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## URANIUM-SERIES DATING OF SPELEOTHEMS: CURRENT TECHNIQUES, LIMITS, & APPLICATIONS

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### 1. ABSTRACT

Carbonate speleothems that contain ppb-ppm levels of uranium can be dated by the  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  and  $^{235}\text{U}$ - $^{231}\text{Pa}$  disequilibrium techniques. Accurate ages are possible if the initial concentrations of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  are well constrained and if the system has remained closed to post-depositional exchange of uranium, thorium, and protactinium. An estimate of the plausible range of initial  $^{230}\text{Th}/^{232}\text{Th}$  values combined with the measured  $^{232}\text{Th}/^{238}\text{U}$  ratio reveal, to first order, whether initial  $^{230}\text{Th}$  is significant. If significant, initial  $^{230}\text{Th}$  can be constrained by monitoring  $^{232}\text{Th}$  and employing isochron techniques to closely estimate the value of the contaminant  $^{230}\text{Th}/^{232}\text{Th}$  ratio. The sensitivity of the age error to uncertainties in the initial  $^{230}\text{Th}/^{232}\text{Th}$  ratio decreases with increasing U concentration, increasing age, and decreasing detrital contamination. For many speleothems, particularly those composed of nearly pure calcite, initial  $^{230}\text{Th}$  may be trivial. Because Pa is more soluble than Th,  $^{232}\text{Th}$  is a poor analog for  $^{231}\text{Pa}$ . Therefore, initial  $^{231}\text{Pa}$  tends to be more significant than initial  $^{230}\text{Th}$  for young samples, although this problem becomes less significant or even insignificant with increasing age. Closed-system behavior can be judged by petrographic considerations, stratigraphic ordering of ages, and  $^{230}\text{Th}$ - $^{231}\text{Pa}$  concordance. Thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) offer significant improvements in counting efficiency and sample throughput compared to traditional decay-counting techniques. For  $\sim 100$  mg samples containing  $\sim 1.0$  ppm  $^{238}\text{U}$ , best-scenario  $^{230}\text{Th}$  age errors, based on the analytical errors ( $2\sigma$ ) of current TIMS and ICP-MS techniques, are approximately:  $500 \pm 6$  yrs,  $10,000 \pm 40$  yrs,  $50,000 \pm 180$  yrs,  $120,000 \pm 500$  yrs, and  $500,000 \pm 15,000$  yrs. Materials as young as tens of years and older than 600,000 years are potentially dateable by the  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  method.

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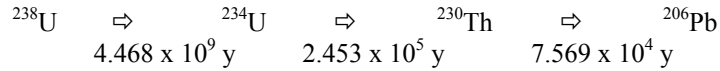
## 2. INTRODUCTION

The principles of uranium-series dating, which include  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  and  $^{235}\text{U}$ - $^{231}\text{Pa}$  disequilibrium dating, have been known since the early part of the last century (Bateman, 1910), shortly after the discovery of radioactivity (Becquerel, 1896; Curie, 1898) and actually before the discovery of isotopes (Thomson, 1914). However, uranium-series dating was not done prior to the 1950's because of problems with measuring concentrations of rare uranium-series isotopes. The first U-Th measurements were made on corals (Barnes et al., 1956), using decay-counting techniques that would become the standard for the next three decades. Although early applications of U-Th-Pa dating included measurements on marine sediment cores (Rosholt et al., 1961) and cave calcites (Rosholt and Antal, 1962; Cherdyntsev et al., 1965), much of the focus was on fossil corals, whose age provided estimates on the timing of past sea levels (e.g. Broecker et al., 1968; Ku, 1968). The routine application of  $^{230}\text{Th}$  dating to speleothems gained prominence in the early 1970's (Ford et al., 1972; Thompson et al., 1974; Harmon et al., 1975), which provided access to a new source of paleoenvironmental information. Dating capabilities advanced in the late 1980's with the development of thermal ionization mass spectrometric (TIMS) techniques for measuring  $^{234}\text{U}$  (Chen et al., 1986) and  $^{230}\text{Th}$  (Edwards et al., 1987). These techniques improved the precision with which  $^{230}\text{Th}$  ages could be determined, decreased sample size requirements, and extended the range of  $^{230}\text{Th}$  dating to both younger and older times. The first mass-spectrometric U-Th measurements on speleothems were made by Li et al. (1989). Since the late 1980's, there have been additional improvements in uranium and thorium isotopic measurements, including measurements made by inductively coupled plasma mass spectrometry (ICP-MS) using instruments with sector magnets (Luo et al., 1997). Another recent advance was the development of TIMS techniques for measuring  $^{231}\text{Pa}$  (Pickett et al., 1994) and the application of these methods to the dating of carbonates (Edwards et al., 1997). The utility of  $^{231}\text{Pa}$  dating lies in its combination with  $^{230}\text{Th}$  dating as a test for age concordance and closed-system behavior (Cheng et al., 1998). By applying these techniques to appropriate materials (e.g. inorganic carbonates, coralline aragonite), one can obtain precise, and potentially accurate ages over the past half million years. These methods promise to place the chronology of a wide range of late Quaternary events on a precise, calendrical time scale.

The extensive number of published  $^{230}\text{Th}$  dates on speleothems has made it clear that well chosen speleothem sub-samples are nearly ideal candidates for  $^{230}\text{Th}$  dating (Schwarcz, 1986; Gascoyne, 1992a). In this regard, three fundamental issues are (1) the precision with which  $^{230}\text{Th}$  ages can be determined, (2) the level of initial  $^{230}\text{Th}$  in samples and methods of correcting for initial  $^{230}\text{Th}$ , and (3) the degree to which diagenesis may affect the accuracy of the ages and methods for detecting diagenesis. The purpose of this paper is to review these three issues in light of current techniques and analytical capabilities. In addition to reviewing current capabilities, we present some of the first high-precision TIMS  $^{231}\text{Pa}$  data on speleothems and some of the first ICP-MS  $^{230}\text{Th}$  data on speleothems. We elaborate on the issue of initial  $^{230}\text{Th}$  using a series of examples and simple isochron techniques. All errors quoted in this paper are given as two standard deviations of the mean ( $2\sigma$ ), including errors on half-life values, which may differ from the original reference. All age determinations reported in this paper are given in years before present.

### 3. BACKGROUND

The activity, or the number of disintegrations per unit time ( $dN/dT$ ), of any radioactive nuclide is equal to  $N\lambda$ , where  $N$  is the number of atoms,  $\lambda$  is the decay constant for that nuclide, and  $T$  is time. The half-life of the nuclide is equal to  $(\ln 2)/\lambda$ .  $^{234}\text{U}$  and  $^{230}\text{Th}$  are the longest-lived intermediate daughters in a decay series that starts with  $^{238}\text{U}$  and ends with stable  $^{206}\text{Pb}$ . That series with only the nuclides pertinent to this discussion and their respective half-lives is:



The half-life of  $^{238}\text{U}$  is four orders of magnitude greater than any of the intermediate daughters. Therefore, any closed system, regardless of the initial state, will approach a state of ‘‘secular equilibrium’’ such that the activities of all the intermediate daughters are the same and are equal to the  $^{238}\text{U}$  activity (Bateman, 1910). External processes that fractionate nuclides within the decay chain disrupt the state of secular equilibrium. The subsequent growth or decay of the intermediate nuclides back towards equilibrium with  $^{238}\text{U}$  can be used to date the fractionation event (see Ivanovich et al., 1992).

Uranium-thorium dating of speleothems is possible because of the extreme fractionation of Th from U in ground water. Uranium is easily oxidized to the  $\text{U}^{6+}$  state and is soluble as the  $\text{UO}_2^{2+}$  (uranyl) ion, and as various uranyl carbonate complexes, but Th is locked into the  $\text{Th}^{4+}$  state and has an extremely low solubility (Langmuir, 1978; Gascoyne, 1992b). Surface waters, therefore, have very low  $^{230}\text{Th}/^{238}\text{U}$  ratios. This condition is examined more fully in a subsequent section, but for the moment we can assume that a growing speleothem includes U into its crystal lattice but incorporates negligible  $^{230}\text{Th}$ . If the crystal lattice remains a closed system with respect to the loss or gain of U and Th, the equations for radioactive production and decay of  $^{238}\text{U}$ ,  $^{234}\text{U}$ , and  $^{230}\text{Th}$  govern the geochemical evolution of the system as follows:

$$\left[ \frac{^{230}\text{Th}}{^{238}\text{U}} \right] = 1 - e^{-\lambda_{230}T} + \left( \frac{\delta^{234}\text{U}_{(m)}}{1000} \right) \left( \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left( 1 - e^{(\lambda_{234} - \lambda_{230})T} \right) \quad (1)$$

