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Measurements of natural uranium concentration and isotopic composition with permil-level precision by inductively coupled plasma–quadrupole mass spectrometry

Chuan-Chou Shen

Department of Geosciences, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106 (river@ntu.edu.tw)

Huei-Ting Lin

Department of Earth Sciences, National Taiwan Normal University, No. 88, Sec. 4, Tingjou Road, Taipei, Taiwan 116

Mei-Fei Chu

Department of Geosciences, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106

Ein-Fen Yu

Department of Earth Sciences, National Taiwan Normal University, No. 88, Sec. 4, Tingjou Road, Taipei, Taiwan 116

Xianfeng Wang

Department of Geology and Geophysics, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, Minnesota 55455, USA

Jeffrey A. Dorale

Department of Geoscience, University of Iowa, 121 Trowbridge Hall, Iowa City, Iowa 52242, USA

[1] A new analytical technique using inductively coupled plasma–quadrupole mass spectrometry (ICP-QMS) has been developed that produces permil-level precision in the measurement of uranium concentration ([U]) and isotopic composition ($\delta^{234}U$) in natural materials. A ^{233}U-^{236}U double spike method was used to correct for mass fractionation during analysis. To correct for ratio drifting, samples were bracketed by uranium standard measurements. A sensitivity of $6-7 \times 10^8$ cps/ppm was generated with a sample solution uptake rate of 30 μL/min. With a measurement time of 15–20 min, standards of 30-ng uranium produced a within-run precision better than 3‰ (±2 R.S.D.) for $\delta^{234}U$ and better than 2‰ for [U]. Replicate measurements made on standards show that a between-run reproducibility of 3.5‰ for $\delta^{234}U$ and 2‰ for [U] can be achieved. ICP-QMS data of $\delta^{234}U$ and [U] in seawater, coral, and speleothem materials are consistent with the data measured by other ICP-MS and TIMS techniques. Advantages of the ICP-QMS method include low cost, easy maintenance, simple instrumental operation, and few sample preparation steps. Sample size requirements are small, such as 10–14 mg of coral material. The results demonstrate that this technique can be applied to natural samples with various matrices.

1. Introduction

[2] The elemental and isotopic abundances of uranium have been extensively used to explore biogeochemical and physical processes in diverse fields of the Earth sciences [e.g., *Bourdon et al.*, 2003]. Low uranium concentrations ([U]) and low abundances of ^{234}U in most natural samples, however, constrain many applications due to measurement limitations. Alpha spectrometry methods have been used to quantify uranium radionuclides for five decades [*Barnes et al.*, 1956; *Ivanovich and Harmon*, 1992], but large sample size requirements and the advent of techniques with vastly improved throughput and analytical precision have pushed alpha-counting techniques toward obsolescence. Thermal ionization mass spectrometry (TIMS) advanced analytical capabilities with permil-level precision in the 1980s [e.g., *Chen and Wasserburg*, 1981; *Edwards et al.*, 1987; *Rubin et al.*, 2005]. Subsequently, various inductively coupled plasma mass spectrometry (ICP-MS) methods have been improved yielding permil-to-sub-permil precision measurements [*Shaw and Francois*, 1991; *Halliday et al.*, 1995; *Stirling et al.*, 1995, 2000; *Luo et al.*, 1997; *Becker et al.*, 1999; *Hinrichs and Schnetger*, 1999; *Becker and Dietze*, 2000; *Pietruszka et al.*, 2002; *Shen et al.*, 2002; *Deschamps et al.*, 2003; *Robinson et al.*, 2004; *Andersen et al.*, 2004; *Fietzke et al.*, 2005]. Merits of ICP-MS techniques include short measurement times, few sample preparation steps, high sample throughput, high ionization efficiency, and mass-dependent discrimination.

[3] With flat-topped peaks, ICP-sector field (SF)-MS and multicollector (MC)-ICP-MS yield high-precision isotopic analyses [*Luo et al.*, 1997; *Stirling et al.*, 2000; *Turner et al.*, 2001; *Pietruszka et al.*, 2002; *Shen et al.*, 2002; *Deschamps et al.*, 2003; *Robinson et al.*, 2004; *Andersen et al.*, 2004; *Fietzke et al.*, 2005]. *Luo et al.* [1997] were the first to develop techniques with a MC-ICP-MS, a Fisons Plasma 54, which yielded 1.2–1.4‰ analytical precision using 300–400 ng of uranium. Secondary ion mass spectrometry (SIMS) and laser-ablation MC-ICP-MS have been used for the in situ analysis of U isotopes in U-rich carbonates [*Stirling et al.*, 2000], zircons [*Reid et al.*, 1997], basalts [*Bourdon et al.*, 1996], and igneous minerals [*Bourdon et al.*, 1994]. These techniques have been reviewed by *Halliday et al.* [1998] and *Goldstein and Stirling* [2003]. Samples with uranium levels of 5–40 ng can be measured with a precision of 0.5–5‰ for $\delta^{234}U$, which is defined as a measure of the fractional deviation of the $^{234}U/^{238}U$ atomic ratio from the value at secular equilibrium (SE) in parts per thousand:

