Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis

 Corey Archer[*1], Morten B. Andersen[1†], Christophe Cloquet[2], Tim M. Conway[1], Shuofei Dong[2], Michael Ellwood[3], Rebekah Moore[4], Joey Nelson[5], Mark Rehkämper[4], Olivier Rouxel[6$], Moneesha Samanta[3], Ki-Cheol Shin[7], Yoshiki Sohrin[8], Shotaro Takano[8] and Laura Wasylenki[9]

[1]Inst. of Geochemistry and Petrology, Dept. of Earth Sciences, ETH Zürich
[*]*Corresponding author (corey.archer@erdw.ethz.ch)*
[2]CRPG, UMR-CNRS 7358, 15 rue Notre Dame des Pauvres, Vandœuvre les Nancy, 54500, France
[3]Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia
[4]Department of Earth Science & Engineering, Imperial College London, London SW7 2AZ, UK
[5]Department of Geological Sciences, Stanford University, Stanford, CA 94305, USA
[6]IFREMER, Dept. Phys. Resources & Deep Sea Ecosyst, Ctr Brest, F-29280 Plouzane, France
[7]Research Institute for Humanity and Nature, 457-4, Motoyama, Kamigamo, Kita-ku, Kyoto, 603-8047, Japan
[8]Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan
[9]Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA

[†]Now at: School of Earth & Ocean Sciences, Cardiff University, Park Place, CF10 3AT, Cardiff
[$]Now at: Deparment of Oceanography, University of Hawaii, Honolulu HI 96822, USA

Abstract

We have prepared a large volume of pure, concentrated and homogenous zinc standard solution. This new standard solution is intended to be used as a primary reference standard for the zinc isotope community, and to serve as a replacement for the near-exhausted current reference standard, the so-called JMC-Lyon Zn. The isotopic composition of this new zinc standard (AA-ETH Zn) has been determined through an inter-laboratory calibration exercise, calibrated against the existing JMC-Lyon standard, as well as the certified Zn reference standard IRMM-3702. The data show that the new standard is isotopically indistinguishable from the IRMM-3702 zinc standard, with a weighted $\delta^{66/64}$Zn value of 0.28±0.02‰ relative to JMC-Lyon. We suggest that this new standard be assigned a value $\delta^{66/64}$Zn of +0.28‰ for reporting of future Zn isotope data, with the rationale that all existing published Zn isotope data are presented relative to the JMC-Lyon standard. Therefore our proposed presentation allows a direct comparison with all previously published data, and that is directly traceable to a certified reference standard, IRMM-3702 Zn. This standard will be made freely available to all interested labs through contact with the corresponding author.

Introduction

The stable isotopes of Zn have, in recent years, emerged as a powerful tracer of natural process in the Earth Sciences. Much of the focus, though by no means exclusively, has been

on investigating the role of Zn and its biogeochemical cycling in the modern ocean [1-5] and on the understanding of processes occurring during planetary formation [6-9]. Common to many of the recently developed non-traditional stable metal isotope systems (e.g. Cu, Mo, Fe, Li), made analytically feasible due to advances in multiple collector inductively coupled plasma-mass spectrometers (MC-ICPMS), comparative studies of Zn and its isotopes have been complicated by the lack of an internationally certified reference standard. However, where rigorous data comparison for other non-traditional stable metal isotope systems such as Mo has been severely hampered in this regard [10, 11], most, if not all Zn isotope data to date has been referenced to the same ICP Zn standard, the so-called JMC-Lyon standard, made available by the authors after the initial high-precision Zn isotope study of Marechal *et al*[12]. Unfortunately the JMC-Lyon standard is nearing exhaustion, and therefore a new reference standard is required.

