppm to 18 ppm and there is no noticeable concentration difference among islands. Tholeiitic basalts from Formosa have similar La concentrations, the range being 10 to 19 ppm.

Alkali basalts from the Hawaiian Islands show a range of La concentrations of 20 to 34 ppm and there is no overlap of these concentrations with those in tholeiitic basalts. The La concentrations in Formosan alkali basalts tend to be higher than in Hawaiian Islands alkali basalts and range from 30 to 54 ppm. As in the Hawaiian Islands, these concentrations do not overlap with those in tholeiitic basalts. Ross Island alkali basalts have still higher La concentrations, the range being 38 to 68 ppm.

These La and Yb concentrations illustrate that when normalized to chondrites, rare earth element trend lines have lower slopes in tholeiites than in alkali basalts. Data for the concentrations of La and Yb in oceanic islands nephelinites is restricted to the analyses reported here and by Kay and Gast (1973) and Schilling and Winchester (1969). Nephelinites always have higher concentrations of La than alkali basalts from the same island, and because the Yb concentrations are not appreciably different from those in alkali basalts, the slopes of trend lines on a normalized

rare earth element plot are always greater than alkali basalts from the same islands.

Ocean ridge tholeiites usually show fairly flat trends when their rare earth element concentrations are normalized to those of chondrites. In some cases they even show a positive slope, which is quite distinct from the negative slope shown by all the data available for oceanic island lavas. The heavy rare earth elements generally show a broad range of concentrations in ocean floor basalts which is in marked contrast to oceanic islands. For example, in basalts from the FAMOUS area, Langmuir et al. (1977) report Yb concentrations ranging from 1.48 to 3.5 ppm and all these lavas are located within 3 km of one another. In a study of Indian Ocean Floor basalts, Fleet et al. (1976) recorded Yb concentrations ranging from 1.6 to 5.1 ppm. Although there are some exceptions (eg. DSDP Leg II, Ayuso et al. 1976) ocean floor basalts generally show a broad range of heavy rare earth element concentrations. An approximate mean value for the concentration of Yb in ocean floor basalts is about 2.5 ppm. This value contrasts noticeably with oceanic island lavas in which the highest mean concentrations for any one island is 2.3 ppm (Ross Island).

Discussion of Other Trace Elements

Analytical Uncertainties

The analytical uncertainties for the data from the Hawaiian lavas are as follows:- $\pm 5\%$ for Hf, Sc and Co. The uncertainty for Th is $\pm 10\%$. Precision and accuracy for Zn, Cu, Ga, Zr and Nb is ± 6 ppm and ± 12 ppm on V, Cr, and Ni. Precision and accuracy on Ba and Pb are $\pm 14\%$ and $\pm 85\%$ respectively. All data from the literature and discussed in this section may be regarded as $\pm 50\%$ at the worst.

Scandium

Sc concentrations show very little variability in Hawaiian lavas, especially those flows which are not differentiated (Table 3-2). The highest concentration recorded is 32 ppm and this occurs in both HW118, an alkali basalt on Maui, and HW127 a tholeiite on Hawaii. Sample HW133, an alkali basalt has the lowest Sc concentration (20 ppm) in the undifferentiated lavas and sample HW116, which is differentiated, had the lowest concentration of Sc (4 ppm) in the suite of rocks. Sc concentrations are rarely documented in the literature. However, Hawaiian concentrations seem to fall between those determined by Le Maitre (1962) for Gough (10 - 20 ppm) in alkali basalts and tholeiites, and those published by McBirney and Williams (1969) for Galapagos basalts (26 - 42 ppm). Sc concentrations in ocean floor basalts determined by Engel et al. (1965) range between 30 to 56 ppm.

Titanium (TiO_2)

Sample HW117, an alkali basalt, has the highest percentage of TiO_2 (2.94%) in the undifferentiated Hawaiian lavas. Sample HW130, a tholeiitic basalt, has the lowest concentration, (1.58%). The highest concentration of TiO_2 occurs in sample HW125 (3.20%) and the lowest concentration occurs in sample HW116 (1.17%). Both of these lavas are differentiated suggesting differentiation initially enriches the lava in TiO_2 , and as new minerals begin to precipitate, it is removed.

The highest percentages of TiO_2 occurring in oceanic island tholeiites are reported by Baker (1974) for Easter Island

and range between 2.51 and 4.41 percent. Some alkali basalts from Tristan da Cunha (Baker et al., 1964), Terceira, Azores (Self and Gunn, 1976), Tenerife, Canaries, (Ridley, 1970), Uapu, Marquesas Arc in the Pacific Ocean (Bishop et al., 1973), Moheli, in the Western Indian Ocean (Strong, 1972a), Easter Island (Baker et al., 1974) and Madeira in the Atlantic Ocean (Hughes and Brown, 1972) have over 4% TiO_2 . Differentiated lavas tend to have the lowest concentrations of TiO_2 in oceanic island lavas with some lavas, such as Saint Helena, having negligible (eg. 0.04%) percentages (Baker, 1969). The ocean floor tholeiites also have very low concentrations of TiO_2 which usually average about 1.0 percent. Oceanic islands with TiO_2 concentrations in alkali basalts and tholeiitic basalts roughly similar to those from the Hawaiian Islands include Grande Comore, Comores Arc (Strong, 1972b), Anjoun, Comores Arc (Flower, 1973) Amsterdam Island (Gunn et al., 1971), the Crozet Arc (Gunn et al., 1970), Reunion (Upton and Wadsworth, 1966, 1972), Mauritius in the Indian Ocean (Baxter, 1976), Galapagos (McBirney and Williams, 1969), and Saint Helena (Baker, 1969).

Zirconium

Sample HW102, a tholeiite, has the lowest Zr concentration (102 ppm) in the Hawaiian suite. In general, tholeiites from the Hawaiian Islands have lower concentrations of Zr than alkali basalts. Sample HW109, a nephelinite has the highest Zr concentration in the undifferentiated lavas (210 ppm). Sample HW116, a differentiated lava, has the highest concentration, 635 ppm, of any sample in the suite.

By far the highest concentrations of Zr in the undifferentiated group of lavas occurs in the alkali basalts from Ua Pu (Bishop et al., 1973) and these range between 200 and 1000 ppm. Many islands have differentiated lavas with over 1000 ppm Zr, but the highest concentration of 1500 ppm is contained in a lava from Ua Pu (Bishop et al., 1973). Concentrations of Zr in tholeiitic and alkalic basalts from Galapagos (McBirney and Williams, 1969) tend to be slightly higher than those from Hawaii. Gough basalts, (LeMaitre, 1962) show similar values, and Iceland basalts (Sigvaldason, 1974) show lower values than those in Hawaiian Islands basalts. The lowest concentrations of Zr (30 - 50 ppm) occur in some ocean floor basalts (Ayuso et al., 1976).

Hafnium

The lowest concentration of Hf (2.3 ppm) in Hawaiian lavas is contained in sample HW130, a tholeiitic basalt. Alkali basalts tend to have higher concentrations of Hf than tholeiitic basalts. Sample HW109, a nephelinite, has the highest Hf concentration, 4.8 ppm, in the undifferentiated lavas. Sample HW119, a differentiated lava, has the highest Hf concentration (18.2 ppm) in the Hawaiian suite.

Very little information is available on Hf concentrations from other oceanic island lavas. McBirney and Williams, (1969) report Hf concentrations ranging from 1.4 to 4.1 ppm in tholeiites and 2.2 ppm to 3.2 ppm in alkali basalts from the Galapagos Islands. Hf concentrations in Atlantic Ocean floor basalts are quite low. Data from Ayuso et al. (1976) suggests a range from 0.9 to 1.5 ppm.

Vanadium

V concentrations in tholeiites from the Hawaiian Islands range from 236 ppm (HW130) to 285 ppm (HW131). Alkali basalts and the nephelinitic sample (HW109) have higher concentrations that range from 267 ppm in sample HW104 to 364 ppm in sample HW117. Sample HW116, a highly differentiated lava, has the lowest concentration of V (27 ppm) in the suite.

Tholeiitic lavas from the Galapagos Islands tend to have higher V concentrations (270 - 310 ppm) than the alkali basalts which range between 120 and 250 ppm (McBirney and Williams, 1969). The range of concentrations in Hawaiian Islands lavas is typical of most oceanic islands. The lowest concentrations of V in oceanic island lavas invariably occur in the more differentiated lavas with some islands such as Mauritius (Baxter, 1976) and the Galapagos Islands (McBirney and Williams, 1969) having lavas with around 5 ppm V. Ocean ridge basalts, and Iceland, have the highest concentrations of V with concentrations between 250 and 495 ppm, (Sigvaldason, 1974 and Kempe, 1976).

Niobium

Nb concentrations vary from 8 ppm (sample HW115) to 11 ppm (samples HW106, HW122, HW129, and HW130) in tholeiites, and from 21 ppm (sample HW118) to 47 ppm (sample HW109) in alkali basalts and nephelinites from the Hawaiian Islands. Sample HW116, a highly differentiated lava, has the highest Nb concentration (62 ppm) in the suite.

These Nb concentrations appear to be relatively low when they are compared with Ua Pu alkali basalts which have concentrations ranging from less than 100 (detection limit) to 150 ppm (Bishop et al., 1973). Lavas from the Galapagos Islands have Nb concentrations similar to those in Hawaiian Islands lavas. The tholeiites have concentrations between 17 and 22 ppm and concentrations in alkali basalts range between 13 and 34 ppm (McBirney and Williams, 1969). Ayuso et al. (1976) record Nb concentrations from Atlantic Ocean floor basalts of between 1 and 3 ppm.

Chromium

Sample HW115, a tholeiitic basalt, has the highest Cr concentration (850 ppm) in the Hawaiian lavas. Cr concentrations in the alkali basalts and nephelinite range between 236 and 564 ppm (samples HW133 and HW118 respectively) and tend to be lower than in the tholeiitic basalts. The differentiated lavas have lower concentrations of Cr than the undifferentiated lavas, with the lowest concentration in sample HW116 (3 ppm).

The concentrations of Cr in Hawaiian basaltic lavas are quite high and are only exceeded by concentrations of over 1000 ppm in a tholeiitic basalt from the Crozet Arc (Gunn et al., 1970) and some nephelinites and alkali basalts from the Samoan Arc (Hawkins and Natland, 1975). Ocean floor tholeiites have Cr concentrations ranging from about 100 to nearly 400 ppm (Fleet, et al., 1976; Ayuso et al., 1976 and Kempe, 1976).

Cobalt

Co concentrations vary from 56 ppm (sample HW131) to 144 ppm (sample HW115) in tholeiites and from 91 ppm (HW109) to 157 ppm (sample HW117) in the nephelinite and alkali basalts. The differentiated lava, HW116, has the lowest concentration of Co (25 ppm). These concentrations are the highest recorded in oceanic basaltic lavas, but some ocean floor lavas reported by Kempe (1976) have concentrations that range from 65 to 100 ppm. Information available from other oceanic islands, such as the Galapagos Islands (McBirney and Williams, 1969), Gough (LeMaitre, 1962), and Amsterdam Island (Gunn et al., 1971) shows that Co usually varies between 20 and 60 ppm in basaltic lavas.

Nickel

Ni concentrations in Hawaiian lavas range from 113 ppm (sample HW131) to 857 ppm (sample HW130) in tholeiitic basalts, and from 152 ppm (sample HW133) to 485 ppm (sample HW102) in the alkali basalts and nephelinites. Ni concentrations are much lower in the differentiated lavas. For example, HW116 has the lowest Ni concentration, 3 ppm. Because olivine is rich in Ni, precipitation of this mineral quickly reduces the Ni concentration of the remaining lava. At the same time, any lavas with an accumulation of olivine will have high Ni concentrations. Sample HW130 has a high MgO content suggesting it may have some accumulated olivine (see major element section, this chapter), and the high Ni concentrations support this.

