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Procedures for accurate U and Th isotope measurements by high precision MC-ICPMS

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Abstract

We present multi-collector (MC) inductively coupled plasma mass spectrometry (ICPMS) protocols developed to obtain high precision, accurate determinations of U and Th isotope ratios that are applicable to a wide range of geological materials. MC-ICPMS provides a means to make high precision measurements but a recent laboratory inter-comparison, Regular European Inter-laboratory Measurement Evaluation Programme (REIMEP)-18, indicates that accurate results for U isotope ratios are not currently achieved by all facilities using MC-ICPMS. We detail a suite of protocols that can be used for a wide variety of U and Th isotope ratios and total loads. Particular attention is devoted to instrument optimisation, instrumental backgrounds, stability and memory effects, multiplier nonlinearity and yield determinations. Our results indicate that the extent of mass fractionation of U and Th analyses run under similar instrumental conditions is 0.48% per amu and 0.45% per amu, respectively, but cannot be distinguished at per mil precision levels. However, we note that multiplier–Faraday cup gain can be significantly different for U and Th by 1% and thus a U standard should not be used to correct Th measurements. For this reason, a combination of thermal ionisation mass spectrometry (TIMS) and MC-ICPMS methods have been used to determine the isotopic ratio of an in-house Th standard (TEDDi). As part of our methods, TEDDi and the U standard NBL-112a are used as bracketing standards for Th and U samples, respectively. While the in-house Th standard has ^{229}Th–^{230}Th–^{232}Th composition specific for bracketing low ^{232}Th analyses, the methods have been also successful for silicates with ^{230}Th/^{232}Th $<10^{-5}$. Using NBL-112a, TEDDi and a gravimetrically calibrated mixed ^{229}Th–^{236}U spike, we demonstrate secular equilibrium in natural materials such as Table Mountain Latite and a Long Valley Glass Mountain sample with a reproducibility of ±3.8 per mil for ^{230}Th/^{238}U and ±2.8 per mil for ^{234}U/^{238}U. We also present results for a variety of U and Th certified reference materials as well as carbonate and silicate standards such as ANU coral (AC-1) and Basalt Columbia River (BCR-2). Furthermore, we find the ^{230}Th–^{238}U ratio of Harwell uraninite slightly greater than unity. This is important because many laboratories use only uraninite for the calibration of their spikes.

Keywords: U–Th isotopes; Disequilibrium; MC-ICPMS; Carbonate; Silicate

1. Introduction

Highly precise and accurate U and Th isotope measurements are very important for establishing the timing of events and determining the rates of a wide variety of natural processes in earth and planetary sciences [1]. Mass spectrometry has largely replaced traditional alpha counting methods for measuring U- and/or Th-isotopes. Technical improvements in the last decade have resulted in a further shift from thermal ionisation mass spectrometry (TIMS) to multi-collector (MC) inductively coupled plasma mass spectrometry (ICPMS) [2].

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Advantages of MC-ICPMS compared to TIMS include higher ionisation efficiencies and thus smaller sample sizes required for a given precision, faster sample throughput and sample-standard switching while keeping instrumental tuning constant, which enables the use of an external standard bracketing procedure for corrections of instrumental biases. However, using MC-ICPMS also has some disadvantages compared to TIMS, such as higher background intensities, potential interferences, greater instrumental mass fractionation and decreased abundance sensitivity. Such effects need careful determination and the measured data must be corrected accordingly. Several protocols to derive U and Th isotope ratios by MC-ICPMS have been reported [3,2] but accurate U and/or Th isotope ratio measurements with dynamic ranges of 10^{-5} or smaller are still a considerable challenge for MC-ICPMS. The problem of inaccuracy has been highlighted by the Regular European Inter-laboratory Measurement Evaluation Programme (REIMEP) 18 campaign [4].

The high dynamic range required to measure typical, natural U and Th isotope ratios such as ^{234}U/^{238}U, or in the case of silicates ^{230}Th/^{232}Th, is typically achieved by using an ion counting system such as a secondary electron multiplier (SEM) in conjunction with Faraday cups. The minor isotope is measured on the SEM while the high intensity ion beam can be measured using a Faraday cup. This poses significant detector cross calibration problems. Moreover, SEM nonlinearity needs careful characterisation and correction [5,6]. Recently, Andersen et al. [7] and Potter et al. [8] have suggested that the measurement of all isotopes statically on Faraday cups can be used to avoid the problem of SEM uncertainty and thus achieve higher precision. However, this approach is restricted to applications that can use large samples or material with high U concentrations. For example, a total consumption of 25 pg of ^{230}Th, as suggested by Potter et al. [8], requires more than 1 g of material at secular equilibrium with U concentration of 1 μg/g, and a 25 ka old stalagmite, for example, with 1 μg/g U contains only around 3 pg/g ^{230}Th, necessitating a rather large sample size of more than 8 g. Such amounts of material are not available in high resolution studies of stalagmites, for example, which have increasingly become a focus of U–Th work [9–12]. For most geological applications, a protocol including SEM or a multi ion counter array [13] is thus required.

At the outset, we intended to develop a flexible suite of methods with the highest achievable precision and accuracy to cover a wide range of potential interests including the age of young and ancient carbonates, Th and U isotope ratios of natural waters or the extent of U–Th disequilibrium in volcanic rocks. This presented a considerable challenge, not only because of the high dynamic range of ^{234}U/^{238}U, for example, but also the extremely wide range in expected ^{230}Th/^{232}Th and ^{230}Th/^{238}U ratios. To be confident in the applicability of our correction procedures across the breadth of potential applications, we have devoted considerable attention to determining the extent of mass fractionation, inter calibration of detectors, response of ion counting systems and background levels in order to correct for each individually. This differs to protocols where all corrections are treated together which can be effective when all samples have similar compositions [14] but is not more generally applicable. Our strategy, outlined below, relies on a variety of both in-house and more widely available standards. We demonstrate that a suitable and well-calibrated Th-standard is essential for accurate U–Th measurements because correction factors such as SEM yield are typically different for U and Th. We present MC-ICPMS U–Th methods used by the Bristol Isotope Group (BIG) and details of our calibration of an in-house isotopic Th standard and of our mixed ^{229}Th–^{236}U spike. We demonstrate differences of SEM–Faraday cup gain between U and Th isotopes and present results of U and Th isotope measurements on certified reference materials (CRM) and secular equilibrium samples. We also present a comparison of U–Th dating results on carbonate samples obtained in the BIG laboratory and, independently, at the isotope facilities of the Heidelberg Academy of Sciences. Due to the increasing precision of mass spectrometric U and Th analyses, the accuracy of spike solution calibration is very important. Thus, such laboratory inter-comparisons are fundamental in U-series geochronology.

2. Experimental

2.1. Instrumentation

The BIG laboratory is equipped with three high precision mass spectrometers: two ThermoFinnigan Neptune MC-ICPMS and a ThermoFinnigan Triton TIMS. The majority of the procedures and results presented below are for measuring U and Th isotopes using a Neptune MC-ICPMS. The sample introduction system on the Neptune instruments incorporates a Cetac Aridus nebuliser with a PFA spray chamber. We use a nebuliser tip with a nominal uptake rate of 50 μl/min. The Neptune collector system consists of eight moveable Faraday cups and a fixed centre cup or SEM. The axial beam can be deflected into either the central Faraday cup or the SEM. The mass spectrometers are now equipped with MasCom multipliers which show significantly smaller intensity effects compared to previously installed ETP multipliers [6]. The SEM is located behind an energy and angular filtering device (Retarding Potential Quadrupole – RPQ) to improve the abundance sensitivity. The RPQ can also be grounded if its use is not required. For review and further technical details about MC-ICPMS instrumentation, see Wieser and Schwieters [15].

2.2. MC-ICPMS U and Th measurements

2.2.1. General procedures

All samples or standards are analysed in 0.6N HCl (see Section 2.2.3), U and Th are routinely measured separately. We adopt a standard-sample bracketing procedure to derive correction factors for mass fractionation and Faraday cup to SEM gain. For U measurements we use NBL-112a (also known as CRM-145 or formerly NBS SRM 960) as the bracketing U-standard. Th measurements are bracketed with an in-house ^{229}Th–^{230}Th–^{232}Th standard (TEDDi). Details of TEDDi are given in Section 3.1.

Table 1
MC-ICP-MS operating parameter settings for ThermoFinnigan Neptune and Cetac Aridus nebuliser

RF power (W)	1200
Cool gas (l/min)	16
Auxiliary gas (l/min)	0.7–0.8
Sample gas (l/min)	0.9–1
Aridus sweep gas (l/min)	4–6
Aridus N_2 (ml/min)	10–20
Sample uptake rate (μl/min)	50
Extraction voltage (V)	−2000

2.2.2. MC-ICPMS settings

The MC-ICPMS system is tuned by adjusting the torch position, instrumental gas flows and the ion lenses to obtain optimal intensity for a ^{238}U beam collected in a Faraday cup. Subsequently, gas flows including Aridus sweep gas and N_2 are optimised to stabilise the beam intensity, reduce noise and minimise oxides which potentially reduces the beam intensity achieved before. Typically, we obtain ∼100 pA intensity of ^{238}U using a 30 ppb solution and 50 μl/min uptake rate. However, we observe regular intensity variations (up to 10% at about 0.01 Hz), probably due to droplet build-up at the nebuliser tip. The nebuliser PFA spray chamber is operated at 80 °C and the desolvator membrane at 160 °C. Typical instrument parameters are given in Table 1.