Recently, efforts have been made to address the problem of a lack of Zn standard, with the creation of a certified reference standard, IRMM-3702 Zn, produced by the Institute for Reference Materials and Measurements (IRMM) in Belgium [13, 14]. Although the IRMM-3702 Zn standard will prove to be an invaluable reference standard for Zn isotope studies, it suffers from two important limitations which would preclude it from being adopted widespread as a primary reference standard. Firstly, it is relatively expensive to purchase because, secondly, at the time of writing it only available for purchase in relatively small aliquots ($\sim$3μmol Zn, or $\sim$200μg Zn). Such an amount of Zn would be of use as a primary reference standard to a laboratory routinely measuring Zn isotopes for only a short period of time. Furthermore, adopting the IRMM-3702 Zn as a primary reference standard would require the IRMM to supply this standard in its current form well into the future, which already seems unlikely given the small quantities in which it is currently distributed. Other potential candidates supplied by international bodies, such as the NIST 3168a Zn standard solution are also unlikely to be useful to the Zn community as a zero-point reference standard, as data suggests that it is isotopically light with a $^{66}Zn/^{64}Zn$ ratio that is approximately 1‰ lower than the JMC-Lyon reference standard (O. Rouxel, *unpbl.*). This composition is, therefore, at an extreme end of the natural range thus far reported for Zn isotopes. A second Zn standard from NIST, SRM 682 has an even more extreme composition, which is approximately 2.5‰ lighter than JMC-Lyon Zn[15, 16]. A third Zn standard supplied by NIST, SRM 683, has a measured composition that falls within the range of natural Zn compositions thus far reported[16, 17], and would therefore likely be useful as a reference standard for the Zn isotope community. But as with IRMM 3702, its availability into the future is not guaranteed. Furthermore, although SRM 683 Zn appears to be isotopically homogeneous[17], purified Zn metal standards have long been known to be extremely variable in their isotopic composition [16]. This potential for heterogeneity therefore precludes, or at the least complicates their adoption as universal zero-point reference standards.

To address this issue, we have prepared a large volume of homogenous Zn solution that we propose to offer as a new reference material for the Zn isotope community. Approximately 9 grams of pure Zn metal (Alfa Aesar Zn foil, Product Code 11912, Lot # I17Z058), which we estimate to be enough Zn to serve the Zn isotope community for the next 50 years, was dissolved in twice distilled 15M nitric acid and diluted to a 5% (v/v) solution with 18.2MΩ.cm de-ionised water (Milli-Q, Merck Millipore). The isotopic composition of this new Zn standard (AA-ETH Zn) was then determined through an inter-laboratory calibration. Participating labs were chosen to ensure a variety in Zn isotope methodology, to ensure that any potential biases produced through analytical protocol are resolved.

Analytical Methodology

A summary of the analytical protocols used by the participating laboratories is shown in Table 1. Most of the participating labs employ a Zn double spike for correction of mass fractionation. An underlying assumption of the using double spike techniques is that mass fractionation occurs according to mass, i.e. all isotopic fractionation is mass dependent. This is expected to be the case for elements with Z<80, such as Zn[18]. This expectation is confirmed by the data obtained from the Brest laboratory, using a non-double spike approach to correct for mass fractionation (Table 2). All participating labs performed measurements of the new AA-ETH Zn standard against both the JMC-Lyon and IRMM-3702 Zn standards. Zn isotopic compositions are reported in the usual δ^{66}Zn (‰) notation, and are reported relative to both the JMC-Lyon and IRMM-3702 Zn standards (Table 2), where

$$\delta^{66}\text{Zn (‰)} = \left[\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard}}} - 1 \right] x\ 1000$$

[1]

Similarly, δ^{67}Zn and δ^{68}Zn are described by the above equation, where ^{66}Zn is replaced by ^{67}Zn or ^{68}Zn respectively. Conversion from δ^{66}Zn to any other Zn isotope pair is achieved by multiplying this value by the factor $\ln(M_2/M_1)/\ln(\text{mass}\ ^{66}\text{Zn}/\text{mass}\ ^{64}\text{Zn})$, where the masses are the true masses, and according to the exponential mass fractionation law. In practice this factor can be approximated to the quotient of the nominal mass difference of the relevant isotope pairs. A brief description of the methodology used by each lab follows.

