Acta Geochim (2024) 43:1054–1064
https://doi.org/10.1007/s11631-024-00729-8

ORIGINAL ARTICLE

Precise and accurate Ga isotope ratio measurements of geological samples by multi-collector inductively coupled plasma mass spectrometry

Yuxu Zhang[1] · **Pan Qiao**[1,3] · **Chuanwei Zhu**[2] · **Haifeng Fan**[1] · **Hanjie Wen**[2,4]

Received: 15 May 2024 / Revised: 5 July 2024 / Accepted: 30 July 2024 / Published online: 22 August 2024

Abstract Gallium isotope is a potential geochemical tool for understanding planetary processes, environmental pollution, and ore deposit formation. The reported Ga isotope compositions ($\delta^{71}Ga_{NIST994}$ values) of some international geological standards, such as BCR-2 and BHVO-2 basalts, exhibit inconsistencies between different laboratories. During mass spectrometry analysis, we found that $\delta^{71}Ga_{NIST994}$ values of geological standards with or without the correction of the interference of $^{138}Ba^{2+}$ (mass/charge ratio = 69) on ^{69}Ga show significant isotope offsets, and thus efficient separation of Ba and correcting the interference of $^{138}Ba^{2+}$ are both crucial to obtain accurate $\delta^{71}Ga$ values. By comparing $\delta^{71}Ga_{NIST994}$ values (relative to NIST SRM 994 Ga) of the same geostandards from different laboratories, we suggest that the isotopic heterogeneity from NIST SRM 994 Ga is one of the key reasons for the inconsistencies in $\delta^{71}Ga_{NIST994}$ values of BCR-2 and BHVO-2. To facilitate inter-laboratory comparisons, we measured the Ga isotopic compositions of 11 geological reference materials (including Pb-Zn ore, bauxite, igneous rocks, and loess) and two Ga solution standards (NIST SRM 3119a and Alfa Aesar). The $\delta^{71}Ga_{NIST994}$ and $\delta^{71}Ga_{IPGP}$ values of these reference materials vary from 1.12 ‰ to 2.63 ‰ and − 0.13 ‰ to 1.38 ‰, respectively, and can be used to evaluate the precision and accuracy of Ga isotope data from different laboratories.

Keywords Ga isotopes · MC-ICP-MS · Reference materials · Chemical purification · Ba interference

1 Introduction

Gallium (Ga) has two stable isotopes, ^{69}Ga and ^{71}Ga, with abundances of 60.1% and 39.9%, respectively (De Laeter 1972). Early studies measured the Ga isotopic compositions of meteorite samples and metallic Ga, and found the fractionation of Ga isotopes in natural samples is minor with high uncertainty (Inghram et al. 1948; De Laeter 1972; Zhang et al. 2016). With the development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and improvements in chemical separation and purification methods (Yuan et al. 2016; Zhang et al. 2016; Kato et al. 2017), accurate analysis of Ga isotope ratios in natural samples has become possible (Yuan et al. 2016, 2018, 2021, 2022; Zhang et al. 2016, 2021; Kato and Moynier 2017a, b; Kato et al. 2017; Feng et al. 2019; Wimpenny et al. 2020, 2022; Wen et al. 2021; Liu et al. 2022; Render et al. 2023; Roland et al. 2023).

Gallium isotopic compositions are usually reported as $\delta^{71}Ga$ values relative to a Ga isotope standard, including NIST SRM 994 Ga (Yuan et al. 2016, 2018, 2021, 2022; Zhang et al. 2016, 2021; Feng et al. 2019; Wimpenny

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11631-024-00729-8.

✉ Hanjie Wen
wenhanjie@vip.gyig.ac.cn

Yuxu Zhang
zhangyuxu98@163.com

[1] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 99 West Lincheng Road, Guiyang 550081, Guizhou Province, China

[2] School of Earth Sciences and Resources, Chang'an University, 126 Yanta Road, Xi'an 710054, Shaanxi Province, China

[3] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 101408, China

[4] College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

et al. 2020, 2022; Wen et al. 2021; Render et al. 2023; Roland et al. 2023) and Institut de Physique du Globe de Paris (IPGP) Ga (Kato and Moynier 2017a, b; Kato et al. 2017; Liu et al. 2022). Similar to other non-traditional stable isotopes, the measurement of Ga isotope ratios has two challenges; i.e., the separation and purification of Ga from samples and the correction of instrumental mass bias. The potential interferences on ^{71}Ga and ^{69}Ga include Ba ($^{138}Ba^{2+}$), Ce ($^{138}Ce^{2+}$ and $^{142}Ce^{2+}$), Nd ($^{142}Nd^{2+}$), La ($^{138}La^{2+}$), $^{54}Fe^{17}O^{+}$, $^{68}Zn^{1}H^{+}$, and etc.

The abundance of Gallium in the crust is ~ 15 µg/g (Tu et al. 2003). Gallium-rich deposits are associated with bauxite and Pb-Zn ore deposits (Liu 1965, 1982; Tu et al. 2003). Chemical separation and purification methods for Ga have been developed in different laboratories (Yuan et al. 2016; Zhang et al. 2016, 2021; Kato et al. 2017; Wimpenny et al. 2020; Roland et al. 2023). However, the reported Ga isotopic compositions of different geological reference materials are still limited, such as sphalerite and bauxite. Meanwhile, the reported δ^{71}Ga values of some international geostandards are varied between different laboratories. For example, the δ^{71}Ga$_{NIST994}$ values of BHVO-2 reported in the literature vary from 0.48 ‰ to 1.21 ‰, and the δ^{71}Ga$_{NIST994}$ values of BCR-2 vary from 0.52 ‰ to 1.20 ‰ (Table 1) (Zhang et al. 2016, 2021; Feng et al. 2019; Wimpenny et al. 2020; Wen et al. 2021; Yuan et al. 2021, 2022; Roland et al. 2023). Among the potential interfering elements (Ba, Ce, Nd, La, Fe, Zn, and etc.), Ba has the lowest ionisation potential, and little Ba ($^{138}Ba^{2+}$; mass/charge ratio = 69) in the separated samples could result in large Ga isotope offsets (Kato et al. 2017). Meanwhile, the National Institute of Standards and Technology (NIST) SRM 994 Ga is likely heterogeneous due to the high uncertainty of the certified value (1.50676 ± 0.00039), this means that different batches of NIST 994 Ga isotopic standard could cause a maximum error of ~ 0.5 ‰. The two factors may result in different reported δ^{71}Ga$_{NIST994}$ values in the literatures. To facilitate interlaboratory comparisons of δ^{71}Ga values, it is necessary to investigate the reasons for these inconsistencies and obtain more Ga isotope data for geological reference materials.

In this study, the potential factors for the differences in the δ^{71}Ga$_{NIST994}$ values of BHVO-2 and BCR-2 were investigated. We also measured the Ga isotopic compositions of nine geological reference materials (including bauxites, Pb-Zn ores, loess, and igneous rocks) and two Ga solution standards (NIST SRM 3119a and Alfa Aesar). The results of this research will improve comparisons of Ga isotope data measured in different laboratories.

2 Materials and methods

The sample digestion, chemical separation, and Ga isotope ratio measurements by Neptune Plus MC–ICP–MS (Thermo Fisher Scientific, Germany) were conducted at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. All sample preparation was carried out in an ISO class 5 clean room facility.

