AU9918492

U-Series Dating Using Thermal Ionisation Mass Spectrometry (TIMS)

Malcolm T McCulloch
Research School of Earth Sciences, ANU

Introduction

U-series dating is based on the decay of the two long-lived isotopes ^{238}U ($\tau_{1/2} = 4.47 \times 10^9$ years) and ^{235}U ($\tau_{1/2} = 0.7 \times 10^9$ years). ^{238}U and its intermediate daughter isotopes ^{234}U ($\tau_{1/2} = 245.4$ ka) and ^{230}Th ($\tau_{1/2} = 75.4$ ka) have been the main focus of recently developed mass spectrometric techniques (Edwards et al., 1987) while the other less frequently used decay chain is based on the decay ^{235}U to ^{231}Pa ($\tau_{1/2} = 32.8$ ka). Both the ^{238}U and ^{235}U decay chains terminate at the stable isotopes ^{206}Pb and ^{207}Pb respectively. Here we will describe some of the applications of the ^{238}U decay chain that have been made possible with TIMS. TIMS has a number of inherent advantages, mainly the ability to measure isotopic ratios at high precision on relatively small samples. In spite of these now obvious advantages, it is only since the mid-1980's when Chen et al., (1986) made the first precise measurements of ^{234}U and ^{232}Th in seawater followed by Edwards et al., (1987) who made combined ^{234}U-^{230}Th measurements, was the full potential of mass spectrometric methods first realised. Interestingly the procedures for U isotopic measurements came from isotopic studies of U in meteorites.

Basic Principles

The basic equation of radioactive decay is given by:

$N_p = N_i e^{-\lambda t}$ and $N_d = N_o - N_p$ where p = parent and d = daughter and N_i refers to the initial number of parent atoms N at time T and λ the decay constant. The halflife ($\tau_{1/2}$) of N_p is given by $N_p = N_o/2$ and hence $\tau^{1/2} = \ln 2/\lambda$. The activity is defined as the number of atoms decaying per unit time and is given by $A = N\lambda$.

Thus in the case of the ^{238}U chain:

$^{230}Th = {}^{234}U(1 - e^{-\lambda_{230}T})$ where the isotopes are given as activities (italics) and at secular equilibrium $^{238}U = {}^{234}U$ and hence $^{230}Th = {}^{238}U(1 - e^{-\lambda_{230}T})$. In general since ^{234}U is produced by alpha decay of ^{238}U, there is recoil, which damages the lattice at the site of ^{234}U and hence often leads to preferential loss of this isotope. For this reason most fossil systems generally incorporate additional ^{234}U and hence the assumption of secular equilibrium is usually not valid. If we assume a closed system with no initial ^{230}Th then a more complicated expression is required to determine the daughter activity:

$$1 - {}^{230}Th/{}^{238}U = e^{-\lambda_{230}T} - \{\delta^{234}U(o)/1000\}\{\lambda_{230}/(\lambda_{230} - \lambda_{234}\}\{1 - e^{(\lambda_{234} - \lambda_{230})T}\} \quad \ldots \; 1$$

where $\delta^{234}U(o) = \{({}^{234}U/{}^{238}U)/({}^{234}U/{}^{238}U)_{eq} - 1\} \times 1000$ where $^{234}U/{}^{238}U_{eq}$ is the atomic ratio at secular equilibrium in parts per thousand and $\delta^{234}U(T) = \delta^{234}U(o)\, e^{-\lambda_{234}T}$. If the value of $\delta^{234}U(T)$ is reasonably well known, as for example in seawater then this ratio can be used as an independent check on whether for example the system (e.g. coral) has acted as a closed system. See Dickin (1995) for more details.

Thermal Ionisation Mass Spectrometry (TIMS) U-series Dating

TIMS U-series dating relies on the direct measurement of the isotope (radioactive or stable) and thus represents a different approach to counting methods. At secular equilibrium: $^{234}U = {}^{208}Th = {}^{226}Ra$. Using the definition of the activity we have:

$^{234}\mathrm{U}\ \ln 2/\tau^{1/2}_{(234)} = {}^{230}\mathrm{Th}\ \ln 2/\tau^{1/2}_{(230)} = {}^{226}\mathrm{Ra}\ \ln 2/\tau^{1/2}_{(226)}$

Thus the atomic ratio of $^{234}\mathrm{U}/^{230}\mathrm{Th} = \tau^{1/2}_{(234)}/\tau^{1/2}_{(230)} = 245.4/75.4 = 3.25$

And $^{230}\mathrm{Th}/^{226}\mathrm{Ra} = \tau^{1/2}_{(230)}/\tau^{1/2}_{(226)} = 75.4/1.6 = 47.1$. That is the abundance is inversely proportion and to the half-life and hence for the short-lived more active isotopes, such as ^{226}Ra measurements by TIMS are increasingly difficult.

