Measurement of $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ in volcanic rocks using the Neptune MC-ICP-MS

Lary Ball,*[a] Kennneth W. W. Sims[a] and Johannes Schwieters[b]

Received 2nd March 2007, Accepted 12th September 2007
First published as an Advance Article on the web 11th October 2007
DOI: 10.1039/b703193a

We present a new multicollector inductively coupled plasma mass spectrometric (MC-ICP-MS) method for measuring isotopic ratios of $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ in volcanic rocks using the Thermo Fisher Neptune. Uranium isotope measurements using SRM U010 as bracketing standard produce agreement within several permil for NBL 112A, REMP-18, as well as for equilibrium rock standards. We also demonstrate that uranium standards are not appropriate for correcting thorium isotopic measurements due to differences between U and Th in both mass bias and mass-dependent ion transmission. Use of the thorium synthetic standard, UCSC ThA, as a bracketing standard produces data that agree well with 'accepted values' for other synthetic Th isotope standards and equilibrium rock standards.

Introduction

^{238}U–^{230}Th disequilibria provide an important geochemical tool for investigating recent volcanologic processes and for dating Quaternary basalts. ^{238}U decay produces ^{234}U and ^{230}Th by alpha decay. In order to assess the disequilibrium, uranium and thorium must be isolated and their isotopic ratios measured. The long half-life nuclide, ^{232}Th, is isolated from the uranium decay series. $^{230}Th/^{232}Th$ ratios in volcanic rocks range from 3 to 8 ppm and are a function of the Th/U ratio of their mantle source ($\sim$2–4) and the short half life of ^{230}Th relative to ^{238}U and ^{232}Th. $^{234}U/^{238}U$ isotope ratios are of the order of 50 ppm, which is again a function of the large difference in ^{238}U and ^{234}U half-lives. Measurement of $^{230}Th/^{232}Th$ in basaltic rocks is difficult because of the large difference in the abundance of the two isotopes. Early alpha counting methods were unsuitable due to the low specific activities of the nuclides, particularly ^{232}Th. High abundance sensitivity thermal ionization mass spectrometry (HAS-TIMS) achieved much better precisions,[1] but was limited in sensitivity by the high first ionization potential of Th. Recent work has shown that alternate ionization sources such as secondary ionization mass spectrometry (SIMS)[2] and inductively coupled plasma mass spectrometry (ICP-MS)[3,4] produce much higher ionization of Th, resulting in higher precision measurements and the ability to work with smaller samples and shorter analysis times.

Reference materials are essential for determining accurate uranium and thorium isotope ratios. Several uranium isotopic standards exist, mainly due to interest by the nuclear industry. Consensus acceptance of uranium isotopic ratios is quite good, although recent advances in mass spectrometry have begun to redefine some previously accepted values.[5,6] As is detailed below, referencing thorium isotopic measurements to known uranium standards is problematic, making acceptance of a thorium reference material for isotopic composition very important. In this paper we detail analytical protocols for multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) measurement of uranium and thorium isotope ratios on the Thermo Fisher Neptune. We address the approach of using uranium standards to optimize Neptune tuning parameters as well as their use for detector drift and yield correction and discuss problems related to intercomparison of various thorium standards and rock standards.

Experimental

Instrumentation

Measurements were made using a Neptune (Thermo Fisher Scientific, Bremen, Germany) MC-ICP-MS. The Neptune has double focusing Nier geometry with mass dispersion of 81 cm, 8 moveable Faraday collectors and a central fixed Faraday with a multiplexing amplifier array featuring a 50 V dynamic range. An axial, discrete dynode ion counter (ETP/SGE, Sydney, Australia) can be used in place of the fixed, central Faraday by use of a deflection lens (FAR/SEM). Ions entering the SEM pass through a tunable repelling potential quadrupole (RPQ) or high abundance sensitivity lens designed to minimize tailing on the low mass side of a peak. SEM detector dead time correction is 20 ns. SEM dead time and linearity are software corrected. The Neptune's sample introduction system, including the cone interface region, operates at ground potential. The ions are accelerated in stages up to 10 kV potential at the detectors. The ICP system is a 27 MHz generator (Seren IPS, Inc., New Jersey, USA) coupled to a standard Fassel style torch with platinum capacitive discharge guard electrode. Samples and standards were, in most cases, introduced with a 60 µl per minute Teflon PFA microconcentric nebulizer (self aspirating mode)

---

[a] MS23, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. E-mail: lball@whoi.edu; Fax: +1-5082892175; Tel: +1-5082893356
[b] Thermo Fisher Scientific, Bremen, Germany. E-mail: johannes.schwieters@thermofisher.com

into a quartz tandem spray chamber (Stable Sample Introduction System, SSIS, Elemental Scientific, Omaha, NB, USA). Desolvating sample introduction systems were tested to increase the ion yield at the detector and will be discussed in this paper. The total ion transmission efficiency for thorium was between 0.1–0.5%, depending on the sample introduction system. Thorium oxide formation relative to thorium metal was 5–20%. Relative amplifier gains for Faraday detectors were determined weekly using an internal current source. Inlet system and ion lens tuning was optimized at the beginning of each day for sensitivity and peak shape. In addition, SEM peak flatness was optimized with the FAR/SEM lens to ensure that the ion beam was orthogonal to the SEM detector. The SEM plateau voltage was checked weekly or when suspected of drifting. Dark noise was also measured regularly and was generally less than 0.1 cps. The RPQ lens was set *via* the suppressor lens voltage. The suppressor voltage of the RPQ filter lens can be varied, allowing 0–100% ion transmission, or can be completely shut off by grounding. Abundance sensitivity improves with decreasing transmission and stronger filter action of the RPQ lens in a non-linear way, as will be discussed. Except for tests, samples were run at ~9960 V suppressor lens setting, achieving ~50 ppb abundance sensitivity at 2 mass units and ~85% ion transmission efficiency. Cup configurations (Table 1) providing optimal simultaneous collection of the isotopes of interest were established for both uranium and thorium. When testing for the possibility of using uranium to correct for thorium, the cups are configured so that no change of cup position is required. In these cases optimization for simultaneous collection is carried out using the dispersion Zoom quad lens. This greatly reduces the time for bracketing thorium with uranium.

