An Inter-Laboratory Assessment of the Thorium Isotopic Composition of Synthetic and Rock Reference Materials

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We present a concerted international effort to cross-calibrate five synthetic Th isotope reference materials (UCSC Th "A", OU Th "U", WUN, IRMM-35 and IRMM-36), and six rock reference materials (UCSC TML, Icelandic ATHO, USGS BCR-2, USGS W-2, USGS BHVO-2, LV18) using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). We then compare our new values with a compilation of literature mass spectrometric data for these reference materials and derive recommended "consensus" $^{230}Th/^{232}Th$ values for each. We also present isotope dilution U and Th concentration data for four rock reference materials (UCSC TML, Icelandic ATHO, USGS BCR-2, USGS W-2).

Keywords: thorium, isotope ratios, rock reference materials, MC-ICP-MS, consensus values.

Received 30 Mar 07 — Accepted 19 Oct 07

Nous présentons une campagne internationale concertée d'inter-calibration de cinq matériaux de référence synthétiques (UCSC Th "A", OU Th "U", WUN, IRMM-35 et IRMM-36) et de six roches de référence (UCSC TML, ATHO Islandais, USGS BCR-2, USGS W-2, USGS BHVO-2, LV18). Cette inter-calibration concerne les isotopes de Th et repose sur la spectrométrie de masse à multi collection couplée à une source plasma (MC-ICP-MS). Nous comparons ensuite nos résultats avec une compilation des données de la littérature obtenues par spectrométrie de masse sur ces matériaux de référence et en déduisons les valeurs $^{230}Th/^{232}Th$ recommandées consensuelles pour chaque matériau. Nous présentons aussi des données de concentrations de U et Th obtenues par dilution isotopique sur quatre matériaux de référence (UCSC TML, Islandais ATHO, USGS BCR-2, USGS W-2).

Mots-clés : thorium, rapports isotopiques, roches de référence, MC-ICP-MS, valeurs de consensus.

^{238}U-^{230}Th disequilibria provide an important geochemical tool for many geological and environmental applications (e.g., Ivanovich and Harmon 1992, Bourdon *et al.* 2003). Determination of ($^{230}Th/^{238}U$) requires measurement of both $^{238}U/^{232}Th$ and $^{230}Th/^{232}Th$. Analytical challenges associated with measuring the extreme $^{230}Th/^{232}Th$ of volcanic rocks (typically ‹ 10^{-5}) are a significant limitation to these applications, and create the need for widely available certified reference materials (CRM) with well-characterised $^{230}Th/^{232}Th$ ratios.

Initially, Th isotopic abundances were measured by alpha spectrometry. However, these early data had

errors ($2s$) of several percent due to the low specific activities of the nuclides in many samples of interest. High abundance sensitivity thermal ionisation mass spectrometry (HAS-TIMS) achieved much better precisions for a given sample size but was limited in sensitivity by the high first ionisation potential of Th (Goldstein *et al.* 1989, McDermott and Hawkesworth 1991, Williams *et al.* 1992). Recent developments utilising alternate ionisation methods such as secondary ionisation mass spectrometry (SIMS) and multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) produce more efficient ionisation of Th, resulting in higher precision measurements and an ability to work with smaller samples and shorter analysis times (England *et al.* 1992, Layne and Sims 2000, Luo *et al.* 1997, Turner *et al.* 2001, Pietruszka 2002, Goldstein and Stirling 2003).

While MC-ICP-MS has significantly improved measurement precision for Th isotope ratios (often ‹ 1 per mil internal standard error), the accuracy of the measurement is limited by our ability to correct for the: (1) tailing of ^{232}Th onto ^{230}Th; (2) instrumental mass bias; (3) SEM/Faraday detector gain calibration and (4) SEM detector linearity. Abundance sensitivity using MC-ICP-MS can be significantly less than achieved on TIMS and SIMS, and for some instruments the tailing of ^{232}Th on ^{230}Th can require a substantial correction (0.1-1%). This effect is easy to quantify and correct, although the error in the correction can approach the overall measurement error. Accounting for mass bias is more difficult because there is only one "effectively" stable isotope, ^{232}Th, so an internal correction cannot be applied. It was initially thought with MC-ICP-MS that U isotopic standards, which have been extremely well calibrated for the nuclear industry, could be used either for bracketing or as an internally doped standard to correct for instrumental mass bias of Th isotopes. However, U does not work as an adequate proxy for Th because of small differences in the U and Th instrumental mass bias and their respective ion energies through high abundance sensitivity filters (Ball *et al.* 2008, Hoffmann *et al.* 2007). Therefore, the most reliable and accurate technique to correct for both instrumental mass fractionations between masses 230 and 232 and the relative difference in the efficiency of the Faraday and SEM detectors is to use a Th isotopic reference material interspersed between each unknown sample (i.e., calibrator-sample-calibrator bracketing).

There are several in-house synthetic Th isotope reference materials (UCSC Th "A", WUN, and OU Th "U"), and two commercially available ones (IRMM 35, IRMM 36) that have ^{230}Th/^{232}Th ratios comparable to volcanic rocks. UCSC Th "A" has been well characterised by several laboratories over many years of TIMS and SIMS analyses (see Rubin compilation 2001), but it is no longer available for distribution. The other in-house synthetic reference materials (WUN, OU Th "U") are less well characterised and have been analysed in only a few laboratories. The IRMM CRMs are relatively new and have large uncertainties, which are based upon a combination of uncertainty in both the gravimetry and TIMS measurement of the low ^{230}Th /^{232}Th stock solution. Because they are commercially available, these IRMM CRMs are critical for the emerging U-series community. However, to be of value for either quality assurance or as a calibrator, the Th isotopic composition of these IRMM CRMs needs to be much better characterised.

We have orchestrated a concerted effort, involving six different laboratories and three different manufacturers of MC-ICP-MS, to measure in multiplicity, the Th isotope ratios of several Th isotopic reference materials (UCSC Th "A", WUN, and OU Th "U"), with particular emphasis on the new IRMM CRMs. We then compare our new values to the compilation of the literature mass spectrometric data for these reference materials and derive recommended ^{230}Th/^{232}Th values.

We also report analyses for several rock reference materials (BCR, W2, TML, BHVO and ATHO) from each laboratory. Three of them (BCR, W2, TML) are important for constraining accuracy as well as precision for both ^{238}U/^{232}Th and ^{230}Th/^{232}Th because their respective (^{230}Th/^{238}U) ratios are close to secular equilibrium. However, until recently the only rock reference material that was measured regularly by U-series laboratories was the UCSC reference sample TML (Williams *et al.* 1992). It is still available upon request but has higher Th and U contents than most rocks and Th-rich accessory phases, so it is slightly heterogeneous in its Th/U and ^{230}Th/^{232}Th ratios. Moreover, its extreme U and Th contents (originally designed to facilitate high precision alpha counting measurements) and evolved matrix make it an inappropriate monitor of accuracy for studies of basaltic rocks. Consequently, this study provides a compilation of Th and U concentrations for volcanic rock reference materials to potentially replace TML.

Table 1.
Thorium isotope measurement protocols for the different "working groups" that participated in this study

	Instrument	2 AMU abundance sensitivity @ masses 230-232	Tail correction	Mass bias and detector gain calibration method	Re-normalisation method
WHOI	ThermoFisher NEPTUNE	~ 50 ppb at 85% transmission was ~ 50 ppb	Exponential. Tailing of ^{232}Th on ^{230}Th was corrected for using an exponential fit of each samples mass scan from 229.5 to mass 231.5. Samples and calibrators corrected independently before applying mass bias and detector gain calibration	Th calibrator-Th sample-Th calibrator bracketing using UCSC Th "A". Combined correction for mass fractionation and gain calibration assuming UCSC Th "A" ^{230}Th/^{232}Th = 5. 856 x 10^{-6} (Rubin 2001)	No re-normalisation
UCSC	ThermoFisher NEPTUNE	25-120 ppb at 70-90% transmission	Linear, uniform. Tail correction combined with mass bias and detector gain correction methods	Th calibrator-Th sample-Th calibrator bracketing using IRMM-035. Combined correction for mass fractionation, gain calibration, and tailing assuming ^{230}Th/^{232}Th of IRMM-035 = 11.407 x 10^{-6}	Re-normalised so UCSC Th "A" ^{230}Th/^{232}Th = 5. 856 x 10^{-6}
GEMOC	Nu Plasma HR MC-ICP-MS	~ 190 ppb at 95-98% transmission (2 AMU values extrapolated from 1 AMU measurements of ~ 450 ppb)	No tail correction	Daily mass bias and gain calibration determination using U standard solution CRM 960 (NBL 112A). Mass fractionation calculated by comparing measured ^{238}U/^{235}U ratio to nominal ratio (137.88) and assuming exponential mass fractionation. Ion counter gain calculated by comparing measured ^{234}U/^{238}U, corrected for mass fractionation, to the published value (5.286 x 10^{-5}). For IRMM-35, W-2 and TML, the ^{230}Th/^{232}Th were secondarily corrected to OU Th "U", assuming its ^{230}Th/^{232}Th ratio = 6.176 x 10^{-6}	Re-normalised so UCSC Th "A" ^{230}Th/^{232}Th = 5. 856 x 10^{-6}
UIUC	Nu Plasma HR MC-ICP-MS	~ 50 ppb at 95% transmission	Linear correction. ^{232}Th tailing on ^{230}Th determined by measuring masses 230.5 and 229.5 for each sample and using a linear interpolation (average) for mass 230	Th calibrator-Th sample-Th calibrator bracketing using UCSC Th "A" spiked with ^{229}Th. Combined correction for mass fractionation and gain calibration assuming UCSC Th "A" ^{230}Th/^{232}Th = 5.856 x 10^{-6} ± 1.2% (Rubin 2001) and ^{232}Th/^{229}Th = 460.20	No re-normalisation

Table 1 (continued).
Thorium isotope measurement protocols for the different "working groups" that participated in this study

	Instrument	2 AMU abundance sensitivity @ masses 230-232	Tail correction	Mass bias and detector gain calibration method	Re-normalisation method
Bristol	ThermoFisher NEPTUNE	~ 20 ppb at ~ 80% transmission	Exponential correction. Tail contributions were calculated for masses 230 and 229 by measuring masses 231, 230.5, 229.5 and 228.5 and interpolating in semi-log space. Samples and calibrators corrected independently before applying mass bias and detector gain calibration	Th calibrator-Th sample-Th calibrator bracketing using in-house Th reference sample TEDDi. Combined correction for mass fractionation and gain calibration assuming TEDDi $230Th/232Th = 4.444 \pm 0.007 \times 10^{-3}$ and $229Th/232Th = 2.927 \pm 0.005$ (Hoffmann et al. 2007)	No re-normalisation. [N.B. - Bristol values were not re-normalised as their measured $230Th/232Th$ for UCSC Th "A" using "TeDDi", was nearly identical to Rubin (2001); see table 2]
LLNL	GV Isoprobe	~ 90 ppb	Linear correction. $232Th$ tailing on $230Th$ determined by measuring masses 230.5 and 229.5 for each sample and using a linear interpolation (average) for mass 230	U calibrator-Th sample-U calibrator bracketing using CRM960 (NBL 112A). Mass fractionation calculated by comparing measured $238U/235U$ ratio to nominal ratio (137.88) and assuming exponential mass fractionation. Ion counter gain calculated by comparing measured $234U/238U$, corrected for mass fractionation, to the published value (5.286×10^{-5})	Re-normalised so UCSC Th "A" $230Th/232Th = 5.856 \times 10^{-6}$

Experimental

All of the new Th isotopic synthetic and rock reference material data presented in this study were measured by MC-ICP-MS. This effort involved six different laboratories (Woods Hole Oceanographic Institution-WHOI; University of California, Santa Cruz- UCSC; GEMOC Centre Macquarie University, GEMOC; University of Bristol; University of Illinois, Urbana Champaign- UIUC; Lawrence Livermore National Laboratory- LLNL) and three different manufacturers (ThermoFisher Neptune; Nu Instruments HR; Micromass Isoprobe). Each laboratory approached this measurement differently, though all from a TIMS background. The analytical protocols and instrument parameters, for each laboratory, are summarised in Table 1 and detailed in Appendix A. The thorium isotope measurement protocols of two groups (UCSC and GEMOC) changed significantly after this study; these changes in their analytical protocols are documented in Appendix A.

Uranium and Th concentration data were measured by isotope dilution ICP-MS. Some groups (Bristol, UIUC) analysed U and Th concentrations concurrent with their U and Th isotopic measurements; while other groups (WHOI, UCSC, GEMOC) spiked separate liquid aliquots of the same dissolution and measured the U and Th IDs separately, and sometimes on different instruments (e.g., WHOI and UCSC used the ThermoFisher Element2 instrument for these analyses). The analytical protocols for the U and Th concentration measurements for each laboratory are detailed in Appendix A.