(modified from Kaufman and Broecker, 1965), and

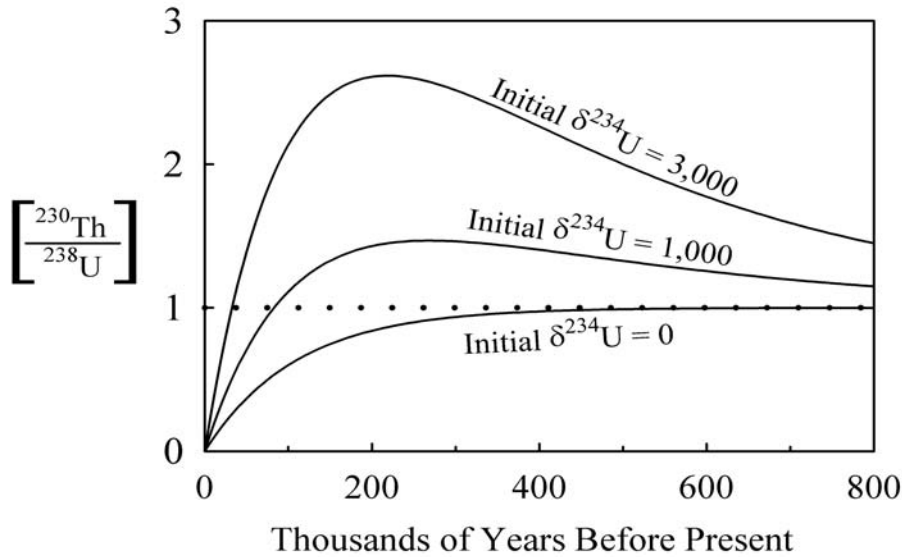
$$\delta^{234}\text{U}_{(t)} = \delta^{234}\text{U}_{(m)} e^{\lambda_{234}T} \quad (2)$$

(modified from Edwards et al., 1987),

where the  $\lambda$ 's denote the decay constants,  $[^{230}\text{Th}/^{238}\text{U}]$  denotes the  $^{230}\text{Th}/^{238}\text{U}$  activity ratio,  $\delta^{234}\text{U}_{(m)} = ([^{234}\text{U}/^{238}\text{U}] - 1) * 1000$ , and  $T$  is the age. Equation (1) shows that the age can be calculated if  $[^{230}\text{Th}/^{238}\text{U}]$  and  $\delta^{234}\text{U}_{(m)}$  can be measured and the decay constants are known. Equation (2) relates the measured  $\delta^{234}\text{U}$  value ( $\delta^{234}\text{U}_{(m)}$ ) to the initial state ( $\delta^{234}\text{U}_{(t)}$ ) when the system was isolated with  $^{230}\text{Th} = 0$ . Figure 1 shows  $[^{230}\text{Th}/^{238}\text{U}]$  plotted as a function of  $T$  and contoured in units of  $\delta^{234}\text{U}_{(t)}$ . This shows that as  $T$  becomes large,  $[^{230}\text{Th}/^{238}\text{U}]$  approaches unity, and that at some point between 400,000 and 800,000 years an age limit to the technique is reached. The

exact limit depends on several factors, including  $\delta^{234}\text{U}_{(i)}$  and the precision of the isotopic measurements.

Reported uncertainties in  $T$  are introduced primarily by uncertainties in the measured values for  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$  and  $\delta^{234}\text{U}_{(m)}$ , but also depend on  $T$  itself, because the slope  $d[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]/dT$ , generally decreases with increasing  $T$ , approaching a slope of zero near secular equilibrium (Fig. 1). The smallest fractional age errors are obtained for materials several thousands to several tens of thousands of years old. Samples of this age are old enough to have enough  $^{230}\text{Th}$  atoms for a high-precision analysis, yet are young enough to fall on the initial high-slope part of the  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$  evolution curve (Fig. 1). For example,  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$  and  $\delta^{234}\text{U}_{(m)}$  measured to the 2.0-3.0 ‰ level yield the approximate age errors:  $\pm 40$  yrs at 10,000 yrs,  $\pm 200$  yrs at 50,000 yrs,  $\pm 1,200$  yrs at 200,000 yrs, and  $\pm 15,000$  yrs at 500,000 yrs.



**Figure 1.** This shows the change in the  $^{230}\text{Th}/^{238}\text{U}$  activity ratio ( $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ ) with time for different initial  $\delta^{234}$  values ( $\delta^{234}\text{U}_{(i)}$ ) and is calculated assuming a closed system and initial  $^{230}\text{Th} = 0$  (Eqs. (1) and (2)). For those cases where  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}] > 1$ , a unique combination of  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$  and  $\delta^{234}\text{U}_{(m)}$  defines the age  $T$ . Initial  $\delta^{234}\text{U}$  values of 0 to 3,000 are common for many of the speleothems discussed in the paper.

The analytical errors in  $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$  and  $\delta^{234}\text{U}_{(m)}$  generally follow counting statistics, such that the fractional error is inversely proportional to the square root of the number of counts per analysis. At the  $2\sigma$  level:

$$2\sigma = \frac{2}{\sqrt{\text{total counts}}} \quad (3)$$

Thus, precision at the 2 % level requires at least  $10^4$  counts, whereas precision at the 2 ‰ level requires at least  $10^6$  counts. Because of their relatively long half-lives, decay counting is on the order of  $10^4$  times less efficient for measuring the abundances of  $^{234}\text{U}$  and  $^{230}\text{Th}$  than is mass spectrometry for the same sample size (Chen et al, 1992).

In practice, measured isotope ratios are reported as mean and standard error. For analyses with stable ion-beam intensities, the “within-run” statistical errors are typically similar to those predicted by counting statistics. Uncertainties in sample weight, spike weight, spike concentration, chemical blanks, and filament blanks are typically small compared to the analytical uncertainty, but are also included in the error propagation through Eq. (1).

Accurate values for half-lives are clearly required for accurate age calculations. Table 1 lists the nuclides discussed in this paper, their half-lives, decay constants, and sources. Of the three pertinent nuclides used in  $^{230}\text{Th}$  dating, the fractional error in the half-life of  $^{238}\text{U}$ ,  $4.4683 \pm 0.0048 \times 10^9$  y (Jaffey et al., 1971), is the smallest. For  $^{234}\text{U}$ , De Bievre et al. (1971) determined a half-life of  $244,600 \pm 730$  years and Lounsbury and Durham (1971) determined a value of  $244,400 \pm 1,200$  years. A commonly used value in geochronology is the mean value: 244,500 years. More recently, Holden (1989) reviewed the available literature on  $^{234}\text{U}$  and proposed a weighted average value of  $245,500 \pm 1,000$  years. A commonly used value for  $^{230}\text{Th}$  is  $75,380 \pm 590$  years (Meadows et al., 1980). Most recently Cheng et al. (2000) re-determined the half-lives of  $^{234}\text{U}$  and  $^{230}\text{Th}$  to be  $245,250 \pm 490$  years and  $75,690 \pm 230$  years. These new values are within error of the previously used values but have smaller errors. We have therefore adopted the Cheng et al. (2000) half-lives and recommend universal use of these values.

It is important to note that uncertainties in decay constants are *not* typically propagated through Eq. (1). This is permissible when comparing ages determined by the same dating technique because any inaccuracy due to decay constants will affect the ages in the same sense. However, when comparing ages determined by different chronometers, it is important to consider errors in decay constants (Renne et al., 1998).

**Table 1.** Half-lives and decay constants and recommended values\*

| Nuclide           | Half-life ( $t_{1/2}$ ) <sup>a</sup> | Decay constant ( $\lambda$ )              | Source                     |
|-------------------|--------------------------------------|---|----------------------------|
| $^{238}\text{U}$  | $4.4683 \pm 0.0048 \times 10^9$ y    | $1.55125 \times 10^{-10}$ y <sup>-1</sup> | Jaffey et al., 1971*       |
| $^{235}\text{U}$  | $7.0381 \pm 0.0096 \times 10^8$ y    | $9.8485 \times 10^{-10}$ y <sup>-1</sup>  | Jaffey et al., 1971*       |
| $^{234}\text{U}$  | $247,500 \pm 3,200$ y                | $2.8006 \times 10^{-6}$ y <sup>-1</sup>   | Fleming et al., 1952       |
| $^{234}\text{U}$  | $244,600 \pm 730$ y                  | $2.8338 \times 10^{-6}$ y <sup>-1</sup>   | De Bievre et al., 1971     |
| $^{234}\text{U}$  | $244,400 \pm 1,200$ y                | $2.8361 \times 10^{-6}$ y <sup>-1</sup>   | Lounsbury & Durham, 1971   |
| $^{234}\text{U}$  | $245,500 \pm 1,000$ y                | $2.8234 \times 10^{-6}$ y <sup>-1</sup>   | Holden, 1989               |
| $^{234}\text{U}$  | $245,250 \pm 490$ y                  | $2.8263 \times 10^{-6}$ y <sup>-1</sup>   | Cheng et al., 2000 *       |
| $^{230}\text{Th}$ | $75,200 \pm 3,200$ y                 | $9.2174 \times 10^{-6}$ y <sup>-1</sup>   | Attree et al., 1961        |
| $^{230}\text{Th}$ | $75,381 \pm 590$ y                   | $9.1953 \times 10^{-6}$ y <sup>-1</sup>   | Meadows et al., 1980       |
| $^{230}\text{Th}$ | $75,690 \pm 230$ y                   | $9.1577 \times 10^{-6}$ y <sup>-1</sup>   | Cheng et al., 2000 *       |
| $^{232}\text{Th}$ | $1.401 \times 10^{10}$ y             | $4.9475 \times 10^{-11}$ y <sup>-1</sup>  | LeRoux & Glendenin, 1963 * |
| $^{231}\text{Pa}$ | $32,760 \pm 220$ y                   | $2.1158 \times 10^{-5}$ y <sup>-1</sup>   | Robert et al., 1969 *      |

\* These are the values used in our calculations and the values we recommend.