The only oceanic island which has higher Ni concentration than those in Hawaiian Islands lavas is Grande Comore

(Strong, 1972b). Alkali basalts from this island have Ni concentrations that range from 540 to 2430 ppm. The highest concentrations are probably due to high olivine content. Some lavas from islands in the Samoan Arc (Hawkins et al., 1975), and lavas from Mauritius (Baxter, 1975, 1976) have Ni concentrations which are broadly similar to those shown by the Hawaiian lavas. Most other oceanic island basalts, as well as those from oceanic ridges, have Ni concentrations significantly below those values recorded from the Hawaiian lavas.

Copper

Cu concentrations in Hawaiian lavas range from 89 ppm (sample HW127) to 134 ppm (sample HW131) in tholeiites and from 78 ppm (sample HW118) to 118 ppm (sample HW117) in alkali basalts and nephelinites. The lowest concentration observed, 28 ppm, occurs in two of the differentiated lavas, samples HW116 and HW128.

Most oceanic lavas have Cu concentrations lower than those observed in the Hawaiian Islands. However, concentrations in basaltic lavas from Ua Pu (Bishop et al., 1973), Iceland (Sigvaldason, 1974), the Crozet Arc (Gunn et al., 1970) and the Galapagos Islands (McBirney and Williams, 1969) are broadly similar to those in Hawaiian lavas. The lowest Cu concentrations in basalts usually occur in ocean floor lavas which range between 12 and 95 ppm (eg. Fleet et al., 1976). Differentiated lavas on oceanic islands invariably have even lower Cu concentrations than ocean floor basalts. Highly differentiated lavas commonly have concentrations below 10 ppm.

Zinc

There is very little variation in the Zn concentrations of Hawaiian lavas. Tholeiites show concentrations that range from 95 ppm (sample HW123) to 109 ppm (sample HW107). The values in alkali basalts that range from 92 ppm (sample HW118) to 114 ppm (sample HW100) are not significantly different. Sample HW109, a nephelinite, has the highest Zn concentration, 116 ppm, in the undifferentiated lavas. Sample HW119, a differentiated lava, has the highest concentration of Zn (124 ppm) in the suite

The limited amount of information available on Zn concentrations in oceanic lavas suggests the concentrations in Hawaiian lavas are typical. Zn concentrations in undifferentiated lavas from Ajouan (Flower, 1973), and Amsterdam Island (Gunn et al., 1971), show that nephelinites tend to have the highest concentrations and tholeiitic basalts the lowest. The concentrations range from about 83 ppm to 155 ppm. The lowest Zn concentrations occur in ocean floor tholeiites and range between 70 and 130 ppm (Fleet et al., 1976 and Kempe, 1976).

Gallium

The Ga concentrations are very similar for most of the Hawaiian lavas. They range from 17 ppm (sample HW127) to 24 ppm (samples HW131 and HW107) in tholeiitic lavas and from 22 ppm (sample HW109) to 26 ppm (sample HW104) in the alkali basalts and nephelinites. Samples HW119, HW126, and HW128, which are differentiated lavas, have 28 ppm Ga, which is the highest concentration in the Hawaiian suite.

Gough and Amsterdam Islands are the only two oceanic islands for which there is information on Ga concentrations. Ga concentrations in alkali basalts and tholeiites from Gough are about the same as those from the Hawaiian Islands and range between 15 and 22 ppm (LeMaitre, 1962). Tholeiitic basalts from Amsterdam Island have concentrations between 13 and 16 ppm (Gunn et al., 1971). Ga concentrations in ocean floor tholeiites are higher than in oceanic island basalts and are generally between 40 and 50 ppm (Ayuso et al., 1976 and Kempe, 1976).

Lead

Pb concentrations in Hawaiian lavas vary between 1.0 (detection limit) ppm for many of the lavas to 10 ppm for the alkali basalt sample HW117. Tatsumoto (1966a) reported concentrations between 1.33 ppm and 5.43 ppm in basaltic and nephelinitic lavas from the Hawaiian Islands. Tatsumoto (1966b) reports Pb concentrations between 1.20 ppm and 1.98 ppm in basaltic lavas from Easter Island and between 1.30 and 3.39 ppm in alkali basalt lavas from Guadalupe. Pb concentrations in ocean floor tholeiites range between 0.49 ppm and 1.29 ppm (Tatsumoto, 1966b).

Thorium

The Th concentrations in lavas from the Hawaiian Islands range between 0.44 ppm (sample HW115) and 1.0 ppm (sample HW122) in tholeiitic basalts and between 1.7 ppm (sample HW133) and 4.0 ppm (samples HW100 and HW102) in alkali basalts. Nephelinites have the highest concentrations of Th in the undifferentiated lavas, the concentrations ranging between 5.9 ppm (sample HW109) and 7.4

ppm (Tatsumoto, 1966b). Some differentiated lavas may have concentrations as high as 7.6 ppm (Tatsumoto, 1966a).

The concentrations in basaltic lavas from Easter Island range between 1.7 and 2.6 ppm and in alkali basalts from Guadalupe they range between 1.8 and 7.2 ppm (Tatsumoto, 1966b). Ocean floor tholeiites have Th concentrations between 0.12 and 0.29 ppm (Tatsumoto, 1966b) indicating they have significantly lower Th concentrations than the Hawaiian lavas.

Barium

Ba concentrations in Hawaiian lavas are generally much lower in tholeiitic basalts than in the alkali basalts and nephelinites. Sample HW130, a tholeiitic basalt, has the lowest concentration of Ba in the suite (59 ppm). The highest concentration, 1470 ppm, is found in sample HW104, an alkali basalt. The highly differentiated samples, HW116 and HW119, also have very high Ba concentrations; 784 and 1030 ppm respectively.

These concentrations are relatively high when they are compared with Ba concentrations in ocean floor basalts which normally contain between 5 and 30 ppm Ba. They can, however, range as high as 200 ppm (Engel et al., 1965; Fleet et al., 1976; Ayuso et al., 1970; and Kempe, 1976). LeMaitre (1962) records Ba concentrations in tholeiitic basalts from Gough Island of between 700 and 900 ppm. These values appear to represent the highest Ba concentrations found in the tholeiitic basalts. Concentrations of Ba in alkali basalts, up to 1600 ppm, have been recorded for the islands of Moheil (Strong, 1972) and Ua Pu (Bishop et al., 1973). Strong (1972a) also reports Ba

concentrations in nephelinites from Moheli between 1100 and 2000 ppm. The highest recorded concentration of Ba in oceanic island lavas, 4100 ppm, is documented from a highly differentiated lava, (potassic phonolite) on Ua Pu (Bishop et al., 1973).

Rubidium and Strontium

Rb and Sr concentrations are extremely variable in oceanic island lavas. They do, however, show a close association with rock type. Data from Hawaii reported here show that Rb varies between 1 ppm (HW107) and 8 ppm (HW131) in tholeiitic basalts and between 7 ppm (HW100) and 27 ppm (HW133) in alkali basalts and the nephelinite. The lavas from Hawaii appear to have higher concentrations of Rb than comparable lavas from Maui and Kauai. The highest concentration of Rb is found in the differentiated sample HW116 from Maui which has 77 ppm Rb.

Sr concentrations vary in the tholeiitic lavas from 225 ppm (sample HW130) to 336 ppm (sample HW131). In the alkali basalt lavas, the concentrations vary from 437 ppm (HW118) to 100 ppm (HW102). Sample HW109, a nephelinite, has the highest concentration of Sr in the undifferentiated lavas (951 ppm). The highest concentrations of Sr in the rock suite is found in the differentiated lava sample HW116 (1605 ppm).

Some interesting relationships exist between rock type and Rb and Sr concentrations in the undifferentiated lavas. Data in this report for Rb and Sr concentrations in lavas from the Hawaiian Islands is supplemented by additional data from Kay and Gast (1973), O'Nions et al. (1977) and Hamilton (1965). The following observations can be

drawn from this data:

1. The lowest Rb and Sr concentrations for each island always occur in the tholeiitic lavas.
2. Alkali basalts which do not contain nepheline have higher concentrations of Rb and Sr than tholeiitic basalts.
3. Rb concentrations increase with Sr concentrations in tholeiites and alkali basalts, but not in nephelinitic alkali basalts and nephelinites.
4. There is correlation between the somewhat constant Rb concentrations and the high Sr abundances in the nephelinitic alkali basalts and nephelinites.
5. Rb and Sr concentrations are much higher in the Oahu tholeiites and alkali basalts than in similar lavas from Kauai.
6. Sr concentrations in nephelinites from Oahu vary from 1300 to over 2000 ppm; Sr concentrations in the same lavas from Kauai range from about 600 ppm to 950 ppm.
7. The range of Rb concentrations in Oahu nephelinites (17 to 55 ppm) is about the same as the range of concentrations in Maui nephelinites and nephelinitic basalts (7 to 50 ppm).

There are some indications that similar conclusions can be drawn from Moheji (Strong, 1972a).

Equally important are the correlations between Rb and Sr in suites of rocks that represent lavas from basaltic composition to those that are highly differentiated, such as trachytes and pantellerites. Figure 3-6 shows the concentrations of Rb and Sr in

lavas from Tristan da Cunha (data from Bell, personal communication, 1979, and O'Nions and Pankhurst, 1974), Hawaii Island (data from this report, Faure and Hurley, 1963; Hamilton, 1965; Hart, 1973 and O'Nions et al., 1977). Terceira (Self and Gunn, 1976) and Easter Island (Baker and Buckley, 1974). Concentrations of Rb and Sr in lavas from Reunion (Upton and Wadsworth, 1972) and Tenerife (Ridley, 1970) are shown in Figure 3-7. The numbers attached to some of the data points correspond to the Thornton and Tuttle (1960) differentiation index. This index is the sum of normative quartz, orthoclase, albite, nepheline, kalsilite and leucite. The higher the differentiation index is, the more differentiated the lava is.

The following observations can be made with reference to Figures 3-6 and 3-7:

1. Tholeiitic basalts have the lowest Rb and Sr concentrations.
2. Alkali basalts with differentiation indices between 28 and 29 have the highest Rb and Sr concentrations.
3. The data from each island appear to approximate to a curve in which Rb and Sr concentrations increase with the differentiation index up to a differentiation index of about 51. At this point, maximum strontium concentrations are reached and after this, Sr concentrations fall off as Rb concentrations and the differentiation indices continue to increase.

Figure 3-6. Concentrations of Rb and Sr in Oceanic Islands. Numbers attached to data points are the differentiation index for that sample. Tristan da Cunha differentiation indexes estimated from rock type names. Dots represent tholeiite triangles are alkalic rocks. References are given in the text.

Figure 3-7. Concentrations of Rb and Sr in Reunion and Tenerife. Numbers attached to the data points are the differentiation index. Dots represent tholeiites, triangles are alkalic rocks. References are in the text.

4. The overall shape of each curve for each island is approximately the same, however, there are large differences in the actual concentrations of Rb and Sr between islands. The highest concentrations are seen in Tristan da Cunha, and the lowest in the Easter Island lavas.

Summary

1. The new major element data for the Hawaiian lavas reveals a suite of rocks of highly variable composition and perhaps complex genetic history.
 2. The rare earth elements, particularly the heavy rare earth elements, show that Kauai and Maui lavas have lower rare earth element concentrations than lavas from the island of Hawaii. Oahu lavas show rare earth element concentrations which encompass the total range shown by Kauai, Maui and Hawaii lavas.
 3. Other than perhaps the rare earths and Rb and Sr concentrations, most of the lavas are similar in composition from one island to another.
 4. The concentrations of the rare earth elements, Hf, Rb, Sr, Ba, Sc, Ti, Zr, Ga, V, Th, and Zn in Hawaiian lavas tend to be intermediate in value, or similar to, those found in other oceanic island lavas.
 5. The Cr, Co, Ni, and Cu concentrations in Hawaiian lavas tend to be higher than most other values
-

observed in other oceanic island and ocean floor basalts.