Results and discussion

Thorium isotopes

Results for ^{230}Th/^{232}Th isotope measurements are presented in Table 2 and shown in Figures 1-8. For comparison we also present (Appendix Table 1 and Figures 1-8) the IRMM "gravimetric" values and a compilation of literature values representing several different laboratories and mass spectrometric techniques: HAS-TIMS (Reida and Ramos 1996, Turner et al. 1997, Thomas et al. 1999, Rubin 2001, Zou et al. 2003, Kokfelt et al. 2003); SIMS (Layne and Sims 2001, Zou et al. 2002) and MC-ICP-MS (Lou et al. 1997, Turner et

Table 2.
Thorium isotopic data for synthetic and rock reference materials from different laboratories

	N	Measured [2] ^{230}Th/^{232}Th (x 10^{-6})	2s RSD (%)	Relative standard error (%)	Corrected [3] ^{230}Th/^{232}Th (x 10^{-6})	2s RSD (%)
WHOI						
Synthetic reference materials						
IRMM-35	28	11.399	0.7%	0.1%	-	-
IRMM-36	28	3.062	0.9%	0.2%	-	-
UCSC Th "A"	-	*	-	-	-	-
OU Th "U"	4	6.173	0.4%	0.2%	-	-
WUN	29	4.350	1.5%	0.3%	-	-
Rock reference materials						
TML	15	5.820	0.8%	0.2%	-	-
ATHO	15	5.495	0.5%	0.1%	-	-
BCR-2	10	4.740	0.6%	0.2%	-	-
W-2	3	3.827	0.8%	0.5%	-	-
BHVO	1	5.843	-	-	-	-
UCSC						
Synthetic reference materials						
IRMM-35	-	11.407	-	-	11.463	-
IRMM-36	3	3.037	0.1%	0.1%	3.051	0.1%
UCSC Th "A"	11	5.828	1.6%	0.5%	-	-
OU Th "U"	11	6.172	1.0%	0.3%	6.203	1.0%
WUN	3	4.301	2.9%	1.7%	4.322	2.9%
Rock reference materials						
TML	11	5.781	1.3%	0.4%	5.809	1.3%
ATHO	3	5.483	0.6%	0.3%	5.510	0.6%
BCR2	-	-	-	-	-	-
W2	-	-	-	-	-	-

Table 2 (continued).
Thorium isotopic data for synthetic and rock reference materials from different laboratories

	N	Measured [2] ^{230}Th/^{232}Th (x 10^{-6})	2s RSD (%)	Relative standard error (%)	Corrected [3] ^{230}Th/^{232}Th (x 10^{-6})	2s RSD (%)
GEMOC						
Synthetic reference materials						
IRMM-35	13	11.261	0.3%	0.1%	11.336	0.3%
IRMM-36	-	-	-	-	-	-
UCSC Th "A"	57	5.817	0.5%	0.1%	-	-
OU Th "U"	159	6.173	1.2%	0.1%	6.214	1.2%
WUN	-	-	-	-	-	-
Rock reference materials						
TML3	9	5.824	0.1%	0.04%	5.863	0.1%
ATHO	-	-	-	-	-	-
BCR-2	-	-	-	-	-	-
W-2	5	3.870	0.2%	0.1%	3.896	0.2%
UIUC						
Synthetic reference materials						
IRMM-35	6	11.362	0.6%	0.2%	-	-
IRMM-36	4	3.044	0.3%	0.2%	-	-
UCSC Th "A"	-	-	-	-	-	-
OU Th "U"	18	6.153	0.7%	0.2%	-	-
WUN	7	4.322	0.4%	0.2%	-	-
Rock reference materials						
TML	37	5.798	0.6%	0.1%	-	-
ATHO	16	5.523	1.0%	0.2%	-	-
BCR-2	17	4.731	0.3%	0.1%	-	-
W-2	-	-	-	-	-	-
BRISTOL						
Synthetic reference materials						
IRMM-35	11	11.384	0.5%	0.1%	-	-
IRMM-36	7	3.047	1.2%	0.5%	-	-
UCSC Th "A"	8	5.856	0.5%	0.2%	-	-
OU Th "U"	8	6.193	0.6%	0.2%	-	-
WUN	12	4.328	0.6%	0.2%	-	-
Rock reference materials						
TML	14	5.794	0.4%	0.1%	-	-
ATHO	-	-	-	-	-	-
BCR-2	11	4.748	0.8%	0.3%	-	-
W-2	-	-	-	-	-	-
LV18	11	8.859	0.7%	0.2%	-	-
LLNL						
Synthetic reference materials						
IRMM-35	8	11.170	0.8%	0.3%	11.334	0.8%
IRMM-36	4	2.987	1.8%	0.9%	3.031	1.8%
UCSC Th "A"	9	5.771	0.7%	0.2%	5.856	0.7%
OU Th "U"	-	-	-	-	-	-
WUN	8	4.223	1.3%	0.5%	4.285	1.3%
Rock reference materials						
TML	6	5.813	0.3%	0.1%	5.899	0.3%
ATHO	-	-	-	-	-	-
BCR-2	-	-	-	-	-	-

[1] See Table 1 and Appendix A for each laboratory's procedures for correcting mass bias, SEM-Faraday yield difference and tail correction.

[2] Values given are averages of each labaoratory's replicate measurements, as given by N. Uncertainites represent 2s standard deviation and standard error about the mean.

[3] WHOI and UIUC used UCSC Th "A" (5.856 x 10^{-6}; Rubin 2001) for sample-calibrator bracketing so only "Measured" values are given; Bristol value for UCSC Th "A", derived from their "independently" characterised Th reference material is essentially identical to Rubin (2001), so "Corrected" values are not given; for UCSC, GEMOC and LLNL both "Measured" and "Corrected" values (i.e., re-normalised to UCSC Th "A" = 5.856 x 10^{-6}; Rubin 2001) are shown. See text for details.
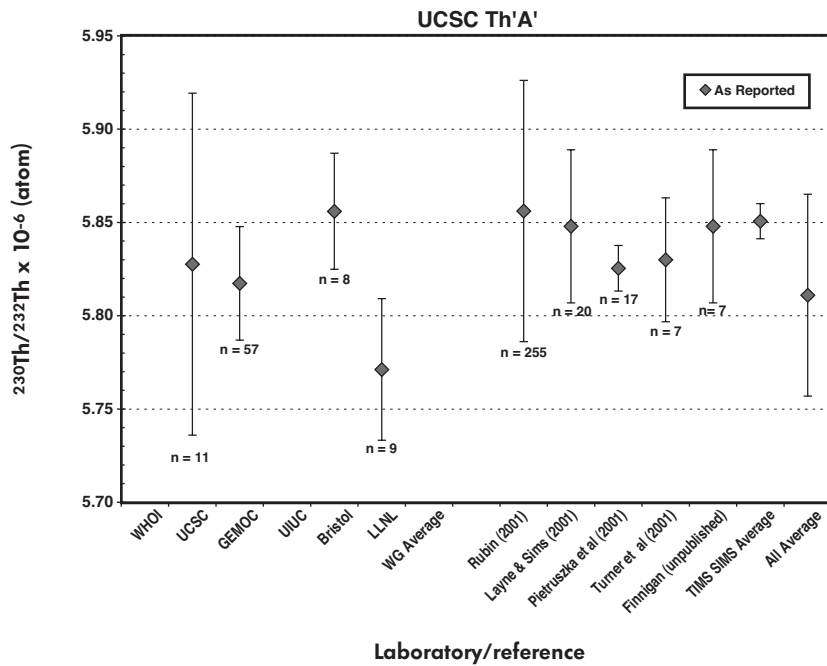
Figure 1. ^{230}Th/^{232}Th for UCSC Th "A' from the working group laboratories that have measured UCSC as an unknown by bracketing measurements with either a U calibrator (GEMOC, LLNL) or another Th calibrator (Bristol). Working groups for which no UCSC Th "A" data are shown used this reference material for sample/calibrator bracketing during Th isotope determinations. Published literature data were measured by TIMS, SIMS or MC-ICP-MS. Also shown is the average and 2s standard deviation for the TIMS/SIMS measurements and MC-ICP-MS U calibrator normalised measurements. To create a self-consistent data set, all other reference materials evaluated in this study have been re-normalised to the Rubin (2001) TIMS compilation for UCSC Th "A". See text for details.
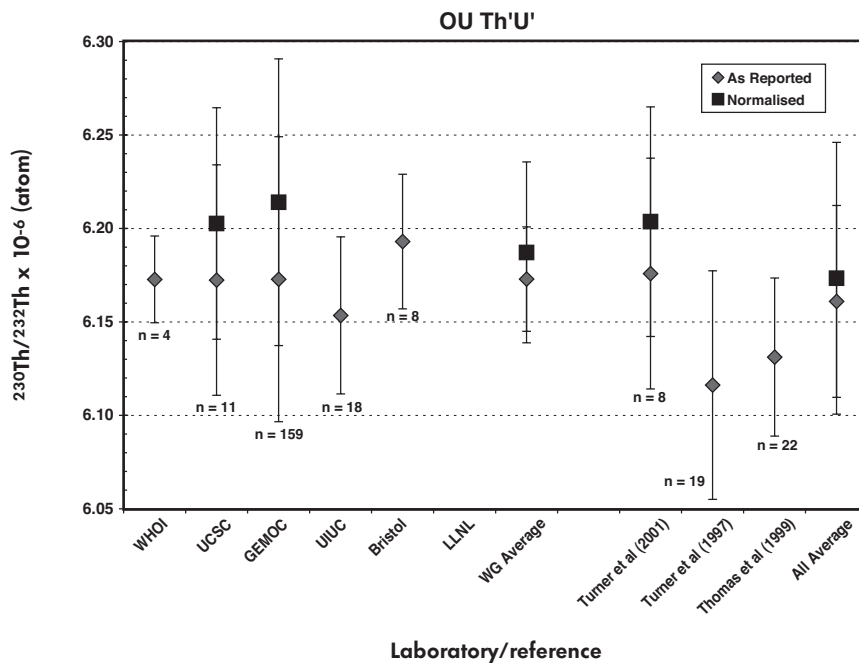

Figure 2. ^{230}Th/^{232}Th for Open University Th "U" synthetic reference material from the working group represented in this study and the literature data. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown. Note that the UCSC Th "A" from the Bristol group is essentially identical to the Rubin (2001) value for UCSC Th "A" and thus their data are not re-normalised. See text for details.
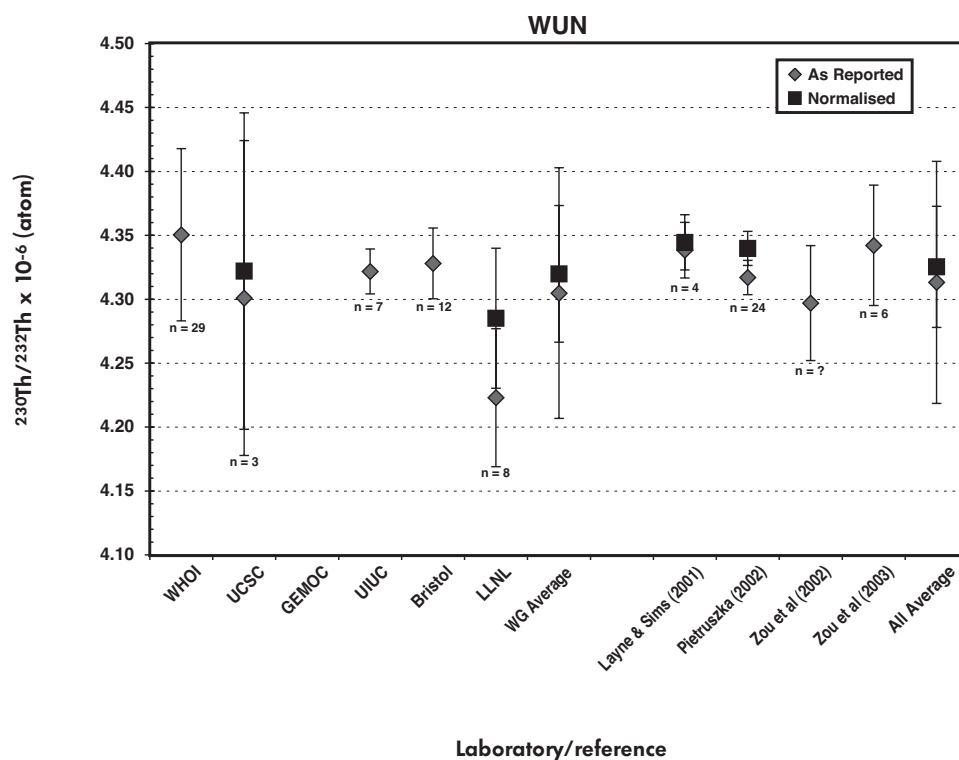
WUN

