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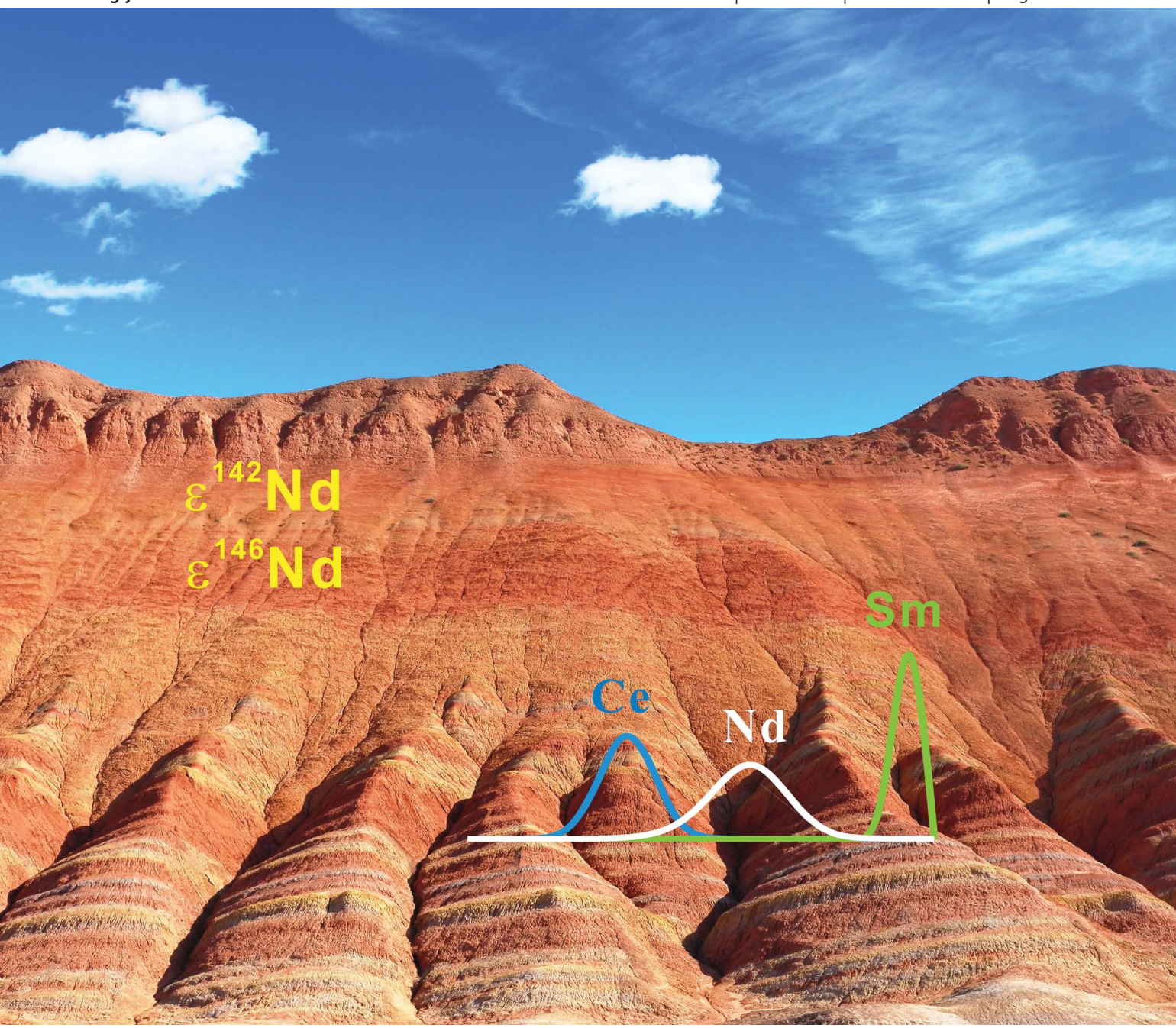

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Precise measurement of stable neodymium isotopes of geological materials by using MC-ICP-MS

