Development and application of a method for U-Th dating of the Bonney Drift, Taylor Valley, Antarctica

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by
David Warwick Smith

University of Waikato
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Abstract.

The lacustrine carbonates of the Bonney Drift, Taylor Valley, Antarctica were deposited in lakes proglacial to glaciers advancing through the valley, and now occur as lag and clasts in the glacial drift formed by the glacier. They commonly contain 8 to 25% detritus, including high levels of silica, titanium, iron, manganese, and other elements; making the extraction and purification of uranium and thorium problematic.

A standard U-Th dating process was adapted to deal with the technical problems peculiar to the samples dated. Silica often formed a gel at the head of the U-Th separation column, and was removed using HF. Titanium frequently precipitated out during the conversion of the thorium fraction from a HCl matrix to HNO_3 form (used for further ion exchange purification) causing very low thorium recovery. This was overcome by using much higher volumes during conversion.

The uranium eluate from the separation column often contained high levels of iron and manganese. These were removed on a small ion exchange column in HNO_3. The resin and wash volumes were adjusted to allow iron and manganese to wash off, but allowing the uranium to be held and eluted subsequently.

An electrodeposition method was developed to achieve the thin plates necessary for alpha spectroscopy. Silver cathode discs were used in a teflon plating cell, with a stirrer rotating on the spiral planar platinum anode. An NH_4Cl/HCl electrolyte was used, adjusted in pH after sample uptake.

Of the 62 samples successfully dated, 13 were eliminated for such reasons as low resolution and spectral shift; leaving 17 duplicates, one triplicate and 12 single analyses for further consideration. Samples with low $^{232}Th/^{230}Th$ levels were corrected for detrital ^{230}Th addition.

The dates obtained were considered in terms of age, geographic distribution, and uranium isotope ratios and concentrations. $\delta^{18}O$ suggested that samples were derived from either Taylor Glacier meltwaters, or possibly Ross Ice Sheet Stage 6 meltwaters, and showed that $\delta^{18}O$ values in the meltwaters increased towards the middle of each event.

Three major events were identified.
(i) an extensive period of deposition around 240 to 300kA (Stage 9?), This may possibly represent two events, in a lake(s) most likely formed proglacial to an expanded Taylor Glacier.
(ii) a short period of lacustrine conditions around 175 to 190 kA ago, correlated with either Taylor Glacier expansion at the end of Stage 7, or Ross Ice Sheet thickening at the start of Stage 6.
(iii) a period of carbonate deposition from 130 to 80 kA(Stage 5), more extensive than that at 175-190 kA. The expanding glacier (Taylor II) then advanced through the carbonates, and those of the earlier events, and redeposited.

The events interpreted appear to correlate with global interglacials, as suggested by Hendy et al (1979). It seems that during interglacials, the East Antarctic Ice Sheet expands (the absence of a sea ice apron allows increased precipitation). As a result, expansion of the East Antarctic Ice Sheet would be expected as a consequence of greenhouse gas warming, offsetting sea level rises caused by melting of temperate glaciers and ice sheets.

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Chapter 1.

Introduction: Uranium-Thorium Dating.

Radiometric Dating.

A number of naturally occurring nuclides are inherently unstable, by virtue of unfavourable balances of protons and neutrons in their nuclei. To achieve a more stable configuration they undergo radioactive decay, spontaneously emitting one of three types of radiation -

(i) alpha particles - two neutrons plus two protons (i.e. a helium nucleus). Alpha particles have a short range, are readily blocked by matter, and have energies in the range of 2-10 MeV.

(ii) beta particles - positively or negatively charged electrons. Although the nucleus contains no electrons, they can be produced by nucleon transformations. Beta particles have energies less than 2MeV and can penetrate matter a short distance, due to their high velocities.

(iii) gamma rays - short bursts of electromagnetic radiation, often accompanying alpha or beta emissions. Such gamma rays have energies from 10keV to 7MeV.

Although individual atoms decay at random, a body of such atoms (N atoms) will display a describable rate of decay. This rate is proportional to the number of atoms present -

i.e the rate of decrease, $-dN/dt = \lambda N$ (1.1)

λ is the decay constant, equivalent to the probability that any atom will decay in the unit of time. This equation can be integrated:

$-dN/dt = \lambda N \Leftrightarrow -\ln N = \lambda t + C$ (1.2)

Since $N=N_0$ at $t=0$ (N_0 = initial no. of atoms), therefore $C = -\ln N_0$.

Therefore, $-\ln N = \lambda t - \ln N_0 \Leftrightarrow N = N_0 \exp(-\lambda t)$ (1.3)

That is, the number of atoms present can be deduced from the initial number, the time elapsed, and the decay constant. A convenient analogue of the decay constant for a nuclide is it's half-life ($t_{1/2}$). This is the time taken for half of any given number of atoms to decay.

The half life is derived from:

$\frac{1}{2}N_0 = N_0 \exp(-\lambda t_{1/2}) \Leftrightarrow \ln(\frac{1}{2}) = -\lambda t_{1/2} \Leftrightarrow t_{1/2} = 0.693/\lambda$ (1.4)

For example, if a body of 100 atoms has a half-life of 5 years, then after 5 years only 50 atoms would be left, after another 5 years only 25 would be left, etc, etc.

This feature of radioactive decay provides the basis for radiometric dating methods. If the initial number of atoms in a system is known, and the half life known, then a determination of the number of atoms currently present gives all the information needed to evaluate the time elapsed since formation of the body of atoms. The half-life of the species determines the period of time over which it is a useful chronometer, since after 6-7 half-lives around 99% of the original atoms will have decayed away. This limits the method, depending on the accuracy of detection of the method (usually determined by the technique and equipment available). A huge range of half-lives are found for different species, ranging from fractions of a second (e.g.^{212}Po, $t_{1/2} = 3\times10^{-7}$s) to millions of years (e.g. ^{147}Sm, $t_{1/2} = 10^{11}$ yrs). Although most short-lived isotopes might be expected to have long since disappeared, some are continually formed -

(i) by interaction with cosmic rays (e.g ^{14}C, ^{10}Be)

(ii) by decay of longer-lived 'parent' nuclides (e.g ^{231}Pa from ^{235}U)

(iii) by artificial means (e.g ^{3}H)

There is a wide range of useful species available for radiometric dating. Some examples are given in table (1.1).

Table 1.1 Some common radiometric geochronometers

Nuclide	Half-life	Useful dating range
^{210}Pb	22 yrs	0 - 100 yrs
^{14}C	5730 yrs	0 - 50 000 yrs
^{230}Th	75 200 yrs	0 - 400 000 yrs
^{40}K	1.25×10^{9} yrs	0 - age of the earth.

The Uranium Series Geochronometers.

Of particular interest in this thesis are the radiometric decay of ^{238}U, ^{235}U and ^{232}Th. All three have half-lives long enough for them to have survived since synthesis, and all three decay to give chains of shorter-lived radioactive daughters. The three decay chains all culminate in different stable isotopes of lead. As described earlier, radioactive decay alters the nucleus - alpha decay decreases mass number by four and atomic number by two units, while beta decay increases the atomic number by one unit, but retains the same mass number.

The three decay chains are given in figure (1.1).

The chaining of decays complicates the simple decay equations given earlier. The first nuclide in the series will decay as predicted by equation (1.3); however the decay of subsequent daughters is limited by their rate of formation from parent nuclides. Their rate of change is the difference between their rate of formation and their own rate of decay i.e $dN_2/dt = \lambda_1 N_1 - \lambda_2 N_2$ (1.5) (N_1, N_2 = number of atoms of parent (N_1) and radioactive daughter (N_2)). Initially the daughter activity will be zero, but will rise rapidly until it becomes limited by the decay rate of it's parent.

In the case of each of the uranium series decay sequences, the half-life of the longest lived daughter is many many times smaller than that of the parent isotope i.e. $\lambda_2 - \lambda_1 \approx \lambda_2$. After several daughter half-lives this gives rise to a special condition, called secular equilibrium. This means that after such time, the activity of the daughters will equal that of the parents, and will continue to be identical thereafter. i.e. at secular equilibrium $\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \lambda_4 N_4 = \ldots \lambda_n N_n$ (1.6) (for a series of decays $N_1 \rightarrow N_2 \rightarrow N_3 \rightarrow \ldots N_n$)

The uranium series decay sequences give rise to three possible methods of dating -

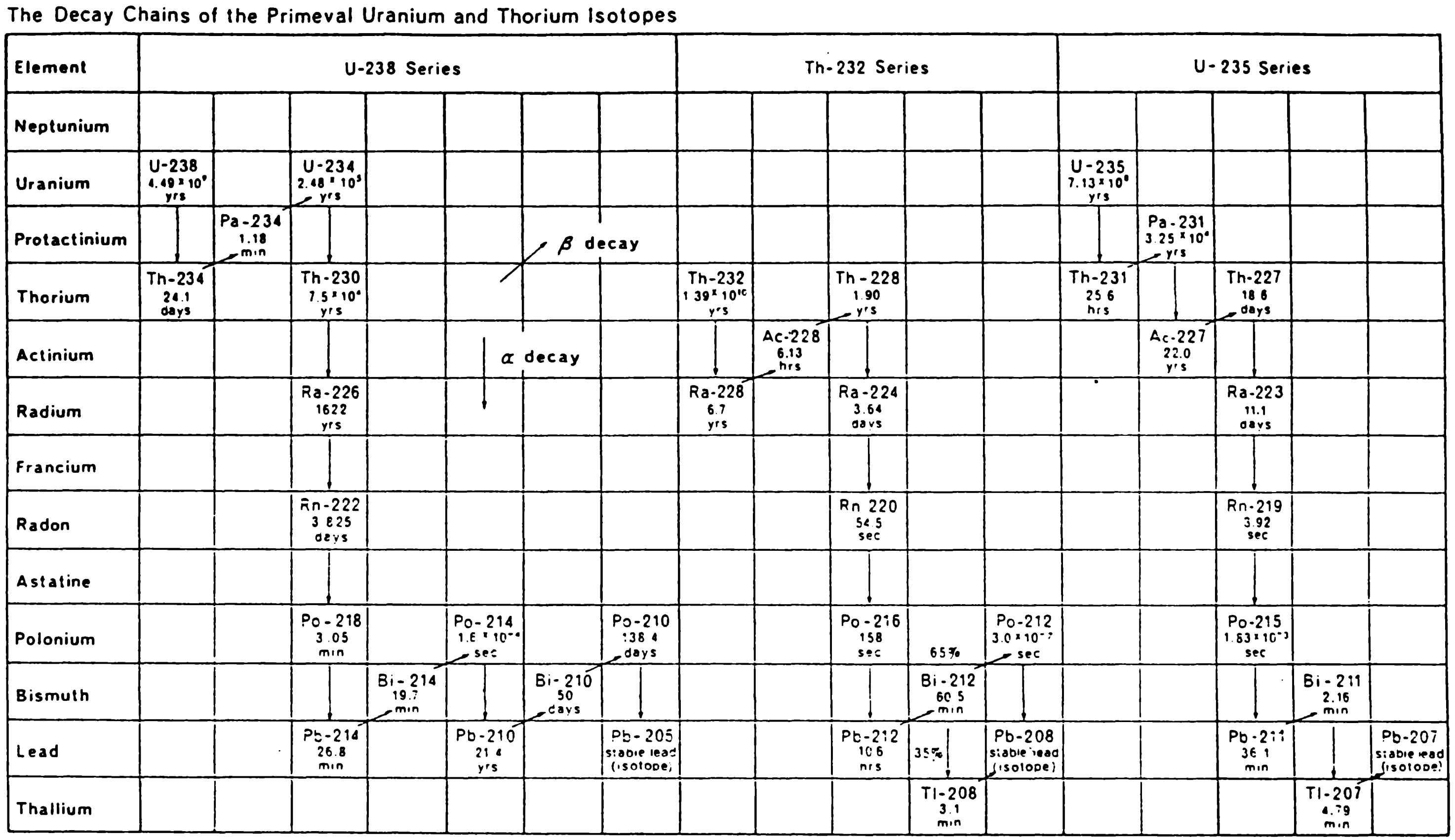
(i) the rate of decay of the parent nuclide. This is generally inapplicable as it is difficult to determine the initial amount of the nuclide present.

(ii) the rate of accumulation of a stable daughter. For example, the amount of ^{206}Pb present in a sample, as a function of the amount of ^{238}U can sometimes be used to estimate the sample age. Rutherford attempted the first ever U-series dating calculations by using the build-up of helium (from alpha particles) to determine the minimum age of the earth.

(iii) the ratio of parent to daughter activity. From the calculations above (eqn 1.6) it can be seen that this will only be useful up to the point of secular equilibrium, beyond which the ratios of activity will be unity at all times (this does, however, give a minimum sample age) The longest lived daughter of any is ^{234}U ($t_{1/2}$ = 248 000 yrs), thus this uranium series dating method is only useful for Pleistocene (0 - 2.5 Myr) samples.

If all samples had been closed since formation of the elements (i.e. no addition or loss of elements by chemical means), it would follow that secular equilibrium would be found in all samples. Fortunately this is not the case. As seen in the decay schemes, daughter species are always different elements from their parents, giving the potential for chemical fractionation and disruption of the decay chain. For example, radon is an inert gas formed in all three decay schemes. It will readily escape most geological bodies, thus there will be a permanent disequilibrium between radon and it's parent (radium). If at any time the system became closed to radon escape, the build-up of the radon daughter polonium could be used to measure the date at which the system became closed (if the sample is younger then the age of radon - polonium secular equilibrium). Furthermore, when the radon escapes to the atmosphere, it produces daughters that readily return to earth. Once they return to earth they are isolated from the parent isotopes and can be used for a short time for dating (e.g. ^{210}Pb is used to date snow and ice)

Of particular interest is the chemical fractionation of uranium and thorium in the ^{238}U series. As discussed below, thorium is separated from the uranium, effectively resetting the geological clock. The return from disequilibrium to equilibrium proceeds as a function of the time since separation of the thorium from the uranium, i.e. the $^{230}Th/^{234}U$ ratio is a function of the age of the sample (with some complications discussed later).



The Decay Chains of the Primeval Uranium and Thorium Isotopes

Figure 1.1 The decay chains of ^{238}U, ^{232}Th and ^{235}U (Kaufman, 1964)

Initial fractionation of Uranium and Thorium.

Disequilibrium can occur due to the highly disparate chemistries of uranium and thorium, particularly in solution. Thorium ([Hg] $6p^66d^27s^2$) favours a +4 oxidation state, while uranium ([Hg] $6p^65f^36d^17s^2$) can exist as U^{4+} or U^{6+}, but in oxidising conditions readily forms the stable $UO_2{}^{2+}$ cation. When initially found in igneous rocks they are often associated, as their large atomic radii make them both late to crystallize in magmas. They are generally found in the more residual phases, such as granites and pegmatites (Goldschmidt, 1954). A number of uranium and thorium rich minerals can form, such as uraninite (UO_2), monazite (Th,Ce,La(PO_4)), and uranothorite ((Th,U)SiO_4).

When weathering occurs, the first major fractionation of the two elements begins. Th^{4+} tends to hydrolyse in solution above pH 3, and very readily adsorbs onto solids. This is usually the way in which thorium is transported. Uranium, however, is quickly oxidised to $UO_2{}^{2+}$, which easily forms soluble complexes, and is transported in the solution phase. At low CO_2 partial pressures uranyl carbonate complexes such as $UO_2(CO_3)_3{}^{4-}$ and $UO_2(CO_3)_2{}^{2-}$ are common, while under some conditions organic acid complexes are favoured. As the weathering solution moves from groundwater, through streams and rivers to a body of water, the separation of the uranium and thorium continues. $^{230}Th^{4+}$ formed by decay of ^{234}U is rapidly scavenged to the solid or particulate phase (about 75% of the thorium in the ocean comes from decay, only 25% is from streams etc (Faure, 1986)). The speed of scavenging of Th is demonstrated by it's residence time in the sea of only 300 yrs, compared to uranium at 500 000 yrs (Faure, 1986).

When the environment becomes depositional it is possible to form sediments free of thorium (or uranium). Precipitation of calcium carbonate is a common depositional process, and it is during this that sediments containing uranium, but initially no thorium, are formed. This occurs by three methods - degassing of the carbon dioxide (e.g. in speleothems), evaporation of the water so as to force precipitation (e.g. in some lacustrine environments), and by biogenic incorporation in the skeleton of organisms, followed by settling of the discarded shell (e.g. in seawater). Uranium is readily incorporated in the calcium carbonate matrix, substituting for Ca^{2+}.

Thorium is also readily substituted for Ca^{2+} but has usually been previously removed from the solution. After the precipitation and sedimentation of the calcium carbonate, any thorium formed by alpha decay of ^{234}U is retained in the carbonate. It builds up as the sediment ages, and after 400 000 yrs ($t_{1/2}{}^{230}Th$ = 75 200 yrs), the thorium reaches secular equilibrium with ^{234}U, and the activity ratio is no longer a function of a unique age.

The fractionation of uranium from thorium can be demonstrated by looking at their relative concentrations at stages of their geochemical cycles (Table (1.2)).

Table 1.2 Fractionation of Uranium and Thorium.

Source	$[^{238}U]$ (ppm)	$[^{232}Th]$ (ppm)	Th/U	Reference
granites	4.8	21.5	4.5	Rogers and Adams, 1969
Mississippi water	1.0	0.01×10^{-5}	0.01×10^{-5}	Moore, 1967
Mississippi sedim.	2.6	10.5	4.04	Scott and Salter, unpub.
Seawater	3.3ppb	8×10^{-6}ppb	2.4×10^{-6}	Kaufman,1969 Ku et al, 1974
Oceanic sand/clay	0.7-4	1-30	0.4 - 10	unref.
limestone - $CaCO_3$	2	v low	0	Heye, 1969
- detritus	2.3	8.2	3.6	Ku et al, 1968

Although limestones are of concern here, the method is in principle applicable to a number of carbonate systems, such as corals, speleothems, and mollusc shells; and also to several non-carbonate systems e.g. peat, marine phosphates, bone, and some volcanic materials.

Complications in the $^{230}Th/^{234}U$ method

1. Necessary assumptions.

For valid dating by the $^{230}Th/^{234}U$ disequilibrium method, two requirements must be met, or approached.

(i) No Th is incorporated into the system i.e. initial $^{230}Th/^{234}U$ ratio = 0. Obviously such Th will contribute to the $^{230}Th/^{234}U$ ratio at the time of analysis. Because of the extremely low solubility of

Th in natural aqueous systems, the presence of ^{230}Th at genesis is almost entirely due to the detrital component of the formation. If such ^{230}Th is present in the system, it will invariably be accompanied by ^{232}Th, which is chemically identical. The ^{232}Th does not decay appreciably over the periods for which ^{230}Th/^{234}U dating is used, and can thus be used as a check for the presence of detrital ^{230}Th. If the initial ^{232}Th/^{230}Th ratio can be deduced, then a correction can be made for the detrital ^{230}Th contribution to the apparent ^{230}Th/^{234}U ratio (see later).

(ii) The sample remains closed to post-depositional migration of the relevant nuclides. In particular, groundwater will readily redissolve the uranium nuclides, or will deposit more uranium. These processes have invalidated much of the use of ^{230}Th/^{234}U dating for molluscs (Broecker, 1963). Evidence for these processes are recrystallization of the sample, and unlikely nuclide ratios (e.g excess ^{230}Th).

The validity of these assumptions for the samples dated is further discussed in Chapter 4. In brief, detrital ^{230}Th contamination needs to be considered, recrystallization is unlikely to be a problem.

2. Decay of ^{234}U.

^{234}U has a half-life of 248 000 years (Evans, 1955), and will thus decay appreciably over the period of usefulness of the method. Initial work on the ^{230}Th/^{234}U method assumed that ^{238}U and ^{234}U would always be in secular equilibrium, due to their activity ratio of unity in source rocks, and presumed identical chemical behaviour. Since ^{238}U would not decay over the period, methods used the ^{230}Th/^{238}U ratios as identical to the ^{230}Th/^{234}U ratio.

It was shown that such equilibrium is not the case (Cherdynstev, 1955), and ^{234}U/^{238}U activity ratios of up to 30 have been found. In sea-water the ratio is 1.15, and in almost all known cases ^{234}U activity exceeds that of ^{238}U. The decay of excess ^{234}U towards secular equilibrium with ^{238}U must be taken into account when calculating the age of the rock.

The reason for the ^{234}U excess is it's preferential leaching by solutions, over ^{238}U. When an alpha particle and two beta particles are ejected from the ^{238}U nucleus to from ^{234}U, the atom must recoil to conserve momentum. Obviously the large mass of the nucleus only need move a small distance (p=mv). However, in moving, the lattice site of the ^{234}U nucleus (previously ^{238}U) becomes slightly distorted, making ^{234}U much more susceptible to leaching and mobilisation.

Equation of Age.

Two contributions must be considered in the age equation; the decay of ^{234}U with time, and the decay of ^{230}Th with time and with decrease in ^{234}U activity. The relationship can be derived:

$$\frac{^{230}Th}{^{234}U} = \frac{1 - \exp(-\lambda_{230}t)}{^{234}U/^{238}U} + \left(1 - \frac{1}{^{234}U/^{238}U}\right) \cdot \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}} \cdot (1-\exp(-(\lambda_{230}-\lambda_{234})t)) \tag{1.7}$$

This cannot be solved directly, either a graphical approach or an iterative method must be used for solving the equation. A computer programme (Appendix A) was used to solve the equation iteratively. Graphical solution isochrons are given in figure (1.2). The graph also shows the need to minimise errors in older samples.

Corrections for Contamination by Detrital Thorium

A number of correction schemes have been proposed to allow for incorporation of detrital ^{230}Th into the sample at the time of depositional, due largely to the widespread occurrence of 'dirty' carbonates that need to be dated. These include travertines, caliches, and (here) lacustrine marls.

Two approaches can be used to correct for detritral thorium.

(i) separation of detrital thorium during processing.

It is very difficult to physically separate the detrital component from the carbonate part, in the solid state. However, by dissolving with dilute acids, it is possible to take the carbonate thorium into solution, and leave much of the detritus intact. There are still problems with this method, as uranium and thorium adsorbed to the detrital surfaces will be leached, and may be of

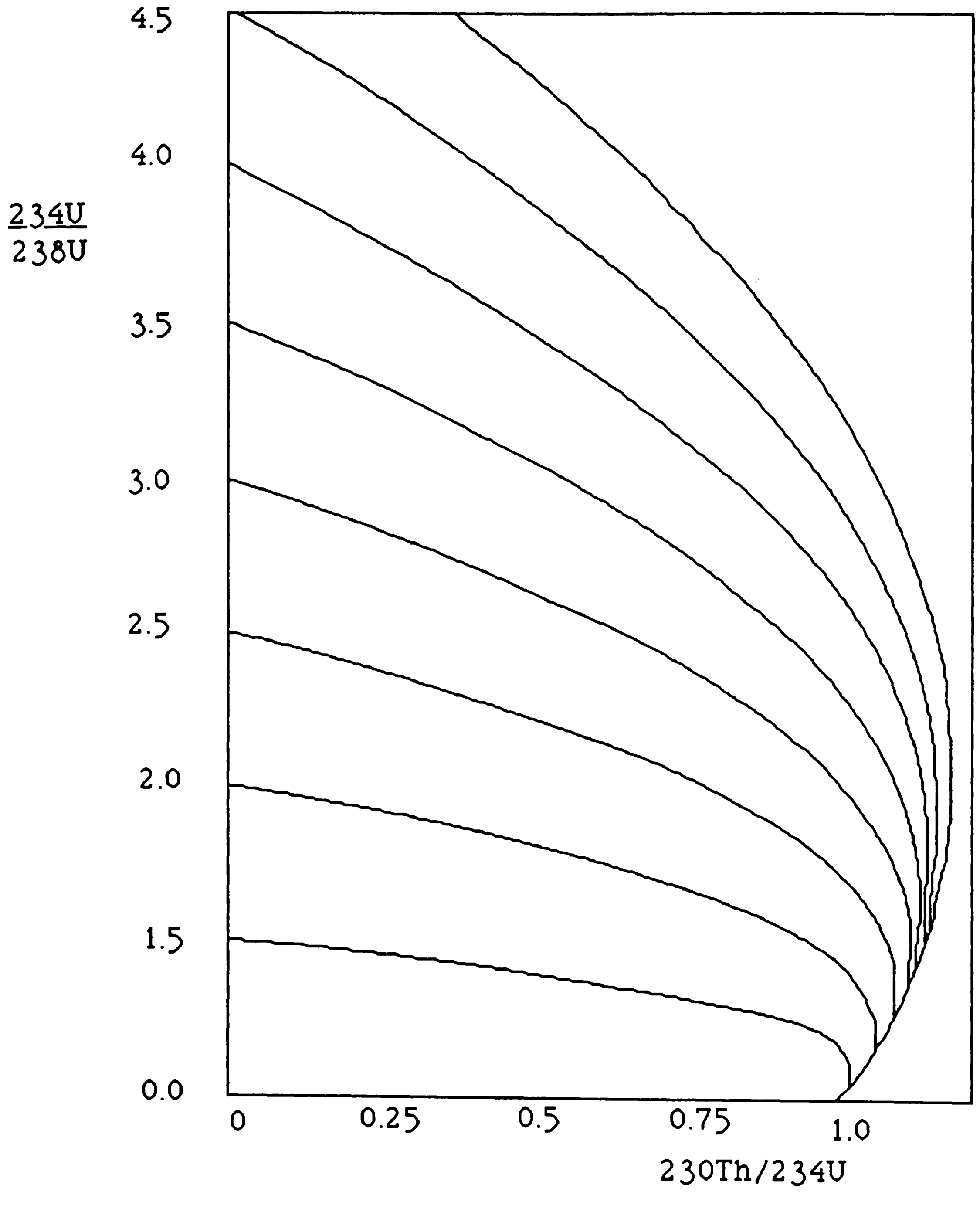


Figure 1.2 Isochron plot for the ^{230}Th-^{234}U age equation (modified by Hendy et al (1979) from Kaufman (1964))

different nuclide ratios to the carbonate phase. Nevertheless, use of dilute acid does help minimise interferences from detritus.

(ii) mathematical corrections.

Using ^{232}Th to estimate ^{230}Th corrections. As suggested above, any ^{232}Th in the detritus (or in the carbonate phase) will be accompanied by ^{230}Th. If the initial ratio of ^{232}Th/^{230}Th were known, then the approximate age determined can be used to calculate the interference of detrital ^{230}Th, and so recalculate the apparent age (assuming that the Th isotopes are retrieved from the detritus in the same ratio as they were incorporated. ^{232}Th will not decay appreciably over the period. Kaufman and Broecker (1965) calculated the true carbonate ^{230}Th activity as follows:

$$^{230}\mathrm{Th}_{true} = {}^{230}\mathrm{Th}_{measured} - R\,.{}^{232}\mathrm{Th}_{measured}\ \exp(-\lambda_{230}t) \qquad (1.8)$$

where $^{230}\mathrm{Th}_{true}$ = ^{230}Th corrected for detrital ^{230}Th
$^{232,230}\mathrm{Th}_{measured}$ = total ^{232,230}Th measured in sample
t = apparent age measured.
R = detritus ^{230}Th/^{232}Th activity ratio at t=0.

R is difficult to estimate with any accuracy, and varies between 1.0 and 3.0 generally. It can often be estimated by looking at a variety of samples that are assumed to have the same R value, but different absolute amounts of ^{232}Th. This could be assumed when geomorphic, physical and temporal proximity of a set of samples suggest a common detritus source.

The method was first used by Kaufman (1971). The true carbonate ^{230}Th/^{234}U ratio is taken from the slope of an isochron plot of ^{230}Th/^{232}Th vs ^{234}U/^{232}Th. It is necessary to have a set of samples of varying detrital content, in order to get a slope (i.e. identical samples will all plot at a point). The ^{230}Th content takes contributions from both the detrital (D) and carbonate (C) phases; and will thus vary with detrital content relative to ^{232}Th, which only comes from the detritus. i.e:

$$\frac{^{230}\mathrm{Th}_{total}}{^{232}\mathrm{Th}_{total}} = \frac{(^{230}\mathrm{Th}_D \pm {}^{230}\mathrm{Th}_C)}{^{232}\mathrm{Th}_{total}} = \frac{^{230}\mathrm{Th}_D}{^{232}\mathrm{Th}_{total}} + \frac{^{230}\mathrm{Th}_C}{^{232}\mathrm{Th}_{total}}$$

and likewise
$$\frac{^{234}\mathrm{U}_{total}}{^{232}\mathrm{Th}_{total}} = \frac{(^{234}\mathrm{U}_D \pm {}^{234}\mathrm{U}_C)}{^{232}\mathrm{Th}_{total}} = \frac{^{234}\mathrm{U}_D}{^{232}\mathrm{Th}_{total}} + \frac{^{234}\mathrm{U}_C}{^{232}\mathrm{Th}_{total}}$$

Therefore
$$\frac{^{230}Th_C}{^{234}U_C} = \frac{\dfrac{^{230}Th_{total}}{^{232}Th_{total}} - \dfrac{^{230}Th_D}{^{232}Th_{total}}}{\dfrac{^{234}U_{total}}{^{232}Th_{total}} - \dfrac{^{234}U_D}{^{232}Th_{total}}} \qquad (1.9)$$

The ratios of $^{230}Th_D/^{232}Th_{total}$ and $^{234}U_D/^{232}Th_{total}$ are assumed to be independent of the amount of detritus present (since $^{232}Th_{total}$ all comes from the detritus as well). The equation is therefore of the standard form m = (x-a) / (y-b), and a plot of x vs y will have a slope of m, and x and y intercepts of a and b respectively. The true carbonate $^{230}Th/^{234}U$ activity, the detrital contribution of thorium, and the true age can then be recalculated for each sample.

A similar plot can be used to find the $^{234}U/^{238}U$ activity for the pure carbonate, since the ratio may be different from that of the detrital phase. Using similar derivation to that above, $^{234}U/^{238}U$ is plotted against $^{232}Th/^{234}U$, giving a slope of $^{234}U_C/^{238}U_C$.

The use of this method for coeval contaminated calcites has been described by Schwarz and Latham (1989).

Other detritus correction schemes have been proposed, including a number that separately analyse the residue and carbonate fractions for the various isotopes. The mixing plot approach outlined above will be further discussed in Chapter 3.

Analytical Methods for U-Th dating.

Because of it's short half-life, the actual concentration of ^{230}Th in any sample is extremely low. For example, if an ancient sample contained 1ppm of ^{238}U, the ^{230}Th concentration would be 5.4×10^{-6} ppm. This has made mass spectrometry impractical for dating until very recently, when Edwards et al (1987) developed a machine capable of such low level measurements. This method is many times more accurate than the traditional method, alpha-spectroscopy, and will doubtless supersede it eventually.

Alpha spectroscopy directly determines the activities of the nuclides. The inaccuracy of alpha spectroscopy is due to it's use of alpha decay counting. Decay counting is based on the random individual decays, where the variance of a given number of alpha events is the square root of the count. Counting is based on surface barrier detectors, which contain thin silicon wafers doped to semi-conductivity. When the alpha particle (ionizing) strikes the detector, it causes a potential difference between the anode and cathode attached to the wafer. The signal sent is a function of the energy of the alpha particle received. Unfortunately ^{230}Th and ^{234}U emit alpha particles of approximately the same energy, and must therefore be completely separated chemically before alpha counting. Alpha spectroscopy requires a uniformly distributed and thin sample to achieve good resolution. Alpha particles are readily diminished in energy by interaction with other matter, and a thick source will have a noticeable low energy tail. It is thus important that the sample for counting be free of any contaminants, as these will absorb alpha particle energy and diminish sample resolution. A number of lower energy particles may run under any nearby lower energy peaks, and such a tail will have to be allowed for when calculating the activity of those peaks.

The brief for the ^{230}Th-^{234}U alpha spectroscopy method is thus to completely separate the uranium in the sample from the thorium, and to isolate both from any other elements; before thinly mounting each on a surface suitable for alpha counting.

Chapter 2

Uranium-Thorium Methodology.

Introduction.

Previous methods used at Waikato were based on a mixture of ion exchange chromatography and organic extraction, culminating in disc preparation by evaporation from an organic medium. Double scavenge coprecipitation led to an anion exchange column where uranium and thorium were separated. The thorium was purified by extraction from hexone using saturated $Al(NO_3)_3$ as a salting out agent, the thorium was then plated out. Iron was separated from the uranium by extraction into di-isopropyl ether, followed by plating of the uranium. This method gave very variable yields, and usually low resolution.

A preliminary attempt at a new U-Th method was based on techniques developed at the Institute of Nuclear Sciences (DSIR) (McCabe et al, 1979) as part of their U-Th and U-Pa dating programme. Their method was based on a cation exchange column, and claimed quantitative yields for uranium and thorium, obviating the need for a spike solution to trace yields. The cation column was designed to work at elevated temperatures in a teflon column, followed by further purification (for uranium); and finally electrodeposition from a sulphate bath, with a rotating cathode system. Attempts at this method were unsuccessful. Leakage problems between the teflon column and water jacket; the difficulty in using polythene beakers as a substitute for teflon; and the attempted use of Al discs as a substitute for stainless steel, all contributed to the failure. Most importantly, the method was unable to deal with the high levels of titanium found in the samples to be dated. A new, simpler, method became available during this time, and was successfully adopted. The method came from the Lamont-Doherty Geological Observatory, Columbia University, where it was developed by Bob Anderson. It was adapted for Antarctic lacustrine carbonates by Dr C. Hendy, and further modified as discussed in this chapter. The method uses standard uranium and thorium processing techniques for the most part; it also features a uranium purification column based on nitric acid, and electroplating from a chloride bath onto silver planchettes. Some emphasis is placed on achieving high yields - such as through multiple rinsing at all stages and through the use of teflon beakers wherever practical. At neutral and near neutral pH conditions thorium exchanges for sodium in ordinary glasses, including borosilicate (i.e laboratory pyrex) glasses. Teflon (polytetrafluoro-ethylene) beakers are quite expensive (currently $18-00 each), but do not chemically adsorb thorium. While high yields are not essential to the process, due to the use of isotope dilution methods, they lead to higher count rates, thus decreasing the statistical error in the dates obtained. High yields are also very important in allowing the method to be readily adapted to samples of low uranium (and thorium) concentration.

All samples were processed in batches of four. However, the method could easily be upgraded to allow batch sizes of eight samples at a time, given more centrifuge bottles, teflon beakers and electroplating units.

The method was developed to cope with a number of problematic trace elements, but to still give high yields of good resolution. Much of the methodology was developed concurrently with routine sample processing, and by the time of processing the final samples had achieved the objectives to a very good degree.

Initial Treatment

Sample Selection.

Samples were selected on several criteria.

(1) the need for a wide range of sites (i.e. sample numbers) to be represented.

(2) sample quality (which limited the first criteria). Samples preferred showed -

(a) pristine appearance (absence of any sign of weathering, oxidation etc (characterized by reddish-brown veneers) - which could mean post-depositional alteration of the nuclide ratios.)

(b) absence of obvious clastic contamination. This was achieved by rejecting samples with obvious non-carbonate inclusions in the matrix e.g. gravels, basalt sands, quartz. Such detritus may contain labile uranium and thorium in ratios independent of the sample age.

However, a number of samples with obviously high levels of detritus were dated to satisfy the need for a range of sample sites.

(3) The final criteria was that a single specimen of the sample must weigh at least 30gms, allowing a margin for duplicate processing of samples. This is as individual specimens from a site may not be homogeneous. Some early samples (nos 87-253a, 87-031-66b, 87-024-48c, 87-017-38b, 87-006-019) were of composite specimens.

Thus the samples dated are not an unbiased selection of the carbonates present in the area.

Pretreatment.

Samples selected were scraped clean to remove any surficial detritus, and any obvious pieces of gravel etc were removed. Samples were crushed (mechanical crusher) and ground in a ring mill grinder for 30s. Although powdering increased the exposure of labile isotopes in the detritus, it made sample dissolution much less time-consuming and ensured homogeneity between duplicates. 10g samples were weighed out accurately, and added to a 600ml beaker. Although sample weight was not critical to the age, all samples weighed from from 9.998g to 10.002g. This allowed $^{228}Th/^{230}Th$ and $^{232}U/^{234}U$ ratios to be used to trace major discrepancies in the ages of replicates.

Spike.

100 mls of distilled water and 10 mls of spike were added. Uranium and thorium are not necessarily extracted quantitatively by the process, thus a spike of non-critical uranium and thorium isotopes was added at the first stage of processing. This allowed the relative yields of the uranium and thorium to be calculated, and hence the true sample $^{230}Th/^{234}U$ ratio to be calculated (the isotope dilution method).

Separation of Uranium and Thorium from Calcium etc.

8N HNO_3 was added to the sample until effervescence ceased. HNO_3 was preferred over HCl because of it's greater oxidising power, ensuring that all uranium was converted to the uranyl form, UO_2^{2+}. This was a critical part of the process, as the acidity was a prime determinant of how much detritus was dissolved or leached along with the carbonate fraction. In all cases this acidification was done very carefully, with minimal excess acid added. The sample was then boiled very gently under a watchglass for approximately one hour, again excessively vigorous conditions would affect the detritus too much. The aim of boiling was to drive off the CO_2 dissolved in the solution, and to ensure that the spike and the natural uranium and thorium isotopes had the same distribution between solution and solid phases.

After cooling for a few minutes the solution was transferred to a 200ml centrifuge bottle, carrying as much of the detritus as possible. Centrifuging was for 10mins at 3000 rpm, the supernatant was then transferred to a 400ml beaker. Any detritus remaining in the 600ml beaker was washed into the centrifuge bottle with a minimum of distilled water. A few drops of 8N HNO_3 were added, and the residues centrifuged again. The supernatant was added to the 400ml beaker, while the residue was filtered on a Buchner funnel, along with washings of any residues from the 600ml beaker. The residue was dried and weighed on the filter paper. A constant filter paper weight of 0.37g was assumed (this was the average of multiple weighings, the distribution was N(0.37g,0.01g)).

The separation of the residue from the acid-soluble phase was completed as rapidly as possible, to minimize excess leaching of the detritus, and to minimize reabsorption of $CO_2(g)$ by the solution after boiling.

Initially the only treatment prior to coprecipitation was to add several drops of $FeCl_3$ (aq). Also tried was the INS solution of 9.7mls $FeCl_3$/200mls 0.1N HCl(McCabe et al, 1979). The $FeCl_3$ acted as a coprecipitant for the uranium and thorium. Although natural Fe levels were very high in many samples, added $FeCl_3$ was used in all samples as a safeguard. The earlier results gave reasonable uranium yields, however these had a maximum value of around 80%. Uranium can readily escape coprecipitation, so the method was modified. The problem was the ability of the uranium to form soluble uranyl complexes with a number of species, such as organic acids and CO_2.

i.e. $CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3^{2-} + 2H^+$

$UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow UO_2\,(CO_3)_3{}^{4-}$ (soluble at pH > 7)

Organic acids form soluble uranyl species above pH 6. These are unlikely to be present in any quantity, if at all, but are possible due to the biogenic source of the carbonates. Thorium coprecipitation is quantitative under most conditions.

To overcome any possible loss of uranium in this part of the process, rigorous conditions were adopted. 10mls of conc HCl was added to the solution, and the solution brought to the boil. The HCl + HNO_3 solution would be strongly oxidising enough to destroy any organic complexing reagents. After 5 mins boiling to expel any CO_2 (the HCl/HNO_3 solution boils very rapidly) the solution was precipitated while still hot.

The coprecipitation stage allows for separation of uranium and thorium (along with Fe, Al and many other trace elements) from all the Group I and Group II elements, particularly Ca. Concentrated ammonia solution was added dropwise, with stirring, until the pH reached 7-7.5 (pH meter). The ammonia may have introduced some CO_2 to the solution, so for some preliminary samples the ammonia was boiled prior to coprecipitation. This did not affect recovery. Gascoyne (1977) made an extensive investigation into this prospect, it seems unlikely that CO_2 in the ammonia is a significant problem.

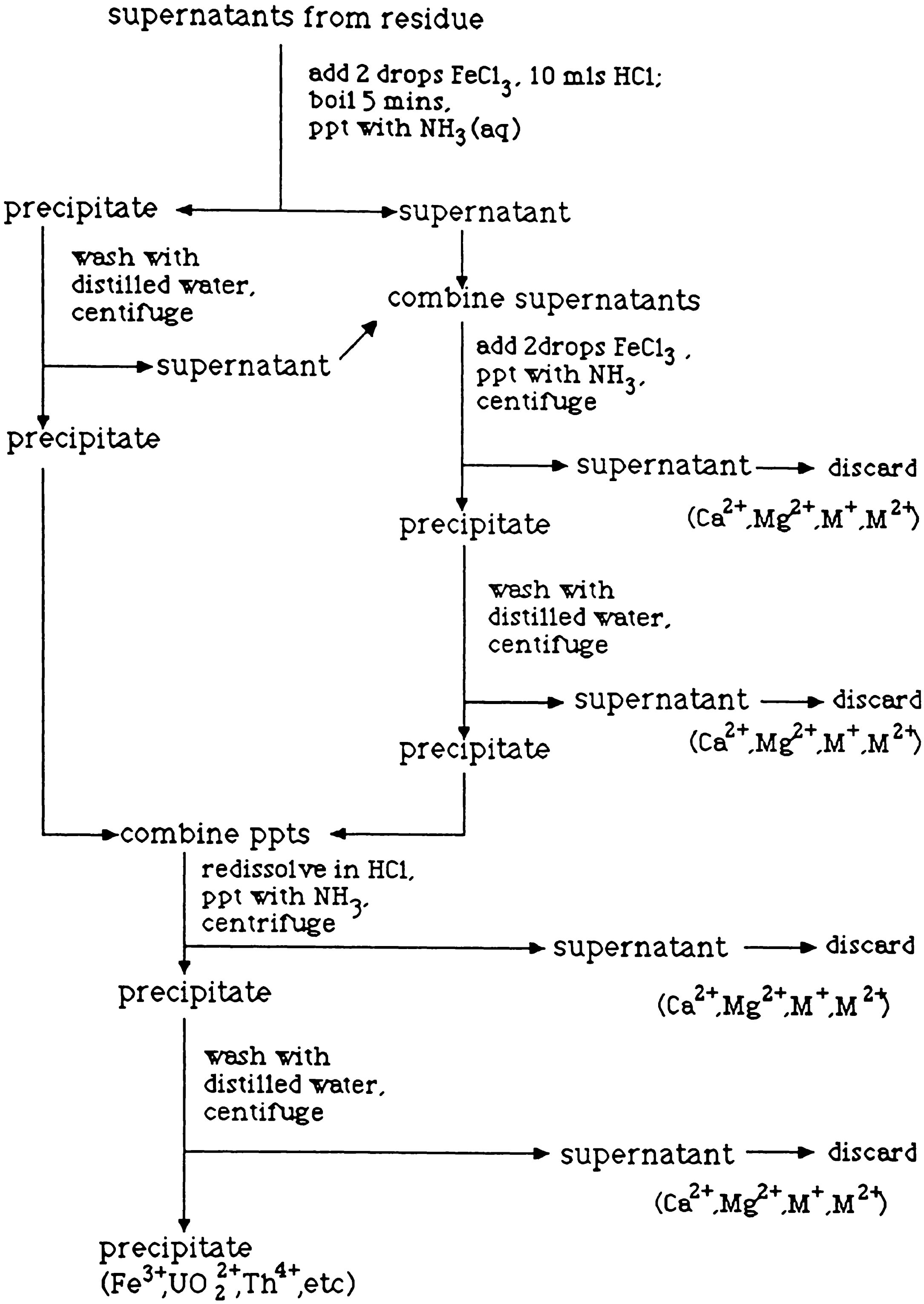
It was of interest here that the precipitate from the HCl/HNO_3 solution was very much visibly finer than that from HNO_3 solution. This gives a greater surface area for coprecipitation, and for some reason gives much less flocculation at the surface, eliminating another small source of uranium and thorium loss.

The precipitate was centrifuged in 200ml plastic bottles. This and all subsequent centrifugation was at 3000 rpm for 10 mins. Higher revolutions were not possible without stressing the centrifuge, shorter times did not always compact the precipitate enough. The supernatant was transferred back to the 400ml beaker; the precipitate was washed with 30mls of distilled water and recentrifuged. This removed any adsorbed Ca back to the aqueous phase. The supernatant was added to the 400 ml beaker. The combined supernatants were reacidified with a minimum of conc HNO_3 (about 2mls was needed). A few drops of $FeCl_3$ (aq) were added, again as a coprecipitant. If necessary more HNO_3 was added to dissolve any solid phase. Some preliminary samples were reboiled at this stage, this was abandoned as having a minimal impact on recovery relative to the extra time needed for reboiling. The supernatant was precipitated with ammonia to pH 7 - 7.5, and added to the centrifuge bottle containing the first precipitate (insufficient centrifuge bottles for separate centrifugation). After centrifuging the supernatant was discarded. The 400ml beaker was rinsed with a minimum of distilled water, and this was added to the precipitate. Again this was centrifuged and the supernatant discarded.

The combined precipitates were redissolved in 8N HCl and diluted to 100mls, in the centrifuge bottle. The solution was reprecipitated with concentrated ammonia in the bottle, centrifuged, and the supernatant discarded. The precipitate was washed with 30mls of distilled water and recentrifuged. Again the supernatant was discarded. The aim of these steps was to ensure complete release of any adsorbed or coprecipitated species that should have been in the aqueous phase; by guaranteed complete dissolution in a new acid, HCl.

The precipitate was dissolved in three times its volume of conc HCl for loading onto the first ion exchange column. The coprecipitation scheme is summarized in figure (2.1).

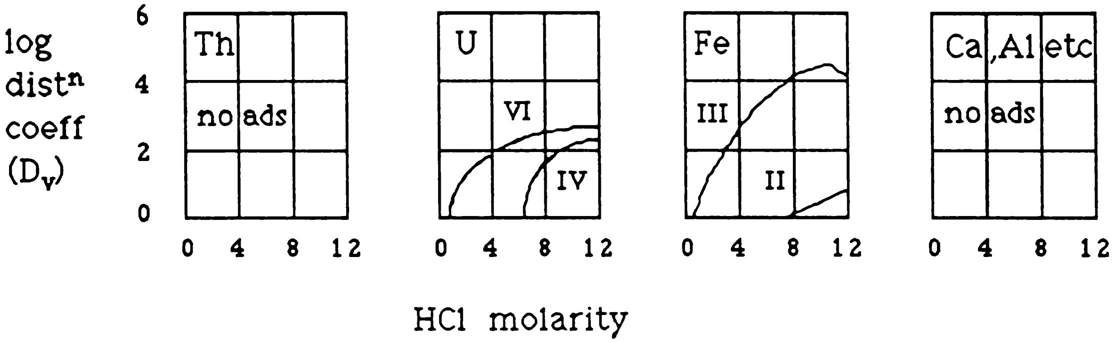
Figure 2.1 Double scavenge coprecipitation scheme



Separation of Uranium From Thorium

Separation of uranium from thorium was achieved by ion exchange chromatography. The distribution of a number of elements between resin and eluant on anion exchange columns in HCl has been investigated by Kraus and Nelson (1955). Some relevant results are given in figure (2.2).

Fig (2.2) Log distribution coefficient vs normality of HCl for several elements. (Kraus and Nelson,1955)



The anionic species formed adhere to the resin, while any cationic or neutral species are washed off. The species of note here are :

$$UO_2^{2+} + 3Cl^- \Leftrightarrow (UO_2Cl_3)^-$$
$$UO_2^{2+} + 4Cl^- \Leftrightarrow (UO_2Cl_4)^{2-}$$
$$Fe^{3+} + 4Cl^- \Leftrightarrow (FeCl_4)^-$$

The resin used was DOWEX 1X8 100-200 mesh (laboratory grade). This was preferred over coarser meshes which although have faster flow, have poorer quality of separation. Analytical grade resin would have been preferable, but was deemed too expensive. A quantity of resin was made into a slurry with distilled water. The slurry was allowed to settle for 5 minutes, after which the supernatant was decanted, taking with it most of the finings. The wash was repeated, again any finings were decanted.

The columns used were BIORAD 20cm x 1.5cm chromatography columns. They were filled with distilled water and allowed to run out, during which time the slurried resin was added. This ensured no air bubbles were trapped in the base of the column.

Approximately half-filled columns were used, generally containing 12-15mls of resin. This was washed with a column volume of distilled water, followed by two volumes of 8N HCl. As in all stages of ion exchange chromatography it was preferable not to allow the head of the resin to run dry. This was largely achieved, but not always. Fortunately 100-200 mesh resin retained the liquid enough that air bubbles did not form in the bed, although some may have worked into the base of the column.

The sample was loaded straight from the centrifuge bottle, and a 100ml teflon beaker (labelled) was placed under the column. When the top of the sample solution was approaching the head of the resin, a wash of 8N HCl was added to the column; followed by two more washes of 8N HCl in like manner. These washes were previously used to thoroughly rinse the original sample centrifuge bottle (or beaker), ensuring complete sample transfer to the column. When the last of the 8N HCl washes were approaching the head of the resin the receiving beaker (containing thorium and other elements) was replaced by another 100ml labelled teflon beaker. A wash of distilled water (column volume) was followed by one of distilled water plus 5 drops conc HCl, followed by a final wash of distilled water. These washes eluted the uranium and iron (and other trace elements) into the beaker. At such low chloride concentrations the uranyl complexes are not held to the resin.