ETH Zürich

All analyses were performed using a Thermo Scientific NeptunePlus MC-ICPMS, using the standard sample and skimmer cones. Prior to analysis, each standard was doped with a mixed ^{64}Zn-^{67}Zn double spike to achieve a standard:spike ratio of ~ 1. Instrumental mass bias correction was performed using the double spike techniques described in Bermin *et al.*[1] Solutions were introduced into the mass spectrometer in a ~0.3M HNO$_3$ (2% v/v) solution via a Cetac Aridus II desolvating system or an Elemental Scientific (ESI) Apex-Q desolvating system, both coupled with a PFA nebuliser with a nominal uptake rate of 50 μL min^{-1}. Isobaric interferences from ^{64}Ni on ^{64}Zn were monitored using ^{62}Ni, but any correction here was always negligible. For data collected with the Apex, an addition correction for small amount of hydrides needed to be made, determined by monitoring the ^{64}ZnH$^+$ hydride produced at mass 65. Typically, hydrides were formed at the 10-20 ppm level. Long term reproducibility including measurements made using both sample introduction systems, as determined by analyses of IRMM-3702 Zn over the course of three years, including those made during each analytical session, is 0.06‰ (2sd).

Australian National University (ANU)

All analyses were performed using a Thermo Scientific NeptunePlus MC-ICPMS using the procedure described in Samanta *et al*[19]. Prior to analysis, each standard was doped with a mixed ^{67}Zn-^{68}Zn double spike to achieve a standard:spike ratio of ~ 0.25. Solutions were introduced into the mass spectrometer in a 2% v/v HNO$_3$ solution via an Elemental Scientific (ESI) Apex-Q desolvating system with a PFA nebuliser (ESI) with a nominal uptake rate of

50 μL min^{-1}. A standard Ni sampler cone and a Ni X-skimmer cone were to enhance instrument sensitivity. At the start of the measurement session, the instrument was tuned for intensities on mass ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{67}Zn and ^{68}Zn. All measurements were made in low resolution mode as 1 block of 30 cycles with a 4 second integration time. All measured ratios were corrected for any interference of ^{64}Ni on ^{64}Zn by monitoring the intensity of ^{62}Ni and subtracting the calculated intensity for ^{64}Ni, based on the natural ^{62}Ni/^{64}Ni ratio, from the measured intensity of ^{64}Zn. These corrections were always negligible compared to the standard/spike signal. The interference corrected data was then blank corrected by subtracting the average intensity of the 30 cycle measurement for each isotope from the intensities measured for the 2% (v/v) HNO$_3$ blank.

Brest

All analyses were performed using a Thermo Scientific Neptune MC-ICPMS. The instrument was tuned for intensities on mass ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{67}Zn and ^{68}Zn. Instrumental mass bias was corrected for by doping the Zn standard solutions with a pure copper standard solution (SRM3114) whose isotopic composition has been calibrated against SRM 976. The data reduction scheme is similar to the approach of Maréchal et al.,[12] which involves measuring ^{65}Cu/^{63}Cu to determine the instrumental mass bias factor using an exponential mass fractionation law. In addition to Cu normalization, Zn isotope ratios were further corrected using a standard bracketing approach, which normalizes the Zn isotope ratio of the sample to the average composition of the standard measured before and after each sample[20]. All measurements were made in low resolution mode as 1 block of 25 cycles with a 4 second integration time. Solutions in 0.28M HNO$_3$ were introduced into the plasma using a double spray quartz chamber system (cyclonic and double pass) and a microconcentric PFA nebulizer operating at a flow rate of about 60 μL min^{-1}. The MC-ICPMS was equipped with high-efficiency Ni-cones (X-cones) and run in medium resolution mode. Using this instrumental set-up, Zn and Cu isotopes were measured at concentrations of 300 ng g^{-1} and 200 ng g^{-1} respectively. Precision of the measurements, determined as the standard deviation values (2SD) of duplicated δ^{66}Zn analysis of the same standard/sample solution over several analytical sessions, generally ranged from 0.02‰ to 0.04‰.