<sup>a</sup> All errors are quoted at the  $2\sigma$  level; this may differ from the original source.

$^{231}\text{Pa}$  is the only long-lived intermediate daughter ( $t_{1/2} = 32,760$  years) in the decay series starting with  $^{235}\text{U}$  and ending with stable  $^{207}\text{Pb}$ .  $^{235}\text{U}$ - $^{231}\text{Pa}$  dating is analogous to  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  dating, but the system only involves two nuclides:

$$\left[ \frac{^{231}\text{Pa}}{^{235}\text{U}} \right] = 1 - e^{-\lambda_{231}T} \quad (4)$$

For a closed-system material at secular equilibrium, the  $^{230}\text{Th}/^{231}\text{Pa}$  atomic ratio is equal to  $(\lambda_{238} * \lambda_{231} * 137.88) / (\lambda_{235} * \lambda_{230}) = 50.9$ , where 137.88 is the present-day value for the natural  $^{238}\text{U}/^{235}\text{U}$  atomic ratio (Steiger and Jäger, 1977). Because  $^{231}\text{Pa}$  is 50 times less abundant than  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$  dating is inherently less precise than  $^{230}\text{Th}$  dating, and because the half-life of  $^{231}\text{Pa}$  is roughly half that of  $^{230}\text{Th}$ , the upper limit to  $^{231}\text{Pa}$  dating is approximately 250,000 years given current capabilities (Edwards et al., 1997).

The discussion thus far has not been restricted to speleothems. Any material that (1) forms with appreciable U, (2) forms with negligible Th and Pa, and (3) remains a closed system, is potentially datable by U-Th-Pa techniques. Despite such simple criteria, few natural materials meet all three conditions. Corals commonly satisfy criteria (1) and (2) exceedingly well but become increasingly likely to violate criterion (3) with increasing age, because coralline aragonite is thermodynamically metastable and is typically highly porous. Materials such as bone, teeth, and mollusk shells also violate criterion (3) because they exclude U while the organism is alive, but then take up U after death (Kaufman et al., 1971; Szabo, 1979). Dense calcite speleothems, on the other hand, are excellent candidates for true closed-system behavior and accurate age dating.

#### 4. SAMPLING CONSIDERATIONS

For  $^{230}\text{Th}$  dating by mass spectrometry, the factors that determine a given level of precision include (1) U concentration, (2)  $\delta^{234}\text{U}_{(t)}$ , (3) sample age, (4) chemical yield (generally > 90%), and (5) ionization/transmission efficiency. For  $^{235}\text{U}$ - $^{231}\text{Pa}$  dating,  $\delta^{234}\text{U}_{(t)}$  is not a factor, and for decay counting, the decay rates of the pertinent nuclides are important. The ionization/transmission efficiency refers to the number of atoms actually detected versus the number of atoms introduced to the system, a variable number dependent on technique but typically in the range of  $10^{-3}$  to  $10^{-5}$  (Chen et al., 1992).

Suppose we seek to measure  $^{234}\text{U}$  with a precision of 2 ‰ ( $2\sigma$ ). Counting statistics predicts a requirement of at least  $10^6$  counts, and assuming a typical ionization efficiency of  $10^{-4}$ , such precision would require  $10^{10}$  atoms of  $^{234}\text{U}$ . Assuming that the sample contains 1 ppm  $^{238}\text{U}$ , the chemical yield is 100 %, and that for simplicity  $^{234}\text{U}$  and  $^{238}\text{U}$  are in secular equilibrium, i.e.  $\delta^{234}\text{U} = 0$  and the  $^{234}\text{U}/^{238}\text{U}$  atomic ratio =  $\lambda_{238}/\lambda_{234}$ . Given these constraints the sample size required for a 2 ‰  $^{234}\text{U}$  analysis is:

$$\text{sample size (g)} = \frac{(10^{10} \text{ atoms } ^{234}\text{U}) \left( 238.051 \frac{\text{g } ^{238}\text{U}}{\text{mole } ^{238}\text{U}} \right)}{\left( 10^{-6} \frac{\text{g } ^{238}\text{U}}{\text{g calcite}} \right) \left( \frac{\lambda_{238}}{\lambda_{234}} \right) \left( 6.022 \times 10^{23} \frac{\text{atoms}}{\text{mole}} \right)} = 0.72 \text{ g calcite} \quad (5)$$

In speleothem and other inorganic calcite work, both sample size and precision are related to the error in age (Ludwig et al., 1992). Deposition rates of speleothems are often low, so that large sub-samples will integrate large time intervals and introduce error in age if uranium concentrations and growth rates are not constant in

that interval. On the other hand, large sub-samples contain more  $^{230}\text{Th}$  atoms and therefore result in higher precision measurements. Thus, there is a tradeoff between spatial resolution in sub-sampling (for which small sub-samples are ideal) and precision in  $^{230}\text{Th}$  age (for which large samples are ideal). The optimal strategy is to balance sampling resolution and analytical precision to obtain the most scientifically useful result.

Improvements in the ionization/transmission efficiency directly result in improved counting statistics and/or smaller sample sizes. Such improvements generally benefit all of the sub-disciplines that utilize isotopic measurements, but hold especially important practical implications for dating slow-growth speleothems.

## 5. EXPERIMENTAL METHODS

### 5.1. Sampling

Sub-samples for dating are typically obtained by either sawing or milling. Milling is generally less destructive to the formation. For high-resolution work, milling from polished surfaces using a hand-held or computerized dental drill offers excellent control. Particularly when the layering is not horizontally uniform, milling allows the tracing of specific layers in a manner that is not possible by sawing. We typically use carbide dental burrs that range in size from 0.5 to 1.2 mm in diameter. Sub-samples smaller than  $\sim 300$  mg can be milled in approximately 20 to 40 minutes. In preparation for sampling, the polished speleothem surface is cleaned with deionized water, and the dental burr is turned in 0.1N HCl and then methanol. The milled powders are gently scraped from the surface of the speleothem onto weighing paper and are then transferred to a pre-weighed polyethylene vial and weighed. For those cases where solid sub-samples are preferable to powders, slow-speed saws and wire saws provide reasonably precise control.

### 5.2. Chemical Separation of Uranium and Thorium

The basic chemical procedure is similar to that described for coral work by Edwards et al., (1987), although the smaller sub-gram sample sizes of the speleothem analyses described here generally involve reduced reagent volumes compared to that described in the reference. Sub-samples are transferred from the polyethylene vials to pre-weighed 30 ml Teflon vials and are re-weighed. The samples are covered with  $\sim 5$  ml of deionized water and are then dissolved by incrementally adding small amounts of 7N  $\text{HNO}_3$ . For clean, powdered samples it is unusual to observe any acid-insoluble residue. For samples with detrital impurities, acid-insoluble residue may remain after nitric acid dissolution. Although in earlier studies the residue was commonly discarded, recent studies have demonstrated that significant and unpredictable exchange of U and Th between the residues and the leachates can take place and render the results inaccurate (Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991). For this reason, the most effective procedure is to completely dissolve the residue with concentrated HF-HCl- $\text{HClO}_4$ . Isochron techniques, to be discussed in a subsequent section, can be used to estimate the U and Th contribution of the detrital phase for those samples with significant contamination.

Once dissolved, the samples are spiked with a mixed  $^{229}\text{Th}$ - $^{233}\text{U}$ - $^{236}\text{U}$  tracer of known concentration and isotopic composition. Organics are destroyed by the addition of 3-6 drops of concentrated  $\text{HClO}_4$ , and the sample is dried on a hot plate. While still hot, the residue is re-dissolved in  $\sim 1\text{N}$  HCl, and  $\sim 0.3$  mg of Fe in

chloride solution is added. The U and Th are co-precipitated with Fe by dropwise addition of concentrated  $\text{NH}_4\text{OH}$ . The mixture is centrifuged and the supernate discarded. The residue is then rinsed 2-3 times, dissolved in 14N  $\text{HNO}_3$ , dried and re-dissolved twice in 14N  $\text{HNO}_3$ , then dried and dissolved in  $\sim 0.5$  ml 7N  $\text{HNO}_3$ . The solution is loaded on an anion exchange column (SPECTRUM Spectra Gel Ion Exchange 1 X 8, chloride form, particle size = 75-150  $\mu\text{m}$ , mesh size = 100-200) with a volume of 0.5 ml. Iron is eluted using 1.5 column volumes of 7N  $\text{HNO}_3$ , thorium is eluted using 2 column volumes of 8N  $\text{HCl}$ , and uranium is eluted using 4 column volumes of water. The U and Th fractions are dried and generally contain only trace amounts of Fe (just visible). Rarely, significant amounts of Fe may require an additional clean-up column, but unless this is the case, the samples are ready either for loading onto rhenium filaments for TIMS analysis or dissolution in a weak nitric acid solution for ICP-MS analysis.

