GEOSTANDARDS and GEOANALYTICAL RESEARCH

Zinc Isotopic Compositions of NIST SRM 683 and Whole-Rock Reference Materials

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In this study the homogeneity of the zinc isotopic composition in the NIST SRM 683 reference material was examined by measuring the Zn isotopic signature in microdrilled sample powders from two metal nuggets. Zinc was purified using AG MP-1M resin and then measured by MC-ICP-MS. Instrumental mass bias was corrected using the "sample-standard bracketing" method and empirical external normalisation with Cu doping. After evaluating the potential effects of varying acid mass fractions and different matrices, high-precision Zn isotope data were obtained with an intermediate measurement precision better than ± 0.05‰ (δ^{66}Zn, 2*s*) over a period of 5 months. The $\delta^{66}Zn_{JMC\text{-}Lyon}$ mean values of eighty-four and fourteen drilled powders from two nuggets were 0.11 ± 0.02‰ and 0.12 ± 0.02‰, respectively, indicating that NIST SRM 683 is a good isotopic reference material with homogeneous Zn isotopes. The Zn isotopic compositions of seventeen rock reference materials were also determined, and their δ^{66}Zn values were in agreement with most previously published data within 2*s*. The δ^{66}Zn values of most of the rock reference materials analysed were in the range 0.22–0.36‰, except for GSP-2 (1.07 ± 0.06‰, *n* = 12), NOD-A-1 (0.96 ± 0.03‰, *n* = 6) and NOD-P-1 (0.78 ± 0.03‰, *n* = 6). These comprehensive data should serve as reference values for quality assurance and interlaboratory calibration exercises.

Keywords: zinc isotopes, NIST SRM 683, multi-collector inductively coupled plasma-mass spectrometry, rock reference materials, isotope fractionation.

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Dans cette étude, l'homogénéité de l'isotope de zinc dans le matériau de référence NIST SRM 683 était examinée par la mesure de la signature isotopique en Zn micro foré poudres d'échantillons provenant de deux pépites métalliques. Zinc a été purifié en utilisant une résine AG MP-1M, puis mesurée par MC-ICP-MS. Biais de masse instrumentale était corrigée en utilisant la méthode de bracketing de l'échantillon-étalon et "empirical external normalisation" avec Cu dopage. Après avoir évalué les effets potentiels des différentes fractions de la masse de l'acide et des différentes matrices, les données isotopiques de Zn de haute précision ont été obtenus avec une précision de mesure intermédiaire meilleure que ± 0.05‰ (de δ^{66}Zn, 2s) sur une durée de 5 mois. Les valeurs moyennes de $\delta^{66}Zn_{JMC\text{-}Lyon}$ en 84 et 14 poudres percés de deux pépites étaient de 0.11 ± 0.02‰ et 0.12 ± 0.02‰, respectivement, indiquant que le NIST SRM 683 est un bon matériau de référence isotopique des isotopes de Zn homogènes. Les compositions isotopiques de zinc de dix-sept matériaux de référence de roche ont également été déterminées, et leurs valeurs de δ^{66}Zn étaient en accord avec les données les plus préalablement publiées au sein de 2 écarts-types. Les valeurs de δ^{66}Zn de la plupart des matériaux de référence de roche analysés se situaient entre 0,22 à 0,36 ‰, sauf pour GSP-2 (1.07 ± 0.06‰, n = 12), NOD-A-1 (0.96 ± 0.03‰, n = 6) et NOD-P-1 (0.78 ± 0.03‰, n = 6). Ces données détaillées doivent servir de valeurs de référence pour l'assurance de la qualité et des exercices de calibration inter laboratoires.

Mots-clés : isotopes de zinc, NIST SRM 683, spectrométrie de masse à source plasma à multi-collection, matériaux de référence de roche, le fractionnement isotopique.

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Over the past decades, with the development of high-precision Zn isotope measurement, Zn isotope geochemistry has been increasingly applied in Earth and planetary sciences. For example, measuring the zinc isotopic signature was a novel tool to study the origin and evolution of the solar system because of the Zn isotopic fractionation produced during volatilisation processes (Humayun and Clayton 1995, Luck *et al.* 2005, Paniello *et al.* 2012a, b, Chen *et al.* 2013a, Day and Moynier 2014); zinc isotopes can be used to explore ore genesis because of a significant Zn isotopic fractionation during the transportation and deposition processes of hydrothermal systems (Mason *et al.* 2005, John *et al.* 2008, Kelley *et al.* 2009, Gagnevin *et al.* 2012, Chen *et al.* 2014, Pašava *et al.* 2014, Zhou *et al.* 2014a, b); and zinc isotope variation can also help track contamination sources in soils, plants and aerosols because some anthropogenic inputs have different Zn isotope signatures compared with natural sources (Cloquet *et al.* 2006, Chen *et al.* 2009a, Fekiacova *et al.* 2015, Thapalia *et al.* 2015). In addition to applications briefly described above, Zn isotopes have also been used to monitor palaeo-pH (Pons *et al.* 2011), used to study the transport mechanisms of Zn in plants (Weiss *et al.* 2005, Viers *et al.* 2007, Moynier *et al.* 2009, Jouvin *et al.* 2012) and even used in life sciences (Balter *et al.* 2013, Moynier *et al.* 2013, Larner *et al.* 2015).

The measurement methods for Zn isotopic determination improved as a result of the broadening of the range of fields of applications. Maréchal *et al.* (1999) developed a high-precision method using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). The analytical method was then progressively modified to accommodate the changing matrix characteristics and element compositions of a variety of terrestrial and extra-terrestrial samples. The Zn purification procedures differed for river water, seawater, plants and rock samples (e.g., Bermin *et al.* 2006, Borrok *et al.* 2007, Chen *et al.* 2009b, Arnold *et al.* 2010, Sossi *et al.* 2015). Furthermore, to limit the problems of mass discrimination effects and time drifts during mass spectrometry measurements, different correction schemes including "sample-standard bracketing" (SSB), external normalisation and the double spike method were introduced (e.g., Maréchal *et al.* 1999, Albarède 2004, Archer and Vance 2004, Mason *et al.* 2004, Makishima and Nakamura 2013).

The use of a common international reference standard should be encouraged to facilitate the comparison of measurement results from the different laboratories performing delta-scale Zn isotopic measurements. Currently, JMC 3-0749L (JMC-Lyon or Lyon) plays this role, but is no longer commercially available, and a new international reference standard should be adopted instead. Several research groups have started using IRMM-3702, a certified zinc nitrate solution produced by the Institute for Reference Materials and Measurements (IRMM). The δ^{66}Zn value of IRMM-3702 against JMC-Lyon was found to be ~ 0.32‰ (e.g., Cloquet *et al.* 2006, Petit *et al.* 2008, Borrok *et al.* 2010, Moeller *et al.* 2012). NIST SRM 683 could also be envisaged to replace JMC-Lyon as a reference measurement standard (Albarède and Beard 2004). NIST SRM 683 is a reference material produced by the National Institute of Standards and Technology as a unit of Zn nuggets (~ 140 g, Figure 1). The large mass of material provided guaranties its availability for a long time. It is, however, critical to ensure that there is a sufficient degree of homogeneity for the Zn isotopic composition in the different nuggets. Tanimizu *et al.* (2002) dissolved NIST SRM 683 metal nuggets and determined the Zn isotopic composition by MC-ICP-MS (using a Nu Plasma 500 instrument), and the relative deviation of ^{66}Zn/^{64}Zn from JMC-Lyon Zn was reported as 1.00007 ± 0.00007. However, whether the NIST SRM 683 Zn nuggets have a homogeneous Zn isotopic composition is still not clear. In this study, we intensively examined the homogeneity of two NIST SRM 683 metal nuggets and their Zn isotopic compositions relative to JMC-Lyon to assess whether this material can be considered a suitable reference measurement standard for future Zn isotope determination.