Reagents, samples, and standards

Rock samples are crushed to <1 mm and then dissolved completely by a series of digestions using HF and HNO_3, followed by HNO_3 + H_3BO_3 and $HClO_4$ to decompose fluorides. During these steps it is essential to attain complete digestion and eliminate all fluorides as incomplete dissolution can perturb the sample's U/Th ratio and fluorides will reduce column yields.

Thorium and uranium are separated and purified in the Woods Hole Oceanographic Institution (WHOI) clean laboratories using two anion columns. The first column is a nitric anion column to separate Th and U from the silicate matrix, while the second column is a HCl anion column to separate Th from U.

Table 1 Neptune collector configurations for uranium and thorium measurements

Detector, *Faraday* or SEM	*L4*	*L3*	*L2*	*L1*	Center (C) SEM	*H1*	*H2*	*H3*	*H4*
Element									
Uranium 1					^{234}U	^{235}U	^{236}U		^{238}U
Uranium 2			^{234}U	^{235}U	^{236}U		^{238}U		
Thorium					^{230}Th		^{232}Th		

Standards and samples are diluted with high purity nitric acid deionized water (SeaStar Chemicals, Inc., Sidney, BC, and Milli-Q, Millipore Corp., Bedford, MA) to 0.2 N HNO_3.

The UCSC ThA standard was obtained from Jim Gill (UCSC), Th standard WUN (Woods Hole-UCLA-National High Magnetics Laboratory) is an in-house standard and the commercially avaliable Th standards IRMM35 and IRMM36 were obtained from the Institute for Reference Materials and Measurements (Geel, Belgium). We also report analyses of the USGS and U-series community rock standards (BCR2, W2, TML, BHVO-1 and ATHO). Three of the rocks standards (BCR2, W2, TML) are important for constraining accuracy as well as precision for both $^{238}U/^{232}Th$ and $^{230}Th/^{232}Th$ because ($^{230}Th/^{238}U$) should be in secular equilibrium due to sample age.

Data acquisition

$^{234}U/^{238}U$

Uranium data was acquired for $^{234}U/^{238}U$ ratios to provide information about the disequilibrium of ^{238}U daughter isotopes. $^{236}U/^{238}U$ ratios were measured only for the synthetic uranium standard U010 (New Brunswick Laboratory, New Brunswick, IL) and were used to calibrate the SEM yield or efficiency and correct for mass bias drift. Time dependent drift correction of both SEM yield and instrumental mass bias are required to produce accurate, reliable data. The suite of uranium standards offered by the New Brunswick Laboratory, such as U010, are well characterized and useful as calibration standards for uranium measurements.[5] We measure ^{238}U and ^{235}U on Faraday collectors and either ^{234}U for $^{234}U/^{230}Th$ disequilibrium determination or ^{236}U for SEM/mass bias correction on the SEM (Table 1). Because of the higher abundances of the minor uranium isotopes, the requirements for ion counting uranium isotopes are not as demanding with regard to abundance sensitivity as those for thorium isotopes. With the RPQ turned off, the tail of ^{238}U on ^{234}U is 50 ppb and the tail of ^{235}U on ^{234}U is 2–5 ppm (depending on instrument performance), making the contribution of ^{238}U and ^{235}U tailing on ^{234}U small relative to other uncertainties. Comparison of $^{234}U/^{238}U$ measurements, made with the RPQ set to 85% transmission, show precisions a factor of two larger than with the RPQ shorted to ground. The degradation of measurement precision with the RPQ on is about one permil, based on 10 measurements each of NBL112A with and without RPQ. Thus, the gains in reducing the small tail contributions of ^{238}U and ^{235}U on ^{234}U are negated by the degradation in precision when using the RPQ filter. Standard–sample–standard bracketing for uranium analysis allows correction for SEM calibration and drift. We find that optimum accuracy is obtained by using ^{234}U in U010 as a yield monitor of SEM efficiency when measuring ^{234}U in unknown samples. We have the option of monitoring instrumental fractionation, either with the same ratio and combining the yield and mass bias correction into one factor, or by tracking the mass bias drift with the $^{235}U/^{238}U$ ratio (approximately 0.01 in U010) on Faraday collectors. We have detected no difference in data quality between the two methods, principally because the SEM yield determination is error limiting.

