The half-lives of uranium-234 and thorium-230

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Abstract

We have re-determined the 234 U and 230 Th half-lives to be 245,250 ± 490 years (2σ) and 75,690 ± 230 years (2σ), respectively. Using high precision thermal ionization mass spectrometric (TIMS) methods, we measured 234 U/238 U and 230 Th/238 U atomic ratios in 4 different materials that were likely to have behaved as closed systems for 10^6 years or more: zircons with concordant 238 U–206 Pb, 235 U–207 Pb, and 232 Th–208 Pb ages, Iceland Spar, Table Mountain Latite, and aliquots of a solution of Harwell uraninite HU-1. We calibrated the TIMS multipliers using U-500, U and Th gravimetric standards, and U double spike. Consistent 234 U/238 U values for all measured materials and consistent 230 Th/238 U values for all materials with the exception of our HU-1 solution support the secular equilibrium status. The new half-lives agree within error with previously determined values; however, errors in our values are generally smaller than those in the earlier determinations. Our 234 U half-life is about 3½ higher than that commonly used in 230 Th dating laboratories and our 230 Th half-life is about 4½ higher. 230 Th ages calculated with the new half-lives are generally older than those calculated with the previously used half-lives. The difference in age, though, is small throughout the 230 Th age range because our revised 234 U and 230 Th half-lives are offset from earlier values in the same sense (both to higher values). In the case of dating materials older than 350 ka in laboratories that rely solely on gravimetric standardization procedures, use of our decay constants and their associated errors will considerably reduce the errors in age arising from uncertainty in the decay constants. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

230 Th dating has been widely used in establishing the absolute chronology of Quaternary climate change (e.g., Edwards et al., 1987; Stein et al., 1993; Gallup et al., 1994; Szabo et al., 1994; Stirling et al., 1995; Adkins et al., 1998), in calibrating the radiocarbon...
time scale (e.g., Bard et al., 1990, 1993; Edwards et al., 1993), and in studies of human evolution (e.g., Swisher et al., 1996; Cheng et al., 1997). The \(^{230}\text{Th}\) method is based on the decay of \(^{238}\text{U}\) through two short lived intermediate daughter isotopes to \(^{234}\text{U}\) and the decay of \(^{238}\text{U}\) to \(^{230}\text{Th}\). The \(^{230}\text{Th}\) age equation (Bateman, 1910; Broecker, 1963) includes terms for the decay constants (or half-lives) of all three nuclides. Therefore, accurate and precise values for the half-lives are essential for accurate and precise age determination. Renne et al. (1998) have recently summarized the issue of the accuracy of half-life determinations and implications for the accuracy of different types of radiometric ages. Of the three pertinent nuclides used in \(^{230}\text{Th}\) dating, the fractional error in the half-life of \(^{238}\text{U}\), \(4.4683 \pm 0.0048 \times 10^9\) years (2\(\sigma\), Jaffey et al., 1971), is the smallest. For the remainder of the text, all quoted errors will be at the 2\(\sigma\) level of uncertainty. For the half-life of \(^{234}\text{U}\), De Bievre et al. (1971) determined a value of \(244,600 \pm 730\) years and Lounsbury and Durham (1971) determined a value of \(244,400 \pm 1200\) years. Because these values are almost identical, a commonly used value in geochronology is the mean of the two: \(244,500\) years. However, Holden (1989) has reviewed all \(^{238}\text{U}\) half-life work and gave a weighted average half-life of \(445,500 \pm 1000\) years using revised data including data from De Bievre et al. (1971) and Lounsbury and Durham (1971). This value differs by 4\% from the commonly used value. The fractional error in the value for the \(^{230}\text{Th}\) half-life is the largest of the three; the most recent and most precise value is \(75,381 \pm 590\) years (Meadows et al., 1980). The uncertainties in the half-lives affect the accuracy of \(^{230}\text{Th}\) ages, particularly for samples older than about 350 ka, in cases where standardization is based solely on gravimetric standards. Thus, by reducing errors in the half-life values we can improve the accuracy of \(^{230}\text{Th}\) ages.

If a system remains closed to chemical exchange for an interval of time long compared to the half-lives of the intermediate daughters in the \(^{238}\text{U}\) decay series, it reaches a state of secular equilibrium (Bateman, 1910). In this state, the activities of all of the nuclides in the decay series are equal: \(\frac{238}\text{U}(\lambda_{238}) = \frac{234}{238}\text{U}(\lambda_{234}) = \frac{230}{238}\text{Th}(\lambda_{230})\), or \(\lambda_{234} = \lambda_{238}/(234\text{U}/238\text{U})\) and \(\lambda_{230} = \lambda_{238}/(230\text{Th}/238\text{U})\). The \(\lambda\)'s are decay constants, the chemical symbols refer to numbers of atoms of the indicated nuclide and the subscripts indicate the mass number of the nuclides. As the value of \(\lambda_{238}\) is well-known, one can determine \(\lambda_{230}\) and \(\lambda_{234}\) by measuring \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{238}\text{U}\) in secular equilibrium materials. With thermal ionization mass spectrometric (TIMS) techniques, one can measure \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{238}\text{U}\) with better precision (Edwards et al., 1987) than the errors for the current values for \(\lambda_{230}\) and \(\lambda_{234}\). Thus, in principle the values for the half-lives of \(^{230}\text{Th}\) and \(^{234}\text{U}\) can be refined by simply measuring \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{238}\text{U}\) in secular equilibrium materials. Using this approach, Ludwig et al. (1992) report a value for the \(^{234}\text{U}\) decay constant that is similar to the Holden (1989) value. In using this approach, the key issues are establishing the accuracy and precision of the mass spectrometric measurements and identifying materials that are likely to have behaved as closed systems over at least the last \(10^6\) years.