$$\delta^{234}U = \left(\left[^{234}U/^{238}U\right] / \left[^{234}U/^{238}U\right]_{SE} - 1 \right) \times 1000 \quad (1)$$

where $[^{234}U/^{238}U]$ is the atomic ratio of ^{234}U and ^{238}U nuclides [*Chen et al.*, 1992].

[4] ICP-quadrupole (Q) MS techniques have also been employed for $\delta^{234}U$ measurements, but typically with a significantly low precision of 10–100‰ [*Shaw and Francois*, 1991; *Becker et al.*, 1999; *Halicz et al.*, 2000; *Ketterer et al.*, 2000; *Kraemer et al.*, 2002]. ICP-QMS, however, provides a low-cost approach and a simple instrumental system compared to ICP-SF-MS, MC-ICP-MS and TIMS. The analytical reproducibility of ICP-QMS is limited by the Gaussian peaks characteristic of these instruments. The best previously reported precision (2σ) of 10‰ for $\delta^{234}U$ abundance in samples with 1 μg uranium was reported by *Kraemer et al.* [2002] using a combination of PERKIN-ELMER ELAN 6000 ICP-QMS with CETAC U6000 AT+ ultrasonic nebulizer.

[5] We have developed a new method using an AGILENT TECHNOLOGIES Agilent 7500s ICP-QMS with a CETAC MCN-6000 introduction system, and have achieved a precision of 1.5–4‰ for samples with 10–100 ng of uranium. This new level of precision was attained by carefully measuring baseline conditions and correcting for biases from mass fractionation and ratio drifting using a double spike technique and standard bracketing methods.

2. Experiment

2.1. Standards and Samples

[6] We measured the uranium isotopic composition and concentration of three different standard materials: (1) the New Brunswick Laboratories Certified Reference Material 112A (NBL-112A, or CRM-145, formerly NBS 960), a uranium metal standard purified from natural uranium ore, dissolved in 1.5 N HNO_3 [Cheng et al., 2000]; (2) Harwell uraninite (HU-1), prepared at the University of Quebec at Montreal from pitchblende powder [Cheng et al., 2000]; and (3) a speleothem carbonate (CAVE-1B) containing approximately 1500 ppb uranium, collected from Crevice Cave, Missouri USA (37°45′N, 89°50′W) and dissolved in 1 N HNO_3 [Shen et al., 2002]. For NBL-112A, the accepted $\delta^{234}U$ value is -36.94 ± 0.45, for HU-1 it is -0.1 ± 0.6 determined by TIMS [Cheng et al., 2000; Shen et al., 2002], and for CAVE-1B it is 2445.9 ± 3.2 determined by ICP-SF-MS [Shen et al., 2002]. NBL-112A was measured in replicate to evaluate the instrumental sensitivity, within-run precision, and reproducibility. To inspect possible memory effects (blanks) in the system, $\delta^{234}U$ and [U] were measured sequentially in NBL-112A, HU-1 and CAVE-1B, which span a large range in $\delta^{234}U$ values.

[7] Natural samples with different matrices were also analyzed. Three 500-ml seawater samples, NW9, NW10 and NW21, were collected from Nanwan, southern Taiwan (21°58′N, 120°42′E). The samples were filtered with an acid-cleaned 0.45-μm acetate cellulose filter and stored acidified in an acid-cleaned polyethylene bottle by adding 0.5–1 g 14 N HNO_3 in the field [Moran et al., 2002]. A speleothem sample, BAU01, was collected from Gruta do Bau, Brazil (10°10′S, 40°50′W) [Wang et al., 2004], and a coral sample, Lg00-1, from Sumatran Islands, Indonesia (0°02′N, 94°28′E). The carbonate samples were dissolved in 1 N HNO_3.

