



Zinc isotope fractionation analyses by thermal ionization mass spectrometry and a double spiking technique

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ABSTRACT

The aim of this work was to develop thermal ionization mass spectrometry (TIMS) isotopic procedures to measure Zn isotope fractionation (δZn) in natural materials. This work represents the most recent development of Zn isotope measurements and the first δZn identification in terrestrial materials using TIMS and a double spike technique. The developed procedures evaluate and solve several critical analytical issues involved in TIMS Zn isotope analysis. For example, no more than 1 μg Zn was used for isotopic analyses which, considering the high ionization potential and low thermal ionization of Zn, represents a useful breakthrough in Zn isotope TIMS analysis. The effect of the ion exchange process on δZn was assessed and found equal to $+0.07 \pm 0.02\% \text{amu}^{-1}$ per column. The ionization efficiency of Zn was enhanced to $0.22 \pm 0.07\%$, which is four times more than what was achieved previously. The magnitude of δZn accompanied by the 95% confidence associated uncertainties were calculated relative to the IRMM 3702, using a Monte Carlo approach for each individual analysis, while the calculated average of δZn for number of analysis was accompanied by a 95% confidence calculated using GUM Workbench software. δZn values were always calculated using two different sets of isotopes which always agreed within uncertainty. These developments enabled sub-per mil δZn to be revealed relative to δZn zero for natural materials. Most of the samples measured are Standard Reference Materials SRMs, where, except for BCR-1 and BIR-1, this is the first time Zn isotopic fractionation has been measured in these samples. No previously published results for Zn isotopic fractionation have been published on these samples using double spiking. Consistent δZn of $\sim +0.3\% \text{amu}^{-1}$ was found in 5 sediments from a range of localities. δZn in two metamorphic samples is similar to that found in igneous rocks but different to that found in sedimentary rocks, which is consistent with our understanding that high temperature and pressure processes do not fractionate the composition of chalcophile elements. The isotope fractionation of Zn in a clay sample is within uncertainties the same as the sediments. The isotope fractionation of Zn of $-0.088 \pm 0.070\% \text{amu}^{-1}$ was also measured in a standard rice sample. δZn in Antarctic Krill of $+0.21 \pm 0.11\% \text{amu}^{-1}$ was found to be similar to the average δZn of $+0.281 \pm 0.083\% \text{amu}^{-1}$ for marine sediments. River water was fractionated by $-1.09 \pm 0.70\% \text{amu}^{-1}$, while restrained tap water yielded the maximum isotope fractionation of $-6.39 \pm 0.62\% \text{amu}^{-1}$. δZn in high pure Zn standard materials ranged from $-5.11 \pm 0.36\% \text{amu}^{-1}$ for AE 10760 to $+0.12 \pm 0.16\% \text{amu}^{-1}$ for Zn IRMM 10440 with some evidence for a relationship between Zn isotope fractionation and its purity. All of the measured isotope fractionation yields an atomic weight within the IUPAC atomic weight of Zn.

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1. Introduction

Zn has five stable isotopes, ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn and ^{70}Zn and twenty four radiogenic nuclides [1]. The main nucleosynthetic production site and processes for Zn have not been clearly identified [2]. The natural abundance of stable Zn isotopes

is $^{64}\text{Zn} = 49.17040 \pm 0.00017\%$, $^{66}\text{Zn} = 27.730629 \pm 0.000096\%$, $^{67}\text{Zn} = 4.040135 \pm 0.000014\%$, $^{68}\text{Zn} = 18.448241 \pm 0.000064\%$ and $^{70}\text{Zn} = 0.000003 \pm 0.610560\%$. Moreover, the atomic weight of Zn; Ar (Zn) = 65.38 ± 0.02 [3,4]. Zinc has a high ionisation potential (9.39 eV) which makes Zn difficult to ionize thermally; it is the reason why few analysts have employed thermal ionization mass spectrometry (TIMS) to measure Zn isotope fractionation (δZn) [5]. Zinc isotopic composition can be used as an environmental tracer [6,7]. The measurements of δZn are of great potential to investigate a wide range of phenomenon, from climate variability to studying the history of the solar system [7–16]. Measurements of δZn can also be useful to more understand biological activities and aspects

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of human health and disease [10,17–20]. The correlation between Zn elemental abundance and δZn is important to understand processes that fractionate Zn in geological materials and relationship between terrestrial and extraterrestrial Zn [21–23].

Early successful δZn measurements were performed using high sensitive Plasma Source Mass Spectrometers (PSMS) [9,12,24–27]. All previous δZn values were relative to in-house laboratory standards; however, the benefit of measuring δZn relative to an international standard “ δ zero” is to allow inter-laboratory comparisons [28].

Many of the samples measured in this work are standard reference materials (SRM's). Measuring the isotopic composition of Zn in SRM's relative to the absolute isotopic composition of Zn (δ zero) will provide baseline metrological results to be exploited for future Zn isotopic investigations. Moreover, δZn values obtained for SRM's will assist analysts for comparative purposes [29].

The double spike technique was used to measure the isotopic fractionation of several elements including Zn, see [12,28,30–32]. The double spike technique is a technique measuring the relative amounts of four isotopes, two of which are enriched. From the knowledge of the isotopic composition of the double spike, it is possible to invert the measurements to calculate the true isotopic composition of the sample corrected for instrumental mass fractionation [33]. Zinc fractionation measurements are possible using the elemental spiking [24] technique [25]; however, double spiking with the same element serves as an internal standard to monitor mass fractionation introduced by any physical or chemical process following the spiking [34]. This is because the isotopes of the double spike will follow exactly the same isotope fractionation behavior as the isotopes of Zn in the sample, which guarantees the accuracy of the measured natural fractionation [34]. δZn can be measured using the double spike approach producing the most robust data [12].

