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THE $^{230}\text{Th}/^{234}\text{U}$ DATING
OF IMPURE TERRESTRIAL CARBONATE
DEPOSITS IN NAMIBIA

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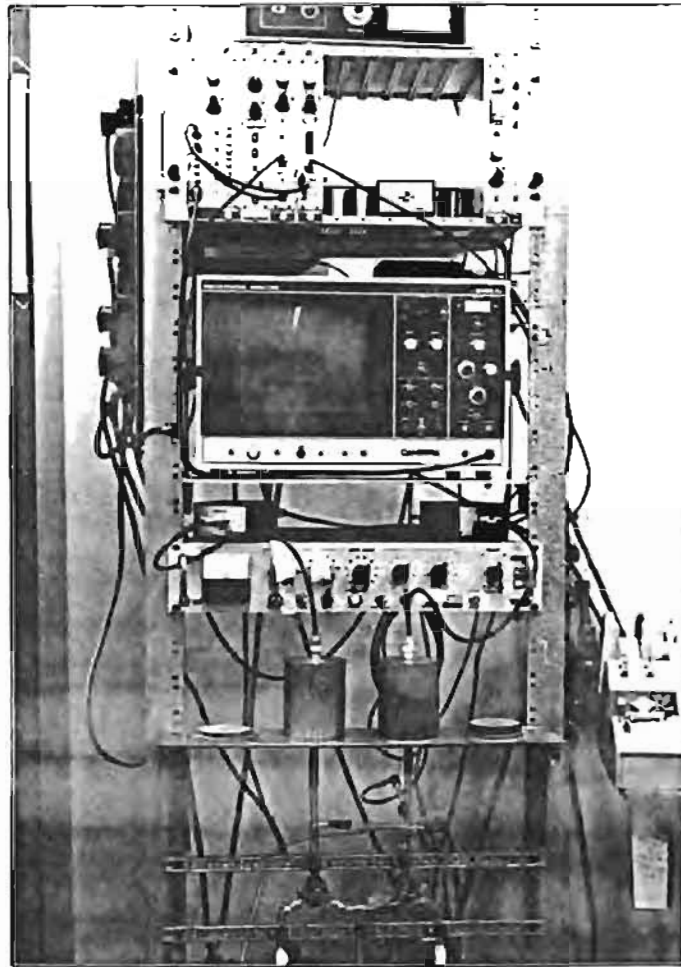
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Frontispiece: Alpha spectrometer in the laboratory of the Quaternary Research Dating Unit (QUADRU), CSIR, where the research work contained in this thesis was undertaken. The multichannel analyser (centre) displays the alpha spectra obtained from the sources placed inside the copper tubes (bottom) which also house the surface-barrier semiconductor detectors.

ABSTRACT

Chemically precipitated calcium carbonates can be dated by means of the ^{230}Th build-up that is produced from co-precipitated ^{234}U . In the case of terrestrial carbonates such as calcretes the calculation of an age is often hampered by the presence of uranium and thorium derived from the detrital component of the sample. Various methods have been used in order to solve this problem, but they all have limitations. In this thesis the possibility is investigated of obtaining meaningful dates by sequential leaching of the carbonate, using material from the Kuiseb River, Namibia.

Different methods of data analysis are applied to the results obtained. The best method of correcting the $^{230}\text{Th}/^{234}\text{U}$ ages was found by comparison with the ^{14}C ages of five samples. The corrected $^{230}\text{Th}/^{234}\text{U}$ ages of the other Kuiseb samples were calculated using the best correction method.

Obtaining corrected $^{230}\text{Th}/^{234}\text{U}$ ages may be used in interpreting climatic changes in the last 350 000 years, although at present too few data are available from the Kuiseb River valley. This study, however, shows that it is possible to obtain reasonably corrected ages from single carbonate samples that contain initial detrital contamination.

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Conventions used

The concentration of radioactive isotopes are expressed in terms of their specific activities, viz. in dpm/kg. Thus ratios, such as $^{230}\text{Th}/^{234}\text{U}$, are always activity ratios and not ratios of atom numbers.

Activities (dpm/kg) and concentrations (ppm) are expressed with respect to the initial total sample mass, as in Ku et al. (1979).

Names of dating methods are used and abbreviated as in current literature, viz. the $^{230}\text{Th}/^{234}\text{U}$ dating method rather than ionium dating, and ^{14}C for the radiocarbon dating method. The chemical leaching procedures are also named as in the current literature, for instance L/L for the so-called Leachate/Leachate method.

C-numbers, eg. C-1117, are sample numbers as used in the Quadru laboratory, C.S.I.R., where the laboratory work for this study was carried out. $^{230}\text{Th}/^{234}\text{U}$ analysis numbers are denoted as U-400. ^{14}C analysis numbers are preceded by Pta-, eg. Pta-1862.

Ages of less than 100 000 years are rounded to the nearest 100 years, while greater ages are rounded to the nearest 1000 years.

CHAPTER 1

INTRODUCTION1.1. THE $^{230}\text{Th}/^{234}\text{U}$ DISEQUILIBRIUM DATING METHOD

The $^{230}\text{Th}/^{234}\text{U}$ method of dating calcium carbonate precipitates has proved to be a most useful technique. The method is based on the radioactive disequilibrium that exists between uranium, which is co-precipitated with calcium from aqueous solutions, and its long-lived daughter isotope, ^{230}Th . Kaufman and Broecker (1965) applied the method to carbonate materials from lake deposits and obtained satisfactory results. It has been especially successful in the dating of coral-reefs that reflect past sea-level stands (eg. Ku et al. 1990), and dating stalagmites in caves (eg. Harmon et al. 1975, Goede and Vogel 1991). The different uranium-series methods, including the $^{230}\text{Th}/^{234}\text{U}$ method, of dating carbonate precipitates have been extensively reviewed over the years by Ku (1976), Ivanovich and Harmon (1982), and Schwarcz (1989).

The three naturally occurring uranium (U) and thorium (Th) decay series consist of nuclides of different nuclear and chemical properties. Figures 1.1 and 1.2 show the half-lives and alpha energies with branching ratios for the ^{238}U and ^{232}Th decay series respectively. In the natural environment these nuclides can be separated through differences in the chemical and physical properties. During the weathering process, alpha recoil can also produce direct separation of nuclides. Thereafter, if the system is closed to nuclide migration, the nuclides tend to restore virtual radioactive equilibrium with each other at rates dictated by their respective half-lives.

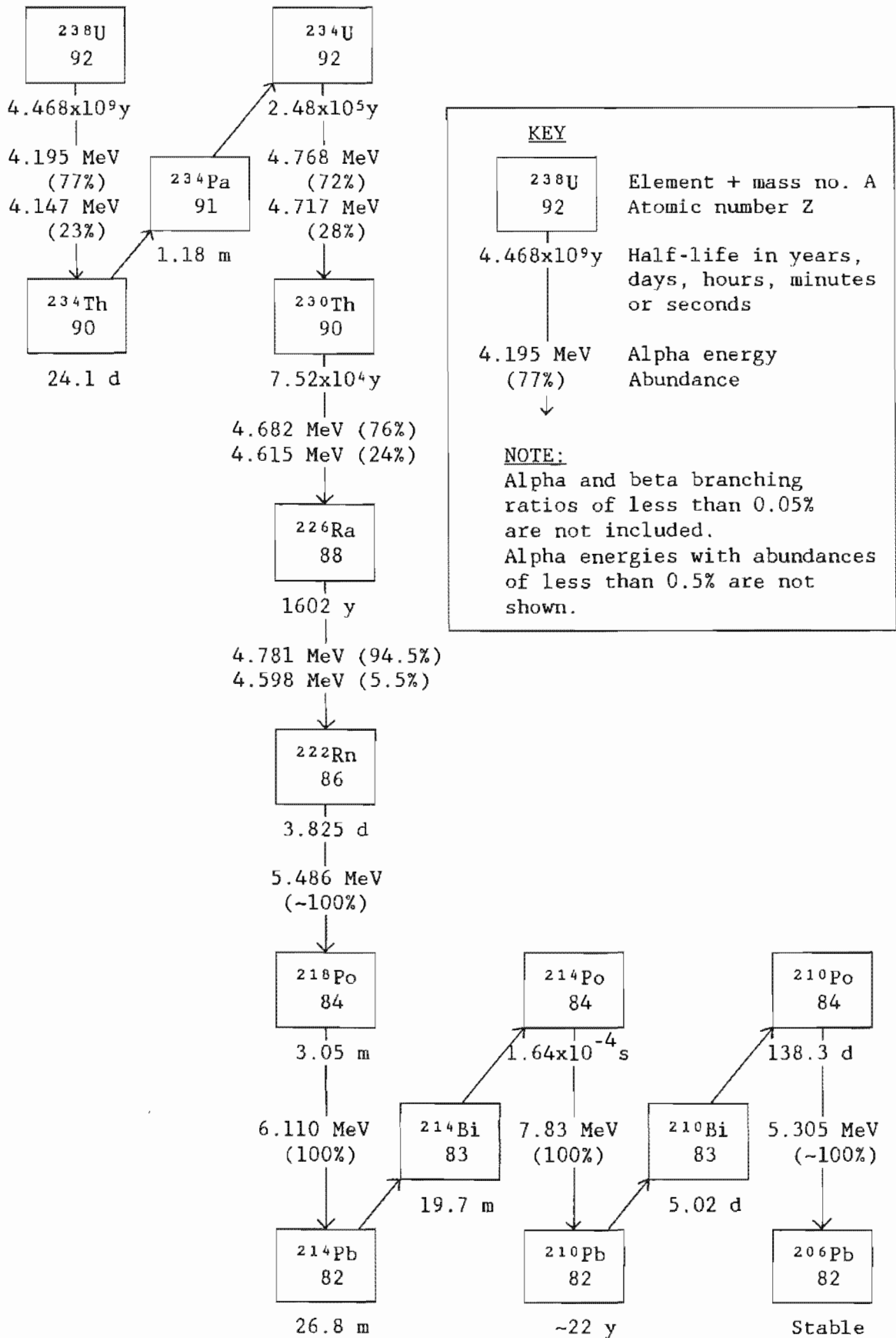


Figure 1.1: ^{238}U decay series (data from Ivanovich and Harmon 1982)

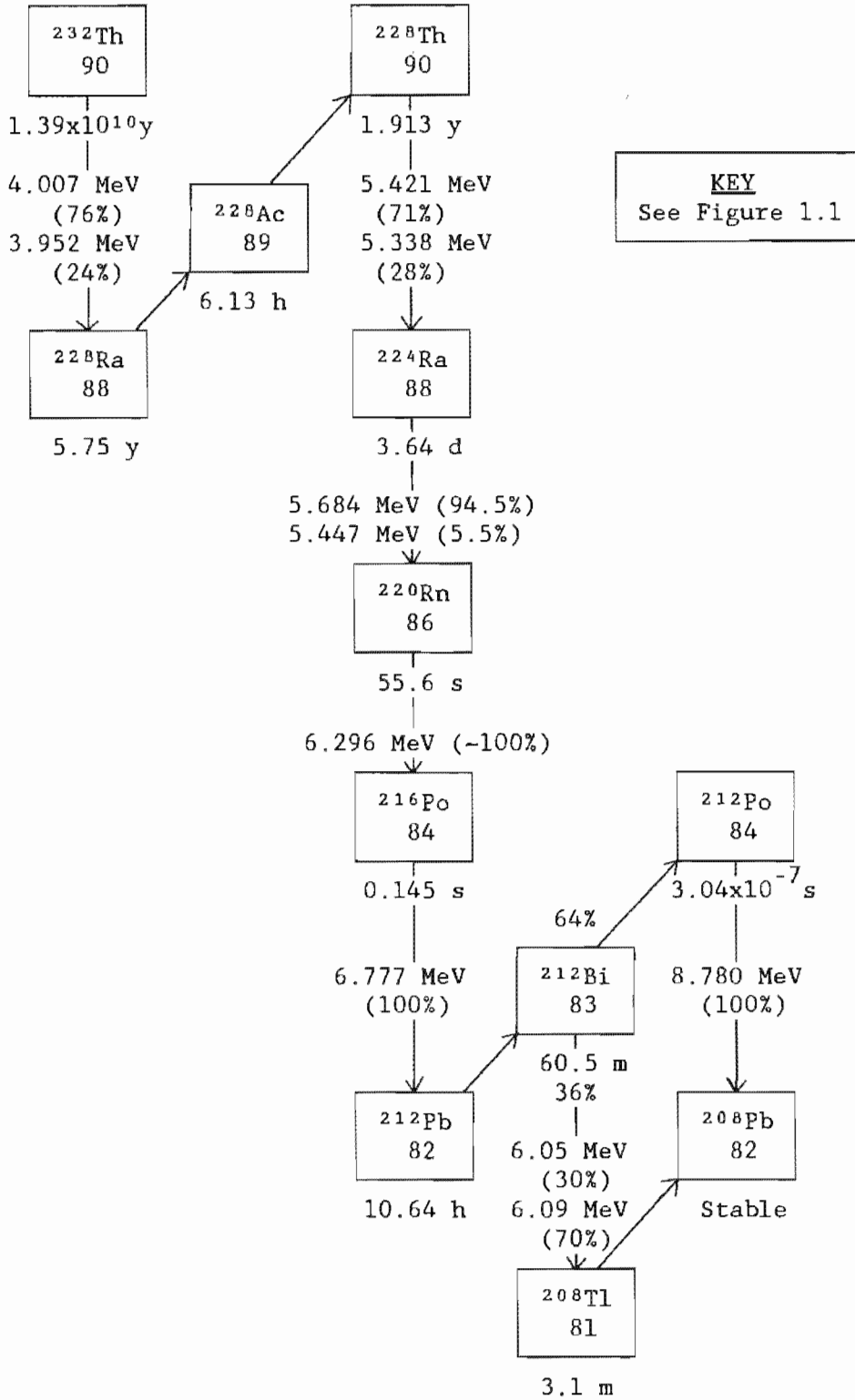


Figure 1.2: ^{232}Th decay series (data from Ivanovich and Harmon 1982)

Natural water contains small amounts of dissolved uranium in the form of uranyl ions, released from weathered rocks. Thorium, however, is extremely insoluble in water and is rapidly removed by absorption onto solid surfaces. Thus, when carbonate is precipitated from such water, the deposit initially contains uranium but little or no thorium. The ^{238}U , however, decays via ^{234}U to ^{230}Th (Figure 1.1). Thus the ^{230}Th in the carbonate builds up from zero activity until the $^{230}\text{Th}/^{234}\text{U}$ activity ratio is approximately unity (Figure 1.3). The half-life of ^{230}Th is 75 200 years, so that equilibrium is restored on this timescale. By measuring the $^{230}\text{Th}/^{234}\text{U}$ activity ratio it is possible to date samples up to about 350 000 years old (Figures 1.3 and 1.4).

It has been found that the $^{234}\text{U}/^{238}\text{U}$ activity ratio of uranium dissolved in water is generally greater than unity and thus this ratio also needs to be measured. This ratio has an average value of 2.03 ± 0.42 in southern African surface waters and a range from 1.29 to 2.59, $n = 16$ (Kronfeld and Vogel 1991). Note that the immediate daughters of ^{238}U , the beta emitters ^{234}Th and ^{234}Pa (Figure 1.1), are very short-lived and will thus effectively be in equilibrium with ^{238}U and do not affect the $^{234}\text{U}/^{238}\text{U}$ ratio. The reasons for the $^{234}\text{U}/^{238}\text{U}$ disequilibrium are the following:

- (a) the ^{234}U atoms may be directly injected into the water by alpha recoil when a ^{238}U atom decays, and
- (b) the ^{234}U atoms that are still in the crystal lattice of the mineral are more easily dissolved than the remaining ^{238}U atoms, due to being dislocated when the parent ^{238}U decayed.

The present day activity ratio between ^{230}Th and ^{234}U is then given by (Ivanovich and Harmon 1982):

$$\frac{^{230}\text{Th}}{^{234}\text{U}} = \frac{^{238}\text{U}}{^{234}\text{U}} \times \left[1 - e^{(-\lambda_0 \times t)} \right] + \frac{\lambda_0}{\lambda_0 - \lambda_1} \times \left[1 - \frac{^{238}\text{U}}{^{234}\text{U}} \right] \times \left[1 - e^{(t \times (\lambda_1 - \lambda_0))} \right]$$

[Eqn 1.1]

where λ_0 and λ_1 are the decay constants for ^{230}Th and ^{234}U respectively in years⁻¹ (values given in Appendix 1) and t is the time in years of ^{230}Th ingrowth (equivalent to the time of carbonate deposition if there was no initial ^{230}Th). The decay of ^{238}U is negligible over the range of dating.

This equation must be solved for time t after measuring the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios (Appendix 1). There is no direct analytical solution of Equation 1.1; thus t must be solved iteratively (Rosenbauer 1991) or graphically (Figure 1.4).

The basic assumptions in using Equation 1.1 to obtain valid $^{230}\text{Th}/^{234}\text{U}$ dates are the following:

- (a) no ^{230}Th may be present in the sample at the time of deposition of the parent. In impure terrestrial carbonates this assumption is invalid, and this problem of "detrital contamination" will be discussed in the remainder of the chapter;
- (b) after calcification the sample must be a closed system, ie. there must be no addition or removal of the relevant radionuclides, ^{238}U , ^{234}U and ^{230}Th , such as could be caused by weathering or recrystallization of the sample.

An additional criterion is that there must be a measurable amount of uranium in the sample, ie. preferably more than 0.05 ppm (= 37 dpm/kg).

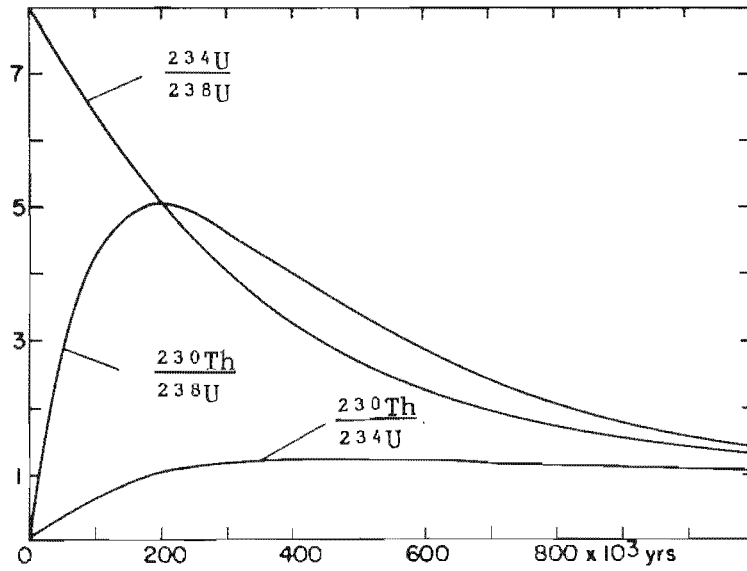


Figure 1.3: Graphical representation of the variation of the $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios, showing how they tend towards secular equilibrium with increasing time, starting with an initial $^{234}\text{U}/^{238}\text{U}$ ratio of 8 and zero ^{230}Th .

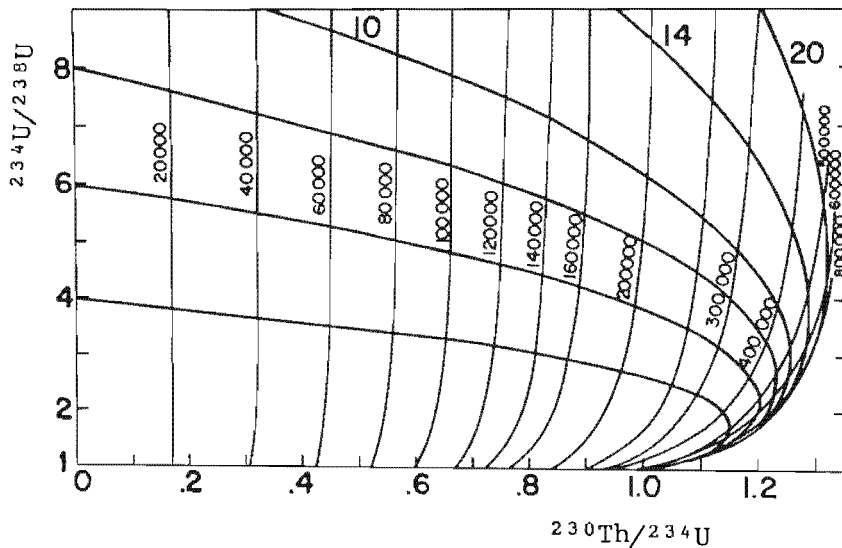


Figure 1.4: Graphical representation of the variation of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios with time in a closed system with no initial ^{230}Th (Kaufman and Broecker 1965). The nearly vertical lines are isochrons, i.e. lines of constant age, obtained from Equation 1.1 but with different initial $^{234}\text{U}/^{238}\text{U}$ activity ratios. The nearly horizontal lines show the change in the nuclide activity ratios as time increases, for different initial $^{234}\text{U}/^{238}\text{U}$ activity ratios.

1.2. THE PROBLEM OF DETRITAL CONTAMINATION

^{230}Th is the daughter of ^{234}U but is not expected to be present in a carbonate deposit initially. Terrestrial calcretes, however, are often found to contain ^{232}Th which is derived from the so-called detritus. In the case of desert calcretes, for instance, the detritus consists of desert sand incorporated in the carbonate. Since ^{232}Th has the same chemical properties as ^{230}Th , it must be assumed that the detritus would also have introduced a certain amount of non-authigenic, ie. initial, ^{230}Th into the sample. This would increase the $^{230}\text{Th}/^{234}\text{U}$ activity ratio and indicate an age that is too large.

Appreciable amounts of ^{232}Th in a sample thus indicates the presence of non-authigenic ^{230}Th . If the $^{230}\text{Th}/^{232}\text{Th}$ ratio is larger than about 15, the age is not seriously affected (Goede and Vogel 1991), but often this does not hold true for impure terrestrial carbonates such as calcrete or lake marl. Several authors have attempted different methods of correcting their results for detrital contamination.

The purpose of the this study is to investigate a different chemical method of obtaining acceptable ages for such impure deposits. More specifically, the approach has been to attempt to separate the uranium and thorium isotopes in the pure carbonate from those associated with the detrital fraction by sequential leaching of the sample with weak acid. The terminology used is defined below, and then the different approaches that have been used are reviewed.

1.3 DESCRIPTION OF CHEMICAL TERMS

The following terms are involved in the chemical processes used by different authors (eg. Schwarcz and Latham 1989) and in the present study.

Carbonate (C): a pure, chemically precipitated carbonate, which, at

the time of deposition, incorporated some uranium but no thorium.

Detritus (D): non-carbonate, detrital minerals which are physically entrapped by the carbonate at the time of the deposition of the latter.