Two major problems arose during this section of work - solid phases on the column and discoloured thorium fractions.

(I) Yellow or yellow-brown washings frequently appeared in the thorium wash, which should be completely clear. This had two sources:

(i) Fe was not retained on the column. The iron complex formed a distinctly brown coloured band at the top of the resin bed. Any movement of the band during the Th washes showed it was not being held to the resin, and was a reasonable proxy for similar uranium movement. This occurred if the chloride activity was less than optimal. Specifically the movement of the Fe band would occur if the sample was loaded in solutions significantly less than 8 molar in HCl. Because the final precipitate from the previous stage was highly hydrated, triple its volume of conc HCl was added to give a total molarity of 8N. Unfortunately this was a subjective measurement and undoubtedly far too little HCl was added on a couple of occasions. When the Fe band was washed off the bottom of the column the washings continued, starting from the first distilled water wash; with all washings combined. The combined eluates were boiled down and dissolved in 8N HCl, before reloading on the column. This was only done on two occasions, as all other discoloured thorium washes were attributed to the other source.

(ii) Colouring by resin products. Frequently the discolour of the thorium fraction was not consistent with that expected for Fe complexes. In these cases drop tests with potassium ferrocyanide gave negative results (whereas Fe^{3+} solutions diluted to the same colour intensity readily turned blue). It seemed likely that byproducts of the resin were being formed by contact with the acid, and that these were the source of the discolour. Further evidence for this was that the colour often disappeared on boiling the solution; and that if boiled to dryness the residue was not red-brown but white. The discolour would also occur when the Fe band was visibly holding at the head of the resin. Strongly discoloured solutions often appeared slightly oily, and sometimes the source of the colour could be partially extracted into hexone.

This effect could be reduced by pre-washing the columns with 8N HNO_3, then with the 8N HCl twice. This discolour was present in virtually all the latter samples, but was not a problem. It was ignored as any organic species would be destroyed when HNO_3 was added to the boiling HCl solution at a latter stage. This was confirmed by the clear colour of the solution after conversion to the HCl form.

(II) Column blockage. It was common in the early samples for the drip rate of the solutions to become very slow, virtually stopping sometimes. Initially this was thought to be due to swelling of the resin with changes in eluant normality. Solutions of 7N or 9N HCl still gave the same result. The precipitate was also boiled to dryness and taken up in 8N HCl to ensure the same normality as subsequent washes. This was also ineffective.

Some samples showed a lightening of colour in the head of the resin, presumed to be a trace element since blank control columns ran satisfactorily. Stirring the head of the resin allowed a short remission in the slowing of the elution rate. A new bulk sample used for preliminary work (87-253a) formed a particularly heinous plug of clear gel up to 3cm long on top of the resin. This was realised to just be a more blatantly manifested form of the earlier lighter colour in the head of the resin.

Samples of the gel were retrieved for further examination. The gel was partially soluble in nitric acid. Atomic absorption analysis suggested high levels of Fe, but gave negative results for Mn, Al, and Si. This was not considered conclusive at the time as there were problems with the AA machine. The gel was found insoluble in organic solvents (CH_2Cl_2, benzene) and had no distinctive smell (as would be expected from the amine products that were the most likely products of resin reaction). This excluded resin byproducts as a source of the gel.

After dessication under vacuum the powdered gel was submitted for X-ray fluorescence analysis. The results showed the powder to be SiO_2, the gel was a hydrated form of the same. The analysis also showed the gel to have taken in high levels of other trace elements, as shown in table (2.1). The identity of the gel was confirmed by it's solubility in HF.

Table 2.1 XRF Results for Silica Gel

Element	Atom %
Silicon	85.4
Aluminium	11.6
Calcium	0.9
Titanium	0.8
Manganese	0.5
Chromium	0.3
Iron	0.3
Zinc	0.1

Processing samples with the SiO_2 levels present in some samples was not practical. The time necessary to pass the needed washes through the solution was of the order of days. Furthermore the retention of Fe by the gel suggested UO_2^{2+} was also likely to be retained, it is uncertain whether or not Th^{4+} would have been affected.

An obvious treatment to remove SiO_2 was to use HF, and the reaction $SiO_2 + 4HF \Leftrightarrow SiF_4\ (g) + 2H_2O$. It was not simple to predict the presence of high SiO_2 levels on the basis of the sample chemistry preceding the first column. Generally, though, high levels of quartz in the residue correlated with high SiO_2 levels. This assessment was not sufficiently explicit, so all samples were treated for SiO_2.

At first the treatment was carried out after the precipitation and scavenge from HNO_3 solution, prior to precipitation from HCl solution. The precipitate was dissolved in 10mls HF, boiled dry, redissolved in 3mls HF and boiled dry. Repeated evaporation with conc HCl (5x) (since HCl was the desired final matrix of the sample) was unsuccessful in removing residual HF, due to the difference in boiling points of the acids (HF 112° , HCl 108°).

Although this was successful in removing SiO_2, traces of HF tended to bleach the top of the resin and sometimes formed a hard white impermeable layer. This led to the use of $HClO_4$ to remove residual HF, followed by evaporation from HCl (which also oxidises any $HClO_4$ not destroyed by the prolonged heating at dryness). In some samples the levels of Ca^{2+} were still too high at this point, and quantities of CaF_2 gel formed - these were unable to be dissolved later. Thus the SiO_2 treatment was moved to beyond the final HCl-NH_3 precipitation, just preceding the first column. Also attempted was the use of boric acid to help break up the more stable fluoride complexes (McCabe et al, 1979) such as the insoluble green FeF_3. This was helpful, but found unneccessary as other aspects of the SiO_2 treatment were refined.

The final method for SiO_2 removal was as follows. After the final precipitate was obtained it was dissolved in conc HNO_3 and transferred to a 100ml teflon beaker. The centrifuge bottle was rinsed with a minimum of HNO_3, and this was added to the beaker. HF was added dropwise until the solution cleared (mainly $FeCl_3.6H_2O$ (yellow) $\Leftrightarrow$ $FeF_3.nH_2O$ (clear)). This was boiled to dryness for about 2-3 hours. 15 mls of $HClO_4$ was added and the beaker was boiled dry at a low heat overnight. A few mls of conc HCl were added, and the solution boiled to dryness. The residue was readily redissolved in 10-20mls of 8N HCl for loading onto the first column.

The final observation of note on the U-Th separation column was the occasional occurrence of a green band in the resin. This would hold just below the Fe band and slowly move downwards with the

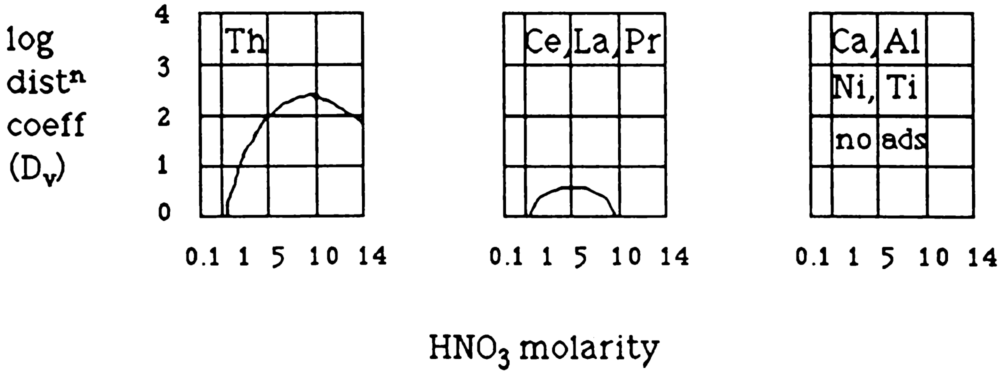
8N HCl washes, often fading in colour. This was seen in samples 87-014-32c, 87-033a, 87-036-76b, and 87-006-019. After fading the green colour was not seen again. It is interesting that the Th fraction often had a slightly green tinge after conversion to the HNO_3 form. The colour was attributed to a trace element in the sample, one that doesn't form a strongly holding anionic chloride complex. Nickel was a possibility.

Unlike some Antarctic carbonates processed in previous years it was never possible to overload the column with high Fe levels. On one occasion two columns were used to reprocess samples, it was found that the apparent overloading was due to suboptimal normality. Correct loading and use of the column always led to the Fe band being held in the top quarter (3-4cm) of the column.

Thorium Purification

After the final eluates of 8N HCl had passed into the uranium-thorium separation column, the beaker was removed to a hot plate. The major elements in the solution were Th, Al, Ti, and any remaining Group I and Group II elements that came through the precipitation stages. To separate these from the thorium an anion exchange column in nitric acid form was used. Some relevant distribution coefficients for a range of acid molarities are given in fig(2.3).

Fig (2.3) Log distribution coefficient vs molarity of HNO_3 for several elements. (Faris and Buchanan, 1964)



The thorium ion forms a very stable nitrate complex that holds well to the column: $Th^{4+} + 6NO_3^- \Leftrightarrow Th(NO_3)_6{}^{2-}$, with a maximum stability around 8N HNO_3.

As in the first column, a 20cm x 1.5cm chromatography column was used, half filled with DOWEX 1X8 100-200 mesh anion exchange resin. The resin was washed with two volumes of 8N HNO_3, in similar manner to that described for the first column. For preliminary samples the same resin as used for the first column was regenerated - the two washes of 8N HNO_3 simply displaced the chloride on the resin. Major problems with overall thorium recovery occurred, and the thorium purification columns were considered a possible source of the loss. This was never proven to be the case, but it became standard practice to use fresh resin for the thorium column. The other advantages of fresh resin were reduced contamination by any residual U or Fe left in the first column (very unlikely), removal of interference by any silica gel left in the resin of the first column, and most importantly, reduced breakdown of the resin. For some reason it seemed that pre-used columns were more disposed to producing discoloured eluates during the thorium elution; possibly due to the oxidising power of mixed traces of the HCl and HNO_3 solutions.

Before running the column the thorium fraction was converted from a chloride matrix (eluate from the first column) to an 8N HNO_3 matrix. When the thorium fractions were first heated, a few mls of conc HNO_3 (and a couple of mls $HClO_4$ in badly discoloured fractions) were added immediately, to aid in oxidising any resin byproducts present. On evaporation of the solution, a white precipitate formed at lower volumes. This was the biggest problem in the whole process - the appearance of titanium precipitates. The species formed was probably hydrated polymeric $(TiO)_n{}^{2n+}$. It would seem that nitrate as a counter-ion gives much lower solubility than the chloride form.

The TiO_2 came from the detrital component of the sample, probably from the basaltic sands and ilmenite present. This is the reason for the great care needed in acidifying and boiling the sample initially. Over vigorous conditions released excessive TiO_2 into solution. There was a clear correlation between titania precipitates at this stage, and little or no recovery of thorium. It was likely that the polymer chains were highly binding for the readily scavenged Th^{4+} ion. It was thus necessary to ensure no (or minimal) precipitation of $(TiO^{2+})_n$ occurred at this stage.

Initially samples were boiled down until a precipitate just started to form, whereupon HNO_3 to three times the volume of HCl present was added. This was boiled under reflux until all the HCl was removed. The solution clears as no more brown nitrogen dioxide was being formed via

$$6HCl + 2HNO_3 \Leftrightarrow 2NOCl + 2Cl_2 + 4H_2O\ (+O_2) \Leftrightarrow 2NO_2 + 4H_2O + 3Cl_2$$

On clearing, the watchglass and beaker walls were washed with HNO3 and boiled for a further 5 minutes. Volumes at this point were typically 20-30 mls, with the precipitate having formed at 10-15 mls. Some samples could be boiled to dryness without a precipitate appearing.

After all the HCl had been removed, an equal volume of distilled water was added, bringing the solution to 8N HNO_3 (conc HNO_3 = 16M). If there was any sign of a precipitate the solution was centrifuged (10mins, 3000rpm). The supernatant was poured off and loaded onto the column. Twenty mls of 8N HNO_3 was used to rinse the beaker, then added to the centrifuge bottle. After dissolving as much of the precipitate as possible, the solution was centrifuged again, and the supernatant added to the column. If any precipitate was still present the step above was repeated. After the last of the sample had been loaded, the column was washed with three column volumes of 8N HNO_3. The three washes were also used to rinse the beaker and centrifuge bottle. After the last washings had passed onto the column, a labelled 100ml teflon beaker was placed under the column. Three column volumes of 9N HCl were used to elute the thorium. Washing with 8N or 10N HCl produced no discernible change in quantity or quality of yield.

This method still frequently gave solid phases on the column, ranging from a distinct layer of white precipitate at the head of the column to a general cloudiness of the loading solution. This invariably led to low thorium yields.

A less retroactive means of dealing with the TiO_2 problem was sought. This entailed using maximal volumes of solution during the matrix conversion in the hope of preventing a precipitate forming in the first place. This was at the expense of solution loading time. The HCl solution was boiled down to about 30mls, at which stage about 50mls of conc HNO_3 was added. This was boiled under reflux until the solution went clear, adding more HNO_3 as necessary, as boiling proceeded. The watchglass and walls were then washed with HNO_3, and the solution boiled for another 5 minutes, to remove final traces of HCl. The watch glass was removed, and the solution was boiled back to a volume of 50 mls. An equal amount of distilled water (by filling a matching beaker to the same level) was added to bring the solution to 8N HNO_3. This gave a total volume of 100mls of sample solution, which could take up to an hour to load onto the column. However, this method produced no visible Ti based solids, and thorium recovery became higher and less variable.

After retrieving the thorium fraction, the same process was repeated on a smaller column, with commensurate volumes. The thorium fraction was boiled down, with 3mls conc HNO_3 added before boiling started, to help oxidise any organic resin products in the washings. When the thorium fraction was almost dry a few mls of conc HNO_3 were added. Again the sample was boiled down to a drop.

A small BIORAD 0.7cm x 10cm chromatography column was used, filled with 2 mls of DOWEX 1X8 100-200 mesh anion exchange resin. This was washed with a column volume of distilled water, followed by two volumes of 8N HNO_3. The resin was prepared in the same way as described for the uranium/thorium separation column. The evaporated thorium fraction was dissolved in 5mls of 8N HNO_3, and loaded onto the column. If any solid residue was still evident, the beaker was gently heated, taking care not to evaporate the H_2O and increase the HNO_3 concentration. After the sample had passed into the column the beaker (heating if necessary) and column were washed with four aliquots of 5mls 8N HNO_3. The effluent was discarded, and the thorium eluted off with three column volumes of 9N HCl, into a labelled 100ml teflon beaker. The sample was covered with a watchglass, since any dust, aerosols etc entering the sample at this point would be electrodeposited as well. The sample was boiled down to a drop of HCl, as described under electrodeposition.

A couple of problems arose with this process.

(1) Due to lack of air circulation, the clamps holding the columns became extremely corroded. Infrequently corrosion products off

the columns would fall into the receiving beakers, during all column stages. It was particularly a problem with the final column, as no further purification would normally take place. On the occasions that this problem arose the sample had to be boiled down and redissolved, often necessitating the use of HF and/or $HClO_4$; before repeating the final column. On one occasion this had to be repeated twice. Fortunately the high stability of the $Th(NO_3)_6^{2-}$ complex on the resin makes this separation quite efficient, and it is unlikely that much thorium is lost by repeating this column, provided all solids were redissolved.

(2) The insolubility of thorium made it susceptible to not being fully retrieved from the beaker by the loading and washing solutions. Often visible deposits were still evident after the four 5ml 8N HNO_3 washes had rinsed the beaker. The loading method was changed to improve thorium recovery.

Instead of dissolving the sample in 5mls 8N HNO_3 it was dissolved in a minimum of conc HNO_3. This was evaporated back to approximately 0.25ml, and 0.25ml distilled water was added. Three mls of conc HNO_3 were added to dissolve the sample, followed by three mls of distilled water. The solution was thus 8N in HNO_3, and was loaded onto the column. The four 5ml washes were replaced by one of 3mls conc HNO_3 plus 3mls distilled water; one of 2mls conc HNO_3 plus 2mls distilled water; followed by two of 5mls 8N HNO_3. This quickly reduced the frequency of residual sample being left in the beaker.

Uranium purification

When the uranium fraction was retrieved from the column, along with Fe, it was boiled down. Prior to this 3mls of conc HNO_3 was added. Although this works against the aim of taking the residue to a chloride matrix, it was found necessary in order to help destroy organic byproducts of the resin. Failure to do this often left a ring of black stain at the maximum volume level of the solution. These were presumed to be organic, and as such may have complexed the uranium. In addition, any organics remaining in the solution may also have complexed uranium, interfering in the following organic extraction step. This step was the first stage of purification of uranium - a separation from iron. Both species are complexed by the chloride ion, however only the ferric chloride complex is soluble in ether. Many methods for U-Th dating extract the iron prior to the column separation of uranium and thorium. Extraction subsequent to separation is preferable, as it allows Fe to act as excellent visual control on the efficiency of the first column.

The solution was evaporated to dryness, 3mls of conc HCl was added (to remove any residual HNO_3) and the solution was boiled to dryness again. It was then dissolved in 3mls 8N HCl. The solution was transferred to a 15ml glass centrifuge tube. A further ml of 8N HCl was used to wash the beaker, this too was added to the centrifuge tube. Five mls of di-isopropyl ether was added to the tube, after being used to wash the last of the sample solution out of the beaker. The sample was emulsified on a vortex mixer for 30s. The upper (ether) phase, containing Fe, was discarded. The extraction was repeated three more times. By this time the chloride concentration had dropped well below the optimum level (about 6-7N). To return to efficient extraction 5 drops of conc HCl were added, and two more extractions with 5mls di-isopropyl ether were performed. The resultant solution was transferred to a new 100ml labelled teflon beaker. The centrifuge tube was washed twice with 3mls 8N HCl, these too were added to the teflon beaker. The ether residues were stored and eventually washed with water to remove Fe, and distilled to recover pure ether.

The problems encountered in this section related to incomplete extraction of the iron - it is unlikely that much, if any, uranium is lost by co-extraction into the ether (Gascoyne, 1977). The samples analysed generally had extremely high natural Fe levels, in addition to the Fe added for coprecipitation. This had two effects. Firstly, if extraction was at all incomplete it meant that levels of Fe would still be unacceptably high. Secondly it could cause three phases to form in the centrifuge tube during the first extraction. The middle layer was a pure iron-chloride-ether compound ($Fe(^iPr_2O)_2Cl_4^-$) (Gascoyne, 1977), and was discarded along with the top layer.

Extraction efficiency was easily monitored visually. The Fe imparts almost all of the orange-yellow colour to the solution. The aqueous solution should be almost clear after the sixth extraction, if extraction is complete. The successive extractions remove Fe at a constant rate (allowing for the small changes in chloride activity), giving an exponential decrease in [Fe]. If extraction works well the aqueous phase will be virtually clear after 4 ether extractions - however, in the preliminary work and first samples the aqueous phases were frequently still very coloured after 6 extractions.

Inefficient extraction took two forms. Extraction would either take place very slowly, leaving a definite yellow colour in the aqueous phase after the final extraction; or else essentially nil extraction would occur, leaving a cloudy orange aqueous phase from start to finish. Attempts to rectify these were based on considering the chloride activity through the process, and on the possibility of trace element interference.

Inconsistency of the method between samples suggested trace element problems (including natural Fe levels). Some samples that extracted poorly were boiled down and extraction repeated. Some of these would clear on the second set, even after 2+2 (i.e two extractions, 5 drops conc HCl, two more extractions); while some would still fail after a second 2+2. This suggested variations between samples. The occasional presence of black solids (in spite of oxidising for resin products) suggested MnO_2 to be present; this was confirmed by the frequent presence of red solids ($MnCl_3$) when the sample was evaporated to dryness. Some samples were tested for Fe by reaction with potassium ferrocyanide, the presence of Fe^{3+} giving a deep blue colour. Some samples were strongly coloured after 4+2 extractions, yet gave negative results for this test. Atomic absorption analysis showed the colour to be due to very high levels of manganese (i.e the extraction was, in fact, efficient for Fe).

However, many samples tested after 4+2 showed Fe to still be present in the aqueous phase. In particular, a spike sample taken through the process was still yellow after 4+2. The only foreign element present was Fe from the coprecipitation stage (this sample also gave three layers in the first extraction).

Chloride concentrations were varied on some samples to improve iron extraction. One ml of conc HCl added after 2 extractions followed by 0.5ml conc HCl after the fourth extraction still gave poor results. Extraction from 9N HCl, with half a ml conc HCl after 2 extractions also failed to improve efficiency. These suggested that decreasing chloride activity was not the source of the problem. After extra acidification had failed on another sample 3mls of distilled water were added, since too higher an acidity would increase the solubility of the ether in the aqueous phase. This also failed to help.

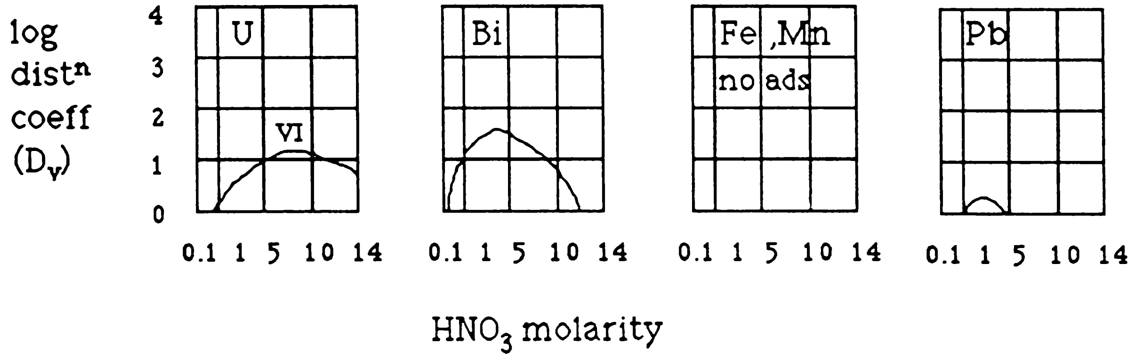
The problem was overcome by changing the relative volumes of the aqueous and organic phases. A sample was dissolved in 6mls 8N HCl and the beaker washed with 1ml 8N HCl, giving a total volume almost double that previously used. To allow for the limited volume of the centrifuge tube the volume of ether was reduced to 3-4 mls per extraction. This worked well on samples of this and a subsequent batch. These volumes were adopted as standard procedure.

It would seem that the volume of 8N HCl used was insufficient to dissolve all the species in some samples, allowing the Fe to retain a form that was not amenable to extraction into di-isopropyl ether. Occasional samples still retained a slight yellow colour after 4+2. This was usually due to the presence of Mn, or sometimes low levels of Fe. Both these circumstances were able to be dealt with by the final uranium purification column.

The sample and washings from the ether extraction stage were boiled down to dryness in a teflon beaker. The residues varied from yellow-brown to grey to a bright green (in the chloride form), suggesting various trace elements to be present. These were often difficult to dissolve, needing a mixture of HCl and HNO_3, and occasionally HF. They were boiled down and eventually the solution was taken up in HNO_3 for the final phase of uranium purification.

This stage was the most critical with respect to uranium yield. It entailed separation of uranium from any residual Fe, Mn, Al, and any other trace elements still present, on an anion exchange column in the nitrate form. The problem is that the maximum distribution coefficient only rises to 100, at 8N HNO_3. Relevant distributions are given in figure (2.4).

Fig (2.4) Log distribution coefficient vs molarity of HNO_3 for several elements. (Faris and Buchanan, 1964)



The method prescribed loading the sample onto the column (a small BIO-RAD chromatography column (0.7cm by 10cm) part filled with DOWEX 1X8 (100-200 mesh) anion exchange resin) in 2mls of 8N HNO_3, then washing three times with 2mls 8N HNO_3. Hydrochloric acid (1.5mls) was added to create a front for the later washings, and the top of the column was allowed to run dry. The uranium was then collected by washing with a column volume of distilled water, the same with a few drops of conc HCl, followed by a final volume of distilled water. The sample was then boiled down for electrodeposition.

Although there were no immediate problems evident with this particular phase of uranium processing, there still remained a general problem with uranium yield. Yields were generally good, and fairly consistent, but had a maximum yield of around 80%. After adjusting the electrodeposition and coprecipitation stages, there was still a problem, this was assumed to be due to the difficult uranium purification column.

Attempts were made to increase the performance of the column, based on the premise that the uranium was being washed off the column before collection. The number of washes of 8N HNO_3 was decreased from 6mls to 5mls, and then to 4mls, with little impact on recovery. A batch of samples was compared by only adding 1ml conc HCl as a chloride front; while adding the standard 1.5mls to the other two samples. The former samples gave higher yields, with no obvious extra residual Fe i.e the reduced front still gave sufficient HCl to wash the uranium off. A further test was with 0.75mls conc HCl on two samples and one ml on the remaining two. There was no difference in yield evident. One ml of HCl became the standard addition for the column. It was also possible that the lower $[Cl^-]$ reduced the subsequent molarity, allowing better retrieval of the uranium. In case uranium was being held by the column, the final distilled water wash was increased to two column volumes.

The volume of resin was also increased 50% from the recommended 2mls of resin to 3mls; in order to help hold any mobilised uranium. Although this in theory could have helped retain Fe, the combined loading solution (2mls), plus washing (6mls) plus HCl (1ml) still gave about three column volumes for Fe removal. There was no visible increase in residual Fe in the uranium fraction.

As in the small thorium column it was preferred to dissolve the initial residue in a concentrated acid, to aid in dissolution of any nuclides particularly adherent to the teflon beaker. Thus the sample was boiled down to a drop, and a few mls of conc HNO_3 were added. This was boiled back to a few drops, beyond which the sample often became insoluble. A matching few drops of distilled water and one ml of conc HNO_3 were added. After dissolving the sample a further 1ml of distilled water was added, bringing the total molarity to 8N HNO_3. Although the final solution in this case may vary slightly from the critical 8 molar normality needed for good separation (cf dissolving in a straight 2mls of 8N HNO_3 from a bulk solution), it was found necessary to ensure retrieval of all the residue from the beaker.

As in the thorium column there were problems with debris from the clamps falling into the beaker, requiring the column to be repeated. In a couple of preliminary samples there seemed to still be high levels of Fe in the sample after the final column, so ether extraction was repeated, with a successful reduction in Fe levels. In all cases 3mls of conc HNO_3 was added to the collected uranium fraction before boiling down for electrodeposition, in order to help oxidise any resin byproducts.

Electrodeposition.

The development of an electroplating method for depositing the samples on discs suitable for alpha-spectroscopy was the major innovation over methods formerly used at Waikato. Previously all samples had been mounted by evaporation of a benzene solution of the thenoyl-trifluoroacetone (TTA) complex in benzene.

Initial attempts to find a suitable electrodeposition method were based on a technique developed by the Institute of Nuclear Sciences (DSIR) as part of their own U-series dating program. Because of the expense of the cathode discs used by the method ($5-00 each), the method was modified. Aluminium discs were used and cell design (fig (2.5)) was modified to a less expensive fixed cathode in the base of the cell, with a separate anode and motor driven teflon stirrer. 10ml samples of spike were taken up in dilute sulphuric acid, and adjusted in pH with dilute NaOH (pH meter). Various pHs were tried, from unadjusted (pH < 1) to pH 3.5. The highest recoveries were , as expected, around pH 3.4. However, these recoveries were still only around 3-4%. These were plated for 2hrs at 3.6V, using a Pt anode (other anodes were previously tried - these decomposed under electrolysis, with spike recoveries less than 2%). Early samples used a magnetic stirrer sitting directly on the Al plate - this caused irregular deposition over the disc, and scour marks. Increasing the deposition time up to 18 hrs had little effect on % recovery. Maximum recovery achieved during this set of experiments was approx. 5%, when an HNO_3/NaOH electrolyte to pH 3.4, with 2hrs deposition , was used. The counting system used included a delay amplifier which was later found to be cutting out a high proportion of alpha counts. Allowing for this, recoveries would still only have approached 10%. Resolution was invariably extremely low.

Most deposits produced in this set of experiments were white and powdery. They adhered poorly to the Al disc and were readily washed off, or sucked away under vacuum in the alpha spectrometer counting chamber. This was probably the major source of failure in this method. Possibly the alumina layer on the discs precluded the normal metal deposition mechanism, and hence reduced adherence. Furthermore, Al was not readily flamed to stabilize and remove polonium - it frequently melted rapidly before glowing red.

It would seem that Al is not a suitable cathode material under these conditions.

A completely new method of U-Th processing was attempted, as described earlier, incorporating a new electrodeposition technique. This was based on an $HCl-NH_4Cl$ electrolyte and Ag discs.

The described method was to dissolve the sample in the minimum of HNO_3 and evaporate to a droplet. 1ml of 0.01N HNO_3 was added, the beaker rinsed and sample transferred to the electroplating cell. 2mls of electrolyte (2N NH_4Cl taken to pH2 with HCl) was used to rinse the beaker and was added to the cell, followed by 1 ml of the same. The sample was plated at 6V, with an initial current of 0.8A. After 45mins the walls of the cell were washed down with distilled water, to recover any uranium or thorium splashed out, and plating was continued for 15mins. At the end a little NH_4OH and distilled water were added (NH_4OH fixes the hydrous oxide film formed to the disc (Mitchell,1960)). The power was turned off, the cell dissembled and the disc washed with distilled water. Finally it was heated to glowing red in a bunsen flame. The prescribed method also alleged the use of silver as an anode. A new cell design (fig (2.6)) was also used, with a spiral anode used to support the magnetic flea stirrer (fleas needed to be trimmed to size).

The first attempts at the new method used the Al discs and the cell constructed for the previous method, with a Pt anode. 2hrs plating of a spike sample evaporated to dryness and treated as above gave a brown deposit on the disc, with a brown electrolyte solution. The disc deposit turned white on heating, although as usual the Al disc was not heated to glowing. The results were of low resolution with a recovery of 37%. On construction of the new cell, testing continued. A qualitative test was to deposit a solution of UO_2Cl_2 for 5mins. This gave a high count rate , but still low resolution. The new cell contained the Ag anode, Al discs were still being used.

The first carbonate samples (run concurrently) invariably gave low results, particularly for thorium. In the deposition stage thick grey sludges up to 3mm thick were often formed on the discs. Some were counted both before and after washing the sludge off with the distilled water - little difference in the low count rate was evident. Continued testing of the electrodeposition method (still using Al discs) continued to give low results, with the added observation of a discolouring/crusting on the Ag anode. Testing of the former INS method using the new cells gave brown solutions and black deposits, but still of low recovery.

At this stage the pH of the electrolyte stock was found to have drifted to pH 3. Deposition with a new stock gave no sludge, but still a low recovery. In retrospect the non-appearance of sludge was coincidental.

Longer plating times were used as an obvious means of increasing the yield. An ammeter was also obtained to monitor current change in the cell. 10mls of spike was evaporated to a drop and taken up as described. It was also standard at this point to add several extra mls of plating solution to cover the anode and so render the stirrer effective. The spike sample was plated for 2hrs, washing with a little distilled water at 45mins and 90mins. The current was initially 40mA, which soon dropped and stabilized at 8mA. At the conclusion the current was 6.5mA. Although the currents observed were much lower than expected, the recovery was 65%. This seemed a reasonable basis for further processing of carbonates, but again thick crusts formed on the cathode discs, with nil Th recovery and low U recovery.

Further testing of spike samples on newly acquired Ag foil discs gave a recovery of 55% for one hour of deposition. Continued processing of carbonate samples gave variable yields, occasionally acceptable, but the majority very low. Again sludges and crusts formed on the discs during electrodeposition. Testing with spike samples (5 replicates) gave very thick deposits of low resolution

Figure 2.5

Electrodeposition cell used with INS method

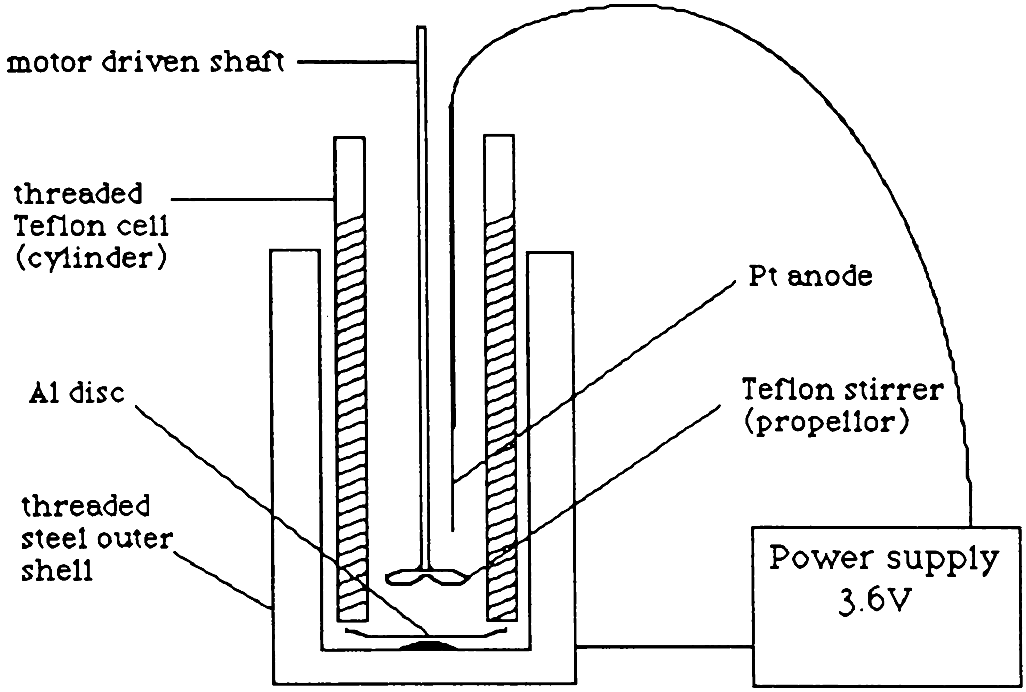
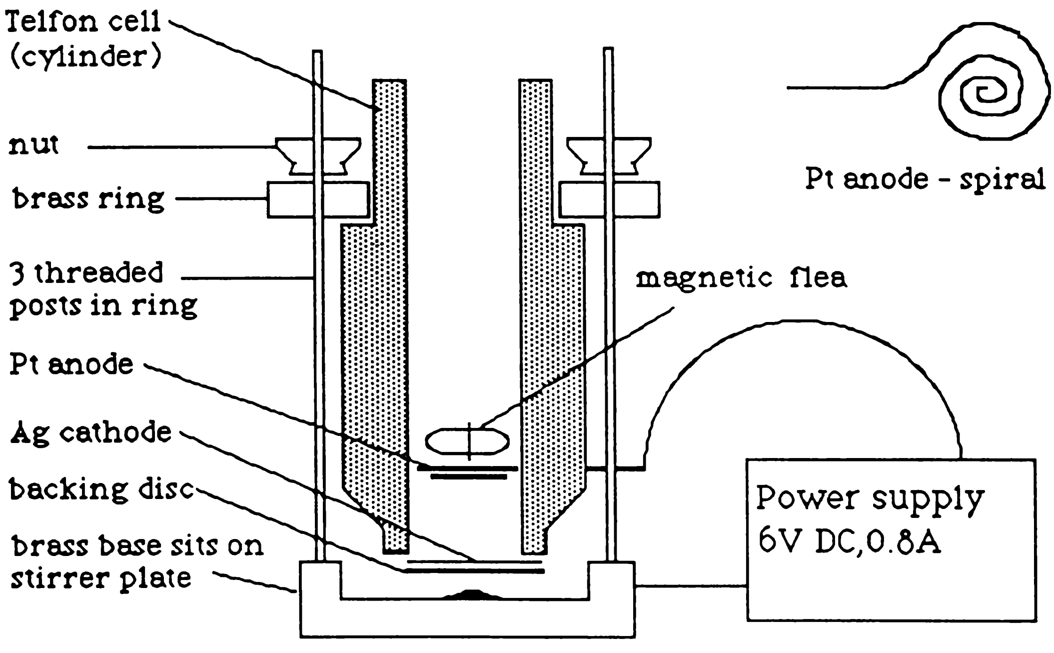


Figure 2.6

Electrodeposition cell used with Lamont-Doherty method



and variable yield. Further carbonate samples gave poor results. Starting currents dropped to 3-10 mA.

A more thorough testing of the electrodeposition process was carried out. Six spike samples were evaporated down and plated as described. Recoveries are presented in table (2.2). Some of the low recoveries correlated with leaking cells. The higher recoveries gave black deposits, others gave grey sludges which were easily washed off. Flaming of these discs removed most of the deposit, with very little left.

Table 2.2. Recovery from electrodepositions.

Sample	Cell	Time	Recovery	
1	2	1hr	5.7%	Cell leaked?
2	1	1hr	16.4%	Cell leaked?
3	3	1hr	10.7%	
4	2	45min	5.9%	Cell leaked?
5	1	1hr	10.6%	
6	3	1.10hr	8.1%	Stirrer erratic.

The grey sludges on the cathodes and anodes, low currents and low recoveries suggested anode passivation, due to the formation of a silver oxide layer. Reversing the potential across one cell for a few minutes caused pitting on the cathode (normally the anode i.e. the Ag spiral), later depositions using this cell were more encouraging. Various treatments to remove the oxide film were attempted, the most successful of which was to soak the cell (containing the anode) in NH_4OH for 4 hours. This removed all the sludge, but still left the Ag wire intact (with a thin white film left on the anode).

Quadruplicate depositions with fresh Ag wire anodes (1.5hrs) gave recoveries from 29% to 40%. Very thick cathode deposits were washed off these discs. After washing the cells in NH_4OH deposition of spike samples was repeated, giving recoveries (3hrs deposition) of 40% to 75%. Again carbonate processing was continued, but results continued to be low. Increasingly low starting currents during plating was cause for further testing of the electrodeposition method. Four spike samples gave recoveries of 13%, 12%, 14%, and 49%; suggesting increasing anode passivation with use. Use of silver anodes was abandoned. Cell performance over this period is presented in table (2.3).

Table 2.3 Performance of Silver Anodes.

Cell Number	Recovery (fresh anode)	Initial Current	Recovery (anodes washed in NH_4OH for time = t)	Recovery (after more samples)
1	29%	0.38A	44% (t=2hrs)	49%
2	36%	0.20A	74% (t=17hrs)	13%
3	40%	0.35A	40% (t=2hrs)	12%
4	38%	0.36A	75% (t=17hrs)	14%

In retrospect the pattern of success of Ag anodes can be interpreted in terms of anode passivation. Fresh anode coils regularly gave good results, but performance decreased with use, as layers of silver oxide built up on the coils. This decreased the current outflow, reducing yield. Build-up of sludge on the cathode was due to decomposition of the anode by electrolysis and by removal of the oxide due to mechanical agitation by the stirrer. The occasional encouraging result for used anodes was probably due to fortuitous exposure of sections of fresh Ag wire (by stirrer agitation); the fresh Ag allowing performance to approach that of a new Ag anode.

It seems extremely unlikely that silver anodes were in fact used in the original Lamont-Doherty process.

One cell was fitted with a platinum spiral electrode. Four consecutive depositions of spike samples were made, each of 1.5hrs. Realistic starting currents of 0.6A to 0.75A were obtained. Recoveries of 45% (first run), 64%, 84%, and 75% were achieved. The low first result was probably due to the unattended stirrer being jammed still in the anode for much of the deposition.

All cells were converted to platinum, three using 1mm wire, and one using 0.5mm wire. No overall difference in results was evident for this latter electrode, however it frequently distorted and bent under the weight of the stirrer. Further testing of the newly converted cells gave recoveries of 49%, 50%, 7%, 96%, 81%, and one negligible recovery (all one hour dep.) Brief counting of discs before and after flaming showed no major loss of uranium nor thorium due to flaming.

Further testing suggested that fresh plating solutions may be necessary for good deposition (plating solutions set the pH, which is critical). These results are summarised in Table (2.4).

Table 2.4 Effect of plating solutions.

Plating Solution	Spike Recovery
6 weeks old	6%
	38%
Fresh solution	97%
	74%

At the time of testing the spike was not calibrated, and calculated recoveries were deemed higher at the time (and suggesting the need for such calibration).

Several other problems were encountered during this period. Some of the lost activity could be attributed to adsorption of the nuclides on the teflon cell walls. This was due to the volumes of solution being used barely covering the anode, such that the stirrer readily splashed solution onto the walls. This was overcome by doubling the volumes of electrolyte used, giving much more even stirring. This required much longer plating times to overcome the lowered diffusion rate due to dilution. The even stirring also led to a large increase in sample resolution, thus overcoming another problem encountered frequently.

Dissolution of the base of the well holding the discs occurred due to leakage of the cells. This deepened the well, making sealing even more difficult. To overcome this, the formerly used Al discs were inverted in the well, and the Ag disc mounted on top. These discs occasionally formed crusts to the point of insulation, requiring the cell to be dissembled and backing disc replaced.

To ensure a reasonable recovery it became standard to deposit all solutions until the current dropped to less than 0.3A (although it was later found that changes in the measured current of 10-20%

could be induced by percussing the ammeter). This generally entailed much longer plating times than prescribed. Flaming the discs was also a difficulty, as 0.013mm Ag foil was used. Several discs were substantially melted, inadvertently, before they had glowed red.

After processing a large number of carbonate samples there seemed to be a systematic problem with thorium recovery. This was traced to the electrodeposition stage, since straight deposition of Th standards frequently gave poor results. Adsorption on the cell walls was a likely problem, so quadruplicate depositions of a thorium standard were carried out, with a watchglass on top of the cell to aid reflux back down the cell walls (although the Th standard had very high levels of ^{230}Th, the tail of which swamped the ^{232}Th peak, recovery was calculated from the ^{228}Th peak, assuming unity between it and the ^{232}Th peak.). Under such refluxing conditions, recoveries were very low.

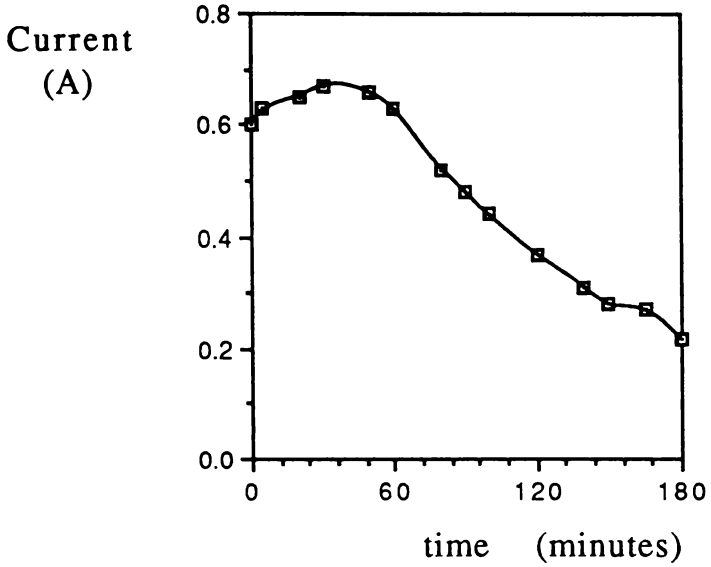
Monitoring the pH of the solution required the cell to be turned off at intervals, to preclude the acidic $Cl_2(g)$ bubbles (from the anode) affecting the reading. Results under reflux showed the pH to drop from 2.5 - 3.0 to less than 0.7 over the course of the deposition (1.35hr), prior to the addition of distilled water. This was probably due to $Cl_2(g)$ being retained, redissolved, and returned to the solution as HCl, thus increasing acidity. (solubility in 100cc H_20 (at STP) of Cl_2 is 310cm^3 while for NH_3 it is only 90 cm^3)

Further testing included the addition of F^- as a complexing reagent, and of hydroxylamine hydrochloride as a plating agent (Talvitie, 1972). Little change in the low recovery was evident.

As part of the process testing the change in current was measured over the course of a deposition. The results (fig 2.7) gave no clues as to the source of the thorium recovery problem.

The electrolyte was tested, as it was presumably retaining the thorium. A qualitative measurement was devised, whereby the electrolyte was made basic with NH_4OH and $FeCl_3$ (aq) was added, to quantitatively precipitate out any thorium or uranium left. This was filtered and the central section of the filter paper counted directly in the alpha spectrometer. This method was validated by straight precipitation of standards.

Fig 2.7 Current vs time for an electrodeposition cell.

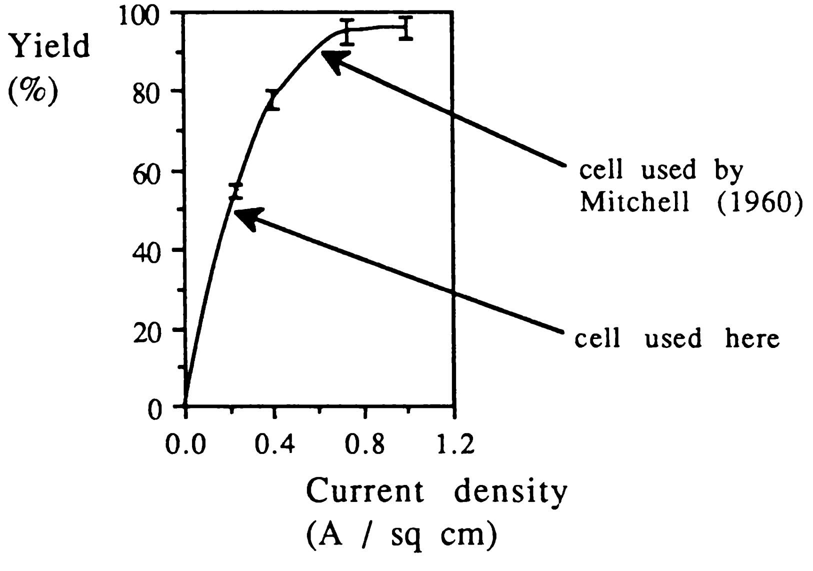


A failed deposition showed no activity in the electrolyte, a re-examination of the beaker used to boil down the standard showed a small but obvious staining in the base. It would seem that much of the standard nuclides were being retained in the beaker, possibly due to excessive evaporation to dryness. The pH of the electrolyte solution (pH 2) was probably insufficient to remove well-adhered thorium from the teflon beakers.

The electrodeposition of actinides was reviewed, looking in particular at some of the pioneering methods in the field. The methods of Mitchell (1960), Talvitie (1972), and Puphal and Olsen (1972) were considered. Mitchell's method was selected as being rapid and simple. It was based on the ammonium chloride/ hydrochloric acid electrolyte previously used, The previous cell design was retained. Mitchell's method used platinum discs, however the Ag discs proved quite satisfactory, and far cheaper. The principal advantage of the method was that the electrolyte was initially unadjusted in pH, allowing samples to be taken up in concentrated acid. The sample was taken up in 1ml of hydrochloric acid, and added to the plating cell. Two 1ml distilled water washes were used to rinse the cell. Methyl red was added as a pH indicator. Ammonium hydroxide was added until the solution just turned yellow, then 2N HCl was added until the solution just turned red again (all dropwise). An extra drop of 2N HCl was added, giving a final pH of 3 - 4 (methyl red: pink (pH4.4) to yellow (pH6.2)).

Mitchell's method used a 2A current, with a disc area of 3cm^2. Voltage was not stated. Recoveries of 98-100% after 15mins were claimed, although this time was not reproducible for Puphal and Olsen (1972). The ratio of current to disc area is critical for rapid deposition (fig (2.8)). Mitchell's method used a ratio of 0.67 Acm^{-2}, while the cell available rated at 0.2 Acm^{-2} (22mm wide discs). This was probably the main reason for the longer plating times found necessary.

Fig 2.8 Current density vs deposition (Mitchell,1960)



Mitchell's method was attempted, using 2mls conc HCl and two 2ml washes of distilled water to bring the volume up. The former supply was used (6V, 0.8A), and Ag discs were used. Current was monitored down to 0.15A, at 5hrs. Distilled water was added 10 mins before the end, to wash down the cell walls. 1ml of NH_3(aq) was added one minute prior to the end, and the electrolyte poured out before turning the cell off. The disc was washed with NH_3(aq), distilled water, and ether, before gently flaming.

Recovery was 96.2% for uranium plus thorium. It is possible that recovery was quantitative for this experiment, as the detector geometry was only known approximately.

Two further tests looked at the effect of 2 drops hydroxylamine hydrochloride, and at shorter deposition times. Results are presented in Table (2.5). Since long deposition times were a simple way to make up for any losses earlier in the system a minimum plating time of 3 hours was adopted.

Table 2.5 Spike Electrodeposition Recovery.

Conditions	Recovery
5 hours electrodeposition	96%
3 hours electrodeposition	91%
5 hours with hydroxylamine-HCl	76%

Final development of the electroplating system was carried out in the course of routine sample processing. Some samples were left to plate overnight, for up to 12 hours. When these were counted they showed a high proportion of low results (particularly for thorium). This practise was discontinued. Failure to remove all HNO_3 from the residue (by repeated evaporation with HCl) gave a yellow solution when HCl was added. The plates for such solutions were invariably thicker, due to dissolution and redeposition of the Ag disc by the powerful HCl/HNO_3 solution.

