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

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

Introduction

The stable isotopes of Zn have, in recent years, emerged as powerful tracers of natural processes in the Earth sciences. Much of the focus, though by no means exclusively, has been on investigating the role of Zn and its biogeochemical cycling in the modern oceani–v and on the understanding of processes occurring during planetary formation.°–v Common to many of the recently developed non-traditional stable metal isotope systems (e.g. Cu, Mo, Fe, and Li), made analytically feasible due to advances in multiple collector inductively coupled plasma-mass spectrometers (MC-ICPMS), comparative studies of Zn and its isotopes have been complicated by the lack of an internationally certified reference standard. However, where rigorous data comparison for other non-traditional stable metal isotope systems such as Mo has been severely hampered in this regard,°,11 most if not all Zn isotope data to date have been referenced to the same ICP Zn standard, the so-called JMC-Lyon standard, made available by the authors after the initial high-precision Zn isotope study of Maréchal et al.12 Unfortunately the JMC-Lyon standard is nearing exhaustion, and therefore a new reference standard is required.

Recently, efforts have been made to address the problem of a lack of Zn standard, with the creation of a certified reference standard, IRMM-3702 Zn, produced by the Institute for Reference Materials and Measurements (IRMM) in Belgium.°,13,14 Although the IRMM-3702 Zn standard will prove to be an invaluable reference standard for Zn isotope studies, it suffers from some important limitations which would preclude it from being adopted widespread as a primary reference standard. At the time of writing it only available for purchase in relatively...
isotopically light with a \( ^{66}\text{Zn}/^{64}\text{Zn} \) ratio, that is the measured zero-point reference standard, as data suggest that it is this standard in its current form well into the future, which a primary reference standard would require the IRMM to supply for mass fractionation (Table 2). All participating labs per-formed measurements of the new AA-ETH Zn standard against a nominal uptake rate of 50 L min\(^{-1}\) via a Cetac Aridus II desolvating system or an Elemental Scientific (ESI) Apex-Q desolvating system, both coupled with a PFA nebuliser with a nominal uptake rate of 50 \( \mu \)L min\(^{-1}\). Isobaric interference from \( ^{65}\text{Ni} \) on \( ^{64}\text{Zn} \) was monitored using \( ^{62}\text{Ni} \), but any correction here was always negligible. For data collected with the Apex, an additional correction for small amounts of hydrides was needed, determined by monitoring the \( ^{64}\text{ZnH}^+ \) hydride produced at mass 65. Typically, hydrides were formed at the 10–20 ppm level. The long term reproducibility of measurements made using both sample introduction systems, as determined by analyses of IRMM-3702 Zn over the course of three years, including those made during each analytical session, is 0.06%\(_{\text{rel}}\) (2SD).

### Analytical methodology

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

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

Similarly, \( \delta^{67}\text{Zn} \) and \( \delta^{68}\text{Zn} \) are described by the above equation, where \( ^{66}\text{Zn} \) is replaced by \( ^{67}\text{Zn} \) or \( ^{68}\text{Zn} \), respectively. Conversion from \( \delta^{66}\text{Zn} \) to any other Zn isotope pair is achieved by multiplying this value by the factor \( \ln(m_{2}/m_{1})/\ln(m_{66}\text{Zn}/m_{64}\text{Zn}) \), where the masses \( m \) are the atomic masses, and according to the exponential mass fractionation law. A brief description of the methodology used by each lab is as follows.

#### ETH Zürich

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

#### Table 1

<table>
<thead>
<tr>
<th>Lab</th>
<th>Instrument</th>
<th>Sample introduction</th>
<th>Mass bias correction(^{15,16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETH Zürich</td>
<td>Neptune Plus</td>
<td>Aridus II, Apex-Q</td>
<td>( ^{64}\text{Zn}–^{67}\text{Zn} ) double spike(^{15} )</td>
</tr>
<tr>
<td>ANU</td>
<td>Neptune Plus</td>
<td>Apex-Q</td>
<td>( ^{67}\text{Zn}–^{68}\text{Zn} ) double spike(^{19} )</td>
</tr>
<tr>
<td>Brest</td>
<td>Neptune Plus</td>
<td>Glass spray chamber</td>
<td>Cu doping(^{20} )</td>
</tr>
<tr>
<td>CPRG – Nancy</td>
<td>Neptune Plus</td>
<td>Glass spray chamber</td>
<td>( ^{64}\text{Zn}–^{67}\text{Zn} ) double spike(^{21} )</td>
</tr>
<tr>
<td>Imperial College</td>
<td>NuPlasmaHR</td>
<td>Aridus II</td>
<td>( ^{64}\text{Zn}–^{67}\text{Zn} ) double spike(^{22} )</td>
</tr>
<tr>
<td>London</td>
<td>NuPlasma II</td>
<td>Aridus II</td>
<td>( ^{64}\text{Zn}–^{67}\text{Zn} ) double spike(^{21} )</td>
</tr>
<tr>
<td>Indiana</td>
<td>Neptune Plus</td>
<td>Aridus II</td>
<td>( ^{64}\text{Zn}–^{67}\text{Zn} ) double spike(^{21} )</td>
</tr>
<tr>
<td>Kyoto</td>
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</tbody>
</table>