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Jinlong Ma,*[a] Gangjian Wei,*[a] Ying Liu,[a] Zhongyuan Ren,[a] Yigang Xu[a] and Yonghong Yang[b]

A method has been developed to determine high-precision stable Nd isotopic compositions in geological samples by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using sample-standard-bracketing (SSB) mode. Nd was pre-concentrated and purified through a two-column ion-exchange chromatographic procedure. The recovery for Nd is generally better than 96%, and the interferences, such as Ce and Sm can be efficiently removed, allowing negligible influence on the stable Nd isotopic composition during mass spectrometry measurement. The internal precision for the stable Nd isotopic compositions, ε^{142}Nd, ε^{145}Nd, ε^{146}Nd and ε^{148}Nd were generally better than $\pm$0.2 (2 SEM), and the external precision was generally better than $\pm$0.2 (1 SD) for ε^{142}Nd, ε^{145}Nd and ε^{146}Nd, and better than $\pm$0.5 (1 SD) for ε^{148}Nd based on the long-term results of the Nd standard solutions, such as La Jolla, Nd-GIG and NIST 3135a. Both the internal and external precisions are comparable to those by double-spike method. The averages of our measured ε^{142}Nd, ε^{145}Nd, ε^{146}Nd and ε^{148}Nd results of La Jolla are identical to those by the double-spike method within analytical error. Thus, our method can provide comparable results with the double-spike method, but does not bring any inconvenience of calibrating double spikes, and the efficiency is greatly improved. This provides a more convenient way for studying stable Nd isotopes in geological processes. By using this method, the stable Nd isotopic compositions for a series of international rock standard references were measured.

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Introduction

The Sm–Nd system is one of the most important isotopic systematics that have been broadly applied in isotope geochronology and geochemistry studies.[1] Nd has seven natural isotopes: ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd and ^{150}Nd. Among them, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd and ^{150}Nd are stable, while ^{142}Nd and ^{143}Nd consist of a radiogenic component derived from the decay of ^{146}Sm and ^{147}Sm, respectively. As the half-life of ^{146}Sm is fairly short ($\sim$68 Ma),[2] radiogenic ^{142}Nd can only be identified in meteorites and rocks of very old age on the Earth.[3–8] The ratios between the stable Nd isotopes are generally considered to be constant during geological processes, and some of them, such as ^{146}Nd/^{142}Nd = 0.63613 and ^{146}Nd/^{144}Nd = 0.7219, have been applied to correct for the mass bias during high-precision Nd isotope measurements.[9–11] Recent studies, however, have indicated that there occurs some significant fractionation for heavy mass isotopes, such as Sr during some geological processes. For example, the stable Sr isotope ratio ^{88}Sr/^{86}Sr has been proven to change significantly during chemical weathering and carbonate concentration.[12–15] Given that the isotopic fractionation is basically controlled by the relative mass difference ($\Delta m/m$), the $\Delta m/m$ for ^{88}Sr/^{86}Sr is of about 0.023, of about 0.014 and 0.028 for ^{146}Nd/^{144}Nd and ^{148}Nd/^{144}Nd, respectively. It is therefore the relative mass differences for the stable Nd isotope ratios that are comparable to that for ^{88}Sr/^{86}Sr. The geological processes that cause stable Sr isotope fractionation may apparently induce stable Nd isotope fractionation. However, the studies on such issues are currently scarce.

The fractionation of the stable Nd isotopes can be described as ε^xNd, defined as follows:

$$\varepsilon^{x}\mathrm{Nd} = \left(\frac{{}^{x}\mathrm{Nd}/{}^{144}\mathrm{Nd}_{\mathrm{sample}}}{{}^{x}\mathrm{Nd}/{}^{144}\mathrm{Nd}_{\mathrm{standard}}} - 1 \right) \times 10\,000$$

where ^{x}Nd could be any of the Nd isotopes rather than ^{144}Nd, and JNdi-1 is generally used as the standard reference material.[16] Great efforts have been made to measure high-precision ^{142}Nd/^{144}Nd ratios in the past decade.[17–19] These methods, however, mostly aim at identifying ε^{142}Nd anomalies for the investigation of the early differentiation of the Earth, and internal mass bias correction using a constant ratio of ^{146}Nd/^{144}Nd = 0.7219 has been applied for all the Nd isotope ratios during mass

