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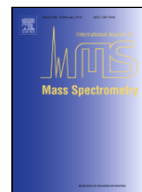
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Full Length Article

Chemical procedure for Zn purification and double spike method for high precision measurement of Zn isotopes by MC-ICPMS

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ABSTRACT

We have developed a new technique for Zn separation and high precision isotope measurement of geological and cosmochemical samples. The protocol includes sample digestion, chemical separation and purification with ion-exchange chromatography and a double spike isotopic measurement using a MC-ICPMS. An analytical precision of 0.02‰ (2SD) for $^{66}\text{Zn}/^{64}\text{Zn}$ was obtained by multiple measurements of a secondary standard (JMC-Lyon). In order to test the accuracy of our method, we analyzed the Zn isotopic composition of the geological reference materials BHVO-2, AGV-2, BIR-1, BCR-2 and JB-2, which are consistent with previous measurements from the literature. The measurements of geological reference standards show an external reproducibility ranging between 0.02 and 0.05‰ (2SD). This study provides a high precision and accuracy Zn isotope double spike technique for geological and cosmochemical rock samples, while requiring only 28 ng Zn per analysis, and is therefore suitable for the study of high temperature igneous or cosmochemical processes.

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1. Introduction

Over the past twenty years, Zn isotopes have emerged as powerful tracers for geological and cosmochemical processes. As a moderately volatile element (50% condensation temperature = 704 K), Zn isotopes have been used to study volatile element depletion in terrestrial planets, meteorites and impact melts [1–4]. Furthermore, Zn isotopes are fractionated during igneous processes which makes them a useful tracer of partial melting and magmatic differentiation [5–7]. In addition, the Zn isotope fractionation during plant uptake is linked to the environmental and physiological status of plants and can be used to characterize the impact of variable Zn supply to plants [8,9]. Also, Zn isotopes have recently appeared to be a useful tracer of marine phytoplankton activity and biogeochemical cycling of micronutrients in the oceans (e.g. Ref. [10,11]). A number of double spike techniques have emerged to study the isotope composition of dissolved Zn in seawater (e.g. Ref. [12–14]), the behavior of Zn in soils during chemical weathering [15], and Zn anthropogenic contamination [16].

Although the double spike technique is applied more and more frequently to various isotope systems in geochemistry, the most commonly used method for Zn isotope analysis of geological samples by MC-ICPMS has been the standard-sample bracketing (SSB) technique that requires the absence of Zn isotope fractionation during chemi-

cal separation of Zn from its matrix (or 100% Zn recovery) and identical matrix effects for sample and standard solutions. A series of Zn isotope studies in magmatic rocks has resulted in a controversy about the Zn isotope composition of the bulk silicate Earth [5–7,17] that justified the development of reliable and more precise analytical methods. An example of the discrepancy in the Zn isotope data is illustrated by the range of measured values for the geological standard BHVO-2 by various groups from $0.21 \pm 0.09\text{‰}$ (2SD) [18] to $0.48 \pm 0.13\text{‰}$ (2SD) [19]. The most recent DS techniques developed for the study of dissolved Zn in seawater has reached a precision of $\sim 0.04\text{‰}$ (2SD) [13,14]. Though such high precision has also been achieved for measurements of geological rock standards [4,15], these analyses were performed with at least 1 μg of Zn, which can be inconvenient for the study of low Zn content samples.

In this study, we developed a new method for determining the Zn isotope composition with a double spike technique specifically targeting geological and cosmochemical applications. In principle, a double spike method corrects for isotope fractionation during the isotope measurement and the sample preparation associated with non-quantitative Zn recovery. To demonstrate the validity of our technique, reference geological materials with a known Zn isotope composition were measured. All isotope measurements will be reported using the following notation:

$$\delta^{66}\text{Zn} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \quad (1)$$

where R_{sample} and R_{standard} are the ratio of $^{66}\text{Zn}/^{64}\text{Zn}$ in the sample and the standard, respectively. The $\delta^{66}\text{Zn}_{\text{JMC}}$ represents the Zn isotope com-

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position of the JMC-Lyon standard solution relative to the in-house standard which is determined by multiple measurements of JMC-Lyon standard solution over a year ($n = 23$).

2. Materials and methods

2.1. Double spike methodology

A double spike solution was added to the sample prior to sample dissolution in order to correct for isotope fractionation during chemical separation and isotopic measurement. The double spike consists of a mixture enriched in two Zn isotopes, ^{64}Zn and ^{67}Zn .

