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Precise determination of U isotopic compositions in low concentration carbonate samples by MC-ICP-MS

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ABSTRACT

We developed a fast and simple analytical procedure for precise determination of U isotopic compositions in low concentration natural samples. The main advantage of the new method is that it requires only 12 ng U and can obtain all U isotopic ratios without using spike. Five carbonate reference materials (JCp-1, RKM-4, RKM-5, GBW04412 and GBW04413) and 3 international standards with different matrices (IAPSO, IRMM-3184 and CRM-U010) were analyzed for (^{234}U/^{238}U) and ^{238}U/^{235}U ratios by MC-ICPMS. Using our method, the results for these standards are in close agreement with the certified values, 1.144 ± 0.004, 0.966 ± 0.004 and 0.990 ± 0.003 for (^{234}U/^{238}U) and 137.72 ± 0.13, 137.64 ± 0.15 and 98.63 ± 0.04 for ^{238}U/^{235}U, in IAPSO, IRMM-3184 and CRM-U010, respectively. The long-term reproducibility of (^{234}U/^{238}U) and ^{238}U/^{235}U is 0.970 ± 0.002 and 137.56 ± 0.09; 1.144 ± 0.004 and 137.72 ± 0.13, respectively, for in-house U solution and IAPSO. The new (^{234}U/^{238}U) results for carbonates show much better precision than previous studies and also reflect their age variability. The obtained ^{238}U/^{235}U ratios, representing the first measurements in these carbonate specimens, are rather constant. The method described here requires only 12 ng of U for analysis and can be completed in 5.2 min. The approach provides a fast method to measure (^{234}U/^{238}U) and ^{238}U/^{235}U ratios in sample matrices commonly encountered in studies of chemical weathering, oceanography and paleoclimatology.

1. Introduction

Although the U isotopes have small differences in mass, several percent (%) to a few per-mil (‰) levels of isotopic fractionations are observed in natural environments. The main mechanisms controlling the fractionation of U isotopes are their variable solubility in different redox states and the α-recoil process. Under oxic conditions in aqueous systems, U forms the soluble uranyl ion UO_2^{2-} that tends to bind with carbonate or phosphate ions to form stable complexes [1]. In anoxic or suboxic conditions, U is reduced from highly soluble hexavalent (U^{VI}) to insoluble tetravalent (U^{IV}) state, which easily precipitates or adsorbs onto solid phases. U isotopic ratios are tools for studying redox conditions, chemical weathering, and paleoclimatology [2,3].

Emission of α-particles leads to the formation of daughter nuclides which can be readily lost from the original mineral [4,5]. Therefore, (^{234}U/^{238}U) (where parentheses denote activity ratio) in continental surface waters are greater than the secular equilibrium value of 1.00 in river water or groundwater, and U isotopic ratios can be used as a proxy for the degree of continental weathering or mixing processes in hydrologic and marine systems. Riverine inputs result in high (^{234}U/^{238}U) values ~1.147 in seawater [6–9]. Differences in seawater (^{234}U/^{238}U) provide information about weathering history and environmental change in the past. For example, elemental and U isotopic measurements of coral skeletons record the evolution of seawater chemistry [7,10]. Therefore precise U compositions of carbonate materials are critical for paleoceanography related studies [11–13].

^{238}U and ^{235}U are parent nuclides of the ^{238}U-decay series and the ^{235}U-decay series, which ultimately decay to stable ^{206}Pb and ^{207}Pb, respectively. Due to their long half-life (^{238}U, $t_{1/2}=4.468\times10^9$ yr and ^{235}U, $t_{1/2}=0.7038\times10^9$ yr), ^{238}U/^{235}U is considered to be invariant throughout the Earth history [14]. In recent years, however, scientists have discovered significant ^{238}U/^{235}U variations of more than 1.3‰ in natural materials [15–17]. Large ^{238}U/^{235}U variations have been reported among speleothem, dolomite chimney deposits, Fe–Mn crust/nodule and black shale, oxidation–reduction was attributed to be the most important factor [15,16]. In other words, ^{238}U/^{235}U ratio can be a potential tool for studying redox variation in the past.

MC-ICP-MS techniques provide high precision and high sample throughput for isotopic measurements, but the precision and accuracy of the results often rely on the selection of calibration method or reference materials. Most of the certified U standards

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are natural U metal, oxide (CRM-112a, CRM-U010 and SRM-950a) or synthetic materials (IRMM-3184). The readily available bulk carbonate standards are not well characterized for high precision ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ values. Given that it is important to use reference materials with similar matrices as the sample, continued improvements and reevaluation of the U isotopic ratios in some commonly used carbonate standards are needed.

In this study, we developed a simplified procedure for the high-precision determination of U isotopic compositions in carbonate, oxide, freshwater and seawater samples. The method was used to analyze ($^{234}U/^{238}U$) and the first $^{238}U/^{235}U$ in carbonate reference materials (JCp-1, RKM-4, RKM-5, GBW04412, and GBW04413). The U purification was carried out using UTEVA resin and subsequent analysis used standard-sample bracketing (SSB) MC-ICP-MS methods to correct for potential mass fractionation. We demonstrate a fast, simple and precise MC-ICP-MS procedure for simultaneously determination of ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ in natural materials with low U content.

2. Experimental

All chemical procedures were performed in a class-10 flow bench in the class-1000 clean room at the Isotope Geochemistry Laboratory (National Cheng Kung University, NCKU), Taiwan. All acids and chemical reagents were double-distilled or sub-boiling, where deionized water (18.3 MΩ) was prepared with an Elix 5 Millipore System. Ultrapure-grade hydrogen peroxide solutions (31%, Merck) were used for removing organic matter. UTEVA resin (100–150 µm, Eichrom Technologies Inc., USA) was used for U and Th separation from all the sample matrices.