High resolution is important for accurate age determination. Thorium discs commonly had high resolution, with the twin peaks of both ^{230}Th and ^{228}Th often obvious. For uranium, however, such minor peaks usually appeared as shoulders, as did the ^{235}U peak in the ^{234}U tail. This is converse to what might be expected. The low activity of ^{232}Th still corresponds to a very high concentration of thorium (due to it's very long half-life). This huge carrier effect could be expected to degrade the resolution as much as for the uranium nuclides. It seems likely that the lower uranium resolution was largely due to Fe sneaking through the uranium purification process. This was partly rectified by changes in the small uranium column process.

A major change in resolution was also achieved by further altering the electrodeposition method. It seemed that the Ag from the disc was being dissolved as the HCl carrying the residue was added to the cell. Evidence for this was the frequent very dark to black (Ag_2O?) colour of the discs. For the latter samples it became standard to add 4mls of distilled water to the conc HCl before it was added to the cell. This achieved the sought increase in resolution. Deposits were mainly translucent, whereas previously they had been mainly opaque. All peak tails were reduced to satisfactory levels, in particular ^{235}U peaks became much sharper.

Finally, the last few discs were made of thicker foil (0.13mm). Although more expensive, it was much easier to work with, less likely to give cell leakage, and scribing of the reverse side did not ridge the plating side (which may give slightly more even plating and better resolution).

The final method for electrodeposition was as follows:

1. Evaporate the sample to a droplet and continue to evaporate down in small volumes of HCl until no more brown fumes/HNO_3 discolouration occurs. Some dried out samples may need HCl+HNO_3, or HF, to be redissolved; in which case extra care is needed to remove the HF or HNO_3.
2. Scribe the back of an Ag foil disc with a unique sample code. Wash and clean the disc with distilled water.
3. Place two Al backing discs in the brass well and assemble the cell with the disc in place. Fill the cell with distilled water and leave for 5 mins to check for leakage. Empty cell. Leakage through the anode port may occur, if so reseal with molten plastic. Retighten nuts if necessary.
4. Dissolve sample in 2mls conc HCl, and add 4mls distilled water. Rinse beaker and add to plating cell. Wash beaker with 1ml conc HCl, add to cell. Repeat with 2 mls distilled water.
5. Add several drops of methyl red solution. Carefully add a magnetic flea to the cell, and stir the solution. Carefully add NH_4OH until the solution just turns yellow. Add 1N HCl until the solution just turns red, add one more drop 1N HCl. If endpoint is badly overshot add more ammonia and repeat.
6. Plate at 6V, 0.8A until the current drops to 0.3A or less (about 3hrs). Wash cell walls with several mls of distilled water and continue plating for 20 minutes.
7. Add 2mls NH_4OH and a few mls distilled water. Continue 30s, then pour electrolyte out of cell. Turn cell off.
8. Wash cell with NH_4OH, then with ample distilled water.

9. Dissemble cell and wash disc with distilled water, and finally acetone (discs only washed with distilled water often give ridged deposits on flaming).
10. Very carefully flame the disc until it just glows red, then store in a small labelled ziplock plastic bag until ready for counting.

Spike Disequilibria

As uranium and thorium were not necessarily extracted quantitatively by the process, isotope dilution techniques were used to determine recovery efficiency. This was carried out by the addition of a spike of ^{232}U and it's daughter ^{228}Th. If the ratio of activity of $^{228}Th/^{232}U$ was known, it was possible to calculate the ratio of $^{230}Th/^{234}U$ in the sample solution. It is important to accurately know the relative activities of the spike members (the spike activity ratio) for age determination. This accuracy is particularly critical for ages near the limit of the method (200-400 kA). It is also useful (although not essential for the age calculation) to know the absolute spike nuclide activities, in order to calculate the yields and hence the uranium and thorium concentrations in the original sample.

The spike used was a trace solution of ^{232}U (half-life = 72yrs), nominally in equilibrium with it's immediate daughter ^{228}Th (half-life = 1.9yrs). The spike activity ratio at equilibrium is not, as could be assumed,actually unity. Due to the use of two of short lived isotopes (i.e. $t_{1/2}$ (^{232}U) - $t_{1/2}$ (^{228}Th) > 0) the activity ratio ($^{228}Th/^{232}U$) approaches 1.0275. But in practice it is common for the spike to be out of equilibrium. This is usually due to complexing of the spike members, which leads to adsorption on the container walls, or settling/non-homogeneity.

The spike solution was purchased from the Radiochemical Centre, Amersham, U.K., stored in 1M HCl. This stock solution was diluted 1:1000 to produce a mother liquor in HNO_3. The mother liquor was diluted 1:500 to produce the working spike solution. Aliquots of 10mls of spike (by volume) were added to each sample analysed.

Disequilibria in both the spike and mother liquor were observed by Judd (1986) ($^{228}Th/^{232}U$ = 0.438, s=0.014) and by Clayton-Greene (1986). A number of experiments were carried out to determine the extent of disequilibria in the spike, as follows -

(1) Direct counting. The spike solution contains a number of nuclides, given in table (2.6).

Table 2.6 Spike nuclides

Nuclide	Alpha energy (MeV)	Emission Intensity
^{232}U	5.32	68.6%
	5.26	31.2%
	5.14	0.3%
^{228}Th	5.42	71.0%
	5.34	28.0%
	5.21	0.4%
^{224}Ra	5.68	94.5%
	5.45	5.5%
^{220}Rn	6.29	100%
^{216}Po	6.78	100%
^{212}Pb	β-emitter	
^{212}Bi	36%	
	α-emitter	
	6.05	25%
	6.09	9%
	5.62	0.6%
	5.55	0.4%
^{212}Po	8.79	64%

(CRC Handbook of Chemistry and Physics, 1969)

Typical resolution of the surface barrier detector is about 25keV, which means that for infinitely thin samples it is possible to resolve the 5.42MeV alpha (^{228}Th) from the 5.32 MeV alpha of ^{232}U, but not possible to resolve the 5.34 MeV alpha of ^{228}Th from the 5.32 MeV alpha of ^{232}U; nor the 5.34 MeV (^{228}Th) from the 5.45 MeV alpha emission of ^{224}Ra.

Thus by directly counting a separated spike sample it was possible to estimate the activity of ^{224}Ra from the 5.68 MeV alpha, subtract 5.8% of this from the combined 5.42 MeV peak, which was multiplied by 1.41 to obtain the activity of ^{228}Th. This can then be subtracted from the total ^{232}U plus ^{228}Th activity (5.42 MeV to 5.26 MeV) to give the ^{232}U activity.

A sample of spike was evaporated down and plated out. A high volume of plating solution and a high stirrer speed were used to give higher resolution, and a long plating time used to approach quantitative deposition of both ^{232}U and ^{228}Th. The results were inconclusive, as insufficient resolution was gained to adequately resolve the two peaks. It is also doubtful that Th was recovered quantitatively, even at longer plating times. Ag anodes were still being used at this stage - causing lower recoveries and massive co-deposition of Ag , hence the low resolution.

(2) Direct plating of spike plus standard. A spike sample with a small amount of U-Th ore DH-1a (described later) was repeatedly evaporated with HF to remove all SiO_2, the small deposit left was plated out. Again a low recovery, low resolution plate was obtained - due to the use of Ag anodes and codeposition of Ag and non U-Th elements from the ore.

(3) Uranium and thorium standards. Standard solutions were made up from AR uranyl acetate and AR thorium nitrate, with standard activities approximately equal to that expected for the spike members. Quadruplicate samples of spike plus both standards (10mls each) were evaporated down and taken up in a few mls of 8N HCl. This was added to a small anion exchange column (2mls resin). Separation was achieved by a commensurate replication of the standard uranium - thorium separation column procedure. The results showed a massive peak at 4.6 MeV in the thorium spectra. This suggested contamination in the standards. ^{226}Ra was possibly present in the uranium standard, while poor separation could have led to a ^{234}U peak- however this could be excluded as no ^{238}U peak was obvious ($^{234}U/^{238}U$ activity = 0.6 in the uranium, which is a byproduct of the nuclear industry).

The suspected source was confirmed by plating in duplicate the uranium and thorium standards. These showed the expected uranium spectrum, but a thorium spectrum with a huge amount of ^{230}Th present. The ^{230}Th should not have been naturally present in the $Th(NO_3)_4$, and suggests that this also was a byproduct of the nuclear industry, perhaps having been used as a carrier in uranium processing. The amount of standard required to give a reasonable ^{232}Th count gave a ^{230}Th count several orders of magnitude higher

- the tail of which was too large to give an accurate ^{232}Th count. The experiment was repeated in quadruplicate with conditions favouring high resolution, the results remained inconclusive. The very poor stoichiometry of thorium nitrate (with respect to water of hydration) would also have precluded accuracy in this experiment.

(4) Spike vs standard ore. DH-1a is a uranium and thorium reference ore developed by the Canadian Certified Reference Materials Project (Steger et al, 1981). It is a (powdered) pebble conglomerate containing feldspathic quartzite and pyrite. In addition many minor minerals are present, including the radioactivity sources uraninite and brannerite (and also some monazite and uranothorite). Uranium and thorium concentrations are certified as 0.2629% and 0.091% respectively (although the ^{230}Th peak was used for the thorium calibration, rather than the ^{232}Th peak), giving a ^{238}U activity of 32.71 Bq g-1. However the independent ^{226}Ra certification gave an activity of 31.5 ±1.5 Bq g-1. Assuming the ^{238}U series is in equilibrium, at least as far as radon, the latter value was taken as the ^{238}U, ^{234}U, and ^{230}Th activity.

Ten mls of spike was added to each of four independently weighed samples of DH-1a. These were boiled down in HF/$HClO_4$ repeatedly, then redissolved in 8N HNO_3. Samples were filtered to remove any residue and processed by the standard procedure.

Results.

One sample (#4) gave marginally disparate counts for ^{234}U and ^{238}U. The uranium result for this sample was derived from the total ^{238}U + ^{234}U + ^{235}U count. Subsequently the other samples were treated in this way for parity. (^{234}U = (^{238}U + ^{234}U + ^{235}U)/2.046) The total peak count was also used for ^{232}U. The ^{234}U count was preferred over ^{238}U as it was more likely to be in equilibrium with ^{230}Th. Results are given in tables (2.7) and (2.8).

Table 2.7 Spike analysis data

Sample	Spike	weight of DH-1a	DH-1a activity
1	last 10mls of spike 1/2/90	0.0501 ±0.0002	1.578 ±0.006
2	10mls of fresh spike 1/5/90	0.0498 ±0.0002	1.569 ±0.006
3	10mls of fresh spike 1/5/90	0.0504 ±0.0002	1.588 ±0.006
4	10mls of fresh spike 1/5/90	0.0499 ±0.0002	1.572 ±0.006

Table 2.8 Spike analysis results.

Sample:	1	2	3	4
[U] Bq/10mls	1.86 ±0.02	1.76 ±0.01	1.84 ±0.02	1.81 ±0.02
[Th] Bq/10mls	1.81 ±0.02	1.74 ±0.02	1.75 ±0.02	1.76 ±0.02
^{228}Th/^{232}U	0.97 ±0.02	0.99 ±0.01	0.95 ±0.02	0.97 ±0.02

Several conclusions could be drawn from these results.

(1) the first sample shows possible enrichment of nuclides. This could be due to dilution differences between spikes 1/2/90 and 1/5/90. This spike was stored in conc HCl, and the sample taken was quite yellow, suggesting leaching of container walls. This would be a precursor to complexing and settling of the nuclides, hence their enrichment. This is far from unequivocal as the results are from one sample only.

(2) there is some disequilibria in the spike. The activities adopted were averages of the last three samples.

i.e. [U] = 1.80 Bq/10mls,
[Th] = 1.75 Bq/10mls,
spike activity ratio (^{228}Th/^{232}U) = 0.97 ± 0.02

(3) the activity is at variance with that expected from dilution calculations. The diluted spike activity would have been 1.48 Bq/10mls at the time of purchase (197?); in 1990 the activity should have been 1.22 Bq/10mls. This gives a 50% variance against the observed activity. Presumably there was less than the recorded dilution made during creation of the mother liquor.

Spike 1/5/90 was used for all the dates reported. This was used over a period of 5 months, and no subsequent checks on disequilibria were carried out.

Cross-contamination.

Frequently staining was observed in the teflon beakers, and was often still present after soaking in a nitric acid bath. Teflon beakers are noted for their non-adsorbent qualities. This may be valid for chemical adsorption, but they would still seem to suffer from physical adsorption at elevated temperatures. Cross-contamination by uranium was noted in teflon beakers in one uranium-thorium laboratory (McCabe et al, 1979). On deposition of one spike sample, the spectra showed a small peak at 4.6 MeV. This was thought to be due to ^{230}Th or ^{234}U, as a cross-contaminant in the teflon beaker used to boil the sample down (it was also possible that the peak was due to a small ^{233}U (alpha emission at 4.8 MeV) impurity in the spike, as has been noted in another U-Th spike (Ivanovich and Warchal, 1981)). Obviously cross-contamination is a potentially major problem, as the contaminants will almost certainly have different uranium and thorium isotope ratios to the current sample.

Assuming cross-contamination, the cleansing method for the teflon beakers was changed. Initially they had been washed in hot water and placed in a conc HNO_3 bath overnight. This was changed to a conc HF bath. A noticeable increase in the cleanliness of the beakers was evident, and no further cross-contamination was found. The bath was later changed to one of 1200mls HF, 500mls HNO_3, 300mls water and 200mls of detergent; for a minimum of 8hrs. This maintained the high cleansing ability of the previous bath, and caused a massive increase in the hydrophobicity of the beakers. Glassware continued to be scoured with Ajax and stored for at least 12hrs in a conc HNO_3 bath.

Final Method for Uranium-Thorium Processing.

Initial Treatment.

1. Take a 30gm specimen (if dating in duplicate), clean the surface, crush and grind to a powder[1].
2. Accurately weigh out about 10gm and add to a 600ml glass beaker.
3. Add about 100ml distilled water and 10ml of $^{232}U/^{228}Th$ spike (pipette).[2]
4. Add 8N HNO_3 until no more effervescence, taking care not to add too much excess acid.[3]
5. Boil gently under a watchglass for one hour to remove CO_2. Do not boil too vigorously, or the detritus will be affected.
6. Remove from heat and centrifuge.
7. Decant aqueous phase into a 400ml glass beaker.
8. Wash residue with distilled water and add a few drops of 8N HNO_3.[4]
9. Centrifuge and add supernatant to the 400ml beaker.
10. Filter residue, dry and weigh.
11. Add 10mls conc HCl and 2 drops $FeCl_3$ to the 400ml beaker.[5]
12. Cover with a watchglass and boil for 5 mins

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[1] Cleaning removes unwanted detritus. Grinding ensures sample homogeneity and decreases dissolution time.

[2] The amount of spike added should generally give count rates similar to that of the sample. 100mls of distilled water helps moderate subsequent acidity.

[3] The 8N HNO_3 releases all the CO_3^{2-} from the sample, and puts the uranium and thorium into solution. However, excess acid will attack the detritus, releasing unwanted uranium, thorium, titania and silica to the solution phase.

[4] These steps separate off the detrital component and also release any carbonate fraction not dissolved in the initial stages.

[5] The HCl, when boiled, destroys any organic uranium complexing reagents; the boiling also ensures all $CO_2(g)$ is driven off. $FeCl_3$ is added as a coprecipitant for uranium and thorium.

13. Remove from heat, add stirrer and stir. While hot add conc NH_4OH dropwise until the pH reaches 7 - 7.5 (use a pH meter).[6]
14. Centrifuge. Return supernatant to the 400ml beaker.
15. Wash the precipitate with distilled water and recentrifuge.[7]
16. Add supernatant to the 400ml beaker.
17. Add 2ml HNO_3 to the beaker, followed by 2 drops $FeCl_3$. Add more HNO_3 if necessary, until all precipitate is dissolved.[8]
18. Repeat precipitation. Centrifuge and discard the supernatant.
19. Wash ppt with distilled water, centrifuge and discard supernatant.
20. Dissolve combined precipitates in a minimum of 8N HCl, and dilute to 100ml with distilled water.
21. Repeat precipitation. Centrifuge and discard the supernatant.
22. Wash ppt with distilled water, centrifuge and discard supernatant.[9]
23. Dissolve ppt in the minimum of 8N HNO_3 and transfer to a 100ml teflon beaker, labelled S1. Rinse centrifuge bottle a few times with a few mls of 8N HNO_3 and add to beaker.
24. Carefully add HF until the solution goes clear, add a couple more drops.
25. Evaporate the solution to dryness and leave at a low heat for a couple of hours.[10]

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[6] A whitish precipitate is initially formed at pH 3 ($Al(OH)_3$), then at pH 4-6 a reddish-brown flock forms, this is $Fe(OH)_3$. The uranium and thorium are quantitatively precipitated by pH 7. The aim of this step is to separate off calcium and any other Group II or Group I metals, which do not form insoluble hydroxides until pH 9- 10.

[7] Washing and recentrifuging ensures that any coadsorbed Ca, Mg etc is returned to the solution.

[8] The supernatants are scavenged once more with extra coprecipitant to recover any uranium or thorium that escaped the first precipitation.

[9] The last few steps completely redissolve the sample (by going to an HCl matrix), again releasing any coadsorbed Ca, Mg, Na etc.

[10] Hopefully all the SiO_2 in the sample is converted to SiF_4, which is gaseous, thus removing Si from the sample. Otherwise it can interfere with the U-Th separation column. Much of the residual HF should be evaporated away due to the higher boiling point of HNO_3.

26. Add 15 mls $HClO_4$ and evaporate at a low heat overnight, or at least until no more fumes are emitted.[11]
27. Add a few mls conc HCl and evaporate to dryness.[12]
28. Dissolve in 10-20 mls of 8N HCl.

Uranium-Thorium Separation Column.

1. Take sufficient resin (BIORAD 1X8 100-200 mesh anion exchange resin) for all the columns in a beaker, and fill the vessel with distilled water.
2. Stir, allow the resin to settle and decant off the finings.
3. Add more distilled water and repeat.[13]
4. Prepare a large ion exchange column with 15 mls resin.[14]
5. Wash with a column volume of distilled water.
6. Wash with two column volumes of 8N HCl.
7. Place a 100ml teflon beaker, labelled Th 1, under the column.
8. Load sample onto column.
9. Wash column with three column volumes of 8N HCl, rinsing the first teflon beaker (S 1) each time.[15]
10. Replace the Th 1 beaker with a fresh 100ml teflon beaker, labelled U1.

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[11] $HClO_4$ has a particularly high boiling point, in it's presence all HF will be preferentially evaporated.

[12] This destroys any $HClO_4$ not already destroyed by the prolonged heating.

[13] The finings interfere with the resin function, as they are not of the certified size range, and may be of foreign composition.

[14] The amount of resin must be enough to easily hold all Fe and U, but should not be so low that the cross-section to length ratio of the resin is so high as to allow Fe and U past. Add distilled water to the column, then the slurry, to prevent air bubbles forming. For the same reason, try never to let the head of the resin run dry.

[15] Thorium, aluminium, nickel,titanium, Scandium group elements, Group II elements and Group I elements are not held on the resin in 8N HCl

11. Wash the Fe and U off the column with a column volume of distilled water, followed by a column volume of distilled water plus 5 drops conc HCl, and a column volume of distilled water.[16]

12. Add a few mls conc HNO_3 to both the Th1 and U 1 beakers and start boiling down.[17]

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[16] In dilute HCl iron, uranium, most remaining transition metals, and many of the metals of Group IV and V are eluted.

[17] The HNO_3 destroys any resin byproducts in the beaker, when boiled with the HCl.

Thorium Purification

1. Evaporate Th 1 fraction down to a volume of about 30mls, add 50 mls of conc HNO_3 and boil under a watchglass.[18]
2. Prepare a fresh large ion exchange column with 15mls of anion exchange resin (BIORAD 1X8 100-200 mesh).
3. Wash the column with one column volume of distilled water, and two of 8N HNO_3
4. Boil until the solution in Th 1 goes clear, and no more brown fumes are given off. It may be necessary to add more HNO_3 if the solution fails to clear.[19]
5. Once clear, wash down watchglass and beaker walls with conc HNO_3. Continue boiling for 5 minutes.
6. Boil the solution back to about 50mls.
7. Add an equal volume of distilled water to bring the solution to 8N in HNO_3.[20]
8. If there is any sign of a precipitate (unusual), centrifuge the solution and load onto the column. Add 20mls 8N HNO_3 to the centrifuge bottle to dissolve any precipitate. If there are still signs of precipitate being present repeat this step until no precipitate is evident. Add all supernatants to the column.[21]
9. If no precipitate, add load solution (approx 100mls) straight onto the column.
10. Rinse the column with 3 column volumes of 8N HNO_3, washing the beaker (Th 1) and centrifuge bottle each time.[22]

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[18] The volumes are kept as large as is practical to prevent titania from precipitating out.

[19] The HNO_3 gives off brown fumes in the presence of HCl, thus when no more such fumes are evident, the solution must be free of HCl, which would have interfered with the following column.

[20] If samples are known to have low titania levels, the volumes can be reduced through these stages. Larger volumes take longer to load onto the column.

[21] The precipitate can sometimes be redissolved in 8N HNO_3, however this is difficult to do. Any undissolved titania precipitate will quickly scavenge thorium from solution.

[22] Species washed off by the 8N HNO_3 are aluminium, nickel, any 3d transition metals that inadvertently came through the first

11. Place a 100ml teflon beaker, labelled Th 2, under the column.
12. Wash off the Th with 3 column volumes of 9N HCl.[23]
13 Add 3mls conc HNO_3 to the beaker and place on hot plate.

Small Thorium Column.

1. Prepare a fresh small ion exchange column, with 2mls of anion exchange resin (BIORAD 1X8 100-200 mesh anion exchange resin)
2. Wash with one column volume of distilled water, and two of 8N HNO_3
3. Boil the solution in Th 2 back to a small volume (until solids start to appear), add 3mls conc HNO_3. Boil back to about 0.25mls HNO_3.
4. Add a matching volume of distilled water, followed by 3mls conc HNO_3 to dissolve the sample. [24]
5. Add 3mls distilled water to bring the solution to 8N in HNO_3.
6. Load onto the column.
7. Rinse the beaker with 3mls conc HNO_3, add 3mls distilled water (heat the beaker very gently to dissolve any solids, only if necessary) and load onto the column.
8. Repeat previous step with 2mls conc HNO_3 and 2mls distilled water.
9. Rinse beaker twice with 5mls 8N HNO_3 and load onto column.
10. Place a 100ml teflon beaker labelled Th 3 under the column.
11. Elute the thorium with 3 column volumes of 9N HCl.[25]
12. Immediately add 3mls conc HNO_3 and cover with a watchglass, to keep out any dust, aerosols etc.
13. Place on the hot plate and start boiling down.

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column, and any Group II or Group I metals present. The only common species held on this column are the actinides, some early lanthanides, zirconium, palladium and gold, the last few are very unlikely.

[23] This should result in only thorium being washed off. With such high levels of contaminants and Gaussian elution profiles, it is likely that some other species may get through.

[24] Dissolving the sample in this way ensures complete retrieval of any sample well adhered to the beaker

[25] This repeats the separation of the previous larger column, just increasing the quality of separation.

Uranium Purification.

1. Boil the sample (U 1) back to dryness, add 3mls conc HCl and boil back to dryness again, to ensure removal of all HNO_3.
2. Dissolve sample in 5mls 8N HCl and add to a small centrifuge tube.
3. Rinse the beaker with 1ml 8N HCl and add to the centrifuge tube.
4. Rinse beaker with 4mls di-isopropyl ether and add to centrifuge tube.
5. Emulsify on a vortex mixer for 15 seconds. Extract the ether phase (top layer) and discard into a waste ether bottle (the ether can eventually be retrieved).[26]
6. Repeat extraction with di-isopropyl ether 3 more times.
7. Add 5 drops conc HCl and extract twice more, each time with 4mls of ether.[27]
8. If the solution is not fairly clear, (i.e. no Fe), it will have to be boiled down and extraction repeated.[28]
9. Transfer to a 100ml labelled teflon beaker (U 2) and wash the centrifuge tube twice with 8N HCl, adding washings to U 2.
10. Add 3mls conc HNO_3 and place U 2 on the hot plate.

Small Uranium Column.

1. Prepare a fresh small ion exchange column, with 3mls of anion exchange resin (BIORAD 1X8 100-200 mesh anion exchange resin)
2. Wash with one column volume of distilled water, and two of 8N HNO_3
3. Boil the solution in U 2 down to a few drops. Add a few mls conc HNO_3 and boil back to a few drops again. Cool and add a matching

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[26] The iron forms an ether-soluble chloride complex, while the uranium chloride complex remains in the aqueous phase.

[27] The chloride concentration drops below optimal as the iron chloride complex is removes. The conc HCl increases the concentration again.

[28] Test a drop of the solution with potassium ferrocyanide to ensure that the discolour is in fact due to Fe, and not to Mn or other species.

volume of distilled water. If there is any insoluble material present the sample may have to be boiled down again and taken up in larger volumes. HCl + HNO_3 may be needed to redissolve, this must then be removed before creating the loading solution.

4. Load the solution onto the column.
5. Add 1ml conc HNO_3 to the beaker, then 1ml distilled water; load onto the column.
6. Rinse the beaker with two 2ml volumes of 8N HNO_3, adding these to the column.[29]
7. Add 1ml of conc HCl to the column, and allow to run until the column head is exposed.
8. Place a 100ml labelled (U 3) teflon beaker under the column.
9. Wash the uranium off with a column volume of distilled water, then a column volume of distilled water plus 3 drops conc HCl, and finally two column volumes of distilled water.[30]
10. Immediately add 3mls conc HNO_3 and cover with a watchglass. Place U 3 on the hot plate.

Electrodeposition

1. Evaporate the sample (U3 or Th3) to a droplet and continue to evaporate down in small volumes of HCl until no more brown fumes/HNO_3 discolouration occurs.[31]
2. Scribe the back of a 22mm Ag foil disc with a unique sample code. Wash and clean the disc with distilled water.
3. Assemble the cell with the disc in place and rinse with distilled water.[32]

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[29] In 8N HNO_3, the uranium is weakly held. Iron, aluminium, Group I and II elements, and all 3d transition metals will pass through the column. Species held are actinides, gold, palladium and zirconium, the last few of which are extremely unlikely to be present.

[30] The uranium is readily washed off the column with most other remaining species.

[31] Presence of HNO_3 in the HCl creates a solution that readily dissolves the Ag disk, so that resolution is reduced by the codepositing Ag.

[32] Ensure that the cell is not leaking, and that it is all very clean.

4. Dissolve sample U3 or Th3 in 2mls conc HCl, and add 4mls distilled water. Rinse beaker and add to plating cell. Wash beaker with 1ml conc HCl, add to cell. Repeat with 2 mls distilled water.
5. Add several drops of methyl red solution. Carefully add a magnetic flea to the cell, and stir the solution. Carefully add NH_4OH until the solution just turns yellow. Add 1N HCl until the solution just turns red, add one more drop 1N HCl.[33]
6. Plate at 6V, 0.8A until the current drops to 0.3A or less (about 3hrs). Wash cell walls with several mls of distilled water and continue plating for 20 minutes.[34]
7. Add 2mls NH_4OH and a few mls distilled water. Continue 30s, then pour electrolyte out of cell. Turn cell off.[35]
8. Wash cell with NH_4OH, then with ample distilled water.
9. Dissemble cell and wash disc with distilled water, and finally wash with acetone.[36]
10. Very carefully flame the disc until it just glows red, then store until ready for counting.[37]

The separation of trace elements by the system is summarised in figure (2.9).

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[33] If the endpoint is badly overshot, then add minimum drops $NH_3(aq)$ and readjust.

[34] This washes down any nuclides splashed onto the cell walls.

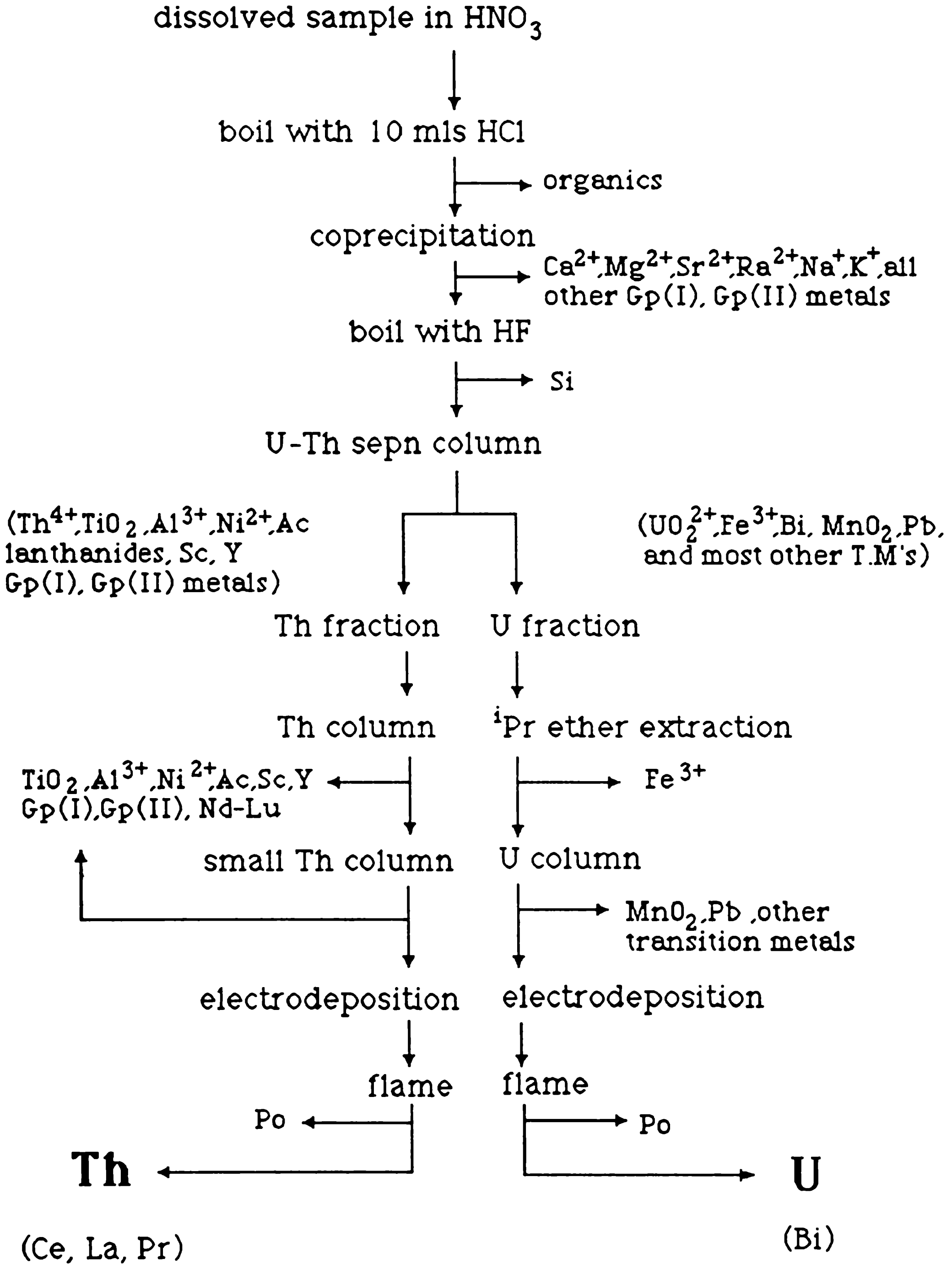
[35] The ammonia fixes the hydrous metal film to the disc.

[36] Acetone evaporates away quickly and doesn't leave a ridged deposit on flaming, unlike distilled water.

[37] The disc must be flamed sufficiently to remove all polonium, but not to the point of melting the disc.

Figure 2.9

Separation and purification of Uranium and Thorium



Future Development of the System.

The method developed has some scope for improvement. The broad structure of the phases seems adequate, but within each stage of separation and purification there is opportunity for development and refinement. Yield is generally satisfactory for most samples, but can be quite variable. There is a general need to identify the remaining areas of uranium and thorium loss in the system. This would obviously lead to improvements in the method, and would make it quite feasible to date samples of quite low uranium concentration. More accurate yield determination would require a better knowledge of the counting geometry of the alpha spectroscopy system (Ch 4), to this end a calibrated alpha source (e.g ^{241}Am) would be needed. Specific refinements possible for the method are as follows.

(1) The spike solution - the presence of disequilibria suggests that there may also be changes in the degree of disequilibria. It would be preferable to work with a spike continually at equilibrium. Use of storage containers guaranteed to be inert and non-leachable for the stock solution, mother liquor, and working spike would be essential. Storage in a dark, refrigerated place would be helpful. Possibly complexing reagents could be investigated for stabilizing the nuclides.

For spike calibration it would be useful to obtain a thorium compound with low or nil levels of ^{230}Th, that is also readily soluble and of known stoichiometry (especially with respect to water of hydration). Such a compound would allow the spike to be quickly and simply calibrated with uranium and thorium standards, using only a small anion exchange column for separation, and electroplating for deposition.

(2) Initial treatment - it would be a great advantage to develop a means of separating the detritus in the sample from the carbonate phase, prior to acidification (which leaches the detritus). In particular the larger gravel inclusions could be removed by mechanical/physical separation. The validity of dates obtained would be greatly enhanced by a study of the effects of different acids, and different acid strengths, on the samples; in order to

assess the contribution of labile uranium and thorium from the detritus to the isotope ratios observed.

The coprecipitation phase is probably close to quantitative. A possible refinement would be to double scavenge the final coprecipitation from HCl solution, and possibly to reboil the solution before doing so. The use of very fine filtering methods to remove silica may be useful.

(3) Uranium - Thorium separation column. The use of analytical grade resin would be a definite advantage in achieving higher quality separation, due to it's narrower particle size range. Analytical grade resin is also pretreated to remove impurities, and would be less likely to produce discoloured washes. A preparatory wash with NaOH or other solutions may also help reduce resin byproducts. It would be productive to examine the effects of low levels of silica (through which the solutions still pass at practical speeds) on the yields of uranium and thorium. It would also be of interest to identify the green band in the resin seen for some samples.

It could be possible to separate off titanium on this column. Data for the activity of titanium on anion exchange columns suggests that titanium is increasingly retained in chloride form at acid strengths of above 8N, although not very strongly (Kraus and Nelson, 1955). If it were held, a simple separation would be possible. The sample could be loaded and washed three times with conc HCl (11.6N) to elute thorium. After this, three washes of, say, 6N - 7N HCl should wash off the titanium but still leave the uranium and iron in place. These could then be eluted with trace HCl solutions, as usual. A number of factors would need to be considered, namely the stability of the resin in conc HCl, the potential for swelling of the resin with changes in normality to block the column, the retention of Ti in multiple washes of conc HCl, and the possible unwanted elution of uranium in 6N -7N HCl. It is nevertheless a potentially promising method.

Use of a partial vacuum could be considered to reduce the lengthy time needed to boil down solutions, at all stages of the process.

(4) Thorium purification. It would be of interest to identify the source of the slight green colour often seen in the thorium fraction.

An improved method of dealing with the titania precipitates is still possible, particularly one that leads to quicker loading of the thorium fraction onto the column than in the current method. Possibly a specific titanium separation stage could be devised.

It would be useful to identify any trace elements that follow thorium through the two columns, possibly via XRF of a few samples after the final Th column, particularly to identify those that make the residue difficult to dissolve. A simple flexible cover attached to the base of the final thorium column would solve the problem of dust, aerosols, and clamp corrosion from entering the beaker, as would also be useful for the final uranium column.

(5) Uranium purification. The ether extraction phase could be further refined to maximise iron extraction, by monitoring changes in chloride activity and Fe concentration through the steps; and by looking at the effect of various trace elements in interfering with this stage.

On boiling down of the uranium solution after ether extraction it would be useful, as for the thorium column, to identify the trace elements still present, particularly the insoluble species. The small uranium column could be checked and refined for yield, looking at both uranium eluted with the 8N HNO_3 washes, and at Fe retained in spite of those washes. Again it would be useful to identify any trace elements that follow uranium past this column, with a view to added separations. In particular polonium-210 is an alpha emitter (half-life = 130 days) in the ^{232}U area, and can add to the ^{232}U count.

(6) Electrodeposition. This stage has the greatest immediate potential for improvement, especially with respect to time taken for deposition. The system of chloride electrolyte with silver discs appears to work adequately. It would also be preferential to retain the current yields for deposition, in excess of 90% for each of uranium and thorium. An investigation into the exact pH and chloride concentration needed for optimal electrodeposition would be helpful, followed by standard use of a pH meter to rigidly set the pH. The Ag discs should be of the thickness used for the last few samples (0.13mm), rather than that used for the bulk of the samples (0.025mm). The thinner discs costed approximately $1-30

each (1990) while the thicker discs were about $3-00 each (1990). This would be a minimal increment in terms of total sample costs. All discs should be cleansed with silver polishing paste prior to use. The use of complexing reagents to block deposition of some trace contaminants could be useful (Puphal and Olsen, 1972).

Cell design has some room for improvement. In the current design, availability of more platinum would allow a more closely spiralled anode to be used, allowing the stirrer to work more smoothly at greater speed.

Ideally, cell design should be based on a rotating cathode, which has multiple advantages over the traditional style (McCabe et al, 1979) for rapidly obtaining a high quality deposit. The use of motors is obviously a more expensive initial cost. Samples could be deposited from reasonable volumes in their beakers at high cathode rotation speeds, giving rapid deposition.

The most pressing need in the current method is to reconsider the current density, which seems to be too low. A current density (i.e. the ratio of current to disc surface area) of around 0.6 A cm^{-2} (cf currently about 0.4A cm^{-2}) would be preferable, giving much more rapid deposition.

Chapter 3.

Spectral Analysis.

Following preparation (Ch. 2), the discs were then analysed by alpha spectroscopy, from which isotope ratios were determined. A number of corrections and adjustments were necessary to the raw data, in order to allow the correct $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios to be calculated. From these the age was determined. The route from uncounted disc to final sample age is here examined in some detail, particularly with regard to some of the standard assumptions.

Alpha spectroscopy.

Samples were analysed on several systems. The majority were performed with one of two Tennelec TC-256 alpha spectroscopy counters linked via a TC-306 router multiplexer to a 2048 channel micro-pulse height multi channel analyser (Nucleus Model 811) on an Apple IIe computer. Several detectors were used in the system, most commonly Tennelec PD-400-100-21-CM (+50V) detectors. These were unused prior to this work. The chambers were dedicated to either uranium or thorium disc counting, in order to render the background due to recoil contamination more constant.

Many of the earlier samples were ‘counted’ on other arrangements, due to difficulties in detector supply and breakdown of most components of the above system at various stages. The alternative was generally an Ortec 121 preamplifier with an Ortec 428 detector bias supply, connected to the sample in a Vollrath counting chamber. The signal was sent to the router and MCA via an Ortec 444 gated biased amplifier (when available) or via an Ortec 451 biased amplifier. Several detectors were used in this system, namely Ortec models BA-040-300-100, BA-030-450-100, and BA-055-450-100. Two uranium discs were counted using a small high resolution detector, a BA-016-50-100. These latter combinations were mainly used for preliminary work, such as spike analysis and electrodeposition testing. Peripheral aspects of the alpha spectroscopy systems included the use of petroleum jelly to seal the chamber doors, and to hold the discs steady under vacuum. This was soon thought to be a possible contribution to detector breakdown, and small tabs of adhesive paper were then used to prevent the very light discs from moving out from beneath the detector under vacuum. For a short time a liquid nitrogen trap was used in the vacuum pump line to prevent pump oils from entering the chamber and breaking down detector surfaces.

Spectra were accumulated at full scale of 3-8 MeV, with two counters operating simultaneously through the multiplexer - giving two spectra of 1024 channels each. Spectra were saved to floppy disc for later analysis. Count times were variable, with a general minimum of either 24 hours or until 10,000 counts (alpha decay events) were accumulated for each major isotope peak. Some low activity samples were counted to only 7-8000 counts for the lowest activity major peak. Since many samples were expected to be at the upper limit of the method (i.e. around 200 - 400 kA), where counting errors were critical, many samples were counted to a minimum of 40,000 counts per major isotope. In many cases individual isotopes had accumulated several hundred thousand counts. Uranium and thorium spectra for sample 87-L1W3 are given in figures (3.1a) and (3.1b). This sample displays typical resolution, although has a lower $^{234}U/^{232}U$ ratio than most.

Isotope Peak Integration.

Integrating the number of counts for each peak gives the activity of the isotope of that energy. Ideally integration should embrace the entire peak for each isotope, with the limits of integration set at those channels above and below the peak at which the count falls to zero. In practice this is not usually practical due to the under-riding of one peak by the low energy tails of another peak. Several criteria for setting the limits of integration for the peaks are available. The same criteria are applied to all the peaks in the spectra of interest. This is not entirely valid due to the small differences in peak shape between peaks of the same spectra, it is however a reasonable approximation for those peaks which make the major contributions to the activity ratios. For example ^{238}U, ^{234}U, and ^{232}U all have twinned peaks, with a minor peak (of 23%

Figure 3.1a Graph of typical uranium spectrum (87-L1W3)

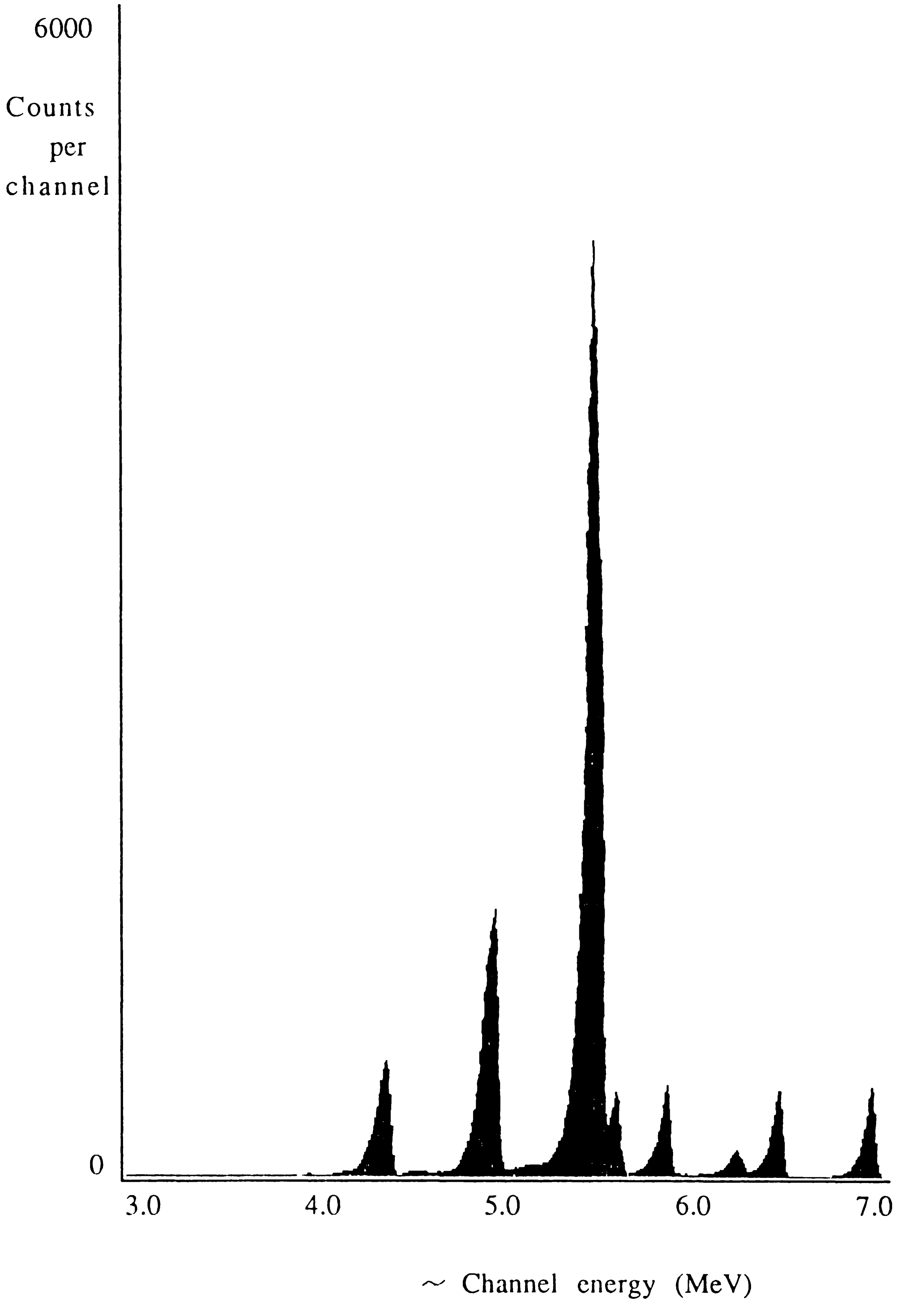


Figure 3.1b Graph of typical thorium spectrum (87-L1W3)

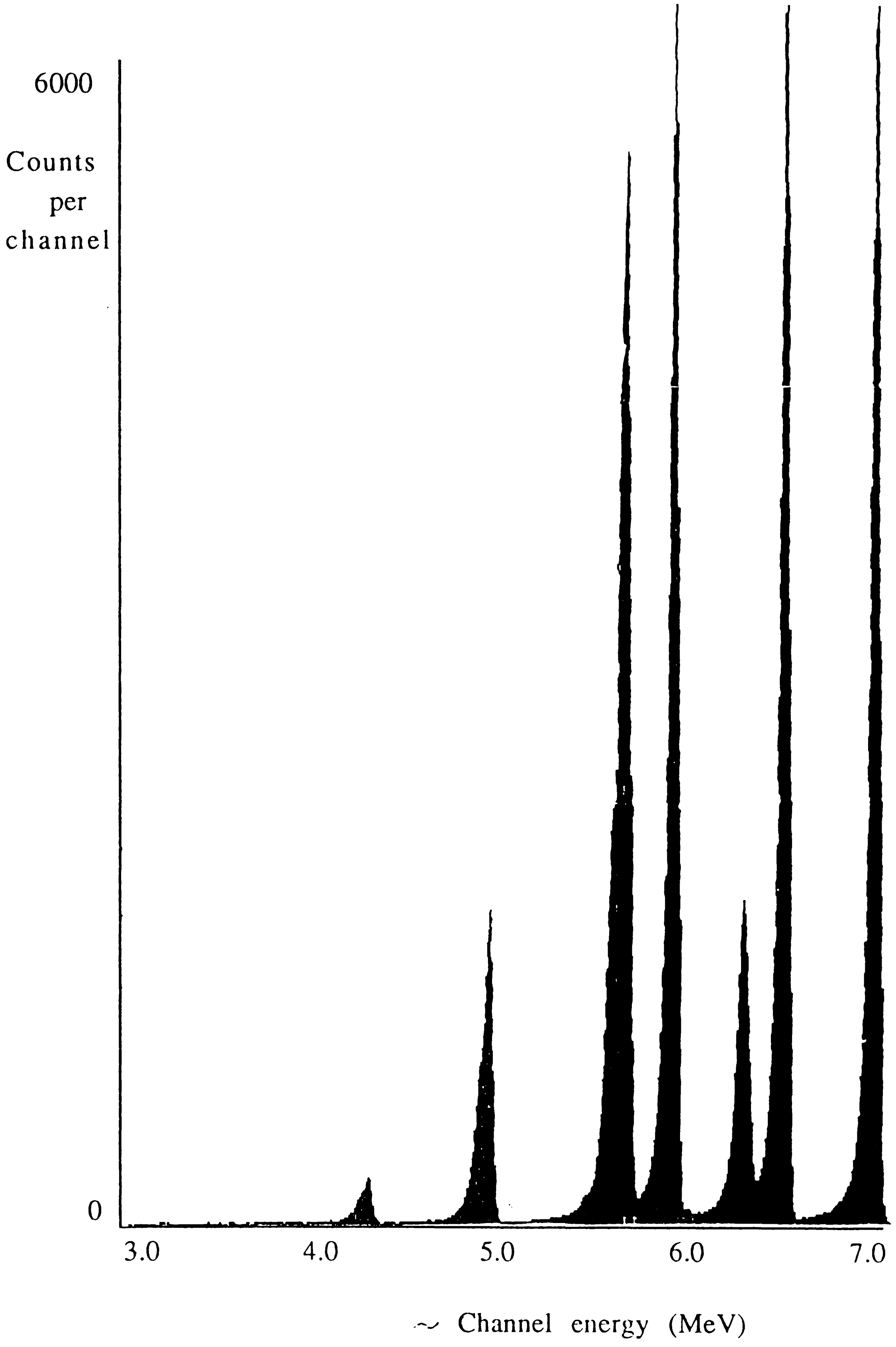


Table 3.1

Integration Limits: Criteria and Standard Errors of sample 87-L1-W3

^{238}U peak

Criteria with respect to apex	^{238}U count	^{238}U bground	^{238}U tail	^{238}U final
(+10,-50)	43923	1157	200	42566
10% of apex counts	40802	561	5	40235
25% of apex counts	37788	421	8	37359
50% of apex counts	31213	275	0	30938
(+10,-40)	43415	964	192	42259
(+10,-30)	42750	731	151	41869
(+5,-30)	40235	608	113	39514
(+5,-20)	38658	503	22	38133
(+5,-10)	32463	298	82	32083

^{234}U peak

Criteria with respect to apex	^{234}U count	^{234}U bground	^{234}U tail	^{234}U final
(+10,-50)	106195	2560	721	102914
10% of apex counts	99324	988	379	97957
25% of apex counts	91374	362	248	90764
50% of apex counts	75242	82	96	75064
(+10,-40)	105003	2069	688	102246
(+10,-30)	103245	1584	407	101255
(+5,-30)	98749	1566	173	97010
(+5,-20)	94714	888	222	93604
(+5,-10)	78155	82	145	77928

^{234}U/^{238}U ratio

Criteria with respect to apex	$\frac{^{234}U}{^{238}U}$	Total error	%error
(+10,-50)	2.4178	0.01437	0.59437
10% of apex counts	2.4346	0.01472	0.60450
25% of apex counts	2.4295	0.01511	0.62191
50% of apex counts	2.4263	0.01649	0.67847
(+10,-40)	2.4195	0.01455	0.60136
(+10,-30)	2.4184	0.01447	0.59822
(+5,-30)	2.4551	0.01505	0.61287
(+5,-20)	2.4546	0.01519	0.61874
(+5,-10)	2.4290	0.01623	0.66833

for ^{238}U, 28% for ^{234}U, and 32% for ^{232}U) just below the main peak (^{238}U at -0.048MeV, ^{234}U at -0.051MeV, and ^{232}U at -0.057MeV).