Figure 3. $^{230}Th/^{232}Th$ for WUN synthetic reference material from the working group represented in this study and the literature data. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown.
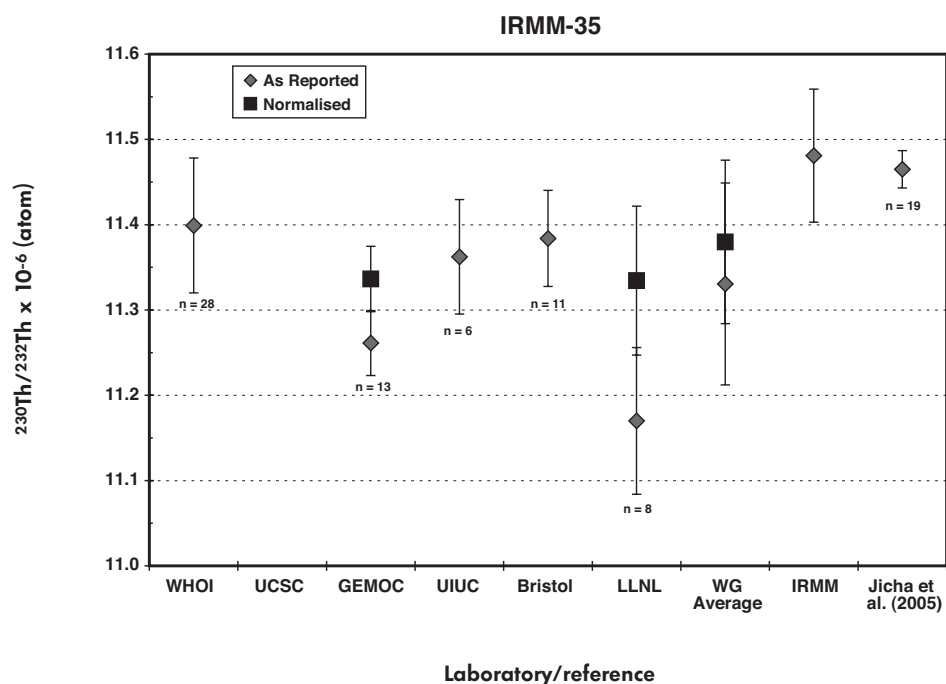
IRMM-35

Figure 4. $^{230}Th/^{232}Th$ for IRMM 35 synthetic reference material from the working group. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown.
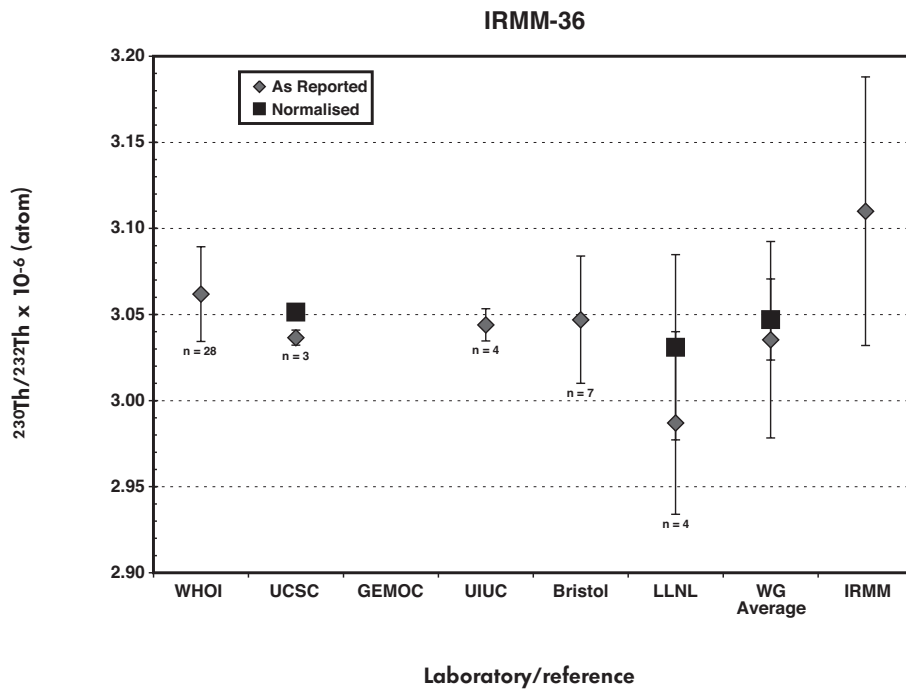
IRMM-36

Figure 5. $^{230}Th/^{232}Th$ for IRMM 36 synthetic reference material from the working group. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown.
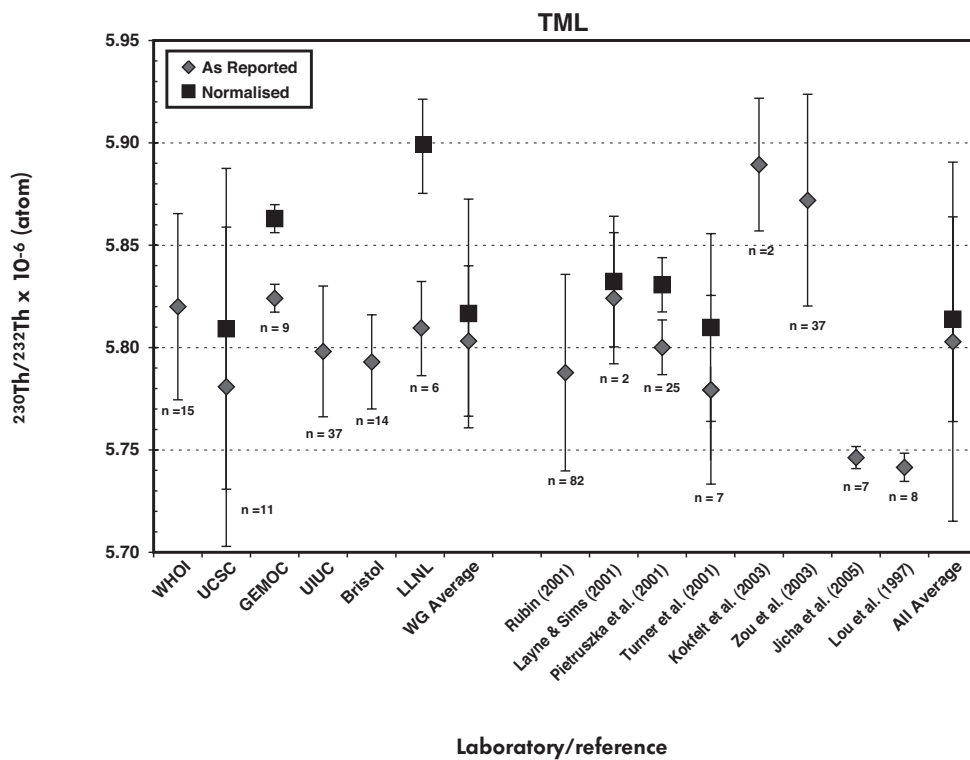

TML

Figure 6. $^{230}Th/^{232}Th$ for TML rock reference material from the working group represented in this study and the literature data. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown.

ATHO

Figure 7. $^{230}Th/^{232}Th$ for ATHO rock reference material from the working group represented in this study and the literature data. Both measured values and re-normalised values (to the consensus value of UCSC Th "A" from Rubin (2001)) are shown. See text for details.
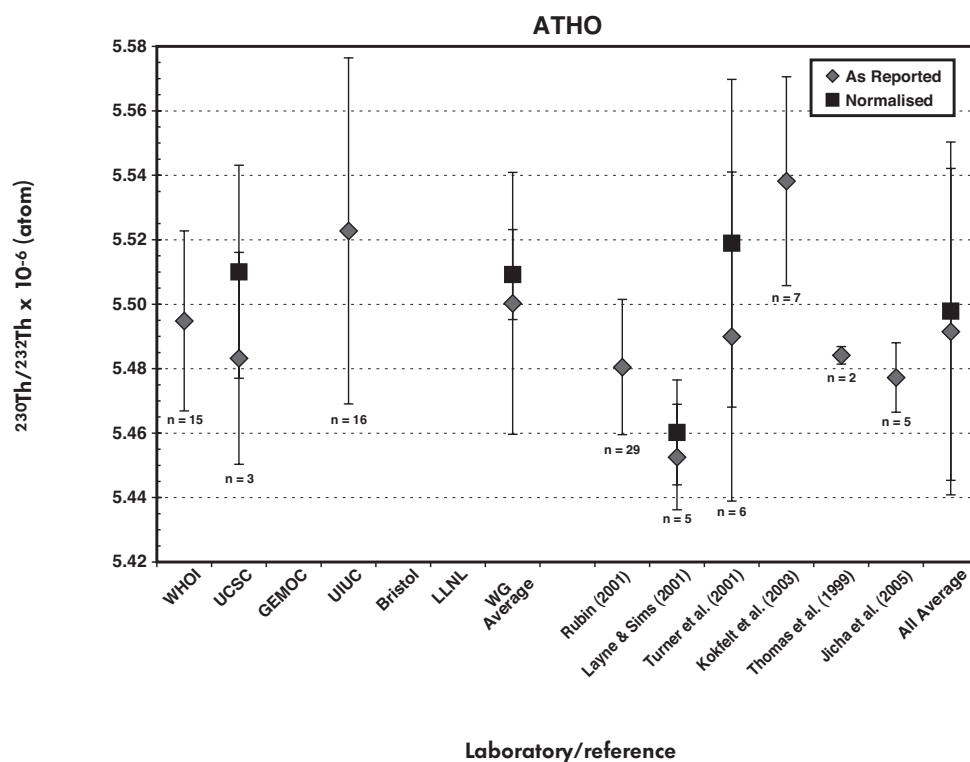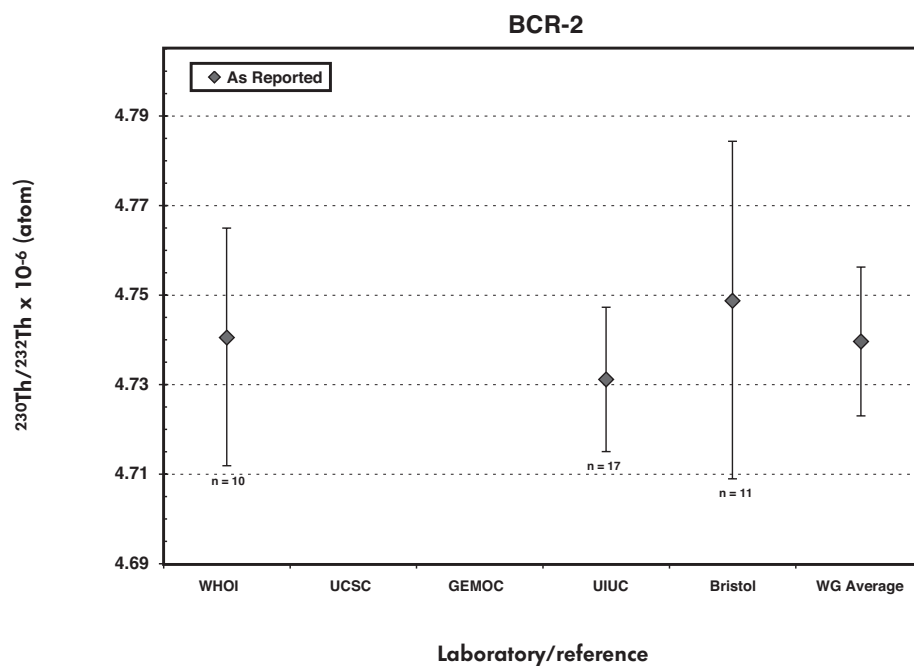
BCR-2

Figure 8. $^{230}Th/^{232}Th$ for BCR-2 rock reference material from the working group represented in this study. Note that none of the data have been re-normalised as WHOI and UIUC used UCSC Th "A" for sample/calibrator bracketing during analyses and the Bristol group is essentially identical to the Rubin (2001) value for UCSC Th "A". See text for details.

al. 2001, Pietruszka *et al.* 2002, Jicha *et al.* 2005). Though this literature compilation is not all-inclusive it is extensive enough to provide a reasonably representative sampling of the published Th reference material data from most of the established U-series laboratories around the globe.