The determination of the isotope proportions in the double spike (DS) solution and their proportions relative to the Zn in the sample were based on the “double spike cocktail list” calculated by Rudge et al. [20]. This list allows the determination of the optimal isotope proportions in the double spike solution that minimize the uncertainty of the natural fractionation factor α . In this list, the optimal double spike mixture includes ^{70}Zn . However, mass 70 has three major interferences, namely $^{54}\text{Fe}^{16}\text{O}^+$, $^{56}\text{Fe}^{14}\text{N}$ and Ge^+ which makes it inconvenient for isotope measurements. To determine the isotopes and their proportion in the double spike solution, two factors must be taken into account: the choice of the four masses involved in the DS technique and the calculated range of proportions (of each spike and of sample relative to the DS mixture) that give the smallest uncertainty. Several studies have designed a double spike method for Zn isotopes measurements for various geochemical applications [12–14,19,21]. Arnold et al. [21] showed that a mixture of ^{64}Zn and ^{67}Zn yields high precision isotope measurements while allowing a large range of sample/spike ratios. According to Rudge et al. [20], ^{62}Zn - ^{67}Zn and ^{66}Zn - ^{68}Zn double spikes should, in principle, be characterized by an even higher precision but the corresponding range of optimal sample/DS ratios is too narrow. In addition, the ^{64}Zn metal that can be obtained commercially has the highest purity compared to other enriched spikes. The optimal $^{64}\text{Zn}/^{67}\text{Zn}$ ratio as calculated in Rudge et al. [20] is 4.88 using ORNL (Oak Ridge National Laboratory) spikes. However, because our spikes were purchased from Isoflex, the composition of the spikes are different, thereby affecting the optimal $^{64}\text{Zn}/^{67}\text{Zn}$ ratio which needed to be recalculated. The optimal $^{64}\text{Zn}/^{67}\text{Zn}$ using Isoflex spikes is 5.96. Moeller et al. [19] developed a technique with a $^{64}\text{Zn}/^{67}\text{Zn}$ ratio of 5.38 with Isoflex spikes which is close to the optimal value. However, Arnold et al. [21] showed that the $^{64}\text{Zn}/^{67}\text{Zn}$ ratio does not drastically affect the uncertainty of the calculated isotope fractionation factor. As an example, both Moeller et al. [19] and Arnold et al. [21] report the same reproducibility for their isotope measurement (0.05%) despite using significantly different $^{64}\text{Zn}/^{67}\text{Zn}$ ratios in their double spike. Therefore, Although the $^{64}\text{Zn}/^{67}\text{Zn}$ value is an important parameter to consider to reach the best precision, it appears that the variability of $^{64}\text{Zn}/^{67}\text{Zn}$ value between different groups does not affect the final precision of the Zn isotope measurement. The DS technique from Arnold et al. [21] was determined with numerical methods based on the geometrical criteria of Galer et al. [22] while other studies [13,14,19] used the optimal spike composition given in Rudge et al. [20]. In this study, we developed a DS technique using the “cocktail list” of Rudge et al. [20] with a $^{64}\text{Zn}/^{67}\text{Zn}$ ratio of 4.50 which is close to the optimal ratio. For our double spike composition, the optimal sample/DS proportions are 58.19% of DS and 41.81% of sample, expressed in moles of Zn.

The double spike solution was prepared by mixing two solutions of enriched ^{64}Zn (196.656 mg, 99.1% purity; Isoflex Corp, USA) and ^{67}Zn (23.144 mg, 89.6% purity; Isoflex Corp, USA). The enriched spikes were dissolved in 19.48 mL and 10.37 mL of 2 N (mol/L) HNO_3 , respectively in order to obtain a concentration of approximately 10 mg/mL of ^{64}Zn and 2 mg/mL of ^{67}Zn . Then, two aliquots of the ^{64}Zn solution and of the ^{67}Zn were mixed and diluted in 2 N HNO_3 in order to obtain a solution containing ~ 350 ppm of Zn. The exact DS composition was calibrated precisely using three different mixtures of DS and Alfa Aesar Zn standard.

2.2. Materials, reagents and instruments

Samples were dissolved and stored in Teflon Savillex® beakers. Anion-exchange resin AG1-X8 (200–400 mesh) were purchased from Eichrom and Polypropylene chromatography columns 2 mL bed volume (0.8×4 cm) from Biorad. For ion-exchange chromatography, we used ultrapure water (Milli-Q®), and Optima™ nitric, hydrochloric, and hydrofluoric acids.

As a primary standard, we prepared a solution of an Alfa Aesar Zn plasma standard solution, Specpure, 1000 $\mu\text{g}/\text{mL}$ (no. 13835, Lot 61300325) diluted in 0.1 N HNO_3 . The accuracy of the DS isotopic measurement was verified before any measurement using a secondary standard JMC (‘JMC-Lyon’, Johnson Matthey, Royston, UK).

The ion-exchange chromatography protocol was determined using a multi-element solution prepared by mixing 1000 ppm mono-elemental solutions. This solution contains elements that can produce isobaric interferences on Zn (Ni^+ , Ba^{2+}) and element potentially forming molecular interferences (Fe, Cr, Al) in order to be sure that our procedure separates Zn from those elements.

Concentration measurements of samples and column calibration were done on an ICPMS Element 2 (Thermo Scientific). An MC-ICPMS Neptune Plus (Thermo Scientific) was used for isotopic measurements at the Laboratoire de Géologie de Lyon.

2.3. Sample dissolution

Samples were first dissolved in 30 mL closed Savillex beakers containing 5 mL of concentrated HF and 5 mL of concentrated HNO_3 at 160 °C for at least 48 h. Samples were then dried down at 120 °C to avoid Zn loss, and dissolved in aqua regia. Finally, the samples were dried down and taken up in concentrated HCl, and then several times in 2 mL of 0.4 N HCl before ion-exchange chromatography. For all samples, we made sure a complete dissolution was obtained, which ensured sample-spike homogenization.