In this work, only 1 μg Zn samples were used for isotopic analyses, thus representing a useful breakthrough in Zn isotope TIMS analysis. A comparison of the amount of sample used relative to the ionization potential of other transition elements can be found in the literature, see [35–39]. This research represents the most recent development of Zn isotopic measurements and the first identification of δZn in terrestrial materials using TIMS and a double spike technique.

2. Materials and methods

2.1. Mass spectrometry

All measurements were performed using a VG 354 TIMS located at Curtin University of Technology. Multi static collection using Faraday multi collector was used. The Daly detector was used for the analysis of smaller (ng) Zn amounts measurements such as blanks and low-level samples.

The observed isotope fractionation is assumed to be mass dependent [40], it is reported as δZn in per mil per atomic mass unit ($\% \text{amu}^{-1}$); such that:

$$\delta\text{Zn} = \frac{\delta^x\text{Zn}}{(x - 64)} = \left(\frac{[(^x\text{Zn}/^{64}\text{Zn})_{\text{Sample}} / (^x\text{Zn}/^{64}\text{Zn})_{\text{Standard}}] - 1}{(x - 64)} \right) \times 1000 \quad (1)$$

where x is the atomic mass number 66, 67, 68 or 70 of Zn.

2.1.1. Samples digestion and separation

All sample preparations were performed at Curtin University of Technology Isotope Dilution Mass Spectrometry (IDMS) laboratory. The laboratory is supplied with High Efficiency Particulate Air (HEPA) filters (Efficiency 99.995% for particles $>0.3 \mu\text{m}$). Sample evaporations took place under a similar HEPA filter clean hood. To

minimize contamination, cleaning procedures were developed for the used Teflon ware. All Teflon beakers and ion exchange columns were leached for weeks in an ultra pure dilute clean HNO_3 and HCl baths before use. A known amount of a sample was mixed with a known amount of double spike in a clean screw-top PFA beaker. Approximately 2 ml of HF acid and 2 ml of HNO_3 acid were added and left overnight. The mixture was heated in a domestic 1200 W microwave oven for about 20 s three to four times. The samples were taken to dryness, and 2 ml of concentrated HNO_3 was added to the residue, again heated in a microwave oven and then taken to dryness. After that, two ml of concentrated HCl was added to the sample and it was heated in a microwave oven for 20–30 s three to four times. The dissolved solution was left to cool to room temperature in-between each stage. The sample was then taken to dryness. The remaining salts were then dissolved with 0.2 ml of $>0.6 \text{ mol L}^{-1}$ HCl and heated on the hot plate for several hours before cooling and separating using ion exchange columns. The resin column volume (CV) used was 0.7 ml of AG1-X8 anion exchange resin, 100–200, or 200–400 mesh size. The resin was washed with 6 full columns of MQ water (FC, 1 FC = 6 ml) followed by 1 FC of 1 mol L^{-1} HNO_3 , 1 FC MQ water, and few column volumes of HCl of concentration $>2 \text{ mol L}^{-1}$. The sample was loaded in HCl of concentration $\sim 0.6 \text{ mol L}^{-1}$, followed by 3 FC of 0.6 mol L^{-1} HCl to remove the Fe, Cu, Ga, Ge and Ni. The Zn was then extracted by 1 FC 1 mol L^{-1} HNO_3 and taken to dryness. Because of the wide variety of samples analyzed, it was important to develop a digestion procedure that worked for most of the samples. All standard reference materials (SRMs) were dissolved using the same technique, except HISS-1 where the HNO_3 was replaced with $\sim 3 \text{ ml}$ of Aqua Regia and the sample was left on a hot plate with the lid on for more than 10 h before proceeding to microwave digestion. Two grams of concentrated HCl was then added to the sample and heated in a microwave oven for 20–30 s, three to four times, with the sample allowed to cool to room temperature in between each stage. After that, the sample was taken to dryness on a hot plate. The remaining salts were then dissolved with 0.2 ml of $>0.6 \text{ mol L}^{-1}$ HCl covered with the beaker lid and heated on the hot plate for several hours leaving the sample ready for chemical purification.

Water samples were loaded to ion exchange columns directly after being weighed and double spiked. Tap water samples, (restrained tap water), were collected in 500 mL containers from a water tap at Curtin University of Technology after keeping the tap shut for more than a week to restrain the water. For the unrestrained tap water experiment, water samples were collected after leaving the same water tap open for more than 20 minutes to make sure that there was no restrained water in the pipes.

By loading a known amount of Zn onto an ion exchange column, the extraction efficiency was determined and found $94 \pm 1\%$, for both 100–200 and 200–400 mesh size resins. The Reagent blanks were $32\text{--}36 \text{ pg g}^{-1}$ for MQ water, $80 \pm 11 \text{ pg g}^{-1}$ for HCl and $55 \pm 15 \text{ pg g}^{-1}$ for HNO_3 . Procedural blanks were measured with every batch of 3–4 samples yielding an average of $8 \pm 5 \text{ ng Zn}$. Exposure blanks were measured in the IDMS laboratory and found to be $<250 \text{ pg/day}$. Though high chemical yields are not required for an accurate double spike analysis [33], the yield was optimized to $93 \pm 4\%$ to avoid loss of sample. The effect of the ion exchange process on fractionation was assessed by passing a sample of Zn through the ion exchange separation process four times in succession, the contribution of the column chemistry to δZn was measured to be $+0.07 \pm 0.02 \% \text{amu}^{-1}$ per column (see Fig. 1). Since all samples were double spiked prior to ion exchange any column induced fractionation had no effect on the results.

