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International Journal of Mass Spectrometry 237 (2004) 107–118

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Toward epsilon levels of measurement precision on ^{234}U/^{238}U by using MC-ICPMS

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Received 3 June 2004; accepted 12 July 2004

Abstract

Variations in ^{234}U/^{238}U have wide-ranging applications as tracers for ground- and river-water fluxes and is an essential component in U-series dating. Analytical developments for measuring ^{234}U/^{238}U have progressed from direct alpha-counting, with precisions at the percent level, to thermal ionization and multiple-collector inductively coupled plasma mass spectrometry (TIMS and MC-ICPMS, respectively) isotopic measurement techniques. However, ^{234}U/^{238}U is difficult to measure with better than permil precision because of the small atomic ratios for most geological samples ($\sim 10^{-4}$ range). Using a Nu Instruments Nu Plasma MC-ICPMS, we have developed two analytical techniques for the precise measurement of ^{234}U/^{238}U: (1) a conventional standard-bracketing protocol using multiple Faraday cups and electron multipliers with ion counting capabilities (FM) and (2) a standard-bracketing Faraday cup protocol (FF). Both are capable of measuring ^{234}U/^{238}U with precisions at the epsilon level (1 epsilon = 1 part in 10^4):

(1) The conventional standard-bracketing FM measurements are conducted as static measurements with the minor ^{234}U isotope measured in a conventional discrete dynode electron multiplier (SEM) equipped with ion counter and a retardation filter. The Faraday-multiplier gain is measured using bracketing measurements of the U metal standard CRM-145. The external reproducibility of ^{234}U/^{238}U (reformulated into δ-notation as δ^{234}U), interspersed with frequent measurements of the gain, is at the ±0.6‰ level (2σ) for both uraninite and carbonate standards, takes ∼75 min and consumes ∼120 ng of U per measurement.

(2) The static standard-bracketing FF protocol measures all three natural U isotopes in Faraday collectors. This is not usually possible using a standard multiple-Faraday array due to the large differences in the abundances of naturally occurring U isotopes. In our study, this is achieved by replacing the standard $10^{11}\ \Omega$ resistor for the ^{238}U Faraday cup with a $10^{9}\ \Omega$ resistor. The $10^{9}\ \Omega$ resistor enables the measurement of ion beams that are ∼100 times larger than can be accommodated by the normal $10^{11}\ \Omega$ resistor, so ^{238}U and ^{234}U are measured simultaneously in Faraday cups with intensities of $\sim 9 \times 10^{-9}$ and $\sim 5 \times 10^{-13}$ A, respectively. All measurements are normalized to bracketing CRM-145 standard measurements (measured with similar ^{238}U signal intensities) thereby correcting for significant tailing from the large ^{238}U ion beam below the smaller ^{234}U beam. Measurements are conducted over 2 min on-peak and 400–650 ng of ^{238}U is required per analysis. External reproducibility for samples with low matrix/U ratios (e.g., uraninites) is better than ±0.3‰ (2σ). Coral samples show a slightly poorer external reproducibility of ±0.4‰ (2σ) due to a higher matrix/U ratios of these samples.

Repeat measurements of CRM-145 give respective δ^{234}U values of -36.44 ± 0.10‰ ($2\sigma_m$, $n = 9$) and -36.50 ± 0.14‰ ($2\sigma_m$, $n = 54$) using the FF and FM analytical technique, assuming Harwell uraninite (HU-1) is in secular equilibrium with respect to ^{234}U/^{238}U. The improved analytical precision achieved in this study for ^{234}U/^{238}U measurement is superior to any other reported measurements and is of great importance for U-series dating errors, particularly for samples older than 300,000 years before present.

Keywords: MC-ICPMS; Uranium; Isotope; U-series

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doi:10.1016/j.ijms.2004.07.004

1. Introduction

Natural uranium (U) has three radioactive isotopes: ^{238}U, ^{235}U and ^{234}U. The isotopes ^{238}U and ^{235}U are radioactive parent nuclides, characterized by relatively long half-lives (4.5 and 0.7 gigayears, respectively), which ultimately decay to stable ^{206}Pb and ^{207}Pb, respectively. The ratio between ^{238}U and ^{235}U is generally assumed to be 137.88 [1] and uniform in the Earth. The ^{234}U and ^{230}Th isotopes are intermediate daughter products of the ^{238}U decay chain, and characterized by "short" half-lives of 245 and 76 ka (kiloyears), respectively. The short half-life of ^{234}U should result in a steady state of secular equilibrium between ^{234}U and ^{238}U at the present day, yielding a constant ^{234}U/^{238}U of 5.4887×10^{-5} or δ^{234}U = 0, where $\delta^{234}\text{U} = ((^{234}\text{U}/^{238}\text{U}_{\text{sample}})/(^{234}\text{U}/^{238}\text{U}_{\text{sec.eq.}}) - 1) \times 10^3$ [2]. However, this is often not the case due to the combined effects of alpha-recoil from mineral grains during ^{238}U decay and subsequent damage to the crystal lattice. As a result, loosely bound ^{234}U is more susceptible to preferential extraction from minerals than lattice-bound ^{238}U [3]. Thus sea-surface water has a ∼15% excess of ^{234}U compared to the secular equilibrium value (e.g., [4]) and more extreme ^{234}U excesses can be found in river- and ground-waters (e.g., [5–7]). These ^{234}U excesses can be used as a tracer for monitoring weathering rates, together with river- and ground-water flow patterns. The disequilibrium of ^{234}U/^{238}U is also used in radioactive waste disposal studies to review the stability of potential geological storage areas (e.g., [8]). For U-series dating purposes, ^{234}U/^{238}U is a necessary component in the U-series age equation, for which accurate and precise measurements of ^{234}U/^{238}U are critical. Good precision on these measurements is especially important for samples approaching secular equilibrium (e.g., 250–600 ka) and significantly reduces age uncertainties. Uranium-series dating has been of major importance for paleoclimate research [9] and for studying the ages and magmatic timescales for young (<600 ka) volcanism [10]. A wide range of carbonate materials, such as sea-surface coral, speleothem and aragonitic slope sediments, have been accurately dated by U-series methods and used as proxies for climate research (e.g., [9,11–13]). For samples where the initial ^{234}U/^{238}U is known, ^{234}U/^{238}U measurements can be used to assess the reliability of the U-series age; diagenesis tends to disturb the U-series isotope systematics, offsetting the ^{230}Th-age from the true sample age (e.g., [14]). In fossil coral, a commonly used method for testing age reliability has been to compare the back-calculated initial ^{234}U/^{238}U with the known present day seawater value, and discard ages with anomalous ^{234}U/^{238}U [15,16]. For the U-series dating of mid-ocean ridge basalt (MORB), the measured ^{234}U/^{238}U has been used for assessing the possibility of seawater interaction [10].

