Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry

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ABSTRACT

We have developed techniques for measuring ^{234}U and ^{230}Th on Faraday cups with precisions of 1–3 epsilon units (1 ε-unit=1 part in 10^4) using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Using a Thermo-Scientific Neptune with desolvation nebulization, we obtained ionization/transmission efficiencies of 1–2% for both U and Th. We set up protocols to correct for tailing, prepared U and Th gravimetric standards, tested a Th mass fractionation correction procedure based on U isotopes, and identified natural calcite samples likely to be in U–Th isotopic secular equilibrium. The measured atomic ratios, ^{234}U/^{238}U=54.970 ($\pm$ 0.019) $\times 10^{-6}$ and ^{230}Th/^{238}U=16.916 ($\pm$ 0.018) $\times 10^{-6}$, for these calcite samples were identical within errors (quoted 2σ uncertainties calculated combining all sources of error). Half-life values calculated from these ratios are consistent with previous values, but have much smaller errors: 245,620 $\pm$ 260 a for ^{234}U and 75,584 $\pm$ 110 a for ^{230}Th (quoted 2σ uncertainties calculated using all sources of error). In calculating a ^{230}Th age, some of the systematic errors included in estimating the full error in the half-lives effectively cancel. Removing these uncertainties (uncertainty in the ^{238}U half-life value, uncertainty in our gravimetric uranium and thorium standards, and uncertainty in the absolute isotopic composition of the uranium standard), yields effective uncertainties for the purposes of ^{230}Th dating of $\pm$ 70 a for the ^{234}U half-life value and $\pm$ 30 a for the ^{230}Th half-life value. Under ideal circumstances, with our methods, the 2σ uncertainty in age, including uncertainty in half-life values is $\pm$ 10 a at 10 ka, $\pm$ 100 a at 130 ka, $\pm$ 300 a at 200 ka, $\pm$ 1 ka at 300 ka, $\pm$ 2 ka at 400 ka, $\pm$ 6 ka at 500 ka, and $\pm$ 12 ka at 600 ka. The isotopic composition of a sample with an age < 800 ka can clearly be resolved from the isotopic composition of a sample in secular equilibrium, assuming closed system behavior. Using these techniques, we analyzed a Sanbao Cave (Hubei, China) stalagmite that formed between 510 and 640 ka ago. As the half-life values were determined independent of the Sanbao Cave ages, the observed co-variation between stalagmite δ^{18}O and Northern Hemisphere summer insolation is consistent with accurate ages and half-life values.

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1. Introduction

^{230}Th dating, also referred to as U/Th dating or ^{238}U–^{234}U–^{230}Th dating, plays an important role in characterizing a broad range of natural processes, including the timing and mechanisms of climate change, the calibration of the radiocarbon timescale, oceanographic processes, human evolution, tectonic and seismic

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processes, and magmatic processes (e.g., Bourdon et al., 2003 and chapters and references therein). This method involves calculating ages from radioactive decay and ingrowth relationships among ^{238}U, ^{234}U and ^{230}Th. Before this work, ^{230}Th dating was used to date materials as young as a few years and in excess of 600 ka (1000 a) (e.g., Edwards et al., 1987; Edwards, 1988; Ludwig et al., 1992; Richards et al., 1994; Henderson and Slowey, 2000; Stirling et al., 2001; Andersen et al., 2004, 2008; Potter et al., 2005; Shen et al., 2008, 2012; Cheng et al., 2009a, 2009b).

In the late 1980s, thermal ionization mass spectrometry (TIMS) techniques with per mil (‰) level precision largely replaced traditional decay counting methods for measuring U and Th isotopes, resulting in an improvement in precision of over an order of magnitude, and a decrease in sample size requirements of 1-2 orders of magnitude (Edwards et al., 1987). ^{230}Th and ^{234}U half-life values with per mil-level precision were determined by applying TIMS techniques to the measurement of $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ in materials thought to be in secular equilibrium (Cheng et al., 2000). The half-life values were then calculated from the measured atomic ratios and the previously measured half-life for ^{238}U (Jaffey et al., 1971).

During the past decade, further technical improvements have resulted from a shift from TIMS methods to techniques of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and ICP-sector field-MS (ICP-SF-MS) with precisions at the per mil or epsilon-unit (ε-unit) level (e.g., Luo et al., 1997; Stirling et al., 2000, 2001, 2006, 2007; Shen et al., 2002, 2003; Robinson et al., 2002; Hellstrom, 2003; Andersen et al., 2004, 2007, 2008, 2010; Potter et al., 2005; Eggins et al., 2005; Fietzke et al., 2005; Mortlock et al., 2005; Hoffmann et al., 2005, 2007; Ball et al., 2008; Weyer et al., 2008; Stirling and Andersen, 2009; Mason and Henderson, 2010; Hiess et al., 2012), including applications of both electron multiplier and Faraday cup measurements.

The main substantive improvement that resulted from the use of mass spectrometric techniques has been an improvement in the proportion of ^{234}U and ^{230}Th atoms in the sample that one can detect. The increase led to higher counts, which in turn, reduced sample size as well as the error from counting statistics. Given the order of the half-lives of ^{230}Th and ^{234}U (10^5 yr), one out of 10^7 of each of these atoms decays during a 1-week counting time. Thus one in 10 million can be counted in a week using decay-counting methods. Using thermal ionization techniques, Edwards et al. (1987) demonstrated an ionization efficiency for Th of 0.1%, improving the number of counts for the same sample size by a factor of 10^4. Esat (1995) reported a TIMS ionization efficiency for Th of ~4%, but we are not aware of other reports of TIMS ionization efficiency (for Th) of this order. For MC-ICP-MS and ICP-SF-MS, previously reported ionization plus transmission efficiencies for U and Th for specific studies are in the 0.1–0.2% range (e.g. Luo et al., 1997; Shen et al., 2002). A review paper notes ICP-MS ionization plus transmission efficiencies of 0.5% in the text and a range of 0.01–1% in a table (Goldstein and Stirling, 2003), but without specific attribution to an instrument or method of nebulization. With our Thermo-Scientific Neptune (MC-ICP-MS), we attain 1–2% ionization plus transmission efficiency for both U and Th using desolvation introduction techniques, about an order of magnitude higher than the original TIMS ionization efficiency of Edwards et al. (1987) and previous ICP-MS studies that specifically mention ionization plus transmission efficiency. The measurements in this study were made at this efficiency. We take advantage of the 1–2% ionization/transmission efficiency in two different ways, depending on sample size. The breakeven point between Faraday cup measurement and electron multiplier measurement is about 5×10^{10} atoms (20 pg) for the lowest abundance isotope (^{230}Th). At this level or higher, the $^{230}Th^+$ beam current exceeds the 2σ noise of the amplifier by a factor of about 10^4, making cup

measurements, with uncertainties of a few ε-units or better possible. For ^{230}Th loads of less than about 5×10^{10} atoms, we make measurements by peak-jumping on a discrete-dynode electron multiplier. For such measurements, uncertainties are close to theoretical counting statistics limits until 2σ counting errors reach values lower than about 1‰. To further reduce total errors, careful multiplier calibration is necessary (see Hayes and Schoeller, 1977; Cheng et al., 2000; Shen et al., 2002).