The "focus quad" ion lens, at the entrance to the magnet, is adjusted to achieve optimal peak shapes on Faraday cups. Minor isotopes such as ^{230}Th and ^{234}U have to be measured with an ion counting system (SEM). The SEM is located behind an RPQ which improves the abundance sensitivity but has an impact on the peak shape obtained with the SEM. There are three focus potentials that control the SEM peak shape independently of the Faraday cup peak shape, namely the voltage applied to deflect the ion beam from Faraday cup to SEM, together with "suppressor" and "decelerator" potentials of the RPQ. The suppressor sets the ultimate level of energy filtering of the RPQ and hence abundance sensitivity and the decelerator provides additional focussing. These three potentials are routinely checked for optimal peak shape prior to a measurement sequence by scanning the magnet and simultaneously comparing the central region of Faraday cup (^{238}U or ^{232}Th) and SEM (^{234}U or ^{230}Th) peaks, to make sure that the plateaux are parallel. We also routinely check whether the SEM is operating within a stable region or "plateau" of the yield relative to the applied operation voltage. The dead time and nonlinearity of our counting system are characterised as described in Hoffmann et al. [6]. We currently observe a nonlinearity of 0.1% per decade intensity for count rates between 100 and 100,000 cps. For count rates exceeding 100,000 cps the nonlinearity is 0.3% per decade.

The RPQ can also respond to the switching on and off of the potential on the "extraction lens". This potential of −2000 V relative to the skimmer cone accelerates positive ions emerging through the skimmer cone aperture from the plasma. As a default, the extraction voltage is switched off at a number of points in the software-controlled analysis routine to preserve the entrance slit from degrading due to the impinging ion flux. We have observed that switching the extraction voltage off and on again can cause a transient effect on the transmission efficiency through the RPQ, lasting more than 10 s up to several minutes. The cause of this phenomenon is obscure but it seems likely that there is some transient change in the energy and/or angular distribution of the ions, since the RPQ strongly discriminates to these parameters. We have modified our voltage supply to ensure that the extraction voltage is never switched off during an analysis sequence.

Table 2
Cup configuration used for ThermoFinnigan Neptune I and II U–Th measurements

	Low 1	Centre (SEM)	High 1	High 2	High 3
Uranium 1		^{234}U			^{238}U
Uranium 2	^{235}U	^{236}U	^{238}U		
Uranium 3[a]		^{235}U		^{238}U	
Uranium 4[a]		^{238}U			
Thorium 1[b]		^{229}Th		^{232}Th	
Thorium 2[b]	^{229}Th	^{230}Th	^{232}Th		
Thorium 3[b,c]		^{232}Th			

[a] Uranium 3 and 4 are only used for background measurements.

[b] Ion optics settings for Th sub-configurations: dispersion voltage = 15 V, focus voltage = −4 V.

[c] ^{232}Th on the SEM is only needed for low ^{232}Th concentration peak jump method and for background measurements.

The cup configuration used for U and Th measurements is shown in Table 2. For isotopic measurements of U and Th we mainly use "sub-configurations" with ^{234}U, ^{236}U, ^{229}Th, and ^{230}Th and, in case of samples with low ^{232}Th concentrations, ^{232}Th in the axial (SEM) position. Sub-configurations with ^{235}U and ^{238}U in the centre are only used for background measurements. Faraday cup amplifiers are internally "gain calibrated" using a highly stable current generator. The baseline of the Faraday cups and the darknoise of the SEM are routinely measured prior to a U–Th measurement sequence. Baseline intensities have a variability of less than ±10 μV.

2.2.3. Background and interferences

Background intensities of U and Th isotopes, as measured in a wash solution, reflect impurities in the carrier solution – we use "supra pure" HCl (Romil Ltd.), diluted with MilliQ H_2O ($R > 18\,M\Omega$) – and "memory" in the sample introduction system. Typical background intensities of pure carrier solution are ^{229}Th, ^{230}Th, ^{234}U and ^{236}U < 0.5 cps, ^{235}U < 5 cps, ^{232}Th < 100 cps and ^{238}U < 500 cps. After a sample or a standard solution has been introduced into the ICPMS system, a wash procedure has to be performed to reduce the background intensities derived from the sample introduction system. The wash procedure is usually done by introducing pure "carrier" solution (0.6N HCl) into the system which effectively reduces U background, but reduction of Th background is more difficult. We have conducted experiments to determine how to minimise the background most efficiently. We tested both 0.6N HCl and 0.6N HNO_3 as carrier solution. Different wash procedures were then tested using various combinations for the wash solution (0.6N HCl, 0.6N HCl + 0.05N HF, 0.6N HNO_3, 0.6N HNO_3 + 0.05N HF). Our results indicate that the washout times are shorter using HCl as carrier solution. However, it is impossible to effectively reduce the background intensities of Th without introducing HF into the wash solution as part of the wash procedure. Currently we employ a combination of (1) 2 min 0.6N HCl, (2) 3 min 0.6N HCl + 0.05N HF and (3) 15 min 0.6N HCl as our standard wash procedure. Step 3 switches the sample introduction system back to the carrier solution and the background intensities of all relevant isotopes are recorded for the correction of subsequent measurements. Using this procedure, background intensities are typically reduced to less than 0.1 per mil of the previous beam intensity. Within a sequence we normally achieve background intensities of: ^{234}U and ^{236}U < 1 cps; ^{235}U < 50 cps; ^{238}U < 5000 cps; ^{229}Th < 5 cps; ^{230}Th < 1 cps; ^{232}Th < 1000 cps. However, if solutions with high ^{232}Th concentrations of about 100 ppb are introduced, which yield beam intensities close to the 50 V maximum on the Faraday cups, the background of the system usually increases. For these cases, we include additional pre-wash cycle(s) with alternating HCl and HF-doped HCl for 1–2 min each.

In addition to background intensities, it is also important to check for any isobaric interferences, for example as a result of molecules that arise from matrix effects. In the plasma many different molecular interferences can arise, for instance, U and Th usually form oxides and/or hydrides. We use the Aridus to reduce the hydrides, and adding N_2 to the Aridus sweep gas reduces the oxides. We usually obtain a UH^+/U^+-ratio in the range of 10^{-7} and an UO^+/U^+-ratio of about 10^{-3}. The extent of oxide formation provides an additional empirical guide to conditions in the portion of the plasma we sample, which we try to make the same for every session. We routinely check standard, sample and wash solutions for other interferences between masses 228 and 240 to monitor possible (organic?) interferences. We do not observe any peaks that influence our measurements.

2.2.4. *Abundance sensitivity*

High abundance sensitivity is essential for U and Th isotope measurements, especially for samples with a low ^{230}Th/^{232}Th ratio (<10^{-5}). The effect of the tail of a high intensity beam (usually ^{232}Th or ^{238}U) on minor isotopes has to be determined experimentally. There are various approaches in the literature. Luo et al. [16], for example, suggest a linear interpolation of ratios measured at masses (*m*/*z*) 229.5 and 230.5 to calculate the ^{232}Th tail on ^{230}Th. Pietruszka et al. [3] use a third order polynomial fit of the tail to achieve the abundance sensitivity at mass 230. Shen et al. [17] demonstrate an exponential shape of the ^{232}Th tailing and use a logarithmic mean of the ratios to ^{232}Th, measured at masses 230.4 and 229.6, to calculate the abundance sensitivity for mass 230.

Our data are consistent with the result of Shen et al. [17]. The tail of ^{238}U and ^{232}Th can be conveniently approximated with an exponential function. In practice, we measure the abundance sensitivity for samples with low ^{230}Th/^{232}Th ratios (<10^{-4}) using the Th-sample solution itself. After measuring the ^{230}Th/^{232}Th and ^{229}Th/^{232}Th ratios, we employ a tail measurement at masses 231, 230.5, 229.5 and 228.5 and use a linear interpolation of the ratios to ^{232}Th in log–linear space (Fig. 1). This is used to derive the tail contribution at masses 229 and 230 to correct the measured ratios of ^{230}Th/^{232}Th and ^{229}Th/^{232}Th, respectively. We usually observe an abundance sensitivity of 2×10^{-8} to 6×10^{-8} of the ^{232}Th intensity at mass 230. For ^{230}Th/^{232}Th > 10^{-4} the influence of abundance sensitivity is sub-per mil and no correction is made.

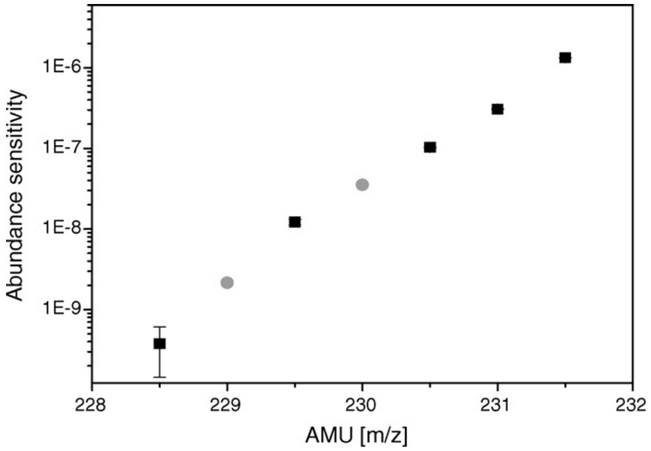

Fig. 1. Abundance sensitivity. ^{232}Th tail in log–linear space and in grey circles calculated values for 230/^{232}Th and 229/^{232}Th as a mean of 228.5/^{232}Th–229.5/^{232}Th and 229.5/^{232}Th–230.5/^{232}Th.

The tail effect of ^{238}U on ^{236}U is obtained by measuring the 236/^{238}U ratio of NBL-112a, as NBL-112a does not contain any ^{236}U. During a sequence the 236/^{238}U ratio of NBL-112a is always simultaneously measured with the ^{235}U/^{238}U ratio. Note that we therefore measure the contribution of the ^{238}U tail and ^{235}U-hydride at the same time as one ratio to ^{238}U. If samples with no natural ^{235}U/^{238}U ratio are measured, the true hydride contribution needs to be calculated using the measured ^{238}UH/^{238}U ratio. We usually obtain an abundance sensitivity of the ^{238}U peak on mass 236 of 2×10^{-8} to 6×10^{-8}, similar to Th. The ^{238}U tailing effect on ^{234}U, which is checked by prior measurements at masses 234.5 and 233.5 using NBL-112a, is found to be negligible.