Leachate (L): the filtered solution produced by partially dissolving a carbonate-detritus mixture in acetic, hydrochloric or nitric acid; this solution contains the isotopes from the carbonate and some of those extracted from the detritus.

Acid-insoluble Residue (R): the material remaining after leaching, consisting of sand or clay. The uranium and thorium of this fraction are contained within the mineral crystals and may be released by total dissolution in a perchloric-hydrofluoric acid mixture.

Boiled solution (S): the filtered solution produced by dissolving the iron oxide coating around sand grains in boiling concentrated acid; the solution contains the isotopes absorbed to the detritus. The uranium and thorium isotopes that remain behind in the residue after this treatment are assumed to be only those contained in the crystal lattices of the mineral grains and as such do not form part of the system (Przybyłowicz et al. 1991).

Differential leaching: the differential isotopic fractionation in a leaching process due to differences in chemical behaviour of the isotopes.

Sequential leach (SL): dissolving successive fractions of a single sample in hydrochloric acid, the final fraction being boiled in acid to remove the iron oxide coating.

1.4 PREVIOUS MODELS TO CORRECT FOR DETRITAL CONTAMINATION

The models used by different authors in attempting to correct for non-negligible detrital contamination are briefly reviewed below. The models differ in the chemical dissolution procedure and also in the method of data analysis. The $^{230}\text{Th}/^{232}\text{Th}$ activity ratio is designated by f in this

work, although several authors use R, eg. Kaufman and Broecker (1965). All the models assume that the ^{232}Th activity is an index of the amount of ^{230}Th belonging to the detrital component. The different approaches involve different assumptions and in some cases require several coeval, ie. of the same age, subsamples to be analysed.

1.4.1 Early models: $^{230}\text{Th}/^{232}\text{Th}$ activity ratio, f (Kaufman and Broecker 1965)

Kaufman and Broecker (1965) wrote the ^{230}Th correction as:

$$^{230}\text{Th}_c = ^{230}\text{Th} - ^{232}\text{Th} \times f_i \times e^{(-\lambda_0 \times t)} \quad [\text{Eqn 1.2}]$$

where c denotes the authigenic ^{230}Th , f_i is the assigned initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, and λ_0 is the decay constant of ^{230}Th . The exponential factor corrects for the decay of the non-authigenic ^{230}Th . ^{232}Th has a very long half-life (Figure 1.2) and may thus be considered to be constant over the last 350 000 years. If the present day $^{230}\text{Th}/^{232}\text{Th}$ ratio, f_r , is known, the correction is simplified to (Lao and Benson 1988):

$$^{230}\text{Th}_c = ^{230}\text{Th} - ^{232}\text{Th} \times f_r \quad [\text{Eqn 1.3}]$$

One can thus find the ^{230}Th of the pure carbonate, $^{230}\text{Th}_c$, if one knows the initial or the present day $^{230}\text{Th}/^{232}\text{Th}$ ratio. Various attempts have been made to estimate these.

f obtained from ^{14}C age

Kaufman and Broecker (1965) calculated f_i by comparing ^{14}C and $^{230}\text{Th}/^{234}\text{U}$ ages in lacustrine carbonates from Lakes Lahontan and Bonneville, obtaining an average of 1.70. Their $^{230}\text{Th}/^{232}\text{Th}$ activity ratios varied from 0.95 to 2.38 for 12 carbonates. Also, this method depends on knowing the ^{14}C ages (which only extend back to 50 000 years).

f obtained from the natural environment

The simplest approach would be to assume that the $^{230}\text{Th}/^{232}\text{Th}$ ratio of the detritus is similar to that of average crustal rock, which is approximately unity (eg. Hendy et. al 1979, Goede and Vogel 1991), with a range between 0.5 and 2, ie. within a factor of two. This can be written as $1 \times/\div 2$ for simplicity. Kronfeld and Vogel (1991) found an average ratio of $0.7 \times/\div 2.2$ for the leachable thorium on river sediment in 19 southern African rivers. This ratio may thus vary from 0.3 to 1.5 or even more widely in the natural environment. One may also use the ratio measured in modern samples as the initial f_i value, eg. 1.84 for modern tufa in Lao and Benson (1988).

If the $^{230}\text{Th}/^{232}\text{Th}$ ratio of a sample is small, eg. less than 15, then the uncertainty of the corrected age is too large to be meaningful.

1.4.2 The Leachate/Leachate (L/L) method (Kaufman 1971, Schwarcz and Latham 1989)

A successful approach to eliminating the effect of initial detrital ^{230}Th has been to separate the sample mechanically into several subsamples with varying amounts of detritus. The carbonate of these subsamples is then boiled in acid and the solutions are analysed.

Kaufman (1971) followed this procedure on the aragonite deposits of the lacustrine Lisan Formation in the Jordan Valley. By applying a suitable graphic procedure to the results of the leachates, the nuclide composition of the pure carbonate can be derived by extrapolation. Plots of $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ each versus $^{232}\text{Th}/^{234}\text{U}$ give straight lines with the y-intercepts being the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios respectively of the pure carbonate - this is referred to as the intercept method. ^{238}U could also be used as the normalising variable, eg. Szabo and Butzer (1979). Osmond et al. (1970) used the same plotting procedure as Kaufman

(1971) but dealt with marine carbonates and did not describe the chemical method used.

Schwarcz and Latham (1989) used effectively the same chemical procedure as Kaufman (1971), but analysed their results by the so-called slope method. They plotted $^{230}\text{Th}/^{232}\text{Th}$ against $^{234}\text{U}/^{232}\text{Th}$, and $^{234}\text{U}/^{232}\text{Th}$ against $^{238}\text{U}/^{232}\text{Th}$, and here the slopes of the graphs are the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios respectively of the pure carbonate. Ku and Liang (1984) and Bischoff and Fitzpatrick (1991) stated that the intercept and slope methods of analysis can be shown to be the same mathematically but the latter method has been the more popular in recent years.

Schwarcz and Latham (1989) justified their graphical approach mathematically, based on the assumption that the leachate fractions are homogenous. The slopes of the isochron plots will not be affected by isotopic fractionation, as long as it is the same for the different leachate fractions. Przybylowicz et al. (1991) showed the validity of the technique experimentally by analysing artificially prepared mixtures of pure calcite of known age and detritus.

The disadvantage of the L/L method is that one needs a spread in the proportion of detritus in the coeval subsamples in order to obtain a reliable age. Also one must assume that the isotopes of a set of subsamples are leached in the same proportion.

1.4.3 The Leachate/Residue (L/R) method (Ku and Liang 1984)

Ku and Liang (1984) reviewed this method which involves dissolving the carbonate, i.e. the acid-soluble fraction, in acid and then totally dissolving the so-called acid-insoluble residue in perchloric and hydrofluoric acid. Two different variations, Schemes I and II, have been applied. Both assume that when the detritus is leached, no fractionation of the

thorium isotopes occurs, ie. $^{230}\text{Th}/^{232}\text{Th}$ in the residue = $^{230}\text{Th}/^{232}\text{Th}$ in the detritus.

Scheme I: (Ku et al. 1979, Ku and Liang 1984)

Ku et al. (1979) analysed leachate and residue pairs of desert pedogenic carbonates in California. In addition to the above assumption, they also assumed that secular equilibrium exists in the detritus, ie. $^{238}\text{U} = ^{234}\text{U} = ^{230}\text{Th}$ in the detritus. Differential extraction of uranium relative to thorium was allowed. The corrected age was then calculated from the following set of equations (Ku and Liang 1984):

$$^{230}\text{Th}_C = ^{230}\text{Th}_R - ^{232}\text{Th}_L \left(^{230}\text{Th}_R / ^{232}\text{Th}_R \right)$$

$$^{234}\text{U}_C = ^{234}\text{U}_L - ^{232}\text{Th}_L \left(^{230}\text{Th}_R / ^{232}\text{Th}_R \right) - \left(^{230}\text{Th}_R - ^{234}\text{U}_R \right)$$

$$^{238}\text{U}_C = ^{238}\text{U}_L - ^{232}\text{Th}_L \left(^{230}\text{Th}_R / ^{232}\text{Th}_R \right) - \left(^{230}\text{Th}_R - ^{238}\text{U}_R \right)$$

The terms $\left(^{230}\text{Th}_R - ^{234}\text{U}_R \right)$ and $\left(^{230}\text{Th}_R - ^{238}\text{U}_R \right)$ correct for fractionation between uranium and thorium. Several leachate-residue pairs with varying detrital amounts may be analysed to obtain a better average.

Scheme II: (Rosholt 1976, Szabo and Sterr 1978, Ku and Liang 1984)

Rosholt (1976) and Szabo and Sterr (1978) analysed caliches and travertines by using one or several leachate subsamples, with varying amounts of detritus, together with only one residue fraction. Secular equilibrium is not required in the detritus, but it is assumed that there is no fractionation between the uranium and thorium when leaching the sample, ie.:

$$\left(^{230}\text{Th} / ^{234}\text{U} \right) \text{ in residue} = \left(^{230}\text{Th} / ^{234}\text{U} \right) \text{ in detritus.}$$

$^{230}\text{Th}/^{232}\text{Th}$ was plotted against $^{234}\text{U}/^{232}\text{Th}$, and $^{234}\text{U}/^{232}\text{Th}$ against $^{238}\text{U}/^{232}\text{Th}$ for each sample pair. The required ratios for the pure carbonate were then obtained from the slopes of these plots. Ku and Liang (1984) derived the mathematical equations which show the validity of the

method if the assumptions hold.

The advantage of Scheme II over Scheme I is that the analysis of the residue for each corresponding leachate fraction is not needed, because it is assumed that there is no U-Th fractionation. The advantage of the L/R method over the L/L method is that in the former single samples may be used while in the latter it is necessary to obtain subsamples with varying detrital amounts.

There have, however, been several criticisms of the L/R method. Luo and Ku (1991) considered it to be analytically demanding in maintaining a high degree of consistency in the leaching process. It has also been shown experimentally to produce incorrect ages (Przykylowitz et al. 1991) since the isotopic composition in the residue is not necessarily related to that of the contaminating nuclides in the leachates. Bischoff and Fitzpatrick (1991) showed in a set of experiments that the condition of isotopic equilibrium in the detritus is not always met, limiting the usage of Scheme 1. Thus to use this method, the above assumptions must first be shown to apply, a requirement that is often not possible.

1.4.4 The Total Sample Dissolution (TSD) method (Lao and Benson 1988, Luo and Ku 1991, Bischoff and Fitzpatrick 1991)

In this method several subsamples, with varying detrital amounts that were deposited at the same time, are required. The subsamples are dissolved completely, using perchloric and hydrofluoric acid. Lao and Benson (1988) totally dissolved tufa subsamples from the Lahontan Basin. They analysed their results by applying the intercept plot for the $^{230}\text{Th}/^{234}\text{U}$ ratio together with the average $^{234}\text{U}/^{238}\text{U}$ ratio. They also applied the f_1 index correction in Equation 1.2 to some of their samples. The initial f_1 used was the average of the f of a modern tufa and of the $^{230}\text{Th}/^{232}\text{Th}$ ratio obtained from the slope of one of the intercept graphs.

Their $^{230}\text{Th}/^{234}\text{U}$ ages compare well with their ^{14}C ages up to 20 000 years. In the older samples the ^{14}C ages were significantly younger than the $^{230}\text{Th}/^{234}\text{U}$ ages.

Bischoff and Fitzpatrick (1991) conducted experiments on artificial mixtures of detritus and pure carbonate with known age. Different mixtures provided subsamples with varying detrital amounts which were completely dissolved. Similar experiments were carried out in order to apply the L/L and L/R methods for comparison. The carbonate ratios were obtained from slope graphs. They concluded that, due to unpredictable isotopic fractionation during leaching, the TSD method gives the best results, followed by the L/L method.

Luo and Ku (1991) used the same chemical procedure and method of analysis as Bischoff and Fitzpatrick (1991) and also provide a mathematical basis for the method. They analysed impure carbonates from Nevada and evaporative sediments from China, obtaining a spread in the proportion of detritus by grinding their samples and choosing different grain size subsamples.

The advantage of this method is that no assumptions need to be made about isotopic fractionation in the leaching process, nor about secular equilibrium in the detritus. The detritus is assumed to be homogeneous. The method can, however, only be applied in cases where a sufficient range of detrital contamination can be achieved.

1.5 PRESENT APPROACH BY SEQUENTIAL LEACHING (SL)

All the above methods are restricted by their assumptions. The "Early models" depend on finding the correct f value, a procedure which may result in large uncertainties. The L/L and TSD methods require several subsamples with varying amounts of detritus to obtain a good age. Although consistent results are produced, it is often not possible to

obtain such sets of samples which differ significantly in their detrital content. This holds especially true in the case of dating calcretes from Namibia. The L/R method has the disadvantage of depending on conditions which are often not met.

A method is needed whereby one can take the detritus into account and obtain a reliable date by analysing a single sample. Thus in this project the possibility of separating the uranium and thorium in the carbonate from that adsorbed to the detritus is investigated by sequential leaching.

The sample is dissolved in weak acid to give the first fraction containing the isotopes belonging to the carbonate. The residue from the weak acid attack is boiled with strong acid to remove the uranium and thorium in the iron hydroxide coating. These two fractions, L and S, together contain all the nuclides of interest, but exclude the nuclides contained in the acid-insoluble residue.

Where possible, ie. for samples of less than 25 000 years, the ages thus obtained are compared with the ^{14}C ages of the same material. Different methods of data analysis are applied as cross-checks.

The following chapters describe the chemical procedure, followed by the method of data analysis, results of the known-age samples, and finally the application to samples of unknown age from the Kuiseb River valley in the central Namib.

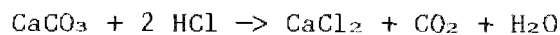
CHAPTER 2

CHEMICAL AND PHYSICAL METHODS

In addition to calcium, a calcrete contains not only uranium and thorium, but also other elements, especially iron. The uranium and thorium need to be chemically separated from these other elements and from each other. The sequence involves acid dissolution, removal of calcium by a co-precipitation process and purification of the uranium and thorium by an ion exchange procedure. These two elements are then electroplated onto stainless steel discs as thin sources so that their alpha activities may be detected and recorded on an alpha spectrometer. There are many variations to the chemical method for $^{230}\text{Th}/^{234}\text{U}$ dating (Ivanovich and Harmon 1982). The method for pure carbonates as used in the Quadru laboratory is described in detail below, followed by the specific techniques of sequential leaching to correct for detrital contamination.

2.1 GENERAL CHEMICAL METHOD

Generally 20-30 g of calcrete contains a sufficient amount of uranium. The sample is dissolved in hydrochloric acid, resulting in the following reaction:



The solution is filtered to retain any acid-insoluble residue which is well rinsed with acid and water. The solution contains all the calcium as well as the uranium and thorium and their daughters, such as radium and polonium (Figure 2.1). Other elements, eg. iron, would cause multilayers when electroplating and result in a thick source. These major elements thus need to be separated before electroplating to obtain good spectra with minimal overlapping of peaks. Since the chemical procedure is not quantitative, a known amount of ^{232}U and ^{228}Th is added to the solution as a spike. This also enables the uranium and thorium concentrations to be

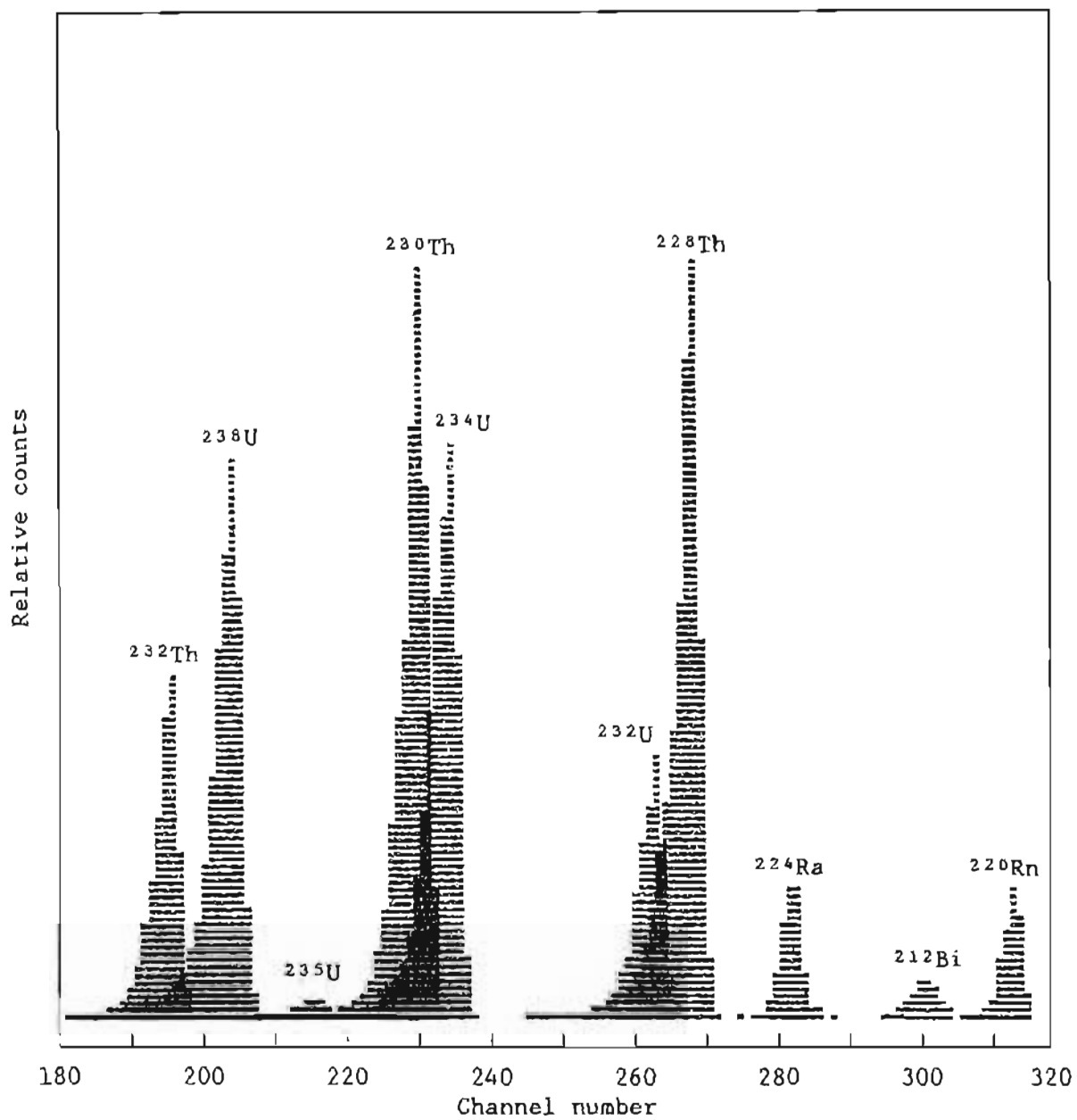


Figure 2.1: Superimposition of typical uranium and thorium alpha spectra showing the extent of overlap of the uranium and thorium isotopes of similar energies (analysis U-452).

calculated.

The next step is to eliminate most of the calcium. Where necessary 5 ml of an iron solution ($\text{Fe}(\text{NO}_3)_3$) is added to the acid solution that is made up to 200 ml volume. The acidic solution is heated and ammonia added until a pH of 7-8 is obtained. At this pH iron hydroxide forms with which the uranium co-precipitates and to which thorium attaches itself, leaving most of the calcium in the solution.

This is centrifuged at 3000 rpm for 10 minutes to separate the solution with the calcium from the iron hydroxide precipitate. The uranium extraction, however, is not very efficient (about 70% U is extracted) and thus the above process is repeated with the decanted solution and the new precipitate is added to the original. This precipitate is dissolved in about 20 ml concentrated HCl and heated to oxidise the iron and uranium before putting it on an ion exchange column.

The ion exchange column consists of a 1x8-200 mesh Dowex-1, chloride form, basic anionic resin. The resin is cleaned with 0.1 N HCl and then equilibrated with 7 N HCl. The sample solution is added to the resin and the thorium, with other ions, are eluted and collected in a beaker while the uranium and iron are retained on the resin. The column is rinsed with 30 ml 7N HCl. The iron is eluted from the column by rinsing with 100 ml acetone (0.05 N HCl in 90% acetone). Not all the iron is eluted at this stage. The uranium, and any remaining iron, is then eluted with 30 ml 0.1 N HCl. The uranium and thorium solutions are evaporated to dryness. Meanwhile the resin is rinsed with 80 ml 1 N nitric acid (to elute ^{210}Po) and equilibrated with 8 N nitric acid.

The thorium needs to be separated from the other ions. The thorium is dissolved in 10 ml 8 N nitric acid and put on the column. The column is rinsed with at least 80 ml of this nitric acid to elute most of the other ions while retaining the thorium. The thorium is eluted with 60 ml 0.1 N HCl and this solution is evaporated to dryness.

Meanwhile the remaining iron is separated from the uranium by using an organic solution iso-Butylmethylketon (BMK). The sample is dissolved in 10 ml 5 N HCl and put in a separation funnel. 10 ml of BMK is added and the solution is thoroughly shaken. The BMK extracts the iron but not the uranium from the acid phase. The denser acid is drained from the funnel. Another 10 ml of 5 N HCl is added to the BMK and shaken again. The new acid is drained and added to the original. This is necessary since the recovery of uranium is not complete. The acid containing the uranium is evaporated on low heat to prevent the traces of organics from burning. When dry, 10 ml of concentrated HCl and a few drops of perchloric acid are added and the solution is heated to oxidise traces of organics. Concentrated HCl is added and heated until all the organics are gone.

2.2 ELECTRODEPOSITION

In order to obtain good resolution in the alpha spectrometry, it is necessary to produce a thin, uniform deposit for a counting source. The source should have a carrier free layer of the alpha emitter with no foreign material above this layer to attenuate alpha radiation. Electrodeposition is used to achieve this. If the above conditions are not met, poor resolution results in greater peak overlap.

For the electrodeposition, the dry uranium and thorium are dissolved in slightly acidic solutions and poured into tubes which are constructed as follows. Stainless steel discs of 28 mm diameter are fitted to glass cylindrical tubes of 65 mm length and 13 mm inside diameter with elastic bands and a glue mixture. The volume contained in the glass tube with the disc as a base is about 8 ml.

The dry uranium is dissolved in 8 ml ammonium chloride solution, pH = 2.5, which is poured into the glass tube. A different electrolytic solution is prepared for the thorium, viz.:

4 ml 2 N NH_4Cl (pH=2.3) + 4 ml oxalic acid (pH=0 to 1)
+ 2 ml 0.01 N HNO_3 (pH=2)

A thin coil of platinum wire is placed in the solution so that the coil end of the wire is about 1 mm above the disc. An applied voltage of 5 to 15V is adjusted to maintain a current of 1A. The uranium is electroplated for 30 minutes and the thorium for 60 minutes.