2.4. Ion-exchange chromatography

After sample dissolution, zinc had to be separated and purified from its matrix using a two-step ion-exchange chromatography before measurement on the MC-ICPMS. The separation protocol was adapted from Wang et al. [23] who developed Sn purification using anion exchange resin. The first column contained 1.5 mL of Eichrom™ AG1-X8 anion-exchange resin (200–400 mesh) and 0.5 mL of pre-filter material from Eichrom™ was loaded on top of the anion-exchange resin bed. The column was washed with 20 mL of 0.5 N HNO_3 , 10 mL of Milli-Q® water, 6 mL 4 N HCl, and conditioned with 6 mL 0.4 N HCl (Table 1). This column was calibrated using the multi-element solution and the results are depicted in Fig. 1.

Most of the matrix was eluted during the first 26 mL 0.4 N HCl while Zn remains on the resin. The elements producing isobaric interferences on ^{64}Zn (i.e. ^{64}Ni and Ba^{2+}) were largely removed during this step. This step also eliminated elements that could produce molecular interferences (Cr, Fe, Mg). Based on existing partition coefficients, Al, Ti and V were also efficiently removed during this stage. Following this first step, 10 mL of 8 N HCl was added in order to remove Ag. Finally, the Zn fraction was eluted with 20 mL of 0.5 N HNO_3 . This solution was evaporated to dryness and taken up in 1 mL 1 N HF for the second column. Two mL of Eichrom™ AG1-X8 anion-exchange resin (200–400 mesh) in the H^+ form was loaded on the second column. Zn is eluted during the first 20 mL of 1 N HF while Sn is separated from Zn during HNO_3 elution. The solution was finally evaporated and taken up in HCl for isotope measurement. In order to check the mass dependence of the Zn isotope fractionation after chemical separation, we measured the $\delta^{66}\text{Zn}$, $\delta^{67}\text{Zn}$, and $\delta^{68}\text{Zn}$ (expressed in ‰/amu) for a granitic reference material (G2) and a peridotite sample from Kilbourne Hole (K1)

Table 1

Protocol for Zn purification by anion-exchange (AG1-X8, 200–400 mesh Eichrom). Column: Polypropylene Biorad 2 mL.

Step	Eluent	Volume (mL)
Column 1		
Wash	0.5 N HNO ₃	20
Rinse	mQ	10
Conditioning	4 N HCl	6
	0.4 N HCl	6
Loading sample	0.4 N HCl	2
Elution of matrix, Ni, Fe, Cr	0.4 N HCl	26
Elution of Ag	8 N HCl	10
Elution of Zn	0.5N HNO₃	20
Column 2		
Wash	0.5 N HNO ₃	20
Rinse	mQ	10
Conditioning	5 N HF	6
	1 N HF	6
Loading sample	1 N HF	1
Elution of Zn	1N HF	20
Elution of Sn	0.5 N HNO ₃	20

with no double spike addition. For both samples, we calculated the three δ/amu values and found that they were identical within uncertainty. This demonstrates that no isobaric interferences are present on the ^{64}Zn , ^{66}Zn , ^{67}Zn and ^{68}Zn masses, with samples having experienced our chemical separation.

The Zn yields were calculated by comparing the Zn amount determined in our BHVO-2 rock powder with the amount of Zn collected at the end of the chemical procedure. The double-spike solution was added before dissolution of the sample and was used to calculate the Zn concentration in BHVO-2 by the isotope dilution technique and found to be 93.1 ± 0.1 ppm. In parallel, the amount of zinc in the final Zn fraction was estimated by comparing the ^{66}Zn and ^{68}Zn intensities in the Zn fraction with those of a known concentration standard solution. Both measurements provided similar Zn contents thereby implying that the total recovery for this procedure is $100 \pm 5\%$. The Zn blank for the total procedure including dissolution and chemical separation was less than 0.5 ng. The total Zn blank was obtained by comparing the total amount of Zn resulting from the whole procedure with the primary standard with known concentration using an MC-ICPMS. This last value was negligible compared to the minimum Zn amount used in a single measurement (28 ng), in particular in the context of high-temperature isotope fractionation applications.

2.5. Mass spectrometry

2.5.1. Measurement protocol

We performed Zn isotope measurements on a MC-ICPMS Neptune Plus (Thermo Scientific) equipped with Jet-X cones and a Cetac Aridus II desolvating system at the Laboratoire de Géologie de Lyon at ENS de Lyon. Measurements were done at high-resolution mostly in order to remove the ArN_2^+ interference on ^{68}Zn (due to the combined use of the Aridus II and Jet-X cones) and other possible remaining interferences.

It is interesting to note that Zn isotope measurements have been performed in low-resolution using an Aridus II without N_2 gas [4,15,16]. We used a PFA nebulizer (135 $\mu\text{L}/\text{min}$) connected to an Aridus II for sample introduction. Table 2 shows the configuration of Faraday collectors (using amplifiers equipped with $10^{11} \Omega$ resistors) for Zn isotope measurements.