2.2.5. *Mass fractionation*

Instrumental mass fractionation is significant in ICPMS analyses and must therefore be carefully determined and corrected. The mass fractionation is largely the result of mass-dependent transmission efficiencies for different isotopes of a particular element through the plasma–vacuum interface region. For ICPMS, heavier isotopes have a better transmission efficiency and so isotopic ratios are biased to the heavy isotopes. We use the exponential law for mass fractionation [18]:

$$\frac{r}{R} = \left(\frac{M_2}{M_1}\right)^{\beta} \tag{1}$$

with r, R are measured, true ratio of isotope2/isotope1, M_2, M_1 atomic masses isotope2 and isotope1 and β is the mass fractionation coefficient.

Maréchal et al. [19] report different mass fractionation coefficients for various elements with values for β around 2. Thus, the mass fractionation coefficients of different elements such as U and Th should ideally be determined separately using a U- and a Th-standard, respectively.

To derive β for U, we measure the $^{235}U/^{238}U$ ratio of NBL-112a statically on two Faraday cups and the mass fractionation correction factor is then calculated using the widely accepted $^{235}U/^{238}U$ ratio of 7.2526×10^{-3} [20]. As no uncertainty is reported for this ratio we assume a minimum uncertainty of 0.1 per mil based on $^{235}U/^{238}U$ data compiled in Cowan and Adler [21]. For Th, we employ our ^{229}Th–^{230}Th–^{232}Th in-house standard TEDDi to measure the mass fractionation. We calculate the mass fractionation factor, β, using the two "known" ratios (see 3.1) $^{229}Th/^{232}Th$ and $^{230}Th/^{232}Th$ of the Th-standard which are measured statically on SEM/Faraday cup combinations. Both Th ratios are biased by mass fractionation and yield. However, if SEM intensities are corrected for nonlinearity effects, the yield should be the same for both ratios and therefore the mass fractionation factor β can be derived. The extent of mass fractionation at the time of sample measurement is estimated by linear interpolation between the values of β obtained for bracketing standards.

2.2.6. SEM nonlinearity and Faraday cup-SEM gain

All data collected with the SEM are corrected for nonlinearity effects as outlined in [6]. Combined use of SEM and Faraday cups also requires the determination of the Faraday cup–SEM gain, also called the yield. The yield can be derived by alternately measuring a beam of appropriate intensity (~5 mV) with the SEM and a Faraday cup (peak jump). However, we use a static measurement routine for MC-ICPMS yield determination because of fluctuations in beam intensity with typical periodicities of seconds to minutes. Furthermore, analysis routines do not necessarily have a beam of suitable intensity to allow a peak jump inter-calibration. Therefore, two isotopes with high dynamic range and a known ratio are simultaneously measured on the SEM and a Faraday cup before and after each sample and used for yield calculation. For U, we use the nonlinearity and mass fractionation corrected $^{234}U/^{238}U$ ratio of NBL-112a and calculate the yield using the $^{234}U/^{238}U$ ratio reported by Cheng et al. [22]. For Th, we use the nonlinearity and mass fractionation corrected $^{230}Th/^{232}Th$ ratio of our standard TEDDi to derive the yield.

2.2.7. Measurement sequence

As discussed, we employ a sample-standard bracketing procedure using NBL-112a or TEDDi as bracketing standards. Every sample or standard measurement is bracketed by a wash procedure (Section 2.2.3). Data collection is started after an uptake time of 90 s. We then allow the SEM to "equilibrate" with the impinging beam for a further 60 s, therefore data collected on the SEM within the first 60 s are usually not used to derive isotopic ratios.

2.2.7.1. Uranium. The isotope ratio measurement protocol for U samples is divided into two static parts:

1. collect only ^{236}U in the SEM to derive the $^{236}U/^{238}U$ ratio, while the $^{235}U/^{238}U$ ratio is measured simultaneously on two Faraday cups;
2. collect only ^{234}U in the SEM to derive the $^{234}U/^{238}U$ ratio.

The same sample solution is therefore used twice with a short (2 min) break between the two measurements. We developed this protocol after significant memory effects were apparent in a particular ETP multiplier [6] and is still our routine protocol. The measurement of the bracketing U-standard is divided in the same way as for the samples. We also monitor the response of the SEM to different beam intensities by measuring the $^{234}U/^{238}U$ ratio of 3 different dilutions (3, 30, 100 ppb) of NBL-112a at the start of every sequence.

2.2.7.2. Thorium. The choice of method for Th mainly depends on the expected $^{230}Th/^{232}Th$ ratio of the sample. For low $^{230}Th/^{232}Th$ ratios, ^{232}Th must be measured on the Faraday cup whereas for high $^{230}Th/^{232}Th$ ratios ^{232}Th is measured on the SEM. The low $^{230}Th/^{232}Th$ method is split into two static measurements:

1. collect only ^{229}Th in the SEM for the $^{229}Th/^{232}Th$ ratio;
2. collect only ^{230}Th in the SEM for the $^{230}Th/^{232}Th$ ratio, followed by
3. tail measurement.

This method is also applied for the bracketing Th-standard, although no tail measurement is needed in this case because the $^{230}Th/^{232}Th$ ratio $>10^{-4}$. Low ^{232}Th intensities require a peak jump routine for Th measurements thus the method for high $^{230}Th/^{232}Th$ involves two measurements using peak jump routines:

1. collect ^{230}Th and ^{229}Th alternately in the SEM for $^{230}Th/^{229}Th$;
2. collect ^{232}Th and ^{229}Th alternately in the SEM for $^{232}Th/^{229}Th$.

All measurements on the SEM can also be done without the RPQ energy filter. This results in a higher SEM–Faraday cup efficiency (yield) but a worse abundance sensitivity. However, we routinely use the setup including the RPQ.

2.2.8. Data reduction and error calculation

All data are corrected online for darknoise (SEM), baseline and gain inter-calibration (Faraday cups). Corrections for background intensities and tail contribution as well as SEM nonlinearity, mass fractionation and yield are conducted offline. Sample data also have to be corrected for spike and chemistry blank contributions.

First, standard data are processed to obtain the mass fractionation coefficient and the yield, then sample data are corrected using linear interpolation between the bracketing standards. In practice, it is not necessary to explicitly calculate both β and yield for Th corrections. We correct the ^{229}Th/^{232}Th, ^{230}Th/^{232}Th (SEM–Faraday cup) and/or ^{230}Th/^{229}Th (SEM–SEM) ratios in one step using measured relative to nominal TEDDi values. Only the correction of the ^{229}Th/^{232}Th measured in a peak jump mode on the SEM requires the mass fractionation factor β.

To calculate activity ratios, we use the half lives for ^{234}U and ^{230}Th of 245250 ± 490 and 75690 ± 230 years as reported by Cheng et al. [22]. Half lives of ^{238}U and ^{235}U are $(4.4683 \pm 0.0048) \times 10^9$ and $(7.0381 \pm 0.0096) \times 10^8$ years [23], for ^{232}Th the half life is reported to be 1.401×10^{10} years [24].

Uncertainties of all variables such as sample mass, spike mass, measured isotopic ratios, spike calibration uncertainty, standard isotope ratios uncertainties or half life uncertainties are propagated using a Monte Carlo procedure to determine the final error of the isotope and activity ratios. Note that the uncertainties of the spike ^{229}Th/^{236}U ratio and of the isotope ratios of the external standards used for sample bracketing add systematic errors to the measured isotope ratios. The final precision of the U and Th ratios is therefore dependent on the precision of the external standards (NBL-112a and TEDDi) used for bias corrections. The precision of the ^{230}Th/^{238}U ratio is also dependent on the spike calibration. All errors quoted in this study are at the 95% confidence level, unless otherwise stated.

2.3. Samples and chemical separation procedures

2.3.1. Samples

2.3.1.1. Gravimetric standards. We prepared a gravimetric U standard solution from a metal bar of NBL-112a. The gravimetric U stock solution in 7N HNO_3 has a concentration of 4.8747 ± 0.0003 mg/g. For Th we used the NIST SRM 3159 solution as starting material for our gravimetric standard. Our Th-solution in 7N HNO_3 has a Th-concentration of 0.4898 ± 0.002 mg/g. From the U stock solution we prepared a diluted gravimetric U solution of 0.4162 ± 0.00003 mg/g and, together with the Th stock, a mixed gravimetric U–Th standard solution with 0.3913 ± 0.00003 mg/g (U) and 0.4505 ± 0.002 mg/g (Th).

2.3.1.2. Isotopic standards. Isotopic uranium standards used in our laboratory are NBL-112a and CRM U500 and U010. We also took part in the recent REIMEP 18 campaign organised by the Institute for Reference Materials and Measurements (IRMM) [4] and measured the isotopic composition of REIMEP 18 A, B, C and D. Isotopic Th standards are CRM IRMM-035 and 036, the Santa Cruz Th "A" standard and the Open University Th "U" standard. Furthermore, we prepared and characterised an in-house isotopic ^{229}Th–^{230}Th–^{232}Th standard TEDDi.

2.3.1.3. Secular equilibrium standards. The accuracy of U–Th measurements can potentially be checked against natural samples sufficiently old to be in a state of secular equilibrium. Unfortunately, it is difficult to be sure the natural samples have behaved as closed systems since formation, despite a range of independent visual and chemical criteria. Only consistent data for a number of different standards is sufficient to infer true secular equilibrium (e.g., [22]). We have thus analysed a range of samples with different U and Th concentrations that have previously been reported to be in secular equilibrium. These include samples with ^{230}Th/^{232}Th ratios in the range of 10^{-5} [25,3] such as the Table Mountain Latite (TML) [26] and Long Valley, Glass mountain sample LV 18. The latter comes from unit OL of Metz and Mahood [27], which represents a lava dome with an age of 1.6 Ma. LV 18 was used by Bourdon et al. [28] as secular equilibrium standard to calibrate their ^{233}Pa spike. We also analysed USGS standard BCR-2 (second generation Columbia River Basalt) for which we present the first U–Th disequilibria data. Harwell Uraninite (HU) (e.g., [22]), which has ^{230}Th/^{232}Th concentration ratio close to unity, was also measured. Note however, that Cheng et al. [22] report a ^{230}Th/^{238}U ratio elevated by 0.3% for their HU sample indicating either that there are differences between batches of HU or that it is not in secular equilibrium. Our uraninite standard solution (Uran 84.5) was provided by UKAEA Harwell in 1990. In Appendix A we provide the addresses of sources from whence the isotopic and secular equilibrium standards were originally obtained.