2.2. Spiking and Chemistry

[8] A double spike, ^{236}U-^{233}U with an atomic ratio of 1.01057 ± 0.00050 [Cheng et al., 2000], was used for mass fractionation correction and uranium quantification. It was added to standards and samples to obtain a $^{235}U/^{233}U$ atomic ratio of $\sim$10 in the mixed solutions, which results in adequate precision for both the $\delta^{234}U$ and [U] determinations [Edwards et al., 1987; Shen et al., 2002]. To evaluate the potential effects on accuracy of large deviations from the target spiking ratio of $\sim$10, samples were over-spiked and under-spiked with various $^{235}U/^{233}U$ ratios ranging from approximately 4 to 104. Chemical separations followed the procedures described in Shen et al. [2003], including Fe co-precipitation and anion-exchange chromatography (AG 1-X8 resin, 100–200 mesh).

2.3. Instrumentation

[9] An AGILENT TECHNOLOGIES Agilent 7500s ICP-QMS, housed at the Department of Geosciences, National Taiwan University, was used in this study. Instrumental settings are listed in Table 1. A desolvation nebulization device, a MCN-6000, was used as a dry sample introduction system to provide a fivefold to tenfold enhancement in sensitivity and to reduce interferences from oxides and hydrides. The optimal uranium ion intensity was achieved with a sweep Ar flow of 3.1–4.0 L/min. No nitrogen was used during the analyses.

[10] The optimal condition of the low resolution mode of our ICP-QMS was determined by analyzing NBL-112A at different peak widths (10%) of 0.5–0.9 atomic mass units (amu) using a standard bracketing method. A consistency of measured $\delta^{234}U$ values was observed between peak widths of 0.6–0.8 amu (Figure 1). In contrast, the measured $\delta^{234}U$ values were 5–6‰ low between 0.50–0.55 amu and slightly high at 0.9 amu. As a consequence, our ICP-QMS was determined to operate optimally using a peak width of 0.70–0.75 (amu) in electrostatic peak hopping mode. Ion beams were detected with a secondary electron multiplier in counting mode. Integration times were 0.1 s, 0.1 s, 0.4 s, 0.05 s, 0.1 s, and 0.025 s for m/z = 228, 233, 234, 235, 236 and 237, respectively. Instrumental background was monitored at m/z = 228, and a typical level was 5–10 cps, which is $\sim$5‰ of the intensity of ^{234}U ion beam. Abundance sensitivity of ^{238}U was 20–40 $\times$ 10^{-6} at m/z = 237 and less than 1 $\times$ 10^{-6} at m/z = 236. Spectral interferences from polyatomic

Table 1. Operating Conditions for ICP-QMS and MCN-6000

	Value/Description
Sample Introduction System MCN-6000	
Sweep Ar	3.1−4.0 L/min
N_2	0 L/min
Sample uptake rate	30 μL/min
Spray chamber temperature	75 °C
Desolvator temperature	160 °C
ICP-QMS: Agilent 7500s	
RF power	1500 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.90 L/min
Sample gas flow	0.4−0.5 L/min
Sample (Torch) depth	8.5−9.0 mm
Torch-H	0.8−1.5 mm
Data Acquisition	
Peak width (10%)	0.70−0.75 amu
Scan mode	Peak hopping
Detection mode	Counting mode
Integration time	0.1 s at m/z = 228, 0.1 s at 233, 0.4 s at 234, 0.05 s at 235, 0.1 s at 236, 0.025 s at 237

complexes and tailing characteristics of the ^{238}U ion beam was examined at m/z = 237. Oxide (UO$^+$/ U$^+$) and hydride (UH$^+$/U$^+$) levels were less than 2×10^{-3} and 2×10^{-6}, respectively. For a 40− 80 ppb uranium solution at a sample uptake rate of 30 μL/min, typical ion beam intensities were: $2-3 \times 10^4$ cps at m/z = 233 and 236, $2-3 \times 10^3$ cps at 234, and $2-3 \times 10^5$ cps at 235. An overall sensitivity (ions counted/atoms introduced) was $3-4 \times 10^{-4}$. Total measurement times were 15−20 min. [U] was calculated using a ^{238}U isotope abundance of 0.99280 and natural ^{238}U/^{235}U atomic ratio of 137.88 ± 0.1 [*Cowan and Adler*, 1977; *Steiger and Jager*, 1977].

[11] After measuring each sample, the spray chamber and nebulizer were removed from the MCN-6000 device and were washed manually using 1% HNO$_3$. This additional 5−10-min cleaning step significantly reduced the instrumental blank to less than 0.01% of the original ion beams. Correction for this trivial blank was not included in the off-line data reduction process.

