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Development of Two New Copper Isotope Standard Solutions and their Copper Isotopic Compositions

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In this study, two new laboratory reference solutions for testing Cu isotopic composition were established and investigated. Two commercially available pure copper products, copper plate and copper wire, were dissolved in 1000-ml Teflon® bottles, to produce 200 μg ml^{-1} stock solutions (hereafter referred to as NWU-Cu-A and NWU-Cu-B), and cryogenically stored. The Cu isotopic compositions of the two samples were determined in three different laboratories using multi-collector inductively coupled plasma-mass spectrometry, and the Cu isotopic compositions obtained from the standard-sample bracketing method were consistent within the two standard deviation (2s) range. The Cu isotopic compositions of the NWU-Cu-A and NWU-Cu-B standard solutions were δ^{65}Cu = +0.91 ± 0.03‰ (2s, n = 42) and δ^{65}Cu = -0.05 ± 0.03‰ (2s, n = 49), respectively, relative to the reference material NIST SRM 976.

Keywords: copper isotopes, MC-ICP-MS, reference material, stable isotope, pure copper metal.

Naturally occurring copper has two stable isotopes, ^{65}Cu and ^{63}Cu, with abundances of 30.83% and 69.17%, respectively (Shields *et al.* 1965, Coplen *et al.* 2002, Liaghati *et al.* 2004). Studies have shown that considerable copper isotope fractionation occurs in the natural environment and that the overall isotopic variability of δ^{65}Cu ranges from -16.49‰ to +19.73‰, while the bulk silicate Earth (BSE) has an average δ^{65}Cu value of +0.06 ± 0.20‰ (2s). Therefore, Cu isotopes can be used as a sensitive geochemical tracing agent to investigate the processes and mechanisms of diagenesis and metallogenesis (Zhu *et al.* 2000, Markl *et al.* 2006, Qian *et al.* 2006, Asael *et al.* 2007, Mathur *et al.* 2009, 2012, Bigalke *et al.* 2010, Li *et al.* 2010, 2015, Wang and Zhu 2010, Navarrete *et al.* 2011, Fellows and Canil 2012, Berkenbosch *et al.* 2015, Liu *et al.* 2015, Mathur and Fantle 2015, Ripley *et al.* 2015, Savage *et al.* 2015, Zhong *et al.* 2015, Lv *et al.* 2016, Song *et al.* 2016). In addition, Cu isotopic studies provide new evidence for metal contaminants in natural soils (Fekiacova *et al.* 2015, Li *et al.* 2015), weathering of black

shale (Mathur *et al.* 2012, Lv *et al.* 2016) and isotope fractionation during biogeochemistry process (Fujii *et al.* 2013, 2014). In recent years, the development and application of multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) has enabled highly accurate determination of the isotopic compositions of metals such as copper, iron, zinc that cannot be precisely determined by traditional thermal ionisation mass spectrometry (Sariego Muniz *et al.* 1999, Zhu *et al.* 2002, 2015, Archer and Vance 2004, Dauphas *et al.* 2009, Liu *et al.* 2014a, Wu *et al.* 2016).

Performing high-accuracy MC-ICP-MS measurement of isotopic composition requires the removal of interferences in MS spectra and calibration of the mass discrimination effects in the instrument (Petit *et al.* 2008). Interferences in the MS system, such as interfering ions or interfering peaks, are normally eliminated by chemical purification. Mass discrimination effects can be calibrated using the standard-sample bracketing (SSB) method as the Cu isotopes in both samples

and standard solutions are purified and any interferences can be ignored. The Cu isotopic composition of a sample measured by SSB method is expressed in δ notation in per mil relative to the reference material:

$$\delta^{65}Cu = \left(\frac{\left(\frac{65_{Cu}}{63_{Cu}}\right)sample}{\left(\frac{65_{Cu}}{63_{Cu}}\right)standard} - 1 \right) \times 1000 \qquad (1)$$

The international reference material for copper isotope tests is National Institute of Standards and Technology reference material NIST SRM 976; however, this reference material is no longer commercially available. Several researchers have investigated potential alternative reference materials. For example, Moeller et al. proposed three new reference materials ERM®-AE633, ERM®-AE647 (Cu) and IRMM-3702 (Zn). The Cu isotope amount ratio of NIST SRM 976 yielded $\delta^{65}Cu$ values of -0.01 ± 0.05‰ and -0.21 ± 0.05‰ relative to ERM®-AE633 and ERM®-AE647, respectively (Moeller et al. 2012); Liu et al. used Chinese National Reference Material GSB Cu as a new laboratory measurement standard; its measured value for $\delta^{65}Cu$ was +0.44 ± 0.04‰ (2s, n = 32) relative to NIST SRM 976 (Liu et al. 2014b). The value of the test sample relative to NIST SRM 976 can be converted from the measured value of the test sample relative to the laboratory standard.