Uranium isotopic measurement is exceedingly difficult due to large differences in abundance between ^{238}U, ^{235}U and ^{234}U (e.g., ^{238}U/^{235}U ∼140 and ^{238}U/^{234}U $\sim 10^4$). Over the last decade, analytical developments in U-series dating by multiple-collector mass spectrometry (both TIMS and MC-ICPMS) have emphasised high precision measurements using small sample sizes. It is now possible to routinely measure both ^{234}U/^{238}U and ^{230}Th/^{238}U with 1–2‰ uncertainties (2σ) using only a few tens of nanograms of uranium [17,18]. Because uranium sample size is no longer a limiting factor for many U-series studies, this study focuses on significantly improving precision in ^{234}U/^{238}U measurement by increasing sample size while maintaining a manageable measurement protocol. Our newly developed techniques allow ^{234}U/^{238}U to be measured with 2σ analytical uncertainties of better than ±0.3 and 0.4‰ in uraninites and coral samples, respectively.

2. Analytical developments

The earliest U isotopic measurements were conducted by alpha-counting spectrometry (e.g., [19]). These methods consumed large amounts of sample material, and required analysis times of up to several weeks to attain analytical precisions at the percent level [17].

The development of direct U isotopic ratio measurement by thermal ionization mass spectrometry (TIMS) in the late 1980s (e.g., [9]) had an enormous impact on U-series analysis, significantly improving precision to the permil level for the best measurements (Table 1) [2,4,8,12,15,20–32]. During the last decade, U-series measurement has further improved with the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS). This reflects four important advantages of MC-ICPMS:

1. Uranium and thorium can be ionized relatively easily in a hot plasma source compared to the inefficiency of surface ionization in TIMS [33].
2. An instrumental mass bias correction can be applied to Th measurements using admixed U [24].
3. Uranium and Th isotopic compositions can be measured in situ using laser ablation [34,35].
4. The use of multiple multiplier systems makes it possible to measure ^{234}U and ^{230}Th simultaneously in the same measurement routine [18].

A fifth advantage, that hitherto has not been fully exploited, is that one can achieve higher precision and overcome the limitations of detector noise, counting statistics and background interferences by simply using a more concentrated solution.

Many of the above issues have focused on measuring Th more precisely. However, the precise and accurate measurement of ^{234}U/^{238}U can also be a limiting factor for U-series studies. This ratio is normally corrected for instrumental mass fractionation by internal normalization of the measured ^{238}U/^{235}U against the assumed natural ratio of 137.88 [9] or by normalization against a well-characterized ^{236}U–^{233}U double U spike [8,10]. The extreme differences in isotopic abundance of the U isotopes, and the very low abundance of ^{234}U, gives rise to two problems that must be overcome.

Table 1
^{234}U/^{238}U measurements of the most commonly used U standards CRM-145 (also known as NIST SRM 960 and NBL 112a) and Harwell uraninite (HU-1) reported by previous workers

	^{234}U/^{238}U ($\times 10^{-5}$)	δ^{234}U (‰)[a]	2σ[b]	$2\sigma_m$[c]	n[d]	U (ng)[e]
Metal standard CRM-145						
TIMS						
(1)[f] Chen et al. [4]	5.267	−40.4	4.2	5–7	6	30
(2) Banner et al. [20]	5.277	−38.6	3.8	6–8	4	50–300
(3) Stein et al. [21]	5.267	−40.4	8.1	6–9	8	150–450
(4) Edwards et al. [22]	5.285	−37.0	1.2	∼1.2	8	–
(5) Eisenhauer et al. [23]	5.310	−32.6	10	5–8	4	–
(6) Stirling et al. [15]	5.288	−36.6	1.7	∼1–2	6	–
(7) Luo et al. [24]	5.284	−37.3	3.0	1–5	14	200–600
(8) Israelson and Wohlrarth [25]	5.29	−36.2	5.7	6	7	–
(9) Cheng et al. [2]	5.286	−36.9	2.2	∼1	21	–
(10) Yokoyama et al. [26]	5.284	−37.3	2.2	1.1–2.5	8	50
(11) Delanghe et al. [27]	5.283	−37.6	1.9	0.8–1.9	33	1000
ICP-MS						
(12) Shen et al. [28]	5.285	−37.1	1.2	1.2–2.4	10	36
MC-ICPMS Faraday–multiplier						
(13) Luo et al. [24]	5.286	−36.9	1.1	1.2–1.4	8	450
(14)	5.286	−36.9	1.5	0.9–1.6	11	300
(15) Robinson et al. [29]	5.287	−36.7	1.7	∼1–2	8	–
(16) Hellstrom [30]	5.290	−36.3	2.7	∼2–6	21	5–40
MC-ICPMS Faradays						
(17) Deschamps et al. [8]	5.289	−36.4	0.8	0.3–0.6	19	>200
Harwell Uraninite HU-1						
TIMS						
Ludwig et al. [12]	5.490	+0.2	3.1	∼0.6	29	–
McCulloch and Esat [31]	5.474	−2.7	3.5	∼1	19	–
Cheng et al. [2]	5.488	−0.1	0.7	0.8–1.1	8	–
Delanghe et al. [27]	5.484	−0.9	1.8	0.6–2.2	19	1000
Neef et al. [32]	5.480	−1.5	3.6	–	16	–
ICP-MS						
Shen et al. [28]	5.491	+0.4	1.4	–	–	–
MC-ICPMS Faraday–multiplier						
Hellstrom [30]	5.482	−1.2	–	–	–	–

[a] Permil deviation of ^{234}U/^{238}U from the assumed value for secular equilibrium; defined as $\delta^{234}\mathrm{U}\ (‰) = (^{234}\mathrm{U}/^{238}\mathrm{U}_{\mathrm{sample}}/^{234}\mathrm{U}/^{238}\mathrm{U}_{\mathrm{sec.eq}}) - 1) \times 1000$, where $^{234}\mathrm{U}/^{238}\mathrm{U}_{\mathrm{sec.eq}} = 5.4887 \times 10^{-5}$ [2].

[b] External reproducibility of measurements.

[c] Internal error of measurements.

[d] Number of measurements.

[e] ng of U used per analysis.

[f] Refs. used in Fig. 8.

First, it is not possible to measure ^{234}U and ^{238}U simultaneously within the limits of a standard multiple-Faraday collector array equipped with $10^{11}\ \Omega$ positive feedback resistors, given the large dynamic range of $\sim 10^4$ (10^{-10} to 10^{-14} A). It is therefore normal to measure the minor ^{234}U isotope on a low-background ion counter (IC), coupled to either a secondary electron multiplier or a Daly detector with photomultiplier, to allow the measurement range to be extended down to $\sim 10^{-14}$ to 10^{-17} A. A major problem for measurements using a mixed Faraday-multiplier array is the calibration of the relative gain. This is generally unstable and must be monitored frequently during the measurement session, in contrast to the relatively stable gain of Faraday detectors. Aside from their inherent instability, ion counter systems require a dead-time correction for amplifiers and can display intensity-dependent non-linearity effects [36].