Integration limits commonly used include those channels containing 1% of the channel count of the peak apex channel (Rosholt,1978), or those channels containing a channel count of 50% of the peak apex channel. The integration scheme chosen was to integrate over a set number of channels with respect to the peak apex. The lower limit of integration was that of the minimum distance between any peak and the point at which the tail of that peak under-rode the next lowest peak. This was always at the ^{235}U-^{238}U confluence for uranium spectra, and the ^{224}Ra-^{228}Th confluence for thorium spectra. A similar criterion was used for upper integration limits i.e. the point at which the upper end of the peak became seriously contaminated by the tail of the next highest peak. The critical points here were the ^{234}U-^{235}U boundary, and the ^{228}Th-^{224}Ra boundary. Reasonable margins within these limits were allowed. The majority of samples were thus integrated to +10,-50 channels with respect to the apex for uranium peaks; and +10,-30 channels for thorium spectra. Typical peak apex separations were 110 channels between ^{232}U and ^{234}U, 105 channels between ^{234}U and ^{238}U, and 70 channels between ^{235}U and ^{234}U; giving a typical resolution of 0.0055 MeV/channel. Typical thorium spectra showed 140 channels between ^{230}Th and ^{228}Th, 120 channels between ^{230}Th and ^{232}Th, and 50 channels between ^{228}Th and ^{224}Ra; giving a typical resolution of 0.0053 MeV/channel. The criteria allowed smaller integration limits to be set for samples of lower resolution, in which marginal increments of integration limits have a higher associated marginal correction. For some individual peaks the apparent peak apex was not truly representative of the peak shape, and an apex was chosen that roughly equated to that which would have been expected from smoothed data.

Although larger integration limits require larger tail and background corrections, they also give a higher count and thus lower final error in the peak activity. The contribution of the higher background and tail corrections can be allowed for by a full error analysis. Results from different integration schemes, with regard to the ^{238}U/^{234}U ratio of a typical sample (87-L1W3), are given in table (3.1). The scheme chosen demonstrates a slightly higher accuracy, i.e. lower standard error, but is not much more accurate then the other 'wide' integration schemes..

Background Correction.

In the absence of sample discs, a noticeable spectra of counts could still be accumulated. This was due to electronic noise in the counting system (minor), defective surface barrier detectors, and recoil contamination of the detector surface. Recoil contamination occurs when nuclei ejected by recoil from alpha decay events become deposited on the detector and counting chamber. The decay of the recoiled nuclei provides the major component of the background. Obviously this will produce highest backgrounds for those nuclei of shortest half-lives. In the region of interest, nuclei of ^{228}Th and it's daughter ^{224}Ra are the most significant. Detectable backgrounds were found under the ^{228}Th peak (due to α-recoiled ^{224}Ra (and possibly ^{222}Rn), ^{234}U and ^{230}Th peak areas (due to α-recoiled ^{226}Ra) and in the ^{232}U region due to α-recoiled ^{210}Po. An apparent defect in the surface barrier detector used for analysing most of the latter uranium discs caused a constantly higher than expected background for these discs in the 4 - 4.5 MeV region.

Background spectra were accumulated periodically, generally at 4 to 6 week intervals, or when different detectors were installed. An appropriate background spectra was integrated over the equivalent area of interest for each isotope peak, multiplied by the ratio of sample count time to background count time, and subtracted from the sample count for each peak.

Tail Corrections.

As evident in figures (3.1a) and (3.1b), low energy tails under-ride lower energy peaks in the spectra. The degree of tail encroachment is unique to each spectra, and is a combined function of sample disc thickness, disc - detector geometry, chamber vacuum etc. The tail of a higher peak must be corrected for to determine the true activity of an isotope. Mathematical equations for modelling peak shapes and subsequent correction by extrapolation of the equation is not yet possible. Two major schemes were used to correct for tail encroachment.

(i) graphical extrapolation of the tail - a graph of the peaks allows the low energy tail to be extrapolated underneath the affected peak, and the tail contribution can be calculated manually.

(ii) by modelling using peaks of similar shape - several of the major peaks show similar shapes, while varying in size. By integrating over the set number of channels at the same number of channels below the 'model' peak apex as the errant tail is below the 'tail' peak apex; followed by multiplying by the size ratio of the two peaks; it is straight-forward to make a reasonable estimate of the tail correction. Integrated peak count ratios without tail corrections provided a more accurate assessment of relative peak size than apex channel count ratios.

Figures (3.2a) and (3.2b) show the applicability of two such models for tail corrections. ^{238}U can be used to correct for the tail of ^{234}U under ^{238}U, and for ^{232}U under ^{234}U. The high correlation between ^{216}Po peak shape and ^{224}Ra peak shape is fortunate, as the tail of ^{224}Ra under ^{228}Th is by far the most significant tail correction that needs to be made. The disparate shape of the ^{228}Th peak shows the inapplicability of ^{216}Po modelling for correction of thorium peak tails. Although ^{232}Th could possibly be used to model the peak shapes of ^{230}Th and ^{228}Th, ^{232}Th count-rates are invariably too low to be statistically useful.

Thus peak modelling on ^{238}U was used to make tail corrections for the ^{238}U and ^{234}U counts; while ^{216}Po modelling was used to correct for the tail under ^{228}Th. Tails under ^{232}Th, ^{230}Th and ^{224}Ra were estimated by graphical extrapolation. No tail correction was made under ^{232}U since isotopes of higher α-energy were absent and almost all of the ^{228}Th peak in any uranium spectrum would have been a background effect; thus the peak tail would also have been included in the background.

Figure 3.2a
Use of 238-U peak shape as a tail model for 232,234-U

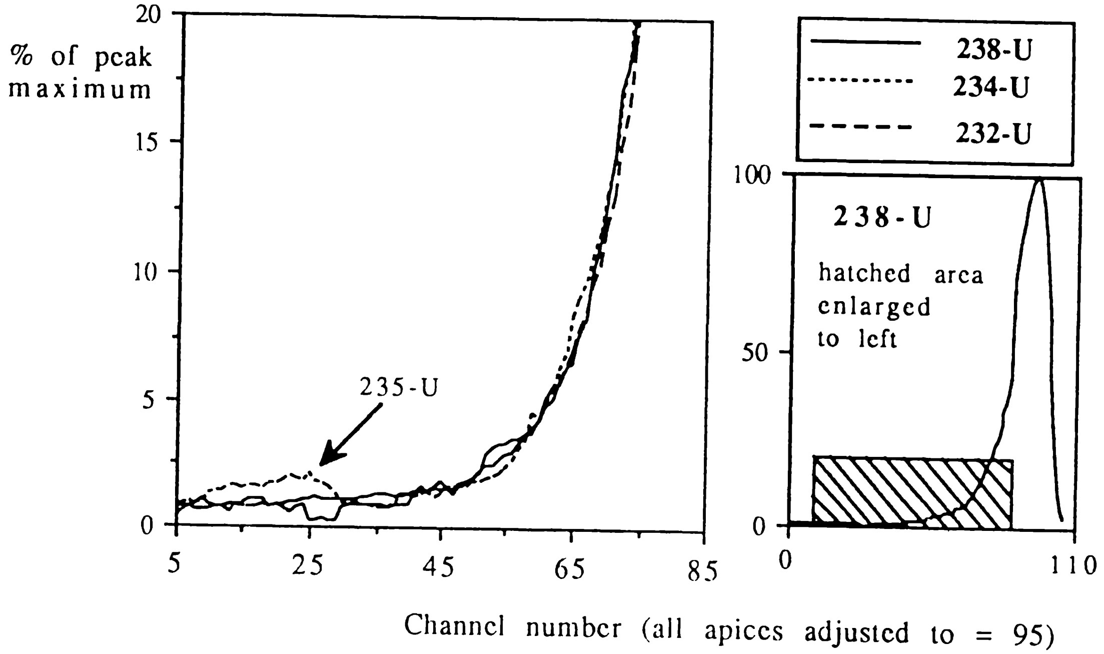
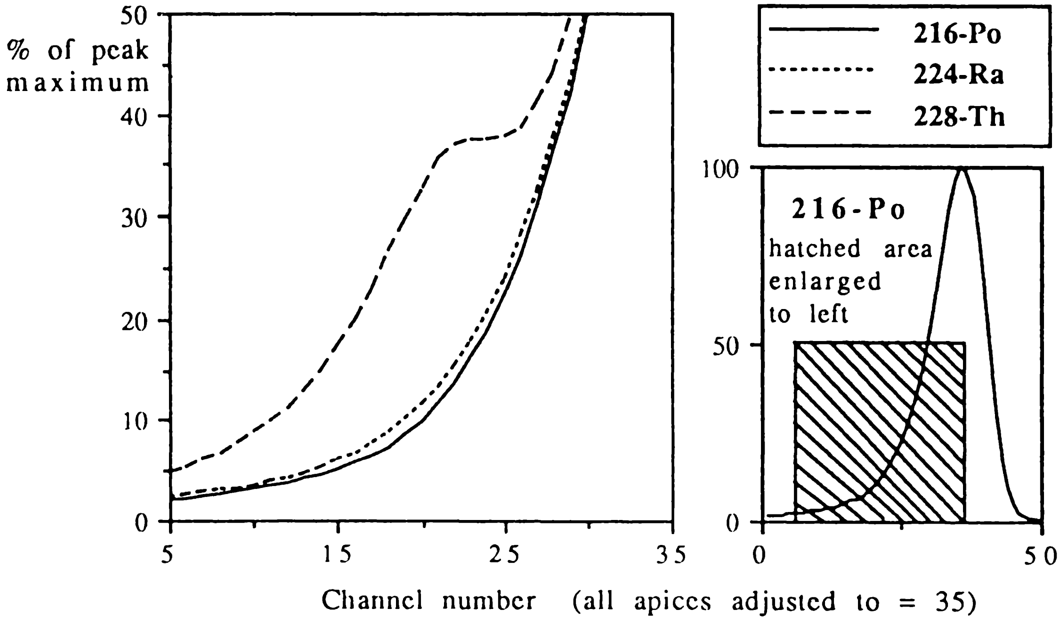


Figure 3.2b
Use of 216-Po peak shape as a tail model for 224-Ra



Corrections to ^{228}Th count.

Several other corrections need to be made to the ^{228}Th count.

(i) A minor peak of ^{224}Ra occurs in the region of integration of ^{228}Th. Since this peak (5.45 MeV) is 5.1% of the total ^{224}Ra count , 0.054 * the ^{224}Ra count (0.054 = 5.1/(100 - 5.1)) was subtracted from the ^{228}Th count.

(ii) The short half-life of ^{228}Th means that it could decay appreciably between separation from it's supporting parent ^{232}U, and counting. This was readily corrected for by the equation $N/N_0 = \exp(-\lambda t)$. ($\lambda = 9.927 \times 10^{-4}$ per day). Given delays of up to 189 days between the U-Th separation column and counting, this meant a maximum correction in one case of $^{228}\mathrm{Th}_{\mathrm{true}} = {}^{228}\mathrm{Th}/0.8289$. However, most corrections were of the order $N/N_0 = 0.95 - 0.99$.

(iii) ^{228}Th occurs naturally in the sample, due to the presence of ^{232}Th (decays to give ^{228}Th). The ^{232}Th/^{228}Th ratio will be unity due to ^{228}Th's short half-life, thus the ^{232}Th count was subtracted from the ^{228}Th count to give the true count of ^{228}Th due to the spike.

Error Analysis.

A full treatment for errors was used for all samples. The Poisson distribution found for decay events has the standard deviation (σ) as the square root of the count. Examples of errors propagated by mathematical functions, as applied to the above measurements, are as follows:

e.g. true count = count - background - tail
σ(true count) = $\sqrt{}$(count + background + tail)

e.g. $^{234}\mathrm{U}/^{238}\mathrm{U}$ = true count (^{234}U)/true count (^{238}U)
$\sigma(^{234}\mathrm{U}/^{238}\mathrm{U}) = (\sqrt{}((\sigma(^{234}\mathrm{U})/^{234}\mathrm{U})^2+(\sigma(^{238}\mathrm{U})/^{238}\mathrm{U})^2))*(^{234}\mathrm{U}/^{238}\mathrm{U})$

e.g. $^{228}\mathrm{Th} = (^{228}\mathrm{Th} - 0.054\,^{224}\mathrm{Ra} - {}^{232}\mathrm{Th})$/decay factor
$\sigma(^{228}\mathrm{Th}) = \sqrt{}((0.054*(\sigma(^{224}\mathrm{Ra})^2)+\sigma(^{232}\mathrm{Th})^2+\sigma(^{228}\mathrm{Th})^2)$/decay factor)

The practice of using the ^{228}Th decay rate as a divisor in the error equation was overlooked at the time of calculating results. This means that in the case of a sample whose ^{228}Th count was much lower than that of any other major peak, the error may be underestimated by several percent. A second deficiency in the error analysis was due to background counts being multiplied by the sample to background count time ratio before the square root was taken as the standard deviation. Again this would have caused a very slight decrease in the errors given.

Errors due to spike composition.

The spike nuclide ratio of ^{228}Th/^{232}U was determined as 0.97 ± 0.02 (Ch. 2). There are convincing arguments both for and against including this error in the analysis. Most obviously, the error should be included to give the true absolute age range of any given sample. A contrary argument is also valid. The spike nuclide ratio can be presumed to have a single fixed value within the error bounds, rather than varying within the error. i.e the error is due to measurement deficiencies rather than the spike itself. Thus were the nuclide ratio 0.96, <u>all</u> samples would be slightly reduced in range, or were it 0.99, <u>all</u> samples would be slightly increased in age. While including the spike error would make the absolute ages more correct, excluding the error makes the relative sample ages more accurate. The latter approach was used, but the validity of both approaches was noted.

Yield and Concentration Calculations.

Yields and concentrations were calculated using the equations:

$$\%\mathrm{U\ yield} = (^{232}\mathrm{U}*100)/(g_f*3600*1.8*(\mathrm{hours}))$$

$$\%\mathrm{Th\ yield} = (^{228}\mathrm{Th}*100)/(g_f*3600*1.75*(\mathrm{hours}))$$

$$[\mathrm{U}]\ (\mathrm{ppm}) = (^{238}\mathrm{U}*1.80)/(0.0123*{}^{232}\mathrm{U}*\mathrm{gms}(\mathrm{CaCO_3}))$$

$$[\mathrm{Th}]\ (\mathrm{ppm}) = (^{232}\mathrm{Th}*1.75)/(0.0041*{}^{228}\mathrm{Th}*\mathrm{gms}(\mathrm{CaCO_3}))$$

where ^{232}U,^{228}Th etc = corrected counts for those nuclides.

g_f = disc - detector geometry factor.

(≈ 0.22 for almost all samples counted)

hours = count time for the disc in hours.

1.80 = ^{232}U activity (Bq) for 10 mls of spike.

1.75 = ^{228}Th activity (Bq) for 10 mls of spike.

gms($CaCO_3$) = weight of the dissolved part of the sample.

0.0123= activity of 10^{-6} gm of ^{238}U.(Bq/10^{-6} gm).

0.0041= activity of 10^{-6} gm of ^{232}Th.(Bq/10^{-6} gm).

Preliminary results of dating.

An initial list of the dates obtained is given in table (3.2). A small number of results are dubious. These are due to three main sources-

(i) - spectral shift. This refers to samples for which there seems to have been a problem in the alpha spectroscopy system. The source of the problem has not been identified, but is clearly evidenced by widely disparate $^{234}U/^{238}U$ ratios. It would seem that one of the counting units was occasionally not recording events in the ^{234}U region. On another occasion, a ^{224}Ra count in a thorium spectra was only about 25% of it's theoretical value from decay laws, given the time between plating and counting. This result (87-017-38b) was adjusted on the basis of the expected ^{224}Ra count. Spectral shift also refers to the observation made in one sample (87-025-51c) of doubled peaks, suggesting the entire spectrum had been translated during counting.

(ii) - low resolution. Several samples had extremely low resolution, generally due to poor electrodeposition, or the presence of large impurities. This caused a tail correction of about 15% for one isotope in one of the samples (87-L1W4). Where such samples disagreed markedly with a replicate, the low resolution sample was disregarded.

(iii) - low recovery. One sample (87-252b) had an extremely low recovery, and produced a date unlikely in the context of the sample set. Although error analysis usually allows for this, the possibility of low levels of cross-contamination or reagent effects suggested that this result should be disregarded.

Table 3.2 Preliminary Results of U-Th analysis

SAMPLE	% residue	[U] ppm	230Th/234U	σ	234U/238U	σ	Age (kA)	(+)	(-)	234U/238U(t=0)	σ	232Th/234U	σ	
87-06-019A	8.2	13.2	0.7432	0.0109	2.0745	0.0279	125.9	3.4	3.2	2.528	0.034	0.0664	0.0016	Three different
87-06-019B	8.3	14.7	1.1398	0.0127	2.0058	0.0200	378.7	29.4	24.1	3.899	0.039	0.0302	0.0003	specimens of sample
87-06-019C	19.9	23.5	1.0331	0.0220	2.1700	0.0260	247.7	18.1	15.8	3.340	0.040	0.0510	0.0020	87-06-019
87-014-32c	33.8	11.7	1.0070	0.0200	2.3160	0.0350	228.6	13.4	12.1	3.490	0.050	0.0730	0.0020	Mixed specimens?
87-014-32c	34.1	12.0	0.9850	0.0220	2.3160	0.0230	216.2	13.0	11.8	3.410	0.030	0.0720	0.0030	
87-033a	13.3	15.2	1.0520	0.0220	2.0720	0.0220	268.4	20.6	17.8	3.270	0.030	0.0240	0.0010	Mixed specimens?
87-033a	10.5	14.8	1.0770	0.0220	2.0530	0.0210	291.6	24.9	20.9	3.380	0.030	0.0320	0.0010	
87-015-34c	23.4	3.4	1.4225	0.0178	1.6428	0.0312	xs Th					0.3400	0.0080	
87-015-34c	22.9	3.2	1.1523	0.0176	1.5858	0.0172	xs Th					0.3989	0.0083	
87-017-38b	8.9	17.7	1.0560	0.0120	2.1580	0.0190	267.5	10.9	10.0	3.446	0.030	0.0240	0.0010	Mixed specimens?
87-017-38b	8.3	17.3	1.0630	0.0130	2.2000	0.0210	271.3	12.1	11.1	3.561	0.034	0.0250	0.0010	
87-024-48c	21.0	14.8	0.9420	0.0120	2.6980	0.0280	189.6	5.6	5.4	3.884	0.040	0.0360	0.0010	Mixed specimens?
87-024-48c	20.2	15.8	0.9140	0.0090	2.5270	0.0240	179.7	4.0	3.9	3.520	0.030	0.0330	0.0010	
87-025-51c	23.3	45.0	1.0017	0.0087	1.7105	0.0088	249.2	7.4	7.0	2.426	0.013	0.0335	0.0003	
87-025-51c	22.0	44.0	0.7477	0.0154	1.7232	0.0082	130.4	4.9	4.7	2.041	0.010	0.0167	0.0016	Low Th, spectral shif
87-031-66b	9.3	16.0	1.0330	0.0130	1.9710	0.0170	258.4	11.4	10.4	2.999	0.026	0.0280	0.0010	Mixed specimens?
87-031-66b	9.5	15.9	1.0400	0.0080	1.9670	0.0110	264.1	7.3	6.9	3.023	0.017	0.0280	0.0010	
87-67a	6.1	64.0	1.2549	0.0136	1.1459	0.0043	infinite					0.0181	0.0006	
87-67a	5.9	64.9	1.1340	0.0085	1.1170	0.0040	infinite					0.0160	0.0003	
87-74a	7.7	14.9	1.0812	0.0034	2.0067	0.0110	299.0	4.4	4.2	3.322	0.018	0.0294	0.0006	
87-74a	7.8	14.6	1.0736	0.0090	2.0432	0.0102	289.0	9.6	8.9	3.340	0.017	0.0261	0.0007	
87-036-76b	9.0	15.0	1.0820	0.0240	2.0660	0.0260	295.7	28.5	23.4	3.440	0.040	0.0260	0.0010	
87-036-76b	7.8	15.6	1.0840	0.0250	2.0070	0.0240	301.9	31.7	25.5	3.340	0.040	0.0330	0.0010	
87-85a	27.1	21.1	0.6578	0.0042	2.6868	0.0116	101.5	1.1	1.0	3.240	0.014	0.0372	0.0005	
87-85a	27.5	20.3	0.6869	0.0069	2.6868	0.0279	108.4	1.8	1.7	3.283	0.034	0.0409	0.0005	

Table 3.2 (cont'd) Preliminary results of U-Th analysis

SAMPLE	%	[U]	230Th	σ	234U	σ	Age	(+)	(-)	234U	σ	232Th	σ	
	residue	ppm	234U		238U		(kA)			238U(t=0)		234U		
87-95a	6.4	23.2	1.0138	0.0110	1.3926	0.0096	294.1	15.9	14.0	1.893	0.013	0.0278	0.0003	Spectral shift
87-95a	6.5	14.8	1.0523	0.0116	2.0412	0.0147	270.2	10.9	10.0	3.216	0.023	0.0251	0.0008	
87-96a	8.1	17.2	0.7680	0.0092	2.4136	0.0164	130.8	2.8	2.7	3.038	0.021	0.0183	0.0007	
87-96a	7.8	41.3	0.7508	0.0087	1.0074	0.0064	150.3	4.2	4.0	1.011	0.006	0.0138	0.0005	Spectral shift
87-61-130b	20.9	11.1	0.7694	0.0059	2.0346	0.0112	133.9	1.9	1.9	2.504	0.014	0.1009	0.0013	
87-61-130b	21.1	11.2	0.7643	0.0063	2.0435	0.0135	132.3	2.0	2.0	2.510	0.017	0.0980	0.0013	
87-69-140b	9.2	14.5	0.7267	0.0098	2.7424	0.0176	118.1	2.6	2.6	3.424	0.022	0.0187	0.0009	
87-69-140b	7.7	13.2	0.7132	0.0051	2.8766	0.0167	114.3	1.3	1.3	2.877	0.017	0.0170	0.0004	
87-82-153b	6.6	11.5	1.0298	0.0146	2.7923	0.0186	232.1	9.1	8.5	4.429	0.030	0.0229	0.0013	
87-85-157b	28.3	21.4	0.6672	0.0044	2.5608	0.0121	104.0	1.1	1.1	3.088	0.015	0.0427	0.0005	
87-85-157b	28.0	20.3	0.6846	0.0049	2.6261	0.0128	108.0	1.2	1.2	3.199	0.016	0.0438	0.0006	
87-86-160c	25.9	21.9	1.0923	0.0115	1.8632	0.0099	325.0	17.0	15.0	3.141	0.017	0.0445	0.0012	
87-86-160c	26.5	18.4	1.0991	0.0069	1.8139	0.0091	340.5	11.9	10.9	3.108	0.016	0.0455	0.0005	
87-91-189b	6.8	15.2	1.0888	0.0126	1.9314	0.0170	313.6	17.4	15.3	3.238	0.029	0.0278	0.0003	
87-91-189b	6.9	14.9	1.0657	0.0119	1.9979	0.0191	284.5	12.9	11.7	3.210	0.031	0.0251	0.0006	
87-105-204	34.2	12.7	0.6853	0.0060	2.6770	0.0234	108.0	1.5	1.5	3.268	0.029	0.0360	0.0009	
87-105-204	36.1	12.9	0.6319	0.0073	2.6697	0.0241	95.7	1.7	1.6	3.182	0.029	0.0397	0.0011	
87-252b	31.3	9.1	0.4977	0.0140	3.2086	0.0707	68.5	2.6	2.5	3.675	0.081	0.0650	0.0041	V. low resn, recovery
87-253a	13.5	22.7	0.6060	0.0130	2.4220	0.0400	90.7	2.9	2.8	2.830	0.050	0.0210	0.0010	/and spectral shift
87-253a	10.5	22.0	0.6530	0.0130	2.4670	0.0100	101.0	3.1	3.0	2.950	0.010	0.0230	0.0010	Lower % residue
87-253a	13.0	24.1	0.5910	0.0140	2.4070	0.0310	87.6	3.0	3.0	2.800	0.040	0.0180	0.0010	
87-253a	13.3	22.6	0.5910	0.0140	2.4470	0.0370	87.5	3.0	3.0	2.850	0.040	0.0170	0.0010	
87-254b	7.6	21.4	0.6588	0.0073	2.5409	0.0149	102.1	1.7	1.7	3.050	0.018	0.0145	0.0004	
87-256b	11.2	12.0	1.0426	0.0154	2.2308	0.0383	254.1	13.1	11.8	3.519	0.060	0.0418	0.0010	

Table 3.2 (cont'd) Preliminary results of U-Th analysis

SAMPLE	%	[U]	230Th	σ	234U	σ	Age	(+)	(-)	234U	σ	232Th	σ	
	residue	ppm	234U		238U		(kA)			238U(t=0)		234U		
87-L1W3	21.8	2.8	1.0048	0.0064	2.3403	0.0118	226.7	4.1	3.9	3.526	0.018	0.1384	0.0021	
87-L1W3	22.2	2.2	1.0114	0.0107	2.3458	0.0281	230.5	7.3	6.9	3.563	0.043	0.1561	0.0030	
87-L1W4	14.6	2.9	1.0704	0.0070	2.2900	0.0167	273.4	6.6	6.3	3.770	0.027	0.0999	0.0015	V.v. low resn
87-L1W4	14.7	3.1	0.9979	0.0049	2.4234	0.0146	221.0	3.1	3.0	3.640	0.022	0.0991	0.0010	
87-L26	18.0	2.1	1.0739	0.0072	2.4048	0.0195	271.8	6.6	6.3	4.002	0.032	0.1566	0.0018	
87-L26	17.8	2.0	1.1151	0.0127	2.3997	0.0324	309.5	15.9	14.2	4.324	0.058	0.1456	0.0038	
87-L28	15.1	18.9	1.0233	0.0031	2.6282	0.0054	231.5	1.9	1.9	4.108	0.008	0.0137	0.0002	
87-S13	27.1	28.8	1.5221	0.0086	3.1299	0.0098	xs Th					0.0108	0.0002	
87-S13	26.4	29.7	1.8515	0.0111	3.0856	0.0110	xs Th					0.0116	0.0002	
87-S30	21.3	25.8	1.5231	0.0110	3.0275	0.0146	xs Th					0.0100	0.0002	
87-S30	20.6	25.0	1.5369	0.0064	3.0030	0.0079	xs Th					0.0116	0.0002	
87-S37	21.6	21.6	1.1124	0.0043	2.9450	0.0083	286.3	3.9	3.8	5.329	0.015	0.0157	0.0002	
87-S37	21.7	21.1	1.1119	0.0033	3.0226	0.0076	283.8	2.9	2.9	5.471	0.014	0.0153	0.0001	

Correction for detrital thorium.

Several samples showed high ^{232}Th/^{234}U ratios, suggesting contamination of the sample by detrital thorium. It could be expected that any ^{232}Th in the detritus was accompanied by ^{230}Th, and thus the apparent age may be in error. This can be corrected for by the methods outlined in Chapter One (and Schwarz and Latham,1989).

A plot of ^{230}Th/^{232}Th vs ^{234}U/^{232}Th for a suite of coeval samples will have a slope equalling the ^{230}Th/^{234}U ratio of the samples, and a y-intercept equalling the initial ^{230}Th/^{232}Th ratio of the detrital component of the sample. Table (3.3) gives those samples having a ^{230}Th/^{232}Th ratio less than 20 (above which any correction should be negligible). Parameters given are for averaged data in the case of duplicates.

Table 3.3 Samples having ^{230}Th/^{232}Th < 20

Sample	^{230}Th/^{232}Th	Age	
87-105-204b	17.3773	101.9	87-254b (102.1kA) used as additional data point to constrain slope error.
87-85a	17.1969	105.0	
87-85-157b	15.6097	106.0	
87-06-019B	11.1928	125.9	87-69-140b (116.2kA) used as additional data point to constrain slope error.
87-61-130b	7.7075	133.1	
87-014-32c	13.7379	222.4	No coeval samples of high ^{230}Th/^{232}Th. Use plot of samples of similar age to obtain $(^{230}\text{Th}/^{232}\text{Th})_0$ value.
87-015-34c	3.4842	infinite	^{230}Th/^{234}U = 1.2874. A correction would still give an infinite age.
87-L1W3	6.8439	228.6	
87-L1W4	10.0696	221.0	
87-L26	7.2435	290.7	No coeval samples of high ^{230}Th/^{232}Th. Use $(^{230}\text{Th}/^{232}\text{Th})_0$ ratio of 87-L1W3/L1W4 plot to obtain correction.

The relevant graphs for each correction are given in figure (3.3 a-g). Although detrital uranium was not expected to be significant, given that much of the detritus was clay (binds Th well, but not U), similar corrections for detrital uranium in the same samples are also given in figure (3.3 a-g).

Figure 3.3a 230Th/232Th vs 234U/232Th

for samples 87-105-204b, 254b, 85a, 85-157b

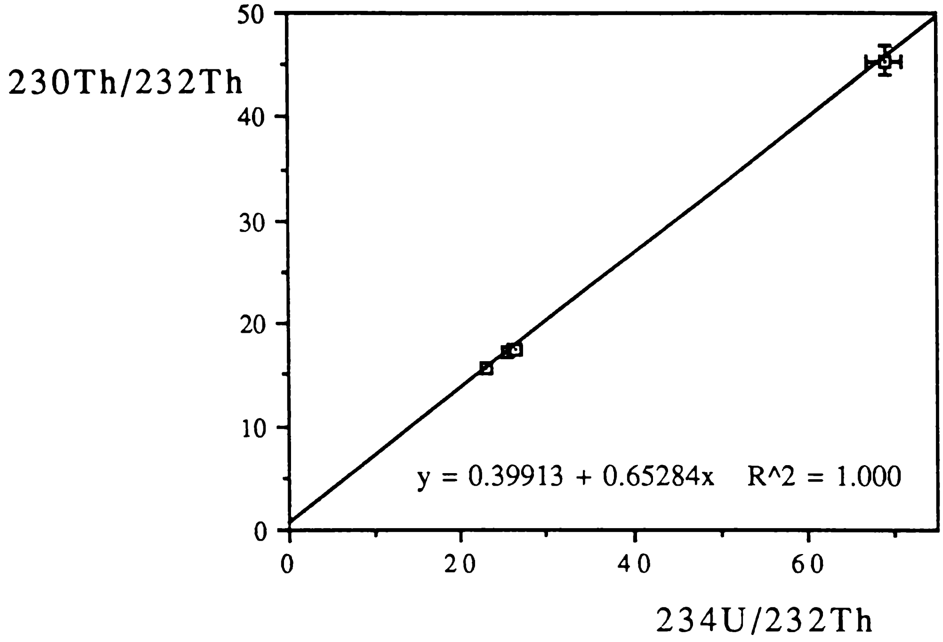


Figure 3.3b 234U/232Th vs 238U/232Th

for samples 87-105-204b, 254b, 85a, 85-157b

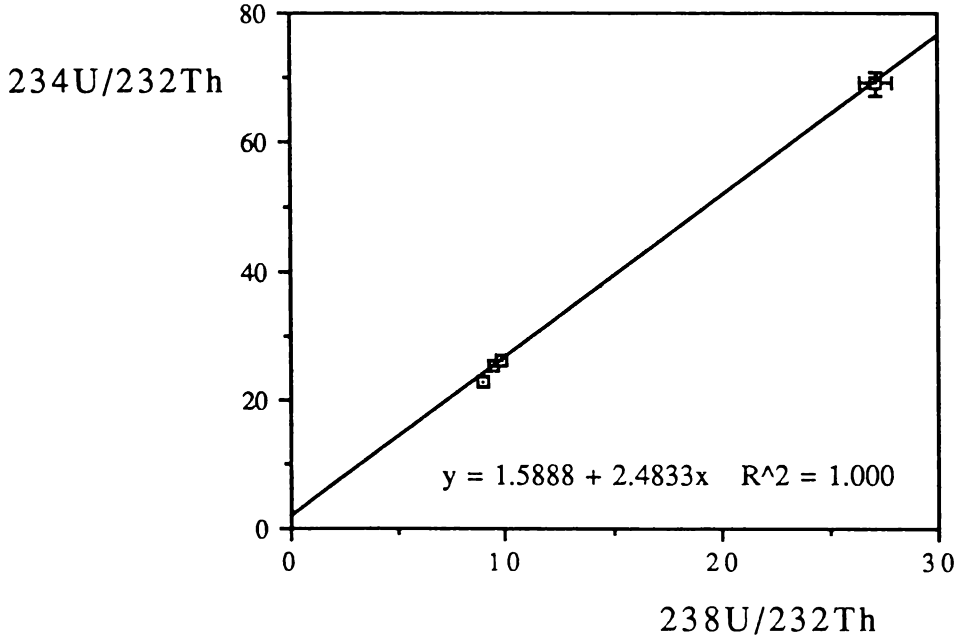


Figure 3.3c 234U/232Th vs 238U/232Th

for samples 87-06-019A, 61-130b, 69-140b

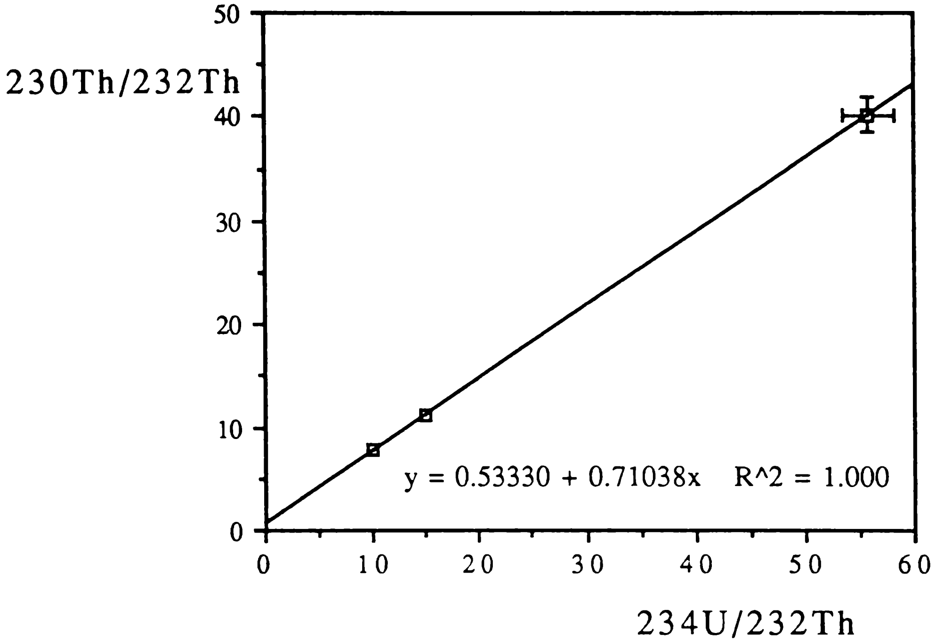


Figure 3.3d 234U/232Th vs 238U/232Th

for samples 87-06-019A, 61-130b, 69-140b

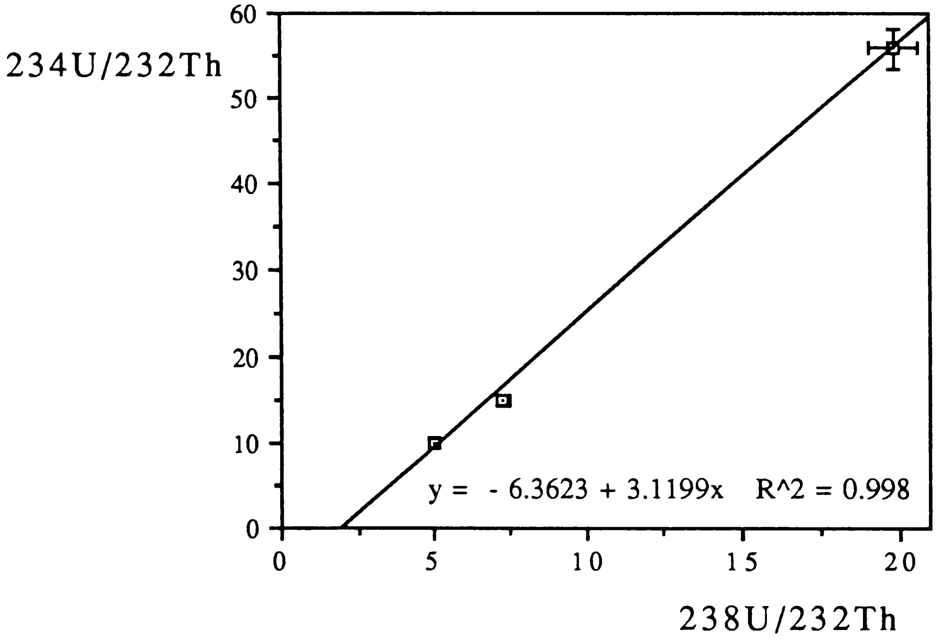


Figure 3.3e 230Th/232Th vs 234U/232Th

for samples 87-014-32c, 82-153b, 33a, 06-019C, 025-51c, 256b
(all 230Th/232Th ratios adjusted to equivalent ages)

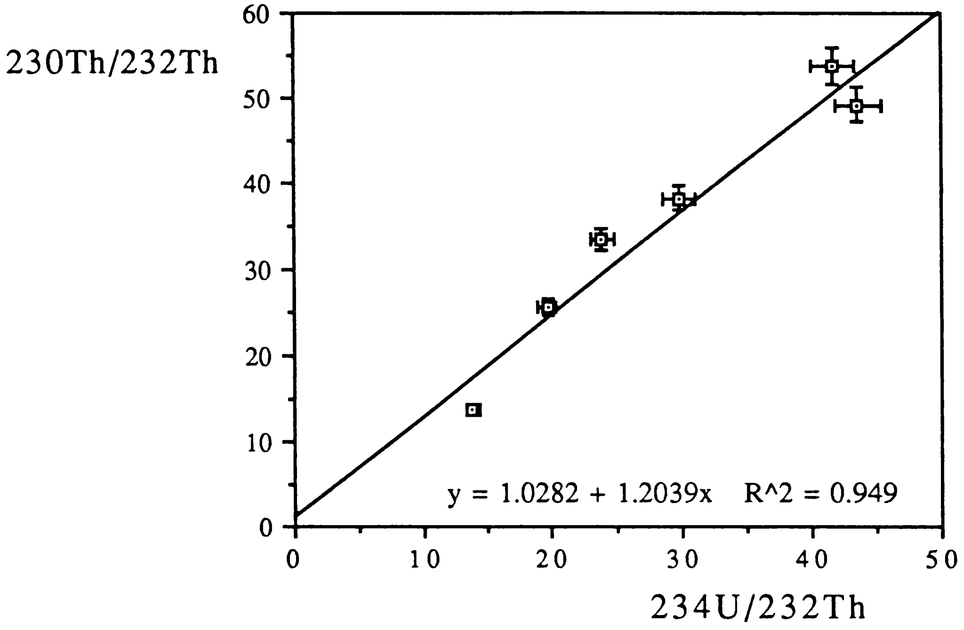


Figure 3.3f 230Th/232Th vs 234U/232Th

for samples 87-L1W3, L1W4

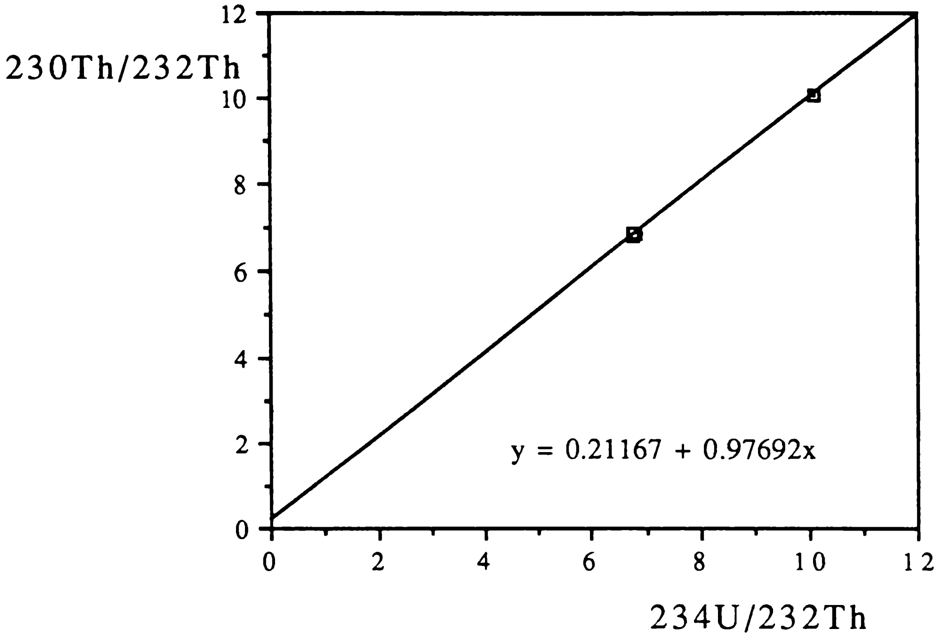
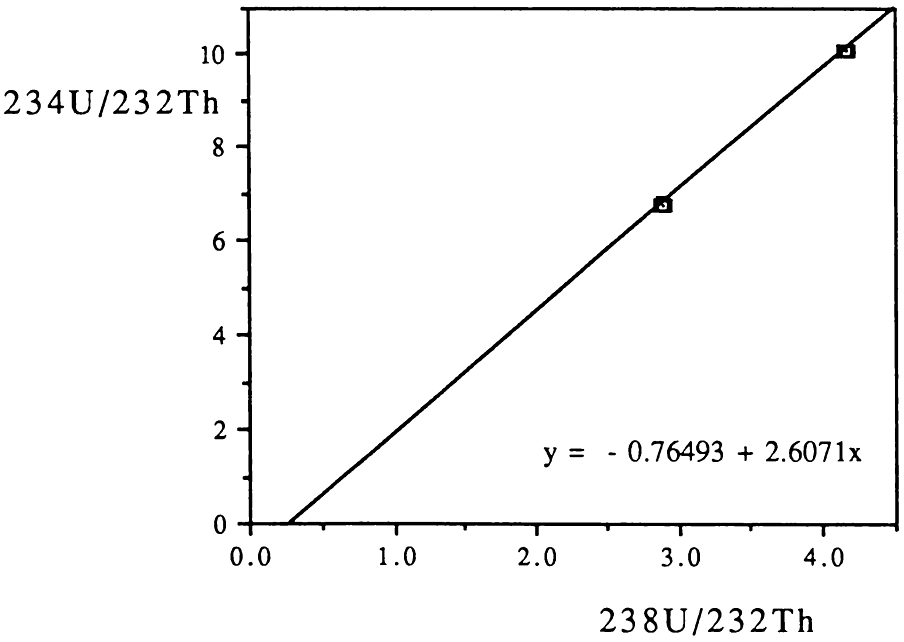


Figure 3.3g 234U/232Th vs 238U/232Th

for samples 87-L1W3, L1-W4



Results of corrections for detrital thorium and uranium are given in table (3.4)

Table 3.4

Selected results corrected for detrital contributions

Sample	Raw Age	Figure	Graph equations **	Corrected age
87-105-204b	101.9	3.3a	Th: $y= 0.39914 + 0.65283x$ ($R^2=1.00$)	100.9 kA
87-85a	105.0	3.3b	U: $y= 1.5887 + 2.4834x$ ($R^2=1.00$)	
87-85-157b	106.0			
87-06-019B	125.9	3.3c	Th: $y= 0.33330 + 0.69658x$ ($R^2=1.00$)	112.9 kA
87-61-130b	133.1	3.3d	U: $y= -6.3623 + 3.1199x$ ($R^2=0.998$)	
87-014-32c	222.4	3.3e	Th: $y= 1.0282 + 1.2039x$ ($R^2=0.949$)	185.5kA
			Let $(230\text{Th}/232\text{Th})_0 = 1.0282$	
87-015-34c	"infinite"		not corrected, too much xs Th	"infinite"
87-L1W3	228.6	3.3f	Th: $y= 0.21167 + 0.9769x$	206.8kA
87-L1W4	221.0	3.3g	U: $y= -0.76493+ 2.6071x$	
87-L26	290.7		Let $(230\text{Th}/232\text{Th})_0 = 0.212$	263.0

** See Chapter One:.

Th = slope equation for plot of $^{230}\text{Th}/^{232}\text{Th}$ vs $^{234}\text{U}/^{232}\text{Th}$.

U = slope equation for plot of $^{234}\text{U}/^{232}\text{Th}$ vs $^{238}\text{U}/^{232}\text{Th}$.

The method used for sample 87-014-32c was to take a set of samples of nearest age that were likely to have a similar detritus source, namely those samples of ages 230-255kA (87-82-153b, 33a, 06-019, 25-51c, and 256b). The $^{230}\text{Th}/^{232}\text{Th}$ ratios for these samples were adjusted to reflect the age differences between each sample and sample 87-014-32c

i.e. $(^{230}\text{Th}/^{232}\text{Th})_{\text{corr}} = (^{230}\text{Th}/^{232}\text{Th})_{\text{orig}} /\exp(-\lambda(t(\text{kA})-222.4))$

The adjusted $^{230}\text{Th}/^{232}\text{Th}$ ratios were plotted against the $^{234}\text{U}/^{232}\text{Th}$ ratios to give the $(^{230}\text{Th}/^{232}\text{Th})_0$ ratio of 87-014-32c, from which the age was recalculated.

Final Results.

After eliminating the dubious results and excess thorium results, averaging the duplicated results (by averaging $^{230}Th/^{234}U$ ratios and recalculating ages), and correcting for detrital ^{230}Th and ^{234}U, a final results list was obtained. This is given in table (3.5), along with the other major parameters useful in further analysis - the uranium concentration and the $^{234}U/^{238}U$ ratio at the time of formation of the sample.

Table 3.5 Final results of U-Th analysis.