2.1 Reagents and materials

Deionised water from a > 18.2 MΩ grade Milli-Q water purification system (Millipore; Bedford, MA, USA) was used. Reagent grade HCl, HF, and HNO_3 were purchased from Sinopharm Chemical Reagent Company Limited, Shanghai, China, and the acids were purified twice using DST-1000 sub-boiling stills (Savillex®; USA). AG 1-X4 anion exchange resin (100–200 mesh; Biorad), Ln-spec resin (50–100 µm; TrisKem), and customised quartz columns (~ 0.52 cm inner diameter and 15 cm resin bed height) were used for the Ga purification.

The National Institute of Standards and Technology (NIST) SRM 994 Ga isotopic standard ($^{69}Ga/^{71}Ga = 1.50676 \pm 0.00039$), NIST SRM 3119a Ga standard solution (lot: 140,124), and Alfa Aesar Ga standard solution (lot: 8,129,898) were used as Ga reference materials. ERM®-AE647 Cu isotopic standard solution (provided by the Institute for Reference Materials and Measurements [IRMM]; $^{65}Cu/^{63}Cu = 0.44560 \pm 0.00074$) was used for the mass bias correction in the external normalisation

Table 1 Ga isotopic compositions of BCR-2 and BHVO-2 reported in the literature

BCR-2		BHVO-2		References
δ^{71}Ga$_{NIST994}$ (‰)	δ^{71}Ga$_{NIST3119a}$ (‰)	δ^{71}Ga$_{NIST994}$ (‰)	δ^{71}Ga$_{NIST3119a}$ (‰)	
0.52 ± 0.07		0.48 ± 0.02		Wimpenny et al. (2020)
0.70 ± 0.03		0.70 ± 0.05		Yuan et al. (2022)
0.76 ± 0.02		0.74 ± 0.02		Zhang et al. (2016)
0.76 ± 0.06	− 1.36 ± 0.08	0.75 ± 0.06	− 1.37 ± 0.09	Feng et al. (2019)
0.89 ± 0.03		0.88 ± 0.04		Roland et al. (2023)
1.19 ± 0.08		1.21 ± 0.05		Wen et al. (2021)
1.20 ± 0.08		1.19 ± 0.04		Zhang et al. (2021)

method. The Ga isotopic compositions of 11 geological reference materials were measured, including two bauxites (GBW07181 and GBW07182; Chinese Reference Materials [CRM]), two Pb–Zn ores (GBW07168 and GBW07372 [CRM]), three basalts (BCR-2 and BHVO-2 from the United States Geological Survey, and GBW07126 [CRM]), one granite (GBW07103 [CRM]), one andesite (GBW07104 [CRM]), one granodiorite (GBW07111 [CRM]), and one loess (GBW07454 [CRM]).

2.2 Sample digestion

An aliquot of each powdered sample containing > 0.5 µg of Ga was placed into a Teflon beaker, and 4 mL of 15 M HNO_3 and 4 mL of 22 M HF were added. The samples were then digested in a closed vessel in a microwave digester (Anton Paar Multiwave 7000; Austria) using the following power-controlled digestion program, 10 min ramp time and 90 min hold time (250 °C; 140 bar). The sample solutions were then evaporated to dryness on a hot plate at 120 °C, and dissolved in 6 M HCl prior to chemical purification of Ga.

2.3 Chemical purification procedure

The chemical purification procedure for separating Ga from the matrix involved two chromatographic columns loaded with AG1-X4 anion exchange resin and Ln-spec resin (Yuan et al. 2016). In this study, the volume of AG1-X4 resin in the first column was increased from 1.8 to 3.0 mL to better remove Zn, and the volume of Ln-spec resin in the second column was increased from 1.4 to 3.0 mL to completely remove Fe and Mo (Wen et al. 2021). In addition, the volume of 6 M HCl washing solution was also increased from 10 to 40 mL to completely remove Cu (Zhang et al. 2021). This allowed to add a Cu isotope standard to the samples to correct the instrumental mass bias. The modified procedures are listed in Table 2.

Table 2 Gallium chemical purification procedures

Process	Reagent	Volume (mL)
Column #1: 3 mL AG1-X4 resin (100–200 mesh, Biorad)		
Clean	H_2O	20
	0.1 M HCl	20
	0.5 M HCl	20
Condition	6 M HCl	10
Load sample	6 M HCl	3 ~ 5
Wash	6 M HCl	10 × 4
Collect Ga	0.5 M HCl	1.5 × 4
Column #2: 3 mL Ln-spec resin (50–100 µm, TrisKem)		
Condition	0.5 M HCl	10
Load sample	0.5 M HCl	6
Collect Ga	0.5 M HCl	2 × 3
Clean (for reuse)	0.25 M oxalic acid + 3 M HCl	30
	0.1 M HCl	30
	4 M HCl	30

2.4 Mass spectrometry

The Ga isotope standards and purified Ga from the samples were dissolved in 1% HNO_3 solution in preparation for Neptune Plus MC–ICP–MS analysis in low-resolution mode using Pt Jet sampler and Ni X-type skimmer cones. A Teflon nebuliser with an uptake rate of 50 µL/min was used for the sample introduction, and the Ga concentrations of the samples and solution standards were ~ 200 ng/mL. $^{63}Cu^+$, $^{65}Cu^+$, $^{66}Zn^+$, $^{137}Ba^{2+}$, $^{69}Ga^+$, and $^{71}Ga^+$ ion beams were collected using Faraday cups at the L3, L1, C, H2, H3, and H4 positions, respectively. The purified Ga from the samples and bracketing standards were each analysed in 4 blocks of 10 cycles with 2.097 s integration periods. After each analysis, the nebuliser and spray chamber were rinsed with 2% HNO_3 until the signal intensity reached the original background level ($^{69}Ga < 0.6$ mV; generally after 4 min).

Due to the low ionisation potential of Ba, the doubly charged ion ($^{138}Ba^{2+}$; mass/charge ratio = 69) generated during ionisation forms a large interference on ^{69}Ga. Kato et al. (2017) reported that the interference of $^{138}Ba^{2+}$ on ^{69}Ga is significant when the Ba/Ga ratio of a sample is $> 4 \times 10^{-4}$. The interference of $^{138}Ba^{2+}$ on ^{69}Ga can be corrected by monitoring the signal intensity of $^{137}Ba^{2+}$ (mass/charge ratio = 68.5). The correction equation is $^{69}Ga_{TRUE} = I69 - {}^{138}Ba^{2+} \approx I69 - (6.39 \times I68.5)$ (where I69 represents the measured intensity of mass 69 and I68.5 represents the intensity of doubly ionised $^{137}Ba^{2+}$ at a mass of 68.5; Kato et al. 2017). We used this method to correct for the interference of $^{138}Ba^{2+}$ on ^{69}Ga, which has been described in detail by Kato et al. (2017).

A method that combines standard–sample bracketing (SSB) with an internal mass bias correction can produce more accurate and precise Ga isotope ratios. Copper is a suitable internal standard for correcting the mass bias during Ga isotope analysis (Yuan et al. 2016; Zhang et al. 2016). ERM®-AE647 Cu solution (IRMM; $^{65}Cu/^{63}Cu = 0.44560 \pm 0.00074$) was used for the correction of the Ga isotope ratios, with a Ga/Cu ratio of ~ 1 for the bracketing standards and purified Ga from the samples.

The Ga isotopic compositions are reported in δ notation relative to a Ga isotope standard:

$$\delta^{71}\text{Ga}\ (‰) = \left[\left({}^{71}\text{Ga}/{}^{69}\text{Ga}\right)_{\text{sample}} / \left({}^{71}\text{Ga}/{}^{69}\text{Ga}\right)_{\text{standard}} - 1\right] \times 1000$$

NIST SRM 994 and IPGP Ga are mainly used as standards for $\delta^{71}Ga$ values reported in the literature (Yuan et al.

2016, 2018, 2021, 2022; Zhang et al. 2016, 2021; Kato and Moynier 2017a, b; Kato et al. 2017; Feng et al. 2019; Wimpenny et al. 2020, 2022; Wen et al. 2021; Liu et al. 2022; Render et al. 2023). In this study, the δ^{71}Ga values are reported relative to the NIST SRM 994 Ga standard. In order to facilitate interlaboratory comparisons, we also calculated the δ^{71}Ga values relative to the IPGP Ga standard.

3 Results and discussion

3.1 Matrix removal and Ga recovery

To achieve accurate and precise Ga isotopic compositions by MC–ICP-MS, it is necessary to add Cu or Zn standards to correct for instrumental mass bias. When the Zn/Ga ratio of the sample is > 10%, $^{68}Zn^{1}H^{+}$ will interfere with the determination of the Ga isotope ratio (Yuan et al. 2016); therefore, Cu is more suitable for instrumental mass bias correction. Accordingly, during the chemical purification of the sample, the actual Cu in the sample needs to be removed, such that it does not interfere with the measurement of the Cu isotope ratio ($^{65}Cu/^{63}Cu$) of the added Cu standard. During the process of removing the interfering elements using an AG1-X4 resin column, the first 10 mL (0–10 mL) of 6 M HCl added removes ~ 50% of the Cu, the second 10 mL (10–20 mL) of 6 M HCl removes an additional ~ 30% of the Cu, the third 10 mL (20–30 mL) of 6 M HCl removes a further ~ 16% of the Cu, and the fourth 10 mL (30–40 mL) of 6 M HCl removes ~ 3.9% of the Cu (Fig. 1; Table S1). Although there is a distinct tailing effect during Cu removal, 40 mL of 6 M HCl can remove ~ 99.9% of the Cu, and the Cu concentration of the purified solution is mostly < 2 ng/mL. For some samples with very high Cu contents (e.g., sphalerite containing a small amount of chalcopyrite [$CuFeS_2$]), it may be necessary to increase the volume of 6 M HCl eluted or to conduct a second anion exchange resin purification. Unlike the tailing effect of Cu, the removal of other elements (Ce, Nd, La, etc.) was effective, and 0–10 mL of 6 M HCl was able to remove > 96% of these elements (Fig. 1; Table S1).

Unlike Cu, Ce, Nd, and La, which were removed by eluting 6 M HCl, Zn was mainly separated from Ga by being adsorbed to the AG1-X4 anion exchange resin and was not eluted (Table S1). We passed a sample solution with a high Zn concentration through the AG1-X4 anion exchange resin to determine the maximum Zn adsorption capacity of the resin. When 6 M HCl is used, 3 mL of AG1-X4 anion exchange resin could adsorb up to 9630 µg of Zn (3210 µg/mL), whereas only 3540 µg of Zn (1180 µg/mL) could be adsorbed when 0.5 M HCl was used (Table S2). In the chemical purification process, to completely remove Zn from the sample, the ratio of total Zn content in the sample to the volume of the anion exchange resin should be < 1180 µg/mL.

The removal of Fe was similar to that of Zn. When the sample passed through the Ln-spec resin (i.e., the second column), Fe was adsorbed on the resin and Ga was not; therefore, Ga and Fe were separated. Our results revealed

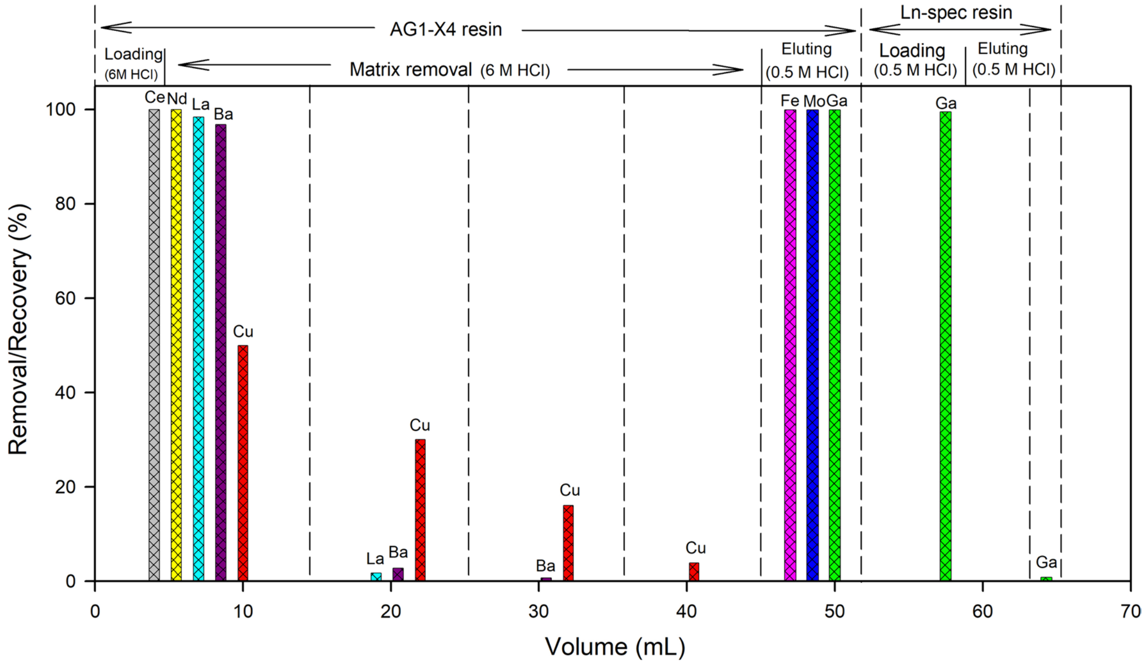


Fig. 1 Elution scheme during Ga separation from the matrix using AG1-X4 resin and Ln-spec resin (additional information available on Table S1)

that the maximum Fe adsorption capacity of 3 mL of Ln-spec resin was ~ 2610 µg (870 µg/mL; Table S2).

In this study, we analysed 11 geological reference materials and 2 procedural blanks. The Ga contents of the procedural blanks ranged from 0.2 to 0.3 ng, and these contents are negligible compared with the Ga contents (> 0.50 µg) of the samples. The recovery of Ga varied from 98.1% to 99.8% (mean = 99.1% ± 0.8%; 2 sd; n = 11).

3.2 Mass bias correction

Just as Cu isotope ratios can be corrected for instrumental mass bias using Ga as an internal standard (e.g., Hou et al. 2016; Lauwens et al. 2018), Ga isotope ratios can be corrected for instrumental mass bias using Cu as an internal standard (e.g., Yuan et al. 2016; Zhang et al. 2016; Feng et al. 2019). If the instrumental isotopic fractionation of Cu and Ga isotopes follows the exponential law, the raw Cu and Ga isotope ratios will form a fractionation line in $\ln(^{65}Cu/^{63}Cu)$ versus $\ln(^{71}Ga/^{69}Ga)$ isotope space, and a theoretical slope can be estimated using the following equation (Wombacher et al. 2003):

$$\text{slope} = ((\ln(^{71}\text{Ga}/^{69}\text{Ga})_{\text{raw}} - \ln(^{71}\text{Ga}/^{69}\text{Ga})_{\text{corrected}})/(\ln(^{65}\text{Cu}/^{63}\text{Cu})_{\text{raw}} - \ln(^{65}\text{Cu}/^{63}\text{Cu})_{\text{ref}}) \quad (1)$$

For our long-term (about 3 years) measurements, the $\ln(^{65}Cu/^{63}Cu)$ versus $\ln(^{71}Ga/^{69}Ga)$ plot exhibits a good positive correlation ($R^2 = 0.97$), with a slope of 0.84 (Fig. 2), which is close to the theoretical slope (0.91) calculated from Eq. (1). This suggests that the instrumental mass bias on the Ga isotope ratios can be corrected using Cu isotopes.

When analysing a standard solution of 0.2 µg/mL NIST SRM 994 Ga with 0.2 µg/mL ERM®-AE647 Cu solution, the $\delta^{71}Ga$ values corrected with Cu and not corrected with Cu were 0.01 ‰ ± 0.02 ‰ (2 sd; n = 24) and 0.00 ‰ ± 0.08 ‰ (2 sd; n = 24), respectively. The precision of the $\delta^{71}Ga$ values corrected with Cu is better than that of the uncorrected $\delta^{71}Ga$ values (Fig. 3).

3.3 Correction of the Ba interference

Analysis of the Ga isotopic compositions of reference materials is an effective means of comparing Ga isotopic measurements conducted in different laboratories. However, the Ga isotopic compositions of geological reference materials reported in the literature differ (Table 1). For example, the $\delta^{71}Ga_{NIST994}$ values of BCR-2 and BHVO-2 reported in the literature vary from 0.52 ‰ to 1.20 ‰ and 0.48 ‰ to 1.21 ‰, respectively (Zhang et al. 2016, 2021; Feng et al. 2019; Wimpenny et al. 2020; Wen et al. 2021; Yuan et al. 2021, 2022; Roland et al. 2023). Among the potential interfering elements, the Ce, Nd, La, Fe, and Zn contents of the purified Ga from the samples do not reach ranges that would interfere with the Ga isotopic measurements (Yuan et al. 2016; Zhang et al. 2016; Kato et al. 2017; Feng et al. 2019; Wimpenny et al. 2020). However, owing to the relatively low ionisation potential of Ba, the interference from the doubly charged ion ($^{138}Ba^{2+}$; mass/charge ratio = 69) on ^{69}Ga can only be ignored when the Ba/Ga ratio of the sample is < 10^{-5} (Kato

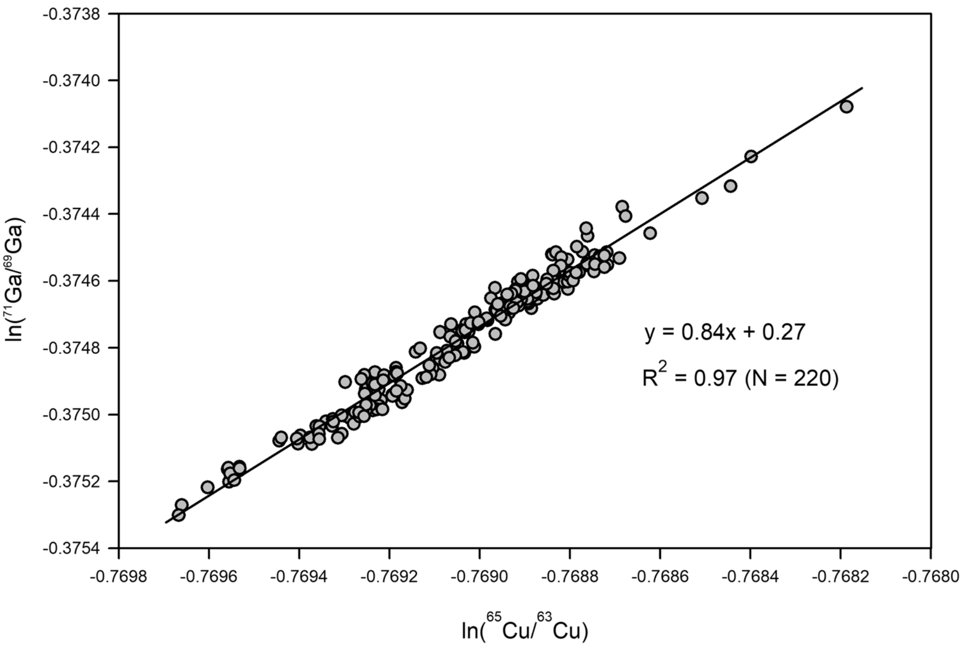
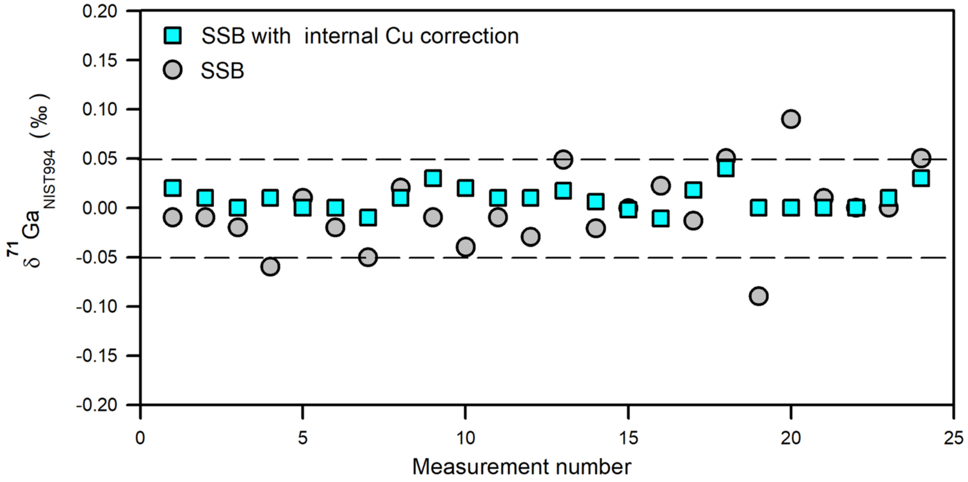


Fig. 2 Correlation between the raw isotope ratios of Ga and Cu

Fig. 3 Accuracy and precision of the data using the SSB method, with and without internal Cu correction



et al. 2017). We conducted multiple analyses of the Ga isotope ratios of BCR-2 and BHVO-2. The $^{137}Ba^{2+}$ signal intensity for the 0.2 µg/mL NIST SRM 994 Ga isotope standard was found to be equal to that of the blank (1% HNO_3 solution). However, the $^{137}Ba^{2+}$ signal intensity of the 0.2 µg/mL Ga separated from BCR-2 and BHVO-2 was 1.5–5.0 times higher than that of the blank.

Over a period of three years, five separate aliquots of BCR-2 and BHVO-2 were purified and measured their Ga isotope ratios (Table 3). We also analysed the Ga isotopic compositions of NIST SRM 3119a and Alfa Aesar (Table 4). For the NIST SRM 3119a and Alfa Aesar, the $\delta^{71}Ga_{NIST994\text{-}mean}$ values (without Ba correction) were 2.60 ‰ ± 0.08 ‰ (2 sd; n = 26) and 1.95 ‰ ± 0.06 ‰ (2 sd; n = 24), and the Ba-corrected $\delta^{71}Ga_{NIST994}$ values were 2.63 ‰ ± 0.07 ‰ (2 sd; n = 26) and 2.00 ‰ ± 0.08 ‰ (2 sd; n = 24), respectively. The corrected and uncorrected $\delta^{71}Ga$ values are the same within error. For BCR-2 and BHVO-2, the $\delta^{71}Ga_{NIST994\text{-}mean}$ values varied from 0.69 ‰ to 1.17 ‰ (average = 0.95 ‰) and 0.61 ‰ to 1.16 ‰ (average = 0.92 ‰), respectively, and the Ba-corrected $\delta^{71}Ga_{NIST994}$ values varied from 1.19 ‰ to 1.29 ‰ (average = 1.24 ‰) and 1.16 ‰ to 1.32 ‰ (average = 1.22 ‰). The $\delta^{71}Ga$ values of BCR-2 and BHVO-2 varied over a wide range when uncorrected for Ba interference but were constant at ~ 1.2 ‰ after correction for the Ba interference (Fig. 4). In the different analytical sessions, there was a large difference in the ratio of the signal intensity of $^{137}Ba^{2+}$ to ^{69}Ga (I68.5/I69) for the same solution (Table 4), which may be related to differences in the MC-ICP-MS set-up during the different analytical sessions (e.g., in the flow rate of Ar gas and X, Y, and Z cone coordinates). Therefore, we divided the ratio of the signal intensity of $^{137}Ba^{2+}$ to that of ^{69}Ga for the sample solution by the ratio of the signal intensity of $^{137}Ba^{2+}$ to that of the signal intensity of ^{69}Ga for the NIST SRM 994 Ga standard to quantify the Ba interference. This ratio is abbreviated as $[(I68.5/I69)_{sample}]$ / $[(I68.5/I69)_{NIST994}]$. During the MC–ICP–MS analysis of NIST SRM 3119a and Alfa Aesar, the average $[(I68.5/I69)_{sample}]$ / $[(I68.5/I69)_{NIST994}]$ values were 1.21 and 1.33, respectively. The Ba concentrations of NIST SRM 3119a and Alfa Aesar are not significantly different from that of the NIST SRM 994 Ga standard, which may be why the corrected and uncorrected $\delta^{71}Ga$ values are the same within error. For BCR-2 and BHVO-2, the $[(I68.5/I69)_{sample}]$ / $[(I68.5/I69)_{NIST994}]$ values varied from 1.57 to 5.21. The Ba contents of these Ga fractions were significantly higher than that of the Ga isotope standard, and the $\delta^{71}Ga_{NIST994}$ value without Ba correction was significantly lower than the corrected value (Table 3). In Fig. 4, the $\delta^{71}Ga_{NIST994}$ values without Ba correction exhibit a negative correlation (for BCR-2, $R^2 = 0.96$; for BHVO-2, $R^2 = 0.94$) with the $[(I68.5/I69)_{sample}]$ / $[(I68.5/I69)_{NIST994}]$ values, but after the Ba correction, the $\delta^{71}Ga_{NIST994}$ values of BCR-2 and BHVO-2 are both constant at ~ 1.2 ‰. Minor $^{138}Ba^{2+}$ could result in a lower $\delta^{71}Ga$ value, and thus efficient separation of Ba and correcting the interference of $^{138}Ba^{2+}$ are both crucial to obtain accurate $\delta^{71}Ga$ values.

During the analysis of Ga isotopes by MC–ICP–MS, when the Fe/Ga ratio is very high, Fe will generate false $^{137}Ba^{2+}$ ion signals (I68.5), thereby affecting the Ba-corrected $\delta^{71}Ga$ values (Roland et al. 2023). By adding different amounts of Fe to the NIST SRM 994 Ga standard and then analysing the Ga isotope ratios by MC–ICP–MS, we found that Fe does not affect the Ba-corrected $\delta^{71}Ga$ values when Fe/Ga (ppm/ppm) is < 100 (Fig. 5; Table S3). The Fe/Ga ratios in the purified Ga from BCR-2 and BHVO-2 were 0.2–1.0, which is much smaller than the Fe/Ga ratio required to affect the Ba-corrected $\delta^{71}Ga$ values.

3.4 Heterogeneity of NIST 994 Ga isotopic standards

The certified value of $^{69}Ga/^{71}Ga$ ratio of NIST SRM 994 Ga isotopic standard is 1.50676 ± 0.00039, this means that different batches of NIST 994 Ga isotopic standard could

Table 3 Barium interference correction data for BCR-2 and BHVO-2

Analytical session	BCR-2				BHVO-2			
	$\delta^{71}Ga_{NIST994}$* (‰)	$\delta^{71}Ga_{NIST994\text{-}mea}$# (‰)	I_{sample} (10^{-5})	I_{sample}/I_{std}	$\delta^{71}Ga_{NIST994}$* (‰)	$\delta^{71}Ga_{NIST994\text{-}mea}$# (‰)	I_{sample} (10^{-5})	I_{sample}/I_{std}
1st	1.21	0.69	10.65	4.08	1.26	0.61	12.90	4.99
	1.22	0.70	10.69	4.17	1.30	0.63	13.09	5.10
	1.23	0.71	10.48	4.35	1.32	0.68	12.38	5.21
	1.20	0.70	10.24	4.22	1.26	0.61	12.61	5.04
	1.19	0.71	10.03	4.06	1.21	0.63	11.42	4.98
2nd	1.25	0.92	7.26	3.47	1.20	0.83	7.70	3.87
	1.23	0.89	7.39	3.53	1.19	0.83	7.51	3.98
	1.24	0.89	8.54	2.83	1.21	0.84	8.71	2.98
	1.27	0.92	8.03	3.14	1.26	0.91	8.26	2.91
3rd	1.21	0.91	7.29	2.93	1.20	1.00	5.72	2.30
	1.26	0.98	6.82	2.86	1.21	1.01	5.51	2.26
	1.25	0.95	7.08	2.92	1.24	1.05	5.43	2.29
	1.25	0.96	6.94	2.89	1.25	1.05	5.59	2.35
4th	1.24	1.03	5.73	2.28	1.16	0.92	6.23	2.49
	1.25	1.05	5.69	2.25	1.18	0.96	6.08	2.32
	1.29	1.08	5.89	2.17	1.19	0.98	5.90	2.32
	1.27	1.08	5.41	2.18	1.19	0.98	5.90	2.31
	1.25	1.05	5.70	2.21	1.20	0.99	5.90	2.35
5th	1.20	1.12	3.17	1.71	1.28	1.16	3.66	1.86
	1.23	1.15	3.05	1.76	1.23	1.13	3.62	2.01
	1.22	1.13	3.09	1.72	1.21	1.08	3.71	1.95
	1.24	1.17	3.05	1.64	1.19	1.10	3.53	1.89
	1.21	1.13	2.98	1.57	1.21	1.09	3.49	1.91
Average	1.24 ± 0.05‰ (2sd,n = 23)	0.95 ± 0.31‰ (2sd,n = 23)	6.75	2.82	1.22 ± 0.08‰ (2sd,n = 23)	0.92 ± 0.35‰ (2sd,n = 23)	7.17	3.03

$\delta^{71}Ga_{NIST994}$* denotes the $\delta^{71}Ga_{NIST994}$ value after correction for Ba interference; $\delta^{71}Ga_{NIST994\text{-}mea}$# denotes the $\delta^{71}Ga_{NIST994}$ value without correction for Ba interference; I_{sample} denotes $[(I68.5/I69)_{sample}]$, i.e., the ratio of the signal intensity of $^{137}Ba^{2+}$ in the sample solution to the signal intensity of ^{69}Ga; and I_{sample}/I_{std} denotes $[(I68.5/I69)_{sample}]/[(I68.5/I69)_{NIST994}]$, i.e., the ratio of the signal intensity of $^{137}Ba^{2+}$ to the signal intensity of ^{69}Ga in the sample solution divided by the ratio of the signal intensity of $^{137}Ba^{2+}$ to that of ^{69}Ga in the NIST SRM 994 Ga isotopic standard

cause a maximum Ga isotope offset up to ~ 0.5 ‰. Feng et al. (2019) obtained $\delta^{71}Ga_{NIST994}$ values of BCR-2 and BHVO-2 are varying from 0.75 ‰ ~ 0.76 ‰, respectively. Here, the $\delta^{71}Ga_{NIST994}$ values of the two geological standards are between 1.22 ‰ and 1.24 ‰. When Ga isotopic compositions of BCR-2 and BHVO-2, obtained from Feng et al. (2019) and this study (Table 5), are reported relative to NIST 3119a or IPGP Ga, the $\delta^{71}Ga$ values of BCR-2 and BHVO-2 are consistent. Thus, we suggest that NIST SRM 994 Ga is likely isotopic heterogeneity.

3.5 Gallium isotopic compositions of geological reference materials

Gallium is mainly enriched in bauxite and Pb–Zn ore deposits, and bauxite is mostly associated with epigenetic weathering of igneous rocks (Liu 1965, 1982; Tu et al. 2003). In this study, we conducted Ga isotope analysis of 11 geological reference materials. BCR-2 and BHVO-2 were digested and analysed in five replicates, and the remaining samples were analysed in triplicate. The results are presented in Table 5. The Ga isotopic compositions of two bauxite reference materials (GBW07181 and GBW07182) are not fractionated, and they have $\delta^{71}Ga_{NIST994}$ values of 1.17 ‰ ± 0.07 ‰ and 1.18 ‰ ± 0.08 ‰ ($\delta^{71}Ga_{IPGP} = -0.08$ ‰ and − 0.07 ‰), respectively. The $\delta^{71}Ga_{NIST994}$ values of the zinc concentrate (GBW07168) and Pb–Zn ore (GBW07372) are 1.12 ‰ ± 0.07 ‰ and 1.21 ‰ ± 0.10 ‰ ($\delta^{71}Ga_{IPGP} = -0.13$ ‰ and − 0.04 ‰), respectively. The $\delta^{71}Ga_{NIST994}$ values of the Emeishan basalt (GBW07126) and andesite (GBW07104) are 1.22 ‰ ± 0.07 ‰ and 1.27 ‰ ± 0.07 ‰ ($\delta^{71}Ga_{IPGP} = -0.03$ ‰ and 0.02 ‰), respectively, similar to the $\delta^{71}Ga$ values for BCR-2 and BHVO-2. The $\delta^{71}Ga_{NIST994}$ values of the granite (GBW07103) and

Table 4 Barium interference correction data for NIST SRM 3119a and Alfa Aesar

Analytical session	NIST SRM 3119a Ga (lot: 140,124)				Alfa Aesar Ga (lot: 8,129,898)			
	$\delta^{71}Ga_{NIST994}$* (‰)	$\delta^{71}Ga_{NIST994\text{-}mea}$# (‰)	I_{sample} (10^{-5})	I_{sample}/I_{std}	$\delta^{71}Ga_{NIST994}$* (‰)	$\delta^{71}Ga_{NIST994\text{-}mea}$# (‰)	I_{sample} (10^{-5})	I_{sample}/I_{std}
1st	2.63	2.58	3.41	1.28	1.99	1.94	3.39	1.36
	2.67	2.63	3.22	1.24	2.03	1.97	3.44	1.31
	2.65	2.62	2.77	1.25	1.99	1.94	3.19	1.34
	2.58	2.54	3.21	1.30	2.00	1.94	3.37	1.33
	2.58	2.52	3.51	1.32				
2nd	2.64	2.60	2.98	1.27	2.03	1.96	3.14	1.45
	2.66	2.62	2.66	1.24	2.00	1.95	2.86	1.40
	2.62	2.58	2.72	1.29	2.04	1.99	2.82	1.33
	2.66	2.62	3.59	1.22	1.99	1.91	4.22	1.40
	2.62	2.58	3.50	1.25	1.99	1.94	3.65	1.33
	2.65	2.61	3.19	1.24				
3rd	2.62	2.59	2.98	1.16	2.03	1.95	4.34	1.43
	2.67	2.65	2.79	1.16	2.02	1.93	4.49	1.47
	2.69	2.67	2.81	1.16	2.05	1.98	4.22	1.38
	2.67	2.65	2.80	1.16	2.06	1.97	4.54	1.45
	2.62	2.59	3.49	1.13	2.03	1.95	4.40	1.42
4th	2.67	2.65	2.92	1.12	1.99	1.93	3.43	1.36
	2.63	2.59	2.94	1.22	2.04	2.00	3.09	1.23
	2.65	2.63	2.96	1.12	2.03	1.99	3.05	1.25
	2.66	2.65	2.72	1.11	2.01	1.97	3.00	1.25
	2.65	2.63	2.91	1.14	2.00	1.97	2.98	1.19
5th	2.61	2.56	2.10	1.29	2.00	1.94	2.28	1.32
	2.64	2.61	2.09	1.21	1.94	1.91	2.12	1.21
	2.61	2.58	2.27	1.18	1.94	1.89	2.28	1.27
	2.55	2.50	2.19	1.17	1.92	1.89	2.22	1.22
	2.59	2.56	2.13	1.17	1.91	1.90	2.24	1.21
Average	2.63 ± 0.07‰ (2sd,n = 26)	2.60 ± 0.08‰ (2sd,n = 26)	2.88	1.21	2.00 ± 0.08‰ (2sd,n = 24)	1.95 ± 0.06‰ (2sd,n = 24)	3.28	1.33

$\delta^{71}Ga_{NIST994}$* denotes the $\delta^{71}Ga_{NIST994}$ value after correction for Ba interference; $\delta^{71}Ga_{NIST994\text{-}mea}$# denotes the $\delta^{71}Ga_{NIST994}$ value without correction for Ba interference; I_{sample} denotes [$(I68.5/I69)_{sample}$], i.e., the ratio of the signal intensity of $^{137}Ba^{2+}$ in the sample solution to the signal intensity of ^{69}Ga; and I_{sample}/I_{std} denotes [$(I68.5/I69)_{sample}$]/[$(I68.5/I69)_{NIST994}$], i.e., the ratio of the signal intensity of $^{137}Ba^{2+}$ to the signal intensity of ^{69}Ga in the sample solution divided by the ratio of the signal intensity of $^{137}Ba^{2+}$ to that of ^{69}Ga in the NIST SRM 994 Ga isotopic standard

granodiorite (GBW07111) are 1.34 ‰ ± 0.11 ‰ and 1.35 ‰ ± 0.09 ‰ ($\delta^{71}Ga_{IPGP} = 0.09$ ‰ and 0.10 ‰), respectively, indicating the granite and granodiorite are slightly more enriched in the heavy Ga isotope than the basalts. The $\delta^{71}Ga_{NIST994}$ value of the loess (GBW07454) is 1.28 ‰ ± 0.08 ‰ ($\delta^{71}Ga_{IPGP} = 0.03$ ‰).

4 Conclusions

We investigated the maximum adsorption capacity of the AG 1-X4 and Ln-spec resin for matrix elements (Zn, Fe) during the purification process, and found that (1) the maximum Zn adsorption capacity of the AG 1-X4 anion resin is ~ 1180 μg/mL; (2) the maximum Fe adsorption capacity of the Ln-spec cation resin is ~ 870 μg/mL; and (3) the Cu

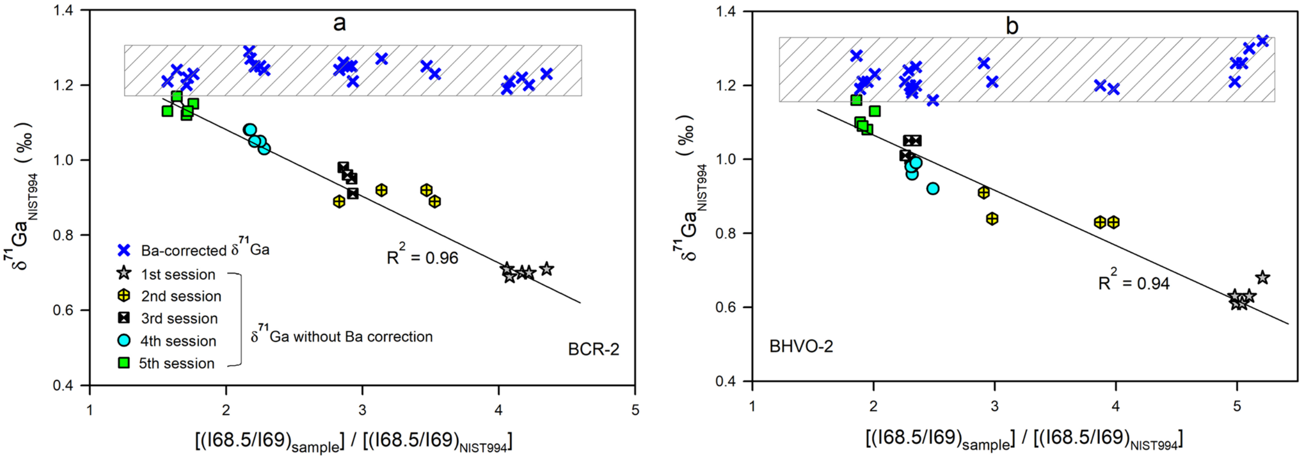


Fig. 4 Ba-corrected and -uncorrected δ^{71}Ga values versus Ba signal intensity

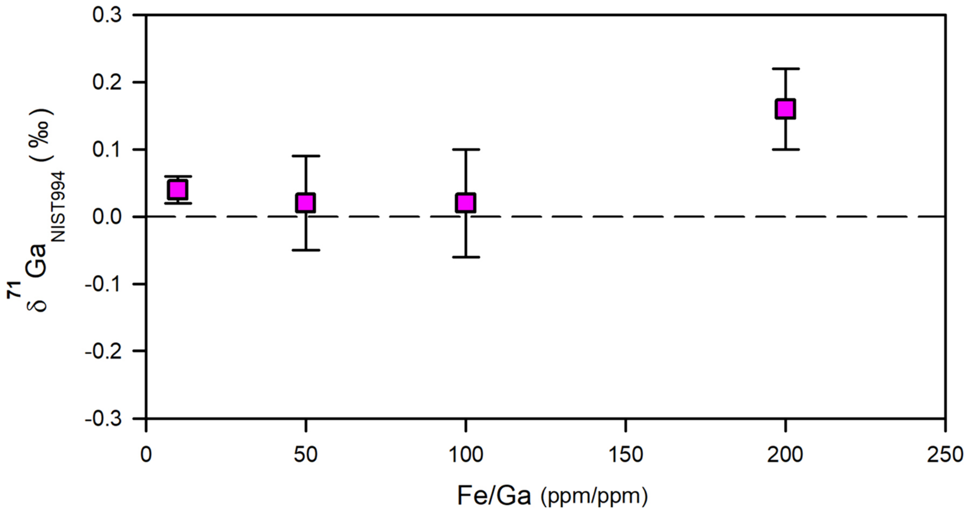


Fig. 5 δ^{71}Ga values of 0.2 μg/mL NIST SRM 994 Ga doped with various amounts of Fe

elution process in the AG 1-X4 anion resin exhibited an obvious ‘tailing effect’. Accordingly, the purification procedure was appropriately modified to make it suitable for Ga isotope measurements of the geological samples with high Zn and Fe contents.

By comparing the Ga isotopic compositions of geological standards (BCR-2 and BHVO-2) with and without Ba correction, the $\delta^{71}Ga_{NIST994}$ values are varied, suggesting that efficient separation of Ba and correcting the interference of $^{138}Ba^{2+}$ are crucial to obtain accurate δ^{71}Ga values. By comparing the Ga isotope data from different laboratories, we suggest that the isotopic heterogeneity from NIST SRM 994 Ga is likely the key reason that results in the differences in $\delta^{71}Ga_{NIST994}$ values for BCR-2 and BHVO-2 reported in the literatures.

The Ga isotopic compositions of 11 geological reference materials were determined, including two Pb-Zn ores (GBW07168 and GBW07372), two bauxites (GBW07181 and GBW07182), three basalts (BCR-2, BHVO-2, and GBW07126), one granite (GBW07103), one andesite (GBW07104), one granodiorite (GBW07111), and one loess (GBW07454). We also measured the Ga isotopic compositions of two standard solutions (NIST SRM 3119a and Alfa Aesar). The $\delta^{71}Ga_{NIST994}$ values of these

Table 5 Gallium isotopic compositions of geological reference materials

Sample	Description	#Ga (μg/g)	$\delta^{71}Ga_{NIST994}$ (‰)	2sd	n	$\delta^{71}Ga_{IPGP}$ (‰)	$\delta^{71}Ga_{NIST3119a}$ (‰)
GBW07181	Bauxite, (CRM, China)	82 ± 15	1.18	0.06	3	−0.07	−1.45
	Parallel sample		1.19	0.03	3	−0.06	−1.44
	Parallel sample		1.13	0.06	3	−0.12	−1.50
Mean			1.17	0.07	9	−0.08	−1.46
GBW07182	Bauxite, (CRM, China)	72 ± 11	1.19	0.11	3	−0.06	−1.44
	Parallel sample		1.21	0.04	3	−0.04	−1.42
	Parallel sample		1.14	0.01	3	−0.11	−1.49
Mean			1.18	0.08	9	−0.07	−1.45
GBW07168	Zinc concentrate (ZnS), (CRM, China)	180 ± 31	1.16	0.06	3	−0.09	−1.47
	Parallel sample		1.12	0.06	3	−0.13	−1.51
	Parallel sample		1.09	0.01	3	−0.16	−1.54
Mean			1.12	0.07	9	−0.13	−1.51
GBW07372	Pb – Zn ore, (CRM, China)	30.7 ± 1.9	1.20	0.11	3	−0.05	−1.43
	Parallel sample		1.26	0.04	3	0.01	−1.37
	Parallel sample		1.17	0.01	3	−0.08	−1.46
Mean			1.21	0.10	9	−0.04	−1.42
GBW07126	Emeishan basalt, (CRM, China)	24.8 ± 2.0	1.19	0.05	3	−0.06	−1.44
	Parallel sample		1.20	0.05	3	−0.05	−1.43
	Parallel sample		1.26	0.04	3	0.01	−1.37
Mean			1.22	0.07	9	−0.03	−1.41
GBW07104	Andesite, (CRM, China)	18.1 ± 1.4	1.28	0.03	3	0.03	−1.35
	Parallel sample		1.23	0.04	3	−0.02	−1.40
	Parallel sample		1.30	0.01	3	0.05	−1.33
Mean			1.27	0.07	9	0.02	−1.36
GBW07103	Granite, (CRM, China)	19 ± 2	1.36	0.02	3	0.11	−1.27
	Parallel sample		1.40	0.05	3	0.15	−1.23
	Parallel sample		1.27	0.01	3	0.02	−1.36
Mean			1.34	0.11	9	0.09	−1.29
GBW07111	Granodiorite, (CRM, China)	20.8 ± 1.6	1.39	0.06	3	0.14	−1.24
	Parallel sample		1.36	0.04	3	0.11	−1.27
	Parallel sample		1.29	0.01	3	0.04	−1.34
Mean			1.35	0.09	9	0.10	−1.28
GBW07454	Loess, (CRM, China)	14.9 ± 0.4	1.31	0.07	3	0.06	−1.32
	Parallel sample		1.23	0.03	3	−0.02	−1.40
	Parallel sample		1.29	0.04	3	0.04	−1.34
Mean			1.28	0.08	9	0.03	−1.35
BCR-2	Basalts, (USGS, USA)	23 ± 2	1.24	0.05	23	−0.01	−1.39
BHVO-2	Basalts, (USGS, USA)	21.7 ± 0.9	1.22	0.08	23	−0.03	−1.41
NIST 3119a Ga	lot: 140,124, (NIST, USA)		2.63	0.07	26	1.38	0
Alfa Aesar Ga	lot: 8,129,898		2.00	0.08	24	0.75	−0.63

CRM: Chinese Reference Materials; *USGS:* United States Geological Survey; *NIST:* National Institute of Standards and Technology. The $\delta^{71}Ga_{IPGP}$ values were calculated in this way. The δ^{71}Ga of NIST 3119a Ga is + 2.63 ± 0.07‰ relative to NIST 994 Ga. Kato et al. (2017) reported that the δ^{71}Ga value of NIST 3119a Ga was + 1.38 ± 0.06‰ relative to the IPGP Ga standard. Thus, we calculated the δ^{71}Ga value of NIST 994 Ga relative to IPGP Ga standard as –1.25‰. Ga content is the recommended values (http://m.crmrm.com/; https://www.nist.gov/srm)

reference materials vary from 1.12 ‰ to 2.63 ‰ (−0.13 ‰ to 1.38 ‰ for $\delta^{71}Ga_{IPGP}$; Table 5).

Acknowledgements This research was financially supported by the National Natural Science Foundation of China (Grant Nos. 42273016 and 41573007) and a special fund managed by the State Key Laboratory of Ore Deposit Geochemistry.

Author contributions Yuxu Zhang and Hanjie Wen designed research; Yuxu Zhang and Chuanwei Zhu provided samples; Yuxu Zhang and Pan Qiao measured samples; Yuxu Zhang provided funding sources; Yuxu Zhang, Hanjie Wen, Chuanwei Zhu, Haifeng Fan and Pan Qiao interpreted data; Yuxu Zhang drafted the paper with comments from other co-authors.

Declarations

Conflict of interest The authors declare no competing interests.

References

De Laeter JR (1972) The isotopic composition and elemental abundance of gallium in meteorites and in terrestrial samples. Geochim Cosmochim Acta 36:735–743.

Feng LP, Zhou L, Liu JH, Hu ZC, Liu YS (2019) Determination of gallium isotopic compositions in reference materials. Geostand Geoanal Res 43:701–714.

Hou QH, Zhou L, Gao S, Zhang T, Feng L, Yang L (2016) Use of Ga for mass bias correction for the accurate determination of copper isotope ratio in the NIST SRM 3114 Cu standard and geological samples by MC-ICP-MS. J Anal at Spectrom 31:280–287.

Inghram MG, Hess DCJ (1948) On the isotopic composition of meteoritic and ter-restrial Gallium. Phys Rev 74:343–344.

Kato C, Moynier F (2017a) Gallium isotopic evidence for extensive volatile loss from the moon during its formation. Sci Adv 3:e1700571.

Kato C, Moynier F (2017b) Gallium isotopic evidence for the fate of moderately volatile elements in planetary bodies and refractory inclusions. Earth Planet Sci Lett 479:330–339.

Kato C, Moynier F, Foriel J, Teng FZ, Puchtel IS (2017) The gallium isotopic composition of the bulk silicate Earth. Chem Geol 448:164–172.

Lauwens S, Costas-Rodríguez M, Vanhaecke F (2018) Ultra-trace Cu isotope ratio measurements via multi-collector ICP-mass spectrometry using Ga as internal standard: an approach applicable to micro-samples. Anal Chim Acta 1025:69–79.

Liu YJ (1965) Several geochemical characters of gallium in some Chinese bauxite deposits. Geological Review 23:42–49 (**in Chinese**).

Liu YJ (1982) Chief genetical types of gallium-bearing deposits in China. Mineral Deposits 1:51–60 (**in Chinese with English abstract**).

Liu JH, Cheng J, Zhou L, Feng LP, Hu TY, Algeo TJ (2022) Copper and gallium isotopic behavior in highly weathered soils. Chem Geol 594:120757.

Render J, Wimpenny J, Borg L (2023) Gallium isotopic constraints for the origin of the earth-moon system. Earth Planet Sci Lett 611:118146.

Roland J, Debaille V, de Jong J, Goderis S (2023) Comparison of two gallium purification procedures for isotopic measurements by MC-ICP-MS in a set of silicate reference materials. Talanta 263:124714.

Tu GC, Gao ZM, Hu RZ, Zhang Q, Li CY, Zhao ZH, Zhang BG (2003) The geochemistry and ore-forming mechanism of the dispersed elements. Geol Publ House 5:368–395 (**in Chinese**).

Wen J, Zhang YX, Wen HJ, Ling KY, Zhu CW, Fan HF (2021) Gallium isotope fractionation in the Xiaoshanba bauxite deposit, central Guizhou Province, southwestern China. Ore Geol Rev 137:104299.

Wimpenny J, Marks N, Knight K, Borg L, Badro J, Ryerson F (2020) Constraining the behavior of gallium isotopes during evaporation at extreme temperatures. Geochim Cosmochim Acta 286:54–71.

Wimpenny J, Borg L, Sio CKI (2022) The gallium isotopic composition of the moon. Earth Planet Sci Lett 578:117318.

Wombacher F, Rehkämper M, Mezger K, Münker C (2003) Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. Geochim Cosmochim Acta 67(23):4639–4654.

Yuan W, Chen JB, Birck JL, Yin ZY, Yuan SL, Cai HM, Wang ZW, Huang Q, Wang ZH (2016) Precise analysis of gallium isotopic composition by MC-ICP-MS. Anal Chem 88:9606–9613.

Yuan W, Saldi GD, Chen JB, Zuccolini MV, Birck JL, Liu YJ, Schott J (2018) Gallium isotope fractionation during Ga adsorption on calcite and goethite. Geochim Cosmochim Acta 223:350–363.

Yuan W, Chen JB, Teng H, Chetelat B, Cai H, Liu J, Wang Z, Bouchez J, Moynier F, Gaillardet J, Schott J, Liu C (2021) A review on the elemental and isotopic geochemistry of gallium. Glob Biogeochem Cycles 35:e2021GB007033.

Yuan W, Gong YZ, Chen JB, Wang ZR, Huang F, Yang XJ, Chetelat B, Teng H, Schott J (2022) Gallium isotope constraints on the intense weathering of basalt. Geochim Cosmochim Acta 333:22–38.

Zhang T, Zhou L, Yang L, Wang Q, Feng LP, Liu YS (2016) High precision measure-ments of gallium isotopic compositions in geological materials by MC-ICP-MS. J Anal at Spectrom 31:1673–1679.

Zhang YX, Liao SL, Tao CH, Wen HJ, Fan HF, Wen J, Yang WF, Li W (2021) Ga isotopic fractionation in sulfides from the Yuhuang and Duanqiao hydrothermal fields on the Southwest Indian ridge. Geosci Front 12:101137.