This is to certify that the

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Dating Quaternary Basalts from Hawaii

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Susan C. Schock

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A METHOD FOR DATING QUATERNARY BASALTS FROM HAWAII

By

Susan C. Schock

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ABSTRACT

A METHOD FOR DATING QUATERNARY BASALTS FROM HAWAII

By

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Uranium-thorium disequilibrium systematics have been used to do quaternary geochronology with speleothems, carbonates and ore bodies. Presently available techniques for chronology, such as K-Ar, cannot give ages for complicated stratigraphic sequences. The islands of Hawaii offered a site where rocks of complicated stratigraphy were uncontaminated by continental rocks. These rocks were excellent candidates upon which to test the application of the uranium-thorium method for basaltic rocks.

In attempting to apply the principles of the method to basaltic lavas, problems arose with incomplete silicate dissolution and iron concentrations, which interfered with the isolation of the uranium and thorium. Yields of both elements were low, which proved to be devastating when dealing with rocks with very small initial concentrations of uranium and thorium. More complete dissolutions are necessary and solvent extractions to overcome the interferences to the method are suggested.

DEDICATION

TO MIKE

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INTRODUCTION

In the study of young rock systems, such as Quaternary basalts, available geochronologic techniques have been unable to help sort out complicated stratigraphic sequences. The potassium-argon dating methods for dating young rocks have been found to have large errors due to small amounts of excess Argon (Damon, 1969; Dalrymple and Lanphere, 1969; Funkhouser, Barnes, and Naughton, 1966). Also, problems of necessary analytical accuracy due to the great length of the half-life of ^{40}K and low ^{40}Ar (rad) factors can cause Quaternary rocks of widely varying ages to appear contemporary (McDougall, 1961; Ku, 1976).

^{14}C dates are limited to occurrences of carbonaceous materials such as wood or charcoal, ashfall or tuff in rocks younger than 40,000 years. The correlation of K-Ar dates with ^{14}C dates have not helped with these problems.

The purpose of this study, therefore, was to determine if uranium-thorium disequilibrium systematics can be used to date Quaternary basaltic rocks. The method has been used successfully for sediments, speleothems, and ore bodies. It has been used for silicic, volcanic rocks by Baranowski (1977) in Long Valley, California. The uranium-thorium systematics method is useable for rocks up to 300,000 years old. Previous work by Baranowski (1977) and Lively (1978) indicate that the most reliable answers are obtained from those rocks which are between 10,000 and 200,000 years old. Basaltic rocks, especially those composed mainly of ferromagnesium minerals, were expected to present greater problems due to the fact that their initial content of uranium and thorium would not be as great as that of the silicic rocks. This proved to be true.

In order to test the validity of this idea, the youngest of the Hawaiian islands, Hawaii itself, was chosen. The rocks of this island are uncontaminated with continental rocks. Continental rock sequences would be more complex in composition since they are accumulated, deposited and accreted from a wide variety of sources. They tend to contain many more silicic minerals. The partitioning of uranium into lighter, more silicic rocks is preferable (Cherdyntsev and Senina, 1970; 1973; Nishimura, 1970). A small amount of contamination from uranium enriched continental rock would therefore further complicate the chemical processing of the rock samples. Since rocks which were not subject to this problem were available in Hawaii, it was the logical choice. Furthermore, the rocks fall into the chronologic range of the chosen method. Lastly, the flows chosen for sampling were thick enough that we were able to sample deeply enough to avoid extensive weathering.

The Kohala volcano, the oldest of the five volcanoes in Hawaii was chosen for sampling since it has volcanic series which occur within the range of the uranium-thorium method based on K-Ar dates. These series have been sampled by Rodd May of the United States Geologic Survey (USGS), who supplied us with explicit cite information for duplication and K-Ar comparison dates.

CHAPTER I

U/Th SYSTEMATICS THEORY

For chronologic uses, there are three uranium-thorium decay series; the ^{238}U series, the ^{235}U series, and the ^{232}Th series. (See Figure 1). The ^{238}U series is mainly of interest for this study. In a closed quaternary volcanic system, an initial disequilibrium exists between the daughter ^{230}Th and its parent ^{238}U. The activity of the thorium gradually returns to secular equilibrium with the activity of the parent uranium. The activity change of ^{230}Th relative to ^{238}U is as follows:

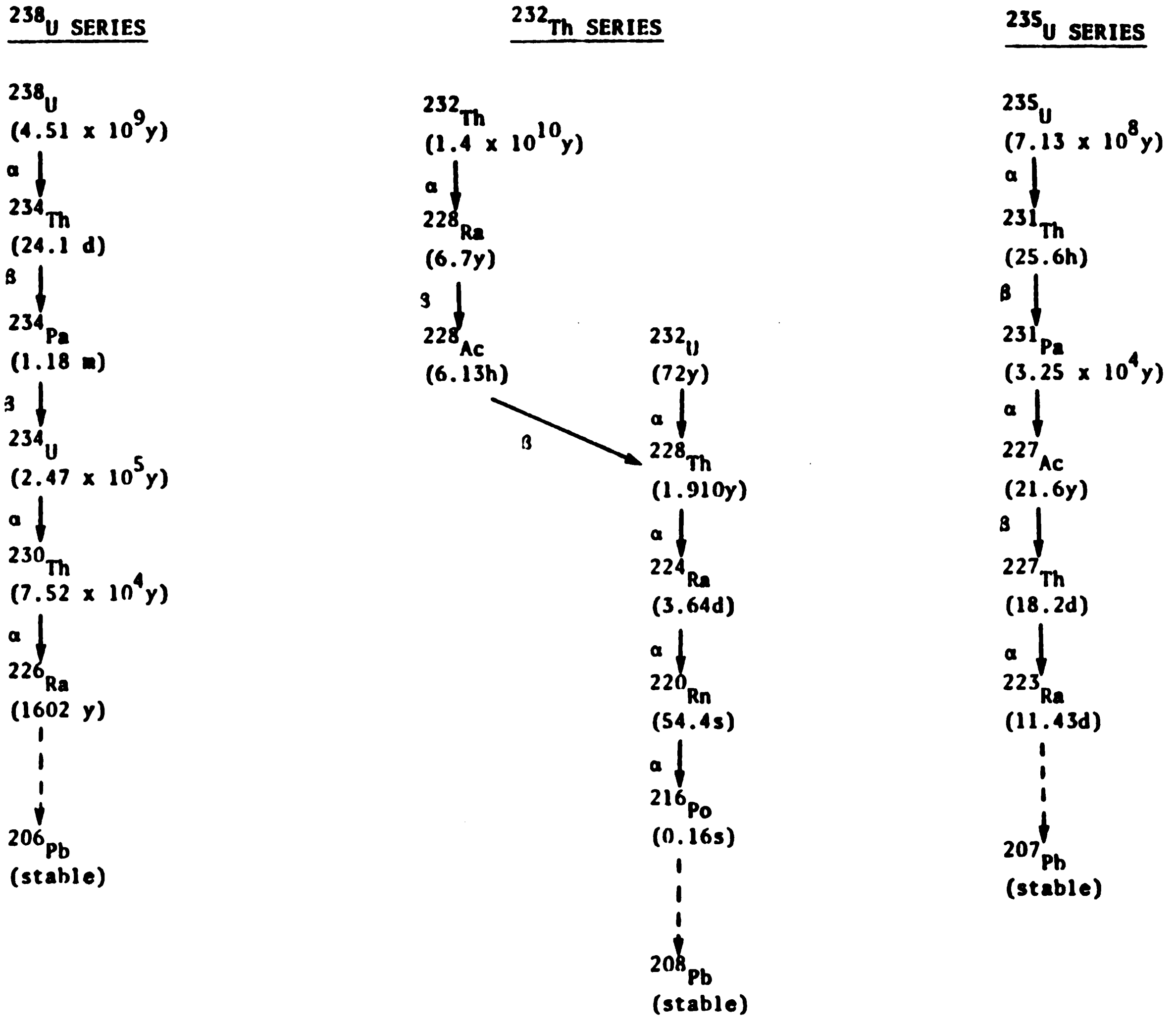
$$^{230}Th_{activity} = {}^{230}Th_{initial} \quad (\exp(-\lambda_{^{230}Th}t)) +$$

$$^{238}U_{activity} \left[1 - (\exp(-\lambda_{^{230}Th}t)) + \left(\frac{^{238}U_{activity}}{^{234}U_{activity}} - 1 \right) \times \right.$$

$$\left. \left(\frac{\lambda_{^{230}Th}}{\lambda_{^{230}Th} - \lambda_{^{234}U}} \right) (1 - (\exp(-\lambda_{^{230}Th} - \lambda_{^{234}U})t)) \right]$$

where λ = decay constant

t = age of the rock



Decay Scheme of the Major Uranium Isotopes

Figure 1

When little or no fractionation of ^{234}U relative to ^{238}U occurs, as is the case in the closed magma system (Somayajulu, et al, 1966), the equation simplifies to:

$$^{230}Th = {}^{230}Th_{initial} (\exp(- \lambda_{^{230}Th} t + {}^{238}U (1 - (\exp(- \lambda_{^{230}Th} t)))))$$

Dividing through by ^{232}Th:

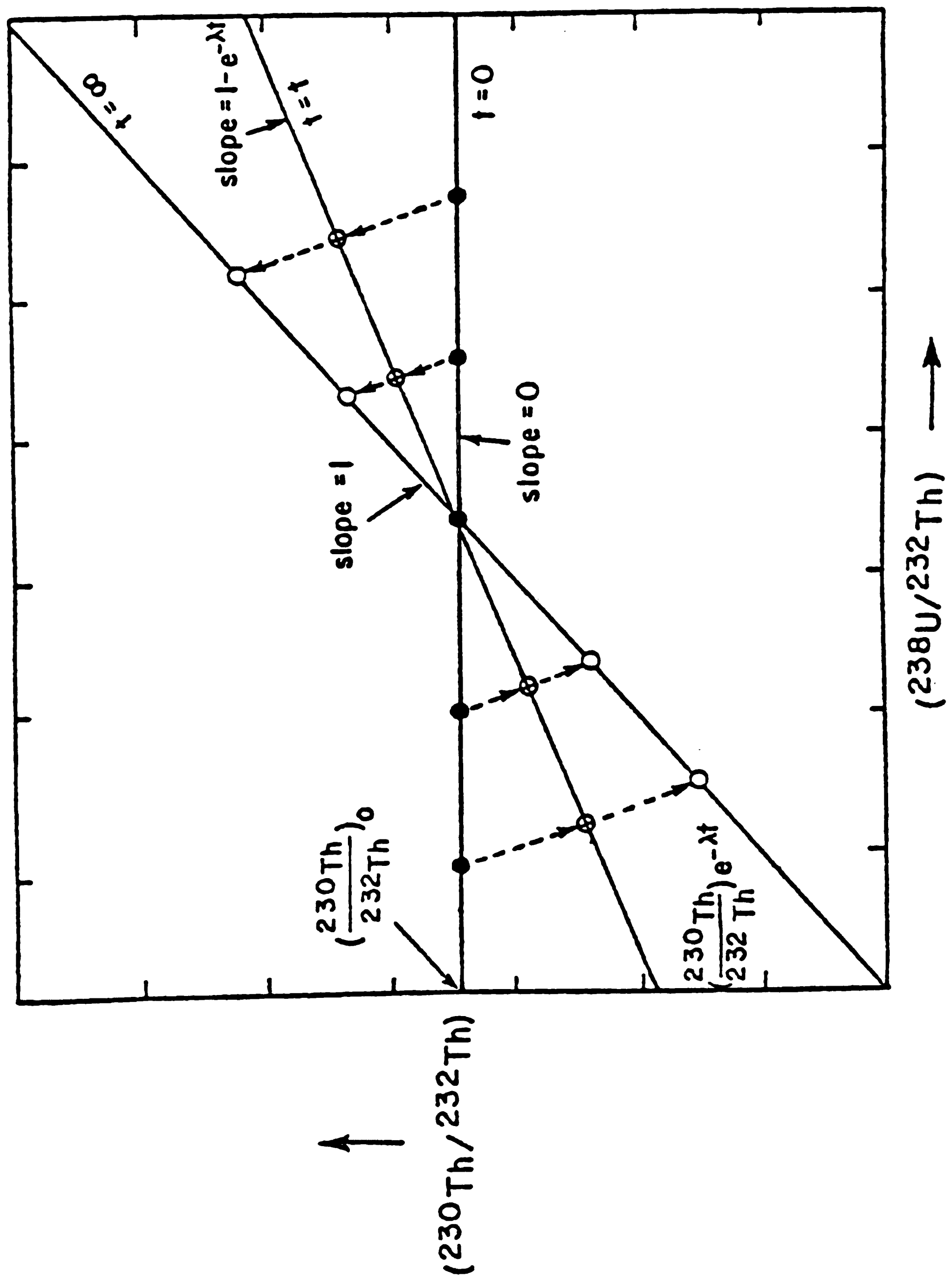
$$\frac{^{230}Th}{^{232}Th} = \left(\frac{^{230}Th}{^{232}Th} \right) (\exp(-\lambda_{^{230}Th} t)) + \frac{^{238}U}{^{232}Th} (1 - (\exp(-\lambda_{^{230}Th} t)))$$

Following the method of Allegre (1968, 1976; Condimines, 1976) these ($^{230}Th/^{232}Th$ and $^{238}U/^{232}Th$) are the ratios used to plot the isochron line to calculate the dates. The $^{230}Th/^{232}Th$ ratio is the y coordinate. The y axis is essentially a range of the possible values of initial isotopes of thorium found for this rock.

The $^{238}U/^{232}Th$ ratio is the x coordinate. The x axis is the range of partitioning found for this rock. By plotting the ratios found for the phases of this rock sample, an isochron line is determined. It's slope is calculated and then substituted into the equation:

$$\text{slope} = 1 - \exp(- \lambda_{^{230}Th} t)$$

The slope will vary from 0 to 1 as a function of time. (See Figure 2). The line with a slope of 0, a horizontal line, represents the initial ratio of $^{230}Th/^{232}Th$. The line with a slope of 1 represents equilibrium. The isochron should fall somewhere between the initial and equilibrium. By solving for t as shown above, the age of the rock is obtained.



Typical Isochron Plot

Figure 2

The major phases of the rocks were separated and the ratios found each one. The assumption is made that the initial $^{230}Th/^{232}Th$ ratios for the phases are the same since the phases are formed at relatively the same time and the system has remained closed with respect to uranium and thorium (Taddeuchi et al, 1967). The $^{238}U/^{232}Th$ ratio is effectively that of the levels U/Th since neither isotope is produced by decay within the range of the method, and therefore the ratio is set by the partitioning of these elements in the original system (Hurley, 1957).

CHAPTER II

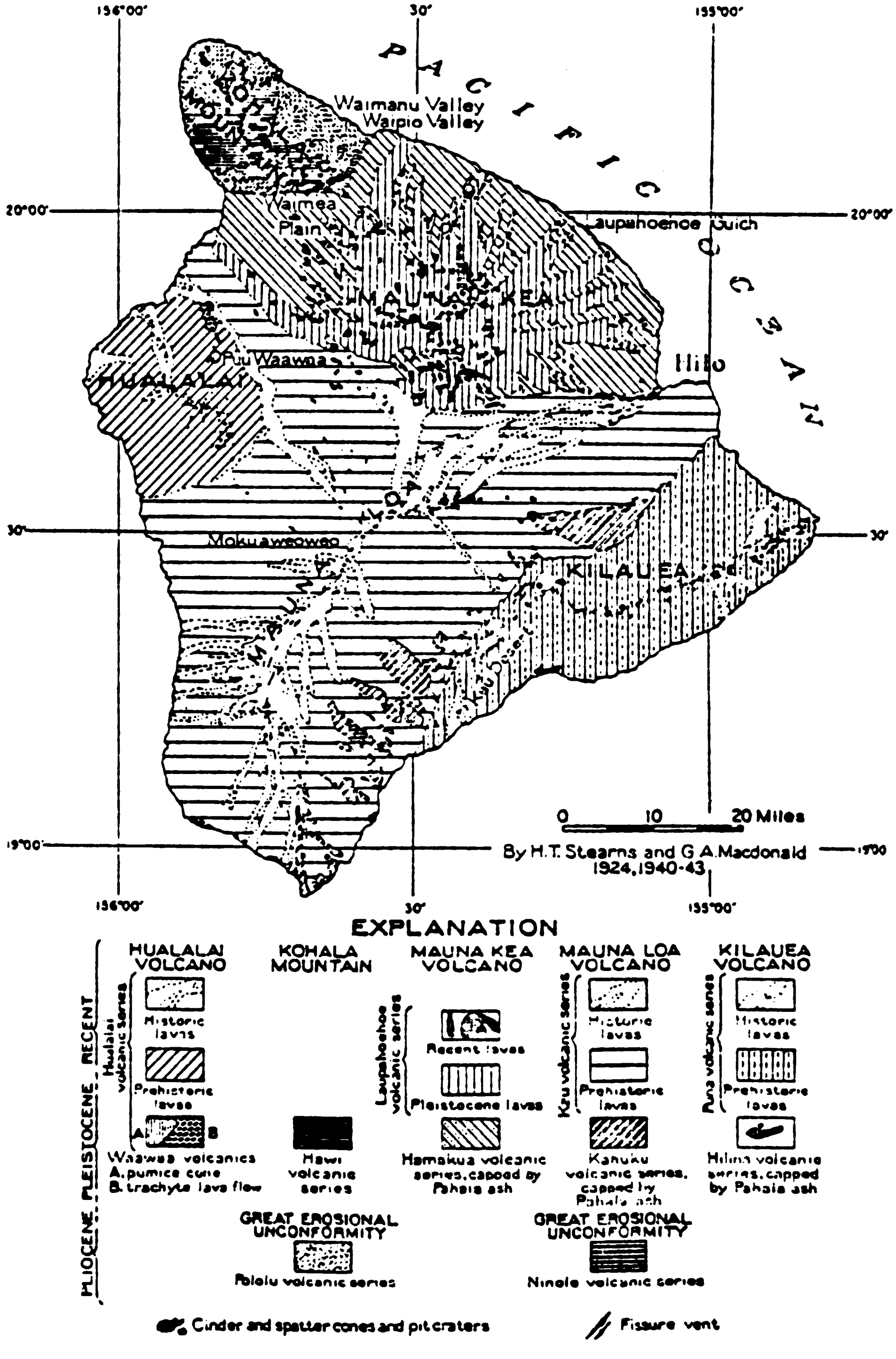
GEOLOGIC SETTING

The Hawaiian Islands are located in the central Pacific Ocean at the southeastern end of a submarine ridge which begins near Midway Island to the northwest and stretches in a relatively straight line to the southeast. The ridge is an example of midplate volcanism, both submarine and subareal, resulting from the movement of the Pacific Plate over a stationary hot spot or mantle plume.