2.1. Instrumentation

U isotopic ratios were measured using a MC-ICP-MS (NEPTUNE, Thermo-Fisher Scientific), with eight movable Faraday cups (10^{11} Ω resistor) and one fixed Faraday cup mounted with a secondary electron multiplier (SEM) at the EDSRC (NCKU). The SEM was equipped with an energy filter, a retarding potential quadruple (RPQ) device, for high abundance sensitivity measurement. An Aridus II™ desolvation system (Cetac) with a PFA nebulizer (Elemental Scientific Inc., uptake rate 50–100 ml min^{-1}), a nickel skimmer cone, an O-ring free sapphire injector and quartz torch (Elemental Scientific Inc.) were connected to the MC-ICP-MS. Sample solution was introduced into the Aridus II™ through a heated PFA spray chamber (110 °C) to maintain the sample in vapor phase before entering a heated PTFE membrane (160 °C). The setting of the RF power in the instrument was controlled at 1200 W and measurements were made using low mass resolution ($R=m/\Delta M=400$) mode. For Neptune, the resolution ($R=m/\Delta M$) is derived from the peak slope of the rising edge measured at 5% and 95% relative peak height. The torch position, instrumental gas flows and the ion lenses of the MC-ICP-MS were tuned to obtain a stable signal and optimal intensity based on the ^{238}U ion beam (about $3.5–4.0\times10^{-11}$ A for 20 ng g^{-1} U). The relevant instrumental settings are listed in Table 1.

2.2. Sample materials

JCp-1 is one of the Geological Survey of Japan (GSJ) standards for carbonate trace element analyses prepared from a living massive coral (*Porites sp.*), collected from the southern Ryukyu Islands. The coral has an average U and Th content of 2.69 ± 0.03 µg g^{-1} and 52 ± 8 ng g^{-1}, respectively. Based on the $^{234}U–^{230}Th$ TIMS dating, an age of approximately 0.82–1.14 ka has been determined for this aragonite standard [11]. Using powder X-ray diffraction methodology, Okaiet al. [18] has not seen the presence of any other mineral.

Table 1
Instrumental setting using Neptune MC-ICP-MS with Aridus II™ for U isotopes measurement.

MC-ICP-MS, Neptune	
Radio frequency power	1200 W
Extraction voltage	2 kV
Guard electrode	On
Skimmer cone	H, Ni cone
Slit resolution	low
mass resolution	~400 m/ΔM
Cup configuration	$^{234}U(C)–^{235}U(H1)–^{238}U(H3)$
Measurement mode	Dynamic
Sample gas (argon)	0.9–1.1 l min^{-1}
Cool gas (argon)	18 l min^{-1}
Auxiliary gas (argon)	0.7 l min^{-1}
cycles/Blocks	10 cycles/6 blocks
integration/Idle time	4.194 s/1.000 s
Wash time	100 s
Uptake time	30 s
Nebulizer flux	50–100 µl min^{-1}
Aridus II™, Cetac	
Nitrogen flow	On
Nebulizer	PFA
Spray chamber/membrane	110 °C/160 °C
Analytic concentration	20 ng g^{-1}
Sensitivity	$\sim3.5–4.0\times10^{-11}$ A/20 ng g^{-1} U
U consumption per analysis	~12 ng (at max. nebulizer flux)

Four other international carbonate standards (RKM-4, RKM-5, GBW04412, and GBW04413) were used in this study. RKM-4 and RKM-5 were collected from Barbados Kendal Hill terrace and Barbados III (Rendezvous Hill) terrace, respectively. The RKM-4, considered as a typical carbonate material, is from the Brown University and McMaster University Pleistocene collections, which were selected based on critical criteria including (1) fresh, free of weathering surfaces and no detrital contamination, (2) not subject to significant re-crystallization and (3) represent a range of ages [19]. The RKM-4 and RKM-5 are 99% aragonite and were used in the first stage of the Uranium-Series Inter-comparison Project (USIP-I), and the second stage of the USIP program (USIP-II) [19–23].

GBW04412 and GBW04413 are speleothem carbonates, collected from the Xiniu cave, Guizhou Province, China. The original GBW04412 had clear growth bands, made of pure aragonite, whereas the GBW04413 consisted of 50% aragonite and 50% calcite [21]. Both standards were measured for their U isotopic compositions during the "The National Comparison Plan on U-series Standard Samples" project [19–21,23]. Detailed information of these carbonate standards are summarized in Table 2.

2.3. Sample preparation

The coral standards and the speleothem standards were analyzed for U isotopic ratios using the following procedures. About 100 mg of carbonate powder was precisely weighed in a clean Teflon vial and ultrapuregrade hydrogen peroxide was added and left overnight to decompose any remaining organic material. The treated carbonate was completely dissolved in 1 ml 3 M HNO_3. We carefully monitored all procedure steps used in the dissolution and confirmed that there was no residue observed. After sample decomposition, an aliquot was evaporated to dryness inside a hood and re-dissolved in 3 M HNO_3 for later U purification using UTEVA resin.

2.4. Standards

The certified international reference seawater IAPSO, coral standard JCp-1, as well as IRMM-3184, and CRM-U010 were

Table 2
Sample materials used in this study.

Reference Material	Type	Composition	Issuing agency	Source location	Age (kyr)	
JCp-1	Coral	Aragonite	GSJ	Ishigaki Island, Japan	0.82–1.14	[11]
RKM-4	Coral	Aragonite	USIP-I	Kendal Hill terrace, Barbados	$210+25/-21$	[19]
					208.1 ± 1.9	[21,23,39]
RKM-5	Coral	Aragonite	USIP-II	Rendezvous Hill terrace, Barbados	131 ± 4	[20]
					129.2 ± 1.2	[23]
					132.6 ± 3.44	[22]
GBW04412	Stalagmite	Aragonite	The National Comparison Plan on U-series Standard Samples	Xiniu cave, China	85 ± 4	[19]
					85 ± 4	[40]
					92.1 ± 0.46	[41]
GBW04413	Stalagmite	50% aragonite +50% calcite	The National Comparison Plan on U-series Standard Samples	Xiniu cave, China	125.7 ± 1.2	[21]
					118 ± 6	[21]
					130 ± 0.16	[41]

prepared as working standards to investigate recovery and potential fractionation effects. Another in-house relative standard solution (RSTD) in a river water matrix was prepared by a series of high-purity standard solutions (1000 μg g^{-1}). The RSTD chemical composition is similar to that of the Kaoping River water. The RSTD was measured for U isotopic ratios and used for calibration and testing for matrix effects of the UTEVA columns. A 20 ng g^{-1} in-house U solution, prepared from 1000 μg g^{-1} high-purity U solution, was used as a bracketing standard during isotopic measurements. The U isotopic compositions of the RSTD and in-house U standards were precisely calibrated using the CRM-U005. The U isotopic values of CRM-U005 were certified by the National Bureau of Standards and the atom percent of U isotopes were ^{234}U: 0.00218 ± 0.00004, ^{235}U: 0.4895 ± 0.0005, ^{236}U: 0.00466 ± 0.00005 and ^{238}U: 99.504 ± 0.001. The fractionation correction was based on the difference between the measured and the certified CRM-U005 and then applied to the in-house U solution as well as the RSTD analyses. Repeated measurements of the in-house U solution obtain the (^{234}U/^{238}U) and ^{238}U/^{235}U of 0.970 ± 0.001 and 137.561 ± 0.001, respectively. We measured the IRMM-3184 and CRM-U010 again, using SSB with the in-house U solution to double check the U isotopic ratios of the in-house U solution. The measured (^{234}U/^{238}U) and ^{238}U/^{235}U of IRMM-3184 and CRM-U010 were 0.966 ± 0.004, 137.64 ± 0.15 and 0.990 ± 0.003, 98.63 ± 0.04, respectively, in excellent agreement with their certified values.