2. “Secular equilibrium” materials

The identification of materials that have behaved as closed systems is not trivial. For example, Rosholt (1983) showed that most of 84 samples of old crystalline rock from the Midwest and Western United States were out of secular equilibrium, indicating open system behavior. Coralline aragonite often exhibits open system behavior as well (Bender et al., 1979; Edwards et al., 1987; Banner et al., 1991; Bard et al., 1991; Henderson et al., 1993; Gallup et al., 1994; Edwards et al., 1997). We have chosen a set of materials for analysis because they have characteristics that indicate that they are likely to have behaved as closed systems or because they have been used by other laboratories as secular equilibrium standards. One test of the secular equilibrium assumption is whether the diverse group of materials that we have analyzed gives consistent results.

We have the strongest evidence for closed system behavior in zircons with concordant \(^{238}\text{U}^{206}\text{Pb}\), \(^{235}\text{U}^{207}\text{Pb}\), and \(^{237}\text{Th}^{208}\text{Pb}\) ages. The concordant ages suggest that \(\text{U}/\text{Pb}, \text{Th}/\text{Pb}\), and consequently \(\text{U}/\text{Th}\) ratios have not changed since crystallization. We analyzed zircons from the Piper Gulch Granodiorite, Santa Rita Mountains, southeastern Arizona (which we call “Zr1”). These give concordant U-
Th–Pb ages of 188 Ma (Asmerom et al., 1990). We also analyzed zircons from Duluth complex intrusive rocks, Northeastern Minnesota (which we call “Zr2”). These give concordant U–Th–Pb ages of 1100 Ma (Paces and Miller, 1993). We also analyzed parts of a 1 × 1 × 1.5 cm macroscopically well-crystallized zircon crystal from Brazil obtained from Wards, (which we call Zr3). No U–Pb data is available for this zircon. In addition to the zircons, we analyzed Iceland Spar, which may have behaved as a closed system because it is coarsely crystalline, has a small surface to volume ratio, and has no macroscopically visible cracks or pores. We also analyzed Table Mountain Latite, which is used in many laboratories for interlaboratory comparison of $^{230}$Th/$^{232}$Th values (Goldstein et al., 1989; Gill et al., 1992; Palacz et al., 1992; Williams et al., 1992; McDermott et al., 1993; Asmerom and Edwards, 1995) and has been used as an U/Pa secular equilibrium standard (Edwards et al., 1997; Pickett and Murrell, 1997; Pickett et al., 1994). Finally, we analyzed aliquots of a solution of Harwell uraninite HU-1, which has been used as a secular equilibrium standard in alpha counting and TIMS laboratories. The HU-1 that we analyzed was an aliquot of a solution that was prepared at the University of Quebec at Montreal from pitchblende powder dissolved according to standard instructions from Harwell.

3. Gravimetric standards

Whereas the accuracy of $^{234}$U/$^{238}$U measurements ultimately depends on the accuracy of uranium isotopic standards, the accuracy of $^{230}$Th/$^{238}$U measurements depends on the accuracy of both isotopic and gravimetric standards. We prepared our uranium gravimetric standard by dissolving approximately 1.5 g of New Brunswick Laboratories Certified Reference Material 112a (NBL-112a, formerly NBS SRM 960) in 1.5 N nitric acid. NBL-112a is a uranium metal standard purified from natural uranium ore. The uranium assay is $99.975 \pm 0.006\%$ and the relative atomic weight is 238.0289. Our thorium gravimetric standard is a solution made from electrotransport purified thorium metal prepared by the Standard Materials Preparation Center, Ames Laboratory (Schmidt et al., 1979). The thorium assay of the metal is about 99.98%, including analysis for anions such as oxygen in the impurities. About 1.5 g of this metal was dissolved in 1.5 N nitric acid mixed with dilute hydrofluoric acid. To check for biases in the preparation of our gravimetric standards, we prepared both standards in duplicate. The measurements reported here are based on a set of standards prepared at the University of Minnesota. A second set of standards was prepared in an analogous fashion at the University of New Mexico. This set of standards was used as a check of the reproducibility of the University of Minnesota set.

4. Sample loading and mass spectrometric analysis

Solutions of spikes, standards, and/or purified uranium and thorium fractions from the secular equilibrium materials were dried down on zone-refined rhenium filaments. Most thorium fractions were dried down from 0.1 N nitric acid solutions, loaded with colloidal graphite as described by Chen and Wasserburg (1981), and run using the single filament technique, at temperatures of 1700 to 1900°C. Some thorium fractions were dried down from HF solutions without graphite as described by Asmerom and Edwards (1995) and run using the double filament technique. The HF-double filament runs were made for comparison with single filament graphite runs to test for systematic biases in fractionation of thorium isotopes in the mass spectrometer source. $^{230}$Th and $^{238}$U loads varied from 5 to 50 pg and from 0.5 to 3 µg, respectively, and were always large enough so that corrections for chemistry blanks (including filament blanks), < 0.4 fg for $^{230}$Th and < 6 fg for $^{238}$U, were negligible. All uranium solutions were dried down from 0.1 N nitric acid solutions without graphite and run using the double filament technique. Evaporation filament currents were 0.8 to 1.2 A and ionization filament currents were 4.4 to 4.9 A.

For sample analysis, we used both of the Finnigan MAT 262 RPQ mass spectrometers at the University of Minnesota. All thorium analyses were performed on the multiplier behind the retarding potential quadrupole (RPQ) in peak-jumping mode. The ura-
nium measurements were either performed on the Faraday Cups in static collection mode or on the multiplier behind the RPQ in peak-jumping mode. Abundance sensitivity on the cups is about $2 \times 10^{-6}$ (tail at mass 237/peak at mass 238). Abundance sensitivity after the RPQ is greater than 95%. Counting efficiency on the multipliers is about 90%; dark noise is less than 5 cpm. Our multiplier measurements on secular equilibrium materials were all performed on MasCom electron multipliers, which have 19 Cu–Be dynodes. We also report on some of the characteristics of ETP multipliers, which have Al dynodes, and on two other brands of Cu–Be dynode multipliers.