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Table 2  Zn isotope results of the AA-ETH standard relative to both JMC-Lyon and the IRMM-3702 Zn standards, with the number of analyses in brackets. 2σ is the calculated twice standard deviation for all measurements across all participating labs, with the exception of the weighted mean, where the error reported is the uncertainty of the weighted mean. The weighted mean and its uncertainty were determined by weighting the values produced by each individual lab according to their individual 2σ uncertainties.

<table>
<thead>
<tr>
<th>Lab</th>
<th>$\delta^{66}$Zn$_{JMC}$</th>
<th>2σ</th>
<th>$\delta^{66}$Zn$_{IRMM}$</th>
<th>2σ</th>
<th>$\delta^{67}$Zn$_{IRMM}$</th>
<th>2σ</th>
<th>$\delta^{68}$Zn$_{IRMM}$</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETH (n = 30)</td>
<td>0.31</td>
<td>0.06</td>
<td>−0.01</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANU (n = 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brest$^a$ (n = 13)</td>
<td></td>
<td></td>
<td>−0.02</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CPRG (n = 20)</td>
<td>0.33</td>
<td>0.12</td>
<td>0.02</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Imperial (n = 18)</td>
<td>0.28</td>
<td>0.05</td>
<td>−0.04</td>
<td>0.05</td>
<td></td>
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</tr>
<tr>
<td>Indiana (n = 32)</td>
<td>0.26</td>
<td>0.10</td>
<td>0.01</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kyoto (n = 10)</td>
<td>0.27</td>
<td>0.03</td>
<td>−0.01</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All (JMC: n = 110, IRMM: n = 129)</td>
<td>0.29</td>
<td>0.09</td>
<td>0.00</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All (weighted)</td>
<td>0.28</td>
<td>0.02</td>
<td>−0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ Data obtained from the Brest lab was obtained via a non-double spike mass bias correction protocol, which allows for independent determination of additional isotope pairs, which are shown here.

Australian National University (ANU). All analyses were performed using a Thermo Scientific Neptune Plus MC-ICPMS using the procedure described in the study of Samanta et al.$^{19}$ Prior to analysis, each standard was doped with a mixed $^{67}$Zn–$^{68}$Zn double spike to achieve a standard:spike ratio of ~0.25. Solutions in a 2% v/v HNO$_3$ solution were introduced into the mass spectrometer via an Elemental Scientific (ESI) Apex-Q desolvating system with a PFA nebuliser (ESI) with a nominal uptake rate of 50 µL min$^{-1}$. A standard Ni sampler cone and a Ni X-skimmer cone were used to enhance instrument sensitivity. At the start of the measurement session, the instrument was optimised for signal intensity on mass $^{62}$Ni, $^{64}$Cu, $^{65}$Cu, $^{64}$Zn, $^{66}$Zn, $^{67}$Zn and $^{68}$Zn. All measurements were made in low resolution mode as 1 block of 30 cycles with a 4 second integration time. All measured ratios were corrected for any interference of $^{64}$Ni on $^{64}$Zn by monitoring the intensity of $^{62}$Ni and subtracting the calculated intensity for $^{64}$Ni, based on the natural $^{64}$Ni/$^{62}$Ni ratio, from the measured intensity of $^{64}$Zn. These corrections were always negligible compared to the standard/spike signal. The interference corrected data were then blank corrected by subtracting the average intensity of the 30 cycle measurement for each isotope from the intensities measured for the 2% v/v HNO$_3$ blank.