[12] In addition to the instrumental background and memory blank, there are three sources of bias: uncertainty of ion counter dead time, mass fractionation (or mass bias) and Gaussian peak shape. The ion counter dead time was set at 46.9 ns with

an uncertainty less than 2.0 ns, determined by measuring ^{235}U/^{238}U ratios with different ^{238}U intensities of $0.2-2 \times 10^6$ cps. When the intensity difference between ^{235}U ion beams in standards and samples is kept below 2×10^5 cps, the dead time uncertainty results in at most a 0.2‰ error in the measured ^{234}U/^{235}U ratio.

2.4. Off-Line Data Reduction

[13] To correct for the mass fractionation, which occurs in mass spectrometers with an ICP source [e.g., *Olesik*, 2000], the measured atomic ratios were normalized to ^{236}U/^{233}U = 1.01057 using an exponential law [*Russell et al.*, 1978]. The characteristics of Gaussian peaks limit the accuracy and precision of isotopic ratio measurements made by mass spectrometers using a quadrupole mass filter. The measured isotopic ratio could vary gradually over time, for instance. We maintained the same analytical condition for 2 hours, for example, and documented a 6‰ drifting for NBL-112A δ^{234}U values (Figure 2a). In addition, an offset of 4‰ is observed between two means of replicate analyses of NBL-112A (Figures 2a and 2b). Accordingly, the NBL-112A standard solution was used to bracket every two samples to correct for the ratio drifting. The mass fractionation-corrected atomic ratios were calibrated with a formula:

$$D_f = \frac{Log\left(\frac{^{234}U}{^{238}U}\right)_{measured}}{Log\left(\frac{^{234}U}{^{238}U}\right)_{true}} \qquad (2)$$

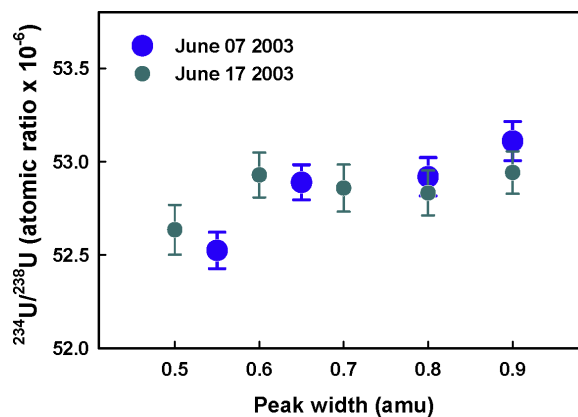where D_f is drift correction factor, calculated by comparing the measured ^{234}U/^{238}U atomic ratio of

Figure 1. The observed relationship between the ^{234}U/^{238}U atomic ratio and peak width. The value of the ^{234}U/^{238}U ratio is 5−6‰ lower at 0.50−0.55 amu and slightly higher at 0.9 amu compared to the value at 0.6−0.8 amu.
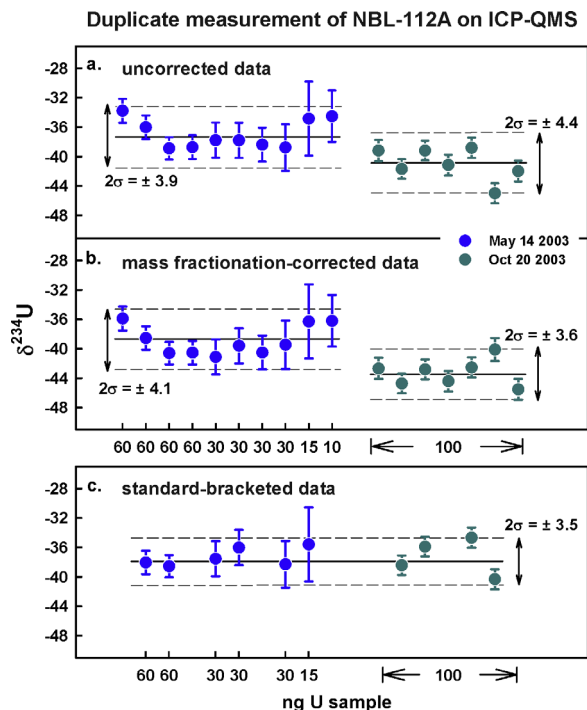
Figure 2. Duplicate ICP-QMS measurements of δ^{234}U on NBL-112A on 14 May 2003 (blue circles) and 20 October 2003 (dark cyan circles). (a) An offset of 4‰ is observed between the means of the two uncorrected measured data sets. (b) After mass fractionation correction, the external precision of δ^{234}U data can be improved for the second data set; however, a 6‰ drifting is still observed for the first data set. (c) The ratio drifting and discrepancy between the means of the two data sets can be corrected with the standard bracketing method.