^{230}Th/^{232}Th

For ^{230}Th/^{232}Th ratio measurements, the H2 Faraday was positioned 2 mass units from the axial channel. ^{230}Th was collected by the SEM discrete dynode ion counter after transition through the RPQ high abundance sensitivity lens. Counting was done in 40 cycles of 16.78 s each. Thus, a sample with 5 kcps of ^{230}Th would be limited in precision to 1‰ (2 sigma) by counting statistics. Automatic baseline subtraction was turned off. Data outliers were rejected using an online two-sigma outlier test. After acquiring the ratio data, a mass scan was done from 229.5 to 231.5 amu in 100 1-s acquisitions in order to extrapolate the peak tail contribution of ^{232}Th on the minor ^{230}Th isotope. For more recent data, a narrower mass range of 229.5–230.7 amu was used to improve the exponential fit. This SEM scan includes the tail of the ^{232}Th into the ^{230}Th peak, the entire ^{230}Th peak, and the residual tail of the ^{232}Th tail on the low mass side of ^{230}Th peak. The 100 data points each for mass, ^{230}Th cps and ^{232}Th volts, are exported to an ASCII file which is then imported into an Excel (Microsoft Corp., Redmond, WA) spreadsheet. The data are divided into 3 plots: SEM points describing the ^{230}Th peak, SEM data outside the ^{230}Th peak delineating the ^{232}Th tail and Faraday voltages outlining the ^{232}Th peak (Fig. 1). The range of points assigned to the 2 SEM plots are chosen by eye to account for slight mass drift so that tail counts are not in the ^{230}Th peak plot and *vice versa*. An exponential curve was fit to the ^{232}Th tail plot using the Excel trendline function, returning an equation for the function. Using the centroid mass of the ^{230}Th peak (nominally 230.033 amu), an explicit solution for the count rate of the tailing at the center mass is calculated. For each thorium standard and sample the raw ratio is corrected for this tailing count rate. The tail corrected ratio for standards is itself ratioed to the theoretical ^{230}Th/^{232}Th ratio. The resultant factor corrects for instrumental mass bias and SEM efficiency. The average of two bracketing correction factors is multiplied by the measured sample ratio to obtain the corrected sample ^{230}Th/^{232}Th value. Because it is so well characterized, we use the UCSC-ThA for standard–sample–standard bracketing. Using UCSC ThA as a normalizing standard, the Th isotopic data for other synthetic and rock standards are in good agreement with their consensus values (see discussion below). It is important to note that improvement of abundance sensitivity using the RPQ lens is necessary not only to reduce the tail correction due to ^{232}Th ions counted as ^{230}Th but also to ensure that the ^{230}Th peak top is not skewed due to the tailing. Flat top peaks are essential for high precision isotope ratio measurements as they reduce changes in count rate caused by slight drift in the mass region that is sampled.

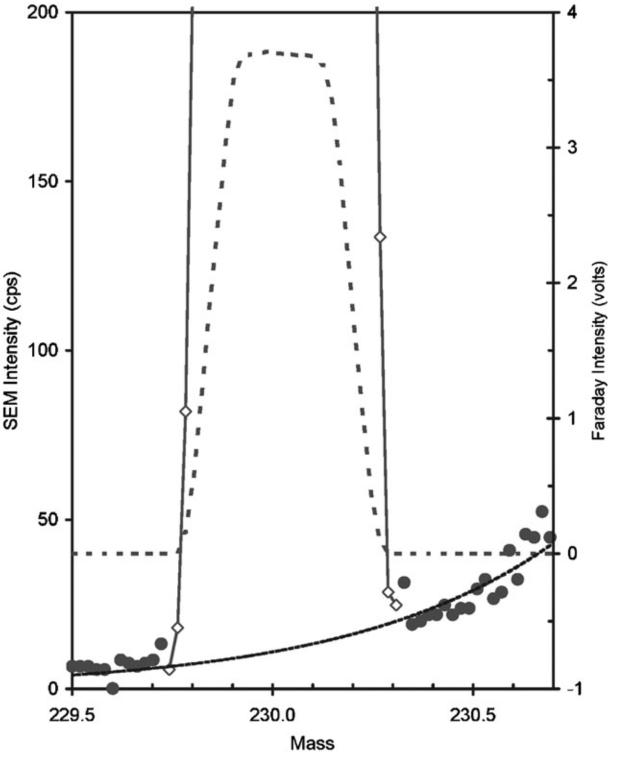

Fig. 1 ^{232}Th tail counts (SEM), closed circles; ^{230}Th peak (SEM), open diamonds; ^{232}Th tail exponential fit, broken line; ^{232}Th peak (Faraday), dotted line.

Use of the U010 standard to bracket the thorium measurements is similar to the thorium bracketing method in that the uranium cup configuration has identical cup positions (^{238}U on H2, ^{236}U on SEM and, additionally, ^{235}U on L1) but uses a unique dispersion and focus lens (collectively called the Zoom lens) setting to exactly center the uranium peaks. Because of the smaller effect of tailing on the larger ^{236}U/^{238}U ratio, no tail correction need be made. At 50 ppb abundance sensitivity, ^{238}U tailing increases the ^{236}U count rate by 0.08%, which is negligible relative to other uncertainities for these measurements. As with Th standard bracketing, we apply a single correction factor for both instrumental mass bias and SEM yield and use an exponential mass bias correction to account for the relative mass difference between ^{236}U/^{238}U and ^{230}Th/^{232}Th.

Results

Uranium data

We employ NBL-U010 as a bracketing standard for the measurement of ^{234}U/^{238}U ratios in samples and NBL-112A (NBS960) as our quality control (QC) reference standard. ^{234}U/^{238}U is used as an SEM yield and mass bias determinant. In early work the ^{234}U/^{238}U mass bias was corrected using an exponential law and the ^{235}U/^{238}U ratio measured on Faraday cups H1 and H3. For NBL-U010, an updated value of ^{235}U/^{238}U (0.010 138 2, Richter and Goldberg[5] *versus* 0.010 140 0, NBS) was used. For all other uranium samples and standards the ^{235}U/^{238}U equilibrium value (0.007 252 7, Cheng and Edwards[6]) is used in the exponential correction. The U010 ^{234}U/^{238}U value of of 5.4483e−5 (Richter and Goldberg[5]) was used for SEM yield correction instead of the value of 5.466e−5 (NIST certification). As was noted above, in later work we forego Faraday measurement of ^{235}U/^{238}U for mass bias correction and use ^{234}U/^{238}U correction for mass