As discussed in detail for each laboratory (Table 1, Appendix A), the accuracy of the ^{230}Th/^{232}Th measurement is limited by our ability to correct for: (1) tailing of ^{232}Th onto ^{230}Th; (2) instrumental mass bias and (3) SEM/Faraday detector gain calibration. For the ^{232}Th tail correction, WHOI and Bristol applied an offline, exponential tail-correction to each sample and reference material, Macquarie, UIUC and LLNL applied an offline, linear tail-correction to each sample and reference material and UCSC combined mass-bias, gain-calibration and tail-correction into one normalising factor. Because of the exponential shape of the ^{232}Th tail, an exponential fit to the data provides the most accurate correction. In contrast, a linear fit overcorrects for the ^{232}Th tail, and combining the tail correction and mass bias correction incorrectly assumes that the relative tailing is uniform between the normalising reference sample and the unknown. However, because these ^{232}Th tail corrections are actually quite small (< 1% - 2% depending on the sample ratio), the effect of these different approaches on the determined ^{230}Th/^{232}Th is small compared to other sources of error.

To account for mass bias and detector gain, all laboratories normalised to a U and/or a Th bracketing calibrator. WHOI and UIUC bracketed "unknowns" with UCSC Th "A" using the nominal Rubin value of 5.856×10^{-6} (± 1.2%; 2*s* RSD). Bristol used an in-house Th std. (TEDDi) with ^{230}Th/^{232}Th = $4.444 \pm 0.007 \times 10^{-3}$ and ^{229}Th/^{232}Th = $2.927 \pm 0.005 \times 10^{-3}$ for their bracketing calibrator. Macquarie bracketed Th "A" and Th "U" with a U-reference material, whereas IRMM-35, W2 and TML were first corrected to a U reference material and then secondarily corrected by bracketing with Th "U" using a nominal value of 6.176×10^{-6}. LLNL used U stynthetic RMs to bracket all Th synthetic RMs analysed in this study.

To create a self-consistent data set we have normalised, or re-normalised all of the Th isotope data to a universal value for the UCSC Th "A" (Figure 1). UCSC Th "A" is probably the best characterised of any synthetic Th reference material and has now been analysed by TIMS, SIMS and MC-ICP-MS in several laboratories. We adopt the average TIMS ^{230}Th/^{232}Th for UCSC Th

"A" (5.856×10^{-6} ± 1.2%; 2*s*) from Rubin (2001) as the nominal value. This Rubin value (n = 255) derives from compiled literature values plus 146 new values and agrees well with more recent SIMS (Layne and Sims 2001) and TIMS data (ThermoFinigan, unpublished). For the "working-group" laboratories that used standards other than UCSC Th "A" we present both the original "reported/measured" values and also the corrected/re-normalised data. The Bristol value for UCSC Th "A", derived from their independently characterised standard, is essentially identical to the Rubin value so re-normalised values are not shown for this laboratory. For the published literature data, any standard compilations containing UCSC Th "A" values were also re-normalised to this adopted nominal value for UCSC Th "A". While correction methods differed between laboratories, the "UCSC Th "A" normalised" data agree within reported uncertainties for all of the measured synthetic and rock reference materials (Figures 2-8). The published TIMS, SIMS and MC-ICP-MS data for these reference materials are also in good agreement, except in a few instances (which are discussed in detail in the appendix).

Agreement between working groups and with previously published data indicates a lack of significant systematic bias in any of the data sources. We therefore report two consensus values based on our chosen value for UCSC Th "A". The first is an average of the working group data and the second is an average of the working group data plus literature data (Table 3). We use three different methods to estimate the error of these consensus values: (1) we calculated the 2*s* standard deviation of the result from each laboratory or each laboratory plus literature sources. This provided an estimate of the reproducibility (interlaboratory errors) of the reference sample, both among our working groups' MC-ICP-MS measurements and the represented larger community; (2) we calculated the average variance from the different laboratories and from the different laboratories plus published data, and then propagate this representative laboratory error with the two-sigma standard deviation in order to obtain a conservative estimate of the combined uncertainty of intra-laboratory errors and inter-laboratory variation; (3) we incorporated the error on the Rubin (2001) value for UCSC Th "A" with the propagated uncertainty calculated in method 2 to provide an estimate of the total uncertainty which includes the uncertainties of both the "known" and unknown reference material.

The results of these calculations are presented in Table 3. In Appendix B, we discuss the pedigree of

Table 3.
Consensus values for synthetic and rock reference materials

	Working group avg. (x 10⁻⁶)	Err. est. 1 (10⁻⁶; rel %)	Err. est. 2 (10⁻⁶; rel %)	Err. est. 3 (10⁻⁶; rel %)	Working group + literature avg. (x 10⁻⁶)	Err. est. 1 (10⁻⁶; rel %)	Err. est. 2 (10⁻⁶; rel %)	Err. est. 3 (10⁻⁶; rel %)
Synthetic reference materials								
IRMM-35	11.380	0.096	0.101	0.170	-	-	-	-
	-	0.84%	0.88%	1.49%	-	-	-	-
IRMM-36	3.047	0.024	0.040	0.054	-	-	-	-
	-	0.77%	1.30%	1.77%	-	-	-	-
OU Th "U"	6.187	0.048	0.075	0.106	6.173	0.073	0.090	0.117
	-	0.78%	1.22%	1.71%	-	1.18%	1.46%	1.89%
WUN	4.321	0.047	0.083	0.098	4.326	0.044	0.074	0.090
	-	1.09%	1.91%	2.26%	-	1.03%	1.71%	2.09%
Rock reference materials								
TML	5.817	0.056	0.071	0.100	5.816	0.047	0.063	0.094
	-	0.96%	1.23%	1.72%	-	0.80%	1.08%	1.61%
ATHO	5.509	0.014	0.055	0.086	5.498	0.052	0.062	0.091
	-	0.25%	1.00%	1.56%	-	0.95%	1.13%	1.65%
BCR-2	4.740	0.017	0.043	0.075	-	-	-	-
	-	0.35%	0.91%	1.51%	-	-	-	-

(1) First set of columns represent the unweighted average and three estimates of the error based on the data from the six working group laboratories of this study; the second set of columns is the unweighted average of the working group plus data compilations and three estimates of error on this average.

(2) Errors are estimated three ways: (1) the 2s standard deviation of the results from each laboratory, or each laboratory plus literature sources; (2) propagates the average variance with the two-sigma inter laboratory standard deviation; and (3) propagates the two sigma error for the Rubin value for UCSC Th "A" (1.2%) with the uncertainty calculated in method 2 to provide an estimate of the total uncertainty that includes the uncertainties of both the "known" and unknown reference material (see text for further details).

Table 4.
Uranium and Th concentration data for rock reference materials (TML, W-2, BCR-2, AThO)

	N	Repl. diss.	[Th] (μg g⁻¹)	± 2s std. dev.	[U] (μg g⁻¹)	± 2s std. dev.	$(^{238}U/^{232}Th)$	± 2s std. dev.	$(^{230}Th/^{232}Th)$	± 2s std. dev.	$(^{230}Th/^{238}U)$	± 2s std. dev.	$(^{234}U/^{238}U)$	± 2s std. dev.
WHOI														
TML	12	8	30.50	0.20	10.79	0.30	1.073	0.004	1.070	0.011	0.998	0.011	1.001	0.002
ATHO	8	5	7.44	0.05	2.26	0.04	0.920	0.017	1.015	0.013	1.104	0.006	1.002	0.003
BCR-2	1	1	5.89	-	1.71	-	0.879	-	0.874	-	0.994	-	-	-
W-2	1	1	2.15	-	0.51	-	0.714	-	0.711	-	0.996	-	1.000	-
UCSC														
TML	2	-	30.01	0.30	10.62	0.11	1.074	0.040	1.068	0.001	0.994	0.008	1.001	-
GEMOC														
TML	9	-	29.70	0.10	10.55	0.03	-	-	-	-	0.999	0.003	0.999	0.001
W-2	5	-	2.15	0.10	0.51	0.00	-	-	-	-	0.998	0.003	1.000	0.002
BRISTOL														
TML	14	3	30.54	0.52	10.72	0.19	1.073	0.004	1.072	0.006	1.000	0.005	1.000	0.003
BCR-2	11	2	5.81	0.08	1.66	0.03	0.875	0.010	0.879	0.005	1.004	0.011	1.005	0.004
UIUC														
AThO	5	5	7.47	0.06	2.23	0.02	0.906	0.008	1.019	0.010	1.125	0.015	0.998	0.001
BCR-2	8	8	5.89	0.02	1.70	0.01	0.874	0.003	0.877	0.002	1.004	0.004	0.996	0.003

Activities calculated using decay constants of Cheng et al. (2000) for ^{230}Th: 9.15771 x 10⁻⁶ yr⁻¹, Jaffey et al. (1971) for ^{238}U: 1.551 x 10⁻¹⁰ yr⁻¹ and le Roux and Gendenin (1963) for ^{232}Th: 4.948 x 10⁻¹¹ yr⁻¹.

each reference material, (RM) highlighting differences and similarities in our results and earlier TIMS and MC-ICP-MS compilations, and detailing our calculations of nominal consensus values and estimates of uncertainty.

U–Th concentrations for rock reference materials

The results for the measured [U], [Th], (^{230}Th/^{232}Th) and (^{234}U/^{238}U), and calculated (^{238}U/^{232}Th) and (^{230}Th/^{238}U) for the rock reference materials BCR, W-2, TML, BHVO and ATHO are presented in Table 4 and shown in Figure 2. Measurement of TML, BCR-2 and W-2 provides verification of accuracy and precision for both ^{238}U/^{232}Th and ^{230}Th/^{232}Th as these rock reference materials are older than 500 ka and have been shown to be in equilibrium with respect to (^{230}Th/^{238}U) and (^{234}U/^{238}U). BHVO-1 and ATHO are younger rocks from Hawaii and Iceland that are not in equilibrium, but that are often used as rock reference materials, and therefore provide further validation of inter-and intra-laboratory reproducibility.

Rock concentrations for even the best characterised rock reference materials are heterogeneous from bottle to bottle and even between aliquots from the same bottle. Therefore, we did not calculate averages for the concentration data presented here, but instead present the observed range for each reference material from each laboratory as a reference for other inter-laboratory comparison. It is important to reiterate that many of these reference materials are old and essentially unaltered with respect to the U-series systematics. As a result, the evidence of radioactive equilibrium within 1% 2s shown in Table 4 for old rocks, with Th isotope ratios normalised to a value of 5.856 x 10^{-6} for UCSC Th "A", provides independent confirmation of that value and, therefore, of the Th isotope ratios for all other RMs reported here, relative to that value.

Summary

(1) We have orchestrated a concerted effort, involving six different laboratories using three different manufacturers of MC-ICP-MS, to measure several synthetic and rock Th isotope reference materials. Despite several different techniques for correcting mass bias, gain calibration and tailing of ^{232}Th onto ^{230}Th, all laboratories results for the "UCSC Th "A" normalised" data agree within reported uncertainties for all measured synthetic and rock reference materials. The published TIMS, SIMS and MC-ICP-MS data for these reference

materials are also in good agreement. Accordingly, we present nominal consensus values and estimates of their error for each of these reference materials.

(2) Although the uncertainties of all the measurements and data compilations often overlap, the U-normalised MC-ICP-MS data typically fall below the Th normalised MC-ICP-MS data and also the TIMS and SIMS literature compilations. This lower ^{230}Th/^{232}Th for the U normalised MC-ICP-MS data is likely due to differences in uranium vs. thorium behaviour with respect to both mass bias and mass dependent ion transmission (Hoffmann *et al.* 2007, Ball *et al.* 2008).

(3) Because referencing thorium isotopic measurements to known uranium reference values is problematic, acceptance of a thorium reference material for isotopic composition determinations is critical. In this study we have chosen to reference our data to the Rubin value for UCSC Th "A". UCSC Th "A" is probably the best characterised of any synthetic Th reference material and has now been analysed by TIMS, SIMS and MC-ICP-MS in several laboratories. Unfortunately this UCSC Th "A" reference sample is no longer available for distribution, so "anchoring" these different reference materials to a common value for UCSC Th "A" provides the community with a long-term reference value against which to compare isotope measurements.

(4) In order to achieve day-to-day and inter-laboratory agreement of ‹ 1% 2s, it is necessary to bracket sample measurements with a Th solution that is well characterised for ^{230}Th/^{232}Th and is ideally within ~ 50% of the unknowns. Despite the growing need within the U-series community for in-house reference samples, many are not widely available. So while commercially available IRMM CRMs are an important first step in fulfilling this need, they have the most extreme values seen/expected for volcanic samples and are thus not an optimum solution. Therefore, the community covets a commercially available reference material with a ^{230}Th/^{232}Th ratio of 5 x 10^{-6} with carefully determined certified gravimetric values.