Furthermore, to compare the data quality of different laboratories, it is critical to measure well-studied rock reference materials, such as those from the USGS and GSJ. However, there is still a lack of systematic determinations for Zn isotopic compositions of these reference materials; indeed, some igneous rocks (e.g., RGM-1, GSP-1 and GSP-2) have no published Zn isotope data. We analysed seventeen reference materials from the USGS and GSJ, namely BCR-2, BHVO-2, BIR-1 and JB-2 (basalts), AGV-1, AGV-2 and JA-2 (andesites), RGM-1 (rhyolite), DTS-2 (dunite), W-2 (diabase), GSP-1, GSP-2 (granodiorites), G-2 (granite), QLO-1 (quartz latite), SDC-1 (mica schist) and NOD-A-1 and NOD-P-1 (manganese nodules). Our measurements provide a high-precision Zn isotope database of reference materials for interlaboratory comparison.

Experimental procedures

Materials, reagents and samples

All high-purity acids used in this study were purified by double sub-boiling distillation of the TraceMetal^{TM} grade acids (from Thermo Fisher Scientific) and then diluted using ultrapure water (18.2 MΩ cm, same below). The Bio-Rad Poly-Prep columns and pipette tips were cleaned by being soaked in 10% *v/v* HCl for 48 hr (at room temperature) and

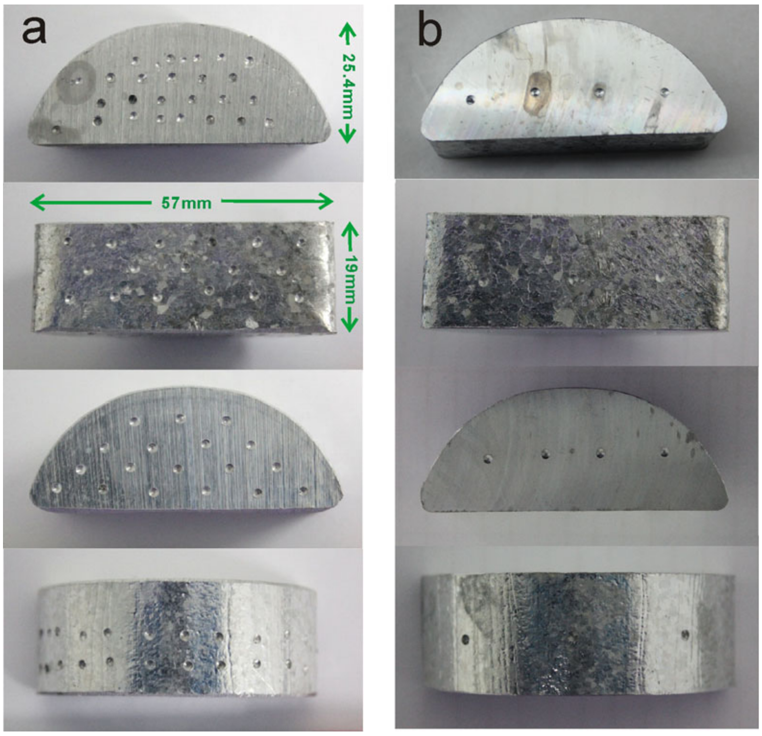

Figure 1. Photographs (with dimensions) of the two NIST SRM 683 metal nuggets drilled for Zn isotope determination.

then rinsed with ultrapure water. All of the Savillex® PFA Teflon beakers were cleaned by boiling in 8 mol l^{-1} HNO_3, 6 mol l^{-1} HCl, 8 mol l^{-1} HNO_3 and ultrapure water, alternately. The temperature for boiling was 130 °C and duration was 6 hr for boiling in each reagent. Between boiling in different reagents, the beakers were sufficiently rinsed using ultrapure water.

NIST SRM 683 preparation: To examine whether NIST SRM 683 is homogeneous in Zn isotopic composition, we drilled two metal nuggets using an electric hand drill with a tungsten carbide bit. Eighty-four and fourteen spots were drilled from the two nuggets (Figure 1), and around 2–3 mg of powder was removed from each spot. To avoid cross-contamination, the drill bit and the metal nugget were rinsed using 2% *m/m* HNO_3 (~ 0.2 mol l^{-1}, same below) followed by ultrapure water before and after each drilling. After rinsing, the drilled Zn metal powder was transferred to a 7-ml Savillex® PFA Teflon beaker and then dissolved in 1 mol l^{-1} HNO_3. The solution was then diluted with ultrapure water to 2% *m/m* HNO_3 for instrumental measurement.

After checking the homogeneity of the Zn isotopes, the Zn metal nugget with the eighty-four drilled spots was dissolved in a 1-l Teflon bottle that was precleaned using HNO_3. Before digestion, the metal nugget's surface was cleaned using diluted HNO_3 to remove possible surface contamination and then rinsed with ultrapure water. After 340 g of ultrapure water was first added to the bottle with the NIST SRM 683 metal nugget, ~ 700 g of 14 mol l^{-1} HNO_3 was slowly added until the metal nugget was completely dissolved, producing a 0.136 g g^{-1} Zn solution. Part of the solution was further diluted to 200 ng g^{-1} with 2% *m/m* HNO_3 for instrumental measurement.

Preparation of whole-rock reference materials: For most reference materials, different amounts of powders (2.5–60 mg) containing ~ 4 µg Zn were digested for chemical separation. For samples with very low Zn mass fractions (RGM-1 and DTS-2), powders containing 2 µg Zn were prepared. Samples were digested in 3 ml of 22 mol l^{-1} HF and 1 ml of 14 mol l^{-1} HNO_3 in 7-ml Savillex® PFA beakers. After the capped beakers were placed on a hot plate at 120 °C for at least 2 days, the samples were dried and then treated with *aqua regia* followed by 11 mol l^{-1} HCl for full digestion. Samples were finally dissolved in 1 ml 6 mol l^{-1} HCl for chemical purification.

The procedure for the digestion of DTS-2 (dunite) was slightly different from the other reference materials because of the existence of a minor amount of chromite. About 60 mg of sample powder was weighed into a Teflon bomb, followed by the addition of 22 mol l^{-1} HF and 14 mol l^{-1} HNO_3 in a 3:1 ratio. The sample was completely dissolved after the capped bomb was heated in an oven at 195 °C at high pressure for 2 days. After cooling, the sample was transferred to a precleaned PFA beaker and treated with the above procedure to digest thoroughly.

Chemical purification procedure

The separation procedure used in this study is modified from Maréchal *et al.* (1999) and Chen *et al.* (2009a). We used a two-step method to purify Zn isotopes from matrices, and Figure 2 shows the elution curves. The first column was a 10-ml Bio-Rad Poly-Prep column with 2 ml of AG MP-1M (100- to 200-mesh) anion-exchange resin, and the second was a 2-ml Bio-Rad Poly-Prep column with 0.5 ml of the same resin. Before loading into the column, the resin was precleaned using 7 mol l^{-1} HNO_3, ultrapure H_2O, 6 mol l^{-1} HCl and ultrapure H_2O, alternately. The details of the chemical purification procedure are given in Table 1. After 2 ml of AG MP-1M resin was loaded into the precleaned first column, it was washed with 0.5 mol l^{-1} HNO_3 (30 ml) and ultrapure H_2O (15 ml) and then conditioned by 6 mol l^{-1} HCl (8 ml). The sample was loaded to the column in 1 ml 6 mol l^{-1} HCl. After Na, Mg, Ti, Al, Ni, K and Ca were eluted using 4 ml 6 mol l^{-1} HCl and Fe and Cu were eluted using 6 ml 0.5 mol l^{-1} HCl, Zn was collected with 10 ml 0.5 mol l^{-1} HNO_3 (Figure 2). Because of the small residue of matrix elements remaining in the collected Zn solutions, a second separation step with 0.5 ml AG MP-1M (100- to 200-mesh) resin was used for further purification following the procedure described in Table 1. Before being introduced into the instrument, a split aliquot of the sample was measured to ensure that the yield of Zn, which is the ratio of Zn content before and after chemical purification, was > 99% and residual matrix elements were negligible. Then, the samples were diluted in 2% *m/m* HNO_3 to 200 ng g^{-1} Zn solutions for isotopic determination.