2.1.2. Loading samples

Mass spectrometer filaments were degassed by heating under vacuum to temperature of $1850 \text{ }^\circ\text{C}$ for at least 30 min. All Zn samples

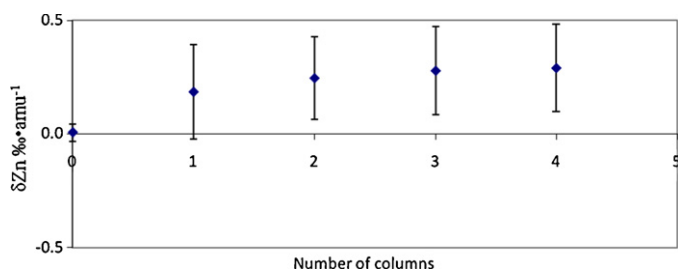


Fig. 1. Contribution of the column chemistry to δZn , where the Y-axis represents δZn induced by the column chemistry and the X-axis represents the number of columns the samples has been through.

were loaded using triple zone refined $0.03 \times 0.76 \text{ mm}$ Re filaments welded onto glass bead filament supports. Less than $1 \mu\text{g}$ of Zn was loaded onto the degassed centre filaments after mixing with $5.6 \mu\text{L}$ activator – $12 \text{ mg g}^{-1} \text{ H}_3\text{PO}_4$ and 8 mg g^{-1} silica gel – solution. The samples were dried by passing an electric current of $<2.4 \text{ A}$ through the central filament. Before measuring isotope ratios at 1560°C , a sample was “degassed” by heating the central and side filaments to a temperature of approximately 1400°C and 1600°C , respectively for about 40 min. An experiment to determine the ionization efficiency of Zn was performed where $1.80 \pm 0.08 \mu\text{g}$ of Zn was mixed with a small amount ($\sim 5.6 \mu\text{L}$ per $1 \mu\text{g}$ of sample) of silica gel and Phosphoric acid activator. This produced an ion beam $>10^{-12} \text{ A}$ for seven continuous hours. This yielded an ionization efficiency of $0.22 \pm 0.07\%$, which is four times more than that measured previously, see [41]. Several other activators such as graphite were trialed but none of them produced ion beams $>4 \times 10^{-13} \text{ A}$ from $\sim 1 \mu\text{g}$ Zn sample. The Silica gel was thus chosen to be the activator in this work. The final sample amount, activator components and analysis temperature matrix were optimized to enable an interference-free ion current $>1 \times 10^{-12} \text{ A}$.

2.1.3. Isotopic analysis

Data collected from the VG 354 was in the form of ratios relative to ^{64}Zn . For Faraday multi collection, atomic masses of ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , ^{69}Ga and ^{70}Zn , were collected in the L3, L1, Axial, H1, H2, H3 Faraday cups respectively. Ion current baselines were measured 0.5 amu either side of the peaks. Integration times of 5 seconds were used to measure individual isotope ratios in blocks of ten before the ion beam was refocussed, and if required, the intensity was re-established. Typically, 80–100 ratios were collected for the isotope measurements. Uncertainties are the 95% confidence levels with no more than 15% of the data rejected, although for most measurements, this was $<5\%$. An internal normalization was applied to the individual ratios to reduce the bias during analyses by calculating a bias factor using the average of $^{68}\text{Zn}/^{64}\text{Zn}$ ratios. Small isobaric interferences of ^{64}Ni on ^{64}Zn , CrO^{16} on ^{66}Zn , ^{68}Zn and ^{70}Zn , $\text{Fe}^{54}\text{O}^{16}$ on ^{70}Zn were minimized by varying the analysis temperature and confirmed to have no effect. An additional sensitive check for contamination effect was the calculation of δZn using two different sets of isotopes, ^{64}Zn , ^{67}Zn , ^{68}Zn , ^{70}Zn and ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{70}Zn . The fractionation was always agreed within uncertainty. The reproducibility of δZn ($0.039\% \text{ amu}^{-1}$) was determined using a mixture of the laboratory standard and the double spike solution. Repeated measurements of this mixture along with the measurements of batches of samples were part of the overall quality control process. The 95% uncertainty on the reproducibility of δZn also effectively presents the isotope fractionation detection limit.

2.1.4. The double spike technique

The double spike solution was already available enriched in the isotopes ^{67}Zn (52%) and ^{70}Zn (27%) and had a concentration of $1.1921 \pm 0.0032 \mu\text{g g}^{-1}$. Since underspiking or overspiking of

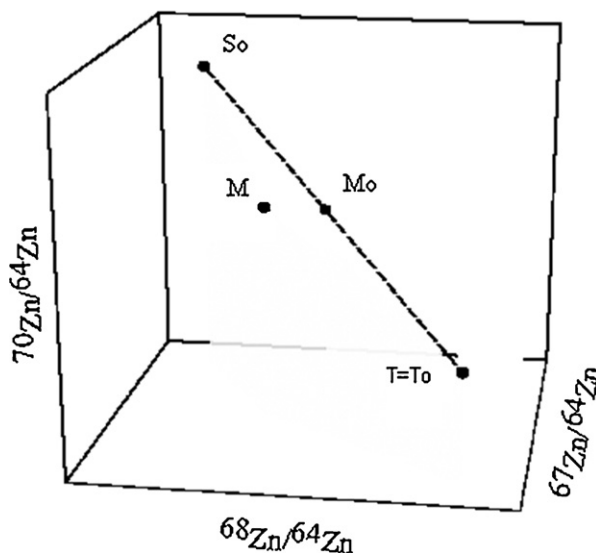


Fig. 2. A three isotope ratio space for Zn. So, Mo and To represent the unfractionated isotopic ratios of the sample, mixture and the tracer, respectively.

samples affects the final uncertainty of the measured δZn , an effort was made to optimize the sample/spike ratio. Initially, a ratio of ^{68}Zn in the sample to ^{67}Zn in the double spike of approximately 1.6 was used, but in the later part of this work the ratio was reduced to ≤ 1 to help reduce the final measured δZn uncertainty. For samples which have unknown Zn concentration, the Zn abundance was predicted by comparing the type of the analyzed sample with a similar type of material from the literature.