(5) It is important to note that the UCSC Th "A" value (TIMS - Rubin 2001) we have adopted has a 1.2% (2s) uncertainty that clearly limits our absolute knowledge of any reference materials normalised to this value. Admixing a well-calibrated ^{229}Th spike to this reference material or any other RM of similar isotopic composition would provide an important absolute constraint on this ratio. The crux of this effort is to

calibrate the ^{229}Th spike to much better than 1% and to correct rigorously for ^{232}Th and ^{230}Th impurities in the spike and ^{229}Th interferences on ^{230}Th. This is similar to the approach taken by Bristol (Hoffmann *et al.* 2007). The observation that the adopted ^{230}Th/^{232}Th from the Rubin (2001) TIMS compilation value agrees extremely well with this new Bristol data, as well as other recent SIMS (Layne and Sims 2001) and HAS-TIMS data (ThermoFinigan, unpublished Triton data) suggests that our knowledge of the accuracy and precision of this reference material is better than 1% [e.g., the average ^{230}Th/^{232}Th of these four data sets (5.852 x 10^{-6}) is only 0.07% different than the Rubin value (5.856 x 10^{-6}) with a two-sigma relative standard deviation of only 0.16%].

(6) The observation that old, unaltered rock reference materials are in radioactive ^{238}U-^{230}Th equilibrium to within 1% (2s) provides independent confirmation of the accuracy of both the Th isotopic and the U and Th concentration measurements. These equilibrium ^{238}U - ^{230}Th measurements also validate the accuracy of the Rubin (2001) TIMS compilation value for UCSC Th "A", against which all of our equilibrium rock reference materials have been normalised.

Acknowledgements

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Appendix A.
Laboratory techniques for measuring Th isotopes and U, Th concentrations

Woods Hole Oceanographic Institution (WHOI)

Thorium isotopes: Thorium was separated and purified in the WHOI clean laboratories using two anion columns. The first column was a nitric anion column to separate Th and U from the silicate rock matrix, and the second column was an hydrochloric anion column to separate Th from U.

Thorium isotopes were measured using the WHOI ThermoFisher NEPTUNE. Analyses were made statically, measuring 232Th on a Faraday cup and 230Th on the axial, discrete dynode ion counter (ETP-SEM/SGE, Sydney, Australia) passing through a tunable repelling potential quadrupole (RPQ) or high abundance sensitivity lens designed to minimise tailing on the low mass side of a peak. Using the RPQ on the ThermoFisher Neptune, the abundance sensitivity at 85% transmission was ~ 50 ppb over 2 AMU, resulting in a tail correction of 232Th on 230Th of 0.7% for 230Th/232Th of

3.3 x 10^{-6} and 0.3% for ^{230}Th/^{232}Th of 6.7 x 10^{-6}. For each sample and calibrator the tailing of ^{232}Th on ^{230}Th was corrected offline using an exponential method, based on a peak scan from mass 229.5 to mass 231.5. These scans showed tail curvature on the NEPTUNE such that a linear extrapolation would significantly overestimate the effect of the ^{232}Th tailing, thereby causing the corrected ^{230}Th/^{232}Th ratio to be too low.

To correct for both instrumental mass fractionation between masses 230 and 232 and the relative difference in the efficiency of the Faraday and SEM detectors, we evaluated two different methodologies: (1) a linear interpolation of the ^{238}U/^{236}U measured in NBS U010 interspersed between each sample and normalised to its certified value (14,535 ± 149), and (2) a linear interpolation of the ^{230}Th/^{232}Th measured in the UCSC Th "A" interspersed between each sample, and normalised to its nominal value 5.856 x 10^{-6} (± 1.2% 2s RSD) from Rubin (2001). Results showed that, due to instrumental mass bias differences and differences of the ion energies through the RPQ filter of U and Th, U did not adequately correct for Th and generally gave results that were too low (Ball et $al.$ 2008). Thus for this study and all Th isotopic analyses at WHOI, Th isotopic measurements were corrected using a linear interpolation of the ^{230}Th/^{232}Th measured in the UCSC Th "A" bracketing each sample, and normalised to a nominal value from Rubin (2001). Sensitivity, based on U using a normal spray chamber (wet plasma) and standard nickel cones, expressed as ion yield was approximately 0.1%. The linear range of the ETP SEM with RPQ was less than 20k cps, with the best linearity achieved by matching samples and calibrators to within a factor of 2. Dead time was measured to be 20 nanoseconds.

Using Th-bracketing (UCSC Th "A"), inter-day reproducibility over a four-year period with multiple instrument operators was 0.4-1.5% (2s) for both synthetic reference materials and processed Th from volcanic samples. Our daily reproducibility for any one solution was 0.2-0.5% (2s) Drift in UCSC Th "A" varied from 0.5 to 1.0% throughout a 10-hour analytical session after a 2-3 hour warm-up period. Temporal variations in drift and abundance sensitivity throughout each session were the most fundamental sources of error.

U-Th concentrations: Uranium and thorium concentrations on separate liquid aliquots from the same rock dissolution were determined by isotope dilution using the Thermo Finnigan Element 2 high resolution sector-field ICP-MS. The dissolved samples were aliquoted so as to contain ~ 10 ng of ^{238}U. Each aliquot was spiked with individual ^{229}Th and ^{233}U spikes and equilibrated, using progressive dry downs and perchloric acid fuming. Samples were spiked to attain ^{232}Th/^{229}Th ≈ 30 and ^{238}U/^{233}U ≈ 10. A nitric anion column was used to separate Th and U from most of the silicate matrix. ^{229}Th and ^{233}U were calibrated against gravimetric solutions of ^{238}U (made from NBS 960 metal) and ^{232}Th (made from Ames metal) and are known to better than 1% (2s).

Uranium and Th were measured in the same aliquot using a peak hopping routine on masses 229, 232, 232.5, 233, 235, 238. The most abundant isotope (typically ^{232}Th) was kept below 5 million counts per second so that all measurements were made in pulse counting mode. Mass 232.5 was monitored to assess tailing of mass 232 onto mass 233 and vice versa. Prior to each analysis, a scan of the spectra from mass 226 to mass 240 was conducted to evaluate background. Because the ^{235}U/^{238}U of the spike was unnatural, instrumental mass fractionation was corrected by sample/calibrator bracketing using a linear interpolation of the ^{235}U/^{238}U measured in NBL-112A interspersed between each sample. Samples were run in triplicate. Thorium and U concentrations given in Table 4 were the average and 2s standard deviation of these triplicate determinations for each separate dissolution. It should be noted that the analyses displayed in Table 4 represent the analytical efforts of various WHOI and visiting students, postdoctoral students and scientists with different powder splits from both WHOI facilities and other institutions.

University of California Santa Cruz (UCSC)

Thorium isotopes: Thorium was separated and purified in the UCSC clean laboratories using only AG1-X8 anion resin. Firstly, Th and Ra were separated from U using 6 mol l^{-1} HCl. Th is then separated from Ra using the same resin and 8 mol l^{-1} HNO$_3$ for Ra, followed by 6 mol l^{-1} HCl for Th. This was repeated with increasingly smaller resin volumes, as necessary. Boric and perchloric acid were added at each drydown to prevent formation of fluorides and to destroy organics, respectively. Uranium was separated from Fe by eluting with 8 mol l^{-1} HNO$_3$ for Fe, followed by 0.5 mol l^{-1} HCl for U.

^{230}Th/^{232}Th ratios were measured statically using the UCSC ThermoFisher NEPTUNE with ^{232}Th on the

H2 Faraday cup and ^{230}Th on the RPQ channel using an ETP SEM. The linear range of the SEM was ‹ 10,000 cps. Samples were dissolved in 2% v/v (0.3 mol l^{-1}) HNO$_3$ + 0.1% v/v HF with intended concentrations of ~ 50-100 ng ml^{-1} Th. Data reported here were obtained using standard Ni cones and a MCN 6000 desolvating nebuliser, but we have since found that an Apex desolvating nebuliser gives a more stable signal without degraded sensitivity or memory. MCN sensitivity was ~ 200-300 V per µg ml^{-1} Th in solution. Rinse times were 10-15 minutes or until backgrounds on ^{230}Th were ‹ 5-10 cps. Total data collection time per analysis was 10-20 minutes, and the total sample consumed was 0.5-1.0 ml (50-100 ng). Data were collected as a single block of twenty-five to fifty 8 s integrations. Internal errors (2s SE) on raw ^{230}Th/^{232}Th were ‹ 0.1%. On-peak backgrounds were measured immediately prior to each analysis on a blank solution of 2% v/v (0.3 mol l^{-1}) HNO$_3$ + 0.1% v/v HF and automatically subtracted from all peaks. Our abundance sensitivity varied inversely with transmission efficiency and with time. Typically, abundance sensitivity was 25-120 ppb at 2 AMU when transmission efficiency was 70-90%. This resulted in a tail correction of ^{232}Th on ^{230}Th of 0.3-1.8% for ^{232}Th/^{230}Th ratios ~ 2 x 10^5 using an exponential correction fit to the mass range 229.5 to 231.0.

Note that for the data reported here, a tail correction was not applied. Rather, results were corrected for mass fractionation, gain calibration, and tailing altogether using calibrator-sample-calibrator bracketing with a synthetic Th reference material and linear extrapolation between standard solutions. IRMM-035 was used as the bracketing calibrator to evaluate its suitability for this purpose. We assumed a ^{230}Th/^{232}Th ratio of 11.407 x 10^{-6} for IRMM-035 rather than the certified value of 11.481 x 10^{-6} in order to present results internally consistent with a ratio 5.856 x 10^{-6} for Th "A" (i.e., Rubin 2001). Thus, our actual bracketed Th "A" value was 5.828 x 10^{-6} ± 1.6% (2s RSD; n = 11). Use of IRMM-035 as a bracketing solution increased the importance of the ^{232}Th tail correction because of the factor of 2-4 difference in ^{230}Th/^{232}Th ratio between calibrator and most natural silicates. When the abundance sensitivity was ‹ 50 ppm at 2 AMU, error on the background correction exceeded 1% such that we obtained better external reproducibility and similar accuracy by bracketing without tail correction for ^{230}Th/^{232}Th ratios › 4 x 10^{-6} in the unknown. At higher abundance sensitivity or ^{230}Th/^{232}Th ratios for unknowns, inter-

day precision was worse for the standard solution WUN than for solutions with lower ratios. Better precision for IRMM-036 results was because this reference material was only analysed on one day. To reduce dependence on abundance sensitivity, we now routinely use UCSC Th "A" as our bracketing calibrator and we make tail corrections for all measurements before bracketing.

We initially explored the use of U isotopes to correct for Th mass fractionation, both by adding NBS 010 to U-free Th solutions, and by analysing it or NBL-112a between analyses of Th solutions. Although our U-normalised ^{232}Th/^{230}Th ratios measured in this way were reproducible to within 1% (2s) during an analytical session, they were usually a few percent too high relative to their nominal accepted values. We could correct for this by normalising to a Th standard solution run in the same way during the same analytical session, but simple Th sample-calibrator bracketing as described above was faster and easier.

Using simple Th-bracketing, inter-day reproducibility over a two year period of 1.0-1.5% (2s) was achieved for both solution calibrators and processed rock reference materials. Reproducibility for any one solution was usually 0.5-1.0% (2s) on any given day. Drift in bracketing solutions varied from 0.5 to 2.0% throughout a 10 hour analytical session after a 2-3 hour warm-up period. Temporal variation in drift and abundance sensitivity throughout each session was our most fundamental source of error, but the stability of our pulse counting system was a persistent problem.

U and Th concentrations: The U and Th concentrations for TML were obtained without isotope dilution, using external calibration of an ELEMENT1 HR-ICP-MS. The method is described by Tepley *et al.* (2006) and Ryder *et al.* (2006). A separate aliquot of sample from that used for isotope ratios was dissolved in HF-HNO$_3$ in an open beaker, and fumed in perchloric acid. Calibration was undertaken against six international reference materials, assuming Th and U concentrations from Eggins (1997) except Th for AGV-1 (we used 6.06 µg g^{-1}: F. Ramos, TIMS-ID). Correction for drift was made internally relative to Bi, and externally using a solution analysed between every four unknowns (i.e., every hour). The 2 standard deviation errors cited are for replicate measurements on four different days using different calibrations. Although this method can achieve comparable accuracy and external precision to TIMS-ID (e.g., ‹ 1% 2s

down to 1 μg ml^{-1}; ± 10-20 ng ml^{-1} at ‹ 1 μg ml^{-1}), we have returned to using TIMS-ID because of recurring and unpredictable exceptions.

