



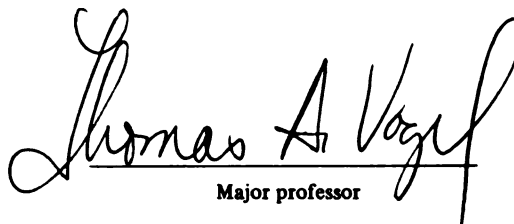
This is to certify that the
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238U/230Th Isotope Systematics of
Rhyolites from Long Valley, California

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James Baranowski

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$^{238}\text{U}/^{230}\text{Th}$ ISOTOPE SYSTEMATICS OF
RHYOLITES FROM LONG VALLEY,
CALIFORNIA

By

James Baranowski

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ABSTRACT

$^{238}\text{U}/^{230}\text{Th}$ ISOTOPE SYSTEMATICS OF RHYOLITES FROM LONG VALLEY, CALIFORNIA

By

James Baranowski

Dates obtained by $^{238}\text{U} - ^{230}\text{Th}$ systematics agree with K-Ar dates for two post collapse intercaldera rhyolites from Long Valley, CA. Analytical precision was not as great as that obtained by K-Ar methods, but the possibility of systematic error present with the use of K-Ar methods was reduced. [$^{230}\text{Th}/^{232}\text{Th}$], [$^{238}\text{U}/^{232}\text{Th}$] values for the glass phase fell above the isochron, possibly due to uranium loss during eruption. The use of hornblende-glass pairs to indicate eruption ages (Allegre, 1968) was not suitable for the rhyolites investigated. Possible $^{234}\text{U}/^{238}\text{U}$ fractionation was observed. This fractionation could only occur before emplacement, as no evidence for post-depositional uranium migration was observed.

($^{230}\text{Th}/^{232}\text{Th}$)_o values were similar, at .94, indicating that Th/U fractionation is not taking place at

James Baranowski

a substantial rate among the rhyolites in the Long
Valley magma chamber.

To Hilary

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Accurate dating of Quaternary igneous rocks has long posed a problem. K/Ar methods are subject to large errors caused by small amounts of excess argon (Damon, 1969; Dalrymple and Lanphere, 1969). Analytical accuracy is also critical due to the long half-life of ^{40}K and low $^{40}\text{Ar}_{\text{rad}}$ abundances encountered. Many dates for samples of different geologic age appear contemporaneous and correlation with ^{14}C dates are poor. ^{14}C dating, though more accurate, is of limited use since only wood, soil profiles, ashfalls, or tuffs may be dated, and the range of the method is limited to rocks younger than 40,000 years.

Uranium-series disequilibrium geochronologic techniques may be applied to volcanic rocks younger than 300,000 years. Given an initial state of isotopic disequilibrium and subsequent maintenance of closed system conditions, nuclides within the ^{238}U , ^{235}U , and ^{232}Th decay series will show a progressive change toward a state of secular equilibrium with time. ^{230}Th is the most useful nuclide in this respect, due to its half-life

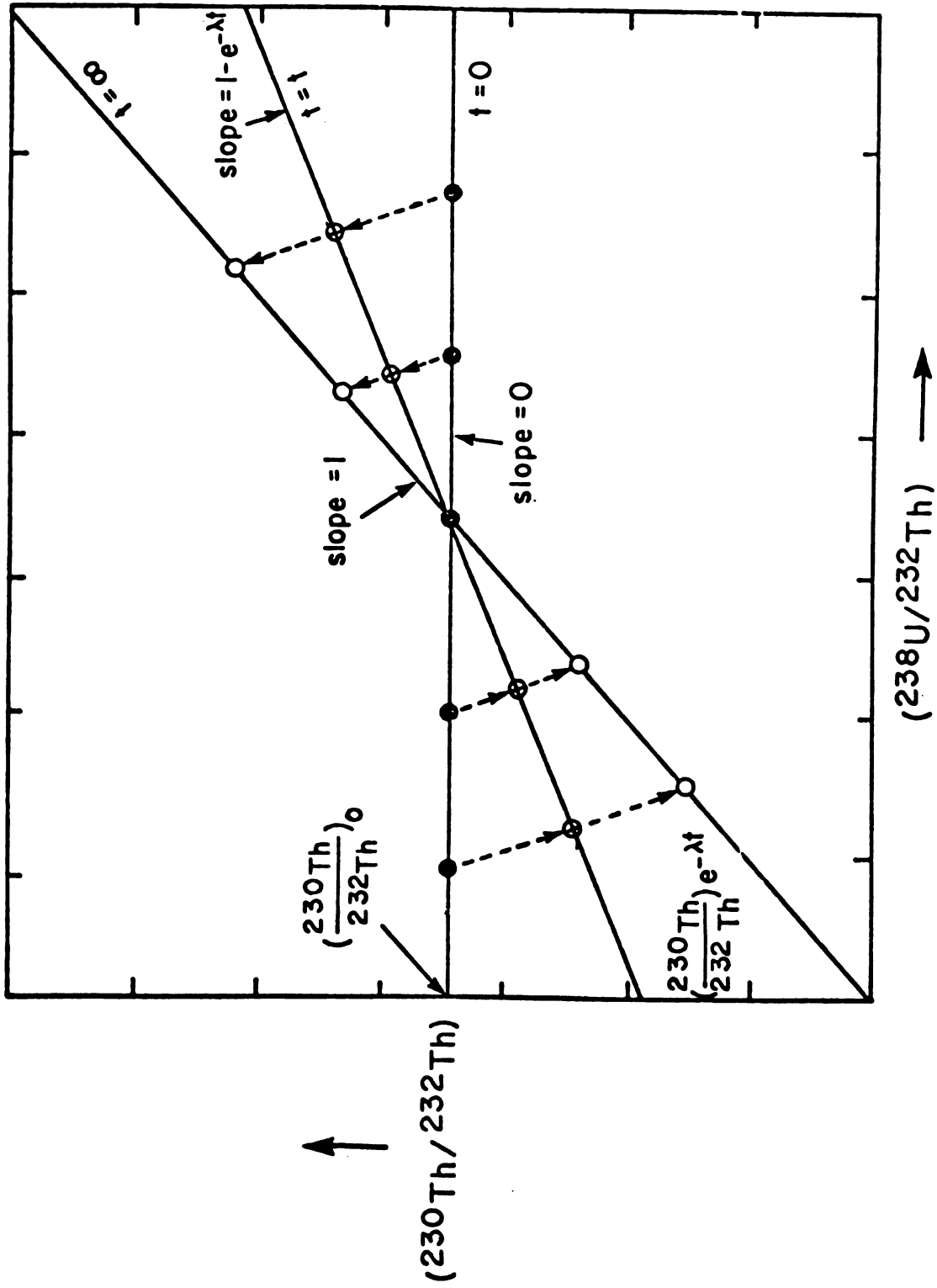
of 75,200 years (Atree et al., 1962). The systematics of ^{230}Th growth back to equilibrium with its parent, ^{238}U , may be treated in a manner similar to Rb/Sr methodology (Allegre, 1968). Thus, the individual $[\ ^{230}\text{Th}/\ ^{232}\text{Th}]$ - $[\ ^{238}\text{U}/\ ^{232}\text{Th}]$ activity ratios for the mineral phases of a rock will describe an isochron, with a slope which changes from 0 to 1 as a function of time (Figure 1). Whole rock and initial whole rock values may also lend insight into the geochemical evolution of a magma chamber (Allegre and Condomines, 1976).

The use of U/Th disequilibrium studies may offer advantages over the use of standard K/Ar geochronology.

These are:

- (i) Migration of U should not occur as readily as migration of Ar.
- (ii) The shorter half-lives of the nuclides involved with U/Th disequilibrium systematics theoretically should result in greater accuracy in age determinations.
- (iii) Many materials unsuitable for K/Ar dating are suitable for U/Th dating.
- (iv) The analysis of several phases is necessary for the construction of an isochron and this provides an internal check on the assumption that the mineral phases have been closed to isotope migration. K/Ar single phase analyses do not possess such an internal check.
- (v) The use of U/Th systematics also provides petrogenetic information in addition to the age determination, whereas K/Ar analysis will only provide age information.

Figure 1.--U/Th isotopic behavior in the system $(^{230}\text{Th}/^{232}\text{Th}) - (^{238}\text{U}/^{232}\text{Th})$ for the separate mineral phases of a volcanic rock initially at isotopic equilibrium with different U/Th ratios, but the same $(^{230}\text{Th}/^{232}\text{Th})$ ratios. Filled circles represent the system at $t = 0$, the crossed circles at some elapsed time $t = t$, and the open circles at secular equilibrium where $t = \infty$. The slope of the line connecting the individual phases is defined by the chromatic function $(1 - e^{-\lambda t})$ and gives the age of the system at any time t .



The post-collapse volcanics of Long Valley caldera, California, have been chosen as a sample site for this study because excellent age control was available for a number of samples suitable for U/Th dating. In addition, various geologic models have been proposed to explain the origin and relationship of the chemically bi-modal suite of volcanic rocks found in Long Valley. The application of the U/Th systematics to the area should provide information concerning the age of the associated magma chamber, as well as the amount of fractionation or mixing that has occurred within the magma chamber. In addition, the source of the magma types may be ascertained.

The primary objective of this thesis was to develop an analytical method for U/Th isotopic analysis of igneous rock and to test the validity and accuracy of the U/Th method as an alternative to K/Ar dating of volcanic rocks between 10,000 and 200,000 years old. A secondary objective was to use the U/Th systematics as a petrogenetic indicator to test various models for the evolution of the bi-modal volcanic suite of the Long Valley, California, resurgent cauldron. The second goal was only partially achieved as it required complete analysis of the total range of rock types present. This was not possible with the time constraints placed upon this study due to problems encountered with the development of the analytical technique.

CHAPTER II

GEOCHEMISTRY OF U AND TH

Chemical Behavior of U and Th

The general geochemical behavior of U and Th is similar in strongly reducing conditions, such as is present in the magmatic environment. This is due to the similarity of ionic radii in the 4+ valence state: $U^{4+} = .93\text{\AA}$ and $Th^{4+} = .96\text{\AA}$. U and Th are not readily partitioned toward the mineral phase, but rather tend to be concentrated in the liquid phase, obtaining their highest concentrations in pegmatites and aplites.

There is usually an increase in U and Th content during differentiation and an increase in Th/U ratio with differentiation over a wide range of intrusive and extrusive rock suites. However, some oceanic island rock suites, such as Hawaii, exhibit a decrease in Th/U ratio (Cherdyntsev and Senina, 1970, 1973; Nishimura, 1970). Cherdyntsev and Senia (1973) attribute this to the eruption of a Th-enriched residual magma. Preliminary data from Long Valley, California (Table 4) indicate that Uranium and Thorium abundances follow a normal pattern. Uranium abundances range from 1 ppm for basalts to over 7 ppm for rhyolites. Thorium abundances range from 2.5

ppm for basalts to over 20 ppm for rhyolites. These abundances were enough to permit measurement of U and Th isotope ratios.

Previous studies (Rogers and Adams, 1957; Taddeucci et al., 1967; Allegre and Condomines, 1976) show that U and Th abundance was distributed evenly throughout the phases present in basic and silicic extrusive rocks. Only small amounts of U and Th are present in uranium minerals. Glass is usually enriched in U and Th relative to the mineral phases, though accessory minerals such as allanite, apatite, zircon, and sometimes magnetite and biotite, act as hosts of U and Th. Quartz and feldspar tend to have low abundances of U and Th. Th/U ratios in phases vary, especially in accessory minerals. Thus, a $^{238}\text{U}/^{230}\text{Th}$ isochron may be constructed using virtually any group of phases present in the Long Valley volcanics.

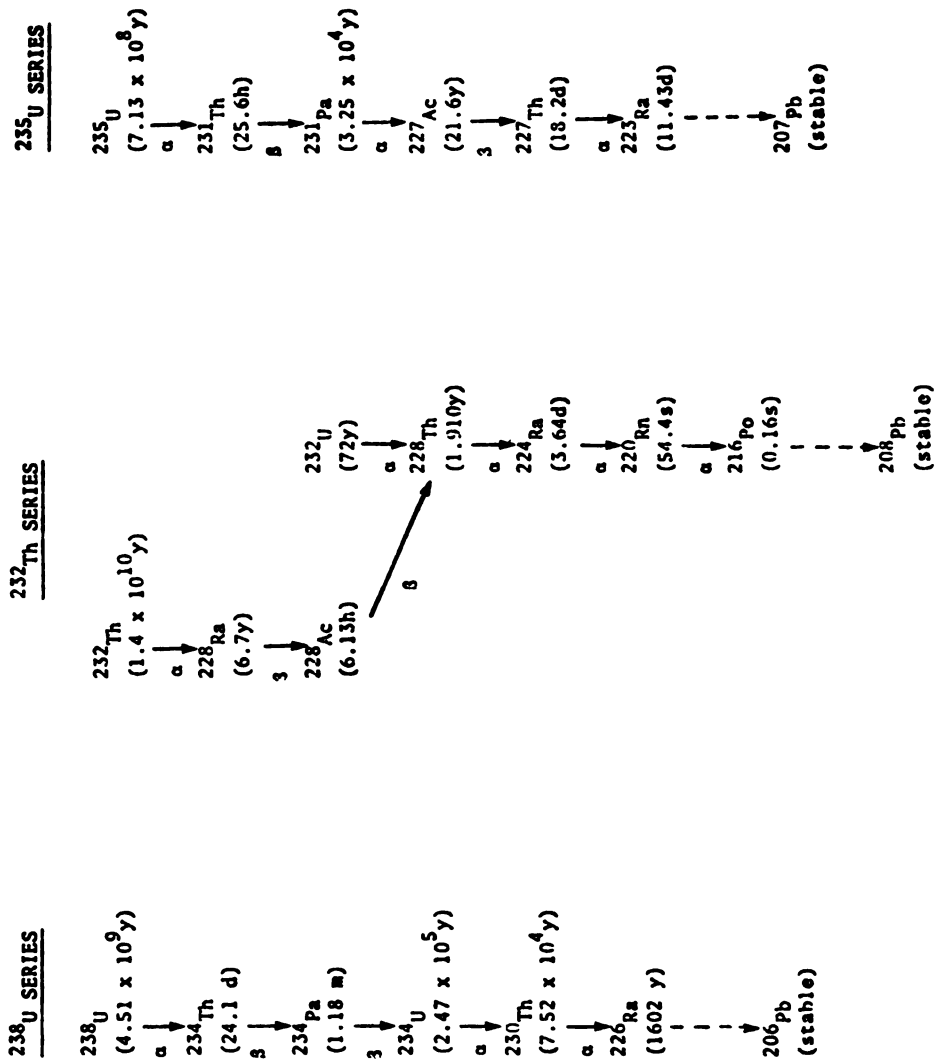
U and Th behave much differently in the near-surface environment. Th is always found in the 4+ oxidation state, whereas U may be oxidized to a 6+ state. Hexavalent U is usually found as the uranyl (UO_2^{2+}) form (Seaborg and Katz, 1954; Christ, et al., 1955), which is discriminated against in the formation of rock-forming minerals, even as a trace element, and tends to remain in solution. In near-surface, hydrothermal, and supergene environments, the amount of U in the 6+ state may reach 100%, which will allow migration of U relative to Th.

U may be leached from mineral phases without destruction of the crystal structure in metamorphic, hydrothermal, and supergene environments (Szalay and Samsoni, 1969; Cherdyntsev, 1971). This is due to the uniform distribution of U and Th in rock-forming and accessory minerals through isomorphous substitution, especially in growth sites, strain defects or microfractures, and microcapillaries (Cherdyntsev, 1971). The behavior of U in glass phases is somewhat different. A study by Kovalev and Malayasova (1971) on extrusive rocks indicate that U exists as uranium oxide compounds rather than silicate chains in vitric glasses. U does not leach as readily from these glasses as from mineral phases. Kovalev and Malayasova attributed this to a protective 'silica gel' coating on vitrified glasses. However, large amounts of U migration accompany the devitrification of glass (Rosholt and Noble, 1969). Therefore, samples showing any evidence of alteration or devitrification must be regarded with caution.

Isotopic Behavior of U and Th

The concentration of the various isotopes of U and Th is controlled primarily by their placement in one of the natural radioactive decay series, shown in Figure 2. ^{238}U , ^{234}U , and ^{230}Th belong to the ^{238}U decay chain. ^{232}Th and ^{228}Th belong to the ^{232}Th decay chain. In a

Figure 2.-- ^{238}U , ^{232}Th , and ^{235}U radioactive
decay series.



system at secular equilibrium, the activities of ^{234}U and ^{230}Th will be equal to ^{238}U activity. ^{228}Th activity will be equal to ^{232}Th activity. Therefore, ^{230}Th activity is related to uranium, not thorium, concentration for a system at secular equilibrium. Since neither ^{238}U nor ^{232}Th are produced by α -decay, the $^{238}\text{U}/^{232}\text{Th}$ ratio in igneous rocks is solely effected by chemical processes controlling the bulk distribution of U and Th in igneous rocks. Thus, $^{238}\text{U}/^{232}\text{Th}$ ratios are effectively the same as the bulk U/Th ratios.

Secular equilibrium may be disturbed by a number of processes. Chemical fractionation of the isotopes may occur. For instance, ^{230}Th may be thrown out of equilibrium with ^{234}U during crystallisation from a melt or any other chemical process that fractionates U relative to Th.

Chemical fractionation of an intermediate element may occur. This is the mechanism for disequilibrium between ^{228}Th and ^{232}Th . ^{228}Ra , intermediate in the decay chain between ^{232}Th and ^{228}Th , is chemically active and subject to migration, which will result in disequilibrium of its daughter product, ^{228}Th .

Isotopic fractionation of chemically identical elements may also occur due to the Slizard-Chalmers, or alpha-recoil, effect (Slizard and Chalmers, 1936; Cherdyntsev, 1971; Kigoshi, 1971). Atoms produced by α -decay occupy damaged sites in the mineral and will be

more subject to migration than an atom that has not undergone decay. This effect is pronounced in the case of ^{234}U , as U is itself initially concentrated in structural defects. As a result, ^{234}U will be preferentially incorporated into microfractures and microcapillaries where it will be more subject to leaching than ^{238}U . In addition, a higher percentage of ^{234}U relative to ^{238}U is found in the 6+ oxidation state, either due to oxidation during decay (Kigoshi, 1971) or to ^{234}U location in microfractures and microcapillaries (Cherdyntsev, 1971).

$^{234}\text{U}/^{238}\text{U}$ fractionation cannot occur in recently formed minerals, since the ^{234}U present is incorporated into the mineral at the time of formation and is in the same state as ^{238}U . Over time, decay-produced ^{234}U will accumulate so that after one half-life, 50% of ^{234}U will be decay-produced.

A similar effect will be encountered if an element is transformed to another element by decay. The daughter nuclide may occupy a position in the mineral that will retain the parent element, but will be unstable when occupied by the daughter element. This occurs in decay produced ^{230}Th .

The $^{234}\text{U}/^{238}\text{U}$ ratio will change in samples undergoing weathering or hydrothermal alteration. Whole-rock leaching experiments show a decrease in $^{234}\text{U}/^{238}\text{U}$ in the sample and a marked enrichment of ^{234}U in the extract

(Szalay and Samsoni, 1969). Basalts and andesites (Cherdyntsev et al., 1967; Cherdyntsev et al., 1968) and rhyolites (Rosholt and Noble, 1969) which have undergone alteration show a decrease in $^{234}\text{U}/^{238}\text{U}$ ratio, whereas waters which drain these areas exhibit ^{234}U enrichment. Fumarole gases and minerals which crystallize from them are also enriched in ^{234}U (Kupstov and Cherdyntsev, 1969).

A controversy exists concerning the operation of the Slizard-Chalmers effect in the magmatic environment. Studies on various volcanic rocks young enough to exhibit ^{230}Th disequilibrium show no fractionation between ^{234}U and ^{238}U (Oversby and Gast, 1968; Nishimura, 1970; Allegre and Condomines, 1976). However, studies by Cherdyntsev et al. (1967; 1968) indicate that ^{234}U fractionation does occur in recent volcanics, in conjunction with Th/U fractionation and $^{230}\text{Th}/^{232}\text{Th}$ fractionation. Cherdyntsev and Senina (1973) attribute this to fractionation of ^{234}U and ^{238}U between the liquid melt and solid phases in contact with the magma either through contamination or at the site of partial fusion. The $^{234}\text{U}/^{238}\text{U}$ ratio was monitored in this study to ascertain if this type of fractionation occurred in the Long Valley volcanics.