In practice, after the instrument parameters are optimised, the stability and measurement accuracy of the instrument must be assessed before testing the sample. Whether a testing instrument is able to accurately analyse the Cu isotopic composition of a sample cannot be verified with only one reference material. In this study, two laboratory standard solutions with the potential to serve as reference materials in Cu isotopic determination were prepared from commercially available copper plate and copper wire. Independent analyses were performed in three laboratories at the University of Science and Technology of China, China University of Geosciences (Beijing) and Northwest University to assess the Cu isotopic compositions of the standard solutions.

Experimental procedure

Reagents and materials

Materials used in this study included the following: copper plate (metallic state; dimensions: 10 × 34 × 0.6 cm; mass: 1.7 kg; stock #43822; lot #E23T019, hereafter referred to as NWU-Cu-A) and copper wire (metallic state; dimensions: 1.0 mm (diameter) × 1 m (length); mass: 7.2 g; stock #10974; lot# I28Q011;

hereafter referred to as NWU-Cu-B) manufactured by Alfa Aesar (Shanghai, China); Geochemical Evolution and Metallogeny of Continents (GEMOC) laboratory standard GEMOC Cu, Macquarie University, Australia (solution state, in 2% HNO_3, courtesy of Kejun Hou); Institute for Materials Research (IMR) Cu manufactured by Johnson Matthey (solution state, in 2% HNO_3, courtesy of Kejun Hou); laboratory standard GSB Cu, Key Laboratory of Isotopic Geology, Ministry of Land and Resources (solution state, in 2% HNO_3, courtesy of Xiangkun Zhu); Chinese Academy of Geological Sciences (CAGS) Cu (solution state, in 2% HNO_3, courtesy of Xiangkun Zhu). These standard solutions were analysed to evaluate the accuracy and precision of Cu isotopic compositions of this work.

Both HCl and HNO_3 used in this work were distilled twice using a Savillex TM DST-1000 sub-boiling still (Minnetonka, MN, USA). The super-pure water that was used was purified using a Milli-Q Element water purification system (Elix-Millipore, Billerica, MA, USA) (resistivity = 18.2 MΩ cm) and then distilled on a quartz sub-boiling still.

Preparation of standard solution

Pure copper metal samples were dissolved as follows: each sample was rinsed successively with anhydrous ethanol and 2% HNO_3 to remove surface pollutants, dissolved in aqua regia in a Savillex Teflon® vial, evaporated at 120 °C to a wet salt state, dissolved in 1 ml of concentrated HNO_3, evaporated to a wet salt state, and finally dissolved in 2% v/v nitric acid, and diluted to obtain a 200 μg ml^{-1} stock solution. The container of stock solution was capped, sealed with parafilm, and stored at 4 °C. Before analysis, the stock solution was diluted to 100 ng ml^{-1} with 2% HNO_3.

Instrumental

Copper isotopes were determined using double-focussing MC-ICP-MS at the State Key Laboratory of Continental Dynamics, Northwest University (Lab 1; Nu Plasma II MC-ICP-MS, Nu Instruments, Wrexham, UK), the State Key Laboratory of Geological Processes Mineral and Resources, China University of Geosciences (Beijing) (Lab 2; Neptune Plus, Thermo Fisher Scientific, Waltham, MA, USA) and the CAS Key Laboratory of Crust-Materials and Environments, University of Science and Technology of China (Lab 3: Neptune Plus, Thermo Fisher Scientific). In this study, all analyses were performed using Faraday cups in static mode. Lab 1 ran all analyses in solution mode, while Lab 2 and Lab 3 ran in dry mode using Aridus II

