

## TECHNICAL NOTE



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## Calibrating NIST SRM 683 as a new international reference standard for Zn isotopes

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Zinc isotopes have been increasingly applied in cosmochemistry, geochemistry, and environmental sciences. A direct comparison of data obtained in different laboratories is a prerequisite to these applications. The JMC 3-0749L Zn solution is the international primary standard for Zn isotopes, but it is nearly exhausted and no longer available. Thus, it is necessary to calibrate a new reference material for Zn isotope analysis. Herein, we measured the Zn isotope composition and examined the homogeneity of the Standard Reference Material 683 of the National Institute of Standard and Technology (NIST SRM 683, a pure Zn metal nugget of 140 grams) with the double-spike method using Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS). Five metal nuggets of NIST SRM 683 were intensively sampled by micro-drilling, and they exhibited  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $0.13 \pm 0.06\text{‰}$  (here and throughout the text, errors are given as two-standard deviation (2SD),  $N = 32$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 31$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ), and  $0.12 \pm 0.06\text{‰}$  ( $N = 30$ ). These values were identical to those of two Zn metal nuggets ( $0.11 \pm 0.02\text{‰}$  and  $0.12 \pm 0.02\text{‰}$ ) previously reported, which confirmed the accuracy of our data and the isotopic homogeneity of NIST SRM 683. We also digested one whole nugget with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $0.12\text{‰} \pm 0.04\text{‰}$  ( $N = 44$ ), which was identical to that of the drilling samples. Our results indicated that within our analytical precision of 0.04, NIST SRM 683 is homogeneous in Zn isotopic compositions with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $0.12 \pm 0.04\text{‰}$  ( $N = 295$ ) at the 95% confidence level, which is close to the Zn isotope value of bulk silicate Earth. Therefore, we believe that NIST SRM 683 is a good candidate for the next primary standard for Zn isotopes.

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## Introduction

Zinc exists in aerosol, hydrosphere, biosphere, and the silicate Earth in the form of bivalent cation:  $\text{Zn}^{2+}$ . The behaviors and cycling of Zn are closely related to various geological processes. In the hydrothermal fluid activities, zinc exists as soluble compounds (e.g.,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnSO}_4$ ) or insoluble compounds (e.g.,  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnS}$ ,  $\text{ZnSO}_3$ ,  $\text{ZnCO}_3$ ,  $\text{ZnSiO}_3$ ,  $\text{Zn}_3(\text{PO}_4)_2$ ).<sup>1</sup> Zinc is moderately incompatible during partial melting of mantle and during magma evolution.<sup>2</sup> Zinc is also widely used in manufacturing, biological medicine, and the food industry. As an essential nutrient for life, Zn plays an important role in growth, reproduction, immune, and endocrine processes. An important group of Zn proteins is the Zn fingers, which are only found in eukaryotes and play a structural

role during transcription.<sup>3</sup> Therefore, understanding the circulation of Zn in natural processes is of great significance.

Zinc isotopes can be fractionated by a number of physical, chemical and biological processes. The wide application of the Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) method for high-precision Zn isotopic analyses has been employed for almost two decades. In 1999, Maréchal *et al.*<sup>4</sup> reported a method for precise analysis of Cu and Zn isotope compositions with plasma-source mass spectrometry. Instrumental mass fractionation was corrected by element doping (Cu for Zn). Since then, Zn isotopes have been widely applied in oceanography, cosmochemistry, magmatism, and environmental studies.<sup>5–9</sup> For example, Zn isotopic composition in the open ocean ( $\sim 0.5\text{‰}$ ) is significantly higher than that of all known input fluxes ( $\sim 0.3\text{‰}$ ), indicating that light Zn isotopes are incorporated into sulphide phases in anoxic settings.<sup>10</sup> Furthermore, Zn isotopes can be used to understand the origin of volatile element depletions during planet accretion because Zn is a moderately volatile element.<sup>11</sup> Clues from major carbonaceous chondrites imply segregation of an isotopically light sulfide phase and loss of the gas phase during chondrule formation.<sup>9</sup> Zn isotope data for continental basalts from eastern China suggest that Zn isotopes have the