Complete repeat analyses of these unknown samples were often required to produce an ion beam $>10^{-12} \text{ A}$. δZn was calculated using the double spike approach of Russell (1971), which requires linearity of the fractionation of the isotopic composition of the element. The isotopic compositions of some samples and standards were measured and this linearity was established within uncertainty. The possibility that Zn analysis using TIMS may not fully exhibit a machine bias that follows a linear law can be ignored. This is because the precision for Zn isotope measurements using TIMS is generally greater than the effect of the difference between the linear law and other correction laws. In practice determining δZn using the double spike, using two different sets of isotopes: ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{70}Zn and ^{64}Zn , ^{67}Zn , ^{68}Zn , ^{70}Zn produce consistent δZn values well within uncertainty. ^{64}Zn was chosen to be the reference isotope because it is the lightest isotope. Any three unique ratios from any four isotopes of Zn describe a vector in a three ratio isotopic compositional diagram (see Fig. 2).

In Fig. 2, “M” represents the measured isotopic composition of the mixture “sample and double spike”. S_0 , M_0 and T_0 represent the unfractionated compositions of the unspiked sample, mixture and double spike respectively, the relation between the two compositions S , M , T and S_0 , M_0 , T_0 , is that the latter can be represented as points that lie in a straight line. This can be represented by:

$$(S_0 - T_0) \otimes (M_0 - T_0) = 0 \quad (2)$$

with errors represented as:

$$\delta S = S - S_0$$

$$\delta M = M - M_0 \quad (3)$$

$$\delta T = 0$$

The measured fractionated isotopic composition (labeled “M” in the diagram) can be corrected using the isotopic composition T , such

that $T = T_0$ [42]. This method uses a three ratio (4 isotope) space. Because Zn has five isotopes, not all isotopes can be represented on the diagram. For example, the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio is not represented in this diagram. This also means that another semi independent isotope space can be generated and double spike calculations performed to cross check the consistency of δZn values.

The surface formed by the three isotopic composition vectors of S , M , and T is considered to form a volume V_1 in the three dimensional isotopic space diagram, the same applies to isotopic composition vectors of S_0 , M_0 and T_0 , which form volume V_2 . The ratio of the V_1 and V_2 is δZn per atomic mass unit. According to the previous assumptions, S , M and T can be represented mathematically as:

$S = (x, y, z)$, $T_0 = (a, b, c)$ and $M = (u, v, w)$. δZn in per mil per atomic mass unit “ f ” and can be written as:

$$f = \left(\frac{V_2}{V_1} \right) \quad (4)$$

This can be represented without taking into account the fourth ratio which is the $^{66}\text{Zn}/^{64}\text{Zn}$.

$$P = \begin{vmatrix} 3 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 6 \end{vmatrix} \quad (5)$$

$$V_1 = \begin{vmatrix} 3 * \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_M & 4 * \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_M & 6 * \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_M \\ 3 * \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_S & 4 * \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_S & 6 * \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_S \\ \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} \end{vmatrix} \quad (6)$$

$$V_2 = \begin{vmatrix} 3 * \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_M & 4 * \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_M & 6 * \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_M \\ \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_S - \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_S - \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_S - \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} \\ \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{67}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{68}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} & \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_M - \left(\frac{^{70}\text{Zn}}{^{64}\text{Zn}} \right)_{T_0} \end{vmatrix} \quad (7)$$

where V_1 , V_2 can be determined by calculating the determinant of each matrix “ Δ ” [42], and δZn can be calculated using Eq. (4).

3. Results and discussion

Results shown in Table 1 are the average of δZn for several dissolutions of the samples. The average of δZn and its associated 95% confidence level uncertainty was calculated using the normal distribution using GUM Workbench software [43]. All results are relative to the IRMM 3702 (Zn δ zero). Individual δZn and its associated 95% confidence uncertainties were calculated using a Monte Carlo approach [44]. The results are discussed relative to average δZn calculated using ^{64}Zn , ^{67}Zn , ^{68}Zn , ^{70}Zn isotopes $\% \text{amu}^{-1}$. Geological SRMs samples measured were chosen to cover the rock cycle of the Earth with the intention of covering a range of materials with significant potential for fractionation. Knowing δZn for SRMs is vital to assess fractionation in similar materials using different analytical techniques e.g., Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Measured δZn relative to IRMM 3702 and the absolute isotopic compositions of the samples are represented in Tables 1–4. The absolute isotopic composition of Zn was calculated by applying the measured average fractionation factor to the absolute isotopic composition of Zn. For all of the samples, δZn was calculated using two sets of isotopes. The obtained δZn for all results agree with each other within individual measurement uncertainties. Calculating the fractionation using different set of isotopes also helped to

determine whether there were any anomalies or interferences on any of the Zn isotopes. Ongoing quality control was also confirmed by measuring the zero fractionation mixture (laboratory standard and double spike) in a number of batches of samples.