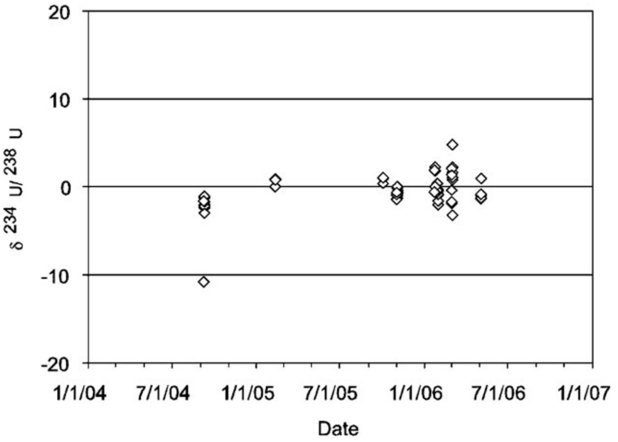

Fig. 2 Historic measured $^{234}U/^{238}U$ for NBL112A ($^{234}U/^{238}U$ accepted = 5.44484e−5, ref. 5) bracketed with U010 ($^{234}U/^{238}U$ = 5.286e−5, ref. 6).

bias and SEM yield. Fig. 2 shows permil differences in values measured for NBL112A over approximately 1 year of analyses. Earlier data from 2004 is a bit noisier and has an obvious outlier of 11 permil on 9/8/04. Subsequent repairs of the accelerating voltage board of the WHOI Neptune resulting in improved mass stability may be responsible for the more recent, higher quality uranium data of about 1–2‰ accuracy (2 SD) with respect to the Richter and Goldberg[5] NBL112A $^{234}U/^{238}U$ value. Data shown for January and March of 2006 were collected using an APEX desolvation system (Elemental Scientific Inc., Omaha, NB, USA) and analyte concentrations approximately one tenth the total uranium concentration (∼10–50 ppb) compared with "wet" aerosol data. The APEX was operated without the optional final membrane desolvator. The data for these runs average −0.14‰ with respect to NBL112A and the precision for 23 measurements is ±4‰, 2 SD. In addition to measurements of NBL 112A for quality assurance, recent data from the uranium isotope ratio inter-laboratory calibration execise, REIMEP-18 (http://www.irmm.jrc.be/html/interlaboratory_comparisons/reimep/reimep-18/index.htm), have become available from the Institute of Reference Materials and Measurements (IRMM, Geel, Belgium). Table 2 compares our measured $^{234}U/^{238}U$ ratios with the IRMM certified values. These samples span a range of $^{234}U/^{238}U$ from 50 to 200 ppm. Differences between measured and certified values are less than 2 permil, and values overlap at the 2 SD confidence interval. As was mentioned previously, the uranium measurements are made with the retardation potential quad lens (RPQ) shorted to ground (no filtering) as tailing effects from ^{235}U and ^{238}U on ^{234}U are insignificant.

SEM operational parameters are crucial to accurate and precise uranium and thorium isotope ratio measurements. The dead time for the WHOI Neptune ETP SEM is 20 ns and is automatically software corrected. The linearity and stability of the ion counting detector needs to be monitored precisely in order to obtain accurate and precise data.[7,8] The Neptune software provides a non-linear algorithm for dead time and linearity correction of the ETP ion counter signal. We choose to implement this default correction (20 ns dead time, 1e5 cps base frequency, and 0.004 dead time factor) and characterize the resultant linearity of the ETP SEM as opposed to disabling all linearity corrections and applying an offline linearity correction. Although not explicitly stated, we believe Hoffman *et al.*[8] utilized the RPQ for their study of linearity in measurements of uranium and thorium ratios using the Neptune. Their quoted abundance sensitivity of 40–50 ppb at 2 amu, with a SEM yield of 80–85%, is typical of Neptune performance with the RPQ on and suppressor voltage optimally set for thorium measurements. We achieve similar non-linearity to Hoffman *et al.*[8] with the RPQ on and set to similar operational parameters, but we achieve much better linearity with it shorted (turned off), as used for the uranium measurements (Fig. 3(a)), and with the default instrument linearity correction active. With a low suppressor voltage the RPQ is essentially off and shows a useful linear range from 3e3 to 1e5 cps. We consider 1e5 cps as our maximum working range of ^{234}U intensities. Slopes of semi-log plots shown in Fig. 3(a) change very little between low count rate data and high count rate data. The 2 sigma standard deviation of the measured $^{234}U/^{238}U$ ratio over the entire intensity range is 8 permil. A more typical working range for uranium isotopes of 2e4–1e5 cps has a 2 SD error of 6 permil. Additionally, if count rates of uranium bracketing standards and samples are matched within a factor of 3, even better linearity is obtained.

The long-term precision and accuracy for uranium measurements for rock samples known to be in secular equilibrium (ATHO and TML) is shown in Table 3. The results show agreement with equilibrium values calculated using the half-life value of ^{234}U from Cheng and Edwards[6] to within 5‰. These samples provide the best measure of our ability to measure uranium isotope ratios as they are influenced by problems of chemical as well as instrumental performance.

Thorium data

Assessing the quality of thorium data is difficult due to the lack of well characterized reference materials certified for $^{230}Th/^{232}Th$. Thorium reference materials considered in this study are noted in Table 4. Our early attempts to correct $^{230}Th/^{232}Th$ data for mass bias and SEM yield using $^{236}U/^{238}U$ (NBL U010) led to data discrepant with existing data from

Table 2 Measured and certified values for uranium isotope ratios in IRMM REIMEP-18 samples

REIMEP-18	Standard error				
Sample	$^{234/238}U$ (measured)	(2 × std error)	$^{234/238}U$ (IRMM)	Error (K = 2)	Δ(‰)
18A	5.66E−05	1.30E−07	5.66E−05	4.10E−08	0.61
18B	3.33E−04	7.50E−07	3.33E−04	2.20E−07	0
18C	7.97E−05	1.80E−07	7.95E−05	6.80E−08	1.87
18D	2.09E−04	4.60E−07	2.09E−04	1.40E−07	−1.09

other instruments and methods (TIMS and SIMS). Rubin's[9] extensive compilation of thorium ratio data for synthetic and igneous rock standards recommends the use of the synthetic standard UCSC ThA, because its ratio is comparable to igneous rocks (5.86 ± 0.02e-6). The Rubin value derived from compiled literature values plus 146 new values is about 1‰ higher than the gravimetric value. Layne and Sims[2] using the Woods Hole Cameca 1270 ion probe reported a value of 5.85 ± 0.03e-6 (2 SD) for UCSC ThA. Data from the Thermo applications laboratory for two different TIMS instruments also yielded a value of 5.85 ± 0.03e-6 (1 SD) for UCSC ThA ^{230}Th/^{232}Th (Dietmar Tutas, personal communication). Our uranium corrected UCSC ThA ^{230}Th/^{232}Th data ranged from 5.68e-6 to 5.78e-6. We investigated possible causes for the discrepancy between our MC-ICP-MS uranium corrected values and literature values for UCSC ThA, as well as other thorium reference materials such as WUN which also tended to lower ^{230}Th/^{232}Th values when normalized to uranium.