In addition to the abundance of the isotope there are several other factors which are important in TIMS measurement. The ionisation efficiency is of key importance and despite its very low abundance the high ionisation efficiency of ^{226}Ra had made possible some TIMS applications. The The ionisation efficiency is probably the single most important factor which limits the precision of ^{230}Th-^{238}U ages, in particular the measurement of the ^{230}Th activity (equation 1). Measurements of ^{230}Th are undertaken using isotope dilution methods with ^{229}Th being used as the reference isotope i.e. the $^{229}\mathrm{Th}/^{230}\mathrm{Th}$ ratio is measured. ^{229}Th is itself unstable with a halflife of ~7 ka, which for laboratory purposes is essentially infinite. For the isotope measurement of ^{238}U enriched isotopes ^{233}U and/or ^{236}U are used. For U it is also possible to correct for the mass fractionation correction that occurs during the thermal ionisation process using the known ratios of either $^{235}\mathrm{U}/^{238}\mathrm{U}$ in the sample or $^{233}\mathrm{U}/^{236}\mathrm{U}$ from the spike. At ANU the former method is generally used. Note however that for Th there is only one ratio available ($^{229}\mathrm{Th}/^{230}\mathrm{Th}$) and hence it is not possible to correct for mass fractionation. The difficulty of producing a relatively long lived enriched isotope for the other systems (e.g. ^{233}Pa has a halflife of 28 days and ^{228}Ra 5.7 years) has made TIMS applications of these latter systems much more restricted.

Some Examples of TIMS Applications

The following examples taken for convenience from the RSES laboratory are given to illustrate various aspects of TIMS U-series.

(i) Duration of the Last Interglacial Using TIMS U-Series Dating of Corals

U-series dating of corals has been the main means by which the duration of the Last Interglacial has been estimated. Due to problems of coral diagenesis, a relatively wide range of ages has been published leading to a long-standing problem that is obviously important to resolve especially in the context of our current interglacial climate regime.