The $^{234}\text{U}/^{238}\text{U}$ ratio was also used as an indicator of radio-element migration in this study. If ^{234}U was fractionated relative to ^{238}U , α -recoil ^{230}Th was probably also fractionated relative to ^{232}Th and large

scale fractionation of U relative to Th will also have occurred. This would result in either a false ($^{230}\text{Th}/^{232}\text{Th}$)_o ratio, or scatter in the isochron plot due to variance in the initial $^{230}\text{Th}/^{232}\text{Th}$ ratios of the phases, or changes in the $^{238}\text{U}/^{232}\text{Th}$ ratios of the phases after formation. For this reason, samples that exhibited non-equilibrium $^{234}\text{U}/^{238}\text{U}$ ratios were regarded with caution.

U/Th Disequilibrium Dating Methods

Uranium series disequilibrium techniques have long been used to date sedimentary rocks. The basis of most methods in disequilibrium of ^{230}Th and ^{231}Pa due to their insolubility in water. Deep sea sediments have been dated using excess ^{230}Th and ^{231}Pa created by decay of soluble uranium in seawater and subsequently incorporated in bottom sediments (Piggot and Urry, 1942; Ku, 1965; Broecker, 1965; Broecker and Ku, 1969; Ku, 1976). Likewise, many carbonates are deposited from water with little or no initial Th. ^{230}Th and ^{231}Pa will grow into equilibrium with their parents ^{234}U and ^{235}U , respectively, after the carbonate has been deposited. This method has been used to date corals and oolites (Broecker and Thurber, 1965; Ku, 1968; Messoilella et al., 1969; Ku et al., 1974), speleothems (Ford, 1973; Schwarcz et al., 1975; Thompson et al., 1975), marls (Kaufman, 1971), caliche (Ku, 1975), and mollusc shells (Broecker, 1963; Broecker et al., 1968; Kaufman et al., 1971).

The change in ^{230}Th activity in relation to ^{238}U activity may be described by:*

$$(1) \quad ^{230}\text{Th} = ^{230}\text{Th}_0 e^{-\lambda_0 t} + ^{238}\text{U} [1 - e^{-\lambda_0 t} + (^{238}\text{U} / ^{234}\text{U} - 1)$$

$$\frac{\lambda_0}{\lambda_0 - \lambda_4} (1 - e^{-(\lambda_0 - \lambda_4)t})]$$

where:

^{230}Th , ^{238}U , ^{234}U = activities of ^{230}Th , ^{238}U ,

and ^{234}U .

$^{230}\text{Th}_0$ = activity of ^{230}Th at time of formation

λ_0, λ_4 = decay constants of ^{230}Th and ^{234}U

t = age of sample

If little or no ^{234}U fractionation relative to ^{238}U has occurred, $(^{238}\text{U} / ^{234}\text{U} - 1)$ becomes small and equation (1) reduces to:

$$(2) \quad ^{230}\text{Th} = ^{230}\text{Th}_0 e^{-\lambda_0 t} + ^{238}\text{U}(1 - e^{-\lambda_0 t}).$$

This equation may be divided by ^{232}Th to obtain:

* Activity units, rather than weight or absolute abundance units, are used throughout when describing isotope ratios or abundances. Elemental ratios or abundances are given in terms of absolute abundances, however.

$$(3) \quad {}^{230}\text{Th}/{}^{232}\text{Th} = ({}^{230}\text{Th}/{}^{232}\text{Th})_0 e^{-\lambda_0 t} + {}^{238}\text{U}/{}^{232}\text{Th} (1 - e^{-\lambda_0 t}).$$

Various means are used to find a value for the unknown quantity ${}^{230}\text{Th}_0$ in the dating methods above. However, complex variations in ${}^{238}\text{U}/{}^{232}\text{Th}$ and ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratios in the formation of igneous rocks make assumptions of $({}^{230}\text{Th}/{}^{232}\text{Th})_0$ ratios impossible.

The comparison of two minerals crystallizing from the same melt may be used to eliminate $({}^{230}\text{Th}/{}^{232}\text{Th})_0$ from equation (3). In order for an accurate date to be obtained, the following conditions must apply.

- (i) The minerals must have identical ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratios at the time of formation.
- (ii) The minerals must have formed at essentially the same time in relation to the total time span.
- (iii) The minerals must behave as a closed system with respect to uranium and thorium after formation.

Previous U-series disequilibrium studies of igneous rocks have yielded mixed results. Cerrari et al. (1965) found that an age obtained for a tuff by analysis of resistate minerals in a beach sand deposited from the tuff was consistent with the age assigned on the basis of geological and geomorphological evidence. Kigoshi (1967), studying successive acid extracts of a whole-rock sample, obtained an age for a rhyolitic tuff which agreed with a K/Ar date for the same sample.

Other results have not been as successful. Taddeucci et al. (1967) obtained only general agreement between U/Th and K/Ar dates for five rhyolites near Long Valley, California. Kupstov et al. (1969) analyzed trachyliparite and basalt, and obtained discordant and unintelligible results, which they attributed to a complex history and different $(^{230}\text{Th}/^{232}\text{Th})_0$ values of minerals at the time of formation. As a result, Kupstov et al. and others (Cherdyntsev et al., 1967, 1968) resorted to calculation of a maximum age based upon the assumption that no ^{230}Th was present in the mineral at the time of formation. Maximum ages so obtained will be considerably older than the actual ages if a considerable amount of ^{230}Th was present at formation.

Allegre (1968) noted that equation (3) described an isochron in coordinates of $[^{238}\text{U}/^{232}\text{Th}]$, $[^{230}\text{Th}/^{232}\text{Th}]$ (figure 1). The slope of the isochron is defined by the relationship:

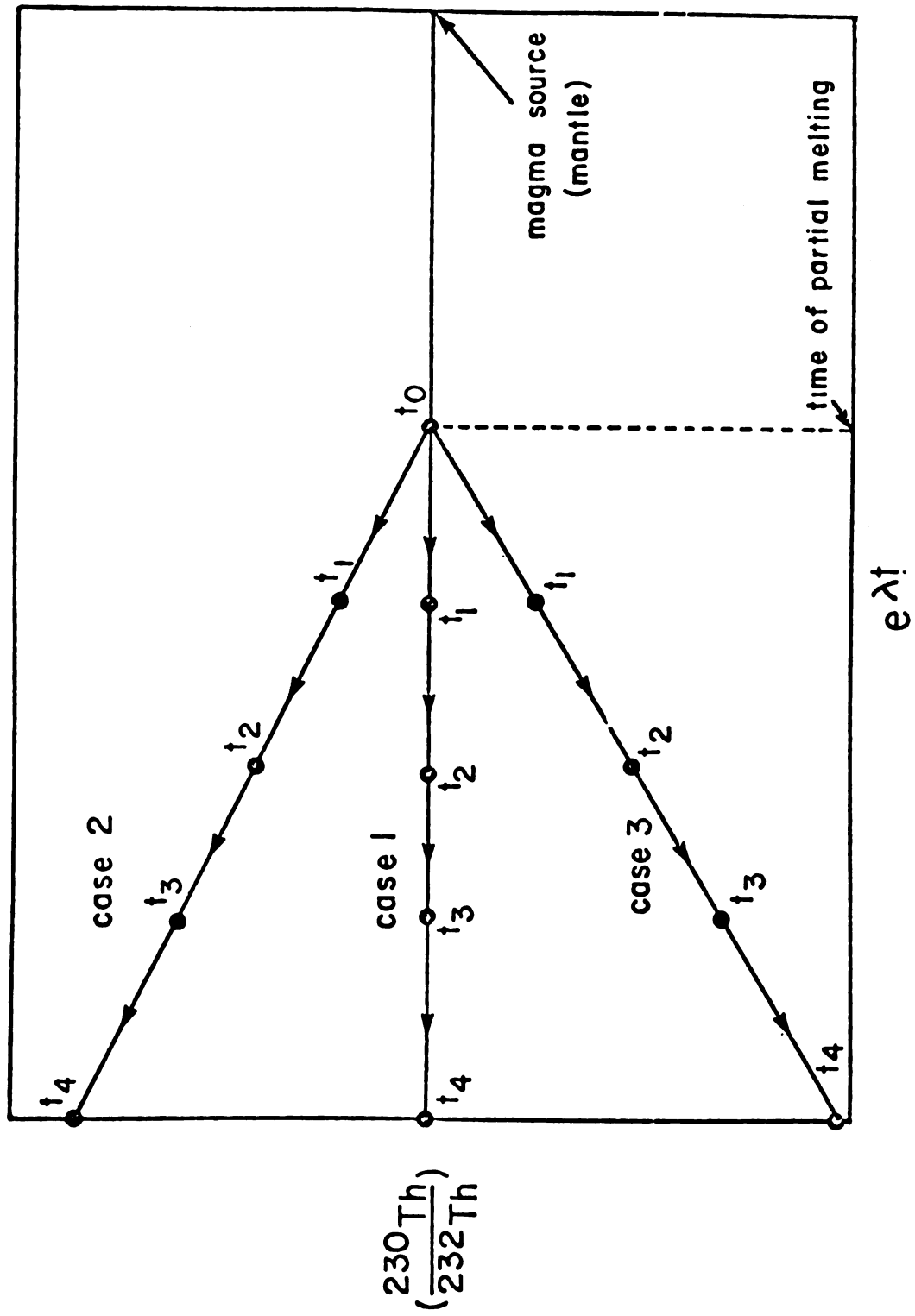
$$(4) \quad \text{slope} = 1 - e^{-\lambda_0 t}.$$

Minerals which do not satisfy the three basic conditions listed previously will plot off the isochron. Fukoka (1974) and Fukoka and Kigoshi (1974) found that zircon plotted off the isochron in a study of dacite pumices. This was interpreted as relic zircon grains included in the dacite lava. Delitala et al. (1975) was able to

construct a separate isochron of infinite age for clinopyroxene and magnetite contained in a pyroclastic tuff with a ^{230}Th date of 41,500 y. using other mineral phases. This was also attributed to the magnetite and clinopyroxene being relics of an earlier event.

Allegre and Condomines (1976) have used initial $^{230}\text{Th}/^{232}\text{Th}$ ratios to derive information concerning the development of a suite of andesites in Costa Rica. If a magma is enriched or depleted in U relative to Th as a result of formation, fractionation, or contamination, the $^{238}\text{U}/^{230}\text{Th}$ ratio of the melt will no longer be at equilibrium. The $^{238}\text{U}/^{230}\text{Th}$ (and $^{230}\text{Th}/^{232}\text{Th}$) ratio to the melt will then progressively change back to a new equilibrium value (Figure 3). This progression will be linear with respect to $e^{-\lambda_0 t}$ if the $^{238}\text{U}/^{230}\text{Th}$ ratio of the melt is disturbed once and the melt subsequently behaves as a closed system. The $(^{230}\text{Th}/^{232}\text{Th})_0$ value of a rock will reflect the $^{230}\text{Th}/^{232}\text{Th}$ ratio of the magma at the time of crystallization (Allegre and Condomines, 1976). Therefore, the $(^{230}\text{Th}/^{232}\text{Th})_0$ ratios of a suite of rocks emanating from a common magma may be used to define the petrogenesis of a magma by analysis of its change in $^{230}\text{Th}/^{232}\text{Th}$ through time.

Figure 3.--Initial $(^{230}\text{Th}/^{232}\text{Th})_0$ ratios as a function of $e^{\lambda t}$. Five arbitrary stages ($t_0 \rightarrow t_4$) are shown for successive eruptions of a magma derived from partial melting in secular equilibrium and rapidly transported to the surface (case 1), successive eruptions of a magma from a differentiating magma chamber with U/Th constant and higher than the source value (case 2) and for a U/Th ratio lower than the source value (case 3).



CHAPTER III

ISOTPOIC ANALYSIS OF U AND Th

One of the goals of this thesis was to develop an analytical method for U/Th isotopic analysis of igneous rock using the facilities available at Michigan State University. Analytical procedures were largely adapted from procedures used by Thompson (1973a, 1973b) and Kaufman (1964) for use with carbonate materials. Modification of these procedures was required due to the complex chemical nature of the volcanic rocks compared to carbonates.

The method developed was satisfactory for the analysis of rhyolitic rock, and splits of biotite, quartz, sanidine, and rhyolitic glass. Rocks with mafic and intermediate composition were subject to low yields and sample loss. Two analyses of whole rock splits from a rim rhyodacite and three analyses of whole rock splits from basalts were attempted. A satisfactory yield was obtained only once, for the uranium split of a basalt. Sample loss also resulted from the use of the method followed by Allegre and Condomines (1976). Subsequently, U/Th isotopic analysis of basic rocks was not attempted.

It is recommended that the analysis of mineral splits only should be considered for future studies of this type.

Sample Collection and Preparation

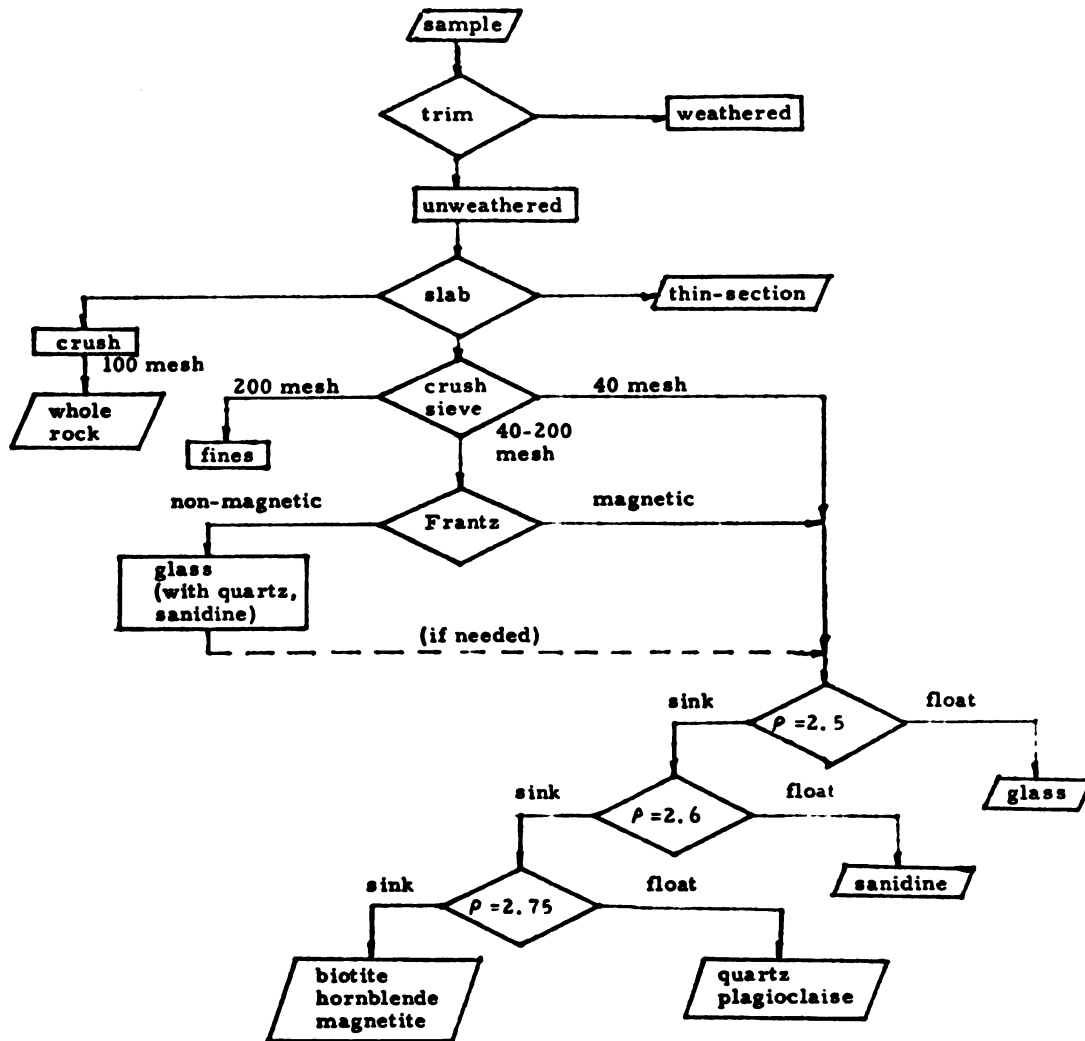
Four silicic samples were analyzed in this study. All were collected from the post-collapse intercaldera rhyolites of Long Valley, California. Samples of basic and intermediate composition were from the basalt and rhyodacite sequences within the caldera. Sample locations and descriptions are given in Appendix I along with a description of the geology of Long Valley.

At the time the samples were collected, it was thought that 5-10 kg samples would yield sufficient material for dating purposes. Due to sample losses in trimming and crushing, and the use of sample splits for thin-section and whole-rock analysis, it became clear that at least 10-20 kg samples should have been collected depending on the relative proportions of mineral phases present in the sample. After weathered surfaces were trimmed, a split was set aside for thin-sectioning. A second split of about 100 g was crushed to less than 100 mesh, first with a metal hammer, then with a ball mill. This split was used for all whole-rock analysis. The remainder of the sample was used for analysis of individual mineral phases. A flow chart of the mineral

separation procedure is given in Figure 4. The sample was crushed to between 40 and 200 mesh, with several smaller size ranges for samples that were to be magnetically separated. Sieving the samples was necessary in order to increase the efficiency of the separation methods and also to keep the apparatus from clogging. Several samples were run through a Frantz isodynamic separator to separate mafic minerals. The magnetic phase included some glass as well as sanidine-magnetite and quartz-magnetite intergrowths. Although several passes through the separator were required, the sample still required density separation. For this reason, later samples were processed entirely by density separation in heavy liquids. Bromoform mixed with dimethylsulfoxide to obtain densities of 2.5, 2.6, and 2.75 g/ml was used. Separations were performed in a separatory funnel in approximately 2 g increments. Glass was separated as the low-density phase at 2.50 g/ml. Sanidine was then separated from heavier minerals at 2.60 g/ml. Quartz plus any plagioclase present in the rock was separated as the light phase from biotite plus any magnetite and hornblende at 2.75 g/ml. An attempt was made to separate enough material to have at least 5 g of each mineral phase except quartz. It was desirable to collect 10 g of quartz. Due to the small quantity of mineral phases present in these samples, this was not

**Figure 4.--Flowchart of sample preparation and
mineral separation procedures.**

SAMPLE FLOW PREPARATION



always possible. No attempt was made to separate plagioclase from quartz or to separate mafic phases. This did not affect the placement of the $[\frac{^{238}\text{U}}{^{232}\text{Th}}] - [\frac{^{230}\text{Th}}{^{232}\text{Th}}]$ isochron for the sample under study if the individual phases plotted on the isochron. The isotope ratios of the mixed phases were averaged and this value was also plotted as a point on the isochron for the sample under consideration. For this reason, very high purity was not required of the mineral splits. Purity was checked by optical methods, and with the exceptions above, was found to be 90% or better.

Chemical Extraction of Uranium and Thorium

Before accurate analyses of the α -spectra of the uranium and thorium isotopes of interest could be performed, chemical purification was required. This was because radioisotopes with α -energies between 4.0 and 5.5 MeV would overlap the α -energies of the nuclides of interest (Figures 7 and 8). The elements responsible for interference are radium, protactinium, radon, and polonium. Uranium will also mask the thorium spectrum and vice versa, as the decay energies of the elements overlap. The activity of interfering nuclides should be reduced to less than .1% of the activity of the desired nuclide in order to reduce systematic errors. Chemical

purification was also required since self-absorption would result if the source contained more than $100 \mu\text{g}/\text{cm}^2$ of material. This would result in attenuation of the sample activity and 'tailing' of the original particle energies, causing loss of resolution. This is known as a 'thick' source. Any element that can be plated on a disc and is present in quantity will cause 'thick source' problems, or problems with the extraction procedure. The elements that must be reduced in quantity by the largest degree, due to their concentrations in rhyolites, are: Si, Al, Fe, Ca, Mg, K, Na, and Mn.