This single line configuration allowed the measurement of ^{60}Ni and ^{62}Ni that could be used to correct for the ^{64}Ni isobaric interference on ^{64}Zn . Each measurement represented one block of 25 cycles with an integration time of 8.389s. Between two measurements, the washing procedure consisted of 10 cycles of 8.389 s in 0.5 N HNO₃ solution and 25 cycles of 8.389 s in 0.1 N HNO₃ with an uptake time of 200 s. This procedure allowed complete recovery of the baseline signal to a level < 1 mV. Finally, an uptake time of 30 s was necessary before the beginning of each measurement in order to obtain a stable signal. The concentrations of samples and standards were adjusted to 40 ppb (with a 10% intensity match), corresponding to a ^{66}Zn intensity ranging from 1.7 to 2 V. The instrumental sensitivity for Zn measurement was usually 75–85 V/ppm. Since we used a nebulizer with a flow rate of 135 $\mu\text{L}/\text{min}$, one measurement required a minimum of 0.74 mL, i.e. 28 ng of Zn. The instrument settings used in our protocol are listed in Table 3.

Prior to each sample measurement, a sequence of primary standard was used to verify the stability of the MC-ICPMS. Following that, an in-house standard (Zn-LGL) was measured using a standard-sample bracketing method in order to check the mass dependence of the measurement. Finally, the accuracy of the DS measurement was verified by measuring regularly the JMC-Lyon standard with the DS technique. Following these tests, a DS measurement sequence consisting of measurements of spiked samples bracketed with spiked standards was used, in order to correct for possible deviation from the exponential mass fractionation law. Indeed, it is known that the exponential law is not perfect for describing instrumental mass bias observed with MC-ICPMS (e.g. Ref. [24]). Such deviation has been observed and corrected for in previous studies ([23,25,26]).

2.5.2. On-peak zero and isobaric interference correction

Before each analysis, the electronic background was determined by measuring the baseline by deflecting the ion beam with the electrostatic analyzer over 15 s. The intensity of all Zn isotopes (in 0.1 N HNO₃) was analyzed before and after standard or sample measurement. The Zn isotope intensity was just above detection limit ($\sim 5.10^{-4}$ V for ^{64}Zn). All isotope intensities were corrected with the average on-peak zero (OPZ) measured before and after standards and samples. However, ArN_2^+ forms an isobaric interference on ^{68}Zn which requires the use of the high-resolution mode because it cannot be corrected properly by on-peak zero.

Isobaric interference of ^{64}Ni on ^{64}Zn is not resolvable and have to be corrected using the measurements of ^{60}Ni and ^{62}Ni peaks. As ^{64}Ni is the least abundant isotope among all Ni isotopes, it produces limited interferences. ^{64}Ni abundance was calculated using the ^{60}Ni peak thanks to its high natural abundance relative to ^{62}Ni :

$$I^{64}\text{Zn} = I^{64} - \left[I^{60}\text{Ni} \times \frac{A^{64}\text{Ni}}{A^{60}\text{Ni}} \times \left(\frac{M^{64}\text{Ni}}{M^{60}\text{Ni}} \right)^f \right] \quad (2)$$

where $I^{64}\text{Zn}$ and $I^{60}\text{Ni}$ are the true intensities of ^{64}Zn and ^{60}Ni , I^{64} is the measured intensity at mass 64, $A^{64}\text{Ni}$ and $A^{60}\text{Ni}$ are the natural abundances of ^{64}Ni and ^{60}Ni , $M^{64}\text{Ni}$ and $M^{60}\text{Ni}$ are the masses of ^{64}Ni and ^{60}Ni , and f is the instrumental fractionation factor determined with Zn isotopes:

$$f = \ln \left(\frac{R_{\text{Zn}66/64}}{\frac{A^{66}\text{Zn}}{A^{64}\text{Zn}}} \right) / \ln \left(\frac{M^{66}\text{Zn}}{M^{64}\text{Zn}} \right) \quad (3)$$

where $R_{\text{Zn}66/64}$ is the ratio of ^{66}Zn and ^{64}Zn in the primary stan-