2.5. Chromatography

In this study, U separation procedures were performed using a simple one-step ion chromatography column modified from Douville et al. [13]. UTEVA resin has been used widely for the extractions of U and some other tetravalent actinides (Th, Pu and Np) [13,24]. It has a maximum capacity of 37 mg ml^{-1} and a bed density of 0.39 g ml^{-1}. About 1 ml UTEVA resin was loaded into an acid-cleaned polypropylene column (4.2 cm height) with an inner diameter of 5.5 mm. The packed column was cleaned with 4 ml 3 M HNO_3, 4 ml 3 M HCl, 4 ml 1 M HCl, and 4 ml deionzied water in sequence before sample loading. The resin was conditioned using 3 ml 3 M HNO_3 and the sample was also loaded in 3 M HNO_3. Matrix elements were eluted with 8 ml 3 M HNO_3 and subsequently washed with 6 ml 3 M HCl to elute Th, and then 6 ml 1 M HCl was added to collect U. The eluted solution containing U was evaporated to dryness and then re-dissolved in 0.3 M HNO_3 for MC-ICP-MS isotopic analyses.

The UTEVA column was calibrated using JCp-1, IAPSO and RSTD (doped with Th) to test the recoveries of U and Th during the chromatographic separation. These standards were used to help understand matrix effects on the UTEVA resin. The U isotopic ratios after column separation were also compared using certified standards IRMM-3184 and CRM-U010. Each sample measurement was duplicated at least twice to double checking any mass fractionation after extraction. The total procedural blank was below 2 pg U (<0.01% U loaded) determined by HR-ICP-MS.

2.6. U isotope measurements

A standard-sample bracketing (SSB) approach was used to correct for mass fractionation and to validate if the ^{238}U/^{235}U is constant [14]. All samples were diluted with 0.3 M HNO_3 to obtain a constant U concentration (20 ng g^{-1}) for isotopic measurements, same as the bracketing standard solution. The gain calibration of the amplifier in MC-ICP-MS was calibrated daily before starting isotopic measurements. The yield factor used to adjust signal transition among the Faraday cups and the SEM was obtained, using a ^{235}U ion beam of about $4-7 \times 10^{-14}$ A to measure the responses of the two kinds of detectors.

Protocols used to ensure quality control and quality assurance (QA & QC) were included by analyzing three sets of certified standards in every sample batch. The analytical order of each set was blank-five standards-blank, and the in-house U standard, IRMM-3184 and CRM-U010 were included in each analytical set. The regular protocol for analyses included blanks and seven replicates of the in-house U standard solution, followed by samples bracketed by the in-house U standard solution. The sample uptake time prior to data acquisition was 30 s, and off-peak baseline and automatic peak centering were performed. One U isotopic measurement involved 60 cycles (10 cycles/6 blocks) with 4.194 s integration and 1.000 s idle per cycle. The total duration of data acquisition was about 5.2 min. The sample introduction rate was 50–100 μl min^{-1}and the total U consumption for each analysis was about 12 ng U for a solution containing 20 ng g^{-1} U (Table 1). The rinse time was 100 s using 0.3 M HNO_3 between each measurement, and the memory effects can be negligible.

We followed the detailed procedures described in Hiess et al. [25] to evaluate the tailing corrections associated with the Neptune MC-ICP-MS. We used the in-house U solution, to evaluate ^{238}U and ^{235}U tailing behavior by measuring intensities at every 0.01 u mass intervals from 233.50 to 237.70 using SEM. The relation between log (intensity) and $-$log (238-mass) showed the tailing for ^{238}U and ^{235}U ion beams as a linear trend in the MC-ICP-MS. The *a* (slope) and *b* (*y*-intercept) coefficients of the linear trend in the log (intensity) vs. $-$log (238-mass) plot were calculated and used for the tail correction. The intensities at masses 237.54 to 236.54 and 234.50 to 233.50 were used to calculate the tailing parameters for ^{238}U and ^{235}U. The tail corrections for all other isotopes were then scaled from their measured on-peak intensities and the sum of the mass tailings was subtracted from all on-peak measurements. For ^{235}U, the

Table 3
Compilation of tail corrections for (^{234}U/^{238}U) and ^{238}U/^{235}U analyzed with the Neptune MC-ICP-MS.

	(^{234}U/^{238}U)	**2*s***	**(^{234}U/^{238}U)^a**	**2*s***	**Difference (‰)**
IRMM-3184	0.967	0.005	0.966	0.004	0.486
U-010	0.989	0.003	0.990	0.003	−0.408
IAPSO	1.143	0.005	1.144	0.004	−0.722
HP-U	0.969	0.003	0.969	0.004	−0.042
Average					−0.171
	^{238}U/^{235}U	**2*s***	**^{238}U/^{235}U^a**	**2*s***	**Difference (‰)**
IRMM-3184	137.64	0.15	137.64	0.15	−0.025
U-010	98.62	0.03	98.63	0.04	−0.081
IAPSO	137.73	0.13	137.72	0.13	0.065
HP-U	137.56	0.14	137.56	0.13	0.014
Average					−0.007

^{a}Data was applied with tail corrections.

^{238}U tailing was 0.003% of the ^{235}U intensity. The data results after tailing correction showed an average difference of 0.007‰ for ^{238}U/^{235}U ratio, which was less than the long-term average analytical precision (0.09, 2*s*). For ^{234}U, the tailing for ^{238}U and ^{235}U was calculated and the tailing effect from ^{238}U was $\sim 10^{-5}$%. The tailing caused an average difference of 0.171‰ on (^{234}U/^{238}U), less than the long-term average analytical precision (0.002, 2*s*) (Table 3).