NBL-112A with the true value, which is assumed to be 52.859×10^{-6} [*Cheng et al.*, 2000]. The values of D_f ranged from 0.998–1.000.

[14] Instrumental background, mass fractionation, and ratio drifting were corrected step by step in an off-line data reduction process, modified from *Shen et al.* [2002]. The interferences of abundance sensitivity tails and hydride levels were less than 0.1‰ and no corrections were employed. Decay constants used were 2.8263×10^{-6} year^{-1} for ^{234}U [*Cheng et al.*, 2000], and 1.55125×10^{-10} year^{-1} for ^{238}U [*Jaffey et al.*, 1971]. All instrumental analyses are given in Table 2. Errors in this paper are two standard deviations (2σ) unless otherwise noted. For comparison, aliquots of standards and samples were also measured by ICP-SF-MS using a Finnigan ELEMENT at the University of Minnesota [*Shen et al.*, 2002] and using a Thermo Electron ELEMENT II at the National

Taiwan University, and/or by TIMS using a Finnigan MAT 262 at the University of Minnesota [*Cheng et al.*, 2000]. A "Student" t-test (p = 0.05) was used for comparison of different instrumental data [*Miller and Miller*, 1988].

3. Results and Discussion

3.1. Standard Measurements

[15] The results of repeated measurements of NBL-112A between May 2003 and October 2003 are shown in Figure 2 and Table 2. Aliquots of NBL-112a ranging from 10 to 100 ng of uranium were measured with an internal precision of ±1.5–4‰ for δ^{234}U. Using the double spike technique and the standard bracketing method, an external precision of ±3.5‰ for δ^{234}U was achieved (Figure 2c).

[16] The average δ^{234}U value of 9 duplicates of HU-1, analyzed over the course of one year, is 0.1 ± 3.3, and is consistent with the data measured by TIMS (-0.1 ± 0.6) and by ICP-SF-MS (0.4 ± 1.4) (Figure 3a) [*Cheng et al.*, 2000; *Shen et al.*, 2002]. For the high-δ^{234}U CAVE-1B standard, a mean of 2438 ± 14, determined by the ICP-QMS technique, shows no difference from ICP-SF-MS data (Figure 3b).

[17] The [U] determinations for the two standards, HU-1 and CAVE-1B, measured by ICP-QMS and by TIMS are not significantly different (Figure 4). For HU-1, there is only an insignificant residual of -1.5 ± 2.4 ppb, for example, between the [U] data of 959 ± 2 ppb determined by ICP-QMS from the value, 960.5 ± 1.3 ppb, determined by ICP-SF-MS [*Shen et al.*, 2002] (Figure 4a). For CAVE-1B, ICP-QMS and ICP-SF-MS data are in agreement within analytical error (Figure 4b).

3.2. Precision and Reproducibility

[18] The δ^{234}U measurements for the standards are reproducible to 3.5‰ for NBL-112A, 3.3‰ for HU-1, and 4‰ for CAVE-1B, even though the within-run error of a single measurement can be as low as 1.5‰ (Figures 2 and 3). Even when the intensity of the ^{235}U beam ranges from 1×10^5–6×10^5 cps (or for ^{234}U, 1–6×10^3 cps), the ICP-QMS method can produce an average between-run reproducibility of 3.5‰. The instrumental memory blanks were evaluated with repeated measurements of HU-1 and CAVE-1B, which have largely disparate δ^{234}U values. Indistinguishable δ^{234}U values of 2424-2452 for CAVE-1B were measured on the ICP-QMS even after analyzing HU-1 with a low

Table 2. Measurements of $^{234}U/^{238}U$ Atomic Ratio, $\delta^{234}U$, and [U] on Mass Spectrometers