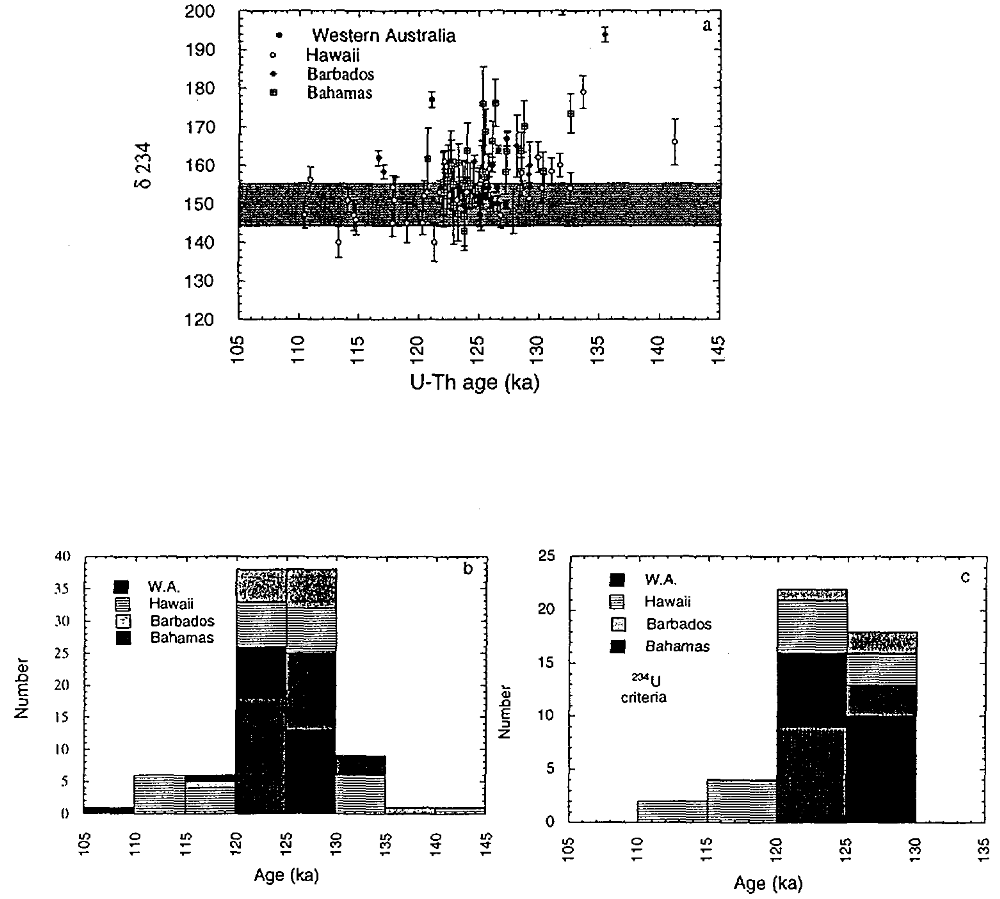

Figure 1 Illustrates the use of δ^{234}U criteria to recognise partial open system behaviour of U-series ages. Using the criteria of δ^{234}U = 149±5 the age range for the Last Interglacial is reduced from 145-105 ka to 130-110 ka. Closer scrutiny of the Hawaii data shows that some of the younger samples were not in situ. The current best estimate for the duration of the Last Interglacial is from 129 to 118 ka (Esat et al., 1999).

Seawater has δ^{234}U = 149 ± 2 per mil and due to the long residence time of uranium in the oceans this ratio is unlikely to have changed by more than ±5 per mil over the last 10^5 years. If coral samples have an initial δ^{234}U(T) ~ 149±5 (the shaded area in Figure 2 a below) then this is a good criteria to indicate that the age is 'reliable'. The precision of a TIMS δ^{234}U measurement for corals (~3 ppm U) is typically ±1 to 2 per mil, a marked improvement over counting methods (±10 to 20 per mil). The age uncertainty (95% CL) is typically ±1 ka which is needed to make useful statements about the duration of the period (~10 ka). Corals can also be dated using the δ^{234}U(T) ratio alone. After four half-lives of ^{234}U (~1 million years) a sample can be dated with a theoretical precision of ~10% (ie ~1,000±100 ka). Diagenesis is however a major limitation of this approach.

(ii) TIMS U-Series Dating of Speleothems and Growth Rate Determinations

Speleothems often have low initial Th, but also very low U concentration, many <0.1 ppm. Furthermore growth rates of cm per 10^{3-4} years are typical, so that larger samples tend to average large-time intervals. This is an especially important limitation in determining growth rates from which hydrological information is inferred. An example is shown in Figure 3 a given below. For TIMS it is possible to determine precise ages on <1 gram of sample at the ~0.1 ppm level (or less). The other use of TIMS U-series ages where greater precision is helpful is in relating the abundance of speleothems to climate stages. For the Last Interglacial to Glacial cycle this requires a precision better than ±5 ka as the Marine Isotope Stages (e.g. interstadials) are typically only separated by 10-15 ka. An example from Ayliffe et al, 1998) is given below (Figure 4).