### 5.3. Instrumental Procedure

Measurements were made at the Minnesota Isotope Lab by TIMS on a Finnigan-MAT 262 instrument, equipped with ion-counting capabilities and a retarding potential quadrupole. Uranium is run using the double-filament technique with an evaporation-filament current of 0.3 to 1.5 amps and an ionization-filament current of 4.0 to 5.3 amps (corresponding to ionization-filament temperatures of 1600-1850  $^\circ\text{C}$ ). Runs typically last 1-2 hours. Because of dead time and intensity bias constraints on the multipliers, ion currents are not allowed to exceed 200,000 counts per second (cps) for  $^{235}\text{U}$ . Ionization efficiencies are typically in the range of  $10^{-4}$  to  $5 \times 10^{-4}$ . Thorium is loaded with colloidal graphite on a single rhenium filament and run at temperatures of 1500-1900  $^\circ\text{C}$  for 1-2 hours. Throughout the course of a Th analysis, both temperature and ion beams increase as the graphite burns away. Typical loads of  $10^{11}$  atoms of  $^{229}\text{Th}$  yield ion currents that range from  $\sim 500$ -2,000 cps at the beginning of a run to  $\sim 10,000$ -40,000 cps near the end of a run, resulting in overall ionization efficiencies that range from  $10^{-4}$  to  $10^{-3}$ .

Measurements made at the Minnesota Isotope Lab by ICP-MS were done on a Finnigan-MAT *ELEMENT*, equipped with a double-focusing sector field/energy filter of reversed Nier-Johnson geometry, and a single electron multiplier. Shen et al. (2001) provide details on the instrumental modifications and procedures. Uranium samples are diluted with 0.1N  $\text{HNO}_3$  to a volume of 1.0 ml and run for  $\sim 20$  minutes at a flow rate of  $\sim 50$   $\mu\text{l}/\text{min}$  using a microconcentric desolvation nebulizer (Cetac MCN 6000). As the nebulized and dried sample is introduced into a plasma, ionization efficiencies are extremely high. However, in this sort of instrument significant losses occur during transmission of the plasma to the high vacuum in the main part of the mass spectrometer. A combined ionization/transmission efficiency of  $\sim 3 \times 10^{-3}$  has been attained for uranium. Thorium samples are diluted with 0.1N  $\text{HNO}_3$  +  $\sim 0.01$ N  $\text{HF}$  to a volume of 0.5 ml and run for  $\sim 10$  minutes at a flow rate of  $\sim 50$   $\mu\text{l}/\text{min}$ . A combined ionization/transmission efficiency of  $\sim 2 \times 10^{-3}$  has been attained for thorium. The implications of the shorter run times and the improved ionization/transmission efficiency of ICP-MS method are significant and are discussed in a subsequent section.

## 6. INITIAL $^{230}\text{Th}$ AND $^{231}\text{Pa}$

The derivations of the  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  and  $^{235}\text{U}$ - $^{231}\text{Pa}$  age equations assume zero initial contents of the daughter isotopes  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ . This assumption is generally



reasonable, because  $\text{Th}^{4+}$  and  $\text{Pa}^{5+}$  (rarely  $\text{Pa}^{4+}$ ) have low solubilities in surface waters. For example, the surface sea water  $^{230}\text{Th}/^{238}\text{U}$  atomic ratio is  $\sim 3 \times 10^{-10}$  and the  $^{231}\text{Pa}/^{235}\text{U}$  ratio is  $\sim 3 \times 10^{-9}$  (Chen et al., 1986 for U; Moran et al., 1995 for  $^{230}\text{Th}$ ; Edmonds et al., 1998 for  $^{231}\text{Pa}$ ). By dating recent corals with low  $^{232}\text{Th}$  concentrations, and whose age was known independently by band-counting, Edwards (1988) demonstrated that the maximum amount of initial  $^{230}\text{Th}$  that could have been incorporated during growth was equivalent to the amount of  $^{230}\text{Th}$  produced by radioactive decay in 3-6 years. A 6-year offset is comparable to the  $2\sigma$  analytical errors for a 500-year-old coral (1 g sample, 3 ppm  $^{238}\text{U}$ ). The age error is  $\sim \pm 3$  years for a 20-year-old coral and  $\sim \pm 20$  years at 4,000 years. Thus, for clean corals older than 20-500 years, initial  $^{230}\text{Th}$  may be negligible.

Although  $\text{Th}^{4+}$  and  $\text{Pa}^{5+}$  have low solubilities, they strongly adsorb to surfaces and may be readily introduced into a growing carbonate matrix with detrital materials such as clays. The initial  $^{230}\text{Th}$  associated with such a detrital component is the main problem with dating "dirty" speleothems and other carbonates. Also, the behavior of  $\text{Th}^{4+}$  and  $\text{Pa}^{5+}$  in karst ground waters is less studied than in ocean surface waters. It is possible that  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  could be carried in solution in colloidal phases (Short et al., 1988; Dearlove et al., 1991), attached to organic molecules (Langmuir and Herman, 1980; Gaffney et al., 1992), or in carbonate complexes (Dervin and Faucherre, 1973a,b; Joao et al., 1987). Thus, multiple sources may potentially contribute variable amounts of initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  to a developing speleothem. Whitehead et al. (1999) suggested that for some young New Zealand speleothems, initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  may account for age offsets from the true age that are larger than 2,000 years, clearly a significant issue.

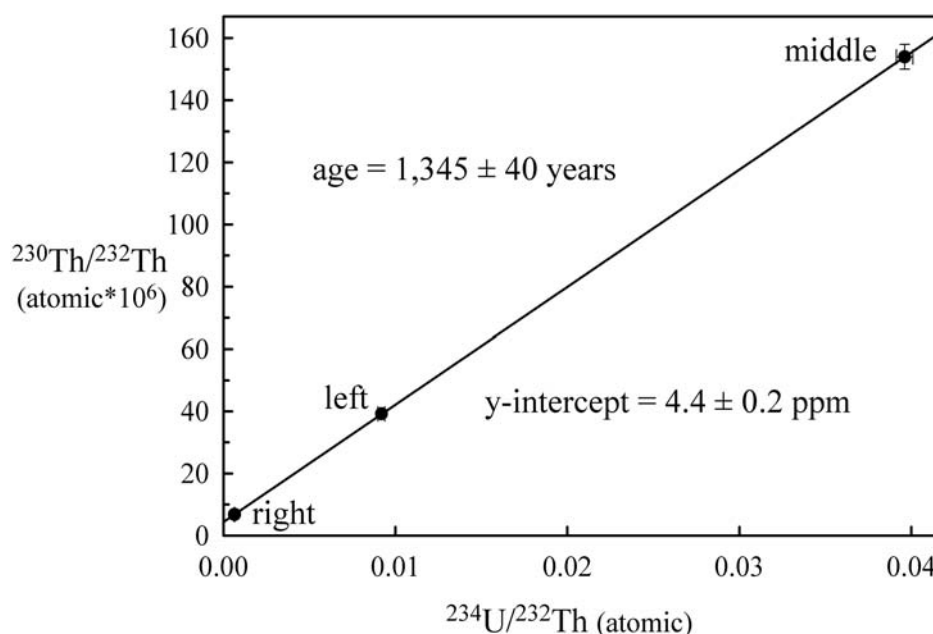
The first step in evaluating initial  $^{230}\text{Th}$  is to measure the  $^{230}\text{Th}/^{232}\text{Th}$  ratio.  $^{232}\text{Th}$  is an abundant radioactive, non-radiogenic isotope with a half-life of  $1.401 \times 10^{10}$  years and is measured during a typical thorium analysis. Because  $^{230}\text{Th}$  and  $^{232}\text{Th}$  are chemically equivalent,  $^{232}\text{Th}$  is a potential monitor of the initial  $^{230}\text{Th}$  content of a growing speleothem if the  $^{230}\text{Th}/^{232}\text{Th}$  ratio of the contamination can be determined.

The  $^{230}\text{Th}/^{232}\text{Th}$  ratio of the contamination can be estimated using an isochron technique (Ludwig, 1993; Kaufman, 1993; Ludwig and Titterton, 1994). The technique depends on the ability to obtain sub-samples of the same age (i.e. carefully milling within the boundaries of a given stratigraphic layer) that differ in  $^{232}\text{Th}/^{238}\text{U}$  values, which generally correlate with detrital content. Many stalagmites lend themselves to such sampling because they are commonly cleanest near the center of a given layer and are dirtier near the edges, presumably because the falling drip flushes particulates away from the point of impact.

The importance of the total sample dissolution technique mentioned earlier becomes apparent because the detrital phase contains Th and U that is both lattice-bound and adsorbed but in unknown proportions. Bischoff and Fitzpatrick (1991) demonstrated that it is not possible to quantitatively separate these two components by selective leaching. Also,  $^{230}\text{Th}$  released from the carbonate phase during acid dissolution may unpredictably adsorb to detrital particles if they are present. For these reasons, both Bischoff and Fitzpatrick (1991) and Luo and Ku (1991) independently concluded that isochron techniques that employ total sample dissolution give the most reliable results.

The isochrons that we depict in this paper are simple two-dimensional isochrons. A rigorous treatment of isochron techniques requires the use of three-dimensional isochrons (e.g. Ludwig and Titterton, 1994). However, for our particular examples, variation in the  $^{234}\text{U}/^{238}\text{U}$  ratio among sub-samples used to construct each isochron is negligible. Therefore, two-dimensional isochrons are advantageous in their simplicity in illustrating the concepts discussed here. Such a two-dimensional,

three-point isochron using total sample dissolution for a stalagmite from Spring Valley Caverns, Minnesota is shown in Fig. 2 (data in Table 2). The regression y-intercept value of 4.4 ppm (the atomic  $^{230}\text{Th}/^{232}\text{Th}$  ratio \*  $10^6$ ) is the present-day  $^{230}\text{Th}/^{232}\text{Th}$  ratio of the contamination. The excellent fit of a straight line to the three points in Fig. 2 is consistent with initial  $^{230}\text{Th}$  being dominated by a single component that has a constant  $^{230}\text{Th}/^{232}\text{Th}$  value.