Brest. All analyses were performed using a Thermo Scientific Neptune MC-ICPMS. The instrument was optimised for signal intensity on mass $^{62}$Ni, $^{64}$Cu, $^{65}$Cu, $^{64}$Zn, $^{66}$Zn, $^{67}$Zn and $^{68}$Zn. Instrumental mass bias was corrected for by doping the Zn standard solutions with a pure copper standard solution (NIST SRM 3114) whose isotopic composition has been calibrated against NIST SRM 976. The data reduction scheme is similar to the approach of Maréchal et al.$^{14}$ which involves measuring $^{65}$Cu/$^{63}$Cu to determine the instrumental mass bias factor using an exponential mass fractionation law. In addition to Cu normalisation, Zn ratios were further corrected using a standard bracketing approach, where measured Zn isotope ratios of the sample are normalised to the average composition of its bracketing reference standard.$^{28}$ All measurements were made in low resolution mode as 1 block of 25 cycles with a 4 second integration time. Solutions in 0.28 M HNO$_3$ were introduced into the plasma using a double spray quartz chamber system (cylindrical and double pass) and a microconcentric PFA nebulizer operating at a flow rate of about 60 µL min$^{-1}$. The MC-ICPMS was equipped with high-efficiency Ni-cones (X-cones) and run in medium resolution mode. Using this instrumental set-up, Zn and Cu isotopes were measured at concentrations of 300 ng g$^{-1}$ and 200 ng g$^{-1}$, respectively. The precision of the measurements, determined as the standard deviation values (2SD) of duplicate $\delta^{66}$Zn analysis of the same standard/sample solution over several analytical sessions, generally ranged from 0.02$^{\pm}$0.005 to 0.04$^{\pm}$0.005.

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

Imperial College London. The isotopic analyses were carried out with a Nu Plasma HR MC-ICPMS instrument at the MAGIC Laboratories using protocols modified from those reported by Arnold et al.$^{22}$ Prior to analysis, a $^{64}$Zn–$^{67}$Zn double spike was added to and equilibrated with each standard solution at a ratio of spike-derived to natural Zn of about 1. The spike–sample mixtures were taken up in 0.1 M HNO$_3$ to achieve total Zn concentrations of ~100 ng mL$^{-1}$. An Aridus II (CETAC Technologies) desolvation system fitted with a nominal 100 µL
min⁻¹ glass nebulizer was used for sample introduction. The analyses involved simultaneous collection of the ion beams of ⁶⁴Zn⁺, ⁶⁶Zn⁺, ⁶⁷Zn⁺, and ⁶⁸Zn⁺, and ⁶²Ni⁺ and ¹³⁷Ba²⁺ for interference correction. Data collection was performed in 3 blocks of 20 × 5 s integrations, with a 15 s electronic background measurement preceding each block. The instrumental mass bias encountered during the analyses was corrected using double spike data reduction methods adapted from those reported by Arnold et al.²⁵ For this, the “raw” measured isotope ratios of ⁶⁶Zn/⁶⁷Zn, ⁶⁸Zn/⁶⁷Zn and ⁶⁶Zn/⁶⁴Zn were processed offline with a spreadsheet-based iterative solver. Corrections for spectral interference from ⁶⁴Ni⁺ and Ba²⁺ ions (¹³²Ba⁺, ¹³⁴Ba⁺ and ¹³⁶Ba⁺) were also subjected to mass bias correction. The required corrections were very small, however, at less than 1 × 10⁻⁵ for both ⁶⁴Ni⁺/⁶⁷Zn⁺ and ¹³⁴Ba⁺/⁶⁷Zn⁺. Additional interspersed analyses of the in-house London Zn standard solution yielded δ²⁶⁶Zn = 0.12 ± 0.06‰ (2SD), in agreement with three previous studies that reported results of 0.08‰ to 0.14‰ for this sample.³²,²³

**Indiana University.** Zinc isotopic standards (AA-ETH Zn, IRMM-3702 Zn and JMC-Lyon Zn) were measured relative to an in-house Zn standard (Sesame Zn) on the NuPlasma II MC-ICPMS in the Sesame Lab at Indiana University Bloomington. Solutions were introduced into the mass spectrometer using a Cetac Aridus II desolvating system. Prior to analysis, standards were doped with a mixed ⁶⁴Zn–⁶⁷Zn double spike, and instrumental mass bias correction was performed using the double spike techniques described in the study of Bryan et al.³¹ Additional analyses of an in-house London Zn standard (δ²⁶⁶ZnSesame = 4.37 ± 0.05‰ (2SD)) simultaneously performed are in agreement with previously reported values of this standard.³³