Sample	no. of samples	[U] (ppm)	Age (kA)	(+)	(-)	$\frac{^{234}U(t=0)}{^{238}U}$	s
87-253a	3	23.1	88.6	3.0	2.9	2.83	0.04
87-105-204b	2	12.8	100.9	1.6	1.6	2.97	0.03
87-85a	2	20.7	100.9	1.3	1.3	2.97	0.02
87-85-157b	2	20.9	100.9	1.1	1.1	2.97	0.02
87-254b	1	21.4	102.1	1.7	1.7	3.05	0.02
87-06-019A	1	13.2	112.9	2.6	2.6	3.91	0.03
87-61-130b	2	11.2	112.9	1.5	1.4	3.91	0.02
87-69-140b	2	13.9	116.2	2.0	1.9	3.50	0.02
87-96a	1	17.2	130.8	2.8	2.7	3.04	0.02
87-024-48c	2	15.3	184.5	4.8	4.6	3.70	0.04
87-L1W3	2	2.5	206.8	4.7	4.6	3.86	0.02
87-L1W4	1	3.1	206.8	2.6	2.6	3.86	0.02
87-L28	1	18.9	231.3	1.9	1.9	4.11	0.01
87-82-153b	1	11.5	232.1	9.1	8.5	4.43	0.03
87-014-32c	2	11.9	241.8	16.1	14.3	3.59	0.04
87-025-51c	1	45.0	249.2	7.4	7.0	2.43	0.01
87-06-019C	1	23.5	247.7	18.1	15.8	3.35	0.04
87-256b	1	12.0	254.1	13.2	11.9	3.50	0.06
87-031-66b	2	16.0	261.2	9.4	8.7	3.01	0.02
87-017-38b	2	17.5	269.4	11.5	10.6	3.50	0.03
87-95a	1	14.8	270.2	10.9	10.0	3.22	0.02
87-033a	2	15.2	279.5	22.6	19.2	3.32	0.04
87-S37	2	21.4	285.1	3.4	3.3	5.40	0.01
87-L26	1	2.1	290.7	11.3	10.3	4.16	0.05
87-74a	2	14.8	293.9	7.1	6.7	3.33	0.02
87-91-189b	2	15.1	298.2	15.0	13.4	3.22	0.03
87-036-76b	2	15.3	298.7	30.1	24.4	3.39	0.04
87-86-160c	2	20.2	332.4	14.7	13.2	3.12	0.02
87-06-019B	1	14.7	378.7	29.4	24.0	3.90	0.04
87-67a	2	64.5	infinite				

Full results are given in Appendix C, with some additional dating carried out reported in Appendix B. Original sample record sheets are given in Appendix D

Additional Results

In addition to those above, a further set of results was available. These were prepared by Dr C. Hendy (Univ. of Waikato) at the Lamont - Doherty Geological Observatory. Although one sample was analysed in common (87-254b), they were apparently different specimens of the sample - thus no cross- calibration of the methods is available. However, samples 87-253b and 253a were different specimens samples from the same site, and gave similar ages, suggesting no major disparity between the analyses. Spike nuclide ratios for both sets of samples were, however, determined with some care. Both data sets are therefore likely to be 'cross-comparable'.

Since the second set of results are from the same sample collection as those prepared here, they have been included for further discussion. The additional results are given in table (3.6). Uranium concentrations were not available.

Table 3.6 Additional U-Th results

Sample	Age (kA)	(+)	(-)	$\frac{234}{238}$	s (t=0)
87-05c	257	50	36	2.42	0.01
87-011	190	10	8	1.24	0.01
87-012	284	14	12	3.26	0.02
87-013c	237	48	34	2.38	0.01
87-087	84	2	2	2.38	0.02
87-087c	97	3	3	3.11	0.04
87-116	177	7	7	3.64	0.03
87-204	178	6	6	3.76	0.02
87-253b	81	4	3	2.84	0.03
87-256b	115	3	3	2.75	0.02
87-257	216	9	9	2.63	0.01
87-L1-W2	125	12	11	3.17	0.13

Chapter 4.

Analysis of Results.

Introduction.

The Taylor Valley.

The samples dated came from the Taylor Valley, one of the Dry Valleys of the Antarctic in the McMurdo Sound region (figure (4.1)). The Taylor Valley runs through the Trans-Antarctic mountains, from the East Antarctic Ice Sheet to the Ross Ice Shelf, and is kept largely ice-free by katabatic winds descending the valleys to the sea. There are several major basins along the length of the valley, of which the "Bonney Basin" is of interest here. The Taylor Glacier, flowing out of the East Antarctic Ice Sheet currently terminates in the Bonney Basin, as do several alpine glaciers on the walls of the valley. Lake Bonney (7km long by 1km wide) occupies part of the basin, receiving meltwater from the Taylor Glacier and alpine glaciers. In addition the valleys contain many deposits assigned to earlier expansions of the Taylor Glacier, and to paleo-lacustrine deposits. Throughout the valley floor thin fragments of limestone (and other lacustrine deposits) are found incorporated in glacial drift. $^{18}O/^{16}O$ determinations on these have been used to distinguish between carbonates deposited from waters derived from the East Antarctic Ice Sheet via the Taylor Glacier ($\delta^{18}0 \approx -42$ per mille) and those derived from local alpine glaciers ($\delta^{18}0 \approx -34$ per mille) (Hendy (1979)). Most of the published results indicate that the carbonate clasts have been derived from the Taylor Glacier. In addition a series of strand lines and moraines on the walls of the basin attest to former limits of glaciation.

Quaternary history of the Taylor Valley.

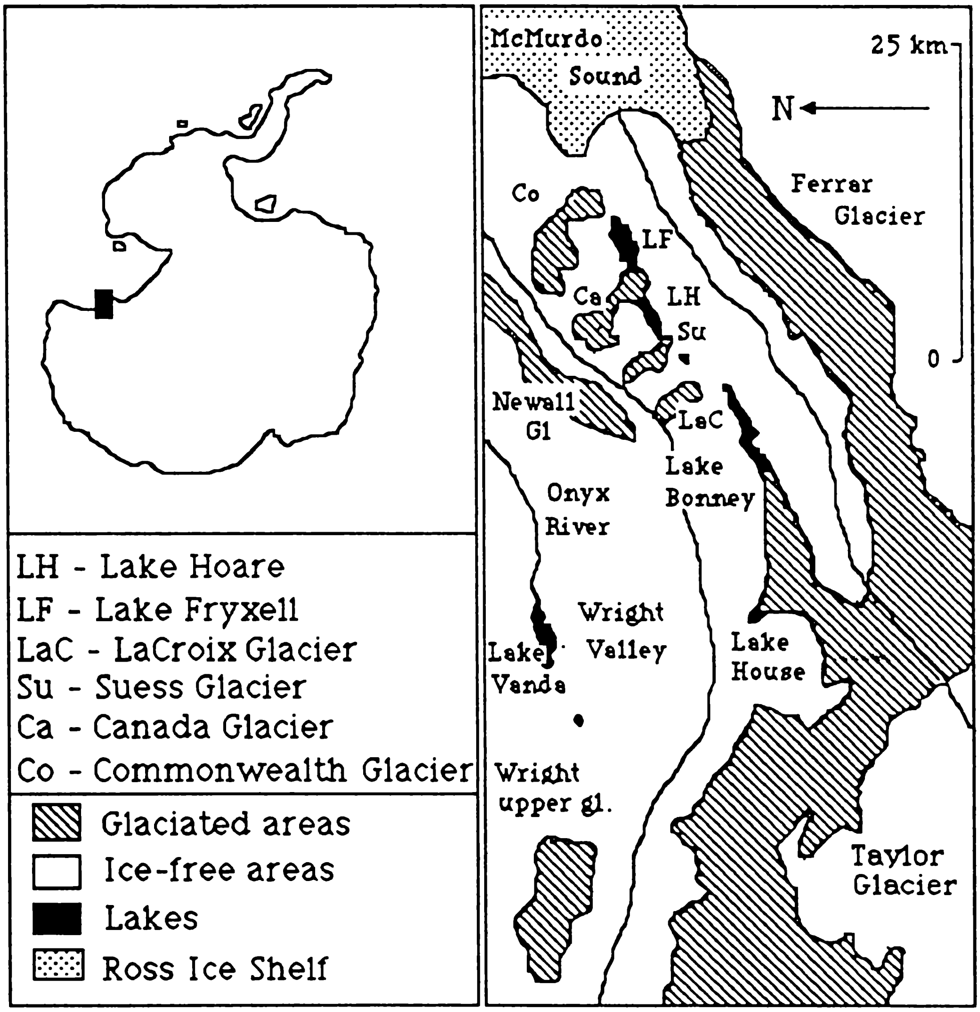
The Taylor Valley is a typical U-shaped glacial valley carved through the TransAntarctic Mountains by an outlet glacier from the interior of the continent. Drilling into the sediments at the eastern end of the valley has yielded fjordal drifts of Miocene age beneath numerous poorly defined younger terrestrial drifts, presumably deposited by glaciers which were cold-based, and doing little or no active cutting of the valley floor. Many of the upper drift sheets contain basaltic lithologies derived from the McMurdo Volcanics, including kenyite, which is only known to outcrop on Ross Island; while the deeper drifts contain lithologies of continental origin. These suggest that the valley floor has been occupied by glaciers of two different origins, namely the East Antarctic Ice Sheet and McMurdo Sound (Robinson, 1985).

Morphology of the valley floor shows numerous subtle glacial/proglacial features, including moraines surrounding the alpine glaciers, a set of at least four drift sheets of increasing age enclosing the Taylor Glacier, and a extensive drifts sheet originating from McMurdo Sound. The most recent of these is also associated with lacustrine features (shorelines, deltas, silt, algae, and drop structures) filling the valley from the Frxyell Basin to the Taylor Glacier. Dating of algae within these sediments reveal that it was an Isotope Stage 2 (25,000 -12,000 yrs old) glaciation. Further to the south, Judd (1986) has found, proglacial to icesheets in McMurdo Sound, sediments dating Isotope Stage 2 (25,000 -12,000 yrs old) and Isotope Stage 6 (135 - 185,000 yrs) in the Marshall Valley.

Clayton-Greene (1989) has found similar Isotope Stage 2 sediments in the Miers Valley. Denton (1989) has demonsrated that these drifts have been caused by the Ross Ice Shelf grounding on the continental shelf of the Ross Sea, flowing around Ross Island into McMurdo Sound and finally terminating in the glacial valleys opening into McMurdo sound. The last such glaciation has been named the Ross Sea Glaciation.

At the upper end of the Taylor Valley, as suggested above, there is evidence for advances of the Taylor Glacier (an outlet to the McMurdo Dome of the East Antarctic Ice Sheet) down into the valley. Pewe (1962) first described the drift sheets and assigned them to four glacial advances; representing expansion of the East Antarctic Ice Sheet during glacial times. He correlated these with the four European Pleistocene glaciations known at the time. Lacustrine deposits were assigned to interglacial periods. Denton et al (1971) assigned the earlier drift sheets on the basis of the K-Ar chronology of lava flows separating the drift sheets. Taylor V, the oldest glaciation was placed at older than 3.5 Myr, at which time

Figure 4.1 Map of the Taylor Valley, Antarctica



the Taylor IV glaciation began. The Taylor III glaciation was dated to at least 1.6 to 2.1 Myr ago. Denton et al (1970) also suggested that the glacial expansions of the Taylor Glacier were out of phase with those of the Ross Sea Ice Shelf (and local alpine glaciers).

The deposits of the younger Taylor Glaciations (the Bonney or, Taylor II, Drift) were dated by Hendy et al (1979), on the basis of the U-Th chronology of limestones found in the western end of the Bonney Basin.*In situ* deposits gave many ages of around 87 - 100 kA, with some 70 - 75 kA samples farthest to the west (upper end of the valley). A few samples gave ages of 120kA, assigned to apossible earlier expansion of the lake (these were assigned to limestones formed in water from the Taylor Glacier, on the basis of oxygen isotope data). Clast and lag deposits suggested lake expansions at 190 - 200 kA (oxygen isotope data suggesting lakes of both alpine and Taylor Glacier origin), and at 300 ± 40 kA (Taylor Glacier expansion). The advance of the Taylor Glacier and alpine glaciers was suggested to tbe synchronous.

Hendy et al (1979) suggested that these deposits were due to thickening of the East Antarctic Ice Sheet causing ice to flow out down the Taylor valley. The 200 kA event appeared to be much less extensive than the 100 kA (Taylor II) event. The distribution of the samples yielding ages around 300kA suggested a very large expansion, possibly right down the valley to the sea (also Hendy (1979)). These expansions were correlated with global interglacial periods (Stages 5, 7, and 9 respectively).

Hendy et al (1979) inferred that during interglacial periods sea ice retreated and atmospheric moisture capacity increased, both causing an increase in precipitation on the interior of the East Antactic Ice Sheet. This outweighed the increase in ablation due to higher temperatures, causing a net advance of the Ice Sheet down the Taylor Valley. Since ablation also increased (although not as much as did accumulation), the proglacial lakes also expanded. As global glacial conditions took over, the precipitation rate decreased relative to the ablation rate, and the glacier retreated by attrition. This has been confirmed by recent ice-core studies (Jouzel et al, 1989) using the ^{10}Be record. They suggested that during the last glacial maximum (16000 yrs ago), the central East Antarctic Ice sheet was several hundred metres thinner than at present.

Further studies in the Arena Valley (off the upper Taylor Glacier) and in the upper Taylor Valley were based on cosmogenic ^{3}He decay in sandstones and granites from moraines (Brook et al, in press) suggested glacial expansion around 68 - 177kA (averaging 116kA), 95 - 280kA (averaging 210kA), 304 - 578kA (averaging 423kA) and 893 - 1550kA (averaging 1130kA).

Sample Description.

The samples analysed were collected during the austral summer of 1987-88 from the Bonney Basin. They are limestones precipitated by algae from lakes formerly in the area; and were collected either from the surface, from within pits dug in mounds on the valley floor, or from stratigraphic sections near the LaCroix and Suess glaciers. The general area was between Lake Bonney and the Suess Glacier outlet (figure 4.2a), and includes recollection from sites dated by Hendy et al (1979). Most came from the area of the valley floor in front of the terminus of the LaCroix glacier. The samples were typically plates ranging from 3 to 15 cm across, and from 1 to 2 cm thick (figure 4.2b). The high uranium and low thorium levels make them suitable for U-Th dating, as evidenced by the results presented. The samples also conform reasonably to the requirements of U-series dating, as discussed in Chapter 1. Post-depositional leaching or addition of critical nuclides is unlikely to have occurred, as the extremely low temperatures in the area preclude groundwater movement - the only reasonable vector for nuclide movement. High levels of ^{230}Th were almost certainly present in several samples at the time of formation, however this has been corrected for in most samples by the methods given in Chapters 1 and 3. Most samples showed no such need for correction.

Time line for sample age distribution.

The principal analysis of the samples dated is their temporal distribution. Samples show a distinct clustering around certain periods. The LaCroix (prefixed 87-L...) and Suess (prefixed 87-S...) section samples are presented separately, as they come from distinct sections exposed by meltwater streams from the respective glaciers. A separate assignment for these samples is also suggested

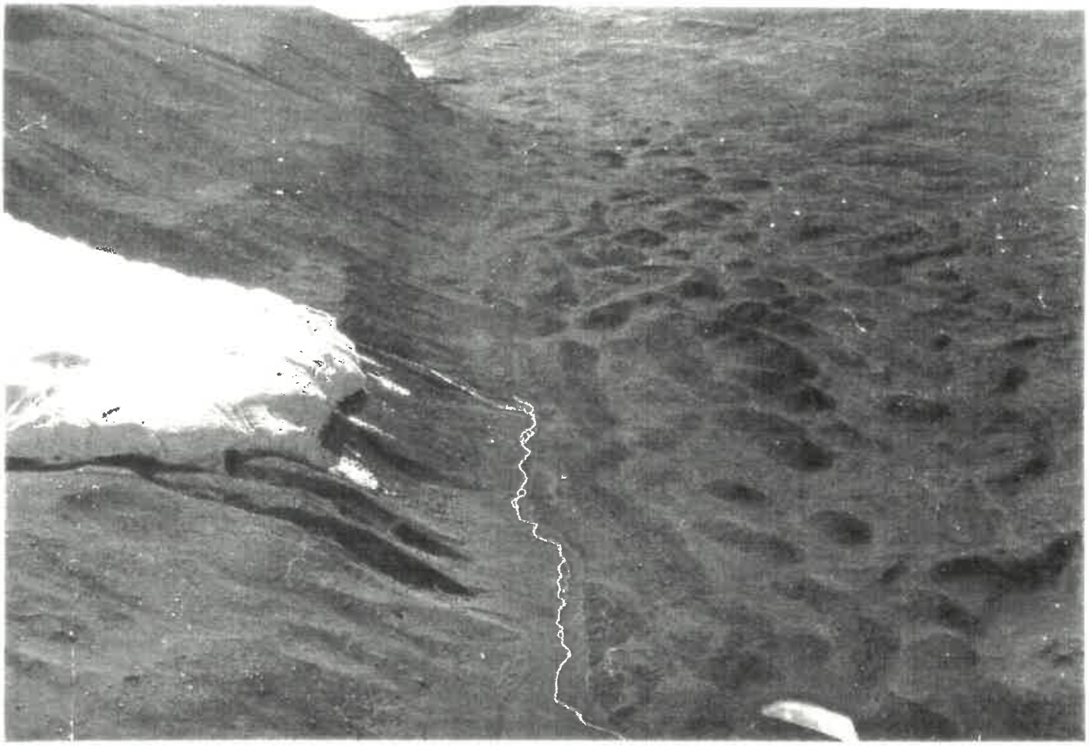


Figure 4.2a Taylor Valley floor and LaCroix Glacier area.
(main sample collection area)

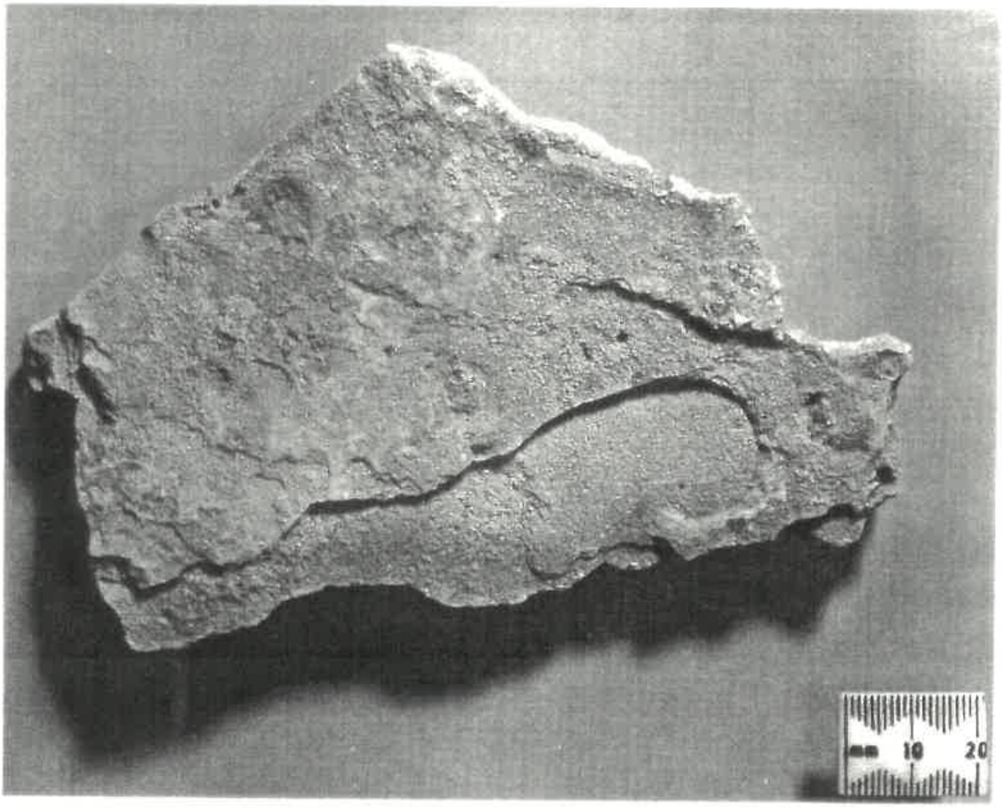


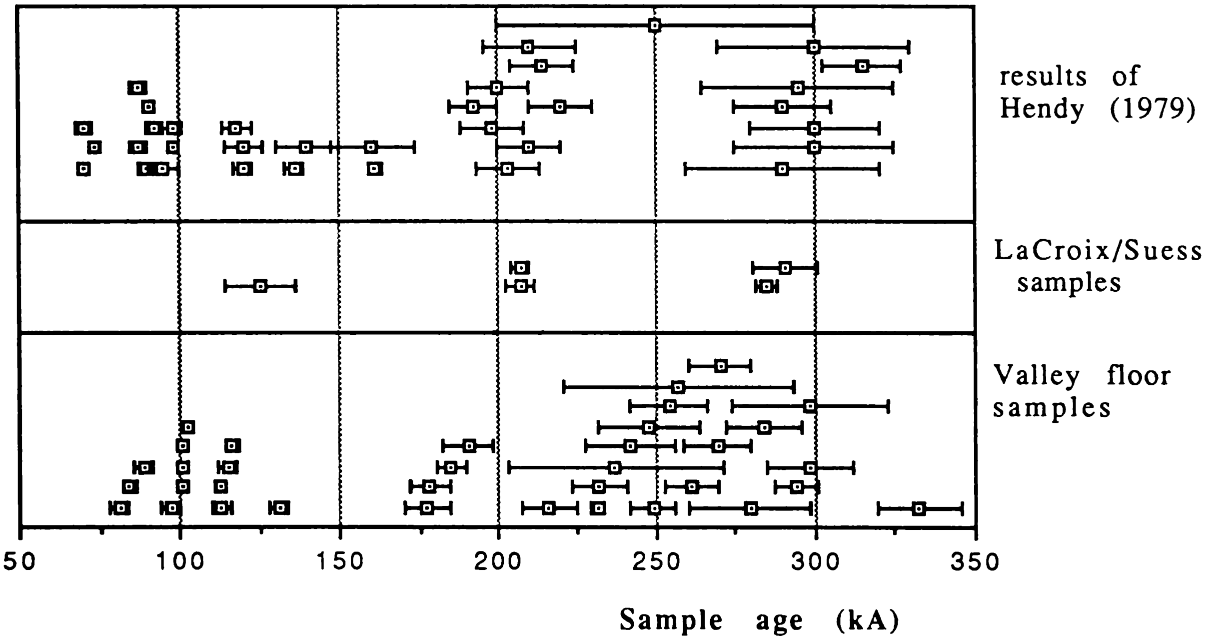
Figure 4.2b Typical lacustrine carbonate used for dating.

on the basis of their uranium concentrations (see below) (less than 4ppm, cf all others > 10 ppm). The initial $^{234}U/^{238}U$ ratios of the LaCroix and Suess samples are all greater than 3.80 (except 87-L1-W2, 3.17), whereas all others are lower then 4.0; 75% of them in the range 2.0 to 3.5.

Samples 87-L28 and 87-82-153b show parameters common to both data sets, with 87-82-153 having a $^{234}U/^{238}U$ ratio comparable to that of a LaCroix section sample, and 87-L28 a much higher uranium concentration than other LaCroix samples. The similar age of these samples, both around 232kA, makes their assignment difficult. The uranium concentration data is more convincing, and both are assigned to the bulk of the samples.

Time lines for the data sets are given in figure (4.3).

Figure 4.3 Time line for sample age distribution



There appear to be several clusters in the data. Definite events are evident at 80 - 130 kA and 175 - 190 kA for the main sample set, while the LaCroix/Suess Section samples show three distinct groups, at 125 kA (one sample), 206kA, and 285 -290 kA. The pattern for the bulk of the samples around 210 to 320 kA is more difficult to decipher. If 87-257 and 87-86-160c are left as an outliers, the rest of the dates fall between 230 kA and 300 kA. Although there are possible clusters around 242 - 261 kA (6 dates, 2 replicated), 269 -

270 kA (2 dates, 1 replicated), 279 - 284 kA (3 dates, 1 replicated) and 294 - 299 kA (3 dates, all replicated), it is also likely that the dates represent a single event from 240 to 300 kA ago, with the spread due to geochemical factors such as ^{230}Th adsorption or U mobility etc etc. These factors become increasingly important as the ^{230}Th/^{234}U ratio approaches secular equilibrium.

Uranium concentration and isotope ratio.

Uranium concentrations and initial ^{234}U/^{238}U ratios are plotted against age in figure (4.4). While no obvious distinguishinging trends are apparent, it is confirmed, as suggested above, that several samples have anomalous parameters relative to the bulk of the data. Samples 87-L26 (290.7 kA), L1-W4 (206.8 kA), and L1-W3 (206.8 kA) all have uranium concentrations an order of magnitude lower than rest of the samples, while 87-S37 has a much higher ^{234}U/^{238}U ratio than the other samples, and 87-025-51c and 87-67a (not plotted) have much higher uranium concentrations than the other samples. It is possible that these samples record extreme conditions with respect to the events recorded by the majority of the samples.

Figure 4.4 Uranium concn and initial^{234}U/^{238}U ratio vs age

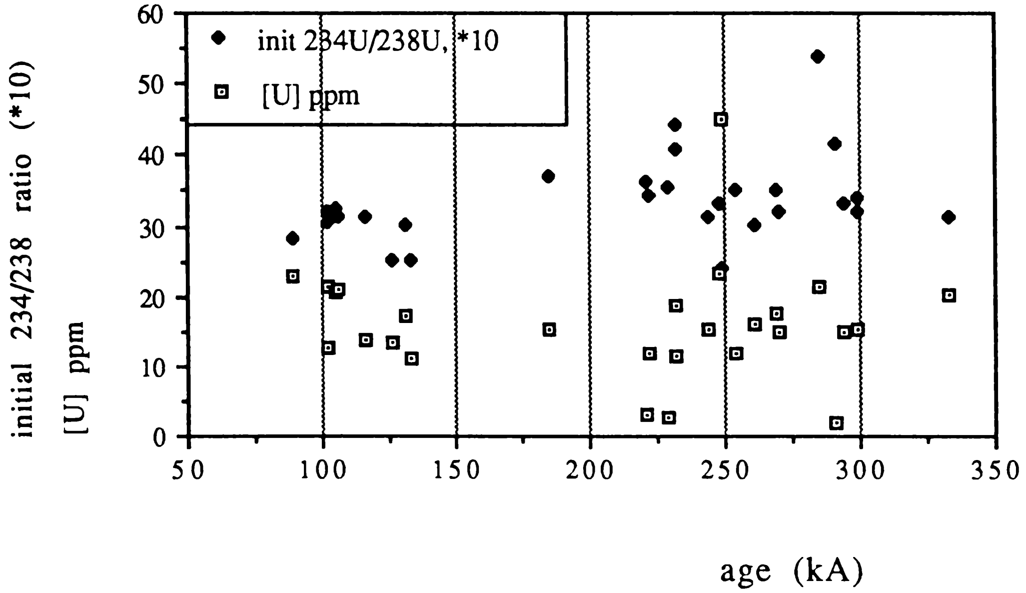
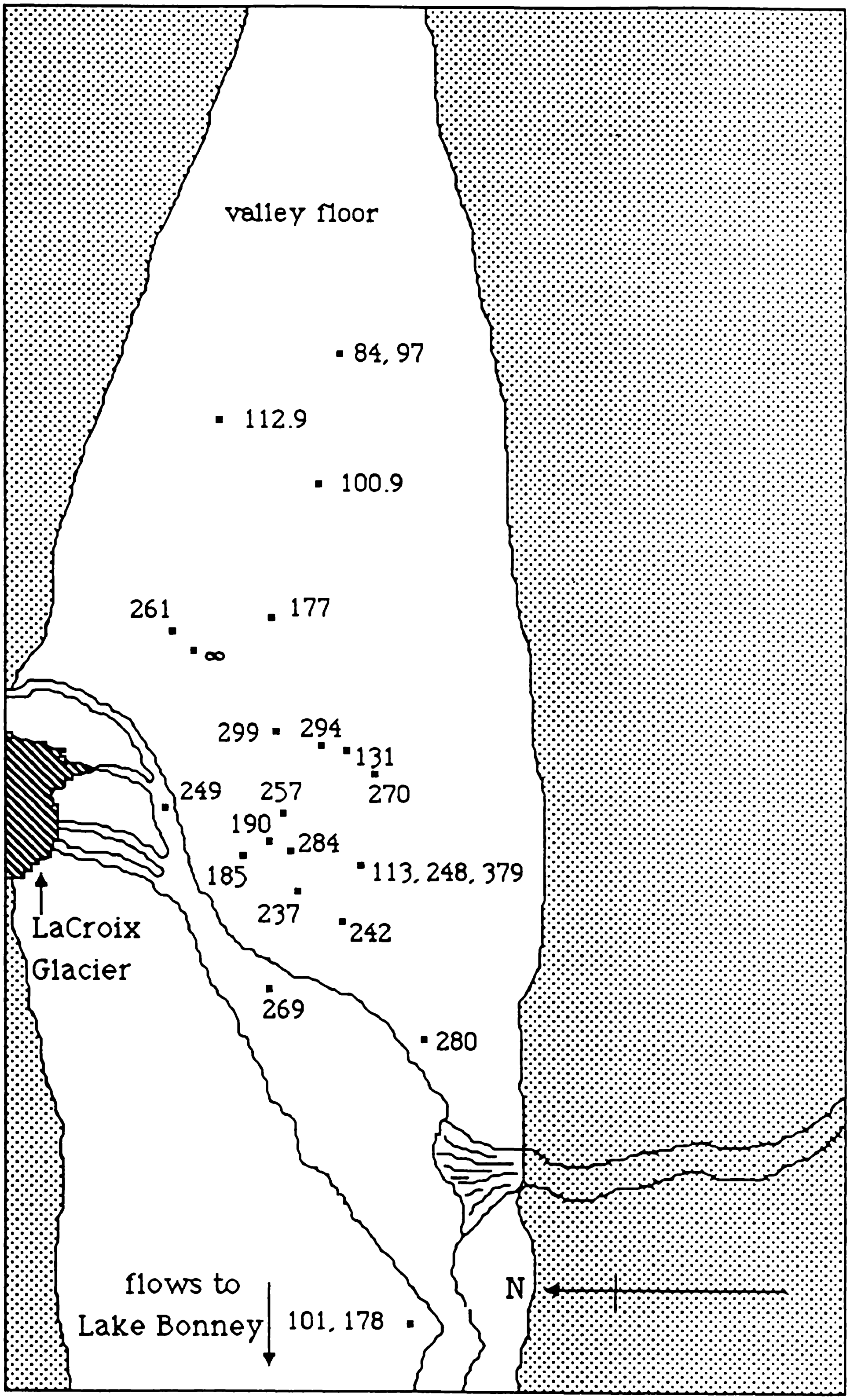


Figure 4.5 Sample Location by Age.



Geographical Distribution of Ages.

The sample ages were plotted with respect to their locations (figure 4.5). A number of samples were obtained outside of the area for which an aerial photograph was available. There is no marked pattern to the age distribution, suggesting that the Taylor Glacier has advanced through the area and ploughed up most of the samples and redeposited them over a wide area. There is, however, a grouping of younger ages at the eastern end of the sampling area. This suggests that the deposits of this age were generally distributed further east than previous glaciations, i.e the proglacial lake around Isotope Stage 5 was more extensive than that of the previous event (175 - 190 kA).

Oxygen Isotope Analysis.

Samples were also analysed for $\delta^{18}0$ content. As oxygen isotopes are fractionated between the hydrosphere and atmosphere, with a temperature-dependent degree of fractionation, it is possible to distinguish between carbonates precipitated from water from different sources (since there is a definable relationship between the $\delta^{18}0$ content of the water and that of the carbonate precipitated out). In the Antarctic region, a variety of $\delta^{18}0$ values have been noted for precipitation, snow and ice. Taking the Standard Mean Ocean Water standard (SMOW) as a reference, values of -40 to -55 per mille are found for current precipitation at the South Pole (Epstein et al 1963; Epstein et al, 1965); values of -40 to -42 per mille are found for the ice currently at the limit of the Taylor Glacier (Hendy et al,1979); -28 to -34 per mille is typical of the alpine glaciers in the Taylor Valley region (Hendy et al,1979); while the Ross Ice Sheet varies from 0 to -30 per mille (Hendy et al,1979). Subsequent analyses (Hendy, in press) have shown that lacustrine carbonates deposited during Isotope Stage 2 in Miers, Marshall and Taylor Valleys had been precipitated from waters with $\delta^{18}0$ values of -30 to -37 per mille (mean of -34), but those deposited in the Marshall valley during Isotope Stage 6 ranged between -38 and -47 per mille (mean -43). If such a lake had occuppied the Taylor Valley, it's carbonates would be difficult to distinguish from those deposited from Taylor Glacier water, but would tend to be slightly more negative. Morgan (1982) also showed that in general the Antarctic Ice Sheets display an increasing $\delta^{18}O$ value with altitude.

The carbonates are compared to the water $\delta^{18}O$ values by the relationships between standards. Samples were analysed with the local Waitomo Limestone Standard (WLS) as a reference. This is converted to the PDB standard, currently accepted as normal for carbonates, by the relationship:

$$\delta^{18}O_{PDB} = 0.999\delta 46 + 0.0098\delta 45 - 1.84$$

This in turn can be converted to the SMOW standard. Assuming the lakes existed at around, say, 4°C, then:

$$\delta^{18}O_{H_2O(SMOW)} = \delta^{18}O_{(CaCO_3)(PDB)} - 3.25 \quad \text{(per mille)}$$

Samples were ground up and reacted with 100% phosphoric acid in a sealed reaction vessel under vacuum at 50°C. The CO_2 formed by the reaction was taken across to a Micromass 602 mass spectrometer for analysis against WLS (above). Results are given in table (4.1).

$\delta^{18}O$ values (wrt to SMOW) were plotted against sample age. Results are given in figure (4.6)

Figure 4.6 Age vs $\delta^{18}O$

(of the water at equilibrium with the carbonate (at 4°C))

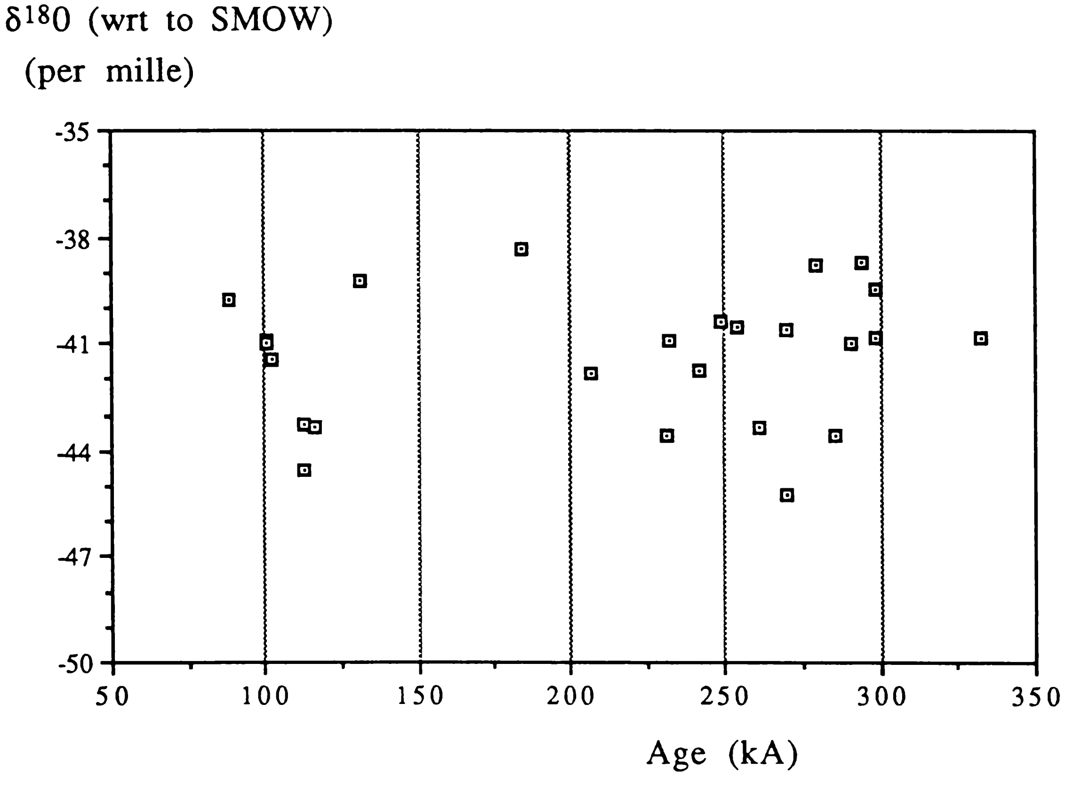


Table 4.1 $\delta^{18}O$ analysis results

SAMPLE	$\delta^{18}O$ wrt PDB (per mille)	$\delta^{18}O$ wrt SMOW (per mille)
87-L26	-37.74	-40.99
87-L1W3	-38.56	-41.81
87-L1W4	-38.56	-41.81
87-L28	-40.31	-43.56
87-86-160c	-37.62	-40.87
87-82-153b	-37.65	-40.90
87-S37	-40.28	-43.53
87-74a	-35.49	-38.74
87-85-157b	-37.69	-40.94
87-67a	-38.08	-41.33
87-253a	-36.52	-39.77
87-024-48c	-35.08	-38.33
87-105-204b	-37.74	-40.99
87-36-76b	-36.20	-39.45
87-96a	-35.98	-39.23
87-256b	-37.29	-40.54
87-06-019	-41.27	-44.52
87-95a	-37.33	-40.58
87-254b	-38.20	-41.45
87-61-130b	-40.02	-43.27
87-91-189b	-37.62	-40.87
87-85a	-37.66	-40.91
87-33a	-35.54	-38.79
87-69-140b	-40.09	-43.34
87-14-32c	-38.50	-41.75
87-31-66b	-40.09	-43.34
87-17-38b	-41.95	-45.20
87-25-51c	-37.14	-40.39

The results suggest that none of the samples could have formed from the Ross Sea Glaciation (Isotope Stage 2) waters, and show little influence from local alpine glaciers. They could have formed from either Taylor glacier or Isotope Stage 6 Ross Ice Shelf meltwaters.

Epstein et al (1970) analysed oxygen isotope ratios from a core taken from Byrd Station. $\delta^{18}0$ values were shown to decrease sharply at the termination of the Wisconsin cold interval (Isotope Stage 2), from about $\delta^{18}0$ = -33 to -about -42 (wrt SMOW), and then to slowly rise again to around -38 at the termination of Stage 5.around 75 kA. At interglacial Stage 5 $\delta^{18}0$ values rose again to around -33 (the latter dates are less certain as they come from the base of the core where thinning due to ice flow occurs). Later results from the Vostok core (Jouzel et al, 1987) confirmed this variation in trend, but suggested a lower magnitude of change.

The results given in figure (4.5) show a possible similarity to the results of Epstein et al (1970). $\delta^{18}0$ values decrease from -39 to -45 through the Stage 5 samples, then rise to around -39 again for the final sample, which is closest to the Stage 5/6 boundary. As the carbonate $\delta^{18}0$ values represent that of the ice terminating in the Taylor Glacier, there are two possible explanations for this. Possibly it represents glacier ice coming from higher altitudes, in which case it could be postulated that the ice reached maximum thickness around 115 - 120 kA, plus the.lag time time between precipitation in the interior and melting from the Taylor Glacier. Jouzel et al (1987) estimated from the ^{10}Be record that precipitation reached a maximum in the interior at 130kA, with an error no more than 5%.

It is also possible that the changes in $\delta^{18}0$ values reflect changes in the flowlines of the ice coming from McMurdo Doome between glacial and interglacial times, i.e during interglacial times the ice terminating in the Taylor Glacier comes from higher up on McMurdo Dome, where $\delta^{18}0$ values are more negative.

The low $\delta^{18}0$ value of the single sample dating around 180 kA confirms the suggestion that this was a minor event compared to the Stage 5 and 230 - 300 kA events. However, $\delta^{18}0$ analysis of the additional samples (table 3.6) dated to this event may show lower $\delta^{18}0$ values.

The $\delta^{18}0$ data for the samples 230 - 300 kA old do not resolve the question of whether one or two events occurred over this period. It would seem that the samples dating around 290 - 300 kA do not represent full interglacial conditions, if compared to the trend through the Stage 5 samples. Possibly the meltwaters forming a lake around this time came from an ice body that attained maximum thickness around 260 - 280 kA.

Chronology of paleo-lake formation.

The absence of any intact stratigraphy makes interpretation of the chronology of lake formation difficult for the earliest cluster of dates, when the scatter in ages approaches the interval between lakes, however there was at least one lake formed by meltwaters from the Taylor Glacier between 300 and 230 kA, from which thin lacustrine carbonates were deposited. Typically these contained 10-25 ppm U with a $^{234}U/^{238}U$ ratio of 3.2 to 3.5 (carbonates from this lake(s) have been incorporated into till by the Taylor II glacier advancing down the Taylor Valley, and left as a prominent part of the drift sheet covering the valley floor and lower valley walls between Lake Henderson and Lake Bonney).

A second, smaller set of dates between 177 and 185 kA, with a $^{234}U/^{238}U$ ratio of 3.70 and a uranium concentration similar to the earlier event above, could have formed from a second lake, around the end of Isotope Stage 7 (Stage 6/7 boundary placed at around 184kA (SPECMAP, 1984)).

A third set of dates ranging between 131 kA and 81 kA; with $^{234}U/^{238}U$ ratios of about 2.5 to 3.5, and a uranium concentration again of 10 to 25 ppm; form a geographically distinct group, presumably corresponding to lacustrine conditions in Isotope Stage 5. $\delta^{18}O$ values suggest that this lake was formed from Taylor Glacier meltwaters. The youngest set of samples include the *in situ* deposit of the Suess Stream Section, and clasts which appear to have been only slightly disturbed on the south wall of the valley (87-252 to 87-257), plus clasts at the eastern (distal) end of the drift sheet.

It would appear that the Taylor II glaciation can be bracketted by the sets of lacustrine carbonates. The glacier advanced into sediments containing 230-300 kA, and 177-185 kA carbonates, incorporating them into it's till. The Isotope Stage 5 carbonates (131-81 kA) are incorporated into drift at the eastern end of the drift sequence, are in place or only slightly disturbed towards it's margins, but are absent from the main body of the drift; suggesting that they were deposited in a lake proglacial to the Taylor II glacier, and thus provide a minimum age of the glaciation at 84 kA, with a maximum age of 131 kA.

Chapter 5

Conclusions.

Methodology.

The Uranium-Thorium dating method has been applied to the lacustrine carbonate deposits of the Taylor Valley, Antarctica. These samples have high levels of detritus, seldom less than 5% and frequently up to 30%. In the past this has made the separation and purification of uranium and thorium particularly difficult. A method has been developed to increase the yields, purity and resolution of the sample mounts required for U-Th analysis by the alpha-spectroscopy technique.

The basic method was a general one used by the Lamont-Doherty Geological Observatory, and was gradually modified to suit the Antarctic lacustrine carbonates samples. Samples were dissolved in dilute nitric acid, with some emphasis placed on the need to minimise excess acidification, and to minimise contact time of the residue with the acidic solution. This was in order to preclude the leaching of uranium and thorium from the detrital phase into the solution phase; but most importantly to prevent titanium and silica from being leached into the solution (which ideally represented only the carbonate part of the sample). Samples were boiled for one hour to drive off CO_2 and to equilibrate the uranium and thorium isotopes in the ^{232}U-^{228}Th spike (added after dissolution) with the sample nuclides in the solution and adsorbed to surfaces. The solution was centrifuged down and the solution phase decanted off. Since organic compounds were a possible source of uranium loss (via complexing), 10mls of HCl was added and the solution boiled for 5 minutes further. $FeCl_3$ (aq) was added in order to help coprecipitate the uranium and thorium. This was done by adding aqueous ammonia to the solution in nitric acid while still hot (to prevent re-adsorption of CO_2). A double scavenge method was used to ensure complete removal of the uranium and thorium, while Ca^{2+}, Mg^{2+} and other ionic cations were left in the solution phase. The uranium-thorium-iron precipitate was redissolved in a hydrochloric acid matrix and reprecipitated to ensure complete removal of Ca, Mg etc.

Initially samples were separated on an ion exchange column at this point, however the column was frequently blocked by a mass of gel at the column head. Analysis suggested this to be a silica gel, this was confirmed by XRF analysis. Since it was difficult to predict the occurrence of this gel, all samples were treated to remove silica prior to loading onto the first column. The method used was to dissolve the final precipitate in HNO_3, add a couple of mls of HF, and boil down to dryness over several hours. A further quantity of HF was added, and the solution boiled down very gradually overnight.

An ion exchange column in chloride form was used to separate the uranium from the thorium. Once silica gels had been removed this column presented no major problems. Loading and washing in 8N HCl eluted thorium, while uranium and iron were washed off with very dilute HCl solutions. Organic breakdown products were found in both eluates, and both were made extremely oxidising with HNO_3 to remove organics. The thorium eluate was further boiled down and converted to an HNO_3 final form, for further separation on another column. Another trace element problem became apparent here, the occurrence of a precipitate of a hydrated form of titanium. This caused very low Th yields, as Th was readily scavenged by the polymeric titania. The suggested method was to centrifuge out the precipitate, load the supernatant onto the column and redissolve the solid phase in more 8N HNO3. Low thorium yields still occurred using this method. An alternative way of dealing with the problem was developed, whereby maximum volumes were maintained throughout the conversion from chloride to nitrate form. The eluate was boiled down to a volume of about 30 mls, at which point nitric acid was added to a volume of around 80mls. This was boiled down gradually until no more colour existed in the solution (all HCl gone).

When distilled water was added to make the solution 8 molar in HNO3, this gave a total volume of 100mls. This took up to an hour to load onto the next ion exchange column, but no further white precipitates were noted during this stage of processing, while yields became higher and more consistent. The thorium was then purified on an anion exchange column (15 mls resin) in nitrate form, to separate out aluminium, and any remaining Group I or II metals. This process was repeated on a second, smaller (2mls resin), thorium column.

The uranium eluate was boiled down and converted to chloride form. The iron was extracted out into an isopropyl ether solution. Although the aqueous phase should have been colourless after 6 extractions with ether, it was still frequently a strong yellow colour. The extraction procedure was varied in a number of ways to maximise iron extraction, however the colour still persisted. Occasionally incomplete iron extraction occurred, but often it seemed that the colour was due to a further trace element, possibly manganese. This was supported by the common occurrence of red crystals on boiling down the solution ($MnCl_3$). The final purification necessary for the uranium was separation from any other remaining trace elements (particularly transition metals) on an ion exchange column in nitrate form. This phase of processing was the most likely cause of the low uranium yields. The parameters of the column process, such as resin quantity, wash volumes, and loading volumes were variously modified, with the aim of losing less of the uranium. The resin volume was halved to around 1ml, while the volume used for washing was also decreased. Uranium yields became more consistent after this.

The final stage of sample preparation was electrodeposition of the sample on planchettes suitable for alpha spectroscopy. The method followed only occasionally gave reasonable yields, and the whole electroplating process was reviewed. The same cell design was retained, however the recommended silver anodes were replaced with platinum anodes. Samples were dissolved in conc HCl, rather than the previously used electrolyte solution pre-adjusted in pH (this solution failed to adequately dissolve the sample). After sample dissolution, the HCl was diluted down with distilled water before being added to the cell. It was then adjusted to around pH 3-4 using a methyl red indicator and aqueous ammonia. Plating times were increased to around 3hrs. This was in order to marginally maximise yields, at no expense in terms of lab work. Distilled water was used to wash down the cell walls shortly before turning the solution off. The work of Mitchell (1960) on current density and deposition rate suggests that the cell used may have been underpowered.

Some time was spent in determining the spike nuclide activity ratio. Various methods of spike calibration were attempted, the successful method used a ground silicate uranium-thorium mineral standard (DH-1a), treated by the above method (with repeated prior evaporation from an HF solution to remove silicon). From four replicates the spike $^{228}Th/^{232}U$ ratio was established as 0.97 (s=0.02).

The success of the methodology developed was evidenced by the increasing yields obtained as dating progressed. Yields for the final three batches of samples counted, at which point no more adjustments were made to the process, averaged 76.7% for uranium, and 75.4% for thorium. Such yields are quite respectable normally, and even more so for samples of such high detrital content. Yields for all samples counted prior to this averaged 52.8% for uranium, and 52.9% for thorium.

Alpha decay spectra were accumulated, and data reduction carried out. The validity of several models used to correct for peaks under-ridden by tails from higher energy peaks were tested. These results suggested ^{216}Po was an excellent model for the tail of ^{224}Ra, but not for the thorium isotopes; while ^{238}U was confirmed as a valid model for the shape of the ^{234}U and ^{232}U tails. Several integration schemes were evaluated, showing the need for as wide an integration limit as possible (at least for the samples dated, which invariably had obvious tails extending through all regions of interest). Errors from the spike analysis were not included in the overall error, in order to preserve the relative accuracy of the ages. Samples with a high ^{232}Th content ($^{232}Th/^{230}Th > 20$) were assumed to have also contained ^{230}Th at the time of formation and were adjusted using plots of $^{232}Th/^{230}Th$ vs $^{234}U/^{232}Th$ and $^{234}U/^{232}Th$ vs $^{238}U/^{232}Th$.

Most samples were dated in duplicate. Results were considered quite rigorously, and a number were eliminated as dubious, due to a variety of reasons; for example, apparent excessive leaching of the detritus, spectral shift, and extremely low resolution. The duplicated results were averaged, while dubious and excess Th results were eliminated; to produce a final date list. A number of other samples were analysed but recovery or resolution was too low to be worth counting This was due to the concurrent experimenting with methodology and sample processing. Of the 62 sample analyses counted, 13 were eliminated for various reasons, leaving a total of 49 valid results, 34 as duplicates, one in triplicate and 12 as single analyses.

Analysis of results.