Separation of Radionuclides

Uranium and thorium were separated quantitatively by the use of the strong-base anion exchange resin Dowex 1-X8 in 9M HCl (Kraus and Nelson, 1956; Kraus et al., 1956). U was adsorbed onto the resin while Th remained in solution in the eluate. U was subsequently eluted by $.1\text{M}$ HCl. Following this, Th was removed from the U eluate by extraction in $.2\text{M}$ thenoyltrifluoroacetone (TTA) (Poskanser and Foreman, 1961). At pH 1.2, 100% of the Th was extracted, while less than 5% of the U was extracted. U was also removed from the Th eluate of the 9M HCl column by feeding the Th solution through the same resin in a 10% 5M HNO_3 - 90% methanol form (Tera et al., 1961). U remained in solution while Th was adsorbed to

be eluted later in 1M HNO_3 . Through these steps U and Th were quantitatively separated.

Since ^{226}Ra contributed to ^{230}Th and ^{234}U activity it was removed. This was accomplished during the $\text{Fe}(\text{OH})_3$ precipitate step where Ra remained in solution. Ra also remained in solution under anion exchange, and was not extracted by TTA (Hagemon, 1950).

A fraction of ^{231}Pa activity will overlap the activities of ^{228}Th , ^{230}Th , ^{232}U , and ^{234}U . The presence of ^{231}Pa can be detected from observation of the 5.01-5.05 MeV peaks, but correction was not necessary since Pa was separated from Th by adsorption with U on the Cl^- column (Kraus et al., 1956) and was separated from U by extraction with Th into TTA at pH 1.2 (Poskanser and Foreman, 1961).

^{210}Po will obscure the ^{232}U and ^{228}Th peaks if present. Po was removed by volatilization during evaporation of the sample onto a planchlet and subsequent heating of the planchlet to red-hot before counting (Kaufman, 1964). However, ^{210}Bi will decay into ^{210}Po with a 138 day half-life. Bi was partially separated from Th by incomplete adsorption onto anion exchange resin in Cl^- media and almost no adsorption in HNO_3^- - methanol media (Kraus and Nelson, 1956; Tera et al., 1965). Bi was partially separated from U by incomplete elution in $.1\text{M HCl}$. Since some ^{210}Bi was present in the

the sample, especially in U samples, the samples were plated and flamed immediately before counting. Thompson (1973a) monitored the presence of ^{210}Pa ($t_{1/2} = 134.8$ days) by counting ^{232}U several months after plating, and no change in U activity was reported.

Since radon is an inert gas, it was not plated on the planchlet and constituted no contamination problem.

Separation of Major Elements

The presence of Si during the chemical extraction process may cause problems as gels will form at many stages of the extraction procedure. Fortunately, Si was volatilized during the dissolution process by production of SiF_4 during HF fuming. In addition, Si did not absorb onto anion resins and tended to remain in solution during $\text{Fe}(\text{OH})_3$ precipitation. When silica or alumina gel was present in small amounts, it was assumed that negligible U or Th was contained in the gel and the gel was discarded. No difference in sample yields were noticed between samples with small amounts of gel and gel-free samples. However, samples with large amounts of gel were frequently lost, either by U or Th loss or the impossibility of continuing the extraction procedure as the presence of gels and precipitates also interfered with solvent extraction steps.

Most gels and precipitates encountered were probably due to the presence of Al, rather than Si. $\text{Al}(\text{OH})_3$ was precipitated along with $\text{Fe}(\text{OH})_3$ in the precipitation step. Al should elute while in 9M HCl form in the anion exchange step, but small quantities were noticed in U eluates from columns that were not rinsed correctly. The presence of large quantities of Al will interfere with the NO_3^- - methanol anion exchange or the Cl^- cation exchange methods. For this reason, Al was removed as $\text{Al}(\text{OH})_4^-$ form by washing the sample while in the hydroxide precipitate form with NaOH before adsorption onto the Th adsorbate columns (Kaufman, 1964). The possibility of large precipitates of insoluble residues was reduced by eliminating evaporation steps from the procedure until relatively pure U or Th absorbates were eluted from their respective columns.

Although iron was added to iron-poor samples as a carrier in the $\text{Fe}(\text{OH})_3$ precipitate step, iron will adsorb onto the anion resin along with U in 9M HCl media, saturating available exchange sites rather quickly. For this reason, Fe was extracted into isopropyl either before the sample was placed on the Cl^- exchange column. Because the initial ether extraction was usually incomplete, and Fe was extracted with U into TTA at pH 3.0 (Poskanser and Foreman, 1961), thick source problems were avoided by a second ether extraction using lower volumes

of liquid before extraction into TTA. The presence of Fe could easily be detected in solution, in precipitate, and on exchange resin by its reddish color.

Any other element that was present in the sample in quantity would also present a problem in analysis, either by creating a thick source or by interfering with the chemical procedure. However, no other steps were taken for removal of these elements as most, with the exception of Mn, Ni, and Mg, were removed in the hydroxide precipitation step by remaining in solution. In addition, the ion exchange and TTA extraction steps further discriminated against other elements present in the rock samples.

Contamination

Reagents

All reagents used in the chemical process were reagent grade obtained from Baker, Fisher, or Mallincrodt. The hydrofluoric acid was Target electronic grade (similar to reagent grade). These reagents were not completely free of uranium or thorium, but any contribution due to reagent or glassware contamination was negligible. This was ascertained in reagent blank runs, spiked with ^{232}U / ^{228}Th , conducted at this lab. All water used was distilled and deionized. Reagents were stored in either polyethelene or factory supplied containers.

Glassware

All evaporations were carried out in vycor or teflon glassware to minimize adsorption of thorium onto the glassware. For other uses pyrex glassware was used as well. No qualitative adsorption problems were encountered provided the samples were in either strong acid or precipitate form. It was noticed during the preparation of thorium standards that thorium could be adsorbed if the standard was not strongly acidic (greater than 1N HCl). Glassware used in the final (TTA) steps of the procedure were cleaned by acetone, followed by vigorous soap scrubbing, 8N HNO_3 wash, 8N HNO_3 rinse, distilled water rinse, and a final acetone rinse. Vycor and teflon glassware were cleaned by storage in 8N HNO_3 , followed by soap wash, acid wash, acid rinse, and distilled water rinse. All other glassware were cleaned by soap, followed by acid and distilled water rinses. Liquinox phosphate-free soap was used, as uranium will complex with phosphorus. Reagent preparation is after Thompson (1973b).

Analytical Procedure--Silicic Samples

Rhyolites were analyzed from the following procedure, adapted in part from Thompson (1973a; 1973b), Kaufman (1964), and Tera, et al. (1961). A flowchart of the procedure is given in Figures 5 and 6.

Figure 5.--Flowchart of chemical procedures
used in chemical extraction of
uranium and thorium.

SAMPLE FLOW - U-Th EXTRACTION

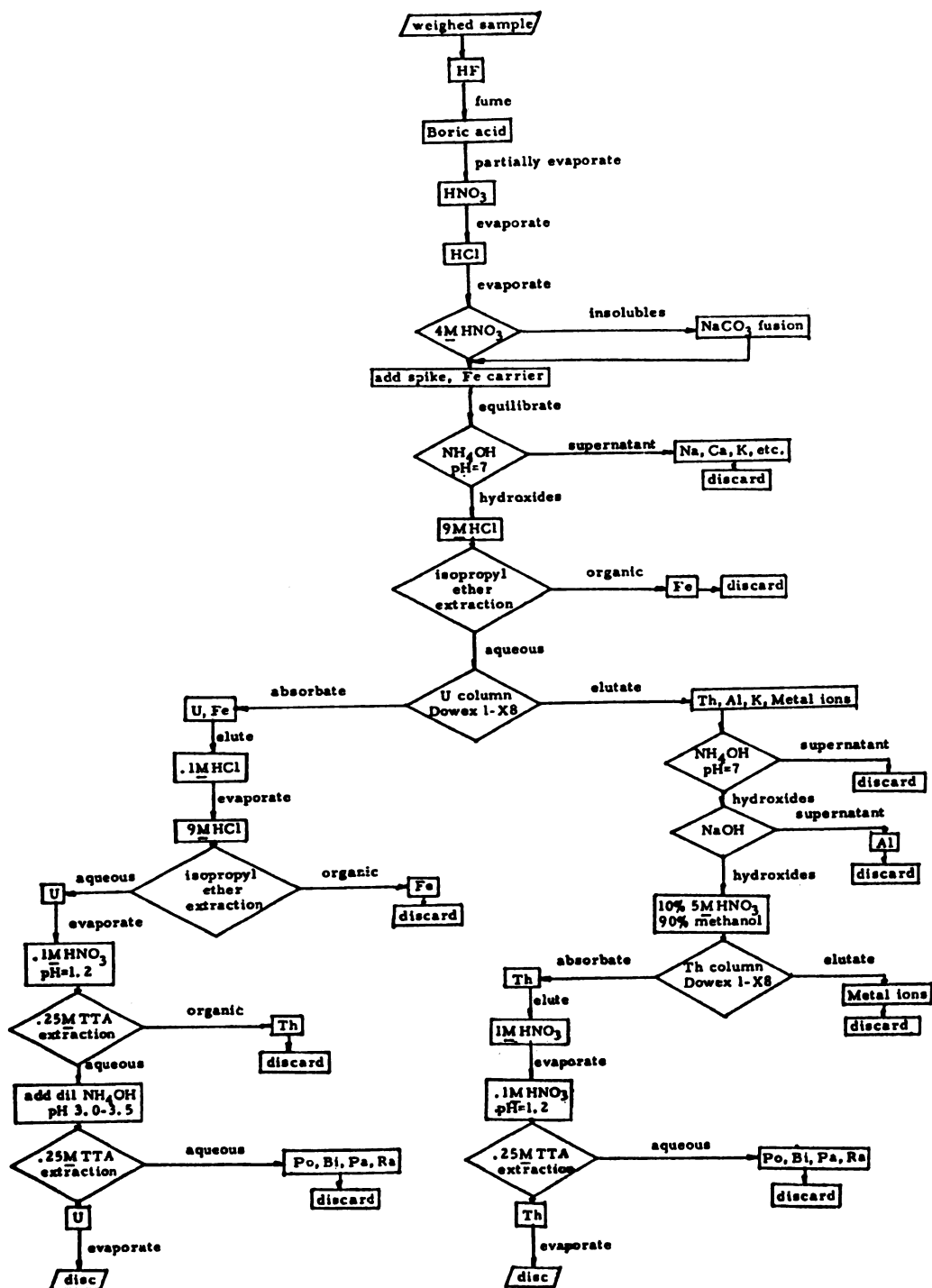
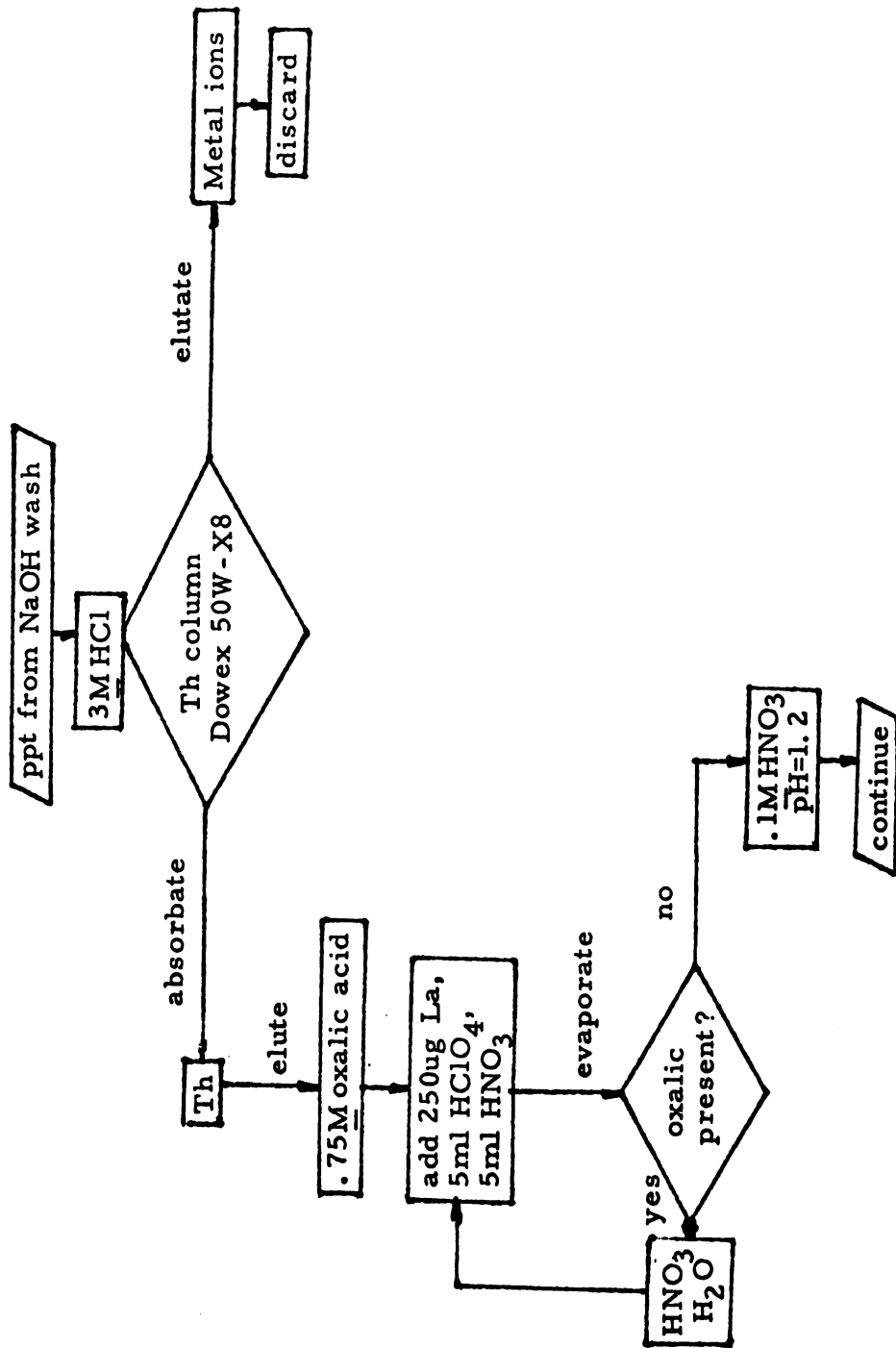


Figure 6.--Flowchart of alternate chemical
procedures used in chemical
extraction of Thorium.

Alternate Method

Th Extraction



1. Weighed samples, preferably between 5-12g (samples in this study ranged from 2-36g) and crushed beyond 100 mesh, were placed in teflon beakers. Approximately 180-200ml concentrated HF was slowly added, with agitation, to minimize splattering. The sample was covered, heated, and fumed for a minimum of 24 hours, with occasional stirring. Additional HF was added to maintain the original volume.

2. After fuming, approximately 1g boric acid was added to neutralize the F^- ion. The sample was then evaporated to $\frac{1}{2}$ volume. To prevent the formation of insoluble fluorides, approximately 100ml concentrated HNO_3 was added and the solution was evaporated. While stirring, 150ml concentrated HCl was added and evaporated. The sample was then wetted with concentrated HNO_3 , stirred and evaporated, and then taken up in approximately 150ml 5M HNO_3 . All solids were stirred into suspension and allowed to settle. A glass stirring rod was placed in the sample to check for F^- . After an hour the supernatant was decanted into a large beaker and more 5M HNO_3 was added to the residue. This process of adding additional 5M HNO_3 was repeated until the sample was quantitatively in solution. Generally 4-5 washes of 5M HNO_3 are required to gain the desired solution. Insoluble residues at this point were fused with $NaCO_3$ at $850^\circ C$ in platinum crucibles. It is important that all the sample

goes into solution, since uranium will be preferentially accumulated in the supernatant before the tracer is added.

3. Once the sample was in solution, it was diluted to 4M HNO_3 and a 2ml Fe^{3+} carrier was added to all Fe-poor samples (all but biotite and mafic whole-rock samples). 2ml dilute spike was added to all samples. This amount of spike results in peaks that are approximately equivalent in size to a 5-10g rhyolite sample. The sample was then allowed to stand for 8 hours to allow the spike to reach chemical equilibrium.

4. The sample was placed on a magnetic stirrer and concentrated NH_3OH was slowly added until the pH reached 6.5. The solution turned brown and a tan to light brown precipitate was formed. This precipitate consisted of Fe, Al, U, Th, Mg, Mn, and other hydroxides. When adding NH_3OH , care must be taken to avoid splattering and also to prevent the formation of localized areas of high pH.

5. The precipitate was allowed to settle. The solution was filtered using a funnel and 19cm Wratten #1 filter paper. The supernatant was discarded.

6. The filtered precipitate was dissolved with 9M HCl into a clean 250ml pyrex or vycor beaker. Frequently, insoluble gel substances were encountered at this point. In that case, the funnels were rinsed and left 4-8 hours to allow all of the supernatant to drain

through, then the gel was discarded. Since no difference in yield was noticed between samples with and without insoluble gels, it was assumed that the gels are composed primarily of silica and alumina and do not contain appreciable uranium or thorium.

7. The 9M HCl sample was placed in a 250ml separatory funnel. An equal amount of isopropyl ether was added, and the funnel was shaken vigorously, venting frequently to relieve pressure. The phases were allowed to separate and Fe was extracted into the organic phase. This step was repeated until the ether showed no change in color. The ether dissolved in the sample was evaporated by warming.

8. An ion exchange column for separation of U and Th was prepared by stopping the bottom of the column with glass wool, slurring 7cm anion exchange resin (BioRad AG1-X8) into it, and rinsing the column with 30ml 9M HCl. The rinse was discarded. The sample, in 9M HCl, was added to the column and the drip rate adjusted to 50ml/hour. 30-50ml 9M HCl was added as rinse. U and Fe were adsorbed on the column, while Th and other elements were eluted. To elute U and Fe, 100ml of .1M HCl was added. When the color band separating the acid phases was 4cm from the bottom of the column, the collecting beaker containing Th was removed and saved. A

clean beaker was placed under the column and the U and Fe was collected.

Note: The adsorbate may be dissolved into solution if too much sample and rinse is allowed to pass through the column. For this reason, the volume of sample and rinse was limited to 170ml for small (8mm x 7cm) columns and 250ml for 12mm x 8cm columns. If the sample was of greater volume, it was split between two columns.

9. The initial eluate containing Th was transferred to a larger beaker and concentrated NH_4OH was added until the pH reached 6.5. Hydroxides were precipitated as in step 4. The solution was filtered and the supernatant discarded.

10. The contents of the funnel were washed twice with 75ml hot 3M NaOH . Al was removed into solution as $\text{Al}(\text{OH})_4^-$ and the supernatant was discarded.

11a. If the remaining precipitate filled more than $\frac{1}{4}$ of the filter paper, it would not go into solution in a small quantity (less than 30ml) of acid and an alternate method (described in 11b) was used. For low volume precipitates, the sample was dissolved in a minimum amount of 5M HNO_3 by adding 10ml 5M HNO_3 to the funnel, taking care to wash the sides of the filter paper. With a spitzer (a disposable 1ml pipet), the precipitate was rinsed down the sides of the paper using the remaining

solution in the funnel. This procedure was repeated, recycling the same solution. 7ml fresh 5M HNO_3 was then added to the funnel and the walls were washed as before. If an insoluble gel remains, it may be presumed to be a silica or alumina gel and discarded. An ion exchange column was prepared as previously described, except the column was set in 10% 5M HNO_3 - 90% methanol instead of 9M HCl . The sample was diluted with methanol to obtain a 10% 5M HNO_3 - 90% methanol mixture and then added to the column. The column was rinsed with 30ml 10% 5M HNO_3 . The eluate containing impurities was discarded. Th had been adsorbed onto the column and was eluted with 100ml 1M HNO_3 . So as not to cook the Th residue, it was evaporated to dryness over low heat or a steam bath in a vycor beaker. The sample was then ready for step 12.

Notes:

(1) The 5M HNO_3 solution should be run through the Th-column as soon as possible or practical. It may be oversaturated and precipitate with time.