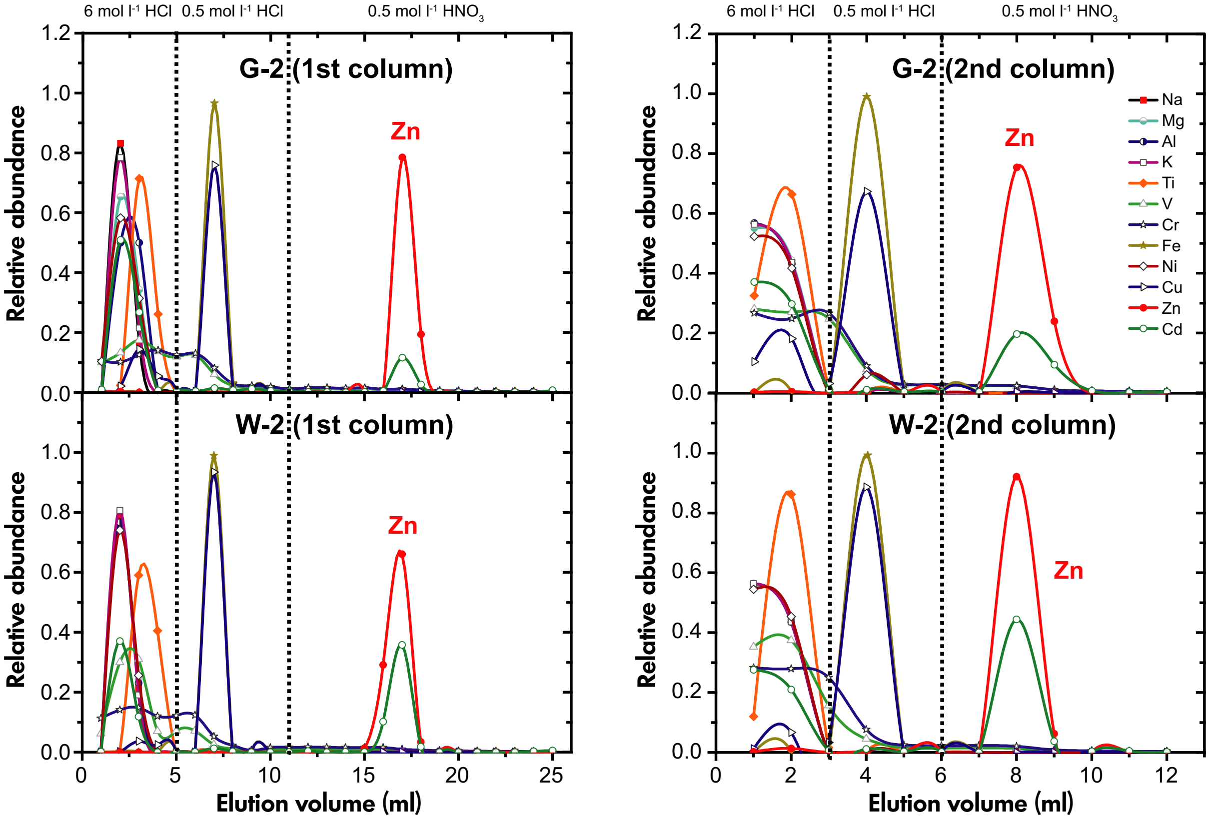

Figure 2. Elution curves of two columns for G-2 and W-2, which contained 4 µg Zn. After loading samples, most matrices were eluted using 6 mol l^{-1} HCl, and Fe and Cu were eluted using 0.5 mol l^{-1} HCl, and then, Zn was collected with 0.5 mol l^{-1} HNO_3. The *x*-axis is the volume of acid used and the *y*-axis is the relative abundance, which is the element content in the cut compared with the total abundance of that element. Element mass fractions were measured using ICP-MS, and Zn yields for G-2 and W-2 were 99.8% and 100%, respectively.

Table 1.
Protocol for Zn purification by anion exchange

Reagent	Volume (ml)
First column	
AG MP-1M (100- to 200-mesh) resin	2
0.5 mol l^{-1} HNO_3	30
Ultrapure water	15
6 mol l^{-1} HCl (conditioning)	8
6 mol l^{-1} HCl (loading sample)	1
6 mol l^{-1} HCl	4
0.5 mol l^{-1} HCl	6
0.5 mol l^{-1} HNO_3 (collect Zn)	10
Second column	
AG MP-1M (100- to 200-mesh) resin	0.5
0.5 mol l^{-1} HNO_3	8
Ultrapure water	4
6 mol l^{-1} HCl (conditioning)	2
6 mol l^{-1} HCl (loading sample)	1
6 mol l^{-1} HCl	2
0.5 mol l^{-1} HCl	3
0.5 mol l^{-1} HNO_3 (collect Zn)	5

This protocol was modified from Maréchal *et al.* (1999) and Chen *et al.* (2009a).

Table 2.
Instrument operating parameters for Zn isotope measurement

Instrument parameters	
RF power	1125–1200 W
Cooling Ar flow rate	~ 16 l min^{-1}
Auxiliary Ar flow rate	~ 0.8 l min^{-1}
Sample Ar flow rate	0.9–1.1 l min^{-1}
Extraction voltage	-2000 V
Vacuum	4–8 × 10^{-9} Pa
Typical ^{64}Zn sensitivity	25 V per µg g^{-1} (LR)
Cones	Ni X skimmer cone, Ni jet sampler cone
Sample uptake	~ 50 µl min^{-1}
Mass resolution	Low resolution

Cup configuration					
Cup	L2-F	C-F	H1-F	H3-F	H4-F
Isotopes	^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn	^{70}Zn

Mass spectrometry

After purification, the sample solutions were analysed using inductively coupled plasma-mass spectrometry (ICP-MS) in the CAS Key Laboratory of Crust-Mantle and Environments at the University of Science and Technology of China (USTC), Hefei, to ensure that the chemical procedure effectively separated matrix elements, and the yield of Zn was > 99%. Then, Zn isotope ratios were measured using MC-ICP-MS (a Neptune Plus instrument from Thermo Fisher Scientific) in the same laboratory. Sample solutions were introduced using a PFA microflow nebuliser (ESI) with an uptake rate of ~ 50 µl min^{-1} and a quartz dual cyclonic spray chamber (Thermo Fisher Scientific). Nickel cones (X skimmer + jet sample cones) were used for all measurements. The cup configuration and parameters for the instrument are summarised in Table 2. Five Zn isotopes (^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn) were collected by L2, C, H1, H3 and H4, respectively, and the sensitivity was ~ 25 V per µg g^{-1} [Zn] at low resolution on the ^{64}Zn ion beam. One block analysis consisted of sixty cycles with an integration time of 2.097 s per cycle. Mass discrimination and time drifts during isotope measurements were corrected using SSB, and empirical external normalisation (EEN; Mason *et al.* 2004) with Cu doping was also applied for the analysis of three samples – BCR-2, AGV-2 and G-2. Each sample was bracketed before and after by the measurement standard (bracketing reference solution or calibrator) JMC-Lyon, with usually three or four repeated analyses of the same sample solution. Between each sample/standard measurement, the introduction system was cleaned using ~ 2% *m/m* HNO_3 for at least 4 min to eliminate potential cross-contamination, until the ^{64}Zn signal was less than 3 mV. In general, samples and measurement standards were diluted to 200 ng g^{-1} by 2% *m/m* HNO_3 and then introduced into the instrument. The total procedural blanks ranged from 7 to 12 ng, which is negligible compared with the ~ 4 µg Zn in samples loaded into the columns.