[a]*State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: jlma@gig.ac.cn; gjwei@gig.ac.cn; Fax: +86-20-85290130; +86-20-85290130; Tel: +86-20-85290116; +86-20-85290093*

[b]*CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China*

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spectrometry measurements. Thus, all these results have removed the information of stable Nd isotope fractionation, and could not be used to investigate the possible fractionation for stable Nd isotopes in geological processes. Currently, high-precision, stable Nd isotopic composition can only be obtained by using double spikes, such as $^{145}Nd + ^{150}Nd$ to correct the mass bias during chemical treatments and mass spectrometry measurements.[16] This method is time-consuming in preparing and calibrating the double spikes and complicated in calculation during measurements. Moreover, the double spikes for Nd isotopes are not easily available for many of the laboratories. This may hinder its broad application in geological studies.

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has the advantage of externally correcting the mass bias by using the standard-sample-standard bracketing (SSB) technique. This provides a more convenient way to measure high-precision isotopic compositions compared to that by using double spikes.[20] This technique, however, requires a more rigid chemical pre-treatment to remove all the matrix and the interference constitutions and to enable a ~100% recovery of the target element. As for Nd, pure Nd should be extracted, and Ce and Sm should be removed entirely to avoid the interference of ^{142}Ce on ^{142}Nd, and ^{144}Sm, ^{148}Sm and ^{150}Sm on ^{144}Nd, ^{148}Nd and ^{150}Nd, respectively. Meanwhile, the recovery of Nd should be close to 100% since the ion-exchange chromatography procedure can induce significant Nd isotope fractionation,[16] and loss of Nd during this procedure may bias the stable Nd isotope results seriously.

We herein report our approaches for measuring the high-precision, stable Nd isotopic composition of geological samples by using the SSB technique on MC-ICP-MS. It will be shown that by carefully handling the ion-exchange chromatography procedure, the Nd recovery is close to 100%, and Sm and Ce could be removed to the level such that the interferences could be effectively corrected to not influence the stable Nd isotopic compositions. More importantly, our results are identical to those using the double-spike method. This provides a convenient means for investigating stable Nd isotope fractionation in geological processes.

Experimental

Samples

Some of the geological standard rock references were selected for stable Nd isotope analysis. These samples cover a wide range of rock styles, from basic rocks such as basalt, to acid rocks such as granite and rhyolite. In addition to these rock samples, some pure Nd solution, including the Nd isotope standard references, JNdi-1, La Jolla Nd and a working Nd isotope standard of our lab, Nd-GIG, as well as NIST 3135a, were used as samples to test the efficiency of chemical treatments and measurement on mass-spectrometry.

Reagents

Water. The water was purified from deionized water using a Millipore system. The purified water (Milli-Q water) yields a resistivity of 18.2 MΩ cm.

Hydrofluoric acid and nitrate acids. BVIII grade (for electronic production) 49% HF and concentrated guaranteed reagent HNO_3 were sub-boiled using a Savillex DST-1000 system, separately. The concentrations of the distilled HF and HNO_3 were generally >30 M and >14 M, respectively. They were used for rock sample digestion.

Hydrochloric acid. Concentrated guaranteed reagent HCl was purified using the method similar to that for HF. The distilled HCl was diluted to appropriate concentrations for chemical treatment.

Sample digestion

About 50–80 mg of rock powder was weighed and poured into a pre-cleaned 15 mL PFA beaker, then 2 mL concentrated HF and 1 mL concentrated HNO_3 were added. The beaker was tightly capped and put onto a hot plate at a temperature of 120 °C for 7 days. After the rock powder was entirely dissolved, the beaker was opened and the solution was dried on the hot plate, and then another 1 mL of concentrated HNO_3 was added and the beaker was tightly capped again and put onto the hot plate overnight to re-dissolve the sample. After that, the solution was dried again and re-dissolved with 2 mL of 6 M HCl for 4 h capped on a hot plate. The solution was then dried again and finally re-dissolved with 1 mL 2.5 M HCl. This procedure enables all the Nd in the rock sample to be dissolved in the solution, and is ready for ion-exchange chromatography treatment.