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potential to trace deep carbonate cycling in the Earth's mantle.<sup>12</sup> The combined record of  $\delta^{114}\text{Cd}$  and  $\delta^{66}\text{Zn}$  in the Nuccaleena cap dolostone samples indicates that Zn could also be used to trace biological process cycles after Marinoan snowball Earth glaciation.<sup>13</sup> Finally, zinc isotope signatures in plants tissues reflect differences in pollution sources, which has provided useful information for improving the environmental and human risk assessment.<sup>14</sup>

The primary reference standard is vital in Zn isotopic analyses. Generally, with the primary reference standard as the nominally "zero point", instrumental mass discrimination can be corrected by three methods: element doping (matrix matching), standard-sample bracketing, and the double spike method.<sup>15</sup> Multiple reference materials should also be measured for data quality control and inter-laboratory comparison. Zn isotope data are reported relative to a primary standard:

$$\delta^x\text{Zn}_{\text{samples(true)}} = \left[ \frac{\left(\frac{x\text{Zn}}{64\text{Zn}}\right)_{\text{samples(measured)}}}{\left(\frac{x\text{Zn}}{64\text{Zn}}\right)_{\text{standard(measured)}}} - 1 \right] \times 1000, (x = 66, 67, 68, 70)(\text{‰}) \quad (1)$$

An ideal international primary standard should be exceedingly homogeneous and widely available, and it should have isotopic composition with natural range in the intermediate of terrestrial reservoirs. Johnson Matthey Corporation (JMC) 3-0749L (hereafter referred to as "JMC-Lyon"), a Zn standard first reported by Bainbridge and Nier (1950),<sup>16</sup> was proposed by Maréchal *et al.* (1999) as the primary reference standard.<sup>4</sup> However, because the JMC-Lyon standard is no longer in production and nearly exhausted, it can no longer serve as an appropriate reference standard. Other materials such as IRMM-3702 produced by the Institute for Reference Materials and Measurements (IRMM) in Belgium may serve as an appropriate standard with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $\sim 0.27\text{‰}$ .<sup>17</sup> However, IRMM-3702 is only available in a relatively small amount ( $\sim 200 \mu\text{g Zn}$ ).<sup>6,18-20</sup> The National Institute of Standard and Technology (NIST) 3168a has a  $^{66}\text{Zn}/^{64}\text{Zn}$  ratio lower than that of JMC-Lyon by  $\sim 1\text{‰}$ ;<sup>20</sup> NIST SRM 682 has an even lower  $^{66}\text{Zn}/^{64}\text{Zn}$  ratio than JMC-Lyon by  $2.5\text{‰}$ .<sup>21,22</sup> Both values are far away from the average value of the bulk silicate Earth ( $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = \sim 0.2\text{‰}$ ).<sup>23,24</sup> Therefore, a new international reference standard is critical for future Zn isotope studies. Table 1 presents the comparison of JMC-Lyon, Alfa Aesar-Eidgenössische Technische Hochschule (AA-

ETH) Zn, IRMM-3702, NIST 3168a, NIST SRM 682 and NIST SRM 683.<sup>25</sup>

Chen *et al.*<sup>26</sup> initially examined the isotopic homogeneity of NIST SRM 683. This standard is a pure zinc nugget. Chen *et al.* measured 98 sample spots from two nuggets on Neptune Plus MC-ICP-MS by the standard bracketing method. However, Archer *et al.*<sup>20</sup> questioned the availability of NIST SRM 683 in the future and also the homogeneity of the Zn isotope composition of NIST SRM 683. Instead, they proposed a new reference that was made of 9 grams of AA-ETH Zn standard. To rigorously examine the homogeneity of the Zn isotopic composition in NIST SRM 683, we intensively measured 153 sample fractions drilled from five NIST SRM 683 nuggets. The aim of this study is to evaluate the isotopic homogeneity of NIST SRM 683 in a larger sample set and to determine its potential as the next-generation international reference standard for Zn isotopes.