6. Nb concentrations in Hawaiian lavas seem low when they are compared to other oceanic island lavas and ocean floor basalts.
7. There are large differences in the trace element composition of similar lavas from different oceanic islands. This is best displayed by the large range of Rb and Sr concentrations from different oceanic islands.

Chapter Four Modelling Trace Element Distribution

Introduction

Gast (1968) first used a trace element distribution model to show that the mantle is probably heterogeneous. This hypothesis was well developed prior to 1968 as a result of lead and strontium isotopes studies of oceanic islands (eg. Powell et al., 1965 and Gast et al., 1964). More recently, however, Sipkin et al. (1975) provided geophysical evidence for mantle heterogeneity. Despite the fact there is fairly good agreement among most workers that the mantle is heterogeneous, its physical scale, chemical extent, and the manner in which the heterogeneity was produced is still not clearly understood.

The concentrations of various trace elements in oceanic island lavas, particularly the Hawaiian Islands, have been examined in detail in the previous chapter. By modelling the rare earth element distributions in Hawaiian lavas, some constraints may be placed on the chemical composition of the mantle, or perhaps on mantle evolution and the information from this modelling can be applied to other trace elements for which partitioning coefficients are available.

Modelling the Effect of Differentiation on REE Concentrations

Mineralogical and chemical evidence suggesting that some lavas are differentiated has been discussed in chapters one and two. In order to show that differentiation is a viable means of explaining the observed rare earth element trends in these lavas, the original undifferentiated composition of sample HW116 from Maui, one of the most differentiated samples, can be estimated and compared with lavas

which have not undergone any differentiation.

Equation I given by Gast (1968) and shown below can be used to find the original concentration of each rare earth element given its concentration in the differentiated lavas:

where $C^L/C^0 = F^k - 1$

C^L/C^0 = the ratio of concentration of an element in the liquid to that of the original concentration before differentiation.

F = the weight fraction of liquid remaining, after differentiation.

K = the distribution coefficient which relates the concentrations in a mineral that has precipitated to the concentration in the liquid. If more than one mineral is precipitated, K is calculated by taking a weighted average of all crystal liquid partitioning coefficients. The weighted average depends on the proportions of phases precipitating.

A literature review (eg. Macdonald and Katsura, 1964; Barberi et al., 1975; McBirney and Williams, 1969) shows that olivine, clinopyroxene, and plagioclase are the first minerals to precipitate from an alkali basaltic magma. Rare earth element crystal/liquid partition coefficients for these phases are given in Table 4-1.

Figure 4-1 shows the rare earth element compositions of the highly differentiated sample HW116 and the undifferentiated alkali basalt sample HW118 normalized to chondrites. Also shown in Figure 4-1 is the calculated original composition of sample HW116 before

Table 4-1. Parameters For the Fractional Crystallization Model.

Mineral	Ol	Cpx	Plag.
D_{Ce}	4.81×10^{-4}	9.17×10^{-2}	1.04×10^{-1}
D_{Nd}	9.11×10^{-4}	1.89×10^{-1}	1.02×10^{-1}
D_{Sm}	1.3×10^{-3}	2.69×10^{-1}	1.00×10^{-1}
D_{Eu}	1.5×10^{-3}	2.99×10^{-1}	5.03×10^{-2}
D_{Yb}	1.1×10^{-3}	2.63×10^{-1}	9.5×10^{-2}
D_{Lu}	9.00×10^{-3}	1.90×10^{-1}	9.7×10^{-2}
Proportions of Phases Removed	30%	50%	20%

D values are estimates and averages derived from:

(1)	Frey et al. (1974).
(2)	Grutzeck et al. (1974).
(3)	Kay and Gast (1973).
(4)	Langmuir et al. (1977).
(5)	Nagasawa and Schnetzler (1971).
(6)	Schnetzler and Philpotts (1970).

differentiation. The proportions of phases used to calculate this trend line were 30 percent olivine, 50 percent clinopyroxene and 20 percent plagioclase and it was assumed that 78 percent crystallization occurred. Other proportions of phases, and percentages of crystallization were tried but this combination produced a rare earth element composition the most similar to sample HW118. Details pertaining to the calculations are given in Appendix III.

Since there is a negligible difference between the estimated original composition of sample HW116 and the observed composition of sample HW118, it may be possible to conclude that fractional crystallization is a viable mechanism for the generation of those

Figure 4-1. Shown is rare earth element composition of sample HW116 as well as an estimate of its original undifferentiated composition. Also shown is sample HW118, an undifferentiated alkali basalt. Note how similar the composition of sample HW118 is to the estimated undifferentiated composition of HW116.

rocks which have heavy rare earth element concentrations. No attempt will be made to understand the rare earth element distribution of those samples previously discussed as "differentiated" in terms of a mantle melting model.

Modelling the Rare Earth Element Distributions in the Melting Process.

In order to model mantle melting, it is necessary to decide what the stable phases are in the mantle. Yoder (1976) has given a strong argument in favour of a garnet peridotite upper mantle.

Evidence for this includes:

1. Garnet peridotite occurs as xenoliths in kimberlite pipes which almost certainly have a deep seated origin.
2. Natural garnet peridotites give partial melts of basaltic composition at high pressure.
3. The mineral assemblages are found to be stable at high pressures and temperatures.
4. Garnet peridotite has appropriate densities and seismic velocities.

Evidence from xenoliths in kimberlite pipes (Chen, 1971) suggests the proportions of these minerals are approximately Ol, 55%; Opx, 25%; Cpx, 10%; Gar, 10%. Kay and Gast (1973) discuss the pressure effects on the proportion of garnet and clinopyroxene and the problem is re-examined here.

In addition to those phases already mentioned, there is abundant evidence to assume that phlogopite is a stable phase in the mantle (Sun and Hanson, 1975b and Yoder, 1976), but because it is only a minor phase, and because its partitioning coefficients suggest it will not control the concentration of any of the rare earth elements, the models proposed here do not include phlogopite. Apatite, which may be an important phase in the mantle, is ignored because it probably entirely melts at the solidus. This assumption is supported by the observation made by Sun and Hanson (1975b) that Ce concentrations are

covariant with P_2O_5 concentrations, for both alkali basalts and nephelinites.

Kay and Gast (1973) used an incremental melting equation (Shaw, 1970) to relate the concentration of a trace element in a lava to its mantle source concentration. The incremental melting relationship removes infinitely small amounts of magma from the mantle and then accumulates these to form a bulk melt. Langmuir et al. (1977) found an incremental melting model unacceptable because the distribution coefficients, for such "incompatible" elements as Rb, and La, are so low that greater than 94 percent of these elements would be removed after only 5 percent melting. A batch melting model, which allows a melt to remain in contact with the residue until melting is completed, enables the mantle to be remelted and still produce reasonable concentrations of these elements.

For similar reasons, Hawksworth et al. (1978) found that an incremental melting model complicates the interpretation of Nd-Sm and Rb-Sr systematics in oceanic rocks. It would thus seem that batch melting best represents the natural process of magma generation.

The following equation given by Shaw (1970) can be used to represent batch melting:

$$\frac{C^L}{C^0} = \frac{1}{D^0 + F(I-P)}$$

where:

$\frac{C^L}{C^0}$ = concentration in the liquid over concentration in the original solid.

D^0 = the bulk distribution coefficient. To calculate D^0 estimates must be made of the phases and their proportions in the mantle as well as the

distribution coefficients for these phases.

P = a correction factor for D^0 , which takes into account that the phases do not melt in the proportions in which they occur in the rock.

F = the weight fraction of melting which takes place.

Table 4-2 gives the distribution coefficients used in calculating D^0 and P . The melting proportions used for the calculation of P come from the 30 Kilobar phase diagram of O'Hara (1968) and are given in Table 4-2.

Kay and Gast (1973) suggested that the modelling of rare earth element concentrations in potassic, nephelinite, and alkali basaltic lavas requires the assumption that different garnet:clinopyroxene ratios exist in the mantle source that gives rise to each of these rock types. The garnet:clinopyroxene ratios they propose for the source region of each rock type are: 17:3 for potassic lavas; 10:10 for nephelinites; 5:15 for alkali basalts.

Because the proportion of garnet to clinopyroxene increases with pressure, they proposed that potassic lavas are generated at greater pressures than nephelinites, and nephelinites at greater pressures than alkali basalts. In order to check their conclusions in the light of the new data, hypothetical curves have been constructed using three different garnet:clinopyroxene proportions and differing percentages of melting. Details pertaining to the actual calculations are given in Appendix III.

Six of the trend lines in Figure 4-2 represent partial melting of a mantle with a constant garnet:clinopyroxene ratio of 1:1 and an arbitrarily chosen rare earth mantle composition of 1.45 times

Table 4-2. Melting Model Parameters For the REE's.

	O ^L	Opx	Cpx	Gar
	50%	30%	3%	17%
<u>% of Mantle</u>	50%	30%	10%	10%
	50%	30%	15%	5%
<u>% of Melt Made From Phase</u>	6%	20%	30%	44%
D* La	3000	800	21.9	914
D Ce	2080	691	10.9	313
D Nd	1098	341	5.28	44.5
D Sm	766	201	3.72	8.54
D Eu	675	125	3.35	4.70
D Dy	638	94.4	3.19	0.788
D Fr	720	73.4	3.60	0.389
D Yb	882	52.0	3.80	0.260

* All D's = Liquid/Crystal

D values are averages and estimates drawn from:

- (1) Frey et al. (1974).
- (2) Grutzech et al. (1974).
- (3) Kay and Gast (1973).
- (4) Langmuir et al. (1977).
- (5) Nagasawa and Schnetzler (1971).
- (6) Schnetzler and Philpotts (1970).
- (7) Shimizu (1975).
- (8) Shimizu and Kashiwa (1975).

Figure 4-2. Hypothetical rare earth element trends produced by various percentages of melting and different garnet:clinopyroxene proportions in a mantle with rare earth element concentrations, 1.45 times chondrites.

chondrites. These were constructed using Shaw's (1970) equation. The light rare earth element concentrations are highly dependent on the degree of partial melting and decrease as the percentage of melting increases. The heavy rare earth element concentrations are, for the most part, independent of the percentage of melting and remain relatively constant.

Gast (1968) pointed out that the relative proportions of garnet and clinopyroxene alone should control the rare earth element trends in most lavas. This point is clearly illustrated in Figure 4-2 where three of the curves represent similar degrees of melting (2%) of three mantle sources with different garnet:clinopyroxene ratios. The actual shape of the curves also changes, but only to a limited extent. As the garnet content increases, the slope of the curve increases; this is essentially brought about by reducing the heavy rare earth element enrichment.

To more clearly illustrate the dependence of the rare earth trends on the garnet:clinopyroxene ratio in the mantle, the requirements for modelling a particular trend with two different garnet:clinopyroxene ratios can be compared. A particular rare earth element trend might be modelled with a garnet:clinopyroxene ratio of one to one, a mantle composition of 1.45 times chondrites, and 2 percent partial melting. This is shown in Figure 4-2. If, however, a seventeen:three mantle garnet clinopyroxene ratio is used to model the trend, the mantle concentrations for such heavy rare earth elements must be increased. In order to produce the same light rare earth element concentrations, the percentage of melting must be increased. High garnet:clinopyroxene ratios produce a trend

line which is quite different in shape from the trend produced by lower garnet:clinopyroxene ratios. In general, the rare earth element trends in Hawaiian lavas suggest these lavas are not generated in a mantle with a high garnet:clinopyroxene ratio. This can be seen by comparing the trends in Figures 3-2 to 3-5 with the trend computed using a garnet:clinopyroxene ratio of seventeen:three as shown in Figure 4-1.

A very small amount of scatter in the heavy rare earth element concentrations in Figure 3-5 suggests the lavas from Kauai, no matter what their composition, are generated from a mantle source with similar rare earth element concentrations and similar garnet:clinopyroxene ratios. This is supported by Figure 4-2 where only curves which represent varying degrees of partial melting with a constant mantle garnet clinopyroxene ratio and a constant mantle composition duplicate the natural relationships observed in Figure 3-4. This is also true of Hawaii and Maui, but rare earth element trends from Oahu suggest the mantle source for these lavas is more variable. Changing the mantle concentrations to explain this variability is preferable to changing the garnet clinopyroxene ratios, because the latter would mean that lavas of nearly identical major element composition on other islands would have to be generated by significantly different degrees of partial melting.