The long-term analytical precision was evaluated by averaging measurements of $10\,\mathrm{ng\,g^{-1}}$ in-house U standard and $20\,\mathrm{ng\,g^{-1}}$ IAPSO over a period of more than 2 years. The mean (^{234}U/^{238}U) and ^{238}U/^{235}U values of in-house U standard were 0.970 ± 0.002 and 137.56 ± 0.09, respectively (Fig. 1A, B). The IAPSO yields mean (^{234}U/^{238}U) and ^{238}U/^{235}U values of 1.144 ± 0.004 and 137.72 ± 0.13, respectively (Fig. 1C, D). The (^{234}U/^{238}U) activity ratio was calculated using the ^{234}U/^{238}U atomic ratio as follows: $(^{234}U/^{238}U) = (^{234}U/^{238}U)_{\text{atomic ratio}} \times (\lambda_{234U}/\lambda_{238U})$, where the decay constant, $\lambda_{234\mathrm{U}} = 2.82629 \times 10^{-6}\,\mathrm{a}^{-1}$, for ^{234}U and $\lambda_{238\mathrm{U}} = 1.551 \times 10^{-10}\,\mathrm{a}^{-1}$ for ^{238}U was adopted from Cheng et al. [26] and Jaffey et al. [27], respectively. All uncertainties reported in this paper, either derived from data acquired in this study or from literature data are shown as 2*s*, where *s* represents the standard deviation [28].

3. Results and discussion

3.1. Column separation efficiency

Compared with previous studies (see Table 4), there are some advantages of our UTEVA resin protocol: (1) The reagents used involve only HNO_3 and HCl which can be easily purified and to control at low blank; (2) effective extraction of U and Th from various sample matrices using a single column; (3) relative simple chemical steps are involved; (4) rather high recovery efficiencies of U and Th. The column procedures were periodically calibrated using international standards and the matrix-matched river water standard. For carbonate matrices, the recoveries of U and Th are better than 99% where U separated successfully from Th in the same specimen. The Ca concentration is less than $10\,\mathrm{ng\,g^{-1}}$ and other trace components (Mg, Sr, Ba) are lower than $2\,\mathrm{ng\,g^{-1}}$ after the UTEVA purification. Douville et al. [13] used UTEVA resin for performed U–Th dating of carbonates. They found no mass fractionation on the U isotopes even at Ca concentration up to $10\,\mu\mathrm{g\,g^{-1}}$. This agrees with our observations that the UTEVA column can circumvent the influence of major element (Ca) and other potential matrix effects in carbonates.

Additionally, the UTEVA resin was tested for seawater and fresh water matrices using IAPSO and RSTD standards, the

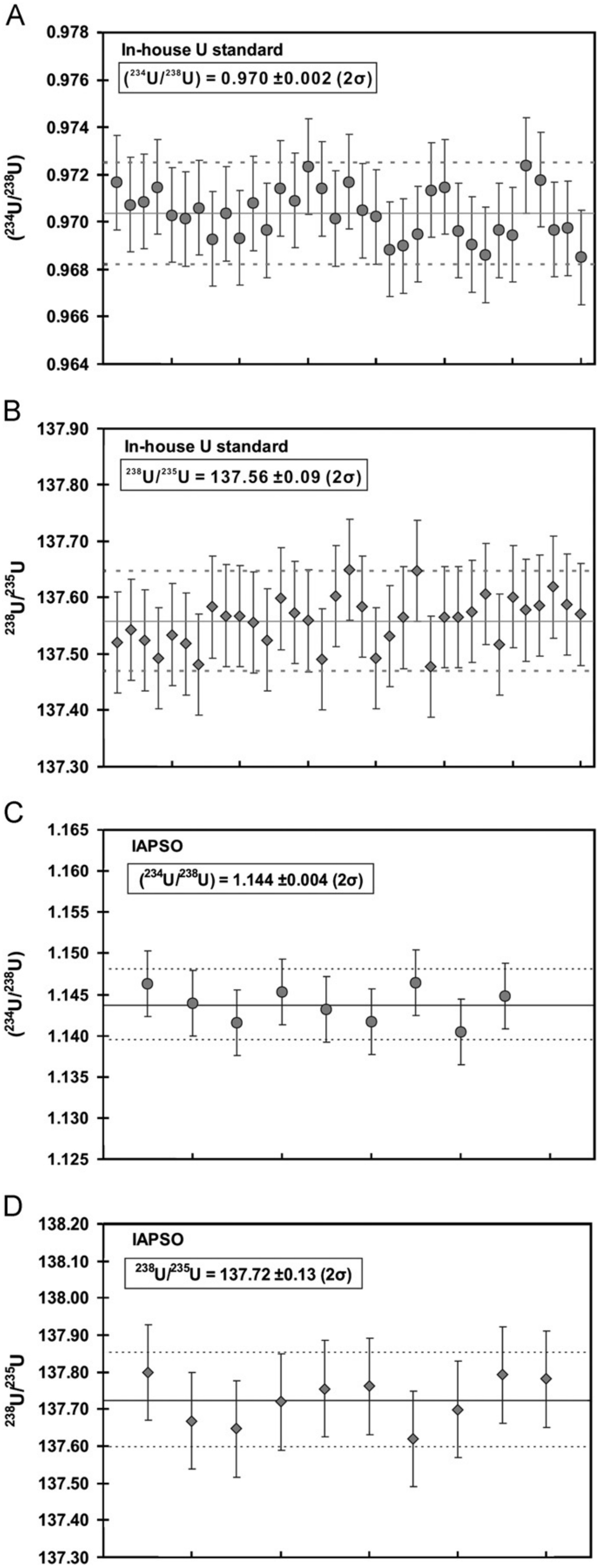

Fig. 1. Long-term analytical results of (A) (^{234}U/^{238}U) and (B) ^{238}U/^{235}U in the in-house U standard. Long-term reproducibility of (C) (^{234}U/^{238}U) and (D) ^{238}U/^{235}U measurements of international seawater standard IAPSO. The data were collected over a period of more than 2 years.

Table 4
Comparison of different approaches with the UTEVA resin method.