CPRG – Nancy

Zn standard solutions (i.e. ETH AA Zn, IRMM-3702 and JMC-Lyon supplied by ETH) with known concentration were doped with ^{64}Zn-^{67}Zn double spike at a sample-spike ratio (m/m ratio) of 1:1.38 for mass bias correction (following the methods described in Bryan *et al.*[21]), then dried and re-dissolved with 0.1 M HNO$_3$ for Zn isotope ratio analysis. The Zn isotope ratios were determined using a Thermo Scientific NeptunePlus MC-ICPMS. The samples were introduced in wet plasma mode and PTFE nebulizer, at concentrations of 200 ng ml^{-1}. Data were collected as 1 block of 30 measurements (5 s integration time for each measurement). The wash out time between samples was 110 seconds using 0.3 M HNO$_3$, followed by a run of the same 0.1 M HNO$_3$ that the samples were re-dissolved in. Isobaric interference from ^{64}Ni on ^{64}Zn was monitored using intensity measurements of ^{62}Ni and was negligible (typically less than 10 ppm).

Imperial College London

The isotopic analyses were carried out with a Nu Plasma HR MC-ICPMS instrument at the MAGIC Laboratories using protocols modified from Arnold et al[22]. Prior to analysis, a ^{64}Zn-^{67}Zn double spike was added to and equilibrated with each standard solution at a ratio of spike-derived to natural Zn of about 1. The spike-sample mixtures were taken up in 0.1 M HNO$_3$ to achieve total Zn concentrations of ~100 ng mL^{-1}. An Aridus II (CETAC Technologies) desolvation system fitted with a nominal 100 μL min^{-1} glass nebulizer was used for sample introduction. The analyses involved simultaneous collection of the ion beams of ^{64}Zn$^+$, ^{66}Zn$^+$, ^{67}Zn$^+$, ^{68}Zn$^+$, and ^{62}Ni$^+$, ^{137}Ba^{2+} for interference correction. Data collection was performed in 3 blocks of 20 x 5 s integrations, with a 15 s electronic background measurement preceding each block. The instrumental mass bias encountered during the analyses was corrected using double spike data reduction methods adapted from Arnold et $al.$[22] For this, the "raw" measured isotope ratios of ^{64}Zn/^{67}Zn, ^{66}Zn/^{67}Zn and ^{68}Zn/^{67}Zn were processed offline with a spreadsheet-based iterative solver. Corrections for spectral interferences from ^{64}Ni$^+$ and Ba^{2+} ions (^{132}Ba^{2+}, ^{134}Ba^{2+} and ^{136}Ba^{2+}) were also subjected to mass bias correction. The required corrections were very small, however, at less 1 x 10^{-5} for both ^{64}Ni$^+$/^{64}Zn$^+$ and ^{134}Ba^{2+}/^{67}Zn$^+$. Additional interspersed analyses of the in-house London Zn standard solution yielded δ^{66}Zn$_{JMC}$ = 0.12 ± 0.06 ‰, in excellent agreement with three previous studies that reported results of 0.08 ‰ to 0.14 ‰ for this sample.[13, 22, 23]

Indiana University

Zinc isotopic standards (AA-ETH Zn, IRMM-3702 Zn and JMC-Lyon Zn) were measured relative to an in-house Zn standard (Sesame Zn) on the NuPlasmaII MC-ICPMS in the Sesame Lab at Indiana University Bloomington. Solutions were introduced into the mass spectrometer using a Cetac Aridus II desolvating system. Prior to analysis, standards were doped with a mixed ^{64}Zn-^{67}Zn double spike, and instrumental mass bias correction was performed using the double spike techniques described in Bryan et $al.$[21] Additional analyses of an in-house London Zn standard (δ^{66}Zn$_{Sesame}$ = 4.37 ± 0.05‰), simultaneously performed are in agreement with previously reported values for this standard.[21]