## Experimental procedures

### Sample information

SRM 683 is a reference material produced by NIST, which was originally established to provide a homogeneous reference material for the analysis of pure zinc and analogous metals; its weight is about 140 grams. This material was prepared by Cominco America Inc. from a special lot of high-grade electrolytic zinc that was homogenized and cast in the form of semi-circular bars (Fig. 1). Each bar was etched, dried, and sealed in a polyethylene pouch to minimize contamination. We purchased 5 pure Zn nuggets from NIST. By comparing the Zn isotope composition of the two nuggets reported in the study by

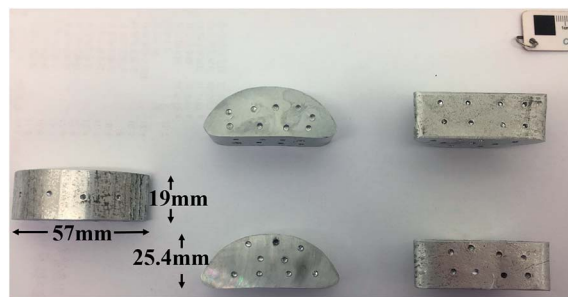
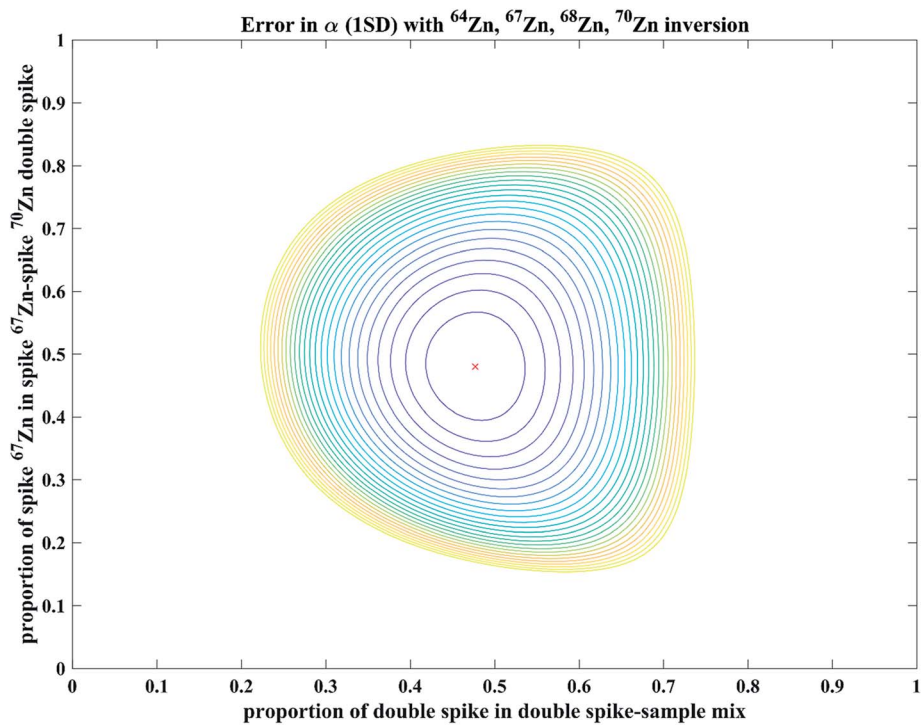