Except for CaCO_3 , all measured natural solid terrestrial samples measured in this work are SRMs. Except for BCR-1 and BIR-1, this is the first time that δZn have been reported in these samples. Isotopic studies of SRMs will improve and increase their exploitation and applications i.e., inter-laboratory comparison. For geological materials, δZn ranges from -0.1amu^{-1} to $+0.5\% \text{amu}^{-1}$ suggesting different geological processes. Zinc in water has special significance in global scale environmental effects, such as the Zn hypothesis [45]. δZn was measured in a variety of high purity Zn metals. The absolute isotopic compositions of Zn for these pure metals were calculated; and hence, serve as valuable sources to provide a metrological base line for Zn isotopic compositions. Moreover, the isotopic composition of Zn in these high purity materials can be exploited to determine the extent of δZn in anthropogenic products and to trace anthropogenic contamination [11,46,47]. The aim of measuring δZn in a Zinc vitamin tablet and Zn plated steel roof fragments was to demonstrate the measurement of δZn . Unfortunately, the measurements for the vitamin tablet and the Zn plated steel roof fragments were performed using the Daly detector. The

obtained values provide results worthy of further investigation. The significance of investigating δZn in the nutritional sample is that Zn vitamin tablets are made from processed chemical compounds like Zn Gluconate and Zn oxides which have undergone some form of purification [11]. As represented in Fig. 4, in this work, all measured isotopic compositions of Zn in natural materials yield an atomic weight within the internationally recognized absolute atomic weight by IUPAC. The isotopic composition of some samples was measured without double spiking to determine if the Zn fractionation could be observed directly and to determine if there were any non-linear effects. While plotting the deviation of the isotopic composition of any sample relative to the laboratory standard is a traditional technique for assessing fractionation, it is not able to detect small sub-permil effects as found for Zn in many samples. In addition this method does not correct accurately for machine induced fractionation, the isotopic composition of unspiked Zn in a CaCO_3 sample relative to IRMM 3702, is shown in Fig. 3.

The deviations show a clear linear dependence and indicate no sign of any isotopic anomaly or interference at any of the Zn isotopes

3.1. Geological materials

As represented in Table 1, none of the Zn minerals appears to be fractionated relative to IRMM 3702 or relative to each other.

Table 1The obtained average for δZn in terrestrial materials; n is the number of independent measurements.

	Sample	Average δZn using ^{64}Zn , ^{67}Zn , ^{68}Zn , ^{70}Zn isotopes ‰ amu^{-1}	Average δZn using ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{70}Zn isotopes ‰ amu^{-1}	n
Zinc pure metals	IRMM 10440	0.12 ± 0.16	0.12 ± 0.16	2
	ZnO6	-4.52 ± 0.13	-4.59 ± 0.13	3
	GF6110	-0.21 ± 0.18	-0.23 ± 0.18	2
	GF6120	-0.09 ± 0.14	-0.10 ± 0.15	3
	IRMM-3702	0.09 ± 0.18	0.03 ± 0.16	2
	JMC-2	0.04 ± 0.14	0.06 ± 0.14	4
Zinc minerals	Sphalerite	-0.01 ± 0.18	-0.02 ± 0.18	2
	HydroZincite	-0.04 ± 0.17	0.04 ± 0.17	2
	Smithsonite	0.02 ± 0.14	0.00 ± 0.14	2
Igneous rocks	Icelandic Basalt BIR-1	-0.01 ± 0.15	0.02 ± 0.15	2
	Basalt BCR-1	0.02 ± 0.12	0.01 ± 0.13	2
	Diabase W-2	0.17 ± 0.10	0.16 ± 0.10	6
	Dolerite DNC-1	-0.09 ± 0.15	-0.13 ± 0.15	4
Sedimentary rocks	Green River Shale, SGR-1	0.30 ± 0.22	0.36 ± 0.23	4
	Cody Shale SCO-1	0.06 ± 0.17	-0.04 ± 0.17	3
	Marine sediment HISS-1	0.31 ± 0.10	0.30 ± 0.10	4
	Murst-Iss-A1	0.305 ± 0.089	0.312 ± 0.093	4
	CaCO ₃	0.43 ± 0.18	0.33 ± 0.18	2
Metamorphic rocks	Mica Schist SDC-1	0.10 ± 0.13	0.09 ± 0.13	5
	Quartz Latite QLO-1	-0.02 ± 0.15	-0.02 ± 0.15	2
Clay	TILL-3	0.12 ± 0.10	0.11 ± 0.11	3
Biological materials	IMEP-19 (Rice)	-0.088 ± 0.070	-0.077 ± 0.071	6
	NIES-9 (Sargasso)	0.090 ± 0.068	0.092 ± 0.070	8
	Murst-ISS-A2	0.21 ± 0.11	0.15 ± 0.12	3
Water	Swan river Victoria Park	-1.37 ± 0.87	-1.8 ± 0.82	1
	Swan river Bayswater	-0.81 ± 1.09	-0.74 ± 1.09	1
	Unrestrained tap water	0.56 ± 2.6	-0.70 ± 2.90	2
	Restrained tap water	-6.39 ± 0.62	-7.22 ± 0.64	1
Anthropogenic materials	Zinc tablet	-2.14 ± 0.48	-2.99 ± 0.54	1
	Zinc plated steel	-1.6 ± 1.0	-1.6 ± 1.0	2

Previous measurements for δZn in sphalerite range from -0.085 to 0.66% amu^{-1} relative to Lyon JMC 3-0749 L [48]. Only Diabase W-2 exhibits a δZn of $+0.17 \pm 0.10\%$ amu^{-1} . This result confirms that igneous rocks would not exhibit significant δZn [14,49]. Igneous rocks form the majority of the Earth's crust, and they are the origin of all other rocks [50]. Since δZn in igneous rocks is within the isotopic composition of Zn for IRMM 3702, we may propose that the laboratory standard Zn IRMM 3702 is a suitable absolute standard and may represent the isotopic composition of Zn of bulk Earth.