Second, a significant "tail" from ^{238}U (and ^{235}U) exists below the ^{234}U ion beam that arises from the scattering of low energy ^{238}U ions caused by particle collisions in the mass spectrometer analyzer. The magnitude of the ^{238}U tail is thus strictly related to the mass spectrometer and expressed as an abundance sensitivity (defined by convention as the contribution from ^{238}U at mass 237) (e.g., [28,37]). This tailing problem is largely eliminated by monitoring background "zeroes" at half-masses and applying a tailing correction to ^{234}U (e.g., [24]). The magnitude of the ^{238}U tail can be further minimized when ^{234}U is measured in a mass spectrometer equipped with an energy filter, deceleration lens or second stage electrostatic analyzer (ESA) to reject the majority of scattered ions. This typically improves abundance sensitivity by an order of magnitude.

The two most widely used MC-ICPMS protocols are a static standard-bracketing procedure and a multi-static approach, initially tested by Luo et al. [24] using a VG Elemental Plasma 54 equipped with a Daly detector. In the standard-bracketing protocol, the measured sample is normalized to a well-characterized standard measured immediately before and after the unknown. The Faraday-IC gain is determined from the standard measurement, by linear interpolation and normalization of the measured $^{234}U/^{238}U$ against the true $^{234}U/^{238}U$ (e.g., [24,29]). The multi-static approach is conducted as a two-cycle measurement, by cycling both ^{234}U and ^{235}U through the ion counting (multiplier or Daly) system. In this case, the Faraday–IC relative gain is determined by normalizing the Faraday–Faraday $^{238}U/^{235}U$ measured in cycle 1 to the Faraday–IC $^{238}U/^{235}U$ measured in cycle 2 [24,34,38]. The standard-bracketing protocol is limited by a possible non-linear drift in the gain between standard measurements. This is not problematic for the multi-static approach where the gain is measured internally. However, the multi-static method can be limited by larger sample requirements and the large difference in abundance between ^{235}U and ^{234}U, as ^{235}U must be sufficiently large to allow it to be measured precisely in both a Faraday cup and electron multiplier.

Using a Nu Instruments Nu Plasma MC-ICPMS (ETH, Zürich), we present two different protocols for the accurate and precise measurement of $^{234}U/^{238}U$. The first is a conventional standard-bracketing protocol using a secondary electron multiplier for measuring ^{234}U, and obtains an extremely good precision (±0.6‰, 2σ). The second is a newly developed, highly precise and accurate standard-bracketing Faraday cup protocol using a $10^9\ \Omega$ resistor for the ^{238}U beam, allowing the simultaneous measurement of all three natural U isotopes in Faraday detectors and improving external reproducibility to better than ±0.3‰ (2σ).

3. Standard and sample preparation

All samples were prepared under clean air conditions (better than Class 100, measured as better than Class 10), using high-purity quartz- and Teflon-distilled reagents for sample dissolution and chemical preparation. Uranium was separated from matrix elements using TRU ion exchange resin (Eichrom) following the chemical protocol of Luo et al. [24]. Up to two TRU resin separations were required to obtain a high-purity U fraction, free of matrix elements. In addition, samples containing a large proportion of organic material, such as old corals, were treated repeatedly with highly oxidizing H_2O_2 (30% concentration) throughout the chemical procedure, in order to break down organic compounds associated with both the sample and the TRU resin. The total chemistry blank is negligible (<10 pg of ^{238}U; 10^{-12} g/g) and removes the necessity for a U blank correction.

4. Analytical procedure

The Nu Plasma MC-ICPMS is equipped with 12 Faraday collectors and 3 discrete dynode secondary electron multipliers (SEM) operating in pulse counting mode with ion counters. The central SEM with ion counter (IC1) is equipped with a retardation filter (Fig. 1). Detailed information on the instrument can be found elsewhere [39–42]. Measurements are conducted using an RF power of 1350 W and at normal mass resolution ($\Delta M/M \sim 400$). Sample solutions are aspirated into the plasma source through an MCN 6000 Cetac micro-concentric nebulizer and desolvator system (aspiration rate ~100 μl/min) with Ar and N_2 support gas. At the time of these experiments, sensitivity for U was ~5‰, and the instrumental mass bias was ~4–6‰ amu^{-1}. Abundance sensitivity is of the order of 2.5–5 ppm amu^{-1} and correlates approximately linearly with the vacuum pressure in the analyzer chamber (~$2\text{–}5 \times 10^{-9}$ mbar). All sample and standard solutions are dissolved in ~0.3N HNO_3 for solution aspiration, and acid washout between measurements is performed over several minutes using alternate solutions of 0.3N HNO_3

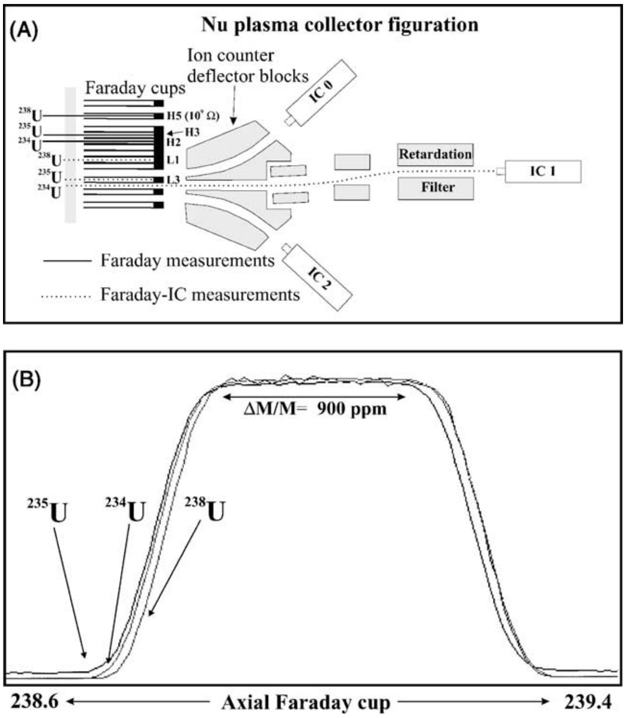

Fig. 1. A. Schematic overview of the collector array for the Nu Instruments Nu Plasma MC-ICPMS. This instrument has an array of 12 Faraday collectors. Collector H5 is equipped with a $10^9\ \Omega$ resistor and the other collectors are fitted with "standard" $10^{11}\ \Omega$ resistors. Low intensity ion beams, such as ^{234}U, can be focused onto one of three secondary electron multipliers with ion counter detector systems, located behind the Faraday array. The central IC1 detector is equipped with a retardation filter, allowing scattered low-energy ions to be rejected. B. Flat-topped peak shapes and alignment of the natural ^{238}U, ^{235}U and ^{234}U isotopes for Faraday–multiplier standard-bracketing measurements. ^{234}U is measured in IC1, while ^{235}U and ^{238}U are measured simultaneously in the L3 and L1 Faraday cups.

and 0.3N HF–0.1N HCl until the ^{238}U intensity diminishes to <0.1‰ of the next running signal intensity.