Sample ID	U, ng	$^{234}U/^{238}U_{atomic\ ratio}$ $\times\ 10^{-6}$	2σ	$\delta^{234}U$ ‰	2σ	[U] ppb	2σ	Method[a]
NBL-112A	60	52.80	±0.09	−38.0	±1.6			ICP-QMS
	60	52.77	±0.08	−38.5	±1.5			ICP-QMS
	30	52.83	±0.13	−37.5	±2.4			ICP-QMS
	30	52.91	±0.13	−36.0	±2.4			ICP-QMS
	30	52.78	±0.17	−38.3	±3.2			ICP-QMS
	15	52.93	±0.28	−35.6	±5.0			ICP-QMS
	100	52.78	±0.07	−38.4	±1.3			ICP-QMS
	100	52.92	±0.07	−35.9	±1.3			ICP-QMS
	100	52.98	±0.08	−34.7	±1.4			ICP-QMS
	100	52.67	±0.07	−40.3	±1.4			ICP-QMS
	100	52.86	±0.03	−37.0	±0.6			TIMS[1]
	50	52.87	±0.06	−36.7	±1.1			TIMS[2]
	30	52.85	±0.07	−37.1	±1.2			ICP-SF-MS[1]
HU-1	80	54.84	±0.16	−0.8	±2.8	961.3	±2.9	ICP-QMS
	35	54.92	±0.11	0.6	±2.0	959.8	±1.4	ICP QMS
	30	54.96	±0.12	1.4	±2.2	960.2	±1.3	ICP QMS
	30	54.92	±0.10	0.6	±1.9	960.5	±1.3	ICP QMS
	50	54.81	±0.14	−1.3	±2.6	958.4	±2.0	ICP-QMS
	70	54.71	±0.15	−3.2	±2.7	959.0	±2.4	ICP-QMS
	60	54.89	±0.13	0.0	±2.4	958.2	±2.0	ICP-QMS
	50	54.98	±0.15	1.8	±2.7	958.1	±2.2	ICP-QMS
	40	54.98	±0.15	1.7	±2.8	959.5	±2.4	ICP-QMS
	100	54.88	±0.03	−0.1	±0.6	960.6	±1.1	TIMS[1]
	20	54.91	±0.08	0.4	±1.4	960.5	±1.3	ICP-SF-MS[1]
CAVE-1B	70	189.35	±0.16	2449.8	±3.0	1537.8	±1.3	ICP-QMS
	30	188.41	±0.27	2432.7	±5.0	1541.4	±2.1	ICP-QMS
	30	188.65	±0.26	2437.1	±4.8	1540.6	±2.1	ICP-QMS
	30	188.95	±0.25	2442.5	±4.6	1539.4	±2.0	ICP-QMS
	40	188.38	±0.35	2432.3	±6.3	1541.7	±3.1	ICP-QMS
	55	188.24	±0.37	2429.6	±6.7	1539.2	±3.4	ICP-QMS
	20	188.81	±0.44	2440.0	±8.1	1541.0	±3.9	ICP-QMS
	15	189.13	±0.18	2445.9	±3.2	1541.7	±2.2	ICP-SF-MS[2]
Seawater								
NW9	23	62.92	±0.26	146.3	±4.7	3.118	±0.014	ICP-QMS
	20	62.99	±0.07	147.6	±1.3	3.121	±0.004	ICP-SF-MS[2]
NW10	19	63.11	±0.26	149.8	±4.8	3.111	±0.015	ICP-QMS
	20	62.93	±0.08	146.5	±1.5	3.112	±0.004	ICP-SF-MS[2]
NW21	15	62.97	±0.33	147.2	±6.0	3.111	±0.017	ICP-QMS
	20	62.93	±0.09	146.5	±1.6	3.121	±0.004	ICP-SF-MS[2]
Coral								
LG00-1	22	62.97	±0.27	147.3	±4.9	2756.4	±18.7	ICP-QMS
	20	62.97	±0.09	147.2	±1.7	2767.1	±6.5	ICP-SF-MS[2]
Speleothem								
BAU01	6	77.17	±0.51	406.0	±9.2	127.9	±0.6	ICP-QMS
	5	77.57	±0.30	413.2	±5.5	127.1	±0.3	ICP-SF-MS[2]

[a] TIMS[1] from *Cheng et al.* [2000]; TIMS[2] from *Rubin et al.* [2005]; ICP-SF-MS[1] from *Shen et al.* [2002]; ICP-SF-MS[2] and ICP-QMS, this study.

$\delta^{234}U$ (Figure 3b). This illustrates that the low instrumental blanks are insignificant and that no contamination was introduced from the preceding sample after physically cleaning the introduction system between runs [*Shen et al.*, 2002]. The reproducibility of [U] determination is 2‰, slightly larger than the within-run precision of 1−2‰ (Figure 4).