The results for δZn in BCR-1 measured in this work is $+0.02 \pm 0.12\%$ amu^{-1} . The only previous measurement for Basalt BCR-1 using a double spiking technique was $+0.11 \pm 1.8\%$ amu^{-1} [30]. The results for δZn in BCR-1 measured in this work demonstrate a fifteen fold improvement in the uncertainty using only $1 \mu\text{g}$ of Zn. Recently δZn in BCR-2-same basalt as BCR-1 [51] – was measured using an un spiked ICP-MS technique and found to be $0.13 \pm 0.01\%$ amu^{-1} relative to JMC 3-0749L [23]. By comparing

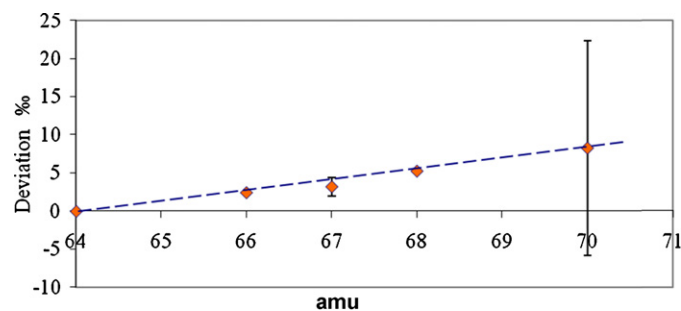


Fig. 3. The deviation of the isotopic composition of CaCO₃ sample relative to IRMM 3702.

the results of this work with the previous un spiked ICP-MS, $\delta\text{Zn} = 0.15 \pm 0.06\%$ amu^{-1} [37], and the results for BCR-2, all relative to Zn JMC 3-0749L. This comparison shows that JMC 3-0749L has the same isotopic composition of IRMM-3702.

Diabase W-2 shows no isotopic variations relative to the rest of the other igneous rocks measured in this work, though it is fractionated relative to IRMM 3702. It appears that high temperatures involved in the formation of igneous rocks do not introduce δZn . For sedimentary rocks, δZn in this work range from $+0.06 \pm 0.17\%$ amu^{-1} SCO-1 to $+0.43 \pm 0.18\%$ amu^{-1} for CaCO₃. Though the measured sediments are from different localities, all sediments measured in this work exhibit similar δZn within uncertainties (average $\delta\text{Zn} = +0.28 \pm 0.08\%$ amu^{-1}). Apart from Cody shale (SCO-1), all of other sediments rocks show a consistent δZn relative to IRMM 3702. A significance to measure δZn in sediments comes from the role of Zn in the limitation of biological activity in the oceans, known as the Zn hypothesis and other oceanic effects, see [45,52]. The results from two metamorphic SRMs indicate a resemblance to δZn of igneous rocks, but also overlap with the Zn in sedimentary rocks. TILL-3 is a clay sample and exhibits $\delta\text{Zn} = +0.12 \pm 0.10\%$ amu^{-1} . It is more likely that TILL-3 will contain Zn similar to that found in sedimentary rocks, because TILL-3 is thought to be formed from mixed glacial sediments.

3.2. Biological materials

For biological materials, IMEP-19 “Rice” and NIES-9 “Sargasso”, $\delta\text{Zn} = -0.088 \pm 0.070$ and $+0.090 \pm 0.068\%$ amu^{-1} respectively, this contradiction suggests different isotopic sources or processes. Sargasso has a δZn similar to that observed for sediments both measured in this work. This similarity could be a reflection for