Using MC-ICP-MS techniques, other groups have demonstrated measurement errors better than 1‰ (Stirling et al., 2001) for ^{230}Th and ^{234}U, in some cases approaching ε-unit precision (e.g., Potter et al., 2005; Stirling and Andersen, 2009). Here, we demonstrate measurement of ^{230}Th and ^{234}U with precisions in the 1–3 ε-unit range. Fundamentally, the main difference between our measurements and previous ICP-MS studies that specifically report ionization plus transmission efficiency is the higher efficiency. Thus, as compared to these studies, our measurements are (a) for comparable sample size, about a factor of two more precise or (b) equally precise using a sample size several times smaller. In the past decade, several studies have reported precisions broadly comparable to those that we report for ^{234}U (Andersen et al., 2004, 2007, 2010; Stirling and Andersen 2009) in natural materials and for ^{230}Th in standard solutions (Potter et al., 2005). None of these studies specifically report ionization plus transmission efficiency, but it is possible that they attained efficiencies similar to ours, as sample size in at least some of these studies is not grossly different from ours. In addition, we apply the same measurement techniques to materials inferred to be in secular equilibrium. By doing so, we determine a self-consistent set of half-life values (with ε-unit levels of precision) for use in the ^{230}Th dating equation, thus improving the accuracy of ^{230}Th ages to levels comparable to the precision of the isotopic measurements.

The main steps in our study include the following: (1) development of protocols for tailing corrections, (2) characterization of U and Th ionization/transmission efficiencies, (3) evaluation of the relationship between instrumental isotopic fractionation of U and Th, (4) standardization using high accuracy U isotopic standards, and (5) identification and measurement of calcites that we infer to be in secular equilibrium. Finally, we tested the accuracy of our methods by analyzing stalagmite samples from Sanbao Cave, Hubei, China. The Sanbao results were determined independent of our new half-life determinations. Dating accuracy (and therefore half-life accuracy) is supported by the agreement of the Sanbao oxygen isotope record with the calculated orbital-based insolation curve.

2. Experimental

2.1. Standards and samples

2.1.1. Isotopic standards

The accuracy of $^{234}U/^{238}U$ and $^{238}U/^{235}U$ measurements ultimately depends on U isotopic standards. Cheng et al. (2000) used a U isotope standard, CRM U-500, from New Brunswick Laboratory, US Department of Energy (Garner et al., 1971). The certified $^{238}U/^{235}U$ value of this standard is 1.00302 with an uncertainty of ≤1‰ (Garner et al., 1971; Garner, 1997 personal communication). Another new U standard, IRMM-074/10, from the Institute for Reference Materials and Measurements (IRMM), Belgium, was employed in this study. The certified value of the $^{238}U/^{235}U$ ratio, which was determined gravimetrically, is 1.000259 with a quoted uncertainty of 1.5 ε-units (Richter et al., 2009). This standard also has trace amounts of other uranium isotopes ($^{233}U/^{235}U=$ $(1.01886 \pm 0.00025) \times 10^{-6}$ (certified value), $^{234}U/^{235}U=(19.558 \pm$

0.035) × 10⁻⁶, ^{236}U/^{235}U=(38.660 ± 0.035) × 10⁻⁶ (last two values calculated from EUR Report 22271EN, IRMM 2006)).

Using the IRMM standard, we determined the isotopic composition of our in-house ^{236}U–^{233}U spike, by measuring mixtures of the spike and standard, using the Faraday cups in static mode. We then used this spike to determine the isotopic composition of CRM U-500 and CRM-112A (formerly NBS SRM 960) from New Brunswick Laboratories. We also used this spike, mixed with a ^{229}Th spike (see below) to determine the U isotopic compositions of three materials commonly used as secular equilibrium standards, Table Mountain Latite (TML), USGS standard Basalt Columbia River, second generation (BCR-2-c) and Harwell uraninite (HU-1), as well as the Th isotopic composition of the latter. Finally, we used this spike to measure the isotopic composition of materials inferred to be in secular equilibrium and then test our 510–640 ka old cave samples.

2.1.2. Gravimetric standards

The accuracy of ^{230}Th/^{238}U or ^{230}Th/^{234}U measurements is dependent on both isotopic and gravimetric standards. Over a decade ago, we prepared a gravimetric U solution by dissolving a weighed piece of CRM-112A metal, obtained from New Brunswick Laboratories (Cheng et al., 2000). Similarly, we prepared a Th gravimetric standard by dissolving a weighed piece of electro-deposited Th metal obtained from the Standard Materials Preparation Center, Ames Laboratory (Cheng et al., 2000). Small aliquots of each concentrated solution were used to make more dilute working standards. Other than the few times each of these bottles was accessed to make more dilute standards, the concentrated standards have remained tightly capped and their weights monitored. For this study, we prepared an additional pair of concentrated gravimetric standards, from which we made a set of dilutions. We dissolved about 3.7 g of CRM-112A in 1.5 N nitric acid to make the concentrated U standard. Prior to dissolution, oxidized surfaces of the uranium metal were cut off and the remaining uranium handled according to protocols described by New Brunswick Laboratories. In addition, we dissolved about 3.3 g of high purity "crystal bar" Th metal obtained from the Ames Laboratory in 1.5 N nitric/0.02 N hydrofluoric acid to make the concentrated Th standard. CRM-112A, purified from natural U ore, has a U assay of 99.978 ± 0.006% and an atomic weight of 238.0289. The Th assay of the crystal bar Th is reported as 99.97%, whereas that of the electro-deposited Th is 99.98%. The calibration of the same mixed spike (^{229}Th–^{233}U–^{236}U) solution using the two sets (old and new) of U and Th gravimetric standards yields consistent results within a few ε-units (Table S1). Nevertheless, we estimate the differential error in our U and Th gravimetric standards, conservatively at ± 1‰.

2.1.3. Calcite standards

In order to improve ^{230}Th dating accuracy, it is critical to identify materials with secular equilibrium isotope ratios, as such materials have atomic ratios directly proportional to half-life values. Thus, by analyzing such materials, one can determine the half-lives of both ^{234}U and ^{230}Th (see Cheng et al., 2000). Old calcite samples were selected from three caves: one set of speleothem calcite samples MO-1, MO-2 and MO-5 from Leana's Breath Cave, beneath the arid Nullarbor Plain of Western Australia, a flowstone sample, WM1-H2 from Wilder Mann Cave in the western part of the Northern Calcareous Alps of Austria, and a calcite wall crust (CA-1) from Jewel Cave, southern Black Hills of South Dakota, USA. U–Pb isochron ages are > 3 million yr for the MO samples (Woodhead et al., 2006), ~2 million yr for the youngest portion of WM1-H2 (Meyer et al., 2009), and 14.7–26 million yr for CA-1 (Palmer et al., 2009). We analyzed a portion of WM1-H2,

separated from the U–Pb-dated younger portion by a hiatus. Thus, the 2 million-yr U–Pb age is a minimum age for the portion of the sample that we analyzed. The ages are, therefore > 8–60 times the half-life of ^{234}U and > 26–200 times the half-life of ^{230}Th. They are coarsely crystalline, with no macroscopic porosity, so are good candidates to have behaved as closed systems. If so, the ratio of ^{230}Th to ^{234}U would not be resolvable from secular equilibrium values. The ratio of ^{234}U to ^{238}U would be very close to secular equilibrium, but plausibly resolvable from equilibrium with measurements of ε-unit precision on the youngest samples.

A series of old calcite samples, likely to have behaved as closed systems and likely old enough to be in U–Th isotopic secular equilibrium were also measured. We chose to analyze calcite because of the likelihood of low ^{232}Th, which would facilitate precise analysis. We further chose large gem-like crystals because of the likelihood that such materials would have behaved as closed systems. The samples represent a random assortment of readily available materials that fit those criteria. They include a mega-crystal calcite (GMC, 25 × 25 × 40 cm³) from Guilin, China, large crystals of Iceland Spar calcite (IS-3, previously reported in Cheng et al., 2000) and NC-1 from Nanjing, China, large green calcites (GC-I, -II and -III) from a giant calcite vein (~40 cm in width and hundreds of meters in length) from Mexico, and a low porosity stalagmite (Kr3) from Krubera Cave, Arabika, Western Caucasus, Crimea, Ukraine.