**Kyoto University.** All isotopic ratios were measured on a Neptune Plus MC-ICPMS with a glass nebuliser (MicroMist 0.1 mL min⁻¹) and an Aridus II desolvating nebulizer system at the Research Institute for Humanity and Nature, Kyoto, Japan. A standard Ni sampler cone and a Ni H-skimmer cone were used. Instrumental mass bias during MC-ICP-MS measurement was corrected using a mixed ⁶⁴Zn–⁶⁷Zn double spike, and isotopic ratios were calculated using the iterative method of Siebert et al.²⁴ The double spike comprised 82.9% ⁶⁴Zn, 0.5% ⁶⁶Zn, 16.2% ⁶⁷Zn, and 0.5% ⁶⁸Zn. The composition of the double spike was calibrated to the AA-ETH Zn standard by measuring AA Zn standard–double spike mixtures in different proportions.²⁵ The standards (JMC Zn or IRMM Zn) were mixed with a double spike in a 1 : 1 weight ratio, and diluted to 200–400 ppb Zn with 2% HNO₃. Data acquisition for each standard consisted of 30 4 s integrations. The intensity of the ⁶⁴Zn beam was ~5 V for 100 ppb natural Zn. In order to correct the instrumental background, a pure 2% HNO₃ w/w solution was measured every four samples, with data collected in 15 4 s integration cycles. The average signal of the pure 2% HNO₃ solutions was then subtracted from the signals of the bracketed standards. Long term reproducibility, estimated by measurement of an in-house Zn standard during the three months surrounding these measurements, is 0.05‰ (2SD).

Results and recommendation

Table 2 and Fig. 1 summarize the data collected by the seven participating inter-calibration labs, representing a total of 126 separate analyses of the AA-ETH standard. Importantly, the results show a clear agreement between participating labs, with the new AA-ETH Zn standard being isotopically indistinguishable from the already calibrated IRMM-3702.¹² Furthermore, both the measured (and implied) offset of IRMM-3702 relative to the JMC-Lyon standard in this dataset are in agreement with previously published values of 0.29 ± 0.05‰ (2SD).¹³,¹⁵,¹⁶ The data presented in this inter-calibration exercise were collected using a variety of techniques, both analytically and in terms of data reduction and specifically the methods used for correcting instrumental mass bias. We can therefore confidently assign a value to our proposed new standard identical to that of IRMM-3702, that is δ²⁶⁶Zn = 0.28 ± 0.02‰, relative to JMC-Lyon Zn, where the uncertainty is given by the uncertainty on the weighted mean – see Table 2.

We thus propose that our new AA-ETH Zn standard, which will be made freely available upon request, be adopted as the new “zero-point” reference standard for future Zn isotopic measurements. In common with the approach used for future Mo isotope studies (see the study of Nagler et al.¹¹ and references therein), we suggest that the AA-ETH standard be assigned a specific reference value of 0.28‰ and not “zero”. This approach facilitates the comparison with existing literature data, provides a direct and traceable link to the already existing and universally adopted JMC-Lyon Zn isotope scale, and therefore allows for common reference values such as 0.3‰ for “lithogenic” Zn to be kept for discussion. Converting δ²⁶⁶Zn values to the JMC-Lyon scale, relative to the AA-ETH = 0.28‰ can be done using the standard conversion identity.²⁶ This is expressed here, for the conversion of a δ value determined relative to the AA-ETH standard to the existing JMC scale as follows:

![Fig. 1 Zn isotope results of the AA-ETH standard relative to both JMC-Lyon and the IRMM-3702 Zn.](image)

This is expressed here, for the conversion of a δ value determined relative to the AA-ETH standard to the existing JMC scale as follows:
Technical Note

\[ \delta^{66}\text{Zn}_{\text{JMCLyon}} (\text{ppm}) = \delta^{66}\text{Zn}_{\text{AA-ETH}} + \delta^{66}\text{Zn}_{\text{AA-ETH JMCLyon}} + \frac{(\delta^{66}\text{Zn}_{\text{AA-ETH}}) \times (\delta^{66}\text{Zn}_{\text{AA-ETH JMCLyon}})}{1000} \]

(2)

where \( \delta^{66}\text{Zn}_{\text{AA-ETH JMCLyon}} = 0.28 \pm 0.02\%_\text{o} \). In practice, this conversion can be approximated to:

\[ \delta^{66}\text{Zn}_{\text{JMCLyon}} (\text{ppm}) = \delta^{66}\text{Zn}_{\text{AA-ETH}} + \delta^{66}\text{Zn}_{\text{AA-ETH JMCLyon}} \]

(3)
as in many cases any systematic errors introduced by this simplification are smaller than analytical uncertainty. Using the AA-ETH Zn standard with either or both of the IRMM or NIST Zn standards as secondary reference materials will therefore allow for simple and rigorous comparison of results generated in different labs moving into the future.

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References