Table 1.
MC-ICP-MS operating conditions for Cu isotopic ratio measurements

MC-ICP-MS parameters	Nu Plasma Laboratory 1: NWU	Neptune Plus Laboratory 2: CUGB	Neptune Plus Laboratory 3:USTC
RF power (W)	1300	1000	1200
Plasma gas flow (l min^{-1})	13	16	16
Auxiliary gas flow (l min^{-1})	0.8	0.8	0.8
Nebuliser gas flow	33 psi	1.0 l min^{-1}	1.0 l min^{-1}
Cones, Sampler + skimmer	Ni(285) + Ni(497)	Ni(X) + Ni(JET)	Ni(X) + Ni(JET)
Total beam intensity, V/µg g^{-1}	4	10–30	10–70
Background of ^{63}Cu (mV)	< 5	< 2	< 2
Mass resolution	Low	Low	Low
Sample uptake rate (µl min^{-1})	100 (wet plasma)	50 (wet plasma)	50 (dry via Aridus II)

desolvator. Specific instrument parameters are shown in Table 1. Trace element mass fractions were determined by quadruple ICP-MS (Varian 820 MS, Analytik Jena, Jena, Germany) using wet plasma mode. Copper distributions of the two metals were measured by energy dispersive spectroscopy (EDS; Oxford instruments, Abingdon, UK), which was installed on a scanning electron microscope (SEM, Quanta 450FEG, FEI, Hillsboro, OR, USA). The magnification was × 5000.

Results and discussion

During the course of Cu isotope measurement with MC-ICP-MS, the general SSB method was used to calibrate the mass discrimination and drifting during analysis without Ni correction and Zn-doping method; nevertheless, the effects of the concentrations of the reference solutions and the sample solutions were assessed, as were the effects of the acidity of the medium on the Cu isotopic ratios.
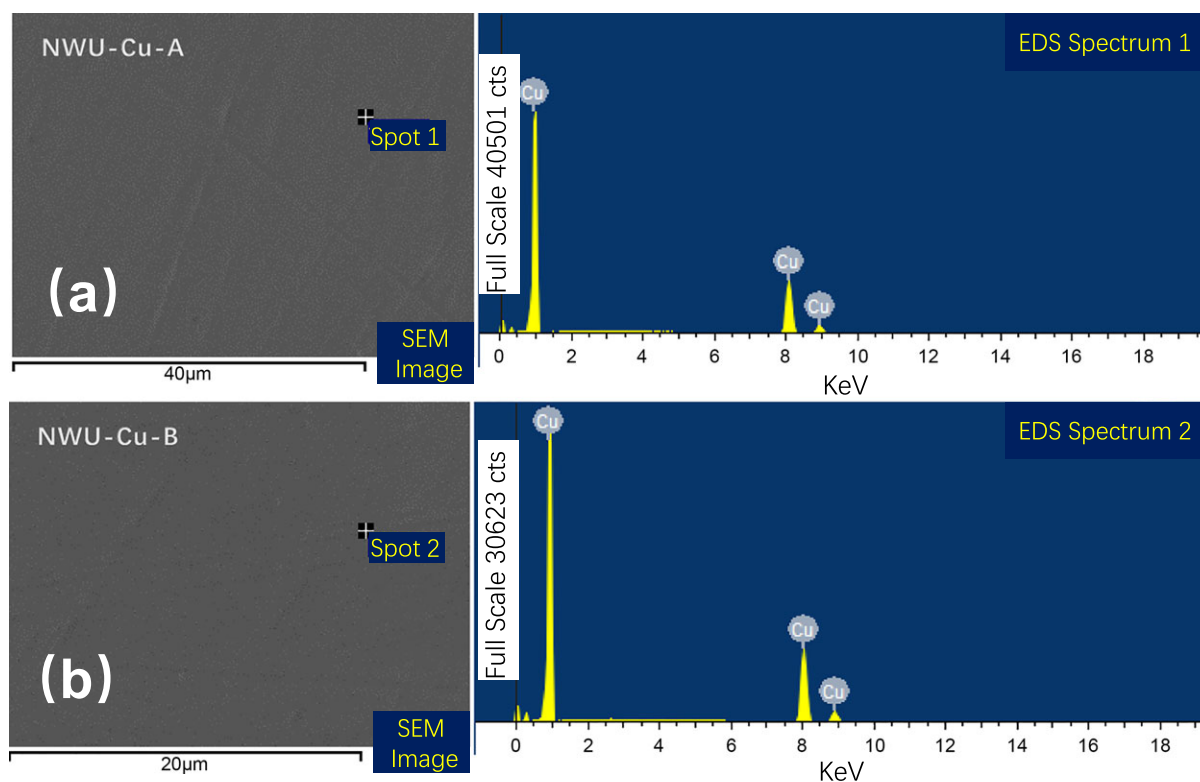