2.3.1.4. Carbonates samples. Examples of applications of our methods to key carbonate samples are presented, including a speleothem sample from Wilder Mann cave, Austrian Alps (WM2, kindly provided by C. Spötl, University of Innsbruck) and a coral sample (ANU coral standard AC-1 [29], kindly provided by T. Esat, ANU). AC-1 was taken from a large porites coral in Aladdin's cave on the Huon Peninsula (Papua New Guinea) and our powder came from the bottom portion. The carbonate samples were independently analysed in Bristol and by TIMS at the Heidelberg Academy of Sciences.

2.3.2. Separation and purification

Samples are spiked with our mixed ^{229}Th–^{236}U spike, kindly provided by S. Turner (GEMOC), but independently calibrated (see below). U and Th are then separated following traditional chemical separation and purification procedures (e.g., [16,30]) and analysed separately in 0.6N HCl solution. Procedural chemistry blank values were typically less than 0.01 ng ^{238}U, 0.1 pg ^{235}U, 1 fg ^{234}U, 0.01 ng ^{232}Th and 1 fg ^{230}Th, respectively.

3. Th standard and spike calibration

3.1. Th standard calibration

The accuracy of MC-ICPMS procedures is highly dependent on the accuracy of calibrated standards used for sample bracketing. Therefore, standards with well-known isotopic composition for both U and Th, are needed to bracket the MC-ICPMS measurements. For U, NBL-112a is an appropriate and widely available standard, for Th, however, no similar standard is readily available. We therefore prepared the in-house TEDDi standard solution. TEDDi was designed to have similar ^{229}Th and ^{230}Th concentrations, the ^{229}Th/^{232}Th and ^{230}Th/^{232}Th ratios were chosen to be in the order of 10^{-3}. TEDDi was specifically mixed to bracket carbonate samples with high ^{230}Th/^{232}Th ratios, with the ^{232}Th concentration of 0.3 ppb chosen to yield an intensity of about 150 mV on the Faraday cups. This allows precise static SEM–Faraday cup measurements of ^{229}Th/^{232}Th and ^{230}Th/^{232}Th, without causing a large ^{232}Th background for subsequent, possibly low ^{232}Th samples. For calibration purposes a concentrated TEDDi solution (20 ppb of ^{232}Th, 10 V intensity on a Faraday cup) was used to allow the measurement of all isotopes statically on Faraday cups.

The isotopic calibration of TEDDi is based on TIMS measurements and static Faraday cup MC-ICPMS measurements. Details of the TIMS measurements of TEDDi are given in Appendix B. In brief, the ^{230}Th/^{229}Th ratio was determined by peak jumping on the SEM, which requires no yield determination. Since ^{229}Th and ^{230}Th have similar intensities, potential nonlinearity effects [6] are negligible. The same is not true for ^{232}Th and therefore ratios involving this nuclide were not determined by TIMS. No significant mass fractionation effect could be detected for TIMS measurements. Running the samples to exhaustion gave no discernable change in the measured ratio. The TIMS measurements give a mean ^{230}Th/^{229}Th ratio of 1.519 ± 0.002.

The precise and accurately measured ^{230}Th/^{229}Th ratio of TEDDi was used for internal mass fractionation corrections of the ^{230}Th/^{232}Th and ^{229}Th/^{232}Th ratios measured statically on Faraday cups of the MC-ICPMS. Measurements on both our Neptune MC-ICPMS instruments over the course of a year yielded mean $^{230}\text{Th}/^{232}\text{Th} = (4.444 \pm 0.007) \times 10^{-3}$ and $^{229}\text{Th}/^{232}\text{Th} = (2.927 \pm 0.005) \times 10^{-3}$.

3.2. U–Th spike calibration

For U–Th analyses we use a mixed ^{229}Th–^{236}U spike. We undertook a careful calibration of the spike concentration and isotopic composition, because all U–Th ratios and therefore age calculations are directly dependent on the accuracy of the spike calibration. Gravimetric NBL-112a and NIST 3159 solutions were used to calibrate the ^{236}U and ^{229}Th concentration of our spike. The secular equilibrium standard TML was additionally used to assess accuracy and precision of the spike calibration. LV 18, BCR-2 and HU were also analysed as further tests of the accuracy of the spike calibration (Section 4.4). Many laboratories use only one secular equilibrium standard, such as HU, to calibrate their spike. Due to the reported uncertainties about HU as secular equilibrium standard [22], we base our calibration principally on assays against gravimetric standards and employ TML measurements to confirm the calibration.

Spike solution was added to 4 aliquots of the dilute gravimetric U standard solution, typically to give a ^{236}U concentration of the same order of magnitude as ^{234}U (^{234}U/^{236}U ~2–3). These mixtures were analysed using methods outlined above in Section 2.2.7. Fig. 2 shows the 46 measured ^{234}U/^{236}U ratios of the different samples, normalised to (sample mass/spike mass). We measure a mean normalised ratio of 50.088 ± 0.023. Using the nominal ^{234}U concentration of the gravimetric NBL-112a solution, the ^{236}U concentration of the spike of 0.4324 ± 0.0002 ng/g can be derived. The ^{234}U/^{236}U ratios of two of the aliquots were also measured using a peak jump routine on a TIMS, which yielded consistent but less precise values (Fig. 2).

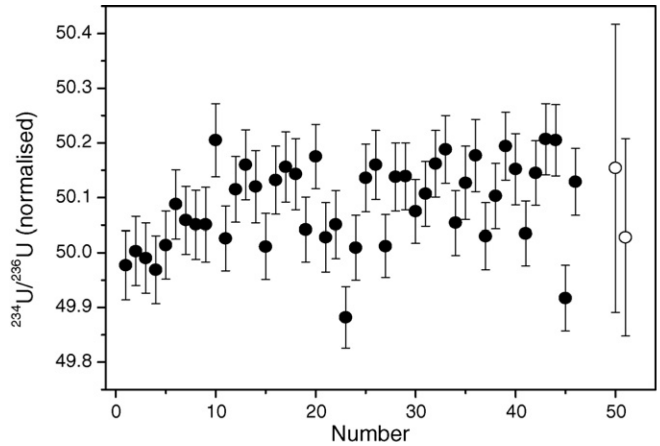

Fig. 2. Calibration of the ^{236}U spike concentration. ^{234}U/^{236}U ratios of spiked gravimetric NBL-112a standard. The ratios are normalised to (standard mass /spike mass) as different solutions with different spike–standard mass ratios were used. The last two values (open symbols) were measured by TIMS.

The ^{229}Th/^{236}U concentration ratio of the spike was then characterised using a mixed NBL-112a-SRM 3159 gravimetric standard. Four aliquots of the mixed standard were spiked with different amounts of spike and then chemically separated in U and Th solutions. Fig. 3 shows the measured ratios of ^{238}U/^{236}U to ^{232}Th/^{229}Th from the combined individual U and Th isotopic measurements. A total of 23 analyses yield an average (^{238}U/^{236}U)/(^{232}Th/^{229}Th) ratio of 2.1325 ± 0.0012 which can be used to calculate the spike ^{229}Th concentration. The resulting value is 1.0644 ± 0.0048 ng/g. This uncertainty is mainly due to the quoted uncertainty of SRM 3159. As we use a mixed ^{229}Th/^{236}U spike, we are interested in the uncertainty of the Th/U ratio. Our final spike ^{229}Th/^{236}U uncertainty is assessed by ^{230}Th/^{238}U uncertainty of TML measurements of 0.14% (Section 4.4). The Th concentration of the spike was also measured using the single element, gravimetric Th standard. Fig. 4 shows 39 analyses of ^{232}Th/^{229}Th normalised to (sam-

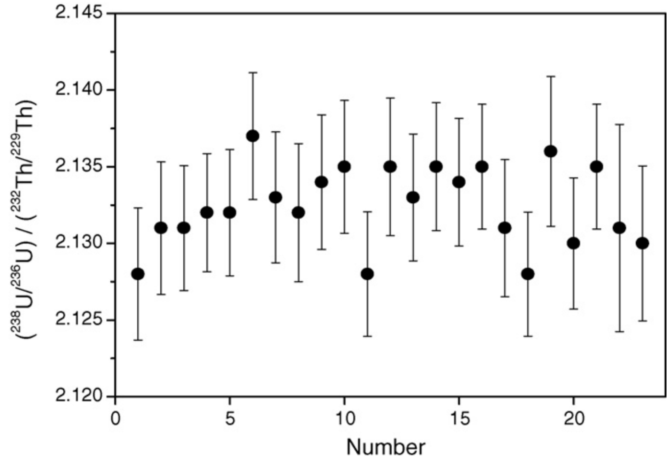

Fig. 3. Calibration of the ^{229}Th/^{236}U spike ratio. MC-ICPMS determined U/Th ratios derived from the spiked mixed gravimetric standard. Shown are the measured ratios of ^{238}U/^{236}U to ^{232}Th/^{229}Th.