(2) If a slightly larger volume of acid is needed to dissolve the sample, use 20ml 5M HNO_3 rinsed with 10ml 5M HNO_3 and feed the sample onto two exchange columns.

(3) Care should be taken to insure that the sample will dissolve while in hydroxide form, as the hydroxides

are much more soluble than the nitrates or chlorides at this stage.

In early trials, the precipitate was taken up into HCl or HNO_3 , evaporated, and taken up in HCl or HNO_3 for placement on the exchange columns. Insoluble residues, gels, and precipitates were common, and Th was often lost.

11b). If the precipitate was too large to dissolve in a small quantity of acid, the following technique was used. The precipitate, after NaOH wash, was dissolved in 100-150ml 3M HCl. The wash was repeated as necessary, using fresh or recycled 3M HCl. If an insoluble gel was present, it was discarded. A column was prepared using cation exchange resin (BioRad 50W-X8) and 3M HCl. The sample was fed onto the column and rinsed with 30ml 3M HCl, followed by 30ml 6M HCl. The original eluate was discarded and the column rinsed. Th was adsorbed on the column and next eluted with .75M oxalic acid. 10ml concentrated HNO_3 and 500 μg La was added and the solution evaporated in a vycor beaker. When approximately 10ml of sample remained, 50ml 8M HNO_3 was added and re-evaporation continued. When 2-5ml remained, the sample was again diluted with 50ml 8M HNO_3 . This step was repeated an additional 3-4 times or until all the oxalic acid had been evaporated. Finally, the sample was carefully evaporated to dryness over low heat. The presence of oxalic acid in the evaporating solution was

characterized by a honey-yellow color and a large amount of white vapor as the solution neared dryness. Small white crystals in the residue also indicated oxalic acid. The sample was now ready for step 12.

Note: Since oxalic acid forms precipitates in benzene which is used in the following step, and thorium oxalate is insoluble, sample loss will result if all oxalic acid is not removed from the solution before residues form during evaporation. For this reason, the 3M HCl columns should be used only when necessary.

12. The Th residue was carefully dissolved in 2ml .1M HNO_3 (pH adjusted to 1.2) and transferred to a centrifuge tube with a spitzer. An additional 1ml .1M HNO_3 was used to rinse the beaker and was transferred to the centrifuge tube. If the sample did not dissolve, it was wetted with 8M HNO_3 , evaporated, and taken up in .1M HNO_3 ; or the sample was dissolved in a small amount of 5M HNO_3 and diluted with a few drops concentrated NH_4OH to adjust to pH 1.2. The pH was brought to 1.2 by a stepwise addition of .3ml dilute NH_4OH . 2ml .25M TTA (thenoyltrifluoroacetone) in benzene was added and the solution was thoroughly mixed using a spitzer and a vortex stirrer for 3 minutes. The time at which mixing was started was recorded to the nearest minute. The contents were centrifuged and Th extracted into the organic phase which was transferred to a 10ml beaker

with a spitzer, care being taken not to transfer any of the aqueous phase. 1ml of the TTA solution was again added to the aqueous phase, the sample was mixed for 5 minutes and centrifuged, and the organic phase was transferred to the 10ml beaker. The aqueous phase was discarded and the organic phase was evaporated to approximately .1ml over low heat. This was taken up with a spitzer and evaporated drop by drop onto a stainless steel planchlet warmed from the edges. Care was taken to insure that evaporation did not go to the edge of the planchlet and was uniformly thin. Lastly, the organics, radon, and polonium were volatilized by flaming the planchet until red-hot over a bunsen burner. The planchet was now ready for the α -counter.

13. The U elutate in .1M HCl from step 8 was carefully evaporated in a vycor beaker to dryness over low heat so as not to overdry the residue. The residue was taken up in 5ml 9M HCl and Fe was again extracted by isopropyl ether using a test tube and spitzer. The aqueous phase was returned to the beaker, carefully evaporated, wetted with several drops concentrated HNO_3 , and carefully re-evaporated.

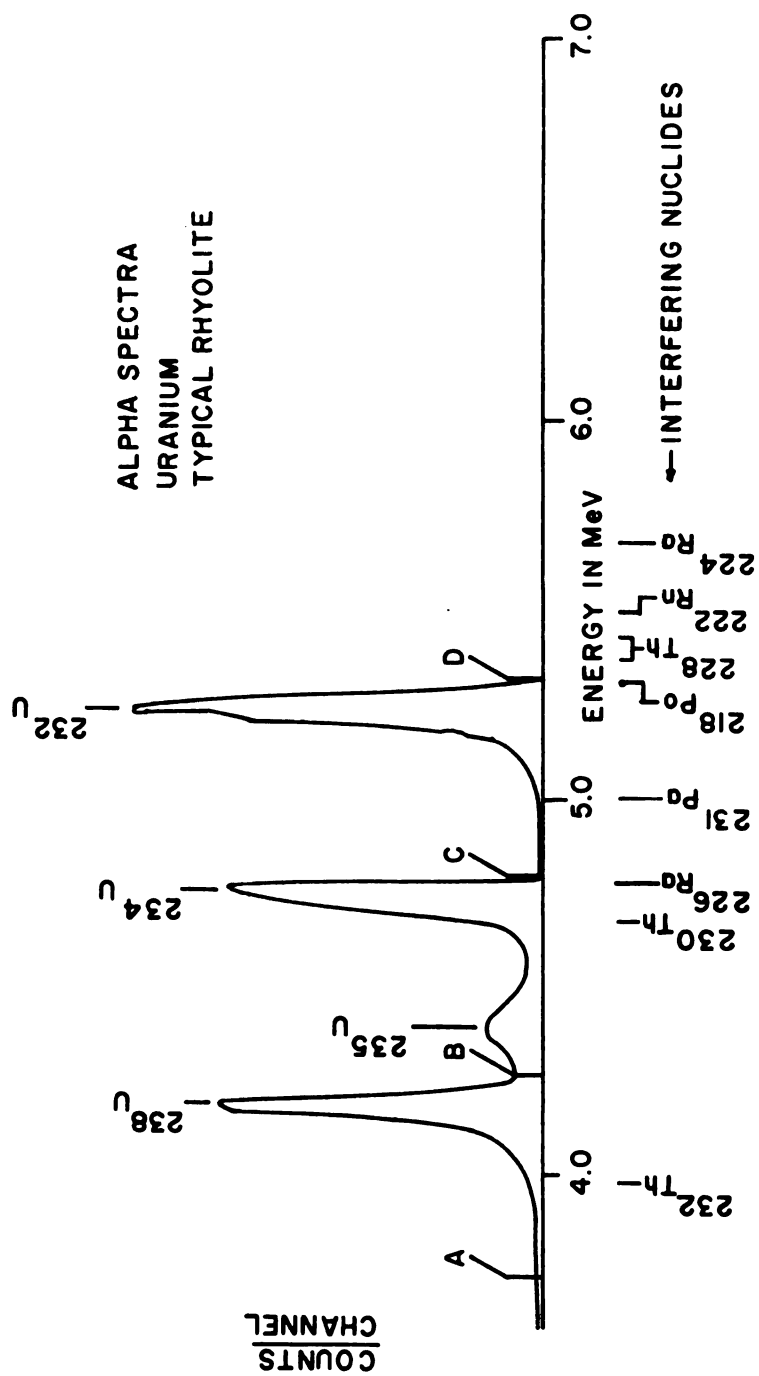
14. The U-containing residue was dissolved in .1M HNO_3 (pH 1.2) and transferred to a test tube the same way as the Th residue. 1ml of the .25M TTA was added, the contents mixed, and centrifuged. The aqueous phase

was then transferred to a second test tube, and the organic phase was discarded. The pH of the aqueous phase was adjusted to between 3.0 and 3.5 by the step-wise addition of $.3M \text{ NH}_4\text{OH}$. Uranium was extracted into the TTA solution and plated onto a stainless steel planchlet in the same manner as the Th split. The plated U disc was then flamed in the same manner and was then ready for α -counting.

Alpha Counting Procedure

A typical U spectrum is shown schematically in Figure 7. ^{232}U activity plus background activity was measured by summing all counts from the base of the ^{232}U peak (D) to the base of the ^{234}U peak (C). In this way, activity due to tailing of ^{232}U was counted. ^{234}U plus 96.7% ^{235}U activity was counted from C (base of ^{234}U peak) to B (base of ^{238}U peak). ^{238}U plus 3.3% ^{235}U activity was counted from A to B. Since ^{238}U and ^{235}U are found in fixed proportion to each other, the ^{235}U contribution to ^{234}U was eliminated by dividing the ^{238}U activity by 21.7 and subtraction of this figure from the ^{234}U activity. ^{235}U contribution to ^{238}U activity is negligible. In order to minimize errors caused by tailing of ^{238}U and ^{234}U , the number of channels included in the ^{238}U and ^{234}U activities were the same. Some error resulted from ^{234}U activity in

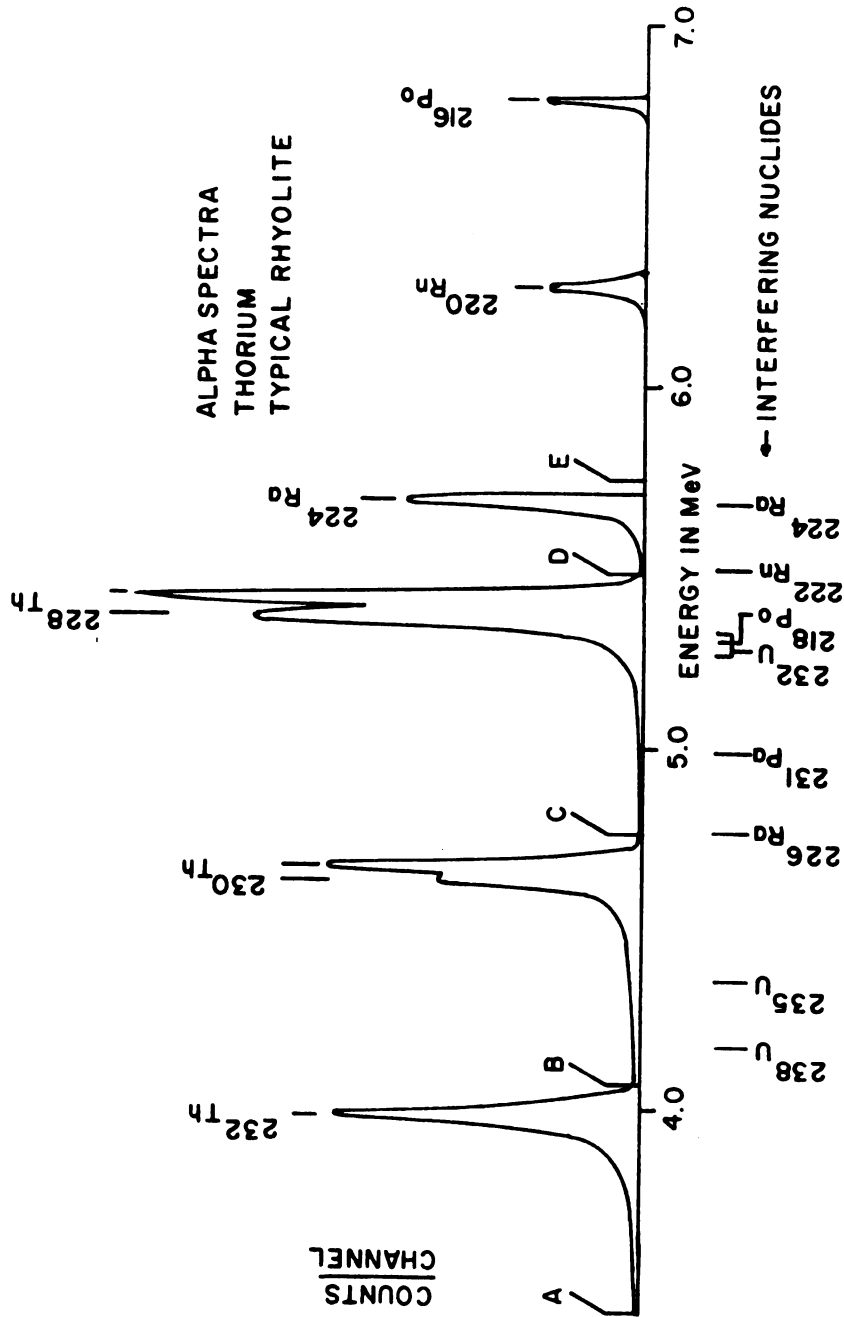
Figure 7.--Graphic representation of the
uranium alpha-spectra of a
typical rhyolite.



the ^{238}U region, and ^{232}U activity in the ^{238}U plus ^{234}U regions, but this was considered negligible for a thin source.

Thorium spectra (Figure 8) were counted in the same manner: 94.5% ^{224}Ra was counted between D and E, 5.5% ^{224}Ra and ^{228}Th was counted between C and D, ^{230}Th was counted between B and C, and ^{232}Th was counted between A and B (same number of channels as ^{230}Th). ^{224}Ra will grow into equilibrium with ^{228}Th with a 3.64 day half-life after TTA extraction. Since a correction for ^{224}Ra activity in the ^{228}Th energy level must be made, and some tailing of ^{224}Ra occurs under ^{228}Th decay, Th samples were counted immediately after TTA extraction. All activities also include a background activity, mostly due to contamination of the detector over time. To compensate for this a blank disc was counted for 12 hours every week. It is important that background counts cover the same channels that the readings cover or substantial errors may result. In this manner a separate background activity for each isotope counted was obtained. These activities were averaged over three consecutive weeks. Sample calculations and error analysis are given in Appendix II.

Figure 8.--Graphic representation of the
thorium alpha-spectra of a
typical rhyolite.



Preparation and Use of Spike

Uranium and thorium yields were monitored by the use of a $^{232}\text{U}/^{228}\text{Th}$ spike. This isotope pair was used because ^{228}Th is the daughter product of ^{232}U , ^{232}U does not occur in nature, and the α -energies of ^{228}Th and ^{232}U are near to those of ^{232}Th , ^{230}Th , ^{238}U , and ^{234}U . However, there are disadvantages to the use of a $^{232}\text{U}/^{228}\text{Th}$ spike, notably that common ^{228}Th occurs in the samples as a member of the ^{232}Th decay chain. However, if it is assumed that common ^{228}Th and ^{232}Th are in equilibrium, ^{232}Th activity may be subtracted from the total observed ^{228}Th activity to obtain only the ^{228}Th activity due to the spike. ^{228}Th and ^{232}Th are separated by ^{228}Ra ($t_{1/2} = 6.7$ years) and ^{228}Ac ($t_{1/2} = 6.13$ hours). In a closed system, ^{228}Th will grow into equilibrium with ^{232}Th within 40 years, therefore, extensive ^{228}Ra migration may occur during the history of the rock, as long as no fractionation has occurred in the last 40 years. Thompson (1973a) and Oversby and Gast (1968) found no evidence of disequilibrium in pleistocene samples. However, Cherdyntsev et al. (1967; 1968) found wide variations in $^{228}\text{Th}/^{232}\text{Th}$ ratios.

This problem was resolved by analysis of two unspiked samples and measurement of their $^{228}\text{Th}/^{232}\text{Th}$ ratios. The data (Table 2) suggest that ^{228}Th is in equilibrium for the rhyolites of Long Valley, California.

When using a ^{228}Th enriched spike, a correction factor must be added to correct for unsupported ^{228}Th decay. Since unsupported ^{228}Th decays with a half-life of 1.90 years, the following correction equation was used:

$$\begin{aligned} {}^{228}\text{Th}_{\text{corr}} &= {}^{228}\text{Th}_{\text{meas}} (1 - e^{-\lambda t}) \\ &= {}^{228}\text{Th}_{\text{meas}} (e^{\lambda t}) \end{aligned}$$

where:

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

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

λ = decay constant ($^{228}\text{Th} = 9.927 \times 10^{-4} \text{d}^{-1}$)

t = elapsed time in days between start of sample counting and uranium separation (9M HCl column for silicic procedures; HF wash for basic procedures)

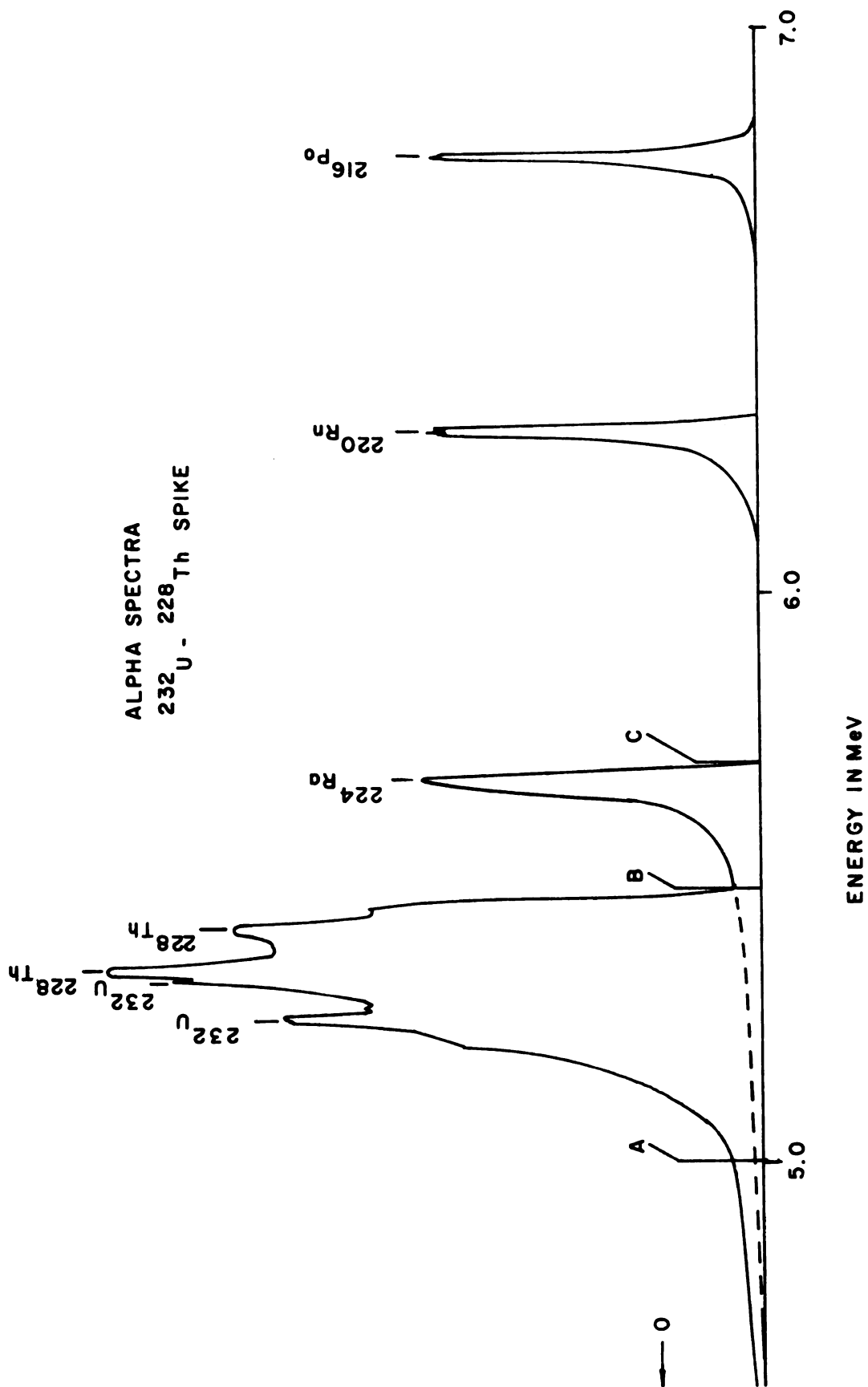
^{228}Th spike is unsupported after it is separated from ^{232}U in the 9M HCl column, but ^{228}Ra supporting the common ^{228}Th is discriminated against in the $\text{Fe}(\text{OH})_3$ precipitation step. Since less than 1% of the original ^{228}Ra will accumulate in one month, and intermediate ^{228}Ac

will decay rapidly, the equation describing the decay of common ^{228}Th simplifies to the equation above. This correction is small for samples counted less than a month after U and Ra separation from Th. Since U was separated from Th only a day or two after Ra was separated from Th and a small amount of Ra remained with the Th after the $\text{Fe}(\text{OH})_3$ precipitation step, the time of U extraction was arbitrarily chosen for use.