GEMOC Centre, Macquarie University

Thorium isotopes: Thorium was separated and purified in the GEMOC clean laboratories. Samples were dissolved through a series of digestions in HF + HNO$_3$ + HCl, HNO$_3$ + H$_3$BO$_3$ and HNO$_3$ (note that high purity acids were used throughout). The samples were then loaded in 7 mol l^{-1} HNO$_3$ (3 ml for 100 mg of sample) on 4 ml of anionic resin AG1-X8 200-400 mesh. The resin was previously washed with 1 column volume (CV) of MQ H$_2$O, 1.5 CV of 6 mol l^{-1} HCl, 1.5 CV of 7 mol l^{-1} HNO$_3$ and 1.5 CV of 0.2 mol l^{-1} HNO$_3$, and pre-conditioned with 3 CV of 7 mol l^{-1} HNO$_3$. Most elements were eluted with 20 ml of 7 mol l^{-1} HNO$_3$ and 4 ml of 6 mol l^{-1} HCl. The Th fraction was then eluted with 4 ml of 6 mol l^{-1} HCl, followed by the U fraction with 7 ml 0.2 mol l^{-1} HNO$_3$.

Thorium isotopes were measured using a Nu Instruments Plasma high resolution multi-collector ICP-MS. Thorium samples were introduced in the source in 2% v/v HNO$_3$ using a desolvating nebuliser (DSN100). A solution with a concentration of ~ 20 ng ml^{-1} of Th commonly yielded ~ 1 V of ^{232}Th on Faraday cups and a few 100 cps for ^{230}Th. Nickel cones were used.

Analyses were made statically, measuring ^{232}Th on a Faraday cup and ^{230}Th on the RPQ channel using an ETP SEM. Using the RPQ on the Nu Plasma, the abundance sensitivity at 95-98% transmission was ~ 450 ppb over 1 AMU (190 ppb at 2 AMU but transmission was not determined).

Prior to Th determination, a solution of the U reference material NBL 112a was run in order to calculate a correction factor for mass bias fractionation and the ion counter gain. The mass bias fractionation correction factor was calculated by comparing the measured ^{238}U/^{235}U ratio to the nominal ratio (137.88) and assuming an exponential relationship between the fractionation and the masses. Ion counter gain was calculated by comparing the measured ^{234}U/^{238}U ratio, corrected for mass bias, to the published value (5.286 x 10^{-5}; Cheng *et al.* (2000). The measured ^{230}Th/^{232}Th ratio was then corrected for mass bias fractionation and ion counter gain using these parameters. Over one day, the calculation of mass bias

fractionation factor and ion counter gain was only required to be performed once; the reproducibility of ^{230}Th/^{232}Th measurements for the standard solution OU Th "U" was 0.1-0.3% (1*s*; n = 5-7). Depending on analysis conditions, it had been observed that measured ^{230}Th/^{232}Th ratios for the standard solution OU Th "U" (corrected from mass bias fractionation and relative ion counter gain) could be different from the published nominal value by up to 1% (Turner *et al.* 2001). Hence, in order to obtain accurate measurements, in addition to the calculation of the mass bias fractionation factor and the ion counter gain at the beginning of the day, each sample or reference material analysis was bracketed by OU Th "U" as a calibrator (6.17665 x 10^{-6} Turner *et al.* 2001). Following this procedure, measured ^{230}Th/^{232}Th ratios deviated from the published value by 0.4% for the rock reference material TML-3 and 0.6% for the synthetic reference material IRMM-35. It was not necessary to run Th "U" between each sample as the measured ^{230}Th/^{232}Th ratio did not vary significantly for a given session. For example, during a session of 32 hours, twenty-three measurements of Th "U" yielded a relative standard error (2*s*) of only 0.06%.

Data presented here were collected using the procedure described above. However, because ^{230}Th was not explicitly corrected for the contribution of the ^{232}Th tail, a new procedure was adopted since early 2007: the measured ^{230}Th/^{232}Th ratio in the sample was corrected by a calibrator-sample- calibrator bracketing with the standard solution Th "U" and linear extrapolation between calibrators. During calibrator and sample measurement, tail correction was performed by collecting at masses 230.5 and 229.5 for each cycle and using a linear extrapolation. The tail correction was about 4% for ^{230}Th/^{232}Th ratios ~ 5-6 x 10^{-6} but could be as high as 8-9% for ^{230}Th/^{232}Th ~ 3 x 10^{-6}. By collecting at 228.5, we were able to determine an exponential fit to the ^{232}Th tail and show that a linear extrapolation could over-correct ^{230}Th by as much as 1% compared to an exponential correction. However, this did not affect the results as samples and calibrators were both corrected using a linear extrapolation. Measurement of selected reference materials using the new procedure yielded ^{230}Th/^{232}Th = 5.847 ± 0.006 x 10^{-6} for Th "A" (n = 3; 2*s*), 1.139 ± 0.009 x 10^{-5} for IRMM35 (n = 1; 2*s*) and 5.79 ± 6 x 10^{-6} for TML (n = 2, 2*s*).

U-Th concentrations: Uranium and thorium concentrations were determined by isotope dilution using the Nu Instruments Plasma high resolution multi-collector

ICP-MS. For [U] and [Th] an amount of rock powder accurately weighed was spiked with ^{229}Th and ^{236}U, these spikes were then equilibrated with sample aliquot through total dissolution. A nitric anion column was used to separate Th and U from most of the silicate matrix (see previous section). The ^{229}Th and ^{236}U had been calibrated against synthetic NIST solutions at The Open University, and cross-checked at Cambridge University. They were known to better than 1%. Aliquots for U and Th were measured separately. Uranium concentrations were measured by collection of ^{236}U on the RPQ channel using an ETP SEM and ^{238}U on a Faraday cup. Thorium concentrations were measured by collection of ^{229}Th on the RPQ channel using an ETP SEM and ^{232}Th on a Faraday cup. In both cases, for the data presented here, a solution of the U reference material NBL-112a was analysed prior to determinations to calculate a correction factor for mass bias fractionation and the ion counter gain (see previous section). As discussed in the previous section, a new procedure had been developed that explicitly accounted for tail correction of ^{232}Th and ^{238}U on ^{229}Th and ^{230}Th, and ^{234}U and ^{236}U, respectively. For U concentrations, the ^{236}U/^{238}U ratio of the sample was corrected by bracketing with calibrator solution U010. For Th concentrations, the ^{229}Th/^{232}Th of the sample was corrected by bracketing with the standard solution OU Th "U" and the difference of mass fractionation between ^{229}Th-^{232}Th and ^{230}Th-^{232}Th was accounted for by running a solution of U solution reference material NBL-112a at the beginning of the day, which yielded a correction factor for mass bias fractionation (variation of this factor over a day induced an error of less than 0.1%). The new procedure yielded for TML: [Th] = 29.73 ± 0.2 (*s*), [U] = 10.56 ± 0.04 and (^{230}Th/^{238}U) = 0.996 ± 0.005 (n = 2).

University of Bristol

Thorium isotopes: Silicate samples were spiked with a mixed ^{229}Th/^{236}U spike, digested in a concentrated HF, HNO_3 and $HClO_4$ mixture and brought into complete solution using a multi-step procedure. Thorium was separated and purified in clean laboratories using a single TRU-spec column with a procedure based on Luo *et al.* (1997). The sample was loaded in 7 mol l^{-1} HNO_3 on a 0.5 ml resin bed and the matrix removed with elution of further 7 mol l^{-1} HNO_3, 1M HNO_3 and 2.5 mol l^{-1} HCl. The Th fraction was collected with 0.5 mol l^{-1} HCl and finally U was eluted with a 0.01 mol l^{-1} HCl-0.01 mol l^{-1} HF mixture. The Th and U fractions were then redissolved in 0.6 mol l^{-1} HCl for measurement on the MC-ICP-MS.

Analytical procedures were reported in full by Hoffmann *et al.* (2007). In brief, Th isotopes were measured using a ThermoFisher NEPTUNE. Two static analyses were made; the first with ^{232}Th on a Faraday cup and ^{230}Th on a SEM that lies behind the RPQ, the second with ^{232}Th on a Faraday cup and ^{229}Th on the RPQ-SEM. We used a MasCom SEM, which had a significantly smaller non-linearity than an earlier, highly non-linear ETP SEM (Hoffmann *et al.* 2005). An apparent memory effect of a more intense on a less intense signal noted on the ETP SEM (Hoffmann *et al.* 2005) led us to chose two separate static analysis measurements rather than jumping between ^{230}Th and ^{229}Th in a single measurement procedure.

Using the RPQ on the ThermoFisher Neptune, the abundance sensitivity at ~ 80% transmission was ~ 20 ppb at two mass units below ^{232}Th. Tail contributions were explicitly calculated for masses 230 and 229 in each sample by measuring masses 231, 230.5, 229.5 and 228.5 and interpolating in semi-log space. To correct for both instrumental mass fractionation and the relative difference in the efficiency of the Faraday cup and SEM detectors, we bracketted our samples with an in-house synthetic Th reference material (TEDDi). Isotopic ratios (^{230}Th/^{232}Th = 4.444 ± 0.007 x 10^{-3}, ^{229}Th/^{232}Th = 2.927 ± 0.005 x 10^{-3}) for this synthetic reference material had been extensively calibrated by TIMS and static Faraday cup measurements on the Neptune (see Hoffmann *et al.* 2007 for details). The isotopic ratios were less extreme than typical silicate samples and the standard solution was originally designed to ensure accurate analysis of low ^{232}Th calcite samples. Thus, the background memory of the intense silicate ^{232}Th beam on the smaller ^{232}Th beam of TEDDi required longer than optimal washout times with alternate HCl and HF-doped HCl solutions. Ultimately, an alternative calibrator with isotope ratios more appropriate for silicate work will be prepared. However, TEDDi has been proven to be a reliable calibrator for silicate samples (Hoffmann *et al.* 2007). Mass bias and Faraday-SEM gain calibration were corrected by dividing ^{229}Th/^{232}Th and ^{230}Th/^{232}Th measurements by the mean ratios of bracketing calibrators, normalised to the true values. Samples were typically run with ^{230}Th and ^{229}Th intensities below 50,000 cps. Non-linearity of the multiplier had been calibrated after Hoffmann *et al.* (2005). Dead time was set to 20 ns and verified as described in Hoffmann *et al.* (2005), although the dead time correction was not a significant parameter for the typical intensities analysed. The effect of instrumental background intensities

and the spike contribution on ^{230}Th was stripped offline and all initial errors were propagated using a Monte Carlo routine to generate a final error. The data reported for reference materials represent measurements made over the ~ 1 year period since the installation of the more stable MasCom SEM.

U–Th concentrations: Thorium concentrations were determined as part of the Th isotopic measurement routine described above. Uranium measurements, for the silicate samples in secular equilibrium, were also made using a sample-calibrator bracketing on the ThermoFisher Neptune. NBL U112a was used as the externally bracketing calibrator for mass bias correction, assuming ^{235}U/^{238}U = 137.88. As with Th, a double static collection routine was used first measuring ^{234}U on the RPQ-SEM simultaneously with ^{238}U on a Faraday cup, followed by ^{236}U on the RPQ-SEM and ^{235}U and ^{238}U simultaneously on Faraday cups. Since NBL U112a does not contain ^{236}U, the measurement of mass 236 on the RM provided a useful abundance sensitivity correction for the samples. The ^{236}U-^{229}Th spike had been calibrated against NIST SRM 3159 (for Th) and an in-house gravimetric calibrator prepared by dissolution of NBL U112a metal (for U). Further details of the calibration are reported in Hoffmann *et al.* (2007). Activity ratios of the silicate reference materials were calculated using the half-lives recommended by Cheng *et al.* (2000).

University of Illinois-Urbana Champaign (UIUC)

Thorium isotopes: Thorium and U were purified from samples using a combination of anion and cation columns as detailed in Lundstrom *et al.* (1998). For Th, one 2 ml cation resin (AG50-X12) column followed by a 150 µl anion resin (AG1-X8) column produced a sufficiently clean sample for Th determination.

Measurements of U and Th concentrations and isotopic compositions at UIUC were made on a Nu plasma HR MC-ICP-MS, manufactured by Nu Instruments. Thorium isotopes were measured in static mode with ^{232}Th (and ^{229}Th when present) measured on Faraday cups and ^{230}Th measured using an ETP SEM behind a decelerating lens abundance sensitivity filter. Nickel cones were used. Abundance sensitivity at mass 231 during measurements of Th "A" ranged from 250 ppb to 400 ppb. The abundance sensitivity at 2 AMU with 95% transmission through the filter was ~ 50 ppb. Determinations of ^{232}Th/^{230}Th used a linear baseline

correction between measurements taken at 229.5 and 230.5. Repeat curve fitting analysis of the distribution of counts at 229.5, 230.5 and 231 on multiple standard runs indicated a curvature of the baseline beneath 230 which could be fitted using an exponential equation (with r^2 of › 0.98). However, the absolute difference in baseline counts subtracted using the linear correction versus the exponential correction resulted in a small change, which was within the uncertainties based on external reproducibility. Therefore, the more simple linear correction was used.