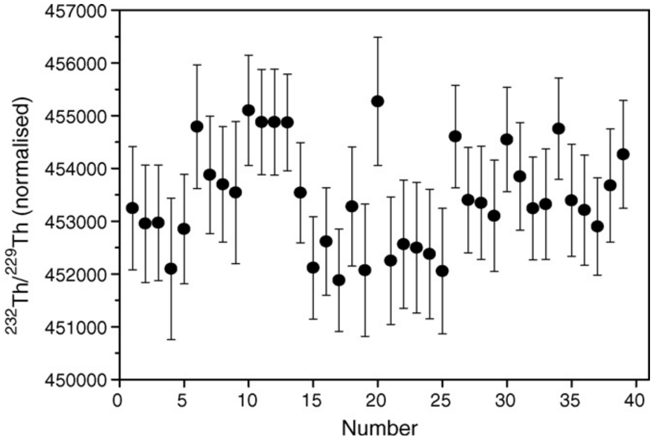

Fig. 4. Calibration of the ^{229}Th spike concentration. MC-ICPMS determinations of ^{232}Th/^{229}Th ratios of spiked gravimetric Th standard. The ratios are normalised to (standard mass/spike mass) as different solutions with different spike–standard mass ratios were used.

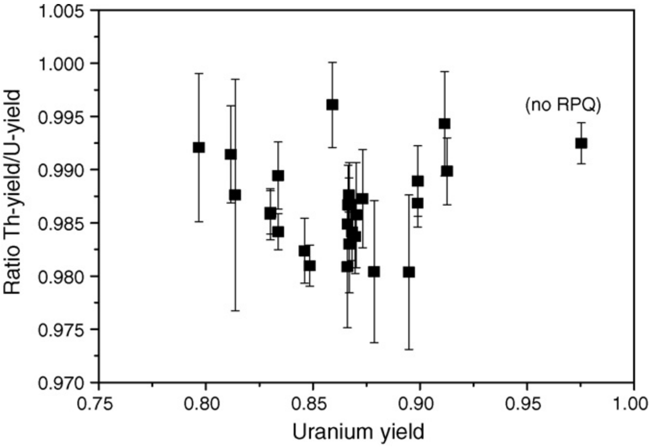

Fig. 5. U and Th yield. Comparison of MC-ICPMS yield of U and Th using a MasCom SEM.

ple mass/spike mass) with a mean of 453,690 ± 330. Again, using the nominal ^{232}Th concentration of the gravimetric standard the ^{229}Th concentration of the spike solution was derived to be 1.0656 ± 0.0044 ng/g. This result is consistent with the mixed gravimetric standard measurements. The ^{238}U/^{236}U, ^{235}U/^{236}U, ^{234}U/^{236}U, ^{232}Th/^{229}Th and ^{230}Th/^{229}Th ratios of the spike were repeatedly measured using MC-ICPMS.

4. U and Th isotope measurements

4.1. Mass fractionation of U and Th

Many U-series laboratories employ a U standard for bracketing both U and Th samples (e.g., [14,31]). Thus, a mass fractionation factor, derived, e.g., from NBL-112a ^{235}U/^{238}U, is used to correct Th isotope data for mass fractionation, assuming identical U and Th mass fractionation. We have used our TEDDi standard to investigate mass fractionation of U and Th. Based on 29 sequences, the average values for the mass fractionation factor β for U is $\beta = 1.13 \pm 0.04$ and for Th we find $\beta = 1 \pm 0.1$. Thus little significant difference in mass fractionation is indicated between U and Th isotopes using measurements of NBL-112a and TEDDi, respectively, the mean mass fractionation per amu being 0.48% for U and 0.45% for Th. The data indicate that a mass fractionation factor derived by U could be reasonably applied for Th mass bias correction within per mil precision, but this is generally not practically applicable given the need to independently correct for SEM–Faraday cup yield (see below).

4.2. SEM–Faraday cup gain of U and Th

As discussed previously, the actual Faraday cup–SEM gain is dependent on various parameters such as SEM operation voltage and the RPQ settings. A different effective yield for U and Th can occur at the same RPQ settings resulting from optimal ionisation in slightly different parts of the plasma. Thus, Th and U ion beams can have slightly different spatial and energy distributions that are notably distinguished by their differential transmission through the RPQ. Furthermore, ions of different elements could have a different yield on the first dynode. Using NBL-112a and TEDDi we compare the yield of U and Th ran in consecutive analyses blocks. Fig. 5 shows the comparison of U- and Th-yield of the MasCom multiplier in Neptune 1 as the mean yield of consecutive 10 h blocks whilst keeping the plasma conditions constant. The yield stability of the SEM is better than 0.5% over 10 h for both U and Th. For this system, the average ratio of Th yield to U yield is about 0.985 ± 0.002.

Without the RPQ, we still find a difference in yield of about 1% indicating that the RPQ is not the sole cause of the difference in yield. Either there is a difference in ion yield on the first dynode, or the difference might be a result of the use of different ion optics settings for U and Th to achieve the same spacing between the ion beams required to use the same cup configuration for both U and Th measurements. However, our results demonstrate the importance of a Th standard for corrections of Th measurements using an ion counting device.

4.3. Isotopic composition of reference materials

U isotope measurements were made on CRM U500 and U010. For both standards, we obtain isotopic ratios that are in good agreement with the reference values or values published elsewhere [32]. Our results are reported in Table 3. We also took part in the REIMEP 18 campaign [4]. For all samples and isotope ratios we obtained results that are in good agreement with the certified range (Table 4). However, the report demonstrates that accuracy of U isotope measurements using MC-ICPMS is still a challenge. The spread of MC-ICPMS results from 16 laboratories for the mean ^{234}U/^{238}U ratio of 5.658×10^{-5} (REIMEP 18 A) is more than 5%. Only 10 results show overlap with the certified range within quoted errors. The results of ^{236}U/^{238}U measurements of REIMEP 18 A and D with ratios of 3×10^{-8} and 1.1×10^{-7} are even worse. The mean MC-ICPMS results span a range of +900% to −50%. One of 13 MC-ICPMS results for sample 18-D has overlap with the certified range due to a

Table 3
Results of U isotope measurements on CRM. U010 data are based on $N = 23$ measurements and for U500 $N = 11$

CRM	Measured	CRM reference	Richter et al. [32]
$^{234}U/^{238}U$			
U010	$5.456 \times 10^{-5} \pm 4 \times 10^{-8}$	$5.466 \times 10^{-5} \pm 5.1 \times 10^{-7}$	$5.448 \times 10^{-5} \pm 8.5 \times 10^{-8}$
U500	$1.0406 \times 10^{-2} \pm 1.2 \times 10^{-5}$	$1.0422 \times 10^{-2} \pm 1.9 \times 10^{-5}$	$1.0425 \times 10^{-2} \pm 1.4 \times 10^{-5}$
$^{235}U/^{238}U$			
U010	$1.0150 \times 10^{-2} \pm 2 \times 10^{-6}$	$1.0140 \times 10^{-2} \pm 1 \times 10^{-5}$	$1.0138 \times 10^{-2} \pm 1 \times 10^{-5}$
U500	$0.99994 \pm 5 \times 10^{-4}$	$0.999698 \pm 1 \times 10^{-3}$	–
$^{236}U/^{238}U$			
U010	$6.9271 \times 10^{-5} \pm 8.3 \times 10^{-8}$	$6.8799 \times 10^{-5} \pm 7.1 \times 10^{-7}$	$6.9287 \times 10^{-5} \pm 1.7 \times 10^{-7}$
U500	$1.5208 \times 10^{-3} \pm 2.2 \times 10^{-6}$	$1.5188 \times 10^{-3} \pm 6.2 \times 10^{-6}$	$1.52334 \times 10^{-3} \pm 1.1 \times 10^{-6}$

Errors are given as 2σ standard errors of the mean except for $^{234}U/^{238}U$ and $^{235}U/^{238}U$ of U010 where the standard errors of replicate measurements are smaller than the systematic errors. In these cases we quote the average 2σ error of individual $^{236}U/^{238}U$ measurements which incorporate these systematic errors.

quoted error of 10%. Two of eight results for 18 A show overlap with the certified range. Note that 16 laboratories submitted MC-ICPMS $^{236}U/^{238}U$ results for samples 18 B and C but only 13 of them submitted a result for sample D and 8 for sample A indicating that the other laboratories were not able to reliably measure ratios for this dynamic range.

Our results for the four U solutions REIMEP 18 A, B, C and D are reported in Table 4. We achieved excellent agreement for all $^{235}U/^{238}U$ ratios. It is interesting that similar to the U500 result our mean $^{235}U/^{238}U$ results are consistently elevated by ~0.3 per mil compared to the middle of the certified range. Our results on the $^{234}U/^{238}U$ ratios are also very good. We find generally slightly (0.1%) elevated $^{234}U/^{238}U$ ratios compared to the middle of the certified range. One measured ratio (REIMEP 18 C) is 2.5 per mil different from the middle of the certified range and does not quite agree within quoted uncertainties. The other $^{234}U/^{238}U$ ratios show good agreement to the certified range.

The $^{236}U/^{238}U$ ratios of the four REIMEP solutions cover a range from 10^{-3} to 10^{-8}. The two solutions with the extreme $^{236}U/^{238}U$ ratios of 1.105×10^{-7} (REIMEP 18 D) and 3.06×10^{-8} (REIMEP 18 A) are a considerable challenge as the ratios yield ^{236}U intensities close to the intensity of abundance sensitivity tailing. Our submitted mean $^{236}U/^{238}U$ result for REIMEP 18 A is 5 per mil smaller than the middle of the certified range which we consider a good result for this dynamic range, considering our 2% measurement error. However, the result for the $^{236}U/^{238}U$ ratio of REIMP 18 D is a good example for the significance of corrections needed for MC-ICPMS data. Our submitted $^{236}U/^{238}U$ result for sample D turned out to be 12% too high. The reason for this is an insufficient correction for the ^{235}U-hydride contribution. The data were corrected for the contribution of the ^{238}U tail and ^{235}U-hydrides on ^{236}U in one step based on a NBL-112a measurement. This procedure is accurate only for natural samples with the same $^{235}U/^{238}U$ ratio as the external NBL-112a standard, but leads to the 12% difference for sample D. Our result for sample A was accurate due to its almost natural $^{235}U/^{238}U$ ratio. In Table 4 we also show the $^{236}U/^{238}U$ ratios derived from our data with the accurate hydride correction required for the enriched $^{235}U/^{238}U$ ratio of REIMEP 18 D based on the $239/^{238}U$ ratio of 6×10^{-7} to 7×10^{-7} measured prior to the sequences. This result now shows excellent agreement with the certified ratio and demonstrates the importance of thorough corrections to raw MC-ICPMS data.