**Figure 2.** A two-dimensional isochron diagram for stalagmite SVC-98-3.B from Spring Valley Caverns, Minnesota (the third dimension, not shown here, would be  $^{234}\text{U}/^{238}\text{U}$ ). The three sub-samples, labeled left, middle, and right, are horizontally spaced 1-1.5 cm from one another within the same stratigraphic layer and are from locations with visually obvious differences in detrital content. Sub-sample widths are about 1.0 mm. The regression y-intercept value of  $4.4 \pm 0.2$  ppm represents the present-day  $^{230}\text{Th}/^{232}\text{Th}$  ratio of the contamination. The true  $^{230}\text{Th}/^{232}\text{Th}$  initial value, that is the value at the actual time of calcite deposition when  $T = 0$ , can be approximated by multiplying the present-day value by  $e^{-\lambda^{230}\text{T}}$ .

**Table 2.** Isochron data for Spring Valley Caverns stalagmite SVC-98-3.B

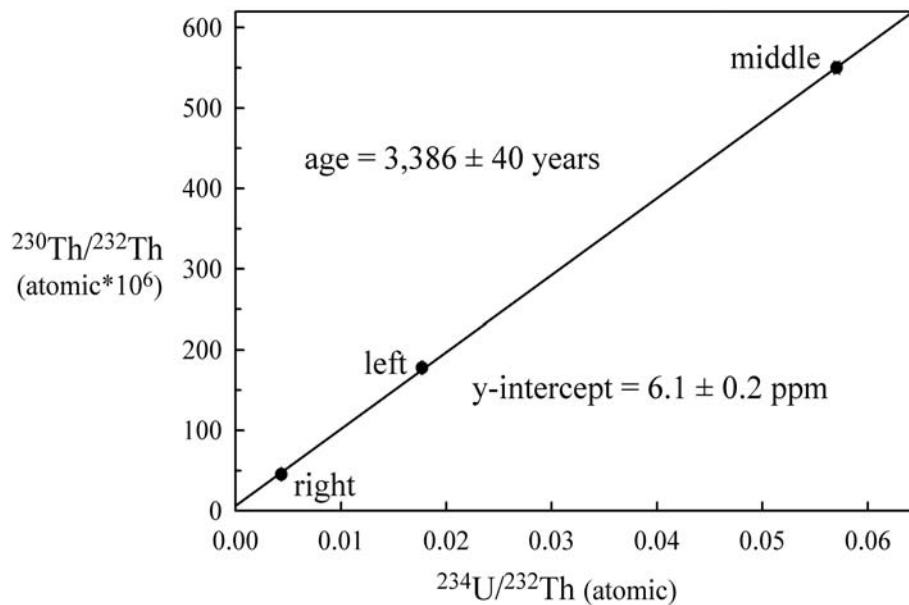
| Isochron Sub-sample | Sample Weight (mg) | $^{238}\text{U}$ conc. (ppm) | $^{232}\text{Th}$ conc. (ppb) | Uncorrected Age | Corrected Age <sup>a</sup> |
|---------------------|--------------------|------------------------------|-------------------------------|-----------------|----------------------------|
| Middle              | 40.5               | 2.55                         | 5.4                           | $1,383 \pm 34$  | $1,344 \pm 34$             |
| Left                | 42.8               | 2.54                         | 22.8                          | $1,519 \pm 46$  | $1,349 \pm 44$             |
| Right               | 37.7               | 2.25                         | 291.6                         | $3,797 \pm 55$  | $1,348 \pm 51$             |

<sup>a</sup> Ages corrected using an initial  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of 4.4 ppm.

The contamination in this particular example is almost certainly clay particles, as such particles were clearly visible in the two dirtier sub-samples. The  $^{230}\text{Th}/^{232}\text{Th}$  ratio of 4.4 ppm is almost the exact value predicted by the chondritic  $^{232}\text{Th}/^{238}\text{U}$

atomic ratio of 3.8, which at secular equilibrium gives a  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio equal to  $\lambda_{238}/\lambda_{230} * 3.8 = 4.44 \times 10^{-6}$ . Such a perfect match is doubtless fortuitous, but it is still reassuring validation of a value commonly used for correcting initial  $^{230}\text{Th}$ . A 4.4 ppm correction results in corrected ages that are impressively concordant (Table 2).

A second isochron example from Crevice Cave, Missouri (Dorale et al., 1998) illustrates a slightly more complex scenario (Fig. 3). The regression y-intercept value of  $6.1 \pm 0.2$  ppm is certainly a reasonable value within the range of common detrital  $^{232}\text{Th}/^{238}\text{U}$  values. As Table 3 shows, however, applying a 6.1 ppm correction to each of the three sub-samples results in ages that are slightly discordant at face value. Such a data set is consistent with the hypothesis that there is more than one source of initial  $^{230}\text{Th}$  and that these multiple sources have different  $^{230}\text{Th}/^{232}\text{Th}$  ratios. The simplest scenario is a two-component system in which the high  $^{232}\text{Th}$  component has a low  $^{230}\text{Th}/^{232}\text{Th}$  ratio and the low  $^{232}\text{Th}$  component has a high  $^{230}\text{Th}/^{232}\text{Th}$  ratio. Indeed, Table 3 illustrates that the two dirtier sub-samples (left and right) give an initial  $^{230}\text{Th}/^{232}\text{Th}$  value of 2.4 ppm, while the two cleaner sub-samples (middle and left) give a value of 11.0 ppm.



**Figure 3.** A two-dimensional isochron diagram for stalagmite CC-99-12-A from Crevice Cave, Missouri. The three sub-samples, labeled left, middle, and right, are horizontally spaced 1-1.5 cm from one another within the same stratigraphic layer and are from locations with visually obvious differences in detrital content. Sub-sample widths are about 2.0 mm. The regression y-intercept value of  $6.1 \pm 0.2$  ppm represents the average, present-day  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of the contamination. Although the scaling of this figure makes it difficult to see, the three points are not exactly co-linear. A two-point line using the two dirtier sub-samples (left and right) gives a regression y-intercept value of 2.4 ppm, and a similar exercise for the two cleaner sub-samples (middle and left) gives a value of 11.0 ppm. Such a data set is consistent with the hypothesis that there is more than one source of initial  $^{230}\text{Th}$  and that these multiple sources have different  $^{230}\text{Th}/^{232}\text{Th}$  ratios. The simplest scenario (one that fits the data in this example) is a two-component system in which the high  $^{232}\text{Th}$  component has a low  $^{230}\text{Th}/^{232}\text{Th}$  value and the low  $^{232}\text{Th}$  component has a high  $^{230}\text{Th}/^{232}\text{Th}$  value.

**Table 3.** Isochron U-Th-Pa data for Crevice Cave stalagmite CC-99-12-A-102.5

|   | Left               | Middle             | Right           |
|---|--------------------|--------------------|-----------------|
| $^{238}\text{U}$ (ppb)  | 1,198              | 1,205              | 1,162           |
| $^{232}\text{Th}$ (ppb)   | 12                 | 3.7                | 47              |
| Uncorrected $^{230}\text{Th}$ age                                 | $3,604 \pm 22$     | $3,453 \pm 20$     | $3,752 \pm 25$  |
| Corrected $6.1 \pm 3.05$ ppm                                      | $3,482 \pm 64$     | $3,415 \pm 28$     | $3,257 \pm 248$ |
| Corrected $2.4 \pm 1.2$ ppm <sup>a</sup>                          | $3,556 \pm 32$     | $3,438 \pm 22$     | $3,557 \pm 100$ |
| Corrected $11.0 \pm 5.5$ ppm <sup>a</sup>                         | $3,385 \pm 111$    | $3,385 \pm 40$     | $2,857 \pm 450$ |
| Uncorrected $^{231}\text{Pa}$ age                                 | $4,815 \pm 210$    | $4,875 \pm 193$    | $3,853 \pm 170$ |
| Corrected $^{231}\text{Pa}$ age <sup>b</sup>                      | $4,689 \pm 219$    | $4,836 \pm 194$    | $3,338 \pm 307$ |
| Calculated initial $^{231}\text{Pa}/^{232}\text{Th}$ <sup>c</sup> | $1,020 \pm 30$ ppb | $3,425 \pm 95$ ppb | $81 \pm 7$ ppb  |

<sup>a</sup> Italicized ages highlight concordant sub-samples for a particular  $^{230}\text{Th}/^{232}\text{Th}$  corrective value.

<sup>b</sup> Corrected for initial  $^{231}\text{Pa}$  using an atomic  $^{231}\text{Pa}/^{232}\text{Th}$  value of  $88.8 \pm 44.4$  ppb. This is the secular equilibrium

value for the chondritic  $^{232}\text{Th}/^{238}\text{U}$  atomic ratio of 3.8.

<sup>c</sup> Calculated using the  $^{230}\text{Th}$  age of  $3,385 \pm 40$  years.