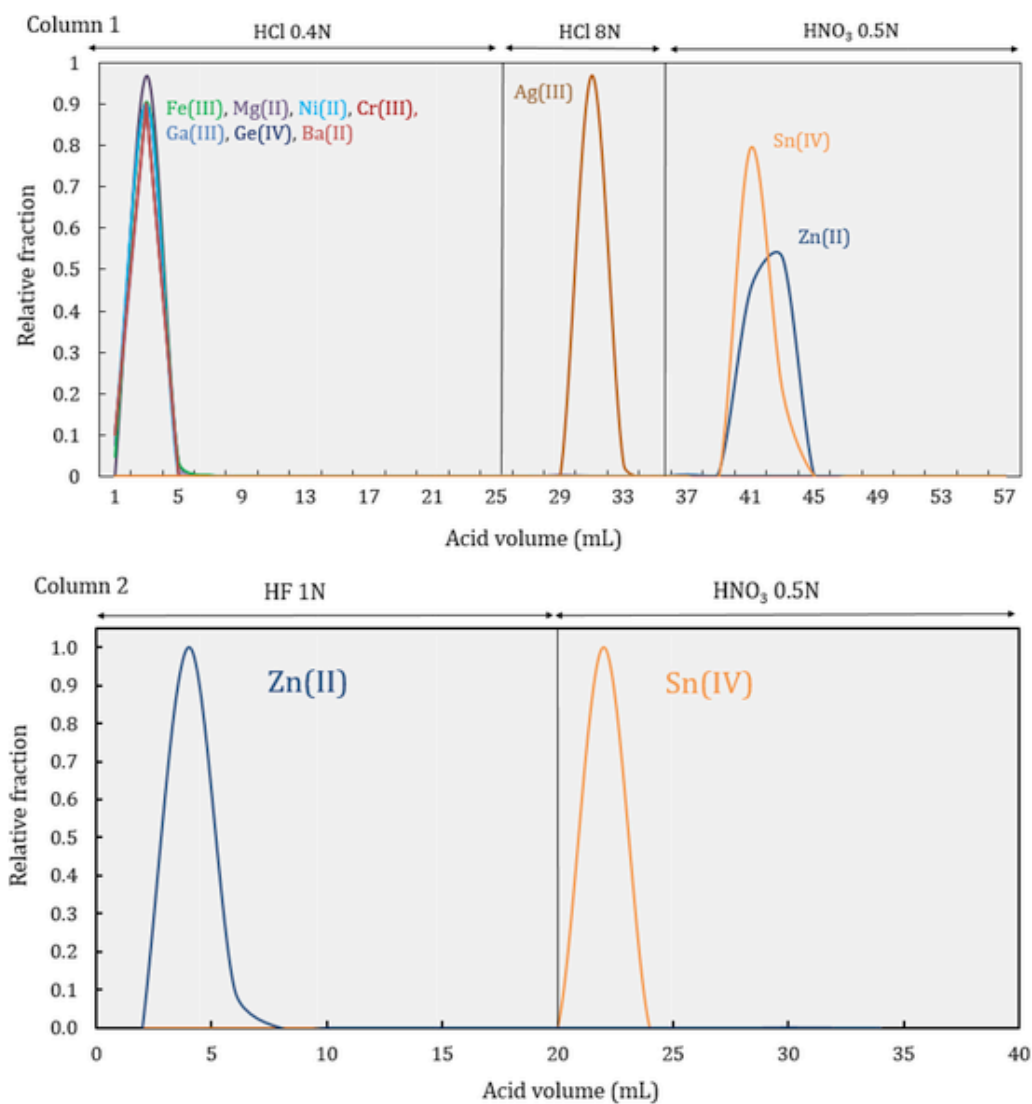


Fig. 1. Elution curve of Zn from synthetic solution. The first column allows $\sim 100\%$ recovery of Zn and separation from isobaric interference created by Ni^+ and Ba^{2+} and possible molecular interferences induced by Cr. The second column allows the separation of Zn from Sn and $\sim 100\%$ recovery of Zn.

Table 2
MC-ICPMS collector configuration.

Collector	L4	L3	L2	L1	Center	H1	H2	H3	H4
Mass		^{60}Ni		^{62}Ni	^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn	
Typical ion beam intensity (V)	n/a	$<10^{-3}$	n/a	$<10^{-4}$	3.4	2	0.3	1.4	n/a

dard, $A^{66}\text{Zn}$ and $A^{64}\text{Zn}$ are the natural abundances of ^{66}Zn and ^{64}Zn , $M^{66}\text{Zn}$ and $M^{64}\text{Zn}$ are the masses of ^{66}Zn and ^{64}Zn . The value of f is calculated using the primary standard every 10 DS measurements. Typical intensity for ^{60}Ni is 10^{-3} V, which corresponds to a signal of 10^{-5} V for ^{64}Ni .

2.5.3. Double spike calibration

The composition of the double spike solution was determined by measuring different mixtures of the primary standard and the double spike solution. The DS-standards mixtures used for the double spike calibration contained 45%, 55% and 65% of DS relative to the primary standard expressed in mole fraction. These DS-standard mixtures were measured three times successively after three analyses of the pri-

mary standard which was used to determine a value of instrumental fractionation β . Finally, the pure DS solution was also measured three times. The measurements of mixtures, pure DS, primary standard, the DS proportion and β values are used as inputs in a MATLAB® code to determine the true composition of the DS as explained in the Appendix of Rudge et al. [20]. The composition of the DS of this study is: $^{64}\text{Zn} = 80.73\%$, $^{66}\text{Zn} = 0.57\%$, $^{67}\text{Zn} = 17.94\%$ and $^{68}\text{Zn} = 0.76\%$. The double spike composition used in this study shows an isotope composition close to the optimal value given by Rudge et al. [20].

In order to check the validity of the double spike method, we measured different DS mixtures with the double spike inversion (Table 4). DS mixtures included DS-standard mixtures used for the calibration and mixtures with low and high DS proportion (Fig. 2). Mixtures with DS proportion ranging from 45 to 75% show $\delta^{66}\text{Zn}$ that are close to

Table 3
Instrument settings of MC-ICPMS Neptune Plus for Zn isotope measurements.