We also measured a variety of Th standard solutions including IRMM-035, IRMM-036 and some widely distributed in-house solution standards such as SC-Th “A” and OU Th “U”. All were measured bracketed and subsequently corrected with TEDDi. For IRMM-035 we derive a $^{230}Th/^{232}Th$ ratio of $(11.383 \pm 0.019) \times 10^{-6}$, and for IRMM-036 $(3.052 \pm 0.015) \times 10^{-6}$. Our results for IRMM-035 and

Table 4
Results of U isotope measurements on REIMEP 18 samples ($N = 7$)

	REIMEP 18 A	REIMEP 18 B	REIMEP 18 C	REIMEP 18 D
$^{234}U/^{238}U$ certified range	0.000056541–0.000056623	0.00033249–0.00033293	0.000079442–0.000079578	0.00020922–0.0002095
$^{234}U/^{238}U$ measured	$5.66203 \times 10^{-5} \pm 6.9 \times 10^{-8}$	$0.0003328 \pm 4.7 \times 10^{-7}$	$7.968810^{-5} \pm 7.3 \times 10^{-8}$	$0.00020958 \pm 4.2 \times 10^{-7}$
$^{235}U/^{238}U$ certified range	0.0072506–0.0072578	0.035452–0.035488	0.0043767–0.0043821	0.024221–0.024245
$^{235}U/^{238}U$ measured	$0.0072564 \pm 9.7 \times 10^{-7}$	$0.03548 \pm 9.6 \times 10^{-6}$	$0.0043808 \pm 1.4 \times 10^{-6}$	$0.02424 \pm 5.9 \times 10^{-6}$
$^{236}U/^{238}U$ certified range	3.0496×10^{-8} to 3.0662×10^{-8}	0.00038815–0.00038841	0.00103326–0.00103414	1.1025×10^{-7} to 1.1083×10^{-7}
$^{236}U/^{238}U$ measured	$3.04296 \times 10^{-8} \pm 5.8 \times 10^{-10}$	$0.00038795 \pm 5.5 \times 10^{-7}$	$0.00103354 \pm 1.6 \times 10^{-6}$	$1.1005 \times 10^{-7} \pm 1.6 \times 10^{-9}$
$^{236}U/^{238}U$ submitted[a]	$3.0433 \times 10^{-8} \pm 5.8 \times 10^{-10}$	$0.00038797 \pm 5.5 \times 10^{-7}$	$0.00103354 \pm 1.6 \times 10^{-6}$	$1.2373 \times 10^{-7} \pm 9.7 \times 10^{-10}$

Errors are given as 2σ standard errors of the mean except for $^{236}U/^{238}U$ of REIMEP 18 D where the standard error of replicate measurements is smaller than the systematic errors. In this case we quote the average 2σ error of individual $^{236}U/^{238}U$ measurements which incorporate these systematic errors.

[a] BIG results originally submitted to IRMM and part of the compilation in Richter et al. [4]. The $^{236}U/^{238}U$ were recalculated with regard to ^{235}UH contribution ($^{236}U/^{238}U$ measured). The result for REIMEP 18 D was originally overestimated by 12% due to insufficient ^{235}UH correction. The result for the $^{236}U/^{238}U$ ratios of REIMEP A, B and C were not significantly affected. See text for details.

Table 5
Results of Th isotope measurements on CRM and other standard samples

Sample	^{230}Th/^{232}Th measured [$\times 10^{-6}$]	^{230}Th/^{232}Th reference [$\times 10^{-6}$]
IRMM-035	11.383 ± 0.02	11.481 ± 0.078[a]
IRMM-036	3.052 ± 0.015	3.113 ± 0.078[a]
UCSC Th“A”	5.856 ± 0.011	5.856 ± 0.07[b] 5.826 ± 0.012[c]
OU Th“U”	6.193 ± 0.013	6.176 ± 0.062[d]
TML	5.793 ± 0.014	5.788 ± 0.058[b] 5.800 ± 0.013[c]
LV 18	8.859 ± 0.02	–
BCR-2	4.748 ± 0.012	–

The data are based on $N = 8$ (IRMM-035), $N = 5$ (IRMM-036), $N = 8$ (UCSC Th“A”), $N = 8$ (OU Th“U”), $N = 10$ (TML), $N = 11$ (LV 18) and $N = 11$ (BCR-2) analyses. Errors are given as 2σ standard errors of the mean except for TML where the standard error of replicate measurements is smaller than the systematic errors. In this case we quote the average 2σ error of individual ^{230}Th/^{232}Th measurements which incorporate these systematic errors.

[a] Certified ratio.

[b] Rubin [34].

[c] Pietruszka et al. [3].

[d] Turner et al. [35].

IRMM-036 are 0.86% and 2%, respectively, different from the certified ratios. However, the certified ratios were calculated using a determination of the low ^{230}Th/^{232}Th gravimetric component measured by TIMS, employing a method of SEM–Faraday cup gain [33] that has been shown to be prone to inaccuracies (e.g., [34]) which might explain the discrepancy. We measured the ^{230}Th/^{232}Th ratio of SC-Th “A” to be $(5.856 \pm 0.011) \times 10^{-6}$ in excellent agreement with Rubin [34]. For OU Th “U” we derive $(6.194 \pm 0.013) \times 10^{-6}$ which is 0.3% higher than the ratio given in Turner et al. [35] but within uncertainties the results are in agreement (Table 5). Furthermore, we also investigated the ^{230}Th–^{232}Th isotope ratio of rock standards TML, LV 18 and BCR-2. Our result for TML is in good agreement with ratios reported by Rubin [34] and Pietruszka et al. [3]. For LV 18 and BCR-2 no literature data on the ^{230}Th/^{232}Th ratio are currently available. All Th standard results are listed in Table 5.

4.4. Measurements of secular equilibrium samples

As highlighted, for example, by McDermott et al. [25], Cheng et al. [22] and Pietruszka et al. [3], a strong test of accuracy for the measurements of U-series isotopes are measurements of secular equilibrium samples. TML seems to be the most reliable secular equilibrium sample [22,3]. We therefore use TML measurements to test the accuracy of our procedures and calibration and to derive the final precision of the spike calibration. Furthermore, we measured LV 18, BCR-2 and HU to test whether these samples can also be used as secular equilibrium standards.

For TML, we find the average activity ratios $^{230}\text{Th}/^{238}\text{U} = 0.9994 \pm 0.0014$ and $^{234}\text{U}/^{238}\text{U} = 1.0005 \pm 0.0007$. This is based on 15 measurements of four separate dissolutions and shows excellent agreement with secular equilibrium ratios. LV 18 has slightly elevated mean ratios close to secular equilibrium. Based on 11 analyses of three different dissolutions we find $^{230}\text{Th}/^{238}\text{U} = 1.0012 \pm 0.001$ and $^{234}\text{U}/^{238}\text{U} = 1.0014 \pm 0.0011$. Another potential secular equilibrium sample is BCR-2. Compared to TML and LV 18 the BCR-2 results are somewhat irregular. The activity ratios of 11 analyses scatter around a mean of $^{230}\text{Th}/^{238}\text{U} = 1.0043 \pm 0.0033$ and $^{234}\text{U}/^{238}\text{U} = 1.0049 \pm 0.0012$. Thus the 16 Ma old BCR-2 must have been recently perturbed from equilibrium. Therefore it is not an appropriate secular equilibrium standard for U–Th analyses. However, this basaltic sample still potentially provides a useful reference close to equilibrium, e.g., for ^{231}Pa/^{235}U disequilibrium measurements, where analytical uncertainties are greater and the deviation from equilibrium thus is not significant [36].

For our Harwell uraninite solution we find $^{230}\text{Th}/^{238}\text{U} = 1.0029 \pm 0.0005$ and $^{234}\text{U}/^{238}\text{U} = 1.0001 \pm 0.0004$, based on 61 measurements of 5 independent prepared aliquots with different sample-spike ratios, measured using two Neptune instruments equipped with different SEM’s (first ETP and now MasCom). Aliquots from the same uraninite stock solution were independently analysed by TIMS in Heidelberg yielding similar results of $^{230}\text{Th}/^{238}\text{U} = 1.0034 \pm 0.0014$ and $^{234}\text{U}/^{238}\text{U} = 0.9982 \pm 0.0018$. Note that the Heidelberg spike was calibrated using another batch of HU-1 (see Appendix C