The Island of Hawaii, the focus of this study is the largest island of the Hawaiian chain. It is comprised of five volcanoes, Kohala, Mauna Kea, Hualalai, Mauna Loa, and Kilauea (See Figure 3).

These volcanoes, as well as the others of the chain, are typically shield volcanoes with summit craters built on fissure systems. The volcanism here is generally mild eruptions of very fluid, hot basalt. Such basalt is characteristically of low viscosity and flows easily, allowing degassing to occur at a reasonably constant rate (Stearns, 1946).

Hawaiian volcanism generally follows a four stage pattern. Not all of the volcanoes of the chain have gone through the complete pattern. The first step is the extrusion of highly fluid picritic basalt to form a shield. All of the volcanoes of Hawaii seem to have gone through this



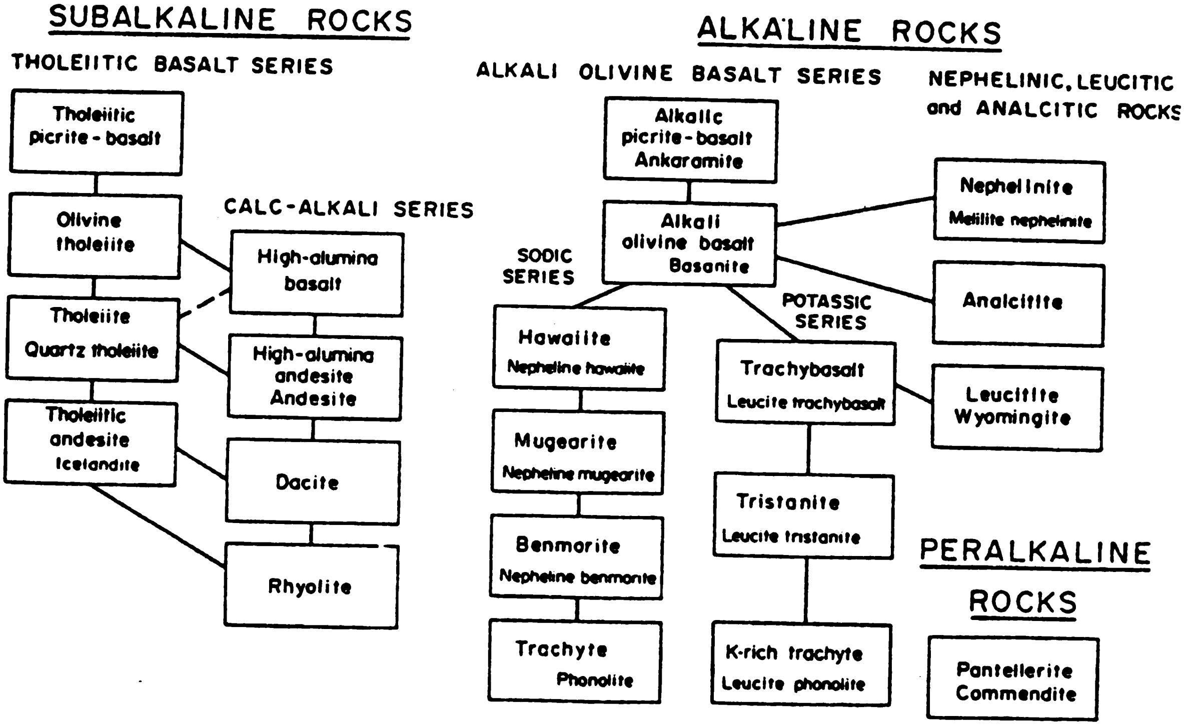
Map of the Collection Area

Figure 3

stage. Second, a caldera is formed and grabens and cliffs develop along the rift zones. These cliffs and grabens usually form during a rapid succession of flows. The Kilauea and Mauna Loa volcanoes are presently in this stage. Both are still visibly active volcanoes. Third, the calderas and grabens are filled by a succession of less frequent flows of a similar basalt. The older volcanoes, Mauna Kea and Kohala, have gone through this phase and are now dormant or extinct. Hualalai had entered this phase before its apparent extinction within historic time. Last, there is a long period of erosion when the activity ceases and then is replaced by an onset of more nephelinic flow (Macdonald and Katsura, 1964). No volcanoes on Hawaii have yet reached this terminal stage of development.

Initially it was the intent of this study to process a suite of basalts encompassing the major rock types found on Hawaii. These samples were collected on two visits in 1977, but analytical difficulties precluded work on all but the Kohala samples. Kohala Mountain is the oldest of the five volcanoes on Hawaii, comprising the northernmost part of the island. Its surface is dotted with a large number of cinder cones from its last period of activity. The rocks of Kohala occur in two volcanic series, both olivine basalts. The oldest series is the Pololu which is composed of basaltic flows, each from five to twenty feet thick. They range in composition from tholeiitic basalt to alkalic basalt (Turner and Verhoogan, 1960). These occur in thinly bedded, highly vesicular flows which weather to a rusty, reddish-brown (Stearns and Macdonald, 1948). This series extends from the floor of the sea to as much as 2000 feet above sea level in some places. There is very little ash found within this series. The Hawi volcanic series is separated from older underlying Pololu series by an erosional unconformity representing a period of little or no volcanic activity. It is more massive than the Pololu series and weathers to greyish soils (Stearns and Macdonald, 1948). Compositionally, the Hawi series is mainly mugearite, an alkali olivine basalt, and a small amount of trachyte (Turner and Verhoogan, 1960). See Figure 4 for a graphic representation of these rock types. There is more ash found in this series than in the Pololu which helps to differentiate them in the field and correlate them stratigraphically. The last flows of the Hawi are interfingered with and overflown by the volcanics of Mauna Kea to the southeast. This interfingering is one of the stratigraphic problems which could be later addressed if the uranium-thorium disequilibrium dating method shows itself to be viable for basalts.

The older Pololu series is considered to be of Pliocene age, which probably began to build up about 0.7 million years ago. The Hawi is considered to be Pleistocene in age. It probably ceased erupting about 0.06 million years ago (Turner and Verhoogan, 1960). These estimates are based mainly on K-Ar dates and stratigraphy.



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General Classification of Volcanic Rocks

Figure 4

CHAPTER III

THE GEOCHEMISTRY OF URANIUM AND THORIUM IN IGNEOUS ROCKS

Uranium and thorium are radioactive elements of the actinide series which have isotopes with long enough half lives that they are still abundant in nature. ^{238}Uranium, the parent of one of the series of interest in this study, has a half-life of 4.51×10^9 years (Attree et al, 1962). ^{232}Thorium has a half-life of 1.4×10^{10} years. ^{235}Uranium, which is not of special relevance in this study, has a half-life of 7.13×10^8 years (Friedlander, Kennedy, Miller, 1955).

Uranium and thorium exhibit very similar geochemical behavior. The similarities are due to their outer electron shell configuations. The ions are similar in size and in the tetravalent form have the same co-ordination with oxygen. Unfilled second shells in the configurations of hexavalent uranium, called uranyl ion, and tetravalent thorium allow their easy participation in chemical reactions. These reactions are commonly oxidation reactions. The shape of the hexavalent uranyl ion (UO_2^{2+}) changes to elongate from the spherical tetravalent form. This ellipsoid with oxygens on the ends is a more soluble form. The properties of uranium which differ from those of thorium are due to its inner unfilled electron shell which can act as valence electrons along with those the outer shell. This situation in uranium allows it to attain the hexavalent state by oxidation (Seaborg and Katz, 1954).

Thorium occurs naturally as ^{232}Th. This major radioisotope has an extremely long half life. It is the parent isotope in the decay series whose final product is ^{208}Pb (see Figure 1). This series undergoes decay so slowly that for the purposes of Pleistocene chronology, we often consider ^{232}Th as constant.

^{230}Th, also known as ionium, is a daughter product of the ^{238}U series whose end member is ^{206}Pb (see Figure 1). It results from the decay of ^{234}U which is in turn a decay product of ^{238}U. ^{234}U can fractionate from ^{238}U during weathering (Cherdyntsev, 1967) due to the easy mobilization of the easily oxidized hexavalent form of uranium. ^{230}Th has a short half-life (7.52×10^4 years) making it useful for the uranium-thorium disequilibrium chronology method.

As described above, the thorium isotopes are tetravalent and relatively insoluble ions. This property makes it possible to assume that the abundance of thorium found in igneous rocks is nearly that of the initial rock (Cherdyntsev, 1968).

The geochemistry of thorium is similar to that of potassium and frequently thorium occurs in association with potassium in silicic igneous rocks (Holland, 1954). The compounds formed in such rocks can more easily migrate towards the surface during crystallization, taking the thorium with them. Therefore magmas held in high chambers in the upper mantle may be enriched upward with respect to thorium (Tatsumoto et al, 1965).

Uranium occurs naturally as three isotopes, ^{238}U with a half-size of 4.49×10^9 years. ^{235}U with a half-life of 7.1×10^9 years, and ^{234}U with a half-life of 2.48 x 10^5 years (see Figure 1).

^{238}U is the most common radioisotope and along with ^{235}U accounts for more than ninety-nine percent of all naturally occuring uranium. The third, much shorter half-lived isotope, ^{234}U, is an intermediate decay product in the ^{238}U series (Ku, 1976).

Uranium occurs in both tetravelent and hexavalent ion forms. The tetravalent ion easily oxidizes to hexavalent form is very soluble and therefore very mobile. This transition from +4 to +6 state occurs easily under the conditions of the geologic surface or near surface environment (Kaufman et al, 1964). Due to the mobility of the hexavalent uranium, it is difficult to determine the original abundance of uranium in heavily weathered rocks or those which have been acted upon for long periods of time by solutions. The uranyl ions are very large and will accumulate during weathering rather than combining quickly into compounds (Tieh et al, 1980). These accumulations are often found as ore bodies.

Uranium and thorium occur in all three major rock types. Their abundance increases as the rocks become more silicic. The range of variations of uranium abundances is very large. The average abundance in continental rocks is approximately 2 ppm. Thorium abundances for granitic continental rocks can be as high as 10-20 ppm, but decreases in the intermediate rocks to 2-5 ppm and is only about 0.05 to 2.2 ppm in the very basic continental rocks (Whitfield, 1958).

The average thorium to uranium ratio for igneous rocks is 3.5 (Rankama, 1954). This is the average of a very large range. Oceanic rocks, basic rocks, have a low thorium to uranium ratio as stated above.

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Continental, acidic, rocks can have abundances as great as 8 ppm thorium and 2 ppm uranium (Cherdyntsev, 1968).

Oceanic crust is usually assumed to be primitive material which approximates the upper mantle. Its thorium to uranium ratio is about 2. This ratio results from the fractional melting of basaltic lava in the upper mantle without fractionating uranium and thorium between the solid and liquid phases (Rogers and Adams, 1957). This means that abundances of uranium and thorium do not represent radiogenic components and are true initial abundances before weathering (Nishamura, 1970).

Accessory minerals such as zircon and sphene are usually the carriers of uranium and thorium. The early forming accessories seldom have a ratio of 3.5. Their ratio is often about 1. However, in magmas where accessory minerals have not crystallized, the ratio is found to be about 3.5, which indicates that the process of formation of accessory minerals allows for this change in distribution (Adams, Osmond and Rogers, 1969) to this study that rocks without accessory minerals be used to determine chronology. The formation of olivine is not a problem with respect to this situation, since olivine incorporates almost no thorium and uranium. There is no evidence that any mineral forms from a basic magma which draws significantly from the original concentrations of thorium and uranium so that we find a relatively uniform distribution of these minerals in all the constituent members of the resultant rocks in intrusive suites. In extrusive rocks, the rapid cooling of the lava allows the major phases to contain the uranium and thorium.

CHAPTER IV

SAMPLE COLLECTION AND PREPARATION

Samples were collected from the Hawi and Pololu series of the Kohala mountain volcano. Specific locations are described in Table 1. As often as possible, an effort was made to correlate samples with those previously collected by Dr. Rodd May of the USGS Geochemical Division, presently at Menlo Park, California. His samples were collected for thermoluminescence work and K-Ar dating two to three years before the collections for this study. For several reasons, many more samples were collected than were used, primarily to ensure that weathering-free samples were collected at each site. The weathering could be more clearly discerned after thin sections were made. Also, samples from the four other volcanoes on the island were collected in case further studies on the "younger" volcanoes became desirable. At each site collections were made of fresh 10-15 kg. samples, as free of weathering as possible in order that the loss of uranium to the weathering process be minimized. Since uranium is easily oxidized to the +6 state and mobilized during weathering, this problem was avoided as much as possible. Relatively unweathered samples are needed for processing to obtain mineral phases so that phase isolation will yield as true a representative of the original as can be obtained. Thin sections were again used to determine what

Table 1

LOCATION DATA

Details of locations are noted here in the event that someone wishes to resample at a duplicated site. I was very grateful to Dr. Rodd May, USGS for this kind of information.

Sample Number	Series and Rock Type	Field Location
761231-8	Pololu series tholeiitic basalt	Mahukona Quadrangle 1 mile north of Mahukona point on old highway 27 on the right roadcut going north
761231-10	Hawi Mugearite	Mahukona Quadrangle in a roadcut 3.8 miles north of Mahukona point on old highway 27 on right side going north
761231-12	Hawi Mugearite	Mahukona Quadrangle in a road at 6.7 miles north of Mahukona point on the right side of old highway 27 going north. This member appears as a sill about 3 feet above the road level
761231-13	Hawi Mugearite	Kamuela Quadrangle on highway 27 in the first roadcut north of Waiaka

phases were present and if any weathering products might interfere with their isolation.

After the collected rocks were returned to the laboratory, hand specimens were taken of the samples, and thin sections were made. Most of the remaining rock was then crushed and pulverized with a Chipmunk Crusher Pulverizer at McMaster University, Ontario, Canada, then milled to less than 200 mesh size with a ball mill.

Five grams of whole rock powder in each case were sent to Dr. Robert McNutt of McMaster University to be analyzed for major elements by x-ray fluorescence (XRF). This was done both to demonstrate the similarity to Dr. Mays' samples, and to check the optical analyses.

Thirty grams of each sample powder were sent to Dr. Hugh Millard of the USGS, Denver for total uranium and thorium abundance analysis by XRF. The results of these analyses appear in Table 2. The results were used to help estimate the amount of sample needed to be processed to get reasonable counts, and to loosely check the components of the rocks as determined by thin section analysis.

About 200 grams of whole rock material were set aside for whole rock analysis. A portion of the remaining powder was cleansed of clay-size particles by gravity settling after washing it with water, allowing the clay particles to remain in suspension and the larger particles to settle out. Centrifuging was not necessary with these rocks because the phases were reasonably discreet and of varied enough densities as to allow them to be separable without it. The clay-size particles were then decanted. The removal of the clay-size particles was necessary since they inter-

Table 2

ELEMENTAL ANALYSES OF SAMPLES USED FOR DATING BY WEIGHT %

	#761231-8	#761231-10	#761231-12	#761231-13
SiO_2	49.01	44.75	49.49	53.94
Al_2O_3	13.96	8.88	16.65	17.14
Fe_2O_3	14.63	17.45	11.85	10.54
MgO	5.21	17.23	4.40	3.48
CaO	10.00	7.31	10.42	6.38
Na_2O	2.74	1.54	3.09	4.24
K_2O	0.80	0.54	0.95	1.85
TiO_2	3.40	1.87	2.92	2.13
MnO	0.20	0.20	0.18	0.20
P_2O_5	0.04	0.22	0.05	0.10

analyses by Dr. Robert McNutt, McMaster University, Canada

ppmTh	0.58	0.00	1.64	3.79
ppmU	0.68	0.41	0.59	2.00
Th/U	0.85	0.00	2.62	1.89

analyses by Dr. High Millard, USGS, Denver, Colorado ferred with mineral phase separation by clogging the Frantz Isodynamic Separator and rendering it useless. The large particle fraction was dried in a drying oven.