Results and discussion

Tolerance to mismatching conditions of acid and zinc mass fractions between the sample and the isotopic standard solutions

The Zn isotope data are reported relative to an isotope standard using the δ notation:

$$\delta^{x}\mathrm{Zn} = ((^{x}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{Sample}}/(^{x}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{Standard}} - 1) \times 1000 \qquad (1)$$

where ^{x}Zn = ^{66}Zn, ^{67}Zn, ^{68}Zn or ^{70}Zn. Previous studies found that the mismatch of acid molarities and element mass fractions between the samples and bracketing measurement standard can produce artefacts when using SSB (Albarède and Beard 2004, Huang *et al.* 2009, An *et al.* 2014). In this study, a series of tests was made to examine these effects. First, a high-purity Zn solution (USTC-Zn), which is an in-house reference solution used in our laboratory, was diluted to 200 ng g^{-1} using 2% *m/m* HNO_3 as a bracketing measurement standard, while aliquots of the same tested

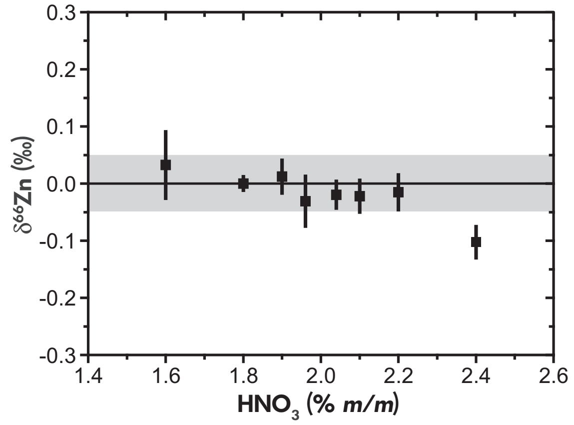

Figure 3. Plot showing the effect of mismatching conditions of acid mass fraction between samples and standard on Zn isotopic measurement. The grey area depicted in this and Figures 4 and 5 represents the intermediate measurement precision (± 0.05‰, 2s) determined during the course of this study.

material were diluted to 200 ng g^{-1} using HNO_3 with mass fractions varying from 1.6% *m/m* to 2.4% *m/m* as unknown samples. As illustrated in Figure 3, when the difference in the acid mass fraction between samples and measurement standard is within 10%, it will not cause an obvious offset in δ^{66}Zn. When the difference is ≥ 20%, the offset in δ^{66}Zn can be 0.10‰, which is significant. To eliminate the possible effect, we always diluted 1 l 2% *m/m* HNO_3 before each batch of analyses and used the same bottle of newly diluted 2% *m/m* HNO_3 for the whole isotope determination process.

We also fixed the Zn mass fraction of the bracketing standard ($[M]_{Standard}$) at 200 ng g^{-1} and varied the mass fractions of aliquots of the same tested material from 40 to 600 ng g^{-1} to test the effect of mass fraction mismatch on Zn isotope determinations. Figure 4 shows that Zn isotope measurements have a large tolerance for mass fraction mismatch when the sample has a greater mass fraction than the measurement standard. No isotopic offset in δ^{66}Zn could be observed when the $[M]_{Sample}/[M]_{Standard}$ ratio increased from 1 to 3. When $[M]_{Sample}/[M]_{Standard}$ was < 0.5, the isotopic offset in δ^{66}Zn was obvious (> 0.14‰). To ensure the precision and accuracy of Zn isotope determination, the Zn mass fraction mismatch between sample and standard solutions was kept at less than ± 10%.

Matrix effects

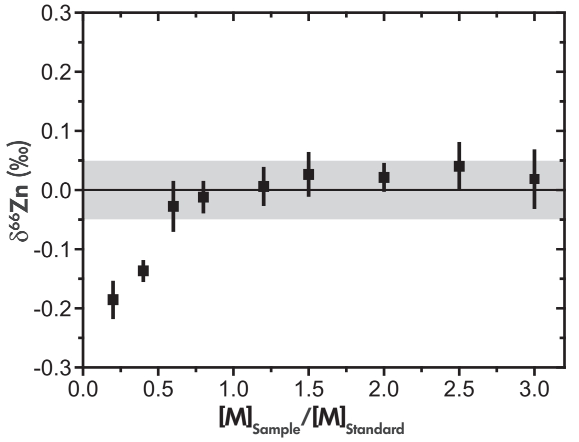

Figure 4. The measured value of δ^{66}Zn with deviation of the Zn mass fractions for samples from the measurement standard. The mass fraction of the measurement standard was 200 ng g^{-1}, and that of the samples varied from 40 to 600 ng g^{-1} ($[M]_{Sample}$/ $[M]_{Standard}$ was from 0.2 to 3).

When using SSB, matrix effects should be rigorously examined to ensure accurate and precise isotope measurement (Albarède 2004). Natural samples usually have quite complex matrices. Although most of the matrix elements can be separated during the chemical purification procedure, some residue might still be collected with the Zn solution. When the mass fractions of these residual matrix elements reach a certain level, they might produce spectral- or nonspectral-related interferences to affect the isotope measurements. In this study, we quantitatively assessed eleven matrix elements (Fe, Mg, Na, Al, Ti, Ni, Cr, Cu, Cd, V and Ba) for their possible effects on Zn isotope measurements with their mass fractions varied in sample solutions. Elements at different mass fractions were doped into 200 ng g^{-1} Zn standard solutions and bracketed using the same pure Zn measurement standard without any doping.

The results show that Zn isotope determinations have different tolerances with different matrix elements. The δ^{66}Zn values are sensitive to Ni and Ti amounts in the sample solutions because $^{64}Ni^{+}$ and $^{48}Ti^{16}O^{+}$ can produce intense isobaric interferences on $^{64}Zn^{+}$. When [Ni]/[Zn] and [Ti]/[Zn] ratios reach 0.001 and 0.01, respectively, an obvious offset of δ^{66}Zn (> 0.07‰) was observed (Figure 5). We did not observe abnormal high mass 64 when monitoring the blank (2% *m/m* HNO_3); this ensured that there was no $^{64}Ni^{+}$ interference produced by the Ni cone used in the instrument. Previous studies have also proved that the contribution of $^{64}Ni^{+}$ (as interference of $^{64}Zn^{+}$) from Ni cones was so small that its effect on Zn isotope measurement was not detectable (Bermin *et al.* 2006, Borrok *et al.* 2007, Balistrieri *et al.* 2008). However, small amounts of Ti and Ni residues in the sample solution will affect Zn isotope determinations.