It may now be possible to estimate the rare earth element composition of the mantle below the Hawaiian Islands but the following uncertainties must be kept in mind. There are un-

certainties in the concentrations of the rare earth data from the lavas themselves. There may be as high as 100% of the quoted value for certain elements. A second source of error is associated with the value chosen for the liquid/crystal partition coefficient. The latter are average values derived from the literature and these may be in serious error. However, any error in estimating D values will mean that estimates of mantle concentrations of a particular element will be higher for all samples or lower for all samples, depending on whether the selected value for D is too high or too low. In addition, the assumption that D_0 and P remain fixed from one part of the mantle to another may be an oversimplification. For example, some authors believe that P_{CO_2} may seriously change the distribution coefficient values and hence, as a result, D_0 and P . Also, changes in the percentages of mineral phases in the mantle could produce differences in the observed concentration of an element from one island to another.

The uncertainties listed above cannot be ignored and cumulatively must cast some doubt on results obtained by using almost any model. However, in spite of this pessimistic situation, estimates are made of the rare earth element concentrations in the mantle below the Hawaiian Islands by making the following assumptions and constraints:

1. Samples HW116, HW119, HW128, HW124, HW125, HW126, JP10, JP15, 1104, and 1102 are assumed to be the result of significant degrees of fractional crystallization and are ignored in estimating the mantle's composition. This assumption is supported by the major element composition, mineralogical composition, and the trace element distribution.
2. Constraints on the clinopyroxene:garnet ratio are based on:
 - (a) The rare earth element patterns in lavas suggest that the garnet:clinopyroxene ratio for the mantle sources of all rock types is limited.
 - (b) The results of melting experiments indicate that the range of melting which produces all rock types is 1 to 30% (eg. Green, 1973). The modelling calculations should produce percentages of melting within this range and this in itself limits the garnet:clinopyroxene ratio.
 - (c) Natural garnet peridotite assemblages from kimberlite pipes suggest that garnet and clinopyroxene each make up about 10 weight percent of the mantle (Chen, 1971).
Given these constraints the garnet and clinopyroxene percentages in the mantle source for all rock types is assumed to be 11:9.
3. La and Yb are used in all calculations for two reasons. Firstly, they represent the opposite ends of the rare earth element spectrum. Secondly, they are fairly well-determined as far as their abundance is concerned, (Appendix II).

4. The three unknowns in the model calculations are the percentages of melting and the concentration in the original solid for both La and Yb (C_{La}^0 and C_{Yb}^0). The percentage of melting, although a product of the calculations, must conform to the guidelines laid down in 2 above.
5. Shaw's (1970) equation for batch melting can be used to calculate C^L/C^0 for both La and Yb provided the percentage of melting is known. In all there are 3 unknowns. A relationship between C^L/C_{La}^0 and C^L/C_{Yb}^0 can be obtained by assuming the mantle's rare earth element composition is, for each lava, some factor times chondrites.

Results of Rare Earth Element Modelling

The results of the modelling calculations, based on the previous assumptions indicate the percentages of melting for the tholeiites are 8.5 to 14.3 percent. Those for alkali basalts are 2.1 to 7.5 percent and the percentages of melting for nephelinites are 0.7 to 2.2. These are in fairly good agreement with many models for generation of basaltic lavas, though for some they are low (eg. Green and Ringwood, 1967).

A difference has been noted between the heavy rare earth element concentrations in lavas from the island of Hawaii as compared with those from Kauai and Maui, in particular. The modelling calculations relate these differences to the mantle composition beneath the islands. This is explicitly shown in Figure 4-3 where the calculated mantle compositions are expressed in terms of chondrites.

Figure 4-3. Shown are the calculated mantle rare earth element concentration, in terms of chondrites, which generated each lava. Each square represents one lava. The lines refer to other possible mantle concentrations between data points.

Hawaiian lavas have a mantle source with rare earth element concentrations between 2.8 and 4.0 times chondrites. Maui and Kauai lavas have estimated mantle source compositions approximately the same and range between 2.2 and 3.0 times chondrites. The source for the Oahu lavas has rare earth element concentrations between 2.0 and 4.8 times chondrites. A t-test shows that the mean mantle compositions for Kauai and Maui are significantly less than the mean for Hawaii at the 99.95 and 99.5 percent confidence levels respectively. The mean composition for the Kauai source is significantly less than the mean for Oahu at the 90.0 percent confidence level. The mean mantle composition for Maui is not different from the means for Oahu and Kauai at the 80 percent confidence level. The mean mantle rare earth element composition for Oahu is not significantly different from the mean for Hawaii at the 80 percent confidence level. Furthermore, there is no significant difference in the rare earth composition of the source for different kinds of lavas from each of the islands. For example, tholeiites have the same mantle source composition as do alkali basalts and nephelinites on Kauai.

Oahu lavas appear to have an extremely heterogeneous source region. Powell and Delong (1966) found that the mean initial ratio of the Koolau Series lavas from Oahu is significantly different from the mean $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios of lavas from the Honolulu and Waianae Series (which overlie and underlie the Koolau Series lavas respectively) at the 99 percent confidence level. Oahu lavas may be placed into two groups using their mantle source rare earth element concentrations. A source represented by the data from five nephelinites, two alkali basalts and two tholeiites has higher rare

earth element concentrations than the source for two tholeiites, two alkali basalts, and one nephelinite at the 99.95 percent confidence level. An analysis of the two mantle source compositions suggested here on the basis of rare earth concentrations reveals absolutely no stratigraphic relationship! The fact remains that the mantle which has produced Oahu lavas is more heterogeneous than that which has produced other island lavas. No explanation is offered for the differences in this thesis.

Kay and Gast (1973) suggested that their mantle concentration estimates are within a factor of two of those actually in the mantle. Their estimate of the mantle rare earth element concentration for sample 04 (Figure 3-4) is approximately two times chondrites. The estimates arrived at here are believed to be more accurate than theirs on two counts. Firstly, they did not use a batch melting model, and secondly, the garnet:clinopyroxene ratios they used are believed to be incorrect and cannot account for the clustering of heavy rare earth element concentrations observed in Hawaiian Islands lavas. Even so, the suggestion is not made that the concentrations here are within a factor of two; this is purely subjective. More important than actual mantle concentrations, however, are the relative mantle concentrations between islands. These are believed to be very good and are considered to be within a factor of two of the true ratio.

A simple La versus Yb plot (Figure 4-4) illustrates and summarizes many of the relationships between the lavas within one island and between islands. All the differentiated lavas (shown as vertical slashes through symbols) plot, as one would expect, towards the upper right hand corner of the diagram. This is because

Figure 4-4. Yb vs La plot for all lavas examined in this report. Vertical slashes through symbols distinguish lavas classed as differentiated. Horizontal slashes correspond to nephelinites.

differentiation enriches the lavas in all the rare earth elements. Even the differentiated lavas from the Island of Hawaii remain distinct from the Maui lavas. In general, they have higher Yb values. This could reflect the higher original Yb concentrations of the undifferentiated Hawaiian lavas.

Kauai and Oahu are not represented by any differentiated lavas in Figure 4-4. The Yb enrichment of a given lava reflects the rare earth element concentration of its mantle source. The source region for Oahu lavas is very heterogeneous because the lavas show a wide range of Yb concentrations. Yb concentrations in Kauai lavas are intermediate, and plot in the middle of the range shown by Oahu lavas. This indicates Kauai lavas have a mantle source with rare earth element concentrations intermediate to the concentrations in the source for Oahu lavas.

The La concentration in a lava is proportional to the percentage of partial melting represented by that lava. For a given Yb concentration lavas representing small percentages of partial melting have high La concentrations whereas lavas representing high percentages of melting have relatively low La concentrations. This is illustrated by the fact that nephelinites plot to the far right (high La) of Figure 4-4. As expected, most tholeiitic lavas fall to the far left hand side of Figure 4-4. The rare occasion when a tholeiite plots in the alkalic field appears to be the result of fractional crystallization of a tholeiitic basalt.

Mantle Concentrations of K, Rb, Sr, Sc, Ti, V, Cr, Co, and Ni.

It is also possible to use Shaw's (1970) equation, which simulates batch melting, to estimate the concentrations of other trace elements in the mantle provided the following parameters are known:

1. Partitioning coefficients for the elements between liquid and phases.
2. The proportions of phases in the mantle.
3. The melting proportions of phases in the mantle.
4. The percentages of partial melting each lava sample represents.
5. The concentration of the trace elements in the lava.

Partitioning coefficients for K, Rb, Sr, Sc, Cr, and Ni are available from the literature for all major mantle phases: olivine, clinopyroxene, orthopyroxene and garnet. These are shown in Table 4-3. The phase proportions are the same as those used for calculating the mantle rare earth element concentrations from the previous section. The garnet:clinopyroxene ratio has not been varied because none of these elements are sensitive to this. The phase melting proportions are also the same as those used for the rare earth elements and are given in Table 4-4.

Partitioning coefficients for Co, between liquid and crystal are available for all phases except garnet. Since it is unlikely that the liquid/crystal partitioning coefficient is lower than that for olivine, and since garnet probably only makes up about 10 percent of the mantle, it is unlikely that it will have a major effect on the Co concentration in lavas. The mantle phase

percentages and melting proportions used in all calculations were somewhat arbitrarily chosen to conform with the proportions of a garnet-bearing mantle and these are given in Table 4-4.

Only liquid/olivine and liquid/clinopyroxene partitioning coefficients are available for Ti and V. Because Ti and V concentrations are rarely very high in garnet and orthopyroxene, it is unlikely that their partitioning coefficients (liquid/crystal) are lower than those for olivine and clinopyroxene, and as a result, olivine and clinopyroxene will, to a first approximation "control" the concentration of these elements in the melt. As long as only relative concentrations of each element between the islands are desired and not absolute mantle abundances, then the melting equation can be used to compensate each lava for the percentage of melting each represents.

The percentage of melting for each lava was calculated from the rare earth element trends and can be used here. As with the rare earth elements, those lavas which have undergone significant fractional crystallization are ignored. One further complication remains. There is good evidence that phlogopite is a residual phase in the mantle for the early percentages of melting. Therefore, K, and Rb concentrations in lavas that represent small amounts of partial melting cannot be related to mantle concentrations using this model. Table 3-2 shows that the Rb concentrations relative to Sr concentrations in samples HW109, HW102, and HW103 are very low. Each of these samples has modal nepheline and the percentage of melting calculated for them from the rare earth element trends is very low. As a result, these samples are not used in the calculation of average Rb and K concentrations of the mantle.

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Table 4-5 gives the calculated average concentrations of K, Rb, Sr, Sc, Ti, V, Cr, Co, and Ni in the mantle sources for Kauai, Maui and Hawaii lavas. The following general observations are made regarding Table 4-5 and discussed in terms of mantle evolution at the end of this chapter:

1. The mantle source for Hawaii lavas appears to be richer in K, Rb, and Sr than the mantle source that produced the Maui and Kauai lavas.
2. The mantle source for lavas from the island of Hawaii seems to be depleted in Ti, V, Cr, Co and Ni relative to Kauai and Maui lavas.
3. The source for Maui lavas appears to be enriched in K, Rb, Sc, Cr and Co relative to Kauai lavas and depleted in Sr, Ti, V, and Ni.
4. The mantle sources for lavas from Hawaii and Kauai seem to have similar Sc concentrations.