Both solutions are quenched with 1 ml of strong ammonia solution to prevent the uranium or thorium from redissolving in the acidic solution after switching off the current. The discs are fired over a bunsen burner to evaporate any ammonium chloride. The discs are then ready to be counted.

2.3 PROBLEMS ENCOUNTERED

(a) The flow rate of liquids through the column is about 8-14 drops per minute. Sometimes, however, this rate decreases or stops when putting thorium on to the column and a waterjet pump is needed to pump the liquid through. The effect on the resin is not known but the yields do not appear to be worse than when no pump is used.

(b) The uranium and thorium sometimes still contain some salts when ready to be electroplated. This results in thick sources and broad alpha peaks which increases the final errors. Putting the sample through the column again helps reduce the salts but may also decrease the yields. Rinsing the discs with acid improves the peak resolution.

(c) In a few samples there were ^{210}Po peaks on the thorium disc. The ^{210}Po overlaps with ^{228}Th , decreasing the accuracy of the ^{228}Th measurement. By rinsing the column with at least 80 ml 1 N nitric acid before adding the thorium solution, this problem was eliminated.

(d) Some carbonates contained organic material which is known to absorb uranium. After precipitation of the iron hydroxide, the remaining solution is yellowish if it contains organics. Sodium chlorite is then added to oxidise the organics and release the uranium. Even so, the yields have been poor for such samples.

(e) Low yields obtained: The $^{234}\text{U}/^{230}\text{Th}$ chemical procedure as a whole involves a complicated sequence, viz. sample dissolution, co-precipitation, ion exchange, and electrodeposition. Losses of uranium and thorium may occur at several stages and the following chemical yields are quoted for the procedure as a whole.

The uranium yield for two of the samples that contained organics ranged from 1% to 34%, mean $16 \pm 14\%$, $n = 5$ fractions. The reliability of these results are discussed later (Section 4.2.2). The uranium yield for all the other samples ranged from 4% to 68%, mean $31 \pm 19\%$, $n = 40$ fractions. The thorium yield for all samples ranged from 7% to 88%, mean $50 \pm 21\%$, $n = 45$ fractions.

The one sample with a particularly low yield was repeated and consistent results were obtained (Section 5.4.2). It thus appears that reliable results are obtained, even in cases where the yields are below 10%. Samples with low yields may be considered to produce acceptable results if there is no laboratory contamination. Other authors have also reported very variable yields: Van der Wijk (1987) obtained yields varying from 5% to 95% for organic material and Ivanovich and Harmon (1982) quote yields of 1 to 90% for different authors for uranium in water samples.

2.4 COUNTING EQUIPMENT

An alpha spectrometer (Frontispiece) is used to determine the

uranium and thorium isotope activities. The source discs are placed a few millimetres below a partially depleted semiconductor detector (450 mm² active area, 32 keV alpha resolution FWHM, 100 micron depletion depth). Alpha particles absorbed in the detector generate electrical pulses proportional to their energy. There are two detectors, DL and DR, both being supplied with a bias voltage of 79V. The electronic amplification is adjusted to produce a convenient spread of the alpha-particle peaks from the different isotopes.

The detection chambers are sealed and evacuated by a rotary oil pump to about 10^{-3} torr to reduce energy loss from the alphas. These signals are fed to separate preamplifiers (Canberra model 2004) and then to the main amplifiers (model 2012 for DL and model 3100-02 for DR). The signals from both amplifiers are then fed through a mixer router (model 8220A) to a multi-channel pulse height analyser (Series 30) which records the numbers of pulses received in each energy interval. The uranium and thorium spectra can be printed out, and the peak values recorded via a HP computer system containing an interface unit, computer, disc drive and printer.

A vacuum gauge is coupled to the preamplifiers via an electrical unit that cuts the voltage if there should be a loss of vacuum (at about 50×10^{-2} torr).

2.5 ANALYSING ALPHA SPECTRA

Typical spectra are shown in Figures 2.2 and 2.3. Generally 14 channels are used to determine the counts in a peak - 10 below and 3 above the peak. When time allows and the yields are sufficient, a disc is counted long enough to obtain several thousand counts per peak. The counts obtained from the peaks need to be corrected for background and for overlapping peaks.

Blank runs which had been through the complete chemical and electrodeposition procedure showed that the reagents used had no detectable levels of uranium and thorium. Blank discs are counted once every month in order to measure the recoil nuclides on the detectors, and the running average is subtracted from the peak counts (Figures 2.2 and 2.3). The errors of the background counts are negligible relative to the errors of the counts.

The following peaks need to be corrected where alpha energies overlap (Figure 2.4). Part of the ^{235}U peak falls on the ^{238}U peak and a small correction must be made using the known $^{235}\text{U}/^{238}\text{U}$ ratio. ^{232}U decays into ^{228}Th , and then ^{228}Th recoils from the source to the detector, resulting in a gradual increase in ^{228}Th background on the uranium detector. 50% of this background ^{228}Th overlaps on to the ^{232}U peak and must be subtracted. In the thorium spectrum, the ^{228}Th spike needs several corrections (made in the following order - see also Figure 2.4):

(a) the ^{224}Ra peak is only a few channels above ^{228}Th and causes an overlap. The ^{216}Po peak is generally in equilibrium with the ^{224}Ra peak and can be used to calibrate the amount of overlap;

(b) 5.1% of ^{224}Ra which has the same energy as ^{228}Th is subtracted;

(c) ^{232}Th also decays into ^{228}Th and thus the ^{232}Th count rate is subtracted from ^{228}Th - assuming that the two nuclides are in equilibrium.

(d) ^{228}Th has a relatively short half life (1.91 years) and thus the number of days between separating ^{228}Th from its parent ^{232}U and counting is used to calculate how much the ^{228}Th has decayed;

The above corrections are small and the errors of the count rates are not affected. In the case of subtracting ^{232}Th from ^{228}Th , however, errors are propagated since this is often significant.

Sometimes the electroplated sources are not sufficiently thin, resulting in overlapping peaks. Corrections can be made by using the tail (on the low energy side) of the ^{238}U or ^{232}Th peaks. In such cases the

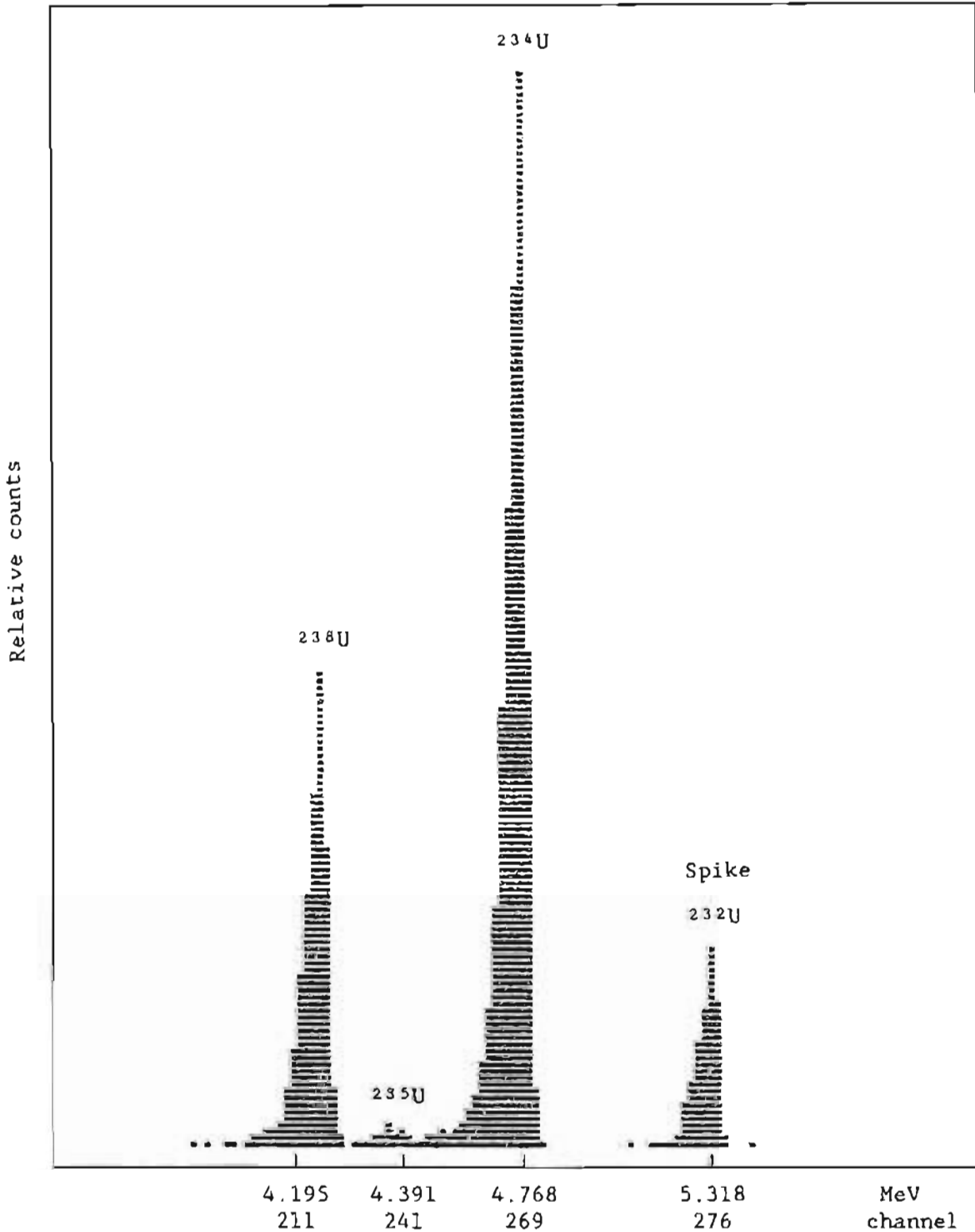


Figure 2.2: Uranium spectrum of Homeb silt fraction 1 (analysis U-446) as an example of a typical uranium spectrum printout.

File: U-446U		Peak channels	Counts	Bkgd
Date: 08/06/92	238U	<201-211-214>	2 568	1
Read time: 90 000 s	234U	<231-241-244>	5 599	1
Max. counts: 1422	232U	<259-269-272>	1 071	11
	part Th	<274-276-278>	22	13

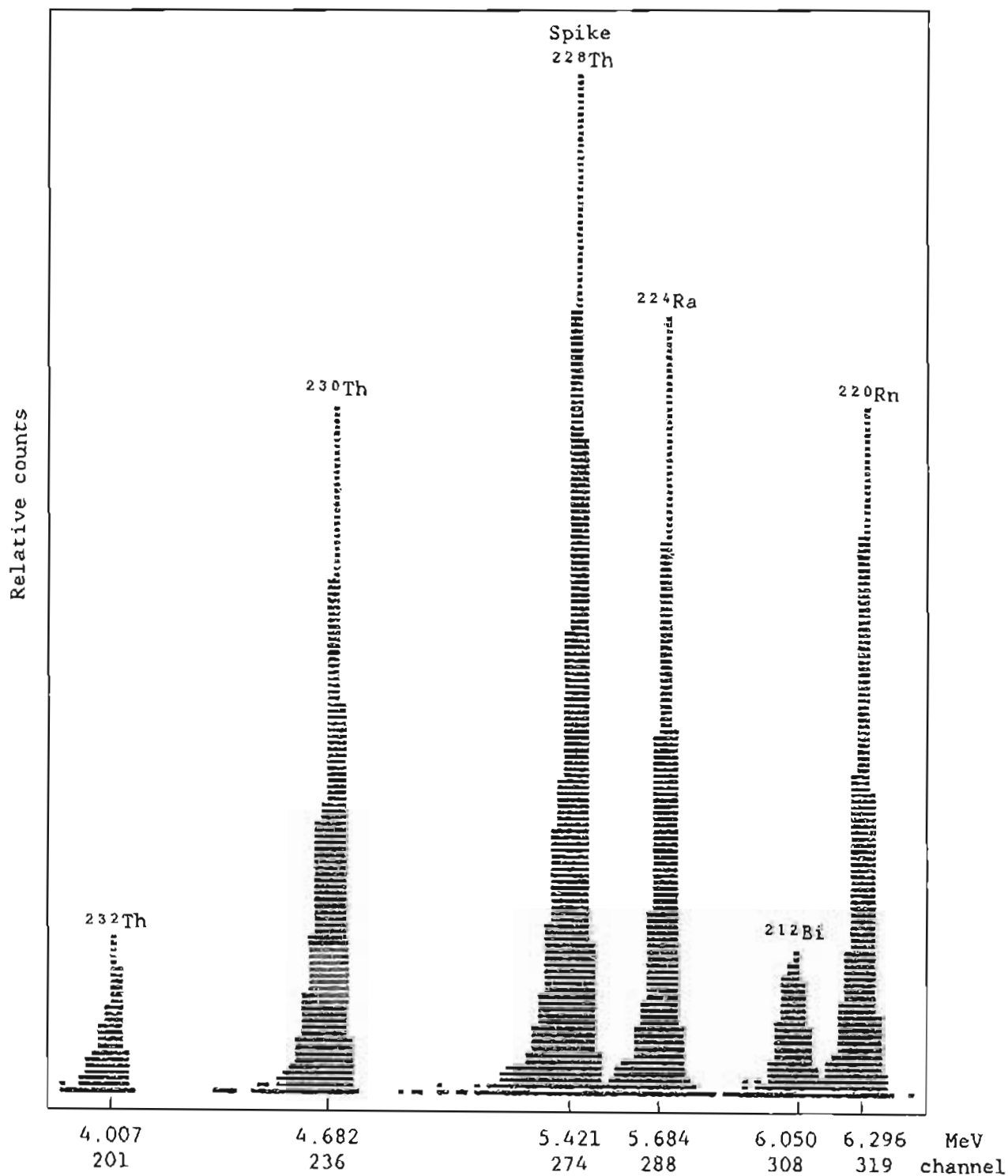


Figure 2.3: Thorium spectrum of Homeb silt fraction 1 (analysis U-446) as an example of a typical thorium spectrum printout. ^{216}Po , with an energy of 6.777 MeV, is not shown in the spectrum.

File:	U-446Th	Peak channels	Counts	Bkgd
Date:	08/06/92	^{232}Th <191-201-204>	438	2
Read time:	90 000 s	^{230}Th <226-236-239>	1 741	2
Max. counts:	667	^{228}Th <264-274-277>	2 746	16
		^{224}Ra <279-288-291>	1 747	

disc is rinsed with acid and recounted. Generally this improves the peaks sufficiently without reducing the count rates too much and the new corrected counts are used.

2.6 CALCULATION OF ACTIVITIES, RATIOS AND AGES

The corrected counts are entered into a Basic program which calculates the activities, activity ratios, ages and all associated errors (Appendix 1). The ages are calculated by iteration (Appendix 1) or determined by reading off from the graph generated by Equation 1.1 (Figure 1.4). An iteration program based on the secant method (written by A. S. Talma of the Quadru laboratory) was used in the present work.

The standard method of error determination in radioactive decay based on counting statistics is applied (Ivanovich and Harmon 1982), ie. the standard deviation in measuring N disintegrations is equal to the square root of N provided that N is large. Errors are propagated in the standard fashion. The actual derived formulas for the errors are given in Appendix 1. Errors are 1σ throughout unless otherwise stated.

2.7 THE SEQUENTIAL LEACH (SL) METHOD

In the Sequential Leach method, a sample is generally covered with 100 ml of distilled water and weak acid (3N HCl) is slowly added to dissolve the carbonate. Generally the carbonate is dissolved in 12 to 48 hours. The sample is filtered and the solution, containing the dissolved uranium and thorium in the carbonate, is processed as described previously. This solution is the WEAK ACID LEACH. The spike solution is added after the solution has been filtered as a standard procedure to prevent problems with spike being reabsorbed onto subsequent fractions. The residue is dried and weighed.

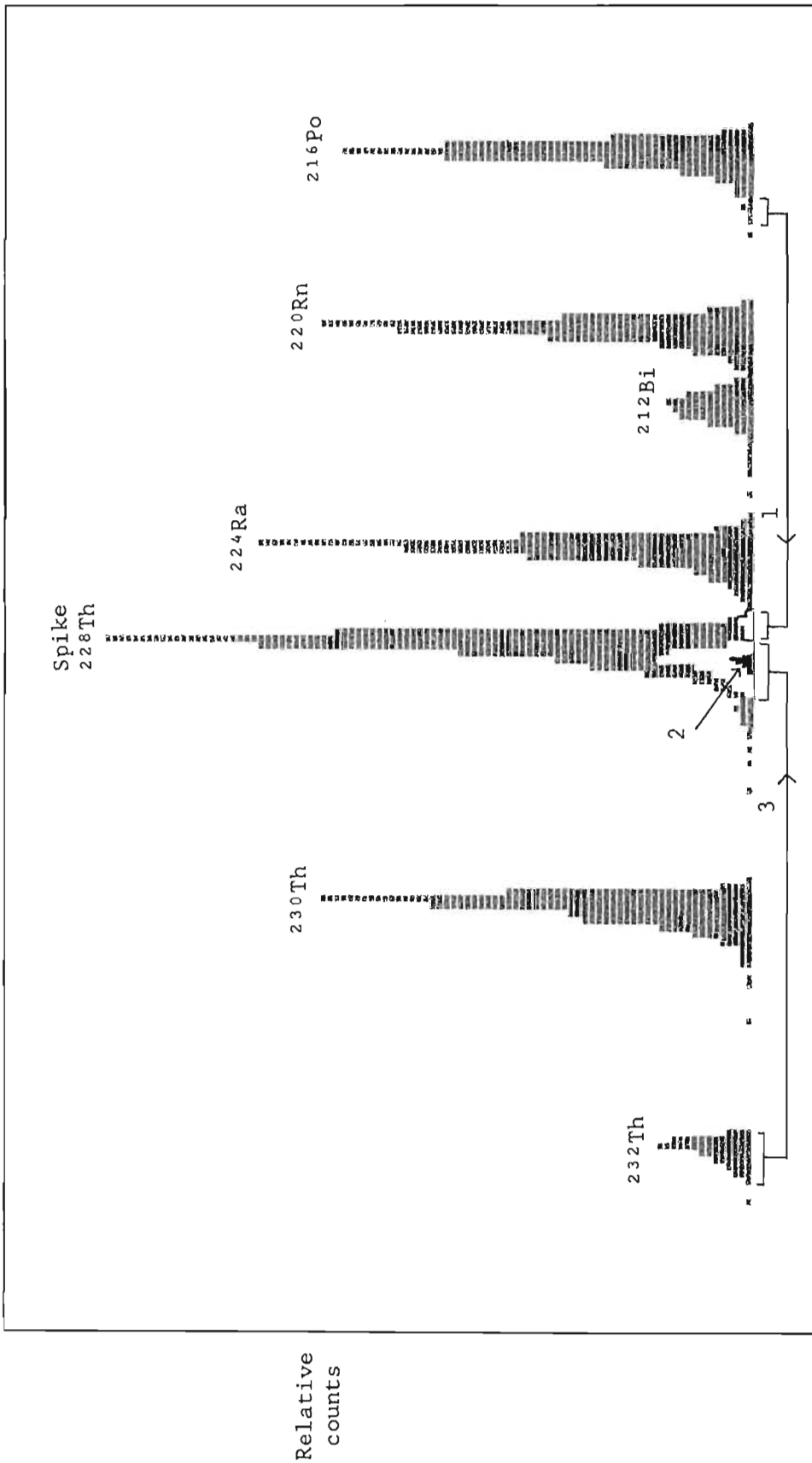


Figure 2.4: Thorium spectrum (analysis U-446) showing the corrections that are made for ^{228}Th (see also text). Some of these corrections are superimposed on the ^{228}Th peak, indicated by the following numerals: 1 (coloured white) indicates the tail overlap of ^{224}Ra on ^{228}Th - the correction is estimated from the ^{216}Po peak; 2 (coloured black) represents 5.1% of the ^{224}Ra peak; and 3 (coloured white) is the ^{228}Th that decayed from its parent ^{232}Th and thus does not belong to the ^{228}Th that was added as spike.

The remaining sand (up to 50% or more of the original sample) is covered with 100 ml of concentrated hydrochloric acid and boiled for at least 10 minutes. This removes the uranium and thorium on the surface of the sand grains and in the iron oxide coating around the sand, giving the BOILED FRACTION. The sample is filtered and the solution is processed as usual.

In some cases two weak leaches were analysed in order to attempt a wider spread of fractions. This was achieved by dissolving only half of the carbonate and filtering the solution to give the first weak leach. Then the remaining carbonate was dissolved to give the solution for the second weak leachate. Finally the residue was boiled as before.

The corrected ages were calculated in several different ways, as described in the next chapter.

CHAPTER 3

METHODS OF DATA ANALYSIS

Five samples of known ^{14}C ages were treated chemically as described in Chapter 2. Several methods of analysis were applied to the data to correct for detrital contamination and the results compared with each other and with the ^{14}C ages. In order to be able to make worthwhile comparisons it is first of all necessary to consider the assumptions underlying these analytical methods, especially in the way they apply to the Sequential Leach method. The ^{14}C age determinations are discussed below, followed by the different methods of correcting the $^{234}\text{U}/^{230}\text{Th}$ ages.

3.1 ^{14}C AGE DETERMINATIONS

The ^{14}C method is a well established dating technique which can provide reliable ages. Since the ^{14}C half-life is only 5 730 years, the method is restricted to the past 50 000 years. During certain periods of the Upper Pleistocene (30 000 to 10 000 years ago) ^{14}C ages have, however, been found to be several thousand years too young (Vogel 1983, 1987, Bard et al. 1990) so that exact correlation with $^{230}\text{Th}/^{234}\text{U}$ dates is not to be expected.

Secondly, problems arise with ^{14}C ages near the dating limit: a sample with an age of 32 000 or 38 000 years contains 2% or 1%, respectively, of the original ^{14}C and the admixture of only a small amount of recent carbonaceous material to an ancient sample can seriously affect the apparent age.

With the dating of terrestrial carbonate material a further complication arises with ^{14}C dates in that the initial ^{14}C content of the carbonate is less than that of the vegetation. It has been shown that

groundwater and pedogenic carbonates commonly contain only about 85% as much ^{14}C as does contemporary organic carbon (eg. Vogel and Ehhalt 1963) with the result that the apparent age of such inorganic carbon is about $1\,500 \pm 500$ years too high. For lacustrine carbonate precipitated in shallow water the discrepancy is more likely to be only 1000 years (Vogel 1982). The ^{14}C dates given in this work have not been corrected for this effect of inorganic carbon.