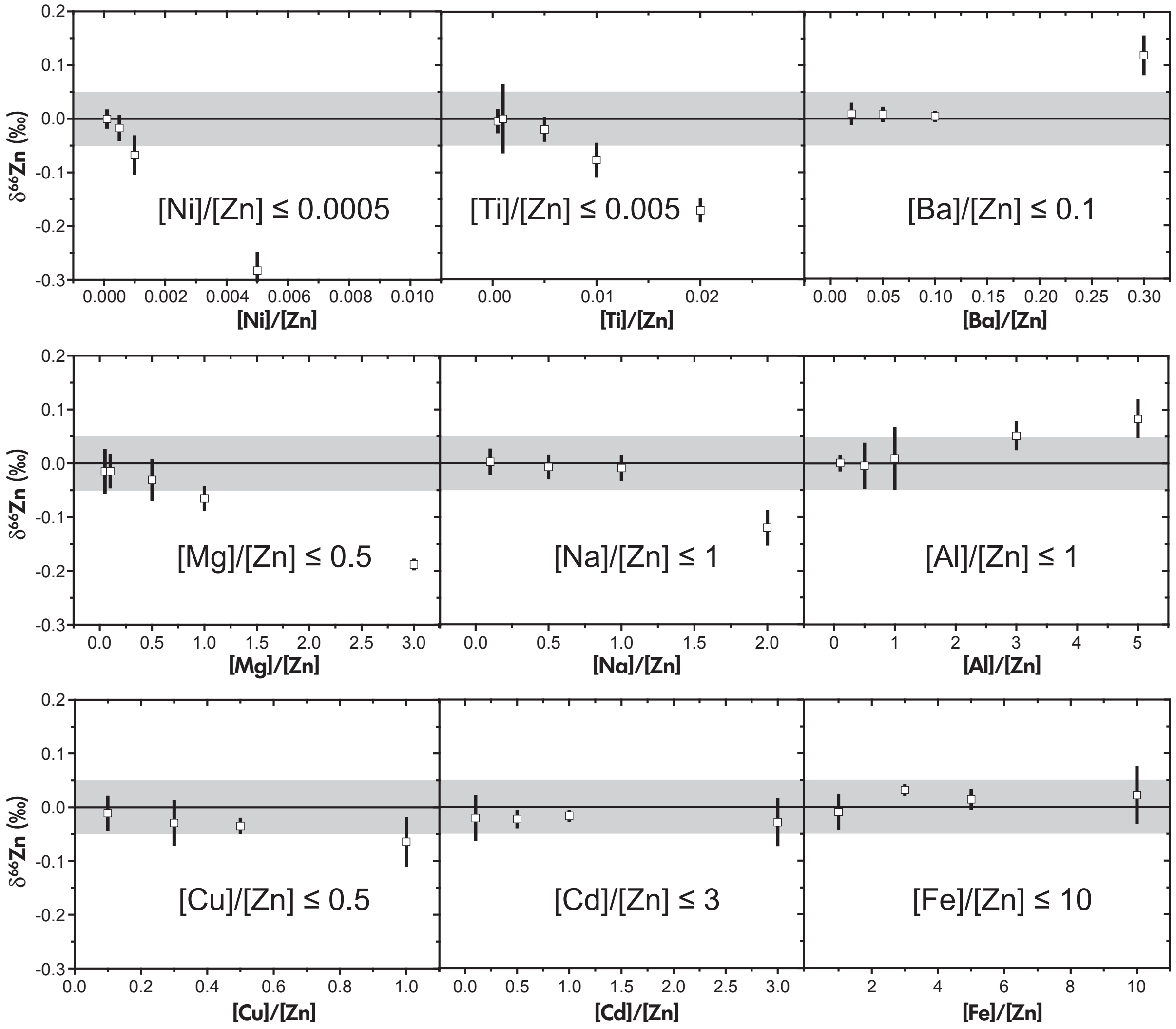

Figure 5. Plots of data from the doping experiment to examine matrix effects on Zn isotope measurement.

Although δ^{66}Zn values are not as susceptible to other elements as to Ni and Ti, the addition of other matrix elements still can noticeably affect the precision and accuracy of Zn isotope determinations. For example, significant drifts in δ^{66}Zn were observed when [Ba]/[Zn] > 0.3, [Mg]/[Zn] > 0.5, [Na]/[Zn] > 2 or [Al]/[Zn] > 3 occurred in sample solutions (Figure 5). When [Cu]/[Zn] reaches 1, there is a small shift of δ^{66}Zn (0.06‰). No observable isotope ratio shift was detected over the range we measured for the other elements ([V]/[Zn] ≤ 0.5, [Cr]/[Zn] ≤ 3, [Cd]/[Zn] ≤ 3 and [Fe]/[Zn] ≤ 10). The doping experiment proved that NIST SRM 683 could be dissolved and used directly as a reference measurement standard without any further purification process. This is because the matrix elements Pb, Cu, Fe, Ag, Cd, Tl and Sn in NIST SRM 683 metal are present only at µg g^{-1} mass fraction levels (i.e., [matrix]/[Zn] ≈ 10^{-6}) and cannot produce offsets of the Zn isotopes.

In general, a one-column purification procedure cannot remove matrix elements completely, especially major elements in igneous rocks (e.g., Mg, Na, Al, Ti). After one-column separation of sample W-2 (diabase), we detected that the [Ti]/[Zn] ratio in the Zn aliquot was greater than 0.02. Based on the experiments above, this high content of Ti residue could produce an obvious offset of δ^{66}Zn (> 0.07‰). Therefore, a second ion-exchange column was necessary to separate Zn further from the matrices. After two column separations, in this study, all purified Zn solutions contained matrices lower than that could produce significant artefacts on Zn isotopes. Nevertheless, to ensure the precision and accuracy of Zn isotope determinations, every purified Zn solution needs to be carefully checked for the matrix element contents. Only when the Zn solution contains matrix element contents lower than certain levels could such a sample be measured using

MC-ICP-MS. Otherwise, a third column would be necessary to purify Zn further to avoid producing significant artefacts (> 0.05‰).

The column separation results also show that part of the Cd could not be separated from Zn (Figure 2), but this would not affect Zn isotopic determination. First, Cd contents in igneous rocks are generally much lower than Zn contents based on the data from GERM (http://earthref.org/GERMRD/e:48/), so the sample solutions did not contain too much Cd. Second, Cd isotopes do not interfere with any Zn isotope. Both our doping experiment and previous studies (Borrok *et al.* 2007) found that residual Cd (i.e., $[Cd]/[Zn] \leq 1$) in the sample solution did not affect Zn isotopic measurements. In this study therefore, we did not further separate Cd from Zn by another step.

Precision and accuracy of Zn isotope measurement

The precision under intermediate measurement conditions for Zn isotope determinations in our laboratory was derived by analysing different aliquots of NIST SRM 683 or independent digestions of the same sample powder over a 5-months period (the number of total analyses is denoted by *M* in Table 3). Each analysis included *n* repeated measurements of the same solution (generally $n \geq 3$, same below). All of the measurement uncertainties reported in this study are expressed as two standard deviations (2*s*) based on *n* of the same solution during each measurement session. All of the data uncertainties from published work listed in this paper were transformed to 2*s*. The δ^{66}Zn value of the NIST SRM 683 measurement after 5 months was 0.12 ± 0.04‰ (2*s*, $M = 18$, *M* is the number of independent analyses of NIST SRM 683 in 5 months, and each analysis includes $n \geq 3$ measurements), and replicates from independent digestions of rock samples agree well with each other within ± 0.05‰ (2*s*, *M* is listed in Table 3). Therefore, the intermediate measurement precision of Zn isotope measurement in our laboratory was better than ± 0.05‰ (2*s*).

Accuracy can be assessed by comparing our data for reference materials with published information. Table 4 shows that δ^{66}Zn values for the reference materials reported in this study are in good agreement with most published data within ± 0.05‰ (2*s*). To prove the validity of the SSB method, BCR-2, AGV-2 and G-2 were analysed and corrected using EEN, following the method described by Mason *et al.* (2004) and Chen *et al.* (2009b). A high-purity Cu solution (ERM-AE647) was added to the bracketing measurement standard and sample solutions to produce mixtures containing 66 ng g^{-1} Cu and 200 ng g^{-1} Zn. According to a matrix examination experiment, when $[Cu]/[Zn] \leq 0.5$, Zn isotopic artefacts are not produced. Table 3 shows that these three samples have the same δ^{66}Zn value after having been corrected by either SSB or EEN, indicating that both methods can provide a reliable instrumental bias correction.

To test the accuracy further, we measured synthetic standard solutions made by mixing NIST SRM 683 with Zn-free matrices. Matrix elements were collected from powders of BHVO-2 (200 mg) and BIR-1, AGV-2, G-2 and NOD-A-1 (50 mg) during the separation of Zn using chromatography. Quantities of 1, 2, 4 and 6 µg of Zn from NIST SRM 683 were mixed with four aliquots of BHVO-2 matrix solutions, while each of the other four matrix solutions was mixed with 4 µg of Zn (NIST SRM 683). The same chromatography procedure described above was then applied to the synthetic solutions. The collected Zn solutions were measured to examine the effects of different sample masses and different sample types. All measurements are shown in Figure 6. There was no Zn isotope offset (within ± 0.05‰) observed from these synthetic solutions, indicating that neither different Zn masses (1–6 µg) with similar matrices nor the same Zn content mass with different matrix compositions (from mafic to felsic) produced Zn isotope artefacts during ion-exchange column purification and instrumental measurement. Our method is reliable for samples with total Zn contents varying from 1 to 6 µg. To reduce the contribution of Zn in the blank, 2 or 4 µg of Zn was prepared depending on the Zn mass fraction of the sample in this study.