Table 4-3. Liquid/Crystal Partition Coefficients

Mineral	K	Rb	Sr	Sc	Ti	V	Cr	Co	Ni
Ol	146.0	40,000.	16,700.	2.0	1.00	5.0	1.25	0.337	0.067
Opx	71.2	3,120.	1,430.	0.34	-	-	0.20	0.481	1.10
Cpx	13.8	625.	15.2	0.81	1.25	0.4	0.17	0.893	0.28
Gar	50.5	435.	3.45	0.10	-	-	0.16	-	15.00

Sources:

- (1) Frey et al. (1974).
- (2) Gast (1968).
- (3) Hawksworth et al. (1978).
- (4) Hakli and Wright (1967).
- (5) Higachi and Nakamura (1969).
- (6) Hodges and Bender (1976).
- (7) Hodges and Papike (1976).
- (8) Muir and Tilley (1964).
- (9) Onuma et al. (1968).
- (10) Philpotts and Schnetzler (1970).
- (11) Shimizu (1974).

Table 4-4. Mantle Mineral Percentages and Melting Proportions Used in Calculations.

Element	Melting Proportions				Mantle Percentages			
	OL	Opx	Cpx	Gar	OL	Opx	Cpx	Gar
K, Rb, Sr, Sc, Cr, Ni	6	20	30	44	50	30	9	11
Co	11	25	64		50	30	20	
Ti, V	26		74		50		50	

Table 4-5. Average Mantle Concentrations (ppm) of Various Trace Elements, Below the Hawaiian Islands.

Element	Kauai	Maui	Hawaii
K	220.	320.	390.
Rb	0.4	0.6	0.8
Sr	37.	33.	40.
Sc	51.	59.	50.
Ti	6,230.	5,920.	5,600.
V	400.	390.	360.
Cr	1,340.	1,400.	870.
Co	250.	310.	210.
Ni	3,410.	2,300.	1,480.

Mantle Evolution

Modelling of the rare earth element distributions as well as the concentrations of Rb, Sr, K, Ti, V, Cr, Co, Ni, and Sc in Hawaiian Islands lavas made it possible to show that the mantle source concentrations of these elements are different for different islands. It remains to be shown how and why these concentration differences might have developed. Other authors have found differences in the trace element concentrations of lavas which are geographically widely

separated and related these to mantle heterogeneity. Gast (1968), for example, proposed that abyssal tholeiites represent between 15 and 30 percent partial melting of a mantle which has been chemically fractionated by previous, less extensive, partial melting events. As evidence in support of this theory, Gast showed that the large ion lithophile elements are largely depleted in abyssal tholeiites relative to their concentrations in oceanic island lavas. As further evidence for the theory, he pointed to the very low Pb and Sr isotopic ratios in abyssal tholeiites which indicate their mantle source, or sources, have been depleted in the parent nucleides by some previous melting event, or events.

Work by previous authors has revealed that individual oceanic islands appear to be characterized by a particular minor element and isotopic signature which is probably related to mantle heterogeneity, (eg. O'Nions and Pankhurst, 1974). Most of the explanations as to how this heterogeneity has come about are extensions of Gast's (1968) ideas and suggest the inhomogeneity has been produced by removing basaltic magma from the mantle in a previous melting event, or events (Schilling, 1973a, b, 1975; Brooks et al. 1976). O'Nions and Pankhurst (1974) proposed that the apparent heterogeneity may be produced by disequilibrium melting of the mantle. This hypothesis has been convincingly refuted by Hofmann and Hart (1978) on the basis of diffusion kinetics. O'Hara (1973, 1975) suggested that the mantle is homogeneous and that the trace element and isotopic differences are produced by fractional crystallization of the basaltic magmas in the mantle. This hypothesis seems unlikely; in order to explain the variation in Pb and Sr isotopic ratios in oceanic islands solely by magmatic crystallization requires that the process take place over a time span of

150 million years (Hofmann and Hart, 1978). It appears that Gast's "depletion theory" best explains the variation in trace element concentrations and isotopic ratios observed in oceanic basaltic lavas.

Mantle concentrations of Rb, Sr, K, Ti, V, Cr, Co, Ni, and Sc, as well as the rare earth elements, for the islands of Hawaii, Maui, and Kauai were calculated earlier. Examination of how these elements behave on melting reveals whether the source is enriched or depleted in each element after a melting event. Sr, Rb, K, Ti, and the rare earth elements are enriched in the liquid in a melting event with the result that the source is left depleted in these elements. V, Cr, Co, Ni, and Sc should be enriched in the mantle after a melting event because their concentrations in the liquid are depleted relative to the solid.

The concentrations of K, Rb, Sr, and the rare earth elements, which are depleted in the residuum in a melting event, are higher in the source for Hawaii lavas than the sources for Maui and Kauai lavas. This suggests the sources for Maui and Kauai lavas has been more affected by a previous melting event, or events, than the source for the Hawaii lavas. The concentrations of Sc, Ti, V, Cr, Co, and Ni are lower in the source for Hawaii lavas than the sources for Kauai and Maui lavas. With the exception of Ti, these elements suggest the Hawaii source has been less "depleted" by previous melting events than the sources for Kauai and Maui lavas because these elements, with the exception of Ti, are enriched in the residuum after a melt is removed.

The relationship between the Kauai and Maui mantle sources is less clear. The concentrations of K and Rb are higher in the source for Maui lavas, suggesting the Kauai source has been more affected by melt extraction. However, Sr and Ti concentrations are higher in the source for Kauai lavas and suggest the Maui source has been more affected by a previous melting event (or events). Sc, Cr, and Co, which should be enriched in the source in a melting event, suggest the Maui mantle is more depleted than the Kauai mantle. However, V, and Ni, which behave in the same manner, suggest the opposite. Approximately half of these elements suggest the source for Maui lavas has been more affected by a previous melting event, (or events), and half suggest the source for Kauai lavas has been most affected. The mantle rare earth element concentrations are approximately the same for the two islands (Figure 4-3) and it may be possible to conclude that the sources for Maui and Kauai lavas are probably very similar in composition and have been affected by similar amounts of previous melting. The small number of samples used in calculating the average mantle concentrations of the elements for Maui may help explain why the mantle concentrations of all the elements are not the same for the two islands.

There are several reasons which might explain why Ti does not seem to fit the model proposed. Ti may be enriched rather than depleted in the mantle in a melting event. This would be the case if there is a phase in the mantle, not accounted for, which holds Ti. Alternatively, one or all of the partitioning coefficients for Ti between the proposed mantle phases and liquid may be in error, which could lead to a misrepresentation of how Ti behaves in a melting event. A final

explanation is that other processes, besides melting of the mantle, have produced the different trace element concentrations between the islands. This explanation seems unfavourable in light of the fact that all the other trace elements seem to support a mantle melting explanation.

Despite the fact that the simple melting hypothesis seems to explain the variation of trace elements within the Hawaiian Islands very well, there are some problems with it when it is applied on a world scale. In the previous chapter, it was noted that the concentrations of Cr, Co, and Ni in Hawaiian lavas are very high compared with the concentrations observed in ocean floor basalts. This is inconsistent with the melting hypothesis which suggests that the concentrations of these elements should be higher in ocean floor basalts than the Hawaiian basalts because the source for the former is more depleted in the large ion lithophile elements than the source for the latter. This discrepancy may be accounted for in several ways:

1. ~~Processes~~ other than simple melting of the mantle have produced the trace element concentration differences.
2. The analysis of how these elements should behave in a melting event is not known precisely. Gast (1968) suggested that chrome-spinels and chrome-rich diopsides are possible mantle phases, and it is, therefore, not valid to assume Cr behaves as a trace element.

There is one further problem with the simple hypothesis that the variations in trace element concentrations are due to

previous melting events. If the assumption is made that the source for Hawaii lavas represents undepleted mantle, then only about 0.25 percent partial melting of this mantle is necessary to produce the trace element concentrations of the Kauai and Maui mantle using Shaw's (1970) equation. This equation relates the concentration in the residual solid to the concentration in the solid before melting and assumes all of the melt formed is removed from the mantle during magma separation. Other authors (e.g. Hawksworth et al., 1978) have come to similar conclusions using the trace element concentration differences between other oceanic islands. They found this value (0.25%) unreasonably low and postulated mantle "fluids" can move some trace elements. The calculated percentage of melting is however, probably fictitious because it does not reflect the way in which melts are made and removed from the mantle. For example, a portion of the mantle may undergo 20 percent partial melting, yet only a very small percentage of the total melt formed may be removed. When Shaw's (1970) equation is used to then estimate the percentage of melting necessary to produce the trace element heterogeneity, a fictitious value is obtained, because it assumes all of the melt is removed from the residuum during magma separation.

In summary, the differences in mantle source concentrations of the rare earth elements Rb, Sr, K, Sc, Cr, Co and Ni can best be explained in terms of a previous melting event or events having depleted the Maui and Kauai source relative to the mantle source for Hawaii lavas. There are some problems with using this simple explanation to explain the differences in concentration of some elements, particularly Cr, Ci and Ni, on a global scale.

Chapter Five Thesis Conclusions

The main objective of this study was to examine the Hawaiian Archipelago lavas for chemical heterogeneity which can only be related to mantle inhomogeneity. This required a careful analysis of the major element geochemistry to eliminate, on geochemical grounds, those lavas which might be differentiated. In addition, an approach was developed that relates the concentration of the trace elements observed in the lavas to the concentration in their source region. The following observations and conclusions can be made:

- (1) On the basis of the modal mineralogy, normative mineralogy and an alkali-silica diagram, all lavas may be generally classified as alkalic or tholeiitic. Thirteen of the lavas belong to the former category and ten to the latter.
- (2) On the basis of both modal and normative mineralogy as well as major and minor element geochemistry, six of the twenty-three lavas are differentiated. The modal and normative mineralogy show that one sample is a nephelinite. Of the remaining sixteen lavas, nine are tholeiitic basalts and eight are alkali basalts.
- (3) Most of the lavas seem to have similar trace element concentrations from one island to another. It would seem that only Rb, Sr, and the heavy rare earth element concentrations vary among islands.
- (4) The concentrations of the rare earth elements, as well as Hf, Rb, Sr, Ba, Sc, Ti, Zr, Ga, V, Th, and Zn

in Hawaiian lavas are similar to those found in other oceanic island lavas. The Cr, Co, Ni, and Cu concentrations in Hawaiian basaltic lavas tend to be higher than most other values observed in ocean island and ocean floor basalts. The Nb concentrations in Hawaiian lavas seem lower than those abundances found in oceanic island lavas and ocean floor basalts.

- (5) The rare earth element distributions in the differentiated lavas from the Hawaiian Islands can be modelled using the equation given by Gast (1968). The mineral proportions which must be removed from an alkali basalt to effect this modelling are 20 percent plagioclase, 30 percent olivine, and 50 percent clinopyroxene.
- (6) By making some assumptions about the mineralogy of the mantle, the melting proportions of the minerals, and the distribution of the rare earth elements in the mantle, hypothetical rare earth element trends were constructed using the equation of Shaw (1970). Comparison of the rare earth element trends in Hawaiian lavas with these hypothetical trends suggests all undifferentiated lava types are generated in a mantle with a limited garnet:clinopyroxene ratio.
- (7) The concentrations of La and Yb in Hawaiian lavas can be used in conjunction with a trace element

modelling equation (Shaw, 1970) to estimate the percentage of melting represented by each lava. Tholeiitic lavas are thought to represent between 8.5 and 14.3 percent melting. Alkali basalts may represent between 2.1 and 7.5 percent partial melting and nephelinites suggest melting percentages of between 0.7 and 2.2

- (8) The same calculations which give the percentages of melting for each lava also indicate the concentrations of the rare earth elements in the mantle source of each lava. The mantle source for Maui, and Kauai lavas are thought to have very similar rare earth element concentrations, substantially lower in concentrations than the source for Hawaii lavas. The source for the Oahu lavas is thought to be very heterogeneous in terms of rare earth element concentrations and encompasses the total range of concentrations shown by the Kauai, Maui and Hawaii sources.
- (9) By using the percentage of melting calculated for each lava from the rare earth element data the mantle concentrations of Rb, Sr, Ti, V, Cr, Sc, Co and Ni have been calculated. Kauai and Maui appear to have sources with lower average concentrations of K, Rb, and Sr, than lavas from Hawaii. V, Cr, Co, Ti and Ni concentrations seem lower in the source for Hawaii lavas than the sources for Maui and Kauai lavas. The average

Sc concentrations in the sources for Kauai and Hawaii lavas are lower in the source for the Maui lavas.