Measurements were made in dry plasma mode using a DSN-100 desolvating nebuliser by uptake of 2% v/v HNO_3 solution. Sensitivities in the U and Th mass range varied from ~ 300 to 450 V/µg g^{-1} at an uptake rate of 0.1 ml min^{-1}. ^{230}Th count rates during analysis were between 1000 and 3000 cps. Repeat analyses of the U960 uranium reference sample over a range of signal intensities showed that the SEM was linear over count rates ranging from 600 to 25000 cps. A 10 ns dead time was applied to all data collected on this SEM.

To calibrate the gain and account for mass bias during Th analysis, we developed a Th calibration solution by combining a known concentration of the UCSC Th "A" isotopic reference solution with a known amount of our ^{229}Th spike, producing a calibration solution with a ^{232}Th/^{229}Th ratio of 460.2. The intensity of ^{229}Th was high enough to be measured on a Faraday cup (at 0.01-0.015 V) such that the measured ^{232}Th/^{229}Th could be used to account for the mass bias during the analysis. ^{230}Th was measured on the high abundance sensitivity ion counting channel with the difference between the measured fractionation corrected ^{232}Th/^{230}Th and the known ^{232}Th/^{230}Th of Th "A" (5.856 x 10^{-6}; Rubin 2001) used to calculate the Faraday cup-ion counter gain during the analysis. Gain and mass bias stability allowed analyses of four samples between each set of two calibration runs. Each analysis reflected twenty-five ratios with 10 s integration times, which followed 30 s baseline measurements at 229.5 and 230.5 AMU.

Note that by adding ^{229}Th to both calibrators and samples, we had to account for two possible analytical effects of the ^{229}Th spike. First, the contribution of ^{230}Th from the spike had to be subtracted from all analyses. The measured ^{229}Th/^{230}Th ratio of the UIUC Th spike was 21,930 ± 100 such that the contribution of ^{230}Th from the spike was relatively minor for samples with

$^{229}Th/^{230}Th$ ‹ 500. In addition, because ^{229}ThH was an isobaric interference on ^{230}Th, accurate assessment of the production of hydride within the DSN-100 was also required. By measuring the count rate at ^{233}U on the ion counter with a › 5 V beam of ^{232}Th present, we found the Th production in the DSN-100 to be 2.5 ppm ± 1 ppm of the ^{232}Th signal. Therefore, both hydride and spike effects were accounted for during our analysis with overall corrections of ~ 1% of the ^{230}Th measured (mostly reflecting the spike contribution). The propagated contributions of these corrections to the analytical error were much smaller than the uncertainty based on repeat analyses; therefore reported errors reflected standard deviations of repeat analyses. The analyses reported here occurred over a 15 month period from October 2005 to August 2007.

U-Th concentrations: Thorium concentrations were determined as part of the Th isotopic measurement routine described above. Uranium measurements were made using a similar sample- calibrator bracketing technique using analyses of NBS U960 (NBL-112A) or IRMM U-A as calibrators to correct for mass bias and gain calibration. Uranium was determined by adding enough ^{236}U to the sample to provide a $^{238}U/^{236}U$ ration of ~ 200 such that ^{236}U was run on a Faraday cup at 0.01-0.015 V. To ensure accurate U and Th concentrations, spiked fully dissolved samples were repeatedly fumed with perchloric acid before chemical separations and purification. To provide quality assurance checks on U measurements, we analysed a purified U solution derived from a modern coral.

Lawrence Livermore National Laboratory (LLNL)

Thorium isotopes: Thorium purification at LLNL was similar to the method described for WHOI (see above). Thorium isotopes were measured using a GV Instruments (originally Micromass, now Thermo-Fisher) IsoProbe MC-ICP-MS. Thorium, in 2% v/v HNO_3 solution, was introduced using a Cetac Aridus desolvating nebuliser. Rinse-out between samples was facilitated using a 5% v/v HNO_3 + 0.01 mol l^{-1} HF solution. The ^{232}Th beam was measured with a Faraday cup and the ^{230}Th beam was measured simultaneously with a Daly detector after it passed through a retarding potential filter to reduce the tailing from ^{232}Th. With the Daly detector and energy filter, the abundance sensitivities at masses 230, 230.5 and 231, were *circa* 90 ppb, 0.5 ppm and 2.2 ppm, respectively, all relative to mass 232. With the sample beam present, the detector baseline

values for ^{230}Th were measured at 229.5 and 230.5, and, for the results reported here, a linear average value was used at mass 230, which over-corrected ^{230}Th for ^{232}Th tailing. For a 60 pA ^{232}Th beam, the overcorrection was roughly 9.8 aA (61 cps) and implied that the $^{230}Th/^{232}Th$ values for IRMM-36 and IRMM-35 should be biased by about -5% and -1.4%, respectively. However, the results for these reference samples, as measured at LLNL, indicated a more consistent bias of -2.6% and -2.1%, relative to the average results normalised to Th "A" (see following discussion). Therefore, it is likely that an offsetting bias enhanced the ^{230}Th signal.

One relatively large component of the signal at mass 230, as measured on the IsoProbe, was the on-peak background. The magnitude of this isobaric interference varied from one analytical session to another, but appeared to be relatively constant on a given day. Typical values were 30 to 200 cps, which may have corresponded to as much as 10% of the total ^{230}Th signal, depending on the sample. The on-peak background was measured before each sample analysis on the matrix used to dilute the sample; 2% v/v HNO_3 in this case, and was subtracted from the sample results. It may be that the isobaric interference at mass 230 was enhanced during introduction of the sample, resulting in a positive bias. Such an effect could explain why the relative deviation from the average normalised value of $^{230}Th/^{232}Th$ measured for IRMM-36 at LLNL was comparable to that for IRMM-35, even though the ratios differed by a factor of about 3.7.

After baseline and on-peak background corrections, the signal at mass 230 was corrected for the relative detector gain factor, and the $^{230}Th/^{232}Th$ ratio was corrected for instrumental mass bias. Both the Daly detector gain factor and the exponent for an exponential mass bias correction were determined using uranium reference samples analysed, at a minimum, before and after the Th sample analyses. The methodology was similar to that utilised at Macquarie. While both the Daly gain factor and the mass bias, as measured using uranium, were very stable over the course of an analytical session (less than 0.2% relative drift in the gain, and less than 0.05% relative drift in the mass bias), the average daily variation for $^{230}Th/^{232}Th$ for replicate reference samples (e.g., UCSC Th "A") was 0.6%. This excess variation was probably caused by a combination of variations in on-peak background, possibly from erratic Th rinse-out of samples run earlier, and variations in the baseline correction due to peak drift (magnetic

field and accelerating voltage instability). Note that no concentration data were reported from LLNL.

Appendix B.
Discussion of the pedigree for synthetic and rock Th isotope reference materials

Here we discuss the pedigree, highlight differences and similarities in our results and earlier TIMS and PIMS compilations, and detail our calculations of nominal consensus values and estimates of uncertainty for each of the synthetic and rock Th isotope reference samples we have investigated.

Synthetic reference samples

UCSC Th "A": UCSC Th "A" was made in 1989 by Ross Williams and Jim Gill from a mixture of NBS ^{230}Th and stock ^{232}Th solutions in proportions of about 5 x10^{-6} (note that the gravimetric ^{230}Th/^{232}Th ratio of this reference sample is unknown, contrary to information given in Rubin 2001). Initial measurement of its ^{230}Th/^{232}Th ratio at UCSC by TIMS was 5.86 x 10^{-6}, which is within error to the now-accepted value. Because this was one of the first synthetic Th isotope reference samples and it was widely distributed and analysed, it is probably the best characterised of any synthetic Th reference material. It is, however, no longer available.

In this study WHOI and UIUC used UCSC Th "A" as a bracketing calibrator and so no data are reported from these laboratories. For the other laboratories that used U calibrators or other Th calibrators for bracketing, their measured UCSC Th "A" data are tabulated in Table 2 and shown in Figure 1. Compiled literature data from Rubin (2001), Layne and Sims (2001), Pietruszka et al. (2002) and Turner et al. (2001) are also shown in Figure 1 and tabulated in Appendix Table A1. The Rubin compilation for UCSC (n = 255) encompasses most (if not all) of the then published TIMS data for this reference sample. The TIMS and SIMS measurements were not fractionation-corrected; however, the convergence of these numbers provides the best justification for using the TIMS compilation number from Rubin (2001).

Although the uncertainties of most measurements and compilations overlap, all of the U-normalised MC-ICP-MS UCSC Th "A" data fall slightly below the tightly clustered TIMS and SIMS compilations. The Th bracketed MC-ICP-MS (Bristol) data is also consistent with the TIMS and SIMS data. This lower ^{230}Th/^{232}Th for the U normalised MC-ICP-MS data is likely to be due to differences in U versus Th behaviour with respect to RPQ transmission and mass bias as well as possible changes in linearity when using U calibrators with count rates that exceed that of the Th samples (Ball et al. accepted; Hoffmann et al. 2007).

Because referencing thorium isotopic measurements to known uranium calibrators is problematic for MC-ICP-MS, acceptance of a thorium reference material for isotopic composition determinations is critical. While UCSC Th "A" is an ideal normalising calibrator in that it is the best characterised of any synthetic Th reference material, it is no longer available for distribution. Thus, one of the goals of this study has been to anchor the other less well-characterised reference materials to a common value for UCSC Th "A", thereby providing the emerging U-series community with a long-term reference against which to compare isotope values.

In this regard is important to note that the Rubin (2001) TIMS value we have adopted has a 1.2% (2s SD) uncertainty, which clearly limits our absolute knowledge of any reference materials normalised to this value. As often discussed, a ^{229}Th spiking of this or another reference material made by IRMM would provide the best absolute constraint on a ratio, if the ^{229}Th spike were calibrated to much better than 1%.

OU Th "U": This reference sample was made by Frank McDermott, Peter van Calsteren and Chris Hawkesworth at Open University in 1993, and has a nominal, but not precisely known gravimetric ^{230}Th/^{232}Th of 5.046 x 10^{-6}. Several subsequent TIMS and MC-ICP-MS data sets have been published for this reference sample and are compiled in van Calsteren and Schweiters (1995), Turner et al. (1997), Thomas et al. (1999) and Turner et al. (2001) (Table A1).

Although all uncertainties overlap, there is better agreement among the "un"-normalised data than there is with the UCSC Th "A" normalised data (Figure 2). However, in both cases the inter-laboratory variability is comparable to most groups' intra-laboratory variability (Tables 2 and 3). The two TIMS compilations (Turner et al. 1997, Thomas et al. 1999) are slightly lower than the MC-ICP-MS data, and thus slightly reduce the "normalised" consensus average (Figure 2; Table 3).