These different factors need to be taken into account when comparing the $^{230}\text{Th}/^{234}\text{U}$ dates with ^{14}C dates of the same material. In the case of terrestrial calcium carbonate deposits, such as pedogenic calcretes, the precipitation can take place over an extended period and/or during successive climatic phases. The radiogenic date obtained will then be a non-linear average for the bulk material. Since the half-life of ^{14}C is much shorter than that of ^{230}Th , the ^{14}C age will tend to be lower than the $^{230}\text{Th}/^{234}\text{U}$ age.

3.2 THE $^{230}\text{Th}/^{234}\text{U}$ CORRECTION METHODS

3.2.1 The slope method

The slope method is currently the most popular method of analysis and has been shown to be mathematically valid, under certain conditions, for analysing coeval leachate samples (Schwarcz and Latham 1989), total samples (Luo and Ku 1991), and leachate/residue pairs (Ku and Liang 1984). It involves plotting $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ (thorium graph) and $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ (uranium graph).

In the case of the L/L and TSD methods, subsamples with proportionately decreasing amounts of detritus will contain less ^{232}Th and thus plot increasingly further from the origin. In the case of the L/R method, the straight line graph is simply based on the difference of two points

(see equations in Section 1.4.3) with the residue point lying closer to the origin. The slopes of the two graphs give the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios, respectively, of the pure carbonate (Schwarcz and Latham 1989, Section 1.4.2).

The slope method of data analysis can be applied in the case of the Sequential Leach chemical technique. If no isotopic fractionation occurs, then the required ratios are directly obtained as in the L/L method (Appendix 2). If differential fractionation does occur, the way in which the slope is affected is shown in Appendix 2. The actual extent to which the Namib samples are affected by fractionation is discussed in Chapter 4.

The following assumptions need to be made in applying the slope method to the SL technique:

(a) assume that there is no ^{232}Th in the pure carbonate fraction;

(b) assume that no reabsorption of specifically thorium onto the undissolved residue occurs;

(c) assume that all the isotopes adsorbed onto the detritus are removed by boiling in acid.

These assumptions imply that there must be no differential fractionation between the isotopes. In plotting the data, the boiled fraction will lie close to the origin and the leachate point further out on a positive slope. If fractionation is present, the leachate points will be affected more than the boiled fraction points.

The best-fit slopes and intercepts and their errors were determined by applying a least-squares regression procedure that takes into account the errors in both the X and Y variables (Harmer and Eglington 1990, Eglington and Harmer 1991). It gives the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios

and associated standard errors. These ratios are then entered into Equation 1.1, which however, then propagates errors slightly larger than standard since ratios rather than counts are used. Also, for large ages the errors become slightly asymmetrical due to the non-linear radioactive decay and the larger relative error is chosen.

3.2.2 The intercept method

This method consists of plotting $^{230}\text{Th}/^{234}\text{U}$ versus $^{232}\text{Th}/^{234}\text{U}$ (thorium graph) and $^{234}\text{U}/^{238}\text{U}$ versus $^{232}\text{Th}/^{238}\text{U}$ (uranium graph) for samples of similar age but with varying detrital amounts, eg. Szabo and Butzer (1979). These graphs are essentially mixing lines representing samples with varying mixtures of carbonate and of detritus. In the case of the thorium graph a sample consisting of carbonate with very little detritus will contain very little ^{232}Th and thus the point will lie close to the y-axis. As more detritus is added to the carbonate, the ^{230}Th and ^{232}Th of the detritus is added in a constant ratio (Kaufman 1971). The y-intercepts represent zero ^{232}Th and thus extrapolating to the y-intercept gives the required ratios of the pure carbonate.

In the case of the SL method the weak acid leach consists of isotopes from the carbonate and some from the detritus. The boiled fraction consists of the remaining detrital isotopes and thus these two points represent a mixing line as described above.

Since the intercept method is mathematically equivalent to the slope method (Ku and Liang 1984, Bischoff and Fitzpatrick 1991), the conditions in using the intercept method may be considered to be the same as for the slope method, in particular that there is no isotopic fractionation. The results of applying the intercept method will be compared with those of the slope method in the case of the SL procedure.

3.2.3 $^{230}\text{Th}/^{234}\text{U}$ ages using the f index

If one takes the ^{232}Th activity in a carbonate sample as an index of the amount of ^{230}Th contamination, a correction may be made to the age equation. The advantage of this method is that only a single sample is needed for analysis.

In the method of Sequential Leaching, more than one fraction of a single sample was analysed in order to use the slope and intercept methods. For each fraction the activities per total sample mass of the uranium and thorium isotopes were calculated. In order to use the f index correction method for comparison, the respective activities of the fractions are added to obtain the total activities of the sample.

The standard age equation may be modified to take into account initial ^{230}Th contamination by combining Equations 1.1 and 1.2 to give:

$$\begin{aligned} \frac{^{230}\text{Th}}{^{234}\text{U}} &= \frac{^{232}\text{Th}}{^{234}\text{U}} \times f_i \times e^{(-\lambda_0 \times t)} + \frac{^{238}\text{U}}{^{234}\text{U}} \times \left[1 - e^{(-\lambda_0 \times t)} \right] \\ &+ \frac{\lambda_0}{\lambda_0 - \lambda_c} \times \left[1 - \frac{^{238}\text{U}}{^{234}\text{U}} \right] \times \left[1 - e^{(t \times (\lambda_c - \lambda_0))} \right] \end{aligned}$$

[Eqn 3.1]

A similar equation is obtained by combining Equations 1.1 and 1.3 if the current $^{230}\text{Th}/^{232}\text{Th}$ activity ratio, f_c is used. The iteration program then calculates the $^{230}\text{Th}/^{234}\text{U}$ age uncorrected for contamination ($f = 0$) or some corrected age by inputting a non-zero f value. Two chief ways of representing this f value are used, although care needs to be taken in distinguishing between using f_i or f_c as defined in Chapter 1 and described below.

The initial ratio, f_i , is effectively the $^{230}\text{Th}/^{232}\text{Th}$ ratio of the contaminating material, ie. the pure detrital desert sand in the case of the Namibian calcretes. This value is found by assuming that the desert sand contains no carbonate. The sand is boiled in concentrated HCl, the solution is analysed as in Chapter 2, and the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio is measured (see Chapter 4).

The current $^{230}\text{Th}/^{232}\text{Th}$ ratio, f_r , of the non-authigenic detrital thorium may be obtained from the intercept graphs since the slope of the $^{230}\text{Th}/^{234}\text{U}$ versus $^{232}\text{Th}/^{234}\text{U}$ graph gives this $^{230}\text{Th}/^{232}\text{Th}$ ratio. Similarly one can also use the $^{230}\text{Th}/^{232}\text{Th}$ intercept of the $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ graph. Since the two graphical procedures are mathematically the same (Section 1.4.2), the f_r values obtained from either graph are also equivalent. In the analysis (Chapter 4) the value from the intercept graph is chosen to compare with the other methods.

Throughout this thesis f_i will refer to the initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, with the value being obtained from desert sand samples, and applying this value to Equation 1.2. Similarly, f_r refers to the current $^{230}\text{Th}/^{232}\text{Th}$ ratio of the non-authigenic thorium, with the values being obtained from the intercept graph, and applying the values to Equation 1.3. The letter f without subscript is a general reference to the $^{230}\text{Th}/^{232}\text{Th}$ ratio.

CHAPTER 4

EXPERIMENTAL TEST RESULTS AND DISCUSSION

The intention in this thesis is to test the applicability of the Sequential Leach method in obtaining valid dates. Since the chief condition for applicability is that no fractionation occurs during the leaching of the detritus, experiments were done on pure desert sands which form the detrital component of the carbonates. Furthermore, the SL technique was tested by analysing some carbonate samples of which the ages were thought to be reasonably well known, and comparing the ages obtained by different correction methods.

4.1 LEACHING EXPERIMENTS ON DESERT SANDS

In order to determine to what extent uranium and thorium are extracted from the detrital fraction of the Namib calcretes by a weak acid leach, three samples of desert dune sand were analysed. Such sand forms the matrix in which the local calcretes developed and thus also constitutes the major fraction of the detritus incorporated in the carbonate cement of the fluvial conglomerates in the Kuiseb River valley.

4.1.1 Sample descriptions

The following three samples of desert sand were investigated:

Lower Tsondap valley (C-2811)

This consists of loose sand from below silt layers in the Lower Tsondap valley that probably are contemporaneous with the Narabeb lacustrine silts, dated to about 200 000 to 240 000 years (Selby et al. 1979).

Khommabes vlei (C-4795)

This is surface dune sand from the Khommabes vlei, 1 km south of the Kuiseb River, and several kilometres west of Gobabeb.

Gobabeb dune sand (C-4188)

This is surface dune sand from the linear dune on the south side of the Kuiseb River opposite Gobabeb.

4.1.2 Chemical procedure

About 10 to 15 g of each sand sample was leached with 100 ml of cold hydrochloric acid (HCl) of about 1 N, giving analyses U-433, U-460 and U-471 for Tsondap, Khommabes and Gobabeb respectively. The residue was then boiled in concentrated HCl for at least 10 minutes until all traces of the iron oxide coating on the grains had dissolved, giving analyses U-433B, U-462 and U-472 for the same sites respectively. The Tsondap and Khommabes samples were left in contact with the 1 N acid for 24 hours, while the third sample, Gobabeb, was left for 48 hours. The leachates of each sample were then processed as described in Chapter 2 and the alpha activities analysed.

The Lower Tsondap sample was also used to determine whether uranium or thorium from the weak acid leachate was reabsorbed onto the residue before separation of the solution. This was achieved by adding the ^{232}U - ^{228}Th spike to the weak acid leachate, U-433, while still in contact with the insoluble sand and not adding spike to the boiled solution, U-433B. The presence of spike in this fraction would then show that reabsorption had taken place. To obtain a measure of the degree of leaching in weak acid for this sample, a separate portion of Lower Tsondap sand was directly boiled in concentrated HCl and the solution analysed. This latter analysis thus gave the total amount of accessible uranium and

thorium in the sample. The results are summarised in Table 4.1 a,b,c.

4.1.3 Reabsorption test

The unspiked boiled fraction of the Lower Tsondap sample U-433B contained no measurable ^{232}U and only $(0.9 \pm 1.2)\%$ of the added ^{228}Th . Thus there is no clear indication of reabsorption of the spike under the leaching conditions that were used.

4.1.4 Initial f_1 ratio of pure detrital desert sands

The $^{230}\text{Th}/^{232}\text{Th}$ activity ratios of the total extractable thorium of the three samples is 0.535, 0.470 and 0.375 (Table 4.1), giving a mean of 0.476 ± 0.105 . If other analyses of similar Namib desert sand are added and the weighted average taken, then the $^{230}\text{Th}/^{232}\text{Th}$ ratio becomes 0.466 ± 0.005 (Vogel, pers. comm.), the total range being 0.375 to 0.591 (total of 9 measurements). A legitimate approach to the dating of the desert calcretes would be to use this latter value to correct for the detrital ^{230}Th (Section 3.2.3).

4.1.5 Leaching proportions - differential fractionation

The results listed in Table 4.1 show that a considerable amount of the uranium and thorium is leached from the sands by cold 1 N HCl. The proportion of the isotopes leached decreases in the order ^{234}U , ^{238}U , ^{230}Th , ^{232}Th . This sequence is understandable in terms of the expected solubility and accessibility of the individual nuclides, although it has possible serious consequences for some of the methods of analysis applied in this work.

The actual percentages of the nuclides extracted with weak acid in the Lower Tsondap sample (Table 4.1a, last column) are somewhat uncertain since U-433 and U-434 are separate portions of the sand, which need not

TABLE 4.1: LEACHING PERCENTAGES FOR DESERT SANDS

Tables (a)-(c) show the percentages of isotopes leached from the sand by weak acid (<1 N HCl). The weak leach times are indicated. The percentages given in the last column of each table are the proportion of activity in the weak leach to the sum of the weak and boiled leaches.

(a) Lower Tsondap Sand (C-2811) - 24 hrs leach

Dpm/kg	U-433 Weak	U-433B Boiled*	U-434 Boiled	$\frac{U-433}{U-434}$ %
^{238}U	67± 4	135± 8	202± 7	33 ± 2
^{234}U	86± 5	158± 9	244± 8	35 ± 2
^{232}Th	98± 5	385± 9	483± 8	20 ± 1
^{230}Th	76± 6	206±11	282± 9	27 ± 2
$\frac{^{230}\text{Th}}{^{234}\text{U}}$	0.883 ±0.084	1.304 ±0.102	1.157 ±0.053	
$\frac{^{234}\text{U}}{^{238}\text{U}}$	1.281 ±0.106	1.170 ±0.096	1.209 ±0.054	
$\frac{^{230}\text{Th}}{^{232}\text{Th}}$	0.773 ±0.073	0.535 ±0.031	0.584 ±0.017	

* Note: activities for U-433B are the difference of the activities of U-434 and U-433B.

(b) Khommabes Vlei (C-4795) - 24 hrs leach

Dpm/kg	U-460 Weak	U-462 Boiled	Sum	$\frac{U-460}{\text{Sum}}$ %
^{238}U	71± 3	223± 9	294± 9	24 ± 1
^{234}U	89± 3	243± 9	332± 9	27 ± 1
^{232}Th	109± 3	672±40	781±40	14 ± 1
^{230}Th	62± 2	305±20	367±20	17 ± 1
$\frac{^{230}\text{Th}}{^{234}\text{U}}$	0.691 ±0.033	1.255 ±0.096	1.105 ±0.067	
$\frac{^{234}\text{U}}{^{238}\text{U}}$	1.258 ±0.057	1.088 ±0.049	1.129 ±0.046	
$\frac{^{230}\text{Th}}{^{232}\text{Th}}$	0.567 ±0.023	0.453 ±0.021	0.470 ±0.035	

TABLE 4.1: LEACHING PERCENTAGES FOR DESERT SANDS - CONTINUED

(c) Gobabeb Dune Sand (G-4188) - 48 hrs leach

Dpm/kg	U-471 Weak	U-472 Boiled	Sum	<u>U-471</u> % Sum
²³⁸ U	73± 6	134± 4	207± 7	35 ± 3
²³⁴ U	82± 6	149± 5	231± 8	36 ± 3
²³² Th	145± 3	450±11	595±11	24 ± 1
²³⁰ Th	62± 2	161± 5	223± 5	28 ± 1
<u>²³⁰Th</u>	0.759	1.082	0.965	
²³⁴ U	±0.062	±0.047	±0.040	
<u>²³⁴U</u>	1.126	1.106	1.116	
²³⁸ U	±0.117	±0.045	±0.054	
<u>²³⁰Th</u>	0.430	0.357	0.375	
²³² Th	±0.013	±0.009	±0.011	

Mass losses:

Total mass lost, ie. values show percentage of iron oxide present on sand (assuming there are no carbonate particles mixed in the sand):

Lower Tsondap	U-433 + U-433B	5%
	U-434	7%
Khommabes	U-460 + U-462	3%
Gobabeb	U-471 + U-472	1%

necessarily be identical. The other two samples suggest that more of the nuclides are extracted in 48 hours than in 24 hours. Applied to the sequential leaching of a calcrete, the results suggest that if the carbonate is dissolved in weak, cold acid as rapidly as possible, then about 1/4 of the detrital uranium and 1/6 of the detrital thorium will be leached, thus substantially increasing the $^{230}\text{Th}/^{232}\text{Th}$ ratio in the carbonate fraction.

4.1.6 Effect of fractionation on the slope method

In Appendix 2 the following equation was obtained for the $^{230}\text{Th}/^{234}\text{U}$ ratio ($= m$) for the pure carbonate, as affected by fractionation:

$$m = \frac{\frac{^{230}\text{Th}_c}{^{234}\text{U}_c} + \left[1 - \frac{r_{0'}}{r_{2'}} \right] \times \frac{^{230}\text{Th}_D}{^{234}\text{U}_D} \times \frac{^{234}\text{U}_D}{^{234}\text{U}_c}}{1 + \left[1 - \frac{r_{4'}}{r_{2'}} \right] \times \frac{^{234}\text{U}_D}{^{234}\text{U}_c}}$$

[Eqn 4.1]

If no isotopic fractionation occurs during the leaching process, then m reduces to $(^{230}\text{Th}/^{234}\text{U})_c$ (Appendix 2). In Section 4.1.5 it was found that the fractions of the isotopes leached from the detritus by weak acid can be written as $r_4 > r_8 > r_0 > r_2$, or equivalently $r_2' > r_0' > r_8' > r_4'$ so the terms $[1 - r_0'/r_2']$ and $[1 - r_4'/r_2']$ will always be positive. The above equation may be simplified by using the data from the sand experiments and making some approximations.

The ratio $(^{230}\text{Th}/^{234}\text{U})_D$ will be close to unity if the uranium adsorbed onto the detritus has been there for a long time. Table 4.1 shows that this ratio lies between 0.965 and 1.157 for the three Namib

desert sand samples. Taking $(^{230}\text{Th}/^{234}\text{U})_D = 1$ and rearranging, gives:

$$\frac{^{230}\text{Th}_C}{^{234}\text{U}_C} = m \times \left[1 + \left[1 - \frac{r_1'}{r_2'} \right] \times \frac{^{234}\text{U}_D}{^{234}\text{U}_C} \right] - \left[1 - \frac{r_0'}{r_2'} \right] \times \frac{^{234}\text{U}_D}{^{234}\text{U}_C}$$

The isotope contribution of the detritus to the Namib calcretes can be estimated from the analyses of desert sand (Table 4.1). These measurements give $r_1'/r_2' = 0.835 \pm 0.019$ and $r_0'/r_2' = 0.942 \pm 0.026$ so that the term $(1 - r_1'/r_2') = 0.165$ and $(1 - r_0'/r_2') = 0.058$. Furthermore, Tables 4.2 and 5.2 show that there was always much more uranium in the carbonate than in the detritus so that $^{234}\text{U}_D/^{234}\text{U}_C$ was always $\ll 1$. These figures suggest that, at least for the samples investigated in this study, the slope m can be expected to be less than 10% smaller than the sought $(^{230}\text{Th}/^{234}\text{U})_C$. Similarly the ratios from plotting the intercept graphs may be expected to be smaller than the actual ratios due to the effect of fractionation.

4.2 SEQUENTIAL LEACHING OF KNOWN-AGE CARBONATES

Impure terrestrial carbonates of well defined known age for comparison with $^{230}\text{Th}/^{234}\text{U}$ dates are not readily available. For this study five samples, three from Namibia and two from Natal, all of which are reasonably well dated by ^{14}C , were analysed. The two Natal samples were used since there were not additional suitably well dated samples from the central Namib. The $^{230}\text{Th}/^{234}\text{U}$ dates obtained from applying the SL method (Chapter 2) to these samples are discussed in this chapter.

4.2.1 Description of the samples

Homeb 15 crust (C-1117)

This sample is a 1 cm thick calcium carbonate crust within the

sequence of silts deposited in the Kuiseb River canyon at Homeb (23°38'S, 15°09'E), 19 km upstream of Gobabeb. Several of these crusts in the sequence were ¹⁴C dated as well as a sample of decayed wood and snail shells (Vogel 1982). The consistent set of dates indicate that the silt accumulated between 23 000 and 19 000 ¹⁴C years ago, placing the age of Homeb 15 at about 21 000 years.

²³⁰Th/²³⁴U analyses:

Three separate subsamples of the Homeb crust were analysed and treated in different ways.

Subsample 1 - cemented silt (28.1 g)

Analysis U-391 was dissolved in weak acid - a boiled fraction was not analysed.

Subsample 2 - cemented silt (12.8 g)

This subsample was analysed by taking two successive weak acid leachates (analyses U-446 and U-447) and then boiling the remaining silt in concentrated HCl to give the boiled fraction (analysis U-449). The sum of the activities of the two carbonate fractions should thus be equivalent to the single weak leach, analysis U-391.

Subsample 3 - loose silt (10.0 g)

Analysis U-451 consisted of loose silt from the Homeb crust, but including some carbonate pieces. This subsample was boiled in acid to compare it with analysis U-449.

Conception Bay reed casts (C-650)

Near Conception Bay (24°01'S, 14°34'E) and Meob Bay (24°31'S, 14°37'E) south of the Kuiseb River the groundwater percolating towards the

sea comes close to the surface so that vegetation can survive here. Following the Last Interglacial a 3 m sand cover was deposited over the beaches in both areas. On top of this surface phragmites reeds grew. At a later stage a drop in groundwater level caused the vegetation to die and an extensive calcium carbonate crust to form on the surface. Subsequent wind erosion has deflated the surface so that only remnants survive. The calcified reed beds have consistently produced ^{14}C dates of about 12 000 years, both at Conception Bay and at Meob Bay (Vogel 1982, 1989) so that this date for the extinction of the reed beds and the calcification is reasonably well established.

The sample selected from Conception Bay consists of calcified reed stalks which must correspond to a relatively short time span of formation.

$^{230}\text{Th}/^{234}\text{U}$ analyses:

One subsample of 40.0 g was analysed in three successive fractions. Fraction 1 (analysis U-454T) - 24.1 g of carbonate was dissolved in weak acid.

Fraction 2 (analysis U-455) - the remaining 13.8 g of carbonate was dissolved in weak acid.

Boiled fraction (analysis U-461) - the remaining sand was boiled in concentrated acid.

Meob Bay calcified crust (C-3359b)

The sample from Meob, 22 km SE of Conception Bay, represents the calcium carbonate crust on the surface of the vegetated flats which were calcified about 12 000 years ago according to the ^{14}C dating (Vogel 1982, 1989).

$^{230}\text{Th}/^{234}\text{U}$ analyses:

One subsample of 30.6 g was analysed in two successive fractions.

Fraction 1 (analysis U-463) - 24.0 g was dissolved in weak acid.

Boiled fraction (analysis U-464) - the remaining sand was boiled in concentrated HCl.

Ngedla stream septarian nodule (C-4640)

Two samples from Natal with ^{14}C dates which were thought to be reliable were also analysed, viz. samples from Ngedla and Hazeldene.

In the banks of a donga on the lower slopes of Ngedla Mountain ($28^{\circ}19'S$, $30^{\circ}37'E$), about 13 km NW of Nqutu, Zululand, large septarian nodules occur. They consist of an inner nodule or nodules enclosed by a calcium carbonate crust. One such nodule with a diameter of 10 cm was ^{14}C dated with the following unpublished results:

Pta-5754	Inner nodule	$27\ 200 \pm 300$ years
Pta-5755	Outer crust	$11\ 250 \pm 70$ years

A portion of the inner nodule was used for $^{230}\text{Th}/^{234}\text{U}$ dating. The formation period of the inner nodule is considered to be relatively short and the outer crust should have isolated it from recent contamination.

$^{230}\text{Th}/^{234}\text{U}$ analyses:

One subsample of 23.7 g of the inner nodule was analysed in two successive fractions.