Another problem in using the spike was that Th tends to adsorb onto glassware, drawing the spike out of equilibrium. For this reason, the spike was stored in borosilicate glass and acidified with 6M HCl. In addition, the spike isotope ratio and activity was calibrated periodically by direct measurement, as described below, after Thompson (1973b).

1ml of prepared spike was evaporated to near dryness, 4 drops distilled H_2O was added, the solution was transferred to a spitzer, and the solution was slowly evaporated onto a stainless steel planchlet. The evaporation must be thin and uniform, as minimal tailing is necessary to resolve the peaks. The planchlet was not flamed. The sample was counted until at least 10,000 counts were recorded on the ^{224}Ra peak (see Figure 9). Although ^{228}Th and ^{232}U cannot be resolved, ^{224}Ra can be considered in equilibrium with ^{228}Th . Therefore:

Figure 9.--Graphic representation of the alpha
spectra of the ^{232}U - ^{228}Th spike.



$$^{228}\text{Th} = ^{224}\text{Ra}$$

$$^{232}\text{U} = (^{232}\text{U} + ^{228}\text{Th}) - ^{224}\text{Ra}$$

and the spike ratio, $^{232}\text{U} / ^{228}\text{Th}$ is:

$$\frac{^{232}\text{U}}{^{228}\text{Th}} = \frac{(^{232}\text{U} + ^{228}\text{Th}) - ^{224}\text{Ra}}{^{224}\text{Ra}}$$

The spectrum was counted as follows: ^{224}Ra was counted from the base of the ^{224}Ra peak to the base of the $^{232}\text{U} + ^{228}\text{Th}$ peak (C to D). $^{232}\text{U} + ^{228}\text{Th}$ was counted from C to channel zero. In addition, the tail due to $^{232}\text{U} + ^{228}\text{Th}$ was counted from channel zero to B, which has the same number of counts as C. Since 5.5% of ^{224}Ra decays occur in the $^{232}\text{U} + ^{228}\text{Th}$ energy range, 5.8% of the ^{224}Ra peak was added to the ^{224}Ra peak and subtracted from the $^{232}\text{U} + ^{228}\text{Th}$ peak. An empirical approximation to correct for ^{224}Ra tailing under the $^{232}\text{U} + ^{228}\text{Th}$ peak was performed as follows: 1/3 of the counts in the $^{232}\text{U} + ^{228}\text{Th}$ tail (O to B) was assumed to be the number of counts in the ^{224}Ra tail. This was subtracted from the $^{232}\text{U} + ^{228}\text{Th}$ peak and added to the ^{224}Ra peak. The [corrected ^{224}Ra peak] was taken to be the ^{228}Th spike activity and the [(corrected $^{228}\text{Th} + ^{232}\text{U}$) - the corrected ^{224}Ra peak] was assumed to be ^{232}U activity.

U-concentration Measurement

U concentration in the samples was determined internally by fitting sample activity to an activity/concentration curve.

This calibration curve was established by direct measurement of U standards for each detector and detector geometry used. Concentration estimates obtained using this method are limited to approximately 5-10% accuracy, the limiting factors being variations in the thickness and geometry of the sample on the planchlet.

For this reason, U and Th abundances of some samples were measured by neutron activation analysis, as described elsewhere. An attempt at estimating Th abundance by α -activity was also made by using the same method. However, problems were encountered in setting up a smooth working curve, possibly due to adsorption of Th onto the glassware. Subsequently, Th abundances were estimated using the U abundance value and $^{238}\text{U}/^{232}\text{Th}$ ratio.

Preparation of uranium standards follows the method of Thompson (1973b).

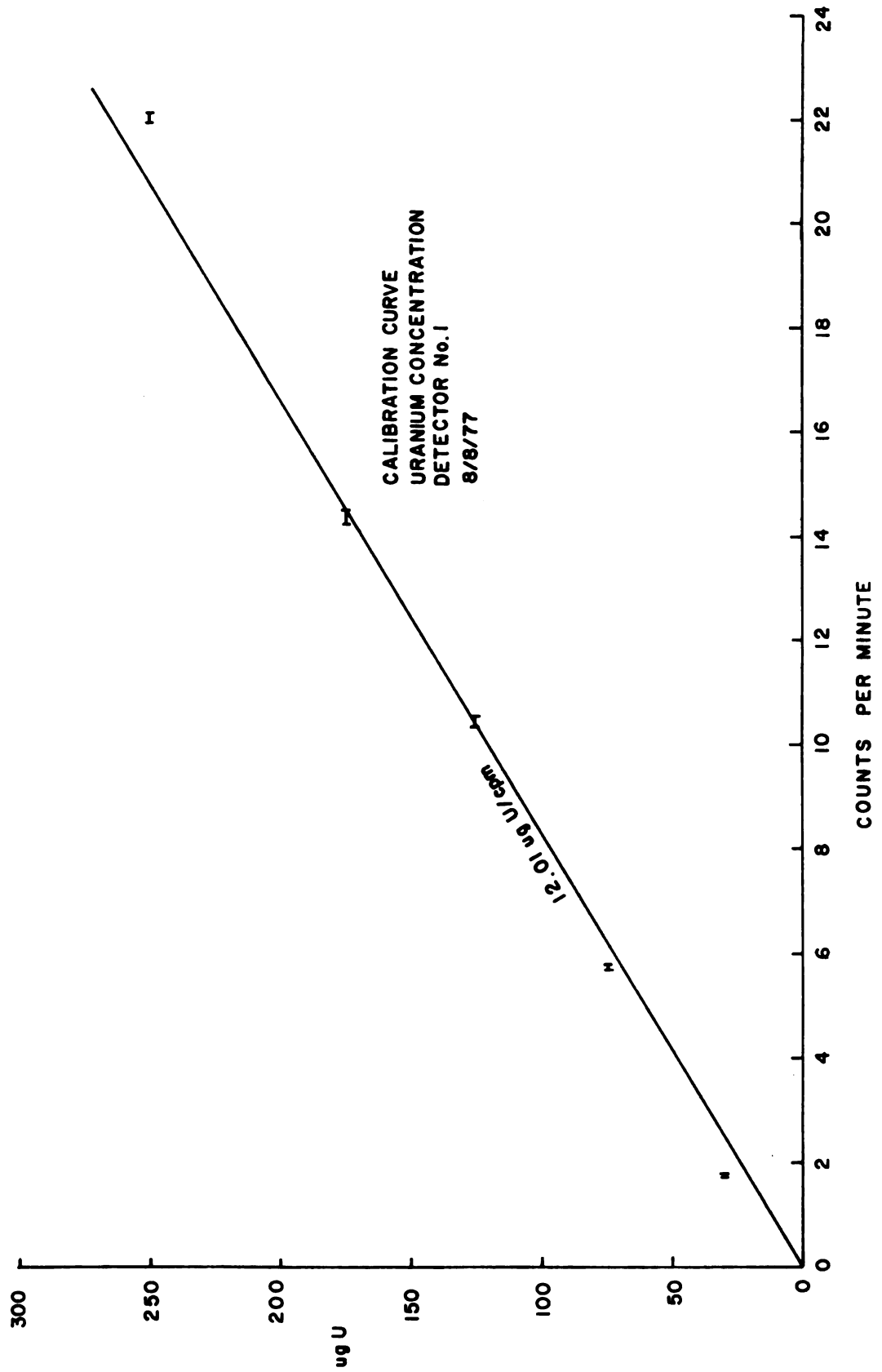
.5273g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in H_2O . 50ml concentrated HNO_3 was added and the solution was diluted to 1 liter giving a 25 μg U/ml stock solution. To obtain a 25 μg U/ml working solution, 10ml of stock solution was diluted to 100ml. 1, 2, 5, 7, and 10 ml of

the working solution was pipetted into separate 10ml beakers and slowly evaporated to dryness. The residue was dissolved in 2ml $.1M$ HNO_3 and the pH of all the solutions was adjusted to 3.0. U was carefully extracted into $.25M$ TTA in benzene three times. The solutions were plated and flamed as before (Step 12, procedure), care being taken not to lose any sample and to keep deposition on the disc as thin and uniform as possible. ^{238}U activity of the samples were counted to an accuracy of $\pm 1\%$. Activity corrected for background μg U was plotted for each sample. The points should describe a straight line (see Figure 10). Scatter in the diagram is most likely a reflection of differences in the geometry of the sample on the disc, indicating the inaccuracy reflected in this determination. Activities must be measured and a new calibration curve must be made for each new detector and source/detector geometry. However, only one set of standards were made, and these were re-used, since no daughter nuclides have energies in the ^{238}U range.

Accuracy of Method

As with most analysis for dating work, the stated error associated with an analysis is based upon the estimated instrumental error, based upon counting statistics or similar variations and is stated at one

Figure 10.--Uranium concentration calibration
curve.



standard deviation. This method will be described in Appendix II. Other sources of error are not accounted for by this estimate.

Systematic errors may result from contamination of the sample, or tailing of other isotope activities under the activity of interest. These errors are kept to a minimum by following the chemical and counting procedures outlined previously. For replicate samples, 67% had activity ratios within one standard deviation of each other. This, plus reagent blank results, indicate that these errors are small compared to the calculated error.

There are two exceptions to this. One is that excessive tailing of ^{224}Ra under $^{232}\text{U} + ^{228}\text{Th}$ is encountered when a spike calibration is analyzed. Although a correction for ^{224}Ra tailing was incorporated into the spike ratio, systematic error may result. This error should increase the error in the $^{234}\text{U}/^{232}\text{Th}$ and $^{238}\text{U}/^{232}\text{Th}$ ratios by no more than 2% (Rosholt and Noble, 1969; Oversby and Gast, 1968).

In addition, several sample splits of 76A021 and 76A017 were processed at the same time as several uranium ore samples, and it is suspected that cross-contamination resulted, either through vapors or improperly washed glassware, since these samples yielded anomalous isotope ratios, approximately the isotope ratios of the ores.

Subsequent re-analysis yielded results in the same range as other samples. For this reason, analysis of 76A017 and 76A021 are considered suspect.

The estimated errors associated with the slope of the isochron line, or t , and the $(^{230}\text{Th}/^{232}\text{Th})_0$ ratio are not directly associated with the isotope ratio errors. The errors are calculated in the scatter of the various mineral phases from the regression line. Therefore, the error associated with the age and $(^{230}\text{Th}/^{232}\text{Th})_0$ values of the sample was indirectly based on the true total error associated with the activity ratios and not the estimated error associated with the activity ratios.

The error for t and $(^{230}\text{Th}/^{232}\text{Th})_0$ was stated at the 90% confidence level. The coefficient of variation of t varies from 12% to 47% depending upon the sample and mineral phases used. This is in the same range of error associated with Allegre and Condomines (1976), using U/Th methods and in the same range or somewhat less accurate as Bailey et al. (1976) using K/Ar methods at the 90% confidence level. Although no replicate isochrons were run, the ages for both samples agree with ages obtained by K/Ar methods (Dalrymple, personal communication) at the 90% confidence level (Figure 13). Sample 76A003 was younger than the K/Ar age, sample 76A004 was older than the K/Ar age.

CHAPTER IV
ISOTOPE RATIOS AND ABUNDANCE
DATA FOR U AND TH

Activity ratios of U and Th isotopes obtained by α -spectrometry are given in Tables 1 and 2.

Preliminary data indicate that the samples analyzed are in equilibrium with respect to ^{228}Th .

$^{234}\text{U}/^{238}\text{U}$ ratios are in equilibrium for most samples, though disequilibrium $^{234}\text{U}/^{238}\text{U}$ values were observed in a few sample splits. $^{234}\text{U}/^{238}\text{U}$ values more than 2 standard deviations greater than 1.00 were noted for the glass and sanidine phases of sample 76A003. $^{234}\text{U}/^{238}\text{U}$ values significantly less than 1.00 were noted in two mineral splits and 76A017 whole-rock. It is possible that variation of this ratio may be due to experimental error.

$[^{238}\text{U}/^{232}\text{Th}] - [^{230}\text{Th}/^{232}\text{Th}]$ internal isochrons for samples 76A003 and 76A004 are given in Figures 11 and 12. Regression data is given in Table 3. The internal isochron for sample 76A004 defines an age of 127,000 $\pm$ 16,000 y.b.p. Sample 76A003 has an age of 89,000 $\pm$ 42,000 y.b.p. when sanidine values were used and

86,500 $\pm$ 20,000 when sanidine values were neglected. ($^{230}\text{Th}/^{232}\text{Th}$)_o values are equivalent for both samples at .94. Glass falls above the line in both cases and was not used in calculation of the isochoron. Sanidine also fell above the isochron in sample 76A003. Since a considerable amount (about 25%) of glass was noted in the sanidine split, the error is likely due to glass contamination. The whole-rock split does not occur at the intersection of the isochron with the equiline and thus is not an average of the phases present in the rock. Instead, the whole-rock value is slightly enriched in U and ^{230}Th .

[$^{234}\text{U}/^{232}\text{Th}$] - [$^{230}\text{Th}/^{232}\text{Th}$] internal isochron data is presented in Table 3 and Figures 13 and 14. An age of 107,000 $\pm$ 38,000 y.b.p. was defined for sample 76A004, while an age of 85,000 $\pm$ 27,000 y.b.p. was defined for sample 76A003. Initial $^{230}\text{Th}/^{232}\text{Th}$ values of .91 were calculated for both samples. Other aspects of the data based upon ^{234}U are similar to data based upon ^{238}U . Isotope data for samples 76A017 and 76A021 was incomplete and did not define an isochron. Problems were encountered in the analysis of these samples as well. For these reasons, internal isochrons were not calculated for these samples.

Uranium and thorium abundance data for whole-rock (Table 4) indicate no major variation in U and Th abundance

among Long Valley rhyolites. Abundance data for mineral and glass splits (Table 1) indicate U and Th partition among the various phases present. Feldspar was slightly depleted in U and Th. Quartz exhibited strong depletion of U and Th. Glass was enriched in U and Th. The mafic phase was strongly enriched in Th, but slightly depleted in U. Other phases did not exhibit strong fractionation between U and Th.

TABLE 1.--Activity ratios, concentrations, and sample yields obtained by alpha-spectrometry.

SAMPLE NO.	LAB. NO.	U CONC.	Th CONC.	U YIELD	Th YIELD	U-234 U-238	+	Th-230 Th-232	+	U-238 Th-232	+	U-234 Th-232	+
<u>76A003</u>													
Whole	191	6.8 ppm	18.1 ppm	37%	16%	.999	.056	1.049	.119	1.155	.147	1.154	.147
Glass	215	10.1 ppm	37.7 ppm	26%	31%	1.186	.051	1.063	.033	.825	.054	.979	.067
Quartz	212	1.3 ppm	5.2 ppm	38%	32%	1.095	.075	.835	.074	.742	.056	.813	.061
Sanidine	214	4.7 ppm	18.4 ppm	34%	34%	1.158	.064	.922	.079	.787	.048	.911	.056
Biotite	213	5.3 ppm		41%	23%	.936	.056	.458	.028	.077	.006	.072	.006
<u>76A004</u>													
Whole	104	5.8 ppm	14.2 ppm	9%	11%	.959	.060	1.156	.073	1.258	.268	1.206	.257
Glass	216	8.9 ppm	30.3 ppm	37%	27%	.993	.035	1.170	.044	.905	.055	.899	.055
Quartz	190		2.1 ppm	31%	31%	1.078	.384	1.122	.503	1.179	.514	1.271	.554
Sanidine	199	6.2 ppm	19.6 ppm	60%	30%	1.002	.061	.956	.103	.973	.102	.975	.102
Biotite	139	1.0 ppm		28%	25%	.761	.111	.423	.045	.186	.046	.142	.035
<u>76A017</u>													
Whole	166	5.1 ppm	11.9 ppm	6%	28%	.745	.124	.959	.057	1.322	.201	.985	.150
Quartz	194	0.0 ppm	0.0 ppm	36%	36%								
Sanidine	167	4.2 ppm	9.7 ppm	9%	32%	.838	.149	1.083	.909	1.336	.203	1.120	.170
Biotite	165	2.0 ppm		15%	0%	.919	.300						
<u>76A021</u>													
Whole	224	8.8 ppm		24%	9%	1.012	.035	.992	.055	.660	.060	.668	.061
Sanidine	177	3.1 ppm	8.2 ppm	37%	5%	.851	.051	1.377	.665	1.273	.576	1.083	.490

TABLE 2.-- $^{238}\text{Th}/^{232}\text{Th}$ activity ratios - unspiked mineral splits.

76A004	Glass	$1.055 \pm .068$
76A004	Quartz	$.990 \pm .070$

TABLE 3.--Regression data for internal isochrons--samples 76A003 and 76A004.

Sample Number	76A003	76A003	76A003	76A004	76A004
Isochron	($^{238}\text{U}/^{232}\text{Th}$)	($^{238}\text{U}/^{232}\text{Th}$)	($^{234}\text{U}/^{232}\text{Th}$)	($^{238}\text{U}/^{232}\text{Th}$)	($^{234}\text{U}/^{232}\text{Th}$)
Mineral splits	biotite whole rock quartz	biotite whole rock quartz sanidine	biotite whole rock quartz sanidine	biotite quartz sanidine whole rock	biotite quartz sanidine whole rock
b_o	.419	.429	.415	.293	.339
b_1	.549733862	.561001630	.544427085	.691015162	.628405595
r^2	.9997	.9903	.998	.9995	.989
$t(y)$	86,500	89,000	85,000	127,000	107,000
$\pm t(y)$	20,000	42,000	27,000	16,000	38,000
C.V. (%)	23	47	32	12	35
$t_U(y)$	108,000	139,000	116,000	144,000	152,000
$t_L(y)$	68,000	55,000	61,000	113,000	76,000
$\frac{^{230}}{(^{232}\text{Th})_o}$	.931	.975	.91340	.948	.912
$\pm$	.095			.062	
K-Ar age (y)	103,000	103,000	103,000	94,000	94,000
$\pm$ (y)	3,000	3,000	3,000	10,000	10,000
C.V. (%)	3	3	3	11	11

TABLE 4.--U and Th abundances.

Sample	Neutron Activation **				α-Spectrometry				Neutron Activation *			
	Th ppm	C.V.	U ppm	C.V.	Th/U	Th ppm	U ppm	Th/U	Th ppm	C.V.	U ppm	Th/U
<u>Rhyolite</u>												
76A003/72G009	--	--	--	--	--	18.1	6.8	2.7	20.6	8	6.9	2 3.0
76A004/72G008	16.2	10	7.6	3	2.1	14.2	5.8	2.5	21.1	7	6.2	2 3.4
76A017	15.0	10	5.3	3	2.8	--	--	--	--	--	--	--
76A019/72G017	--	--	--	--	--	--	--	--	15.9	8	3.9	3 4.1
76A020/72G007	--	--	--	--	--	--	--	--	16.0	9	6.3	2 2.5
76A021	--	--	--	--	--	--	--	--	--	--	--	--
<u>Rhyodacite</u>												
76A010/73G022	8.8	13	2.9	4	3.0	--	--	--	11.2	15	2.2	6 5.0
<u>Basalt</u>												
76A006	3.8	22	1.2	8	3.1	--	--	--	--	--	--	--
76A007	2.6	32	1.0	10	2.6	--	--	--	--	--	--	--
76A018	4.1	21	1.1	9	3.8	--	--	--	--	--	--	--

* R May (personal communication)

** H.T. Millard, U.S.G.S., Denver, Colorado

c.v. = coefficient of variation = one standard deviation expressed as percentage of contraction, based on counting statistics.

Figure 11.--[$^{230}\text{Th}/^{232}\text{Th}$], [$^{238}\text{U}/^{232}\text{Th}$] internal
isochrons for sample 76A003.

