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High Precision Measurements of Gallium Isotopic Composition in Geological Materials by MC-ICP-MS

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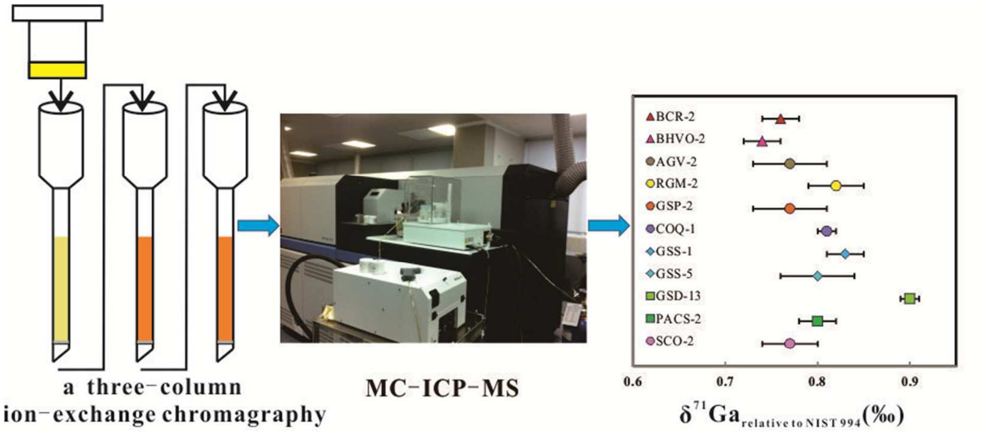
Content entry

A new MC-ICP-MS approach is reported for the high precision and accuracy determination of Ga isotope ratio in geological samples.



Abstract

An analytical protocol for the accurate and precise determination of gallium isotope ratio in geological materials is presented for the first time by using multi–collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Separation of Ga from natural sample matrices was achieved by using a three-column ion-exchange chromatography with one anion exchange AG MP-1M column and two cation exchange AG 50W-X8 columns. This approach provides an efficient purification of Ga from an excess amount of Fe existed in geological samples, with low blank and high yield. The instrument mass bias was monitored and corrected by using a model of standard-sample bracketing with internal normalization, and copper was used as an internal standard which was added to both sample and standard solutions. The long-term external reproducibility of $\delta^{71/69}$Ga obtained is 0.04‰ (2SD). Ga isotopic compositions of geological reference materials including basalt, andesite, rhyolite, granodiorite, soil, sediment, carbonatite and shale were measured using the proposed approach. The ^{71}Ga/^{69}Ga ratio in these geological reference materials spanned over a rather narrow range between 0.74‰ and 0.90‰, relative to NIST SRM 994.

Keywords: gallium isotope, MC-ICP-MS, instrument mass bias correction, matrix effects, geological samples

Introduction

Gallium is a wide-spread trace element in the curst, and the abundance of gallium is about 16 ppm in the crust.[1] Gallium has two stable isotopes of *m/z* 69 and 71, with relative abundances of 60.10% and 39.90%, respectively.[2, 3] Since the electric charge, ion diameter, coordination number and electronic configuration are similar between Ga^{3+} and Fe^{3+}, thus the chemical behavior of these two is very similar.[4] As a siderophile element, the Ga isotopic composition in chondrites and the terrestrial samples is significantly different.[5, 6] Therefore, gallium isotopic composition can be used as a potential geochemical tracer in the study of the early history of the solar system and the processes of nucleo-synthesis. In addition, Ga is extensively used in the semiconductor industries and medical field, and combustion of fossil fuels can contribute to the Ga discharge to the environment.[7-11] Because of the Ga-associated waste may result in environmental problems,[10, 12] the investigation of Ga isotope ratio may be applied in the field of the environment. Up to date, very few measurements have been made on the isotopic composition of Ga since the early work of Aston *et al.*[13] and Sampson *et al.*[14] Furthermore, the high precision Ga isotope ratio measurements using MC-ICP-MS is rare, apart from Kato *et al.*[6] used MC-ICP-MS for obtaining Ga isotopic composition of iron meteorites.

The main challenges in high precision isotope ratio measurements are to obtain pure Ga through purification procedure and to correct the instrument mass bias properly. For gallium purification from sample matrices, chemical precipitation,[15] complexation,[16] solvent extraction,[17] and ion exchange,[18] have been developed to extract of gallium in industrial applications. Ion exchange resin was used for the separation of Ga in previous studies[19-21], but these studies focused on the Ga isotope fractionation on the column. De Laeter *et al.* first reported to use Dowex AG1 X10 and Dowex AG 50 X8 to purify Ga from iron meteorites sample.[5] To date, there is no systematic protocol available for the separation/purification of gallium from geological samples.

In the early days, gallium isotopic composition measurements were undertaken with thermal ionization mass spectrometry (TIMS), and the precision of the ^{69}Ga/^{71}Ga ratio is $\leq$ 0.01% (1SD).[22, 23] Compared to TIMS, the advantages of MC-ICP-MS, especially its high sample throughput and simple sample introduction process, have made it a powerful tool for the accurate determination of isotopic compositions of several elements, such as copper[24, 25], iron[26, 27], zinc[28, 29], molybdenum[30, 31], strontium[32, 33], neodymium[34], lead[35, 36] and so on. However, MC-ICP-MS suffers larger mass bias but much smaller drift over time than TIMS, proper correction of the mass bias is of importance to generate accurate isotope ratio results. In addition to instrument mass bias, matrix-depended non-spectral mass discrimination induced by changes in sample matrix would also influence the accuracy of isotope ratios. To compensate non-spectral mass discrimination, it requires near a perfect analyte separation to eliminate matrix elements. In terms of correction of mass bias, various methods have been employed, such as the direct sample-standard bracketing (SSB) model[27] and the internal mass bias correction model[37] whereas a pair of isotopes of another “suitable” element was added with use of Russell equation for mass bias correction. As demonstrated in previous studies[32, 33, 38, 39], the model of combined SSB with internal mass bias correction can produce more accurate and precise isotope ratios, where by an internal standard element is added to both sample and standard; and close matching of concentrations of both analyte and internal standard element in the sample and standard is required. The main advantage of this model is that short-term fluctuations in the instrument mass bias during bracketing standard are corrected.

The purpose of this work was to develop a protocol for high precision Ga isotope ratio measurements in geological samples by MC-ICP-MS after column separation. A three-column ion-exchange setup was employed to purify Ga from sample matrices; anion-exchange column was used to separate most matrix elements from Ga followed by cation-exchange column to separate all of Fe from Ga, and finally another same cation-exchange column to further remove residual Fe. The MC-ICP-MS measurement protocol utilizes the model of combined SSB with internal normalization of Cu to correct for instrument mass bias. The certified reference value of $^{71}Ga/^{69}Ga$ in NIST SRM 994 was employed to calibrate the $^{65}Cu/^{63}Cu$ ratio in the two adjacent bracketing standards; their average value of $^{65}Cu/^{63}Cu$ was then used to correct the $^{71}Ga/^{69}Ga$ ratio in the sample. This developed protocol was applied successfully for the determination of Ga isotope ratio in geological samples.

Experimental

Sample dissolution, chemical separation and measurements by MC-ICP-MS were done at the State Key Laboratory of Geological Processes and Mineral

Resources, Wuhan, China. In order to reduce the process blank, all sample preparation was conducted in a metal-free clean room with an HEPA-filtered air supply and under laminar flow hoods.

Instrumentation

A quadrupole ICP-MS (POEMS Ⅲ ICP-MS, Agilent Technologies, Yokogawa, Japan) was used to measure matrix element concentrations in collected Ga fractions from three columns. Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) was used for the Ga isotope ratio measurements. The instrument is equipped with nine moveable Faraday cups and a PFA Teflon self-aspirating nebulizer MCN50 (Elemental Scientific, Omaha NE) operating at $50 \mu L \cdot min^{-1}$.

Reagents

Nitric acid and hydrofluoric acid were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a DST-1000 acid purification system (Savillex, Eden Prairie, USA). Hydrochloric acid was prepared by dilution of Suprapur® grade hydrochloric acid (Merck KGaA., Darmstadt, Germany) with High-purity deionized water (Millipore, Billerica MA, USA).

The isotopic certified reference material NIST SRM 994 Ga and the isotopic material solution NIST SRM 3114 Cu were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg MD, USA). The certified value of $^{69/71}$Ga = 1.50676 ± 0.00039 (U, at 95% confidence interval) in NIST SRM 994 Ga was determined by thermal-ionization mass spectrometry[22], which was used as standard. The plasma standard gallium solution (Alfa Aesar, Karlsruhe, Germany, batch 626491D) was used as an in-house (shelf) standard. The internal standard element used was NIST 3114 Cu with $^{65}Cu/^{63}Cu = 0.4470 \pm 0.0013$ (2SD, *n = 37*) by Hou *et al*.[39]

A 2000 $mg \cdot kg^{-1}$ stock solution of NIST SRM 994 was prepared by quantitative dissolution of Ga in concentrated HNO_3 and HCl with heating, and then diluted with deionized water. NIST SRM 3114 Cu was used as the internal standard, and was added to both the sample and standard solutions. Gallium standard solution of 200 $ng \cdot g^{-1}$ Ga was prepared by diluting the Ga stock solution in 2% HNO_3 followed by spiking with the Cu standard solution, NIST SRM 3114 Cu, yielding a mass fraction of 200 $ng \cdot g^{-1}$. The purified Ga solutions from geological samples were diluted to 200 $ng \cdot g^{-1}$ and spiked with Cu standard solution, yielding a mass fraction of 200 $ng \cdot g^{-1}$ for Cu.

Geological reference materials of BCR-2, BHVO-2 (Basalt) and AGV-2 (Andesite), RGM-2 (Andesite), COQ-1 (carbonatite), SCO-2 (shale) and GSP-2 (granite) purchased from United States Geological Survey (Reston, VA, USA), including GSS-1, GSS-5 (soil) and GSD-13 (sediment) from GBW (China) and PACS-3 (sediment) from National Research Council Canada (Ottawa, Canada) were used as test samples for Ga isotope ratio measurements.

Sample Dissolution

Gallium concentrations in tested geological samples are roughly at 20 $\mu g \cdot g^{-1}$, and thus each 50 mg of samples was used to contain approximately 1μg Ga for isotope ratio measurements. All samples were digested using Teflon capsules sealed in stainless steel bombs. In brief, each 50 mg of powdered rock samples was dissolved in 3 ml concentrated HF-HNO_3 (1:1) mixture at 190℃ for 48 hours in an oven. The contents were transferred to Teflon beakers and were evaporated to dryness on a hot plate at 100^{o}C, and then each sample was treated with a small amount of concentrated HNO_3 and was evaporated to dryness to drive off fluorides completely. Contents were re-dissolved in 1ml 7 N HCl + 0.03% H_2O_2 solution and maintained at 120℃ for 12 hours in an oven. The contents were then heated at 100℃ on the hot plate to dryness. Each 0.25 ml 7 N HCl + 0.03% H_2O_2 was added to the sample and then evaporated to dryness in order to achieve complete HCl surroundings. This procedure was repeated three times to ensure that all cations were converted to chloride species. Note that H_2O_2 was added to aid the digestion of any possible organic substances existing in the sample matrices and to maintain metals in high oxidation states for column separation. At 0.03% H_2O_2 concentration level, no visible bubbles and aversive effects were observed during the column separation. Finally, each 1ml 7 N HCl + 0.03% H_2O_2 solution was added to dissolve the residue prior to the purification of gallium from sample matrices.

Chemical Separation

Purification of Ga from sample matrices was achieved by using three column separation with one anion exchange column containing 1.5 ml pre-cleaned AG MP-1M anion exchange resin (Bio-Rad, 100–200 mesh) to remove most matrix elements, second column containing 1.5 ml cation exchange resin AG 50W-X8 (Bio-Rad, 200-400 Mesh) to remove most Ge and Fe, and the third column containing the same AG 50W-X8 resin to further remove the residual amount of Fe. The column separation procedure is summarized in Table.1.

The anion AG MP-1M column was first cleaned twice with 10 ml of 2 N HNO_3 and 10 ml of 2 N HCl, respectively. Prior to loading the sample, the column was conditioned in 7 N HCl + 0.03% H_2O_2. The sample was loaded and the column was washed with 14 ml 7 N HCl + 0.03% H_2O_2 to remove matrix elements (e.g., Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Pr, Nd, Cu and Co). All Ga along with Ge and Fe eluted with 4 ml of 2 N HCl + 0.03% H_2O_2. This collected Ga fraction in Teflon vial was heated to dryness, and then re-dissolved in 1ml 2.1 N HCl + 0.03% H_2O_2 solution prior to the second column separation.

Similarly, the second cation exchange AG 50W-X8 column was cleaned with twice 10 ml 6 N HCl. The column was conditioned in 2.1 N HCl + 0.03% H_2O_2. It was found that Ge and most of Fe were effectively rinsed off with 2.8 ml of 2.1 N HCl + 0.03% H_2O_2, and Ga fraction was collected with another 5 ml 2.1 N HCl + 0.03% H_2O_2. The collected Ga fraction was heated to dryness and re-dissolved in 1ml 2.1 N HCl + 0.03% H_2O_2 solution prior to the third column separation which is identical to the second column separation, in order to remove the residual amount Fe. The final collected Ga fraction was dried completely, and re-dissolved in 1 ml 2% HNO_3 prior to ICP-MS measurements.

The efficiency of Ga separation was evaluated using five geological reference materials BCR-2, AVG-2, BHVO-2, RGM-2 and GSP-2 which contain Fe_2O_3 9.65%, 8.63%, 4.68%, 1.3% and 3.43%, respectively. Collected Ga fractions from three columns were analyzed by a quadrupole ICP-MS (POEMS Ⅲ ICP-MS, Agilent Technologies, Yokogawa, Japan) to obtain matrix elements concentrations relative to Ga concentration (expressed as the ratio of the individual matrix element concentration to the Ga concentration).

MC-ICP-MS measurements

Optimization of the Neptune was performed daily, and typical operating conditions are summarized in Table.2. The gain calibration for each Faraday cup was performed daily to ensure correction for its efficiency. Instrumental background and acid matrix blank were monitored by on-peak acid blank measurements taken before every sample and standard. Samples were introduced into the plasma through a self-aspiration nebulizer at a flow rate of 50 $\mu L \cdot min^{-1}$, connected to a combined Scott spray chamber on top and cyclonic spray chamber on the bottom. Prior to each sample analysis, 2% HNO_3 was introduced for 2 min to reduce background. Intensities of Ga and all other measured isotopes of interest (see below) obtained from a blank solution of 2% HNO_3 was subtracted from those of both samples and standard. A static run was employed to collect ^{69}Ga and ^{71}Ga, and ^{63}Cu and ^{65}Cu isotopes simultaneously using the Faraday cup configuration shown in Table 2. Samples and standard were introduced into MC-ICP-MS in the following sequence: NIST 994 – sample – NIST 994. The Ga isotopic composition of the samples was expressed relative to the standard reference material NIST SRM 994 in a delta (per mil) notation:

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

Three replicate measurements or more of each sample was performed.

Results and discussion

Mass bias correction

To achieve accurate and precise Ga isotope ratio measurements by MC-ICP-MS, instrument mass bias needs to be corrected. In this study, mass bias correction was followed previous studies[32, 39], using a model of combined standard-sample bracketing and internal normalization (C-SSBIN). The main advantage of this model is that short-term fluctuations in the instrument mass bias during bracketing standards are corrected, but matrix induced mass bias cannot be compensated. In order to ensure accurate measurement results, concentrations of the analyte Ga and the internal standard element Cu in the sample and standard were matched within 5%. The certified value of 1.50676 ± 0.00039 for ^{69}Ga/^{71}Ga of SRM 994 ($R^{69/71}_{SRM\ 994}$) and the measured (uncorrected) value of ^{69}Ga/^{71}Ga of SRM 994 ($r^{69/71}_{SRM\ 994}$) were used to calculate the fractionation factor of Ga (f^{Ga}) in two adjacent bracketing standard solutions using equ (2) of Russell's law.[40] Assuming identical mass bias for two elements, $f^{Ga} = f^{Cu}$, the fractionation factor (f^{Ga}) and the measured value of ^{65}Cu/^{63}Cu of SRM 3114 ($r^{65/63}_{SRM\ 994}$) were used to calculate the mass bias corrected ratio of ^{65}Cu/^{63}Cu in standard solution of SRM 994 using eqn (3) of Russell's law.

$$f^{Ga} = \frac{ln\left(\frac{R^{69/71}_{SRM\ 994}}{r^{69/71}_{SRM\ 994}}\right)}{ln\left(\frac{m_{71}}{m_{69}}\right)} \qquad (2)$$

$$R^{65/63}_{SRM\ 994} = r^{65/63}_{SRM\ 994}\left(\frac{m_{63}}{m_{65}}\right)^{f^{Ga}} \qquad (3)$$

$$f^{Cu} = \frac{ln\left(\frac{R^{65/63}_{SRM\ 994}}{r^{65/63}_{Sample}}\right)}{ln\left(\frac{m_{63}}{m_{65}}\right)} \qquad (4)$$

$$R_{Sample}^{71/69} = r_{Sample}^{71/69}\left(\frac{m_{69}}{m_{71}}\right)^{f^{Cu}} \qquad (5)$$

Here R is the true isotope ratio, r is the measured (uncorrected) isotope ratio, m is the nuclide masses[2], and f is the fractionation factor. The average value of ^{65}Cu/^{63}Cu in two adjacent standard solutions was then used to calculate the mass bias corrected Ga isotope ratio in the sample using eqns (4) and (5). Note that Cu internal standard in the sample serves as the mass-bias correction proxy to allow for correction of time-dependent variation of the mass bias. Thus, the absolute value of the Cu isotope ratio is not needed. Even though the absolute value obtained for the Cu isotope ratio may itself be biased due to the limitations of the employed mass-bias correction model (e.g., assumption $f^{Ga}=f^{Cu}$), this bias is largelynegated in the second step of the calibration (Cu → Ga). This assumption is only fully valid if matrix and concentration matching is fully attained.

Results from the measurements of an in-house standard Alfa Ga solution relative to NIST SRM 994 using direct SSB (Fig.1a) and C-SSBIN (Fig.1b) mass bias correction models, respectively, are presented in Fig.1. Values of δ^{71}Ga of 1.71 ± 0.07‰ (2SD, $n = 14$) and δ^{71}Ga of 1.72 ± 0.03‰ (2SD, $n = 14$) in the in-house standard Alfa Ga were obtained using mass bias models of SSB and C-SSBIN, respectively, an approximate 2-fold improvement in precision of δ^{71}Ga obtained by C-SSBIN compared to that obtained by only SSB approach. Therefore, the model of C-SSBIN mass bias correction was selected for all subsequent analysis.

As shown in Fig.2, a long-term reproducibility of Ga isotope ratio measurements during a period of four months using the chosen C-SSBIN mass bias correction was found to be better than 0.04% (2SD) for ^{71}Ga/^{69}Ga.

Fractionation of chemical separation

Isotopic fractionation on ion-exchange resin was observed for gallium by Machlan *et al.*[19] However, Maréchal *et al.*[24] study on column separation of copper found no significant isotopic fractionation induced by ion-exchange purification when quantitative (near 100%) recovery of the copper is obtained. The recovery of purification procedure for Ga in this study was assessed by using five geological reference materials (BCR-2, AVG-2, BHVO-2, RGM-2, GSP-2), quantitative recovery from 94.7% to 99.0% (the average of 97.5 ± 3.0 %, 2SD, *n=10*) was obtained.

To investigate whether the isotopic fractionation of Ga occurred during the purification procedure, NIST SRM 994 Ga was added to the collected column fractions contain no Ga but all matrix elements from GSD-13 or SCO-2, respectively. These NIST SRM 994 Ga spiked matrix samples were purified using the proposed three-column ion-exchange separation procedure. Purified samples were then measured against pure SRM 994 Ga standard, and values of 0.04 ± 0.02‰ (2SD, $n = 3$) in the Ga spiked GSD-13 and 0.02 ± 0.03‰ (2SD, $n = 4$) in the Ga spiked SCO-2 for δ^{71}Ga were obtained, in agreement with the expected value of zero. These results confirmed that no isotopic fractionation occurred during the three-column separations. In addition, accurate Ga isotope ratio results can be obtained in geological samples using the proposed column separation procedure and measurement protocol.

Spectral interferences and matrix effects

Note that the C-SSBIN mass bias correction technique requires matrix and analyte concentrations matching between the sample and the standard solutions to ensure accurate measurement results. Matrix elements could induce spectral interferences and non-spectral mass discrimination (known as matrix effect). Potential polyatomic interferences on Ga isotopes include $^{53}Cr^{16}O^+$, $^{68}Zn^{1}H^+$, $^{29}Si^{40}Ar^+$, $^{32}S^{37}Cl^+$, $^{57}Fe^{12}C^+$ and $^{138}Ba^{2+}$ on $^{69}Ga^+$, and $^{55}Mn^{16}O^+$, $^{70}Ge^{1}H^+$, $^{31}P^{40}Ar^+$, $^{54}Fe^{16}O^{1}H^+$, $^{142}Ce^{2+}$ and $^{142}Nd^{2+}$ on $^{71}Ga^+$.[41] Clearly, elements such as Na, Mg, Al, Si, P, Ti and Mn are abundant in natural geological samples, and many polyatomic interferences arising from them could not be eliminated even with use of high resolution mode. Thus, purification of Ga from sample matrices is important to achieve accurate Ga isotope ratio measurements.

Polyatomic interferences arising from Te, Ba, Ce, La, Pr, Nd, Cr and V, are considered to be low since these elements are at trace levels in geological samples. Fortunately, the more abundant elements, including Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cs, Ba, La, Pr and Nd, were efficiently reduced to insignificant levels ($X/Ga < 0.001$) after the first anion exchange column separation. In addition, measured intensities for Ga isotopes in the 2% HNO_3 solution was at background levels of < 0.001 V, confirming insignificant contributions from $^{40}Ar^{14}N^{18}O^+$ and $^{40}Ar^{15}N^{16}O^+$ on ^{71}Ga. However, it was found that a small amount of residual Fe ($3 < Fe/Ga < 30$) still remained in the collected Ga fraction after passing the first anion AG MP-1M column and the second cation AG50W-X8 column. When the Fe/Ga concentration ratio is greater than 2, significant effect on Ga isotope ratio measurements is evident (see Fig. 3). In order to further remove the residual amount of Fe, third time cation AG50W-X8 column separation is necessary. The Fe/Ga in the final purified solution was found to be less than 0.06, its influence on Ga isotope measurements can be neglected. The overall procedure blank from three column separation was found to be 30 ± 2pg (*n* = *5*), sufficiently low for Ga ratio measurements in geological samples.

In order to assess the influence of matrix effects of the residual Fe and Ge in purified solutions on Ga isotope ratio measurements, 200 $ng \cdot g^{-1}$ Ga NIST 994 standard solutions were spiked with various amounts of Fe or Ge and Ga isotope ratio was measured against a pure 200 $ng \cdot g^{-1}$ Ga NIST 994 standard. As shown in Fig.3a, no significant effect was observed on δ^{71}Ga when concentration ratio of Fe/Ga was less than 2. Biased results for Ga isotope ratio (towards a lighter isotopic composition) were evident at higher concentration ratios of Fe/Ga. In this study, the geological samples were purified by passing through three columns to efficiently remove Fe and Ge, resulting in Fe/Ga ratio less than 0.06 in the final purified solutions, which has no significant effect on Ga isotope ratio measurements. Similarly, as shown in Fig.3b, the effect of Ge on δ^{71}Ga was insignificant when concentration ratio of Ge/Ga was less than 3. Significant effect on δ^{71}Ga was evident at higher Ge/Ga concentration ratios. The concentration ratios of Ge/Ga in purified solutions from geological samples were found to be less than 0.001. These observations confirm that accurate Ga isotope ratio results in geological samples can be obtained using the proposed three-column separation and MC-ICP-MS measurements since residual amounts of Fe and Ge in the final purified solutions are insignificant and their effects on Ga ratio measurements are negligible.

Results for geological reference materials

For the final Ga isotope ratio measurements in geological reference materials, three-column ion-exchange separations were applied to purify Ga from sample matrices. C-SSBIN mass bias correction was employed for obtaining Ga isotope ratio by MC-ICP-MS. Intensities of all measured isotopes obtained from the process blank were subtracted from those of all samples. The results of Ga isotopic composition in different types of geological reference materials are presented in Table 3. The δ^{71}Ga values for geological reference materials (basalt, andesite, rhyolite, granodiorite, soil, sediment, carbonatite, shale) show a narrow range from 0.74‰ to 0.90‰. The in-house standard Alfa Ga has a different value of δ^{71}Ga (1.71 ± 0.04‰, 2SD, *n = 94*), compared to NIST 994 Ga standard. Commercially available high-purity gallium is generally purified by electrolytic refining, fractional crystallization, electrolytic crystallization, vacuum rectification or vacuum pyrolysis. Results obtained in this study suggest that there might be someisotopic fractionation effects associated with these anthropogenic purification processes of Ga. These results are similar to the isotopic variation in commercial high-purity gallium observed by Gramlich *et al.*[23] Ga isotope ratio may potentially provide an isotopic marker for distinguishing anthropogenic smelter emissions from natural Ga contaminants.

Conclusion

A new, accurate and precise approach for the determination of Ga isotope ratio in geological samples is presented based on three column separations of matrices and MC-ICP-MS measurements. One anion exchange AG MP-1M column in combination with two cation exchange AG 50W-X8 columns provide an efficient and low blank purification of Ga from an excess of Fe in geological samples. No significant Ga isotopic fractionation is observed during column separation. The C-SSBIN mass bias correction approach, utilizing Cu as the internal standard element, provides approximate 2-fold improvement in the precision of δ^{71}Ga compared to that obtained by using the only SSB approach. A δ^{71}Ga value of 1.71 ± 0.04‰ (2SD, *n = 94*) of in-house standard Alfa Ga relative to NIST 994 is obtained. The proposed method is expected to have wide potential applications in geochemical and environmental research.

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Table.1 Column Separation Procedure

Anion exchange AG MP-1M column	**Step**	**Elements found**
2 × 10 ml 2 N HNO_3	clean	
10 ml 2 N HCl	clean	
3 ml DIW	clean	
3 ml 7 N HCl + 0.03% H_2O_2	condition	
Sample in 1 ml 7 N HCl + 0.03% H_2O_2	load	
14 ml 7 N HCl + 0.03% H_2O_2	rinse	Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Pr, Nd, Cu and Co
4 ml 2N HCl + 0.03% H_2O_2	elute	Ga, Fe and Ge
Cation exchange AG50W-X8column*	**Step**	**Elements found**
2 × 10 ml 6 N HCl	clean	
10 ml DIW	clean	
3 ml 2.1 N HCl + 0.03% H_2O_2	condition	
Sample in 1 ml 2.1 N HCl + 0.03% H_2O_2	load	
2.8 ml 2.1 N HCl + 0.03% H_2O_2	rinse	Ge and Fe
5 ml 2.1 N HCl + 0.03% H_2O_2	elute	Ga

* Third column separation is the same as the cation exchange AG 50W-X8 column

Table.2MC-ICP-MS Operating Conditions

Instrument Settings	
Forward power	1200W
Plasma gas flow rate	16.0 L Ar min^{-1}
Auxiliary gas flow rate	1.0 L Ar min^{-1}
Carrier gas flow rate	1.02 L Ar min^{-1}
Sample cone (H)	Nickel, 1.1 mm (orifice)
Skimmer cone (X)	Nickel, 0.88 mm (orifice)
Lens settings	Optimized for maximum analyte signal intensity and flat top peak
Date Acquisition Parameters	
Faraday cup configuration	L4 (^{63}Cu), L2 (^{65}Cu), C (^{67}Zn), H2 (^{69}Ga), H4 (^{71}Ga)
Mass resolution, $m/\triangle m$ at 5 and 95%	~300
sensitivity	7 V for ^{69}Ga at 200 ng·g^{-1}
Blank signal (2% HNO_3)	1 mV for ^{69}Ga
Signal integration time	4.194 s
No. of integrations, cycles, blocks	1, 10, 5

Table.3 Ga isotopic composition (mean, 2SD) of geological reference materials

Samples	Characters	δ^{71}Ga (‰)
NIST 994 Ga	Certified reference material	0.00 ± 0.03 (*n = 20*)
Alfa Ga	**In-house standard**	1.71 ± 0.04 (*n = 94*)
NIST 994 Ga	Add the matrix of GSD-2 and separated again	0.04 ± 0.02 (*n = 3*)
NIST 994 Ga	Add the matrix of SCO-2 and separated again	0.02 ± 0.03 (*n = 4*)
BCR-2	Basalt	0.76 ± 0.02 (*n = 4*)
BHVO-2	Basalt	0.74 ± 0.02 (*n = 8*)
AGV-2	Andesite	0.77 ± 0.04 (*n = 8*)
RGM-2	Rhyolite	0.82 ± 0.03 (*n = 10*)
GSP-2	Granodiorite	0.77 ± 0.04 (*n = 6*)
COQ-1	carbonatite	0.81 ± 0.01 (*n = 4*)
GSS-1	Soil	0.83 ± 0.02 (*n = 3*)
GSS-5	Soil	0.80 ± 0.04 (*n = 4*)
GSD-13	Sediment	0.90 ± 0.01 (*n = 3*)
SCO-2	shale	0.77 ± 0.03 (*n = 4*)
PACS-2	Sediment	0.80 ± 0.02 (*n = 4*)

Figure captions

Fig.1 Precision and accuracy of the two mass bias correction models for Ga isotope ratio in the Alfa Ga in-house standard relative to bracketing standard NIST 994 Ga, error bars are 2SD. (a) Direct SSB mass bias correction approach; (b) Proposed C-SSBIN mass bias correction approach. The measured solutions have Ga and Cu concentrations of 200 ng·g^{-1}.

Fig.2 Long-term reproducibility of Ga isotope ratio for Alfa Ga in-house standard in four months of eight measurement sessions. The measured solutions have Ga and Cu concentrations of 200 ng·g^{-1}. C-SSBIN mass bias correction approach was used.

Fig.3 Evaluation effects on δ^{71}Ga measurements from Fe (a) and Ge (b). The errors (2SD) were calculated based on at least three separate analytical sessions. C-SSBIN mass bias correction approach was used.

Figure 1

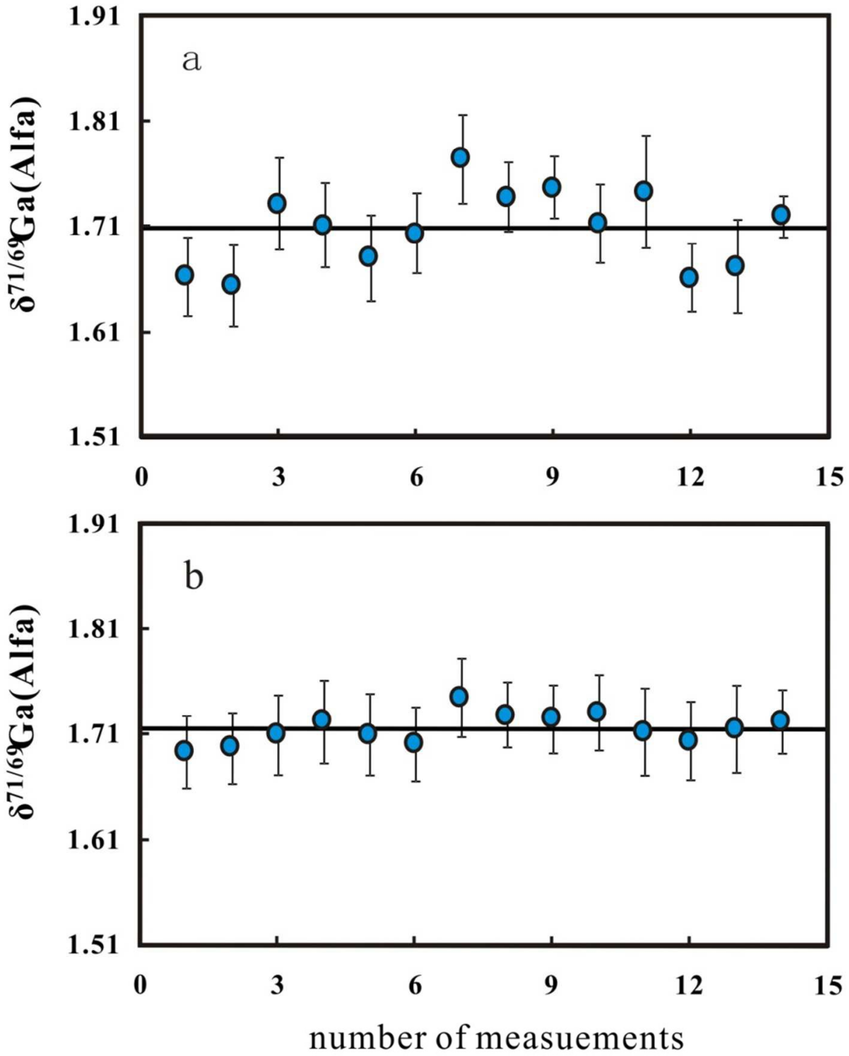

a
b
$\delta^{71/69}$Ga(Alfa)
1.91
1.81
1.71
1.61
1.51
0
3
6
9
12
15
number of measuements

Figure 2

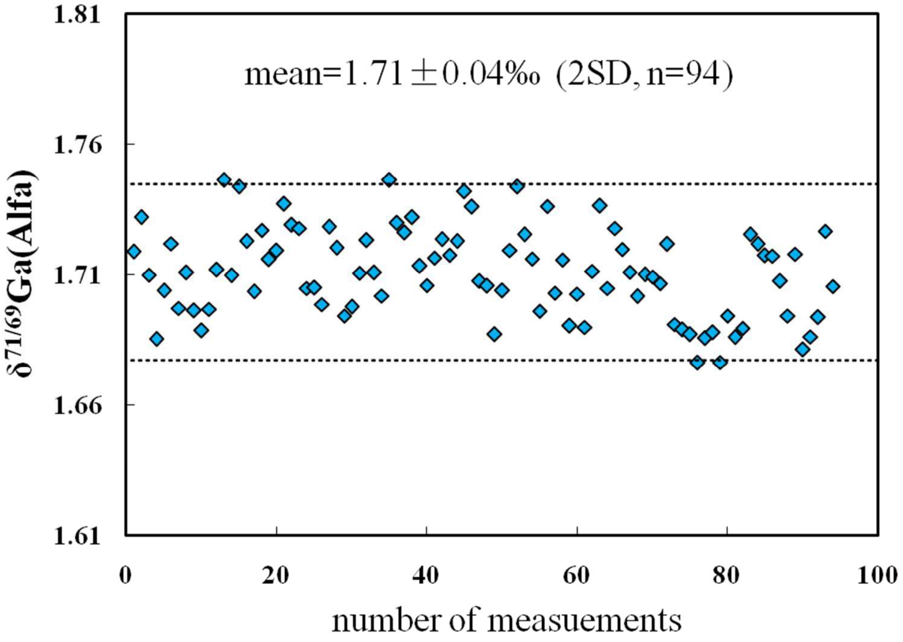
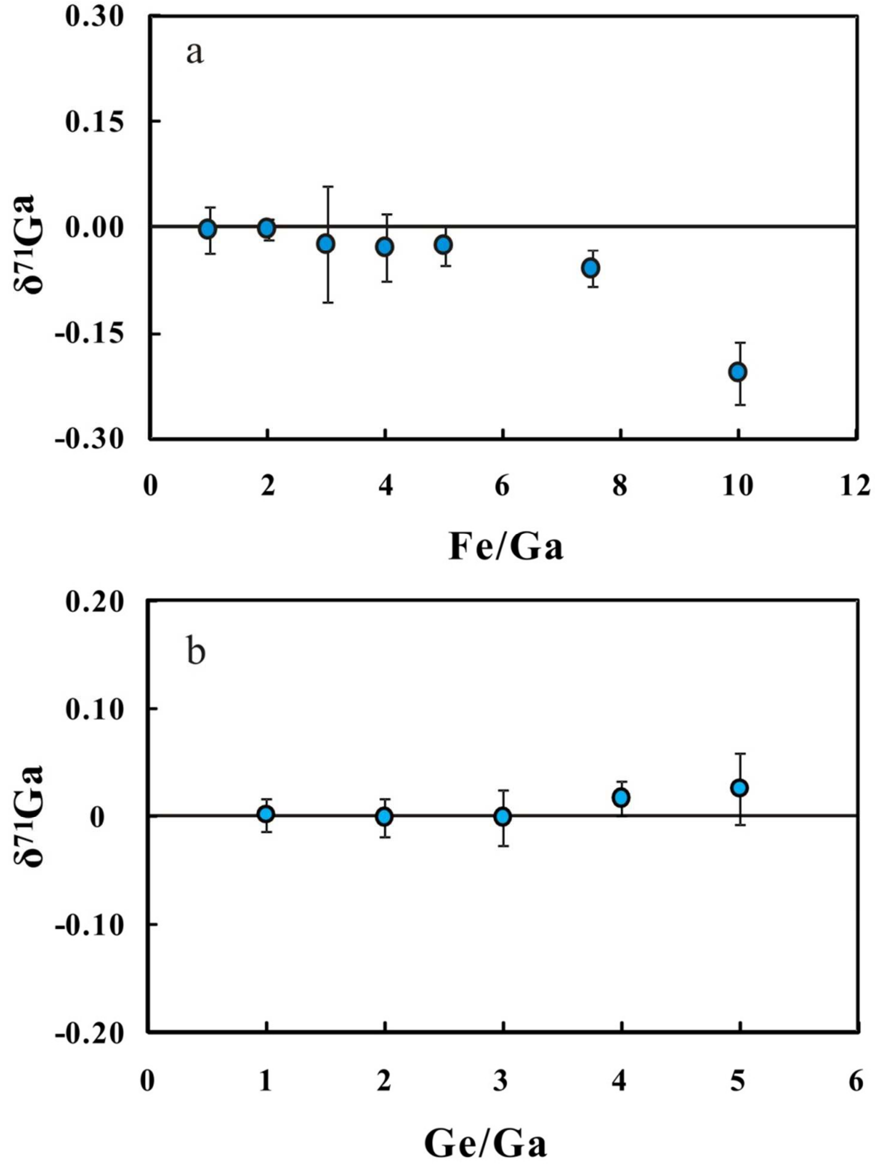

mean=1.71±0.04‰ (2SD, n=94)
1.81
1.76
1.71
1.66
1.61
δ71/69Ga(Alfa)
0
20
40
60
80
100
number of measuements

Figure 3


a
0.30
0.15
0.00
-0.15
-0.30
$\delta^{71}Ga$
0
2
4
6
8
10
12
Fe/Ga
b
0.20
0.10
0
-0.10
-0.20
$\delta^{71}Ga$
0
1
2
3
4
5
6
Ge/Ga