Speleothems from other regions help provide perspective for the midwestern examples given here. Richards et al. (1999) analyzed a stalagmite from the Bahamas and calculated an initial  $^{230}\text{Th}/^{232}\text{Th}$  ratio of 89 ppm, significantly higher than the Minnesota and Missouri examples. The carbonate platforms that comprise the Bahamas are expected to have significantly lower silicate-related  $^{232}\text{Th}$ . The high initial  $^{230}\text{Th}/^{232}\text{Th}$  values of these speleothems most likely reflect the production of  $^{230}\text{Th}$  by uranium decay in a ground water setting that is deficient in  $^{232}\text{Th}$ , or indicate that the primary limestone itself has high  $^{230}\text{Th}/^{232}\text{Th}$  ratios. The transport mechanism for this excess  $^{230}\text{Th}$  is possibly by colloids, organic complexes, or carbonate complexes as mentioned earlier. Other workers have referred to a high  $^{230}\text{Th}$  component such as this as “hydrogenous” (e.g. Lin et al., 1996).

$^{231}\text{Pa}$  dating adds another dimension to the issue of initial daughter/parent ratios. Whitehead et al. (1999) described discordant  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  ages for several young New Zealand speleothems (measured by  $\alpha$ -counting) and reinforced earlier suggestions that  $\text{Pa}^{5+}$  and  $\text{Th}^{4+}$  may have slightly different behaviors in ground water. Gascoyne (1985), for example, measured  $^{227}\text{Th}$  as a proxy for  $^{231}\text{Pa}$  and suggested the possibility of  $^{231}\text{Pa}$  excess in speleothems. We also observe small but significant  $^{231}\text{Pa} - ^{230}\text{Th}$  discordance for our Holocene Crevice Cave stalagmite, as the uncorrected  $^{231}\text{Pa}$  ages are older than the  $^{230}\text{Th}$  ages, suggesting  $^{231}\text{Pa}$  excess (Table 3).

For the two sub-samples with lower  $^{232}\text{Th}$  concentrations,  $^{231}\text{Pa} - ^{230}\text{Th}$  discordance remains after initial  $^{231}\text{Pa}$  is corrected assuming secular equilibrium and a  $^{232}\text{Th}/^{238}\text{U}$  value of 3.8 ( $^{231}\text{Pa}/^{232}\text{Th} = \lambda_{235}/(\lambda_{231} * 3.8 * 137.88) = 8.9 \times 10^{-8}$  (89 ppb)). This indicates that  $^{232}\text{Th}$  is a poor analog for  $^{231}\text{Pa}$  in these samples. Using the  $^{230}\text{Th}$  age of  $3,385 \pm 40$  years as the true age, we calculate initial  $^{231}\text{Pa}/^{232}\text{Th}$  ratios of  $3,425 \pm 95$  ppb,  $1,020 \pm 30$  ppb, and  $81 \pm 7$  for the middle (low  $^{232}\text{Th}$ ), left (moderate  $^{232}\text{Th}$ ), and right (high  $^{232}\text{Th}$ ) sub-samples, respectively. This suggests that a hydrogenous  $^{231}\text{Pa}$  component is significant for those samples with low  $^{232}\text{Th}$  concentrations, and that  $^{231}\text{Pa}$  is considerably more soluble than  $^{230}\text{Th}$  in karst ground waters. This observation is consistent with the significantly longer residence time of  $^{231}\text{Pa}$  (~ 200 years) versus  $^{230}\text{Th}$  (~ 20 years) in the oceans (Broecker and Peng, 1982; Yu et al., 1996).

To what extent do initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  affect the validity of disequilibrium ages? In some cases initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  can cause an offset from the true age that

is significantly larger than the analytical error. However, these tend to be unusual cases for samples that are young, have low U concentrations, have a high hydrogenous component, have high detrital content, or have a combination of the four factors. The sensitivity of the age error to uncertainties in the initial concentrations of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  decreases with the sample age because (1) *in situ* radiogenic production of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  and (2) the unsupported decay of the initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , gradually shift the radiogenic/initial ratio toward higher values. Our data suggest that initial  $^{231}\text{Pa}$  is more problematic in young speleothems than initial  $^{230}\text{Th}$ , because  $^{230}\text{Th}$  is less soluble than  $^{231}\text{Pa}$ , and because we can correct for initial  $^{230}\text{Th}$  using estimates of the initial  $^{230}\text{Th}/^{232}\text{Th}$  ratio.

The Spring Valley Caverns stalagmite provides an excellent example of initial  $^{230}\text{Th}$  sensitivity. Using an isochron technique (Fig. 2; Table 2), we calculated an initial  $^{230}\text{Th}/^{232}\text{Th}$  value of 4.4 ppm for this particular stalagmite. We can test the sensitivity of the three sub-samples to uncertainties on this initial  $^{230}\text{Th}/^{232}\text{Th}$  value as shown in Table 4. The exercise clearly shows that the most sensitive sample is the right sub-sample, which has the highest  $^{232}\text{Th}$  concentration. For the cleanest sub-sample (middle), initial  $^{230}\text{Th}/^{232}\text{Th}$  uncertainties of 100% (e.g.  $4.4 \pm 4.4$  ppm), after propagation through Eq. (1), are relatively small and are comparable to the analytical error (34 yrs vs. 52 yrs).

**Table 4.** Sensitivity to initial  $^{230}\text{Th}$  corrections for stalagmite SVC\98-3.B

| Sample ID | $^{232}\text{Th}$ (ppb) | $[^{230}\text{Th}/^{232}\text{Th}]$ activity | Uncorrected Age | Corrected 4.4 ppm | Corrected $4.4 \pm 2.2$ ppm | Corrected $4.4 \pm 4.4$ ppm |
|-----------|-------------------------|--|-----------------|-------------------|-----------------------------|-----------------------------|
| Middle    | 5                       | 29   | $1,383 \pm 34$  | $1,344 \pm 34$    | $1,344 \pm 39$              | $1,344 \pm 52$              |
| Left      | 23                      | 7  | $1,519 \pm 46$  | $1,349 \pm 44$    | $1,349 \pm 95$              | $1,349 \pm 175$             |
| Right     | 291                     | 1  | $3,797 \pm 55$  | $1,348 \pm 51$    | $1,348 \pm 1,220$           | $1,348 \pm 2,450$           |

By alpha-counting techniques, the general rule of thumb was that samples with  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios  $> \sim 20$  did not have significant initial  $^{230}\text{Th}$  corrections relative to analytical error (Schwarcz, 1986). However, because mass spectrometric techniques have increased the precision of the isotopic measurements, the  $[^{230}\text{Th}/^{232}\text{Th}] > 20$  guideline no longer accurately reflects the relationship between initial  $^{230}\text{Th}$  corrections and the magnitude of the analytical errors. Table 5 lists a number of examples in order of increasing  $[^{230}\text{Th}/^{232}\text{Th}]$  to help illustrate the spectrum of this relationship. Sample 97-8-K-4.5, for example, has a  $[^{230}\text{Th}/^{232}\text{Th}] = 48$ , yet the initial  $^{230}\text{Th}$  correction ( $\pm 45$  years) is still larger than the analytical error ( $\pm 17$  years). Sample 99-12-3-3.0, because of its young age (it was collected while active and the sub-sample is from very near the top surface) and relatively high  $^{232}\text{Th}$  concentration, demonstrates extreme initial  $^{230}\text{Th}$  sensitivity. Using a 4.4 ppm corrective value results in a negative age ( $-13 \pm 9$  years), so clearly the 4.4 ppm value can not be correct. A 4.2 ppm corrective value, however, results in an age of  $18 \pm 9$  years. This particular example is clearly a good candidate for the type of careful isochron work described above, as the sample age is extremely sensitive to the initial  $^{230}\text{Th}/^{232}\text{Th}$  ratio. On the opposite end of the spectrum, sample CC-99-3-Y-485.5 is corrected using an initial  $^{230}\text{Th}/^{232}\text{Th}$  value of  $4.4 \pm 2.2$  ppm, but the difference between the corrected and uncorrected ages is less than one year, far smaller than the analytical error of  $\pm 375$  years. Most speleothem samples fall somewhere between these two extremes, although, generally speaking, speleothems with sufficiently high  $^{238}\text{U}/^{232}\text{Th}$  ratios commonly have initial  $^{230}\text{Th}$  corrections that range from moderate

(i.e. comparable to the analytical error) to trivial (e.g. the last four entries in Table 5). As mentioned earlier, exceptions to this general statement typically involve samples that are very young and/or those that have an unusually high hydrogenous  $^{230}\text{Th}$  component.