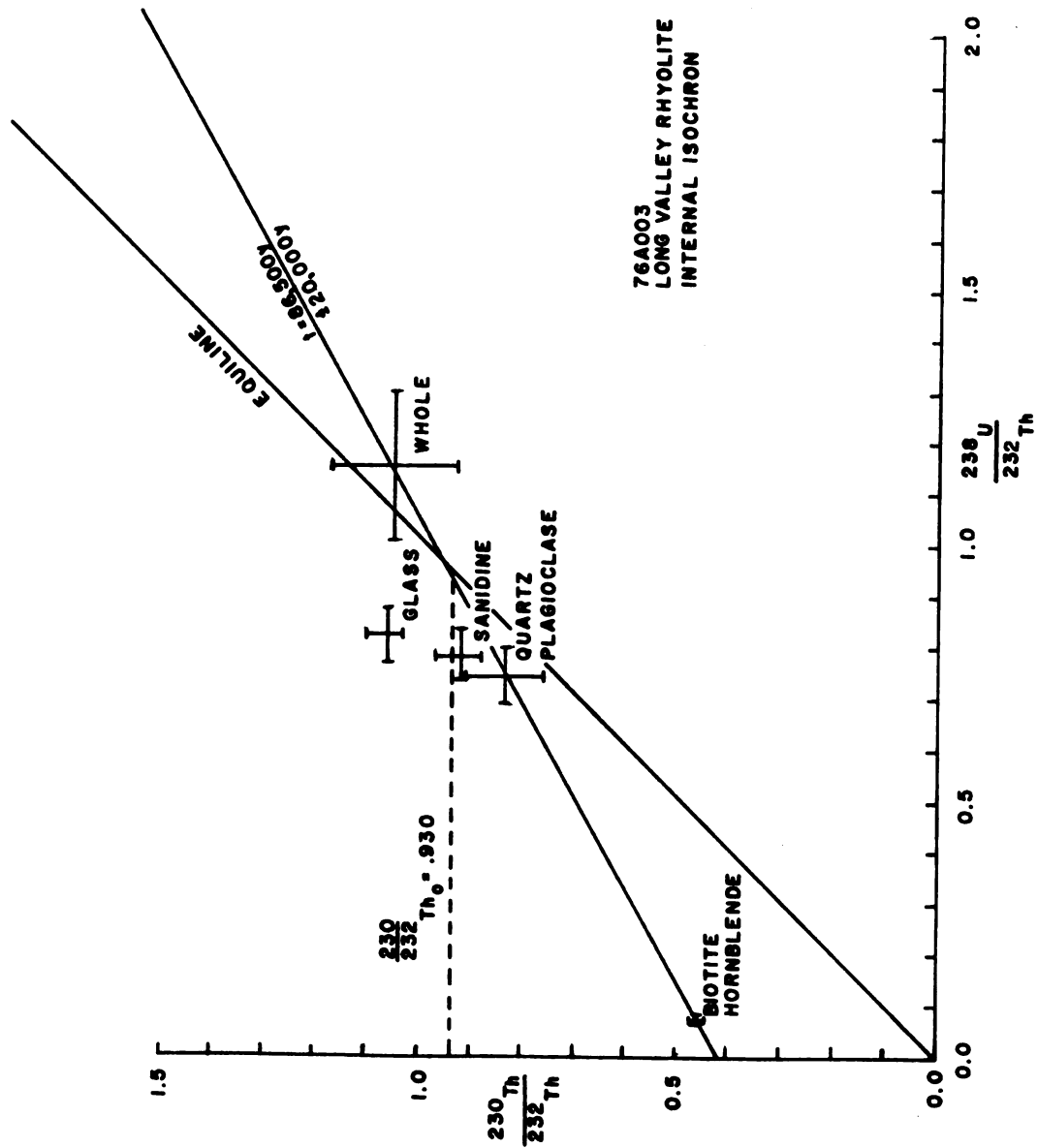


Figure 12.--[$^{230}\text{Th}/^{232}\text{Th}$], [$^{238}\text{U}/^{232}\text{Th}$] internal
isochrons for sample 76A004.

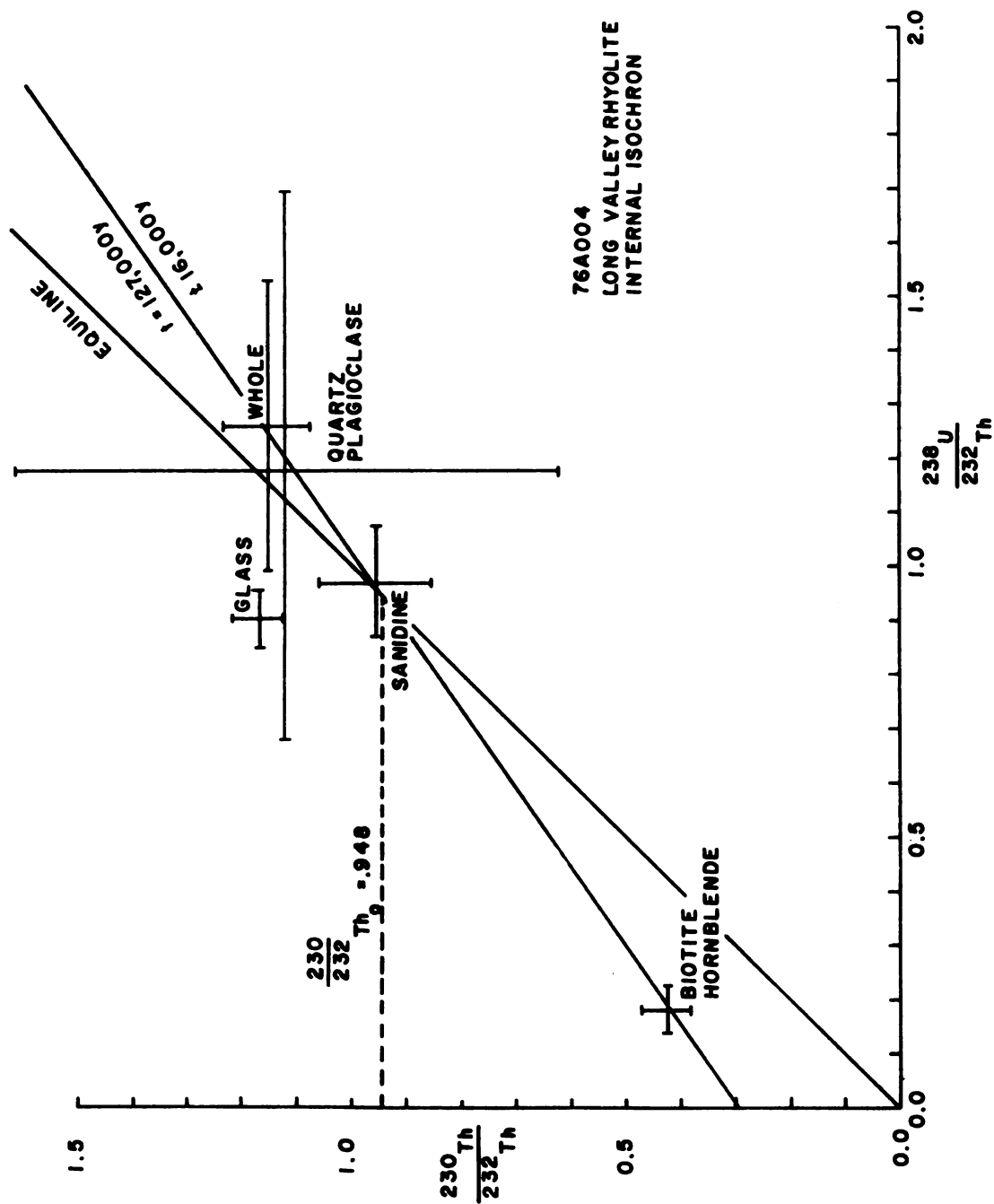


Figure 13.--[$^{230}\text{Th}/^{232}\text{Th}$], [$^{234}\text{U}/^{232}\text{Th}$] internal
isochrons for sample 76A003.

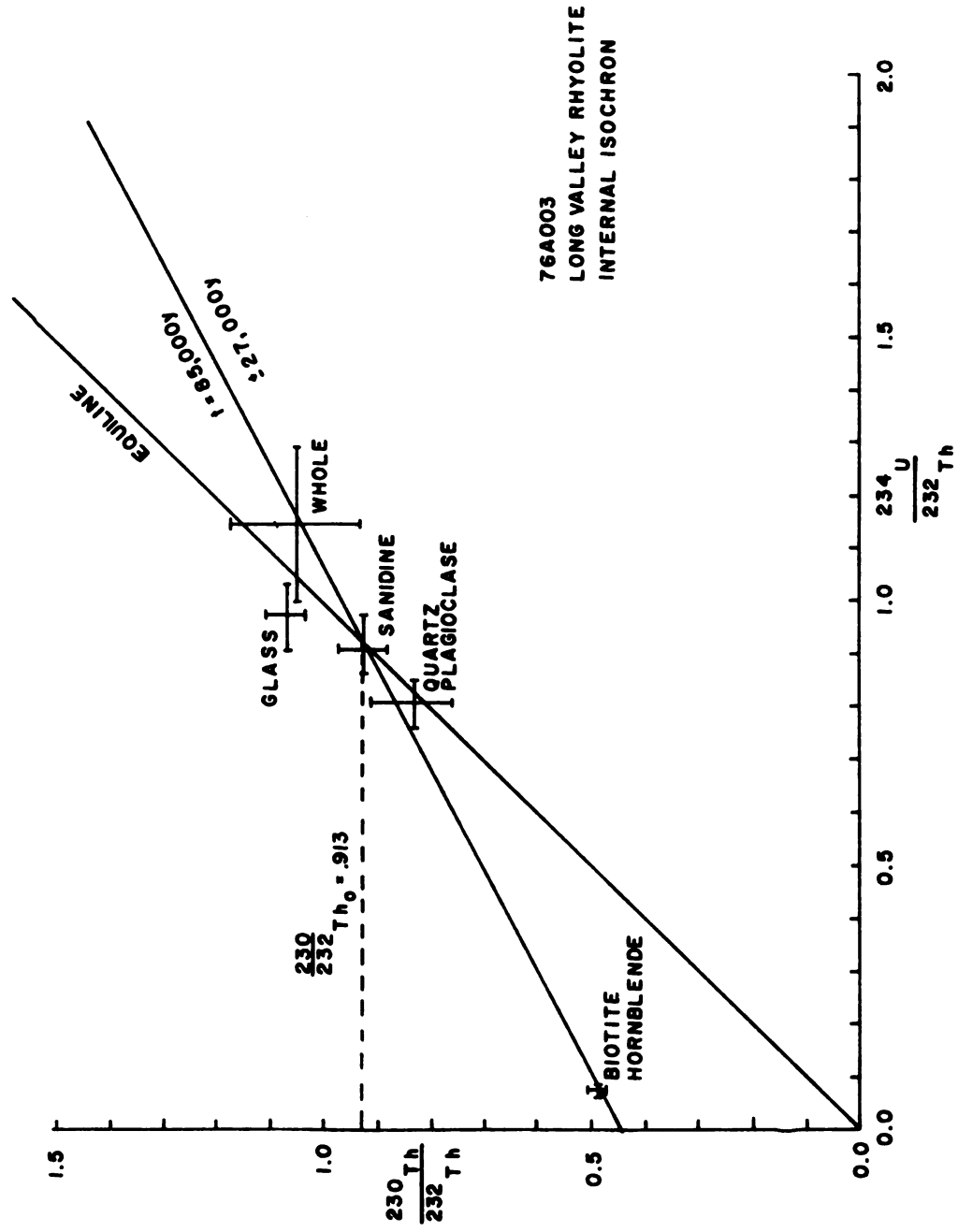
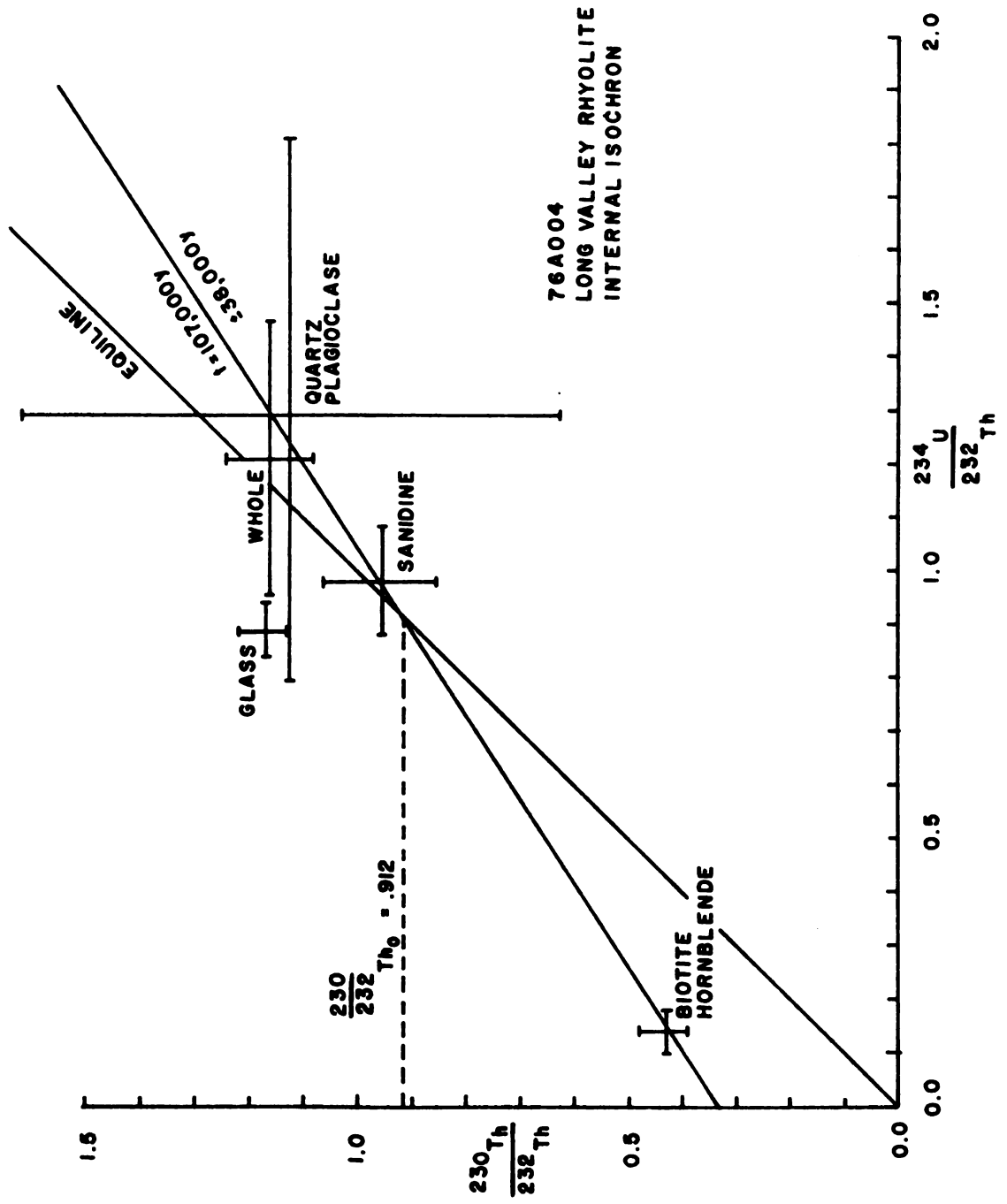


Figure 14.-- $[^{230}\text{Th}/^{232}\text{Th}]$, $[^{234}\text{U}/^{232}\text{Th}]$ internal
isochrons for sample 76A004.



CHAPTER V

DISCUSSION AND CONCLUSIONS

Discussion of Sample Results

It is unlikely that recent uranium loss occurred in samples 76A003 and 76A004. Equilibrium $^{228}\text{Th}/^{232}\text{Th}$ ratios indicate little or no alteration within the past 60 years. ^{234}U depletion, indicative of U loss, was observed only once, for the biotite split of 76A004. Textural evidence indicates little or no deuteric exchange with either hydrothermal or meteoric waters, and the sample locations are located on a topographical and structural high away from the locus of current hydrothermal activity.

There is a slight possibility that uranium migration occurred soon after eruption. Bailey et al. (1976) and Lachenbruch et al. (1976) suggest that the possibility of hydrothermal alteration was greatest at that time. $^{234}\text{U}/^{238}\text{U}$ fractionation should not accompany alteration at this time, since only a small amount of ^{234}U will have been created by radioactive decay and will be occupying α -recoil damaged sites. Uniform uranium abundances, linear sample isochrons, and textural and

field evidence tend to argue against uranium migration after formation.

Disequilibrium ^{234}U observed in several samples may occur before eruption of emplacement. Such fractionation could occur in several ways. Excess uranium may be introduced into the melt during initial partial melting, as residual minerals are leached in U, and the melt is preferentially enriched in ^{234}U by the Szliard-Chalmers effect. Excess ^{234}U may also result from leaching of the wall rock. The above mechanisms would probably give similar $^{234}\text{U}/^{238}\text{U}$ ratios for all mineral splits of the same sample. Early formed minerals could be leached of U by the remaining melt. The melt composition could also change with time, either through addition of new material, fractional crystallization, or loss of volatiles. These processes could lead to variation of $^{234}\text{U}/^{238}\text{U}$ ratios in mineral phases from the same sample.

Mineral phases used in this study were well suited for U/Th disequilibrium geochronology. Sufficient spread was present in the Th/U ratio to allow reasonably accurate internal isochrons. The linearity of all phases, except glass, indicated that formation of phases took place at approximately the same time, that initial $^{230}\text{Th}/^{232}\text{Th}$ fractionation did not occur, and that subsequent U migration either did not occur or was minimal.

The anomalous appearance of glass above the isochron was probably a result of chemical fractionation of the liquid after crystal formation close to the time of eruption or emplacement. It is possible that U was preferentially incorporated into a gas phase and subsequently lost through fumarole activity, consequently the remaining melt was depleted in U. Upon cooling of the melt, the system with respect to glass closed. However, glass remained open to chemical exchange longer than the minerals, which crystallized at depth, causing glass to fall off the isochron line.

The glass in the samples analyzed was probably not leached of U by modern rain water, as the glass was vitric and showed no evidence of alteration in thin-section. $^{234}\text{U}/^{238}\text{U}$ ratios were not less than unity which indicated that large scale U leaching of the glass had not occurred.

There was a possibility that U was lost as UF_4 gas during dissolution of the glass phase. No isotopic fractionation was present due to complete dissolution of the sample. Such a uranium loss would result in the displacement of the glass phase to the right, above the isochron. However, the dissolution of silicate glass by HF for U analysis has been used successfully in the past (Tadeucci et al., 1967; Allegre and Condomines, 1976). In addition, similar behavior would result from

dissolution of whole-rock samples or mineral phases. This was not the case. U loss during dissolution is therefore improbable.

With one exception, ages obtained in this study were equivalent to corresponding K/Ar ages at the 90% confidence level (Table 3). Sample 76A004 yielded a U/Th age older than the corresponding K/Ar age, however, the reverse was true of sample 76A003. Better fit of mineral phases to the regression line were obtained through the use of the $^{238}\text{U}/^{232}\text{Th}$ ratio. This resulted in lower experimental error. However, no significant difference was found between $[^{238}\text{U}/^{232}\text{Th}]$ $[^{230}\text{Th}/^{232}\text{Th}]$ ages and $[^{234}\text{U}/^{232}\text{Th}]$ $[^{230}\text{Th}/^{232}\text{Th}]$ ages.

Similar initial $^{230}\text{Th}/^{232}\text{Th}$ values indicated a common origin for the two rhyolites studied. Three models may be proposed to explain the lack of change in initial $^{230}\text{Th}/^{232}\text{Th}$ value for samples erupted at least 10,000 years apart.

- (i) The samples were erupted from an old magma chamber that had reached isotopic equilibrium with respect to U and Th.
- (ii) The samples were erupted from a magma chamber where relative fractionation between U and Th had not taken place.
- (iii) The samples were produced from separate partial melting events from a homogeneous source, subsequently with identical petrogenesis.

The possibility of the third model is remote due to the coincidences involved. The second model may possibly have occurred, but the first model is in agreement with existing evidence that magma has existed continuously in the Long Valley chamber for over 10^6 years (Bailey et al., 1976; Lachenbruch et al., 1976).

Models (i) and (ii) require that isotopic equilibrium was maintained for some time preceeding and during the eruption of samples 76A003 and 76A004. Consequently, the source magma did not undergo change in U or Th content through fractionation or contamination.