5. Spike preparation

We prepared a $^{233}$U–$^{236}$U double spike as described by Chen and Wasserburg (1981). $^{235}$U oxide and $^{236}$U oxide powders were obtained from Oak Ridge National Laboratory, dissolved in 1.5 N nitric acid and mixed so that the $^{235}$U/$^{236}$U ratio was close to one. Initially, we had problems with increasing $^{236}$U concentration with time in the spike solution, presumably because the $^{236}$U oxide had not dissolved completely. We solved this problem by filtering the solution. The isotopic composition of this spike was determined by (1) mixing the spike with certified reference material CRM U-500 US Department of Energy, New Brunswick Laboratory (Garner et al., 1971) and analyzing the mixture on the cups in static collection mode, and (2) measuring the spike’s isotopic composition in peak-jumping mode on the multiplier. The first measurement provided the $^{233}$U/$^{236}$U ratio of the spike, normalized for instrumental fractionation to the known 238 U/$^{235}$U value of U-500. The spike isotopic composition is: $^{236}$U/$^{233}$U = 1.0106 ± 0.0010, $^{234}$U/$^{233}$U = 0.016808 ± 0.000017, $^{235}$U/$^{233}$U = 0.10539 ± 0.00011, and $^{234}$U/$^{233}$U = 0.003185 ± 0.000005. The absolute concentration of $^{233}$U in the spike was determined by mixing an aliquot of the spike with an aliquot of our NBL-112a gravimetric standard and measuring the mixture on the multiplier in peak-jumping mode.

Our $^{229}$Th spike was prepared by diluting a solution of $^{229}$Th obtained from Oak Ridge National Laboratory in 1.5 N nitric acid. The isotopic composition of this spike was determined on the electron multiplier in peak-jumping mode: $^{230}$Th$/^{229}$Th = 0.0000402 ± 0.0000011 and $^{232}$Th$/^{229}$Th < 0.0018. The absolute $^{229}$Th concentration of our spike was determined by mixing an aliquot of the spike with an aliquot of our thorium gravimetric standard and measuring the isotopic composition of the mixture using the multiplier in peak-jumping mode.

We also prepared a mixed U–Th spike by mixing the two spike solutions. To minimize weighing errors and eliminate errors due to differential evaporation of spike solutions, our mixed spike was used for all measurements of $^{230}$Th/$^{238}$U in secular equilibrium materials. The $^{233}$U and $^{229}$Th concentrations in the mixed spike were confirmed several times by mixing gravimetric standards with the spike and measuring the isotopic composition of the mixture using the multiplier in peak-jumping mode.

6. Characterizing the multipliers

Our measurements on secular equilibrium materials require electron multipliers because $^{230}$Th and $^{234}$U concentrations in natural materials are too low to yield ion beams large enough for precise measurement on the cups. As such, the accuracy of our measurements depends on the linearity of the multipliers. We have tested for multiplier bias using two types of uranium solutions of known isotopic composition. The isotopic composition of these solutions is known from NBL certification, gravimetry, our measurement of the solutions on the cups, or some combination of the three. The first type of solution (which we call a ‘‘Type I solution’’) is natural uranium (NBL-112a) mixed with our spike so that the $^{233}$U/$^{235}$U ratio in the mixture is about 2. In this kind of mixture, the $^{238}$U/$^{235}$U ratio can be mea-
sured, using the known $^{233}\text{U}/^{236}\text{U}$ ratio to normalize for mass fractionation (see Chen and Wasserburg, 1981 for an extensive set of these sorts of measurements). Type I solutions are particularly useful because the natural $^{238}\text{U}/^{235}\text{U}$ ratio (about 138) is well-known and is similar to the value of the uranium isotope ratio that we would like to measure in secular equilibrium materials, the $^{235}\text{U}/^{234}\text{U}$ ratio (about 132). Thus, any multiplier biases related to differential ion beam intensity should be of similar magnitude for both. Before testing multipliers with Type I solutions, we measured the $^{238}\text{U}/^{235}\text{U}$ ratio of a number of natural materials on the cups. The $^{238}\text{U}/^{235}\text{U}$ values of NBL-112a, HU-1, Zr1, and a twentieth century coral all were within 0.4‰ of the nominal value for natural uranium of 137.88 (see Cowan and Adler, 1976; Garner, personal communication, 1997). These measurements indicate that the certified $^{238}\text{U}/^{235}\text{U}$ value for U-500 (upon which our spike $^{235}\text{U}/^{238}\text{U}$ value is based) is consistent with the nominal $^{238}\text{U}/^{235}\text{U}$ value for natural uranium, well within the quoted uncertainties of $\pm 1\%$ for each (Garner, personal communication, 1997; Garner et al., 1971). The measurements also indicate that (1) the procedure by which we determined the $^{235}\text{U}/^{238}\text{U}$ ratio in our spike did not introduce significant inaccuracy or imprecision and (2) a sampling of materials in which we are measuring uranium isotopic composition have the same $^{235}\text{U}/^{238}\text{U}$ values (within $\pm 0.4\%$). The latter finding is consistent with those of Cowan and Adler (1976), who found that $^{238}\text{U}/^{235}\text{U}$ values of a range of uranium-rich natural materials differed by no more than $\pm 0.3\%$.

The second set of solutions ("Type II solutions") that we used for checking multiplier biases, are a set of mixtures of our spike and U-500, in different proportions. U-500 is essentially 50% $^{235}\text{U}$ and 50% $^{238}\text{U}$ and the spike is essentially 50% $^{233}\text{U}$ and 50% $^{236}\text{U}$. Therefore, all mixtures of the two solutions have both $^{235}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ equal to approximately 1. By varying the proportions of spike and U-500, we made a set of mixtures with this characteristic and varying ratios of $^{235}\text{U}$ (or $^{238}\text{U}$) to $^{233}\text{U}$ (or $^{236}\text{U}$). We made four such solutions with $^{235}\text{U}/^{233}\text{U}$ equal to approximately 10, 50, 100, and 150. We calculated the isotopic compositions of the four solutions by gravimetry and verified the compositions of the first two with measurements on the cups. Type II solutions were particularly useful in separating out multiplier biases that correlated with mass from those that correlated with ion beam intensity. In the course of establishing the isotopic compositions of our Type II solutions, we also analyzed U-500 separately on the cups in static collection mode. We normalized to the certified $^{235}\text{U}/^{238}\text{U}$ value of 1.000302 and obtained the following results: $^{236}\text{U}/^{235}\text{U} = 0.001524 \pm 0.000002$ and $^{234}\text{U}/^{235}\text{U} = 0.010431 \pm 0.000010$. These values are consistent with the certified values of $^{236}\text{U}/^{235}\text{U} = 0.001519 \pm 0.000006$ and $^{234}\text{U}/^{235}\text{U} = 0.010425 \pm 0.000019$, but have smaller errors.