Uranium standard bracketing of thorium samples, as described, uses the ^{236}U/^{238}U ratio of SRM U010. The ^{236}U is measured on the SEM with the RPQ set for optimum ^{230}Th transmission and ^{232}Th low mass tail rejection. Typically the count rate of ^{236}U in the bracketing standard runs is higher than the ^{230}Th count rate by about a factor of ten. Linearity differences between decadal differences in count rate can be of the order of two per cent. if the difference in count rate spans the region of drastic slope change (Fig. 3(b)). A high count rate ^{236}U/^{238}U standard would drive calculated ^{230}Th/^{232}Th values lower. Matching ^{236}U count rates to ^{230}Th count rates is possible but only for high concentration thorium samples and requires pre-screening of the samples. Tests of uranium bracketing for correction of ^{230}Th/^{232}Th measurements with variable count rates of ^{236}U relative to ^{230}Th (with ^{236}U standard count rates ranging from 2–10 times higher than the ^{230}Th sample count rates) did not reveal any systemic difference in the determined ^{230}Th/^{232}Th outside the external reproducibility of the ratio measurement (0.4% 2 SD). However, regardless of the intensity of the ^{236}U in the uranium standard, the ^{230}Th/^{232}Th ratios derived from the uranium bracketing were uniformly lower than values for the UCSC ThA bracketed samples.

Recent work at the ThermoFisher Scientific Neptune Applications Laboratory in Bremen, Germany (Johannes Schwieters, personal communication) showed that the ion transmission of the RPQ filter depends on the mass of the ion such that at an RPQ suppressor lens voltage yielding 80% transmission for ^{238}U, the ^{208}Pb transmission could be as much as 6% lower (Fig. 4(a)). Our own experiments of ^{236}U *versus* ^{230}Th transmission show that the ion transmission of Th

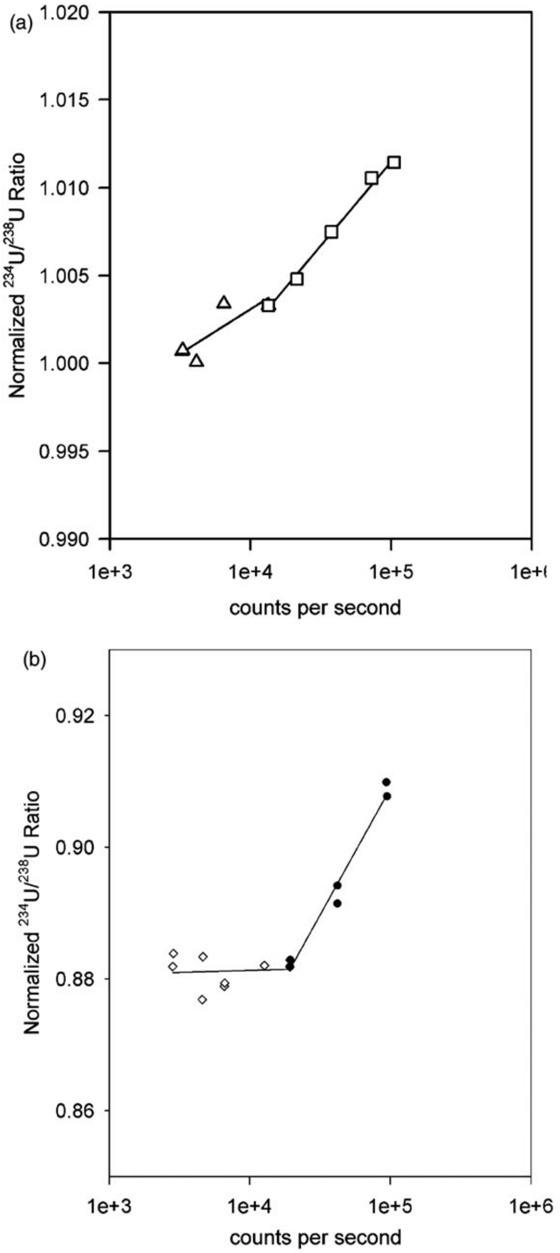

Fig. 3 (a) SEM linearity at low RPQ suppressor voltage (100% transmission); open triangles, count rates from 4E3 to 2E4 cps, slope = 0.002; open squares, count rates from 2E4 to 1E5 cps, slope = 0.004. (b) SEM linearity at moderate RPQ suppressor voltage (85% transmission); open diamonds, count rates from 3e3 to 4e4 cps, slope = 0.0002; closed circles, count rates from 4e4 to 1e5 cps, slope = 0.017.