- (10) The apparent differences in the mantle source concentrations of the rare earth elements, Rb, Sr, K, Sc, Cr, Co and Ni can best be interpreted in terms of a previous melting event, or events, having depleted the Maui and Kauai source relative to the mantle source for Hawaii lavas. Ti concentrations are at variance with this interpretation. However, the behaviour of Ti in a melting event is not, as yet, precisely understood.

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Appendix I: Petrography and Sample Locations

Given are the detailed petrographic descriptions, names, and sampling locations for the Hawaiian lavas. The sample locations are shown in Figures 1-2, 1-3, and 1-4, Chapter I.

Sample names are based on modal mineralogy using the classification of Yoder and Tilley (1962). Petrographic criteria for distinguishing alkaline and tholeiitic rock types are given in Chapter 2. In those cases where petrographic criteria were difficult to find, and the modal name disagrees with the name based on the normative mineralogy, the rock is also given a name, in brackets, based on the norm.

HW100

Description: Fine-grained, porphyritic, hypocrystalline, basalt.

Euhedral olivine phenocrysts (Fog5-88) make up 22% of the rock, have an average length of 2.6 mm, and are rimmed with iddingsite. Matrix olivine and clinopyroxene are anhedral and make up 3% and 27% of the sample respectively. Both the olivine and pyroxene average about 0.15 mm in size.

Plagioclase is restricted to the matrix, makes up 24% of the sample, and has an average size of approximately 0.15 mm.

Opakes make up 4% of the sample, are subhedral to anhedral, and average 0.03 mm in size. Glass makes up the remaining 20% of the rock.

Name: Alkali Basalt.

Location: Kauai. The sample was collected 1.9 km. west of Kaumakani, towards Waimea, along highway 50, close to where a bridge crosses over the highway. It belongs to the Koloa Series.

HW102

Description: Microporphyritic, holocrystalline, basalt.

Olivine phenocrysts (Fo_{80-85}) make up 25% of the rock, and average 0.18 mm in length. They are euhedral and have an iddingsite alteration rim. Smaller grains may be completely altered. Matrix olivine makes up 5% of the sample, averages about 0.08 mm in size, and is anhedral. Clinopyroxene of indeterminate composition, makes up about 34% of the sample, is anhedral, and averages about 0.08 mm in length.

Nepheline up to 1.70 mm in size occurs in the ground-mass and poikilitically encloses clinopyroxene and olivine. Grains average about 1.0 mm in size and make up 26% of the sample. About 2% of the sample is plagioclase averaging about 0.12 mm in size.

Opaques make up about 3% of the sample and glass about 5%.

Name: Alkali Basalt.

Location: Kauai. The sample comes from a site overlooking Hanapepe along highway 50, and belongs to the Koloa Series.

HW103

Description: Holocrystalline, porphyritic, basalt.

Olivine phenocrysts (Fo_{87}) make up 28% of the sample, are euhedral, and average 0.30 mm. Most olivine grains have a rim of iddingsite alteration. A small percentage of olivine occurs in the matrix.

Clinopyroxene is restricted to the matrix and makes up 35% of the sample. It is anhedral and averages about 0.05 mm in length.

Plagioclase (An_{54}) makes up 28% of the sample, is anhedral, and occurs in the form of long thin laths. Some grains are zoned. The average length of the grains is 0.24 mm. Extremely fine nepheline grains (0.05 mm) make up about 2% of the matrix.

Opaques make up less than 5% of the sample, are fairly euhedral, and average 0.07 mm in length.

In addition to iddingsite alteration a small amount of carbonate was found in the matrix of the thin section examined.

Name: Alkali Basalt.

Location: Kauai. Same location as HW102.

HW104

Description: Fine-grained, porphyritic, holocrystalline, basalt.

Olivine phenocrysts (Fo_{88}) make up 33% of the sample. They are euhedral and often surrounded by a thin rim of iddingsite. Phenocrysts reach 1.30 mm in length but average about 0.35 mm.

Matrix clinopyroxene, and small amounts of matrix olivine form 37% of the sample. Grains are subhedral. The clinopyroxenes average 0.07 mm, while the olivine grains vary from 0.02 mm to phenocryst size.

Plagioclase grains form about 25% of the sample and are anhedral. The average grain size is 0.07 mm and the composition is probably An_{38} .

Opaques have an average size of 0.10 mm, are euhedral, and constitute about 5% of the sample.

Along with the minor alteration of olivine to iddingsite, some olivine grains show minor hematite as well.

Name: Alkali Basalt.

Location: Kauai. The sample comes from an outcrop on the south side of highway 580, 4.8 mm from the junction between highways 580 and 56 near Wailua. It belongs to the Koloa Series.

HW106

Description: Fine-grained, holocrystalline, porphyritic, basalt.

Anhedral to euhedral olivine phenocrysts (For_{87}) make up 28% of the sample. The grains average 0.75 mm in size, and most show thin iddingsite rims. Skeletal olivine grains occur as phenocrysts.

Plagioclase (An_{60}) is restricted to the matrix and is subhedral to anhedral. The longest grains are 0.50 mm in length and the average about 0.14 mm. Plagioclase makes up about 36% of the rock.

Clinopyroxene occurs only in the matrix, is anhedral, and has an average length of 0.03 mm. Most grains do not exceed 0.30 mm in size. Clinopyroxene makes up 32% of the rock.

Opaques make up 4% of the sample, are anhedral, and average 0.05 mm in length.

Alteration is restricted to iddingsite on the rims of olivine grains.

Name: Olivine Tholeiite

Location: Kauai. The sampling location is approximately 1 km west on the shoreline from the northern end of highway 56. The sample comes from the Waimea Canyon Series lavas.

HW107

Description: Holocrystalline, fine-grained, porphyritic, basalt.

Euhedral olivine phenocrysts (Fo_{87}) make up 25% of the sample. The largest grains are about 1.70 mm long, but average 0.60 mm. There is a rim of iddingsite alteration around most of the olivine grains.

Orthopyroxene (En_{77}) phenocrysts make up 7% of the sample. They are subhedral, and have an average length of 0.20 mm. The largest grains are about 1.30 mm. Orthopyroxene appears to mantle some of the olivine grains.

Plagioclase (An_{57}) occurs only in the matrix, and makes up 40% of the sample. The grains are mostly anhedral and the average length is 0.10 mm.

Clinopyroxene is the only pyroxene in the matrix. The grains are anhedral, measure 0.05 mm, and make up 25% of the sample.

Opaques make up 3% of the sample, are anhedral, and average about 0.04 mm in length.

Name: Olivine Tholeiite.

Location: Kauai. Same location as for HW106.

HW109

Description: Fine-grained, holocrystalline, vesicular, and porphyritic.

Euhedral olivine phenocrysts (For_{88}) average 0.30 mm in size, and make up 15% of the sample. Most olivine is surrounded by a rim of iddingsite.

Anhedral augite occurs in the matrix, averages 0.09 mm in length, and makes up 41% of the sample. The augite is

purplish brown in color suggesting a titaniferous variety.

Olivine in the matrix makes up 10% of the sample, is anhedral, and has an average grain length of 0.10 mm.

Nepheline makes up 28% of the sample. The grains are anhedral, average 0.66 mm in size, and surround the pyroxene and olivine grains.

Anhedral opaques make up 6% of the sample, and average 0.10 mm in size.

Nodules occurring in the rock (but separated from the rock portions analyzed) were examined petrographically. They contain large nepheline grains averaging 1.44 mm in size. Titaniferous augite forms small blebs in the nepheline grains and also forms euhedral grains averaging 0.15 mm in size. These two minerals plus olivine occur in the host rock, but olivine is absent in the nodule.

Name: Alkali Basalt (Nephelinite).

Location: Kauai. Sample comes from the cinder cone Puu Hunihuni which is near Koloa.

HW115

Description: Fine-grained, holocrystalline, porphyritic, and vesicular.

Olivine phenocrysts (Fe_{88}) make up 15% of the sample. The grains are euhedral, and average about 1.60 mm in length. The largest grains are 7.0 mm long.

Augite phenocrysts make up 17% of the sample. The grains are euhedral and have an average length of 1.20 mm but some are as long as 3.0 mm.

Clinopyroxene and olivine in the matrix make up 33% and 2% of the sample respectively. The clinopyroxene is anhedral and averages about 0.02 mm in length whereas the olivine grains are also anhedral but average 0.04 mm in size.

Plagioclase (An_{54}) makes up 30% of the sample. The grains are subhedral to anhedral and average 0.05 mm in length.

Euhedral to subhedral opaques make up 3% of the sample and average 0.08 mm in length.

There is no alteration visible in thin section.

Name: Olivine Tholeiite.

Location: Maui. The sample was collected 7.5 km north of Olowalu on highway 30. It comes from the Wailuku Volcanic Series.

HW116

Description: Holocrystalline, pilotaxitic, equigranular, and fine grained.

Plagioclase (An_{44}) makes up about 75% of the sample. The grains are subhedral to anhedral, equigranular, and average about 0.40 mm in length. The plagioclase laths are all oriented in the same direction producing a pilotaxitic texture.

Olivine forms about 6% of the sample. The grains are euhedral and average 0.28 mm in length.

Opaques make up about 7% of the sample. They are euhedral to subhedral, and average 0.06 mm in length.

Anhedral clinopyroxene averages 0.01 mm in size and makes up 12% of the sample.

The sample is fresh in thin section.

Name: Alkali Basalt.

Location: Maui. The sample was collected at McGregor Point on highway 30. It belongs to the Honolua Series volcanics.

HW117

Description: Fine-grained, highly vesicular, porphyritic, and hypocrystalline basalt.

Euhedral augite phenocrysts, averaging 2.0 mm in length, make up 29% of the sample. The phenocrysts show some zoning and brown pleochroism.

Olivine phenocrysts (Fe_{80}) make up about 10% of the sample. The grains are euhedral and average 1.0 mm in length.

Matrix clinopyroxene makes up about 20% of the sample. It is anhedral and averages 0.06 mm in size. Matrix olivine makes up about 8% of the sample, is anhedral, and averages 0.06 mm in size.

Anhedral to subhedral plagioclase (An_{54}) occurs only in the matrix. It makes up 28% of the sample, and averages 0.14 mm in length.

Opaques are euhedral, make up about 4% of the sample, and average 0.07 mm in length. Glass makes up about 1% of the sample and is most apparent near vesicles. The vesicles average 2 mm in size but are as large as 1.2 cm. They make up 35% of the sample by volume.

Name: Olivine Tholeiite (Alkali Basalt).

Location: Maui. The sample is from the 1790 flow of Haleakala Volcano, along the road to La Perouse Bay.

HW118

Description: Fine-grained, holocrystalline, and porphyritic.

Euhedral augite phenocrysts make up 30% of the sample. They have an average size of 1.9 mm and can reach up to 8 mm in length. They also show some light brown pleochroism and some zoning. The centers of most augite crystals have very few inclusions, but toward the outside there is usually a prominent line outside of which the crystal is full of inclusions.

Euhedral olivine phenocrysts (Fe_{86}) average 1.0 mm in length but some grains can reach 3 mm in size. Olivine phenocrysts make up 15% of the sample.

Plagioclase (An_{59}) occurs only in the matrix, is anhedral, makes up 24% of the rock, and averages 0.15 mm in length.

Olivine and clinopyroxene make up 6% and 19% of the matrix respectively. Both are anhedral and have an average size of 0.06 mm.

Opaques make up 6% of the sample, are anhedral to subhedral and average 0.05 mm in length. Minor hematite in the matrix suggests slight alteration.

Name: Alkali Basalt.

Location: Maui. The sample comes from the Haleakala Crater, very close to the summit and visitor center.

HW119

Description: Fine-grained, pilotaxitic, and porphyritic.