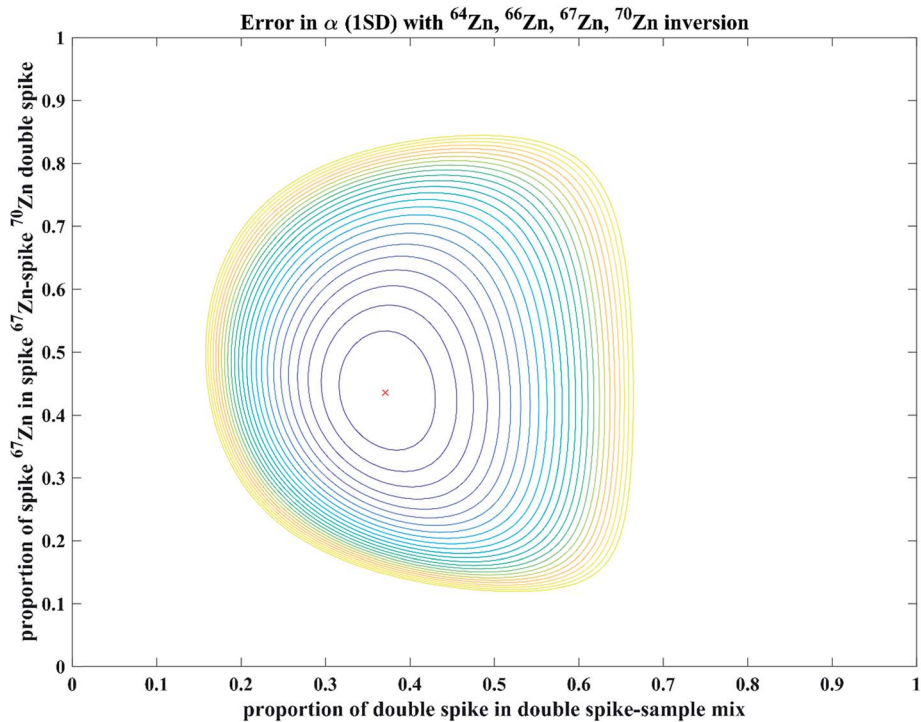
Fig. 1 NIST SRM 683 nuggets measured in this study with five spots drilled. Each nugget is in the form of a semicircular bar segment, 57 mm diameter, 25.4 mm deep at mid-diameter and 19 mm long.

Table 1 Measured isotope ratios of commercial Zn reagents

Sample name/source	Form or nominal purity	$\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$	Amount
JMC/Johnson Matthey, UK	Zinc metal wire	0	Exhausted
IRMM-3702/Institute for Reference Materials and Measurements, Belgium	Acidified aqueous solution	0.27‰	$\sim 200 \mu\text{g Zn}$
AA-ETH Zn/Alfa Aesar, USA	Acidified aqueous solution	0.28‰	$\sim 9 \text{ g Zn}$
NIST 3168a/NIST Chemical Sciences Division, USA	Acidified aqueous solution	$\sim -1\text{‰}$	$\sim 0.5 \text{ g Zn}$
NIST SRM 682/Cominco American, Canada	Zinc metal bar/99.9999%	$-2.5\text{‰}$	
NIST SRM 683/Cominco American, Canada	Zinc metal bar/1.00027	0.13‰	$> 900 \text{ g Zn}$



(a)



(b)

**Fig. 2** Influence of isotopic composition of DS and proportion of DS in DS-sample mix. The horizontal axis gives the proportion of double spike in the double spike-sample mixture, and the vertical axis gives the proportion of  $^{67}\text{Zn}$  in the double spike. (a) is the result of  $^{68}\text{Zn}/^{64}\text{Zn}$ - $^{67}\text{Zn}/^{64}\text{Zn}$ - $^{70}\text{Zn}/^{64}\text{Zn}$  isotope space, (b) is the result of  $^{66}\text{Zn}/^{64}\text{Zn}$ - $^{67}\text{Zn}/^{64}\text{Zn}$ - $^{70}\text{Zn}/^{64}\text{Zn}$  isotope space.

Chen *et al.* (2016), we can rigorously test the homogeneity of Zn isotopic composition for seven individual fractions.