Table 3 Measured uranium isotope ratios and deviations from calculated equilibrium values in rock standards

Date	Reference material	^{234}U/^{238}U measured	Deviation from equilibrium (‰)
9/9/2004	AThO	5.51E-05	4.29
9/9/2004	TML	5.50E-05	1.51
9/10/2005	TML	5.51E-05	4.15
9/10/2005	TML	5.52E-05	4.88
2/11/2005	TML	5.50E-05	1.06
2/11/2005	AThO	5.50E-05	2.16

Table 4 Thorium reference material measurements with thorium and uranium bracketing

Reference material	$^{230}Th/^{232}Th^{a}$	N	$^{230}Th/^{232}Th^{b}$	N	$^{230}Th/^{232}Th^{c}$	N	$^{230}Th/^{232}Th^{d}$
AthO	(5.495 ± 0.029)E-06	14	5.35E-06	1	(5.480 ± 0.021)E-06	29	
IRMM35	(1.152 ± 0.017)E-05	20					(1.148 ± 0.0078)E-05
IRMM36	(3.086 ± 0.036)E-06	20					(3.113 ± 0.078)E-06
TML	(5.826 ± 0.047)E-06	13	5.68E-06	1	(5.787 ± 0.048)E-06	42	
WUN	(4.358 ± 0.040)E-06	26	(4.195 ± 0.092)E-06	21			
Th U	(6.167 ± 0.023)E-6	3	(6.031 ± 0.112)E-06	5			
W2	(3.827 ± 0.032)E-6	3					
BCR2	(5.495 ± 0.029)E-06	7					
UCSC ThA	(5.837 ± 0.044)E-06[e]	5	(5.740 ± 0.129)E-06	31	(5.856 ± 0.070)E-06	255	

[a] = UCSC ThA bracketing standard.[9] [b] = U010 ($^{236}U/^{238}U$) bracketing standard. [c] = Ref. 9 compiled value. [d] = IRMM certificate. [e] = Thermo Finnigan TIMS value.

and U differ by up to 3–4% (Fig. 4(b)). This mass dependent transmission through the RPQ filter lens is a function of the mass dependent energy of the ions generated at the ICP interface. Basically, all ions enter the mass spectrometer through the cones with the same velocity and hence the lighter ions have a smaller kinetic ion energy compared with the heavier ions. As a result, the heavier ions have a higher transmission through the energy filter lens (RPQ). When the filter action of the RPQ lens is enhanced by increasing the suppressor lens voltage, the mass dependent transmission is even more enhanced. Most methods using $^{236}U/^{238}U$ to correct for $^{230}Th/^{232}Th$ mass bias and ion counter yield assume equal transmission of thorium and uranium ions through the RPQ. Since this correction scheme is linear and the heavier ions are transmitted through the RPQ preferentially, the U-corrected $^{230}Th/^{232}Th$ ratio of the unknown sample will be systematically low by an amount equal to the difference in transmission between ^{230}Th and ^{236}U. Our measured transmission difference of 3–4% between ^{230}Th and ^{236}U accounts for the difference we obtain for the U-corrected $^{230}Th/^{232}Th$ values (Table 4) and the nominal consensus values for these standards determined by SIMS and TIMS compilations,[2,9] suggesting that this effect is probably the largest source of error in the U-corrected $^{230}Th/^{232}Th$ ratios. Finally, we note that the temporal drift in RPQ transmission can be up to a per cent. over the course of a day. This significant shift highlights the need to bracket every unknown sample with a known standard and explains why the external reproduciblity of ratios measured with the RPQ on show a larger variability: for example, $^{230}Th/^{232}Th$ have greater external reproducibility than ratios measured with the RPQ disabled as for $^{234}U/^{238}U$.

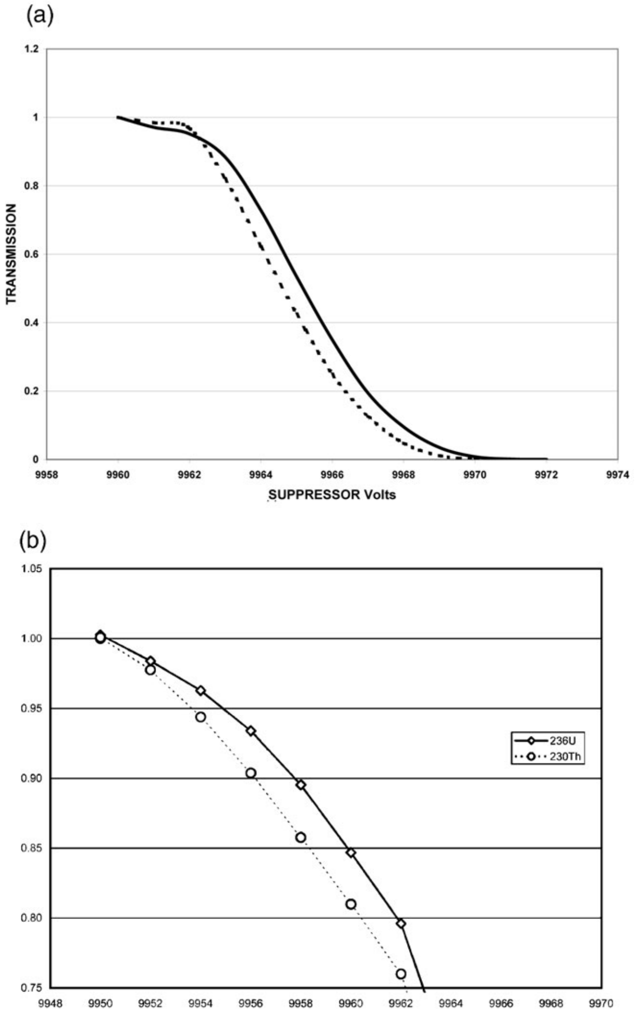

Fig. 4 (a) Ion transmission of Pb (dotted line) and U (continuous line). Note U/Pb and U/Th plots do not have the same suppressor voltage scales. (b) Ion transmission of ^{236}U (diamonds) *versus* ^{230}Th (circles). Suppressor voltage range expanded to show working range for optimum ^{230}Th measurement. Note that the ^{230}Th transmission is not corrected for tailing.