Magnetite was separated from the large particles by repeated hand magnet removal. The product of this removal was washed, settled and dried again for further purification.

The rest of the large particle fraction was run through the Frantz Isodynamic Separator several times to isolate the pyroxene, and then the plagioclase. The pyroxene was magnetic and the plagioclase, which was virtually non-magnetic, dropped out. The Frantz settings used are listed in Appendix B.

The separated pyroxene and plagioclase were washed, settled and dried several more times to remove impurities. The resulting products were examined optically to insure eighty percent purity or greater. The only exception to the purity was possibly the plagioclase, which was frequently so finely grained that it retained microscopic particles of other mineral phases. Other phases were much freer of contamination. The mineral separates were then dried and weighed. It was decided that ten gram splits would be analyzed for uranium and thorium. This was decided because the trial runs of up to 100 grams required prohibitively large volumes of residue to form during dissolution. Since the mathematics of the method deal with the isotope ratios within each phase, it is not necessary to be strictly quantitative with the separations. The optimization of yields is therefore more important than large volumes of total material processed, as long as accurate weighing of the final amount was done. The yield is the percent of the actual amount of isotope which is extracted from a given phase by the chemical processing. The way in which the yield is determined is through the use of a spike of a known amount of an isotope which is not contained in the sample. The spike is discussed in Appendix A. After their determination by counting, yields were normalized to one hundred percent.

CHAPTER V

URANIUM AND THORIUM ISOLATION

The final chemical processing of the prepared powders to isolate uranium and thorium evolved through trials and adjustments. The original method was patterned after that of Peter Thompson (1973a, 1973b). As the work proceeded and problems arose, alternatives were sought. A flow chart of the final process appears in Figures 6-9 at the end of this section.

The magnetite phase was taken into solution with about 100 mL of hydrochloric acid (HCl) on a stirrer overnight. The result was complete dissolution. The solution was then taken to dryness on a hotplate and then redissolved in concentrated nitric acid (HNO_3) and diluted with enough deionized water to make a 4N solution.

Ten to fifteen grams of whole rock sample or silicate mineral separate was digested with 50 mL of concentrated hydrofluoric acid (HF). Sample and acid were fumed on a hot plate in a covered 250 mL teflon beaker for twelve hours. Due to the residues which formed about the lip of the beaker and the rim of the cover plate, it was feared that uranium was being lost as a volatile fluoride compound. The probability was confirmed by discussions with members of the Chemistry faculty.

Consequently, a fusion with sodium carbonate flux was done. The sample powder was ground to less than 200 mesh, mixed with ten parts flux to one part sample, and then divided into ten gram splits and placed in platinum crucibles in a muffle oven at 850°C for eight to twelve hours.

The fusions should have produced an easily dissolved product. This was not the case, however, and insoluble residues recurred over the course of two to three refusions. These residues were finally subjected to hydrofluoric acid fuming. After the dissolution had been achieved, the solution was taken to dryness on the hotplate while still in the teflon beaker. The resulting product was taken into solution with 4N nitric acid. If residues were left behind, as they often were, they were filtered or centrifuged off, dried and fused once again. The solution was then added to the original dissolution volume in a 4000 mL pyrex beaker.

After the sample was totally in solution, 2 mLs of a dilute spike of known uranium and thorium isotopic content was added. The spike is discussed in Appendix A. The volume of dissolved sample at this point was usually slightly less than 2000 mL. The volume was raised to 2000 mL with 4N nitric acid. Also added at this point were forty mL of a solution of 250 mg lanthanum oxide, 5 mL $HClO_4$ and 5 mL HNO_3, whose purpose it was to carry the thorium with it through a later step, preventing it from combining into insoluble products.

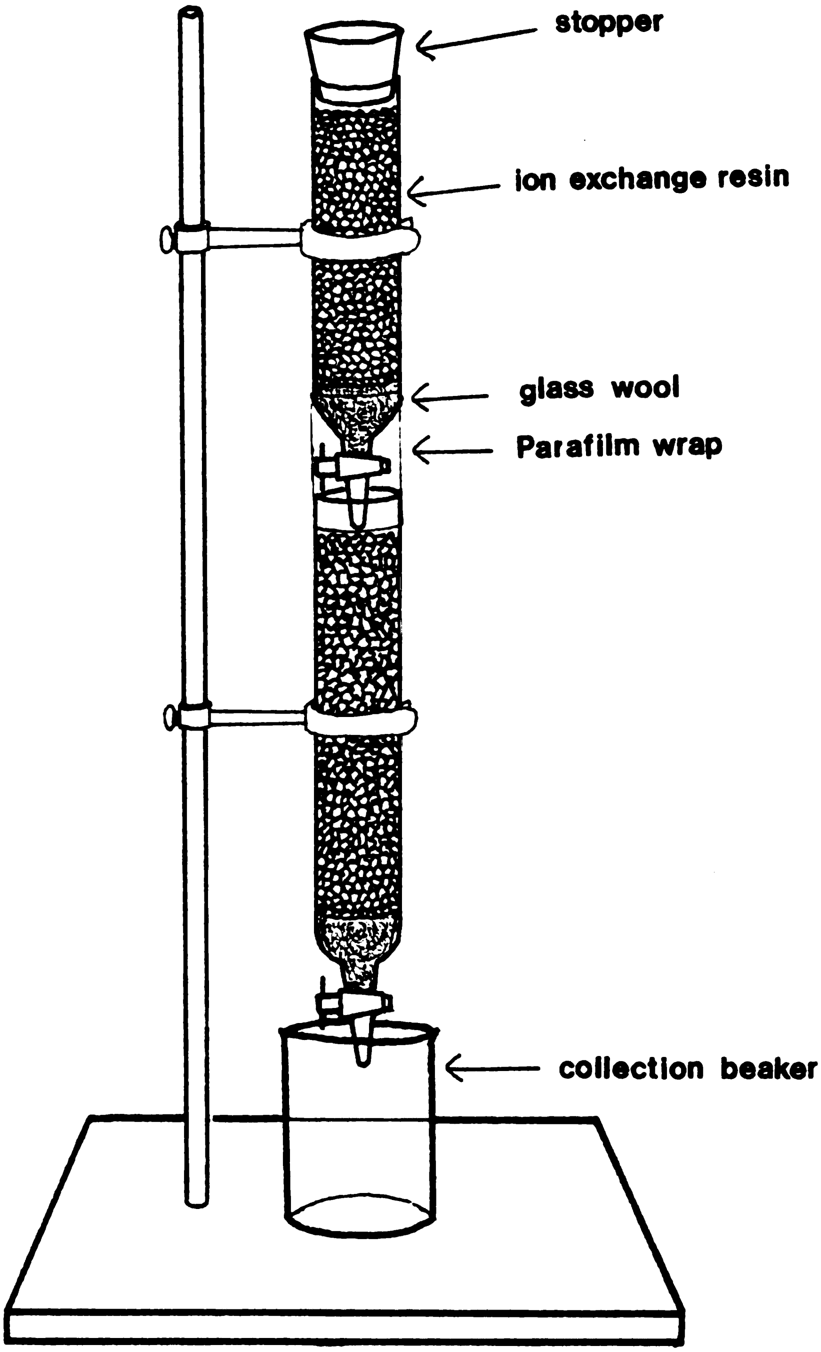
The spike and lanthanum oxide were stirred into the sample solution and allowed to equilibrate for at least 24 hours. The use of magnetic stirring equipment shortened the time necessary for equilibration to about twelve hours.

After equilibration was achieved, concentrated ammonium hydroxide (NH_4OH) was added, slowly, through a glass funnel while stirring with a magnetic stirrer. This caused the precipitation of iron hydroxide at precisely the point when a pH of 7 was reached. This reaction was extremely exothermic, and the addition of the NH_4OH had to be done slowly or spattering and even breakage of the container could take place. The precipitated iron hydroxide carried the uranium and thorium with it. Unfortunately aluminum and manganese were also carried along. These elements complicated later steps.

In an attempt to remove the aluminum, a hot sodium hydroxide wash was done (Kaufman, 1964). Uranium loss caused the abandonment of this step.

In a later ion exchange step to overcome the aluminum problem, longer columns of greater diameter, and therefore greater resin capacity were used. The individual columns available were not long enough to allow the alumnimum to be taken up by the resin and still to have sites left for the uranium. To overcome this problem, two columns were mounted, one above the other, and the solution not taken up by the first was allowed to pass directly into the second below it. (See Figure 5).

After the iron hydroxide precipitation step, the precipitate was next dissolved in 9N hydrochloric acid (HCl) (after Thompson, 1973) and the resulting solution purged of iron by extraction with isopropyl ether. This was done by putting 75-100 mL of sample solution and an equal volume of isopropyl ether into a 250 mL separatory funnel and vigorously shaking them for several minutes being careful to aspirate the pressure created by agitating the mixture, at 30-60 second intervals. The iron was reduced and taken in the ether, which was then allowed to stand for several seconds to gravity separate from the solution. The ether and iron were



Ion Exchange Column Arrangement

Figure 5

then discarded. This procedure was repeated until the ether no longer took on a yellow color after agitation or until no further change of color to the sample indicated that no more iron was being extracted. It did not mean, however, that there was no more iron in the sample solution. In basic rocks, like the Hawaiian basalts, later steps yielded enough iron to interfere with the alpha counting process. Since this iron was not available for reduction in the ether extraction step, it must not have been existing as free ion in solution, and therefore could not be reduced and extracted.

After ether extraction, the sample was gently heated on a hotplate to drive off the remaining ether. Then the solution was fed onto an anion exchange column of Dowex AG1-X8 Resin which had already been conditioned to the chloride form with 9N HCl. The column was then rinsed with about 30 mL of 9N HCl. The uranium remained on the resin column at that time. The fluid that passed through the column contained the thorium and was, therefore, retained in a vycor beaker. Vycor was used for this part of the procedure since it is made of a high silica glass and the uranium and thorium were less likely to be lost to adsorption on the beaker.

At this point it was important to note the time when the uranium was separated from the thorium. Thorium^{228} is produced in both the decay of uranium^{232} and thorium^{232}. Therefore, it is necessary to include a correction for the change in the thorium^{228} contributing factors after separation when doing subsequent calculations.

Uranium was eluted from the ion exchange column with 100 mL of 0.1N HCl into a separate vycor beaker.

The thorium bearing fluid was fed onto an anion exchange column which had been conditioned to the nitrate form with 8N HNO_3. The thorium was taken onto the resin column. After rinsing with 30 mL of 8N HNO_3, the waste was discarded and the thorium eluted with 100 mL of 0.1 N HNO_3 into a vycor beaker. There was discoloration of the resin and loss of flow through the column.

An anion exchange column, conditioned with a solution of 5 mL of 5N HNO_3 and 45 mL of methanol was used to isolate the thorium after Tera et al. (1961). The fluid left behind after the separation of the uranium was evaporated to dryness on a hotplate and then brought back up in 5 mL of 5N HNO_3. It was added to 45 mL of methanol. This solution was immediately fed onto the HNO_3-methanol column. After rinsing with another 30 mL of 90% methanol solution and discarding the passed fluid, the thorium was eluted with 100 mL of 0.1 N HNO_3. The resultant thorium yields were not high, but were better than those previously obtained. The interference from elements or complexes not removed in earlier steps caused the resin sites to be occupied before the thorium was taken up completely. Prohibitively large amounts of resin would have been needed to correct this problem, if indeed it could be corrected. The use of consecutive columns, as used before, still did not alleviate the situation.

Personal communication with Dr. Allegre and Dr. Condomines from Paris, France led to another change which is described here and was incorporated into the final process. The early steps of the adapted Thompson method remain the same until the filtering of the iron hydroxide precipitate. At that time a plastic funnel was substituted for the glass one for filtration. The precipitate was then dissolved with 100 mL of concentrated hydrofluoric acid into a teflon beaker. This solution contained the uranium and iron. The white residue left behind in the filter paper contained the thorium and lanthanum. Again, the time of the separation of the uranium and thorium was noted in order to correct the thorium^{228} value.

The uranium bearing hydrofluoric acid solution in a covered teflon beaker was evaporated to half its original volume. About a teaspoon of boric acid powder was added and the solution raised to 100 mL with concentrated nitric acid, thereby yielding soluble nitrates rather than insoluble fluorides. This solution was evaporated to dryness on a hotplate. The residues that were left were wetted with a few drops of concentrated nitric acid and once again evaporated to dryness. This step was repeated twice more to insure that all the residues were in a soluble form.

Next, the residue was taken into solution with 9N HCl and this solution extracted for iron as previously described. Once the iron had been removed and the ether driven off, the uranium bearing solution was run on a 9N HCl anion exchange column and eluted as described before. The final uranium bearing solution was evaporated to dryness in a vycor beaker, covered and set aside until the final steps were performed. The amount of occurring uranium isotopes were not changed with respect to each other over the time they were held. The thorium on the other hand, was subject to change, making it important to process it first.

The thorium bearing residue left behind in the filter paper in the plastic funnel was treated with concentrated nitric acid to liberate the thorium. After this acid drained into a teflon beaker, the residue was rinsed again with 5N HNO_3 into the same beaker to free any remaining thorium. The gel remaining in the filter paper was discarded after it was found to be mainly aluminum by XRF analysis. The acid containing the thorium was evaporated to dryness, then the residue brought up in 5 mL of 5N HNO_3, and added to 45 mL of methanol. This solution was processed on a 90% methanol column as described before. The resulting elutate was evaporated to dryness in a vycor beaker.

The thorium was brought back up in a small amount of 8N HNO_3 and reevaporated. Then about 2 mL of 0.1N HNO_3 acid were added. The pH of this solution was checked to determine if it was 1.2. If not, it was adjusted using more 0.1N HNO_3 or dilute NH_4OH as needed. The method available for this check was pH paper, which was a source of gross error. The acid was then transferred to a test tube and 2 mL of triethylenetetraamine (TTA) and benzene solution added to it. These liquids were mixed on a test tube mixer for several minutes to extract the thorium into the organic phase. The tube was centrifuged briefly to separate the acid and organic phases. Then the organic upper layer was carefully drawn off with a disposable pipette, being careful not to take up any of the acid phase. The organic phase was placed in a 10 mL beaker. This extraction step was repeated several times to assure complete extraction. The organic phase was then evaporated to a small volume (about 1 mL) and drawn up into a warmed, clean disposable pipette and evaporated a drop at a time onto the center of a stainless steel planchette. The planchette was then heated to a dull red over a Bunsen burner flame to drive off the organics and any interferring U^{235} which may have been present. After it was cool, the disc was counted as described in the next section. Thorium discs were counted first beginning as few minutes as possible after separation from uranium to minimize the Th^{228} correction needed. The uranium residue was raised in 0.1N HNO_3, as was the thorium, but the pH was adjusted with dilute NH_4OH to 3.4. The acid was then transferred to a test tube and 2 mL. of TTA and benzene added. The same procedure used before was followed here except at the higher pH with several extractions, evaporation and transferral to the stainless steel planchete.

Anywhere along the way in the process after the first ether extraction, if there appeared to be a great deal of iron in the sample, it was possible to take the solution to dryness, raise it in 9N HCl and ether extract again, then pick up the procedure at the point it had reached when the iron had become apparent.

All evaporations, precipitations and platings were done in fume hoods to prevent the inhalation of fumes.

A flow chart of the procedure appears in Figures 6-9.