### Sample preparation

Five metal nuggets were drilled for high-density sampling using an electric hand drill with a tungsten carbide bit (Fig. 1). Each nugget was extensively sampled by 30–32 drilling fractions. Before sampling, the drill bit was rinsed successively by ethanol, 10% m m<sup>-1</sup> HNO<sub>3</sub>, and ultrapure water (18.2 MΩ cm, same below). Then, the drill bit was placed in a clean beaker, immersed in ultrapure water, and cleaned twice under sonication for 15 minutes. To avoid cross contamination, the drill bit and the metal nugget were carefully cleaned using ethanol, followed with ultrapure water before and after each drilling. The drilled Zn metal powder was then transferred to a 7 ml Savillex® PFA Teflon beaker and dissolved in 1 ml 10% m m<sup>-1</sup> HNO<sub>3</sub>. All of the used Teflon beakers were previously cleaned by heating in 8 mol l<sup>-1</sup> HNO<sub>3</sub>, 6 mol l<sup>-1</sup> HCl, 8 mol l<sup>-1</sup> HNO<sub>3</sub>, and ultrapure water, successively. Finally, the solution was diluted to 2% m m<sup>-1</sup> HNO<sub>3</sub> for instrumental measurement.

### Double spike (DS) method and mass spectrometry

Because zinc has five stable isotopes, namely, <sup>64</sup>Zn (48.63%), <sup>66</sup>Zn (27.90%), <sup>67</sup>Zn (4.10%), <sup>68</sup>Zn (18.75%), and <sup>70</sup>Zn (0.62%), the DS method was used to correct instrumental mass bias in mass spectrometry for Zn isotope analysis of NIST SRM 683. The key controls on the precision of the DS method are the choices of double spike composition and the mixing fractions of the spike and the sample. Here, we have chosen <sup>67</sup>Zn–<sup>70</sup>Zn as the spikes. We used MATLAB codes provided by Rudge *et al.*<sup>27</sup> to calculate the suitable isotopic composition for <sup>67</sup>Zn–<sup>70</sup>Zn DS. The results indicated that the optimal composition of <sup>67</sup>Zn–<sup>70</sup>Zn DS was <sup>70</sup>Zn/<sup>67</sup>Zn = 1.08, and the optimal molar fraction of DS derived to total Zn was 0.48 for the <sup>68</sup>Zn/<sup>64</sup>Zn–<sup>67</sup>Zn/<sup>64</sup>Zn–<sup>70</sup>Zn/<sup>64</sup>Zn isotope space (Fig. 2a). For the <sup>66</sup>Zn/<sup>64</sup>Zn–<sup>67</sup>Zn/<sup>64</sup>Zn–<sup>70</sup>Zn/<sup>64</sup>Zn isotope

space, the optimal composition of <sup>67</sup>Zn–<sup>70</sup>Zn DS was <sup>70</sup>Zn/<sup>67</sup>Zn = 1.30, and the optimal molar fraction of DS derived to total Zn was 0.37 (Fig. 2b). The effect of <sup>70</sup>Zn/<sup>67</sup>Zn variation on error propagation and range of optimal spike-sample ratios was small, and the influence of spike-sample ratios on error propagation was not significant (Fig. 2).

Zn DS was prepared as a mixture of two concentrated spike solutions that were enriched in <sup>67</sup>Zn and <sup>70</sup>Zn. Briefly, 2.78 mg of <sup>67</sup>Zn metal (89.60% purity; Oak Ridge National Laboratory, USA) and 2.18 mg of <sup>70</sup>Zn metal (95.41% purity; Oak Ridge National Laboratory, USA) were dissolved in 2 N HNO<sub>3</sub>. The individual spikes were then mixed to obtain a DS solution. Finally, the solution was diluted to 2% HNO<sub>3</sub> for measurement. The Zn concentration and isotopic composition were determined by comparison with those of the reference material IRMM 3702. The final Zn isotopic composition was characterized by <sup>70</sup>Zn/<sup>67</sup>Zn = 1.02, and the total Zn concentration was 2.67 ppm. The molar fraction of DS derived to total Zn was approximately 0.45; this yielded molar ratios of about 1 : 0.6 : 0.8 : 0.5 : 0.8 for <sup>64</sup>Zn/<sup>66</sup>Zn/<sup>67</sup>Zn/<sup>68</sup>Zn/<sup>70</sup>Zn for the sample-spike mixture.