Fraction 1 (analysis U-444) - 10.1 g of carbonate was dissolved in weak acid.

Boiled fraction (analysis U-445) - the remaining sand was boiled in concentrated HCl.

Hazeldene donga nodule (C-3813c)

This is the second sample dated from Natal. Hazeldene donga is situated on Hazeldene farm about 20 km east of Dundee ($28^{\circ}10'S$, $30^{\circ}14'E$), Natal. On the west side of the donga there is a colluvium remnant with

exposed stratified layers. The sample consists of calcrete nodules from the vertic palaeosol which is 3.6 to 3.8 m below the surface.

The organics in the palaeosol were ^{14}C dated to $14\,070 \pm 290$ years (Pta-4883). Carbonate nodules from below the vertic soil gave ^{14}C dates of $10\,980 \pm 80$ (fr1, Pta-4818) and $11\,930 \pm 110$ years (fr2, Pta-4819).

The ^{14}C dates suggest that the soil that developed during the End-Glacial period (16 000 to 10 000 years), became dry at about 11 000 years ago and was buried by colluvium shortly thereafter. The formation period of the nodules should thus have been reasonably short and well defined.

$^{230}\text{Th}/^{234}\text{U}$ analyses:

Two subsamples of a piece of this nodule were analysed.

Subsample 1 - (18.4 g)

Two small nodules were boiled in concentrated acid, thus dissolving the carbonate and the iron oxide coating in one analysis (U-431).

Subsample 2 - (15.2 g)

This subsample again consisted of two small nodules, analysed by a weak and a boiled fraction. Thus the sum of the activities should be equivalent to the activity of analysis U-431.

Fraction 1 (analysis U-473) - 10.3 g of carbonate was dissolved in weak acid.

Boiled fraction (analysis U-474) - the remaining sand was boiled in concentrated HCl.

4.2.2 Discussion of the results of the $^{230}\text{Th}/^{234}\text{U}$ analyses

The activities and the activity ratios obtained in the $^{230}\text{Th}/^{234}\text{U}$ analyses are given in Tables 4.2 and 4.3. Before discussing the ages calculated by the different methods of analysis (Table 4.4), a comment on

the low yields obtained for the Conception Bay sample is appropriate. This sample contained some organic matter which is known to absorb uranium (Section 2.3), and the two weak acid leachates had uranium yields of only 4% and 1% respectively. The consistency in the activities of these two leachates, however, show that the isotope ratios were not seriously affected (Table 4.2) - compare the consistency in the activities of the two leachates of Homeb. The boiled fraction of Ngedla also had a low uranium yield of 4% but since this sample produced anomalous thorium results (see below), it is difficult to assess the reliability of the uranium measurement.

The Homeb and Hazeldene samples had high yields for all fractions measured. In the other case where very low yields were obtained (Kuisseb Kl), a repeat sample gave completely compatible results. These are discussed in Section 5.4.2.

Thus the $^{230}\text{Th}/^{234}\text{U}$ ages in Table 4.4 are not considered to be affected by the chemical yields. Also the ^{14}C ages are considered to be reliable as the samples used are all less than 30 000 years old. Three of the corrected $^{230}\text{Th}/^{234}\text{U}$ dates are very similar to the ^{14}C ages, viz. in samples Homeb, Conception and Hazeldene. In the other two cases, however, there are distinct differences. The corrected $^{230}\text{Th}/^{234}\text{U}$ ages for Ngedla are much lower, at up to 11 000 years, than the ^{14}C age of 27 200 years. Meob, on the other hand, has corrected $^{230}\text{Th}/^{234}\text{U}$ ages of over 45 000 years while the ^{14}C age is only 12 000 years. The probable reasons for these differences in Meob and Ngedla will be discussed below, and then the different correction methods for the $^{230}\text{Th}/^{234}\text{U}$ ages will be compared in the other three samples.

Special case of Meob and Ngedla

The corrected $^{230}\text{Th}/^{234}\text{U}$ dates obtained from Meob are drastically different from the ^{14}C ages of the same carbonate. The only explanation

TABLE 4.2: ACTIVITIES FOR THE KNOWN-AGE SAMPLES

Sample	U-no	Fr.	Dpm/kg			
			²³⁸ U	²³⁴ U	²³² Th	²³⁰ Th
Homeb silt G-1117	U-391	1	857 ± 22	2057 ± 48	137 ± 3	340 ± 5
	U-451	T	634 ± 11	906 ± 15	1022 ± 42	564 ± 25
	U-446	1	765 ± 28	1675 ± 56	65 ± 4	261 ± 9
	U-447	2	700 ± 25	1481 ± 48	113 ± 3	315 ± 6
	U-449	B	227 ± 6	218 ± 6	499 ± 13	300 ± 8
	SUM	S	1692 ± 38	3374 ± 74	677 ± 14	876 ± 13
Conception C-650	U-454T	1	372 ± 15	385 ± 15	5 ± 0	43 ± 1
	U-455	2	483 ± 35	540 ± 39	7 ± 1	46 ± 2
	U-461	B	22 ± 1	30 ± 1	37 ± 1	33 ± 1
	SUM	S	877 ± 38	955 ± 42	49 ± 1	122 ± 2
Meob Bay C-3359b	U-463	1	2061 ± 56	2326 ± 63	69 ± 8	899 ± 61
	U-464	B	86 ± 3	100 ± 4	103 ± 3	94 ± 3
	SUM	S	2147 ± 56	2426 ± 63	172 ± 9	993 ± 61
Ngedla C-4640	U-444	1	1345 ± 23	1612 ± 27	241 ± 5	482 ± 8
	U-445	B	494 ± 18	655 ± 23	708 ± 24	1022 ± 34
	SUM	S	1839 ± 29	2267 ± 35	949 ± 25	1504 ± 35
Hazeldene C-3813c	U-431	T	1028 ± 25	1374 ± 32	686 ± 12	455 ± 8
	U-473	1	870 ± 26	1228 ± 35	332 ± 15	288 ± 13
	U-474	B	83 ± 3	109 ± 4	379 ± 8	205 ± 5
	SUM	S	953 ± 26	1337 ± 35	711 ± 17	493 ± 14

Note:

The fractions are referred to as follows: weak leaches 1 and 2, boiled fraction B, total leach T (boiling a sample without a weak leach first), sum S of the weak and boiled fractions of a single subsample. See text for specific details on the different fractions.

TABLE 4.3: ACTIVITY RATIOS FOR THE KNOWN-AGE SAMPLES

Sample	U-no	Fr.	$^{230}\text{Th}/^{234}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	% CO_3
Homeb silt C-1117	U-391	1	0.165±0.005	2.399±0.036	2.479±0.041	42
	U-451	T	0.623±0.029	1.429±0.024	0.552±0.016	17
	U-446	1	0.156±0.008	2.188±0.052	3.989±0.214	5
	U-447	2	0.213±0.008	2.115±0.051	2.793±0.060	
	U-449	B	1.373±0.052	0.962±0.029	0.601±0.009	
SUM	S	0.259±0.007	1.994±0.063	1.293±0.032		
Conception C-650	U-454T	1	0.111±0.006	1.035±0.034	8.113±0.772	98
	U-455	2	0.084±0.007	1.117±0.060	6.208±0.516	
	U-461	B	1.112±0.059	1.343±0.085	0.887±0.032	
	SUM	S	0.127±0.006	1.088±0.067	2.439±0.079	
Meob Bay C-3359b	U-463	1	0.386±0.028	1.129±0.014	12.96±1.319	88
	U-464	B	0.938±0.045	1.167±0.054	0.912±0.030	
	SUM	S	0.409±0.027	1.130±0.042	5.755±0.455	
Ngedla C-4640	U-444	1	0.299±0.007	1.199±0.012	2.001±0.028	63
	U-445	B	1.560±0.076	1.325±0.042	1.443±0.019	
	SUM	S	0.663±0.019	1.233±0.027	1.585±0.056	
Hazeldene C-3813c	U-431	T	0.331±0.010	1.336±0.023	0.664±0.007	70
	U-473	1	0.235±0.013	1.411±0.034	0.867±0.036	70
	U-474	B	1.878±0.079	1.319±0.062	0.541±0.012	
	SUM	S	0.369±0.014	1.403±0.054	0.694±0.026	

Note:

The fractions 1, 2, B, T, S are referred to as in Table 4.2.

% CO_3 is the amount of material (mainly carbonate) that was dissolved, as a percentage of the initial sample mass.

TABLE 4.4: ^{14}C AND $^{230}\text{Th}/^{234}\text{U}$ AGES FOR KNOWN-AGE SAMPLES

Sample	Homeb C-1117	Conception C-650	Meob C-3359b	Ngedla C-4640	Hazeldene C-3813c
^{14}C age (years)	19 000 - 23 000	12 000	12 000	27 200 \pm 300	10 980 - 11 930
U-no's	U-446,447, 449,(391, 451)	U-454T, 455,461	U-463, 464	U-444, 445	U-473, 474, (431)
% mass loss	12%	3%	9%	20%	2%
U ppm	2.293 \pm 0.052	1.189 \pm 0.052	2.910 \pm 0.076	2.491 \pm 0.040	1.291 \pm 0.036
Uncorrected age	31 800 \pm 1 000	14 700 \pm 800	56 500 \pm 4 900	112 500 \pm 5 600	48 700 \pm 2 400
Intercept age	17 700 \pm 800	9 900 \pm 700	49 400 \pm 5 000	11 000 \pm 2 400	10 900 \pm 2 200
Slope age	18 000 \pm 900	9 100 \pm 1 200	46 400 \pm 10 700	10 400 \pm 700	10 300 \pm 1 400
$f_i =$ 0.466	21 500 \pm 800	12 000 \pm 700	52 900 \pm 4 900	-	-
f_t	0.524	0.820	0.552	1.353	0.514
Age with f_t	17 900 \pm 700	9 500 \pm 500	49 600 \pm 4 600	11 000 \pm 2 600	10 800 \pm 1 500
Silt f_i	0.552				
Age with f correc.	19 500 \pm 800				

Note:

f ages: f_i is the initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, and f_t the current $^{230}\text{Th}/^{232}\text{Th}$ ratio.

% mass loss: the percentage mass lost only in the boiled fraction, thus indicating how much carbonate was still in the boiled fraction.

The silt f_i value is similar to the sand value (see text).

for this discrepancy is that the uranium had accumulated over a long period of time while the vegetated surface existed, as supported by the relatively high uranium concentration (Table 4.2). Organic matter is known to absorb and bind uranium and if this surface supported vegetation since, say, the beginning of the Last Glacial period, the $^{230}\text{Th}/^{234}\text{U}$ age would be an average age over the whole period of time until the soil ceased to support plants and became calcified. The ^{14}C age of the carbonate crust then is the date of final desiccation while the $^{230}\text{Th}/^{234}\text{U}$ age is the average age of the soil.

In the case of Ngedla there was about 20% mass loss in the boiled fraction (Table 4.3); most of this would be carbonate since the iron oxide coating only accounts for a few percent of the mass. The ^{230}Th activity of the boiled fraction is double that of the first fraction, suggesting thorium reabsorption. This could explain why the f values are too high, giving ages too young compared to the ^{14}C age. Also the age is very sensitive to the actual f value used - a small change in f results in a large change in the age, viz. $f_r = 1.353$ gives an age of 11 000 years (Table 4.4) while $f_r = 1.050$ gives $27\,300 \pm 2\,700$ years which is similar to its ^{14}C age. Ngedla and Meob will not be considered further in comparing the different correction methods.

Slope and intercept method ages

The slope and intercept results are given in Table 4.4. The graphs of a representative sample, viz. Hazeldene, are shown in Figure 4.5. The graphs for the other samples are similar. Note that the error ellipses shown for the points are 95% confidence limits (2σ), while the age calculations are based on 1σ limits.

In the case of Homeb all the subsamples are used for the slope and intercept graphs. They are all valid points, coming from the same

sample. Including subsamples 1 and 3 in this way gives the same age as when using only the fractions of subsample 2.

The slope and intercept ages are equivalent when compared to each other, as is to be expected since these two methods may be considered mathematically the same. In the three samples, Homeb, Conception and Hazeldene, these ages are younger than the ^{14}C ages by some 10 to 20%. These figures are larger than the estimate of less than 10% derived from analysis of the pure sand samples given in Section 4.1.6.

Bearing in mind that the conditions under which the various samples were leached in these initial experiments, it is perhaps not surprising that considerable variations occurred in the degree of separation between the carbonate and detrital fractions and in the amounts of isotopic fractionation.

The results show, however, that useful information may be obtained with this method. In many instances where the age of a deposit is completely unknown, a date that may be up to 20% too young is well worth the effort. In the specific case of the Namib calcretes where the isotopic composition of the detrital contamination can be estimated with some confidence, the use of the f index is, however, probably more appropriate.

f index ages

Here again the results will be discussed chiefly for Homeb, Conception and Hazeldene. The uncorrected $^{230}\text{Th}/^{234}\text{U}$ ages are all greater than the ^{14}C ages due to detrital contamination. Applying current or initial f values (Section 3.2.3) decreases the age by correcting for the non-authigenic detrital ^{230}Th .

Using an initial $f_1 = 0.466$ obtained from pure desert sands (Section 4.1.4) gives excellent results for two of the Namib samples,

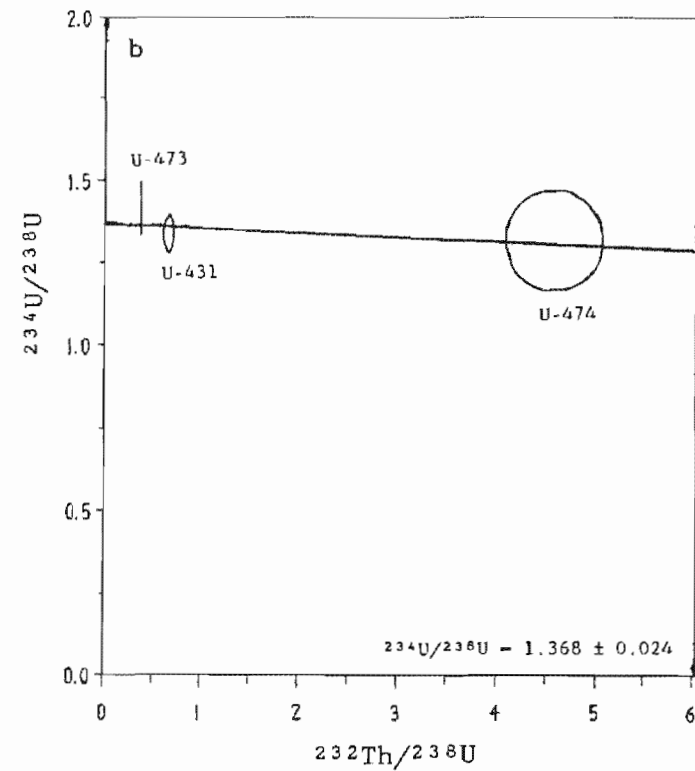
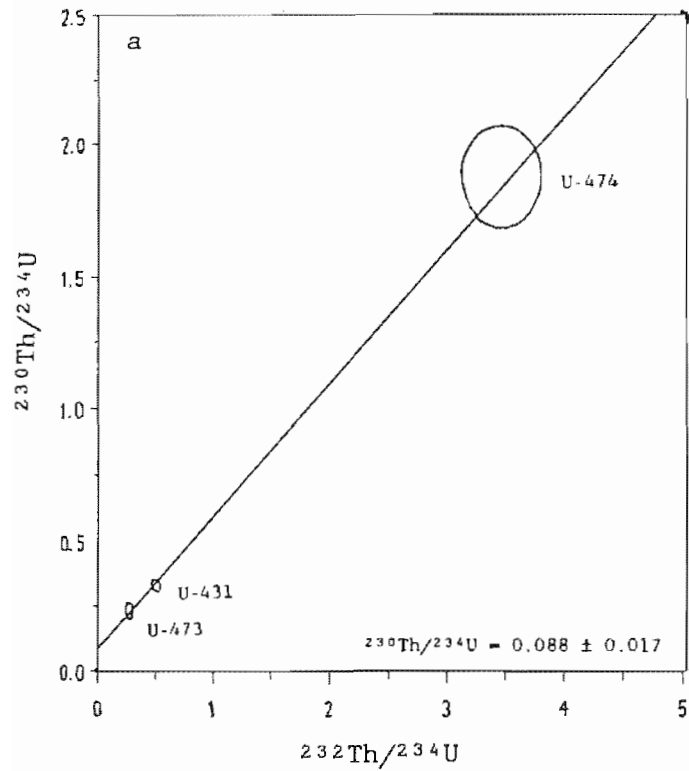


Figure 4.1: Intercept graphs for the Hazeldene nodules, with a leachate fraction (U-473), a boiled fraction (U-474), and a total boiled sample (U-431). The intercept of graph (a) gives the $^{230}\text{Th}/^{234}\text{U}$ ratio, and that of graph (b) gives the $^{234}\text{U}/^{238}\text{U}$ ratio, of the pure carbonate. The error ellipses are shown at 2σ .

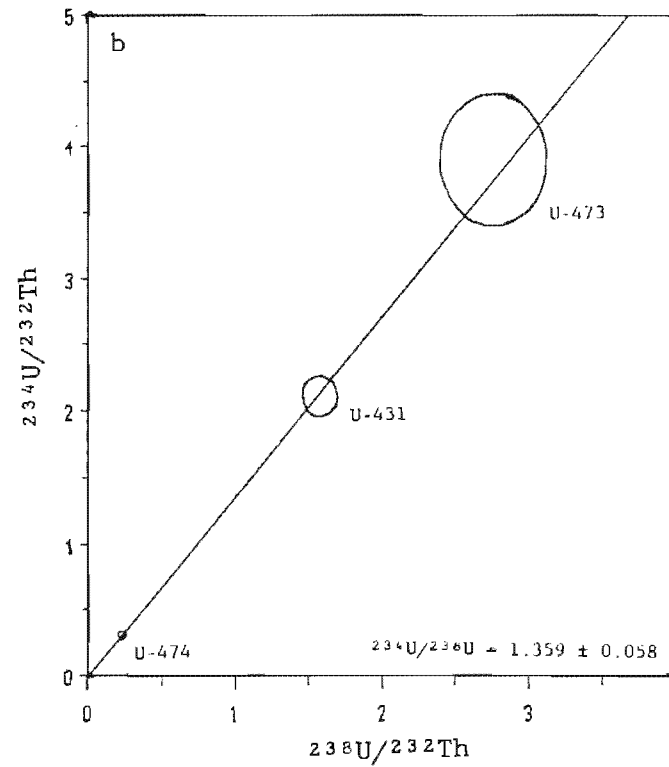
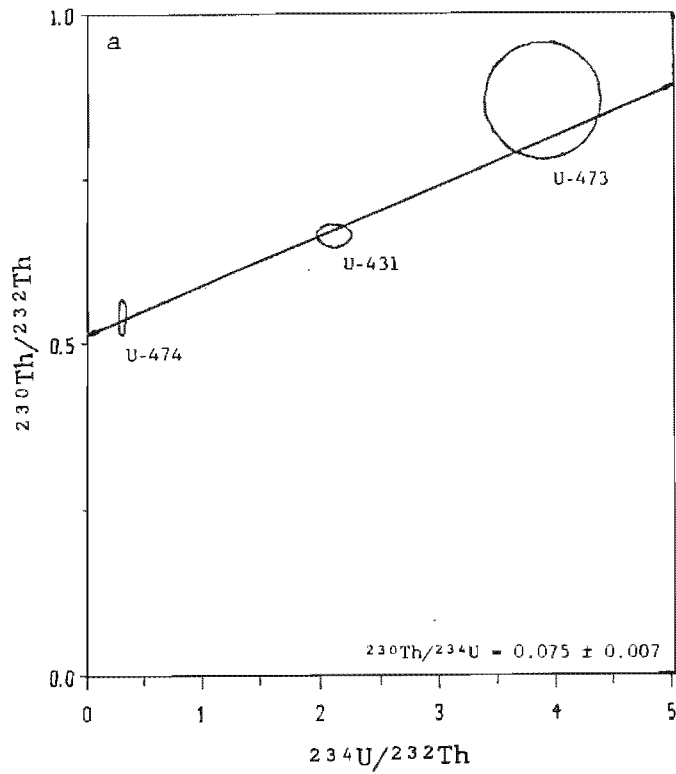


Figure 4.2: Slope graphs for the Hazeldene nodules, with a leachate fraction (U-473), a boiled fraction (U-474), and a total boiled sample (U-431). The slope of graph (a) gives the $^{230}\text{Th}/^{234}\text{U}$ ratio, and that of graph (b) gives the $^{234}\text{U}/^{238}\text{U}$ ratio, of the pure carbonate. The error ellipses are shown at 2σ .

viz. Homeb and Conception. This value cannot be used for the Natal sample, Hazeldene, since the detrital sand matrix is not necessarily the same as the desert sand.

The $^{230}\text{Th}/^{232}\text{Th}$ ratio of the total boiled Homeb silt (analysis U-451) is 0.552 and represents the f_1 of silt, except that this sample did contain some carbonate and thus this f will be slightly too high. This latter fact taken into consideration, it seems that it is very similar to the f_1 of actual desert sands.

The f_e values obtained from the slope of the intercept graphs give ages slightly younger than those obtained from the f_1 values and than the ^{14}C ages. This must, again, be due to the differential fractionation influencing the graphical plots.

4.3 CONCLUSION

The ages obtained by the slope and intercept graphs are generally too young by up to 20% due to the effect of differential fractionation from the detritus to the leachates. This then also results in errors when using the f_e values from the intercept graphs. The initial f_1 values obtained from the desert sands provides the best results, and may be used in correcting the other samples collected in the Kuiseb River valley (Chapter 5). The ages obtained from the graphical procedures may still be useful as lower limits and thus these methods are included in the next chapter for comparison with the ages obtained from the f_1 values.

CHAPTER 5

APPLICATION TO THE KUISEB RIVER

In this chapter several calcretes and conglomerates of the Kuiseb River canyon are analysed, correcting the $^{230}\text{Th}/^{234}\text{U}$ ages by the f_1 index, as discussed in Chapter 4. The other methods of correction are also applied for comparative purposes. In order to interpret the data it is first necessary to briefly discuss the general climate and situation of the Kuiseb River. The samples included in this chapter differ from those in the previous chapter in not having "single ages", but having formed over long periods of time. The implications of this fact are discussed, whereafter the specific samples are described and the results discussed.

5.1 THE KUISEB RIVER SYSTEM

The Kuiseb River in Namibia (Figure 5.1) is an ephemeral watercourse that arises above the Great Escarpment about 20 km south-west of Windhoek and crosses the central Namib Desert to drain into the Atlantic Ocean after some 300 km (Ward 1984). The river forms the northern boundary of the Namib Sand Sea, while gravel plains overlie the shist bedrock north of the river.