The Zn three-isotope plots of all reference materials and NIST SRM 683 are shown in Figure 7. The equation of the δ^{66}Zn (*X*) and δ^{67}Zn (*Y*) fractionation line ($y = (1.48 \pm 0.02)x + (0.03 \pm 0.01)$, $R^2 = 0.986$) is consistent with the slope values of kinetic (1.48) and equilibrium (1.49) fractionation within error (Young *et al.* 2002), and the Zn isotopes of all of these reference materials show mass-dependent fractionation.

Zn isotopic compositions of NIST SRM 683

The average δ^{66}Zn value of the eighty-four drilled powders from the first NIST SRM 683 metal nugget was 0.11 ± 0.02‰ ($M = 84$), and that of the fourteen drilled powders from another NIST SRM 683 metal nugget was 0.12 ± 0.02‰ ($M = 14$). Both are consistent with the results obtained for the solution of the first whole metal nugget

Table 3.
Zinc isotope compositions of seventeen rock reference materials reported in this study

Reference materials	Zn (µg g^{-1})	δ^{66}Zn (‰)	2*s*	δ^{67}Zn (‰)	2*s*	δ^{68}Zn (‰)	2*s*	*n*
Dunite								
DTS-2	45	0.27	0.04	0.43	0.01	0.51	0.04	3
Basalt								
BCR-2	127	0.24	0.06	0.36	0.11	0.49	0.13	4
		0.24	0.03	0.37	0.03	0.51	0.05	4
		0.27	0.03	0.39	0.04	0.54	0.07	3
		0.24	0.03	0.34	0.00	0.49	0.07	3[†]
Average (M = 4)		0.25	0.04	0.37	0.07	0.51	0.09	14[a]
BHVO-2	103	0.28	0.05	0.48	0.10	0.57	0.08	4
		0.30	0.01	0.46	0.09	0.61	0.05	4
		0.31	0.03	0.49	0.07	0.65	0.05	4
		0.30	0.03	0.50	0.03	0.63	0.02	4
		0.32	0.01	0.46	0.05	0.63	0.04	6
		0.32	0.03	0.51	0.02	0.64	0.03	4
		0.30	0.01	0.50	0.07	0.62	0.03	4
		0.33	0.01	0.51	0.05	0.65	0.02	4
		0.31	0.03	0.50	0.04	0.62	0.03	4
		0.31	0.02	0.47	0.04	0.62	0.02	4
		0.31	0.00	0.47	0.03	0.63	0.04	4
Average (M = 11)		0.31	0.03	0.49	0.06	0.62	0.06	46[a]
BIR-1	70	0.21	0.05	0.33	0.05	0.46	0.07	4
		0.20	0.02	0.41	0.04	0.49	0.04	4
		0.21	0.03	0.36	0.06	0.45	0.02	4
		0.25	0.02	0.39	0.02	0.52	0.04	4
		0.24	0.03	0.38	0.13	0.47	0.05	3
		0.25	0.04	0.35	0.05	0.48	0.08	4
Average (M = 6)		0.23	0.05	0.37	0.08	0.48	0.06	23[a]
JB-2	108	0.21	0.02*	0.33	0.05*	0.43	0.04*	2
		0.23	0.04	0.36	0.04	0.46	0.08	7
Average (M = 2)		0.23	0.04	0.35	0.05	0.46	0.08	9[a]
Diabase								
W-2	80	0.20	0.04	0.32	0.04	0.44	0.05	3
		0.21	0.05	0.38	0.10	0.44	0.10	4
		0.24	0.03	0.39	0.03	0.49	0.02	4
Average (M = 3)		0.22	0.05	0.37	0.09	0.46	0.08	11[a]
Andesite								
AGV-1	88	0.29	0.05	0.46	0.11	0.60	0.10	4
		0.29	0.02	0.46	0.05	0.56	0.04	3
		0.28	0.02	0.44	0.02	0.57	0.03	3
		0.28	0.02	0.43	0.05	0.58	0.04	3
Average (M = 4)		0.29	0.03	0.45	0.07	0.58	0.06	13[a]
AGV-2	86	0.28	0.01	0.44	0.01	0.56	0.02	4
		0.29	0.03	0.43	0.03	0.60	0.02	4
		0.28	0.02	0.44	0.02	0.56	0.02	3
		0.29	0.04	0.49	0.04	0.60	0.12	4
		0.23	0.03	0.36	0.03	0.48	0.02	3[†]
Average (M = 5)		0.28	0.05	0.43	0.09	0.56	0.10	18[a]
JA-2	64	0.27	0.04	0.39	0.03	0.56	0.03	3
		0.28	0.02*	0.46	0.00*	0.58	0.06*	2
Average (M = 2)		0.28	0.03	0.42	0.07	0.57	0.05	5[a]
Quartz latite								
QLO-1	61	0.27	0.01	0.42	0.06	0.55	0.04	3
		0.26	0.02	0.45	0.02	0.52	0.03	3
		0.26	0.05	0.38	0.07	0.52	0.11	4
		0.28	0.05	0.43	0.09	0.55	0.11	4
Average (M = 4)		0.27	0.04	0.42	0.08	0.53	0.09	14[a]

Table 3 (continued).
Zinc isotope compositions of seventeen rock reference materials reported in this study

Reference materials	Zn (µg g^{-1})	δ^{66}Zn (‰)	2*s*	δ^{67}Zn (‰)	2*s*	δ^{68}Zn (‰)	2*s*	*n*
Granodiorite								
GSP-1	104	0.29	0.05	0.50	0.07	0.62	0.07	4
		0.33	0.03	0.52	0.06	0.64	0.08	4
Average (M = 2)		0.31	0.05	0.51	0.06	0.63	0.08	8[a]
GSP-2	120	*1.15*	*0.03*	*1.66*	*0.05*	*1.89*	*0.04*	*3*
		1.01	*0.04*	*1.42*	*0.11*	*1.66*	*0.08*	*4*
		0.99	*0.01**	*1.40*	*0.05**	*1.62*	*0.01**	*2*
		1.07	0.02	1.56	0.01	1.76	0.02	3
		1.06	0.03	1.52	0.03	1.73	0.06	3
		1.10	0.02	1.57	0.03	1.79	0.04	3
		1.03	0.01	1.45	0.03	1.67	0.05	3
Average (M = 4)[#]		1.07	0.06	1.53	0.11	1.74	0.10	12[a]
Granite								
G-2	86	0.33	0.06	0.56	0.10	0.66	0.13	4
		0.34	0.03	0.52	0.03	0.70	0.05	4
		0.33	0.06	0.48	0.07	0.67	0.12	4
		0.34	0.03	0.54	0.06	0.69	0.06	4
		0.35	0.04	0.55	0.09	0.69	0.05	4
		0.35	0.03	0.53	0.02	0.69	0.07	3[†]
Average (M = 6)		0.34	0.04	0.53	0.08	0.68	0.08	23[a]
Rhyolite								
RGM-1	32	0.37	0.05	0.57	0.04	0.74	0.04	3
		0.37	0.06	0.57	0.11	0.72	0.12	6
		0.35	0.01	0.57	0.02	0.71	0.03	3
Average (M = 3)		0.36	0.05	0.57	0.07	0.72	0.09	12[a]
Manganese nodule								
NOD-A-1	590	0.96	0.02	1.59	0.10	1.99	0.04	3
		0.96	0.04	1.60	0.04	2.00	0.07	3
Average (M = 2)		0.96	0.03	1.59	0.07	2.00	0.05	6[a]
NOD-P-1	1600	0.78	0.04	1.19	0.01	1.59	0.05	3
		0.78	0.02	1.20	0.08	1.53	0.06	3
Average (M = 2)		0.78	0.03	1.20	0.05	1.56	0.09	6[a]
Mica schist								
SDC-1	103	0.27	0.01	0.40	0.02	0.52	0.03	3
		0.26	0.02	0.42	0.04	0.51	0.04	3
		0.26	0.03	0.43	0.06	0.53	0.06	3
Average (M = 3)		0.26	0.02	0.42	0.04	0.52	0.05	9[a]

n is the times of repeated measurement of the same solution.
M is the times of independent digestions of the same reference material powder.
2*s* = 2 times the standard deviation of the population of *n* repeat measurements.
[a] The total number of repeated runs of the same sample, including different digestions.
* The difference between two samples instead of two standard deviations.
[†] The sample corrected by EEN method with doping Cu.
[#] The first three results (in italics) were not taken into account for the calculation of the average (because of possible instability of the instrument during measurements, see details in text).