Most isotopic ratio measurements of this study were performed with a MC-ICP-MS (Neptune Plus from Thermo-Fisher Scientific) in the Chinese Academy of Science (CAS) Key Laboratory of Crust-Mantle Materials and Environments at the University of Science and Technology of China (USTC) in Hefei, China. An Aridus II desolvator (CETAC Technologies, Omaha, U.S.A.) was connected to a 50 μL min<sup>-1</sup> PFA MicroFlow Teflon nebulizer (Elemental Scientific Inc, Omaha, U.S.A.). Jet sampling and H-skimmer cones were used during the measurement. <sup>64</sup>Zn, <sup>66</sup>Zn, <sup>67</sup>Zn, <sup>68</sup>Zn, and <sup>70</sup>Zn were simultaneously collected in the Faraday cups of L3, L1, C, H1, and H3, respectively. The high-resolution mode was used to avoid the interferences of <sup>68</sup>Zn.

The sample and standard solutions were diluted in 2% HNO<sub>3</sub>. The typical sensitivity of <sup>64</sup>Zn was ~18 V ppm<sup>-1</sup>. The data acquisition sequence comprised 1 block with 60 cycles, and the integration time was 4.197 s for each cycle. The baseline was

Table 2 Instrument parameters

instrumental parameters	Neptune plus (USTC)				
RF power	~1200 W				
Cooling Ar flow rate	~16 L min <sup>-1</sup>				
Auxiliary Ar flow rate	~0.8 L min <sup>-1</sup>				
Nebuliser Ar flow rate	~0.85 L min <sup>-1</sup>				
Extraction voltage	-2000 V				
Vacuum	4–8 × 10 <sup>-9</sup> Pa				
Resolution	High-resolution				
Typical <sup>64</sup> Zn sensitivity	~18 V ppm <sup>-1</sup> (LR)				
Background of <sup>64</sup> Zn	<1 mV				
Cones	H-skimmer cone, Jet-sampler cone				
Ion lens setting	Optimized for max intensity				
Desolvator	Aridus II				
Argon flow rate	2.5–2.8 mL min <sup>-1</sup>				
Installed nebulizer	Teflon self-aspirating micronebulizer system				
Sample uptake	~50 μl min <sup>-1</sup>				
Detector mode	Faraday cup static mode				
Cup	L3-F	L1-F	C-F	H1-F	H3-F
Isotopes	<sup>64</sup> Zn	<sup>66</sup> Zn	<sup>67</sup> Zn	<sup>68</sup> Zn	<sup>70</sup> Zn
Amplifier resistor	10 <sup>11</sup> Ω	10 <sup>11</sup> Ω	10 <sup>11</sup> Ω	10 <sup>11</sup> Ω	10 <sup>11</sup> Ω