The present day climate of the central Namib Desert is hyperarid to arid. The mean annual rainfall increases from about 12 mm at Walvis Bay to about 23 mm at Gobabeb, 57 km from the coast, to about 100 mm below the escarpment. Fog from the coast provides some additional precipitation - about 31 mm annually at Gobabeb (Vogel 1989). The potential annual evaporation rate is as high as 3000 mm (Teller et al. 1990).

Rainfall occurs mainly in light to moderate showers during late summer, resulting in annual river flow in the upper reaches of the Kuiseb. The water carried by the river decreases as the flood moves downstream and

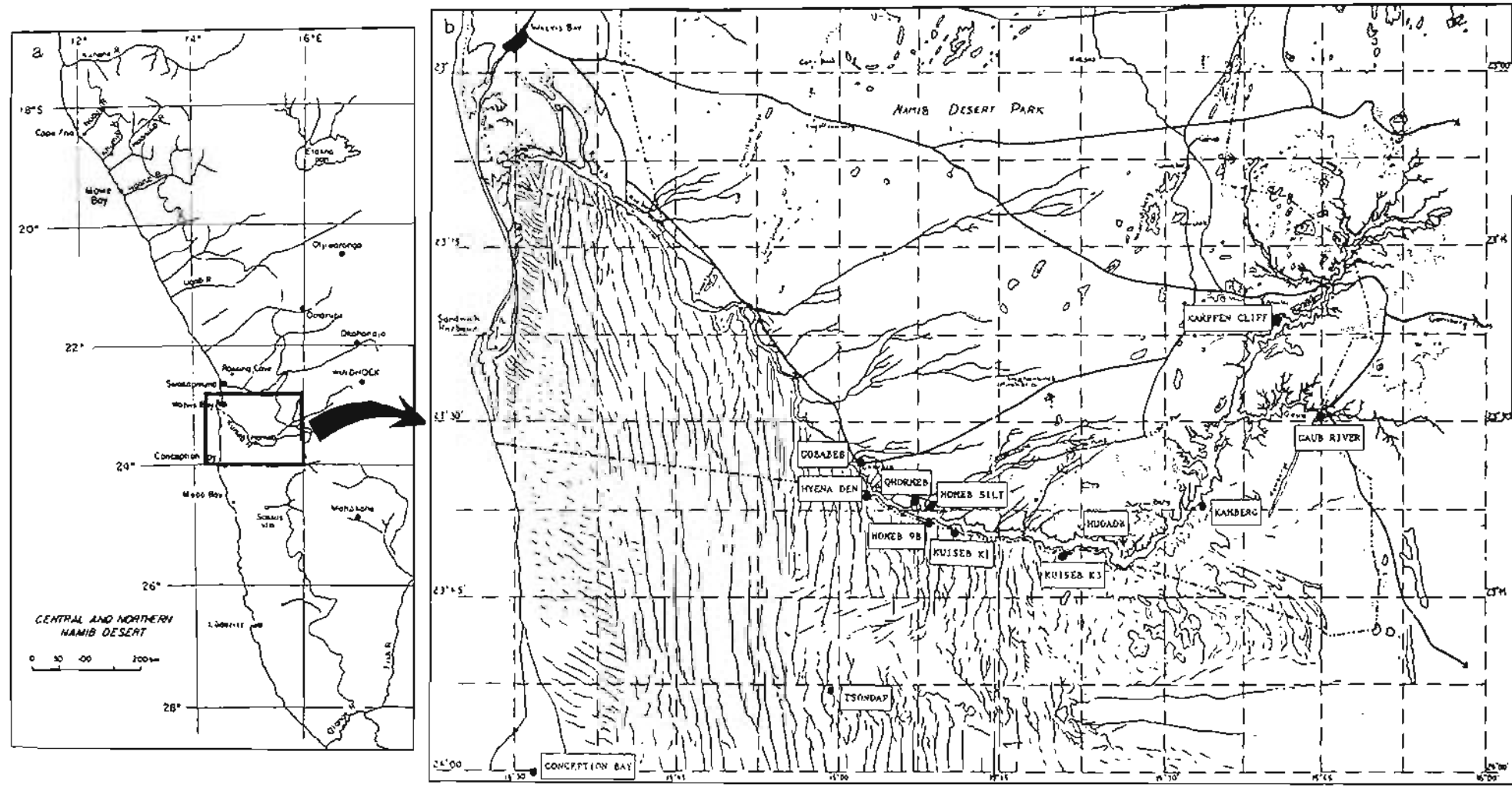


Figure 5.1: Location of the Namibian sample sites. Figure (a) shows the location of the Kuisieb River and also indicates the position of Meob Bay which lies outside the area shown in figure (b). The black dots in figure (b) show the site positions where the Kuisieb River samples were collected.

sinks into the sandy riverbed so that it only occasionally reaches the flats behind the coastal dune barrier. The result of this flow pattern is that the Kuiseb River tends to drop its sediment load in specific regions along its course, corresponding to the average reach of the floods (Vogel 1989).

In the mid-reaches of the Kuiseb, west of the escarpment, the river valley is deeply incised, up to 200 m depth, but becomes much less so between Gobabeb and the coast.

The canyon deposits

Above the south bank of the canyon between Oswater and Hudaob (Figure 5.1) a 1-2 m thick layer of calcrete, the Homeb calcrete, extends for some distance away from the river bank (Figure 5.2). More massive calcrete, up to 8 m thick, occurs further upstream on top of the Karpfen Cliff conglomerate which was deposited in large alluvial fans below the escarpment. Exposures of this calcified conglomerate are accessible at, for instance, Karpfen Cliff, Kamberg Cliffs and above the roadbridge over the Gaub River (Figure 5.1).

At many places within the canyon, upstream of Gobabeb, remnants of a younger conglomerate, the Oswater conglomerate, are exposed to a height of about 40 m. The river cobbles are highly cemented with calcium carbonate. This cementing may or may not have taken place during the original fluvial stage of deposition.

Finally, the Homeb silts (Figure 5.2) were deposited in the mid-reaches of the canyon during a low-energy phase of the river after most of the Oswater conglomerate had been removed by down-cutting.

5.2 DATING CALCRETES AND INTERPRETING DATES

The materials analysed in Chapter 4 were silt deposits, reedcasts

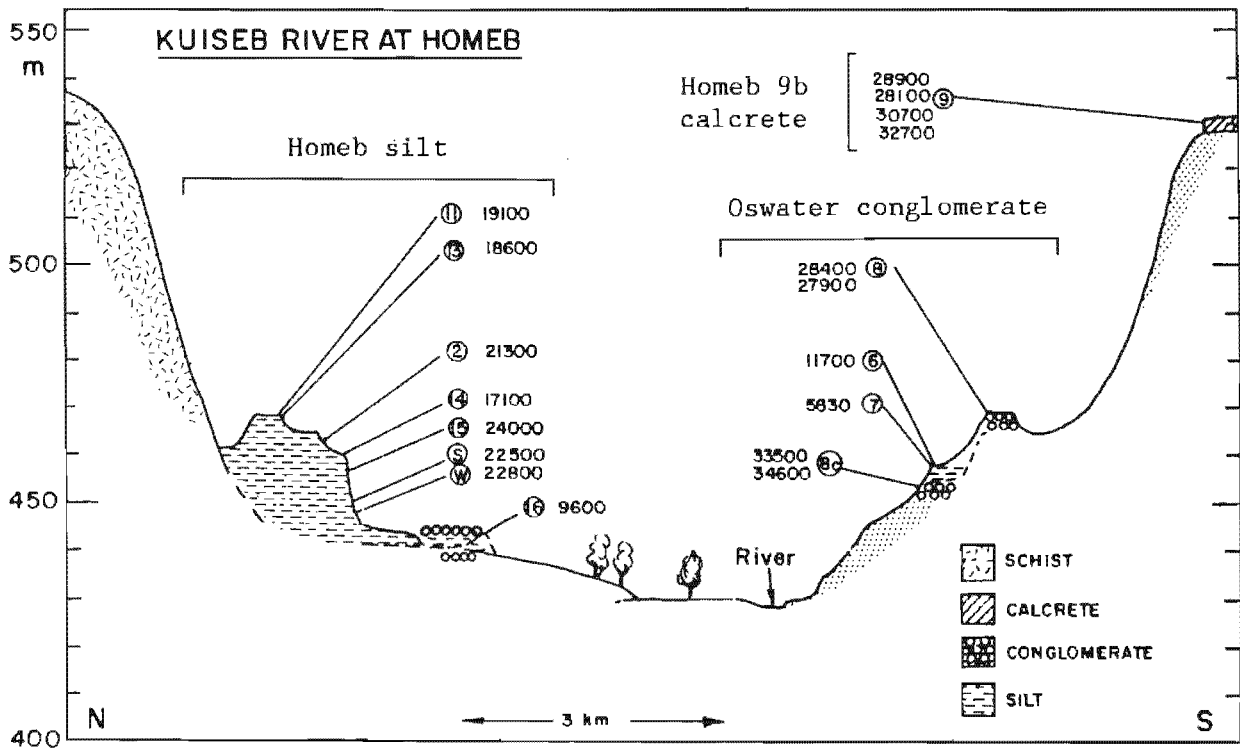


Figure 5.2: Schematic cross-section through the Kuiseb River valley at Homeb. The circled sample numbers and ^{14}C ages are those of Vogel (1982). The relative positions of three chief deposits found in the Kuiseb valley, the Oswater conglomerate, the Homeb 9b calcrete and the Homeb silts, are indicated in the figure.

and carbonate nodules. The sample materials included in this chapter may be defined as follows. A calcrete is a subsurface deposit of calcium carbonate which is precipitated from groundwater, replacing the soil in which it forms. Calcretes may be found in various stages of development, from slight calcification of soil layers to nodules forming in the soil, to hardpans. The other type of terrestrial carbonate that was investigated is conglomerate which is an accumulation of fragments. In the case of the Kuiseb River, the conglomerates consist of river pebbles and cobbles which have become cemented by carbonate. The precipitation of carbonate in a fluvial cobble accumulation must be expected to occur only gradually, either during accumulation or even during later degradation. The different types of calcrete found in southern Africa have been described and classified in an extensive review by Netterberg (1980).

In Chapter 4 the samples of known-age represented "single" ages, i.e. short growth periods due to the material type being analysed. Calcretes and conglomerates cannot be represented by a single age because the calcification may have taken place over a long period of time. The age obtained by measuring the uranium and thorium in such carbonate will be some average time of the total period of formation. There are several factors that determine the "average" age obtained. Firstly, for samples of ages of up to about 75 000 years, the change in the $^{230}\text{Th}/^{234}\text{U}$ ratio with time is fairly linear (Figures 1.3 and 1.4) and the measured age will lie more or less in the middle of the period of formation, without indicating the length of the growth period. Beyond 75 000 years, the measured age will be closer to the end stage of formation. ^{14}C has a much shorter half-life and thus the measured ^{14}C age will lie even closer to the end of the formation period than the $^{230}\text{Th}/^{234}\text{U}$ age. Thus, for carbonates that are datable by the ^{14}C method, viz. with ages up to 40 000 years, the measured ^{14}C age will be younger than the measured $^{230}\text{Th}/^{234}\text{U}$ age, without implying any contradiction.

Secondly, there may be more than one period of calcrete formation in the history of a calcrete layer. If there are alternate periods of active and inactive calcrete formation, due to changes in climatic conditions, then the measured $^{230}\text{Th}/^{234}\text{U}$ and ^{14}C ages will depend on the length of time of these periods, with the ^{14}C age again being younger than the $^{230}\text{Th}/^{234}\text{U}$ age. Similarly, if a period of active calcrete formation is followed by recrystallization of the carbonate, the measured $^{230}\text{Th}/^{234}\text{U}$ age will be older if uranium is leached out and ^{14}C ages will be younger if additional ^{14}C is incorporated, than the age of the initial formation.

Both calcrete and cemented conglomerate by their nature contain a considerable amount of detritus, viz. desert sand, which adds substantial amounts of leachable uranium and thorium to the sample. It is therefore to be expected that significant corrections for detrital ^{230}Th will be required.

Dating the formation periods of alluvial deposits and calcretes in desert areas may provide a time-scale for climatic reconstruction of wet-dry cycles. This has been done in the Kuiseb area by ^{14}C dating for the last 40 000 years (Vogel 1989) but the time-scale may possibly be extended to about 300 000 years by $^{230}\text{Th}/^{234}\text{U}$ dating.

Calcretes are found mostly in warm areas with limited precipitation, more specifically in areas where the annual rainfall is 400 to 600 mm (Goudie and Pye 1983). Since it is much drier in the Namib Desert at present (Section 5.1), the climate must have been wetter at some past stages for the Kuiseb calcretes to have formed. Flood activity itself, causing river incision and carrying river pebbles and sediment, is related to rainfall in the catchment area, ie. above the escarpment, rather than rainfall in the desert (Ward et al. 1983). Thus care needs to be taken in correlating geomorphic features with local climatic events.

5.3 DESCRIPTION OF THE SAMPLE SITES

The samples covered in this section are from either the top surface deposit (the Homeb calcrete and Karpfen Cliff conglomerate) or from the Oswater conglomerate terrace along the Kuiseb River. The ^{14}C ages are given where available. The $^{230}\text{Th}/^{234}\text{U}$ results are given in Tables 5.1 and 5.2.

5.3.1 Homeb 9b calcrete C-1413 (Figures 5.1, 5.2)

This is a hardpan calcrete from about 110 m above the riverbed above the south bank at Homeb ($23^{\circ}38'S$, $15^{\circ}09'E$). It consists of two phases which are visibly distinct - the older white nodules, cemented together by younger pinkish cement. The ^{14}C ages are:

Pta-1494	Pink		$28\ 900 \pm 490$ years
Pta-2419	Pink	repeat	$28\ 100 \pm 480$ years
Pta-2426	White	fr1	$30\ 700 \pm 510$ years
Pta-2427	White	fr2	$32\ 700 \pm 600$ years

$^{230}\text{Th}/^{234}\text{U}$ analyses:

Two subsamples were taken.

Subsample 1 (84.5 g) consisted of the older white nodule and was divided into two fractions - a weak acid leach (U-393) and a boiled fraction (U-396).

Subsample 2 (82.5 g) consisted of two fractions of the pink cement - a weak acid leach (U-394) and a boiled fraction (U-395).

5.3.2 Kuiseb K1 calcrete C-1424 (Figure 5.1)

This is calcrete from the surface layer on the south bank, about 5 km upstream from Homeb. No phases can be distinguished visibly. The ^{14}C ages are as follows:

Pta-3656	total	32 300 ± 810 years
Pta-5373	fr1	37 000 ± 1100 years
Pta-5376	fr2	43 300 ± 2000 years

$^{230}\text{Th}/^{234}\text{U}$ analyses:

Two subsamples were measured.

K1: Subsample 1 (72.2 g) consisted of two weak acid leaches (U-384B and U-385), and of a boiled fraction (U-386).

K1R: Subsample 2 (23.3 g) was a repeat measurement but with only one weak acid leach (U-438) and a boiled fraction (U-439).

5.3.3 Kuiseb K3 calcrete C-1426 (Figure 5.1)

This sample is similar to K1, being pink calcrete from the surface layer on the south bank, about 20 km upstream from Homeb. The ^{14}C ages are:

Pta-5912	fr1	40 700	+ 2500 - 1900	years
Pta-5913	fr2	39 600	+ 2600 - 1900	years

$^{230}\text{Th}/^{234}\text{U}$ analyses:

One $^{230}\text{Th}/^{234}\text{U}$ sample of 66.2 g was measured, consisting of two weak acid leaches (U-408 and U-409), and a boiled fraction (U-425)

5.3.4 Kamberg Cliff conglomerate C-2602/3 (Figure 5.1)

This sample consists of carbonate from the surface pebble conglomerate on top of Kamberg Cluff. It is an 8 metres thick layer, lying on top of fluvial Tsondap sandstone. Samples were taken from the top and just below the bottom of the conglomerate layer at -8 m. The ^{14}C ages are:

Pta-5952	Top (C-2602)	37 800 ± 1400 years
Pta-6011	-8 m (C-2603)	>44 000 years

$^{230}\text{Th}/^{234}\text{U}$ analyses:

Two $^{230}\text{Th}/^{234}\text{U}$ samples were measured, taken from different depths.

Sample 1 (C-2602, 20.0 g) from the top of the calcrete layer, consisted of a weak acid leach (U-465), and a boiled fraction (U-466).

Sample 2 (C-2603, 22.2) from the top of the fluvial sandstone just below the 8 m thick conglomerate, consisted of a weak acid leach (U-452), and a boiled fraction (U-453).

5.3.5 Karpfen Cliff conglomerate C-2599/C-2601 (Figure 5.1)

This 8 m thick calcified conglomerate is on top of the fluvial Tsondap sandstone and is exposed on the north bank, about 75 km upstream of Homeb. Samples from different depths of the layer have been analysed. The unpublished ^{14}C ages are:

Pta-5953	Top (C-2599)	total	23 100 ± 290 years
Pta-6055	"	fr1	27 300 ± 350 years
Pta-6056	"	fr2	30 900 ± 630 years
Pta-6009	-8 m (C-2601)	fr1	29 000 ± 550 years
Pta-6010	"	fr2	28 800 ± 780 years

 $^{230}\text{Th}/^{234}\text{U}$ analyses:

One $^{230}\text{Th}/^{234}\text{U}$ sample of 23.0 g from the top (C-2599) was measured, consisting of a weak acid leach (U-456), and of a boiled fraction (U-458). The -8 m sample (C-2601) was not measured.

5.3.6 Gaub River calcrete C-4803 (Figure 5.1)

The Gaub River is a tributary of the Kuiseb and the surface calcrete layer in the top of the Karpfen Cliff conglomerate along the Kuiseb extends along the Gaub for some distance. The sample chosen was a large white piece of calcrete. No ^{14}C analysis has been done on this site.

 $^{230}\text{Th}/^{234}\text{U}$ analysis:

One $^{230}\text{Th}/^{234}\text{U}$ sample of 19.6 g was measured, consisting of a weak acid leach (U-457), and a boiled fraction (U-459).

5.3.7 Qhormeb 10 conglomerate C-1678 (Figure 5.1)

This is part of the Oswater conglomerate. The cemented river gravel forms a compact layer at Qhormeb, 11.5 km east of Gobabeb, just downstream from Homeb, on the north bank. It forms part of the Oswater conglomerate (Ward 1984). Seven ^{14}C ages for this deposit range from 28 900 to 47 800 years (Vogel 1989), with the ages decreasing from the bottom upwards. Where two fractions were measured, the second was generally older, indicating a long period of calcification.

$^{230}\text{Th}/^{234}\text{U}$ analysis:

One $^{230}\text{Th}/^{234}\text{U}$ sample of 20.0 g was measured, consisting of a weak acid leach (U-448), and a boiled fraction (U-450).

5.3.8 Hyena Den conglomerate C-2595 (Figure 5.1)

This sample also belongs to the Oswater conglomerate, but is located on the south bank, a few kilometres downstream from Qhormeb. No ^{14}C analysis has been done on this material. The sample was collected from cemented dune sand, underlying the conglomerate at about 8 m from the top.

$^{230}\text{Th}/^{234}\text{U}$ analysis:

One $^{230}\text{Th}/^{234}\text{U}$ sample of 20.2 g of basal dune sand was measured, consisting of a weak acid leach (U-467), and a boiled fraction (U-468).

5.4 RESULTS AND DISCUSSION

Table 5.1 shows the activities and ratios of the individual fractions of the samples that were measured. Also shown is the percentage of carbonate in the samples which ranged from 41% to 86% of the initial

TABLE 5.1: ACTIVITIES FOR THE KUISEB RIVER SAMPLES

Sample	U-no	Fr.	Dpm/kg			
			^{238}U	^{234}U	^{232}Th	^{230}Th
Homeb 9b C-1413 (white)	U-393	1	647 ± 12	807 ± 15	116 ± 2	522 ± 7
	U-396	B	105 ± 2	156 ± 3	148 ± 3	264 ± 5
	SUM	S	752 ± 12	963 ± 15	264 ± 4	786 ± 9
Homeb 9b C-1413 (pink)	U-394	1	175 ± 2	224 ± 2	33 ± 2	90 ± 5
	U-395	B	119 ± 2	171 ± 2	169 ± 3	200 ± 3
	SUM	S	294 ± 3	395 ± 3	202 ± 4	290 ± 6
Kuisseb K1 C-1424	U-384T	1	275 ± 11	459 ± 18	27 ± 1	141 ± 2
	U-385	2	270 ± 12	468 ± 19	87 ± 1	269 ± 4
	U-386	B	241 ± 11	281 ± 13	567 ± 13	376 ± 9
	SUM	S	786 ± 20	1208 ± 29	681 ± 13	786 ± 10
Kuisseb K1R C-1424 (repeat)	U-438	1	687 ± 24	868 ± 29	106 ± 3	377 ± 6
	U-439	B	240 ± 7	246 ± 7	560 ± 11	344 ± 8
	SUM	S	2147 ± 25	1114 ± 30	666 ± 11	721 ± 10
Kuisseb K3 C-1426	U-408	1	210 ± 5	273 ± 7	10 ± 1	91 ± 3
	U-409	2	678 ± 19	853 ± 24	211 ± 6	484 ± 12
	U-425	B	130 ± 3	155 ± 3	400 ± 5	384 ± 5
	SUM	S	1018 ± 20	1281 ± 25	621 ± 8	959 ± 13
Kamberg C-2602 (calcrete)	U-465	1	617 ± 19	669 ± 20	121 ± 2	428 ± 5
	U-466	B	211 ± 6	220 ± 6	518 ± 11	369 ± 9
	SUM	S	828 ± 20	889 ± 21	639 ± 11	797 ± 10
Kamberg C-2603 (sandstone)	U-452	1	775 ± 22	820 ± 23	309 ± 8	671 ± 14
	U-453	B	191 ± 8	232 ± 10	309 ± 6	256 ± 5
	SUM	S	966 ± 23	1052 ± 25	618 ± 10	927 ± 15
Karpfenkl. C-2599	U-456	1	509 ± 13	538 ± 14	145 ± 4	545 ± 10
	U-458	B	62 ± 4	84 ± 5	109 ± 3	93 ± 3
	SUM	S	571 ± 14	622 ± 15	254 ± 5	638 ± 10
Gaub River C-4803	U-457	1	3370 ± 111	3271 ± 108	274 ± 8	3215 ± 62
	U-459	B	197 ± 7	176 ± 7	128 ± 3	222 ± 4
	SUM	S	3567 ± 111	3447 ± 108	402 ± 9	3437 ± 62
Qhormeb C-1678	U-448	1	630 ± 14	824 ± 17	313 ± 6	647 ± 10
	U-450	B	105 ± 5	121 ± 5	226 ± 4	134 ± 3
	SUM	S	735 ± 15	945 ± 18	539 ± 7	781 ± 10
Hyena Den C-2595	U-467	1	429 ± 6	537 ± 8	33 ± 1	118 ± 3
	U-468	B	104 ± 3	144 ± 3	236 ± 4	498 ± 6
	SUM	S	533 ± 7	681 ± 9	269 ± 4	616 ± 7

Note:

The fractions 1, 2, B, T, S are as in Table 4.2.