**Table 5.** Corrected vs. uncorrected ages for some Crevice Cave stalagmite sub-samples

| Sample ID               | $^{238}\text{U}$ (ppb) | $^{232}\text{Th}$ (ppb) | $[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$ activity | Uncorrected Age | Corrected Age <sup>a</sup> |
|-------------------------|------------------------|-------------------------|--|-----------------|----------------------------|
| 99-3-B-3.8 <sup>b</sup> | 840                    | 83                      | 1  | 682 ± 8         | -13 ± 9                    |
| 99-3-B-3.8 <sup>c</sup> | 840                    | 83                      | 1  | 682 ± 8         | 18 ± 9                     |
| 94-DBL-S-199.0          | 444                    | 132                     | 18   | 66,651 ± 493    | 64,521 ± 1,167             |
| 99-12-J-3.0             | 405                    | 28                      | 26   | 18,259 ± 153    | 17,741 ± 300               |
| 97-8-K-4.5              | 822                    | 4.4                     | 48   | 2,662 ± 17      | 2,617 ± 28                 |
| 99-12-B-19.0            | 1,652                  | 0.6                     | 77   | 332 ± 6         | 329 ± 6                    |
| 99-3-B-251.9            | 1,454                  | 1.6                     | 290  | 2,364 ± 10      | 2,358 ± 10                 |
| 99-3-B-203.0            | 973                    | 0.2                     | 1,000  | 1,514 ± 8       | 1,513 ± 8                  |
| 99-3-W-382.5            | 1,208                  | 2.2                     | 3,480  | 99,479 ± 389    | 99,466 ± 389               |
| 99-3-E-119.5            | 445                    | 0.3                     | 23,800   | 244,072 ± 1,759 | 244,070 ± 1,759            |
| 99-3-Y-485.5            | 2,102                  | 0.02                    | 560,000  | 83,172 ± 375    | 83,172 ± 375               |

<sup>a</sup> All ages except the first two entries are corrected using a  $^{230}\text{Th}/\text{}^{232}\text{Th}$  atomic ratio of  $4.4 \pm 2.2$  ppm.

<sup>b</sup> Corrected using a  $^{230}\text{Th}/\text{}^{232}\text{Th}$  atomic ratio of 4.4 ppm.

<sup>c</sup> Corrected using a  $^{230}\text{Th}/\text{}^{232}\text{Th}$  atomic ratio of 4.2 ppm.

Isochron data in Fig. 3 was used to suggest that initial  $^{230}\text{Th}$  in some cases likely has more than one component. A two-component system was inferred in which the high  $^{232}\text{Th}$  component has a low  $^{230}\text{Th}/\text{}^{232}\text{Th}$  ratio (e.g. clays) and the low  $^{232}\text{Th}$  component has a high  $^{230}\text{Th}/\text{}^{232}\text{Th}$  ratio (e.g. hydrogenous forms). How is this knowledge best accommodated in the initial  $^{230}\text{Th}$  correction procedure? For many speleothems, such as the Spring Valley Caverns example, isochron-derived  $^{230}\text{Th}/\text{}^{232}\text{Th}$  initial values that are low and are close to the chondritic secular equilibrium value of 4.4 ppm suggest that the high  $^{230}\text{Th}/\text{}^{232}\text{Th}$  hydrogenous component, although it likely exists, is of secondary importance. For many samples such as these, using a single appropriate value with generous errors of 50-100 % (i.e.  $4.4 \pm 2.2$  or  $4.4 \pm 4.4$  ppm) is a reasonable way of correcting for initial  $^{230}\text{Th}$ . For the Crevice Cave isochron example, the range of 2.4-11.0 ppm implied a moderate two-component contribution of initial  $^{230}\text{Th}$ . This situation can be addressed either by (1) applying different initial  $^{230}\text{Th}/\text{}^{232}\text{Th}$  corrective values to the dirtier and cleaner sub-samples within the guidelines provided by the isochron data, and then remaining conservative with respect to the errors, or (2) using a single  $^{230}\text{Th}/\text{}^{232}\text{Th}$  value with errors that encompass the range of initial values. For those exceptional cases where hydrogenous  $^{230}\text{Th}$  is more significant, such as the Bahamas example, multiple isochrons may be required for any given speleothem.

On the basis of the arguments presented above, we disagree with some of the conclusions of Whitehead et al. (1999), who dated several speleothems presumed to be close to zero-age but gave ages from 2,000-3,000 years. They concluded that because of initial  $^{230}\text{Th}$ , *all* speleothem ages less than 2,000-3,000 years are possibly inaccurate and should be viewed with suspicion. Based on the same data, they also concluded that a speleothem sample dated by Li et al. (1989) at  $40,000 \pm 700$  years

could have systematic errors (related to initial  $^{230}\text{Th}$ ) that would increase the age error to  $\pm 2,000$  years. The authors imply that the initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  conditions specific to their cave settings in New Zealand have general application to other cave systems worldwide. We have shown that initial  $^{230}\text{Th}$  corrections for many of the speleothems we have studied are orders of magnitude smaller than the inferred New Zealand values, and therefore stress that each cave system and perhaps each speleothem demands individual evaluation.

## 7. TIMS VERSUS ICP-MS

Table 6 lists three stalagmite sub-samples dated by both TIMS and ICP-MS. Both methods give the same ages within error. These sub-samples contained between 0.8 and 1.0 ppm  $^{238}\text{U}$ , and  $\sim 80\%$  of the U and Th fractions was loaded for the TIMS analysis and  $\sim 20\%$  was reserved for analysis by ICP-MS. Comparable precision for the two methods attests to the higher ionization efficiency of the ICP-MS method. Shorter analysis times also allow higher throughput on the ICP-MS. TIMS analyses are more labor intensive (e.g. filament loading) and more prone to accident (e.g. filament burn-out, premature graphite loss). By comparison, source stability of the ICP-MS is generally inferior to TIMS. For ultra-high precision work ( $\sim 1\%$ ) on sufficiently large samples, the source stability of TIMS is a distinct advantage. For analyses in the 2-3  $\%$  range, however, ICP-MS offers some distinct advantages over TIMS and has particular appeal to speleothem work, which typically benefits from analyzing very small sub-samples.

**Table 6.** Comparison between TIMS and ICP-MS methods

| Sample ID  | Sample Size (g) | Method | Measured $\delta^{234}\text{U}$ | $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ activity | Corrected Age <sup>a</sup> |
|------------|-----------------|--------|---------------------------------|---|----------------------------|
| DBL-L-27.5 | 0.3004          | TIMS   | $3,031.9 \pm 3.4$               | $1.2234 \pm 0.0039$                                       | $37,710 \pm 140$           |
|            |                 | ICP-MS | $3,037.7 \pm 5.8$               | $1.2303 \pm 0.0046$                                       | $37,890 \pm 170$           |
| DBL-L-75.2 | 0.2997          | TIMS   | $2,509.0 \pm 4.6$               | $1.2375 \pm 0.0044$                                       | $45,000 \pm 200$           |
|            |                 | ICP-MS | $2,506.0 \pm 5.5$               | $1.2424 \pm 0.0050$                                       | $45,260 \pm 230$           |
| VA2-1-BR   | 0.1831          | TIMS   | $427.0 \pm 1.8$                 | $1.2787 \pm 0.0086$                                       | $198,170 \pm 3,420$        |
|            |                 | ICP-MS | $427.4 \pm 2.8$                 | $1.2768 \pm 0.0053$                                       | $197,300 \pm 2,310$        |

<sup>a</sup> Ages corrected for initial  $^{230}\text{Th}$  using a  $^{230}\text{Th}/^{232}\text{Th}$  value of  $4.4 \pm 2.2$  ppm. All corrections are  $< 25$  years.

Prospects for further improvements in sensitivity and precision of mass spectrometric measurements of these nuclides require improvements in either ionization efficiency or transmission efficiency or both. For TIMS methods, the possibility exists for increasing ionization efficiencies using different loading techniques. In addition, small but significant increases in transmission efficiency could plausibly be obtained with improved TIMS instruments, perhaps including the Finnigan *TRITON*. For ICP-MS methods, it is likely that small but significant improvements will continue to be made through modifications in "front end" design. Recent improvements include the use of micro-concentric nebulizers, desolvation nebulizers, guard electrodes, and refinements in cone geometry (see refs in Shen et al., 2001). The use of larger geometry ICP-MS instruments may also lead to significant improvements in transmission. Finally, the use of multiple electron multipliers or channeltrons (on a multi-collector ICP-MS, MC-ICP-MS), obviates the

problems associated with the ICP source instability and also maximizes the amount of time that the isotope of interest can be counted. While requiring careful work to cross-calibrate multipliers, this will lead to an improvement of on the order of a factor of two in numbers of ions counted. Taken together, all of these potential improvements bode well for yet additional improvements in the precision and sensitivity with which we will be able measure rare uranium-series nuclides in coming years.

## 8. ACCURACY OF AGES

The issues of initial  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  are ones of accuracy, that is, how close the age determination is to the true age of the sample. A second concern, one that increases with the sample age, is the closed-system behavior of the U-Th-Pa decay chains. In general, older samples are more at risk because of the longer opportunity for diagenetic changes to have taken place. Speleothems with significant porosity are poorer candidates for closed-system behavior than are speleothems with dense fabrics. Fluid inclusions are a ubiquitous source of micron-scale fabric porosity but are generally isolated and thus do not translate to permeability with diagenetic implications.

Combined  $^{230}\text{Th}$ - $^{231}\text{Pa}$  dating is a powerful test of open-system behavior because diagenesis will often result in discordant ages (Cheng et al., 1998). Table 7 shows U-Th-Pa data for a Crevice Cave stalagmite that suggests closed-system behavior for at least the last 90,000 years. The larger errors of the  $^{231}\text{Pa}$  ages reflect both the lower  $^{231}\text{Pa}$  concentrations (compared to  $^{230}\text{Th}$ ) and the larger fractional errors related to large  $T$  for the  $^{235}\text{U}$ - $^{231}\text{Pa}$  clock (limit  $\sim 250$  ka). Initial  $^{230}\text{Th}$  is insignificant for these sub-samples because of their relatively old age and low  $^{232}\text{Th}$  content. The age concordance also indicates that any offset from the true age due to initial  $^{231}\text{Pa}$  is insignificant relative to the analytical error for these particular (old) sub-samples.