(0.12 ± 0.04‰, *M* = 18, Figure 8) and previously published data (0.07 ± 0.07‰) (Tanimizu *et al.* 2002). Each drilled powder was analysed four times (*n* = 4), and the whole metal solution was analysed eighteen times independently with four single runs for each analysis. The small analytical errors of these independent analyses and consistent δ^{66}Zn values of different metal pieces indicate that NIST SRM 683 metals in our laboratory are homogeneous in Zn isotopic composition.

To assess our data further, we performed chemical separation for two aliquots of NIST SRM 683 solution, using the same processes described above. The δ^{66}Zn values of the two parallel samples were 0.12 ± 0.02‰ (*n* = 3) and 0.11 ± 0.02‰ (*n* = 3), which are the same within ± 0.05‰ compared with the unpurified NIST SRM 683 samples (Figure 8). This experiment further proved that the minor matrix elements in the NIST SRM 683 metal nugget are negligible.

Table 4.
Comparison of data from this study with previously published data

Reference materials	δ^{66}Zn (‰)	2*s*	References
BCR-2	0.25	0.04	This study
	0.33	0.09	Herzog *et al.* (2009)
	0.23	0.08	Bigalke *et al.* (2010)
	0.25	0.02	Moynier *et al.* (2011)
	0.33	0.13	Moeller *et al.* (2012)
	0.25	0.01	Sossi *et al.* (2015)
BIR-1	0.23	0.05	This study
	0.26	0.09	Herzog *et al.* (2009)
	0.31	0.04	Chen *et al.* (2013b)
	0.20	0.04	Sossi *et al.* (2015)
BHVO-2	0.31	0.03	This study
	0.29	0.09	Herzog *et al.* (2009)
	0.21	0.09	Moynier *et al.* (2010)
	0.17	0.09	Moynier *et al.* (2010)
	0.48	0.13	Moeller *et al.* (2012)
	0.33	0.04	Chen *et al.* (2013b)
	0.27	0.06	Sossi *et al.* (2015)
JB-2	0.23	0.04	This study
	0.19	0.08	Makishima and Nakamura (2013)
	0.22	0.07	Sossi *et al.* (2015)
AGV-1	0.29	0.03	This study
	0.50	0.06	Moeller *et al.* (2012)
	-1.58	0.30	Makishima and Nakamura (2013)
JA-2	0.28	0.03	This study
	-0.01	0.14	Makishima and Nakamura (2013)
AGV-2	0.28	0.05	This study
	0.32	0.04	Chen *et al.* (2013b)
	0.25	0.09	Moynier *et al.* (2010)
G-2	0.34	0.04	This study
	0.32	0.09	Paniello *et al.* (2012a)
	0.30	0.09	Paniello *et al.* (2012b)
	0.44	0.09	Moeller *et al.* (2012)
	0.43	0.05	Moeller *et al.* (2012)
NOD-P-1	0.78	0.03	This study
	0.78	0.09	Chapman *et al.* (2006)
	0.87	0.08	Bigalke *et al.* (2010)
	0.63	0.07	Gagnevin *et al.* (2012)

Zinc isotopic compositions of reference materials

The Zn isotopic compositions of seventeen reference materials are listed in Table 3. One to eleven replicated analyses (independent digestions) were performed for them, and all measurements for each sample agree well with each other within analytical error. Data comparison of our data and previously published data is shown in Table 4.

The δ^{66}Zn values of three basalts, BCR-2 (0.25 ± 0.04‰, *n* = 14), BHVO-2 (0.31 ± 0.03‰, *n* = 46) and BIR-1 (0.23 ± 0.05‰, *n* = 23), are consistent with previously reported data (Herzog *et al.* 2009, Bigalke *et al.* 2010, Moynier *et al.* 2010, 2011, Moeller *et al.* 2012, Chen *et al.* 2013b, Sossi *et al.* 2015). The analyses of two separately digested JB-2 samples yielded an average δ^{66}Zn of 0.23 ± 0.04‰ (*n* = 9), consistent with 0.19 ± 0.08‰ reported by Makishima and Nakamura (2013) and 0.22 ± 0.07‰ by Sossi *et al.* (2015). We report δ^{66}Zn values for dunite DTS-2 (0.27 ± 0.04‰, *n* = 3) and diabase W-2 (0.22 ± 0.05‰, *n* = 11) for the first time.

The andesite reference materials analysed in this study included AGV-1, AGV-2 and JA-2, which have consistent Zn isotopic compositions. The average δ^{66}Zn value of AGV-2 was 0.28 ± 0.05‰ (*n* = 18), in agreement with the value 0.25 ± 0.09‰ reported by Moynier *et al.* (2010) and 0.32 ± 0.04‰ by Chen *et al.* (2013b). The average δ^{66}Zn value for AGV-1 was 0.29 ± 0.03‰ (*n* = 13), showing an indistinguishable Zn isotopic composition with AGV-2 within ± 0.05‰. However, it is slightly lighter than 0.50 ± 0.06‰ reported by Moeller *et al.* (2012) and much heavier than -1.58 ± 0.30‰ reported by Makishima and Nakamura (2013). The average δ^{66}Zn value for JA-2 in this study was 0.28 ± 0.03‰ (*n* = 5), also inconsistent with data from Makishima and Nakamura (2013) (-0.01 ± 0.14‰). However, our data for AGV-1 and JA-2 are consistent with other previously published data for andesites (Chen *et al.* 2013b, Zhu *et al.* 2013).

The average δ^{66}Zn value of granite G-2 was 0.34 ± 0.04‰ (*n* = 23), in agreement with 0.32 ± 0.09‰ reported by Paniello *et al.* (2012a) and 0.30 ± 0.09‰ reported by Paniello *et al.* (2012b), but lighter than 0.44 ± 0.09‰ and 0.43 ± 0.05‰ reported by Moeller *et al.* (2012). The average δ^{66}Zn value for RGM-1 was 0.36 ± 0.05‰ (*n* = 12), and that for QLO-1 (quartz latite) was 0.27 ± 0.04‰ (*n* = 14). The average δ^{66}Zn values of two granodiorites, GSP-1 and GSP-2, were 0.31 ± 0.05‰ (*n* = 8) and 1.07 ± 0.06‰ (*n* = 12), respectively. These two samples were collected from the same location, but they have different geochemical characteristics (Raczek *et al.* 2001, 2003). In Table 3, the first three independent digestion solutions of GSP-2 (italics in the table) have very large 2*s* values for δ^{66}Zn (0.18‰), possibly due to the instability of the instrument during measurement. To ensure the precision of Zn isotopes determined in our laboratory, we digested GSP-2 four more times and measured them under better instrumental conditions. The average δ^{66}Zn value of GSP-2 for these four independent digestions was 1.07 ± 0.06‰ (*n* = 12), which is the datum reported in this study.