Instrumental mass bias significantly alters measured isotope ratios from their true values. For heavy isotopes such as uranium and thorium, the Neptune mass bias is approximately 0.5% per amu and must be corrected to produce accurate data. Owing to the lack of well-calibrated Th isotope reference materials, it is common to assume equivalent mass bias between U and Th.[4,10,11] In order to test this assumption we prepared a mixture of uranium (NBL 112A, 0.3 ppm total uranium) and a solution containing 2 sources of Th, a solution standard with $^{232/230}Th > 2e5$ (with undetectable ^{229}Th) and a ^{229}Th spike yielding ~ 1 ppm total thorium. The ^{229}Th was added to give a $^{232}Th/^{229}Th$ of ~ 90, similar to the $^{238/235}U$ ratio of the NBL 112A of ~ 140. The minor isotopes of each element gave Faraday voltages of 70–80 mV. The ΔM for each pair is the same and the relative ΔM ($\Delta M/M$) only differs by 0.03%. Assuming the mass bias obeys an exponential law, a log plot of the measured ratios divided by the log of the ratio of the isotopic masses, $\ln(R_m)/\ln(R_{Mass})$, should produce a line

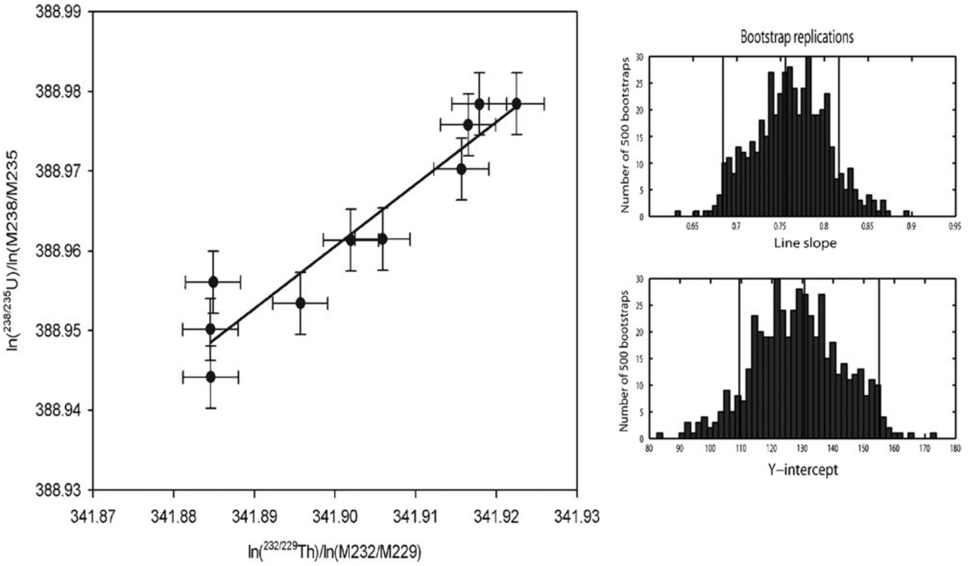

Fig. 5 Instrumental mass bias of uranium *versus* thorium and bootstrap analysis of slope and intercept. Slope (f_U/f_{Th}) = 0.76. Individual points in the regression plot represent block averages of 100 ratios. Bootstrap replicates represent the entire sample population: vertical lines show the 95% confidence for the slope and intercept (ref. 12).

with a slope of one if the uranium and thorium mass biases are equally covariant. For this experiment, the Neptune was warmed up with plasma on for one hour. Uranium and thorium ratios were measured simultaneously and the mass bias was allowed to vary over the 5 hour run without perturbing any operational parameters. Pooling the 1000 data points into 10 blocks gives a plot with a slope of ~0.76 (Fig. 5). Monte Carlo analyses and bootstrap regression of this data[12] verifies that the slope is significantly less than 1. Clearly the mass biases of these 2 elements are quite different. Earlier experiments in which the instrumental mass bias was changed by de-tuning gas flows showed extreme and non-reproducible mass bias effects.[13,14] We feel the experiment presented in Fig. 5 is most representative of measurements which utilize uranium as a proxy to mass bias correct for thorium. However, the lesson taken from earlier experiments forcing a mass bias deviation is that a plasma mass spectrometer not optimally tuned, for example with an unstable gas flow, will produce disparate results that may not follow a predictable mass bias law. Typically, analytical schemes using U as a proxy for Th assume that $f_U/f_{Th} = 1$ (see, for example, White *et al.*[15]), whereas our results show that $f_U/f_{Th} \neq 1$. The resulting $^{230}Th/^{232}Th$ based on the effect measured here ($f_U/f_{Th} = 0.76$) will be too low by as much as 1% for a $^{230}Th/^{232}Th$ ratio of 5.9 ppm and mass bias fractionations typical of the Neptune (0.5% per amu). These results indicate that U is not a good mass bias proxy for Th. Making such an assumption is erroneous and can lead to systematic offsets in the corrected $^{230}Th/^{232}Th$. Temporal difference of f_U/f_{Th} over longer time scales will only exacerbate this effect.

It is clear from the above discussion that U does not work well as a proxy for Th when making Th isotopic measurements, and that linearity, ion transmission and mass bias are best characterized using Th. Our present method for analysing thorium isotopic ratios brackets each unknown with a thorium reference material. We use the thorium reference material UCSC ThA as its ratio is an optimal match for work with basaltic rocks and is well characterized in the literature. We have endeavored to include a variety of thorium reference materials in our daily analyses to build a data set of these other reference materials. Particularly useful are the IRMM35 and IRMM36 as these bracket the range of igneous rock ratios $^{230}Th/^{232}Th$ and are commercially available.