	Purification	Spike use	U Recovery (%)	Reagent for UTEVA resin	Sample species
Carter et al. [22]	(1) Co-precipitation, (2) UTEVA resin	Yes	61–106	HNO_3, HCl, ammonium oxalate	U ore, coral, granite, U standard
Yokoyama et al. [42]	(1) UTEVA resin, (2) TEVA resin	No	92–106	HF, HNO_3, HCl	silicate rocks
Potter et al. [24]	(1) TRUspec resin, (2) UTEVA resin	Yes	–	HNO_3, HCl, HF	Coral
Stirling et al. [15]	(1) TRUspec resin, (2) UTEVA resin	Yes	–	HNO_3, HCl, HF	Carbonate, seawater, river water, Fe–Mn deposit, shale, U standard
Weyer et al. [16]	(1) UTEVA resin	Yes	97–100	HNO_3, HCl, Oxalic acid	Seawater, granite, basalt, black shale, Mn-crust, suboxic sediment, U standard
Douville et al. [13]	(1) UTEVA resin	Yes	~100	HNO_3, HCl	Carbonate
Not et al. [43]	(1) Co-precipitation, (2) AG1 × 8 resin, (3) UTEVA resin	Yes	–	HNO_3	Seawater, sea ice and brine
This study	(1) UTEVA resin	No	91–99	HNO_3, HCl	Carbonate, river water, seawater, U-standard

recoveries are better than 91% (U: 92.6% and Th: 91.1%). After purification,the major ions concentrations (Na, Mg, Ca) in seawater and fresh water were lower than 200 ng g^{-1} and 20 ng g^{-1}, respectively. The measured trace elements concentrations (Li, Sr, Ba, B) in seawater and fresh water are all below 2 ng g^{-1}. The measured ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ in IAPSO and RSTD were 1.144 ± 0.004, 137.72 ± 0.13 and 0.969 ± 0.004, 137.56 ± 0.13, respectively. These ratios are in excellent agreement with open ocean seawater ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ of 1.147 [6–8,29] and 137.819 [15,16]. For RSTD, the U isotopic ratios of ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ are 0.970 ± 0.001 and 137.561 ± 0.001, respectively.

The measured average ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ values in standards IRMM-3184 and CRM-U010 are 0.966 ± 0.004, 137.64 ± 0.15 and 0.990 ± 0.003, 98.63 ± 0.04, which agree well with the certified values of 0.968 ± 0.007, 137.697 ± 0.041 and 0.996 ± 0.011, 98.619 ± 0.098, respectively [30,31]. Condon et al. [17] and Brennecka et al. [32] used TIMS with double spiked IRMM-3636 for $^{238}U/^{235}U$ analysis in IRMM-184 and obtained $^{238}U/^{235}U$ ratios of 137.682 ± 0.024 and 137.696 ± 0.035, respectively. Our measured values fall within the analytical error of the certified results.

3.2. U isotopic ratios

($^{234}U/^{238}U$) in carbonates is a useful proxy for sealevel reconstruction, paleo climatology and environmental changes. Its ratios in cave carbonates were used as archives for chemical weathering processes in the past or source tracers in various hydrological systems. $^{238}U/^{235}U$ variation in ground water is a potential tool for studying redox changes in environments. Several international reference carbonate standards, including coral and speleothem, were analyzed in this study (Table 2). A small sample size, requiring less time and no spike was used, which obtained better precision than previous results (Table 5). These results are compared with previous data for the U isotopic compositions of carbonates (Table 6). All carbonates materials show higher ($^{234}U/^{238}U$) than the secular equilibrium value of 1.00. The ($^{234}U/^{238}U$) values range from 1.096 to 1.143 in coral standards and 1.423 to 1.848 in stalagmite standards. The $^{238}U/^{235}U$ ratios in these carbonates are rather constant, ranged between 137.71 and 137.77 (Table 6).

The coral standards JCp-1, RKM-4 and RKM-5 show average ($^{234}U/^{238}U$) of 1.143 ± 0.002, 1.096 ± 0.002 and 1.108 ± 0.007, respectively (Table 6). After normalization using the secular equilibrium value, we found that JCp-1 has a similar $\delta^{234}U$ as IAPSO ($\delta^{234}U = 143.7 \pm 4.3‰$) and the $\delta^{234}U$ in RKM-4 and RKM-5 is lower than the open ocean seawater. There is no clear change of ($^{234}U/^{238}U$) over the last three hundred thousand years, in contrast to marine corals [10] where living coral incorporate the same ($^{234}U/^{238}U$) as ambient seawater [7]. The initial ($^{234}U/^{238}U$) in marine carbonates can be used to constrain whether diagenesis has occurred after formation [7,33]. The measured ($^{234}U/^{238}U$) of JCp-1 coincides with the value of modern seawater (1.147 ± 0.001, [7,8]), reflecting closed system conditions without subsequent diagenetic influences. These results are consistent with Watanabe and Nakai [11] using HNO_3, $HF/HClO_4$ and HCl/H_3BO_3 digestion. This supports that the HNO_3–H_2O_2 method can be used for carbonate dissolution without detrital silicates contamination.

RKM-4 and RKM-5 standards show ($^{234}U/^{238}U$) lower than the seawater value. If the ages of RKM-4 and RKM-5 were exactly known, then the deviation of their U isotopic ratios must be related to open system conditions or diagenetic effects in these materials. The ($^{234}U/^{238}U$) of RKM-4 and RKM-5 are negatively correlated with their ages. The low ($^{234}U/^{238}U$) can be explained by the preferential loss of ^{234}U relative to ^{238}U by α-recoil and the ^{234}U decay results in the ($^{234}U/^{238}U$) tending to approach the secular equilibrium with age. We estimate ^{234}U loss via α-decay from carbonate formation using a simple decay function derived from Calsteren and Thomas [34], using the following equation:

$$\left(\frac{^{234}U}{^{238}U}\right)_t = \left\{\left(\frac{^{234}U}{^{238}U}\right)_{sec-eq} - \left(\frac{^{234}U}{^{238}U}\right)_{init}\right\} \times \left(1 - exp^{-t\lambda_{234}}\right) + \left(\frac{^{234}U}{^{238}U}\right)_{init}$$

where t is the average age as shown in Table 2, λ_{234} is the decay constant of ^{234}U and $(^{234}U/^{238}U)_{sec-eq}$ is 1.00. We assume that the initial ($^{234}U/^{238}U$) of RKM-4 and RKM-5 is the same as seawater. The calculated $(^{234}U/^{238}U)_t$ of RKM-4 and RKM-5 are 1.080 and 1.100, respectively, which is in agreement with the measured results reported here. Thus, we argue that the low ($^{234}U/^{238}U$) relative to the seawater value in RKM-4 and RKM-5 can be interpreted as resulting from the loss of ^{234}U due to the decay process.