In summary, the δ^{66}Zn values derived for igneous rock reference materials, except GSP-2, fell in the range 0.22–

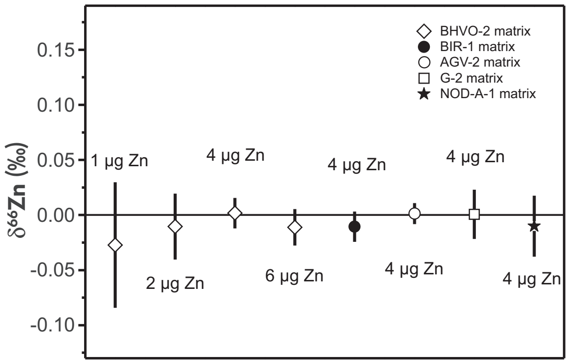

Figure 6. Zinc isotopic composition of synthetic standards. Different symbols represent different compositional matrix solutions. The first four were the matrix solutions from 50 mg BHVO-2, and the others were the matrix solutions from 50 mg BIR-1, AGV-2, G-2 and NOD-A-1. Different amounts of NIST SRM 683 Zn were doped into these solutions, and then, Zn was separated using chromatography. The bracketing measurement standard was the pure NIST SRM 683 solution without any doping element.

0.36‰, consistent with most previously reported data for igneous rocks (Paniello *et al.* 2012a, Chen *et al.* 2013b, Zhu *et al.* 2013). The δ^{66}Zn value for GSP-2 is much heavier than that of the other igneous rock reference materials.

The schist reference material SDC-1 gave an average δ^{66}Zn value of 0.26 ± 0.02‰ (n = 9), which is similar to most igneous rocks. The Zn isotopic compositions of two manganese nodules (NOD-P-1 and NOD-A-1) and one schist (SDC-1) were determined. NOD-P-1 had an average δ^{66}Zn of 0.78 ± 0.03‰ (n = 6), agreeing well with 0.87 ± 0.08‰ reported by Bigalke *et al.* (2010) and 0.78 ± 0.09‰ by Chapman *et al.* (2006) within 2*s*, but slightly heavier than 0.63 ± 0.07‰, reported by Gagnevin *et al.* (2012). Currently, there are no published Zn isotopic data for NOD-A-1. δ^{66}Zn value for NOD-A-1 measured in this study was 0.96 ± 0.03‰ (n = 6), similar to the mean value for ferromanganese nodules (0.90 ± 0.28‰) reported by Maréchal *et al.* (2000) and for Fe–Mn crusts (1.04 ± 0.08‰) reported by Little *et al.* (2014). Compared with the δ^{66}Zn value of deep seawater (~ 0.5‰) (Little *et al.* 2014, Zhao *et al.* 2014), Zn isotopic compositions of manganese nodules have heavier Zn isotopes. This might be related to the formation process of manganese nodules.

Conclusions

The Zn isotopic compositions of ninety-eight drilled metal powders and the whole metal measured in this study clearly prove that the NIST SRM 683 metal nuggets have a homogeneous Zn isotopic composition, which is only slightly heavier than JMC-Lyon ($\delta^{66}Zn_{JMC\text{-}Lyon}$ = 0.12 ± 0.04‰, M = 18). Because the JMC-Lyon material is no longer available, the NIST SRM 683 metal is a good choice to be a reference measurement standard for Zn isotope determinations because of its homogeneity, availability, reserve and isotopic composition. We examined the potential parameters that might affect the precision and accuracy of Zn isotope determinations, including mismatching conditions of acid and zinc mass fractions between samples and

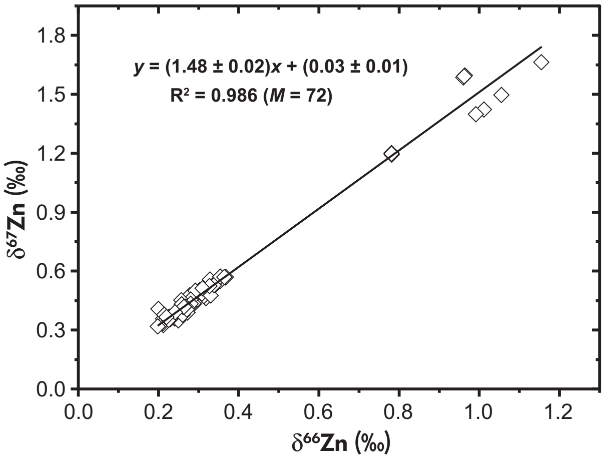

Figure 7. Zinc three-isotope plot (δ^{67}Zn vs. δ^{66}Zn) of all reference materials and NIST SRM 683 analysed in this study. The slope of the linear regression is 1.48 ± 0.02, which is consistent with the slope values of kinetic (1.48) and equilibrium (1.49) fractionation within error (2*s*, *M* = 72) (Young *et al.* 2002).

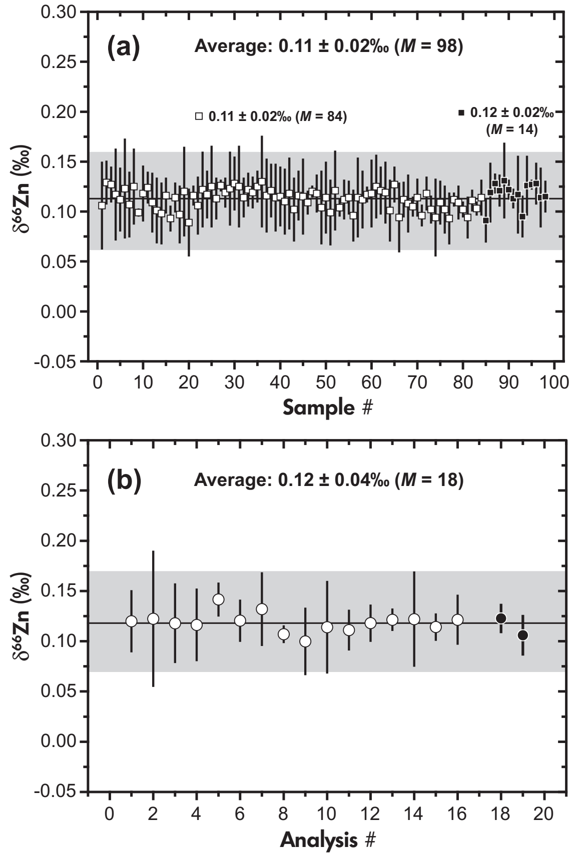

Figure 8. Zinc isotopic composition of NIST SRM 683. (a) The data of drilled NIST SRM 683 metal powders: open and filled square symbols represent the two different metal nuggets. Each square represents the average δ^{66}Zn value of one drilled powder, which was determined four times (n = 4). The average δ^{66}Zn value of eighty-four samples from the first metal was 0.11 ± 0.02‰ (M = 84), and that of fourteen samples from the other metal was 0.12 ± 0.02‰ (M = 14). The average δ^{66}Zn value of all the ninety-eight drilled powders was 0.11 ± 0.02‰ (M = 98). (b) The δ^{66}Zn data of the bulk solution of the first metal nugget. The open circle symbols represent unpurified NIST SRM 683 solution, while the two filled circle symbols represent purified samples with additional chemical separation. A total of eighteen measurements (n = 3 for each measurement) of the same solution over 5 months yielded an average of 0.12 ± 0.04‰ (M = 18).

bracketing measurement standard, and matrix effects. No significant analytical artefact was observed when $[M]_{Sample}/[M]_{Standard}$ varied from 0.5 to 3, or there was less than 10% difference in acid mass fractions. Zinc isotope determinations are sensitive to the matrix elements, especially to Ni and Ti, which can produce an obvious offset of δ^{66}Zn when [Ni]/[Zn] and [Ti]/[Zn] ratios reach 0.001 and 0.01, respectively. Significant drifts in δ^{66}Zn were also observed when the ratio values [Ba]/[Zn] > 0.3, [Mg]/[Zn] > 0.5, [Na]/[Zn] > 2 or [Al]/[Zn] > 3 occurred in sample solutions. We also report Zn isotopic compositions of a broad range of reference materials, which are suitable for interlaboratory comparison and quality control for future Zn isotopic studies in geoscience. The significant Zn isotope fractionation found in igneous rocks (0.85‰) might reflect different mantle sources, and Zn isotopes could potentially be used to trace their sources. It is also possible that later geological processes produced the Zn isotope fractionation.

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