Settings	
Cone	Ni jet cone
Resolution	10,000
Aridus II parameters	
Argon sweep gas flow	7 L min ⁻¹
Nitrogen gas	< 10 mL min ⁻¹
Spray chamber temperature	110 °C
Membrane oven temperature	160 °C
Sample rate	135 µL min ⁻¹
Medium	0.1 N HNO ₃
Concentration	40 ppb
Instrument parameter	
Cool Ar	15 L min ⁻¹
Auxiliary Ar	0.8 L min ⁻¹
Sample Ar	1.1 L min ⁻¹
RF power	1200 W
Cones	Ni
Sensitivity	75–85 V ppm ⁻¹
Sequence parameter	
Number of blocks	1
Cycles per block	25
Integrations	1
Idle time	3s
Integration time	8.389s

Table 4

The Zn isotope composition of DS-standard mixtures and their different DS proportion relative to the primary standard Alfa Aesar. Errors are expressed as 2SD (%). DS-Standards in blue are used in the DS calibration. Note the increase of errors for mixtures with too low DS proportion and a shift of $\delta^{66}\text{Zn}$ values for mixtures with too high DS proportion.

Mixtures	DS molar abundance (%)	$\delta^{66}\text{Zn}$ (‰)
DS 25	25	-0.05 ± 0.24 ‰
DS 35	35	-0.01 ± 0.14 ‰
DS 45	45	-0.01 ± 0.03 ‰
DS 55	55	0.00 ± 0.03 ‰
DS 65	65	0.02 ± 0.04 ‰
DS 75	75	-0.02 ± 0.04 ‰
DS 85	85	-0.07 ± 0.03 ‰

zero indicating that the double spike calibration is valid. However, mixtures with DS proportion lower than 45% exhibited an increase of the 2SD while mixtures with DS proportion higher than 75% had lower $\delta^{66}\text{Zn}$ values, thereby revealing a systematic error. This suggests that a Zn isotope measurement is valid if the DS proportion relative to the sample ranges between 45 and 75%.

2.5.4. Data reduction

The intensities of ^{64}Zn , ^{66}Zn , ^{67}Zn and ^{68}Zn are corrected from OPZ and ^{64}Ni interference. The average ratios of the 25 cycles are calculated with the Neptune software which beforehand suppresses values outside the 2SD.

The calculation of the $\delta^{66}\text{Zn}$ is done with a MATLAB® code of double spike inversion based on equations of Rudge et al. [20]. This allows the correction of instrumental and chemical fractionation that can occur during isotope measurement on the MC-ICPMS and during chemi-

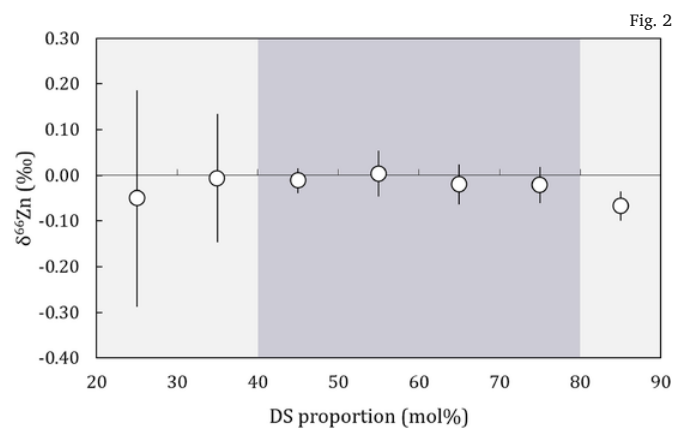


Fig. 2
Zn isotope composition of mixtures and their different DS proportion in double spike-sample mix. The purple area highlights the range of DS proportion that allows the maximum precision and accuracy. Samples with low DS proportion (< 45%) have a higher 2SD while standard with high DS proportion (> 80%) show poor accuracy. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cal purification. The isotope fractionation factor is the output of the program based on the measured ratios ($^{66}\text{Zn}/^{64}\text{Zn}$, $^{67}\text{Zn}/^{64}\text{Zn}$ and $^{68}\text{Zn}/^{64}\text{Zn}$), the isotope composition of the DS and the primary standard. Furthermore, a DS-standard with a DS proportion of 58.19% by mole of Zn is measured before and after every sample in order to correct the possible deviation from the exponential mass fractionation law. Finally, the Zn isotope composition of the sample is calculated with:

$$\delta^{66}\text{Zn}_{\text{sample final}} = \delta^{66}\text{Zn}_{\text{sample}} - \delta^{66}\text{Zn}_{\text{std}} \quad (4)$$

where $\delta^{66}\text{Zn}_{\text{sample}}$ is the returned value of the sample measurement and $\delta^{66}\text{Zn}_{\text{std}}$ is the mean value of the standard before and after the sample (this correction is smaller than 0.05‰). Finally, the Zn isotope composition is calculated relative to the JMC-Lyon standard with:

$$\delta^{66}\text{Zn}_{\text{sample final JMC}} = \delta^{66}\text{Zn}_{\text{sample final}} + \delta^{66}\text{Zn}_{\text{JMC}} \quad (5)$$

where $\delta^{66}\text{Zn}_{\text{JMC}} = 0.27 \pm 0.02\text{‰}$.