Multiplier biases can be separated into two types, those that correlate with mass and those that correlate with ion beam intensity. One can further sub-divide intensity biases into a well-known bias due to the dead time of the counter and biases due to factors that are poorly understood. First, we address the question of dead time. We measured the width of the square wave emerging from the pre-amplifier directly and obtained values of 20 to 22 ns. The value for dead time should be greater than or equal to the square wave width. We determined the dead time of our multipliers empirically by measuring the $^{238}\text{U}/^{236}\text{U}$ values of Type I solutions at $^{235}\text{U}^+$ beam intensities of 100,000 and 550,000 cps. We then adjusted the dead time so that the dead time-corrected $^{238}\text{U}/^{236}\text{U}$ values of the low and high intensity runs were identical. By propagating the error in the isotopic ratio determinations through the equation for dead time correction, we calculated the error in our dead time determination: $\pm 2$ ns. We have determined dead time in this fashion for over 10 Cu–Be dynode multipliers (mainly MasCom multipliers, but also multipliers made by Phillips and by EMI) and two ETP Al dynode multipliers. The dead time values for all of the multipliers fall between 26 and 28 ns.

We then compared the dead time corrected $^{238}\text{U}/^{235}\text{U}$ value to the true $^{238}\text{U}/^{235}\text{U}$ value of NBL-112a (137.88). We found that on Cu–Be dynode multipliers the measured value was generally within 2‰ of the known value. However, on the ETP Al dynode multipliers that we tested, the value was typically about 8‰ high and varied temporally by about 3‰, over time scales of days. For this reason, all of the multiplier isotope ratio measure-
ments that we report here were determined on MasCom (Cu–Be dynode) multipliers. Whereas $^{238}\text{U}/^{235}\text{U}$ ratios as measured on the MasCom multipliers, were generally within 2‰ of the known value, in some cases the measured value could be resolved from the known value, indicating a small but resolvable bias.

To learn more about this bias, we measured Type II solutions. In one set of experiments, we measured $^{238}\text{U}$ and $^{235}\text{U}$ on the cups and $^{232}\text{U}$, $^{234}\text{U}$, and $^{236}\text{U}$ on the multiplier during the same mass spectrometer run. We used the $^{238}\text{U}/^{235}\text{U}$ ratio (as measured on the cups) to normalize for fractionation in the source. We then compared the $^{236}\text{U}/^{233}\text{U}$ ratio normalized in this fashion to the known ratio of the solution. On the MasCom (Cu–Be dynode) multipliers, we observed that the measured $^{236}\text{U}/^{233}\text{U}$ ratio was slightly lower than the true ratio. The magnitude of the offset was the same for different MasCom multipliers and independent of the intensity of the $^{236}\text{U}$ (or $^{233}\text{U}$) ion beam (between 5000 and 400,000 cps). As the $^{236}\text{U}/^{233}\text{U}$ ratio is approximately 1, this offset is a mass bias, not an intensity bias. The magnitude of this bias is 0.9 ± 0.4‰ per mass unit (at about mass 233). The lighter isotope is over-counted relative to the heavier isotope by this factor.

Next, we performed a second set of experiments on Type II solutions. Instead of measuring $^{238}\text{U}$ and $^{235}\text{U}$ on the cups and the other isotopes on the multiplier, we measured all of the isotopes on the multiplier in peak-jumping mode. Again, we used the $^{238}\text{U}/^{235}\text{U}$ ratio to normalize for fractionation and compared the normalized $^{232}\text{U}/^{236}\text{U}$ ratios to the known value. In this set of experiments, the normalized $^{232}\text{U}/^{236}\text{U}$ ratios were indistinguishable from the known value within the measurement precision of about ±0.5‰. Thus, the normalization procedure for mass fractionation, also corrects for multiplier mass bias, as long as the isotopes used for normalization are measured on the multiplier. For this reason, we apply the 0.9 ± 0.4‰ per mass unit correction to our thorium isotopic measurements (which are not normalized for instrumental fractionation), but not to our uranium isotopic measurements (which are normalized for instrumental fractionation).

As the normalization procedure corrects for mass bias, the offsets between measured and known $^{238}\text{U}/^{235}\text{U}$ ratios in Type I solutions cannot result from mass bias. We presume that this small offset is associated with intensity differences, and additional data discussed below supports this idea. To summarize the discussion to this point, the MasCom Cu–Be dynode multipliers all have small and consistent mass biases. Some also have small intensity biases that are consistent over the course of months but may change over the approximately 2-year lifetime of the multiplier. The two ETP Al dynode multipliers had no detectable mass bias, but had relatively large and variable intensity biases. Because of the latter characteristic of the ETP multipliers, we chose to use MasCom Cu–Be dynode multipliers instead of ETP Al dynode multipliers for our measurements on secular equilibrium materials. However, for other applications, in which isotope ratios are close to one, ETP multipliers, with their lack of detectable mass bias, might be preferable.