FLOW CHART OF ANALYSIS I

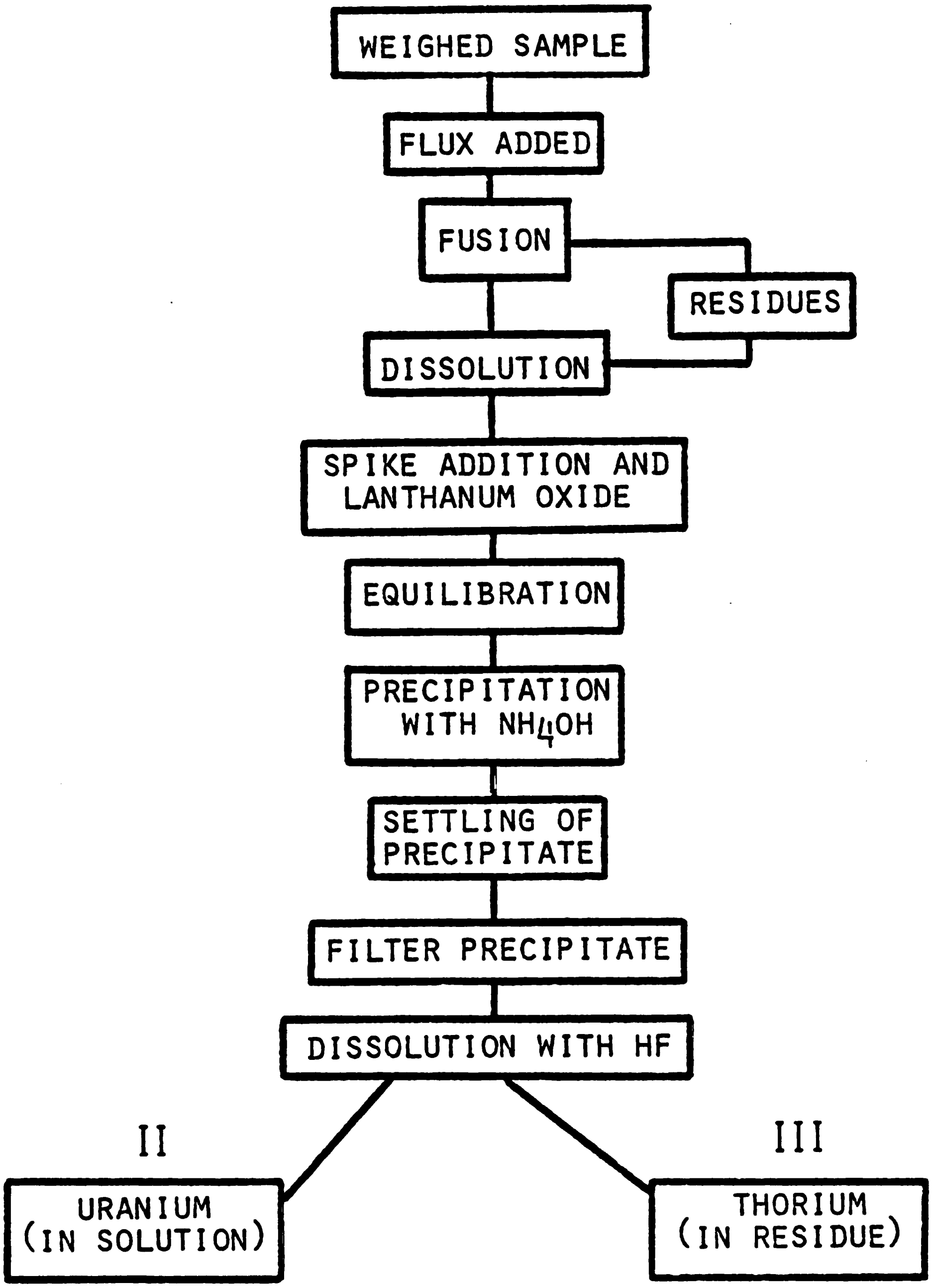


Figure 6

URANIUM PROCEDURE II

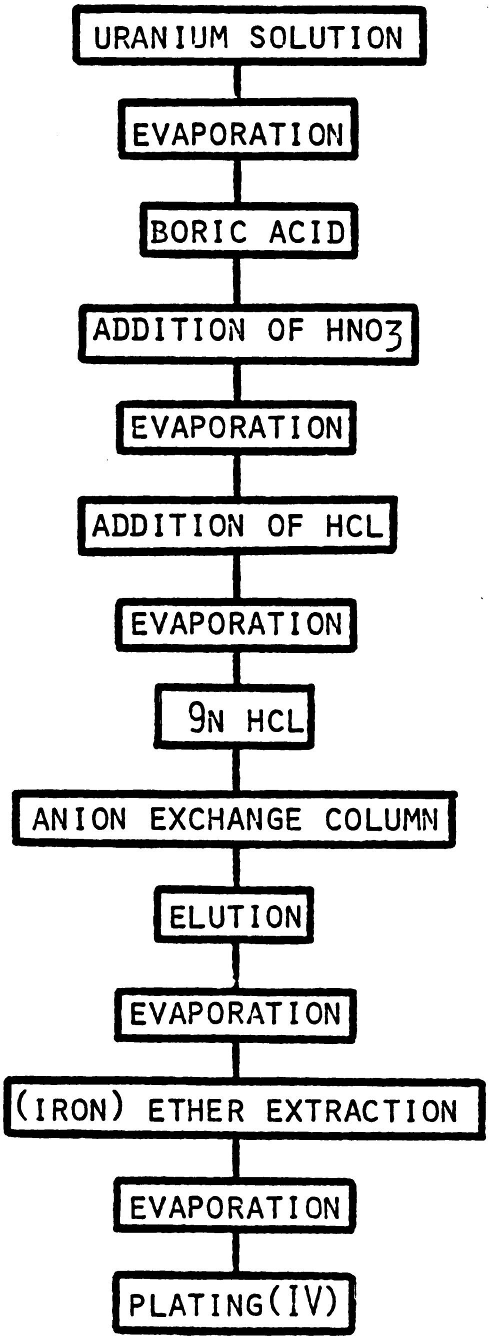


Figure 7

THORIUM PROCEDURE III

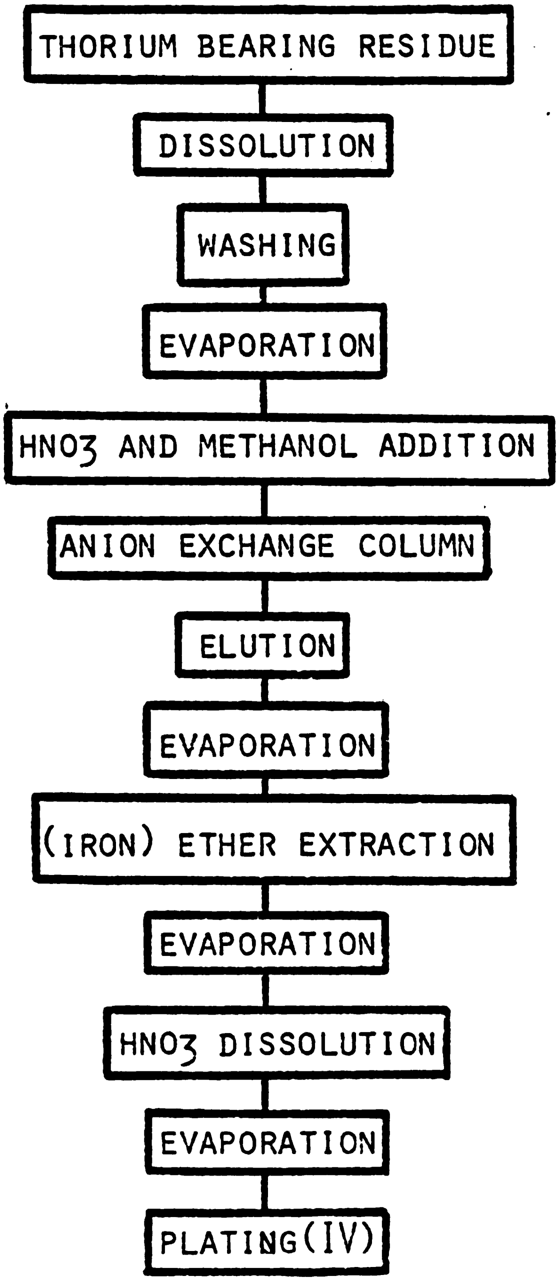


Figure 8

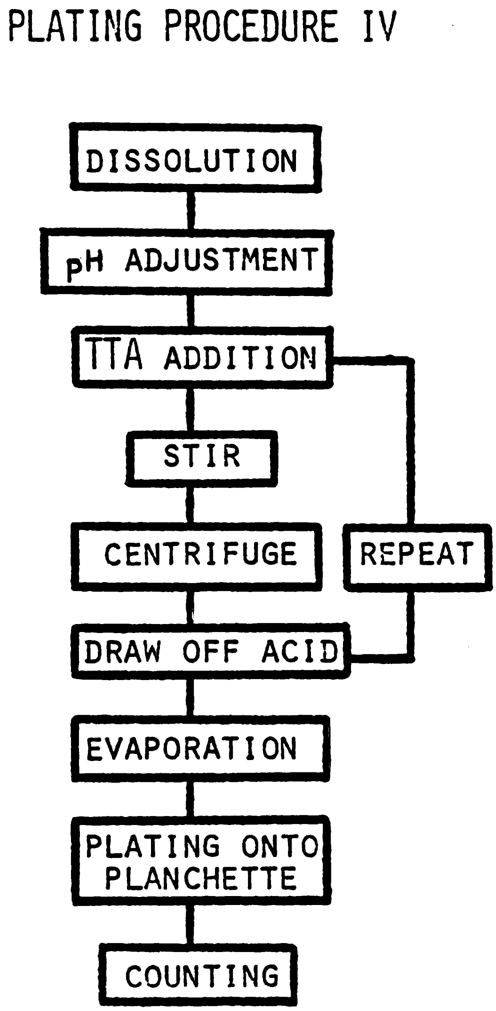

PLATING PROCEDURE IV
DISSOLUTION
pH ADJUSTMENT
TTA ADDITION
STIR
CENTRIFUGE
REPEAT
DRAW OFF ACID
EVAPORATION
PLATING ONTO PLANCHETTE
COUNTING

Figure 9

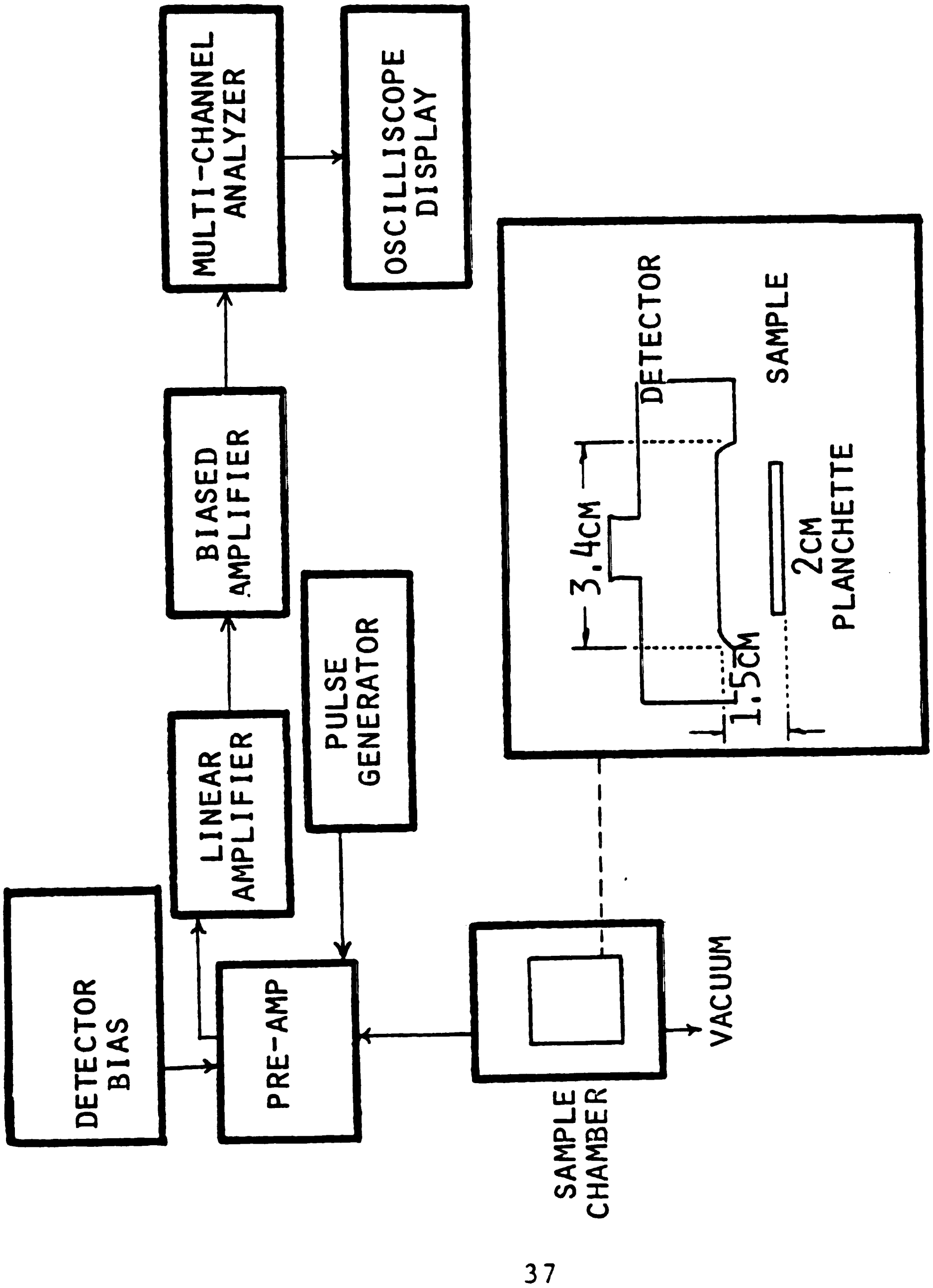
CHAPTER VI

ALPHA COUNTING PROCEDURE

Once the stainless steel planchettes were prepared, they were counted on an ORTEC Ca-070-950-100 spectrometer. (See Figure 10). This is a surface-barrier semi-conductor detector which is a solid state instrument which affords high resolution. The spectrometer provides a 0-10 volt linear signal which is sent to the vacuum chamber containing the sample. The sample planchette is mounted on a holder inside the detector. It is important that the area of the planchette containing the sample be centered as well as possible on the holder to optimize the geometry. The detection chamber is cooled with dry ice to maintain low backgrounds which are due to buildup of contaminants from alpha recoil nucleii. As was mentioned before, background was measured throughout the data acquisition period by counting blank planchettes over the same channels as had been determined for the isotopes of interest.

The signal from the detector is passed through a pre-amplifier and an amplifier and then onto a multichannel analyzer (MCA). After at least twenty four hours, the spectrum gathered for a planchette was counted over the channels corresponding to the various isotopes of interest. The raw counts, time and correlated background values were then entered into data sheets to be used with the computer program in Appendix E.

Figure 10



SCHEMATIC DIAGRAM OF α-PARTICLE SPECTROMETER

Thorium planchettes which contained the much shorter half life isotopes, were counted as soon as possible after their plating. The corresponding uranium - that is, the one from the same aliquot of sample was counted after the thorium.

The data sheets for each sample appear in Appendix F. The count rates for the isotopes are very low in most cases. This occurs for several reasons. First, the content of total uranium and total thorium in these samples was extremely low. Even if a high yield of the elements had been obtained, it would have been necessary to count the samples for much longer periods of time in order to achieve the high counts (approximately 1000) which yield good counting statistics. The unfortunate situation was that the work load and schedule of the research group allowed only a short time for the completion of the counting before the removal of the equipment took place. For this reason, every time a planchette was put in the detector, the spectrum acquisition was viewed for several minutes to half an hour. If no decays appeared during that time, the final steps of the plating were repeated on the undisturbed containers and the new planchettes counted. The chemical interferences discussed in the previous chapter attenuated the decays almost completely in some cases. The procedure should have been suspended and redone from the beginning at this point, but time constraints made this option impossible so the counts were done on the samples at hand in hopes that some data might be obtained.

The intention of this thesis was to determine whether this method could be applied to basic volcanic rocks to obtain chronology information. Under the conditions of this work, the answer to that question seems to be that it cannot. However, I feel that complete fusions and solvent extraction could provide good data.

Fusions with an alternate flux, potassium flouride (KF), have been used (Sill, 1977) in processing thorium for alpha spectrometry. This may be a viable alternative.