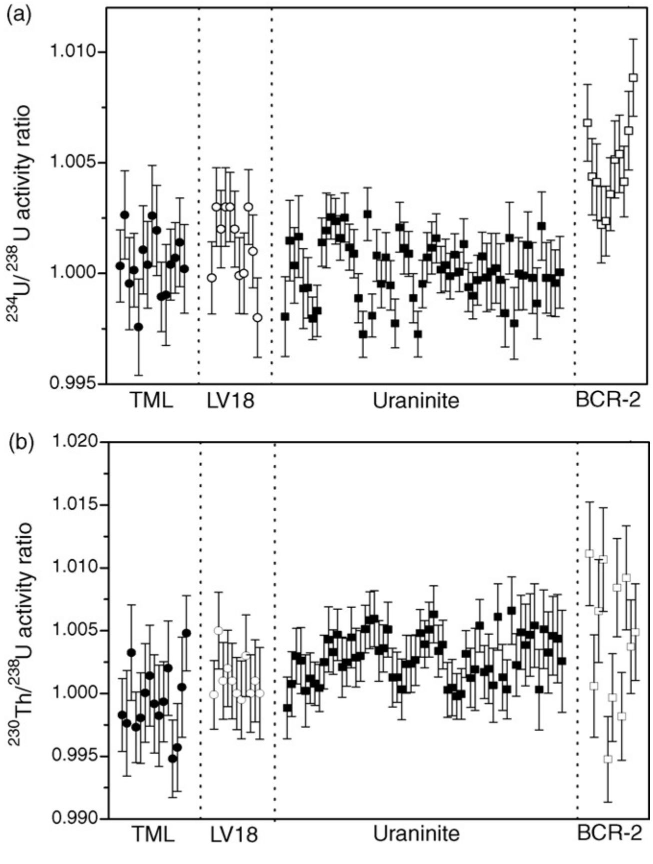

Fig. 6. Secular equilibrium standards. (a) MC-ICPMS determinations of ^{234}U/^{238}U ratios of TML (circles), LV 18 (open circles), Uran 84.5 (squares) and BCR-2 (open squares). (b) MC-ICPMS determinations of ^{230}Th/^{238}U of TML, LV 18, Uran 84.5 and BCR-2.

for details). As Heidelberg obtains the same results on Uran 84.5 as Bristol with the gravimetrically calibrated BIG spike, we conclude that the different batches of Harwell uraninite show significant differences in isotopic composition. Therefore, HU seems not to be a reliable secular equilibrium standard and a spike calibration based on HU needs independent confirmation. Our laboratory inter-comparison results indicate that the Heidelberg spike calibration is accurate. Fig. 6a and b show a compilation of our results on secular equilibrium samples.

4.5. U–Th isotope measurements on carbonate samples

We have applied our U–Th methods to a coral sample as part of a laboratory inter-comparison study using the ANU coral standard AC-1 [29]. The comparison of measurements on carbonate samples addresses potential differences due to spike and standard calibration as well as sample preparation procedures and potential matrix effects. Three different sub-samples were prepared from a powdered aliquot and analysed at least twice each by MC-ICPMS in Bristol. In addition, six sub-samples of AC-1 from the same stock were prepared and analysed by TIMS in Heidelberg. The reported results agree well with those from Bristol. In Bristol, based on 7 analyses, we obtain a mean δ^{234}U value of 101.9 ± 1.4, a ^{230}Th/^{238}U activity ratio of 0.760 ± 0.001 and an age of 124.3 ± 0.25 ka. In Heidelberg we measure a mean δ^{234}U value of 102.3 ± 0.9, a ^{230}Th/^{238}U activity ratio of 0.759 ± 0.0032 and an age of 123.98 ± 0.82 ka. Fig. 7a and b show the measured ratios and the dating results.

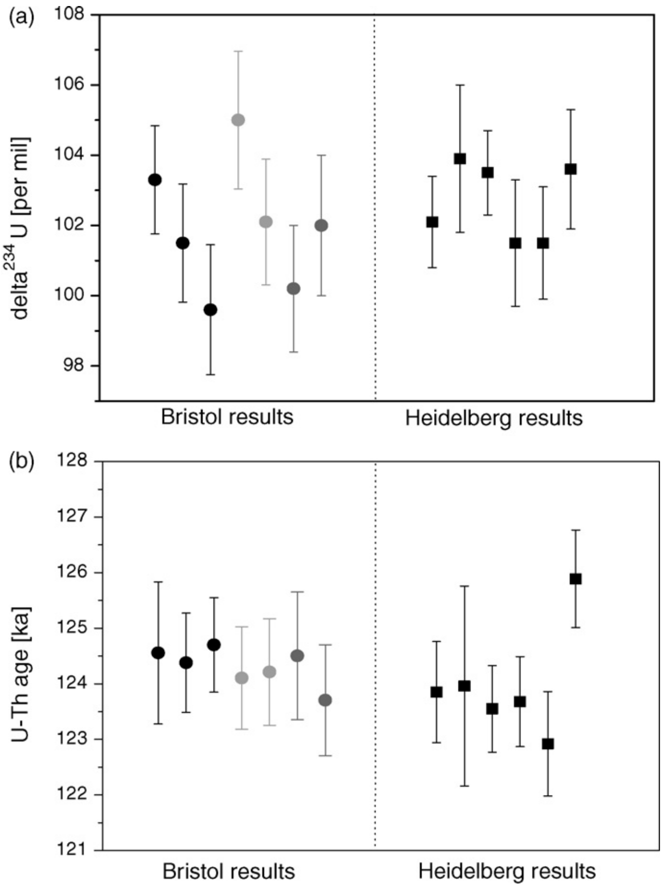

Fig. 7. Laboratory inter-comparison. (a) Results of δ^{234}U measurements of AC-1, measured in Bristol (circles, different grey scale for 3 different sub-samples) and Heidelberg (squares). (b) Dating results of AC-1 measured in Bristol and Heidelberg. ($\delta^{234}\mathrm{U} = ([^{234}\mathrm{U}/^{238}\mathrm{U}]_{\mathrm{activity}} - 1) \times 1000$).

AC-1 has a ^{238}U concentration of 3.22 ± 0.01 μg/g. The typical sample mass for one analysis of AC-1 in Bristol was equivalent to ∼9 mg. We usually prepare enough to be able to do a repeat analysis of the same solution. In the case of the 3 AC-1 sub-samples, we prepared 90 mg samples that can be used for 10–15 repeat measurements. In Heidelberg the typical sample mass for an analysis was 300–500 mg. The typical uncertainties of a single measurement are similar for both laboratories. We derive uncertainties for the ^{234}U/^{238}U ratio of 0.2% and 0.4% for the ^{230}Th/^{238}U ratio. The age uncertainty is 0.8%.

We also employed a secular equilibrium carbonate sample for inter-laboratory comparison. A speleothem sample from Wilder Mann cave, Austrian Alps (WM2) has been independently analysed in Bristol and Heidelberg. The sub-sample analysed for the comparison has relatively high U concentration (25.3 μg/g of ^{238}U). Within uncertainties the sample is in secular equilibrium as measured in Bristol ($^{234}\mathrm{U}/^{238}\mathrm{U} = 1.0009 \pm 0.0016$ and $^{230}\mathrm{Th}/^{238}\mathrm{U} = 1.0013 \pm 0.003$) and in Heidelberg ($^{234}\mathrm{U}/^{238}\mathrm{U} = 1.0000 \pm 0.002$ and $^{230}\mathrm{Th}/^{238}\mathrm{U} = 1.0021 \pm 0.0033$).

5. Conclusions

MC-ICPMS is an extremely valuable tool for precise U–Th isotope measurements but instrumental biases need careful assessment and correction in order to obtain accurate results. We demonstrate the accuracy and applicability of our methods to a wide range of different samples including U and Th isotope standards, carbonate and silicate rock samples. An accurately calibrated Th standard is essential for accurate Th measurements using MC-ICPMS and conventional combination of SEM and Faraday cups and is also likely to be important for a multi ion counting (MIC) procedure. An accurate mass bias correction for Th isotopes using a Th standard is also likely to be important for very high precision static Faraday cup protocols [8]. Our in-house Th standard TEDDi is optimised for samples with small ^{232}Th concentrations. However, our results show that this standard is suitable to derive precise and accurate Th isotope ratios for low ^{232}Th carbonates as well as high ^{232}Th silicate rocks.

An accurate spike calibration is also important for reliable U–Th dating. We demonstrate that the most reliable calibration is based on a combination of gravimetric standards and a reliable secular equilibrium standard such as TML. Laboratories that used HU for the spike calibration should independently confirm that their HU batch is in secular equilibrium as we find significant differences between batches of HU.

Our protocols are designed for MC-ICPMS measurements including the use of an ion counting system. Therefore, we can use samples as small as 20 mg, with U-concentration of less than 1 μg/g (<20 ng U). The methods outlined above can be used to date samples covering all ages from Holocene to those that reached secular equilibrium with both high and low ^{232}Th concentrations. We can also reliably measure U–Th composition of silicate rocks. Our results for the REIMEP 18 samples demonstrate that we can accurately determine non-natural U isotope ratios over a wide dynamic range. A laboratory inter-comparison for U–Th dating as between BIG and Heidelberg Academy of Sciences would be desirable on a wider scale between all laboratories working in that field.

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Appendix A. Addresses of sources for standards

1. Standards U010, U500 and NBL-112a
   New Brunswick Laboratory (NBL), U.S. Department of Energy, New Brunswick Laboratory, Bldg 350, ATTN: Reference Materials Sales, 9800 South Cass Avenue, Argonne, IL 60439, USA. http://www.nbl.doe.gov/.
2. Standard SRM3159
   National Institute of Standards and Technology (NIST), 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2330, USA. http://www.nist.gov/.
3. Standards IRMM-035, IRMM-036 and REIMEP 18
   European Commission, Directorate-General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Retieseweg 111, B-2440 Geel, Belgium. http://www.irmm.jrc.be/html/homepage.htm.
4. Standard BCR-2
   U.S. Geological Survey (USGS), Box 25046, MS 973, Denver, CO 80225, USA. http://www.usgs.gov/.
5. In-house standard SC Th“A”
   Zenon Palacz, then at University of California, Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA.
6. In-house standard OU Th“U”
   Simon Turner, then at Open University, Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK.
7. TML
   James B. Gill, Earth and Planetary Sciences, University of California, Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA
8. LV 18
   Gareth Davies, Faculteit der Aard-en Levenswetenschappen, Vrije Universiteit, De Boelelaan 1085, 1081 HV Amsterdam, Netherlands
9. Harwell Uraninite
   UKAEA Harwell (decommissioned), http://www.ukaea.org.uk/index.htm.

Appendix B. TIMS procedures

For the calibration of the Th-standard we conducted TIMS measurements. The Th sample was taken up in 1N HNO_3 and loaded on a Re-filament. Th measurements were made using the double filament technique. We usually performed measurements on the ThO^+ species. However, to ensure we use the best beam intensity, we routinely check the intensities for both Th^+ and ThO^+.