As noted above, we presumed that the small offset between measured and known $^{238}\text{U}/^{235}\text{U}$ values of Type I solutions was related to ion beam intensity. We tested this idea with data from peak-jumping measurements on Type II solutions. These data confirmed this idea. On multipliers for which the measured and known $^{238}\text{U}/^{235}\text{U}$ ratio in Type I solutions were the same, the measured and known ratios of $^{235}\text{U}$ (or $^{238}\text{U}$) to $^{233}\text{U}$ (or $^{236}\text{U}$) in Type II solutions were also the same. On multipliers for which the measured $^{238}\text{U}/^{235}\text{U}$ ratio in Type I solutions was offset from the known ratio, the measured $^{235}\text{U}$ (or $^{238}\text{U}$) to $^{233}\text{U}$ (or $^{236}\text{U}$) ratios in Type II solutions were also offset. For a given multiplier the measured ratio of a higher intensity to a lower intensity beam would always be offset from the known ratio in the same sense. Because these offsets are so small (largest biases are about 2‰ and the precision of our isotope ratio measurements are typically ±0.5‰), we could not determine the relationship between beam intensity and intensity bias precisely. However, the following relationship fits all of our data for Type II solutions within measurement precision of about ±0.5‰: $$(A/B)_M = (A/B)_0 X,$$ where “$A/B$” is an isotope ratio, the subscript “$C$” refers to the corrected ratio, the subscript “$M$” refers to the measured ratio, and the exponent “$X$” is an empirically determined variable that is specific to each multiplier. As examples, the “$X$” values for three of our current multipliers are 0.99968, 0.99996.
and 1.00022. Therefore, the difference between measured and corrected values for an isotope ratio around 100 is 1.5, 0.2, and 1.0% for each of the three multipliers and the difference between measured and corrected values for an isotope ratio around 10 is 0.7, 0.1, and 0.5% for each of the three multipliers. For an isotope ratio of 1, the form of the equation requires no correction, consistent with our observations. We apply this intensity bias correction to all of the isotope ratio measurements performed on our multipliers. When $^{235}\text{U}/^{238}\text{U}$ values of Type I solutions are corrected in this manner, the corrected value agrees with the known value to within 1%, suggesting that the correction is valid.

7. $^{234}\text{U}/^{238}\text{U}$ measurements in NBL-112a

After characterizing our multipliers, we measured $^{234}\text{U}/^{238}\text{U}$ values for NBL-112a. Solutions of NBL-112a were spiked with our uranium double spike so that $^{235}\text{U}/^{234}\text{U}$ was about 10 (see Chen et al., 1986). $^{233}\text{U}$, $^{234}\text{U}$, $^{235}\text{U}$, and $^{236}\text{U}$ were then measured on the multiplier in peak-jumping mode. The intensity of the most intense beam ($^{238}\text{U}^+$) was maintained at or below 200,000 cps so that the error in our dead time correction was negligible. Each sample was run until at least 4 million $^{234}\text{U}$ ions had been counted ($\pm 1\%$ ($2\sigma$) counting statistics). The $^{234}\text{U}/^{235}\text{U}$ value was normalized for fractionation using the known $^{233}\text{U}/^{236}\text{U}$ ratio of the spike and corrected for intensity bias using the relationship discussed above. We then divided by the natural $^{238}\text{U}/^{235}\text{U}$ value of 137.88.

Twenty-one measurements of NBL-112a gave a mean $^{234}\text{U}/^{238}\text{U}$ value of $(52.860 \pm 0.025) \times 10^{-6}$, where the error is $2\sigma$ of the mean of the 21 measurements. This corresponds to a $\delta^{234}$U value of $-33.96 \pm 0.46\%$, using the values for decay constants commonly used prior to this work ($\lambda_{234} = 2.835 \times 10^{-6}\text{ yr}^{-1}$ (average of the values from De Bievre et al. (1971) and Lounsbury and Durham (1971), $\lambda_{235} = 1.55125 \times 10^{-10}\text{ yr}^{-1}$ (Jaffey et al., 1971)) or a value of $-36.94 \pm 0.45\%$, using the revised value for $\lambda_{234}$ that we propose below. This value agrees with previously reported values from this laboratory (Gallup et al., 1994; Edwards et al., 1997), as well as values reported by other laboratories (Chen et al., 1986; Goldstein et al., 1991; Stirling et al., 1995).

It is important to note that the error that we quote is a measure of the reproducibility of our measurements. If systematic errors are included, the error estimate becomes larger. There are two significant sources of systematic error. The first is the error in the absolute $^{238}\text{U}/^{235}\text{U}$ ratio of U-500. The accuracy of our normalization for instrumental fractionation is ultimately based on the accuracy of this value. As $^{235}\text{U}$ differs by 3 mass units from $^{238}\text{U}$, and $^{234}\text{U}$ differs by 4 mass units from $^{238}\text{U}$, the $\pm 1\%$ error in the U-500 $^{238}\text{U}/^{235}\text{U}$ value (Garner et al., 1971) contributes $\pm 1.3\%$ to the error in our measured $^{234}\text{U}/^{238}\text{U}$ values. The other significant source of error is the error in our correction for multiplier bias, which we estimate to be no larger than $\pm 1\%$ based on the fact that individual measurements of $^{238}\text{U}/^{235}\text{U}$ ratios of Type I solutions agree with the value measured on the Faraday Cups to better than $\pm 1\%$.

Combining these two errors, the error in the dead time correction, and the error discussed in the previous paragraph, we arrive at a total error of $\pm 1.8\%$. Thus, our value for the $^{234}\text{U}/^{238}\text{U}$ ratio in NBL-112a, including all systematic errors is: $(52.860 \pm 0.095) \times 10^{-6}$, corresponding to a $\delta^{234}$U value of $-34.0 \pm 1.7\%$ with the commonly used value for $\lambda_{234}$ (mean of the values of De Bievre et al. (1971) and Lounsbury and Durham (1971)) or a $\delta^{234}$U value of $-36.9 \pm 1.7\%$ using the value for $\lambda_{234}$ that we propose below.

8. $^{234}\text{U}/^{238}\text{U}$ measurements on secular equilibrium materials

Zircons were dissolved in HF, HClO$_4$, and HNO$_3$ in Teflon bombs in the presence of our mixed ($^{233}\text{U}--^{236}\text{U}--^{237}\text{Th}$) spike. Table Mountain Latite was also dissolved in Teflon bombs with HF, HClO$_4$, and HNO$_3$, and spike was added subsequent to dissolution. Iceland Spar was dissolved in HNO$_3$, and spike was added subsequent to dissolution. HU-1 was obtained in a solution. We added spike to aliquots of
this solution. All samples were processed through anion exchange columns in order to purify uranium and thorium fractions, using procedures similar to those described by Edwards et al. (1987) and Asmerom and Edwards (1995).