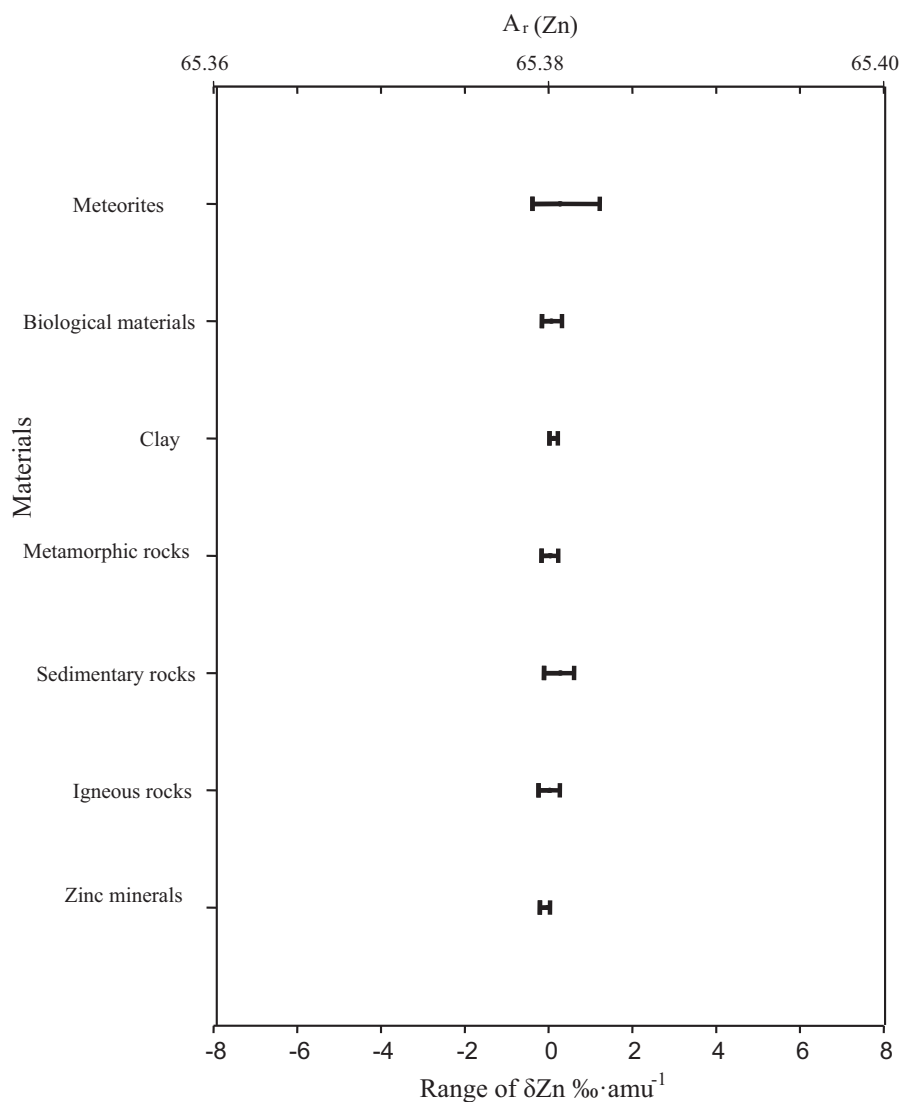


Fig. 4. Range of average δZn in natural materials measured in this research using ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{70}Zn isotopes, also compared to that found in meteorites [22]. The full length of the upper x-axis represents the range of the IUPAC Zn atomic weight uncertainty.

the oceanic conditions under which Sargasso grows, see [9]. IMEP-19 “Rice” is negatively fractionated and barring significant external contamination related either to the soil, or related to a growth-associated process. MURST-Iss-A2 “Antarctic Krill” was taken from the Southern Ocean. The result obtained for MURST-Iss-A2 ($\delta\text{Zn} = +0.21 \pm 0.11\text{‰}\cdot\text{amu}^{-1}$) is similar to the average δZn results obtained for marine sediments. One explanation for this is that these animals simply reflect the same δZn as of the environment in which they live. There has been a presumption that the range of δZn is larger in organic materials than in inorganic materials [53]. In this work, only three biological materials were measured for their δZn ; thus, such presumption cannot be established. Previous δZn measurements in biological materials concluded the potential of Zn isotopes analysis to trace and better understand biological activities [17,19,53].

3.3. Water samples

Accurate and precise measurements of δZn in water samples are hampered by a number of considerable analytical challenges that are generally related to the very low concentration of Zn in water. This low concentration necessitates pre-concentration

of the metals from large water samples. A good chemical separation is required in order to eliminate isobaric interferences [12]. The concentration of Zn in water samples measured in this work was measured using the very accurate IDMS technique [29]. In this work, the relatively large δZn values obtained for water samples promise future exploitation for δZn measurements of low-level ng g^{-1} Zn concentration potable and river waters [29]. The average δZn in the Swan River water measured in this work is $-1.09 \pm 0.70\text{‰}\cdot\text{amu}^{-1}$. Although the uncertainty in this measurement is big, δZn in Swan River waters is larger than in all other natural samples. It is possible that δZn is due to the Zn leached into the river from fertilizers used on nearby agricultural land and other anthropogenic sources. This confirms the possibility of using this approach to investigate the mixed natural and anthropogenic Zn sources in the environment [54]. Restrained tap water ($\delta\text{Zn} = -6.39 \pm 0.62\text{‰}\cdot\text{amu}^{-1}$) is opposite in sign but similar in magnitude to that found in some of the high purity Zn materials. The unrestrained water presents the isotopic composition of the water source, while the Zn in restrained water contains an additional source of Zn, which is most likely from the water pipes. This explanation is supported by the results of the measured concentration of Zn in the tap water, where the unrestrained tap water is about 400

Table 2
Proposed absolute isotopic composition of Zn in Zn pure standard metals.

Standard Zn metal		Ratio	±
IRMM-Ac AE 10760	$^{66}\text{Zn}/^{64}\text{Zn}$	0.55821	0.00051
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.080907	0.000097
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.36753	0.00057
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012037	0.000035
10440	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56411	0.00035
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082196	0.000052
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37537	0.00029
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012427	0.000026
ZnO6	$^{66}\text{Zn}/^{64}\text{Zn}$	0.55887	0.00033
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.081052	0.000047
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.36841	0.00025
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012081	0.000024
GF6110	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56373	0.00036
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082114	0.000057
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37487	0.00032
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012402	0.000027
GF6120	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56387	0.00034
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082144	0.000049
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37506	0.00026
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012411	0.000025
IRMM3702	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56407	0.00036
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082188	0.000056
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37533	0.00032
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012425	0.000026
JMC-2	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56401	0.00034
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082175	0.000048
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37524	0.00026
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012421	0.000025
IRMM Alfa Aesar 10759	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56398	0.00030
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.08217	0.00004
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37520	0.00017
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.01242	0.00002

times less than the concentration of Zn in the restrained tap water [29].

3.4. High purity Zn metals and anthropogenic materials

All high purity Zn metals samples fit into two groups. In group I, (IRMM 10440 with purity 99.99%, AE 10760 purity 99.9999% and ZnO6 purity 99.999%). Group II, (IRMM 3702, AE 10759, GF 6110, GF 6120, with purity 99.999%, 99.999%, 99.9998%, 99.99% respectively, also JMC-2 with unknown purity). Fig. 5 shows a “three isotope plot” of $^{68}\text{Zn}/^{64}\text{Zn}$ versus $^{66}\text{Zn}/^{64}\text{Zn}$ for the measured high purity metals. It is important to mention that; this group includes IRMM 3702, which is presumed to have the isotopic composition of Zn in bulk earth. The groups are not characterized by common metal purities, but may be grouped according to their metal sources, or more likely, according to common production processes.