The final step was the measurement of the ages and oxygen isotopic composition of a stalagmite, which grew over an extended period of time in the older portion of the ^{230}Th dating range. Stalagmite SB-32, 26 cm in diameter and 118 cm in length, was collected about 1500 m from the cave entrance of Sanbao Cave, Hubei, China (Wang et al., 2008; Cheng et al., 2009a). It grew continuously between about 640 and 510 ka ago and is composed of dense, clean calcite. Chip subsamples for ^{230}Th dating were cut along growth bands, using a diamond saw blade. The accuracy of our method was tested by comparing the Sanbao stalagmite δ¹⁸O time series with N. Hemisphere summer insolation. The basis for this test is the known close, inverse, in-phase relationship between the Sanbao stalagmite δ¹⁸O time series and N. Hemisphere summer insolation over the past 380 ka (Wang et al., 2008; Cheng et al., 2009a). If our ages and half-life values were accurate, we would expect to observe a similar relationship further back in time, as recorded in SB-32. Oxygen isotope analyses were made at Nanjing Normal University, China.

2.1.4. Zircons

To examine the secular equilibrium assumption of the calcite samples, ^{234}U/^{238}U atomic ratios for various zircons were analyzed, including several unaltered zircons (ZrSiO₄) and altered zircons (cyrtolite, Zr[(SiO₄),(OH)₄]). Two red-brown gem zircons (hyacinths, Z-VIII, 1.0 × 0.8 × 0.6 cm³ from Madagascar, and EZ-5-b, 1.0 × 0.8 × 0.6 cm³ from Afghanistan) and one brown zircon EZ-1 (0.7 × 0.4 × 0.4 cm³ from Ontario, Canada) were used. The altered zircons include zircon EZ-7 from Africa, cyrtolite Z7 from Ontario, Canada, cyrtolite C-II from Ontario, Canada, and cyrtolite EC-X from Brazil.

2.2. Spike calibration

The U isotopic composition of our ^{236}U–^{233}U double spike was determined by measuring the isotopic composition of mixtures of spike and the IRMM-074/10 U standard (Table S2). All of our uncertainties are quoted at the 2σ level. This strategy was originally employed by Chen and Wasserburg (1981) to calibrate a ^{236}U–^{233}U spike relative to CRM U-500. If the only uncertainty that we consider is the uncertainty in our mass spectrometer

Table 1
CRM U-500 calibrations against Minnesota double spike (based on IRMM 074/10).

	$^{238}U/^{235}U$	P/C	$^{234}U/^{238}U$	P/C	$^{236}U/^{238}U$	P/C
U-500-Uspk-I	0.99990	± (4)/(16)	0.0104295	± (5)/(20)	0.001521	± (2)/(3)
U-500-Uspk-II	0.99988	± (4)/(16)	0.0104305	± (5)/(20)	0.001523	± (2)/(3)
U-500-Uspk-III	0.99988	± (4)/(16)	0.0104300	± (5)/(20)	0.001522	± (2)/(3)
Average	**0.99989**	**± (4)/(16)**	**0.0104300**	**± (4)/(20)**	**0.001523**	**± (2)/(3)**
U-500 Certificate value	**1.0003**	**± _/(10)**	**0.01043**	**± _/(2)**	**0.001519**	**± _/(6)**
Condon et al. (2010)	**0.99978**	**± (8)/(16)**	**0.0104259**	**± (3)/(20)**	**0.001520**	**± (2)/(5)**
Richter et al. (2009)	**0.99991**	**± _/(37)**	**0.010431**	**± (1)/(14)**	**0.001524**	**± (1)/(4)**
Cheng et al. (2000)	*1.0003*		**0.010431**	**± (10)/(10)**	**0.001524**	**± _/(3)**

I, II and III are different mixtures from this study. Uncertainties of the ratio means are presented as $\pm P/C$ (2σ). The first set of errors (P) only accounts for the imprecision of our mass spectrometry measurements. The second set of errors (C) represents the combined uncertainty including the quoted accuracy of IRMM-074/10.

measurement, the $^{236}U/^{233}U$ ratio of our spike is 1.01014 ± 0.00004. If we also include the quoted uncertainty in the $^{238}U/^{235}U$ ratio of IRMM-074/10, the uncertainty becomes ± 0.00015. Using the IRMM-074/10-based spike isotopic compositions, we measured the isotopic composition of CRM U-500 (Table 1). For each isotope ratio, our values are the same as the certified values within the original quoted uncertainties, verifying the accuracy of the original CRM U-500 values. However, the new values are nominally different and have significantly smaller uncertainties. Richter and Goldberg (2003), Richter et al. (2009) and Condon et al. (2010) previously reported the results of a similar set of measurements and our results are consistent with the results of both of these studies (Table 1).

Calibrated to IRMM-074/10, our ^{236}U–^{233}U double spike has the following compositions (with errors including the quoted errors for IRMM-074/10): $^{236}U/^{233}U = 1.01014 \pm 0.00015$, $^{238}U/^{233}U = 0.016756 \pm 0.000004$, $^{235}U/^{233}U = 0.10522 \pm 0.00003$, $^{234}U/^{233}U = 0.003180 \pm 0.000002$. The isotopic compositions of our mixed U–Th (^{236}U–^{233}U–^{229}Th) spike are as follows: $^{236}U/^{233}U = 1.01013 \pm 0.00015$, $^{238}U/^{233}U = 0.01700 \pm 0.00001$, $^{235}U/^{233}U = 0.10521 \pm 0.00003$, and $^{234}U/^{233}U = 0.003180 \pm 0.000003$. The concentrations of U and Th in the mixed spike were calibrated with our CRM-112A and Ames gravimetric standards.

2.3. Chemistry

Procedures for U and Th chemical separation and preparation of reagent solutions are similar to those described by Edwards et al. (1987) and Shen et al. (2002, 2003). For high-precision measurement on the Faraday cups, the Th fraction was always passed through a second anion-exchange column to ensure clear separation from U. Routine chemical yields are about 90% or better for both U and Th. Upon dry down, U and Th separates had no visible residue or no more than a film on the order of half a mm in diameter or less. An aliquot of ^{236}U–^{233}U double spike solution was admixed (so that $^{233}U/^{229}Th \sim 1$) with each Th fraction just prior to analysis for use in correcting for mass fractionation. Because we use the $^{236}U/^{233}U$ ratio to correct for instrumental fractionation of Th, we were concerned about the possibility of differential fractionation of isotopes of U and isotopes of Th during chemical separation. We tested for this fractionation and saw no evidence for this process using our standard chemical procedures (see Supplementary material and Table S3).

2.4. Instrumentation

U and Th isotopic measurements were made on our Thermo-Scientific Neptune MC-ICP-MS. This instrumentation has been described by Wieser and Schwieters (2005). The collector system has 8 moveable Faraday cups and an off-axis fixed center cup. The axial beam can be deflected into either the center Faraday cup or a secondary electron multiplier (SEM) with copper–beryllium dynodes.

The SEM is located behind a retarding potential quadrupole (RPQ), which improves abundance sensitivity. All measurements were made using an Aridus or Aridus II desolvating nebulizer. Detailed operating conditions are described in the Supplementary material.