The CRM-145 U metal standard is used for optimizing intensity and achieving aligned flat-topped peak shapes for the three natural U isotopes (Fig. 1). CRM-145 is also used as a bracketing standard for both analytical protocols, assuming it has a ^{234}U/^{238}U of 5.285×10^{-5} (δ^{234}U = −37.1‰), based on the average of 17 values published by earlier workers (Table 1). All measurements of ^{234}U/^{238}U were corrected for the instrumental mass bias using the exponential mass fractionation law [43], by normalising the measured ^{238}U/^{235}U to the assumed natural ratio of 137.88. In the present study, analytical performance is primarily based on the external reproducibility of a series of measurements for the same sample/standard, reported here as two standard deviations of the mean or 2σ. Twice the standard error of the mean, or $2\sigma_{\mathrm{m}}$, is reported for: (a) the internal precision of a single analysis, and (b) the mean of a suite of replicate analyses, in order to compare measurement accuracy.

5. Conventional Faraday cup—multiplier measurements

5.1. Analytical procedure

Measurements of ^{234}U/^{238}U were conducted by measuring ^{238}U and ^{235}U in Faraday cups and ^{234}U simultaneously in the IC1 ion counter (Fig. 1, Table 2). The gain determined from the bracketing standard was applied as an average to the unknown sample. Count rates for ^{234}U were kept below 1×10^{5} cps (1.6×10^{-15} A) for two main reasons. First, determining ion counter dead-time settings accurately and precisely becomes unimportant. Second, the effect of non-linearity in the response of the SEM to variable intensities can be reduced (e.g., [36]). The IC1 retardation filter improves the abundance sensitivity to ∼0.5–1.0 ppm amu^{-1}. However, even at this level, the abundance sensitivity still produces a significant tailing effect under the ^{234}U beam. Therefore, further corrections for tailing are made by measuring baseline zeroes at half-mass and determining the background beneath each U isotope by linear interpolation. For ^{238}U intensities of $\sim 1.7 \times 10^{-10}$ A (17 V), the half-mass zero measurement yields backgrounds on 234.5 and 233.5 of ∼100 and 30 cps, respectively, which represents a significant proportion (up to ∼2‰) of the ^{234}U intensity (∼50,000 cps for samples in secular equilibrium). The interpolated background below ^{234}U is thus different if the tail profile is modeled as a linear or exponential function, changing the background corrected ^{234}U/^{238}U by up to 250 ppm. However, given that the sample is normalised to a bracketing standard, the difference in ^{234}U/^{238}U between the two zero correction methods is negligible (<25 ppm) and the more simple average background correction is used.

Table 2
Analytical protocols for ^{234}U/^{238}U measurements

	Collectors used (see Fig. 1)		
	L1, H5	L3, H2	IC1, H1
Standard (CRM-145)	*238*	*235*	234
Unknown	***238***	*235*	**234**
Standard (CRM-145)	*238*	*235*	234

Collectors L1, L3 and IC1 are used in the static Faraday-multiplier standard-bracketing mode, while H5, H2 and H1 are used in the static Faraday–Faraday standard-bracketing mode. Underlined isotopes are used for gain or tail corrections. Italicized isotopes are used for mass bias correction. Bold isotopes are used for the measured ratios.

All FM measurements are performed over 40-cycles with signal integration times of 5 s. Total acquisition times are ∼8 min (including the measurement of the background zeros) and ∼40 ng of ^{238}U is consumed per analysis. The CRM-145 standard and unknown samples are measured at similar intensities ((1.4–1.9) × 10^{-10} A, ∼60 ppb ^{238}U) to minimize possible systematic errors arising from non-linearity in the IC1 response (Table 3).

The above-mentioned analytical approach (40 cycles at (1.4–1.9) × 10^{-10} A) was found to yield the best results, based on a comparison of self-bracketing measurements of CRM-145 with varying measurement duration and signal size (Table 4):

(1) A shorter, higher intensity analysis yields better reproducibility than a longer, low intensity analysis consuming the same amount of uranium, presumably because the gain is measured more frequently.
(2) Counting statistics place a lower limit on the duration of an analysis for a given desired precision. This is demonstrated in Table 4, where the internal uncertainty increases with decreasing analysis duration.

Table 3
Analytical parameters used for the measurement protocols

	Faraday–multiplier	Faraday–Faraday
Background parameters		
Background “zero” method	Half-mass	Deflected beam
Zero integration time (s)	2 × 20	60
On-peak measurement parameters		
On-peak data integration time per cycle (s)	5	0.2
Number of cycles	2 × 20	∼600
Analysis time per measurement (min)	∼8	∼3
Washout time (min)	2–5	2–5
Total analysis time (std-sample-std)—single (min)	∼30	∼20
Total analysis time—integrated (min)	∼75	∼50
Intensity of ^{238}U (A)	(1.4–1.9) × 10^{-10}	(5.0–9.0) × 10^{-9}
U concentration	∼60 ppb	∼2–3 ppm
U sample size per single measurement	∼40 ng	∼400–650 ng

Table 4
Static Faraday–multiplier standard-bracketing

	Number of ratios	$^{234}U/^{238}U$ ($\times 10^{-5}$)	$\delta^{234}U$ (‰)	$\pm 2\sigma$[a]	$\pm 2\sigma_m$[b]	n	Sessions ratios
CRM-145 self-bracketed							
7.5 V	20	5.283	−37.4	±1.9	1.3	74	2
	40	5.284	−37.3	±1.8	0.9	36	2
	80	5.285	−37.1	±1.2	0.7	18	2
15 V	20	5.285	−37.2	±1.2	0.9	48	2
	40[c]	5.285	−37.2	±1.1	0.6	23	2
	80	5.285	−37.2	±0.9	0.4	11	2
CRM-145-sample-CRM-145							
Uraninites							
HU-1[d]	40	5.485	−0.6	±1.3	0.7	18	2
(Integrated)	120			±0.8	0.4	6	
HU-1[e]	40	5.485	−0.6	±0.9	0.7	36	10
(Integrated)	120			±0.6	0.4	12	
CZ-1	40	5.495	+1.2	±0.6	0.7	7	2
CU-1	40	5.485	−0.6	[f]	0.8	3	1
Barbados coral							
B1	40	6.142	+118.9	±1.1	0.7	9	3
B2	40	6.033	+99.1	[f]	0.7	3	1
B3	40	6.022	+97.0	[f]	0.7	3	1
Speleothem							
KOZ	40	2.940	−464.3	±0.4	0.4	6	2

[a] External reproducibility.
[b] Internal error (average).
[c] Preferred method of analysis.
[d] Non-optimized data acquisition.
[e] Optimized data acquisition.
[f] Insufficient number of measurements to use 2σ as a statistically valid uncertainty.