WUN: Woods Hole, UCLA, National High Magnetics Laboratory synthetic Th isotope reference

Table A1.
Reported literature values for synthetic and rock Th isotope reference materials

	Method	N	Reported $^{230}Th/^{232}Th$ (x 10⁻⁶)	Abs. std. dev. (2s) (x 10⁻⁶)	Corrected $^{230}Th/^{232}Th$ (x 10⁻⁶)	Abs. std. dev. (2s) (x 10⁻⁶)	Reference
Synthetic reference material							
IRMM-35	Gravimetry	-	11.481	0.078	-	-	IRMM (1997)
	MC-ICP-MS	19	11.465	0.022	-	-	Jicha *et al.* (2005)
IRMM-36	Gravimetry	-	3.113	0.078	-	-	IRMM (1997)
OU Th "U"	MC-ICP-MS	8	6.176	0.062	6.204	0.061	Turner *et al.* (2001)
	TIMS	19	6.116	0.061	-	-	Turner *et al.* (1997)
	TIMS	22	6.131	0.042	-	-	Thomas *et al.* (1999)
WUN	MC-ICP-MS	24	4.317	0.013	4.340	0.013	Pietruszka *et al.* (2002)
	SIMS	4	4.338	0.022	4.344	0.022	Layne and Sims (2001)
	SIMS	?	4.297	0.045	-	-	Zou *et al.* (2002)
	TIMS	6	4.342	0.047	-	-	Zou *et al.* (2003)
UCSC Th "A"	TIMS	255	5.856	0.070	-	-	Rubin (2001)
	SIMS	20	5.848	0.041	-	-	Layne and Sims (2001)
	MC-ICP-MS	17	5.825	0.012	-	-	Pietruszka *et al.* (2001)
	MC-ICP-MS	7	5.830	0.033	-	-	Turner *et al.* (2001)
	TIMS	7	5.848	0.041	-	-	Finnigan (unpublished)
Rock reference material							
ATHO	TIMS	29	5.481	0.021	-	-	Rubin (2001)
	SIMS	5	5.453	0.016	5.460	0.016	Layne and Sims (2001)
	MC-ICP-MS	6	5.490	0.051	5.519	0.051	Turner *et al.* (2001)
	TIMS	7	5.538	0.032	-	-	Kokfelt *et al.* (2003)
	TIMS	2	5.484	0.003	-	-	Thomas *et al.* (1999)
	MC-ICP-MS	5	5.477	0.011	-	-	Jicha *et al.* (2005)
TML	TIMS	82	5.788	0.048	-	-	Rubin (2001)
	SIMS	2	5.824	0.032	5.832	0.032	Layne and Sims (2001)
	MC-ICP-MS	25	5.800	0.013	5.831	0.013	Pietruszka *et al.* (2001)
	MC-ICP-MS	7	5.780	0.046	5.810	0.046	Turner *et al.* (2001)
	TIMS	2	5.889	0.032	-	-	Kokfelt *et al.* (2003)
	TIMS	37	5.872	0.052	-	-	Zou *et al.* (2003)
	MC-ICP-MS	8	5.742	0.007	-	-	Lou *et al.* (1997)
	MC-ICP-MS	7	5.746	0.005	-	-	Jicha *et al.* (2005)
AGV-1	TIMS	3	4.947	0.006	4.956	0.006	Reid and Ramos (1996)
JB-1	TIMS	3	2.967	0.007	2.972	0.007	Reid and Ramos (1996)

(1) Most of these references represent compilations taken from other publications.
(2) Samples with reported UCSC Th "A" data are corrected to Rubin (2001) value for UCSC Th "A" of 5.856 x 10⁻⁶.
(3) Reid and Ramos (1996) UCSC Th "A" and TML data are compiled in Rubin (2001).

material (WUN) was made by Alan Zindler in collaboration with Ken Sims and Mary Reid. When it was initially distributed the nominal gravimetric $^{230}Th/^{232}Th$ was given as 4.35 x 10⁻⁶, but no uncertainties were ever reported.

There are several reported compilations from different TIMS, SIMS and MC-ICP-MS efforts shown in Figure 3 and tabulated in appendix Table A1. Layne and Sims (2001) report data from WHOI measured by Cameca IMS 1270; Zou *et al.* (2002) are a compila-

tion of Th isotope data from the National High Magnetics Laboratory measured by SIMS using the VG ISOLAB; Zou *et al.* (2003) is the UCLA compilation measured by HAS-TIMS using the VG Sector 54/354; and Pietruszka *et al.* (2002) were measured by MC-ICP-MS using the VG P54-30 at Department of Terrestrial Magnetism at Carnegie in Washington DC.

As observed for most Th isotopic reference materials (except OU Th "U") the U-normalised MC-ICP-MS data (particularly LLNL) are lower than the SIMS or

TIMS data and the Th-calibrator bracketed MC-ICP-MS data. It is also worth noting that both intra-laboratory variability and inter-laboratory variability for WUN is larger than the other synthetic reference materials. The large propagated error estimate for our consensus value of this reference material (Table 3) is driven by the large uncertainty from UCSC (Table 1, Figure 3).

IRMM 35 and 36: These synthetic reference materials were made gravimetrically and certified by the Institute for Reference Materials and Measurements (IRMM). They are the only commercially available Th isotopic reference materials. The certified gravimetric values and attendant information can be found at http://www.irmm.jrc.be/html/reference_materials_catalogue/catalogue/IRMM/index.htm. Because these samples' uncertainties are based on errors in gravimetry, the absolute uncertainty is the same for both (7.8 x 10^{-8}), which translates into 0.7% relative uncertainty for IRMM 35 and a 2.5% relative uncertainty for IRMM 36 (Table A1).

The isotopic ratios of these reference materials are not very typical of volcanic rock values, with IRMM 35 being at the extreme low end and IRMM 36 being at the extreme high end of values found in volcanic samples.

For both IRMM 35 and IRMM 36, the measured values using U normalisation are lower than the Th normalised and reported IRMM gravimetric values. When these U-normalised values are re-normalised to our adopted UCSC reference value the inter-laboratory agreement is better than 1%. When all sources of error are considered, our consensus values (Table 3) overlap the IRMM reported gravimetric values, but are significantly lower (~ 1% for IRMM 35 and ~ 2.5% for IRMM 36).

Rock reference materials

TML: Table Mountain Latite (TML) is from a stratigraphic unit by that name that includes the type locality of "latite" as defined by Ransome in 1898 as an alternative to the term trachyandesite. This reference material was collected by Ross Williams near the city of Sonora in the western foothills of the Sierra Nevada, CA, in 1986, and has been distributed by UCSC. About 70 g was crushed in tungsten carbide at UCSC to ~ 200 mesh and made available by request. The Rubin compilation is based on this material. Other aliquots of the original material were re-crushed recently and are again available upon request from J.

Table A2.
Major and trace element composition of TML

Major Element	(% m/m)
SiO_2	57.13
TiO_2	1.38
Al_2O_3	18.69
FeO^*	6.12
MnO	0.04
MgO	1.29
CaO	6.47
Na_2O	4.12
K_2O	3.44
P_2O_5	0.68
Sum	99.36

Trace element	(μg g^{-1})
Sc	15.0
Rb	167.0
Sr	782.0
Y	31.0
Zr	401.0
Nb	20.0
Cs	11.5
Ba	1314.0
La	65.0
Ce	123.0
Pr	15.4
Nd	55.0
Sm	9.63
Eu	1.84
Gd	9.36
Tb	1.03
Dy	5.34
Ho	0.95
Er	2.64
Tm	0.39
Yb	2.40
Lu	0.36
Hf	9.47
Ta	1.40
Pb	27.0
Th	30.0
U	10.5

Major elements were measured by XRF at WSU with estimated precision and accuracy of 1%. Trace elements were measured by HR-ICPMS at UCSC with estimated precision and accuracy of 1-3%. Full analytical details are given by Ryder *et al.* (2006).
* Total Fe.

Gill. Table A2 provides its chemical composition (J. Gill, analyst). TML has large plagioclase phenocrysts accompanied by augite phenocrysts of variable size. Its age is 10.2 ± 0.1 Ma and it is part of a suite of high-K, high-HFSE magmas that spread southward through the Sierras in the Miocene (Busby *et al.* 2008). TML was sampled from a single lava flow that extends from the Sierra crest to the eastern edge of the Great Valley, and was erupted during cryptochron C5n.2n-1 with a distinctive palaeomagnetic direction (equivalent to Flow 14 in Busby *et al.* 2008). A different sample

from the same flow was used as an in-house INAA reference material by A. Smith at LBL.

The Rubin compilation for TML (n = 42) encompasses most of the then published TIMS data for this reference material. Subsequent compilations also included here are: Layne and Sims (2001) WHOI compilation of SIMS data using the Cameca IMS 127O; Zou *et al.* (2003) UCLA compilation measured by HAS-TIMS using the VG Sector 54/354; Kokefelt *et al.* (2003) compilation measured by HAS-TIMS using Finnigan MAT 262 (with RPQ-II); and Pietruszka *et al.* (2002) DTM compilation measured by MC-ICP-MS using the VG P54-30. Also included is the MC-ICP-MS compilation of Turner *et al.* (2001), which is not included in the Rubin (2001) compilation.

Despite this sample's heterogeneity, the inter-laboratory and intra-laboratory variability of this rock reference material is ‹ 1%, which is comparable to the synthetic Th reference samples. The GEMOC U normalised number is similar to the working group and overall consensus value (Table 3), whereas the re-normalised number is shifted toward the upper limit of this consensus value. The TIMS values from Kokfelt *et al.* (2003) and Zou *et al.* (2003) are on the high end, but still within the collective uncertainties of the consensus values (Table 3, appendix Table A1).

An important characteristic of this reference material is that it is in radioactive equilibrium with respect to U- decay series nuclides, thus measurement of $(^{238}U/^{232}Th)$ and $(^{230}Th/^{232}Th)$ provide important constraints on both accuracy and precision (Table 4).

ATHO: ATHO is a Holocene Icelandic rhyolite obsidian provided to the U-series community by M. Condomines and O. Sigmarsson. The Rubin (2001) compilation for AThO (n = 29) encompasses most of the then published TIMS data for this reference material. Other data in our compilation include recent HAS-TIMS measurements (Thomas *et al.* 1999, Kokfelt *et al.* 2003, Zou *et al.* 2003), SIMS measurements (Layne and Sims 2001) and MC-ICP-MS data (Turner *et al.* 2001).

Inter-laboratory agreement for the three working group laboratories (WHOI, UCSC, UIUC) that measured this reference material (0.14% 2*s*) is better than their intra-laboratory reproducibility. Overall reproducibility, including the literature data, is better than 1%. While this reference material appears to be slightly more homogeneous than TML and lower in U and Th

concentrations, it is too young to be in equilibrium with respect to ^{238}U-^{230}Th (Table 4).

BCR-2: BCR-2 is a USGS basalt reference material from the Columbia River and was collected in 1996 from the Bridal Veil Flow Quarry. The quarry, located approximately 29 miles east of Portland, Oregon, is the same collection site used to provide material for BCR-1. Details of sample collection, mineralogy, and elemental concentrations can be found at: http://minerals.cr.usgs.gov/geo_chem_stand/basaltbcr2.html

For the three working groups (WHOI, UIUC, Bristol) that measured this reference material (Figure 8) the inter-laboratory agreement is better than their intra-laboratory reproducibility (Tables 1 and 2). Like TML, an important characteristic of BCR-2 is that the U-series nuclides are in radioactive equilibrium, so that measurement of $(^{238}U/^{232}Th)$ and $(^{230}Th/^{232}Th)$ provide important constraints on both accuracy and precision (Table 4). This reference material has the additional advantage of having lower concentrations than TML, making it a better quality assurance measure for low concentration basaltic measurements.

W-2: W-2 is a USGS diabase reference material collected in 1976 from the Bull Run quarry near Centreville, Virginia. This is the same collection site as USGS reference materials W-1. Details of sample collection, mineralogy, and elemental concentrations can be found at: http://minerals.cr.usgs.gov/geo_chem_stand/diabase.html

To our knowledge the data presented here are the first reported U-series data for this reference material (Tables 1-3). Since only two laboratories measured W-2 (WHOI, GEMOC), average consensus values were not calculated; however, the measurements of these two laboratories agree within 1%. Again, this reference material is in radioactive equilibrium with respect to ^{238}U-^{230}Th and its low concentrations of Th and U make it an ideal quality assurance RM for basaltic measurements.

BHVO-2: BHVO-2 is a USGS Hawaiian basalt reference material (Basalt Hawaiian Volcanic Observatory) that was taken from the surface layer of the pahoehoe lava that overflowed from the Halemaumau crater in the autumn of 1919. This is the same location used to provide material for BHVO-1. Details of sample collection, mineralogy and elemental concentrations can be found at: http://minerals.cr.usgs.gov/geo_chem_stand/basaltbhvo2.html

Pietruszka *et al.* (2002) report a compilation of Th isotope and U and Th concentrations for this same 1919 lava flow measured at University of Hawaii in Rubin's laboratory and at DTM. Though these measurements are not from the official reference material distributed by the USGS, the Th isotopes reported by Pietruszka *et al.* (2002) (Table A1) are in excellent agreement with the WHOI data reported here (Table 2).

AGV-1: AGV-1 is a USGS andesite reference material, collected from the eastern side of Guano Valley in Lake County, Oregon (see http://minerals.cr.usgs.gov/geo_chem_stand/andesite1.html).

This reference material has been replaced by AGV-2. The only U-series data reported for AGV-1 that we know of come from Reid and Ramos (1996).

JB-1: JB-1 is a Japenese basalt reference material, collected from the 7.6 Ma Kitamatsuura basalt, from Sasebo, of the Nagasaki Prefecture (Kurasawa 1968). This reference material, which was first issued in 1968 by the Geological Survey of Japan (GSJ), has been replaced by JB-1a (1984), which was collected at the same locality. Details of sample collection, mineralogy, and elemental concentrations (Sims *et al.* 1989) can be found at: http://riodb02.ibase.aist.go.jp/geostand/. To our knowledge Reid and Ramos (1996) have published the only U-series data reported for this sample.