Ion-exchange chromatography

A two-column procedure was adopted for pre-concentrating and purifying the Nd of the rock samples. The first column is to pre-concentrate rare earth elements (REEs). AG50W-X12 strong cation resin of the Bio-Rad company was selected. Each 1 g of AG50W-X12 resin with 200–400 mesh in size was loaded into an Eichrom 0.8 × 8 cm polypropylene column. The ion-exchange chromatography procedure was summarized in Table 1. The eluted REE was dried on a hot plate for further Nd purification on column 2. The Nd recovery during this column procedure was tested by using a basalt standard reference, BHVO-2. A dissolved BHVO-2 solution was separated into two parts with one being treated by the above ion-exchange procedure. The Nd amounts both in the elution and the un-treated aliquot were tested using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Element), and the results indicated that the Nd recovery is >99%.

The dried REE was re-dissolved in 0.2 mL of 0.25 M HCl to further purify the Nd from other REEs on column 2 using Ln resin with di(2-ethylhexyl) orthophosphoric acid (HDEHP) of the Eichrom company. Each 1 g of Ln Spec resin of 50–100 mesh size was loaded into a Bio-Rad 0.7 × 20 cm glass Econo-column. Details of the ion-exchange chromatography procedure are summarized in Table 1 (column 2). The elution curves of this ion-exchange chromatographic procedure for Nd, Ce and Sm were calibrated by using the elution of BHVO-2 after the second column procedure. All the elutions, including sample loading, rinsing and Nd elutions were collected, and the concentrations

Table 1 Ion-exchange chromatography procedure

Column 1: AG50W-X12 resin	
Step	Operation
Step 1	Resin washing and condition 6 M HCl 5 mL × 4 Milli-Q water 5 mL × 1 2.5 M HCl 5 mL × 1
Step 2	Loading sample (1 mL)
Step 3	Washing 2.5 M HCl leaching 5 mL × 5
Step 4	Collecting REE 6 M HCl collecting REE 5 mL × 3
Column 2: LN resin (HDEHP)	
Step	Operation
Step 1	Resin washing and condition 6 M HCl 5 mL × 4 Milli-Q water 5 mL × 1 0.25 M HCl 5 mL × 2
Step 2	Loading sample (0.2 mL)
Step 3	Washing 0.25 M HCl rinsing 0.25 mL × 4 0.25 M HCl rinsing 1.5 mL × 6
Step 4	Collecting Nd 0.25 M HCl 2 mL × 7
Step 5	Washing (remove Sm) 6 M HCl rinsing 2 mL × 3

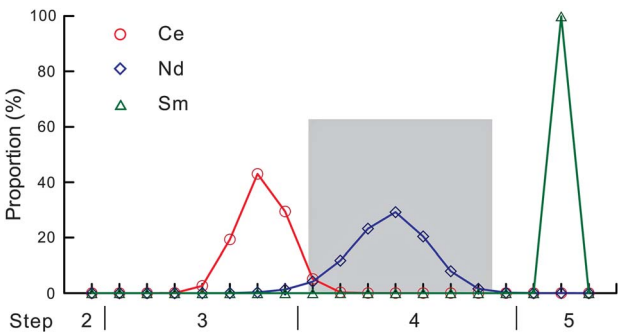

Fig. 1 The elution curves of column 2 of the ion-exchange chromatographic procedure for Nd purification. The point in Step 2 represents the elution of sample loading. The first point in Step 3 represents the total elution of the rinsing of 0.25 mL × 4, and the following 6 points represent each of the elutions of 1.5 mL × 6. The first 7 points in Step 4 represent each of the elutions of 2 mL × 7, and the last point in Step 4 represents the extra 2 mL rinsing to test whether there is still Nd in the elution. The 3 points in Step 5 represent each of the elutions of 2 mL × 3.

of Nd, Ce and Sm in each elution were measured using a Thermo Element ICP-MS. The proportion of each element relative to its total amount in each elution was then calculated from the measured concentrations, and are shown in Fig. 1.