5.2. Limiting factors

5.2.1. Memory effects

Acid washout between measurements normally reduces ^{238}U background signals quickly (<4 min) to <0.1‰ of the following measurement intensity. However, washout can be hindered by the accumulation of U-rich droplets in the spray chamber and desolvator system. These memory effects can accumulate from much earlier measurements, introducing large systematic offsets in the measured isotopic composition (Fig. 2). Such U-rich droplets can be effectively removed by heating the entire spray chamber to ∼70 °C.

5.2.2. Matrix effects

The presence of residual matrix elements in the eluted uranium following TRU resin column separation can degrade analytical performance. This is noticeable in $^{234}U/^{238}U$ measurements for a high-matrix coral sample from Barbados, B1, that has been processed only once through TRU resin chemistry. Results for this coral show a poor long-term reproducibility compared with the CRM-145 standard (Fig. 3). A mass scan of the aspirated solution shows that Ca is the only significant matrix component (Ca/U = 10). However, the solution was not treated with H_2O_2 and also contained a significant amount of organic material. The degraded reproducibility of this solution is therefore considered to be due to the Ca matrix, combined with a significant amount of organic residue, the latter of which disturbs the uptake rate of the aspirated solution. Purifying the solution with a second TRU resin separation step lowers the Ca/U ratio to <1 and combining this with an H_2O_2 oxidation step is likely to improve reproducibility to the level of low matrix samples (see Section 5.3).

5.3. Sample measurements

5.3.1. Uraninites

Before careful control of the above-mentioned memory and matrix effects, initial measurements of the Harwell Uraninite HU-1 standard, assumed to be in secular equilibrium for $^{234}U/^{238}U$, yielded an external reproducibility of ±1.3‰ (2σ). By heating the entire spray chamber, thereby minimizing memory effects, the external reproducibility for a second aliquot of HU-1 was improved to ±0.9‰ (2σ). Importantly, both HU-1 data sets yielded identical mean $\delta^{234}U$ values (Table 4). The difference between the mean $\delta^{234}U$ values for HU-1 and CRM-145 is -36.50 ± 0.14 ($2\sigma_m$, $n = 54$) in agreement with ratios obtained in other studies (Table 1). The in-house uraninite standard CZ-1 gave an external reproducibility of ±0.6‰ (2σ) (Fig. 4).

5.3.2. Carbonates

Measurements of the B1 coral, with a Ca/U ratio of 10, gave an external reproducibility of ±1.1‰, slightly

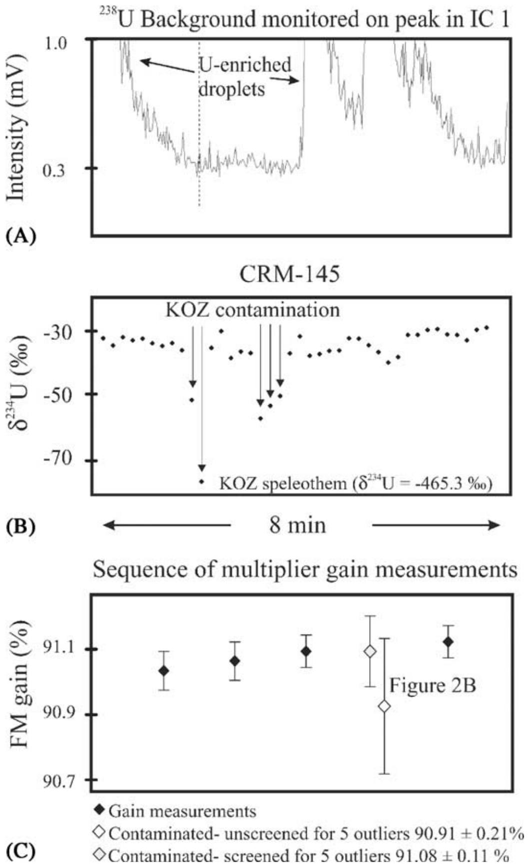

Fig. 2. (A) Intensity of ^{238}U background during acid washout. In this example the background shows a base level of ∼0.3 mV, however, condensed U-enriched droplets create episodic U "spikes" of 1–100 mV. The majority of such droplets are condensates in the spray chamber, which can be removed by heating the spray chamber to 70 °C. (B) Example of a CRM-145 measurement that has been disturbed by memory from U-enriched droplets of a speleothem sample (KOZ), highly depleted in ^{234}U, that had been measured during the previous day. Contamination from the depleted speleothem could be seen as sudden excursions in δ^{234}U to anomalously low values. These outlying data points could be readily identified and removed from the measurement sequence to improve analytical reproducibility, as shown in (C). (C) Comparison of the Faraday–multiplier gain during an analytical session, including the measurement shown in (B), which displays an anomalously low value. When screened for outliers, this gain measurement is indistinguishable from the other data points.

worse than that obtained for uraninite samples. In contrast, a well-purified, U-rich speleothem (KOZ) highly depleted in ^{234}U, shows very good behaviour with internal errors of ±0.4–0.5‰ ($2\sigma_m$) and similar reproducibility for six measurements (±0.4‰, 2σ).

5.3.3. *Integrated measurements*

In order to minimize scatter in the data caused by outliers arising from an abrupt change in the multiplier gain and improve counting statistics, single measurements can be integrated as the composite of three repeat measurements. The combined data set is treated statistically as a single measurement consisting of 120 cycles, and using the interspersed CRM-145 measurements between each set of 40-cycles to frequently monitor the gain. An integrated measurement therefore requires an analysis time of ∼75 min and consumes ∼120 ng of sample U. Integrated measurements of HU-1 improve reproducibility to ±0.6‰ (2σ) (Fig. 4, Table 4). Integrated measurements of B1 yield the same level of precision as HU-1 (±0.6‰), even including the measurements that showed a degraded reproducibility as single measurements (Fig. 3).