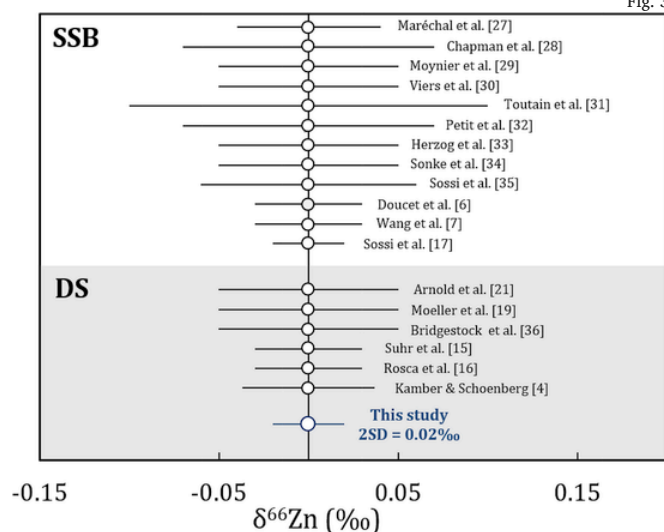
2.5.5. Precision of the Zn isotope measurements

The secondary standard JMC-Lyon was measured several times during every sequence in order to evaluate the accuracy of the DS measurement and was used to estimate a measurement reproducibility of 0.02‰ (2SD) and 0.005‰ (2SE, n = 23). This standard was measured at least two times during each run for a total of 11 runs over a year. Fig. 3 shows a comparison of Zn isotope measurement reproducibility (2SD) between existing methods of Zn isotope measurements in geological samples and this study [4,6,7,15–17,19,21,27–36]. This method provides a high Zn measurement reproducibility for the study of Zn isotopes in geological and cosmochemical rock samples. The most recently published SSB method has shown a comparable precision to this study (0.02‰, 2SD) [17]. However, Sossi et al. [17] measurements are based on a method from Sossi et al. [35] which requires the use of ~85 ng of Zn while only 28 ng are necessary in our method, which represents a significant improvement. Therefore, our method can be used to analyze precious samples with complexes matrices.

3. Application to geological reference materials

This technique has been used to measure the Zn isotope composition of five largely studied geological reference materials in order to estimate the accuracy of our method (Table 5). The $\delta^{66}\text{Zn}$ value of USGS reference samples BHVO-2, BCR-2, BIR-1 and AGV-2 was $0.33 \pm 0.03\text{‰}$, $0.33 \pm 0.05\text{‰}$, $0.28 \pm 0.04\text{‰}$ and $0.34 \pm 0.02\text{‰}$ respectively (2SD), which is consistent with existing measurements (

Fig. 3



A comparison of measurement reproducibility (2SD) of existing methods for Zn isotope measurements.

Table 5

Zn isotope composition of BHVO-2, BIR-1, BCR-2, AGV-2 (USGS standards) and JB-2 (GSJ standard) measured in this study. δ values (‰) are calculated relative to the Alfa Aesar standard (in-house) and JMC standard.

Sample	$\delta^{66}\text{Zn}$ (in-house)	$\delta^{66}\text{Zn}$ (JMC)	2SD	2SE	n	Zn (ppm)
BHVO-2	0.06	0.33	0.03	0.02	3	93.1
BIR-1	0.01	0.28	0.04	0.02	3	74.1
BCR-2	0.06	0.33	0.05	0.02	4	133.7
AGV-2	0.07	0.34	0.02	0.01	3	92.6
JB-2	-0.09	0.18	0.04	0.03	3	114.9

Fig. 4) [3,5–7,15–19,33,35,37–39]. The variability of the precision obtained during the measurements of geological standards likely reflect matrix effects affecting the stability of the measurements. Note that Moeller et al. [19] measured a $\delta^{66}\text{Zn}$ value of $0.48 \pm 0.13\text{‰}$ (2SD) for BHVO-2 which appears to be an outlier compared to our and other studies and shows a large error. Although recent studies (based on Moeller et al. [19] method) allowed the determination of Zn isotope composition with high precision and accuracy [4,15,16], the minimum Zn amount used for one Zn isotope analysis was at least 9 times higher than in this study. The study of Weis et al. [40] showed that BHVO and BCR were heterogeneous for Sr, Nd and Pb isotopes and possibly contaminated for a number of trace elements during sample preparation (e.g. Sn, Pb, W and Mo) but this was not the case for Zn which is more abundant than these trace elements. The Zn isotope composition of BHVO-2 measured by Sossi et al. [17] ($0.28 \pm 0.06\text{‰}$) exhibits a larger uncertainty than our measurement ($0.33 \pm 0.03\text{‰}$) while requiring approximately 3 times more material. Finally, JB-2 from the Geological Survey of Japan (GSJ) JB-2 was $0.18 \pm 0.04\text{‰}$ (2SD) which was also found to be very similar to measurements from Wang et al. [7], Sossi et al. [17] and Chen et al. [5]. All geological reference materials measured here are consistent with existing data which proves the accuracy of our method.

4. Conclusion

We have developed a new analytical method for the measurement of Zn isotopes by mass spectrometry providing high accuracy and precision. A total Zn recovery close to 100% is obtained using a two-step ion-exchange chromatography with AG1-X8 anion resin. A ^{64}Zn – ^{67}Zn double spike was used to correct for mass-dependent fractionation pro-

duced during chemical separation or during analysis on the MC-ICPMS. The double spike solution developed in this study is close to the optimum value given in Rudge et al. [20]. An internal reproducibility of 0.02‰ (2SD) for ^{66}Zn – ^{64}Zn was determined by multiple analyses of a secondary standard (JMC-Lyon). The external reproducibility obtained on geological reference materials ranged between 0.02 and 0.05‰ (2SD). A minimum of 28 ng of Zn is necessary for one isotope measurement, a factor of 9 less than double spike methods with similar precision reported in the literature. The Zn isotope composition of five geological standards was measured and was found to be in good agreement with previous literature data. This analytical method should be applicable to the determination of Zn isotope fractionation during high temperature geological and cosmochemical processes.