Instrumental calibration of SEM darknoise, Faraday cup gain calibration and baseline are performed before a measurement. To tune the TIMS, the currents on the ionisation filament (IONI) and evaporation filament (EVA) are set to achieve a $^{232}Th^{16}O^+$ beam of a few kcps (filament currents about 4 and 2 A, respectively, $T \sim 1700\,^\circ C$ depending on filament and sample loading). The tuning is performed using filament position, ion source settings and the lens stack. The peak shape is checked on both Faraday cup and SEM. The mass calibration is also checked. For TEDDi calibration we measure only the $^{230}Th/^{229}Th$ ratio using a peak jump routine on the SEM so that no yield characterisation was needed.

To monitor a potential mass fractionation, we check the isotope ratios for any trend from start to the end of a measurement. We find that mass fractionation is negligible for the mean isotope ratios by running the samples to exhaustion. For TEDDi, the contribution of ^{232}Th tail is negligible as $^{230}Th/^{232}Th \sim 10^{-3}$. All measured ratios are corrected for filament blank contribution and interfering oxide isotopes.

U samples for the spike calibration are also taken up in 1N HNO_3 and are loaded on a Re-filament, U measurements are made using the double filament technique. To tune the TIMS for U, the currents of ionisation filament (IONI) and evaporation filament (EVA) are set to achieve a ^{238}U beam of about 200 kcps (currents about 3.5 and 0.4 A, respectively, $T \sim 1650\,^\circ C$ depending on filament and sample loading).

The SEM–Faraday cup yield characterisation must be done individually using each sample itself. Usually a beam with an appropriate intensity is switched between SEM and Faraday cup to obtain the SEM to Faraday cup yield. We measure the yield after tuning with a ^{238}U beam always at the same intensity of about 2×10^5 cps. However, the accuracy of this yield characterisation is limited and not used for calibration measurements. After the yield was determined the filament was carefully heated to currents of usually 3.8 A (IONI) and 1A (EVA) with a temperature around 1660 °C for U. During a U measurement the current of the evaporation filament usually needs to be adjusted to keep the U intensity within a certain range. To monitor potential mass fractionation, we check the isotope ratios for any trend from start to the end of a measurement. As for Th, we find that mass fractionation is negligible. For spike calibration, we measured the $^{234}U/^{236}U$ of spiked gravimetric NBL-112a samples only using a peak jump routine with similar intensities applied to the SEM.

Appendix C. Calibration of the U and Th spikes used in the Heidelberg laboratory

The TIMS laboratory at the Heidelberg Academy of Sciences uses a ^{233}U–^{236}U-double spike and a ^{229}Th spike. These spike solutions were carefully calibrated against a gravimetric U standard solution and a secular equilibrium standard solution. Similarly as described for the Bristol laboratory (see Section 2.3.1.), we prepared a gravimetric U standard solution from a NBL-112a metal bar. This solution in 7N HNO_3 has a ^{238}U concentration of 1.1455 ± 0.0001 mg/g. From this U solution we prepared a diluted gravimetric U solution with a ^{238}U content of 5.7809 ± 0.0005 μg/g. This diluted solution was used to calibrate the ^{233}U–^{236}U-double spike.

Aliquots of the U standard solution were spiked with sufficient amounts of the ^{233}U–^{236}U-double spike, so that the ^{236}U concentration was in the same order of magnitude as the ^{235}U concentration (i.e., ^{235}U/^{236}U ~1) and measured by TIMS. Using the known ^{235}U concentration of the gravimetric solution, the ^{236}U concentration of the ^{233}U–^{236}U-double spike was calculated. The ^{233}U concentration of the spike was then calculated from the precisely determined isotopic ratio of ^{233}U/^{236}U. The resulting concentrations are 0.3988 ± 0.0002 ng/g for ^{233}U and 47.79 ± 0.03 ng/g for ^{236}U. The ^{229}Th concentration of the ^{229}Th-spike was calibrated against a HU secular equilibrium standard solution, kindly provided by N. Frank ((LSCE)/CNRS-CEA, Gif-sur-Yvette). Aliquots of the HU standard solution were spiked with sufficient amounts of the ^{233}U–^{236}U-double spike, so that the ^{236}U concentration was in the same order of magnitude as the ^{235}U concentration (i.e., ^{235}U/^{236}U~1). Similarly, ^{229}Th spike was added, so that the ^{229}Th/^{230}Th isotopic ratio was ~1. U and Th isotope ratios were measured by TIMS. Assuming that the HU standard is in secular equilibrium and using the U spike concentrations calculated as described above, the ^{229}Th spike concentration was calculated. The resulting value is 0.1759 ± 0.0002 ng/g.

References

[1] B. Bourdon, G.M. Henderson, C.C. Lundstrom, S.P. Turner (Eds.), Uranium-Series Geochemistry, Reviews in Mineralogy and Geochemistry, vol. 52, The Mineralogical Society of America, Washington, 2003.

[2] S.J. Goldstein, C.H. Stirling, Rev. Mineral. Geochem. 52 (2003) 23.

[3] A.J. Pietruszka, R.W. Carlson, E.H. Hauri, Chem. Geol. 188 (2002) 171.

[4] S. Richter, A. Alonso, J. Truyens, H. Kühn, A. Verbruggen, R. Wellum, Office for official publications of the European Communities EUR 22529, Luxemburg, 2006, http://www.irmm.jrc.be/html/interlaboratory_comparisons/reimep/reimep-18/EUR22529EN.pdf.

[5] S. Richter, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, Int. J. Mass Spectrom. 206 (2001) 105.

[6] D.L. Hoffmann, D.A. Richards, T.R. Elliott, P.L. Smart, C.D. Coath, C.J. Hawkesworth, Int. J. Mass Spectrom 244 (2-3) (2005) 97.

[7] M.B. Andersen, C.H. Stirling, E.-K. Potter, A.N. Halliday, Int. J. Mass Spectrom. 237 (2004) 107.

[8] E.-K. Potter, C.H. Stirling, M.B. Andersen, A.N. Halliday, Int. J. Mass Spectrom. 247 (2005) 10.

[9] Y.J. Wang, H. Cheng, R.L. Edwards, Z.S. An, J.Y. Wu, C.-C. Shen, J.A. Dorale, Science 294 (2001) 2345.

[10] C. Spötl, A. Mangini, Earth Planet. Sci. Lett. 203 (2002) 507.

[11] D. Genty, D. Blamart, R. Ouahdi, M. Gilmour, A. Baker, J. Jouzel, S. Van-Exter, Nature 421 (2003) 833.

[12] S. Holzkämper, C. Spötl, A. Mangini, Earth Planet. Sci. Lett. 236 (2005) 751.

[13] J. Fietzke, V. Liebetrau, A. Eisenhauer, C. Dullo, J. Anal. At. Spectrom. 20 (2005) 395.

[14] L.F. Robinson, G.M. Henderson, N.C. Slowey, Earth Planet. Sci. Lett. 196 (2002) 175.

[15] M.E. Wieser, J.B. Schwieters, Int. J. Mass Spectrom. 242 (2005) 97.

[16] X. Luo, M. Rehkämper, D.C. Lee, A.N. Halliday, Int. J. Mass Spectrom. 171 (1997) 105.

[17] C.C. Shen, R.L. Edwards, H. Cheng, J.A. Dorale, R.B. Thomas, S.B. Moran, S.E. Weinstein, H.N. Edmonds, Chem. Geol. 185 (2002) 165.

[18] W.A. Russell, D.A. Papanastassiou, T.A. Tombrello, Geochim. Cosmochim. Acta 42 (1978) 1075.

[19] C.N. Maréchal, P. Télouk, F. Albarède, Chem. Geol. 156 (1999) 215.

[20] R.H. Steiger, E. Jäger, Earth Planet. Sci. Lett. 36 (1977) 359.

[21] G.A. Cowan, H.H. Adler, Geochim. Cosmochim. Acta 40 (1976) 1487.

[22] H. Cheng, R.L. Edwards, J. Hoff, C.D. Gallup, D.A. Richards, Y. Asmerom, Chem. Geol. 169 (2000) 17.

[23] A.H. Jaffey, K.F. Flynn, L.E. Glendenin, W.C. Bentley, A.M. Essling, Phys. Rev. C 4 (1971) 1889.

[24] N.E. Holden, Pure Appl. Chem. 62 (5) (1990) 941.

[25] F. McDermott, T.R. Elliott, P. van Calsteren, C.J. Hawkesworth, Chem. Geol. 103 (1993) 283.

[26] R. Williams, K. Collerson, J. Gill, C. Deniel, Earth Planet. Sci. Lett. 111 (1992) 257.

[27] J.M. Metz, G.A. Mahood, Contrib. Mineral. Petrol. 106 (1991) 379.

[28] B. Bourdon, J.-L. Joron, C.J. Allègre, Chem. Geol. 157 (1999) 147.

[29] M.T. McCulloch, T. Esat, Chem. Geol. 169 (2000) 107.

[30] M. Ivanovich, R.S. Harmon (Eds.), Uranium-Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, Oxford University Press, Oxford, 1992.

[31] S. Nakai, S. Fuduka, S. Nakada, Analyst 126 (2001) 1707.

[32] S. Richter, S.A. Goldberg, Int. J. Mass Spectrom. 229 (2003) 181.

[33] K. Raptis, K. Mayer, F. Hendrickx, P. De Bièvre, Fresenius J. Anal. Chem. 361 (1998) 400.

[34] K.H. Rubin, Chem. Geol. 175 (2001) 723.

[35] S. Turner, P. van Calsteren, N. Vigier, L. Thomas, J. Anal. At. Spectrom. 16 (2001) 612.

[36] J. Prytulak, T. Elliott, D.L. Hoffmann, C.D. Coath, Geostand. Geoanal. Res., submitted for publication.