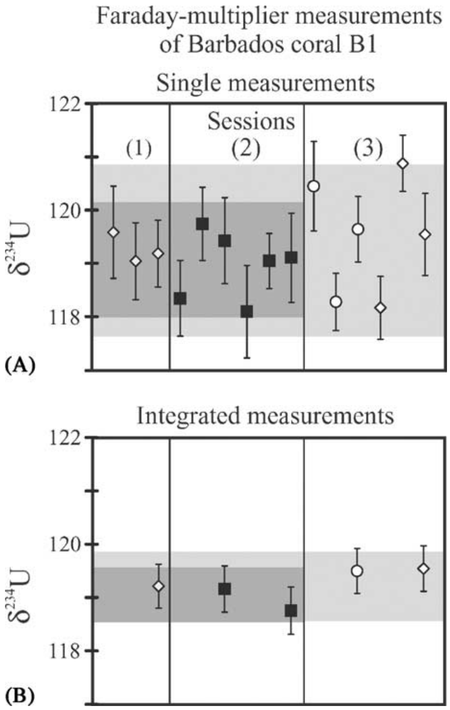

Fig. 3. δ^{234}U acquired over three independent measurement sessions for the Barbados coral B1. The result of individual 40-cycle measurements is shown in (A), whereas in (B) the same data are displayed as integrated blocks of three 40-cycle data sets. In (A), the first two sessions yield a 2σ = ±1.1‰ (dark grey band), however the reproducibility degrades during the last measurement session (2σ = ±1.6‰, lighter grey band) due to a comparatively larger proportion of Ca and organics in this sample with respect to the other two aliquots. Subsequent experiments show that a better purification of the sample would improve the reproducibility to the same level as shown by the other aliquots. Importantly, the scatter shown by the third data set is eliminated when the data are integrated over three measurements (B).

6. Multiple Faraday cup measurements

6.1. *Measurement protocol*

A previous attempt to eliminate electron multipliers from U-series isotopic measurements has been conducted by Deschamps et al. [8] who tested a static ^{235}U/^{234}U Faraday cup measurement protocol. Using a Micromass Isoprobe MC-ICPMS, this study retained the usual 10^{11} Ω resistor array, and monitored ^{234}U and ^{235}U in Faraday collectors, while simultaneously deflecting the large ^{238}U ion beam into a gap between Faraday cups to avoid saturating the collectors with

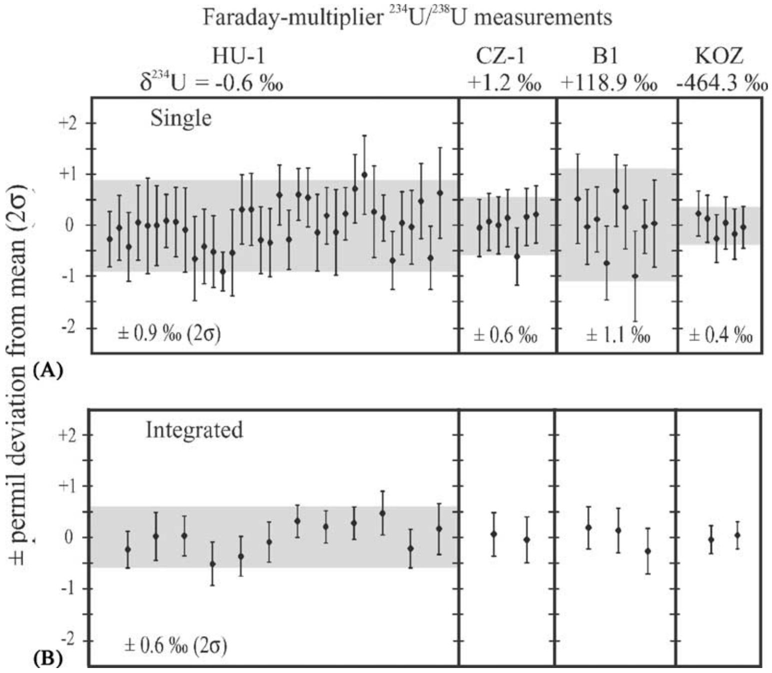

Fig. 4. Long-term 2σ reproducibility (grey bands) of the Faraday–multiplier standard-bracketing measurements for (A) single measurements, and (B) integrated measurements.

an excessively large ^{238}U signal. A ^{236}U/^{233}U spike was then used to monitor the mass bias correction. The tail contribution from the ^{238}U ion beam is significantly below the other U isotopes and was corrected for by monitoring a tail profile for a mono-isotopic solution of ^{236}U spike tracer, assuming the ^{236}U profile is identical to that for ^{238}U. The final ^{234}U/^{238}U ratio was obtained from the measured ^{234}U/^{235}U assuming a natural ^{238}U/^{235}U of 137.88. Although eliminating the dependence on ion counters, this method is still limited by small ^{234}U intensities ($\sim 5 \times 10^{-14}$ A), which only just overcome the Faraday background noise. Consequently, the reported analytical reproducibility is comparable to the one permil level that can be achieved using conventional MC-ICPMS and multiplier protocols.

For the multiple Faraday (FF) protocol developed in this study, the preamplifier connected to the ^{238}U Faraday cup was fitted with a 10^9 Ω resistor, which allows ^{238}U intensities of up to 10^{-8} A to be measured. This is a factor of 100 larger than can be accommodated by Faraday systems equipped with the usual 10^{11} Ω resistors, and makes it possible to make simultaneous Faraday cup measurements of ^{238}U ($\sim 9 \times 10^{-9}$ A), ^{235}U ($\sim 7 \times 10^{-11}$ A) and ^{234}U ($\sim 5 \times 10^{-13}$ A) in the same analysis sequence (Fig. 1, Table 2).

Uranium isotopic measurement using Faraday cups is complicated by two factors. First, the tailing of the large ^{238}U beam below the ^{234}U isotope is significant due to the lack of a retardation filter. Second, the normal procedure for minimizing tailing effects by measuring zeroes at half-mass is no longer possible due to a scattering of ions across the entire collector array when the large ^{238}U beam is deflected between collectors. To overcome these limitations, all samples are normalized to the CRM-145 bracketing standard, measured at similarly high intensities, and assuming an identical ^{238}U tailing behaviour for both sample and standard.

Measurements are conducted using a "time-resolved" protocol provided with the Nu Plasma. In time-resolved mode, background zeroes can be measured before the solution is introduced, thereby lowering sample requirements. Background zeroes are monitored for 60 s by deflecting the ion beams from the axial optical plane. The solution is then introduced and on-peak data are acquired over a 2 min period (Fig. 5). A solution containing 2–3 ppm ^{238}U yields a ^{238}U intensity of (5–9) $\times 10^{-9}$ A, and consumes ∼400–650 ng of U per analysis (Table 3). Using this technique, measurements of ^{234}U/^{238}U for the CRM-145 standard are extremely precise, with analytical errors of ±0.2‰ (2σ_m), but are generally 5–10‰ higher than the normalizing ratio (5.285 $\times 10^{-5}$) due to the ^{238}U tailing below ^{234}U. Tailing from the ^{238}U ion beam is also significant below ^{235}U, and contributes ∼1 ppm to the ^{235}U peak intensity, elevating it by ∼0.1‰. Correcting for this lowers the ^{234}U/^{238}U by a similar magnitude. However, given that all ratios are normalized to the bracketing standard, the ^{235}U correction affects both sample and standard in an identical manner and is negligible. The ^{238}U tail profile is strictly correlated with vacuum conditions in the analyzer chamber. The accuracy of the ^{234}U/^{238}U measurement is thus highly sensitive to subtle variations in the analyzer pressure over relatively short timescales spanning the duration of an analysis. The analyzer entrance valve is opened at least 30 min before the start of an analytical session to "equilibrate" the pressure in the chamber.