The results obtained were analysed with the hope of building up a picture of both the chronology and nature of past events in the Taylor Valley. Previous work on the Bonney Drift (from where these samples were collected) (Hendy et al, 1979) had suggested advance of the Taylor Glacier, correlated to thickening of the East Antarctic Ice Sheet, in interglacial Isotope Stages 5 and 7, and possibly at Stage 9. The dates derived here largely supported that contention, with the dates clustering at around 90 - 130 kA, 175 to 185 kA, and 240 - 300 kA. The large number of samples falling into the latter cluster were difficult to resolve, as there were possible groupings within this cluster at 240 to 260 kA, 270 to 285 kA and 290 to 300 kA. It seemed most likely that the data represented one extensive event, although two events at 230 to 250 kA and 270 to 300 kA were also possible.

Uranium concentrations and $^{234}U/^{238}U$ data were used to pick out anomalous results, which probably reflected extreme conditions within the events described. Of particular interest were the samples from the stratigraphically intact LaCroix and Suess Sections from the valley walls, which had uranium concentrations an order of magnitude lower than the bulk of the samples from the valley floor. These could represent the first stage of paleo-lake formation.

The geographical distribution of the samples ages revealed that the last major glacier to advance through the area had ploughed up most of the samples and redeposited them. However a general grouping of younger ages to the eastern end of the area sampled suggested that the lake associated with the Taylor II glaciation of Isotope Stage 5 was a more extensive event than that of Stage 7.

Oxygen isotope analysis was carried out on all of the samples dated. $\delta^{18}O$ values were of a quite restricted range, from -38 per mille to -45 per mille. this confirmed that none of the carbonates were deposited from lakes proglacial to a thickened Ross Ice Sheet (Stage 2), nor from lakes formed by local alpine glacier meltwaters (from which far less negative $\delta^{18}O$ values would be expected). There was some evidence for $\delta^{18}O$ values decreasing towards the middle of an interglacial period, due to either changes in surface altitude of the interior ice-sheet or with changes in the flow-lines of the ice coming from the interior.

By combining the results acquired here with those of Hendy et al (1979), the late Quaternary events contributing to the components of the Bonney Drift can be summarised as follows.

(i) An extensive period of lacustrine conditions from 230kA to 300kA, formed proglacial to the Taylor Glacier. The carbonates deposited contained 10 to 25 ppm uranium, and a $^{234}U/^{238}U$ ratio of 3.2 to 3.5. It is possible that two lakes are represented by the data, or one lake with two periods of extended volume. However, there is evidence that on this occasion the Taylor Glacier advanced at least to the coast at New Harbour (Chapman-Smith, 1975; Powell, 1976, 1981); suggesting that one large event is most likely. Possibly this event climaxed around 260kA. All the carbonates deposited in the lakes at this time were redeposited by the Taylor II glacier (and possibly other glaciers).

(ii) a less extensive event occurred around 210 to 175 kA ago, when again a lake proglacial to the Taylor Glacier formed in the Bonney Basin. The results of Hendy et al (1979) suggested that the earlier carbonates (210 to 190 kA) were deposited from alpine glacier meltwaters, while results here suggest that the later dates were from samples deposited from a lake largely composed of either Taylor Glacier meltwater, or possibly Ross Sea Ice-sheet (Marshall Drift) meltwater. The carbonates deposited by the lake from 190 to 175 kA typically had a uranium concentration of10 to 25 ppm, and a $^{234}U/^{238}U$ ratio of about 3.70.

It would seem that a change in conditions, probably due to the precipitation change caused by an increase in the proximity of open sea, was initially only responded to by the alpine glaciers, but later on may have caused the Taylor Glacier (representing the East Antarctic Ice Sheet) to expand (if the later dates were due to Taylor Glacier and not Ross Sea Ice-sheet meltwaters. As stated above, this event was probably less extensive than the other events interpreted here. The carbonates deposited were later ploughed up by the Taylor II glacier.

(iii) an extensive lake existed in the Bonney basin, the Hoare Basin, and probably the Fryxell Basin from around 75 kA to 130 kA. This proglacial lake was formed by meltwaters from the Taylor glacier.

Carbonates were deposited from the lake, typically containing 10 to 25 ppm uranium, with a $^{234}U/^{238}U$ ratio of around 3.2 to 3.5. If the abundance of samples reflected the extent of carbonate deposition, this lake was probably at it's most extensive around 85 to 105 kA ago.

The Taylor II Glacier advanced through it's own proglacial lake, shifting the lake down valley and ploughing up the carbonates deposited and redepositing them further down the valley.

(iv) a couple of samples suggest that at least one other Quaternary event also occurred; given the pattern above it is likely that several other glacial advances have also occurred during the Pleistocene.

Interpretation of glacial chronology.

Assuming that the proglacial lakes described above are related, as seems likely, to advance of the Taylor glacier, it is reasonable to infer that they also correlate with thickening of the McMurdo Dome, and probably hence with thickening of much of the interior of the East Antarctic Ice Sheet. The dates obtained suggest that this thickening occurs during global interglacial periods. This is supported by the currently observed increasing lake level of Lake Bonney and increase in interior accumulation rates (Jouzel et al,1987) since the last glacial maximum. The 80 to 130kA event clearly correlates with Stage 5 of the marine $\delta^{18}0$ record, while the 175 to 210kA event relates to the Stage 7 interglacial. The 230 to 300kA event does not conform to the marine record. It is likely that this due to both the sample age spread exceeding the actual timeframe of the event, due to geochemical factors in the samples and the inherent lower resolution of the U-Th method around these ages; and due to the poor absolute chronological control of the marine record around this time. Isotope stage 9 is placed at around 300kA in the marine record, the dates above suggest that it may have been more recent than this.

This can be explained by the mechanism of Hendy et al (1979). During global interglacial conditions sea ice around the continent retreats and atmospheric moisture content increases, allowing more precipitation to reach the interior of the East Antarctic Ice Sheet - this exceeds any increase in ablation rate caused by increased temperature. this causes the ice sheet to thicken, whereas in global glacial times, the extent of sea-ice prevents much precipitation from the open sea reaching the interior. Although this says nothing about the lateral extent and coastal thickening of the ice-sheet, it would seem that one parameter, interior thickness, of the East Antarctic Ice Sheet (containing 76% of the world's fresh water) could act to moderate such interglacial features as increased sea-level.

Appendix A

Calculation of U - Th ages

Ages and initial $^{234}U/^{238}U$ ratios were derived from the calculated $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios, using the BASIC programme listed below. This is the Apple Macintosh listing, in practice the programme was rewritten for, and used on, an Apple IIe. The programme uses an iterative method of solution.

Other BASIC computer programmes were written for the Apple IIe. A simple programme integrated a spectrum between entered channel limits. A data manipulation programme was written, giving options of subtracting a background spectrum file (or any other file), with allowance for time ratios; smoothing a spectrum file; subtracting or adding a constant to a spectrum; multiplying or dividing a spectrum by a constant; and saving the resultant file so it could be loaded back into the multichannel analyser programme.

Computer programme for age equation solving.

```
10 REM U_TH AGE CALCULATION
20 REM V 02/23/1989 LDGO
23 INPUT "SAMPLE NUMBER";SN$
25 INPUT "230TH/U234 =";TU
35 INPUT "+/-";ETU
40 INPUT "234U/238U";UU
45 INPUT "+/-";EUU
50 CA=.009219
55 REM HALF-LIFE 230TH = 75,200 YRS
60 CB=.002795
65 REM HALF-LIFE 234U = 248,000 YRS
70 MT=0
80 GOSUB 800
90 A0=X
100 TU=TU+ETU
110 UU=UU-EUU
120 MT=0
130 GOSUB 800
135 REM COMPUTE MAXIMUM AGE
140 A1=X
150 TU=TU-2*ETU
160 UU=UU+2*EUU
170 MT=0
180 GOSUB 800
190 REM COMPUTE MINIMUM AGE
200 A2=X:AE1=A1-A0:AE2=A0-A2
230 PRINT "AGE = ";A0;" kA"
240 PRINT "+";AE1
250 PRINT "-";AE2
```

```
260 PRINT " (1 s.d.)"
290 REM CALCULATE ORIGINAL 234U/238U RATIO
300 UU=UU-EUU:TU=TU-ETU
330  IUR=(UU-1)*EXP(CB*A0)+1
340  EIUR=(IUR*EUU)/UU
350 PRINT "INITIAL 234/238 =";IUR;"+/-";EIUR
600 GOTO 10000
790 REM THIS SUBROUTINE COMPUTES
795 REM THE AGES
800  DEF FNC(X) = (1-EXP(-CA*X))/UU+(1-1/UU)*CA/(CA-CB)*(1-
     EXP((CB-CA)*X))-TU
810 B1=1:B2=600:V1=FNC(B1):S1=SGN(V1)
820  V2=FNC(B2):S2=SGN(V2)
825 REM CHECKING FIT OF ITERATIONS
830 IF S1*S2=O THEN GOTO 920
840 IF S1*S2<0 THEN GOTO 875
850 GOTO 810
875  D(2+S1)=B1:D(2-S1)=B2
885  X=(D(1)+D(3))/2:MT=MT+1
890 S3=SGN(FNC(X))
895 IF S3=0 THEN GOTO 940
900 D(2+S3) = X
905   RE=ABS(D(1)-D(3))/(ABS(D(1))+ABS(D(3)))
910 IF RE<.00001 THEN GOTO 940
912 REM IF ERROR <0.0001 THEN AGE CALCULATED
913 REM IF ERROR LARGER THEN ADJUST AGES AND
914 REM RECALCULATE
915 GOTO 885
920 IF S1=0 THEN GOTO 935
925 X=B2
930 GOTO 940
935 X=B1
940 RETURN
10000 END
```

Appendix B

Dating of some Kidnappers Group molluscs.

In addition to the Taylor Valley lacustrine carbonates dated, four samples (in duplicate) of molluscs were analysed by the U-Th method. The samples were collected by Dr P. Kamp, University of Waikato. Sample KD came from the base of the Te Awanga Formation in the Kidnappers Group, while samples KA, KB, and KC outcropped several metres apart in the Clifton Sandstone of the same Group. The samples were expected to reflect periods of marine or estuarine deposition in the largely terrestrially sourced Kidnappers Group. Ages of around 120 - 125 kA (Isotope Stage 5e) for the KA sample, and around 180 kA (≈ Isotope Stage 7) for samples KD, KC, and KB; were expected. Results of dating are given in Table (B). Carefully chosen multiple specimens were used for each sample (≈ 20gms each).

Table B Results of dating Kidnappers Group molluscs.

Sample	KA	KB	KC	KD
%residue	0.18	0.28	0.20	0.31
[U] ppm	1.75	1.12	1.71	1.29
$^{234}U/^{238}U$ (s)	1.71 (0.04)	1.67 (0.05)	1.71 (0.04)	1.61 (0.05)
$^{230}Th/^{234}U$	0.149	0.127	0.145	0.161
s	0.006	0.005	0.008	0.009
Age (kA) (+/-)	17.3 (0.8)	14.6 (0.6)	16.8 (1.0)	18.8 (1.1)
init. $^{234}U/^{238}U$ (s)	1.75 (0.04)	1.70 (0.05)	1.74 (0.04)	1.64 (0.05)

The ages obtained were inconsistent with sample stratigraphy, and are ascribed to post-depositional migration of critical nuclides. This is commonly the case for mollusc samples (Kaufman et al, 1971). The low $^{230}Th/^{234}U$ ratios suggest post-depositional uptake of uranium, either throughout or late in the sample history. The $^{234}U/^{238}U$ ratios observed are inconsistent with those expected for marine/estuarine samples (marine $^{234}U/^{238}U$ = 1.15), and suggests that the uptake of uranium was from groundwater; which could be expected to have a much higher $^{234}U/^{238}U$ ratio than the sea/estuary in which the molluscs formed.

Despite the failure of the effort to date these important samples, it should be noted that the analytical technique worked well, yielding good recoveries of uranium and thorium.

Appendix C

Full Results of U-Th dating

SAMPLE	weight (g)	% resid	[U] ppm	[Th] ppm	% U recov	% Th recov	Th decay	230Th/228Th	σ	234U/232U	σ	230Th/234U	σ	234U/238U	σ	232Th/234U	σ
87-06-019	10.001	8.2	13.2	6.3	45.4	20.7	0.9678	1.3173	0.0141	1.7193	0.0173	0.7432	0.0109	2.0745	0.0279	0.0664	0.0016
87-06-019	10.001	8.3	14.7	2.7	70.2	85.0	0.9823	2.1730	0.0119	1.8493	0.0183	1.1398	0.0127	2.0058	0.0200	0.0302	0.0003
87-06-019	10.001	19.9	23.5	1.5	44.8	41.7	0.9870	1.7900	0.0200	1.6800	0.0180	1.0331	0.0220	2.1700	0.0260	0.0510	0.0020
87-014-32c	10.000	33.8	11.7	5.8	74.8	72.5	0.9900	1.2690	0.0090	1.2230	0.0160	1.0070	0.0200	2.3160	0.0350	0.0730	0.0020
87-014-32c	9.999	34.1	12.0	5.8	80.4	62.0	0.9810	1.2690	0.0150	1.2500	0.0130	0.9850	0.0220	2.3160	0.0230	0.0720	0.0030
87-033a	10.000	13.3	15.2	2.2	66.2	67.8	0.9870	1.9660	0.0210	1.8680	0.0190	1.0520	0.0220	2.0720	0.0220	0.0240	0.0010
87-033a	10.000	10.5	14.8	2.9	87.7	34.7	0.9840	2.0590	0.0210	1.8540	0.0190	1.0770	0.0220	2.0530	0.0210	0.0320	0.0010
87-015-34c	10.000	23.4	3.4	5.7	15.4	42.6	0.9736	0.4275	0.0047	0.2915	0.0039	1.4225	0.0178	1.6428	0.0312	0.3400	0.0080
87-015-34c	9.999	22.9	3.2	7.0	82.8	28.9	0.9745	0.3150	0.0042	0.2652	0.0020	1.1523	0.0176	1.5858	0.0172	0.3989	0.0083
87-017-38b	10.001	8.9	17.7	2.6	57.1	80.1	0.9850	2.5930	0.0210	2.3820	0.0200	1.0560	0.0120	2.1580	0.0190	0.0240	0.0010
87-017-38b	9.999	8.3	17.3	2.8	54.5	90.6	0.9900	2.6140	0.0210	2.3850	0.0230	1.0630	0.0130	2.2000	0.0210	0.0250	0.0010
87-024-48c	10.000	21.0	14.8	4.2	59.6	91.5	0.9840	2.0980	0.0170	2.1610	0.0190	0.9420	0.0120	2.6980	0.0280	0.0360	0.0010
87-024-48c	10.001	20.2	15.8	4.0	72.8	72.1	0.9920	2.0510	0.0100	2.1780	0.0190	0.9140	0.0090	2.5270	0.0240	0.0330	0.0010
87-025-51c	10.002	23.3	45.0	7.8	42.8	69.5	0.9852	4.1692	0.0216	4.0374	0.0280	1.0017	0.0087	1.7105	0.0088	0.0335	0.0003
87-025-51c	10.002	22.0	44.0	3.9	83.4	2.5	0.9630	3.1196	0.0622	4.0470	0.0273	0.7477	0.0154	1.7232	0.0082	0.0167	0.0016
87-031-66b	9.999	9.3	16.0	2.7	19.2	85.8	0.9800	2.0810	0.0180	1.9550	0.0170	1.0330	0.0130	1.9710	0.0170	0.0280	0.0010
87-031-66b	10.001	9.5	15.9	2.6	66.6	77.1	0.9920	2.0730	0.0100	1.9330	0.0110	1.0400	0.0080	1.9670	0.0110	0.0280	0.0010
87-67a	10.000	6.1	64.0	3.9	64.5	28.1	0.9338	6.0870	0.0572	4.7052	0.0257	1.2549	0.0136	1.1459	0.0043	0.0181	0.0006
87-67a	10.000	5.9	64.9	3.5	49.5	77.9	0.9209	5.4370	0.0273	4.6500	0.0260	1.1340	0.0085	1.1170	0.0040	0.0160	0.0003
87-74a	10.000	7.7	14.9	2.6	33.4	46.5	0.9356	2.0966	0.0106	1.8810	0.0100	1.0812	0.0034	2.0067	0.0110	0.0294	0.0006
87-74a	9.999	7.8	14.6	2.3	87.9	59.2	0.9478	2.0786	0.0141	1.8781	0.0094	1.0736	0.0090	2.0432	0.0102	0.0261	0.0007
87-036-76b	10.000	9.0	15.0	2.3	64.7	45.1	0.9860	2.1550	0.0220	1.9320	0.0230	1.0820	0.0240	2.0660	0.0260	0.0260	0.0010
87-036-76b	10.001	7.8	15.6	3.0	62.3	57.9	0.9790	2.2090	0.0240	1.9770	0.0240	1.0840	0.0250	2.0070	0.0240	0.0330	0.0010

SAMPLE	weight (g)	% resid	[U] ppm	[Th] ppm	% U recov.	% Th recov.	Th decay	230Th / 228Th	σ	234U / 232U	σ	230Th / 234U	σ	234U / 238U	σ	232Th / 234U	σ
87-85a	9.999	27.1	21.1	6.3	57.5	72.4	0.9544	1.9132	0.0089	2.8211	0.0119	0.6578	0.0042	2.6868	0.0116	0.0372	0.0005
87-85a	10.001	27.5	20.3	6.7	7.0	81.7	0.9611	1.9176	0.0330	2.7080	0.0255	0.6869	0.0069	2.6868	0.0279	0.0409	0.0005
87-95a	10.001	6.4	23.2	2.7	69.0	15.6	0.9611	2.1565	0.0168	2.0634	0.0155	1.0138	0.0110	1.3926	0.0096	0.0278	0.0003
87-95a	10.002	6.5	14.8	2.3	84.7	76.3	0.9554	2.0921	0.0177	1.9284	0.0135	1.0523	0.0116	2.0412	0.0147	0.0251	0.0008
87-96a	10.001	8.1	17.2	2.3	77.2	55.2	0.9554	2.0610	0.0202	2.6032	0.0181	0.7680	0.0092	2.4136	0.0164	0.0183	0.0007
87-96a	10.002	7.8	41.3	1.7	49.8	12.4	0.9687	2.0303	0.0159	2.6231	0.0225	0.7508	0.0087	1.0074	0.0064	0.0138	0.0005
87-61-130b	10.001	20.9	11.1	6.9	40.3	33.6	0.9697	0.9692	0.0059	1.2219	0.0057	0.7694	0.0059	2.0346	0.0112	0.1009	0.0013
87-61-130b	10.001	21.1	11.2	6.7	57.6	72.0	0.9573	0.9710	0.0059	1.2323	0.0070	0.7643	0.0063	2.0435	0.0135	0.0980	0.0013
87-69-140b	10.001	9.2	14.5	2.2	38.1	14.0	0.9639	1.8520	0.0222	2.4720	0.0150	0.7267	0.0098	2.7424	0.0176	0.0187	0.0009
87-69-140b	10.001	7.7	13.2	2.0	70.4	92.2	0.9497	1.7629	0.0093	2.3976	0.0123	0.7132	0.0051	2.8766	0.0167	0.0170	0.0004
87-82-153b	10.002	6.6	11.5	2.2	66.3	20.3	0.9544	2.1854	0.0283	2.0586	0.0117	1.0298	0.0146	2.7923	0.0186	0.0229	0.0013
87-85-157b	10.001	28.3	21.4	7.1	46.5	55.8	0.9273	1.8599	0.0093	2.6980	0.0127	0.6672	0.0044	2.5608	0.0121	0.0427	0.0005
87-85-157b	10.001	28.0	20.3	6.8	38.7	40.2	0.9459	1.8507	0.0104	2.6223	0.0121	0.6846	0.0049	2.6261	0.0128	0.0438	0.0006
87-86-160c	9.999	25.9	21.9	4.3	82.8	34.9	0.9412	1.8928	0.0173	1.6809	0.0085	1.0923	0.0115	1.8632	0.0099	0.0445	0.0012
87-86-160c	10.000	26.5	18.4	4.6	33.2	61.7	1.9020	0.0073	1.6786	0.0083		1.0991	0.0069	1.8139	0.0091	0.0455	0.0005
87-91-189b	10.000	6.8	15.2	2.4	54.7	78.4	0.9620	2.0936	0.0162	1.8652	0.0160	1.0888	0.0126	1.9314	0.0170	0.0278	0.0003
87-91-189b	10.000	6.9	14.9	2.2	52.4	90.4	0.9535	2.0811	0.0122	1.8942	0.0176	1.0657	0.0119	1.9979	0.0191	0.0251	0.0006
87-105-204b	3.933	34.2	12.7	3.7	86.5	83.1	0.9459	0.4247	0.0029	0.6011	0.0034	0.6853	0.0060	2.6770	0.0234	0.0360	0.0009
87-105-204b	10.000	36.1	12.9	4.1	45.8	51.6	0.9544	0.9797	0.0087	1.5038	0.0110	0.6319	0.0073	2.6697	0.0241	0.0397	0.0011
87-252b	10.001	31.3	9.1	5.7	3.8	2.7	0.9630	0.6999	0.0167	1.3642	0.0402	0.4977	0.0140	3.2086	0.0707	0.0650	0.0041
87-253a	10.003	13.5	22.7	3.4	11.8	38.4	0.9910	2.0340	0.0240	3.2540	0.0600	0.6060	0.0130	2.4220	0.0400	0.0210	0.0010
87-253a	10.001	10.5	22.0	3.7	19.9	18.8	0.9900	2.2330	0.0380	3.3200	0.0110	0.6530	0.0130	2.4670	0.0100	0.0230	0.0010
87-253a	9.999	13.0	24.1	3.1	18.8	15.1	0.9890	2.0980	0.0370	3.4430	0.0510	0.5910	0.0140	2.4070	0.0310	0.0180	0.0010
87-253a	9.995	13.3	22.6	2.7	11.6	17.3	0.9880	1.9910	0.0370	3.2680	0.0560	0.5910	0.0140	2.4470	0.0370	0.0170	0.0010
87-254b	10.002	7.6	21.4	2.6	49.6	38.7	0.9563	2.3336	0.0207	3.4358	0.0220	0.6588	0.0073	2.5409	0.0149	0.0145	0.0004
87-256b	10.000	11.2	12.0	3.4	29.3	79.4	0.9535	1.7442	0.0115	1.6227	0.0214	1.0426	0.0154	2.2308	0.0383	0.0418	0.0010

SAMPLE	weight (g)	% resid	[U] ppm	[Th] ppm	% U recov.	% Th recov.	Th decay	$\frac{\text{230Th}}{\text{228Th}}$	σ	$\frac{\text{234U}}{\text{232U}}$	σ	$\frac{\text{230Th}}{\text{234U}}$	σ	$\frac{\text{234U}}{\text{238U}}$	σ	$\frac{\text{232Th}}{\text{234U}}$	σ
87-L1W3	10.001	21.8	2.8	2.7	103.7!	46.9	0.9046	0.3643	0.0020	0.3517	0.0011	1.0048	0.0064	2.3403	0.0118	0.1384	0.0021
87-L1W3	10.000	22.2	2.2	2.5	92.8	85.3	0.9136	0.2921	0.0022	0.2801	0.0021	1.0114	0.0107	2.3458	0.0281	0.1561	0.0030
87-L1W4	10.001	14.6	2.9	2.3	68.7	60.4	0.8948	0.4221	0.0020	0.3825	0.0018	1.0704	0.0070	2.2900	0.0167	0.0999	0.0015
87-L1W4	9.999	14.7	3.1	2.2	62.5	91.7	0.9173	0.4494	0.0014	0.4368	0.0017	0.9979	0.0049	2.4234	0.0146	0.0991	0.0010
87-L26	10.001	18.0	2.1	2.3	83.8	94.2	0.9073	0.3059	0.0014	0.2763	0.0013	1.0739	0.0072	2.4048	0.0195	0.1566	0.0018
87-L26	9.999	17.8	2.0	2.1	81.8	75.1	0.8289	0.3058	0.0024	0.2660	0.0022	1.1151	0.0127	2.3997	0.0324	0.1456	0.0038
87-L28	10.001	15.1	18.9	2.0	97.0	92.8	0.8781	3.0452	0.0069	2.8868	0.0057	1.0233	0.0031	2.6282	0.0054	0.0137	0.0002
87-S13	10.000	27.1	28.8	2.9	75.5	53.3	0.8364	7.0533	0.0326	4.4948	0.0149	1.5221	0.0086	3.1299	0.0098	0.0108	0.0002
87-S13	10.000	26.4	29.7	3.9	87.8	68.8	0.9182	8.8014	0.0404	4.6110	0.0177	1.8515	0.0111	3.0856	0.0110	0.0116	0.0002
87-S30	10.000	21.3	25.8	2.4	40.3	59.6	0.8389	6.6213	0.0308	4.2167	0.0230	1.5231	0.0110	3.0275	0.0146	0.0100	0.0002
87-S30	9.999	20.6	25.0	2.6	81.8	87.4	0.8877	6.5372	0.0194	4.1259	0.0120	1.5369	0.0064	3.0030	0.0079	0.0116	0.0002
87-S37	10.000	21.6	21.6	3.0	74.7	81.6	0.8833	3.9044	0.0108	3.4046	0.0093	1.1124	0.0043	2.9450	0.0083	0.0157	0.0002
87-S37	10.001	21.7	21.1	2.9	46.6	83.8	0.8720	3.9194	0.0068	3.4193	0.0083	1.1119	0.0033	3.0226	0.0076	0.0153	0.0001

Appendix D.

Sample record sheets

The laboratory records for each radiometric analysis are reproduced below.

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-006-019 Lab number: 18/7/90 3
Sample: Taylor Valley lacustrine carbonate
Sample weight: 10.00g
Residue weight: 0.831 %residue: 8.3%
Weight dissolved: 9.170 %soluble: 91.7%
Sample treatment: —

Date of U-Th sepn: 19/7/90 Counting delay: 18 days ^{228}Th decay factor: 0.9823
Spike activity: U: 1.808 dpm/ml Th: 1.751 dpm/ml Mls spike: 10
Date of plating U: 26/7/90 Th: 24/7/90

URANIUM Count time: 52 2/3 hrs Start: 11.45a 15/8/90 Stop: 4.25p 17/8/90
Channels counted: -30, +10 (small hi-res detector)(gp ~ 0.07?)

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	15801		37 / 45	295	15461	0.0082
^{234}U	31276		63 / 77	188	31011	0.0057
^{232}U	16873		85 / 104	—	16769	0.0078

Bground : 21/8/90 43h (x 52 2/3/43)
Tail method: 238U modelling

THORIUM Count time: 50h Start: 12.40p 6/8/90 Stop: 2.40p 8/8/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	3657	1	17 / 20	240	3397	0.0184
^{230}Th	128257		40 / 47	200	128010	0.0028
^{228}Th	66251		90 / 105	1780	64366	0.0041
^{224}Ra	59527		293 / 341	600	58586	0.0042

Bground: 21/8/90 43h (x 50/43)
Tail method: 216Po model for 228Th.
graphically for 232,230Th; estimate 224Ra

RESULTS:

234U/238U: 2.0056 std dev: 0.0200 234U/232U: 1.8493 std dev: 0.0185

[U] ppm: 14.7 U yield: ~ 70.2% ?

228Th-0.054Ra: 61202 228Th/decay factor: 62305 228Th-232Th: 58908 (0.0047)

230Th/228Th: 2.1730 std dev: 0.0119

[Th] ppm: 2.7 Th yield: 85.0%

230Th/234U: 1.1751 std dev. 0.0130 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.1398 std dev: 0.0127 232Th/234U: 0.0302 std dev: 0.0005

Age (kA): 378.7 (+) 29.4 (-) 24.0

(234U/238U)t=0: 3.899 std dev: 0.059 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87·006·014 Lab number: 21/6/90 4
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 1.990 %residue: 19.9
Weight dissolved: 8.011 %soluble: 80.1
Sample treatment: ---

Date of U-Th sepn: 22/6/90 Counting delay: 13days 228Th decay factor: 0.987
Spike activity: U: 1·80 Bq/10ml Th: 1·75 Bq/10mls Mls spike: 10
Date of plating U: Th:

URANIUM Count time: 40½h. Start: ~~6.40p 29/6~~ 5 15p 2/7 Stop: ~~5.10p 2/7~~ 9.45a 4/7
Channels counted: -60, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	20693		280	325	20088	0.007
234U	44436		681	202	43553	0.005
232U	25994		105	–	25889	0.006

Bground : 6/7/90 73h (x40½/73)
Tail method: 238U modelling

THORIUM Count time: 47h Start: 12p 9/7 Stop: 11a 11/7
Channels counted: -35, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	2577		175	80	2322	0.023
230Th	49265		683	100	48482	0.005
228Th	31625		167	1177	30481	0.006
224Ra	26081		319	400	25362	0.006

Bground: 6/7/90 73h x47/73
Tail method: 216Po model for 224Ra
others graphically

RESULTS:

234U/238U: 2.170 std dev: 0.026 234U/232U: 1.680 std dev: 0.018

[U] ppm: 23.5 U yield: 44.5

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 27142

230Th/228Th: 1.7900 std dev: 0.0200

[Th] ppm: 1.5 Th yield: 41.7

230Th/234U: 1.065 std dev. 0.023 Spike 228Th/232U: 0.97

Correct 230Th/234U: ·01 std dev: 0.023 232Th/234U: 0.0510 std dev: 0.002

Age (kA): 247.7 (+) 18.1 (-) 15.8

(234U/238U)t=0: 3.34 std dev: 0.04 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-014-32c Lab number: 10/7/90 1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 9.944g
Residue weight: 3.402 %residue: 34.1
Weight dissolved: 6.541 %soluble: 65.9
Sample treatment:

Date of U-Th sepn: 11/7/90 Counting delay: 19 days 228Th decay factor: 0.981
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: Th:

URANIUM Count time: 43½h Start: 7.30p 23/7 Stop: 3p 25/7
Channels counted: -60, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	27438		231	302	26905	0.006
234U	63377		223	751	62303	0.004
232U	49957		116	–	49841	0.004

Bground : 73h (×43½/73)
Tail method: 210Po modelling

THORIUM Count time: 29h Start: 11.30a 30/7 Stop: 4.30p 31/7
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	2387		102	40	2245	0.022
230Th	32168		393	140	31635	0.006
228Th	28668		45	614	27959	0.006
224Ra	24093		148	500	24093	

Bground: 73h × 29/73
Tail method: 210Po model for 224Ra
graphical for others

RESULTS:

234U/238U: 2.316 std dev: 0.023 234U/232U: 1.250 std dev: 0.030

[U] ppm: 12.0 U yield: 80.4

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 24929

230Th/228Th: 1.2690 std dev: 0.0150

[Th] ppm: 5.0 Th yield: 62.0

230Th/234U: 1.015 std dev. 0.023 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.985 std dev: 0.022 232Th/234U: 0.072 std dev: 0.003

Age (kA): 216.2 (+) 13.0 (-) 11.8

(234U/238U)t=0: 3.41 std dev: 0.05 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-014-32c Lab number: 28,6,90 1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.000g
Residue weight: 3.382 %residue: 33.8
Weight dissolved: 6.618 %soluble: 66.2
Sample treatment: —

Date of U-Th sepn: 29/6/90 Counting delay: 9 days 228Th decay factor: 0.990
Spike activity: U: 1.50 dpm/ml Th: 1.75 dpm/ml Mls spike: 10
Date of plating U: Th:

URANIUM Count time: 21h Start: 6pm 22/7 Stop: 3pm 23/7
Channels counted: +10, -60

	Count	std dev	bground	tail	net	%std dev/100
238U	12238		143	276	11819	0.009
234U	27974		358	245	27371	0.006
232U	22437		54	--	22383	0.0067

Bground : 6/7/90 73h (x21/73)
Tail method: 230U modelling

THORIUM Count time: 71h Start: 11.55a 13/7 Stop: 10.55a 16/7
Channels counted: +10, -40

	Count	std dev	bground	tail	net	%std dev/100
232Th	6862		279	350	6233	0.0133
230Th	89408		1151	250	88007	0.0039
228Th	80120		264	3077	76779	0.0057
224Ra	38125		497	1250	36378	

Bground: 6/7/90 73h (x71/73)
Tail method: 210Po model for 224Ra, others graphically

RESULTS:

234U/238U: 2.316 std dev: 0.055 234U/232U: 1.225 std dev: 0.016

[U] ppm: 11.7 U yield: 74.8

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 69358

230Th/228Th: 1.2690 std dev: 0.09

[Th] ppm: 5.8 Th yield: 71.5

230Th/234U: 1.058 std dev. 0.021 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.007 std dev: 0.020 232Th/234U: 0.0730 std dev: 0.0020

Age (kA): 228.6 (+) 13.4 (-) 12.1

(234U/238U)t=0: 3.49 std dev: 0.05 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-033a Lab number: 28/6/90 2
Sample: Taylor Valley lac. carb

Sample weight: 10.000
Residue weight: 1.327 %residue: 13.3
Weight dissolved: 8.673 %soluble: 86.7
Sample treatment: —

Date of U-Th sepn: Counting delay: 13 days 228Th decay factor: 0.9070
Spike activity: U: 1.805 Bq/10ml Th: 1.75 Bq/10ml Mls spike: 10ml
Date of plating U: Th:

URANIUM Count time: 29½h Start: 1pm 20/7 Stop: 6.30pm 21/7
Channels counted: -50, +15

	Count	std dev	bground	tail	net	%std dev/100
238U	25799		190	489	25120	0.0064
234U	52786		488	257	52043	0.0044
232U	27926		68	—	27858	0.0060

Bground: 6/7/90 15h (×29½/73)
Tail method: 238U modelling

THORIUM Count time: 27h Start: 11.35a 17/7 Stop: 2.35 18/7
Channels counted: -35, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	1437		88	250	1096	0.0546
230Th	48390		392	135	47863	0.0046
228Th	27390		95	1161	26134	0.0065
224Ra	20052		183	670	19199	0.0066

Bground: 6/7/90 15h (×27/73)
Tail method: 216Po model for 224Ra
~~[illegible]~~ graphically for others

RESULTS:

234U/238U: 2.0720 std dev: 0.0220 234U/232U: 1.868 std dev: 0.019

[U] ppm: 15.2 U yield: 66.2

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 24345

230Th/228Th: 1.966 std dev: 0.021

[Th] ppm: 2.2 Th yield: 67.8

230Th/234U: 1.052 std dev. 0.022 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.020 std dev: 0.022 232Th/234U: 0.0240 std dev: 0.0010

Age (kA): 268.4 (+) 20.6 (-) 17.8

(234U/238U)t=0: 3.270 std dev: 0.050 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-033a Lab number: 10/7/90 2
Sample: Taylor Valley lac. carbonate

Sample weight: 10.000g
Residue weight: 1.051 %residue: 10.5
Weight dissolved: 8.949 %soluble: 89.5
Sample treatment: —

Date of U-Th sepn: Counting delay: 16 ^{228}Th decay factor: 0.984
Spike activity: U: 1.80 Bq/10ml Th: 1.75 Bq/10ml Mls spike: 10
Date of plating U: Th:

URANIUM Count time: 23h Start: 5.30p 25/7 Stop: 4.30p 26/7
Channels counted: +10, -60

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	26540		159	420	25961	0.006
^{234}U	53905		382	216	53307	0.004
^{232}U	28818		61		28757	0.006

Bground : (×23/73)
Tail method: 238U modelling

THORIUM Count time: 65h Start: 6p 27/7 Stop: 11a 30/7
Channels counted: +10, 35

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	2128		251	0	1877	0.023
^{230}Th	65429		880	150	64399	[illegible]
^{228}Th	35239		219	978	34042	0.006
^{224}Ra	27120		436	300	26384	0.006

Bground:
Tail method: 228 model for 224Ra
others graphically.

RESULTS:

234U/238U: 2.053 std dev: 0.021 234U/232U: 1.854 std dev: 0.019

[U] ppm: 14.8 U yield: 87.7

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 31271

230Th/228Th: 2.0590 std dev: 0.0210

[Th] ppm: 2.9 Th yield: 34.7

230Th/234U: 1.111 std dev. 0.023 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0770 std dev: 0.022 232Th/234U: 0.032 std dev: 0.001

Age (kA): 241.6 (+) 24.9 (-) 20.9

(234U/238U)t=0: 3.38 std dev: 0.03 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-015-34-c Lab number: 26/7/90 1

Sample: Taylor Valley lacustrine carbonate

Sample weight: 9.999

Residue weight: 2.285 %residue: 22.9

Weight dissolved: 7.714 %soluble: 77.1

Sample treatment: HCl – TiO$_2$.

Date of U-Th sepn: 27/7/90 Counting delay: 26 days ^{228}Th decay factor: 0.9745

Spike activity: U: 1.80 dpm/mls Th: 1.75 dpm/mls Mls spike: 10

Date of plating U: 31/7 Th: 2/8

URANIUM Count time: 74h Start: 1.45p 22/8/90 Stop: 3.45p 25/8/90

Channels counted: -30 +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	14990		18 / 26	351	14613	0.0085
^{234}U	24445		12 / 17	1254	23174	0.0067
^{232}U	87402		17 / 25		87377	0.0054

Bground : 27/8/90 51h (×74/51)

Tail method: 232U modelling

THORIUM Count time: 74h Start: 1.45p 22/8/90 Stop: 3.45p 25/8/90

Channels counted: -30,+10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	4154		114 / 165	240	3749	0.0180
^{230}Th	10015		374 / 543	120	9352	0.0110
^{228}Th	38526		215 / 312	3835	34379	0.0060
^{224}Ra	35502		1019 / 1479	720	33503	0.0058

Bground: 27/8/90 51h (×74/51)

Tail method: ^{228}Th, model for ^{228}Th.
^{232,230}Th graphically; estimate ^{224}Ra.

RESULTS:

234U/238U: 1.5858 std dev: 0.0172 234U/232U: 0.2652 std dev: 0.0020

[U] ppm: 3.2 U yield: 82.8%

228Th-0.054Ra: 32581 228Th/decay factor: 33433 228Th-232Th: 24684 (0.0075)

230Th/228Th: 0.350 std dev: 0.0042

[Th] ppm: 7.0 Th yield: 28.9%

230Th/234U: 1.1880 std dev. 0.0181 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.1523 std dev: 0.0176 232Th/234U: 0.3989 std dev: 0.0083

Age (kA): ∞ (+) (-) Age at -1σ = 508.5 kA

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments: ~~Cross-contamination in Th counts~~ high bg; high ^{232}Th

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-015-34c Lab number: 18/7/90 1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.000g
Residue weight: 2.341 %residue: 23.4
Weight dissolved: 7.659 %soluble: 76.6
Sample treatment:
— —

Date of U-Th sepn: 19/7/90 Counting delay: 27days 228Th decay factor: 0.9736
Spike activity: U: 1.00dpm/10mls Th: 1.75dpm/10mls Mls spike: 10
Date of plating U: 25/7/90 Th: 24/7

URANIUM Count time: 137h Start: 6.50p 9/8/90 Stop: 11.30a 15/8/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	5715		33 / 105	285	5325	0.0147
234U	9882		57 / 182	952	8745	0.0120
232U	30229		68 / 217	—	30012	0.0056

Bground : 21/8/90 43h (×137/43)
Tail method: model on 232U

THORIUM Count time: 52⅔hrs. Start: 11.45a 15/8/90 Stop: 4.25p 17/8/90
Channels counted: -35, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	3283		19 / 23	80	3180	0.0183
230Th	13481		46 / 56	120	13305	0.0088
228Th	36324		101 / 124	1027	35173	0.0055
224Ra	33618		410 / 502	240	32876	0.0056

Bground: 21/8/90 43hrs. $(\times \frac{52⅔}{43})$
Tail method: 210Po, model for 228Th. graphically for 232,230Th; estimate 224Ra

RESULTS:

234U/238U: 1.6428 std dev: 0.0312 234U/232U: 0.2915 std dev: 0.0039

[U] ppm: 3.4 U yield: 15.4%

228Th-0.054Ra: 33398 228Th/decay factor: 34305 228Th-232Th: 31123 (0.0060)

230Th/228Th: 0.4275 std dev: 0.0047

[Th] ppm: 5.7 Th yield: 42.6%

230Th/234U: 1.4665 std dev. 0.0163 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.4225 std dev: 0.0178 232Th/234U: 0.3400 std dev: 0.0080

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-017-38b Lab number: 12/6/90 3
Sample: Antarctic carbonate

Sample weight: 9.999
Residue weight: 0.831 %residue: 8.3%
Weight dissolved: 9.168 %soluble: 91.7%
Sample treatment: Th fraction slightly yellow [illegible] by Th/Al column

Date of U-Th sepn: 14/6/90 Counting delay: 9 228Th decay factor: 0.990
Spike activity: U: 0.188 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: ~17/6 Th: 19/6

URANIUM Count time: 21½h Start: 11.40pm 20/6/90 Stop: 9.10pm 21/6/90
Channels counted: +10, -60

	Count	std dev	bground	tail	net	%std dev/100
238U	18678	137	14	542	18122	0.006
234U	40188	200	38	289	39861	0.005
232U	16808	130	92	—	16716	0.008

Bground : 25/6/90 24h (2/2) (×21½/24)
Tail method: 232U model

THORIUM Count time: 18½h Start: 9.30pm 21/6/90 Stop: 4pm 22/6/90
Channels counted: +15, -35

	Count	std dev	bground	tail	net	%std dev/100
232Th	1522	39	60	15	1447	0.028
230Th	62619	250	175	25	62419	0.004
228Th	25927	161	171	60	25696	0.006
224Ra	3433				(11215)	0.009

Bground: 25/6/90 24h (1/2) (× 70½/24)
Tail method: 216Po model for 228Th, others graphically

RESULTS:

234U/238U: 2.200 std dev: 0.021 234U/232U: 2.385 std dev: 0.023

[U] ppm: 17.3 U yield: 54.5%

228Th-0.054Ra: 25090 228Th/decay factor: 23882 (± 007) 228Th-232Th: 23643

230Th/228Th: 2.614 std dev: 0.028

[Th] ppm: 2.82 Th yield: 90.6%

230Th/234U: 1.096 std dev. ± 0.014 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.063 std dev: 0.013 232Th/234U: 0.025 std dev: 0.001

Age (kA): 271.3 (+) 12.1 (-) 11.1

(234U/238U)t=0: 3.561 std dev: 0.034 234U/238U age: / std dev:

Comments: 224Ra count is only ~2238 (corr). ~~[illegible]~~
Decay laws suggest that after 3 days, should be at least 11215 counts if sep at plating
Is system cutting out some high E rays?)

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-017-38b Lab number: 21/6/90 3
Sample: Antarctic carbonate c.c from pit 38. Silt + dropstones

Sample weight: 10.001
Residue weight: 0.885 %residue: 8.9%
Weight dissolved: 9.116 %soluble: 91.1%
Sample treatment: Black skins in 7h bkr before small AG 1X column
soluble in HCl, difficult in HNO3

Date of U-Th sepn: 26-6-90 Counting delay: 15 days ^{228}Th decay factor: 0.985
Spike activity: U: 0.18 Bq ml⁻¹ Th: 0.175 Bq ml⁻¹ Mls spike: 10
Date of plating U: 28-6-90 Th: 29-6-90

URANIUM Count time: 24h Start: 10 15am 4/7/90 Stop: 10 15am 5/7/90
Channels counted: -60, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	22107	149	171	384	21552	0 007
^{234}U	47046	217	415	121	46510	0.005
^{232}U	19587	140	65	-	19522	0 007

Bground : 6/7/90 Bh(1/2) (x 24/73)
Tail method: 238U model.

THORIUM Count time: 24h Start: 11 20am 11/7/90 Stop: 11 25am 12/7/90
Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1746	42	96	150	1500	0.030
^{230}Th	69651	264	389	120	69142	0 004
^{228}Th	31193	177	90	1932	29171	0.006
^{224}Ra	27020	164	169	750	26101	0.006

Bground:
Tail method:

RESULTS:

234U/238U: 2.158 std dev: 0.019 234U/232U: 2.382 std dev: 0.020

[U] ppm: 17.7 U yield: 57.1%

228Th-0.054Ra: 27762 228Th/decay factor: 26661 (0.009) 228Th-232Th: 26262

230Th/228Th: 2.593 std dev: 0.021

[Th] ppm: 2 6 3 Th yield: 80.1%

230Th/234U: 1.089 std dev. 0.013 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.056 std dev: 0.012 232Th/234U: 0.024 std dev: 0.001

Age (kA): 267.5 (+) 10.9 (-) 10.0

(234U/238U)t=0: 3.446 std dev: 0.030 234U/238U age: — std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-024-48c Lab number: 21/6/90 2
Sample: Antarctic carbonate

Sample weight: 10.000g
Residue weight: 2.099 %residue: 21.0
Weight dissolved: 7.901 %soluble: 79.0
Sample treatment: Sandy residue
U still quite yellow after ether extraction.

Date of U-Th sepn: 26-6-90 Counting delay: ^{228}Th decay factor: 0.984
Spike activity: U: 0.18 Bq/ml/Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 19/6 Th: 20/6

URANIUM Count time: 22h Start: Stop:
Channels counted: +10, -45

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	16219	127	117	1130	14972	0.009
^{234}U	41110	203	328	395	40387	0.005
^{232}U	18743	137	52	–	18691	0.007

Bground :
Tail method:

THORIUM Count time: 25h Start: Stop:
Channels counted: +10, -35

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	2157	46	86	45	2026	0.024
^{230}Th	55334	235	341	90	54903	0.004
^{228}Th	30076	173	81	815	29180	0.006
^{224}Ra	26615	163	156	360	26099	0.006

Bground:
Tail method:

RESULTS:

234U/238U: 2.698 std dev: 0.028 234U/232U: 2.161 std dev: 0.019

[U] ppm: 14.8 U yield: 59.6% yf = 0.22

228Th-0.054Ra: 27771 228Th/decay factor: 26163 (0.007) 228Th-232Th: 25745

230Th/228Th: 2.098 std dev: 0.017

[Th] ppm: 4.18 Th yield: 91.5% yf = 0.22

230Th/234U: 0.971 std dev. 0.013 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.942 std dev: 0.012 232Th/234U: 0.036 std dev: 0.001

Age (kA): 189.56 (+) 5.62 (-) 5.38

(234U/238U)t=0: 3.884 std dev: 0.040 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-024-48c Lab number: 12/6/90 2
Sample: Antarctic carbonate

Sample weight: 10.001
Residue weight: 2.024 %residue: 20 2
Weight dissolved: 7.976 %soluble: 79 8
Sample treatment:

Date of U-Th sepn: 14/6/90 Counting delay: 8 days ^{228}Th decay factor: 0 942
Spike activity: U: 0.48 dpm/ml Th: 0.75 dpm/ml Mls spike: 10
Date of plating U: 19/6 Th: 21/6

URANIUM Count time: 21½ h Start: Stop:
Channels counted: 210-70

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	20084	142	122	739	19223	0 008
^{234}U	49206	222	273	362	48571	0 005
^{232}U	22387	147	82	—	22305	0 007

Bground : 25/6/90 24h (½) (x 21½/24)
Tail method: model on 232U

THORIUM Count time: 70½ h Start: Stop:
Channels counted: 410-30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	5401	73	24	160	5217	0.014
^{230}Th	144637	380	88	120	144429	0 003
^{228}Th	77307	278	361	596	76350	0 004
^{224}Ra	27304	165	2949	800	23555	0.007

Bground: 25/6/90 24h (2/2) x 70½/24
Tail method: 216Po model for 224Ra, others graphically.

RESULTS:

234U/238U: 2.527 std dev: 0.024 234U/232U: 2.178 std dev: 0.019

[U] ppm: 15.8 U yield: 72.8% gf = 0.22

228Th-0.054Ra: 75078 228Th/decay factor: 70424 (0.004) 228Th-232Th: 69861

230Th/228Th: 2.051 std dev: 0.010

[Th] ppm: 396 Th yield: 72.1% gf = 0.22

230Th/234U: 0.942 std dev. 0.009 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0 914 std dev: 0.009 232Th/234U: 0.033 std dev: 0.001

Age (kA): 179.69 (+) 4.00 (-) 3.87

(234U/238U)t=0: 3.52 std dev: 0.03 234U/238U age: std dev:

Comments:

232U peak was in outlier
so integration limits shifted.

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-025-51c Lab number: 18/7/90 2
Sample: Taylor Valley lacustrine carbonate
Sample weight: 10.002g
Residue weight: 2.334 %residue: 23.3
Weight dissolved: 7.668 %soluble: 76.7
Sample treatment: Dig'd in HCl, [illegible] to rem residue

Date of U-Th sepn: 19/7/90 Counting delay: 15 days 228Th decay factor: 0.9852
Spike activity: U: 1.60Bq/10mls Th: 1.75Bq/10mls Mls spike: 10
Date of plating U: 26/7/90 Th: 23/7

URANIUM Count time: 137h Start: 6.30p 9/8/90 Stop: 11.30a 15/8/90
Channels counted: -30, +10 (small hi-res detector),(3f ~0.05)

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	64615		40/127	1646	62842	0.0041
^{234}U	108072		54/172	409	107491	0.0051
^{232}U	26837		67/213	–	26624	0.0062

Bground : 21/8/90 43h (×137/43)
Tail method: 232U modelling

THORIUM Count time: 67h Start: 12.30p 3/8/90 Stop: 5.30p 6/8/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	9368		16/25	340	9003	0.0110
^{230}Th	269490		41/64	220	269206	0.0019
^{228}Th	79580		77/120	3337	76123	0.0038
^{224}Ra	68570		241/376	800	67394	0.0039

Bground: 21/8/90 43h (×67/43)
Tail method: 216Po model for 228Th.
estimate 224Ra graphically for 232,230Th

RESULTS:

234U/238U: 1.7105 std dev: 0.0088 234U/232U: 4.0374 std dev: 0.0280

[U] ppm: 45.0 U yield: ~42.8% ?