Differentiation of a silicic magma to produce intermediate rock types, as proposed by Bailey et al. (1976) is not in agreement with the data presented here, unless differentiation proceeded so slowly that the change in the $^{230}\text{Th}/^{232}\text{Th}$ ratio was undetected for the samples analyzed. The production of intermediate magma types through contamination as proposed by Eichelberger and Gooley (1977) is in agreement with the data presented in this paper, if the contamination did not affect the parent magma of the rocks used in this study.

If ^{230}Th was at equilibrium during mineral formation, then an initial Th/U value of 3.3 may be calculated for the parent magma at the time of mineral formation.

Comparison with Previous Results

The ages calculated in this study are in far greater agreement with K/Ar dates than previous U/Th ages presented by Taddeucci et al. (1967) and Allegre (1968). This is partially due to the inaccuracy of the method of calculation used by Taddeucci et al. (1967) and Allegre (1968), but may also be a reflection of the unreliability of K/Ar dates of such young rocks. Glass in this study falls above the isochron, while glass fell below the isochron in the data presented by Taddeucci et al. (1967). This casts doubt on the possibility of using glass-hornblende pairs to estimate the eruption age, as suggested by Allegre (1968). Analytical error associated with the ages calculated in this study was higher than analytical error for corresponding K/Ar ages. The correlation of U-Th ages with previous K-Ar studies lend support to the accuracy of both U-Th and K-Ar ages.

Suggested Improvements

The accuracy of the dates obtained in this study could be improved in several ways. Samples could be counted with greater accuracy through slightly higher sample sizes, longer count times, and the use of detectors with lower background count rates and greater sensitivity. A greater amount of data points may be obtained through separation and analysis of more mineral phases, such as

magnetite. Artificial "phases" may be separated, possibly by separating the glass by various physical methods, including color, magnetic susceptibility, or sample size after crushing. Slight differences in U and Th content may result, even if the glass is essentially homogeneous. Several splits of the same sample or several samples of the same cooling unit may be analyzed and placed on the isochron, increasing the power of confidence and possibly increasing the accuracy of the age.

Isochron slope and intercept has been calculated by linear regression using the least-squares technique. This is a completely unbiased estimator of slope and intercept only if the standard deviation of the errors in the data points are equal. Since this error varies somewhat from sample split to sample split, another method would be to weight individual samples on the basis of analytical error and perform a linear regression on the isochron points using the method of maximum likelihood. This has been used to treat Rb/Sr data (York, 1969; Brooks et al., 1972).

Errors associated with the determination of the $^{228}\text{Th}/^{232}\text{U}$ spike may be reduced by plating .1ml instead of 1ml of spike to insure minimum tailing, and counting for long periods of time, up to one week.

The partial success of one basalt sample and preliminary success by another worker at Michigan State

University (S. Leo, in preparation) with isotopic analysis of Hawaiian basalts indicates that further studies of the caldera rocks are possible. Analysis of contemporaneous rhyodacites and basalts in addition to the rhyolites would yield information on the relationship of the rhyodacites to the basalts and rhyolites.

In summary, this thesis has shown that excellent correlation between U/Th and K/Ar dates may be obtained for silicic volcanic rocks. Analytical accuracy will not be significantly better than K/Ar accuracy with the present procedures and instrumentation, however. U/Th dating may reduce the possibility of systematic error inherent with K/Ar dating of young rocks due to argon loss or experimental error by the use and correlation of many different sample splits to obtain an age.

In addition, it has been shown that two rhyolites in Long Valley caldera were erupted approximately 100,000 years ago. The major mineral phases were formed at roughly the same time, after which U was lost from the magma, probably at emplacement. Migration of U or Th after emplacement probably did not take place. The original magma had a Th/U ratio around 3.3 and subsequently lost Th relative to U prior to emplacement.

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APPENDICES

APPENDIX I

GEOLOGY OF LONG VALLEY, CALIFORNIA

APPENDIX I

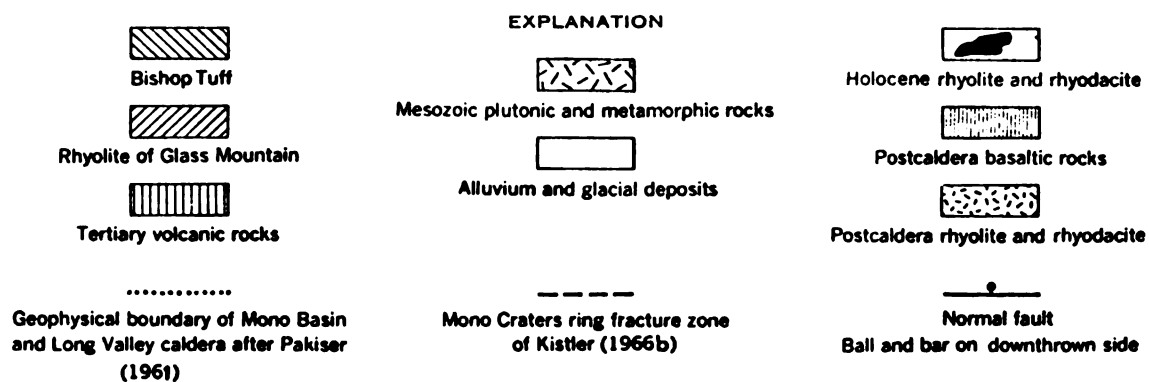
GEOLOGY OF LONG VALLEY, CALIFORNIA

Long Valley caldera is a 450 km² elliptical depression on the east front of the Sierra Nevada which straddles the Sierra Nevada and the Owens Valley (Figure 15). The caldera is approximately 30 km south of the Mono craters area, the postulated location of a submerged magma chamber in an earlier stage of development than Long Valley (Bailey et al., 1976).

The dimensions of the caldera are 17 km north-south and 32 km east-west. The walls of the caldera are well-defined, ranging from 500 to 1200 m with lower elevations to the east and southeast where the area is drained.

Pre-caldera host rocks in the vicinity of the caldera (Figures 15 and 16) include the Jurassic and Cretaceous granites and granodiorites of the Sierra Nevada batholith and Paleozoic and Mesozoic metamorphic rocks of the Mount Morrison and Ritter range roof pendants (Bateman et al., 1963; Rinehart and Ross, 1964). Basalt and andesite flows ranging in age from 2.6 to 3.2 m.y.b.p. by K/Ar methods which reach thicknesses of 250 m

Figure 15.--Geologic map of the region around
Long Valley, from Bailey et al. (1976).



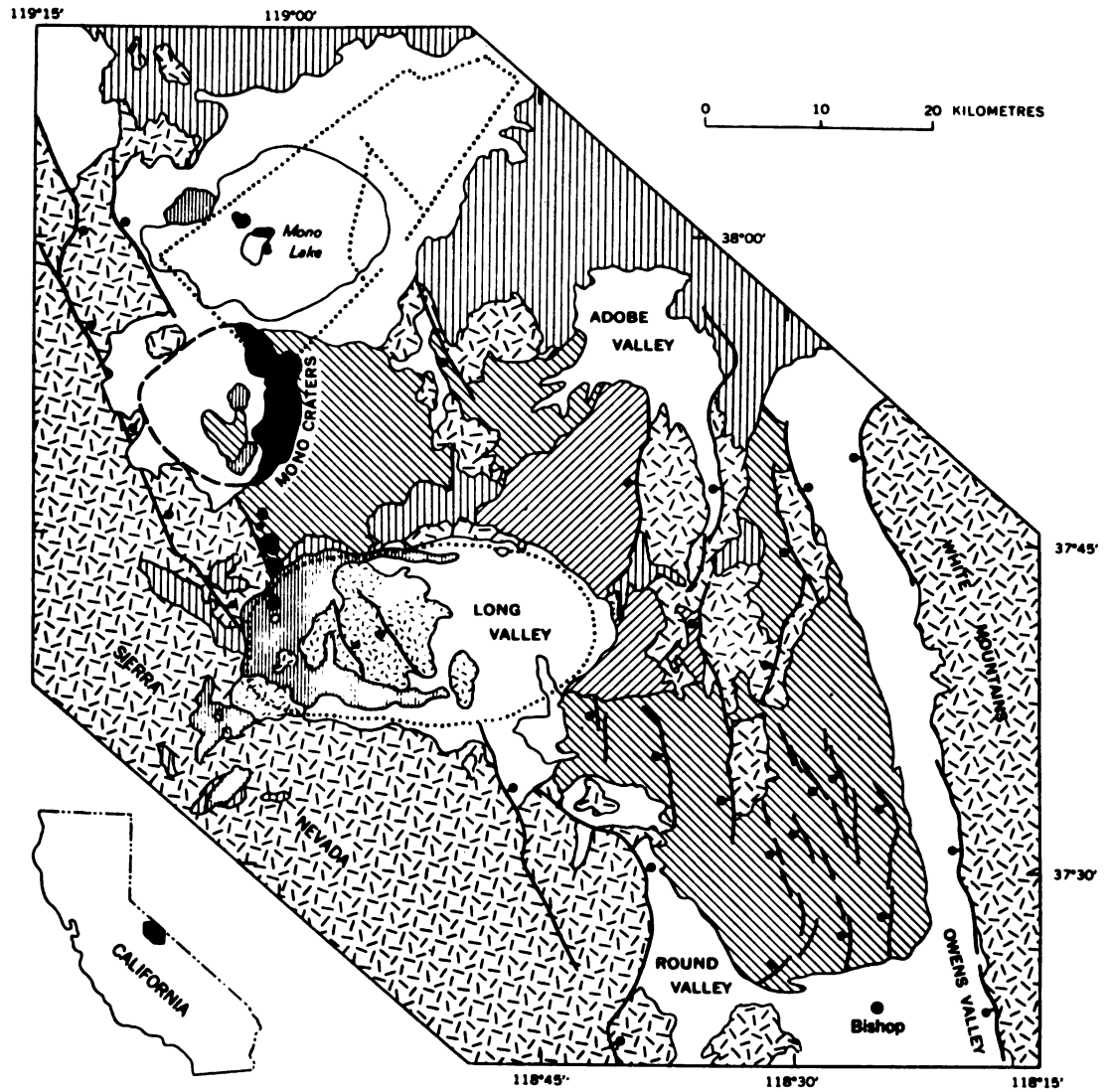
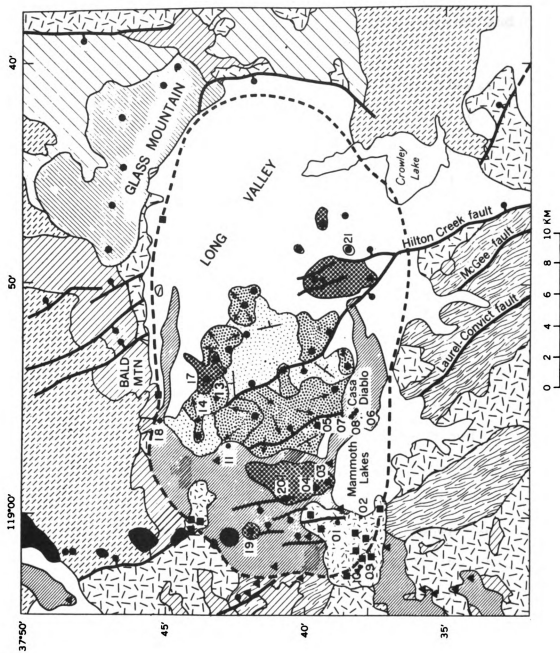


Figure 16.--Geologic map of Long, Valley,
California, showing sample locations.
Numbers on map correspond to the last
two digits of the sample number.

E X P L A N A T I O N

	Alluvium, glacial deposits, and caldera fill		
	Holocene rhyolite-rhyodacite	Volcanic vents	● rhyolite ■ rhyodacite ▲ basalt-andesite
	Late basaltic rocks	3.	sample locality
	Rim rhyodacites	⊗	Drill hole
	Moat rhyolites	└─	Direction of dip of strata
	Early rhyolites	↗	General direction of flowage of lava
	{ tuffs: fine dotted flows: coarse dotted		
	Bishop Tuff		Normal fault - ball and bar on downthrown side
	Rhyolite of Glass Mtn		
	{ dome flows: fine lined tuffs: coarse lined		
	Tertiary volcanic rocks		Outline of Long Valley caldera floor
	Jurassic-Cretaceous granitic rocks		
	Paleozoic-Mesozoic metamorphic rocks		



occur in the caldera area, including the caldera itself. The distribution of the mafic flows does not suggest a direct correlation with the associated magma chamber and caldera itself (Bailey et al., 1976).

A thick sequence of rhyolites on the northeast rim of the caldera can be related to the Long Valley chamber (Bailey et al., 1976). These rhyolites, which underlie Glass Mountain, range in age from .9 to 1.9 m.y. old. The rhyolites are aphyric to sparsely porphyritic, high in silica, peraluminous, and highly differentiated (Noble et al., 1972).

The Bishop tuff is a rhyolitic ash flow sheet which erupted from vents in the caldera. The tuff is crystal-rich, rhyolitic, and homogeneous in composition (Huber and Rinehart, 1967; Sheridan, 1968). Based on geochemical and mineralogical evidence (Hildreth and Spera, 1974), Bailey et al. (1976) calculated that 600 km³ of magma was ejected. Although great volumes of material were ejected in more than one event (Sheridan, 1968), K/Ar dates and geochemical evidence indicate that the Bishop tuff was emplaced within a time span of a few centuries, or less, about 700,000 years ago (Dalrymple et al., 1965). Formation of the caldera took place immediately after or during eruption of the Bishop tuff, as the roof of the magma chamber collapsed.

Crystal-poor rhyolite tuffs, flows, and domes were erupted within the caldera almost immediately after collapse. K/Ar dates indicate that these early rhyolites had been erupted over a span of 100,000 years and less than 100,000 years after eruption of the Bishop tuff and collapse of the chamber. Chemical analyses (Table 5) show that the rhyolite is homogeneous in chemical composition and high in silica, although Bailey (1974) was able to map three mineralogical facies. Glass in the early rhyolite domes and flows is partially devitrified.

Uplift into a resurgent dome in the west-central part of the caldera accompanied emplacement of the early rhyolites (Bailey et al., 1976; Smith and Bailey, 1968).

After resurgence, hornblende-biotite rhyolite, richer in phenocrysts and slightly poorer in silica than the early rhyolites, was erupted. These rhyolites are highly pumacious with a vitrophyric texture. Three groups of rhyolites were erupted, in the south-east around 300,000 years ago, in the north-east about 500,000 years ago, and in the west around 100,000 years ago by K/Ar dating.

Basaltic magma was erupted in the west moat associated with a chain of basaltic magmatism extending from Devil's Postpile to the south-west of Long Valley (Huber and Rinehart, 1967), to the Mono basin, 45 km

TABLE 5.--Bulk chemical data.

	Early Rhyolites		Moat Rhyolites		Rim Rhyodacites			Late Basalts					
	76A014	M-111	76A004	76A017	M-174	76A002	76A010	M-340	M-920	76A006	76A018	M-665	M-166
SiO ₂	74.95	74.2*	76.36	73.22	74.4*	67.19	72.59	65.8*	64.7*	56.02	52.19	54.7*	48.8*
Al ₂ O ₃	13.78	14.3	13.06	14.33	13.5	16.51	15.52	16.8	17.0	17.20	17.72	16.4	17.8
Fe ₂ O ₃	1.47	1.46	1.12	2.02	1.21	3.60	1.38	3.7	4.0	9.63	9.68	9.1	8.8
MgO	.19	.16	.27	.54	.28	1.07	.42	1.0	1.1	.82	4.80	3.4	7.3
CaO	.77	.79	.69	1.18	.78	2.31	.82	2.7	2.7	6.25	8.84	6.1	10.3
Na ₂ O	3.34	3.7	3.44	3.49	3.8	4.22	2.87	5.0	4.5	4.10	3.44	4.8	3.3
K ₂ O	5.18	5.2	4.75	4.80	4.5	4.14	5.78	3.9	4.8	1.84	1.42	2.2	1.0
TiO ₂	.16	.18	.14	.26	.15	.69	.46	.70	.64	1.97	1.70	2.0	1.4
MnO	.03	.02	.04	.04	.05	.05	.04	.08	.06	.15	.16	.16	.12
P ₂ O ₅	.14	.05	.14	.14	.04	.25	.15	.22	.16	.05	.05	5.8	.34
H ₂ O	--	.50	--	--	1.9	--	--	.18	.60	.13	.56	--	--
L.O.I	.78	--	2.08	2.48	--	.41	4.46	--	--	.70	4.15	--	--

* Rinehart and Ross (1964).

L.O.I. = Loss on Ignition @ 1000°C for 30 minutes.

north (Christensen and Gilbert, 1964). Eruption of the basalt was contemporaneous with the eruption of the last group of moat rhyolites. These rocks are similar to other Cenozoic mafic rocks occurring throughout the basin and range province and are thought to have a common upper mantle origin (Leeman and Rogers, 1969; Christiansen and Lipman, 1972).

Also contemporaneous with eruption of rhyolite and basalt is the eruption of crystal-rich rhyodacite along the caldera rim and moat. Textural and field relationships as well as discordant K/Ar dates on sanidine and biotite for some samples suggest that these rocks are at least partially a product of mixing of a rhyolitic or rhyodacitic magma with the basalt magma (Bailey et al., 1976; Eichelberger and Gooley, 1977). Several stages of differentiation may also exist, as suggested by Bailey et al. (1976). The effect of these processes on the petrogenesis of the intermediate magma is unclear, however.

The most recent volcanic products of Long Valley are the Inyo domes, a series of rhyolite-rhyodacite domes, related in time (12,000-720 y.b.p.; Dalrymple, 1967; Friedman, 1968; Wood, 1977) to the rhyolites of the Mono craters. The domes are chemically and petrogenetically heterogeneous, consisting of rhyolite obsidian similar to the rhyolites of Mono craters and rhyodacite similar

to the earlier rim rhyodacites of Long Valley. These textures suggest an incomplete mixing of the two magmas.

In summary, the Long Valley caldera was formed .7 m.y.b.p. during the eruption of the Bishop tuff. Volcanism continued within the caldera in the form of crystal-poor rhyolite flows and tuffs in conjunction with doming in the west-central area of the caldera. This was followed by eruption of three groups of rhyolites near the caldera most with higher amounts of H_2O and phenocryst content. Contemporaneous with the last group of rhyolites, rhyodacites exhibiting disequilibrium crystallization textures were erupted along the caldera rim, and basalts were erupted in the caldera area in conjunction with basalt eruption in other areas. Recent eruption of rhyolite-rhyodacite in the caldera is similar to the volcanism at Mono craters to the north.

The basaltic, rhyodacitic, and last of the three moat rhyolite sequences are suitable for age dating by the U/Th disequilibrium method, because they were erupted within the age range of the method (10,000-200,000 y.b.p.). They possess a sufficient number of phases, and they have undergone little alteration. In addition, U/Th disequilibrium dating of the rhyodacite phase of the Inyo dome holocene volcanics may reveal the presence of relic minerals of an older age than that given by K/Ar dating.

Sample Collection

At the time sample collection was undertaken, it was assumed that the U/Th isotope analysis of at least 5 or 6 samples of felsic and mafic composition would be possible. Consequently, a sampling program was set up to define the compositional and isotopic changes exhibited within the caldera with composition and with time. Nineteen samples averaging 10 kg each were collected from within the caldera (Figure 15 and Table 6).

Six basalts were collected with as wide a spread in location and time as possible. Four rim rhyodacites were collected, two from the flanks of Mammoth Mountain and two from the summit of Mammoth Mountain. Six moat rhyolites were collected, one from the north-east, one from the south-east, and four from a wide variation of locations in the west, including one from a rhyolite dome (76A020). In addition, two early rhyolites were collected. Samples were taken from identical locations of samples used for K/Ar dates. Control was established using field maps and notes of B. Dalrymple and R. May. Samples were taken from fresh, unweathered surfaces when possible.

Chemical and Petrographic Description

Major element chemical data for the moat rhyolites is given in Table 5. The moat rhyolites are high in

TABLE 6.--Sample Descriptions.