Values of selected thorium reference materials measured relative to UCSC 'ThA' compare well with published data (Table 4). Since we use UCSC 'ThA' as a bracketing standard, we do not report a measured value for it except relative to uranium normalization. Our chosen accepted value of $^{230}Th/^{232}Th = (5.856 \pm 0.070)e{-}06$ derives from Rubin's 2001[9] average of 255 measurements. Five TIMS analyses in May 2004 at the Thermo Finnigan demo lab in Bremen, Germany, yielded a slightly more precise value of $(5.837 \pm 0.044)e{-}06$ that is within the range of Rubin's value. Rubin's value is also within the error of the ion probe measurements of Layne and Sims.[2] Measured ATHO and TML values fall well within the analytical uncertainty. The measured IRMM values can be compared with the recommended certified values and fall within the published uncertainty. In the case of our measured value for IRMM36, the external reproducibility in our 16 measured values is less than half the published uncertainty, which is based on gravimetry.

The uranium corrected $^{230}Th/^{232}Th$ values reported in Table 4 are 2–3% lower than UCSC ThA corrected values. Given that ^{236}U has higher transmission through the RPQ than ^{232}Th by up to 4% (Fig. 4(b)), higher transmission of the ^{236}U with respect to ^{230}Th would result in an SEM efficiency closer to one than would a ^{230}Th SEM correction. Thus, the ^{236}U correction would produce a lower corrected $^{230}Th/^{232}Th$ ratio.

Conclusions

(1) MC-ICP-MS provides an accurate, precise and sensitive technique for measuring U isotopes with high sample throughput. Uranium ratio measurements referenced to certified/newly published[5] values for U010 are precise and accurate to the level of several permil, based on comparison with well accepted gravimetric SRMs as well as equilibrium rock standards.

(2) MC-ICP-MS also provides a precise and sensitive technique for measuring Th isotopes with high sample throughput. However, the accuracy of these measurements is limited by our ability to correct for: (i) the tailing of ^{232}Th onto ^{230}Th; (ii) instrumental mass bias; (iii) SEM/Faraday detector gain calibration; and (vi) temporal variations in the RPQ ion transmission and SEM efficiency.

(3) Use of uranium SRMs to correct for mass bias and SEM yield for ^{230}Th/^{232}Th is shown to be problematic. Differences in uranium *versus* thorium behavior with respect to RPQ transmission and mass bias, as well as changes in linearity when using uranium standards with count rates that exceed those of the thorium samples, is shown to produce anomalously low ^{230}Th/^{232}Th ratios. The dominant factor is differences resulting from the mass dependent transmission of ions through the RPQ. These differences are likely to be unique for each instrument and need to be evaluated systematically. In this regard it is important to note that this study describes our evaluation of one particular MC-ICP-MS, the WHOI Thermo Fisher Neptune: however, the systematic approach we use is applicable to all MC-ICP-MSs.

(4) Thorium measurements of a variety of solutions and equilibrium rock standards are referenced to thorium standard UCSC ThA and show good agreement with consensus values from other laboratories using a variety mass spectrometric techniques.

(5) We note that measurement of thorium isotopes requires a well-calibrated thorium standard. While the UCSC ThA standard fits this purpose it is no longer available for distribution. The commercially available standards from IRMM are an important step forward. However, their values are not similar to typical volcanic samples, nor are they well calibrated. Clearly, there exists an important need in the community for a well-calibrated, readily available, synthetic standard with a thorium isotope ratio more suitable to measurements of volcanic rocks.

Acknowledgements

Formal and informal reviews by Stephan Richter and 3 anonymous reviewers contributed to the accuracy and clarity of this contribution. This work was funded in part by NSF grants OCE-9730967 (KWWS) and NSF-EAR/IF-0318137 (KWWS, LAB).

References

1 S. J. Goldstein, M. T. Murrell and D. R. Janecky, *Earth Planet. Sci. Lett.*, 1989, **96**, 134–146.

2 G. D. Layne and K. W. Sims, *Int. J. Mass Spectrom.*, 2000, **203**, 187–198.

3 A. N. Halliday, D. Lee, J. N. Christensen, A. J. Walder, P. A. Freedman, C. E. Jones, C. M. Hall, W. Yi and D. Teagle, *Int. J. Mass Spectrom.*, 1995, **146/147**, 21–33.

4 S. Turner, P. van Calsteren, N. Vigier and L. Thomas, *J. Anal. At. Spectrom.*, 2001, **16**, 612–615.

5 S. Richter and S. A. Goldberg, *Int. J. Mass Spectrom.*, 2003, **229**, 181–197.

6 H. Cheng, R. L. Edwards, J. Hoff, C. D. Gallup, D. A. Richards and Y. Asmerom, *Chem. Geol.*, 2000, **169**, 17–33.

7 S. Richter, S. A. Goldberg, P. B. Mason, A. J. Traina and J. B. Schwieters, *Int. J. Mass Spectrom.*, 2001, **206**, 105–127.

8 D. L. Hoffman, D. A. Richards, T. R. Elliott, P. L. Smart, C. D. Coath and C. J. Hawkesworth, *Int. J. Mass Spectrom.*, 2005, **244**, 97–108.

9 K. H. Rubin, *Chem. Geol.*, 2001, **175**, 723–750.

10 J. Helstrom, *J. Anal. At. Spectrom.*, 2003, **18**, 1346–1351.

11 A. J. Pietruszka, R. W. Carlson and E. H. Hauri, *Chem. Geol.*, 2002, **188**, 171–191.

12 R. A. Sohn and W. Menke, *Geochem., Geophys. Geosyst.*, 2002, 3, 10.1029/2001GC000253.

13 L. Ball, K. Sims, J. B. Schwieters and D. Tuttas, *Geochim. Cosmochim. Acta*, 2004, **68**(11S), 542.

14 H. Andren, I. Rodushkin, A. Stenburg, D. Malinovsky and D. Baxter, *J. Anal. At. Spectrom.*, 2004, **19**, 1217–1224.

15 W. White, F. Albarede and P. Telouk, *Chem. Geol.*, 2000, **167**, 257–270.