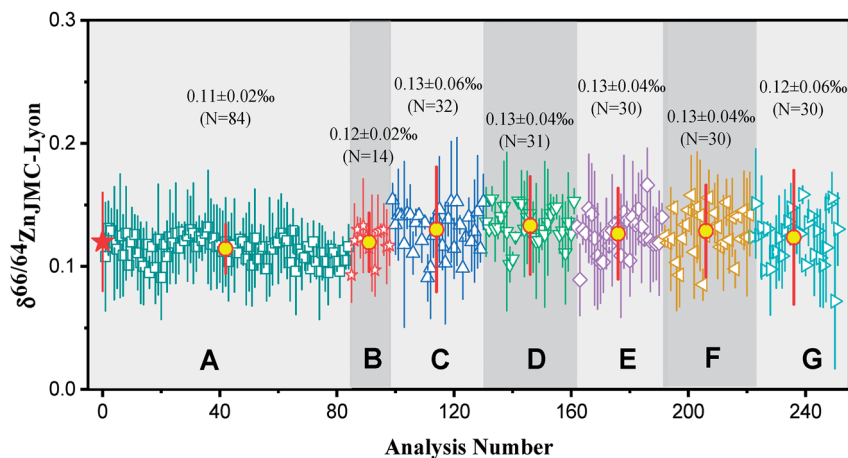


Fig. 3 Measurements of 251 sample fractions from seven metal nuggets of NIST SRM 683 including 98 fractions previously measured by Chen *et al.* (2016). The seven nuggets have  $\delta^{66}\text{Zn}$  of  $0.11 \pm 0.02\text{‰}$  ( $N = 84$ ),  $0.12 \pm 0.02\text{‰}$  ( $N = 14$ ),  $0.13 \pm 0.06\text{‰}$  ( $N = 32$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 31$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ) and  $0.12 \pm 0.06\text{‰}$  ( $N = 30$ ). These data agree with an average  $\delta^{66}\text{Zn}$  of  $0.12 \pm 0.04\text{‰}$  relative to that of JCM-Lyon ( $N = 295$ ). The red solid star represents the average  $\delta^{66}\text{Zn}$  data of the bulk solution of the first metal nugget (A).

Table 3  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of seven NIST SRM 683 Zn nuggets

No.	$\delta^{66}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$	$\delta^{67}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$	$\delta^{68}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$
A <sup>a</sup> ( $n = 84$ )	0.11	0.02			0.24	0.08
B <sup>a</sup> ( $n = 14$ )	0.12	0.03			0.23	0.10
C ( $n = 32$ )	0.13	0.06	0.18	0.08	0.24	0.08
D ( $n = 31$ )	0.13	0.04	0.19	0.07	0.25	0.07
E ( $n = 30$ )	0.13	0.04	0.18	0.08	0.25	0.08
F ( $n = 30$ )	0.13	0.04	0.18	0.08	0.24	0.08
G ( $n = 30$ )	0.12	0.06	0.17	0.12	0.23	0.13
H <sup>b</sup> ( $n = 44$ )	0.12	0.04	0.18	0.06	0.24	0.06

<sup>a</sup> A and B are data measured by Chen *et al.* (2016) by the standard bracketing method. <sup>b</sup> H denotes the data of the first metal nugget (A) measured by the double spike method.

measured prior to each block. The analyses were repeated at least twice for each sample solution. Before each measurement, the sample introduction system was cleaned three times with 5%  $\text{HNO}_3$  ( $\text{m m}^{-1}$ , 20 s), 5%  $\text{HNO}_3$  ( $\text{m m}^{-1}$ , 60 s), and 2%  $\text{HNO}_3$  ( $\text{m m}^{-1}$ , 60 s) to eliminate any potential cross-contamination. After rinsing, the  $^{64}\text{Zn}$  background was found to be lower than 1 mV, and it was much lower than the signal of samples (about 15 V). The instrumental parameters used in USTC during measurements are summarized in Table 2.

We digested the first nugget (nugget A in Fig. 3 and Table 3) measured by Chen *et al.* (2016) to obtain an in-house reference material. A total of forty-four measurements of the same solution over 2 months yielded an average of  $0.12 \pm 0.04\text{‰}$  (two-standard deviation (2SD),  $N = 44$ ). These data were identical to Chen *et al.*'s measurement using the standard bracketing method. Therefore, we used the solution of NIST SRM 683 standard as the in-house "zero-delta" reference material for Zn isotope measurements with the  $\delta^{66}\text{Zn}_{\text{JMC-SRM 683}}$  value fixed as  $0.12\text{‰}$  (Fig. 3). The results were then reported in delta notation relative to JMC-Lyon:

$$\delta^x\text{Zn}_{\text{sample-JMC}} = \delta^x\text{Zn}_{\text{sample-SRM 683}} - \delta^x\text{Zn}_{\text{JMC-SRM 683}}, \quad (x = 66, 67, 68, 70) \quad (2)$$

Each measurement section has four spiked samples and a spiked standard (*e.g.*, IRMM 3702 or AAS) for data monitoring. To test the accuracy of Zn isotope data, the NIST SRM 683 solution was also measured using the standard bracketing method on *Neptune Plus* MC-ICP-MS at the China University of Geosciences of Beijing (CUGB, detailed instrument parameters can be found in studies reported by Liu *et al.* (2014)<sup>28</sup> and Lv *et al.* (2016)<sup>29</sup>) and the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS, detailed instrument parameters can be found in the study reported by Yuan *et al.* (2016)<sup>30</sup>). This can provide laboratory bias and in turn external precision of the SRM 683 standard.