A data acquisition protocol using either Faraday cups or SEM was chosen according to the intensities of smallest isotope beams, i.e., ^{234}U for U and ^{230}Th for Th. If we could attain a beam intensity of 3×10^{-13} A (30 mV using a 10^{11} Ω resistor) or more for 300 s or longer, we measure the beams with the cups; otherwise we measure the beams by peak-jumping on the SEM (see Supplementary material and Shen et al. (2012) for discussion of SEM techniques). With our 1–2% efficiency, this criterion corresponds to 1 μg of ^{238}U and 20 pg of ^{230}Th. These amounts would be found in 1 g of cave calcite older than about 100 ka, containing 1 ppm of ^{238}U.

3. Results and discussion

3.1. Faraday cup measurements

3.1.1. U measurement protocols

The cup configurations used for U and Th measurements are illustrated in Fig. S1. For U isotopic measurements, we made measurements at 3 magnetic field values: one for which we measured ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U on the cups, one for which we measured the tail at mass 234.5 and one for which we measured the tail at mass 237. The tail measurements were made on the axial SEM with the RPQ off. The ^{238}U beam was measured at ~50 V on cup H2 with a 10^{10} Ω resistor (5×10^{-9} A). The other U isotopes were measured on cups with 10^{11} Ω resistors. SEM dark noise (~0.01–0.02 cps) and counting efficiency (with daily variability of ≤1%) were routinely monitored. During cleaning prior to each U or Th measurement, baselines of the Faraday cups were measured for about 16 min, approximately equal to typical U data acquisition time. Baseline variability for 16 min integrations is about ± 4 μV at the 2σ level, and is a significant source of uncertainty. Daily external errors on baseline measurements are on the same order (Fig. S2). To minimize this uncertainty, the amplifier with the least noise was connected to cup L2 for measuring the small beams, ^{234}U or ^{230}Th (Fig. S1). If possible, we increased ^{234}U and ^{230}Th beam intensities above the minimum currents required for cup measurements (30 mV or 3×10^{-13} A) to further reduce this source of error. The gain of each amplifier/resistor was determined with standard internal voltages. For U measurements, this sometimes required measurements of two aliquots of the U fraction. For the more concentrated aliquot, we measured all of the U isotopes except ^{238}U, which was too large to measure, but was collected in a grounded cup. For the more dilute aliquot, we measured all of the U isotopes except ^{234}U, which was too small for useful data at the required precision. We then combined the data from the two runs.

3.1.2. U tailing

For the cup U isotopic determinations, another important issue is correction for tailing effects from ^{238}U and ^{235}U, under the small beams (^{233}U, ^{234}U and ^{236}U; see Edwards et al., 1987; Cheng et al., 2000; Shen et al., 2002). In developing our measurement and tailing correction protocol, we started with the idea that the large $^{238}U^+$ beam needed to be collected in a Faraday cup any time that we were measuring an ion beam or tail. By doing so, we would prevent reflected beams or charged particles generated by the large $^{238}U^+$ beam from causing measurement artifacts. We then characterized the $^{238}U^+$ tail carefully and developed a measurement protocol in which we characterize the tail in detail daily, then characterize aspects of the tail during the mass spectrometer runs (see Supplementary material for details) and use all of this information in making the tail corrections.

3.1.3. Th measurement protocols and correction for instrumental fractionation

The challenges of the Th measurements differ from those of the U measurements. Most of our samples have extremely low ^{232}Th concentrations (generally less than hundreds of parts per trillion) and consequently very high $^{230}Th/^{232}Th$ ratios (0.05–2). As a result, there are no Th beams larger than 1 V and tailing corrections are trivial. On the other hand, it is not possible to correct for instrumental fractionation of Th isotopes without an additional Th isotope. Thus, we use U isotopes (our ^{236}U–^{233}U spike) to correct for instrumental fractionation of Th. Tests of this procedure showed no evidence for inaccuracy at our measurement precision of $\pm 2\,\varepsilon$ units (see Supplementary material and Table S4).

Our measurement protocols for Th on the cups are similar to those described by Potter et al. (2005). Amplifier baselines are measured with the accelerating voltage off before and after sample measurement for 16 min, as with the U measurements. After baseline measurement, intensities of ^{229}Th–^{230}Th–^{232}Th and admixed ^{236}U–^{233}U spike were determined on the cups in static mode (Fig. S1). Each sample was measured for about 4 min with a ^{230}Th beam intensity of 40 mV (4×10^{-13} A) or more. Although tailing is generally insignificant, we do apply ^{232}Th tail corrections based on measurement the ^{232}Th tail of our Ames-Th electrodeposited standard solution, which has a low $^{230}Th/^{232}Th$ ratio of 0.603 (± 0.004) $\times 10^{-6}$ (Cheng et al., 2000; Shen et al., 2002).

3.1.4. Reproducibility

The external error for our $^{234}U/^{238}U$ measurements is also about 2 ε-units (2σ) as shown by repeat measurements of CRM-112A during a 3-yr period between January 2007 and February 2010 (Fig. 1). This is also consistent with the performance of many duplicate measurements of calcite samples that typically agree within internal errors of about 2 ε-units (Table S5).

3.2. Isotopic compositions of CRM U-500 and CRM-112A

As noted above, we determined the isotopic composition of our ^{236}U–^{233}U spike by measuring mixtures of our spike and the IRMM-074/10 standard. We then determined the $^{238}U/^{235}U$ ratio of the CRM U-500 standard by measuring mixtures of CRM U-500 and our spike. Our measured value is 0.99989 ± 0.00004, only considering the uncertainty in our mass spectrometer measurements. If we also consider the quoted uncertainty in IRMM-074/10, the error increases to ± 0.00016 (Table 1). Our $^{238}U/^{235}U$ value agrees within uncertainties with the value of Condon et al. (2010), 0.99978 ± 0.00016, and the value of Richter et al. (2010), 0.99991 ± 0.00037 and the original certified value (1.000302 with an uncertainty of about 1‰, Garner et al., 1971). However, our value is about 4 ε-units smaller than the certified value and has significantly smaller error. After normalization to our $^{238}U/^{235}U$ value, we obtained the following isotope ratio values for CRM U-500: $^{236}U/^{235}U = 0.001523 \pm 0.000003$ and $^{234}U/^{235}U = 0.010430 \pm 0.000002$ (Table 1). Again, using our spike, calibrated to IRMM-074/10, we measured the following isotope ratios for CRM-112A: $^{234}U/^{238}U = 52.852$ (± 0.015 or ± 0.018) $\times 10^{-6}$ and $^{238}U/^{235}U = 137.832$ (± 0.015 or ± 0.026) (Table 2), where the smaller of each pair of errors only includes the uncertainty in our mass spectrometric measurements and the larger of each pair of errors also includes the quoted uncertainty in the IRMM standard. Using the new ^{234}U half-life (see Section 3.4), the $^{234}U/^{238}U$ activity ratio is 0.9615 ± 0.0003 and $\delta^{234}U = -38.5 \pm 0.3$. Note that these uncertainties only include our measurement uncertainties, as these values are essentially a comparison of our values for $^{234}U/^{238}U$ in CRM-112A and in our "secular equilibrium" materials. As both $^{234}U/^{238}U$ values are based upon the same IRMM standard, the uncertainty that the IRMM standard contributes to both values is highly correlated and normalized out in the comparison.