CHAPTER VII

PROBLEMS OF DATA RESULTS AND CONSIDERATIONS

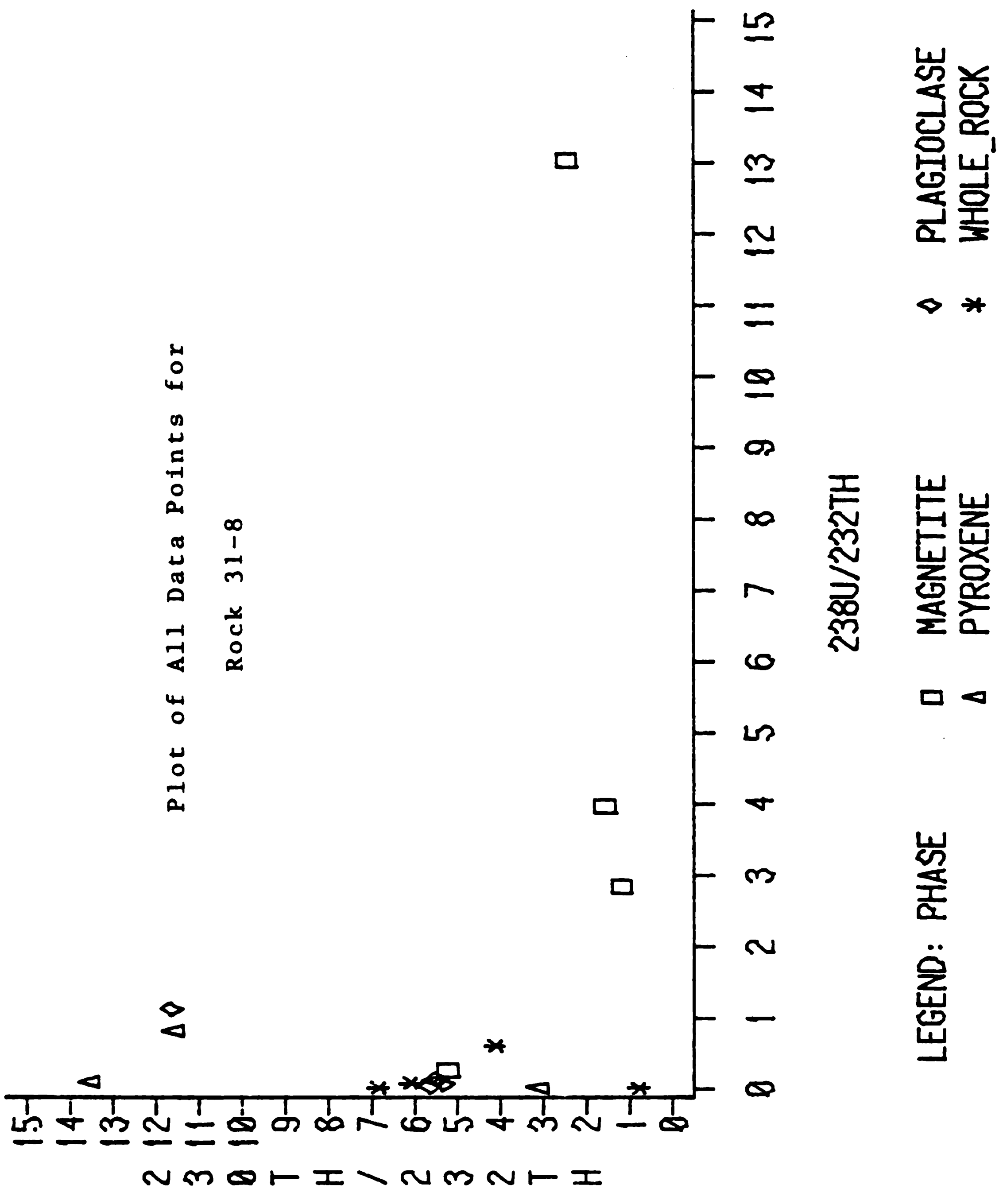
After counting samples for at least twenty-four hours, the data were entered into a computer program and run on an IBM 370 computer to calculate the $^{238}U/^{232}Th$ ratio, the $^{230}Th/^{232}Th$ ratio, and the errors in each of these ratios. The computer program, as used, appears in Appendix E.

The calculations take the following general pattern. The raw counts for the isotope of interest are divided by the counting time for that isotope. Background counts for the corresponding channels, divided by its count time are substracted from the raw counts per minute. If correction factors are to be applied to the particular isotope, they are done at this point. Finally, the corrected amount is divided through by the yield for the element being treated.

Ratios of yield corrected values are determined next and the errors for each value calculated in double precision. The exact equations used to do each of these steps are laid out in the program in Appendix E.

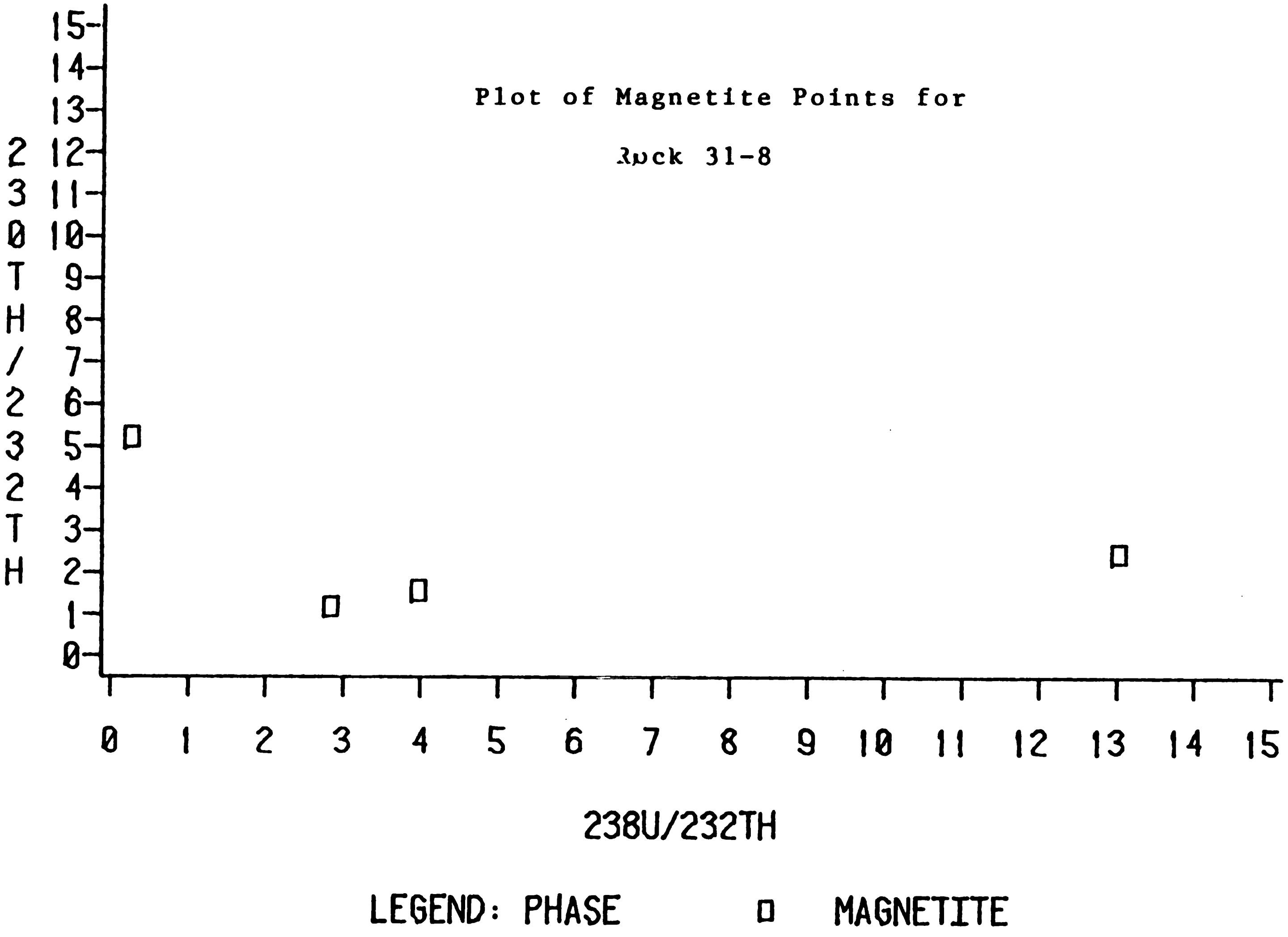
The results of the first runs of the data showed very clearly that there were significant problems. These were mainly that the data points plotted far from the region of the diagram where they were expected to plot. Figure 11 is a plot of the data points found for repeated analyses of each of the four phases of rock number 31-8. The points cluster along the y axis in all but 3 cases. A more pronounced pattern emerged when each phase is plotted separately, as in Figures 12, 13, 14 and 15. Figure 12 shows that the magnetite points are reasonably distributed closer to the 45 degree 'equiline' and the x-axis closer to where they should fall. The plagioclase points, on Figure 13, cluster close to the y axis, as do the pyroxene (Figure 14) and whole rock points (Figure 15). Each phase can be found in an area of the graph progressively higher on the y axis and each may be related to a similarly progressively worse problem in the dissolution chemistry.

The magnetite (Fe_3O_4), a simple iron oxide rather than a silicate, was easier to take into solution than the other phases. It was possible to take each aliquot of this phase into solution in hydrochloric acid overnight. However, the predominance of the iron in the solution, once attained, was so overwhelming that repeated isopropyl ether extractions throughout the procedure could not remove it. Enough excess iron came off onto the ion exchange columns in the later steps of the process after several extractions to 'clog' the columns. This demonstrated that not all of the iron had been extractable into the ether and remained as an iron complex rather than as free, extractable iron ion. At the final planchette plating step, the iron remaining was once more ether extracted and when absolutely no more could be removed, plating was done. An iron residue formed during the evaporation of the final drops of solution. This residue was thick enough to attenuate the alpha counts severely.



Plot of All Data Points for Rock 31-8

Figure 11



Plot of Magnetite Points for

Rock 31-8

Figure 12

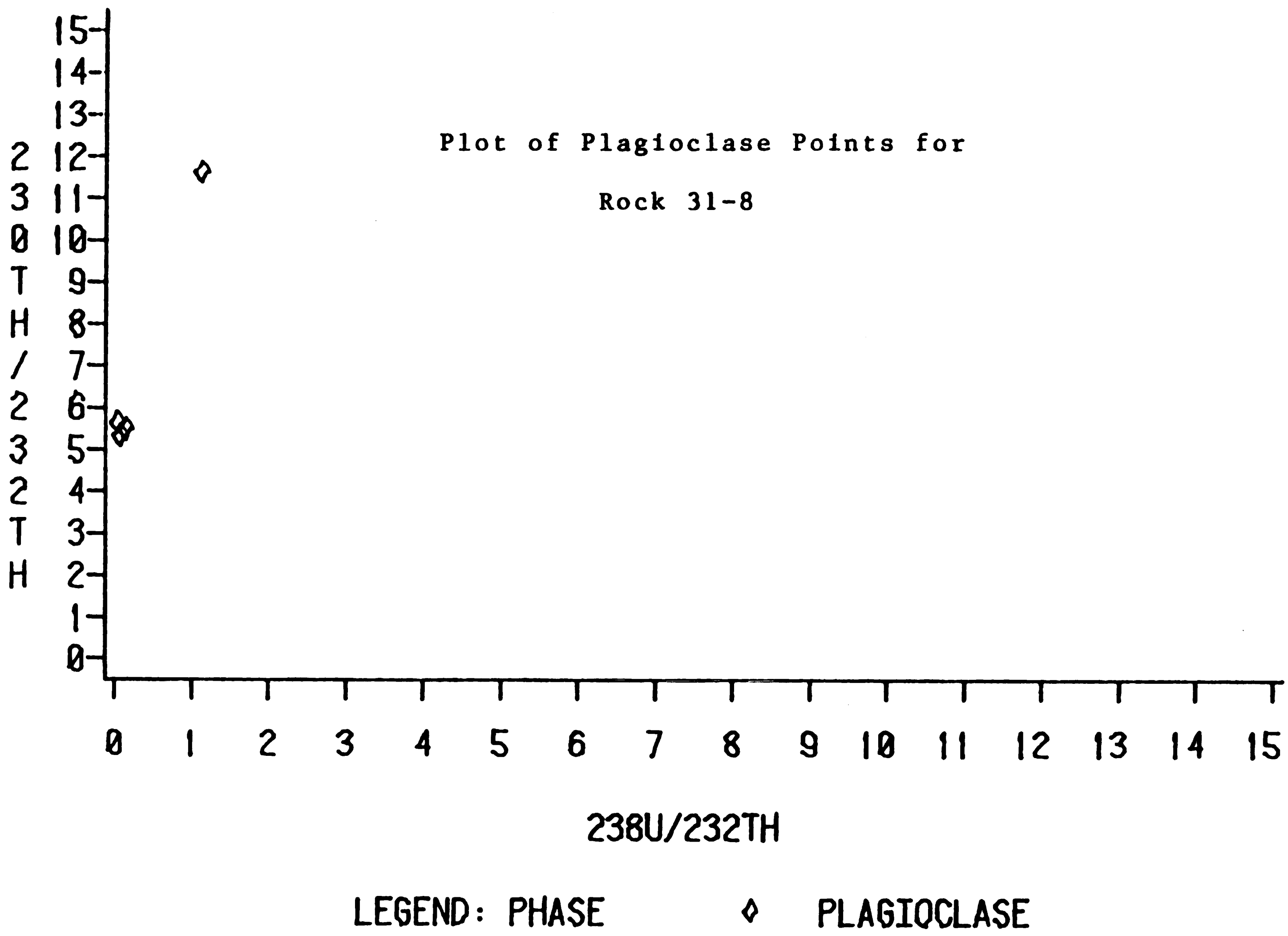
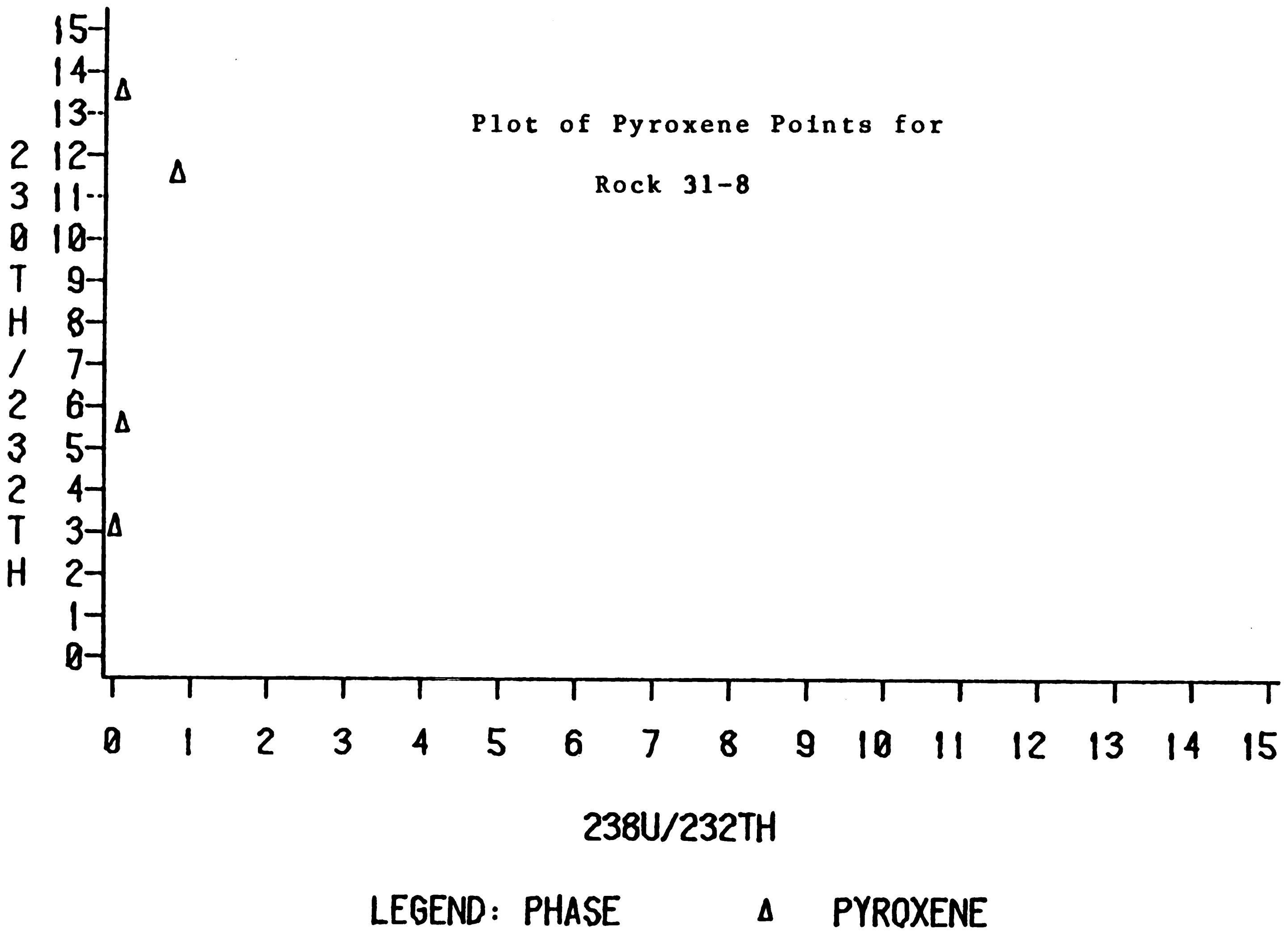

Plot of Plagioclase Points for
Rock 31-8
230TH/232TH
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
238U/232TH
LEGEND: PHASE
◊ PLAGIOCLASE