TABLE 5.2: ACTIVITY RATIOS FOR THE KUISEB RIVER SAMPLES

Sample	U-no	Fr.	$^{230}\text{Th}/^{234}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	% CO_3
Homeb 9b C-1413 (white)	U-393	1	0.646±0.020	1.247±0.011	4.485±0.058	74
	U-396	B	1.688±0.063	1.491±0.025	1.787±0.029	
	SUM	S	0.816±0.016	1.281±0.029	2.977±0.057	
Homeb 9b C-1413 (pink)	U-394	1	0.401±0.025	1.277±0.009	2.749±0.208	49
	U-395	B	1.170±0.039	1.436±0.019	1.184±0.017	
	SUM	S	0.734±0.016	1.344±0.017	1.436±0.041	
Kuisseb K1 C-1424	U-384T	1	0.308±0.013	1.667±0.047	5.162±0.137	86
	U-385	2	0.576±0.026	1.735±0.051	3.084±0.045	
	U-386	B	1.338±0.111	1.165±0.042	0.663±0.010	
	SUM	S	0.651±0.018	1.537±0.054	1.154±0.026	
Kuisseb K1R C-1424 (repeat)	U-438	1	0.434±0.017	1.262±0.034	3.553±0.086	74
	U-439	B	1.401±0.065	1.026±0.033	0.616±0.012	
	SUM	S	0.647±0.020	1.202±0.035	1.083±0.023	
Kuisseb K3 C-1426	U-408	1	0.335±0.015	1.297±0.026	8.830±0.739	66
	U-409	2	0.568±0.031	1.259±0.019	2.300±0.047	
	U-425	B	2.473±0.090	1.190±0.023	0.959±0.008	
	SUM	S	0.749±0.018	1.258±0.035	1.544±0.029	
Kamberg C-2602 (calcrete)	U-465	1	0.639±0.021	1.084±0.029	3.522±0.066	77
	U-466	B	1.675±0.073	1.044±0.031	0.712±0.016	
	SUM	S	0.897±0.024	1.074±0.036	1.247±0.027	
Kamberg C-2603 (sandstone)	U-452	1	0.819±0.034	1.058±0.023	2.172±0.048	41
	U-453	B	1.106±0.054	1.210±0.059	0.829±0.017	
	SUM	S	0.881±0.025	1.089±0.037	1.500±0.034	
Karpfenkl. C-2599	U-456	1	1.012±0.034	1.058±0.024	3.767±0.093	59
	U-458	B	1.108±0.069	1.356±0.102	0.848±0.029	
	SUM	S	1.026±0.030	1.089±0.037	2.512±0.063	
Gaub River C-4803	U-457	1	0.983±0.043	0.971±0.015	11.73±0.271	74
	U-459	B	1.257±0.054	0.894±0.038	1.730±0.044	
	SUM	S	0.997±0.036	0.966±0.043	8.550±0.246	
Qhormeb C-1678	U-448	1	0.785±0.024	1.309±0.023	2.064±0.036	61
	U-450	B	1.105±0.053	1.150±0.062	0.593±0.013	
	SUM	S	0.826±0.019	1.286±0.036	1.449±0.026	
Hyena Den C-2595	U-467	1	0.220±0.006	1.251±0.017	3.621±0.148	48
	U-468	B	3.464±0.094	1.376±0.040	2.107±0.031	
	SUM	S	0.905±0.016	1.278±0.024	2.290±0.043	

Note:

The fractions 1, 2, B, T, S are as in Table 4.2.

% CO_3 is the amount of material (mostly carbonate) that was dissolved, as a percentage of the initial sample mass.

TABLE 5.3: AGES FOR THE KUISEB RIVER SAMPLES

Sample	H9b white C-1413	H9b pink C-1413	Kuiseb K1 C-1424	K1R repeat C-1424	Kuiseb K3 C-1426
^{14}C age (years)	30 700 - 32 700	28 100 - 28 900	32 300 - 43 300	32 300 - 43 300	39 600 - 40 700
U-no's	U-393,396	U-394,395	U-384B, 385,386	U-438,439	U-408,409 425
% mass loss	10%	2%	14%	4%	8%
U ppm	1.019 \pm 0.016	0.398 \pm 0.003	1.065 \pm 0.027	1.244 \pm 0.034	1.378 \pm 0.027
Uncorrected age	164 800 \pm 9 500	132 200 \pm 7 200	105 400 \pm 7 100	108 700 \pm 6 500	139 400 \pm 9 400
$f_t =$ 0.466	152 000 \pm 9 000	106 000 \pm 7 000	75 800 \pm 7 100	75 200 \pm 5 700	114 000 \pm 9 000
Intercept age	65 000 \pm 5 800	33 300 \pm 4 900	36 800 \pm 2 300	50 600 \pm 3 300	39 800 \pm 2 400
Slope age	60 700 \pm 4 100	31 400 \pm 6 400	51 100 \pm 2 800	47 500 \pm 3 300	43 100 \pm 3 600
f_e	1.301	0.913	0.467	0.449	0.824
Age with f_e	64 900 \pm 3 700	33 400 \pm 3 600	51 600 \pm 4 700	51 000 \pm 3 100	45 900 \pm 3 900

Note:

f ages: f_i is the initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, and f_t is the current $^{230}\text{Th}/^{232}\text{Th}$ ratio.

% mass loss: the percentage mass lost only in the boiled fraction, thus indicating how much carbonate was still in the boiled fraction.

TABLE 5.3: AGES FOR KUISEB RIVER SAMPLES - CONTINUED

Sample	Kamberg C-2602	Kamberg C-2603	Karpfenk. C-2599	Gaub R. C-4803	Qhormeb C-1678	Hyena Den C-2595
^{14}C age (years)	37 800 $\pm 1\ 400$	-	23 100 -30 900	-	28 900 -47 800	-
U-no's	U-465,466	U-452,453	U-456,458	U-457,459	U-448,450	U-467,468
% mass loss	8%	6%	15%	2%	4%	3%
U ppm	1.122 ± 0.027	1.309 ± 0.031	0.774 ± 0.019	4.833 ± 0.151	0.997 ± 0.019	0.724 ± 0.010
Uncorrected age	230 000 $\pm 27\ 000$	217 000 $\pm 25\ 000$	>348 000	>343 000	169 000 $\pm 11\ 000$	213 000 $\pm 12\ 000$
$f_1 =$ 0.466	189 000 $\pm 25\ 000$	185 000 $\pm 24\ 000$	>350 000	>340 000	140 000 $\pm 10\ 000$	194 000 $\pm 12\ 000$
Intercept age	132 000 $\pm 22\ 000$	86 100 $\pm 6\ 100$	>289 000	>248 000	122 000 $\pm 12\ 000$	10 800 $\pm 1\ 100$
Slope age	120 000 $\pm 17\ 000$	79 400 $\pm 6\ 700$	>217 000	>194 000	111 000 $\pm 11\ 000$	10 300 $\pm 1\ 200$
f_τ	0.299	0.477	0.092	0.426	0.216	2.049
Age with f_τ	121 000 $\pm 8\ 000$	98 200 $\pm 6\ 900$	>350 000	>340 000	123 000 $\pm 7\ 000$	10 800 $\pm 2\ 200$

Note:

f ages: f_1 is the initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, and f_τ is the current $^{230}\text{Th}/^{232}\text{Th}$ ratio.

% mass loss: the percentage mass lost only in the boiled fraction, thus indicating how much carbonate was still in the boiled fraction.

sample mass, indicating that the proportion of sand is high in these calcretes. The sums of the fractions (Table 5.1) for each sample allow the ratios (Table 5.2) and the uncorrected $^{230}\text{Th}/^{234}\text{U}$ ages to be calculated (Table 5.3).

5.4.1 The ^{14}C ages

In all of the samples (Table 5.2) the ^{14}C ages are substantially lower than the uncorrected $^{230}\text{Th}/^{234}\text{U}$ dates or even the ages corrected by f_1 . The most plausible explanation lies in the fact that these thick calcretes must have formed over many thousands of years and the difference in half-lives used in the two dating methods results in different average ages (Section 5.2). The extent of the growth periods will be referred to below.

5.4.2 The $^{230}\text{Th}/^{234}\text{U}$ ages

Since the carbonates considered here started their formation before the time covered by ^{14}C dating, there is no independent check on the $^{230}\text{Th}/^{234}\text{U}$ ages. The uncorrected age at least sets an upper limit since it is a maximum average age. In Chapter 4 the correction using the initial f_1 of desert sand was found to be the best approach. It is considered valid to use this for all the samples covered in this chapter since desert sand forms the detrital component of the carbonate samples in this study. Thus it is assumed that the ages obtained in this way are the best average ages and the ages obtained by other methods will be briefly compared with these ages.

The average ages obtained by using $f_1 = 0.466$ (Section 4.1.4) and listed in Table 5.2 suggest that the calcrete covering the Karpfen Cliff conglomerate dates to beyond the range of the $^{230}\text{Th}/^{234}\text{U}$ dating method, while the calcretes in the Homeb area are much younger. The

carbonate cementing the Oswater conglomerate may be intermediate.

It is satisfying to note the consistency obtained in a repeat sample, Kuiseb K1 and K1R (Tables 5.1, 5.2 and 5.3). The first subsample consisted of two weak leaches and the repeat subsample of only one. Both K1 and K1R included some fractions with low chemical yields for the uranium (4% to 7%), but the fact that the ages are the same shows that the results are reliable despite the low yields. The other samples covered in this chapter had acceptable yields (> 7%).

Length of the formation periods

For two samples, namely Kuiseb K1 and K3, two weak leachates, rather than only one, were analysed. The ratios for the individual fractions are given in Table 5.2 and these correspond to the following ages, corrected by $f_1 = 0.466$:

K1	fr1	U-384B	36 000 years
	fr2	U-385	77 600 years
K3	fr1	U-408	41 700 years
	fr2	U-409	75 200 years

These results clearly illustrate that there is a mixture of several ages in a single piece of Kuiseb calcrete, i.e. it formed over many thousand years. In these two samples the period of formation, not necessarily continuous, is more than 40 000 years.

Slope and intercept ages

In Chapter 4 it was shown that the slope and intercept ages are too young due to differential fractionation and it may be safely assumed that it will also be the case here (Table 5.3). This is also confirmed by comparing the age corrected with f_1 . The slope and intercept ages are always younger, sometimes drastically so, than the f_1 ages. Assuming

that the nuclides in the detritus are in equilibrium, as was found in the sand experiments (Section 4.1), the $^{230}\text{Th}/^{234}\text{U}$ ratios of the boiled fractions often exceed 1.2 (Table 5.2) which indicates extensive fractionation between uranium and thorium during the leaching process. The ages obtained are thus too young.

The slope and intercept ages are all similar to each other with the exception of Kuiseb Kl and KLR, which difference may be explained as follows. The first measurement of Kl consisted of two weak leaches and a boiled fraction. The first and second acid leachates represent different average ages, viz. 36 000 and 77 600 years, as shown above. The different ages are also clearly demonstrated in Figure 5.3 in that the points do not lie on a single straight line. The graphs for KLR (Figure 5.4) have only one leachate and a boiled point and thus the slopes are the average ages. In the intercept graph of Kl the first leachate point strongly determines the intercept of the best straight line and thus gives an age close to that of the outer carbonate. The intercept age (36 800 years, Table 5.3) is therefore less than that given by the slope method (51 100 years) for Kuiseb Kl.

Ages corrected using f_{τ} values

Using the f_{τ} values from the intercept graph give younger ages than those obtained from the f_{α} values of the desert sand (Section 4.1.6). This may be explained by the fact that the f_{τ} value is obtained from the intercept graph which is known to be influenced by differential fractionation. Generally the ages obtained by applying the f_{τ} values are similar to the ages obtained from the actual intercept and slope graphs (Table 5.3), as would be expected.

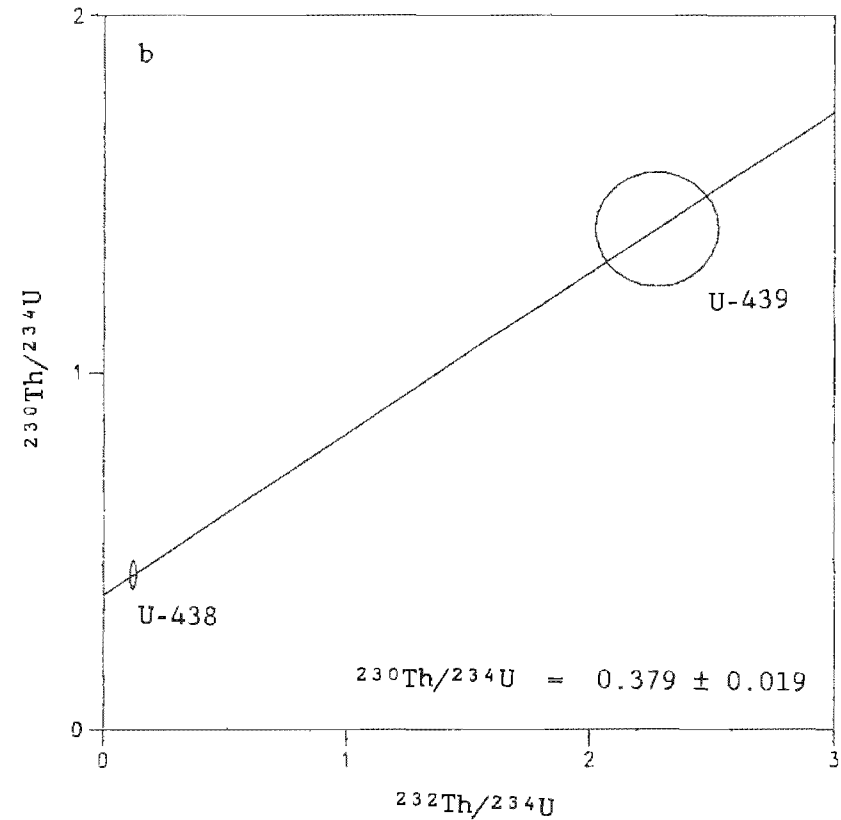
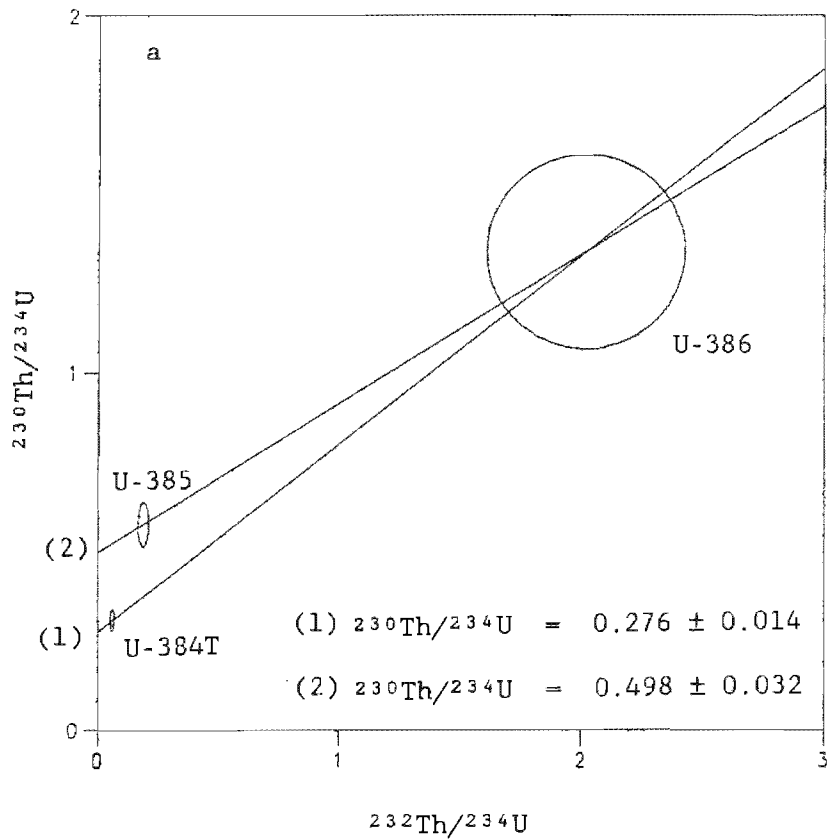


Figure 5.3: Intercept graphs for (a) the Kuiseb K1 and (b) the K1R calcretes. The intercepts give the $^{230}\text{Th}/^{234}\text{U}$ ratio of the pure carbonate. Figure (a) shows the two slopes and y-intercepts, indicating the ages of the two leachate fractions (see text), while the intercept in figure (b) gives the average age of sample K1R. The error ellipses are shown at 2σ .

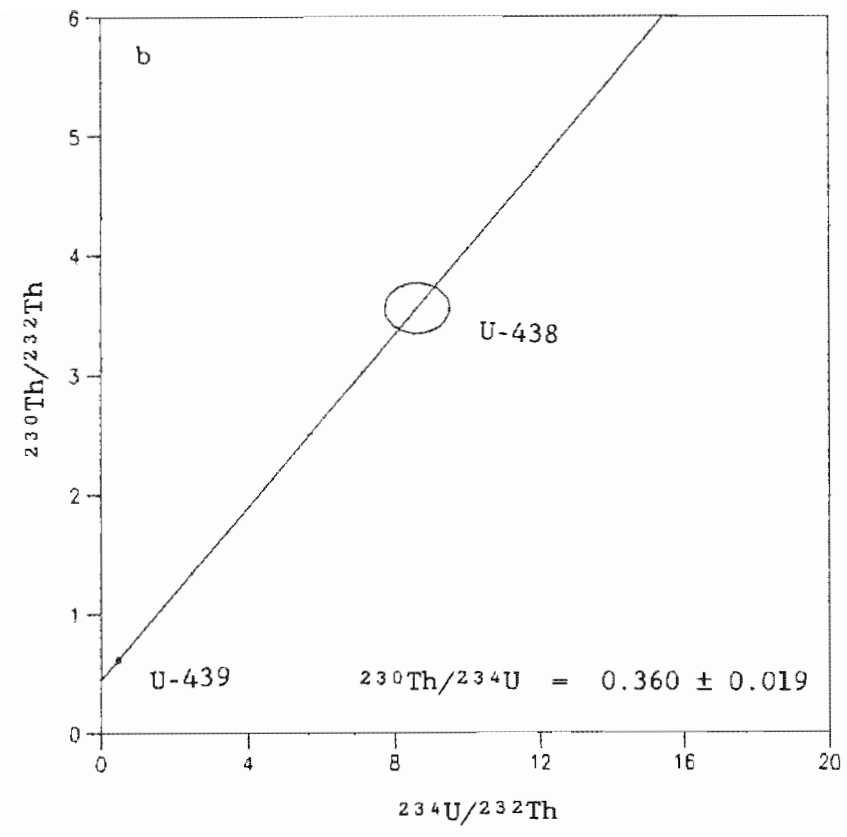
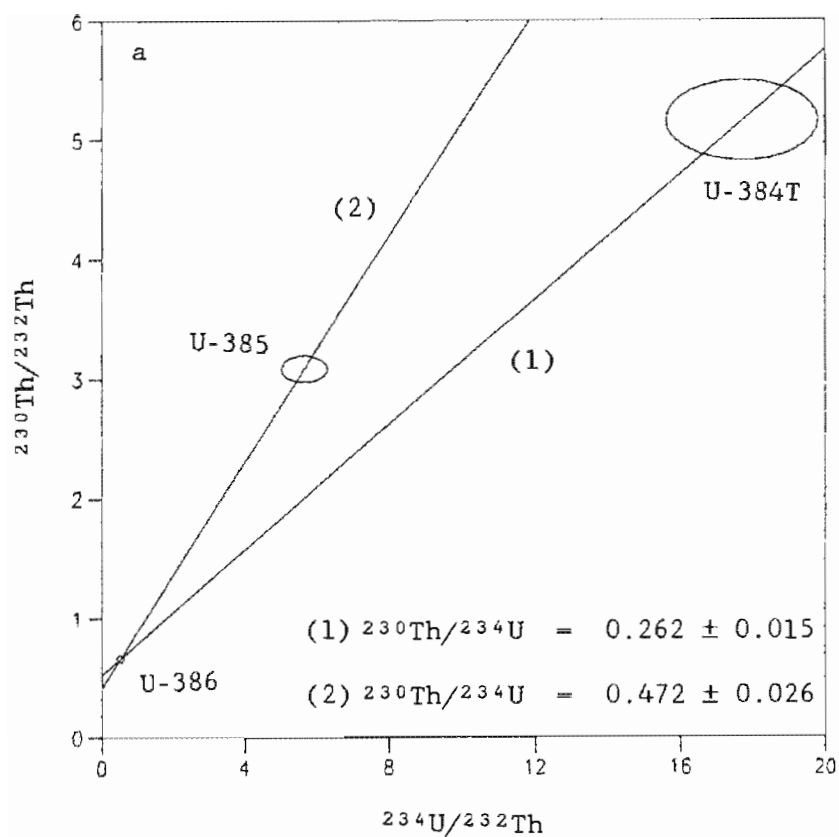


Figure 5.4: Slope graphs for (a) the Kuiseb Kl and (b) the KlR calcretes. The slopes give the $^{230}\text{Th}/^{234}\text{U}$ ratio of the pure carbonate. Figure (a) shows two slopes indicating the ages of the two leachate fractions (see text), while the slope in figure (b) gives the average age of sample KlR. The error ellipses are shown at 2σ .

5.4.3 Discussion of the corrected ages

Top calcrete surface

Samples H9b, K1 and K3 all lie on the surface above the Kuiseb canyon on the south bank. They lie within several kilometres of each other and comprise the same calcrete layer of 1-2 m thickness. The combined results for these samples suggest that the calcrete probably formed in the time range 150 000 to 30 000 (Table 5.3, K1 fr1). The oldest date is for the visibly older nodules in the H9b sample.

The oldest samples measured are the Karpfen Cliff and Gaub calcretes, both being beyond the dating range of the $^{230}\text{Th}/^{234}\text{U}$ method, as was assumed by Ward (1984). The ^{14}C age of Karpfen Cliff is fairly young and thus suggests fairly extensive recrystallization.

The Kamberg pebble conglomerate is a 8 m thick layer overlying basal sandstone. The similar ages of the sandstone (C-2602) and the conglomerate (C-2603) indicate that, although the sand of the sandstone must have been laid down much earlier, both were cemented at the same time and possibly to a large extent at a time after the cementing of the Karpfen Cliff and Gaub conglomerates.