3.3. $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ of "secular equilibrium" materials

3.3.1. Testing of calcite samples

Replicate measurements of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ atomic ratios of U–Pb dated 2–26 million yr old calcites, MO-1, MO-2 and MO-5 from Leana's Breath Cave, Australia (Woodhead et al., 2006), WM1-H2 from Wilder Mann Cave, Austria (Meyer et al., 2009), and CA-1 from Jewel Cave, S. Dakota, USA are given in Table S5. The consistency of $^{234}U/^{238}U$ values, 54.97 (± 0.01) $\times 10^{-6}$, and $^{230}Th/^{238}U$ values, 16.916 (± 0.003) $\times 10^{-6}$ (where quoted errors
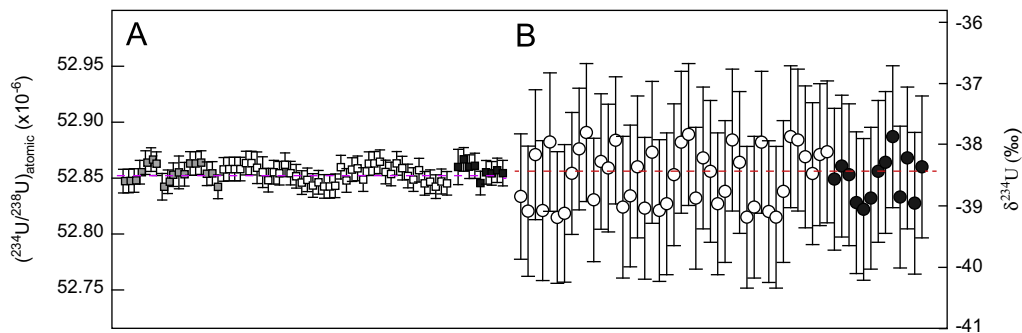
Fig. 1. (A) Repeat measurements of the $^{234}U/^{238}U$ ratio, for CRM-112A using Faraday cup protocol between January 2007 and May 2008 (gray squares with H cones, open squares with X cones), and in February 2010 (solid squares with X cones). (B) Duplicate measurements with internal precision of 0.8–1.2‰ using single SEM protocol between May 2007 and May 2008 (open circles), and between December 2009 and January 2010 (solid circles). The long-term 2σ reproducibility is ~2 ε-units for the Faraday-cup protocol and ~1‰ for the SEM protocol, consistent with the typical internal precision of individual measurements. Dash lines show mean values of $^{234}U/^{238}U$ atomic ratios: 52.852 (± 0.015) $\times 10^{-6}$ and 52.86 (± 0.05) $\times 10^{-6}$ for the cup and SEM protocols, respectively.

Table 2
U isotope compositions of CRM−112A, Table Mountain Latite (TML), basalt (BCR − 2) and uraninite (HU − 1).

Material	$^{234}U / ^{238}U$ (atomic × 10^{-6})	^{234}U (‰)	$^{238}U / ^{235}U$ (atomic)	$\varepsilon^{238}U$ (ε-units)	$^{230}Th / ^{238}U$ (activity)
CRM-112A					
This study	**52.852 ± 0.015**	− 38.5 ± 0.3	**137.832 ± 0.015**	0.0 ± 1.1	
Certificate value	**52.841 ± 0.082**	− 38.7 ± 1.5	**137.849 ± 0.079**	1.2 ± 5.7	
Condon et al. (2010)			**137.844 ± 0.011**	0.9 ± 0.8	
Richter et al. (2010)	**52.853 ± 0.016**	− 38.5 ± 0.4	**137.836 ± 0.023**	0.3 ± 1.7	
Hiess et al. (2012) (TIMS)	**52.99 ± 0.16**	− 36.0 ± 2.9	**137.832 ± 0.022**	0.0 ± 1.6	
Hiess et al. (2012) (ICPMS)	**52.870 ± 0.050**	− 38.2 ± 0.9	**137.829 ± 0.022**	0.0 ± 1.6	
Cheng et al. (2000)	**52.860 ± 0.050**	− 38.4 ± 1.0			
TML					
Table	54.920 ± 0.011	− 0.89 ± 0.21	137.813 ± 0.012	− 1.4 ± 0.8	
Mountain	54.922 ± 0.015	− 0.85 ± 0.27	137.778 ± 0.011	− 3.9 ± 0.8	
Latite	54.920 ± 0.018	− 0.89 ± 0.32	137.799 ± 0.006	− 2.4 ± 0.4	
	54.910 ± 0.011	− 1.07 ± 0.19	137.799 ± 0.006	− 2.4 ± 0.4	
Average	**54.918 ± 0.011**	**− 0.92 ± 0.19**	**137.797 ± 0.011**	**− 2.5 ± 0.4**	
HU-1					
Harwell	54.890 ± 0.010	− 1.43 ± 0.18	137.767 ± 0.010	− 4.7 ± 0.7	1.00468 ± 0.00020
Uraninite	54.890 ± 0.010	− 1.43 ± 0.18	137.765 ± 0.010	− 4.8 ± 0.7	1.00474 ± 0.00022
	54.910 ± 0.010	− 1.07 ± 0.18	137.764 ± 0.010	− 4.9 ± 0.7	1.00430 ± 0.00033
	54.900 ± 0.010	− 1.25 ± 0.18	137.760 ± 0.020	− 5.2 ± 1.5	1.00413 ± 0.00033
	54.910 ± 0.010	− 1.07 ± 0.18	137.765 ± 0.010	− 4.9 ± 0.7	1.00489 ± 0.00028
	54.900 ± 0.013	− 1.25 ± 0.24	137.757 ± 0.010	− 5.5 ± 0.7	1.00480 ± 0.00025
	54.900 ± 0.013	− 1.25 ± 0.24	137.768 ± 0.010	− 4.7 ± 0.7	1.00459 ± 0.00020
	54.900 ± 0.010	− 1.25 ± 0.18	137.770 ± 0.010	− 4.5 ± 0.7	1.00474 ± 0.00028
	54.910 ± 0.010	− 1.07 ± 0.18	137.780 ± 0.010	− 3.8 ± 0.7	1.00438 ± 0.00035
Average	**54.903 ± 0.011**	**− 1.20 ± 0.18**	**137.766 ± 0.010**	**− 4.8 ± 0.7**	**1.00458 ± 0.00020**
BCR-2-c					
Columbia	55.030 ± 0.030	1.11 ± 0.54	137.789 ± 0.017	− 3.2 ± 1.3	
River Basalt	55.020 ± 0.030	0.93 ± 0.55	137.768 ± 0.020	− 4.6 ± 1.5	
	55.030 ± 0.042	1.11 ± 0.77	137.791 ± 0.025	− 3.0 ± 1.8	
Average	**55.027 ± 0.030**	**1.05 ± 0.55**	**137.783 ± 0.020**	**− 3.6 ± 1.3**	

include only our measurement errors) shows that external reproducibility is close to internal precision (Table S5, Fig. 2). The three different sets of samples from caves in Australia, Austria, and the US have identical measured $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ atomic ratios within analytical precisions of 1–3 ε-units (Table S5), consistent with the assumption that these materials are in secular equilibrium.

We also measured $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ ratios in a series of presumed old (not U–Pb dated) calcite samples from diverse locations worldwide, including GMC, IS-3, and NC-1 from China, GC-I, GC-II and GC-III from Mexico, and Kr3 from Ukraine (Table S5). These samples give $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ atomic ratios, indistinguishable from those of the previous three sets of calcites, consistent with the assumption that these samples are also in secular equilibrium.