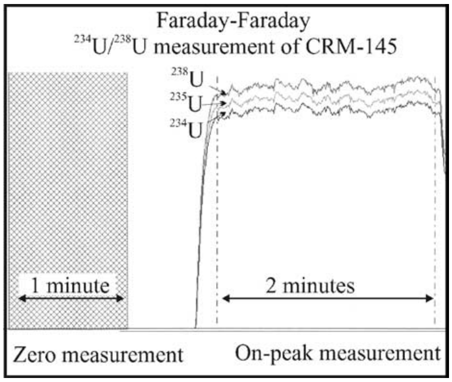

Fig. 5. Faraday–Faraday $^{234}U/^{238}U$ measurement of the CRM-145 standard. First, background zeroes are measured on-peak for 60 s while the ion beams are deflected off-axis. Thereafter, the sample or standard solution is introduced and the ion beams "grow in" and stabilize. Data are then acquired over a 2 min period as a series of 0.2 s integrations giving ∼600 ratios. The measured isotope ratios are calculated and corrected for instrumental mass fractionation off-line using a 2σ rejection criteria. In this example, measurement intensities are 9.1×10^{-9} A for ^{238}U, 6.5×10^{-11} A for ^{235}U and 4.7×10^{-13} A for ^{234}U. The measured $\delta^{234}U$, uncorrected for ^{238}U tailing beneath ^{234}U, gives a value of −27.04 ± 0.14‰ ($2\sigma_m$), ∼10‰ larger than the normalisation value of −37.12‰.

6.2. *Limiting factors for multiple Faraday cup measurements*

One of the main factors limiting accuracy and precision in $^{234}U/^{238}U$ measurement using Faraday collectors is the inherent assumption of a similar ^{238}U tail profile between the sample and CRM-145 standard. The character of the tail is significantly altered by the presence of residual matrix elements in the eluted U fraction. This is because trace impurities in the sample change the loading and energy conditions in the plasma, which can defocus the beam and create a different tail profile, yielding inaccurate results. This effect is mainly a function of the absolute amount of matrix introduced into the plasma source. This implies that for relatively "dilute" sample solutions (e.g., with ppb levels of U), accurate results can be obtained with solutions containing trace impurities. However, because our multi-Faraday measurements require sample solutions containing high ∼3 ppm concentrations of U, any residual matrix elements are also highly concentrated. For example, an aliquot of the CZ-1 uraninite (∼60 wt.% U), which had not been processed through TRU resin ion exchange chemistry, yielded $^{234}U/^{238}U$ ratios ∼1.5% higher than the true value because of a significantly larger ^{238}U tailing contribution beneath ^{235}U and ^{234}U for CZ-1 than observed for the bracketing CRM-145. Ideally it would be useful to estimate the tailing profile by monitoring the abundance sensitivity at mass 237. However, this is not possible using our current instrument configuration for U isotopic analysis. Instead, large discrepancies between tailing profiles can be monitored by measuring the tailing contribution at mass 236, expressed as a function of 236 (tail)/^{238}U. Normally, this value is ∼1 ppm and significantly different 236 (tail)/^{238}U values between CRM-145 and the unknown samples provide criteria for rejecting inaccurate results. For example, the above-mentioned CZ-1 had a 236 (tail)/^{238}U that is ∼0.7 ppm higher than the abundance effect observed for the bracketing CRM-145.

This makes it necessary to have ultra-purified U solutions. For coral samples, Ca/U ratios of ≤1 are sufficient for obtaining accurate results using this technique. Furthermore, samples should be free of organic material thereby avoiding changes in the solution uptake rate and the requirement of longer washout time between samples.

6.3. *Sample measurements*

6.3.1. *Uraninites*

Measurements of CZ-1 yield a long-term reproducibility of ±0.26‰ (2σ) (Fig. 6, Table 5). CZ-1 was measured over

Table 5
Static Faraday–Faraday standard-bracketing

	$^{234}U/^{238}U$ ($\times 10^{-5}$)	$\delta^{234}U$ (‰)	$\pm 2\sigma$[a]	$2\sigma_m$[b]	n	Sessions
Uraninites						
HU-1	5.485	−0.68	±0.31	0.24	9	3
CZ-1	5.495	+1.21	±0.26	0.23	29	7
(Integrated)			±0.14	0.13	9	
CU-1	5.485	−0.58	[c]	0.27	1	1
Corals						
B3	6.021	+96.97	[c]	0.23	2	1
B4	6.074	+106.64	±0.38	0.19	28	4
(Integrated)			±0.30	0.11	9	
B5	6.138	+118.36	±0.38	0.21	12	2
(Integrated)			±0.29	0.12	4	
Speleothem						
KOZ	2.940	−464.36	[c]	0.24	2	1

[a] External reproducibility.
[b] Internal error (average).
[c] Insufficient number of measurements to use 2σ as a statistically valid uncertainty.

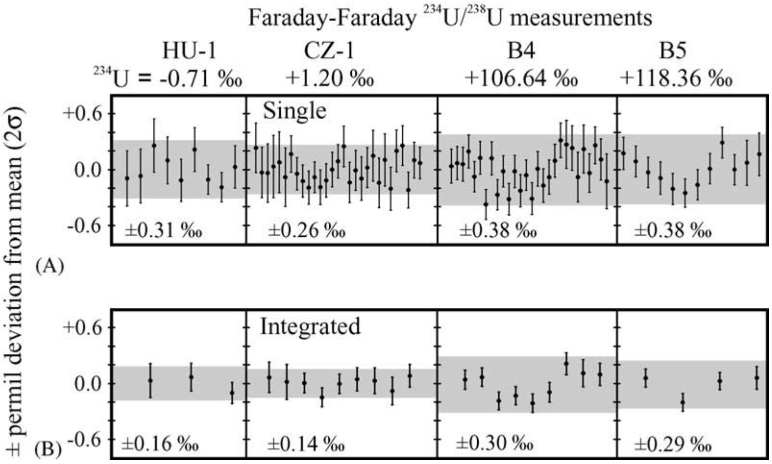

Fig. 6. Long-term 2σ reproducibility (grey bands) of the Faraday–Faraday (FF) standard-bracketing measurements for (A) single measurements, and (B) integrated measurements.

seven separate analytical sessions and on two independently processed aliquots. Repeat measurements of HU-1 give rise to a ±0.31‰ (2σ) reproducibility, and the mean values for both uraninites are in perfect agreement with the conventional FM measurements (Fig. 7).