3.3. Seawater, Coral, and Speleothem Samples

[19] The $\delta^{234}U$ data of three 5−8-g aliquots of seawater samples, NW9, NW10 and NW21, measured by ICP-QMS are 146.3 ± 4.7, 149.8 ± 4.8, 147.2 ± 5.9, respectively, consistent with the ICP-SF-MS data with a precision of 1−2‰ (Figure 5a). This compares favorably with the $\delta^{234}U$ values of
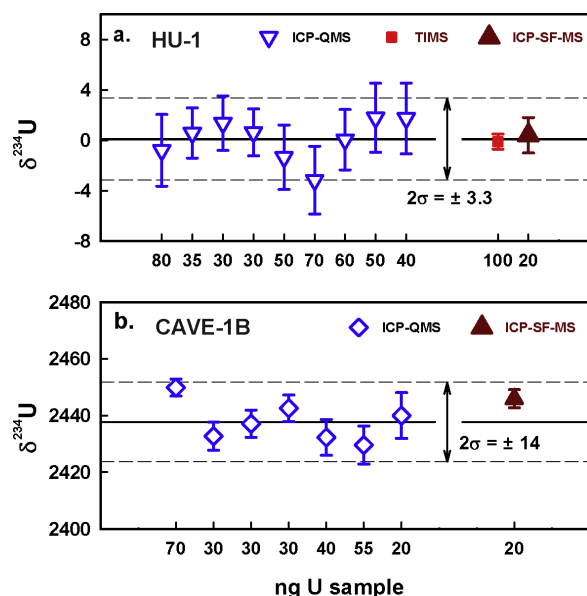
Figure 3. Repeated ICP-QMS measurements of δ^{234}U on (a) HU-1 (hollow triangles) and (b) CAVE-1B (diamonds) using the standard bracketing method. ICP-QMS values show no significant difference from the data measured by ICP-SF-MS (solid triangles) and TIMS (square).

open ocean seawater which is 146 ± 2 [*Chen et al.,* 1986]. The δ^{234}U data of coral Lg00-1 (147.3 ± 4.9) and speleothem BAU01 (406.0 ± 9.2) also agree with ICP-SF-MS data. [U] data of five
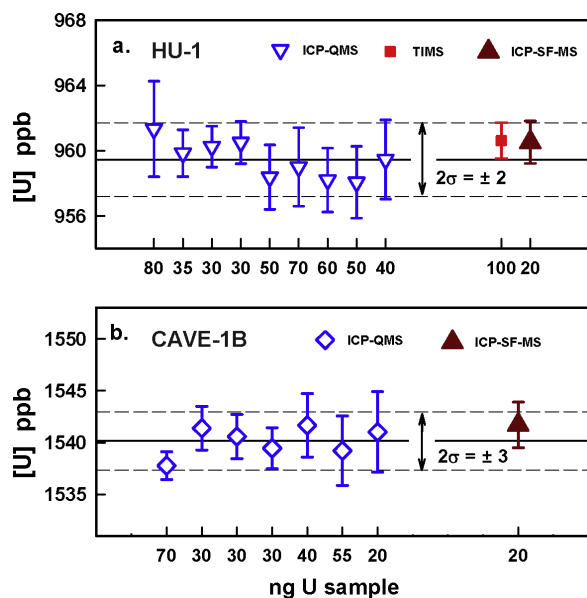

Figure 4. Duplicate ICP-QMS measurements of [U] on (a) HU-1 (hollow triangles) and (b) CAVE-1B (diamonds). ICP-QMS data closely match those measured by ICP-SF-MS (triangles) and TIMS (square).
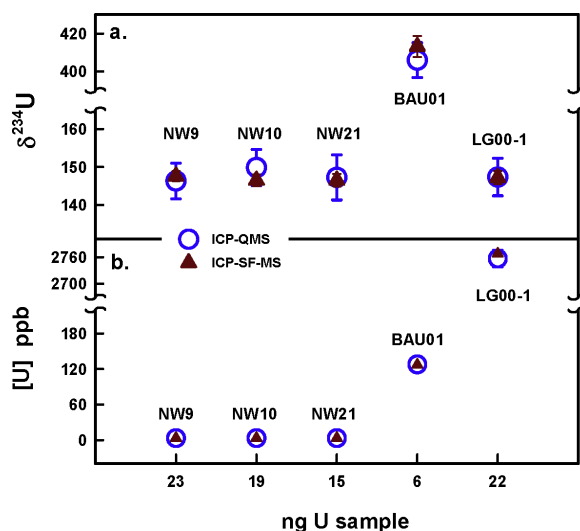

Figure 5. Comparison of ICP-QMS (circles) and ICP-SF-MS (triangles) measurements of δ^{234}U and [U] on three seawater samples (NW9, NW10, and NW21), one speleothem sample (BAU01), and one coral sample (LG00-1). All data are all consistent within error.

natural samples with analytical errors of 4–7‰, all match ICP-SF-MS data even for under-spiked (^{235}U/^{233}U = 104 for Lg00-1) and over-spiked (^{235}U/^{233}U = 3.9 for BAU01) samples (Figure 5b). The two ICP-MS data sets are consistent within error and provide further evidence that permil-level precision isotopic measurements can be achieved by ICP-QMS for samples with different matrices. The amount of uranium analyzed ranged from 6–23 ng.