Kyoto University

All isotopic ratios were measured on a Neptune Plus MC-ICPMS with a glass nebuliser (MicroMist 0.1 mL min^{-1}) and an Aridus II desolvating nebulizer system at the Research Institute for Humanity and Nature, Kyoto, Japan. A standard Ni sampler cone and a Ni H-skimmer cone were used. Instrumental mass bias during MC-ICP-MS measurement was corrected using a mixed ^{64}Zn-^{67}Zn double spike, and isotopic ratios were calculated using the iterative method of Siebert et al[24]. The double spike comprised 82.9% ^{64}Zn, 0.5% ^{66}Zn, 16.2% ^{67}Zn, and 0.5% ^{68}Zn. The composition of the double spike was calibrated to the AA-ETH Zn standard by measuring AA Zn standard–double spike mixtures in different proportions [25]. The standards (JMC Zn or IRMM Zn) were mixed with double spike in 1:1 weight ratio, and diluted to 200−400 ppb Zn with 2% HNO$_3$. Data acquisition for each standards consisted of 30 4-s integrations. The intensity of the ^{66}Zn beam was ~5 V for 100 ppb natural Zn. In order to correct the instrumental background, a pure 2% HNO$_3$ (w/w) solution was measured every four samples, with data collected in 15 4-s integration cycles. The average signal of the pure 2% HNO$_3$ solutions were then subtracted from signals of the bracketed standards. Long term reproducibility including measurements of an in-house Zn standard during 3 months surrounding these measurements is 0.05‰ (2sd).

Results and Recommendation

Table 2 and Figure 1 summarises the data collected by the seven participating inter-calibration labs, representing a total of 126 separate analyses of the AA-ETH standard. Importantly, the results show a clear agreement between participating labs, with the new AA-ETH Zn standard being isotopically indistinguishable from the already calibrated IRMM-3702 [13]. Furthermore, both the measured (and implied) offset of IRMM-3702 relative to the JMC-Lyon standard in this dataset are in agreement with previously published values of 0.29 ± 0.05‰[13, 15, 16]. The data presented in this inter-calibration exercise were collected using a variety of techniques, both analytically and in terms of data reduction and specifically the methods used for correcting instrumental mass bias. We can therefore confidently assign a value to our proposed new standard identical to that of IRMM-3702, that is $\delta^{66}Zn = 0.28 \pm 0.02$‰, relative to JMC-Lyon Zn.

We thus propose that our new AA-ETH Zn standard, which will be made freely available upon request, be adopted as the new "zero-point" reference standard for future Zn isotopic measurements. In common with the approach used for future Mo isotope studies (see Nagler *et al.*[11] and references therein), we suggest that the AA-ETH standard be assigned a specific reference value of 0.28‰, and not "zero". This approach facilitates the comparison with existing literature data, provides a direct and traceable link to the already existing and universally adopted JMC-Lyon Zn isotope scale, and therefore allows for common reference values such as 0.3‰ for "lithogenic" Zn to be kept for discussion. Converting $\delta^{66}Zn$ values to the JMC-Lyon scale, relative to the AA-ETH = 0.28‰ can be done using the standard conversion identity[26]. This is expressed here, for the conversion of a δ value determined relative to the AA-ETH standard to the existing JMC scale as follows:

$$\delta^{66}Zn_{JMC\text{-}Lyon} \text{ (‰)} = \delta^{66}Zn_{AA\text{-}ETH} + {}^{66}Zn_{AA\text{-}ETH\text{ - }JMC\text{-}Lyon} + \frac{(\delta^{66}Zn_{AA\text{-}ETH}).({}^{66}Zn_{AA\text{-}ETH\text{ - }JMC\text{-}Lyon})}{1000}$$

$$[2]$$

where $\delta^{66}Zn_{AA\text{-}ETH\text{ - }JMC\text{-}Lyon} = 0.28 \pm 0.02$‰. In practice, this conversion can be approximated to:

$$\delta^{66}Zn_{JMC\text{-}Lyon} \text{ (‰)} = \delta^{66}Zn_{AA\text{-}ETH} + \delta^{66}Zn_{AA\text{-}ETH\text{ - }JMC\text{-}Lyon} \qquad [3]$$

as in many cases any systematic errors introduced by this simplification are smaller than analytical uncertainty. Using the AA-ETH Zn standard with either or both of the IRMM or NIST Zn standards as secondary reference materials will therefore allow simple and rigorous comparison of results generated in different labs moving into the future.

Lab	Instrument	Sample introduction	Mass bias correction[ref]
ETH Zürich	Neptune Plus	Aridus II, Apex-Q	^{64}Zn-^{67}Zn double spike[1]
ANU	Neptune Plus	Apex-Q	^{67}Zn-^{68}Zn double spike[19]
Brest	Neptune Plus	Glass spray chamber	Cu doping[20]
CPRG - Nancy	Neptune Plus	Glass spray chamber	^{64}Zn-^{67}Zn double spike[21]
Imperial College London	NuPlasmaHR	Aridus II	^{64}Zn-^{67}Zn double spike[22]
Indiana	NuPlasma II	Aridus II	^{64}Zn-^{67}Zn double spike[21]
Kyoto	Neptune Plus	Aridus II	^{64}Zn-^{67}Zn double spike

Table 1. Summary of analytical protocols employed by participating labs.

Lab	δ^{66}Zn$_{JMC}$	2σ	δ^{66}Zn$_{IRMM}$	2σ	δ^{67}Zn$_{IRMM}$	2σ	δ^{68}Zn$_{IRMM}$	2σ
ETH (n=30)	0.31	0.06	-0.01	0.07				
ANU (n=5)			-0.03	0.05				
†Brest (n=13)			-0.02	0.04	-0.02	0.07	-0.07	0.06
CPRG (n=20)	0.33	0.12	0.02	0.08				
Imperial (n=18)	0.28	0.05	-0.04	0.05				
Indiana (n=32)	0.26	0.10	0.01	0.10				
Kyoto (n=10)	0.27	0.03	-0.01	0.02				
All (*JMC: n=110, IRMM: n=129*)	0.29	0.09	0.00	0.07				
All (weighted)	0.28	0.02	-0.02	0.02				

Table 2. Zn isotope results of the AA-ETH standard relative to both JMC-Lyon and the IRMM-3702 Zn standards, with number of analyses in brackets. 2σ is the calculated twice standard deviation for all measurements across all participating labs, with the exception of the weighted mean, where the error reported is the uncertainty of the weighted mean. The weighted mean and its uncertainty were determined by weighting the values produced by each individual lab according to their individual 2σ uncertainties. †Data obtained from the Brest lab was obtained via a non-double spike mass bias correction protocol, which allows independent determination of additional isotope pairs, which are shown here.

Figure 1. Zn isotope results of the AA-ETH standard relative to both JMC-Lyon and the IRMM-3702 Zn. Filled circles show data on the JMC scale and open circles show data on the IRMM scale. The grey bands represent twice the standard deviation of all the measurements made. The dashed line represent the weighted average for each set of measurements. The star shows the value obtained for IRMM-3702, relative to JMC-Lyon from Moeller *et al.*[13]