## Results and discussion

The summary of our results is presented in Table 3 and Fig. 3. The five nuggets have  $\delta^{66}\text{Zn}$  values of  $0.13 \pm 0.06\text{‰}$  ( $N = 32$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 31$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ),  $0.13 \pm 0.04\text{‰}$  ( $N = 30$ ) and  $0.12 \pm 0.06\text{‰}$  ( $N = 30$ ) (Table 3C-G and Fig. 3 C-G). Within our analytical precision, we did not observe heterogeneity of Zn isotope compositions in different nuggets of NIST SRM 683. These values are identical to those of the two Zn metal nuggets previously reported by Chen *et al.*<sup>26</sup> (Table 3A and B and Fig. 3 A

Table 4 Zinc isotopic composition of NIST SRM 683 measured in three different labs

Lab	$\delta^{66}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$	$\delta^{68}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$	$\delta^{67}\text{Zn}_{\text{JMC-Lyon}}/\text{‰}$	2SD/ $\text{‰}$
USTC ( $n = 295$ )	0.12	0.04	0.24	0.08	0.18	0.07
CUGB ( $n = 20$ )	0.12	0.04	0.24	0.07	0.18	0.08
IGCAS ( $n = 48$ )	0.12	0.04	0.23	0.09	0.17	0.11

and B). We also digested the first nugget (A) with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $0.12\text{‰} \pm 0.04\text{‰}$  ( $N = 44$ ) at the 95% confidence level (Table 3H and the red solid star in Fig. 3). Thus, the Zn isotopic compositions of NIST SRM 683 could be marked as  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = 0.12 \pm 0.04\text{‰}$  ( $N = 295$ ) at the 95% confidence level. Zn isotopic ratios of NIST SRM 683 measured at CUGB and IGCAS are summarized in Table 4 for comparison among the three laboratories. This indicates a total of 363 separate analyses of the NIST SRM 683 standard. The results measured in the three labs show good agreement with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  of  $0.12 \pm 0.04\text{‰}$  ( $N = 295$ ),  $0.12 \pm 0.04\text{‰}$  ( $N = 20$ ) and  $0.12 \pm 0.04\text{‰}$  ( $N = 48$ ).

In summary, intensive measurements for seven nuggets of NIST SRM 683 showed that no heterogeneity of Zn isotopic composition could be found in this standard with the current analytical precision of  $0.04\text{‰}$ . The Zn isotopic composition ( $\delta^{66}\text{Zn}$ ) was slightly higher than that of JMC-Lyon by  $0.12\text{‰}$ . This value was closer to that of the bulk silicate Earth (average  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = 0.15\text{--}0.20\text{‰}$ )<sup>31,32</sup> compared with that of JMC-Lyon. Furthermore, because the weight of each NIST SRM 683 nugget was 140 grams, it is much more abundant and more easily obtained than the standards previously calibrated. Therefore, due to the advantages of NIST SRM 683, this standard could be used as the next-generation reference standard for Zn isotope analyses.

## Conclusions

Five NIST SRM 683 Zn metal nuggets have been separately measured in three labs from USTC, CUGB, and IGCAS. The results show that within the analytical precision of  $0.04\text{‰}$ , NIST SRM 683 is extremely homogenous in Zn isotopic compositions with  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = 0.12 \pm 0.04\text{‰}$  ( $N = 295$ ) at the 95% confidence level. This value is closer to the average value of the bulk silicate Earth. More importantly, NIST SRM 683 has weight of up to 140 grams for each nugget, and it can be available for long-term usage for labs all over the world. The split of the SRM 683 nugget is available from the corresponding author upon request. Therefore, we believe that NIST SRM 683 can be the new “zero-point” reference standard for future Zn isotopic measurements.

## Conflicts of interest

There are no conflicts to declare.

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