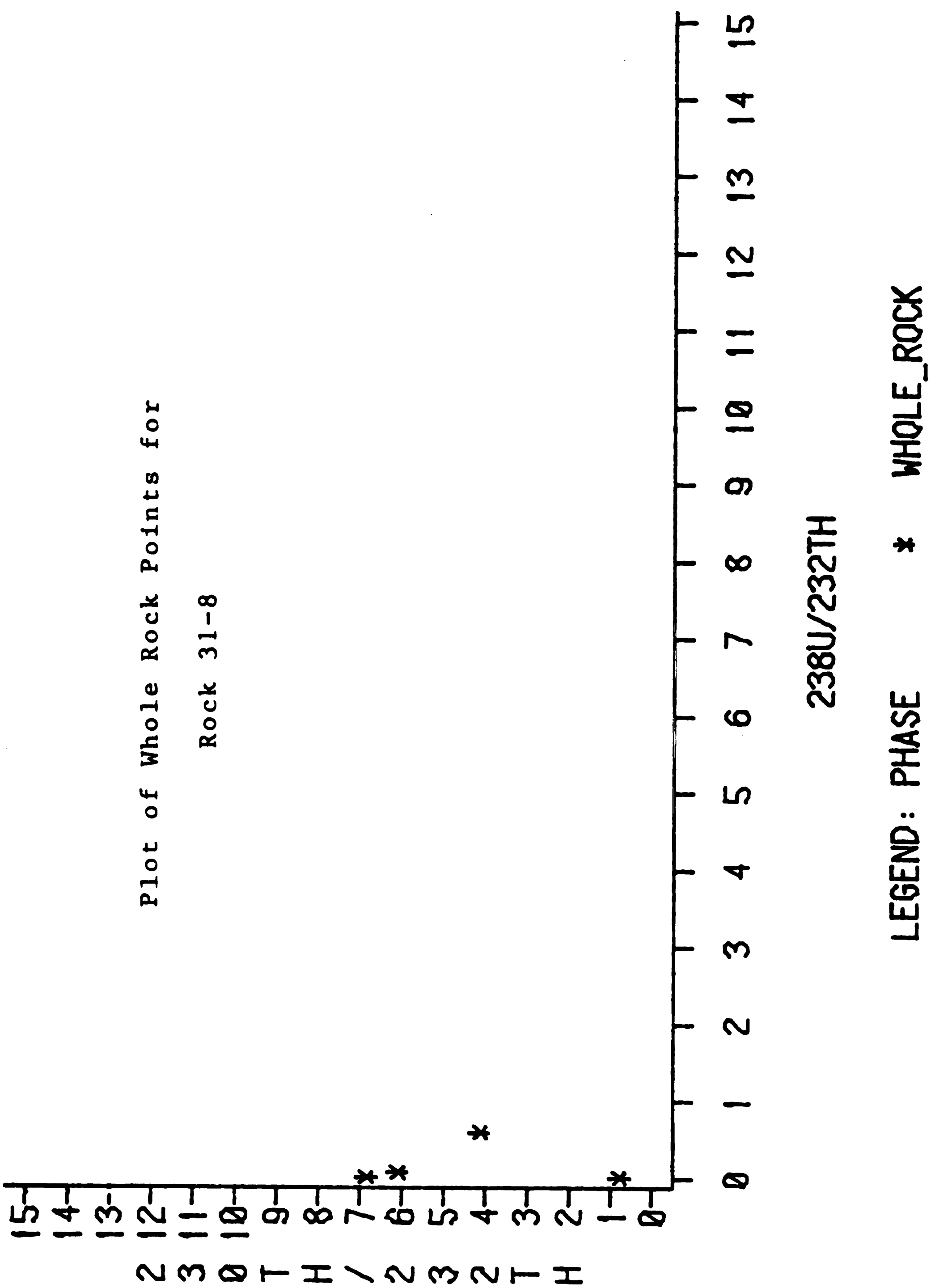
Figure 13



Plot of Pyroxene Points for

Rock 31-8

Figure 14


Plot of Whole Rock Points for

Rock 31-8

Figure 15

This problem of excess iron was not a problem in the work done on speleothems or light rocks since the iron content of those materials is proportionally so much lower than that of magnetite that the problem had not been seen in this magnitude before during the work of this research group. In fact, iron was added in processing those kinds of rock in order to facillitate the iron hydroxide precipitation step.

The other phases of the rock; plagioclase, pyroxene and whole rock, in addition to their iron content are silicates. This fact is the other of the two most serious problems faced in the chemistry which produced this data. After the initial attempt to take each phase into solution with hydrofluoric acid and perchloric acid followed by nitric acid, the residue which was left behind clearly required more intensive treatment. To this end, a fusion with sodium bicarbonate was attempted. The other available flux material was lithium metaborate. In discussions with the head of the research team it was decided that the lithium in the flux would interfere with the carriage of the thorium through the procedure. Therefore, the fusions were done with the sodium bicarbonate. According to the texts on fusions, the optimum temperature for fusion of these phases was 850°C. The recommended flux-to-phase proportions ranged from 4:1 to 10:1. Experimental trials with whole rock were run since whole rock was the one phase which needed the least processing and virtually unlimited amounts were available. Successive trials with different combinations of flux, time, and temperature were run. When any combination which involved a temperature greater the 850°C was tried, a black, pastey looking, insoluble coating, probably iron, formed around the edge of the crucible and on the underside of the cover. A temperature of lower than 850°C produced no noticeable change in the powder at all, even if left for longer than 10 to 12 hours.

Flux proportions lower than 8:1 produced little if any noticeable change in the powder and no improvement in the total amount of residue left behind after the dissolution. The final combination was the one which produced the best results with the fewest problems. That combination was 10:1 flux to sample heated to 850°C for 4 hours for phases like plagioclase and pyroxene and for six hours for whole rock.

The results of the fusions never reached the glass bead stage about which I had read, but all attempts to better them with the materials available resulted in no better products. Never was it possible to reduce the residues appreciably. The clustering of the silicate phases along the y-axis, may possibly be explained by their compositions. The inability to breakdown the phases, coupled with the loss of uranium in the fuming hydrofluoric acid step could account for the extreme vertical displacement of the points. The thorium loss, as well as additional uranium loss, during the many times solutions were taken to dryness and redissolved could account for the horizontal displacement and further vertical displacement of the points on the graph. Since attempts to mathematically correct the values back to 100 percent yields were relatively unsuccessful and the use of weighted linear regression techniques only increased the problem, (Table 3 and Figures 16-19) chemical interferences were the reasonable causes.

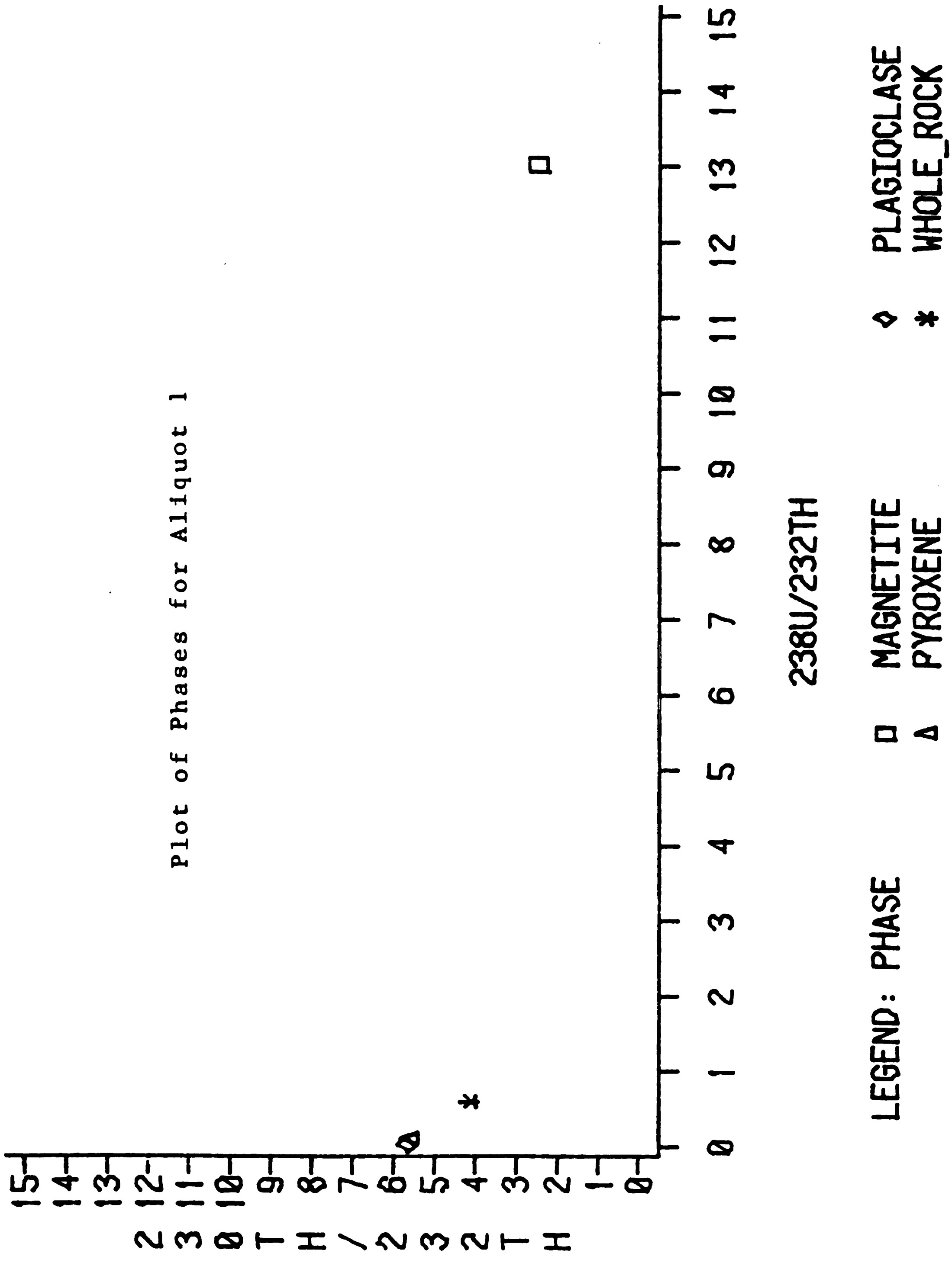
Table 3

REGRESSION DATA FOR 31-8 PHASES

Phase	Y Intercept	Slope	R Square
Magnetite	2.935590	-0.49	0.07487
Plagioclase	5.072947	16.58	0.98920
Whole Rock	4.52390	-0.13	0.00530
Pyroxene	8.39158	0.60	0.10582

PHASE DATA

Lab Number	Th/Th Ratio	Error	U/Th	Ratio
MSU251	1.1897	0.371	2.8435	0.451
MSU252	1.5590	0.688	3.9705	1.034
MSU253	5.2106	0.162	0.2597	0.034
MSU256	2.4733	0.133	13.0218	0.658
MSU255	11.6556	0.422	1.1170	0.061
MSU292	5.4999	0.056	0.1355	0.011
MSU293	5.3464	0.025	0.0610	0.003
MSU294	5.6379	0.017	0.0224	0.002
MSU261	6.0872	0.046	0.0775	0.006
MSU267	0.7885	0.006	0.0063	0.003
MSU268	6.8489	0.021	0.0112	0.001
MSU269	4.1110	0.320	0.5970	0.099
MSU257	13.5426	0.153	0.092	0.009
MSU258	3.1521	0.013	0.0197	0.002
MSU259	11.6146	0.040	0.8095	0.005
MSU295	5.5927	0.104	0.1042	0.021



Plot of Phases for Aliquot 1

Figure 16

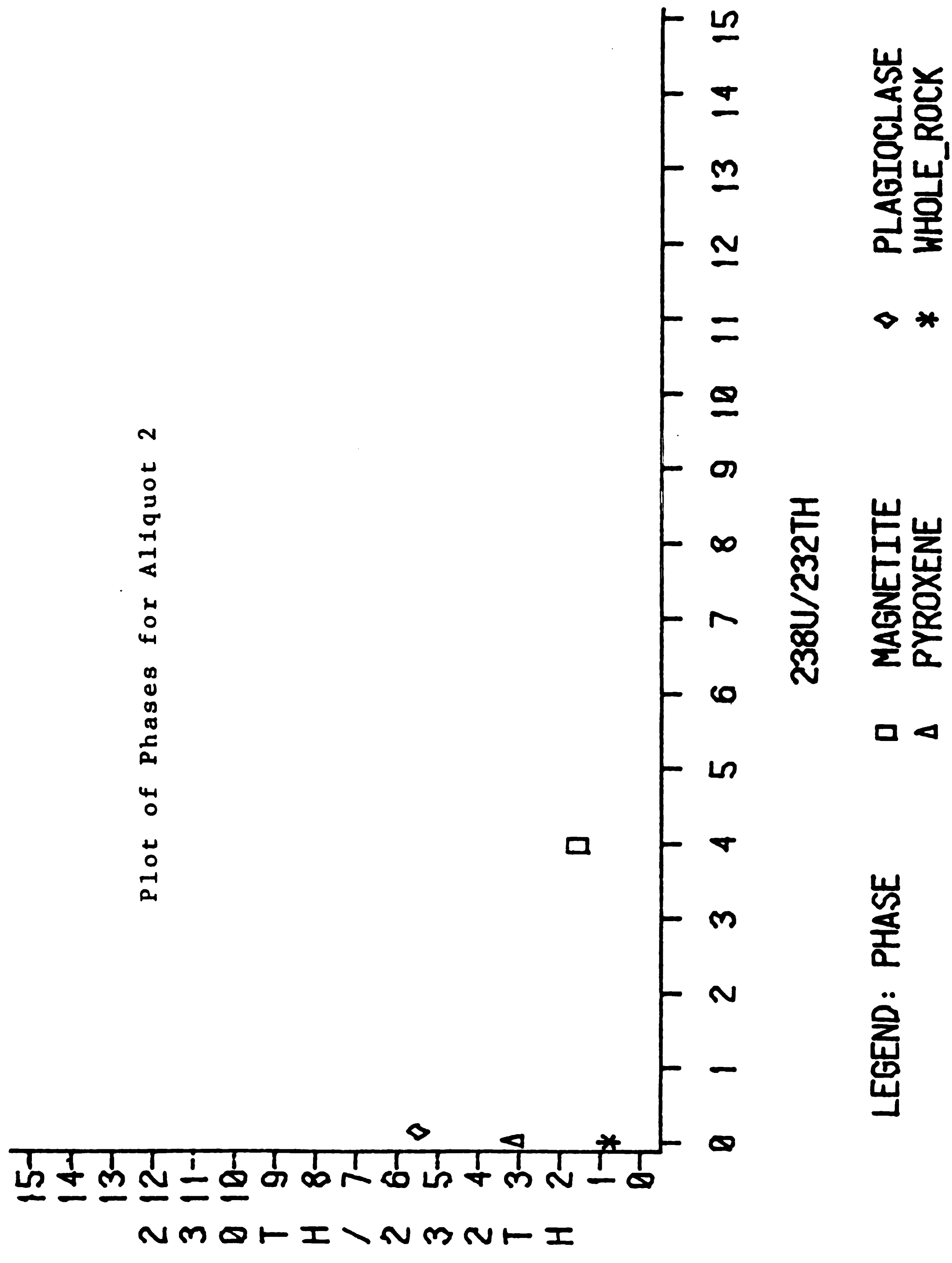

Plot of Phases for Aliquot 2
230TH/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
238U/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
LEGEND: PHASE
□ MAGNETITE
◇ PLAGIOCLASE
△ PYROXENE
* WHOLE_ROCK