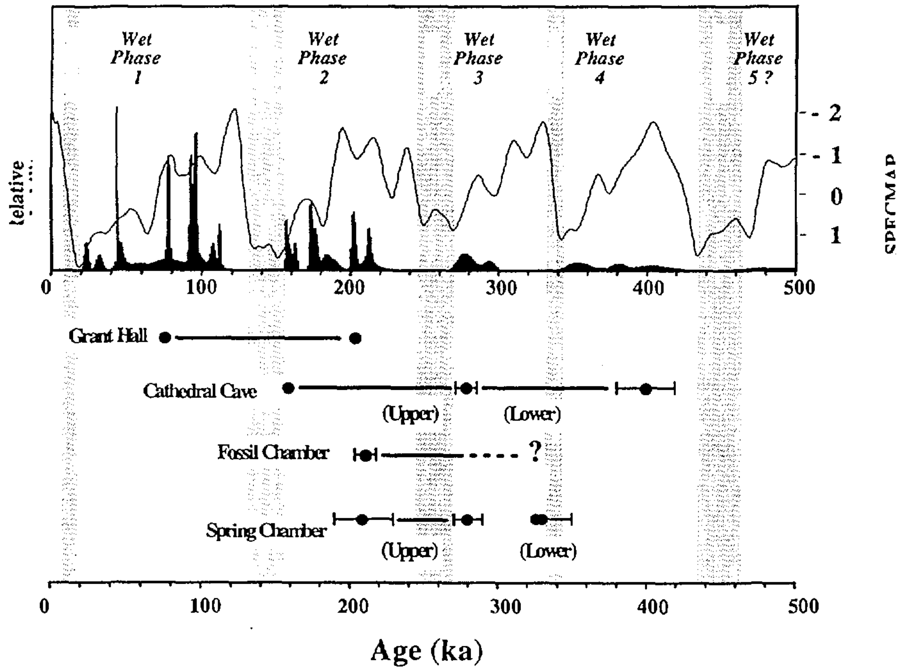

Figure 2. Ages of flowstones constraining the age of bone-bearing sedimentary units in the limestone caves at Naracoorte (large black dots) compared with (1) massive speleothem growth phases, (filled black curve) and (2) SPECMAP composite $\delta^{18}O$ curve for marine sediments. Error bars shown are ± 2σ. The filled black curve is an age-probability histogram of U/Th ages for 45 massive speleothem samples from caves in the Naracoorte region, and is thought to represent an increase in effective precipitation and soil CO_2 productivity.

(iii) U-Series Dating of *Genyornis* Shells

The shells of the now extinct megafuana *Genyornis* provide one of the few opportunities to place age constraints on the timing of this event/s. The difficulty however is that the shells fragments are typically 0.1-0.5 grams, have low U (0.1 ppm) and occasionally contain significant quantities of detrital ^{232}Th. Despite these limitations TIMS dating using the U-Th isochron approach (e.g. Bischoff and Fitzpatrick, 1991) has provided valuable information (Miller et al., 1999) and an example is shown below.

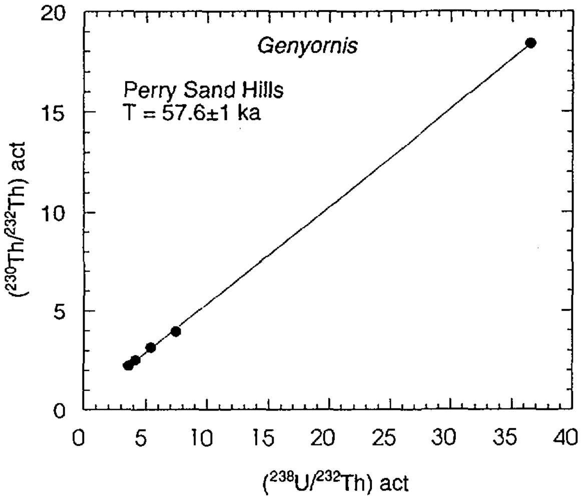

Figure 3. U-Th isochron diagram for *Genyornis* eggshell fragments from the same stratigraphic horizon in a Quaternary dune sequence in South Australia.

(iv) TIMS Dating of Open Systems?

It is sometimes assumed that because an analytical method is relatively precise and that analysis can be undertaken on small samples, that it is an inherently *accurate* result regardless of whether the sample has in fact been a closed system (ie not open to exchange of U or Th). In fact all that is achieved is a more precise measurement of the degree of open system behaviour. Whether this can be translated into a more reliable age constraint is debateable, but in any case it is necessary to use another system such as ESR so that some modelling of the extent of open system behaviour can be undertaken with several independent parameters (e.g. Grun and McDermott, 1994). In some systems where redistribution of U ands Th can be shown to occur on a restricted spatial scale, a closed system may in fact be better approximated by a larger sample size. Demonstrating the scales over which redistribution of U and Th occurs is itself a challenging task and fraught with uncertainties and not generally recommended for TIMS applications.

References

Ayliffe L., Marianelli P., Moriarty K.C., Wells R.T., McCulloch M.T., Mortimer G.E. and Hellstrom J.C., (1998) Geology, 26, 147-150.

Bischoff J.L and Fitsgerald J.A. (1991 Geochim Cosmo Chim Acta, 55, 543-554.

Chen J.H., Edwards R.L. and Wasserburg G.J. (1986) Earth Planet Science Letters, 80, 241-251.

Dickin A.P. (1995) Radiogenic Isotope Geology. Cambridge University Press.

Edwards R.L Chen J.H. and Wasserburg G.J. (1987) Earth Planet Science Letters, 81, 175-192.

Esat T.M., McCulloch M.T., Chappell J., Pillans B., and Omura A. (1999) Science, 283, 199-202.

Grun R. and McDermott, F. (1994). Ancient TL. 14, 21-25.

Miller G.H., Magee J.W., Johnson B.J., Fogel M.L., Spooner N.A., McCulloch M.T. and Ayliffe L.K. (1999) Science, 283, 205-208.

McCulloch M.T., Tudhope A.W., Esat T.M., Mortimer G.E , Chappell J., Pillans B., Chivas A.R. and Omura A. (1999) Science, 283, 202-204.