228Th-0.054Ra: 72483 228Th/decay factor: 73573 228Th-232Th: 64570 (0.0048)

230Th/228Th: 4.1692 std dev: 0.0216

[Th] ppm: 7.8 Th yield: 69.5%

230Th/234U: 1.0527 std dev. 0.0089 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0017 std dev: 0.0087 232Th/234U: 0.0355 std dev: 0.0005

Age (kA): 249.2 (+) 7.4 (-) 7.0

(234U/238U)t=0: 2.426 std dev: 0.0125 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-025-5/c Lab number: 26/7/90 #2
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.002g
Residue weight: 2.198g %residue: 22.0
Weight dissolved: 7.804g %soluble: 78.0
Sample treatment: Still high Fe in U after U-Th column due to column overload.
High Ti in Th column

Date of U-Th sepn: 27/7/90 Counting delay: 38 days 228Th decay factor: 0.9630
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 31/7/90 Th: 1/8/90

URANIUM Count time: 24h Start: 4.30p 25/8/90 Stop: 4-30p 26/8
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	73669		18 / 8	6646	67015	0.0042
234U	117586		10 / 5	2103	115478	0.0030
232U	28539		11 / 5		28534	0.0059

Bground : 27/8/90 51h (× 24/51)
Tail method: 238U modelling

THORIUM Count time: 165h Start: 12.10p 3/9/90 Stop: 9.10a 10/9/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	1001		110 / 356	240	405	0.0987
230Th	19144		393 / 1271	100	17773	0.0081
228Th	7357		153 / 495	700	6162	0.0150
224Ra	8597		949 / 3070	240	5287	0.0206

Bground: 27/8/90 51h (× 165/51)
Tail method: 216Po, model for 228Th
graphical for 232,230Th; estimate 224Ra

RESULTS:

234U/238U: ~~1.7461~~ 1.7232 std dev: 0.0082 234U/232U: ~~4.1202~~ 4.0470 std dev: 0.0273

[U] ppm: 44.0 U yield: 83.4%

228Th-0.054Ra: 5877 228Th/decay factor: 6102 228Th-232Th: 5697 (0.0182)

230Th/228Th: 3.1196 std dev: 0.0622

[Th] ppm: 3.9 Th yield: 2.5%

230Th/234U: 0.7708 std dev. 0.01599 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7477 std dev: 0.0154 232Th/234U: 0.0167 std dev: 0.0016

Age (kA): 130.4 (+) 4.9 (-) 4.7

(234U/238U)t=0: 2.041 std dev: 0.010 234U/238U age: std dev:

Comments: Th unreliable - low recovery
· some spectral shift?

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-031-66b Lab number: 21/6/90 1
Sample: Ant Taylor valley lacustrine carbonate.

Sample weight: 9.999g
Residue weight: 0.928 %residue: 9.3
Weight dissolved: 9.071 %soluble: 90.7
Sample treatment: --

Date of U-Th sepn: 26/6/90 Counting delay: 20 days 228Th decay factor: 0.980
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 28/6/90 Th: 24/6/90

URANIUM Count time: 71h Start: 6 10pm 24/6/90 Stop: 5 10pm 2/7/90
Channels counted: -65, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	19762	141	495	0	19267	0.007
^{234}U	39161	198	1194	0	37973	0.005
^{232}U	19621	140	143	0	19428	0.007

Bground : 6/7/90 73h (×71/73)
Tail method: modelling on 238U

THORIUM Count time: 17h Start: 5 40pm 16/7/90 Stop: 10 40am 17/7/90
Channels counted: -35, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1289		63	75	1151	0.053
^{230}Th	42432		252	90	42090	0.005
^{228}Th	23020		60	840	22120	0.007
^{224}Ra	21683		116	300	21267	0.007

Bground: 6/7/90 73h (1/2) .17/73
Tail method: 228Th by 216Po model
others graphically

RESULTS:

234U/238U: 1.971 std dev: 0.017 234U/232U: 1.955 std dev: 0.017

[U] ppm: 16.0 U yield: 19.2%

228Th-0.054Ra: 20972 228Th/decay (2) factor: 20226 (0.007) 228Th (1) -232Th: 19821

230Th/228Th: 2.081 std dev: 0.018

[Th] ppm: 2.68 Th yield: 85.8%

230Th/234U: 1.064 std dev. 0.013 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.033 std dev: 0.013 232Th/234U: 0.028 std dev: 0.001

Age (kA): 258.4 (+) 11.4 (-) 10.4

(234U/238U)t=0: 2.997 std dev: 0.026 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-031-666 Lab number: 12/6/90 1
Sample: Antarctic carbonate c.c clast, pt 66

Sample weight: 10.001
Residue weight: 0.953 %residue: 9.5%
Weight dissolved: 9.048 %soluble: 90.5%
Sample treatment: U formed 3 layers with ether.

Date of U-Th sepn: 14/6/90 Counting delay: 8 days 228Th decay factor: 0.992
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 14/6 ? Th: 21/6 ?

URANIUM Count time: 50½ h Start: 4.05p 18/6/90 Stop: 6.35p 20/6/90
Channels counted: +10, -70

	Count	std dev	bground	tail	net	%std dev/100
238U	48456	220	38	1336	47082	0.005
234U	93267	305	97	574	92596	0.003
232U	48131	219	217	–	47914	0.005

Bground : 25/6/90 24h (1/2) (x 50½/24)
Tail method: modelling on 238U

THORIUM Count time: 70 ½ h Start: 4.30p 22/6/90 Stop: 3p 25/6/90
Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
232Th	4523	67	185	240	4098	0.017
230Th	156923	396	611	160	156153	0.003
228Th	82188	287	546	1561	80081	0.004
224Ra	28815	170	4251	1000	23564	0.008

Bground: 25/6/90 24h (2/2) (x 70½/24)
Tail method: 216Po model for 228Th, others graphically.

RESULTS:

234U/238U: 1.967 std dev: 0.011 234U/232U: 1.933 std dev: 0.011

[U] ppm: 15.9 U yield: 66.6% yf = 0.22

228Th-0.054Ra: 78809 228Th/decay factor: 75313 (0.004) 228Th-232Th: 74711

230Th/228Th: 2.073 std dev: 0.010

[Th] ppm: 2.57 Th yield: 77.1% yf = 0.22

230Th/234U: 1.073 std dev. 0.006 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.040 std dev: 0.008 232Th/234U: 0.028 std dev: 0.001

Age (kA): 264.08 (+) 7.25 (-) 6.85

(234U/238U)t=0: 3.023 std dev: 0.017 234U/238U age: std dev:

Comments: Sample mixture of specimens
from bag 87-031-666??.

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-67a Lab number: 19/9/90 4

Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.000g

Residue weight: 0.608 %residue: 6.1

Weight dissolved: 9.392 %soluble: 93.9

Sample treatment: low int mA for electroplating U & Th.

Date of U-Th sepn: 20/9/90 Counting delay: 27/11 69days ^{228}Th decay factor: 0.9338

Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10mls

Date of plating U: 23/9 Th: 25/9

URANIUM Count time: 46hrs Start: 4.10p 27/11/90 Stop: 2.10p 29/11/90

Channels counted: -50, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	217150		204 → 209	43274	173667	0.0029
^{234}U	209881		482 → 493	10386	199002	0.0024
^{232}U	42387		91 → 93	—	42294	0.0049

Bground : 19/12/90 45h (x 46/45)

Tail method: model on ^{238}U

THORIUM Count time: 46hrs Start: 4.10p 27/11/90 Stop: 2.10p 29/11/90

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1842		74 → 76	240	1526	0.0304
^{230}Th	109258		157 → 160	80	109018	0.0030
^{228}Th	20619		545 → 557	1071	18991	0.0078
^{224}Ra	19172		3353 → 3428	~~[illegible]~~ 160	15584	0.0097

Bground: 19/12/90 45h (x 46/45)

Tail method: ^{216}Po model for 224/228
graphically for 232, 230 ; 224 estimate

RESULTS:

234U/238U: 1.1459 std dev: 0.0043 234U/232U: 4.7052 std dev: 0.0257

[U] ppm: 64.0 U yield: 64.5%

228Th-0.054Ra: 18149 228Th/decay factor: 19436 228Th-232Th: 17910, 0.0089

230Th/228Th: 6.0870 std dev: 0.0572

[Th] ppm: 3.9 Th yield: 28.1%

230Th/234U: 1.2937 std dev. 0.0141 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.2549 std dev: 0.0136 232Th/234U: 0.0181 std dev: 0.0006

Age (kA): ∞ (+) (-)

(234U/238U)i=0: [illegible] std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-67a Lab number: 24/9/90 4
Sample: Taupo Valley lacustrine carbonate

Sample weight: 10.000g
Residue weight: 0.591 %residue: 5.9
Weight dissolved: 9.409 %soluble: 94.1
Sample treatment:

Date of U-Th sepn: 25/9/90 Counting delay: 83days ^{228}Th decay factor: 0.9209
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 27/9 Th: 28/9

URANIUM Count time: 55h Start: 10.55a 17/12 Stop: 3.55p 19/12
Channels counted: -50, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	164016	411	(202) 247	6834	161935	0.0026
^{234}U	183194	428	(502) 614	1646	180594	0.0024
^{232}U	38905	197	(90) 110	—	38795	0.0051

Bground : 14/12/90 45hrs × $\frac{55}{45}$
Tail method: modelling on ^{238}U

THORIUM Count time: 55h Start: 10.55a 17/12 Stop: 3.55p 19/12
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	5140	72	(64) 78	480	4582	0.0165
^{230}Th	323731	569	(152) 186	240	325005	0.0018
^{228}Th	64613	254	(501) 612	1899	62102	0.0042
^{224}Ra	63916	253	(3317) 4152	1000	58764	0.0045

Bground: 19/12/90 45hrs × $\frac{55}{45}$
Tail method: modelling on ^{216}Po for ^{224}Ra under ^{228}Th
graphical for others

RESULTS:

234U/238U: 1.117 std dev: 0.0040 234U/232U: 4.650 std dev: 0.026

[U] ppm: 64.9 U yield: 49.5%

228Th-0.054Ra: 58929 228Th/decay factor: 65990 228Th-232Th: 59408

230Th/228Th: 5.437 std dev: 0.0273

[Th] ppm: 3.50 Th yield: 77.9% yp = 0.22

230Th/234U: 1.169 std dev. 0.0088 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.134 std dev: 0.0085 232Th/234U: 0.0160 std dev: 0.0005

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-74a Lab number: 24/9/90 1
Sample: Taylor Valley Lacustrine carbonate

Sample weight: 10.000g
Residue weight: 0.767 %residue: 7.7
Weight dissolved: 9.233 %soluble: 92.3
Sample treatment:

Date of U-Th sepn: 25/9/90 Counting delay: 29/11 67days ^{228}Th decay factor: 0.9356
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10ml Mls spike: 10
Date of plating U: 27/9 Th: 28/9

URANIUM Count time: 116hrs Start: 2.15p 29/11/90 Stop: 10.15a 4/12/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	52746		204 → 526	435	51785	0.0045
^{234}U	105322		427 → 1101	303	103918	0.0031
^{232}U	55487		94 → 242	—	55245	0.0043

Bground : 19/12/90 45h ($\times \frac{116}{45}$)
Tail method: model on ^{238}U

THORIUM Count time: 116hrs Start: 2.15p 29/11/90 Stop: 10.15a 4/12/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	4705		68 → 175	400	4130	0.0176
^{230}Th	157442		156 → 402	240	156800	0.0025
^{228}Th	81658		525 → 1353	2836	77469	0.0038
^{224}Ra	76609		3375 → 8700	800	67309	0.0044

Bground: 19/12/90 45h ($\times \frac{116}{45}$)
Tail method: ^{216}Po model for 224/228
others graphically; 224 estimated

RESULTS:

234U/238U: 2.0067 std dev: 0.0110 234U/232U: 1.8810 std dev: 0.0100

[U] ppm: 14.9 U yield: 33.4%

228Th-0.054Ra: 73834 228Th/decay factor: 78917 228Th-232Th: 74787, 0.0044

230Th/228Th: 2.0966 std dev: 0.0106

[Th] ppm: 2.6 Th yield: 46.5%

230Th/234U: 1.1146 std dev. 0.0035 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0812 std dev: 0.0034 232Th/234U: 0.0299 std dev: 0.0006

Age (kA): 299.0 (+) 4.4 (-) 4.2

(234U/238U)t=0: 3.322 std dev: 0.018 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-74a Lab number: 19/9/90 1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 9.994g
Residue weight: 0.783g %residue: 7.8%
Weight dissolved: 9.217g %soluble: 92.2%
Sample treatment: 7 hours plating Th

Date of U-Th sepn: 20/9/90 Counting delay: 54 days 228Th decay factor: 0.9478
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 23/9 Th: 25/9

URANIUM Count time: 49½hrs Start: 1.06p 12/11/90 Stop: 2.36p 14/11/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	58186		125 → 258	525	57405	0.0043
234U	117417		284 → 586	278	116553	0.0030
232U	62180		59 → 122	—	62058	0.0040

Bground: 18/9/90 24h ×49½/24
Tail method: model on 238U

THORIUM Count time: 49½hrs Start: 1.06p 12/11/90 Stop: 2.36p 14/11/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	2462		24 → 50	360	2052	0.0261
230Th	84739		41 → 85	240	84414	0.0035
228Th	45282		246 → 507	2102	42673	0.0051
224Ra	44471		1317 → 2840	200	41431	0.0053

Bground: 18/9/90 24h ×49½/24
Tail method: 216Po model for 228Th
graphical for 232, 230
estimate for 224Ra

RESULTS:

234U/238U: 2.0432 std dev: 0.0102 234U/232U: 1.8781 std dev: 0.0094

[U] ppm: 14.6 U yield: 87.9%

228Th-0.054Ra: 40436 228Th/decay factor: 42663 228Th-232Th: 40611, 0.0058

230Th/228Th: 2.0786 std dev: 0.0141

[Th] ppm: 2.3 Th yield: 59.2%

230Th/234U: 1.1068 std dev. 0.0093 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0736 std dev: 0.0090 232Th/234U: 0.0261 std dev: 0.0007

Age (kA): 289.0 (+) 9.6 (-) 8.9

(234U/238U)t=0: 3.340 std dev: 0.017 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-036-76b Lab number: 28/6/90 3
Sample: Antarctic lacustrine carbonate

Sample weight: 10.000g
Residue weight: 0.896 %residue: 9.0
Weight dissolved: 9.104 %soluble: 91.0
Sample treatment: Green phase on 1st column
Still strong yellow colour after 1st column
Brown soln when collected to small Cl column.

Date of U-Th sepn: 4/7/90 Counting delay: 14 days 228Th decay factor: 0.986
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 13/7/90 Th: 11/7/90

URANIUM Count time: 23h Start: 6.45pm 21/7/90 Stop: 5.45pm 22/7/90
Channels counted: +15, -45

	Count	std dev	bground	tail	net	%std dev/100
238U	22835		135	2707	19993	0.008
234U	42606		344	1175	41087	0.005
232U	21268		56	-	21212	0.007

Bground : BGROUND 6/7/90 1/2 23H (x23/23)
Tail method: model on 238U

THORIUM Count time: 43h Start: 5.40p 18/7/90 Stop: 12.40pm 20/7/90
Channels counted: +10, -35

	Count	std dev	bground	tail	net	%std dev/100
232Th	1546		160	90	1296	0.033
230Th	56042		625	135	55282	0.004
228Th	28628		151	643	27834	0.006
224Ra	22806		295	450	22061	0.007

Bground: BGROUND 6/7/90 1/2 23H (x43/23)
Tail method: 216Po model of 224Ra, others graphically

RESULTS:

234U/238U: 2.055 std dev: 0.019 234U/232U: 1.937 std dev: 0.017

[U] ppm: 15.2 U yield: 64.7%

228Th-0.054Ra: 26643 228Th/decay factor: 25706 (0.007) 228Th-232Th: 25347

230Th/228Th: 2.151 std dev: 0.017

[Th] ppm: 2.36 Th yield: 43.1%

230Th/234U: 1.110 std dev. 0.014 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.077 std dev: 0.013 232Th/234U: 0.025 std dev: 0.001

Age (kA): 291.5 (+) 14.6 (-) 13.1

(234U/238U)t=0: 3.43 std dev: 0.051 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-036-766 Lab number: 10/7/90 3
Sample: Taylor Valley lacustrine carbonate.
Sample weight: 10.001g
Residue weight: 9 222 %residue: 7.8
Weight dissolved: 0.779 %soluble: 92.2
Sample treatment: —

Date of U-Th sepn: 11-7-90 Counting delay: 21days ^{228}Th decay factor: 0.979
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: Th:

URANIUM Count time: 25¼h Start: Stop:
Channels counted: -60, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	22547		181	280	22086	0.007
^{234}U	44897		414	156	44327	0.005
^{232}U	22487		71		22416	0.007

Bground : (125¼/73)
Tail method: 238U modelling

THORIUM Count time: 30h Start: Stop:
Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	4299		120	2600	1579	0.025
^{230}Th	54416		468	800	53148	0.004
^{228}Th	35830		111	9182	26537	0.007
^{224}Ra	29232		209	2400	26623	

Bground:
Tail method: 216Po model for 224Ra
others graphically.

RESULTS:

234U/238U: 2.007 std dev: 0.024 234U/232U: 1.977 std dev: 0.024

[U] ppm: 15.6 U yield: 62.3%

228Th-0.054Ra: 228Th/decay factor: 228Th-232Th: 24059

230Th/228Th: 2.2090 std dev: 0.0240

[Th] ppm: 3.0 Th yield: 57.9%

230Th/234U: 1.117 std dev. 0.026 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0840 std dev: 0.025 232Th/234U: 0.0350 std dev: 0.0010

Age (kA): 301.9 (+) 31.7 (-) 25.5

(234U/238U)t=0: 3.34 std dev: 0.04 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-85a Lab number: 14/9/90 2
Sample: Taylor Valley Lacustrine Carbonate

Sample weight: 9.999g
Residue weight: 2.713 %residue: 27.1
Weight dissolved: 7.286 %soluble: 72.9
Sample treatment:

Date of U-Th sepn: 15/9/90 Counting delay: 47 days ^{228}Th decay factor: 0.9544
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 20/9 Th: 21/9

URANIUM Count time: 93h Start: 1.52p 1/11/90 Stop: 10.52a 5/11
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	83132		126 -> 488	2662	79982	0.0037
^{234}U	217132		288 -> 1116	1117	214899	0.0022
^{232}U	76397		57 -> 221	—	76176	0.0036

Bground : 18/9/90 24h $(\times\frac{93}{24})$
Tail method: model on ^{238}U

THORIUM Count time: 93h Start: 1.52p 1/11/90 Stop: 10.52a 5/11
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	11011		27 -> 105	800	10106	0.0108
^{230}Th	179131		42 -> 163	480	178488	0.0024
^{228}Th	109801		220 -> 853	4900	104048	0.0033
^{224}Ra	106823		1416 -> 5445	2000	99328	0.0034

Bground: 18/9/90 24h $(\times\frac{93}{24})$
Tail method: ^{210}Po model for ^{228}Th; estimate ^{224}Ra; others graphically

RESULTS:

234U/238U: 2.6868 std dev: 0.0116 234U/232U: 2.8211 std dev: 0.0119

[U] ppm: 21.1 U yield: 57.5%

228Th-0.054Ra: 98684 228Th/decay factor: 103399 228Th-232Th: 93293, 0.0040

230Th/228Th: 1.9132 std dev: 0.0089

[Th] ppm: 6.3 Th yield: 72.4%

230Th/234U: 0.6782 std dev. 0.0043 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6578 std dev: 0.0042 232Th/234U: 0.0372 std dev: 0.0005

Age (kA): 101.5 (+) 1.0 (-) 1.0

(234U/238U)t=0: 3.240 std dev: 0.014 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-85a Lab number: 1/9/90 2
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 2.746 %residue: 27.5
Weight dissolved: 7.255 %soluble: 72.5
Sample treatment: Left one week after HF treatment
The yellow solution on plating uranium, v. high gas discharge in cell ([illegible]?)

Date of U-Th sepn: 10/9/90 Counting delay: 40days 228Th decay factor: 0.9611
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 17/9 Th: 18/9

URANIUM Count time: 166½hrs Start: 4.32p 20/10/90 Stop: 3.02p 27/10/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	19887		129 875	2294	16698	0.0091
234U	47571		267 1852	855	44864	0.0050
232U	17004		63 / 437	—	16567	0.0080

Bground : 18/9/90 24h (× 166½/24)
Tail method: model on 238U

THORIUM Count time: 166½hrs Start: 4.32p 20/10/90 Stop: 3.02p 27/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	22273		25 / 173	600	21500	0.0071
230Th	362070		40 / 278	400	361392	0.0017
228Th	220610		168 / 1166	7183	212261	0.0023
224Ra	206064		1416 / 9824	2400	193840	0.0024

Bground: 18/9/90 24h (× 166½/24)
Tail method: 214Pb model for 224/228
estimate for 228, graphical for 232, 230Th

RESULTS:

234U/238U: 2.6868 std dev: 0.0279 234U/232U: 2.7080 std dev: 0.0255

[U] ppm: 20.5 U yield: 70%

228Th-0.054Ra: 201794 228Th/decay factor: 209961 228Th-232Th: 188461, 0.0028

230Th/228Th: 1.9176 std dev: 0.0330

[Th] ppm: 6.7 Th yield: 81.7%

230Th/234U: 0.7081 std dev. 0.0071 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6709 std dev: 0.0069 232Th/234U: 0.0409 std dev: 0.00[illegible]5

Age (kA): 108.4 (+) 1.8 (-) 1.7

(234U/238U)t=0: 3.283 std dev: 0.054 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-95a   Lab number: 1/8/90 2
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 0.641   %residue: 6.4
Weight dissolved: 9.360   %soluble: 93.6
Sample treatment:

Date of U-Th sepn: 2/8/90   Counting delay: 40days   228Th decay factor: 0.9611
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls   Mls spike: 10
Date of plating U: 5/8   Th: 6/8

URANIUM Count time: 27h   Start: 12.35p 11/9/90   Stop: 3.35p 12/9
Channels counted: -45, +15

	Count	std dev	bground	tail	net	%std dev/100
238U	41559		176 / 93	2089	39377	0.0053
234U	56227		390 / 206	1185	54836	0.0044
232U	26641		124 / 66		26575	0.0061

Bground : 27/8/90 51h   (×27/51)
Tail method: 238U modelling

THORIUM Count time: 138h   Start: 3.45p 12/9/90   Stop: 9.45a 18/9
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	1794		12 / 32	0	1762	0.0243
230Th	64205		14 / 38	0	64167	0.0040
228Th	34336		23 / 62	2116	32158	0.0059
224Ra	35206		16 / 43	600	34563	0.0055

Bground: 27/8/90 51h   (×138/51)
Tail method: 216Po model for 232Th
graphical for 230,228Th; estimate 224Ra

RESULTS:

234U/238U: 1.3926   std dev: 0.0096   234U/232U: 2.0634   std dev: 0.0155

[U] ppm: 23.2   U yield: 69.0%

228Th-0.054Ra: 30292   228Th/decay factor: 31518   228Th-232Th: 29756 (0.0067)

230Th/228Th: 2.1565   std dev: 0.0168

[Th] ppm: 2.7   Th yield: 15.6%

230Th/234U: 1.0451   std dev. 0.0113   Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0138   std dev: 0.0110   232Th/234U: 0.0278   std dev: 0.0003

Age (kA): 244.1   (+) 15.9   (-) 14.0

(234U/238U)t=0: 1.893   std dev: 0.013   234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-95a　　Lab number: 6/8/90 2
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.002g
Residue weight: 0.649　　%residue: 6.5
Weight dissolved: 9.353　　%soluble: 93.5
Sample treatment:

Date of U-Th sepn: 7/8/90　　Counting delay: 46 days　　^{228}Th decay factor: 0.9554
Spike activity: U: 1.80Bq/10mls Th: 1.75Bq/10mls Mls spike: 10
Date of plating U: 9/8　　Th: 10/8

URANIUM Count time: 26h　　Start: 3.10 20/9/90　　Stop: 5.10 21/9
Channels counted: -40, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	30328		39 / 42	672	29614	0.0059
^{234}U	60803		58 / 63	293	60447	0.0041
^{232}U	31537		132 / 143		31394	0.0057

Bground : 18/9/90 24h　　(×26/24)
Tail method: ^{238}U modelling

THORIUM Count time: 24h　　Start: 5.30p 21/9/90　　Stop: 5.30p 22/9/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1370		23	80	1267	0.0303
^{230}Th	53263		43	120	53100	0.0044
^{228}Th	28691		206	1679	26806	0.0065
^{224}Ra	26769		1433	400	24936	0.0068

Bground: 18/9/90 24h　　(×24/24)
Tail method: model on ^{224}Ra for ^{228}Th
graphical for 232,230Th; estimate for ^{224}Ra

RESULTS:

234U/238U: 2.0412 std dev: 0.0147 234U/232U: 1.9284 std dev: 0.0135

[U] ppm: 14.8　　U yield: 84.7%

228Th-0.054Ra: 25459　　228Th/decay factor: 26648　　228Th-232Th: 25381 (0.0072)

230Th/228Th: 2.0921 std dev: 0.0177

[Th] ppm: 2.3　　Th yield: 76.5%

230Th/234U: 1.0849　　std dev. 0.0119　　Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0523　　std dev: 0.0116　　232Th/234U: 0.0259　　std dev: 0.0008

Age (kA): 270.2　　(+) 10.9 (-) 10.0

(234U/238U)t=0: 3.216　　std dev: 0.023　　234U/238U age:　　std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-96a Lab number: 6/8/90 1

Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 0.808g %residue: 8.1
Weight dissolved: 9.193g %soluble: 91.9
Sample treatment:

Date of U-Th sepn: 7/8/90 Counting delay: 46days ^{228}Th decay factor: 0.9554
Spike activity: U: 1.88Bq/10ml Th: 1.75Bq/10ml Mls spike: 10ml
Date of plating U: 4/8/90 Th: 10/8/90

URANIUM Count time: 26h Start: 3.10 20/9/90 Stop: 5.10 21/9
Channels counted: -40, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	31356		118 / 128	353	30875	0.0057
^{234}U	75445		272 / 295	630	74520	0.0037
^{232}U	28679		49 / 53	—	28626	0.0059

Bground : 18/9/90 24h (× 26/24)
Tail method: model on ^{238}U

THORIUM Count time: 24h Start: 5.30 21/9 Stop: 5.30 22/9
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1058		77	80	901	0.0387
^{230}Th	38106		255	40	37811	0.0052
^{228}Th	20220		77	769	19374	0.0075
^{224}Ra	18605		198	160	18247	0.0075

Bground: 18/9/90 24h (× 24/24)
Tail method: ^{224}Ra model after ^{228}Th
graphical for ^{232,230}Th, estimate ^{224}Ra

RESULTS:

234U/238U: 2.4136 std dev: 0.0164 234U/232U: 2.6052 std dev: 0.0181

[U] ppm: 17.2 U yield: 77.2%

228Th-0.054Ra: 18389 228Th/decay factor: 19247 228Th-232Th: 18346 (0.0083)

230Th/228Th: 2.0610 std dev: 0.0202

[Th] ppm: 2.3 Th yield: 55.2%

230Th/234U: 0.7917 std dev. 0.0045 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7680 std dev: 0.0042 232Th/234U: 0.0183 std dev: 0.0007

Age (kA): 130.8 (+) 2.8 (-) 2.7

(234U/238U)t=0: 3.038 std dev: 0.021 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-96a Lab number: 1/8/90 1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.0029
Residue weight: 0.777 %residue: 7.8
Weight dissolved: 9.225 %soluble: 92.2
Sample treatment: some SiO_2 in first column.

Date of U-Th sepn: 2/8/90 Counting delay: 32days ^{228}Th decay factor: 0.9687
Spike activity: U: 180 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 4/8 Th: 5/8

URANIUM Count time: 27h Start: 9.25a 10/9/90 Stop: 12.25p 11/9
Channels counted: -35, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	50503		176 / 43	554	49856	0.0045
^{234}U	50663		345 / 209	177	50277	0.0045
^{232}U	19241		140 / 74		19167	0.0073

Bground : 27/8/90 51h (× 27/51)
Tail method: ^{238}U modelling

THORIUM Count time: 165h Start: 12.10p 3/9/90 Stop: 9.10a 10/9
Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1216		11 / 36	120	1060	0.0349
^{230}Th	57755		14 / 45	160	57550	0.0042
^{228}Th	31532		23 / 74	1416	30042	0.0060
^{224}Ra	29300		18 / 58	400	28842	0.0060

Bground: 27/8/90 51h (× 165/51)
Tail method: ^{216}Po model fit ^{228}Th.
graphical fit ^{232,230}Th; estimate ^{224}Ra

RESULTS:

234U/238U: 1.0074 std dev: 0.0064 234U/232U: 2.6231 std dev: 0.0225

[U] ppm: 41.3 U yield: 49.8%

228Th-0.054Ra: 28485 228Th/decay factor: 29405 228Th-232Th: 28345 (0.0066)

230Th/228Th: 2.0303 std dev: 0.0159

[Th] ppm: 1.7 Th yield: 12.4%

230Th/234U: 0.7740 std dev. 0.0090 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7508 std dev: 0.0087 232Th/234U: 0.0136 std dev: 0.0005

Age (kA): 150.3 (+) 4.2 (-) 4.0

(234U/238U)t=0: 1.011 std dev: 0.006 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-61-1306 Lab number: 1/9/90 01/Th1
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 2.093 %residue: 20.9
Weight dissolved: 7.908 %soluble: 79.1
Sample treatment: –

Date of U-Th sepn: 10/9/90 Counting delay: 31 days ^{228}Th decay factor: 0.9697
Spike activity: U: 1.80 Bq/10ml Th: 1.75 Bq/10ml Mls spike: 10
Date of plating U: 13/9 Th: 14/9

URANIUM Count time: 149hrs Start: 12.42p 11/10/90 Stop: 5.42p 17/10/90
Channels counted: -60, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	52707		144 / 894	437	51376	0.0045
^{234}U	106723		304 / 1887	308	104528	0.0032
^{232}U	85952		66 / 410	—	85542	0.0034

Bground : 18/9/90 24h 149/24
Tail method: model on ^{232}U

THORIUM Count time: 149hrs Start: 12.42p 11/10/90 Stop: 5.42p 17/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	9293		26 / 161	320	8812	0.0112
^{230}Th	67844		41 / 256	400	67188	0.0039
^{228}Th	84587		235 / 1447	3804	79336	0.0038
^{224}Ra	76036		1415 / 8785	1200	66051	0.0044

Bground: 16/11/90 24h (×149/24)
Tail method: ^{224}Ra model for ^{228}Th.
estimate ^{224}Ra; graphical for ^{232,230}Th

RESULTS:

234U/238U: 2.0346 std dev: 0.0112 234U/232U: 1.2219 std dev: 0.0057

[U] ppm: 11.1 U yield: 40.5%

228Th-0.054Ra: 75769 228Th/decay factor: 78137 228Th-232Th: 69325, 0.0047

230Th/228Th: 0.9692 std dev: 0.0059

[Th] ppm: 6.9 Th yield: 33.6%

230Th/234U: 0.7932 std dev. 0.0061 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7694 std dev: 0.0059 232Th/234U: 0.1009 std dev: 0.0013

Age (kA): 133.9 (+) 1.9 (-) 1.9

(234U/238U)t=0: 2.504 std dev: 0.014 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-61-1306 Lab number: 14/9/90 1

Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g

Residue weight: 2.107 %residue: 21.1

Weight dissolved: 7.894 %soluble: 78.9

Sample treatment: v. high in Fe,, possibly in MnO$_2$
U electroplated for 12hrs

Date of U-Th sepn: 15/9/90 Counting delay: 44 days ^{228}Th decay factor: 0.9573

Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10

Date of plating U: 20/9 Th: 21/9

URANIUM Count time: 70½ hrs Start: 3.15p 29/10/90 Stop: 1.45p 1/11

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	35481		129 → 379	196	34906	0.0054
^{234}U	72286		275 → 808	149	71329	0.0038
^{232}U	58056		59 → 173	—	57883	0.0042

Bground : 18/4/90 24h (× 70½/24)

Tail method: model on ^{238}U

THORIUM Count time: 70½ hrs Start: 3.15p 29/10/90 Stop: 1.45p 1/11

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	9145		24 → 71	320	8754	0.0112
^{230}Th	68634		42 → 123	240	68271	0.0038
^{228}Th	84127		212 → 623	3716	79788	0.0037
^{224}Ra	81101		1418 → 4165	1000	75936	0.0039

Bground: 18/4/90 24h (× 70½/24)

Tail method: ^{216}Po model for ^{228}Th;
estimate for ^{224}Ra; others graphically

RESULTS:

234U/238U: 2.0435 std dev: 0.0135 234U/232U: 1.2323 std dev: 0.0070

[U] ppm: 11.2 U yield: 57.6%

228Th-0.054Ra: 75687 228Th/decay factor: 79063 228Th-232Th: 70309, 0.0047

230Th/228Th: 0.9710 std dev: 0.0059

[Th] ppm: 6.7 Th yield: 72.0%

230Th/234U: 0.7880 std dev. 0.0065 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7643 std dev: 0.0063 232Th/234U: 0.0980 std dev: 0.0013

Age (kA): 132.3 (+) 2.0 (-) 2.0

(234U/238U)t=0: 2.510 std dev: 0.017 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-69-1406 Lab number: 1/9/403
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 0.921 %residue: 9.2
Weight dissolved: 9.080 %soluble: 90.8
Sample treatment: ½ml HF added to Th to dissolve cloudiness before large Th (nitrate) column

Date of U-Th sepn: 10/9/90 Counting delay: 57 days ^{228}Th decay factor: 0.9659
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 14/9/90 Th: 18/9/90

URANIUM Count time: 70½h Start: 5.55p 17/10/90 Stop: 4.25p 20/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	35225		126/370	555	34500	0.0055
^{234}U	95590		170/493	183	94614	0.0035
^{232}U	58448		59/173	—	58275	0.0051

Bground : 18/9/90 24h × 70½/24
Tail method: model on ^{238}U

THORIUM Count time: 70½hrs Start: 5.55p 17/10/90 Stop: 4.25p 20/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	819		36/106	80	633	0.0501
^{230}Th	25539		42/123	80	25336	0.0065
^{228}Th	15905		227/667	724	14514	0.0091
^{224}Ra	17683		1415/4157	240	13286	0.0112

Bground: 18/9/90 24h (×70½/24)
Tail method: 228/232 model for 228Th, estimate for 224Ra, graphical for 232Th, 230Th.

RESULTS:

234U/238U: 2.7424 std dev: 0.0176 234U/232U: 2.4720 std dev: 0.0150

[U] ppm: 14.5 U yield: 38.1%

228Th-0.054Ra: 13797 228Th/decay factor: 14313 228Th-232Th: 13680, 0.0102

230Th/228Th: 1.8520 std dev: 0.0222

[Th] ppm: 2.2 Th yield: 14.0%

230Th/234U: 0.7492 std dev. 0.0101 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7207 std dev: 0.0098 232Th/234U: 0.0187 std dev: 0.0009

Age (kA): 118.1 (+) 2.6 (-) 2.6

(234U/238U)t=0: 3.424 std dev: 0.022 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-69-1406 Lab number: 14/9/90 3
Sample: Taylor valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 0.771 %residue: 7.7
Weight dissolved: 9.230 %soluble: 92.3
Sample treatment:

Date of U-Th sepn: 15/9/90 Counting delay: 52 days ^{228}Th decay factor: 0.9497
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10mls
Date of plating U: 20/9 Th: 21/9

URANIUM Count time: 53h Start: 10.56a 5/11/90 Stop: 3.56 7/11
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	47590		121 → 267	2996	44327	0.0051
^{234}U	129372		285 → 629	1234	127509	0.0028
^{232}U	53311		59 → 130	—	53181	0.0043

Bground : 18/9/90 24h (×53/24)
Tail method: model on ^{238}U

THORIUM Count time: 53h Start: 10.56a 5/11/90 Stop: 3.56p 7/11
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	3345		27 → 60	320	2965	0.0206
^{230}Th	119965		41 → 91	480	119394	0.0029
^{228}Th	74820		220 → 486	3574	70760	0.0040
^{224}Ra	71849		1415 → 3125	1600	67124	0.0041

Bground: 18/9/90 24h (×53/24)
Tail method: ^{216}Po model for ^{228}Th
graphical for 232,230; estimate for ^{224}Ra

RESULTS:

234U/238U: 2.8766 std dev: 0.0167 234U/232U: 2.3976 std dev: 0.0123

[U] ppm: 13.2 U yield: 70.4%

228Th-0.054Ra: 67135 228Th/decay factor: 70691 228Th-232Th: 67726, 0.0044

230Th/228Th: 1.7629 std dev: 0.0093

[Th] ppm: 2.0 Th yield: 92.2%

230Th/234U: 0.7353 std dev. 0.0054 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.7132 std dev: 0.0051 232Th/234U: 0.0170 std dev: 0.0004

Age (kA): 114.3 (+) 1.3 (-) 1.3

(234U/238U)t=0: 3.583 std dev: 0.021 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-82-153b Lab number: 15/8/90 2

Sample: Taylor Valley lacustrine carbonates.

Sample weight: 10.002

Residue weight: 0.656 %residue: 6.6%

Weight dissolved: 9.346 %soluble: 93.4%

Sample treatment: Both Th & U covered with Ag while plating

Date of U-Th sepn: 16/8/90 Counting delay: 47 days ^{228}Th decay factor: 0.9544

Spike activity: U: 1.80 dpm/10mls Th: 1.75 dpm/10mls Mls spike: 10

Date of plating U: 22/8 Th: 23/8

URANIUM Count time: 49½ hrs Start: 9.38a 3/10/90 Stop: 10.48a 5/10/90

Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	37174		104 / 213	2712	34249	0.0058
^{234}U	98268		266 / 545	2041	95652	0.0033
^{232}U	46548		46 / 94	—	46454	0.0046

Bground : 16/9/90 24h (x49½/24)

Tail method: model on ^{232}U

THORIUM Count time: 49½ hrs Start: 9.38a 3/10/90 Stop: 10.48a 5/10/90

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1044		24 / 49	320	675	0.0557
^{230}Th	30775		119 / 244	240	30289	0.0058
^{228}Th	18325		212 / 434	3293	14598	0.0102
^{224}Ra	17175		1432/2934	800	13441	0.0108

Bground: 18/1/90 24h (x49½/24)

Tail method: ^{216}Po model for ^{228}Th, estimate for ^{224}Ra. graphical for ^{230,232}Th

RESULTS:

234U/238U: 2.7923 std dev: 0.0186 234U/232U: 2.0586 std dev: 0.0117

[U] ppm: 11.5 U yield: 66.3%

228Th-0.054Ra: 13872 228Th/decay factor: 14535 228Th-232Th: 13860, 0.0116

230Th/228Th: 2.1854 std dev: 0.0283

[Th] ppm: 2.2 Th yield: 20.5%

230Th/234U: **1.0616** std dev. 0.0450 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0298 std dev: 0.0146 232Th/234U: 0.0229 std dev: 0.0013

Age (kA): 232.1 (+) 9.1 (-) 8.5

(234U/238U)t=0: 4.429 std dev: 0.030 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-85-157b Lab number: 24/9/90 2
Sample: Taylor Valley lacustrine carbonate.

Sample weight: 10.001g
Residue weight: 2.827 %residue: 28.3
Weight dissolved: 7.173 %soluble: 71.7
Sample treatment: high in SiO_2
extra 1ml HN washing in small U column

Date of U-Th sepn: 25/9/90 Counting delay: 7/12 76days ^{228}Th decay factor: 0.9273
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10mls
Date of plating U: 27/9 Th: 28/9

URANIUM Count time: 95h Start: 7/12/90 1.35p Stop: 11/12/90 12.40p
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	67513		202 → 426	1006	66081	0.0040
^{234}U	170599		438 → 925	451	169223	0.0025
^{232}U	63231		95 → 201	—	63030	0.0040

Bground : 19/12/90 45h (x95/45)
Tail method: model on ^{238}U

THORIUM Count time: 95h Start: 7/12/90 1.35p Stop: 11/12/90 12.40p
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	9012		68 → 144	150	8714	0.0111
^{230}Th	136766		153 → 323	200	136243	0.0027
^{228}Th	83648		521 → 1100	2508	80040	0.0037
^{224}Ra	79535		3385 → 7146	400	71989	0.0041

Bground: 19/12/90 45h (x95/45)
Tail method: ^{216}Po model for 224/228
others graphically

RESULTS:

234U/238U: 2.5608 std dev: 0.0121 234U/232U: 2.6980 std dev: 0.0127

[U] ppm: 21.4 U yield: 46.5%

228Th-0.054Ra: 76153 228Th/decay factor: 82123 228Th-232Th: 73409, 0.0042

230Th/228Th: 1.8559 std dev: 0.0093

[Th] ppm: 7.1 Th yield: 55.8%

230Th/234U: 0.6879 std dev. 0.0046 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6672 std dev: 0.0044 232Th/234U: 0.0437 std dev: 0.0005

Age (kA): 104.0 (+) 1.1 (-) 1.1

(234U/238U)t=0: 3.088 std dev: 0.0156 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-85-157b Lab number: 19/9/90 2
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 2.799g %residue: 28.0%
Weight dissolved: 7.203 %soluble: 72.0%
Sample treatment: Blockage in U Th sepn column - probably SiO_2. unexpensive
High Fe in U plating cell (insuff. flux hrs?)

Date of U-Th sepn: 20/9/90 Counting delay: 56 days ^{228}Th decay factor: 0.4459
Spike activity: U: 1.30 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 22/9 Th: 25/9

URANIUM Count time: 117½ hrs Start: 2.40p 14/11/90 Stop: 12.10p 19/11/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	68435		129 → 632	3152	64851	0.0042
^{234}U	172352		284 → 1340	1179	169833	0.0025
^{232}U	65041		60 → 294	—	64747	0.0039

Bground : 18/9/90 24h $(\times \frac{117\frac{1}{2}}{24})$
Tail method: model on ^{238}U

THORIUM Count time: 117½ hrs Start: 2.40p 14/11/90 Stop: 12.10p 19/11/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	8239		25 → 122	600	7517	0.0126
^{230}Th	121652		42 → 206	400	121246	0.0029
^{228}Th	78618		241 → 1180	4457	72981	0.0040
^{224}Ra	80163		1374 → 6727	1200	72236	0.0041

Bground: 18/9/90 24h $(\times \frac{117\frac{1}{2}}{24})$
Tail method: 216,218 model for 228Th
graph for 232, 230; estimate for 224Ra.

RESULTS:

234U/238U: 2.6261 std dev: 0.0128 234U/232U: 2.6223 std dev: 0.0121

[U] ppm: 20.3 U yield: 38.7%

228Th-0.054Ra: 69080 228Th/decay factor: 73051 228Th-232Th: 65514, 0.0048

230Th/228Th: 1.8507 std dev: 0.0104

[Th] ppm: 6.8 Th yield: 40.2%

230Th/234U: 0.7057 std dev. 0.0051 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6846 std dev: 0.0049 232Th/234U: 0.0438 std dev: 0.0006

Age (kA): 108.0 (+) 1.2 (-) 1.2

(234U/238U)t=0: 3.199 std dev: 0.016 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-86-160c Lab number: 19/9/90 3
Sample: Taylor Valley lacustrine carbonate

Sample weight: 9.999g
Residue weight: 2.590 %residue: 25.9
Weight dissolved: 7.409 %soluble: 74.1
Sample treatment:

Date of U-Th sepn: 20/9/90 Counting delay: 19/11 61 days ^{228}Th decay factor: 0.9412
Spike activity: U: 1.80 dpm/10mls Th: 1.75 dpm/10mls Mls spike: 10
Date of plating U: 22/9 Th: 25/9

URANIUM Count time: 52h Start: 12.28p 19/11/90 Stop: 4.28p 21/11/90
Channels counted: -50, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	56246		137 → 297	561	55388	0.0043
^{234}U	104162		303 → 657	305	103200	0.0031
^{232}U	61531		63 → 137	—	61394	0.0040

Bground : 18/9/90 24h ($\times \frac{52}{24}$)
Tail method: model on ^{238}U

THORIUM Count time: 52h Start: 12.28p 19/11/90 Stop: 4.28p 21/11/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	2095		25 → 54	160	1881	0.0255
^{230}Th	47814		41 → 89	120	47605	0.0046
^{228}Th	28837		241 → 522	1500	26815	0.0066
^{224}Ra	28877		1374 → 2977	480	25420	0.0071

Bground: 18/9/90 24h ($\times \frac{52}{24}$)
Tail method: ^{216}Po model for ^{228}Th
graph for ^{232,230}Th; estimate for ^{224}Ra

RESULTS:

234U/238U: 1.8632 std dev: 0.0099 234U/232U: 1.6809 std dev: 0.0085

[U] ppm: 21.9 U yield: 82.8%

228Th-0.054Ra: 25442 228Th/decay factor: 27031 228Th-232Th: 25150, 0.0079

230Th/228Th: 1.8928 std dev: 0.0173

[Th] ppm: 4.3 Th yield: 34.9

230Th/234U: 1.1261 std dev. 0.0118 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0923 std dev: 0.0115 232Th/234U: 0.0445 std dev: 0.0012

Age (kA): 325.0 (+) 17.0 (-) 15.0

(234U/238U)t=0: 3.141 std dev: 0.017 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-86-100c Lab number: 24/9/90 3
Sample: Taylor Valley lac. carbonate

Sample weight: 10.000g
Residue weight: 2.650 %residue: 26.5
Weight dissolved: 7.350 %soluble: 73.5
Sample treatment: high in SiO2

Date of U-Th sepn: 25/9/90 Counting delay: 80 days ^{228}Th decay factor: 0.9237
Spike activity: U: 1.80 Bq/10ml Th: 1.75 Bq/10ml Mls spike: 10
Date of plating U: 27/9 Th: 28/9

URANIUM Count time: 142hrs Start: 12.58p 11/12/90 Stop: 10.58a 17/12/90
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	61732	·	204/644	238	62138	0.0040
^{234}U	114263		427/1347	203	112713	0.0030
^{232}U	62446		95/300	—	62146	0.0039

Bground : 14/12/90 45h (x 142/45)
Tail method: 236U modelling

THORIUM Count time: 142hrs Start: 12.58p 11/12/90 Stop: 10.58a 17/12/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	10101		70/221	320	9560	0.0108
^{230}Th	231832		155/489	400	230943	0.0021
^{228}Th	133383		536/1691	4354	127338	0.0029
^{224}Ra	124496		3375/10650	1200	117646	0.0052

Bground: 14/12/90 45h (x 142/45)
Tail method: 216Po, model for 228Th
others graphically.

RESULTS:

234U/238U: 1.8139 std dev: 0.0091 234U/232U: 1.6786 std dev: 0.0083

[U] ppm: 18.4 U yield: 33.2%

228Th-0.054Ra: 120905 228Th/decay factor: 130979 228Th-232Th: 121419 (0.0032)

230Th/228Th: 1.9020 std dev: 0.0073

[Th] ppm: 4.6 Th yield: 61.7%

230Th/234U: 1.1331 std dev. 0.0071 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.099 std dev: 0.0066 232Th/234U: 0.0455 std dev:

Age (kA): 340.5 (+) 11.9 (-) 10.9

(234U/238U)t=0: 3.108 std dev: 0.0156 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-91-1896 Lab number: 1/8/90 3
Sample: Taylor Valley lacustrine carbonate.