Oswater Terrace

Both Qhormeb and Hyena Den are terraces belonging to the Oswater conglomerate. Their ages, being similar to the white nodules at Homeb and Kamberg respectively, are quite high. It must be pointed out, however, that their ages only apply to the carbonate cement and do not date the deposition of the river gravels.

CHAPTER 6

CONCLUSION

In conclusion several important considerations may be discussed and summarised in terms of the validity and usefulness of obtaining corrected $^{230}\text{Th}/^{234}\text{U}$ dates for carbonate materials from arid areas, specifically Namibia.

6.1 SATISFYING THE DATING CONDITIONS

All the samples contained sufficient uranium (Tables 4.1 and 5.1), satisfying the additional criterion for $^{230}\text{Th}/^{234}\text{U}$ dating (Section 1.1). The condition of having zero initial ^{230}Th is obviously violated in all samples and thus the need for the different correction procedures. The condition of the samples being in closed systems is satisfied in the case of the "single-age samples" considered in Chapter 4 since the ages corresponded well with the ^{14}C ages in 3 of 5 cases; special conditions applied to the other two samples. In the case of the calcretes and conglomerates closed conditions cannot really be considered to apply due to the continuous addition of uranium over long formation periods. The dates thus obtained represent intermediate ages within the times of formation.

6.2 IMPORTANCE OF THE CHEMICAL PROCEDURE

Since samples of varying amounts of detrital ^{230}Th could not be obtained from the Kuiseb, single samples with leachate-boiled fractions were used. The Sequential Leach method as applied here was found to be limited due to differential fractionation of isotopes and seeming reabsorption of thorium to the boiled fraction in some cases. The SL method may

be improved by firing the carbonate in a furnace of about 800°C. This will convert the calcium carbonate to calcium oxide which may dissolve much more readily in acid. This should substantially decrease the leaching time and thus reduce the effect of fractionation and reabsorption, as noted by Bischoff and Fitzpatrick (1991) but not appreciated at first when developing the SL method.

Other improvements could be made by using the weaker acid, eg. acetic acid, for the carbonate leaches, and rinsing the sand more carefully.

Improving the chemistry could in future give improved agreement between the different correction procedures, giving greater confidence to the results obtained.

6.3 CORRECTING $^{230}\text{Th}/^{234}\text{U}$ DATES

This study shows that it is possible to obtain corrected ages for single impure terrestrial carbonates. If a range of coeval samples with differing amounts of detritus is available then the Leachate/Leachate method would probably be the most suitable method of analysis, since it is not affected by differential fractionation. In the case of not having samples with a wide spread of detrital contamination, as is the situation in the Kuiseb River valley, the Sequential Leach chemical method is usable. The data may be analysed by the intercept or slope methods if strict chemical control is exercised so as to reduce differential fractionation to a negligible degree. Alternatively, if the source of detrital contamination is known, this fact may be used to correct the ages. This last approach was found to be the most suitable, the detritus being the local desert sand which was easily obtained. In this latter approach, it is not even necessary to apply the chemical Sequential Leach method, unless a check on the method of data analysis is required.

6.4 SUMMARY OF THE $^{230}\text{Th}/^{234}\text{U}$ DATES OBTAINED

Reliable $^{230}\text{Th}/^{234}\text{U}$ dates may indeed be obtained from calcretes in arid areas. Some conclusions may be made about the analyses of the samples from the Kuiseb River valley. The Oswater samples (140 000 and 194 000 years) are older than the Homeb surface calcretes, but more samples from Oswater should be measured. The Homeb calcretes formed mainly during the Late Pleistocene, i.e. the last 130 000 years, and thus are younger than the calcification of the Karpfen Cliff conglomerate. These dates are in contradiction to Ward (1983, 1988) who considers, based on his geological interpretation, that most of the Kuiseb calcretes formed before the Late Pleistocene.

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BIBLIOGRAPHY

- Bard, E., B. Hamelin, R.G. Fairbanks and A. Zindler. 1990. Calibration of the ^{14}C timescale over the past 30 000 years using mass spectrometric U-Th ages from Barbados corals. *Nature* 345:405-410.
- Bischoff, J.L. and J.A. Fitzpatrick. 1991. U-series dating of impure carbonates: An isochron technique using total-sample dissolution. *Geochimica et Cosmochimica Acta* 55:543-554.
- Eglinton, B.M. and R.E. Harmer. 1991. GEODATE: a program for the processing and regression of isotope data using IBM-compatible microcomputers. CSIR Manual EMA-H 9101, 57 pp.
- Goede, A. and J.C. Vogel. 1991. Trace element variations and dating of a Late Pleistocene Tasmanian speleothem. *Palaeogeography, Palaeoclimatology, Palaeoecology* 88:121-131.
- Goudie, A.S. and K. Pye (eds). 1983. Chemical sediments and geomorphology: precipitates and residua in the near-surface environment. Academic Press, London. 439 pp.
- Harmer, R.E. and B.M. Eglinton. 1990. A review of the statistical principles of geochronometry: towards a more consistent approach for reporting geochronological data. *South African Journal of Geology* 93:845-856.
- Harmon, R.S., P. Thompson, H.P. Schwarcz and D.C. Ford. 1975. Uranium-series dating of speleothems. *The NSS Bulletin* 37:21-33.
- Hendy, C.H., T.R. Healy, E.M. Rayner, J. Shaw and A.T. Wilson. 1979. Late Pleistocene Glacial Chronology of the Taylor Valley, Antarctica, and the global climate. *Quaternary Research* 11:172-184.
- Ivanovich, M. and R.S. Harmon (eds). 1982. Uranium series disequilibrium: Applications to environmental problems. Clarendon Press, Oxford. 571 pp.
- Kaufman, A. 1971. U-series dating of Dead Sea Basin carbonates. *Geochimica et Cosmochimica Acta* 35:1269-1281.
- Kaufman, A. and W. Broecker. 1965. Comparison of Th230 and C14 Ages for Carbonate Materials from Lakes Lahontan and Bonneville. *Journal of Geophysical Research* 70(16):4039-4054.
- Kronfeld, J. and J.C. Vogel. 1991. Uranium isotopes in surface waters from southern Africa. *Earth and Planetary Science Letters* 105:191-195.
- Ku, T.-L. 1976. The uranium-series methods of age determination. *Annual Review of Earth and Planetary Sciences* 4:347-379.
- Ku, T.-L., W.B. Bull, S.T. Freeman and K.G. Knauss. 1979. Th230-U234 dating of pedogenic carbonates in gravelly desert soils of Vidal Valley, southeastern California. *Geological Society of America Bulletin* 90:1063-1073.

- Ku, T.-L. and Z.-C. Liang. 1984. The dating of impure carbonates with decay-series isotopes. *Nuclear Instruments and Methods in Physics Research* 223:563-571.
- Ku, T.-L., M. Ivanovich and S. Luo. 1990. U-series dating of Last Interglacial High Sea Stands: Barbados revisited. *Quaternary Research* 33:129-147.
- Lao, Y. and L. Benson. 1988. Uranium-Series Age Estimates and Paleoclimatic Significance of Pleistocene Tufas from the Lahontan Basin, California and Nevada. *Quaternary Research* 30:165-176.
- Luo, S. and T.-L. Ku. 1991. U-series isochron dating: A generalized method employing total-sample dissolution. *Geochimica et Cosmochimica Acta* 55:555-564.
- Mandel, J. 1967. The statistical analysis of experimental data. Interscience Publishers, New York.
- Netterberg, F. 1980. Geology of Southern African calcretes: 1. Terminology, description, macrofeatures, and classification. *Transactions of the Geological Society of South Africa* 83:255-283.
- Osmond, J.K., J.P. May and W.F. Tanner. 1970. Age of the Cape Kennedy Barrier-and-Lagoon Complex. *Journal of Geophysical Research* 75:469-479.
- Przybylowicz, W., H.P. Schwarcz and A.G. Latham. 1991. Dirty calcites 2. Uranium-series dating of artificial calcite-detritus mixtures. *Chemical Geology (Isotope Geoscience Section)* 86:161-178.
- Rosenbauer, R.J. 1991. UDATE1: A computer program for the calculation of uranium-series isotopic ages. *Computers and Geosciences* 17:45-75.
- Rosholt, J.N. 1976. Th²³⁰/U²³⁴ dating of travertine and caliche rinds. *Geological Society of America Abstracts with Programs* 8:1076.
- Schwarcz, H.P. 1989. Uranium series dating of Quaternary deposits. *Quaternary International* 1:7-17.
- Schwarcz, H.P. and A.G. Latham. 1989. Dirty calcites 1. Uranium-series dating of contaminated calcite using leachates alone. *Chemical Geology (Isotope Geoscience Section)* 80:35-43.
- Selby, M.J., C.H. Hendy and M.K. Seely. 1979. A late Quaternary lake in the central Namib desert, southern Africa, and some implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* 26:37-41.
- Szabo, B.J. and K.W. Butzer. 1979. Uranium-series dating of lacustrine limestones from pan deposits with Final Acheulian Assemblage at Rooidam, Kimberley District, South Africa. *Quaternary Research* 11:257-260.
- Szabo, B.J. and H. Sterr. 1978. Dating caliches from southern Nevada by ²³⁰Th/²³²Th versus ²³⁴U/²³²Th and ²³⁴U/²³²Th versus ²³⁸U/²³²Th isochron-plot method: in R.E. Zartman (ed.), Short papers of the fourth International conference, Geochronology, Cosmochronology, Isotope Geology: U.S. Geological Survey Open-File Report 78-701:416-418.

Teller, J.T., N. Rutter, and N. Lancaster. 1990. Sedimentology and paleohydrology of late Quaternary lake deposits in the northern Namib sand sea, Namibia. *Quaternary Science Reviews* 9:343-364.

Van der Wijk, A. 1987. Radiometric dating by alpha spectrometry on uranium series nuclides. PhD, Rijksuniversiteit, Groningen.

Vogel, J.C. 1982. The age of the Kuiseb river silt terrace at Homeb. In: JA Coetzee and EM van Zinderen Bakker (eds.), *Palaeoecology of Africa* 15:201-209.

Vogel, J.C. 1983. ^{14}C variations during the Upper Pleistocene. *Radiocarbon* 25:213-218.

Vogel, J.C. 1987. Calibration of radiocarbon dates beyond 10 000 BP. In: *Chronologies in the Near East*. O. Aurenche, J. Evin and F. Hours (eds), BAR International Series:319-322.

Vogel, J.C. 1989. Evidence of past climatic change in the Namib Desert. *Palaeogeography, Palaeoclimatology, Palaeoecology* 70:355-366.

Vogel, J.C. and D. Ehhalt. 1963. The use of the carbon isotopes in groundwater studies. *Radioisotopes in Hydrology, Proceedings of symposium held by IAEA in Tokyo, March 1963, Vienna:383-395*

Ward, J. 1984. A reappraisal of the Cenozoic stratigraphy in the Kuiseb valley of the central Namib desert. In: J.C. Vogel (ed.), *Late Cainozoic Palaeoclimates of the Southern Hemisphere*. Balkema, Rotterdam, pp 455-463.

Ward, J. 1988. On an interpretation of the Oswater Conglomerate Formation, Kuiseb Valley, Namib Desert. *Palaeoecology of Africa* 19:119-125.

Ward, J., M.K. Seely and N. Lancaster. 1983. On the antiquity of the Namib. *South African Journal of Science* 79:175-183.

APPENDIX 1; CORRECTIONS AND CALCULATIONS

This appendix gives the calculations as used in this thesis. They are similar to those given in Rosenbauer (1991).

DECAY CONSTANTS (Ivanovich and Harmon 1982)

$$\begin{aligned}\lambda_2 &= \text{decay constant for } ^{232}\text{U} = \ln 2/72 \text{ y} \\ \lambda_4 &= \text{decay constant for } ^{234}\text{U} = \ln 2/248 \text{ 000 y} \\ \lambda_0 &= \text{decay constant for } ^{230}\text{Th} = \ln 2/75 \text{ 200 y} \\ \lambda_8 &= \text{decay constant for } ^{228}\text{Th} = \ln 2/1.913 \text{ y}\end{aligned}$$

ACTIVITIES

The activity calculation depends on measuring and comparing the alpha count rates of the isotopes with those of the added ^{232}U and ^{228}Th spikes. The counting times do not actually enter into the calculations.

Since the parent ^{232}U decays with a half-life of 72 years, its specific activity needs to be adjusted on an annual basis. In 1980 the activity was determined as 8.856 dpm/ml so that:

$$A_{u2} = 8.856 \times \exp(-\lambda_2 \times t_2) \text{ dpm/ml}$$

where t_2 is the number of years since 1980.

The daughter isotope, ^{228}Th , is in secular equilibrium with ^{232}U so that its specific activity is:

$$\begin{aligned}A_{T8} &= A_{u2} \times \lambda_8 / (\lambda_8 - \lambda_2) \\ &= A_{u2} \times 1.027\end{aligned}$$

The specific activity of the ^{238}U isotope (given in square brackets to distinguish it from the counts in its alpha peak) is given by:

$$[^{238}\text{U}] = \frac{^{238}\text{U} \times A_{u2} \times V}{^{232}\text{U} \times M} \pm [^{238}\text{U}] \times \text{SQRT} \left[\frac{(E_{u8})^2}{(^{238}\text{U})^2} + \frac{(E_{u2})^2}{(^{232}\text{U})^2} \right] \text{ dpm/g}$$

where:

- ^{238}U and ^{232}U are the total number of counts
- A_{u2} is the known ^{232}U spike activity in dpm/ml
- V is the spike volume used in ml (usually 1 ml)
- M is the total (ie. initial) sample mass in g
- SQRT is the square root function
- E_{u8} and E_{u2} are the errors in ^{238}U and ^{232}U respectively

Similar expressions may be written for $[^{234}\text{U}]$, $[^{232}\text{Th}]$, and $[^{230}\text{Th}]$.

The errors in measuring the mass and the amount of spike are assumed to be negligible.

CONCENTRATIONS

The uranium and thorium concentrations in the samples are given by:

$$[U] = [^{238}\text{U}]/0.738 \pm (\text{error in } [^{238}\text{U}])/0.738 \text{ ppm}$$

$$[\text{Th}] = [^{232}\text{Th}]/0.2427 \pm (\text{error in } [^{232}\text{Th}])/0.2427 \text{ ppm}$$

YIELDS

The thorium yield is given by:

$$Y_{\text{Th}} = \frac{^{228}\text{Th} \times 60 \times 100}{T \times 0.34 \times A_{\text{Th}} \times V} \%$$

where:

100 converts the yield to a percentage value

T is the total counting time in seconds

the factor 0.34 is the detector efficiency

V is the volume of spike used

Similarly the uranium yield is given by:

$$Y_{\text{U}} = \frac{^{232}\text{U} \times 60 \times 100}{T \times 0.34 \times A_{\text{U}2} \times V} \%$$

ACTIVITY RATIOS

The $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ ratios are obtained simply by dividing the relevant counts.

The $^{230}\text{Th}/^{234}\text{U}$ ratio is given by:

$$\frac{[^{230}\text{Th}]}{[^{234}\text{U}]} = \frac{^{230}\text{Th}}{^{234}\text{U}} \times \frac{^{232}\text{U}}{^{228}\text{Th}} \times 1.027$$

where the spikes and spike factor are included to make the uranium and thorium compatible with each other since their counts originate from different spectra. The error is obtained by simple propagation of the counting errors.

AGE CALCULATION

The age equation is given by Equations 1.1 and 3.1. For the computer program this equation is written as a function $F(t) = 0$. The secant method is used to solve for t iteratively. The initial estimate of the time is found from:

$$t = [-\ln(1 - \{^{230}\text{Th}/^{234}\text{U}\}/1.2)]/\lambda_0$$

where the factor 1.2 is used to begin with a slightly lower $^{230}\text{Th}/^{234}\text{U}$ ratio.

The secant equation is given by:

$$t(i+1) = t(i) - F(t(i)) \times \frac{t(i) - t(i-1)}{F(t(i)) - F(t(i-1))}$$

This new calculated age is compared to the previous estimate and convergence is taken when there is no difference in ages in the first decimal point.

APPENDIX 2: JUSTIFICATION FOR THE SLOPE METHOD

When plotting $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ for the points of the leachate and the boiled fractions of a sample, the slopes of the straight lines are assumed to give the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios of the pure carbonate. This may be considered valid if differential fractionation does not influence the slopes of the graphs, as Schwarcz and Latham (1989) showed to be true for the L/L method.

The following set of equations may be written for the activities (per gram of sample dissolved) of the respective isotopes in the weak acid leachate solution:

$$\begin{aligned}^{238}\text{U}_L &= ^{238}\text{U}_C + r_8 \times ^{238}\text{U}_D \\ ^{234}\text{U}_L &= ^{234}\text{U}_C + r_4 \times ^{234}\text{U}_D \\ ^{230}\text{Th}_L &= ^{230}\text{Th}_C + r_0 \times ^{230}\text{Th}_D \\ ^{232}\text{Th}_L &= 0 + r_2 \times ^{232}\text{Th}_D\end{aligned}$$

where (see also Section 1.3):

C refers to the nuclides of the pure carbonate
D refers to the nuclides adsorbed on the detrital minerals
L refers to the nuclides leached from C and D into the solution
 r_i are the fractions of the respective isotopes taken into solution from the detritus

Similarly the set of equations for the activities of the isotopes in the boiled fraction may be written as follows, assuming that all the nuclides belonging to the carbonate have been removed in the weak acid leachate, and assuming that all the detrital isotopes are in the solution:

$$\begin{aligned}^{238}\text{U}_S &= r_8' \times ^{238}\text{U}_D \\ ^{234}\text{U}_S &= r_4' \times ^{234}\text{U}_D \\ ^{230}\text{Th}_S &= r_0' \times ^{230}\text{Th}_D \\ ^{232}\text{Th}_S &= r_2' \times ^{232}\text{Th}_D\end{aligned}$$

where:

S refers to the nuclides leached from D into the solution
 r_i' are the fractions of the respective isotopes remaining on the detritus after the first leach, ie. $r_i' = (1 - r_i)$.

Now the slope m of the $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ graph is:

$$m = \frac{\Delta y}{\Delta x} = \frac{\left[\frac{^{230}\text{Th}}{^{232}\text{Th}} \right]_L - \left[\frac{^{230}\text{Th}}{^{232}\text{Th}} \right]_S}{\left[\frac{^{234}\text{U}}{^{232}\text{Th}} \right]_L - \left[\frac{^{234}\text{U}}{^{232}\text{Th}} \right]_S}$$

Now substitute the equations written above:

$$m = \frac{\Delta y}{\Delta x} = \frac{\left[\frac{^{230}\text{Th}_C + r_0 \times ^{230}\text{Th}_D}{r_2 \times ^{232}\text{Th}_D} \right]_L - \left[\frac{r_0' \times ^{230}\text{Th}_D}{r_2' \times ^{232}\text{Th}_D} \right]_S}{\left[\frac{^{234}\text{U}_C + r_4 \times ^{234}\text{U}_D}{r_2 \times ^{232}\text{Th}_D} \right]_L - \left[\frac{r_4' \times ^{234}\text{U}_D}{r_2' \times ^{232}\text{Th}_D} \right]_S}$$

Multiply throughout by $(r_2 \times r_2' \times ^{232}\text{Th}_D)$:

$$m = \frac{(r_2' \times ^{230}\text{Th}_C + r_0 \times r_2' \times ^{230}\text{Th}_D) - (r_2 \times r_0' \times ^{230}\text{Th}_D)}{(r_2' \times ^{234}\text{U}_C + r_4 \times r_2' \times ^{234}\text{U}_D) - (r_2 \times r_4' \times ^{234}\text{U}_D)}$$

$$= \frac{r_2' \times \boxed{^{230}\text{Th}_C} + (r_0 \times r_2' - r_2 \times r_0') \times ^{230}\text{Th}_D}{r_2' \times \boxed{^{234}\text{U}_C} + (r_4 \times r_2' - r_2 \times r_4') \times ^{234}\text{U}_D}$$

Now putting $r_1 = (1 - r_1')$ simplifies the expression for the slope to:

$$m = \frac{r_2' \times ^{230}\text{Th}_C + (r_2' - r_0') \times ^{230}\text{Th}_D}{r_2' \times ^{234}\text{U}_C + (r_2' - r_4') \times ^{234}\text{U}_D}$$

Dividing by $(r_2' \times {}^{234}\text{U}_C)$ gives:

$$m = \frac{\frac{{}^{230}\text{Th}_C}{{}^{234}\text{U}_C} + \left[1 - \frac{r_{0'}}{r_2'} \right] \times \frac{{}^{230}\text{Th}_B}{{}^{234}\text{U}_B} \times \frac{{}^{234}\text{U}_B}{{}^{234}\text{U}_C}}{1 + \left[1 - \frac{r_{1'}}{r_2'} \right] \times \frac{{}^{234}\text{U}_B}{{}^{234}\text{U}_C}}$$

Thus $m = ({}^{230}\text{Th}/{}^{234}\text{U})_C$ if the $r_{0'}/r_2'$ and $r_{1'}/r_2'$ ratios are unity, ie. if there is no differential fractionation.

Similarly, the slope m of the ${}^{234}\text{U}/{}^{232}\text{Th}$ versus ${}^{238}\text{U}/{}^{232}\text{Th}$ graph is:

$$m = \frac{\Delta y}{\Delta x} = \frac{\left[\frac{{}^{234}\text{U}}{{}^{232}\text{Th}} \right]_L - \left[\frac{{}^{234}\text{U}}{{}^{232}\text{Th}} \right]_S}{\left[\frac{{}^{238}\text{U}}{{}^{232}\text{Th}} \right]_L - \left[\frac{{}^{238}\text{U}}{{}^{232}\text{Th}} \right]_S} = \frac{\frac{{}^{234}\text{U}_C}{{}^{238}\text{U}_C} + \left[1 - \frac{r_{A'}}{r_2'} \right] \times \frac{{}^{234}\text{U}_B}{{}^{238}\text{U}_C}}{1 + \left[1 - \frac{r_{B'}}{r_2'} \right] \times \frac{{}^{238}\text{U}_B}{{}^{238}\text{U}_C}}$$

Once again, $m = ({}^{234}\text{U}/{}^{238}\text{U})_C$ if the $r_{0'}/r_2'$ and $r_{A'}/r_2'$ ratios are unity, ie. if there is no differential fractionation.

In Chapter 4 the extent of differential fractionation is investigated and discussed.

Although the above equations apply to a leachate-boiled fraction pair, the equations are based on the difference of two points. If two leachates and a boiled fraction are measured, the above may be applied to any two of these points. Thus, as long as all three points lie on a straight line, the above equations may be applied in the case of more than one leachate fraction.