Three minerals occur as phenocrysts. Olivine phenocrysts make up 4% of the rock, are anhedral, and average 1.6 mm in size. Augite phenocrysts are subhedral, average 1.80 mm in length, and make up 3% of the rock. Hornblende phenocrysts are anhedral, average 1.68 mm in length and make up 2% of the rock.

The hornblende phenocrysts do not seem to have been in equilibrium with the melt. Several of the olivines have augite mantling them.

Olivine in the matrix makes up about 5% of the sample. The grains are anhedral, and average 0.04 mm in size. Clinopyroxene in the matrix makes up 17% of the sample, is anhedral, and has an average grain size of less than 0.01 mm.

Plagioclase (An_{49}) makes up 60% of the sample. The grains are equigranular, subhedral to anhedral, and average 0.30 mm in size. The grains are oriented, producing a pilotaxitic texture.

Opakes make up 10% of the sample, are subhedral, and average 0.30 mm in size.

The sample is very fresh in thin section.

Name: Alkali Basalt

Location: Maui. Same location as for HW118.

HW122

Description: Fine-grained, vesicular and porphyritic basalt.

Euhedral olivine phenocrysts (Fo_{88}) have an average size of 0.80 mm and make up 23% of the sample. Augite also forms euhedral phenocrysts which make up 7% of the sample and average 0.60 mm in length. The smaller phenocrysts form glomeroporphyritic masses. Phenocrysts of plagioclase (An_{53}) make up less than 1% of the sample. These tend to be glomeroporphyritic, euhedral, and average about 0.16 mm in length.

Olivine and clinopyroxene form 7% and 25% of the matrix respectively. Both are anhedral and average about 0.02 mm in size. Plagioclase in the matrix (An_{50}) makes up 30% of the sample, is anhedral, and averages 0.07 mm in size.

Anhedral opaques average 0.01 mm in size and make up 7% of the sample.

There is no alteration apparent in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample comes from the January 1974 flow at the end of the Chain of Craters Road and is a lava from Mauna Loa Volcano.

HW123

Description: Fine-grained, holocrystalline, microporphyritic, basalt.

Plagioclase phenocrysts (composition varies from An_{76} for larger grains to An_{68} for grains approaching matrix size) make up 12% of the sample, are euhedral, and average 0.54 mm in length.

Olivine phenocrysts (Fo_{87}) make up 6% of the sample, are euhedral, and have an average size of 0.35 mm. Augite phenocrysts make up 4% of the rock, are euhedral, and have an average size of 0.22 mm.

The matrix is composed of anhedral plagioclase, anhedral clinopyroxene, and opaques. The matrix plagioclase makes up 33% of the sample, and has an average grain size of about 0.01 mm. Clinopyroxene in the matrix makes up 38% of the sample, and has an average grain size of 0.01 mm.

Opaques make up 7% of the sample, have an average grain size of 0.03 mm, and are subhedral to anhedral.

The sample is fresh in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample comes from the southwest side of highway 11, 1.6 km south of the junction with the branch road to Hoopulua and Milolii. It is from the 1926 flow from Mauna Loa.

HW124

Description: Fine-grained, holocrystalline, pilotaxitic, basalt.

Olivine phenocrysts (Fo_{87}) make up 4% of the rock sample, are anhedral, and have an average size of 0.30 mm. They occur, along with small plagioclase phenocrysts, as small glomeroporphyritic masses. Euhedral, zoned plagioclase phenocrysts (An_{86}) make up 16% of the sample, and have an average length of 1.7 mm.

Matrix clinopyroxene makes up 25% of the sample. It is anhedral and has an average size of 0.03 mm. Matrix olivine

makes up 16% of the sample. It is anhedral, and has an average length of 0.04 mm.

Plagioclase in the matrix makes up 40% of the sample. The grains are subhedral to anhedral, and have an average length of 0.16 mm. The laths show a pilotaxitic texture.

Opaques are anhedral, average 0.04 mm in length, and make up 9% of the sample.

The sample appears fresh in thin section.

Name: Olivine Tholeiite (Alkali Basalt).

Location: Hawaii. The sample comes from the east side of highway 25, 1.8 km from the junction with highway 19 near Waimea. It belongs to the Pololu Series lavas.

HW125

Description: Fine-grained, holocrystalline, porphyritic basalt.

Olivine phenocrysts make up about 1% of the rock. The grains are euhedral, and have an average length of 0.50 mm. Most grains are surrounded by a rim of iddingsite.

Euhedral augite phenocrysts make up 10% of the sample. The grains average 0.80 mm in size, show a light yellow brown phenocrism, and exhibit some zoning.

Plagioclase phenocrysts (An_{68}) are euhedral, average 2.1 mm in length, and make up 25% of the sample. Some of the phenocrysts are highly zoned.

Matrix olivine and clinopyroxene make up 17% of the sample. Both exhibit anhedral grains which average 0.02 mm in length.

Matrix plagioclase (An_{55}) make up 38% of the sample.

The grains are anhedral and average 0.12 mm in length.

Opaques make up 9% of the sample, are subhedral to anhedral, and average 0.04 mm.

Apart from the alteration rims on olivine grains, the sample is fresh.

Name: Olivine Tholeiite.

Location: Hawaii. The sample comes from the east side of highway 25, 2.4 miles north of the junction with highway 19 near Waimea. It belongs to the Pololu Series.

HW126

Description: Fine-grained, holocrystalline, and porphyritic.

Euhedral to subhedral olivine phenocrysts (Fo_{85}) average 0.78 mm in size and make up 18% of the rock.

Plagioclase phenocrysts (An_{76}) make up 14% of the sample, are euhedral, and average 0.54 mm in length. These crystals often show some zoning.

Olivine in the matrix makes up about 5% of the sample, is anhedral, and averages 0.02 mm in length. Plagioclase (An_{58}) in the matrix makes up 39% of the sample. It is anhedral, and averages 0.12 mm in length. Clinopyroxene in the matrix makes up about 20% of the sample, is anhedral, and has an average size of 0.01 mm.

Subhedral to anhedral opaques make up 4% of the sample, occur in the matrix, and average 0.03 mm in length.

Except for minor alteration of olivine grains, the sample is fresh in thin section.

Name: Olivine Tholeiite (Alkali Basalt).

Location: Hawaii. Sample location is 6.9 km north of the junction between highway 25 and highway 19. It belongs to the Hamakua Series.

HW127

Description: Fine-grained, holocrystalline, and porphyritic.

Olivine phenocrysts (Fe_{88}) are euhedral to anhedral. They have an average size of 1.5 mm and make up 25% of the rock. Euhedral augite phenocrysts make up 18% of the sample, have an average size of 0.9 mm, and show a light yellow brown pleochroism. Plagioclase phenocrysts (An_{82}) are euhedral, average 0.4 mm in length, and make up 3% of the sample.

Olivine makes up at least 1% of the matrix. It is anhedral, and has an average grain size of 0.01 mm. Clinopyroxene in the matrix is anhedral, has an average size of 0.01 mm, and makes up 22% of the sample. Plagioclase in the matrix (An_{70}) has an average size of about 0.01 mm and makes up 24% of the sample.

Opagues in the matrix are subhedral, average 0.02 mm in length and make up 7% of the sample.

There is no alteration apparent in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample location is 5.6 km south of the junction between Saddle Road and highway 190. This is the same site as U.S.G.S. sample site 17. This sample belongs to the Hamakua Series.

HW128

Description: Fine-grained, holocrystalline, and pilotaxitic.

Plagioclase (An_{49}) makes up 68% of the sample. The grains are anhedral, average 0.14 mm in size, and form a pilotaxitic

texture.

Anhedral clinopyroxene makes up 15% of the sample, and averages 0.02 mm in size. Euhedral to anhedral olivine, averaging 0.04 mm in size makes up 7% of the sample.

Opaques make up 10% of the sample, are subhedral to anhedral, and average 0.03 mm in length.

The sample is fresh in thin section.

Name: Alkali Basalt.

Location: Hawaii. The sample location is 11.4 km south of the junction between Saddle Road and highway 190. It is a lava from Mauna Kea Volcano and belongs to the Hamakua Volcanic Series.

HW129

Description: Fine-grained, holocrystalline, vesicular and porphyritic.

Olivine phenocrysts (Fog7) make up less than 1% of the sample. The grains are euhedral, and average 0.40 mm in size.

Olivine makes up 3% of the matrix, averages 0.04 mm in size, and is anhedral. Clinopyroxene occurs in the matrix as anhedral grains averaging 0.04 mm, and makes up 42% of the sample. Plagioclase (An₅₀) forms anhedral grains in the matrix averaging 0.10 mm in length. It makes up 48% of the sample.

Opaques make up 7% of the sample, are anhedral, and average 0.03 in size.

The sample is fresh in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample location is 17.6 km south of the

junction between highway 190 and Saddle Road. It is a lava from Mauna Loa Volcano.

HW130

Description: Medium-grained, holocrystalline, vesicular, and porphyritic.

Olivine phenocrysts (Fe_{80}) make up 35% of the sample. The grains are euhedral to anhedral, and average 1.6 mm in size. A few grains have a "skeletal" texture. Pigeonite tends to surround the grains and olivine does not occur in the matrix.

Clinopyroxene in the matrix forms 35% of the sample. It occurs as anhedral grains that average 0.10 mm in size. Plagioclase (An_{54}) occurs as anhedral to subhedral grains that average 0.22 mm in length. It forms about 28% of the rock.

Opaques make up 2% of the sample, are anhedral, and average 0.07 mm in size.

The sample is fresh in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample location is 18.7 km south of the junction between highway 190 and Saddle Road on highway 190. It is a lava from Mauna Loa Volcano.

HW131

Description: Medium-grained, holocrystalline, vesicular, and porphyritic.

Euhedral olivine phenocrysts (Fe_{69}) averages 1.7 mm in size and makes up 1% of the sample.

Matrix olivine is anhedral, averages 0.15 mm in length,

and makes up 4% of the sample. Clinopyroxene in the matrix is anhedral, averages 0.15 mm in length, and makes up 40% of the sample. Matrix plagioclase (An_{65}) forms 48% of the sample. The grains are anhedral and average 0.25 mm in size.

Opaques occur in the matrix as anhedral grains averaging 0.15 mm in size and make up approximately 7% of the rock.

The sample is fresh in thin section.

Name: Olivine Tholeiite.

Location: Hawaii. The sample location is 20.5 km south along highway 190 from the junction with Saddle Road. It is from the 1859 eruption of Mauna Loa.

HW133

Description: Fine-grained, holocrystalline, and porphyritic.

Olivine phenocrysts (For_{88}) form 1% of the sample. The crystals are euhedral and average 0.66 mm in size.

Matrix olivine is anhedral, averages 0.09 mm in size, and forms 10% of the sample. Clinopyroxene forms anhedral grains in the matrix averaging 0.03 mm in length. It makes up 43% of the sample. Anhedral plagioclase (An_{44}) in the matrix averages 0.11 mm in size, and makes up 40% of the rock.

Opaques make up 6% of the sample, are anhedral, and average 0.01 mm in length.

The sample is fresh in thin section.

Name: Alkali Basalt.

Location: Hawaii. The sample location is approximately 32.6 km south on highway 190 of the junction with Saddle Road. It comes from the 1801 Flow of Kaupulehu Volcano.

Appendix II Laboratory Procedure

Sample Preparation

As a first step in the preparation procedure, thin sections were made of all samples, and examined to confirm their freshness. The powders used in all chemical analyses were prepared by first removing any weathering surfaces from the rock samples. Those rocks containing "nodules" were carefully prepared so as to remove the foreign material from the lava being analyzed. The samples were crushed to coarse gravel size chips and then powdered to 200 mesh in a tungsten carbide Bleuler mill. All equipment was meticulously washed with distilled water and acetone after each sample in order to minimize contamination.