The uranium fractions were analyzed on the multiplier as described above. Of the six secular equilibrium samples that we analyzed, we performed two separate dissolutions for both Table Mountain Latite and Zr-1. For HU-1, we ran two separate aliquots through anion exchange columns. For each sample that we processed through anion exchange columns, we performed four separate mass spectrometer runs. The results of the 36 mass spectrometer runs are shown in Fig. 1 and Table 1. The internal error for a single run is typically ±1‰. All $^{234}\text{U}/^{238}\text{U}$ values agree within error, indicating analytical reproducibility and suggesting that the samples have behaved as closed systems. The mean and 2σ of the mean of these runs is $54.887 \pm 0.007 \times 10^{-6}$. This error is a measure of the reproducibility of our measurements. If systematic errors are considered, the value becomes $54.891 \pm 0.094 \times 10^{-6} \ (2\sigma)$. From this value, we calculate $\lambda_{234} = \lambda_{238}/(^{234}\text{U}/^{238}\text{U}) = (2.8262 \pm 0.0057) \times 10^{-6} \ \text{yr}^{-1}$, using the value of Jaffey et al. (1971) for $\lambda_{238}$. This corresponds to a half-life of 245,250 ± 490 years (2σ). Considering errors, our value agrees with those of De Bievre et al. (1971), Lounsbury and Durham (1971), Holden (1989), and Ludwig et al. (1992). The error in our value is smaller than the quoted errors for the first

Fig. 1. $^{234}\text{U}/^{238}\text{U}$ atomic ratios of secular equilibrium samples. See text and Table 1 for sample numbers. The open diamonds refer to single analyses and shaded diamonds refer to the average for each sample. The error bars indicate 2σ analytical precision. The shaded bars on the left are $^{234}\text{U}/^{238}\text{U}$ values (including errors) predicted for secular equilibrium materials assuming the value of Jaffey et al. (1971) for $^{238}\text{U}$ half-life and indicated values for $^{234}\text{U}$ half-life. The bar for the $^{234}\text{U}$ half-life value for this study is derived from the data illustrated here. The error estimate for this $^{234}\text{U}$ half-life value includes systematic errors.
Table 1
The analytical results from secular equilibrium samples

<table>
<thead>
<tr>
<th>Sample number*</th>
<th>238U (ppm)**</th>
<th>(234U / 238U)_{atomic} \times 10^6</th>
<th>(230Th / 238U)_{atomic} \times 10^9***</th>
<th>Single filament</th>
<th>Double filament</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-1 (I)</td>
<td>1141.5 ± 0.8</td>
<td>54.909 ± 0.052</td>
<td>16.940 ± 0.032 (10)</td>
<td>16.927 ± 0.036</td>
<td></td>
</tr>
<tr>
<td>Zr-1 (II)</td>
<td>1191.3 ± 0.6</td>
<td>54.853 ± 0.045</td>
<td>16.952 ± 0.034 (8)</td>
<td>16.935 ± 0.034</td>
<td></td>
</tr>
<tr>
<td>Zr-2</td>
<td>478.90 ± 0.35</td>
<td>54.898 ± 0.054</td>
<td>16.940 ± 0.032 (10)</td>
<td>16.927 ± 0.036</td>
<td></td>
</tr>
<tr>
<td>Zr-3</td>
<td>17.316 ± 0.013</td>
<td>54.878 ± 0.046</td>
<td>16.930 ± 0.042 (10)</td>
<td>16.918 ± 0.051</td>
<td></td>
</tr>
<tr>
<td>TML (I)</td>
<td>10.658 ± 0.006</td>
<td>54.887 ± 0.057</td>
<td>16.930 ± 0.042 (10)</td>
<td>16.883 ± 0.046</td>
<td></td>
</tr>
<tr>
<td>TML (II)</td>
<td>10.657 ± 0.006</td>
<td>54.875 ± 0.052</td>
<td>16.906 ± 0.042 (10)</td>
<td>16.918 ± 0.051</td>
<td></td>
</tr>
<tr>
<td>IS</td>
<td>0.3073 ± 0.0002</td>
<td>54.940 ± 0.042</td>
<td>16.930 ± 0.029 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HU-1 (I)</td>
<td>1.3186 ± 0.0008</td>
<td>54.880 ± 0.060</td>
<td>17.004 ± 0.029 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HU-1 (II)</td>
<td>0.9511 ± 0.0007</td>
<td>54.870 ± 0.048</td>
<td>16.987 ± 0.028(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>54.887</td>
<td>16.950</td>
<td>16.916</td>
<td></td>
</tr>
</tbody>
</table>

* See text for sample numbers. I and II refer to different fractions of the same sample. Zr-1 (I) and (II) are different fractions of the same zircon (mesh size 150–200, Asmerom et al., 1990). TML (I) and (II) are the powder fractions of the same Table Mountain Latite. HU-1 (I) and HU-1 (II) are different dilutions from the same concentrated solution.

** ppm = \((238U \text{ mass/sample mass}) \times 10^6\).

*** The data of single filament measurements are the weighted averages, and the numbers in parentheses are the numbers of replicate analyses.

three of these four earlier determinations. In comparison to our value, the value of Ludwig et al. (1992) is identical and the value of Holden (1989) is virtually identical (200 years or 0.9% higher). However, the values of De Bievre et al. (1971) and Lounsbury and Durham (1971), which are commonly used by many laboratories are about 800 years or more than 3% lower than our value.
9. The $^{234}$U decay constant and $\delta^{234}$U values

$\delta^{234}$U values are calculated from measured $^{234}$U/$^{238}$U atomic ratios with the following equation:

$$\delta^{234} = \left(\frac{^{234}}{^{238}}\right) \left(\frac{\lambda_{^{234}}}{\lambda_{^{238}}} - 1\right) \times 1000.$$ 

Thus, calculated $\delta^{234}$U values depend on the value of $\lambda_{^{234}}$ that is used. As our new $\lambda_{^{234}}$ value is about 3% smaller than the commonly used value, $\delta^{234}$U values calculated with the new $\lambda_{^{234}}$ value will be smaller (by about three $\delta$-units for materials close to secular equilibrium) than $\delta^{234}$U values calculated with the old $\lambda_{^{234}}$ value. We have previously reported a marine $\delta^{234}U$ value from modern reef-building corals of 149.3% (Galewsky et al., 1996). This value was calculated with the old $\lambda_{^{234}}$ value of 2.835 $\times$ 10$^{-6}$ yr$^{-1}$. Use of our new $\lambda_{^{234}}$ value revises our value for our best estimate of the modern marine value to 145.8 ± 1.7% (the mean and 2$\sigma$ of the population of 22 measurements on modern reef-building corals).