The stalagmite standards GBW04412 and GBW04413 have average ($^{234}U/^{238}U$) of 1.848 ± 0.006 and 1.423 ± 0.005, similar to previous reports, but the analytical precision is improved by a factor of 10 (Table 6). The GBW04412 and GBW04413 have notably high $\delta^{234}U$ relative to RKM-4, RKM-5 and seawater. The measured ($^{234}U/^{238}U$) of GBW04412 and GBW04413 might imply a high degree of interaction between groundwater and soils, further reflecting the degree of chemical weathering and past

Table 5
Comparison between U measurements for the sample consumption, time cost and analytical precision.

	Technique	Spike use	U consumption per analysis (ng)	Time per analysis (min)	δ^{234}U Analytical precision (‰, 2σ)	δ^{238}U Analytical precision (‰, 2σ)
Fietzke et al. [44]	MC-ICP-MS (MIC)	Y	5	30	1.0	–
Deschamps et al. [45]	MC-ICP-MS (FF)	Y	>200	4.1	1.3	–
Andersen et al. [46]	MC-ICP-MS (FF)	Y	400–650	3	0.3	–
Stirling et al. [15,47,48]	MC-ICP-MS (FF)	Y	3	1	–	0.2
	MC-ICP-MS (FF)	Y	20	10	–	0.1–0.2
	MC-ICP-MS (FF)	Y	50	10	–	0.04
Weyer et al. [16]	MC-ICP-MS (FF)	Y	50–200	5	–	0.06
Hiess et al. [25]	MC-ICP-MS (FF)	Y	1000	<30	–	0.01
Luo et al. [49]	MC-ICP-MS (FM)	N	450	–	1.1	–
Robison et al. [50]	MC-ICP-MS (FM)	Y	–	10	1.7	–
Hellstrom [51]	MC-ICP-MS (FM)	Y	5–40	–	2.7	–
Andersen et al. [46]	MC-ICP-MS (FM)	Y	40	8	0.6	–
Hoffmann et al. [52]	MC-ICP-MS (FM)	Y	<20	–	2.8	–
Makishima et al. [53]	MC-ICP-MS (FM)	Y	0.5–21	7	1.7–10.4	–
	MC-ICP-MS (FM)	N	0.2–9	3	1.3–5.3	–
This Study	MC-ICP-MS (FM)	N	12	5.2	2.0	0.64

MIC, multiple ion counting; FF, Faraday–Faraday; FM, Faraday–Multiplier.

Table 6
Uranium isotopic ratios of the sample materials.

Name	(^{234}U/^{238}U)	2*s*	δ^{234}U[a]	2*s* (‰)	^{238}U/^{235}U	2*s*	δ^{238}U[b]	2*s* (‰)			
JCp-1	1.15	0.01	152	10	137.798	0.001	−0.595	0.01	MC-ICP-MS	Spike	[11]
	1.143	0.002	143.0	2.2	137.72	0.15	−1.18	1.08	MC-ICP-MS	SSB	This study
RKM-4	1.11	0.02	110	20	–	–	–	–	α spectrometry	Spike	[19]
	1.118	0.004	118.0	4.0	–	–	–	–	TIMS	Spike	[21,23,39]
	1.13	0.01	130	10	–	–	–	–	SF-ICP-MS	Spike	[41]
	1.096	0.002	96.1	2.2	137.75	0.12	−0.94	0.86	MC-ICP-MS	SSB	This study
RKM-5	1.114	0.02	114.0	20	–	–	–	–	α spectrometry	Spike	[19]
	1.1	0.04	100	40	–	–	–	–	α spectrometry	Spike	[20]
	1.093	0.06	93.0	60	–	–	–	–	α spectrometry	Spike	[22]
	1.11	0.005	110	5.0	–	–	–	–	TIMS	Spike	[23]
	1.14	0.01	140	10	–	–	–	–	SF-ICP-MS	Spike	[41]
	1.108	0.007	108.0	6.7	137.71	0.14	−1.2	0.98	MC-ICP-MS	SSB	This study
GBW04412	1.86	0.08	860	80	–	–	–	–	α spectrometry	Spike	[19]
	1.86	0.08	860	80	–	–	–	–	TIMS	Spike	[40]
	1.903	0.0078	903.0	7.8	–	–	–	–	SF-ICP-MS	Spike	[41]
	1.848	0.006	847.9	5.5	137.72	0.19	−1.15	1.39	MC-ICP-MS	SSB	This study
GBW04413	1.42	0.04	420	40	–	–	–	–	α spectrometry	Spike	[21]
	1.411	0.006	411.0	6.0	–	–	–	–	TIMS, spike	Spike	[21]
	1.499	0.0064	499.0	6.4	–	–	–	–	SF-ICP-MS	Spike	[41]
	1.423	0.005	422.8	5.0	137.77	0.11	−0.82	0.81	MC-ICP-MS	SSB	This study

Analytical uncertainties for (^{234}U/^{238}U) and ^{238}U/^{235}U are given by 2*s* (standard deviation).

[a] $\delta^{234}U=\{(^{234}U/^{238}U)_{sample}/(^{234}U/^{238}U)_{equillbrium})-1\}\times 10^3$
where (^{234}U/^{238}U)$_{\text{sample}}$ denotes the mean determined ^{234}U/^{238}U activity ratio for sample material in this study. The δ^{234}U is the variation of (^{234}U/^{238}U) relative to the radioactive secular equilibrium value. Analytical uncertainties of δ^{234}U are given by 2*s* (‰).

[b] $\delta^{238}U=\{(^{238}U/^{235}U)_{sample}/^{238}U/^{235}U)_{standard})-1\}\times 10^3$
where (^{238}U/^{235}U)$_{\text{standard}}$ denotes the ^{238}U/^{235}U isotopic ratio (137.880) for SRM-950a [38]. The δ^{238}U reflects the ^{238}U/^{235}U variation relative to the U isotopic ratio of SRM-950a. Analytical uncertainties of δ^{238}U showed by 2*s* (‰).

climatic conditions. Cave stalagmitescan provide an archive of environmental change through the Quaternary. The initial (^{234}U/^{238}U) and δ^{18}O from the speleothem in the Soreq cave, Israel were correlated and the variation of U isotopic ratio can be explained in terms of climatic changes affecting the drip water discharge rate, which reflects precipitation and weathering conditions of the local soil and soil water [35]. Temporal (^{234}U/^{238}U) records in stalagmites can be applied as excellent tools for paleoclimate and paleohydrology [35–37].