1. J. Bermin, D. Vance, C. Archer and P. J. Statham, *Chemical Geology*, 2006, 226, 280-297.
2. D. Vance, C. Archer, J. Bermin, J. Perkins, P. J. Statham, M. C. Lohan, M. J. Ellwood and R. A. Mills, *Earth and Planetary Science Letters*, 2008, 274, 204-213.
3. T. M. Conway and S. G. John, *Global Biogeochemical Cycles*, 2014, 28, 1111-1128.
4. S. H. Little, D. Vance, C. Walker-Brown and W. M. Landing, *Geochimica Et Cosmochimica Acta*, 2014, 125, 673-693.
5. C. N. Marechal, E. Nicolas, C. Douchet and F. Albarede, *Geochemistry Geophysics Geosystems*, 2000, 1.
6. C. Kato, F. Moynier, M. C. Valdes, J. K. Dhaliwal and J. M. D. Day, *Nature Communications*, 2015, 6.
7. P. S. Savage, M. Boyet and F. Moynier, *Meteoritics & Planetary Science*, 2014, 49, 353-353.
8. R. C. Paniello, J. M. D. Day and F. Moynier, *Nature*, 2012, 490, 376-+.
9. J. M. Luck, D. Ben Othman and F. Albarede, *Geochimica Et Cosmochimica Acta*, 2005, 69, 5351-5363.
10. T. Goldberg, G. Gordon, G. Izon, C. Archer, C. R. Pearce, J. McManus, A. D. Anbar and M. Rehkamper, *Journal of Analytical Atomic Spectrometry*, 2013, 28, 724-735.
11. T. F. Nagler, A. D. Anbar, C. Archer, T. Goldberg, G. W. Gordon, N. D. Greber, C. Siebert, Y. Sohrin and D. Vance, *Geostandards and Geoanalytical Research*, 2014, 38, 149-151.
12. C. N. Marechal, P. Telouk and F. Albarede, *Chemical Geology*, 1999, 156, 251-273.
13. K. Moeller, R. Schoenberg, R.-B. Pedersen, D. Weiss and S. Dong, *Geostandards and Geoanalytical Research*, 2012, 36, 177-199.
14. E. Ponzevera, C. R. Quetel, M. Berglund, P. D. P. Taylor, P. Evans, R. D. Loss and G. Fortunato, *Journal of the American Society for Mass Spectrometry*, 2006, 17, 1412-1427.
15. T. M. Conway, A. D. Rosenberg, J. F. Adkins and S. G. John, *Analytica Chimica Acta*, 2013, 793, 44-52.
16. C. Cloquet, J. Carignan, M. F. Lehmann and F. Vanhaecke, *Analytical and Bioanalytical Chemistry*, 2008, 390, 451-463.
17. S. Chen, Y. Liu, J. Hu, Z. Zhang, Z. Hou, F. Huang and H. Yu, *Geostandards and Geoanalytical Research*, 2016, DOI: 10.1111/j.1751-908X.2015.00377.x, n/a-n/a.
18. N. Dauphas and E. A. Schauble, in *Annual Review of Earth and Planetary Sciences, Vol 44*, eds. R. Jeanloz and K. H. Freeman, 2016, vol. 44, pp. 709-783.
19. M. Samanta, M. J. Ellwood and G. E. Mortimer, *Microchemical Journal*, 2016, 126, 530-537.
20. S. G. John, O. J. Rouxel, P. R. Craddock, A. M. Engwall and E. A. Boyle, *Earth and Planetary Science Letters*, 2008, 269, 17-28.
21. A. L. Bryan, S. F. Dong, E. B. Wilkes and L. E. Wasylenki, *Geochimica Et Cosmochimica Acta*, 2015, 157, 182-197.
22. T. Arnold, M. Schonbachler, M. Rehkamper, S. F. Dong, F. J. Zhao, G. J. D. Kirk, B. J. Coles and D. J. Weiss, *Analytical and Bioanalytical Chemistry*, 2010, 398, 3115-3125.
23. F. Larner and M. Rehkaemper, *Environmental Science & Technology*, 2012, 46, 4149-4158.
24. C. Siebert, T. F. Nagler and J. D. Kramers, *Geochemistry Geophysics Geosystems*, 2001, 2, art. no.-2000GC000124.

25.   J. F. Rudge, B. C. Reynolds and B. Bourdon, *Chemical Geology*, 2009, 265, 420-431.
26.   R. E. Criss, *Principles of Stable Isotope Distribution.*, Oxford University Press, Oxford. UK, 1999.