10. $^{230}$Th/$^{238}$U measurements on secular equilibrium materials

We performed thorium isotopic measurements on a subset of the samples on which we analyzed $^{234}$U/$^{238}$U. We measured the thorium fractions for the two dissolutions of Zr1, the two dissolutions of Table Mountain Latite, the single dissolution of Iceland Spar, and the two aliquots of HU-1. For the first

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**Secular Equilibrium Samples**

Fig. 2. Atomic $^{230}$Th/$^{238}$U ratios of secular equilibrium samples. Sample numbers are as indicated in Table 1 and Fig. 1. The open circles refer to thorium isotopic measurements using the single filament graphite loading technique and solid squares refer to thorium isotopic measurements using single the double filament loading technique without graphite. The error bars indicate 2$\sigma$ analytical precision. The shaded bars on the left indicate $^{230}$Th/$^{238}$U values (including errors) predicted for secular equilibrium materials, assuming the value of Jaffey et al. (1971) for $^{234}$U half-life and indicated values for $^{230}$Th half-life. The bar for the $^{230}$Th half-life value for this study is derived from the data illustrated here. The error estimate for this $^{230}$Th half-life value includes systematic errors.
dissolution of Zr1, we performed 10 thorium runs using the single filament graphite technique and one run using the double filament technique. For the second dissolution of Zr1, we performed eight thorium runs using the single filament graphite technique and one run using the double filament technique. For each of the two Table Mountain Latite dissolutions, we performed 10 single filament graphite runs and one double filament run. For Iceland Spar, we performed four single filament graphite runs, and for each of the aliquots of HU-1, we performed two single filament graphite runs. 230 Th concentrations were determined from the measured 238 U concentrations were determined from the measured 238 U ratios and the standard isotope dilution equations. 238 U concentrations were determined from the measured 236 U/238 U ratios (measured as described above) and the standard isotope dilution equations.

Measured 230 Th/238 U ratios are shown in Fig. 2 and Table 1. Errors for each set of measurements range from ±1.5 to ±3%. All of the values agree within error except for the values of HU-1, which have higher 230 Th/238 U values than the other samples. The fact that the double filament runs without graphite give the same values as the single filament runs with graphite indicates that mass-dependent isotopic fractionation in the mass spectrometer source is the same (within errors) for two different loading techniques. The higher 230 Th/238 U value for HU-1 suggests that our solution of HU-1 did not behave as a closed system. It is possible that the original HU-1 powder was not in secular equilibrium. It is also possible that the high value for the solution that we analyzed results from the preparation or aliquoting of this particular solution and is unique to this solution. If so, it is possible that HU-1 solutions in different laboratories could have different 230 Th/238 U values. The consistent 230 Th/238 U values of the materials other than HU-1 suggest that these other materials have behaved as closed systems. If so, we may use measurements on any or all of these other materials to calculate λ230. We choose to use the data from Zr1 as the basis for our λ230 calculation because we have independent evidence (concordant U–Th–Pb ages discussed above) that indicates that this material has behaved as a closed system for uranium and thorium. However, inclusion of the Table Mountain Latite and Iceland Spar data would not change the calculated λ230 value significantly.

The average of the four determinations of 230 Th/238 U for Zr1 is (16.939 ± 0.017) × 10−6. The quoted error is a measure of reproducibility and does not include systematic errors. Systematic errors and our estimates of their magnitudes include: systematic instrumental fractionation during thorium runs (±2%), error in uranium and thorium concentrations in gravimetric standards (±1%), and error in corrections for multiplier bias in thorium runs (±1.5%). Combining all errors, we calculate a total error of ±2.9%, or a Zr1 230 Th/238 U value of (16.939 ± 0.049) × 10−6. From this value, we calculate λ230 = λ238/(230 Th/238 U) = (9.158 ± 0.028) × 10−6 yr−1, using the value of Jaffey et al. (1971) for λ238, and propagating all errors including those from λ238. This corresponds to a half-life of 75,690 ± 230 years. Considering errors, our value agrees with that of Meadows et al. (1980); however, the error in our value is smaller. In comparison to our value, the value of Meadows et al. (1980) is about 300 years smaller or 4% lower.

11. Half-life values and 230 Th ages

The reduction in the errors in the half-life values and the shift in the nominal values for the half-lives can affect calculated 230 Th ages substantially. There are two types of standards in general use: gravimetric standards and secular equilibrium standards. The errors in half-lives propagate differently depending on which types of standards are used. For instance, if gravimetric uranium and thorium standards are used, the fractional error in 230 Th age due to error in the 230 Th half-life is less than the fractional error in the half-life for ages significantly less than 105 years, but greater than the fractional error in the half-life for ages significantly larger than 105 years (Edwards et al., 1987). However, if materials assumed to be in secular equilibrium are used for uranium and thorium standards, the fractional error in age due to error in the 230 Th half-life is similar to the fractional error in the half-life regardless of age (Ludwig et al., 1992). The error in age due to error in half-lives (using errors from earlier half-life determinations) is shown in Fig. 3. With gravimetric standardization, the error in age due to error in half-lives becomes
Fig. 3. Error in $^{230}$Th age due to error decay constants, calculated with previous values for the errors in decay constants ($\pm 8\%$ for $\lambda_{230}$ and $\pm 3\%$ for $\lambda_{234}$). (a) and (b) are the same plots except for the scales. Error is contoured as a function of measured $\delta^{234}$U value. The shaded area shows the whole range of error in age due to error in decay constants, if measurements are standardized using a secular equilibrium solution. In this case, errors in age resulting from errors in decay constants are small. However, the secular equilibrium assumption must be valid in order to avoid systematic errors of unknown magnitude. The contours indicate errors in age due to error in decay constants, if measurements are standardized by gravimetry. Contours with positive ordinate values indicate maximum possible offsets toward older age, considering errors. Contours with negative ordinate values indicate maximum possible offsets toward younger age, considering errors.