Figure 17

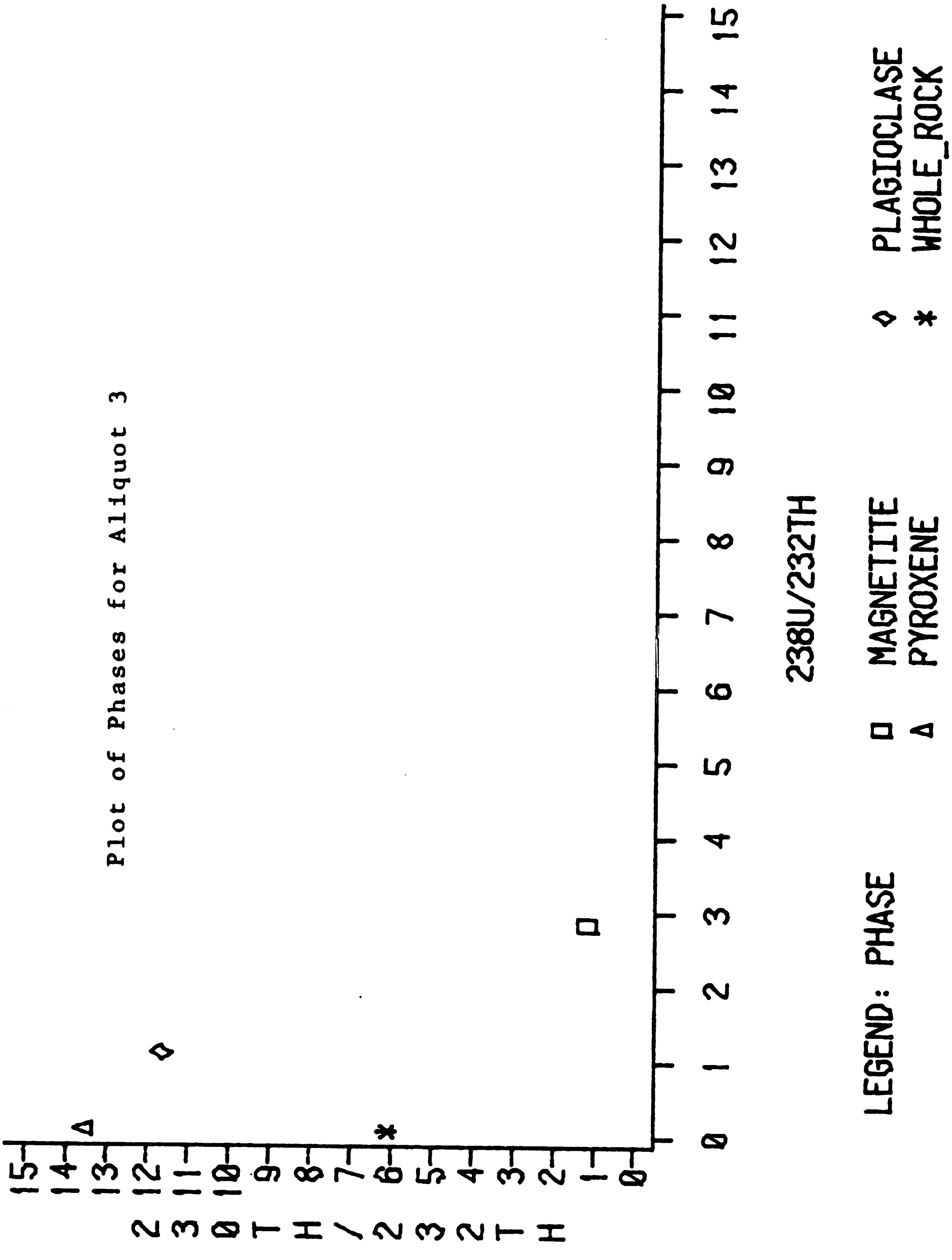

Plot of Phases for Aliquot 3
230TH/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
238U/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
LEGEND: PHASE
□ MAGNETITE
◇ PLAGIOCLASE
△ PYROXENE
* WHOLE_ROCK

Figure 18

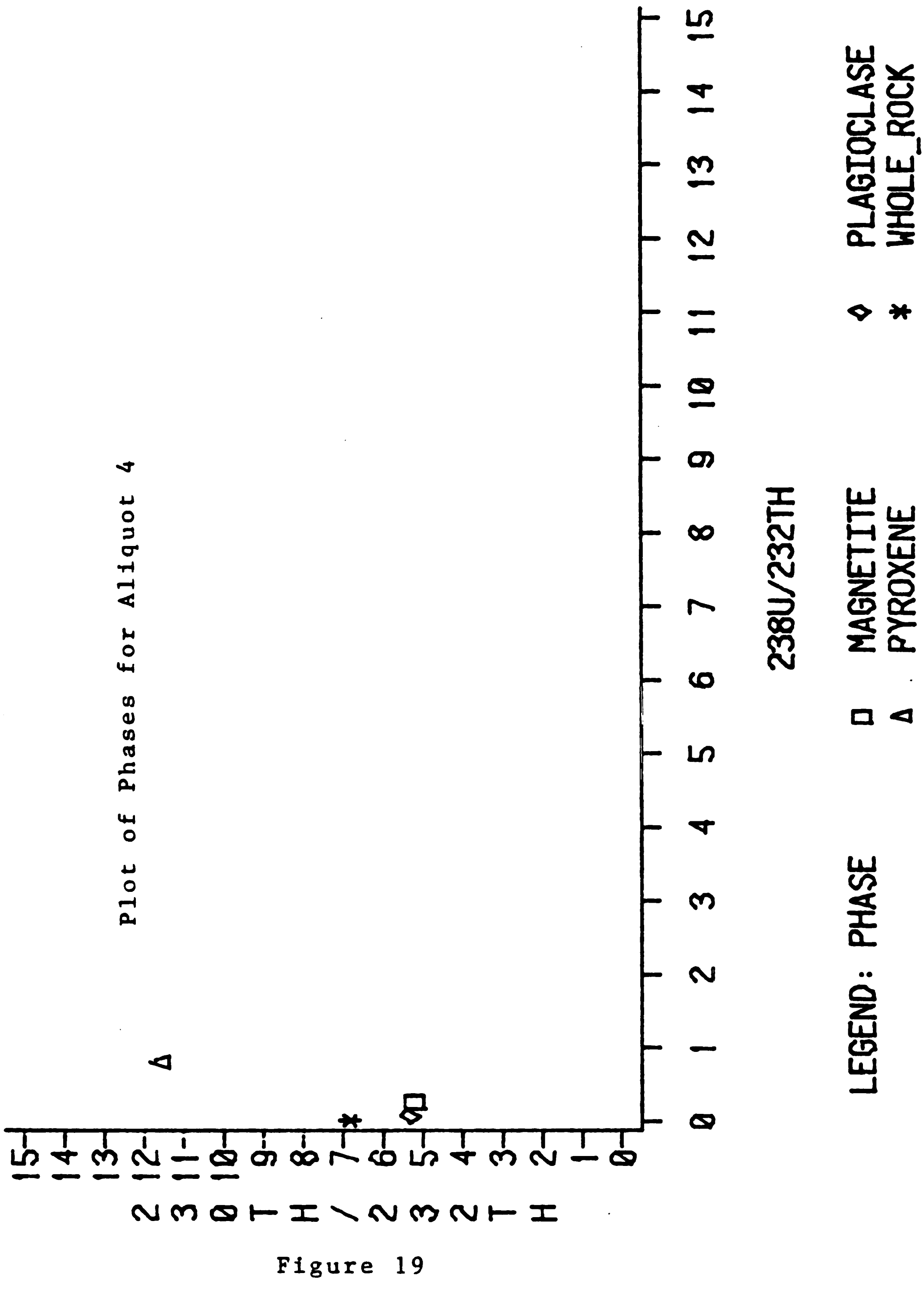
Plot of Phases for Aliquot 4
230TH/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
238U/232TH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
LEGEND: PHASE
□ MAGNETITE
◇ PLAGIOCLASE
Δ PYROXENE
* WHOLE_ROCK

Figure 19

In the general sense, it seems unreasonable to take a rock into solution, even given that dissolution is complete, and then to remove everything except a minute portion, in order to analyze that portion. It would seem to be much more reasonable to remove the trace elements of interest by some method, such as solvent extraction, early in the processing, leaving all the rest behind.

A type of solvent extraction was tried at one point in this work. Several telephone conversations with the chemists at one of Atlantic Richfield's Research and Development Laboratories yielded samples of four quaternary amines which are commonly used in industrial uranium solvent extraction. Attempts to facilitate solvent extractions in the laboratory were failures. The equipment necessary could not by synthesized and the technique was too cumbersome to miniaturize with no real understanding of the procedure and no guidance aside from phone conversations with some very well meaning scientists. It remains my conviction that the technique of solvent extraction is the way to proceed if this approach to basic volcanic rocks is to be used. Work by Gunyon, 1975; Jenkins 1969, and others seem to show the viability of this approach.

Whatever method is used, however, primary dissolution is necessary. Fusions or pressure bombs to break down the silicates must be successfully carried out in order to assure the release of the extremely small fractions or uranium and thorium from the rock or phase.

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APPENDICES

APPENDIX A

^{228}Th/^{232}U SPIKE

^{228}Th/^{232}U SPIKE

In order to quantitatively evaluate the yields of the uranium and thorium, a spike of ^{228}Th and ^{232}U in known quantity was added to the dissolved samples. These isotopes were best used since they were relatively non-existent in the system considered. Small corrections were made for the presence of both in the calculation of the age.

^{228}Th is a short lived daughter product of ^{232}U and therefore the two are reasonably considered to be at equilibrium in a closed system such as this.

It was also advantageous to use these isotopes because their energies fall into an easily used part of the spectrum for counting purposes.

Since known quantities of spike were used, the percent yield could be determined from the samples. Therefore, a normalized value would give the abundance of uranium and thorium in the original rocks.

The concentrated spike was diluted with 6N HCl to prevent it from adsorbing into the glass of the storage recepticle. Exactly 10.0 mL of concentrated spike was pipetted into a solution composed of 10 mL of concentrated HCl and 500 mL of concentrated HNO_3 contained in a 1-liter volumetric flask. This solution was then brought to volume with distilled water. A 5.0 mL aliquot of this solution at a time was then diluted to one liter with distilled water in a pyrex beaker. This was called the "dilute spike" and was stored in a dark brown pyrex glass bottle, refrigerated.

When using a spike of ^{228}Th, it becomes necessary to correct for the unsupported ^{228}Th decay with a half-life of 1.90 years. This correction is made by the following equation:

$$^{228}\mathrm{Th}_{corr} = \mathrm{cpm}\ ^{228}\mathrm{Th} - (^{232}\mathrm{U} \times .055)\ \exp(\lambda_{^{228}\mathrm{Th}} \times \mathrm{DECT})$$

where:

$^{228}\mathrm{Th}_{corr}$ = activity corrected for unsupported decay

$^{228}\mathrm{Th}_{meas}$ = measured activity

λ = decay constant for ^{228}Th (9.927×10^{-4}) yrs

DECT = the time which elapses between the chemical separation of uranium from thorium and when the actual counting beings

cpm = counts per minute corrected for background

The spike was periodically analyzed to determine the change of isotopic ratios in it and its activity.

APPENDIX B

USE OF FRANTZ ISODYNAMIC SEPARATOR

USE OF FRANTZ ISODYNAMIC SEPARATOR

Whole rock samples, crushed to less than 200 mesh size and cleansed of clay size particles, were dried and then passed through the Frantz Isodynamic Separator at the following settings:

Range: always set on low for mafic rocks
Side-side angle: approximately 18 degrees
Front-back angle: approximately 27 degrees

Mineral	Amps	Vibrator Setting
Magnetite	.025	4-6
Pyroxene	.08-1.0	6-7
Plagioclase	two runs at 1.0	5-6
	two runs at 1.5	5-6

If the rock was relatively free of altered minerals, several runs at each setting removed the discreet grains of more magnetically susceptible minerals. Then a setting of 1.5 amps cleared the remaining plagioclase of grains which were amalgams of mafic and non-mafic minerals. Glass, if present, could be removed by heavy liquids or water-gravity settling. For the Hawaiian basalts, water washes were at least as successful as heavy liquids separations. For obvious reasons, water separations were preferred.

APPENDIX C

REAGENTS

REAGENTS

I. Water was distilled and deionized.

II. Prepared reagents:

Reagent	Strength	Ingredients
A. Nitric Acid	8N	510 mL conc. to 1 L w/ H_2O
	0.1N	6.4 mL conc. to 1 L w/ H_2O
	5N	320 mL conc. to 1 L w/ H_2O
measured with graduated cylinders or class A pipettes		
B. Hydrochloric Acid	9N	710 mL conc. to 1 L w/ H_2O
	0.1N	8.6 mL conc. to 1 L w/ H_2O
C. Ammonium Hydroxide	0.3N	20 mL conc. to 1 L w/ H_2O
D. TTA Solution		25 gms + 500 mL benzene

all stocks were reagent grade

III. Spike:

from: Radiochemical Centre
Amersham, England

APPENDIX D

CLEANING OF GLASSWARE

CLEANING OF GLASSWARE

All glassware was scrubbed with phosphate free detergent and hot water. Next it was rinsed with tap water, then scrubbed with 8N HNO_3. It was then rinsed with tap and finally with distilled water.

Centrifuge tubes, test tubes, and 10 mL beakers were rinsed with acetone, detergent scrubbed and tap water rinsed. Next they were scrubbed with 8N HNO_3, rinsed with tap water and then rinsed with distilled water. An acetone rinse and final distilled water rinse followed.

Vycor beakers and teflon beakers were soaked overnight in 2:1 HNO_3:H_2O before washing.