[20] [U] was 3.1 ± 0.1 ppb for the three Nanwan seawater samples with a salinity of 33.8–34.0 (H.-J. Lee, personal communication, 2004). A value of 3.2 ± 0.1 ppb seawater [U], normalized to a salinity of 35, is consistent to those, 3.2–3.3 ppb, in the previous reports [*Chen et al.,* 1986; *Robinson et al.,* 2004]. [U] in the coral, LG00-1, is 2.75 ppm, within an overall range of 1.5–4.0 ppm [*Shen and Dunbar,* 1995; *Edwards et al.,* 2003].

3.4. Advantages and Disadvantages

[21] Samples ranging in sizes from 10 to 100 ng of uranium are generally required to attain an analytical precision of 1‰ by MC-ICP-MS and ICP-SF-MS [*Goldstein and Stirling,* 2003]. Although the reproducibility of 2–3.5‰, demonstrated here by our new ICP-QMS technique, is slightly higher than those by other ICP-MS's using magnetic-sector mass analyzers, our method offers the dis-

tinct advantages of low cost, easy maintenance, and simple instrument operation. As compared with previous ICP-QMS techniques [*Shaw and Francois*, 1991; *Ketterer et al.*, 2000; *Kraemer et al.*, 2002], the analytical improvement includes signal enhancement and effective corrections for mass fractionation and ratio drifting. Our new technique far exceeds the previous best precision of 10‰ using 1 μg of uranium for $\delta^{234}U$ measurements, published by *Kraemer et al.* [2002]. Using only 30 ng of uranium (or 1.5 pg of ^{234}U), $\delta^{234}U$ and [U] data with errors better than 4‰ can be achieved using this newly developed method. This corresponds to 10 g of seawater [*Robinson et al.*, 2004], 10–14 mg of coral [*Edwards et al.*, 1987; *Shen et al.*, 2005],<15 mg of marine sediment [*Moran et al.*, 2005], or 10–300 mg of speleothem material [*Dorale et al.*, 2004; *Wang et al.*, 2004].

[22] This technique, however, is still constrained by the relative lower sensitivity and higher instrumental background compared to the ICP-SF-MS technique [*Shen et al.*, 2002]. An overall sensitivity of $3-4 \times 10^{-4}$ is significantly lower than the $1-10 \times 10^{-3}$ sensitivities of MC-ICP-MS and ICP-SF-MS techniques [*Stirling et al.*, 2000; *Turner et al.*, 2001; *Pietruszka et al.*, 2002; *Shen et al.*, 2002; *Deschamps et al.*, 2003; *Robinson et al.*, 2004; *Andersen et al.*, 2004; *Fietzke et al.*, 2005]. The instrumental background of 5–10 cps at m/z = 220–240 of the Agilent 7500s requires a ^{234}U ion beam intensity of 1,000 cps or higher for 3–4‰ precision.

[23] Examples of applications include (1) the oceanic budgets and fluxes of U-series nuclides, (2) evolution of global oceanic circulations, (3) geochronology, and (4) paleoclimatology. In combination with measurements of the thorium isotopic composition, Holocene carbonate samples with ppm levels of uranium could be dateable with a precision better than ∼100 years. A possible instrumental procedure is as follows. After chemical separation, the collected Th and U fractions would be analyzed consecutively, bracketed with a standard of known $\delta^{234}U$ value. Counts at m/z = 228, 229, 230 and 232 would be measured for the Th fraction. With a 0.5-g subsample of Holocene coral, for example, an ^{230}Th ion beam of >1,000 cps can be measured in 10 min with an expected precision of 5–10‰. For corals younger than 50–100 years, the intensity of ^{230}Th ion beam will be 100 cps or less

and the analytical precision will be limited by the background counts of 5–10 cps.

4. Conclusions

[24] A simple and precise analytical method of determining the uranium isotopic composition and concentration of natural materials using ICP-QMS has been developed. Measurement time is 15–20 min per sample. A precision better than 3‰ for $\delta^{234}U$ and better than 2‰ for [U] can be achieved for samples with 30-ng uranium. Although the ultimate precision and sensitivity offered by this ICP-QMS is slightly less than that of other ICP-MS techniques, such as ICP-SF-MS and MC-ICP-MS, permil-level precision allows its ready application in various fields of the earth sciences.

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