Sample No.	Earlier Sample No.*	K/Ar Age*	Sample Description and Location
<u>Most Rhyolites</u>			
76A003	72G009	.103 $\pm$.002 m.y.b.p.	White, vitrophyric rhyolite with phenocrysts of sanidine, quartz, biotite, and hornblende. From a flow in the western eruptive sequence. Collected from a knoll north of Mammoth Lakes, SE $\frac{1}{4}$, NE $\frac{1}{4}$, SE $\frac{1}{4}$, S. 27, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A004	72G008	.094 $\pm$.006 m.y.b.p.	Same as 76A003, except from NE $\frac{1}{4}$, NW $\frac{1}{4}$, SE $\frac{1}{4}$, S. 27, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A017	72G011	.468 $\pm$.010 m.y.b.p.	White, vitrophyric rhyolite similar to 76A003, except showing some signs of alteration. From a flow in the northeastern eruptive sequence, 1.5m. SSW of Aclarius Ranch, SE $\frac{1}{4}$, NE $\frac{1}{4}$, SW $\frac{1}{4}$, S. 32, T. 2S., R. 28E., Mt. Morrison Quadrangle.
76A019	72G017	.113 $\pm$.004 m.y.b.p.	White, vitrophyric rhyolite with abundant phenocrysts of feldspar, quartz, biotite, and hornblende. Phenocrysts are larger in size than in other areas. From the western eruptive sequence, on the SW side of Deer Mountain, NW $\frac{1}{4}$, SE $\frac{1}{4}$, SE $\frac{1}{4}$, S. 8, T. 3S., R. 27E., Devil's Postpile Quadrangle.
76A020	72G007	.106 $\pm$.003 m.y.b.p.	Hornblende-biotite rhyolite with phenocrysts of plagioclase. The matrix consists of plagioclase and sanidine microclites. From a rhyolite dome in the western eruptive sequence, located north of Mammoth Lakes, center of the S $\frac{1}{2}$, NW $\frac{1}{4}$, NW $\frac{1}{4}$, S. 22, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A021	72G005	.324 $\pm$.010 m.y.b.p.	Vitrophyric rhyolite similar to sample 76A003, except slightly more rich in phenocrysts. From a flow in the southeastern eruptive sequence, .9m NNW of Whitmore Hot Springs, center of S $\frac{1}{2}$, NW $\frac{1}{4}$, SW $\frac{1}{4}$, S. 32, T. 3S., R. 29E., Mt. Morrison Quadrangle.
<u>Rim Rhyodacites</u>			
76A001	73G018	.145 $\pm$.029 m.y.b.p.	Glaasy, grey flow banded rhyodacite with phenocrysts of plagioclase, biotite, minor magnetite and pyroxene. Collected from inside "earthquake fault" tourist area, SW $\frac{1}{4}$, SE $\frac{1}{4}$, S. 28, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A002	73G026	not dated	Same as 76A001, from a roadcut 1 mile north of Lake Mary, NW $\frac{1}{4}$, SE $\frac{1}{4}$, NW $\frac{1}{4}$, S. 9, T. 4S., R. 27E., Devil's Postpile Quadrangle.

76A009	73G023	.050 ± .010 m.y.b.p. on sanidine .095 ± .024 m.y.b.p. on biotite	Light, glassy rhyodacite with plagioclase and altered biotite phenocrysts. From summit of Mammoth Mountain, Devil's Postpile Quadrangle
76A010	73G022	.068 ± .012 m.y.b.p. on sanidine .126 ± .062 m.y.b.p. on biotite	Same as 76A009, except that alteration is not present. From summit of Mammoth Mountain, Devil's Postpile Quadrangle.
<u>Late Basalts</u>			
76A006	73G012	.126 ± .025 m.y.b.p.	Fine-grained basalt, with matrix consisting of magnetite, plagioclase, hornblende, and pyroxene. Collected from N. side of stream .9 miles WSW of Casa Diablo Hot Springs, stratigraphically below Casa Diablo Till, SW ¼, NE ¼, SW ¼, S. 31, T. 3S., R. 28E., Mt. Morrison Quadrangle.
76A007	73G014	.062 ± .013 m.y.b.p.	Fine-grained basalt with pyroxene and plagioclase phenocrysts. Matrix similar to 76A006. Collected from N. side of stream 1.1 mile WSW of Casa Diablo Hot Springs, stratigraphically above Casa Diablo Till, SW ¼, NE ¼, SW ¼, S. 31, T. 3S., R. 28E., Mt. Morrison Quadrangle.
76A008	73G013	not dated	Fine-grain, vesicular basalt with large olivine, pyroxene, and plagioclase phenocrysts. From N. side of stream .9 mile WSW of Casa Diablo Hot Springs, SW ¼, NW ¼, SE ¼, S. 31, T. 3S., R. 28E., Mt. Morrison Quadrangle.
76A011	73G008	.145 ± .015 m.y.b.p.	Highly glassy and vesicular basalt with small pyroxene and plagioclase phenocrysts, on a small knoll from BM 7651, SW ¼, SW ¼, NW ¼, S. 1, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A012	73G006	not dated	Glassy basalt with imbedded pyroxene and plagioclase phenocrysts. From a small knoll W. of U.S. 395, center of S ¼, NE ¼, NW ¼, S. 12, T. 3S., R. 27E., Mt. Morrison Quadrangle.
76A018	73G009	.104 ± .011 m.y.b.p.	Glassy, vesicular basalt with large plagioclase and pyroxene phenocrysts. Hornblende forms reaction rings on pyroxene, sometimes completely replacing pyroxene. Matrix contains abundant plagioclase microlites. Collected from S. shore of creek at Big Spring Campground .1 mile W. of bridge, center of NE ¼, NE ¼, S. 25, T. 2S., R. 27E., Cowtrack Mountain Quadrangle.

* After Bailey et al. (1976), Dalrymple (personal communication). Analytical error in the K/Ar age is one standard deviation, based upon analytical precision.

silica, approximately the same amount as the early rhyolites. The most rhyolites contained lower amounts of K_2O and higher amounts of volatiles when compared to the early rhyolites.

Thin-section petrographic analysis indicated that the early rhyolites were suitable for dating, though K/Ar data indicated that the north-east rhyolite group was too old to date by U/Th disequilibrium. None of the samples taken showed evidence of major alteration, and the glass in the flows was vitrophyric. Phenocrysts of sanidine (about 15% by volume), plagioclase (5-15%), lesser amounts of quartz, and biotite or hornblende (1-2%) were present. Phenocrysts averaged up to 5 mm in length. Minor fine-grained magnetite was also present. Glomeroporphyritic textures were uncommon. Sample 76A020, collected on a rhyolite dome, was slightly different, with a matrix of plagioclase and sanidine microlites, with no void space. Plagioclase phenocrysts were zoned, and plagioclase rather than sanidine was the primary phenocryst phase.

The last basalts analyzed were similar in composition to other basin and range basalts. Two types were present, quartz normative tholeiite, represented by sample 76A006, and olivine normative basalt, represented by sample 76A018.

Thin-section petrographic analysis indicated that the basalts were suitable for U/Th dating, though mineral separation could be difficult due to the fine grain size. The basalts were fine grained, usually with abundant glass. Pyroxene was the predominant mineral phase, occupying 5-20% of the whole rock. Minor amounts of olivine were observed in some samples. Hornblende was found in all samples, in places as reaction rings on pyroxene. Mafic phenocrysts were generally less than 1 mm in length, though larger in some samples (76A008, 76A018). The matrix consisted of roughly equal amounts of andesine plagioclase microlites less than .5 mm and glass, with 1-5% fine-grained magnetite. Only minor amounts of alteration were present. Sample 76A018, from the north moat, was slightly different. It contained 10% plagioclase (An 35) phenocrysts, in addition to pyroxene, and the matrix was almost totally crystallized. The crystallized matrix consisted of 70% andesine plagioclase microlites, 10% pyroxene, and minor amounts of hematite, magnetite, and glass.

Chemical analysis of the rim rhyodacites indicated that the rhyodacites were of intermediate composition and show some chemical variation. Sample 76A010, from the summit of Mammoth Mountain, was richer in silica, K_2O , and volatiles while poorer in Fe_2O_3 , TiO_2 , Na_2O , CaO , and MgO . This may have been due to hydrothermal alteration.

The mineralogical composition of the rim rhyodacites varied, but they generally contained 10-20% zoned plagioclase, 15% or less hornblende, and varied amounts of augite, hypersthene, biotite, magnetite, sanidine, quartz, and olivine in some places. Reaction rings and embayed reaction surfaces were prevalent. The matrix consisted of high Fe glass with varied amounts of plagioclase microlites. In some samples, the groundmass exhibited a heterogeneous flow banded texture. Alteration was present in some areas (76A009).

APPENDIX II

CALCULATION OF ANALYTICAL ERROR

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The number of alpha-decays produced or counted in a given time always follows the Poisson distribution,

$$W(N) = \frac{(N_0)^N}{N!} \exp (-N_0)$$

which approximates a Gaussian distribution in N is large (Jenkins and DeVries, 1969). The standard deviation (σ) of the distribution is equal to N_0 or approximately equal to N . This means that, neglecting background effects, the standard deviation of: 100 counts is ± 10 counts, or $\pm 10\%$; 1,000 counts is ± 31.7 counts, or $\pm 3.17\%$; 10,000 counts is ± 100 counts, or $\pm 1\%$. With this relationship as a rule of thumb, an effort was made to count until 1000 decays had accumulated under each peak to be counted. Samples used for calibration were counted until 10,000 decays had accumulated under each analyzed peak. Since $N = RT$ where R is the activity and T is the counting time,

$$\frac{\sigma(R)}{R} = \frac{\sigma(N)}{N}$$

if $\sigma (T)$ is considered negligible. Therefore,

$$\sigma (R) = \frac{R}{T}.$$

There is a similar error associated with the counts due to background. When the background is subtracted from the total count rate, the errors are propagated according to:

$$\sigma_T = \sqrt{\left(\frac{\sigma_s}{R_s}\right)^2 + \left(\frac{\sigma_b}{R_b}\right)^2}$$

where: σ_T = error in corrected activity
 σ_s = error in sample activity
 σ_b = error in background activity
 R_s = sample activity
 R_b = background activity

since $\sigma = \sqrt{\frac{R}{T}}$, this may be reduced to:

$$\sigma_T = \sqrt{\frac{R_s}{T_s} + \frac{R_b}{T_b} + \frac{R_b}{T_s}}$$

where: T_s = sample count time
 T_b = background count time
 T = error in the sample activity

The first term expresses the uncertainty in the total activity. The second term is an expression of the uncertainty in the background activity calculated from the background runs. The third term expresses the uncertainty in the number of background counts contribution to the sample activity.

Error in activity ratios are propagated according to:

$$\sigma_{A/B} = \frac{A}{B} \sqrt{\left(\frac{\sigma_A}{R_A}\right)^2 + \left(\frac{\sigma_B}{R_B}\right)^2}$$

where: $\frac{A}{B}$ is the activity ratio
 R_A, R_B are the activities
 σ_A, σ_B are the errors

It should be noted that all errors of isotope activities or ratios discussed are 1 standard deviation, or at the 68.3% confidence level. All errors are approximately twice as large at the 95% confidence level.

Ages and $(^{230}\text{Th}/^{232}\text{Th})_0$ ratios are calculated by the method suggested by Allegre (1968) and Kigoshi (1967). The slope (b_1) of the regression line is calculated by a least-squares linear regression in two dimensions, using $^{238}\text{U}/^{232}\text{Th}$ or $^{234}\text{U}/^{232}\text{Th}$ as X and $^{230}\text{Th}/^{232}\text{Th}$ as Y:

$$b_1 = \frac{\sum (X_i - \bar{X}) (Y_i - \bar{Y})}{\sum (X_i - \bar{X})^2}$$

The Y-intercept (b_0) is calculated as:

$$b_0 = \frac{1}{n} (\sum Y_i - b_1 \sum X_i)$$

The $(^{230}\text{Th}/^{232}\text{Th})_0$ value is the point where the isochron meets the equiline, or $X = Y$ for the isochron.

Error in the slope is calculated as:

$$s^2(b_1) = \frac{\text{MSE}}{\sum (X_i - \bar{X})^2}$$

$s(b_1)$ is distributed as t with $n-2$ degrees of freedom. This means that $s(b_1)$ cannot be treated as one standard deviation of a Gaussian distribution, which is the way most errors associated with isotope ratios and K-Ar dates are expressed. Direct comparison may be made by comparing similar confidence intervals, however.

Error in the $(^{230}\text{Th}/^{232}\text{Th})_0$ ratio was found by estimating a confidence interval at h , the $^{238}\text{U}/^{232}\text{Th}$ value at the intersection of the isochron and equiline:

$$s^2(\hat{Y}_h) = \text{MSE} \frac{1}{n} + \frac{(X_h - \bar{X})^2}{\sum (X_i - \bar{X})^2}$$

These positive and negative values were then extrapolated parallel to the isochron until they intersected the equiline. The difference between the $^{230}\text{Th}/^{232}\text{Th}$ ratios at these points was then divided by two and used as the error associated with the $(^{230}\text{Th}/^{232}\text{Th})_0$ ratio.

The age of the sample is related to the slope of isochron by:

$$b_1 = 1 - e^{-\lambda_0 t}$$

where λ_0 = decay constant of ^{230}Th . The sample age does not vary linearly with the isochron slope, with more variation in age for a given change in slope as the sample is older. Since the error in the slope is symmetric around b_1 , the calculated lower age limit is closer to the calculated age than the upper limit. These ages have been averaged by calculating ages for the upper and lower slope limits, taking the difference, and dividing by two.

Sample Calculation

- (1) Raw counts were calculated from instrument read-outs as follows:

$$^{238}\text{U} = 1350$$

$$^{235}\text{U} = ^{238}\text{U} / 21.7 = 62$$

$$^{234}\text{U} = ^{234}\text{U}_{\text{raw}} - ^{235}\text{U} = 1382 - 62 = 1320$$

$$^{232}\text{U} = 1272$$

$$^{232}\text{Th} = 2117$$

$$^{230}\text{Th} = 2327$$

$$^{224}\text{Ra} = ^{224}\text{Ra}_{\text{raw}} - (^{224}\text{Ra}_{\text{background activity}})$$

$$(\text{Th}_{\text{count time}})$$

$$= 667 - (.1597) (1479) = 431$$

$$^{228}\text{Th} = ^{228}\text{Th}_{\text{raw}} - (^{224}\text{Ra}) (.06)$$

$$= 4587 - 26 = 4561.$$

(2) Raw counts were converted to counts per minute:

$$^{238}\text{U}_{\text{cpm}} = ^{238}\text{U}_{\text{counts}} / ^{238}\text{U}_{\text{count time (minutes)}}$$

$$= 1350 / 953.07 = 1.4165 \text{ cpm}$$

$$^{238}\text{Th}_{\text{cpm}} = ^{238}\text{Th}_{\text{counts}} / ^{238}\text{Th}_{\text{count time (minutes)}}$$

$$= 2117 / 1479 = 1.4314 \text{ cpm.}$$

all other activities were treated in a similar manner.

(3) Background activity was subtracted:

$$^{238}\text{U} = ^{238}\text{U}_{\text{sample}} - ^{238}\text{U}_{\text{background}}$$

$$= 1.4165 - .0240 = 1.225_{\text{cpm}}$$

all other activities were treated in a similar manner.

- (4) ^{228}Th activity was corrected for decay of unsupported ^{228}Th as follows:

$$^{228}\text{Th} = (^{228}\text{Th}_{\text{uncorrected}}) e^{-\lambda_{228}t}$$

$$^{228}\text{Th} = (2.7690 \text{ cpm}) e^{-(9.927 \times 10^{-4} \text{ d}^{-1})(18\text{d})}$$

$$^{228}\text{Th} = 2.8217$$

- (5) Error in sample activity was calculated as follows:

$$\begin{aligned} \sigma_{238} &= \frac{^{238}\text{U}}{t_{\text{U}}} + \frac{^{238}\text{U}_{\text{bgd}}}{t_{\text{bgd}}} + \frac{^{238}\text{U}_{\text{bgd}}}{t_{\text{U}}} \\ &= \frac{1.225}{953.07} + \frac{.0240}{2089.33} + \frac{.0240}{953.07} = .0352 \text{ cpm} \end{aligned}$$

other activities are calculated similarly.

- (6) ^{228}Th activity due to spike addition was calculated as follows:

$$^{228}\text{Th}_{\text{spike}} = ^{228}\text{Th} - (^{232}\text{Th}) (^{228}\text{Th}/^{232}\text{Th})_{\text{unspiked}}$$

$^{228}\text{Th}/^{232}\text{Th}$ ratio in an unspiked sample is usually 1.

$$= 2.8217 - (1.4197)(1) = 1.4020 \text{ cpm}$$

error:

$$\begin{aligned}\sigma_{228 \text{ spike}} &= \sqrt{(\sigma_{228})^2 + (\sigma_{232})^2} \\ &= \sqrt{(.0450)^2 + (.0314)^2} = .0549 \text{ cpm}\end{aligned}$$

(7) $^{230}\text{Th}/^{232}\text{Th}$ activity ratio was calculated as follows:

$$\frac{^{230}\text{Th}}{^{232}\text{Th}} = \frac{1.5088}{1.4197} = 1.063$$

error:

$$\begin{aligned}\sigma_{\frac{^{230}\text{Th}}{^{232}\text{Th}}} &= \frac{^{230}\text{Th}}{^{232}\text{Th}} \sqrt{\left(\frac{\sigma_{^{230}\text{Th}}}{^{230}\text{Th}}\right)^2 + \left(\frac{\sigma_{^{232}\text{Th}}}{^{232}\text{Th}}\right)^2} \\ &= 1.186 \sqrt{\left(\frac{.0337}{1.5088}\right)^2 + \left(\frac{.0314}{1.4197}\right)^2} = .034\end{aligned}$$

$^{234}\text{U}/^{238}\text{U}$, $^{228}\text{Th}/^{232}\text{Th}$ ratios are calculated in the same manner.

(8) $^{238}\text{U}/^{232}\text{Th}$ activity ratio was calculated as follows:

$$\frac{^{238}\text{U}}{^{232}\text{Th}} = \frac{^{238}\text{U}}{^{232}\text{Th}} \times \frac{^{228}\text{Th spike}}{^{232}\text{U}} \times \text{spike}$$

$$\frac{^{238}\text{U}}{^{232}\text{Th}} = \left(\frac{1.1225}{1.4197}\right) \left(\frac{1.4020}{1.3176}\right) (.998) = .825$$

spike = measured $^{232}\text{U}/^{228}\text{Th}$ ratio in spike
calibration

associated error:

$$\begin{aligned} \sigma_{238/232} &= \frac{^{238}\text{U}}{^{232}\text{Th}} \sqrt{\left(\frac{\sigma_{238}}{^{238}\text{U}}\right)^2 + \left(\frac{\sigma_{232}}{^{232}\text{Th}}\right)^2 + \left(\frac{\sigma_{228 \text{ spike}}}{^{228}\text{Th spike}}\right)^2} \\ &\quad + \frac{\left(\frac{\sigma_{232}}{^{232}\text{U}}\right)^2 + \left(\frac{\sigma_{\text{spike}}}{\text{spike}}\right)^2}{2} \\ &= .825 \sqrt{\left(\frac{.0352}{1.1225}\right)^2 + \left(\frac{.0314}{1.4197}\right)^2 + \left(\frac{.0549}{1.4020}\right)^2 + \left(\frac{.0378}{1.3176}\right)^2} \\ &\quad + \left(\frac{.02}{.998}\right)^2 = .054. \end{aligned}$$

$^{234}\text{U}/^{232}\text{Th}$ ratio was calculated in the same manner.

(9) Sample yield was calculated as follows:

$$\begin{aligned} \% \text{ yield} &= \frac{{}^{232}\text{U}}{(S_U)(X)} \times 100 = \frac{1.3176 \text{ cpm}}{(12.76 \text{ cpm/ml})(.2 \text{ ml})} \times 100 \\ &= 26\% \end{aligned}$$

S_U = measured activity of 1 ml concentrated spike

X = amount of concentrated spike added to the sample.

Th yield was calculated in the same manner.

(10) Uranium concentration was calculated as follows:

$$\begin{aligned} \text{U concentration (ppm)} &= \frac{({}^{232}\text{U})(C)}{(\% \text{ yield})(\text{sample weight})} \\ &= \frac{(1.3176 \text{ cpm})(12.01 \text{ g/cpm})}{(26\%)(5.3 \text{ g})} \\ &= 10 \text{ ppm} \end{aligned}$$

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