Figure 1. SEM-EDS single spot analysis of NWU-Cu-A and NWU-Cu-B metals: (a) SEM image and EDS spectrum of NWU-Cu-A, (b) SEM image and EDS spectrum of NWU-Cu-B. [Colour figure can be viewed at wileyonlinelibrary.com]

Purity of NWU-Cu-A and NWU-Cu-B metals

The two copper metals were measured using both SEM-EDS and ICP-MS for copper and trace element mass fractions. The EDS spectrum showed that there were only copper peaks detected on the two metals (Figure 1). Several portions of the two copper metals were dissolved and Rh was used as an internal standard element during ICP-MS measurement. The results revealed that all trace elements of the two metals were lower than 0.05 ng g^{-1} except Zn and Ni. Nickel concentration in NWU-Cu-A and NWU-Cu-B were 0.12 and 0.80 ng g^{-1}, respectively. This was probably caused by Ni cones applied in this work. Zinc concentration in NWU-Cu-A and NWU-Cu-B was 0.55 and 0.77 ng g^{-1}, respectively. These trace elements could not affect the Cu isotope measurement as they were too low to be detected by the Faraday cups in MC-ICP-MS when the stock solution was diluted 10^6 times for Cu isotope determination.

Effects of acidity

In this study, 2% HNO$_3$ was used as the medium for Cu isotope measurement with MC-ICP-MS. The effect of acidity was tested using a series of NWU-Cu-B solutions with different acidity. The NWU-Cu-B solution (1 μg ml^{-1}) with 2% HNO$_3$ was analysed as a reference, while those contained 0–4% HNO$_3$ were analysed as 'samples'. The results indicated that changes in the acidity clearly affected the results of the Cu isotopic compositions (Figure 2). When the medium was ultrapure water, the Cu isotopic composition was 0.5‰ lighter than that in 2% HNO$_3$. The correlation coefficient of the acidity ratio and the δ^{65}Cu value was 0.93. This result may have occurred because changes in the acidity of the sample solution altered the ionisation efficiency of the plasma, leading to changes in mass discrimination by the instrument. Therefore, during sample testing, the acidity of the sample solutions was strictly set to match with that of the reference standard solution when the analyses were run in wet plasma mode.

Effects of concentration

A series of NWU-Cu-B solutions of different Cu concentrations ('samples') were measured, while a NWU-Cu-B solution of 1 μg ml^{-1} Cu content was analysed as the bracketed standard. The Cu isotopic ratio of each 'sample' was calculated relative to the standard solution. When the Cu concentration ratio between 'samples' and standard changed within a range of 0.08–12 times, the Cu ion signal intensity of the samples ranged from 5 to 50 V, but the fractioning coefficient (β) of the MS system was not correlated with the signal intensity (which changed within the
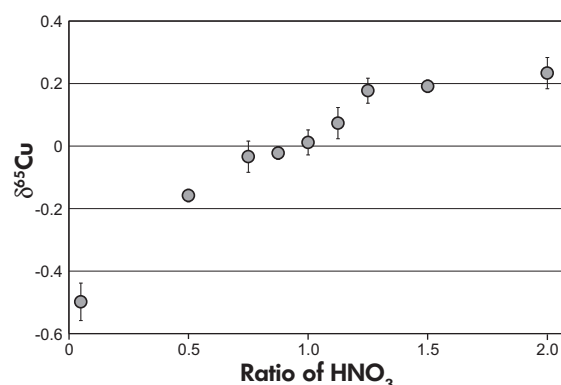

Figure 2. Effects of different acidities of sample solutions/standard solution on Cu isotopic ratio. Both the sample and the standard were NWU-Cu-B.

range of 1.81–1.91, Figure 3). The Cu isotopic ratios of all 'samples' agreed well within the two standard deviation (2*s*) range. Because suitable signal intensity ensured highly accurate and precise analysis by the MS system, the concentrations of the solution were typically 1 μg ml^{-1} for wet plasma mode and 100–200 ng ml^{-1} for dry plasma mode, which was equilibrated to the extent that the signal intensity was within a range of 10–20 V.