Sample weight: 10.000g
Residue weight: 0.683 %residue: 6.8
Weight dissolved: 9.317 %soluble: 93.2
Sample treatment:

Date of U-Th sepn: 2/8/90 Counting delay: 39days ^{228}Th decay factor: 0.9620
Spike activity: U: 1.80Bq/10mls Th: 1.75Bq/10mls Mls spike: 10
Date of plating U: 4/8 Th: 4/8

URANIUM Count time: 27h Start: Stop:
Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	20871		15 / 8	512	20351	0.0072
^{234}U	39655		24 / 13	316	39306	0.0051
^{232}U	21080		13 / 7		21073	0.0069

Bground : 27/8/90 51h (×27/51)
Tail method: 238U modelling

THORIUM Count time: 27h Start: Stop:
Channels counted: - 30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1566		12 / 6	40	1520	0.0264
^{230}Th	61524		13 / 7	60	61457	0.0040
^{228}Th	32529		22 / 12	1193	31324	0.0059
^{224}Ra	30544		17 / 9	480	30055	0.0059

Bground: 27/8/90 51h (×27/51)
Tail method: 216Po model for 228Th, graphical for 230,232Th, estimate 224Ra

RESULTS:

234U/238U: 1.9314 std dev: 0.0170 234U/232U: 1.8852 std dev: 0.0160

[U] ppm: 15.2 U yield: 54.7%

228Th-0.054Ra: 29701 228Th/decay factor: 30874 228Th-232Th: 29354 (0.0066)

230Th/228Th: 2.0936 std dev: 0.0162

[Th] ppm: 2.4 Th yield: 78.4%

230Th/234U: 1.1225 std dev. 0.0130 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0888 std dev: 0.0126 232Th/234U: 0.0278 std dev: 0.0003

Age (kA): 313.6 (+) 17.4 (-) 15.3

(234U/238U)t=0: 3.238 std dev: 0.029 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-91-1896 Lab number: 6/8/90 3
Sample: Taylor Valley lacustrine carbonate
Sample weight: 10.000g
Residue weight: 0.694 %residue: 6.9
Weight dissolved: 9.306 %soluble: 93.1
Sample treatment:
U sample discoloured, lots of gas evolving while plating

Date of U-Th sepn: 7/8/90 Counting delay: 48days ^{228}Th decay factor: 0.9535
Spike activity: U: 1.80Bq/10mls Th: 1.75Bq/10mls Mls spike: 10
Date of plating U: 9/8 Th: 10/8

URANIUM Count time: 24h Start: 10.15a 19/9/90 Stop: 10.15a 20/9/90
Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	17260		31	225	17004	0.0078
^{234}U	34394		52	369	33973	0.0055
^{232}U	18041		100	—	17935	0.0075

Bground : 18/9/90 24h (×24/24)
Tail method: model on ^{238}U

THORIUM Count time: 40h Start: 5.35p 22/9/90 Stop: 9.35a 24/9/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	2739		77/128	160	2451	0.0224
^{230}Th	104949		262/437	240	104272	0.0031
^{228}Th	54560		77/128	1656	52776	0.0045
^{224}Ra	50282		197/328	600	49354	0.0046

Bground: 15/9/90 24h (×40/24)
Tail method: ^{216}Po, model for ^{228}Th
graphical for ^{232,230}Th; estimate ^{224}Ra

RESULTS:

234U/238U: 1.9479 std dev: 0.0180 234U/232U: 1.8942 std dev: 0.0176

[U] ppm: 14.9 U yield: 52.4%

228Th-0.054Ra: 50111 228Th/decay factor: 52555 228Th-232Th: 50104 (0.0050)

230Th/228Th: 2.0811 std dev: 0.0122

[Th] ppm: 2.2 Th yield: 90.4%

230Th/234U: 1.0987 std dev. 0.0123 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0057 std dev: 0.0119 232Th/234U: 0.0257 std dev: 0.0006

Age (kA): 284.5 (+) 12.9 (-) 11.7

(234U/238U)t=0: 3.210 std dev: 0.031 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-105-2046 Lab number: 14/9/90 4
Sample: Taylor valley lacustrine carbonate

Sample weight: 3.933g
Residue weight: 1.347 %residue: 34.2%
Weight dissolved: 2.586 %soluble: 65.8%
Sample treatment: U plated for ~12hrs

Date of U-Th sepn: 15/9/90 Counting delay: 56 days ^{228}Th decay factor: 0.9459
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 20/9 Th: 21/9

URANIUM Count time: 69h Start: 3.53p 9/11/90 Stop: 12.53p 12/11
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	19765		126→362	309	19094	0.0075
^{234}U	52238		267→768	354	51116	0.0045
^{232}U	85209		58→167	—	85042	0.0034

Bground : 18/9/90 24h ×69/24
Tail method: model on ^{238}U

THORIUM Count time: 69h Start: 3 53p 9/11/90 Stop: 12.53p 12/11
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1960		24→69	120	1771	0.0262
^{230}Th	34059		41→118	200	33741	0.0055
^{228}Th	84773		246→707	3131	80935	0.0037
^{224}Ra	81008		1373→3947	1000	76121	0.0039

Bground: 18/9/90 24h ×69/24
Tail method: ^{210}Po model for ^{228}Th
graphical for ^{232,230}Th; estimate ^{224}Ra

RESULTS:

234U/238U: 2.677 std dev: 0.0234 234U/232U: 0.6011 std dev: 0.0034

[U] ppm: 12.7 U yield: 86.5%

228Th-0.054Ra: 76824 228Th/decay factor: 81218 228Th-232Th: 79447, 0.0039

230Th/228Th: 0.4247 std dev: 0.0029

[Th] ppm: 3.7 Th yield: 83.1%

230Th/234U: 0.7065 std dev. 0.006 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6853 std dev: 0.006 232Th/234U: 0.0360 std dev: 0.0009

Age (kA): 108.0 (+) 1.5 (-) 1.5

(234U/238U)t=0: 3.268 std dev: 0.029 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-105-204b Lab number: 1/9/90 4
Sample: Taylor Valley lacustrine carbonate.

Sample weight: 10.000g
Residue weight: 3.610g %residue: 36.1
Weight dissolved: 6.390 %soluble: 63.9
Sample treatment: Low starting current for Th electrodeposition

Date of U-Th sepn: 10/9/90 Counting delay: 47 days ^{228}Th decay factor: 0.9544
Spike activity: U: 1.80 Bq/10 mls Th: 1.75 Bq/10 mls Mls spike: 10
Date of plating U: 13/9 Th: 17/9

URANIUM Count time: 48h Start: 3.05p 27/10/90 Stop: 3.05p 29/10/90
Channels counted: -50, 110

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	18043		129 → 258	141	17644	0.0077
^{234}U	47830		270 → 540	186	47104	0.0047
^{232}U	31439		58 → 116	—	31323	0.0057

Bground: 18/9/90 24h (× 48/24)
Tail method: model on ^{238}U

THORIUM Count time: 48h Start: 3.05p 27/10/90 Stop: 3.05p 29/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	2764		25 → 50	600	2114	0.0276
^{230}Th	35629		42 → 84	480	35065	0.0054
^{228}Th	44363		226 → 452	7185	36726	0.0062
^{224}Ra	40409		1416 → 2832	2000	35577	0.0060

Bground: 18/9/90 24h (× 48/24)
Tail method: ^{216}Po model for ^{228}Th
estimate ^{224}Ra; graphically for 232, 230

RESULTS:

234U/238U: 2.6697 std dev: 0.0241 234U/232U: 1.5038 std dev: 0.0111

[U] ppm: 12.9 U yield: 45.8%

228Th-0.054Ra: 34805 228Th/decay factor: 36468 228Th-232Th: 34354, 0.0070

230Th/228Th: 0.9797 std dev: 0.0087

[Th] ppm: 4.1[illegible] Th yield: 51.6%

230Th/234U: 0.6515 std dev. 0.0075 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6319 std dev: 0.0073 232Th/234U: 0.0397 std dev: 0.0011

Age (kA): 95.7 (+) 1.7 (-) 1.6

(234U/238U)t=0: 3.182 std dev: 0.029 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-2526 Lab number: 15/8/90 3
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.001g
Residue weight: 3.128 %residue: 31.3
Weight dissolved: 6.873 %soluble: 68.7
Sample treatment:
high in SiO$_2$
Th plated overnight, 10h

Date of U-Th sepn: 16/8/90 Counting delay: 38 days ^{228}Th decay factor: 0.9650
Spike activity: U: 1.808 dpm/10ml Th: 1.75 dpm/10ml Mls spike: 10
Date of plating U: 23/8/90 Th: 24/8/90

URANIUM Count time: 168⅔ hrs Start: 10.10a 24/9/90 Stop: 10.50a 1/10/90
Channels counted: -40, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	4745		111 / 780	129	3836	0.0196
^{234}U	13869		241 / 1539	22	12308	0.0101
^{232}U	9409		55 / 387	—	9022	0.0110

double peaks from bground due to long count time??

Bground: 18/9/90 24h (x 168⅔/24)
Tail method: model on 238U

THORIUM Count time: 168⅔ hrs Start: 10.10a 24/9/90 Stop: 10.50a 1/10/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	871		24 / 14	280	577	0.0592
^{230}Th	9516		40 / 295	200	9021	0.0111
^{228}Th	11015		205 / 1441	2724	6850	0.0180
^{224}Ra	14768		1423 / 10001	800	3967	0.0405

Bground: 18/9/90 24h (x 168⅔/24)
Tail method: 212Po model for 228Th, estimate for 224Ra, graph used for 232,230Th.

RESULTS:

234U/238U: 3.2086 std dev: 0.0701 234U/232U: 1.3642 std dev: 0.0204

[U] ppm: 4.1 U yield: 3.8%

228Th-0.054Ra: 6636 228Th/decay factor: 6891 228Th-232Th: 6314, 0.0211

230Th/228Th: 0.6999 std dev: 0.0167

[Th] ppm: 5.7 Th yield: 2.7%

230Th/234U: 0.5130 std dev. 0.0144 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.4977 std dev: 0.0140 232Th/234U: 0.0650 std dev: 0.0041

Age (kA): 68.5 (+) 2.6 (-) 2.5

(234U/238U)t=0: 3.675 std dev: 0.081 234U/238U age: std dev:

Comments: Large double peaks in U spectrum. Low res.
Very low solubility result, ∴ low yield.

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-253a Lab number: 12/3/90 1

Sample: Antarctic carbonate

Sample weight: 9.995
Residue weight: 1.331 %residue: 13.5 %
Weight dissolved: 8.664 %soluble: 86.7 %
Sample treatment:
top layers of resin bleached in both U columns. HF?

Date of U-Th sepn: 13/3/90 Counting delay: 12 days ^{228}Th decay factor: 0.988
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 15/3 Th: 16/3

URANIUM Count time: 48h Start: 6p.m 16/3/90 Stop: 6pm 18/3/90
Channels counted: +20, -95

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	6039	78	14	115	5910	0.013
^{234}U	14523	121	30	34	14459	0.008
^{232}U	4522	67	98	–	4424	0.015

Bground : 21/3/90 24H (× 48/24)
Tail method: modelling on ^{238}U

THORIUM Count time: 24h Start: 1.10p.m 25/3/90 Stop: 1.10p.m 26/3/90
Channels counted: +15, -80

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	425	21	5	135	285	0.083
^{230}Th	10569	103	15	90	10464	0.010
^{228}Th	6001	77	79	166	5756	0.014
^{224}Ra	5469	74	206	100	5165	0.015

Bground: 21/3/90 24h (× 24/24)
Tail method: modelling on ^{224}Ra for 228
graphically for ^{232}Th, ^{230}Th

RESULTS:

234U/238U: 2.447 std dev: 0.037 234U/232U: 3.268 std dev: 0.056

[U] ppm: 22.56 U yield: 11.6 %

228Th-0.054Ra: 5477 228Th/decay factor: 5255 228Th-232Th: 5192

230Th/228Th: 1.991 std dev: 0.037

[Th] ppm: 2.67 Th yield: 17.3 %

230Th/234U: 0.609 std dev. 0.015 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.591 std dev: 0.014 232Th/234U: 0.017 std dev: 0.001

Age (kA): 87.47 (+) 3.04 (-) 2.97

(234U/238U)t=0: 2.85 std dev: 0.04 234U/238U age: — std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-253a Lab number: 12/3/90 2
Sample: Antarctic carbonate

Sample weight: 9.999
Residue weight: 1.303 %residue: 13.0
Weight dissolved: 8.696 %soluble: 87.0
Sample treatment:

Date of U-Th sepn: 13/3/90 Counting delay: 11 days 228Th decay factor: 0.989
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 15/3 Th: 16/3

URANIUM Count time: 24h Start: 5.45pm 15/3/90 Stop: 5.45pm 16/3/90
Channels counted: +30, -100

	Count	std dev	bground	tail	net	%std dev/100
238U	9713	99	7	521	9185	0.011
234U	22273	149	19	150	22104	0.007
232U	6477	80	57	–	6420	0.013

Bground : 21/3/90 24h (x 24/24)
Tail method: modelling on 232U

THORIUM Count time: 26h Start: 11am 24/3/90 Stop: 1pm 25/3/90
Channels counted: +20, -70

	Count	std dev	bground	tail	net	%std dev/100
232Th	429	21	5	80	344	0.067
230Th	11516	107	15	113	11388	0.009
228Th	6180	79	100	131	5949	0.013
224Ra	4767	69	228	140	4399	0.016

Bground: 21/3/90 24h (x 26/4)
Tail method: 216Po model for 228Th, graphically for 232Th, 230Th. Approx for 224Ra

RESULTS:

234U/238U: 2.407 std dev: 0.031 234U/232U: 3.443 std dev: 0.051

[U] ppm: 24.08 U yield: 18.8%

228Th-0.054Ra: 5711 228Th/decay factor: 5427 (counts) 228Th-232Th: 5367

230Th/228Th: 2.098 std dev: 0.037

[Th] ppm: 3.11 Th yield: 15.1%

230Th/234U: 0.609 std dev. 0.014 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.591 std dev: 0.014 232Th/234U: 0.018 std dev: 0.001

Age (kA): 87.56 (+) 3.04 (-) 2.96

(234U/238U)t=0: 2.80 std dev: 0.09 234U/238U age: — std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-253a Lab number: 12/3/90 3
Sample: Antarctic carbonate

Sample weight: 10.001
Residue weight: 1.052 %residue: 10.5%
Weight dissolved: 8.949 %soluble: 89.5%
Sample treatment: centrifuge bottle leaks, ~10% lost.

Date of U-Th sepn: 13/3/90 Counting delay: 10 days 228Th decay factor: 0.990
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 15/3 Th: 16/3

URANIUM Count time: 39h Start: 6.15p 18/3/90 Stop: 10.18p 20/3/90
Channels counted: +20, -100 (stopped for 55 min)

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	15607	125	11	717	14879	0.009
^{234}U	36931	192	28	196	36707	0.005
^{232}U	11133		78	--	11055	0.010

Bground : 21/3/90 24h (x 39/24)
Tail method: model on ^{238}U

THORIUM Count time: 23h Start: 10.50a 23/3/90 Stop: 9.50a 24/3/90
Channels counted: +15, -60

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	521	23	4	56	462	0.052
^{230}Th	13591	117	11	25	13555	0.009
^{228}Th	6924	83	81	132	6711	0.013
^{224}Ra	4750	69	189	115	4446	0.016

Bground: 21/3/90 24h (x 23/24)
Tail method: ^{216}Po model for ^{228}Th, others graphically

RESULTS:

234U/238U: 2.467 std dev: 0.010 234U/232U: 3.320 std dev: 0.011

[U] ppm: 22.0 U yield: 19.9% (of ≥ 0.22)

228Th-0.054Ra: 6471 228Th/decay factor: 6070 (0.015) 228Th-232Th: 6009

230Th/228Th: 2.233 std dev: 0.038

[Th] ppm: 37 Th yield: 18.6

230Th/234U: 0.673 std dev. 0.014 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.653 std dev: 0.013 232Th/234U: 0.023 std dev: 0.001

Age (kA): 101.01 (+) 3.06 (-) 2.99

(234U/238U)t=0: 2.95 std dev: 0.012 234U/238U age: — std dev:

Comments: U low resn. Less % residue than other 253a samples
Th high.

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-253a Lab number: 12/3/90 4
Sample: Antwchi carbonate

Sample weight: 10.005
Residue weight: 1.348 %residue: 13.5%
Weight dissolved: 8.655 %soluble: 86.5%
Sample treatment:

Date of U-Th sepn: 13/3/90 Counting delay: 9 days ^{228}Th decay factor: 0.991
Spike activity: U: 0.18 Bq/ml Th: 0.175 Bq/ml Mls spike: 10
Date of plating U: 15/3 Th: 16/3

URANIUM Count time: 24h Start: 10.10 am 20/3/90 Stop: 10.10 am 21/3/90
Channels counted: 125, -110

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	5517	74	7	98	5412	0.014
^{234}U	13162	115	20	33	13109	0.009
^{232}U	4090	64	61	-	4029	0.016

Bground : 21/3/90 24h (× 24/24)
Tail method: modelling on ^{230}U

THORIUM Count time: 24¼h Start: 10.30 am 22/3/90 Stop: 10.45 am 23/3/90
Channels counted: 120, -60

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1010	32	4	120	886	0.038
^{230}Th	26544	162	11	100	26283	0.006
^{228}Th	14478	120	89	261	14128	0.009
^{224}Ra	8726	93	207	200	8319	0.011

Bground: 21/3/90 24h (× 24¼/24)
Tail method: model on ^{210}Po for ^{224}Ra, graphical for others.

RESULTS:

234U/238U: 2.422 std dev: 0.040 234U/232U: 3.254 ([illegible]) std dev: 0.060

[U] ppm: 22.7 U yield: 11.8%

228Th-0.054Ra: 13679 228Th/decay factor: 12922 ([illegible]) 228Th-232Th: 12793

230Th/228Th: 2.034 std dev: 0.024

[Th] ppm: 3.58 Th yield: 38.4%

230Th/234U: 0.625 std dev. 0.014 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.606 std dev: 0.013 232Th/234U: 0.021 std dev: 0.001

Age (kA): 90.70 (+) 2.92 (-) 2.84

(234U/238U)t=0: 2.83 std dev: 0.05 234U/238U age: — std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-2546 Lab number: 15/8/90 4
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.002g
Residue weight: 0.762 %residue: 7.6%
Weight dissolved: 9.240 %soluble: 92.4%
Sample treatment: Th plated overnight (16h), with watchglass atop
U covered while plating

Date of U-Th sepn: 16/8/90 Counting delay: 45 days ^{228}Th decay factor: 0.9565
Spike activity: U: 1.206Bq/mark Th: 1.75 Bq/mark Mls spike: 10
Date of plating U: 22/8 Th: 25/8

URANIUM Count time: 45hs Start: 12 27p 1/10/90 Stop: 9.27a 3/10/90
Channels counted: -45, +15

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	44427		119/223	1666	43058	0.0050
^{234}U	110517		294/551	669	104357	0.0031
^{232}U	31430		54/101	–	31629	0.0056

Bground : 18/10/90 24h (x45/24)
Tail method: model on ^{238}U

THORIUM Count time: 45hs Start: 12 27p 1/10/90 Stop: 9 27a 3/10/90
Channels counted: -45, +15

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	1460		24/45	100	1360	0.0290
^{230}Th	58224		42/79	40	58105	0.0042
^{228}Th	28012		199/373	1241	26398	0.0065
^{224}Ra	26949		1428/2676	450	23821	0.0073

Bground: 18/10/90 24h (x45/24)
Tail method: ^{210}Po model for ^{228}Th, estimate ^{224}Ra
graphical for ^{232,230}Th

RESULTS:

234U/238U: 2.5409 std dev: 0.0144 234U/232U: 3.4358 std dev: 0.0220

[U] ppm: 21.4 U yield: 49.6%

228Th-0.054Ra: 25112 228Th/decay factor: 26260 228Th-232Th: 24900, 0.0075

230Th/228Th: 2.3536 std dev: 0.0207

[Th] ppm: 2.6 Th yield: 38.7%

230Th/234U: 0.6792 std dev. 0.0075 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.6588 std dev: 0.0073 232Th/234U: 0.0145 std dev: 0.0004

Age (kA): 102.1 (+) 1.7 (-) 1.7

(234U/238U)t=0: 3.050 std dev: 0.018 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-2566 Lab number: 6/8/90 4
Sample: Taylor Valley lacustrine carbonate

Sample weight: 10.000g
Residue weight: 1.123g %residue: 11.2
Weight dissolved: 8.877g %soluble: 88.8
Sample treatment:

Date of U-Th sepn: 7/8/90 Counting delay: 48 days 228Th decay factor: 0.9535
Spike activity: U: 1.808 dpm/10mls Th: 1.75 dpm/10mls Mls spike: 10
Date of plating U: 9/8 Th: 10/8

URANIUM Count time: 24h Start: 10.15a 19/9/90 Stop: 10.15a 20/9
Channels counted: -40, +15

	Count	std dev	bground	tail	net	%std dev/100
238U	9416	+	100	2055	7261	0.0148
234U	17788		233	1305	16250	0.0086
232U	10063		49		10014	0.0100

Bground : 18/9/90 24h (×24/24)
Tail method: 238U modelling

THORIUM Count time: 40h Start: 5.35p 22/9/90 Stop: 9.35a 24/9/90
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	3319		24 / 40	200	3079	0.0144
230Th	77007		42 / 70	120	76817	0.0036
228Th	49568		206 / 343	1949	47276	0.0048
224Ra	46666		1432 / 2387	800	43479	0.0051

Bground: 18/9/90 24h (×40/24)
Tail method: 216Po model for 228Th
graphical for 232,230Th, estimate 224Ra

RESULTS:

234U/238U: 2.2380 std dev: 0.0503 234U/232U: 1.6227 std dev: 0.0214

[U] ppm: 12.0 U yield: 29.3%

228Th-0.054Ra: 44928 228Th/decay factor: 47119 228Th-232Th: 44040 (0.0055)

230Th/228Th: 1.7442 std dev: 0.0115

[Th] ppm: 3.4 Th yield: 79.4%

230Th/234U: 1.0749 std dev. 0.0158 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0426 std dev: 0.0154 232Th/234U: 0.0418 std dev: 0.000

Age (kA): 254.1 (+) 13.1 (-) 11.8

(234U/238U)t=0: 3.519 std dev: 0.000 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-21 W3 Lab number: 1/10/90 1
Sample: Jayla valley lacustrine carbonate, La Croix section

Sample weight: 10.001g
Residue weight: 2.180g %residue: 21.8
Weight dissolved: 7.821g %soluble: 78.2
Sample treatment: High in SiO$_2$; some TiO$_2$

Date of U-Th sepn: 2/10/90 Counting delay: 10 days ^{228}Th decay factor: 0.9046
Spike activity: U: 1.50 dpm/10mls Th: 1.75 dpm/10mls Mls spike: 10
Date of plating U: 4/10 Th: 6/10

URANIUM Count time: 266h Start: 10.50a 11/1/91 Stop: 12.50p 22/1/91
Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	60858		146/1159	629	59070	0.0042
^{234}U	143295		445/2630	2425	138240	0.0028
^{232}U	393625		95/562	–	393063	0.0016

Bground: 14/12/90 45h (× 266/45)
Tail method: 238U modelling

THORIUM Count time: 266h Start: 10.50a 11/1/91 Stop: 12.50p 22/1/91
Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	12587		68/402	3500	8685	0.0148
^{230}Th	70014		150/867	6100	63027	0.0044
^{228}Th	228294 (228294)		444/2920	52362	173012	0.0031
^{224}Ra	199423		3397/20080	19200	160143	0.0031

Bground: 14/12/90 45h (× 266/45)
Tail method: ^{216}Po model for ^{228}Th.
^{232}Th, ^{230}Th graphically; estimate ^{224}Ra

RESULTS:

234U/238U: 2.3405 std dev: 0.0118 234U/232U: 0.3517 std dev: 0.0011

[U] ppm: **2.8** U yield: 103.7% (yf ~0.22 ...4)

228Th-0.054Ra: 164364 228Th/decay factor: 181698 228Th-232Th: 173013 (0.0033)

230Th/228Th: 0.3643 std dev: 0.0020

[Th] ppm: **2.7** Th yield: 46.9%

230Th/234U: 1.0558 std dev. 0.0066 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0048 std dev: 0.0064 232Th/234U: 0.1384 std dev: 0.0021

Age (kA): 226.7 (+) 4.1 (-) 3.9

(234U/238U)t=0: 3.526 std dev: 0.018 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-L1W3 Lab number: 27/9/90 1
Sample: Taylor Valley lacustrine carbonate, LaCroix section.

Sample weight: 10.000g
Residue weight: 2.223g %residue: 22.2
Weight dissolved: 7.777g %soluble: 77.8
Sample treatment: —

Date of U-Th sepn: 20/9 Counting delay: 91 days ^{228}Th decay factor: 0.9136
Spike activity: U: 1.80 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 2/10/90 Th: 3/10/90

URANIUM Count time: 70h Start: 1.10p 21/12/90 Stop: 11.10a 24/12/90
Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	11627		160/249	**322**	11056	0.0100
^{234}U	27575		438/681	955	25935	0.0066
^{232}U	92736		96/149		92587	0.0053

Bground : 14/12/90 45h (× 70/45)
Tail method: modelling on ^{234}U

THORIUM Count time: 70h Start: 1.10p 21/12/90 Stop: 11.10a.m 24/12/90
Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	3935		68/106	100	3729	0.0173
^{230}Th	24596		153/238	200	24158	0.0065
^{228}Th	85678		497/773	1862	83043	0.0056
^{224}Ra	81654		3397/5284	1000	75350	0.0059

Bground: 14/12/90 45h (× 70/45)
Tail method: ^{216}Po modelfit - ^{228}Th; ^{232,230}Th graphically, estimate ^{224}Ra

RESULTS:

234U/238U: 2.3458 std dev: 0.0281 234U/232U: 0.2801 std dev: 0.0021

[U] ppm: 2.2 U yield: 92.8%

228Th-0.054Ra: 78974 228Th/decay factor: 86443 228Th-232Th: 82714 (0.0058)

230Th/228Th: 0.2921 std dev: 0.0022

[Th] ppm: 2.5 Th yield: 85.3%

230Th/234U: 1.0427 std dev. 0.0110 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0114 std dev: 0.0107 232Th/234U: 0.1561 std dev: 0.0050

Age (kA): 230.5 (+) 7.3 (-) 6.9

(234U/238U)t=0: 3.563 std dev: 0.043 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-L 1W4 Lab number: 1/10/90 2

Sample: Taylor Valley lacustrine carbonate, [illegible] section

Sample weight: 10.00g
Residue weight: 1.457 %residue: 14.6
Weight dissolved: 8.544 %soluble: 85.4
Sample treatment: High in undissolved fine element (clay?)
Thick U disc

Date of U-Th sepn: 2/10/90 Counting delay: 112 days 228Th decay factor: 0.8948
Spike activity: U: 1.80 dpm/10mls Th: 1.75 dpm/10mls Mls spike: 10
Date of plating U: 4/10 Th: 7/10

URANIUM Count time: 220h Start: 1pm 22/1/91 Stop: 5pm 31/1/91
Channels counted: 10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	41658		192/439	5874	35685	0.0061
^{234}U	99742		440/2151	14077	82403	0.0041
^{232}U	215882		89/435		215447	0.0022

Bground: 14/12/90 45h (x 220/45)
Tail method: 238U modelling

THORIUM Count time: 220h Start: 1pm 22/1/91 Stop: 5pm 31/1/91
Channels counted: 10, 30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	8646		67/528	1000	7260	0.0158
^{230}Th	79758		153/748	1230	77780	0.0037
^{228}Th	205801		527/2576	23316	179909	0.0027
^{224}Ra	183143		3385/16549	6600	157844	0.0029

Bground: 14/12/90 45h
Tail method: 224Ra model for 228Th,
estimate 224Ra, 232,230Th graphically

RESULTS:

234U/238U: 2.2900 std dev: 0.0167 234U/232U: 0.3825 std dev: 0.0018

[U] ppm: 2.4 U yield: 68.7%

228Th-0.054Ra: 171385 228Th/decay factor: 191534 228Th-232Th: 184274 (0.0028)

230Th/228Th: 0.4221 std dev: 0.0020

[Th] ppm: 2.5 Th yield: 60.4%

230Th/234U: 1.1035 std dev. 0.0073 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0104 std dev: 0.0040 232Th/234U: 0.0999 std dev: 0.0015

Age (kA): 273.4 (+) 6.6 (-) 6.3

(234U/238U)t=0: 3.770 std dev: 0.027 234U/238U age: std dev:

Comments: V low resn Unreliable

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-L1W4 Lab number: 27/9/90 2
Sample: Taylor Valley lacustrine carbonate, La Croix Section
Sample weight: 9.999g
Residue weight: 1.466 %residue: 14.7
Weight dissolved: 8.533 %soluble: 85.3
Sample treatment: -

Date of U-Th sepn: 28/9/90 Counting delay: 87days ^{228}Th decay factor: 0.9173
Spike activity: U: 1.803/10mls Th: 1.753/10mls Mls spike: 10
Date of plating U: 2/10/90 Th: 3/10/90

URANIUM Count time: 263h Start: 11.20a 24/12/90 Stop: 10.20a 4/1/91
Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	43955		198/1157	588	42210	0.0051
^{234}U	106226		438/2560	1374	102292	0.0032
^{232}U	234761		97/567	–	234194	0.0021

Bground : 19/12/90 45h
Tail method: ^{232}U modelling

THORIUM Count time: 263h Start: 11.20a 24/12/91 Stop: 10.20a 4/1/91
Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	16121		62/362	830	14929	0.0088
^{230}Th	152185		153/894	1000	150291	0.0026
^{228}Th	346375		518/3027	6257	337091	0.0018
^{224}Ra	328689		3408/14910	720	308051	0.0019

Bground: 14/12/90 45h
Tail method: ^{216}Po modelled for ^{228}Th. ^{232,230}Th graphically; estimate ^{224}Ra.

RESULTS:

234U/238U: 2.4234 std dev: 0.0146 234U/232U: 0.4366 std dev: 0.0017

[U] ppm: 3.1 U yield: 62.5%

228Th-0.054Ra: 320456 228Th/decay factor: 349347 228Th-232Th: 334418 (0.0019)

230Th/228Th: 0.4494 std dev: 0.0014

[Th] ppm: 2.2 Th yield: 91.7%

230Th/234U: 1.0288 std dev. 0.0051 Spike 228Th/232U: 0.97

Correct 230Th/234U: 0.9979 std dev: 0.0049 232Th/234U: 0.0991 std dev: 0.0010

Age (kA): 221.0 (+) 3.1 (-) 3.0

(234U/238U)t=0: 3.640 std dev: 0.022 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-L26 Lab number: 9/10/90 4
Sample: Taylor Valley lacustrine carbonate, LaCroix section.
Sample weight: 9.999g
Residue weight: 1.784g %residue: 17.8
Weight dissolved: 8.215g %soluble: 82.2
Sample treatment: High in SiO$_2$; some TiO$_2$.

Date of U-Th sepn: 10/10/90 Counting delay: 189 days ^{228}Th decay factor: 0.8289
Spike activity: U: 1.80 dpm/10 ml Th: 1.75 dpm/10 ml Mls spike: 10
Date of plating U: 13/10/90 Th: 12/10/90

URANIUM Count time: 69h Start: 5.45pm 17/4/91 Stop: 2.45pm 20/4/91
Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	9527		138 / 302	311	8914	0.0113
^{234}U	23092		298 / 653	1048	21391	0.0074
^{232}U	80605		80 / 175		80430	0.0055

Bground : 17/4/91 31½ hrs (× 69/31½)
Tail method: ^{236}U modelling

THORIUM Count time: 69h Start: 5.45pm 17/4/91 Stop: 2.45pm 20/4/91
Channels counted: +20, -20 (1 low energy detector gone)

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	3368		45 / 99	400	2869	0.0217
^{230}Th	22333		77 / 169	200	21964	0.0069
^{228}Th	69103		353 / 773	3200	65130	0.0042
^{224}Ra	66351		2329 / 5102	1800	59449	0.0046

Bground: 17/4/91 31½ hrs (× 69/31½)
Tail method: ^{224}Ra modelled for ^{228}Th
^{232,230}Th graphically, straight (both sides) ^{224}Ra

RESULTS:

234U/238U: 2.3997 std dev: 0.0324 234U/232U: 0.2660 std dev: 0.0022

[U] ppm: 2.0 U yield: 81.8%

228Th-0.054Ra: 61920 228Th/decay factor: 74701 228Th-232Th: 71832 (0.0040)

230Th/228Th: 0.3058 std dev: 0.0024

[Th] ppm: 2.1 Th yield: 75.1%

230Th/234U: 1.1446 std dev. 0.0131 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.1151 std dev: 0.0127 232Th/234U: 0.1456 std dev: 0.0038

Age (kA): 309.5 (+) 15.9 (-) 14.2

(234U/238U)t=0: 4.324 std dev: 0.058 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87L26 Lab number: 27/9/90 3

Sample: Taylor Valley lacustrine carbonate, LaCroix Section

Sample weight: 10.001g

Residue weight: 1.803 %residue: 18.0

Weight dissolved: 8.198 %soluble: 82.0

Sample treatment:

Date of U-Th sepn: 28/9/90 Counting delay: 98days ^{228}Th decay factor: 0.9073

Spike activity: U: 1.80 dpm/mls Th: 1.75 dpm/mls Mls spike: 10

Date of plating U: 3/10/90 Th: 5/10/90

URANIUM Count time: 168h Start: 10.30a 4/1/91 Stop: 10.30a 11/1/91

Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	23994		191 / 713	223	23058	0.0068
^{234}U	58159		445 / 1661	1047	55451	0.0044
^{232}U	201056		95 / 355	–	200701	0.0022

Bground : 19/12/90 45h (x 168/45)

Tail method: ^{238}U modelling

THORIUM Count time: 168h Start: 10.30a 4/1/91 Stop: 10.30a 11/1/91

Channels counted: +10, -30

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	10420		64 / 239	400	9781	0.0108
^{230}Th	68198		152 / 567	560	67071	0.0039
^{228}Th	225551		518 / 1934	4896	218721	0.0022
^{224}Ra	217421		3397 / 12682	3200	201539	0.0024

Bground: 19/12/90 45h (x 168/45)

Tail method: ^{210}Po model for ^{228}Th;
$^{232, 230}$Th graphically; estimate ^{224}Ra

RESULTS:

234U/238U: 2.4048 std dev: 0.0195 234U/232U: 0.2763 std dev: 0.0013

[U] ppm: 2.1 U yield: 83.8%

228Th-0.054Ra: 207838 228Th/decay factor: 229073 228Th-232Th: 219292 (0.0023)

230Th/228Th: 0.3059 std dev: 0.0014

[Th] ppm: 2.3 Th yield: 94.2%

230Th/234U: 1.1071 std dev. 0.0074 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0739 std dev: 0.0072 232Th/234U: 0.1566 std dev: 0.0018

Age (kA): 271.8 (+) 6.6 (-) 6.3

(234U/238U)t=0: 4.002 std dev: 0.052 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-228 Lab number: 5/10/90 4

Sample: LaCroix Section, Taylor Valley lacustrine carbonate

Sample weight: 10.000g

Residue weight: 1.511g %residue: 15.1%

Weight dissolved: 8.490g %soluble: 84.9%

Sample treatment:

3rd Th column repeated, since SiO2 in first column.

Date of U-Th sepn: 6/10/90 Counting delay: 131days ^{228}Th decay factor: 0.8781

Spike activity: U: 1.80Bq/10mls Th: 1.75Bq/10mls Mls spike: 10mls

Date of plating U: 9/10/90 Th: 12/10/90

URANIUM Count time: 238½hrs Start: 11-30am 15/2/91 Stop: 10a 25/2/91

Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	391298		185 / 981	28102	362215	0.0018
^{234}U	965826		476 / 2523	11330	951973	0.0010
^{232}U	330229		86 / 456		329773	0.0017

Bground : 19/12/90 45h (≈232½/45)

Tail method: ^{238}U modelling

THORIUM Count time: 238½hrs Start: 11-30am 15/2/91 Stop: 10a 25/2/91

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	16173		65 / 345	3340	12488	0.0113
^{230}Th	935643		153 / 811	1700	934132	0.0010
^{228}Th	319740		518 / 2745	21687	295308	0.0020
^{224}Ra	301363		3392 / 17970	6000	277385	0.0021

Bground: 19/12/90 45h (≈232½/45)

Tail method: ^{232,230}Th graphically; ^{224}Ra estimate
^{216}Po model fr. ^{228}Th

RESULTS:

234U/238U: 2.6282 std dev: 0.0054 234U/232U: 2.8868 std dev: 0.0057

[U] ppm: 18.9 U yield: 97.0%

228Th-0.054Ra: 280329 228Th/decay factor: 319245 228Th-232Th: 3007.57 (0.0020)

230Th/228Th: 3.0452 std dev: 0.0069

[Th] ppm: 2.0 Th yield: 92.8%

230Th/234U: 1.0549 std dev. 0.0051 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.0233 std dev: 0.0051 232Th/234U: 0.0137 std dev: 0.0002

Age (kA): 231.3 (+) 1.9 (-) 1.9

(234U/238U)t=0: 4.108 std dev: 0.008 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-513 Lab number: 9/10/90 1

Sample: Taylor Valley lacustrine carbonate, Suess section

Sample weight: 10.000g

Residue weight: 2.710g %residue: 27.1

Weight dissolved: 7.290g %soluble: 72.9

Sample treatment: Th fraction light green in 2N HNO3

Date of U-Th sepn: 10/10/90 Counting delay: 180 days ^{228}Th decay factor: 0.8364

Spike activity: U: 1.80 dpm/10ml Th: 1.75 dpm/10ml Mls spike: 10

Date of plating U: 13/10/90 Th: 12/10/90

URANIUM Count time: 102hrs Start: 11.25a 8/4/91 Stop: 5.25p 12/4/91

Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	177560		134/450	19484	157626	0.0028
^{234}U	498168		344/1130	36.79	493359	0.0014
^{232}U	109989		70/227	—	109762	0.0050

Bground : 17/4/91 31½hrs (x 102/31.5)

Tail method: 232U modelling

THORIUM Count time: 102hrs Start: 11.25a 8/4/91 Stop: 5.25p 12/4/91

Channels counted: +20, -20 (low resn) (detector poor)

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	4841		48 / 155	920	3766	0.0204
^{230}Th	532727		73/236	1200	531291	0.0014
^{228}Th	82517		338/1094	10953	70470	0.0044
^{224}Ra	40431		2260/7344	~~2730~~	79967	0.0040

Bground: 17/4/91 31½hrs (x 102/31.5) 5120

Tail method: 228/232 model for 228Th, 232,230Th graphically; estimate 224Ra (tail both sides)

RESULTS:

234U/238U: 3.1299 std dev: 0.0098 234U/232U: 4.4948 std dev: 0.0149

[U] ppm: 28.8 U yield: 75.5%

228Th-0.054Ra: 66152 228Th/decay factor: 79091 228Th-232Th: 75325 (0.0044)

230Th/228Th: 7.0535 std dev: 0.0326

[Th] ppm: 2.9 Th yield: 53.3%

230Th/234U: 1.5692 std dev. 0.0089 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.5221 std dev: 0.0086 232Th/234U: 0.0108 std dev: 0.0002

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-513 Lab number: 5/10/90 1

Sample: Taylor Valley lacustrine carbonate, Swiss Section.

Sample weight: 10.000g

Residue weight: 2.644g %residue: 26.4

Weight dissolved: 7.356g %soluble: 73.6

Sample treatment: —

Date of U-Th sepn: 6/10/90 Counting delay: 86days ^{228}Th decay factor: 0.9182

Spike activity: U: 1.80Bq/10ml Th: 1.75Bq/10ml Mls spike: 10

Date of plating U: 9/10/90 Th: 11/10/90

URANIUM Count time: 67h Start: 5.15p 31/1/91 Stop: 12.15p 3/2/91

Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	141843		189/281	16240	125322	0.0032
^{234}U	391167		480/715	3488	386694	0.0016
^{232}U	84007		96/143	–	83864	0.0055

Bground : 19/12/90 45h (x 67/45)

Tail method: modeled on ^{238}U

THORIUM Count time: 67h Start: 5.15p 31/1/91 Stop: 12.15p 3/2/91

Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	4594		64/45	310	4189	0.0169
^{230}Th	553586		153/228	180	553178	0.0013
^{228}Th	65964		369/549	1540	63875	0.0041
^{224}Ra	80343		3392/5050	600	74743	0.0059

Bground: 19/12/90 45h (x 67/45)

Tail method: ^{216}Po modeled for ^{228}Th.
estimate ^{224}Ra, ^{232,230}Th graphically

RESULTS:

234U/238U: 3.0856 std dev: 0.0110 234U/232U: 4.6110 std dev: 0.0177

[U] ppm: 29.7 U yield: 87.8%

228Th-0.054Ra: 61928 228Th/decay factor: 67445 228Th-232Th: 62851 (0.0044)

230Th/228Th: 8.8014 std dev: 0.0404

[Th] ppm: 3.9 Th yield: 68.8%

230Th/234U: 1.9088 std dev. 0.0114 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.8515 std dev: 0.0111 232Th/234U: 0.0140 std dev: 0.0003

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES. UNIVERSITY OF WAIKATO.

Sample no: 87-530 Lab number: 5/10/90 2
Sample: Taylor Valley lacustrine carbonate, Siass Section
Sample weight: 9.999g
Residue weight: 2.064g %residue: 20.6%
Weight dissolved: 7.935g %soluble: 79.4%
Sample treatment: Third Th column repeated

Date of U-Th sepn: 6/10/90 Counting delay: 120days 228Th decay factor: 0.8877
Spike activity: U: 1.80Bq/10mls Th: 1.75Bq/10mls Mls spike: 10
Date of plating U: 9/10/90 Th: 12/10/90

URANIUM Count time: 124h Start: 12.30p 3/2/91 Stop: 4.30p 8/2/91
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
238U	207567		189/521	8477	198569	0.0023
234U	600046		480/1323	2416	596307	0.0013
232U	144765		86/237	—	144528	0.0026

Bground : 19/12/90 45h (x 124/45)
Tail method: 238U modelling.

THORIUM Count time: 124h Start: 12.30p 3/2/91 Stop: 4.30p 8/2/91
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
232Th	8160		96/265	500	7345	0.0128
230Th	982691		153/422	350	981919	0.0040
228Th	152094		521/1436	3461	147197	0.0027
224Ra	146427		3392/9347	2000	135080	0.0029

Bground: 19/12/90 45h (x 124/45)
Tail method: 2-step model for 228Th. estimate 224Ra, graphically for 232,230Th

RESULTS:

234U/238U: 3.0030 std dev: 0.0079 234U/232U: 4.1259 std dev: 0.0120

[U] ppm: 25.0 U yield: 81.8%

228Th-0.054Ra: 139902 228Th/decay factor: 157601 228Th-232Th: 150206 (0.0028)

230Th/228Th: 6.5372 std dev: 0.0194

[Th] ppm: 2.6 Th yield: 87.4%

230Th/234U: 1.5844 std dev. 0.0066 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.5369 std dev: 0.0064 232Th/234U: 0.0116 std dev: 0.0002

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-530 Lab number: 9/10/90 2
Sample: Taylor Valley lacustrine carbonate, Suess section.
Sample weight: 10.000g
Residue weight: 2.134g %residue: 21.3%
Weight dissolved: 7.866g %soluble: 78.7%
Sample treatment: Light green colour in Th fraction - as on others

Date of U-Th sepn: 10/10/90 Counting delay: 177 days ^{228}Th decay factor: 0.8389
Spike activity: U: 1.80 Bq/10.mls Th: 1.75 Bq/10.mls Mls spike: 10
Date of plating U: 13/10/90 Th: 12/10/90

URANIUM Count time: 74½ hrs Start: Stop:
Channels counted: +10, -50

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	61461		135/315	1728	59418	0.0042
^{234}U	181185		301/726	569	179890	0.0024
^{232}U	42968		70/166	–	42802	0.0049

Bground : 17/4/91 31½hrs (×74½/31½)
Tail method: model on 238U

THORIUM Count time: 74½ hrs Start: 8.50a 5/4/91 Stop: 11.20a 8/4/91
Channels counted: +15, -20 (low resn - detector gone)

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	3117		40/95	350	2672	0.0223
^{230}Th	407817		64/151	450	407216	0.0016
^{228}Th	60283		311/736	2901	56646	0.0045
^{224}Ra	59149		2067/4936	2100	52113	0.0049

Bground: 17/4/91 31½hrs (× 74½/31½)
Tail method: 224Ra modelled for 228Th.
estimate 224Ra (both sides); 232,230Th graphically

RESULTS:

234U/238U: 3.0275 std dev: 0.0146 234U/232U: 4.2167 std dev: 0.0230

[U] ppm: 25.8 U yield: 40.5%

228Th-0.054Ra: 53852 228Th/decay factor: 64172 228Th-232Th: 61500 (0.0044)

230Th/228Th: 6.6213 std dev: 0.0508

[Th] ppm: 2.4 Th yield: 59.6%

230Th/234U: 1.5703 std dev. 0.0113 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.5231 std dev: 0.0110 232Th/234U: 0.0100 std dev: 0.0002

Age (kA): ∞ (+) (-)

(234U/238U)t=0: std dev: 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES.
UNIVERSITY OF WAIKATO.

Sample no: 87-537 Lab number: 9/10/90 U3
Sample: Taylor Valley lacustrine carbonate, Suess section
Sample weight: 10.001g
Residue weight: 2.173g %residue: 21.7
Weight dissolved: 7.828g %soluble: 78.3
Sample treatment: High in Fe, Mn.

Date of U-Th sepn: 10/10/90 Counting delay: 138 days ^{228}Th decay factor: 0.8720
Spike activity: U: 1.808 Bq/10mls Th: 1.75 Bq/10mls Mls spike: 10
Date of plating U: 13/10/90 Th: 12/10/90

URANIUM Count time: 342.5hrs Start: 10.15a 25/2/91 Stop: 4.45p 11/3/91
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	294613	~~198~~	198/1507	35793	257313	0.0022
^{234}U	792932	~~444~~	444/3379	11795	777758	0.0012
^{232}U	228181	~~95~~	95/723		227458	0.0021

Bground : 14/12/90 45h (× 342½/45)
Tail method: 238U modelling

THORIUM Count time: 342.5hrs. Start: 10.15a 25/2/91 Stop: 4.45p 11/3/91
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	23670		64/487	1800	21383	0.0075
^{230}Th	1561203		150/1142	1500	1558561	0.0001
^{228}Th	395175		501/3813	7377	383985	0.0017
^{224}Ra	374089		3397/25855	4000	344234	0.0018

Bground: 14/12/90 45h (× 342½/45)
Tail method: 216/8 model for 228Th; estimate 224Ra; 232,230Th graphically

RESULTS:

234U/238U: 3.0226 std dev: 0.0076 234U/232U: 3.4193 std dev: ~~3.97650~~ 0.0083

[U] ppm: 21.1 U yield: 46.6%

228Th-0.054Ra: 365396 228Th/decay factor: 419033 228Th-232Th: 397650 (0.0017)

230Th/228Th: 3.9194 std dev: 0.0068

[Th] ppm: 2.9 Th yield: 83.8%

230Th/234U: 1.1463 std dev. 0.0054 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.1119 std dev: 0.0053 232Th/234U: 0.0153 std dev: 0.0001

Age (kA): 283.8 (+) 2.9 (-) 2.9

(234U/238U)t=0: 5.471 std dev: 0.014 234U/238U age: std dev:

Comments:

URANIUM-THORIUM SAMPLES, UNIVERSITY OF WAIKATO.

Sample no: 87-537 Lab number: 5/10/90 3
Sample: Taylor Valley lacustrine carbonate, Suess section
Sample weight: 10.000g
Residue weight: 2.156g %residue: 21.6
Weight dissolved: 7.844g %soluble: 78.4
Sample treatment: —

Date of U-Th sepn: 6/10/90 Counting delay: 125days ^{228}Th decay factor: 0.8833
Spike activity: U: 1.80 Bq/10mL Th: 1.75 Bq/10mL Mls spike: 10
Date of plating U: 9/10/90 Th: 11/10/90

URANIUM Count time: 163¼ hrs Start: 4.35p 8/2/91 Stop: 11.20a 15/2/91
Channels counted: -50, +10

	Count	std dev	bground	tail	net	%std dev/100
^{238}U	224485		185 / 671	22969	200845	0.0025
^{234}U	599965		498 / 1807	6662	591496	0.0013
^{232}U	174015		77 / 279	—	173736	0.0024

Bground : 19/12/90 45h (x 163¼/45)
Tail method: 238U modelling

THORIUM Count time: 163¼ hrs Start: 4.35p 8/2/91 Stop: 11.20a 15/2/91
Channels counted: -30, +10

	Count	std dev	bground	tail	net	%std dev/100
^{232}Th	10736		62 / 225	340	10171	0.0105
^{230}Th	721354		152 / 551	240	720563	0.0012
^{228}Th	186423		501 / 1818	3497	181108	0.0024
^{224}Ra	182606		3397 / 12324	1600	168682	0.0026

Bground: 15/12/90 45h (x 163¼/45)
Tail method: 216Po model for 228Th.
estimate 224Ra, 232,230Th graphically

RESULTS:

234U/238U: 2.9450 std dev: 0.0083 234U/232U: 3.4046 std dev: 0.0093

[U] ppm: 21.6 U yield: 74.7 %

228Th-0.054Ra: 171999 228Th/decay factor: 194723 228Th-232Th: 184552 (0.0025)

230Th/228Th: 3.9044 std dev: 0.0108

[Th] ppm: 3.0 Th yield: 81.6%

230Th/234U: 1.1468 std dev. 0.0044 Spike 228Th/232U: 0.97

Correct 230Th/234U: 1.1124 std dev: 0.0043 232Th/234U: 0.0157 std dev: 0.0002

Age (kA): 286.3 (+) 3.9 (-) 3.8

(234U/238U)t=0: 5.329 std dev: 0.015 234U/238U age: std dev:

Comments:

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