3.3.2. Zircons

Measured $^{234}U/^{238}U$ atomic ratios of zircon samples, Z-VIII, EZ-5 and EZ-1, are 54.96×10^{-6}–54.97×10^{-6} (Table S6). The values within precisions of ± 2 ε-units are consistent with the above calcite data. However, one zircon sample, EZ-7, and three cyrtolite samples, 7-b, C-II and EZ-X, show systematically low $^{234}U/^{238}U$ atomic ratios ranging from 54.36×10^{-6} to 54.90×10^{-6}, decreasing generally from visibly slightly altered zircon to clearly altered zircons, cyrtolites (Table S6). This is consistent with preferential ^{234}U loss during diagenesis.

3.3.3. Other standards: TML, HU-1 and BCR-2

Determinations of ^{238}U and ^{234}U abundances for three materials that have been used as secular equilibrium standards, TML, BCR-2 and HU-1, and ^{230}Th abundances of the latter are listed in Table 2. $^{234}U/^{238}U$ atomic ratios are 54.92 (± 0.01) $\times 10^{-6}$ for TML, 55.03 (± 0.03) $\times 10^{-6}$ for BCR-2-c, and 54.90 (± 0.01) $\times 10^{-6}$ for HU-1 (Table 2). The values for TML and HU-1 are about 1‰ lower than the calcite value and that for BCR-2-c is about 1‰ higher than the calcite values. Considering errors, $^{234}U/^{238}U$ values for all three are distinct, outside of analytical errors, from our calcite values, suggesting that these materials are not in secular equilibrium. The measured mean of $^{230}Th/^{238}U$ atomic ratio from Minnesota's aliquot of HU-1 is 16.993 (± 0.004) $\times 10^{-6}$, similar to the result documented in Cheng et al. (2000) and about 4.6‰ higher than the values for our calcite samples. Note that HU-1 was originally distributed as a solid, with directions for dissolution. Typically, after dissolution, there would be some remaining insoluble residue from which the solution was separated. We obtained our aliquot of HU-1, already in solution, from the University of Quebec at Montreal. It is possible and perhaps likely, that solutions of HU-1 prepared from different dissolutions would have different $^{230}Th/^{238}U$ ratios (and plausibly different $^{234}U/^{238}U$ ratios) due to fractionation between solution and residue.

3.4. ^{234}U and ^{230}Th half-lives

3.4.1. ^{234}U half-life

If we assume that the measured $^{234}U/^{238}U$ value for our calcites and well-preserved zircons is the secular equilibrium value, we can calculate the ^{234}U decay constant: $\lambda_{234} = \lambda_{238}/(^{234}U/^{238}U)$ using $\lambda_{238} = 1.55125 \times 10^{-10}$ a^{-1} as determined by Jaffey et al. (1971). However, we should first consider the full set of errors involved in determining a value for the decay constant. In addition to the uncertainty of our mass spectrometric measurements (2 ε-units), the uncertainty in the IRMM standard contributes 2 ε-units (1.5 ε-units quoted uncertainty over 3 mass units, so 2 ε-units over 4 mass units), and we assume an additional up to 2 ε-units uncertainty to account for the possibility that some of the "secular
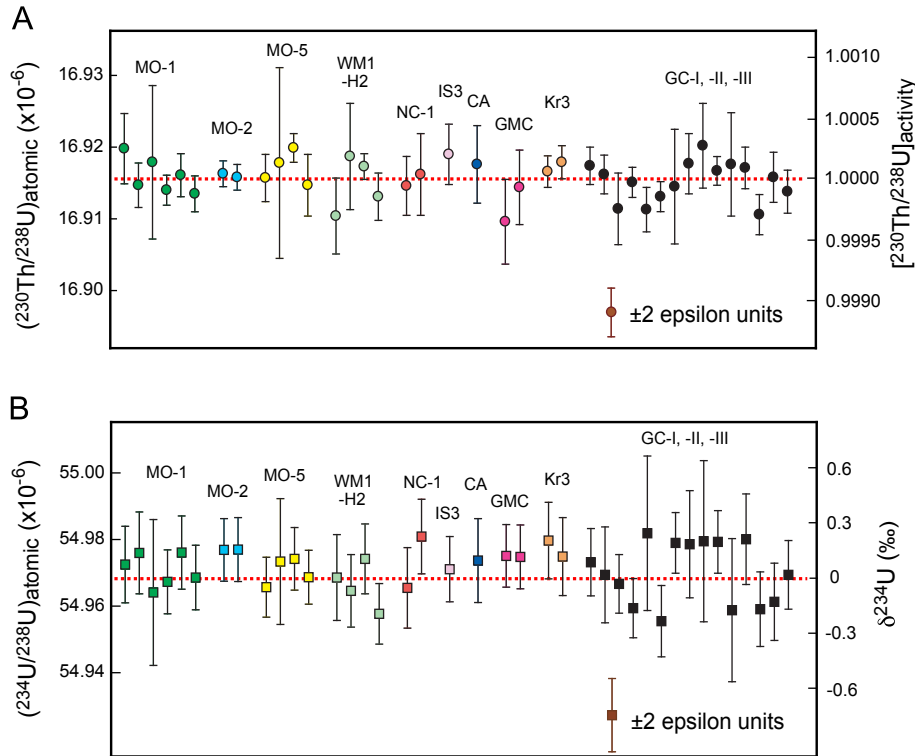
Fig. 2. (A) ^{230}Th/^{238}U and (B) ^{234}U/^{238}U atomic ratios of calcites in U–Th isotopic secular equilibrium. The sample numbers are indicated at the top. The error bars indicate analytical precisions (2σ). An error bar of 2 ε-units is also shown in (A) and (B) for comparison.

equilibrium" materials in our average may be altered a small amount, but not identified as distinct given our 2 ε-unit measurement uncertainty. Combining all of these uncertainties quadratically, yields a ^{234}U/^{238}U$_{secular\ equilibrium}$ = (54.970 ± 0.019) × 10^{-6}. From this, we calculate a value for λ_{234} of (2.82206 ± 0.00302) × 10^{-6} a^{-1}, the uncertainty of which is dominated by the additional uncertainty in λ_{238} (10.7 ε-units, Jaffey et al., 1971), and corresponds to a ^{234}U half-life of 245,620 ± 260 a. Included in all of these uncertainties are a number of systematic errors, which largely cancel for purposes of calculating ^{230}Th ages. Those that do not effectively cancel are our measurement uncertainty and the uncertainty in whether all of the "secular equilibrium" samples are truly in secular equilibrium. Keeping only these sources of uncertainty, for the purposes of ^{230}Th dating, the error in ^{234}U half-life reduces to ± 70 a corresponding to an uncertainty in λ_{234} of ± 0.00080 × 10^{-6} a^{-1}. Our new half-life value is consistent with and more precise than our previous determination of 245,250 ± 490 a (2σ) (Cheng et al., 2000) and with earlier determinations (De Bievre et al., 1971; Lounsbury and Durham, 1971; Holden, 1989). The nominal shift of 370 a (or about 1.5‰) from the Cheng et al. (2000) value results from (1) the use of the more accurate U isotopic standard (IRMM-074/10) as opposed to CRM U-500, which resulted in a shift of about 0.5‰ and (2) a shift of about 1‰ due to the difference in materials used as "secular equilibrium" standards. In particular, measurements of ^{234}U/^{238}U in TML and HU-1 were averaged into the Cheng et al. (2000) secular equilibrium value. We show above that these materials have ^{234}U/^{238}U ratios that are distinctly outside of the self-consistent values for calcite and unaltered zircon of this study, and we have, therefore, not used their ^{234}U/^{238}U in calculating our secular equilibrium ^{234}U/^{238}U value.