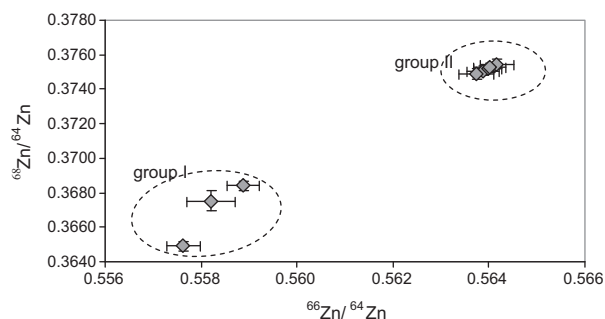


Fig. 5. Three-isotope plot for pure Zn standard metals. Uncertainties in graph are 2σ 95% confidence level.

Table 3
Proposed absolute isotopic composition of Zn in Zn minerals, igneous, marine SRMs and CaCO_3 .

Mineral		Ratio	±
Sphalerite	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56397	0.00036
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082166	0.000057
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37519	0.00032
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012418	0.000026
HydroZincite	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56392	0.00036
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082156	0.000055
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37513	0.00030
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012415	0.000026
Smithsonite	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56399	0.00034
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082171	0.000050
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37522	0.00027
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012419	0.000025
Basalt BCR-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56399	0.00033
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082171	0.000046
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37522	0.00024
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012419	0.000025
Icelandic Basalt BIR-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56397	0.00034
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082166	0.000051
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37519	0.00028
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012418	0.000025
Diabase W-2	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56416	0.00032
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082207	0.000043
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37544	0.00022
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012430	0.000024
Dolerite DNC-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56387	0.00035
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082144	0.000051
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37505	0.00028
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012411	0.000025
Green River Shale, SGR-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56431	0.00039
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082240	0.000064
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37564	0.00036
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012440	0.000028
Cody Shale SCo-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56404	0.00036
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082181	0.000055
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37528	0.00030
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012422	0.000026
Marine sediment HISS-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56432	0.00032
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082242	0.000043
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37566	0.00022
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012441	0.000024
Murst-Iss-A1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56431	0.00032
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082241	0.000041
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37565	0.00021
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012441	0.000024
CaCO_3	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56446	0.00037
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082272	0.000057
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37584	0.00032
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012450	0.000027

Fig. 5 shows δZn applicability to trace the movement and source of natural and anthropogenic Zn in the environment. This requires the isotopic composition of anthropogenic Zn to be known, so the processes that mix anthropogenic and other sources can be explored as an environmental tracer [11]. The average δZn in a Zn plated steel sample and in a Zinc vitamin is $-1.6 \pm 1.0\text{‰}$ and $-2.14 \pm 0.48\text{‰}$, respectively. Both are similar in magnitude to δZn found in high purity metal samples, and most likely reflect different industrial processes.

The internationally recognized atomic weight of Zn is 65.38 ± 0.02 [55]. As represented in Fig. 4, the largest δZn value measured in this work is $-6.39 \pm 0.62\text{‰}$ for restrained tap water yields an atomic weight 65.3614 ± 0.0025 . This atomic weight is within the uncertainty of the International Union for Pure and Applied Chemistry (IUPAC) value. All uncertainties in the

Table 4
Proposed absolute isotopic composition of Zn for measured metamorphic rocks, Clay and biological SRMs.

Sample	Ratio	±	
Mica Schist SDC-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56408	0.00033
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082191	0.000048
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37534	0.00025
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012425	0.000025
Quartz Latite QLO-1	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56395	0.00035
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082161	0.000051
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37516	0.00028
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012417	0.000025
TILL-3	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56411	0.00032
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082196	0.000043
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37537	0.00022
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012427	0.000024
IMEP-19 (Rice)	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56387	0.00031
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082144	0.000039
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37506	0.00019
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012411	0.000024
NIES-9 (Sargasso)	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56407	0.00031
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082188	0.000039
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37533	0.00019
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012425	0.000023
Murst-ISS-A2 (Antarctic Krill)	$^{66}\text{Zn}/^{64}\text{Zn}$	0.56420	0.00032
	$^{67}\text{Zn}/^{64}\text{Zn}$	0.082217	0.000045
	$^{68}\text{Zn}/^{64}\text{Zn}$	0.37550	0.00023
	$^{70}\text{Zn}/^{64}\text{Zn}$	0.012433	0.000025

calculated atomic weight were the 95% confidence determined using GUM software.

4. Conclusion

The procedure developed in this work is the most recent development of Zn isotopic measurements and the first identification of δZn in natural and anthropogenic materials using TIMS and a double spiking technique. The procedures developed solve several analytical issues involved in TIMS Zn isotopic measurements. The procedures allowed sub-per mil δZn to be revealed from a $1\ \mu\text{g}$ Zn sample relative to Zn δ zero. The double spike solution was enriched in the isotopes ^{67}Zn (52%) and ^{70}Zn (27%). The ionization efficiency of Zn was enhanced to $0.22 \pm 0.07\%$. The calculated average of δZn for number of analyses was accompanied by a 95% confidence calculated using GUM Workbench software. δZn values where calculated using two different sets of isotopes, ^{64}Zn , ^{67}Zn , ^{68}Zn , ^{70}Zn and ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{70}Zn , which always agreed within uncertainty. The reproducibility of δZn ($0.039\% \text{amu}^{-1}$) was determined using a mixture of the laboratory standard and the double spike solution. The 95% uncertainty on the reproducibility of δZn also effectively presents the isotope fractionation detection limit. The developed procedure opens the way for isotopic analysis to be applied to wide variety of biological samples, including human samples. These findings emphasize the strong potential of Zn isotopic composition as an environmental tracer. Of the eight high purity materials analyzed, five show a relationship between δZn and the degree of impurity. All of the measured δZn yield an atomic weight within the uncertainty of the IUPAC value (65.38 ± 0.02) [55].

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