It can be shown in Fig. 1 that the collected Nd eluted by 14 mL of 0.25 M HCl generally accounts for about 98.3% of the total Nd loaded on the column with no Sm being eluted. However, there is about 5% loaded Ce being eluted into this

Table 2 Neptune typical operating parameters for measuring stable Nd isotopes

Parameter	Value
RF forward power	1305 W
Cooling gas	15 L min^{-1}
Auxiliary gas	1.1 L min^{-1}
Sample gas	1.0 L min^{-1}
Extraction	−2000 V
Focus	−726 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Torch setting	
X-pos	−3.310 mm
Y-pos	−2.213 mm
Z-pos	1.103 mm
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	100 μL min^{-1}
Perri-pump	−12.75 rpm
Instrument resolution	400 (low)
Integration time	4.194 s
Idle time	3 s

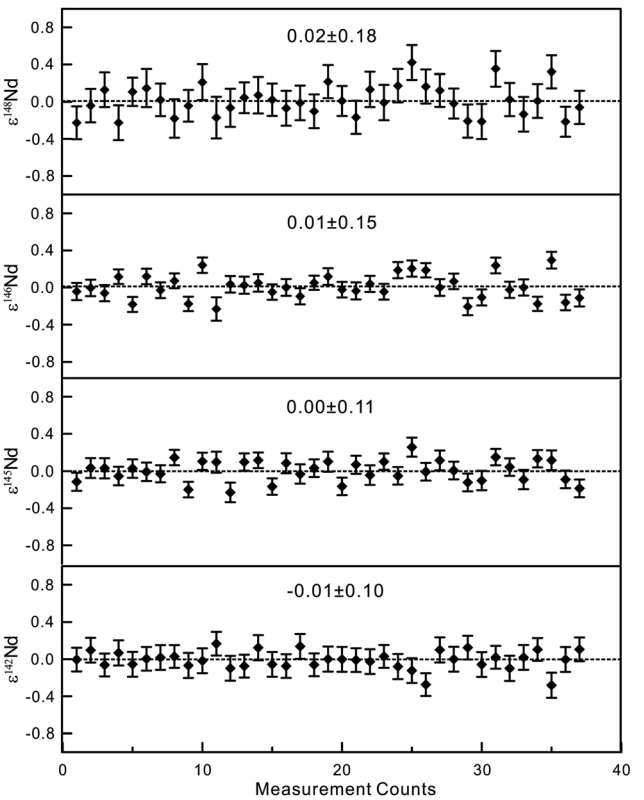

Fig. 2 The stabilities of ε^{142}Nd, ε^{145}Nd, ε^{146}Nd and ε^{148}Nd of the ~10 h continuous measurements for JNdi-1.

solution. As the Ce/Nd ratio of BHVO-2 is about 1.6, the ^{142}Ce may contribute about 2% to the total *m*/*z* 142 in this elution. It will be shown in the following discussion that the interference of ^{142}Ce could be adequately corrected when its contribution to the total *m*/*z* 142 is less than 0.5%. Therefore, the efficiency to separate Ce from Nd is not enough after the column 2

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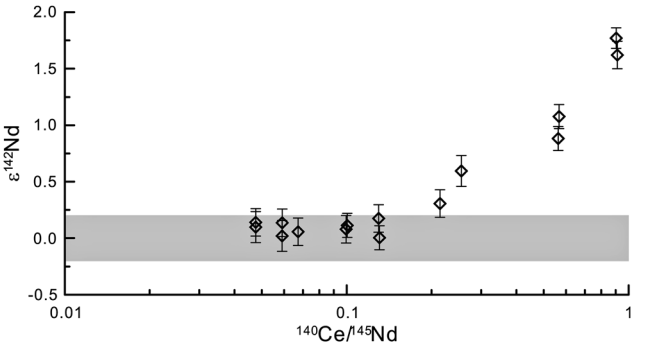

Fig. 3 The influence of ^{142}Ce isobaric interference on ^{142}Nd to the ε^{142}Nd value for JNdi-1.

procedure. We then dried the elution and performed the Column 2 procedure for the second time. The Nd recovery was still >96%, and the ^{142}Ce contribution to the total *m*/*z* 142 is generally about 0.1%. This enables the accurate measurement of ε^{142}Nd as well as the other stable Nd isotopes for most of the rock samples. The elution was dried on a hot plate and then 0.5 mL concentrated HNO_3 was added, dried again and finally re-dissolved in 2% HNO_3 for mass spectrometry measurement.