Uncited references

[27]; [28]; [29]; [30]; [31]; [32]; [33]; [34]; [36]; [37]; [38]; [39].

CRedit authorship contribution statement

Quentin Amet: Methodology, Writing - original draft, Writing - review & editing. **Caroline Fitoussi:** Conceptualization, Resources, Methodology, Writing - review & editing.

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Quentin Amet: Methodology, Writing - original draft, Writing - review & editing. **Caroline Fitoussi:** Conceptualization, Resources, Methodology, Writing - review & editing.

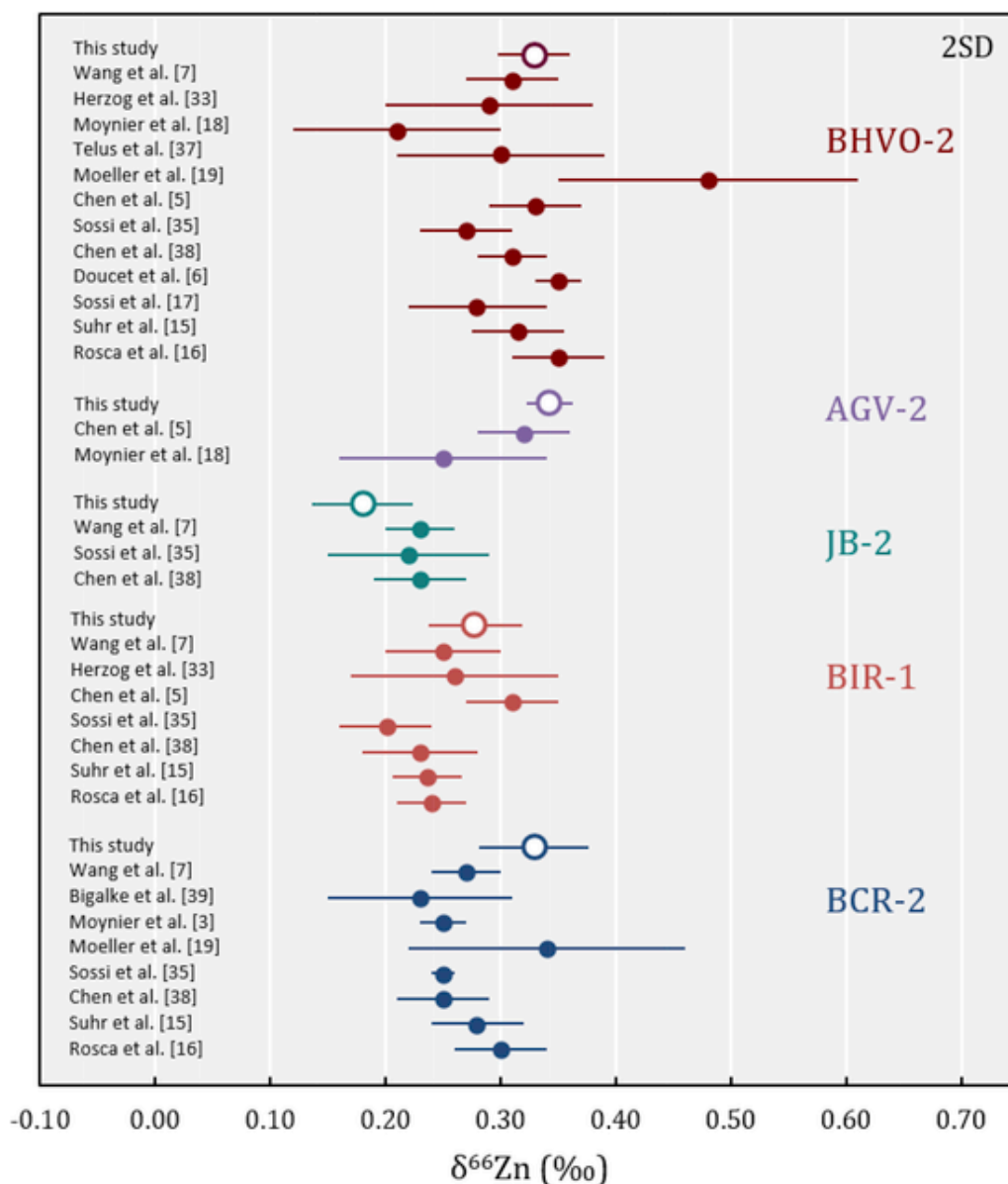
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 4



A comparison of Zn isotope composition of geological rock standards BCR-2, BIR-1, JB-2, AGV-2 and BHVO-2 measured in this study (open circles) and in the literature (dots). The $\delta^{66}\text{Zn}$ of all geological standards are consistent with available data from the literature thereby confirming the accuracy of our method.

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