Analysis for Rb and Sr

The Rb and Sr concentrations were determined by X-ray fluorescence analysis at Carleton University. Rb/Sr ratios were determined on boric acid backed pellets (Doering, 1968)¹ and analyzing on a Siemens Kristolloflex 2H using a lithium fluoride crystal and a molybdenum tube. Mass absorption coefficients were measured directly using a method described by Norrish and Chappell (1977)². The analytical uncertainties are considered to be $\pm 2\%$ for the Sr concentrations and ± 1 ppm for Rb.

¹ Doering 1968. A Rapid Method For Measuring the Rb/Sr ratio in Silicate Rocks, in Geological Survey Research, 1968. United States Geological Survey Professional Paper 600-C, Pages C164 to C168.

² Norrish, K. and Chappell, B.W. 1979. X-Ray Fluorescence Spectrometry in Physical Methods in Determinative Mineralogy. Edited by Zussman, J. 2nd ed. Academic Press, London, 1977. Pages 201 to 272.

Analysis for La, Ce, Nd, Sm, Eu,
Tb, Yb, Lu, Hf, Sc, Co, and Th

Samples were sealed in quartz ampoules, and irradiated at the McMaster Nuclear Reactor Facility at a flux of about 1×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ for 24 hours. Counting was done at Erindale College using a 4096 channel analyzer in conjunction with a Ge(Li) detector. The first counting was done after 10 days cooling, at which time La, Lu, Nd, Sm, and Yb were determined via ^{140}La , ^{177}Lu , ^{147}Nd , ^{152}Sm , and ^{175}Yb . Samples were counted a second time, 40 days following irradiation for determination of Ce, Co, Eu, Hf, Sc, Tb, and Th via ^{141}Ce , ^{60}Co , ^{152}Eu , ^{181}Hf , ^{46}Sc , ^{160}Tb , and ^{233}Pa . Accuracy and precision are estimated to be ± 1 to 5% for Sm, Yb, La, Ce, Hf, Sc, Co, and Eu, and ± 6 to 10% for Lu, Nd, Th, and Tb.

Analysis for the Major Element Oxides,
Nb, Zr, Pb, Ga, Zn, Ni, Cu, Ba, V, and Cr

The major element analyses were done by atomic absorption on a Perkin Elmer 360 at The Memorial University of Newfoundland. 0.1 grams of sample were dissolved in 5.0 ml. of hydrofluoric acid and 50 ml. of saturated boric acid solution and made up to 200 ml. with distilled water. Samples were compared with a suite of standards with approximately the same concentrations as the samples.

Analysis for Nb, Zr, Pb, Ga, Zr, Ni, Cu, Ba, V, and Cr was carried out at The Memorial University of Newfoundland on a Phillips 1450 automatic X-ray fluorescence spectrometer. The peak intensities were compared with those of U.S.G.S. rock standards. The correction for mass absorption was based on measurements of the Compton scatter peak of the silver tube. Precisions and accuracy is believed to be

$\pm$ 6 to 12 ppm for V, Cr, Zn, and Ni, $\pm$ 2 to 6 ppm for Cu, Ga, Zr, and Nb, $\pm$ 1 to 14 percent for Ba and $\pm$ 50 to 100 percent for Pb.

Appendix III Sample Calculations

This appendix acts as a guide to the calculations discussed in chapter four.

Fractional Crystallization

In Figure 4-1 the rare earth element concentrations of sample HW116 are shown along with the original undifferentiated concentration of HW116 normalized to chondritic meteorites. Calculation of the latter concentrations from the former is illustrated here using Yb. The calculation of the original undifferentiated concentrations of the other elements is done in a similar manner. From Gast (1968) we know that

$$\frac{C^L}{C^0} = F^{(K-1)} \quad (\text{Eq. 1})$$

where: F = the weight fraction of liquid remaining.

K = the bulk distribution coefficient. It is an average of individual distribution coefficients weighted according to the proportion of phases crystallizing.

Since the percentage of crystallization was estimated to be 78%, F must be:

$$F = 1 - .78 = .22.$$

K is calculated using the distribution coefficients for Yb given in Table 4-1 and by assuming the weight fractions of olivine, clinopyroxene, and plagioclase are .30, .50, and .20 respectively. The calculation is as follows:

<u>Mineral</u>	<u>Distribution Coefficient Yb</u>	<u>Weight Fraction</u>	<u>Total</u>
Ol	1.1×10^{-2}	.30	0.0033
Cpx	2.6×10^{-1}	.50	0.1315
Plag	9.5×10^{-2}	.20	<u>0.0190</u>
K = Bulk Distribution Coefficient =			<u>0.1538</u>

The concentration of Yb in sample HW116 is 4.2 ppm (Table 3-3), the unknown quantity is the original undifferentiated concentration. From equation 1:

$$C^0 = \frac{C^L}{F(K-1)}$$

Substituting

$$C^0 = \frac{4.22 \text{ ppm}}{.22 (.154-1)} = \frac{4.22}{3.60} = 1.17 \text{ ppm}$$

In order to plot this concentration in Figure 4-1a, it must be normalized to chondrites as follows:

$$\frac{C^0}{\text{Concentration Chondrites}} = \frac{1.17 \text{ ppm}}{0.22 \text{ ppm}} = 5.32.$$

Partial Melting

To illustrate how the curves in Figure 4-2 were arrived at, the Yb data point, for a mantle with 10% Gar and 10% Cpx and representing 20% partial melting is calculated from Shaw (1970) we know:

$$\frac{C^L}{C^0} = \frac{1}{D^0 + F(1-P)} \quad (\text{Eq. 2})$$

where: $\frac{C^L}{C^0} = \frac{\text{Concentration in the liquid}}{\text{Concentration in the original solid}}$

$$D^0 = \frac{x^a}{K^{L/a}} + \frac{x^b}{K^{L/b}} + \dots \text{ and } x^a = \text{weight fraction of phase}$$

$K^{L/a}$ = liquid/crystal partitioning coefficient.

$$P = \frac{p^a}{K^{L/a}} + \frac{p^b}{K^{L/b}} + \dots \text{ and } p^a = \text{fraction of melt contributed by phase.}$$

$K^{L/a}$ = the liquid/crystal partitioning coefficient.

The phase proportions, phase melting proportions, and partitioning coefficients used in calculating D^0 and P are given in Table 4-2 and used as follows:

	OL	Opx	Cpx	Gar					
D_{Yb}^0	$\frac{0.50}{882}$	$+$	$\frac{0.30}{52.0}$	$+$	$\frac{0.10}{3.80}$	$+$	$\frac{0.10}{0.26}$	$=$	0.4153
P_{Yb}	$\frac{0.06}{882}$	$+$	$\frac{0.20}{52.0}$	$+$	$\frac{0.30}{3.80}$	$+$	$\frac{0.44}{0.26}$	$=$	1.7752

Substituting into Shaw's equation:

$$\begin{aligned} \frac{C^L}{C^0} &= \frac{1}{D^0 + F(I - P)} \\ &= \frac{1}{0.4153 + 0.20(1 - 1.7752)} \\ &= 3.84 \end{aligned}$$

The mantle's concentration in rare earth elements is 1.45 times chondrites. Because the chondritic Yb concentration is 0.220 ppm the melt's concentration is:

$$\begin{aligned} C^L &= C^0 \times 3.84 \\ &= 0.220 \text{ ppm} \times 1.45 \times 3.84 \\ &= 1.23 \text{ ppm.} \end{aligned}$$

Since Figure 4-2 is normalized to chondrites the calculation may be simplified:

$$\frac{0.220 \times 1.45 \times 3.84}{0.220 \text{ ppm}} = 5.57.$$

Estimation of Percent Melting and Mantle Concentrations

To illustrate estimation of the percent partial melting sample HW110, an alkali basalt is used as the appropriate garnet and clinopyroxene percentages are 11 and 9 respectively. We know from Shaw (1970):

$$\frac{C_{La}^L}{C_{La}^O} = \frac{1}{D_{La}^O + F (I - P_{La})}$$

and

$$\frac{C_{Yb}^L}{C_{Yb}^O} = \frac{1}{D_{Yb}^O + F (I - P_{Yb})}$$

There are three unknowns C_{La}^O , C_{Yb}^O , and F , but only two equations. By assuming the mantle's concentrations of rare earth elements is chondritic, the following relationship can be derived:

$$\frac{\frac{C_{La}^L}{C_{La}^O}}{\frac{C_{Yb}^L}{C_{Yb}^O}} = \frac{\frac{C_{La}^L}{x \cdot 0.329}}{\frac{C_{Yb}^L}{x \cdot 0.220}} = \frac{\text{Lava La normalized to chondrites}}{\text{Lava Yb normalized to chondrites}} = R$$

where x = the unknown mantle concentration factor of rare earth elements in terms of chondrites

0.329 = the chondritic concentration of La

0.220 = the chondritic concentration of Yb

R = the ratio of normalized La to normalized Yb.

Solving for F by division:

$$\frac{\frac{1}{D_{La}^O + F (I - P_{La})}}{\frac{1}{D_{Yb}^O + F (I - P_{Yb})}} = R$$

$$\frac{D_{Yb}^0 + F(1-P_{Yb})}{D_{La}^0 + F(1-P_{La})} = R$$

$$D_{Yb}^0 + F(1-P_{Yb}) = R \times D_{La}^0 + R \times F(1-P_{La})$$

$$D_{Yb}^0 - R D_{La}^0 = RF(1-P_{La}) - F(1-P_{Yb})$$

$$D_{Yb}^0 - R D_{La}^0 = F(R(1-P_{La}) - (1-P_{Yb}))$$

$$F = \frac{D_{Yb}^0 - R D_{La}^0}{R(1-P_{La}) - (1-P_{Yb})}$$

And solving for x, which is the mantle's concentration of rare earth elements:

$$\frac{C_{La}^L}{C_{La}^0} = \frac{1}{D_{La}^0 + F(1-P_{La})}$$

$$\text{since } C_{La}^0 = x \cdot 0.329$$

$$x \cdot 0.329 = C_{La}^L \times (D_{La}^0 + F(1-P_{La}))$$

$$x = \frac{C_{La}^L \times (D_{La}^0 + F(1-P_{La}))}{0.329}$$

To calculate F and x for sample HW100, P_{Yb} , P_{La} , D_{Yb}^0 and D_{La}^0 are necessary. The data given in Table 4-2 is used as follows:

	O1	Opx	Cpx	Gar	
D_{Yb}^0	$= \frac{0.50}{882}$	$+ \frac{0.30}{52.0}$	$+ \frac{0.09}{3.80}$	$+ \frac{0.11}{0.26}$	$= 0.4512$
P_{Yb}	$= \frac{0.06}{882}$	$+ \frac{0.20}{52.0}$	$+ \frac{0.30}{3.80}$	$+ \frac{0.44}{0.26}$	$= 1.7752$
D_{La}^0	$= 0.00467$				
P_{La}	$= 0.0144$				

The La and Yb concentrations in Sample HW100 are 34 and 1.3 ppm and the chondrite normalized values are 103 and 5.9 respectively.

$$\frac{\text{Normalized La}}{\text{Normalized Yb}} = R = \frac{103}{5.9} = 17.5$$

Substituting and solving for F:

$$\begin{aligned} F &= \frac{D_{Yb}^0 - R \cdot D_{La}^0}{R(1-P_{La}) - (1-P_{Yb})} \\ &= \frac{0.451 - 17.5 \times 0.00467}{17.5(1 - 0.0144) - (1 - 1.7752)} \\ &= 0.0205 \text{ or } 2.0\% \text{ melting.} \end{aligned}$$

This corresponds to the lowest percentage of melting obtained for any alkali basalt. Solving for the mantle's concentration in rare earth elements

$$\begin{aligned} x &= \frac{C_{La}^L}{0.329} \times D_{La}^0 + F(1-P_{La}) \\ x &= 103 \times (0.00467 + 0.0205(1 - 0.0144)) \\ &= 2.56 \end{aligned}$$

The concentration of rare earth elements in the mantle where this lava was generated is calculated to be 2.56 times chondrites.

END

08 12 80

FIN