3.4.2. ^{230}Th half-life

The uncertainties in the secular equilibrium ^{230}Th/^{238}U value are measurement precision (2 ε-units), uncertainty in the IRMM U

standard (1.5 ε-unit), uncertainty in the secular equilibrium assumption (2 ε-units), uncertainty in the use of U isotopes to calculate instrumental fractionation for Th (2 ε-units), and uncertainty in the Th and U gravimetric standards (10 ε-units). Combining these uncertainties quadratically yields ^{230}Th/^{238}U$_{secular\ equilibrium}$ = (16.916 ± 0.018) × 10^{-6}. The value of ^{230}Th decay constant is: $\lambda_{230} = \lambda_{238}/(^{230}$Th/^{238}U$) = 9.1705$ (± 0.0138) × 10^{-6} a^{-1} (2σ), corresponding to a ^{230}Th half-life of 75,584 ± 110 a, including uncertainty in λ_{238} (Jaffey et al., 1971). The new half-life value is consistent within uncertainty with our previous determination of 75,690 ± 230 a (2σ) (Cheng et al., 2000) and with an earlier determination by Meadows et al. (1980). Keeping only those sources of uncertainty that do not effectively cancel for the purposes of ^{230}Th dating (measurement precision, uncertainty in secular equilibrium assumption, and uncertainty in instrumental fractionation correction) yields a half-life uncertainty of ± 30 a, corresponding to an uncertainty in λ_{230} of ± 0.0032 × 10^{-6} a^{-1}.

3.5. ^{230}Th dating precision and accuracy

3.5.1. Dating precision

Given the precision with which we measure ^{230}Th/^{238}U and ^{234}U/^{238}U using our Faraday cup protocol, under ideal circumstances, the 2σ error in age is ± 10 a at 10 ka, ± 100 a at 130 ka, ± 300 a at 200 ka, ± 1 ka at 300 ka, ± 2 ka at 400 ka, ± 6 ka at 500 ka, and ± 12 ka at 600 ka (Fig. 3). The isotopic composition of a sample with an age < 800 ka can clearly be resolved from the isotopic composition of a sample in secular equilibrium, assuming closed system behavior.

3.5.2. Strategy for accuracy test

We designed a test of our half-live values, measurement techniques, and the degree to which our "secular equilibrium" materials were truly in secular equilibrium. The isotopic
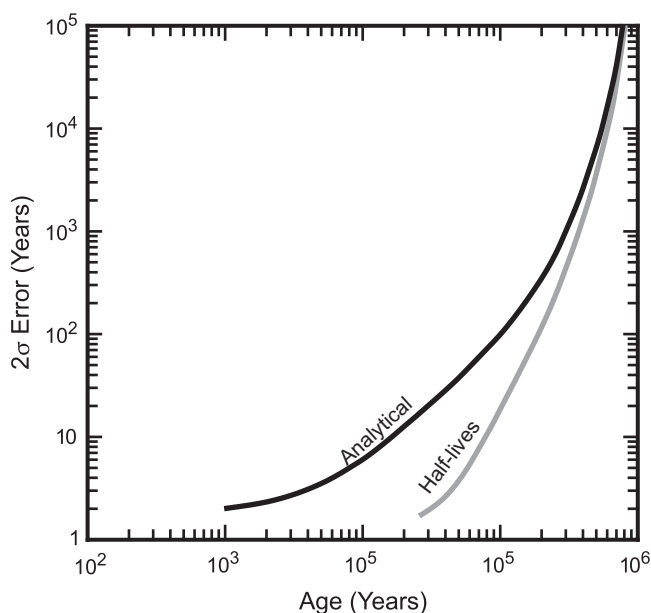
Fig. 3. Error in age vs. age (both on log scales). Plotted are the errors in age from analytical error in the measurement precision of a particular sample and error in age due to imprecision in the half-life values. Note that the error resulting from half-life uncertainty is small compared to analytical error in measuring the sample isotopic compositions.

Fig. 4. An age model for stalagmite sample SB-32 from Sanbao Cave. The chronology is based on a polynomial fit of all 84 [230]Th dates. Vertical error bars depict [230]Th dating errors (2σ).

Fig. 5. $\delta^{18}O$ time series of stalagmite SB-32 (black) in comparison with July 21st insolation at 65°N (grey, Berger, 1978). The Sanbao $\delta^{18}O$ time series broadly matches the ~23-ka cycle. In contrast, for example, had we simply used the previous half-life values, the $\delta^{18}O$ time series would have been shifted younger by 25 ka at 500ka, 37 ka at 550 ka, and 54 ka at 600 ka. See Supplementary material for the full data set.

composition of rainfall has tracked summer solar insolation for the past 380 ka in those regions of China currently affected by Asian monsoon rainfall (see Wang et al., 2008; Cheng et al., 2009a). We expect that this relationship would have continued further back in time. If so, an accurately dated Chinese speleothem in this time range should yield an oxygen isotope record that follows the calculated summer insolation. In addition, because of the nature of the [230]Th age equation, the offset of a secular equilibrium standard from secular equilibrium would result in progressively larger shifts in [230]Th ages for progressively older samples. For example, a 5 ε-unit offset in the "secular equilibrium" material will result in an age offset of about 1 ka at 300 ka; 2 ka at 400 ka; 5 ka at 500 ka; 15 ka at 600 ka and 30 ka at 650 ka (Fig. S5). Thus, a 5 ε-unit offset in our secular equilibrium value should show up as a systematical offset between a Chinese stalagmite oxygen isotope record and summer insolation, an offset that would increase with age.
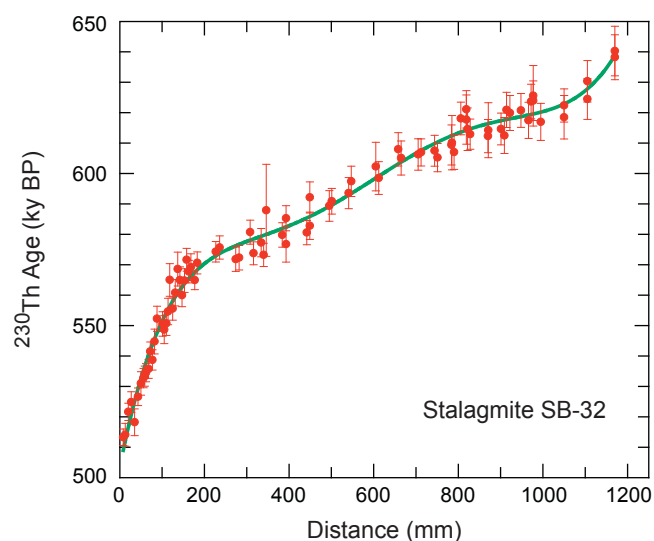
3.5.3. Relationship between oxygen isotope record and summer insolation

We first identified a stalagmite (SB-32 from Sanbao Cave (see Wang et al., 2008)) that grew continuously between about 640 and 510 ka ago. We then obtained 84 [230]Th dates using the methods described in this paper. To avoid any possible problems associated with drilling, we cut a column along the growth axis of this sample, and then sliced this column into subsamples that we dated. We first showed that the dates were in stratigraphic order, consistent with closed system behavior for the samples (Fig. 4, Table S7). The oxygen isotope time series broadly follows summer solar insolation (Berger, 1978), with no indication of progressive offset with age (Fig. 5), consistent with accurate ages based on the new decay constants.
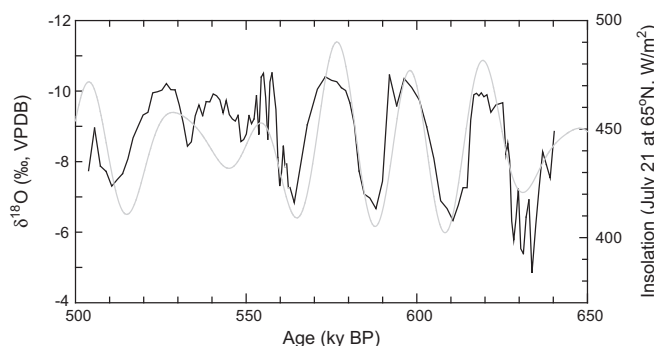
3.6. [238]U/[235]U variation in nature