The δ^{238}U reflects ^{238}U/^{235}U variation relative to the U isotopic ratio of SRM-950a [38]. Most δ^{238}U values incarbonate standards are higher than seawater, where the largest variation occurred in stalagmite specimens (Table 6). The results of Stirling et al. [15] are rather similar to this study. Except for JCp-1, the data reported here are the first published ^{238}U/^{235}U ratios for RKM-4, RKM-5, GBW04412 and GBW04413. The ^{238}U/^{235}U ratios in JCp-1, RKM-4 and RKM-5 are 137.72 ± 0.15, 137.75 ± 0.12 and 137.71 ± 0.14, respectively. Our JCp-1 results are similar to the published ^{238}U/^{235}U ratio, 137.798 ± 0.001 from Watanabe and Nakai [11]. ^{238}U/^{235}U in GBW04412 and GBW04413 are rather similar, 137.72 ± 0.19 and 137.77 ± 0.11, respectively. The published ^{238}U/^{235}U in natural coral and speleothem ranges from 137.741 ± 0.018 to 137.890 ± 0.012 [15,16,25]. Our measured ^{238}U/^{235}U in coral and speleothem standards fall within a similar range or slightly lower, the slightly poor precision is possibly due to smaller amount of U used.

In this study, thedetermination of $^{238}U/^{235}U$ ratios and ($^{234}U/^{238}U$) is possibly limited to the following reasons: (1) The large differences in natural U isotopic abundances (^{238}U: 99.28%, ^{235}U: 0.72% and ^{234}U: 0.0054%) make it difficult to measure the high precise $^{238}U/^{235}U$ and ($^{234}U/^{238}U$) simultaneously without using spikes. (2) Low U concentration exists in most natural materials, such as seawater, river water, groundwater and rain water. The average U concentration is in the range of several ng g^{-1} to pg g^{-1}. Therefore, a method which requires a smaller amount of U is of benefit for many research applications. In this new approach, only12 ng U was used for $^{238}U/^{235}U$ and ($^{234}U/^{238}U$) measurement without spike. This is 1.6-80 times lower than the methods in Stirling et al. [15], Weyer et al. [16] and Hiess et al. [25]. The $^{238}U/^{235}U$ natural variation in the five carbonate standards is small and cannot be distinguished with this method. However, this method is sensitive enough to quantify the variation in ($^{234}U/^{238}U$) in many natural samples. Future high-precision techniques for $^{238}U/^{235}U$ measurement are still necessary for detecting minor variations in those standards. However, the analytical approach shown here can provide a fast, simple and precise determination for ($^{234}U/^{238}U$) and $^{238}U/^{235}U$, which are useful for many relevant studies related to chemical weathering, oceanography and climatic changes.

4. Conclusions

In this study, we developed a UTEVA separation protocol and standard-sample bracketing MC-ICP-MS analytical procedures for a rapid and simple analysis of U isotopic measurement in different natural materials.Our major conclusions are as follows: (1) A routine UTEVA column procedure is available for U and Th separation in carbonates, seawater and fresh water. (2) We determined precise ($^{234}U/^{238}U$) and $^{238}U/^{235}U$ ratios for carbonate reference standards JCp-1, RKM-4 and RKM-5, GBW04412 and GBW04413. (3) The measured ($^{234}U/^{238}U$) of JCp-1 is the same as the value of modern seawater, reflecting no diageneticartifacts in this standard. The ($^{234}U/^{238}U$) in RKM-4 and RKM-5 shows large variations, possibly due to potential α-recoil artifacts. A rather large ($^{234}U/^{238}U$) difference were measured in GBW04412 and GBW04413, reflecting the degree of weathering and ground water/ soil interaction. (4) Only a small variability in $^{238}U/^{235}U$, within analytical uncertainty, was measured in the carbonates analyzed.