Reproducibility of preparation method and copper isotopic composition

The Cu isotopic compositions of the prepared NWU-Cu-A and NWU-Cu-B solutions were analysed by different operators in three different laboratories at the State Key Laboratory of Continental Dynamics, Northwest University; the State Key Laboratory of Geological Processes Mineral and Resources, China University of Geosciences (Beijing); and the CAS Key Laboratory of Crust-Materials and Environments, University of
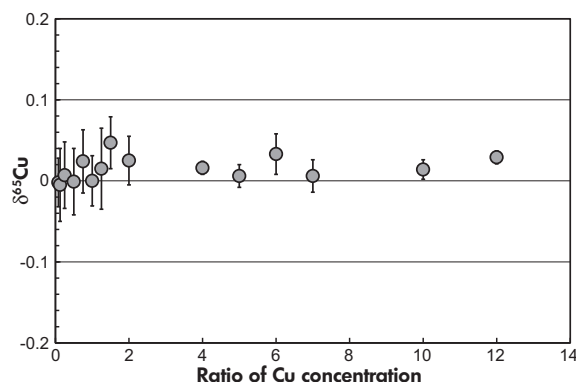

Figure 3. δ^{65}Cu of various concentrations of Cu in NWU-Cu-B relative to fixed Cu content in NWU-Cu-B (1 μg ml^{-1}).
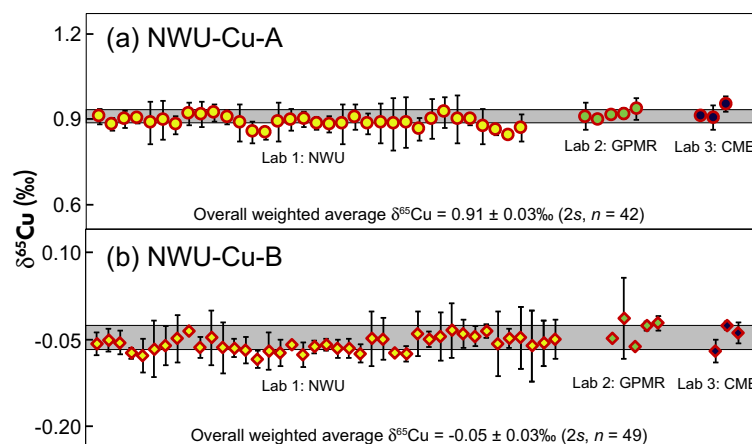
Figure 4. Copper isotopic compositions of NWU-Cu-A and NWU-Cu-B reported by three different laboratories. Lab 1 is the State Key Laboratory of Continental Dynamics, Northwest University; Lab 2 is the State Key Laboratory of Geological Processes Mineral and Resources, China University of Geology (Beijing); Lab 3 is the CAS Key Laboratory of Crust-Materials and Environments, University of Science and Technology of China. [Colour figure can be viewed at wileyonlinelibrary.com]

Science and Technology of China (results shown in Figure 4). The results for NWU-Cu-A from the three laboratories were as follows: $\delta^{65}Cu$ = +0.89 ± 0.04‰ (2s, n = 34), $\delta^{65}Cu$ = +0.92 ± 0.03‰ (2s, n = 5) and $\delta^{65}Cu$ = +0.92 ± 0.05‰ (2s, n = 3), respectively; the weighted mean for the results from the three laboratories was +0.91 ± 0.03‰ (2s). The measurement results for NWU-Cu-B from the three laboratories were as follows: $\delta^{65}Cu$ = -0.06 ± 0.03‰ (2s, n = 41), $\delta^{65}Cu$ = -0.02 ± 0.01‰ (2s, n = 5) and $\delta^{65}Cu$ = -0.05 ± 0.05‰ (2s, n = 3), respectively; the weighted mean for the results from the three laboratories was -0.05 ± 0.03‰ (2s).