significant for materials older than about 200 ka and becomes quite large for materials older than 350 ka. With secular equilibrium standardization, the error in age due to error in half-lives is relatively small throughout the time range appropriate for $^{230}$Th dating (see Ludwig et al., 1992). However, a fundamen-
tal issue associated with secular equilibrium standardization is the secular equilibrium assumption itself. If the standard is not, in fact, in secular equilibrium (as appears to be the case with our aliquot of HU-1) this introduces a systematic error of unknown magnitude.

Fig. 4 shows the error in age due to errors in half-lives with our values for half-lives. Errors in age due to errors in half-lives are generally reduced by factors of two to three (compare Fig. 3a and Fig. 4a) over previous errors. The most striking improvement is for materials older than about 350 ka with ages over 350 ka, in laboratories using gravimetric standardization procedures.

Fig. 4. Similar to Fig. 3 except the calculation uses our values for the error in decay constants (±3% for $\lambda_{230}$ and ±2% for $\lambda_{234}$). Errors in age are reduced significantly for materials older than about 350 ka, in laboratories using gravimetric standardization procedures.
standardized using gravimetric methods. For example, considering materials with measured $\delta^{234}\text{U}$ values close to zero, using the old half-life errors, all such materials older than about 480 ka had ages indistinguishable from infinite age. However, with the new half-life errors, materials with $\delta^{234}\text{U}$ values close to zero and ages as old as 570 ka have ages resolvable from infinity. 480 ka materials have errors

Fig. 5. $^{230}\text{Th}$ age calculated using our proposed values for decay constants minus $^{230}\text{Th}$ age calculated using commonly used values for decay constants. The calculation assumes gravimetric standardization. Contours indicate measured $\delta^{234}\text{U}$ values. The age calculated using new values for decay constants are older than those calculated using old values for decay constants. However, the difference in age is small throughout the age range because our revised $\lambda_{230}$ and $\lambda_{234}$ values are offset from earlier values in the same sense (both are revised to lower values).
in age due to errors in half-lives of +60/-40 ka. Thus, the reduction in half-life errors improves our ability to date materials in the older portion of the 230Th time range.

It is important to note that in our estimate of half-life errors, we have included systematic errors. Had we only included errors based on the reproducibility of our measurements, the errors would be smaller by factors of 3 (for 230Th half-life) to 10 (for 234U half-life). One can envision a situation (for example, in our laboratories) where the systematic errors in routine sample analysis are essentially the same as the systematic errors in the measurements upon which our decay constant determinations are based. Both types of analysis use the same spike calibrated with the same gravimetric and isotopic standards as well as similar multipliers with similar biases. In propagating errors through the age equation, the systematic errors in our half-life determinations largely cancel out against the same systematic errors in the determination of the 230Th/238U and 234U/238U values of a routine sample. In this case, the main sources of age error are the reproducibility of the half-life values and the reproducibility of the 230Th/238U and 234U/238U values of a routine sample. The reproducibility of the half-life values are significantly better than the typical reproducibility of the 230Th/238U and 234U/238U values of a routine sample. Thus, in this case, the error in age due to error in half-life values are negligible (compared to the error in age due to analytical errors in routine sample measurement).

Fig. 5 shows the differences between 230Th ages calculated using our half-lives and those calculated with commonly used values for half-lives (half-life for 230Th = 75,381 years and for 234U = 244,500 years), for analyses based on gravimetric standards. The ages calculated with the new half-lives are older than those calculated with currently used half-lives. Despite the fact that the new half-life values differ by 3 to 4% from the old values, the shift in age is generally small. The relatively small shift results from the fact that both half-life values have shifted in the same direction (to larger values). Thus the shift in the ratio of the decay constants is small. The age difference is largest for materials with 234U/238U values close to zero and smallest for materials with high 234U/238U values. The age difference generally increases with age. Unaltered marine samples always have measured 234U/238U values between 0 and 150%. For such materials, the difference in age at 1 ka is 4 years, at 10 ka is 35 years, at 100 ka is 340 years, at 200 ka is 700 years, at 300 ka is 1300 years, at 400 ka is 2300 years and at 500 ka is 4000 years (Fig. 5).

12. Conclusions

We have measured 234U/238U and 230Th/238U ratios in a number of materials that may have behaved as closed systems for 10^6 years or more. Consistent 234U/238U values for all measured materials and consistent 230Th/238U values for all materials (with the exception of our HU-1 solution) generally support the closed system assumption. 234U and 230Th half-lives calculated from the two isotope ratios agree within errors with previously determined values; however, errors in our determinations are generally smaller than errors in the earlier determinations. Our value for the 234U half-life is about 3% higher than the value commonly used in 230Th dating laboratories and our value for the 230Th half-life is about 4% higher. The small upward revision of the 234U half-life requires a small downward revision of 234U/238U ratios calculated from atomic 234U/238U ratios. 230Th ages calculated with the new half-lives are generally older than those calculated with the old half-lives. However, revisions in ages are small throughout the 230Th age range because the revisions in 230Th and 234U half-lives have the same sign. From a practical standpoint, the main impact of this work relates to the dating of materials older than 350 ka in laboratories that rely solely on gravimetric standardization procedures. In this case, use of our decay constants and their associated errors will reduce errors in age due to errors in decay constants considerably. For any laboratories with systematic errors similar to ours, use of our decay constant values will reduce age error due to decay constant error to insignificant levels.

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