**Table 7.** Comparison between  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  ages for Crevice Cave stalagmite CC-J

| ID    | $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$<br>activity | $[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$<br>activity | $[\text{}^{231}\text{Pa}/\text{}^{235}\text{U}]$<br>activity | $^{230}\text{Th}$ Age                 | $^{231}\text{Pa}$ Age                 |
|-------|--|---|--|---------------------------------------|---------------------------------------|
|       |  |   |  | corrected <sup>a</sup><br>uncorrected | corrected <sup>a</sup><br>uncorrected |
| 222.0 | $1.4176 \pm 0.0042$  | 9,990   | $0.8101 \pm 0.0058$  | $78,860 \pm 330^a$                    | $78,520 \pm 1,470^a$                  |
|       |  |   |  | $78,870 \pm 330$                      | $78,530 \pm 1,470$                    |
| 315.5 | $1.8191 \pm 0.0065$  | 3,020   | $0.8507 \pm 0.0053$  | $89,740 \pm 530^a$                    | $89,900 \pm 1,720^a$                  |
|       |  |   |  | $89,770 \pm 530$                      | $89,920 \pm 1,720$                    |

<sup>a</sup> Ages are corrected for initial  $^{230}\text{Th}$  using an atomic  $^{230}\text{Th}/\text{}^{232}\text{Th}$  value of  $4.4 \pm 4.4$  ppm and for initial  $^{231}\text{Pa}$  using an atomic  $^{231}\text{Pa}/\text{}^{232}\text{Th}$  value of  $88.8 \pm 88.8$  ppb. These are the secular equilibrium values for the chondritic  $^{232}\text{Th}/\text{}^{238}\text{U}$  atomic ratio of 3.8.

Another indication of closed-system behavior is the stratigraphic ordering of ages and the absence of any age reversals. Although simple, this straightforward criterion becomes an impressive argument for those speleothems with a large number of densely spaced ages such as is shown for stalagmite CC-94-9-DBL-L in Table 8. Stalagmite CC-94-9-DBL-L is composed of dense, yellowish, translucent calcite with ubiquitous fluid inclusions in the 3-10 micron range. The stalagmite stopped growing  $\sim 23,000$  years ago and was found in the cave lying in a stream. A 0.5-1.0



mm rind indicates leaching of the outer surface but the interior is pristine and optically unaltered. The U-Th systematics also suggest it has remained a completely closed system. The stalagmite contains a high-resolution record of past changes in climate and vegetation in the form of stable carbon and oxygen isotopic variations (Dorale et al., 1998). The importance of a precise and accurate  $^{230}\text{Th}$  chronology for records such as this cannot be overstated. Dense calcite that remains completely closed to the diagenetic loss and/or gain of both parent and daughter isotopes is a key reason why speleothems can be dated with great accuracy.

**Table 8.** U-Th data for stalagmite CC-94-9-DBL-L from Crevice Cave, Missouri<sup>a</sup>

| ID <sup>b</sup> | Sample Size (mg) | $^{238}\text{U}$ (ppb) | Measured $\delta^{234}\text{U}$ | $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ activity | $[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$ activity | Corrected Age <sup>c</sup> |
|-----------------|------------------|------------------------|---------------------------------|---|--|----------------------------|
| 1.5             | 180              | 556                    | 3,555.4 ± 8.6                   | 0.9410 ± 0.0067   | 690  | 24,530 ± 190               |
| 4.0             | 284              | 561                    | 3,452.7 ± 3.2                   | 1.0033 ± 0.0037   | 320  | 26,990 ± 110               |
| 7.9             | 203              | 803                    | 3,365.6 ± 6.6                   | 1.0969 ± 0.0050   | 1,430  | 30,450 ± 160*              |
| 11.0            | 293              | 928                    | 3,321.5 ± 3.4                   | 1.1183 ± 0.0034   | 7,800  | 31,470 ± 110               |
| 18.5            | 185              | 843                    | 3,182.9 ± 5.1                   | 1.1571 ± 0.0041   | 5,580  | 33,930 ± 140               |
| 27.5            | 300              | 812                    | 3,032.4 ± 2.5                   | 1.2264 ± 0.0033   | 1,050  | 37,810 ± 120**             |
| 30.8            | 230              | 957                    | 2,973.3 ± 2.8                   | 1.2315 ± 0.0035   | 1,800  | 38,650 ± 130               |
| 41.8            | 220              | 1,026                  | 2,813.6 ± 3.0                   | 1.2282 ± 0.0032   | 12,100   | 40,420 ± 130               |
| 50.0            | 279              | 1,000                  | 2,774.1 ± 10.7                  | 1.2540 ± 0.0116   | 20,900   | 41,920 ± 470*              |
| 67.2            | 212              | 915                    | 2,567.8 ± 5.2                   | 1.2172 ± 0.0041   | 22,600   | 43,270 ± 190               |
| 75.2            | 300              | 796                    | 2,508.3 ± 2.8                   | 1.2400 ± 0.0036   | 7,500  | 45,120 ± 160**             |
| 80.2            | 242              | 753                    | 2,477.1 ± 3.4                   | 1.2529 ± 0.0035   | 9,700  | 46,170 ± 160               |
| 95.1            | 197              | 571                    | 2,303.0 ± 3.3                   | 1.2372 ± 0.0059   | 6,360  | 48,400 ± 280               |
| 116.0           | 318              | 605                    | 2,357.8 ± 5.8                   | 1.3316 ± 0.0055   | 6,170  | 51,810 ± 280*              |
| 133.6           | 220              | 643                    | 2,303.3 ± 4.5                   | 1.3455 ± 0.0046   | 3,470  | 53,540 ± 250               |
| 143.1           | 293              | 631                    | 2,352.0 ± 4.0                   | 1.3881 ± 0.0045   | 9,630  | 54,620 ± 230*              |
| 150.2           | 225              | 646                    | 2,337.6 ± 2.6                   | 1.3880 ± 0.0039   | 7,110  | 54,900 ± 200               |
| 160.9           | 309              | 760                    | 2,411.0 ± 3.7                   | 1.4349 ± 0.0045   | 1,820  | 55,650 ± 230*              |
| 173.8           | 238              | 641                    | 2,336.4 ± 2.6                   | 1.4189 ± 0.0048   | 320  | 56,430 ± 240               |
| 191.0           | 246              | 649                    | 2,336.6 ± 3.4                   | 1.4540 ± 0.0044   | 420  | 58,160 ± 230               |
| 202.0           | 366              | 566                    | 2,249.4 ± 4.0                   | 1.4458 ± 0.0051   | 290  | 59,730 ± 280*              |
| 225.5           | 238              | 521                    | 2,191.4 ± 8.1                   | 1.4741 ± 0.0102   | 91   | 62,630 ± 580               |
| 238.0           | 435              | 433                    | 2,274.2 ± 4.6                   | 1.5541 ± 0.0100   | 44   | 64,780 ± 540*              |
| 247.8           | 296              | 489                    | 2,444.2 ± 13.0                  | 1.6485 ± 0.0291   | 15   | 65,370 ± 1,500             |

<sup>a</sup> All measurements made by TIMS except those denoted \* which were made by ICP-MS and those denoted \*\* which were made by both TIMS and ICP-MS.

<sup>b</sup> ID denotes distance in mm from the top surface of stalagmite to the midpoint of the sub-sample boring.

<sup>c</sup> Ages are corrected for initial  $^{230}\text{Th}$  using a  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of  $4.4 \pm 2.2$  ppm.

## 9. CONCLUSIONS

The range over which useful age data on speleothems can be obtained by uranium-series disequilibrium techniques extends from tens of years to ~ 600,000 years. Compared to decay-counting, TIMS and ICP-MS techniques have significantly extended the dateable time range, greatly reduced age errors, reduced sample-size requirements to a level more compatible with the slow growth rates common to many speleothems, and reduced the time and effort invested per analysis. These improvements now allow for high-resolution dating that is typically more

precise than that obtained by  $^{14}\text{C}$ . For the past half million years, U-Th dated speleothem records represent an excellent source of Quaternary paleoenvironmental information.

Accurate dating is possible if the initial concentrations of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  are well constrained and the system remains closed to post-depositional loss and/or gain of U, Th, and Pa. Initial  $^{230}\text{Th}$  can be constrained by monitoring  $^{232}\text{Th}$  and employing isochron techniques. The small sample size requirements of mass spectrometry allow effective application of precise isochron sub-sampling on slow-growth speleothems. The sensitivity of the age error to uncertainties in initial  $^{230}\text{Th}$  decreases with increasing U concentration, increasing age, and decreasing detrital contamination. For many speleothems the uncertainties regarding initial  $^{230}\text{Th}$  are smaller than those associated with the analytical precision of the measurements and are trivial. Because Pa is more soluble than Th,  $^{232}\text{Th}$  is a poor analog for  $^{231}\text{Pa}$ . Therefore, initial  $^{231}\text{Pa}$  is more problematic than initial  $^{230}\text{Th}$  for young samples, although this problem becomes less significant or even insignificant with increasing age. Closed-system behavior can be judged by petrographic considerations, stratigraphic ordering of ages, and  $^{230}\text{Th}$ - $^{231}\text{Pa}$  concordance. Dense, calcite speleothems seem capable of maintaining closed-system U-series behavior over the timescales of effective U-Th-Pa dating.

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