3.6.1. Notation

Natural variation in the ratio of [238]U/[235]U has been studied for several decades, but has received renewed attention in recent

years. In an early study, Cowan and Adler (1976) demonstrated natural variation in this ratio. The main mechanism that they discuss is depletion of [235]U as a result of natural fission chain reactions. However, their results do not preclude variations due to mass dependent (or nuclear volume dependent) fractionation. Soon thereafter, a number of studies focused on the possibility of variability of [238]U/[235]U due to the decay of [247]Cm (through short-lived daughters to [235]U) in the early solar system. Arden (1977) and Tatsumoto and Shimaraura (1979) reported large anomalies. However, Chen and Wasserburg (1980, 1981) found no evidence of anomalous [238]U/[235]U, at a level of about 5‰ in similar materials. The [236]U–[233]U double spike technique developed by Chen and Wasserburg (1981) became the standard method for measuring U isotopic composition up to the present, including this publication. The evidence for [247]Cm in the early solar system has been pursued, with higher precision measurements in recent years (Stirling et al., 2006; Brennecka et al., 2010). Brennecka et al. (2010) showed evidence for [238]U/[235]U variation of about 4‰, likely related to decay of [247]Cm. In addition, terrestrial studies following up on the work of Cowan and Adler (1976) have studied variation in [238]U/[235]U in terrestrial samples (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Hiess et al., 2012). The observed variability, in excess of 5‰ (Hiess et al., 2012), likely results from

mass-dependent fractionation, with nuclear volume effects playing an important role. In most of the mass/nuclear volume dependent studies and some of the studies of possible radiogenic anomalies, different ε and δ notations and $^{235}U/^{238}U$ or $^{238}U/^{235}U$ reference values have been employed. As the community moves forward, this situation is untenable.

As a consequence, we would like to suggest a common notation based upon precedent and common sense. First, it seems to us that the search for ^{247}Cm anomalies is a special case in which the use of absolute ratios, following Brennecka et al. (2010) and more than half a century of radiogenic isotope dating studies, makes sense. If the radiogenic studies are taken as a special case, then our choice of notation for the remaining mass dependent/nuclear volume studies should follow the precedent of stable isotope studies, which traditionally have employed a high mass/low mass isotope ratio, as opposed to the reverse, hence the choice of $^{238}U/^{235}U$ as opposed to $^{235}U/^{238}U$. From here, we choose to examine a relatively early notational definition and ask if additional changes might be warranted. Stirling et al. (2007) define $\varepsilon^{235}U$ with CRM 145 as the standard. Based on our previous argument, we suggest that it should instead be defined as $\varepsilon^{238}U$. The choice of ε rather than δ seems reasonable to us as precisions of better than an ε-unit are clearly now possible and the known range of natural variability of $^{238}U/^{235}U$ in ε-units is on the order of several tens. The choice of CRM 145 also is reasonable, as this standard is readily available to the community. It also has the same certified isotopic composition as CRM-112A, which is also readily available and has a long history as an isotopic and gravimetric U standard. Furthermore, the $^{238}U/^{235}U$ value of CRM-112A has now been measured at high precision relative to the IRMM standards, independently by several laboratories (Richter et al., 2010; Condon et al., 2010; Hiess et al., 2012; this study). In sum, we recommend $\varepsilon^{238}U$ notation with CRM 145/CRM-112A defined as $\varepsilon^{238}U = 0$.

3.6.2. Consideration of $^{238}U/^{235}U$ fractionation on ^{230}Th dating

Recent observations show an approximately 50 ε-unit variation in $^{238}U/^{235}U$ ratios in natural materials (Hiess et al., 2012). A survey of low-temperature precipitates yields a range of about 20 ε-units (Stirling et al., 2007). Our calcite samples show a similar range, from $\varepsilon^{238}U = -6$ to $+11$ (Table S5). This variability has implications regarding age accuracy (Stirling et al., 2007). Our laboratory and others have traditionally measured the $^{234}U/^{235}U$ ratio and calculated a $^{234}U/^{238}U$ ratio presuming a nominal $^{238}U/^{235}U$ ratio of 137.88. Similarly, we have directly measured a ^{235}U concentration (via isotope dilution) and calculated a ^{238}U concentration and $^{230}Th/^{238}U$ ratio using the nominal $^{238}U/^{235}U$ value. Of note is the fact that, with our technical procedures, any inaccuracies in the 137.88 value are perfectly correlated when used in calculating $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios. Also of note is the fact that the $^{238}U/^{235}U$ value has no bearing on the $^{230}Th/^{234}U$ ratio. ^{230}Th ages are, to first order, dependent on the $^{230}Th/^{234}U$ ratio (not ^{238}U per se). For this reason, with our technical procedures, errors in age due to natural variability in $^{238}U/^{235}U$ value are relatively small. Using our procedures, a 10 ε-unit inaccuracy in $^{238}U/^{235}U$, results in the following inaccuracies in age for carbonates with an initial $\delta^{234}U$ value of 150‰: 20 a for a 100 ka old sample, 0.15 ka at 200 ka; 0.45 ka at 300 ka; 1.5 ka at 400 ka; and 4 ka at 500 ka. Note that our calculated age inaccuracies are much smaller than those calculated by Stirling et al. (2007) for the same inaccuracy in $^{238}U/^{235}U$. It is likely that the discrepancies are the result of differences in analytical procedures used in the different laboratories.

In summary, for our multiplier measurements, in which the highest possible precision for any pertinent isotope ratio is ± 1‰, the inaccuracy in age introduced by a nominal $^{238}U/^{235}U$ ratio, is small compared to the error in age due to measurement precision. Thus, for our multiplier measurements, a nominal $^{238}U/^{235}U$ value is sufficient, or, for the higher precision multiplier measurements a generic stalagmite or cave-specific value is fine. However, for our Faraday cup measurements, potential inaccuracies in a nominal value are significant. Thus, we measure $^{238}U/^{235}U$ directly for all samples measured on the Faraday cups.

4. Conclusions

We have developed techniques for precisely measuring ^{234}U and ^{230}Th to precisions of 1–3 ε-units by MC-ICP-MS, which can now be applied to dating calcites with U concentrations as low as a few hundred ppb. On the basis of systematic experiments and precise measurements of diverse materials, likely to be in U–Th isotopic secular equilibrium, we determined new half-life values for ^{234}U and ^{230}Th as $245,620 \pm 260$ and $75,584 \pm 110$ a (including all uncertainties), or errors of ± 70 and ± 30 a respectively, considering only uncertainties that will not effectively cancel in calculating ^{230}Th ages. The measurement techniques allow for determination of high-precision ^{230}Th ages; the new half-life values improve the accuracy of ^{230}Th ages. Correlation between N. Hemisphere summer insolation and the Sanbao Cave $\delta^{18}O$ record between 510 and 640 ka ago, as determined using our new half-life values, supports both the accuracy of our half-life values and the closed system assumption for these stalagmites at the new levels of precision. It also illustrates the application of this new generation of ^{230}Th dating techniques.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.04.006.

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