APPENDIX E

COMPUTER PROGRAMS USED TO PROCESS THE DATA AND TO CALCULATE THE ERRORS

COMPUTER PROGRAMS USED TO PROCESS THE DATA AND TO CALCULATE THE ERRORS

```
C        THIS PROGRAM CORRECTS RAW COUNT RATE DATA AND COMPUTES U-238/TH-232,
C        U-234/U-238 AND TH-230/TH-232 ISOTOPE RATIOS. YIELDS OF U AND TH ARE
C        CALCULATED AND THE ERRORS IN THE RATIOS CALCULATED.
C        N1=U-238 COUNT RATE
C        N2=U-234 COUNT RATE
C        N3=U-232 COUNT RATE
C        N4=TH-232 COUNT RATE
C        N5=TH-230 COUNT RATE
C        N6=TH-228 COUNT RATE
C        N7=RA-224 COUNT RATE
C        CN1=CORRECTED U-238 COUNT RATE YIELD CORRECTED
C        CN2=CORRECTED U-234 COUNT RATE YIELD CORRECTED
C        CN3=CORRECTED U-232 COUNT RATE YIELD CORRECTED
C        CN4=CORRECTED TH-232 COUNT RATE YIELD CORRECTED
C        CN5=CORRECTED TH-230 COUNT RATE YIELD CORRECTED
C        CN6=CORRECTED TH-228 COUNT RATE YIELD CORRECTED
C        CNTU = ACCUMULATION TIME FOR U SPECTRUM (MINS)
C        CNTT = ACCUMULATION TIME FOR TH SPECTRUM (MINS)
C        CNBD = ACCUMULATION TIME FOR BLANK DISC (MIN)
C        SAR=ACTIVITY OF 1.0 ML U-232/TH-232  SPIKE
C        WT=WEIGHT OF SAMPLE USED
C        SPIKE=TH-228/U-232 ACTIVITY RATIO IN SPIKE
C        THALF8=THE DECAY CONSTANT FOR TH-228=9.94E-04
C        DECT=DELAY BETWEEN COUNTING TH228 AND SEPARATION FROM U
C        B1=COUNTER BACKGROUND CORRECTION FOR U-238
C        B2=COUNTER BACKGROUND CORRECTION FOR U-234
C        B3=COUNTER BACKGROUND CORRECTION FOR U-232
C        B4=COUNTER BACKGROUND CORRECTION FOR TH-232
C        B5=COUNTER BACKGROUND CORRECTION FOR TH-230
C        B6=COUNTER BACKGROUND CORRECTION FOR TH-228
      DOUBLE PRECISION N1,N2,N3,N4,N5,N6,N7,CN1,CN2,CN3,CN4,CN5,CN6,
     2   CNTU,CNTT,CNBD,SAR,SAU,SAT,B1,B2,B3,B4,B5,B6,DECT,ML,WT,YU,
     3   YT,R21,R14,R54,YUP,YTP,PPMU,ER1,ER2,ER4,ER5,ER14,ER54,ER21,YI,
     4   YII,THALF8,Y2,Y3,Y4,Y5,Y6,Y7
      DIMENSION TITLE(10)
```

```
100   READ(5,101,END=999)TITLE,CNTU,CNTT,SPIKE,DECT,ML,WT
101   FORMAT(10A1,6E10.4)
      WRITE(6,1000)TITLE,CNTU,CNTT,DECT,ML,WT
1000  FORMAT(1X,10A1,2X,2(1PE20.10),/,13X,3(1PE20.10))
102   READ(5,103)N1,N2,N3,N4,N5,N6,N7
103   FORMAT(7F10.4)
      WRITE(6,103)N1,N2,N3,N4,N5,N6,N7
104   READ(5,105)B1,B2,B3,B4,B5,B6,CNBD
105   FORMAT(7F10.4)
      WRITE(6,105)B1,B2,B3,B4,B5,B6,CNBD
      THALF8=9.94E-04
      SAU=25.39
      SAT=22.62
      SAR=SAU/SAT
      WRITE(6,140)SAR
140   FORMAT(2X,'SAR=',1PE20.10)
C     CORRECT FOR BACKGROUND, CALCULATE COUNTS PER MINUTE AND NORMALIZE
      YU=(((N3/CNTU)-(B3/CNBD))/(SAU*.2))
       Y2=N6/CNTT
       Y3=B6/CNBD
       Y4=Y2-Y3
       Y5=N7/CNTT
       Y6=B6/CNBD
       Y7=(Y5-Y6)*.055
       YI=(Y4-Y7)
      YII=YI*(YI*DEXP(THALF8*DECT))
      YT=(YII/(SAT*.2))
      WRITE(6,6000)YI
6000  FORMAT(2X,'YI=',1PE20.10)
      WRITE(6,6001)YII
6001  FORMAT(2X,'YII=',1PE20.10)
C     CORRECT COUNTS FOR BACKGROUND AND PEAK TAILING AND YIELD CORRECT
      CN1= ((N1/CNTU)-(B1/CNBD))/YU
      CN2=(((N2/CNTU)-(B2/CNBD))/YU)-(CN1/21.7)
      CN3=((N3/CNTU)-(B3/CNBD))/YU
      CN4=((N4/CNTT)-(B4/CNBD))/YT
      CN5=((N5/CNTT)-(B5/CNBD))/YT
      CN6=(YII)/YT
C       CALCULATION OF ISOTOPE RATIOS AND ERRORS IN THESE RATIOS
C        DUE TO STATISTICAL ERRORS IN THE COUNT RATE
C     R21=U234/U238
C     R14=U238/TH232
C     R54=TH230/TH232
      R21=CN2/CN1
      R14=(CN1/CN4)
      R54=CN5/CN4
C          CORRECTED COUNTS IN ORDER 1-6
125   WRITE(6,126)CN1,CN2,CN3,CN4,CN5,CN6
126   FORMAT(2X,'CN1=',1PE20.10,2X,'CN2=',1PE20.10,2X,'CN3=',1PE20.10,/,
     1  2X,'CN4=',1PE20.10,2X,'CN5=',1PE20.10,2X,'CN6=',1PE20.10)
```

```
      YUP=YU*100
117   WRITE(6,118)YUP
118   FORMAT(10X,'YU= ',1PE10.2,'PERCENT')
      PPMU=((.2)*(CN1)*(304.93))/(CN3*WT)
      WRITE(6,251)PPMU
251   FORMAT(' PPMU= ',1PE10.2)
C     CALCULATION OF THE ERROR IN THE RATIOS
C        ER = TOTAL ERROR IN U-TH COUNT RATES DERIVED FROM U-TH COUNT RATES
C        , BLANK DISC COUNT RATE FOR U-TH COUNT TIMES
C        , BLANK DISC COUNT RATE FOR BLANK DISC COUNT TIMES
      ER1=DSQRT((CN1/CNTU)+(B1/CNBD)+(B1/CNTU))
      WRITE(6,5000)ER1
5000  FORMAT(2X,'ERROR IN CN1=',1PE20.10)
      ER2=DSQRT((CN2/CNTU)+(B2/CNBD)+(B2/CNTU))
      WRITE(6,5001)ER2
5001  FORMAT(2X,'ERROR IN CN2=',1PE20.10)
      ER4=DSQRT((CN4/CNTT)+(B4/CNBD)+(B4/CNTT))
      WRITE(6,5002)ER4
5002  FORMAT(2X,'ERROR IN CN4=',1PE20.10)
      ER5=DSQRT((CN5/CNTT)+(B5/CNBD)+(B5/CNTT))
      ER14=(CN1/CN4)*DSQRT(ER1*ER1/(CN1*CN1)+ER4*ER4/(CN4*CN4))
      WRITE(6,5003)ER5
5003  FORMAT(2X,'ERROR IN CN5=',1PE20.10)
      ER21=(CN2/CN1)*DSQRT(ER2*ER2/(CN2*CN2)+ER1*ER1/(CN1*CN1))
      ER54=(CN5/CN4)*DSQRT(ER5*ER5/(CN5*CN5)+ER4*ER4/(CN4*CN4))
      YTP=YT*100
119   WRITE(6,120)YTP
120   FORMAT(10X,'YT= ',1PE10.2,'PERCENT')
106   WRITE(6,107)R14
131   WRITE(6,132)ER14
108   WRITE(6,109)R54
133   WRITE(6,134)ER54
107   FORMAT(10X,'U238/TH232=',1PE20.10)
109   FORMAT(10X,'TH230/TH232=',1PE20.10)
110   WRITE(6,111)R21
135   WRITE(6,136)ER21
111   FORMAT(10X,'U234/U238=',1PE20.10)
132   FORMAT(2X,'ERROR U238/TH232= ',1PE20.10)
134   FORMAT(2X,'ERROR TH230/TH232= ',1PE20.10)
136   FORMAT(2X,'ERROR U234/U238=',1PE20.10,//)
      WRITE(6,7000)TITLE,R54,ER54,R41,ER41
7000  FORMAT(2X,2A4,2X,4(1PE20.10,2X,//)
      GO TO 100
999   STOP
      END
```

```
MSU251    1328.8    1382.53   0.99      3.977     00.2       10.0
235.0     226.0     493.0     499.0     644.0     1990.0    236.0
9.0       31.0      6.0       6.0       32.0      20.0      682.97
MSU252    1494.95   1534.63   0.99      1.826     00.2       15.0
48.0      94.0      92.0      163.0     305.0     1558.0    235.0
9.0       31.0      6.0       6.0       32.0      20.0      682.97
MSU253    2456.43   3104.0    0.99      4.388     00.2       10.0
183.0     305.0     658.0     41.0      153.0     220.0     109.0
23.0      61.0      21.0      18.0      62.0      40.0      1627.43
MSU255    1336.0    1577.8    0.99      31.038    00.2       10.0
128.0      159.0     236.0     60.0     670.0     420.0     170.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU256    1516.12   2899.33   0.99      3.216     00.2       10.0
1121.0    1565.0    326.0     110.0     264.0     1032.0    220.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU257    2685.05   1809.02   0.99      38.213    00.2       10.0
267.0     319.0     1548.0     12.0     123.0     98.0      31.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU258    1585.2    1430.18   0.99      8.994     00.2       10.0
105.0      139.0     465.0     24.0     70.0      59.0      36.03
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU259    1315.93   2607.35   0.99      11.01     00.2       10.0
336.0     432.0     54.0      20.0      184.0     82.0      54.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU261    1275.93   1594.0    0.99      5.001     00.2       10.0
28.0      61.0      92.0      27.0      150.0     108.0     45.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU267    1205.03   1262.0    0.99      14.111    00.2       10.0
25.0      232.0     500.0     275.0     217.0     244.0     515.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU268    1473.0    1393.3    0.99      40.01     00.2       10.0
79.0      109.0     391.0     24.0      150.0     48.0      36.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU269    1553.83   1427.35   0.99      19.021    00.2       10.0
160.0     210.0     1166.0    36.0      140.0     444.0     92.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU292    1431.18   2439.0    0.99      19.078    00.2       10.0
55.0      102.0     208.0     27.0      129.0     177.0     45.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU293    2819.3    2957.48   0.99      27.949    00.2       10.0
43.0      107.0     128.0     66.0      330.0     198.0     87.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU295    1393.1    1880.88   0.99      9.360     00.2        2.5
128.0     204.0     1223.0    36.0      186.0     249.0     60.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
MSU294    1342.68   3007.88   0.99      26.08     00.2       10.0
16.0      62.0      64.0      20.0      88.0      82.0      33.0
11.0      23.0      16.0      7.0       6.0       23.0      4065.65
```

APPENDIX F

DATA SHEETS FROM THE LABORATORY RESULTS

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 252 Sample Number 31-8 Mag. Sample Weight 15 gms.

Sample Identification Magnetite from Pololu Basalt

Date Preparation Began 9/11/77 Date & Time of U/Th Separation 9/16/77

Amount of Tracer 2 ml. 1525

Date & Time of Completion 9/18/77

DECT 1.8799 Method of Dissolution HCl

ASSAY:

	U		Th	
Date & Time of Chemical Extraction	10/21/77	1150	9/18/77	1136
Begin Count Time	10/21/77	1250	9/18/77	1232
End Count Time	10/22/77	1350	9/19/77	1412
Actual Count Time (min)	1494.95		1534.63	

	Channels	Counts		Channels	Counts
^{238}U	123-223	48	^{232}Th	92-193	163
^{235}U			^{230}Th	194-316	305
^{234}U	224-324	94	^{228}Th	317-446	1558
^{232}U	325-435	92	^{224}Ra	447-494	235

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 292 Sample Number 31-8 plag. Sample Weight 10 gms.

Sample Identification plagioclase from Pololu Basalt (1)

Date Preparation Began 10/15/77 Date & Time of U/Th Separation 10/21/77

Amount of Tracer 2 ml. 1155

Date & Time of Completion 10/27/77 fusion

DECT 19.078 Method of Dissolution & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/3/77 1155	11/6/77 2003
Begin Count Time	11/3/77 1348	11/7/77 2108
End Count Time	11/4/77 1343	11/9/77 1347
Actual Count Time (min)	1431.18	2439.0

	Channels	Counts		Channels	Counts
^{238}U	124-224	55	^{232}Th	70-188	27
^{235}U			^{230}Th	189-307	129
^{234}U	225-326	102	^{228}Th	308-436	177
^{232}U	327-425	208	^{224}Ra	437-493	45

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 259 Sample Number 31-8 pyroxl Sample Weight 10 gms.

Sample Identification pyroxene (1) from Pololu Basalt

Date Preparation Began 9/15/77 Date & Time of U/Th Separation 9/28/77 1530

Amount of Tracer 2 ml.

Date & Time of Completion 10/9/77

DECT 12.2388 Method of Dissolution fusion & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/12/77 1430	10/10/77 1945
Begin Count Time	11/14/77 1559	10/10/77 2044
End Count Time	11/15/77 1400	10/12/77 1625
Actual Count Time (min)	1315.93	2607.35

	Channels	Counts		Channels	Counts
^{238}U	127-227	336	^{232}Th	70-189	20
^{235}U			^{230}Th	190-307	184
^{234}U	228-328	432	^{228}Th	308-441	82
^{232}U	329-429	54	^{224}Ra	442-490	54

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 261 Sample Number 31-8 WR1 Sample Weight 10 gms.

Sample Identification Whole Rock Pololu Basalt

Date Preparation Began 9/22/77 Date & Time of U/Th Separation 9/29/77 1345

Amount of Tracer 2 ml.

Date & Time of Completion 10/3/77

DECT 36.001 Method of Dissolution fusion & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/4/77 1250	11/4/77 1250
Begin Count Time	11/5/77 1626	11/4/77 1347
End Count Time	11/6/77 1342	11/5/77 1621
Actual Count Time (min)	1275.93	1594.0

	Channels	Counts		Channels	Counts
^{238}U	121-221	28	^{232}Th	69-189	27
^{235}U			^{230}Th	190-307	150
^{234}U	222-324	61	^{228}Th	308-448	108
^{232}U	325-425	92	^{224}Ra	439-490	45

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 253 Sample Number 31-8 mag2 Sample Weight 10 gms.

Sample Identification Magnetite (2) from Pololu Basalt

Date Preparation Began 9/15/77 Date & Time of U/Th Separation 9/23/77 1105

Amount of Tracer 2 ml.

Date & Time of Completion 9/27/77

DECT 6.202 Method of Dissolution HCl

ASSAY:

	U	Th
Date & Time of Chemical Extraction	10/26/77 1358	9/28/77 1638
Begin Count Time	10/26/77 1455	9/29/77 1556
End Count Time	10/28/77 937	9/30/77 2112
Actual Count Time (min)	2546.43	3104.0

	Channels	Counts		Channels	Counts
^{238}U	123-227	183	^{232}Th	72-193	31
^{235}U			^{230}Th	194-316	153
^{234}U	228-324	305	^{228}Th	317-442	220
^{232}U	325-431	658	^{224}Ra	443-496	109

COMMENTS: Thorium was re-extracted and replated for counting due to a problem in the electronics of the counter which caused the element to need changing; and the count to be restarted.

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 293 Sample Number 31-8 plag2 Sample Weight 10 gms.

Sample Identification Plagioclase (2) from Pololu Basalt

Date Preparation Began 10/15/77 Date & Time of U/Th Separation 10/21/77 1300

Amount of Tracer 2 ml.

Date & Time of Completion 10/25/77

DECT 27.012 Method of Dissolution fusion & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/23/77 1145	11/18/77 1045
Begin Count Time	11/23/77 1446	11/18/77 1147
End Count Time	2819.3	2957.48
Actual Count Time (min)	2819.3	2957.48

	Channels	Counts		Channels	Counts
^{238}U	124-224	43	^{232}Th	70-188	66
^{235}U			^{230}Th	189-307	330
^{234}U	225-324	107	^{228}Th	308-436	198
^{232}U	325-425	128	^{224}Ra	437-495	87

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 257 Sample Number 31.8 pyrox2 Sample Weight 10 gms.

Sample Identification Pyroxene (2) from Pololu Basalt

Date Preparation Began 9/15/77 Date & Time of U/Th Separation 9/23/77

Amount of Tracer 2 ml. 1115

Date & Time of Completion 10/1/77

DECT 38.213 Method of Dissolution HF & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	10/22/77 1256	10/31/77 1532
Begin Count Time	10/22/77 1358	10/31/77 1622
End Count Time	10/23/77 1055	11/1/77 1325
Actual Count Time (min)	2685.05	1809.02

	Channels	Counts		Channels	Counts
^{238}U	128-228	267	^{232}Th	75-193	12
^{235}U			^{230}Th	194-315	123
^{234}U	229-329	319	^{228}Th	316-440	98
^{232}U	330-429	1548	^{224}Ra	441-495	31

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 268 Sample Number 31-8WR2 Sample Weight 10 gms.

Sample Identification Whole Rock (2) Pololu Basalt

Date Preparation Began 9/18/77 Date & Time of U/Th Separation 10/9/77 1130

Amount of Tracer 2 ml.

Date & Time of Completion 10/16/77

DECT 30.101 Method of Dissolution fusion & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/15/77 1325	11/8/77 1130
Begin Count Time	11/17/77 1102	11/8/77 1355
End Count Time	11/18/77 1133	11/9/77 1308
Actual Count Time (min)	1473.27	1393.93

	Channels	Counts		Channels	Counts
^{238}U	123-223	79	^{232}Th	72-186	24
^{235}U			^{230}Th	187-308	150
^{234}U	224-325	109	^{228}Th	309-441	48
^{232}U	326-431	391	^{224}Ra	442-494	36

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 256 Sample Number 31-8 mag3 Sample Weight 10 gms.

Sample Identification Magnetite Replicate (3) from Pololu Basalt

Date Preparation Began 9/15/77 Date & Time of U/Th Separation 9/23/77 1110

Amount of Tracer 2 ml.

Date & Time of Completion 9/26/77

DECT 3.216 Method of Dissolution HCl

ASSAY:

	U	Th
Date & Time of Chemical Extraction	10/28/77 1330	9/26/77 1545
Begin Count Time	10/30/77 1445	9/26/77 1621
End Count Time	10/31/77 1605	9/28/77 1658
Actual Count Time (min)	1516.12	2899.33

	Channels	Counts		Channels	Counts
^{238}U	121.221	1121	^{232}Th	75-193	110
^{235}U			^{230}Th	194-315	264
^{234}U	222-325	1565	^{228}Th	316-445	1032
^{232}U	326-426	326	^{224}Ra	446-493	220

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 294 Sample Number 31-8 plag3 Sample Weight 10 gms.

Sample Identification Plagioclase (3) from Pololu Basalt

Date Preparation Began 10/15/77 Date & Time of U/Th Separation 10/25/77 1130

Amount of Tracer 2 ml.

Date & Time of Completion 10/28/77

DECT 26.08 Method of Dissolution fusion & HNO$_3$

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/23/77 1130	11/20/77 1215
Begin Count Time	11/28/77 1310	11/20/77 1325
End Count Time	11/28/77 1337	11/22/77 1541
Actual Count Time (min)	1342.68	3007.88

	Channels	Counts		Channels	Counts
^{238}U	124-224	16	^{232}Th	72-186	20
^{235}U			^{230}Th	187-308	88
^{234}U	225-325	62	^{228}Th	309-440	82
^{232}U	326-426	64	^{224}Ra	441-494	33

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 258 Sample Number 31-8 pyrox3 Sample Weight 10 gms.

Sample Identification Pyroxene (3) from Pololu Basalt

Date Preparation Began 9/15/77 Date & Time of U/Th Separation 9/23/77

Amount of Tracer 2 ml. 1330

Date & Time of Completion 10/1/77

DECT 8.994 Method of Dissolution HF & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	10/27/77 1530	10/2/77 1230
Begin Count Time	10/28/77 945	10/2/77 1321
End Count Time	10/29/77 1226	10/3/77 1551
Actual Count Time (min)	1585.2	1430.18

	Channels	Counts		Channels	Counts
^{238}U	125-225	105	^{232}Th	71-190	24
^{235}U			^{230}Th	191-308	70
^{234}U	226-324	139	^{228}Th	309-438	59
^{232}U	325-425	465	^{224}Ra	439-490	36

COMMENTS:

Michigan State University

RADIOACTIVE DATING DATA SHEET

DATA:

Laboratory Number 269 Sample Number 31-8WR3 Sample Weight 10 gms.

Sample Identification Whole Rock (3) Pololu Basalt

Date Preparation Began 9/18/77 Date & Time of U/Th Separation 10/4/77

Amount of Tracer 2 ml. 1530

Date & Time of Completion 10/16/77

DECT 19.816 Method of Dissolution fusion & HNO_3

ASSAY:

	U	Th
Date & Time of Chemical Extraction	11/2/77 1030	10/23/77 1630
Begin Count Time	11/2/77 1135	10/24/77 1100
End Count Time	11/3/77 1343	10/25/77 1105
Actual Count Time (min)	1553.83	1427.35

	Channels	Counts		Channels	Counts
^{238}U	122-223	160	^{232}Th	70-189	36
^{235}U			^{230}Th	190-307	140
^{234}U	224-325	210	^{228}Th	308-441	444
^{232}U	326-428	1166	^{224}Ra	442-491	92

COMMENTS: