# Precise Analysis of Gallium Isotopic Composition by MC-ICP-MS

Wei Yuan,[†,‡] Jiu Bin Chen,[*,†] Jean-Louis Birck,[§] Zuo Ying Yin,[†] Sheng Liu Yuan,[†,‡] Hong Ming Cai,[†,‡] Zhong Wei Wang,[†,‡] Qiang Huang,[†] and Zhu Hong Wang[†]

[†]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guiyang 550081, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

[§]Laboratoire de Géochimie et Cosmochimie, Institute de Physique du Globe de Paris (IPGP), 75252 Paris, France

Ⓢ *Supporting Information*

ABSTRACT: Though an isotope approach could be beneficial for better understanding the biogeochemical cycle of gallium (Ga), an analogue of the monoisotopic element aluminum (Al), the geochemistry of Ga isotopes has not been widely elaborated. We developed a two-step method for purifying Ga from geological (biological) samples for precise measurement of Ga isotope ratio using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Ga was thoroughly separated from other matrix elements using two chromatographic columns loaded with AG 1-X4 and Ln-spec resin, respectively. The separation method was carefully calibrated using both synthetic and natural samples and validated by assessing the extraction yield (99.8 ± 0.8%, 2SD, $n = 23$) and the reproducibility (2SD uncertainty better than 0.05‰, $n = 116$) of the measured isotopic ratio (expressed as $\delta^{71}Ga$). The validation of the whole protocol, together with instrumental analysis, was confirmed by the investigation of the matrix effect, the result of a standard addition experiment, and the comparison of Ga isotope measurement on two mass spectrometers—Nu Plasma II and Neptune Plus. Although the measurements using the sample-standard bracketing (SSB) correction method on both instruments resulted in identical $\delta^{71}Ga$ values for reference materials, the modified empirical external normalization (MEEN) method gave relatively better precision compared to SSB on Neptune. Our preliminary results showed large variation of $\delta^{71}Ga$ (up to 1.83‰) for 10 standards, with higher values in industrially produced materials, implying potential application of Ga isotopes.
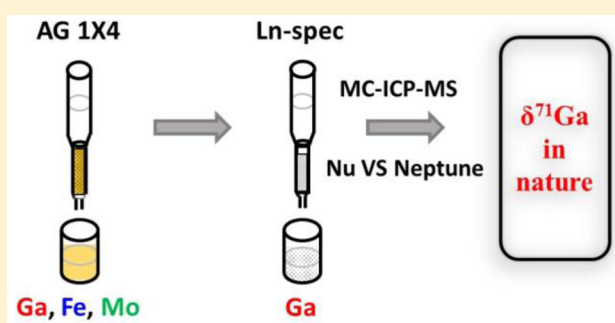
Discovered by P. E. Lecoq de Boisbaudran in 1875,[1] gallium (Ga) is a metallic element close to the nonmetals in the periodic table and has special physiochemical characteristics and important economic value; therefore, it is of great interest in many research aspects. Over the past decades, significant advancements about Ga geochemistry have been achieved based mainly on the analysis of Ga concentration and species. Generally, Ga exists primarily in a trivalent state (Ga^{3+}), and its free elemental form (Ga^0) is rarely found in nature.[1,2] As the third element of the Group IIIA, Ga has chemical properties similar to aluminum (Al) and is frequently used as a geochemical analogue of Al.[3−7] However, unlike Al which is a major element, the trace element Ga sometimes behaves differently, and the fractionation between Ga and Al (Ga/Al ratio) was usually used to investigate the transport and behaviors of trace elements in the ocean,[4,5,8,9] rivers,[5,10] and during weathering processes.[10,11] The ratio of B/Ga was also employed in paleoclimate research, for example, to distinguish the terrigenous from the marine environment.[12] Though Ga is involved in many biological processes and is detected in almost all plants and even enriched in some certain species, the exact role of Ga in biological metabolism still remains unclear.[13]

Moreover, the distribution of Ga in the mantle and core of the earth may be an indicator of the material source, physiochemical condition, and dynamic processes during differentiation.[14] Ga is also useful in the cosmochemical studies; for example, the concentration measurement of Ga (with other elements) helps to classify iron meteorites.[15−19] Though these studies significantly improved our knowledge on the Ga geochemistry, many processes and mechanisms involved in the transportation and transformation of Ga in nature remain unidentified and/or unquantified.

Economically, Ga is largely used in high-tech applications,[2,20] including electronics, the missile industry, and the power sector.[21−23] The wide application of Ga in human activities would not only lead to a growing demand for Ga, resulting in the urgent exploration of more potential sources beside bauxite or purification and enrichment techniques for low level minerals,[24−26] but also modify the biogeochemical cycle of Ga by for example increasing the continental input of Ga to the

ocean. Thus, more research is required to better constrain the anthropogenic impact on the biogeochemical cycle of Ga.

Since the past decade, the development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) and the analyte purification techniques have allowed for accurate and precise measurements of isotopic ratios of many metals,[27−32] which significantly improved our knowledge on different sectors of earth science. Theoretical, experimental, and applicable studies have reported large variations of metal stable isotope ratios in a variety of environments and have shown significant fractionation of these isotopes induced by many biogeochemical processes, such as adsorption,[33,34] biological uptake,[35−38] diffusion,[39] precipitation,[40−43] and weathering.[44] A Ga isotope approach could also provide a better understanding of Ga geochemistry. Ga has two stable isotopes, ^{69}Ga and ^{71}Ga, with the abundances of 60.1% and 39.9%, respectively.[19] Previous studies have demonstrated that the species as well as the chemical bond (and lattice) that incorporate Ga can change under different geological conditions (pH, temperature, etc.), or can be modified in many physiochemical processes.[6,7,45−47] These changes or processes may fractionate Ga isotopes and thus induce different Ga isotopic signatures in diverse geological (and biological) reservoirs. Ga isotopic composition may be also modified by some specific biological processes; for example, the preferential uptake and accumulation of Ga by some lichens and mosses than other plants could induce different isotopic effects.[13] Thus, Ga isotopes may be useful for variable studies of its geochemical behaviors in nature. However, apart from several comparative studies on the abundance and distribution of Ga isotopes around the middle of last century,[19,48−52] the geochemistry of Ga isotopes has not been widely elaborated up to now, due to probably the lack of an effective and reliable method for separating Ga from complex matrices and measuring Ga isotope ratio on the new generation mass spectrometers (MC-ICP-MS).

This work is devoted to a new chromatographic method to purify Ga from geological (biological) samples for precise measurement of Ga isotopic composition on MC-ICP-MS. The two-stage separation method is based on a series of tests using various types of elution and even resin, and carefully calibrated by assessing the extraction yield and the reproducibility of the measured isotopic ratio. The whole protocol, together with instrumental analysis, is validated by the investigation of the matrix effect, the results of a standard addition experiment, and the comparison of Ga isotope measurement on two mass spectrometers (Nu Plasma II and Neptune Plus).

■ EXPERIMENTAL SECTION

Materials and Reagents. All materials and reagents including resins, Milli-Q water (18.2 MΩ, Millipore, U.S.A.), oxalic acid solution (made by oxalic powder), and distilled acids (HCl, HNO$_3$ and HF) were prepared in the clean room (Class 100). The anion exchange resin AG1-X4 (200−400 mesh, Biorad) and the cation exchange resin Ln-spec (50−100 μm, TrisKem) were used in this study for Ga separation. Both resins were carefully washed with Milli-Q water, and the fine floating grains were discarded before loading into the column. All reagent blanks were determined after evaporation of a 10 mL solution and were 0.001, 0.001, 0.001, 0.002, 0.002, 0.009, 0.001, and 0.003 μg/L for H$_2$O, 0.1 M HCl, 0.5 M HCl, 1 M HCl, 4 M HCl, 6 M HCl, 2% HNO$_3$ and "3 M HCl + 0.25 M oxalic acid", respectively, being negligible in comparison to the amounts of Ga in both standards and samples. NIST SRM 994

Ga concentration standard (NIST, U.S.A.), GBW(E) 08056 industrial synthetic concentrated solution (prepared by Shandong Metallurgical Science Research Institute, China) were used as Ga reference materials. The high pure Ga metal standard, NIST SRM 994, was digested by concentrated HNO$_3$ and HCl with heating, then diluted to 1000 ppm by Mill-Q water. Multielement standard GBW 081531 (National Institute of Metrology, China), monoelement Fe standard (GBW(E) 080364, The Department of Water Environment, IWHR, China), and Mo standard (GBW(E) 080218, National Institute of Metrology, China) were employed to model natural samples or for matrix effect tests. Cu standard (Alfa Aesar, Germany) was used for mass bias correction in the modified empirical external normalization (MEEN) method. All Teflon labware was cleaned with ultrapure HNO$_3$ and rinsed with Mill-Q water just before their use.

Except for GBW(E) 08056 solution, nine reference standards were acid-digested for the measurements of Ga isotope compositions. Except for the in-house Ga standard solution (GBW(E) 08056), eight reference materials, including JB-2 (basalt), JG-2 (granite), BHVO-2 (basalt), G-2 (granite), GXR-2 (soil), GXR-3 (Hot springs deposit), MAG-1 (marine mud), GBW07405 (soil), and one gallium(III) nitrate hydrate (Alfa Aesar, Germany) were also prepared and measured for δ^{71}Ga against the international standard NIST 994 Ga. Before analysis, 100 mg of these geological materials were digested with first 4 mL of concentrated HNO$_3$ and HF (1:1) in Teflon vials (48 h at 140 °C), then 1 mL of concentrated HNO$_3$, and lastly, 1 mL of 6 M HCl, respectively. After dryness, the last residue was dissolved in 1 mL of 6 M HCl and ready for the column chemistry. Elemental concentrations were measured on ICP-MS NexION 300X (PerkinElmer, U.S.A.), with the precision better than 5% (2SD) based on repeated analysis of the geostandard SLRS-5.

Ga Separation Protocol. For precise Ga isotope measurement, it was crucial to thoroughly separate Ga from the matrix and other elements in natural samples, especially from Mg, Al, Fe, Ba, Ce, Cr, and Zn, because the presence of these elements could generate spectral effects on Ga isotopes in argide form (Mg, Al), hydro form (Zn), (hydro)-oxide form (Cr, Fe), and double-charged species (Ba, Ce) (see below "Matrix effect on Ga isotopic measurement"). To ensure the matrix-matched principle on Ga isotopic measurement, both Mo and Cu, which are often present in natural samples, should also be separated from Ga.[30,53] The protocol was composed of two chromatographic steps: the first step for purifying Ga from most major and minor elements, and the second step for separating Ga from Fe and Mo, respectively. The elution scheme for the whole purification process was summarized in Table 1. Both steps were carried out on a polypropylene column (inner diameter 0.8× 4 cm, length 9 cm, Biorad).

For the first step, the column charged with 1.8 mL of AG1-X4 resin was first rinsed with 10 mL of H$_2$O and 10 mL of 0.1 M HCl, then conditioned with 10 mL of 6 M HCl; subsequently, the sample was loaded in 6 M HCl. After matrix rinsing with 10 mL of 6 M HCl, it was eluted in 5 mL of 0.5 M HCl. Because this Ga elution still contained substantial amounts of Fe and Mo (measured by ICP-MS), a second purification was required.

The second separation of Ga from Fe and Mo was achieved on the column loaded with 1.4 mL of Ln-spec resin. The column was conditioned with 10 mL of 0.5 M HCl. The previously obtained 5 mL Ga-contained 0.5 M HCl solution

Table 1. Elution Sequence of the Two-Step Separation

eluant	volume (mL)	eluted
first column charged with 1.8 mL AG1-X4 resin		
H$_2$O	10	cleaning
0.1 M HCl	10	cleaning
6 M HCl	10	cleaning + conditioning
sample (6 M HCl)	1	loading
6 M HCl	10	matrix
0.5 M HCl	5	Ga (Fe and Mo)
second column charged with 1.4 mL Ln-spec resin		
0.5 M HCl	10	conditioning
0.5 M HCl sample solution	5	loading + Ga
1 M HCl	6	Ga
0.25 M oxalic acid + 3 M HCl	20	cleaning (Mo, Fe)
0.1 M HCl	20	cleaning
4 M HCl	20	cleaning (Fe)

was loaded onto the column. Because Mo and Fe were well-retained by the Ln-spec resin but not Ga, the liquid passed through the column was immediately collected into the Teflon vial. Another 6 mL of 1 M HCl was introduced to elute the remaining Ga still retained in the resin into the same Teflon vial. The 11 mL Ga elution was further evaporated to dryness, and the residual was dissolved in 2% HNO$_3$ for isotope and concentration measurements. To reuse the Ln-spec resin, the column was cleaned by 20 mL of a mixed solution of 0.25 M oxalic acid and 3 M HCl, as well as 20 mL of 0.1 M HCl and 20 mL of 4 M HCl to strip Fe and Mo. The total procedure blank was 0.3 ng for the whole protocol and 0.2 ng and 0.1 ng for the first and the second steps, respectively, being negligible compared to the mass (at least 200 ng and 80 ng on Nu and Neptune MC-ICP-MS, respectively) needed for a precise isotope analysis.

Ga Isotope Measurement on the Nu MC-ICP-MS. Ga isotope measurement was performed on the Nu Plasma II MC-ICP-MS (Nu Instruments Ltd., U.K.) at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). The Ga standards and samples were measured in 2% HNO$_3$, and the concentration of Ga was fixed to 50 μg/L.

The instrument setting was shown in Table 2. For the cup's configuration, mass dispersion was adjusted to allow collection of two Ga isotopes (^{69}Ga and ^{71}Ga), three Zn isotopes (^{66}Zn, ^{67}Zn, ^{68}Zn), and four double-charged isotopes including

Table 2. Nu Plasma II ICP-MS Operating Conditions

component	parameter
stage control	back/forward: 8.83; in/out: 3.97; up/down: 2.93
vacuum capacitor	lighting: 2330; running: 2160
gas panel	coolant (L/min): 13.0; Aux (L/min): 0.80; Neb (Psi): 27.6; mix gas (L/min): 0.00; mix gas 2 (L/min): 0.00
RF power	forward (W): 1300
quads	quad1:6.3; quad2:74.5
high voltage	HV1: 5999; HV2: 4412; HV3: 3671; HV4: 1700; HV5: 2814; HV6: 2408
Faraday cups setting	^{146}Ge^{2+} (H7); ^{71}Ga (H4); ^{140}Ce^{2+} (H2); ^{69}Ga (Ax); ^{137}Ba^{2+} (L1); ^{68}Zn (L2); ^{135}Ba^{2+} (L3); ^{67}Zn (L4); ^{66}Zn (L5)

^{135}Ba^{2+}, ^{137}Ba^{2+}, ^{140}Ce^{2+}, and ^{146}Ge^{2+} in variable cups. An Aridus II desolvator (CETAC, U.S.A.) was used as sample introduction system, and the low-resolution entrance slit was chosen throughout the study. The instrumental baseline and peak centering were done before every sample (standard) analysis. Each measurement included 60 integrations of 6s in 5 blocks of 12 cycles, followed by a 3 min of washing with 0.5 M HNO$_3$ to lower the Ga signal to an insignificant level (<1 mV). The instrumental sensitivity was about 7 V on ^{69}Ga for a 50 μg/L solution. In this study, the sample-standard bracketing (SSB) method was employed to correct the mass bias for all measurements, because our Nu instrument mostly had a perfect stability, as reported in previous study.[30,53] Ga isotope results in this study were expressed as δ^{71}Ga, in units per mil (‰):

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

here we chose the NIST SRM 994 solid metal Ga as the reference standard, as it was well calibrated (Ga$^{69/71}$ = 1.50676 ± 0.00039, at 95% confidence interval) and adopted for an ideal international standard purpose.[54−56]

Comparison between Nu and Neptune Instruments. Ga isotope measurement was also carried out on a Neptune Plus mass spectrometer, another commonly used instrument for comparison. This was done on the Neptune Plus (Thermo Finnigan, Germany) at the Institute de Physique du Globe de Paris (IPGP), France. The machine setting of Neptune Plus was summarized in Table 3. The desolvator Apex HF (without nitrogen flow) was instead employed as sample inlet system, equipped with a self-aspiring microconcentric PFA nebulizer. The samples (standards) were measured also in 2% HNO$_3$, but the Ga concentration was set to 20 μg/L, because the Neptune Plus had a better sensitivity (8 V on ^{69}Ga for a 20 μg/L solution) compared to the Nu Plasma II. Limited by the detector configuration of this particular Neptune Plus, the Faraday cups were set for measuring two Ga isotopes (^{69}Ga, ^{71}Ga), two Cu isotopes (^{63}Cu, ^{65}Cu), three Zn isotopes (^{66}Zn, ^{67}Zn, ^{70}Zn), and only one double-charged Ba isotope (^{137}Ba^{2+}) (see Table 3).

In addition to the conventional SSB, the modified empirical external normalization (MEEN) method that has been well-described and used in previous studies was also employed for the mass bias correction on the Neptune Plus.[27,30,31,57−59] The general observation from these studies was that, though SSB and MEEN gave similar results for mass bias correction under relatively stable instrumental conditions (the case of our Nu Plasma II), the MEEN approach produces better precision when the Neptune instrument was not very stable due to for example the instability of Apex desolvator.[30,53,54] Two previous studies have reported the usefulness of Ga for correcting mass bias in Cu and Zn isotope analysis.[60,61] Here, Cu was alternatively employed for the correction during Ga isotope determination. In this method, the AAS Cu solution provided by IPGP (France)[30] was used with the radio of Ga/Cu of 0.5 at Ga concentration of 20 μg/L.

■ RESULTS AND DISCUSSION

Efficiency and Reproducibility of Ga Separation Protocol. Ga was separated from the geological matrix by two ion-exchange chromatography steps: a first preconcentration using AG 1-X4 resin and a second purification on the

Table 3. Neptune Plus ICP-MS Operating Settings

component	parameter
zoom optics parameter	focus quad [V]: 10.00; dispersion quad [V]: 0.00
center cup	decelerator [V]: 8199.9; suppressor [V]: 9965.0
source lenses	extraction [V]: −2000; focus [V]: −611.0; X-defl [V]: 6.49;
	Y-defl [V]: −4.30; shape [V]: 206.00 rot quad [V]: 18.93;
inlet system	source offset [V]: −6.00
	cool gas [L/min]: 16.00; aux gas [L/min]: 0.88;
	sample gas [L/min]: 1.065; add. gas1 [L/min]: 0.00;
	add. gas 2 [L/min]: 0.00; X-pos [mm]: 0.010;
	Y-pos [mm]: −3.300; Z-pos [mm]: −1.850; peri. pump [rpm]: 5.00;
	RF power [W]: 1200
Faraday cups setting	^{71}Ga (H4); ^{70}Zn (H3); ^{69}Ga (H2); ^{137}Ba^{2+} (H1); ^{67}Zn (RPQ/IC1); ^{66}Zn (L1); ^{65}Cu (L2); ^{63}Cu (L4)

special Ln-spec resin. The anion-exchange resin AG1-X4, which was a lower cross-linked (4%) resin, has been successfully used to separate target elements such as Fe, Zn, and Hg from natural sample.[30,31,62] In this study, the resin volume was set to 1.8 mL to give a compromise between a good purification (partially depending on the volume) and the short elution time. The theoretical capacity of AG1-X4 resin was 1 mequiv/ml, thus with 1.8 mL resin, 41.4 mg Ga^{3+} could be retained, which allows for separating Ga from a large amount of geological samples, given the average Ga abundance of 17 ppm in the Earth Crust.[1]

For precise Ga isotope measurement, the identical matrix should be guaranteed between standard and sample, thus natural samples need to be thoroughly purified, with a particular goal of separating Ga from major (e.g., Fe) and trace elements such as Ba, Ce, Zn, Cu, and Mo (see below discussion on the matrix effect). To establish an appropriate elution scheme, the solution volume V_{elu} needed for eluting the target element can be calculated using the following equation:

$$V_{elu} = V_0 + M \times Kd \tag{9}$$

where V_0 is the dead volume of resin, M is the dry mass of resin, and Kd is the partitioning coefficient of Ga in a given solution, defined as[63]

$$Kd = \frac{\text{amount of Ga in resin/g of resin}}{\text{amount of Ga in solution/ml of solution}} \tag{10}$$

In hydrochloric acid medium, the partitioning coefficient Kd of Ga^{3+} between AG1-X4 resin and the solution increase correspondingly.[64] As Kd was already higher than 5×10^4 at 6 M HCl, we chose to load samples in this acidity in order to avoid the volatility of concentrated HCl (>7 M). Theoretically, 50 L of 6 M HCl could be introduced into the column before Ga breakthrough. The Kd of Ga^{3+} was below 5 at 0.5 M HCl, and thus, Ga could be eluted in about 5 mL 0.5 M HCl. In order to test the above theoretical calculations, a series of experiments were carried out on both synthetic and natural sample solutions, and element concentrations were measured for every elution fraction collected 1 mL by 1 mL. The primary elution curves showed that major elements, such as Na, Mg, Ba and Ca, were not retained by the resin at 6 M HCl (Figure 1A).

However, almost all of Fe and some of Mo went into the 0.5 M Ga fraction (Figure 1A), because of the similar partition coefficient for Fe^{3+} and Mo^{6+} in the same HCl medium, with their Kd of about 10^4 and 5×10^2 at 6 M HCl, and both below 5 at 0.5 M HCl, respectively. A further separation step is thus needed to separate Ga from Fe (and Mo). We first attempted to use the same resin (AG1-X4) to achieve this separation by
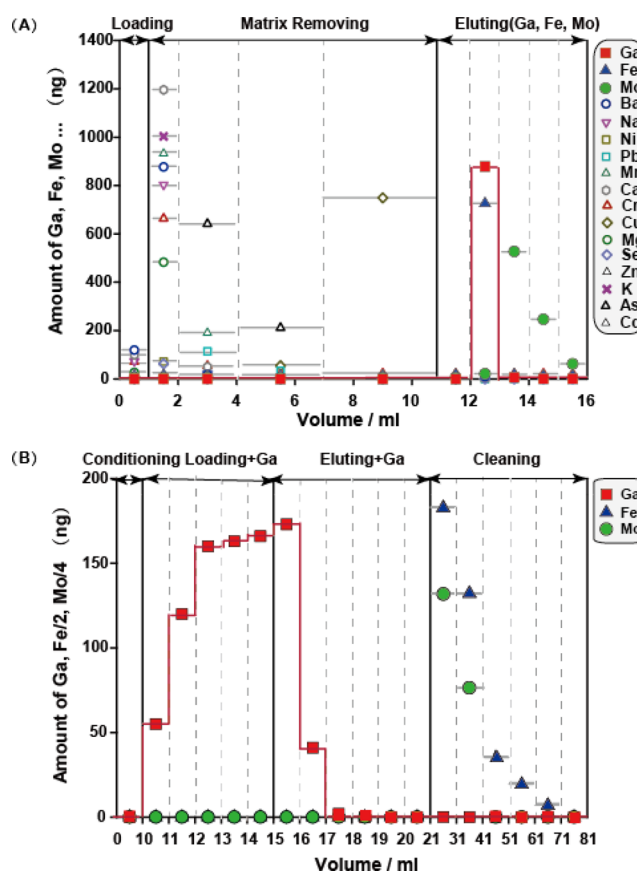
Figure 1. Elution curve of Ga separation from matrix on the AG 1 × 4 resin (A) and the Ln-spec resin (B). Though most of the major and trace elements were removed in the first step, Ga fraction still contained Fe and Mo, requiring a second purification, which was done on the column charged with Ln-spec resin. The detailed procedure was described in the text.

changing the concentration or kind of acid, and by adding other reactants. Though the small Kd difference between Fe^{3+} and Ga^{3+} signified a possibility to effectively separate these two elements by modifying the HCl concentration (1 M ∼ 2 M), our experimental data showed that Fe^{3+} was promptly and almost simultaneously eluted in Ga^{3+} solution. Alternatively, we performed the elution using nitric acid and got similar results. Because the Kd of Fe^{2+} was very different from Ga^{3+} in HCl solution, we then tried to transfer Fe^{3+} to Fe^{2+} in column by adding reductants, (ascorbic acid and hydrazine dihydro-chloride), but the results showed that only part of Fe^{3+} was reduced to Fe^{2+}, likely caused by the loss of reducing ability for

Table 4. Potential Species Interfering Ga Isotope Measurement on MC-ICP-MS

species	mass-69	mass-71
monoisotopic species	^{69}Ga	^{71}Ga
argides	$^{40}Ar^{29}Si^+$, $^{37}Cl^{16}O_2^+$	$^{40}Ar^{15}N^{16}O$
(hydro)-oxides	$^{51}V^{18}O^+$, $^{52}Cr^{17}O^+$, $^{68}Zn^1H^+$,	$^{53}Cr^{18}O^+$, $^{54}Cr^{17}O^+$, $^{55}Mn^{16}O^+$,
	$^{50}Ti\ ^{18}O^1H^+$, $^{50}V\ ^{18}O^1H^+$,	$^{54}Fe^{17}O^+$, $^{70}Zn^1H^+$, $^{52}Cr^{18}O^1H^+$,
	$^{50}Cr\ ^{18}O^1H^+$, $^{51}V^{17}O^1H^+$,	$^{53}Cr^{17}O^1H^+$, $^{54}Cr^{16}O^1H^+$,
	$^{52}Cr^{16}O^1H^+$,	$^{54}Fe^{16}O^1H^+$
elemental species	$^{33}S^{36}S$	
double-charged species	$^{138}Ba^{2+}$, $^{138}La^{2+}$, $^{138}Ce^{2+}$	$^{142}Nd^{2+}$, $^{142}Ce^{2+}$

these reductants in relatively concentrated acid. Finally, we tried to modify the Kd of metals (here Ga, Fe, and Mo) to get a good Ga isolation by adding oxalic acid, which generally forms strong metal complexes in HCl elution.[65] The tests showed that this addition did change the Kds but failed to achieve a complete separation (Fe trailing in Ga elution). Thus, another chromatographic column loaded with different resin should be chosen and employed.

We first chose the column charged with 1.2 mL cation exchange AG 50W-X12 resin (200−400 mesh, Biorad) that was widely used for separating metals in HF medium.[66] Though Ga would theoretically be separated from Fe on this resin in dilute HF, the tests using 1 or 1.5 M HF for both loading and eluting showed that, although most of Fe^{3+} was eventually eluted prior to Ga^{3+}, there was still a small Fe^{3+} fraction present in the following Ga eluent.

Finally, the Ln-spec resin that was commonly used to separate radium and lanthanides from geological samples was chosen to achieve the second separation in dilute HCl medium.[67] Given the theoretical capacity of 0.16 mmol/mL for this resin, up to 15 mg of Ga could be retained with a resin volume of 1.4 mL. Interestingly, Ga^{3+}, Fe^{3+}, and Mo^{6+} displayed quite different Kd on this resin in dilute HCl or HNO_3 medium; for example, their Kds were about 0.3 (Ga^{3+}) and 5 × 10^3 (Fe^{3+}) at 0.5 M HCl, and 0.8 (Ga^{3+}), 5 × 10^3 (Fe^{3+}), and 7 × 10^2 (Mo^{6+}) at 0.5 M HNO_3, respectively. In fact, the specific "phosphoric acid" from the Ln-Spec resin form more stable complexes with Fe (having incomplete "d" electron shell) than Ga (with complete "d" electron shell). Loading in 0.5 M HCl, Fe^{3+} (and Mo^{6+}) could be retained by the resin, but Ga^{3+} should directly go through. Thus, the last 0.5 M HCl elution containing Ga, Fe, and Mo from the first preconcentration step could be loaded directly on the Ln-spec column without any additional step (e.g., evaporating to dryness and/or changing the acid medium), which allowed for completing the two step separation in a single day. However, the first tests showed that a small fraction of Ga^{3+} still remained in the Ln-spec resin posterior to the loading, requiring another eluent. We chose 6 mL of 1 M HCl to elute the remaining Ga^{3+}, because at 1 M HCl, the Kd of Ga^{3+} reached its minimum value of about 0.2, much lower than that of Fe^{3+} (about 10^3). The concentration measurement showed that Fe and Mo were still retained on the Ln-spec resin and were not found in the 11 mL (5 mL loading 0.5 M HCl plus 6 mL 1 M HCl eluent) Ga fraction at all (Figure 1B). Finally, in order to reuse the Ln-spec resin and avoid the possible presence of Fe (and Mo) in the Ga fraction,[65] a mixture of 0.25 M oxalic acid and 3 M HCl was used to elute all Mo and most of Fe, the rest of Fe was further removed from the column in 4 M HCl, because the Kd of Fe in this acid medium was the lowest (about 15). A 0.1 M HCl

solution was inserted before 4 M HCl to clean the possible presence of other elements (such as REEs) (Table 1).

In order to check the recovery of Ga, a series of experiments (n = 23) were done using our purification protocol on synthetic solutions (5 ng to 100 μg of GBW(E) 08056 Ga mixed with other elements such as Fe, Mo, Ba, Na, Zn, etc.). The recoveries of Ga varied from 98.8% to 100.6% with a mean value of 99.8 ± 0.8% (2SD, n = 23). Except for some synthetic samples with very low Ga concentration (<200 ng), Ga isotopic ratios were measured on the Nu Plasma II instrument for all elution derived from the above tests. The results showed that $\delta^{71}Ga$ varied from 1.69‰ to 1.78‰, averaging 1.74 ± 0.05‰ (2SD, n = 21).

Matrix Effect on Ga Isotopic Measurement. The effect of matrix such as Ga concentration and other species that may interfere Ga isotopic measurement were systematically investigated. The primary experiments on varying Ga concentration from 5 μg/L to 50 μg/L showed that the Ga content should be set to higher than 20 μg/L, because a continuous decrease of $\delta^{71}Ga$ with Ga concentration down to 5 μg/L was determined, probably due to the instrumental blank effect, as reported in previous work.[30]

Removing the possible spectral interferences derived from elemental isobars, major argides, trace oxides, and doubly charged species was another critical issue for precise Ga isotopic analysis. The potential spectral interferences were summarized in Table 4. According to this table, Ga should be thoroughly separated from elements such as Ba, Ce, Zn, Fe, because they may generate spectral interferences in doubly charged species ($^{138}Ba^{2+}$, $^{138}Ce^{2+}$ and $^{142}Ce^{2+}$) or polyatomic forms ($^{54}Fe^{16}O^1H^+$, $^{68}Zn^1H^+$ and $^{70}Zn^1H^+$).
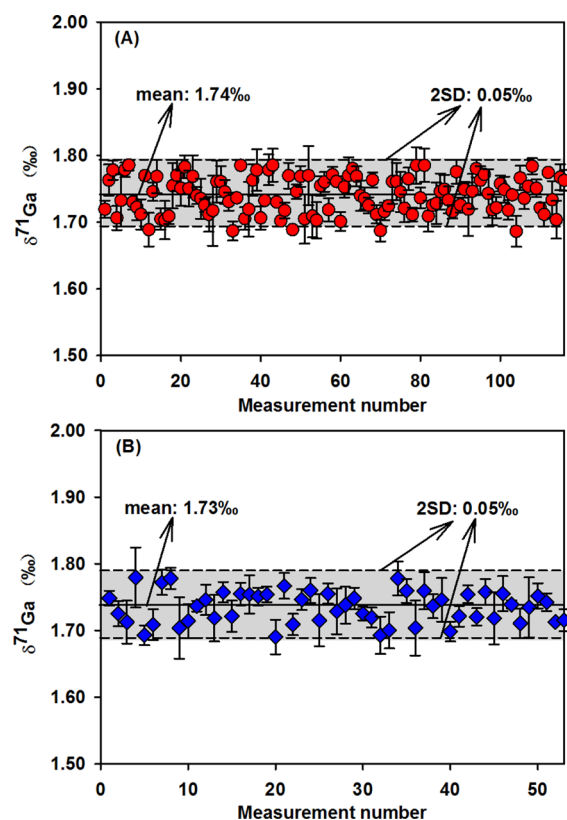
Though our two-step method would well purify Ga from other major and trace elements, we still investigated the effect of the possible presence of certain elements such as Ba, Ce, Cu, Zn, Fe, and Mo on Ga isotope measurements. This was done by fixing Ga concentration to 50 μg/L and by changing the ratios of element/Ga (thus the percentage) in standard solutions. As shown in Figure 2A,B, the presence of Ba and Ce induced a significant deviation of $\delta^{71}Ga$ from the actual value (around zero) of the initial Ga standard. This is caused by the doubly charged interferences of ^{138}Ba $(71.698)^{2+}$, ^{138}Ce $(0.251)^{2+}$ on ^{69}Ga and ^{142}Ce $(11.114)^{2+}$ on ^{71}Ga, which would result in lower and higher $\delta^{71}Ga$ values, respectively. Therefore, Ga isotope analysis should be done on solutions absolutely free of Ba and Ce. In the study, the final Ga eluent from the two-column purification contained hardly any Ba and Ce. The effects of the presence of Cu, Zn, Fe, and Mo on $\delta^{71}Ga$ were also shown in Figure 2C−F. Unlike Ba and Ce, no clear influence was found within the measurement uncertainty (0.05‰, see below) for the given element/Ga ratio range, except for Zn that could interfere with Ga isotopes in hydride
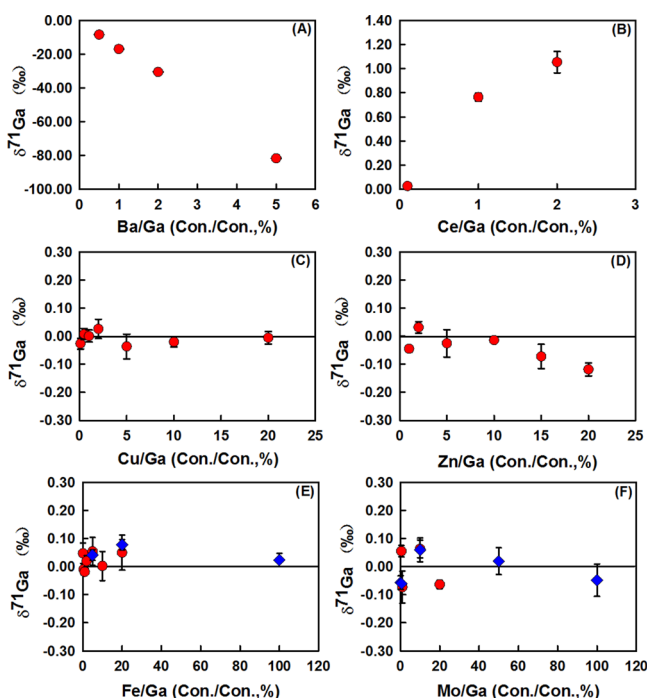
Figure 2. Assessment of the influence of Ba (A), Ce (B), Cu (C), Zn (D), Fe (E), and Mo (F) on Ga isotopic measurements. The δ^{71}Ga data was the average value of five replicate analyses, and the error bars represented the 2SD uncertainty of all measurements. The effects of Fe and Mo were investigated on both Nu Plasma II (red dots) and Neptune Plus (blue rhombi) machines.

Figure 3. Reproducibility of Ga isotope ratio (δ^{71}Ga) for long-term measurements of the standard GBW(E) 08056 on the Nu Plasma II (A, red dots) and the Neptune Plus (B, blue rhombi) using SSB correction method, respectively. The dashed lines and solid line represented the external long-term standard deviations (2SD) and mean for all tests, respectively. The error bars (2SD) were also given for each measurement and were generally better than 0.05‰.

forms (^{68}ZnH$^+$ and ^{70}ZnH$^+$) when the ratio of Zn/Ga was higher than 10%. The fact that the abundance of ^{68}Zn (18.75%) is much higher than ^{70}Zn (0.62%) might explain the lower δ^{71}Ga values in test solutions with higher Zn/Ga ratio (>10%), supposing that both Zn isotopes trended to equally form hydrides. In fact, the concentration ratios of Cu/Ga, Zn/Ga, Fe/Ga, and Mo/Ga in the last elution of all tests were very small (far below 2%) for both synthetic and sample solutions, implying no significant impact on Ga isotopic measurement. The tests on the Neptune gave similar results to those on Nu instrument (Figure 2E,F). Finally, our measurement data showed no argide interferences (e.g., ^{40}Ar^{29}Si$^+$ and ^{40}Ar^{15}N^{16}O) on Ga isotopes, as the background Ga level was generally lower than 0.1 mV. Though the presence of Mo did not show clear influence on Ga isotopic measurement (Figure 2F), Mo was removed in our protocol in order to guarantee the identical medium in sample to standard solution and avoid an unexpected matrix effect.

Validation of Ga Isotopic Measurement. The standard GBW(E) 08056 was calibrated against the international standard NIST 994 Ga and was measured regularly as in-house standard on the Nu plasma II to control the analysis quality. Figure 3A showed the results of δ^{71}Ga for 116 measurements in 1 year. All measurements gave an average δ^{71}Ga of 1.74‰ with a long-term external 2SD uncertainty of 0.05‰ (Figure 3A). In order to confirm the accuracy and precision of this calibration (Ga isotopic measurement), a standard addition experiment, similar to a previous study,[68] was carried out by making six mixture solutions of GBW(E) 08056 Ga and NIST 994 Ga, with GBW(E) 08056 Ga proportions of 0% (pure NIST 994 Ga solution), 10%, 20%, 50%, 80%, and 100% (pure GBW(E)08056 Ga), respectively. The Ga isotope

ratio (and concentration) of all mixtures was measured on Nu MC-ICP-MS using the SSB method. The results showed similar δ^{71}Ga values for both pure standards as the long-term measurements, and more importantly, a linear correlation between δ^{71}Ga and Ga fraction with the correlation coefficient (R^2) of 0.997 (Figure 4), attesting the accurate analysis of this in-house standard and that the use of SSB method for mass bias correction was adequate.

Application to the Reference Materials. Ga was carefully purified from the 10 standards using our newly developed protocol, and Ga isotopic composition was measured on either Nu or Neptune ICP-MS or both (Table 5). As seen in Table 5, our shorter-term measurements gave the external 2SD uncertainty of <0.05‰ for all samples, comparable to the long-term reproducibility (0.05‰, 2SD, n = 116, Figure 3). As a whole, all reference materials displayed a large δ^{71}Ga variation of about 1.83‰, with generally higher values for standards of industrial processes than natural geological materials. Though the exact mechanism enriching heavier Ga isotopes in industrial materials remains unknown, the large difference of δ^{71}Ga between artificial standards and natural materials implies the usefulness of Ga isotopes in studying some aspects of Ga geochemistry, for example, for distinguishing natural from anthropogenic sources.

Nu versus Neptune. For comparison, Ga isotope measurement was carried out on both Nu and Neptune MC-ICP-MS but with completely different instrumental setting (see Table 2
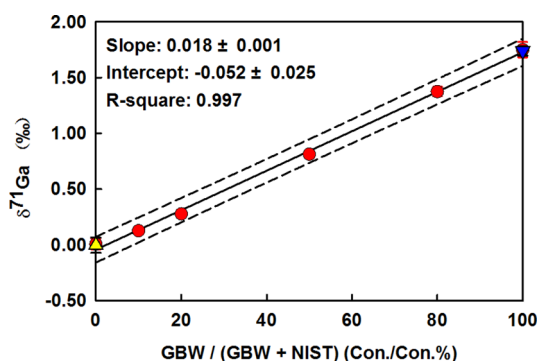
Figure 4. Standard addition experiment for validation of the whole purification and isotopic analysis protocol. The experiment was carried out on six mixture solutions of GBW(E) 08056 Ga and NIST 994 Ga. The δ^{71}Ga values measured here (red points with red error bars, $n = 5$) for the two pure standards (0.00 ± 0.05‰ and 1.75 ± 0.06‰) were consistent with the results (0.00 ± 0.04‰ and 1.74 ± 0.05‰) of long-term measurements. The linear fit validated the accuracy of Ga isotope analysis. The blank dotted lines were the confidence interval of six measurements at 95% confidence levels.

and Table 3). Concomitant with the best optimization (tuning) of instrument conditions, the Neptune had a better sensitivity (e.g., 8 V on ^{69}Ga for 20 μg/L solution) compared to the Nu ICP-MS (about 7 V on ^{69}Ga for a 50 μg/L solution). Thus, the Neptune consumed relatively less Ga mass (to give the same signal intensity and results with good precision, see below) and was more adaptable for dilute samples. Regarding the reference control, the cup configuration and the collector design of the Nu Plasma II at IGCAS allowed for measuring more isotopes (nine isotopes, Table 2) than the Neptune Plus at IPGP (eight isotopes, Table 3). An especially important point was the ability to measure ^{140}Ce^{2+} on the Nu Plasma II, which allowed recognition of the interferences of ^{138}Ce^{2+} and ^{142}Ce^{2+} on Ga isotopes (Figure 2B, Table 4). Therefore, complete removal of Ce must be guaranteed, or sample solution must be scanned prior to Ga isotopic analysis on Neptune.

Despite the above-mentioned difference, 53 measurements of GBW(E) 08056 Ga using the SSB method on the Neptune displayed similar reproducibility (long-term 2SD < 0.05‰) as the Nu instrument (Figure 3B, Table 5). Moreover, the analysis of four reference materials (JB-2, BHVO-2, Ga nitrate, and GBW(E) 08056) on Neptune using the same SSB correction gave almost identical δ^{71}Ga values to those on Nu (Table 5),

implying that Ga isotope ratio can be readily measured on both instruments. The Table 5 also showed that, though measured on the same Neptune ICP-MS at IPGP, for the four references, the MEEN correction method gave relatively better precision (0.02 to 0.03‰) than the SSB method (0.03 to 0.06‰).

CONCLUSION

The new two-step method allows for separating Ga from complex geological matrix, especially from elements such as Ba, Ce, Zn, Cu, and Fe that may interfere with Ga isotope measurement. The separation protocol was thoroughly calibrated and optimized using both synthetic and natural samples and has been proven to be reproducible and satisfactory for precise Ga isotope ratio determination on MC-ICP-MS. The short-term analysis performed on both Nu and Neptune spectrometers gave identical δ^{71}Ga values for natural materials and a precision better than 0.05‰, comparable to that (0.05‰, 2SD, $n = 116$) of the long-term in-house standard calibration. Our preliminary results revealed large variation of δ^{71}Ga (up to 1.83‰) in 10 natural and industrial reference materials, stimulating further investigation of Ga isotopic composition in natural reservoirs and the relative fractionation mechanisms. The application of isotope approach would provide new insight into the study of the geochemical cycle of Ga.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.anal-chem.6b02317.

> Modified empirical external normalization, tests of Ga recovery using our separation protocol and the reproducibility of δ^{71}Ga for the whole separation procedure, effect of the Ga concentration on the measurements of δ^{71}Ga (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: chenjiubin@vip.gyig.ac.cn. Tel.: +86 851 85892669.

Notes

The authors declare no competing financial interest.

Table 5. Results of Comparison between Nu and Neptune Mass Spectrometers[a]

	δ^{71}Ga-SSB (‰)		δ^{71}Ga-MEEN (‰)
sample	Nu (mean ± 2SD)	Neptune (mean ± 2SD)	Neptune (mean ± 2SD)
JB-2 (basalt)	0.11 ± 0.03 ($n = 9$)	0.10 ± 0.04 ($n = 10$)	0.11 ± 0.02 ($n = 9$)
BHVO-2 (basalt)	0.08 ± 0.02 ($n = 9$)	0.07 ± 0.03 ($n = 10$)	0.08 ± 0.02 ($n = 10$)
gallium(III) nitrate hydrate	1.83 ± 0.04 ($n = 10$)	1.81 ± 0.06 ($n = 6$)	1.82 ± 0.03 ($n = 9$)
GBW(E) 08056	1.74 ± 0.05 ($n = 21$)	1.73 ± 0.03 ($n = 5$)	1.72 ± 0.02 ($n = 9$)
G-2 (granite)	0.03 ± 0.03 ($n = 5$)		
JG-2 (granite)	0.02 ± 0.03 ($n = 3$)		
MAG-1 (marine mud)	0.06 ± 0.04 ($n = 5$)		
GXR-2 (soil)	0.04 ± 0.05 ($n = 4$)		
GXR-3 (deposit)	0.03 ± 0.05 ($n = 4$)		
GBW 07405 (soil)	0.02 ± 0.04 ($n = 5$)		

[a]n, the number of repeated measurements for the same sample including different column procedures (2 or 3). 2SD, 2 times the standard deviation of the population of n repeated measurements.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Shaw, D. M. *Phys. Chem. Earth* **1957**, *2*, 164−211.
(2) Moskalyk, R. R. *Miner. Eng.* **2003**, *16*, 921−929.
(3) Burton, J. D.; Culkin, F.; Riley, J. P. *Geochim. Cosmochim. Acta* **1959**, *16*, 151−180.
(4) Orians, K. J.; Bruland, K. W. *Nature* **1988**, *332*, 717−719.
(5) Shiller, A. M. *Geochim. Cosmochim. Acta* **1988**, *52*, 1879−1882.
(6) Diakonov, II; Pokrovski, G. S.; Benezeth, P.; Schott, J.; Dandurand, J. L.; Escalier, J. *Geochim. Cosmochim. Acta* **1997**, *61*, 1333−1343.
(7) Pokrovsky, O. S.; Pokrovski, G. S.; Schott, J. *J. Colloid Interface Sci.* **2004**, *279*, 314−325.
(8) Yamamoto, T.; Otsuka, Y.; Uemura, K. *J. Oceanogr. Soc. Jpn.* **1976**, *32*, 182−186.
(9) Orians, K. J.; Bruland, K. W. *Geochim. Cosmochim. Acta* **1988**, *52*, 2955−2962.
(10) Shiller, A. M.; Frilot, D. M. *Geochim. Cosmochim. Acta* **1996**, *60*, 1323−1328.
(11) Hieronymus, B.; Boulegue, J.; Kotschoubey, B. *Chem. Geol.* **1990**, *84*, 78−82.
(12) Chen, Z. Y.; Chen, Z. L.; Zhang, W. G. *Quat. Res.* **1997**, *47*, 181−191.
(13) Poledniok, J. *Chemosphere* **2008**, *73*, 572−579.
(14) McDonough, W. F.; Sun, S. s. *Chem. Geol.* **1995**, *120*, 223−253.
(15) Lovering, J. F.; Nichiporuk, W.; Chodos, A.; Brown, H. *Geochim. Cosmochim. Acta* **1957**, *11*, 263−278.
(16) Wasson, J. T. *Geochim. Cosmochim. Acta* **1967**, *31*, 161−180.
(17) Wasson, J. T.; Kimbeblin, J. *Geochim. Cosmochim. Acta* **1967**, *31*, 2065−2093.
(18) Wasson, J. T.; Schaudy, R. *Icarus* **1971**, *14*, 59−70.
(19) De Laeter, J. R. *Geochim. Cosmochim. Acta* **1972**, *36*, 735−743.
(20) Lovik, A. N.; Restrepo, E.; Muller, D. B. *Environ. Sci. Technol.* **2015**, *49*, 5704−5712.
(21) Font, O.; Querol, X.; Juan, R.; Casado, R.; Ruiz, C. R.; Lopez-Soler, A.; Coca, P.; Garcia Pena, F. *J. Hazard. Mater.* **2007**, *139*, 413−423.
(22) Gupta, B.; Mudhar, N.; Singh, I. *Sep. Purif. Technol.* **2007**, *57*, 294−303.
(23) Chou, W.-L.; Wang, C.-T.; Yang, K.-C.; Huang, Y.-H. *J. Hazard. Mater.* **2008**, *160*, 6−12.
(24) Katrak, F.; Agarwal, J. *J. Met.* **1981**, *33*, 33−36.
(25) Ibragimov, A.; Budon, S. *ENRC Annual Report and Accounts*; Eurasian Natural Resources Corporation PLC: Luxembourg, 2010.
(26) Gladyshev, S.; Akcil, A.; Abdulvaliev, R.; Tastanov, Y.; Beisembekova, K.; Temirova, S. *Hydrometallurgy* **2013**, *140*, 95−101.
(27) Marechal, C. N.; Telouk, P.; Albarede, F. *Chem. Geol.* **1999**, *156*, 251−273.
(28) Zhu, X. K.; O'Nions, R. K.; Guo, Y.; Belshaw, N. S.; Rickard, D. *Chem. Geol.* **2000**, *163*, 139−149.
(29) Hintelmann, H.; Foucher, D.; Evans, R. D.; Dillon, P. *Geochim. Cosmochim. Acta* **2003**, *67*, A147.
(30) Chen, J.-B.; Louvat, P.; Gaillardet, J.; Birck, J.-L. *Chem. Geol.* **2009**, *259*, 120−130.
(31) Chen, J.-B; Hintelmann, H.; Dimock, B. *J. Anal. At. Spectrom.* **2010**, *25*, 1402−1409.
(32) Liu, S.-A.; Teng, F.-Z.; Li, S.; Wei, G.-J.; Ma, J.-L.; Li, D. *Geochim. Cosmochim. Acta* **2014**, *146*, 59−75.
(33) Pokrovsky, O. S.; Viers, J.; Freydier, R. *J. Colloid Interface Sci.* **2005**, *291*, 192−200.
(34) Juillot, F.; Maréchal, C.; Ponthieu, M.; Cacaly, S.; Morin, G.; Benedetti, M.; Hazemann, J. L.; Proux, O.; Guyot, F. *Geochim. Cosmochim. Acta* **2008**, *72*, 4886−4900.
(35) Weiss, D. J.; Mason, T. F. D.; Zhao, F. J.; Kirk, G. J. D.; Coles, B. J.; Horstwood, M. S. A. *New Phytol.* **2005**, *165*, 703−710.
(36) Gélabert, A.; Pokrovsky, O. S.; Viers, J.; Schott, J.; Boudou, A.; Feurtet-Mazel, A. *Geochim. Cosmochim. Acta* **2006**, *70*, 839−857.
(37) Black, J. R.; Yin, Q.-z.; Rustad, J. R.; Casey, W. H. *J. Am. Chem. Soc.* **2007**, *129*, 8690−8691.
(38) Viers, J.; Oliva, P.; Nonell, A.; Gélabert, A.; Sonke, J. E.; Freydier, R.; Gainville, R.; Dupré, B. *Chem. Geol.* **2007**, *239*, 124−137.
(39) Rodushkin, I.; Stenberg, A.; Andrén, H.; Malinovsky, D.; Baxter, D. C. *Anal. Chem.* **2004**, *76*, 2148−2151.
(40) Galy, A.; Bar-Matthews, M.; Halicz, L.; O'Nions, R. K. *Earth Planet. Sci. Lett.* **2002**, *201*, 105−115.
(41) Immenhauser, A.; Buhl, D.; Richter, D.; Niedermayr, A.; Riechelmann, D.; Dietzel, M.; Schulte, U. *Geochim. Cosmochim. Acta* **2010**, *74*, 4346−4364.
(42) Li, W.; Chakraborty, S.; Beard, B. L.; Romanek, C. S.; Johnson, C. M. *Earth Planet. Sci. Lett.* **2012**, *333−334*, 304−316.
(43) Saulnier, S.; Rollion-Bard, C.; Vigier, N.; Chaussidon, M. *Geochim. Cosmochim. Acta* **2012**, *91*, 75−91.
(44) Bullen, T. D. In *Treatise on Geochemistry*, 2nd ed., Vol. 7; Holland, H., Turekian, K., Eds.; Elsevier: Amsterdam, 2014.
(45) Baes, C. F.; Mesmer, R. E. *Hydrolysis of cations*; John Wiley & Sons: Hoboken, NJ, 1976.
(46) Van Gaans, P.; Oonk, H.; Somsen, G. *J. Solution Chem.* **1990**, *19*, 831−854.
(47) Benézéth, P.; Diakonov, I. I.; Pokrovski, G. S.; Dandurand, J.-L.; Schott, J.; Khodakovsky, I. L. *Geochim. Cosmochim. Acta* **1997**, *61*, 1345−1357.
(48) Aston, F. W. *Proc. R. Soc. London, Ser. A* **1935**, *149*, 396−405.
(49) Sampson, M. B.; Bleakney, W. *Phys. Rev.* **1936**, *50*, 456.
(50) Inghram, M. G.; Hess, D. C., Jr; Brown, H. S.; Goldberg, E. *Phys. Rev.* **1948**, *74*, 343.
(51) Hibbs, R. *Mass Spectrometric Measurements of Natural Isotopic Spectra*; United States Atomic Energy Commission, Technical Information Service: Oak Ridge, TN, 1949.
(52) Antkiw, S.; Dibeler, V. H. *J. Chem. Phys.* **1953**, *21*, 1890−1891.
(53) Mason, T. F. D.; Weiss, D. J.; Horstwood, M.; Parrish, R. R.; Russell, S. S.; Mullane, E.; Coles, B. J. *J. Anal. At. Spectrom.* **2004**, *19*, 218−226.
(54) Yang, L.; Meija, J. *Anal. Chem.* **2010**, *82*, 4188−4193.
(55) Machlan, L.; Gramlich, J.; Powell, L.; Lambert, G. *J. Res. Natl. Bur. Stand.* **1986**, *91*, 323−331.
(56) Brand, W. A.; Coplen, T. B.; Vogl, J.; Rosner, M.; Prohaska, T. *Pure Appl. Chem.* **2014**, *86*, 425−467.
(57) Woodhead, J. *J. Anal. At. Spectrom.* **2002**, *17*, 1381−1385.
(58) Archer, C.; Vance, D. *J. Anal. At. Spectrom.* **2004**, *19*, 656−665.
(59) Vance, D.; Archer, C.; Bermin, J.; Kennaway, G.; Cox, E. J.; Statham, P. J.; Lohan, M. C.; Ellwood, M. J. *Geochim. Cosmochim. Acta* **2006**, *70*, A666−A666.
(60) Hou, Q.; Zhou, L.; Gao, S.; Zhang, T.; Feng, L.; Yang, L. *J. Anal. At. Spectrom.* **2016**, *31*, 280−287.
(61) Roehl, R.; Gomez, J.; Woodhouse, L. R. *J. Anal. At. Spectrom.* **1995**, *10*, 15−23.
(62) Strelow, F. W. E. *Talanta* **1980**, *27*, 727−732.
(63) Kiriyama, T.; Kuroda, R. *Fresenius' Z. Anal. Chem.* **1988**, *332*, 338−340.
(64) Tremillon, B. *Mir, Moscow* **1967**, 33.
(65) Strelow, F.; Weinert, C.; Eloff, C. *Anal. Chem.* **1972**, *44*, 2352−2356.
(66) Chang, V. T.-C.; Makishima, A.; Belshaw, N. S.; O'Nions, R. K. *J. Anal. At. Spectrom.* **2003**, *18*, 296−301.
(67) Horwitz, E.; Bloomquist, C. *J. Inorg. Nucl. Chem.* **1975**, *37*, 425−434.
(68) Huang, Q.; Liu, Y. L.; Chen, J. B.; Feng, X. B.; Huang, W. L.; Yuan, S. L.; Cai, H. M.; Fu, X. W. *J. Anal. At. Spectrom.* **2015**, *30*, 957−966.