Both NWU-Cu-A and NWU-Cu-B were homogeneous in terms of their Cu isotopic compositions. The difference of $\delta^{65}Cu$ between the two standards was 0.96‰, which ensured the application of these two standards for quality control (QC) purpose or running as bracketing standard. As the initial state of these two standards was metal, they could be used as QC or bracketing standard in microbeam analysis, for example, laser ablation.

The Cu isotopic ratios of four laboratory reference materials, GEMOC Cu, IMR Cu, CAGS Cu and GSB Cu,

Table 2.
Copper isotopic compositions of Institute for Materials Research (IMR) Cu, GEMOC Cu, Chinese Academy of Geological Sciences (CAGS) Cu and GSB Cu using NWU-Cu-A and NWU-Cu-B as calibration materials

Sample	$\delta^{65}Cu$		$\delta^{65}Cu_{Reported}$	Sources
	Measured, this work	**Recalculated to NIST SRM 976**		
Calibrator: NWU-Cu-A				
IMR Cu	-0.56 ± 0.04 (n = 34)	0.35 ± 0.05	0.34 ± 0.08 (n = 32)	Hou *et al.* (2008)
GEMOC Cu	-0.92 ± 0.06 (n = 46)	-0.01 ± 0.07	-0.06 ± 0.09 (n = 105)	Li *et al.* (2008)
			-0.04 ± 0.07 (n = 10)	Hou *et al.* (2008)
CAGS Cu	-0.37 ± 0.06 (n = 17)	0.54 ± 0.07	0.57 ± 0.08 (n = 13)	Li *et al.* (2008)
			0.55 ± 0.05 (n = 9)	Hou *et al.* (2008)
GSB Cu	-0.44 ± 0.05 (n = 12)	0.47 ± 0.06	0.44 ± 0.04 (n = 32)	Liu *et al.* (2014a, b)
Calibrator: NWU-Cu-B				
IMR Cu	0.39 ± 0.03 (n = 25)	0.34 ± 0.04	0.34 ± 0.08 (n = 32)	Hou *et al.* (2008)
GEMOC Cu	0.03 ± 0.04 (n = 54)	-0.02 ± 0.05	-0.06 ± 0.09 (n = 105)	Li *et al.* (2008)
			-0.04 ± 0.07 (n = 10)	Hou *et al.* (2008)
CAGS Cu	0.58 ± 0.07 (n = 27)	0.53 ± 0.08	0.57 ± 0.08 (n = 13)	Li *et al.* (2008)
			0.55 ± 0.05 (n = 9)	Hou *et al.* (2008)
GSB Cu	0.49 ± 0.06 (n = 24)	0.44 ± 0.07	0.44 ± 0.04 (n = 32)	Liu *et al.* (2014a, b)

were measured using NWU-Cu-A and NWU-Cu-B as the standards (Table 2). The Cu isotopic compositions of the above-mentioned laboratory standard materials relative to NIST SRM 976 were calculated from the Cu isotopic compositions of NWU-Cu-A and NWU-Cu-B relative to NIST SRM 976 and were consistent with the reported values within the 2s range.

Conclusions

In this study, two different copper isotope solutions were prepared using commercially available pure copper plate and copper wire; their Cu isotopic compositions were measured in three different laboratories using MC-ICP-MS, and the mass discrimination effects were calibrated using the SSB method. Differences in the acidity of the medium between the sample solution and the standard solution considerably affected the isotopic ratio; thus, it was necessary that the concentration of the medium acid in the sample solution was identical to that of the standard solution. However, differences in the copper concentration between the sample solution and the standard solution scarcely influenced the measurements of the Cu isotopic composition. The Cu isotopic ratios of the copper standard solutions NWU-Cu-A and NWU-Cu-B, prepared using commercially available sources of copper in solid state, were measured in three different laboratories and were $\delta^{65}Cu_{NWU-Cu-A} = +0.91 \pm 0.03$‰, (2s, $n = 42$), and $\delta^{65}Cu_{NWU-Cu-B} = -0.05 \pm 0.03$‰, (2s, $n = 49$) (reference material, NIST SRM 976). These results indicate that NWU-Cu-A and NWU-Cu-B may be used as reference materials for testing Cu isotopes in laboratories and may be provided to laboratories that require laboratory reference materials for method studies and microdomain analysis using laser ablation MC-ICP-MS or SIMS.

Acknowledgements

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