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References

[1] M. Ivanovich, R.S. Harmon, Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, 2nd ed., Clarendon Press Oxford, 1992.
[2] N. Kumar, R.F. Anderson, R.A. Mortlock, P.N. Froelich, P. Kubik, B. Dittrichhannen, M. Suter, Nature 378 (1995) 675–680.
[3] F. Sirocko, D. Garbe-Schönberg, C. Devey, Global Planet. Change 26 (2000) 217–303.
[4] R.L. Fleischer, O.G. Raabe, Geochim. Cosmochim. Acta 42 (1978) 973–978.
[5] P. Swarzenski, P. Campbell, D. Porcelli, B. McKee, Cont. Shelf Res. 24 (2004) 2357–2372.
[6] J.H. Chen, R. Lawrence Edwards, G.J. Wasserburg, Earth Planet. Sci. Lett. 80 (1986) 241–251.
[7] L.F. Robinson, N.S. Belshaw, G.M. Henderson, Geochim. Cosmochim. Acta 68 (2004) 1777–1789.
[8] M.B. Andersen, C.H. Stirling, D. Porcelli, A.N. Halliday, P.S. Andersson, M. Baskaran, Earth Planet. Sci. Lett. 259 (2007) 171–185.
[9] M.B. Andersen, C.H. Stirling, B. Zimmermann, A.N. Halliday, Geochem. Geophys. Geosyst. 11 (2010).
[10] G.M. Henderson, Earth Planet. Sci. Lett. 199 (2002) 97–110.
[11] Y. Watanabe, Si Nakai, Microchim. Acta 156 (2006) 289–295.
[12] M. Bar-Matthews, C.W. Marean, Z. Jacobs, P. Karkanas, E.C. Fisher, A.I.R. Herries, K. Brown, H.M. Williams, J. Bernatchez, A. Ayalon, P.J. Nilssen, Quat. Sci. Rev. 29 (2010) 2131–2145.
[13] E. Douville, E. Sallé, N. Frank, M. Eisele, E. Pons-Branchu, S. Ayrault, Chem. Geol. 272 (2010) 1–11.
[14] G.A. Cowan, H.H. Adler, Geochim. Cosmochim. Acta 40 (1976) 1487–1490.
[15] C.H. Stirling, M.B. Andersen, E.-K. Potter, A.N. Halliday, Earth Planet. Sci. Lett. 264 (2007) 208–225.
[16] S. Weyer, A.D. Anbar, A. Gerdes, G.W. Gordon, T.J. Algeo, E.A. Boyle, Geochim. Cosmochim. Acta 72 (2008) 345–359.
[17] D.J. Condon, N. McLean, S.R. Noble, S.A. Bowring, Geochim. Cosmochim. Acta 74 (2010) 7127–7143.
[18] T. Okai, A. Suzuki, H. Kawahata, S. Terashima, N. Imai, Geostand. Newslett. 26 (2002) 95–99.
[19] R.S. Harmon, T.L. Ku, R.K. Matthews, P.L. Smart, Geology 7 (1979) 405–409.
[20] J.W. Pickett, T.L. Ku, C.H. Thompson, D. Roman, R.A. Kelley, Y.P. Huang, Quat. Res. 31 (1989) 392–395.
[21] Z.C. Peng, Z.R. Wang, W.D. Sun, Z.B. Ma, M. Xia, C.H. Zhang, W.J. Chen, Z.L. Zhang, Z.H. An, Chin. Sci. Bull. 43 (1998) 333–336.
[22] H.E. Carter, P. Warwick, J. Cobb, G. Longworth, Analyst 124 (1999) 271–274.
[23] Z.B. Ma, J.L. Xiao, X.T. Zhao, Z.C. Peng, M. Xia, G.P. Zhang, Z.R. Wang, Z.S. An, J. Coastal Res. 19 (2003) 296–303.
[24] E.K. Potter, C.H. Stirling, M.B. Andersen, A.N. Halliday, Int. J. Mass Spectrom. 247 (2005) 10–17.
[25] J. Hiess, D.J. Condon, N. McLean, S.R. Noble, Science 335 (2012) 1610–1614.
[26] H. Cheng, R.L. Edwards, J. Hoff, C.D. Gallup, D.A. Richards, Y. Asmerom, Chem. Geol. 169 (2000) 17–33.
[27] A. Jaffey, K. Flynn, L. Glendenin, W. Bentley, A. Essling, Phys. Rev. C 4 (1971) 1889–1906.
[28] S.L. Goldstein, P. Deines, E.H. Oelkers, R.L. Rudnick, L.M. Walter, Chem. Geol. 202 (2003) 1–4.
[29] D. Delanghe, E. Bard, B. Hamelin, Mar. Chem. 80 (2002) 79–93.
[30] S. Richter, A. Alonso, W.D. Bolle, H. Kühn, A. Verbruggen, R. Wellum, P.D.P. Taylor, Int. J. Mass Spectrom. 247 (2005) 37–39.
[31] S. Richter, R. Eykens, H. Kühn, Y. Aregbe, A. Verbruggen, S. Weyer, Int. J. Mass Spectrom. 295 (2010) 94–97.
[32] G.A. Brennecka, L.E. Borg, I.D. Hutcheon, M.A. Sharp, A.D. Anbar, Earth Planet. Sci. Lett. 291 (2010) 228–233.
[33] R. Lawrence Edwards, J.H. Chen, G.J. Wasserburg, Earth Planet. Sci. Lett. 81 (1987) 175–192.
[34] P. van Calsteren, L. Thomas, Earth-Sci. Rev. 75 (2006) 155–175.
[35] A. Kaufman, G.J. Wasserburg, D. Porcelli, M. Bar-Matthews, A. Ayalon, L. Halicz, Earth Planet. Sci. Lett. 156 (1998) 141–155.
[36] J. Zhou, C.C. Lundstrom, B. Fouke, S. Panno, K. Hackley, B. Curry, Chem. Geol. 221 (2005) 1–20.
[37] O.M. Göktürk, D. Fleitmann, S. Badertscher, H. Cheng, R.L. Edwards, M. Leuenberger, A. Fankhauser, O. Tüysüz, J. Kramers, Quat. Sci. Rev. 30 (2011) 2433–2445.
[38] K.J.R. Rosman, P.D.P. Taylor, Pure Appl. Chem. 70 (1998) 217–235.
[39] Z.R. Wang, Z.F. Zhang, Z.C. Peng, Z.B. Ma, Chin. J. Geochem. 20 (2001) 138–143.
[40] Z.B. Ma, M. Xia, C.H. Zhang, Z.C. Pen, Z.R. Wang, W.D. Sun, Z.S. An, Chin. Sci. Bull. 44 (1999) 937–941.
[41] M.L. Shen, Department of Earth Sciences, National Chen Kung University, Tainan, 2007, pp. 65.
[42] T. Yokoyama, A. Makishima, E. Nakamura, Anal. Chem. 71 (1999) 135–141.
[43] C. Not, K. Brown, B. Ghaleb, C. Hillaire-Marcel, Mar. Chem. 130–131 (2012) 33–39.
[44] J. Fietzke, V. Liebetrau, A. Eisenhauer, C. Dullo, J. Anal. Atom. Spectrom. 20 (2005) 395.
[45] P. Deschamps, R. Doucelance, B. Ghaleb, J.-L. Michelot, Chem. Geol. 201 (2003) 141–160.
[46] M.B. Andersen, C.H. Stirling, E.K. Potter, A.N. Halliday, Int. J. Mass Spectrom. 237 (2004) 107–118.
[47] C.H. Stirling, A.N. Halliday, D. Porcelli, Geochim. Cosmochim. Acta 69 (2005) 1059–1071.
[48] C. Stirling, A. Halliday, E. Potter, M. Andersen, B. Zanda, Earth Planet. Sci. Lett. 251 (2006) 386–397.
[49] X. Luo, M. Rehkamper, D.C. Lee, A.N. Halliday, Int. J. Mass Spectrom. Ion Process. 171 (1997) 105–117.
[50] L.F. Robinson, G.M. Henderson, N.C. Slowey, Earth Planet. Sci. Lett. 196 (2002) 175–187.
[51] J. Hellstrom, J. Anal. Atom. Spectrom. 18 (2003) 1346.
[52] D.L. Hoffmann, J. Prytulak, D.A. Richards, T. Elliott, C.D. Coath, P.L. Smart, D. Scholz, Int. J. Mass Spectrom. 264 (2007) 97–109.
[53] A. Makishima, T.A. Chekol, E. Nakamura, J. Anal. Atom. Spectrom. 22 (2007) 1383.