6.3.2. Coral samples

The B3 Barbados coral yielded a δ^{234}U of +96.97 ± 0.18 (2σ_m, n = 2), in agreement with ion counter measurements on the same sample (δ^{234}U = +97.04 ± 0.47‰, 2σ_m, n = 3). The long-term reproducibility for coral samples was tested using three solutions; two independently processed aliquots of Barbados coral B4 and another Barbados coral B5. The 2 aliquots of B4 yielded identical results (δ^{234}U = +106.66 and +106.63, respectively) and the external reproducibility of the combined 28 measurements was ±0.38‰ (2σ) (Fig. 6). Sample B5 yielded a similar reproducibility of ±0.38‰ (2σ). The poorer reproducibility for coral compared to CZ-1 (±0.26‰, 2σ) is apparently due to the higher matrix/U ratio and organic content.

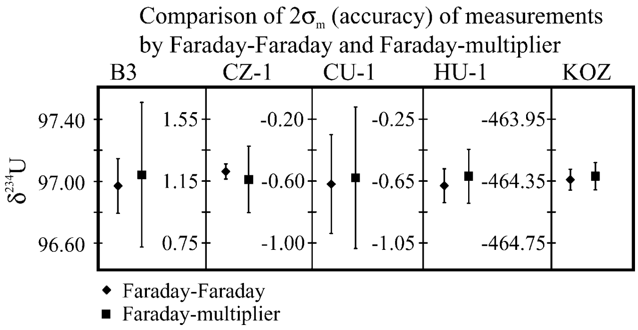

Fig. 7. Comparison of accuracy (2σ_m) between our newly developed Faraday–Faraday ^{234}U/^{238}U measurement protocol and the conventional Faraday–multiplier measurements. Consistent results are obtained.

6.3.3. Integrated measurements

If three measurements are integrated (using 1200–1850 ng U), as described earlier for the Faraday-multiplier standard-bracketing measurements, the external reproducibility of the CZ-1 uraninite and B4 coral improves to ±0.14‰ (2σ) and ±0.30‰ (2σ), respectively (Fig. 6).

7. Concluding remarks

The results presented here show that both the Faraday–multiplier (FM) and Faraday–Faraday (FF) standard-bracketing analytical protocols yield precise results. Furthermore, δ^{234}U values obtained using both protocols are in excellent agreement within the 2σ_m analytical errors (Fig. 7).

Faraday–Faraday measurements of ^{234}U/^{238}U using a 10^9 Ω resistor for the ^{238}U beam yields high precision and reproducibility and is furthermore very fast, requiring only ∼20 min for the combined analyses of the sample and bracketing standards. The external reproducibility of the CZ-1 uraninite using our Faraday–Faraday protocol is ±0.26‰ (2σ) and is superior to all other TIMS and MC-ICPMS measurements of samples/standards with similarly low matrix/U ratios (e.g., HU-1 and CRM-145) (Fig. 8). For the Faraday–Faraday measurements, a poorer reproducibility for corals compared to high U standards is also reported by others (e.g., [8]). Even careful purification procedures did not improve the reproducibility to the same level as observed for the uraninite standards. This demonstrates that external reproducibility tests should be based on standards characterized by similar matrix compositions as the unknown samples. In this study, the external reproducibility for coral samples is ±0.38‰ (2σ) and represents a significant improvement compared to earlier measurements.

The advantage of our conventional Faraday–multiplier protocol over the Faraday–Faraday approach is that it can be

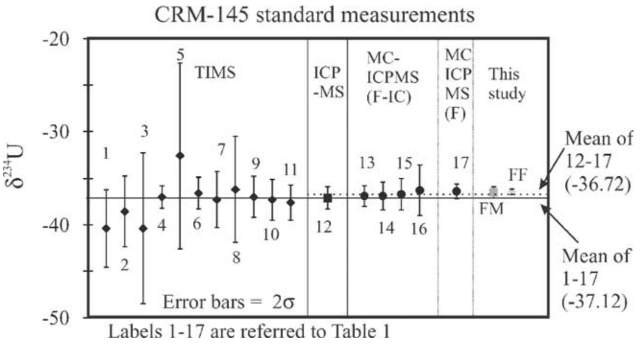

Fig. 8. Measurements of δ^{234}U for CRM-145 reported by others (see Table 1) and in this study. The error bars reflect the 2σ external reproducibility. The Faraday–multiplier and Faraday–Faraday measurements acquired in this study yield mean values of $\delta^{234}U = -36.5 \pm 0.6‰$ (2σ) and $-36.44 \pm 0.31‰$ (2σ), respectively. The δ^{234}U for both methods are marginally higher than the overall average of Refs. [1–17] ($\delta^{234}U = -37.12$) but are very consistent with other measurements conducted by ICPMS/MC-ICPMS ($\delta^{234}U = -36.72$).

conducted without a $10^9\ \Omega$ resistor, requires only moderate purification, and consumes less sample, while still yielding good reproducibility of ±0.6‰ (2σ) for integrated measurements.

Both the static Faraday–Faraday and Faraday–multiplier measurements protocols presented in this study require relatively large U sample sizes (∼400–650 and ∼120 ng of ^{238}U, respectively). This is often not problematic for samples with ppm levels of U, such as corals and many speleothem samples. For seawater samples containing ∼3 ppb U a Faraday–Faraday measurement requires the extraction of U from ∼250 ml of seawater. In U-series geochronology, the superior precision in δ^{234}U measurement significantly improves the 2σ error associated with the U-series age determination, particularly for old samples with ^{238}U–^{234}U–^{230}Th systematics approaching secular equilibrium. For example, δ^{234}U uncertainties of ±1.5‰ (typically reported for MC-ICPMS), 0.6‰ (FM) and 0.30‰ (FF) assuming ±1‰ uncertainties in the $^{230}Th/^{238}U$ ratio in each case, improves the U-series age uncertainty from ±3.2 to ±2.0 and ±1.8 ka, respectively, in a 300 ka old sample. U-series dating uncertainties will further benefit from analytical advances in Th isotope measurements.

Acknowledgements

The authors wish to thank Christoph Spötl for providing the KOZ Speleothem; Ole V. Petersen and Henrik Mortensen for the CZ-1 uraninite (Geological Museum Copenhagen, sample number 1984.436); Felix Oberli for technical support and the rest of the IGMR group at ETH for keeping the clean lab and mass spectrometers running. This manuscript benefited from helpful comments from an anonymous reviewer. This research was primarily funded by the ETH Forschungskomission and Swiss National Fonds.

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