Instrumentation

The stable Nd isotope analysis in this study was carried out using a Thermo Fisher Scientific Neptune Plus MC-ICP-MS in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). This instrument is a double-focusing magnetic sector field mass spectrometer equipped with 9 Faraday cups and 4 ion counters. Sample solutions in 2% nitric acid were introduced through a Micromist PFA nebulizer and buffered in a glass cyclonic spray chamber. The spray was inlet to a torch directly without any membrane desolvator.

Measuring strategies

All the nine Faraday cups were used in our measurement. The axial Faraday cup was assigned to ^{145}Nd, and L4, L3, L2 and L1 Faraday cups were assigned to ^{140}Ce, ^{142}(Ce + Nd), ^{143}Nd and ^{144}(Nd + Sm), respectively, and H1, H2, H3 Faraday cups were assigned to ^{146}Nd, ^{147}Sm and ^{148}(Nd + Sm), respectively. The H4 Faraday cup was intended to assign to ^{150}(Nd + Sm). Unfortunately, the H3 and H4 Faraday cups were bound together on our machine. The H4 Faraday cup could not reach to the position of *m*/*z* 150 when H3 was at the position of *m*/*z* 148. We therefore gave up the measurement of ^{150}Nd. The isobaric interference of ^{142}Ce on ^{142}Nd was corrected by monitoring ^{140}Ce as $^{142}\text{Ce} = 0.125226 \times {}^{140}\text{Ce}$, and the interferences of Sm on ^{144}Nd and ^{148}Nd were corrected by using $^{144}\text{Sm} = 0.206667 \times {}^{147}\text{Sm}$ and $^{148}\text{Sm} = 0.753352 \times {}^{147}\text{Sm}$,[21] respectively.

The typical instrument parameters during the stable Nd isotope measurement are shown in Table 2. The intensity of ^{145}Nd was generally optimized to about 1.2 V by using a Nd standard of 50–80 ng mL^{-1} before each measurement session, while the background of 2% HNO_3 on *m*/*z* 145 was generally lower than 0.2 mV. Prior to measurement, the measured samples were adjusted to a ^{145}Nd intensity of ~1.2 V, similar to those of the bracketing JNdi-1 standards. This enables a perfect intensity match between the sample and the bracketing

Table 3 The measured stable Nd isotopic compositions of the rock samples and the Nd standard solutions

Sample ID	Sample style	ε^{142}Nd	ε^{145}Nd	ε^{146}Nd	ε^{148}Nd	n^a
Pure Nd standard						
La Jolla		2.10 ± 0.20[b]	−1.10 ± 0.11	−2.06 ± 0.17	−4.16 ± 0.41	13
(Reference)[c]		2.11 ± 0.18	−1.00 ± 0.09	−1.97 ± 0.23	−3.84 ± 0.48	2
Nd-GIG		−2.33 ± 0.19	1.17 ± 0.13	2.25 ± 0.20	4.36 ± 0.33	13
NIST 3135a		0.10 ± 0.25	−0.06 ± 0.15	−0.16 ± 0.19	−0.40 ± 0.57	11
Rock samples						
JA-2	Andesite	−0.43	0.17	0.52	0.59	1
BCR-2	Basalt	0.69 ± 0.20	−0.46 ± 0.09	−0.74 ± 0.08	−1.62 ± 0.32	5
BHVO-2	Basalt	0.98 ± 0.18	−0.59 ± 0.12	−0.72 ± 0.10	−1.72 ± 0.41	5
JB-1	Basalt	0.97	−0.57	−1.00	−2.30	1
JB-3	Basalt	1.09 ± 0.16	−0.69 ± 0.09	−1.05 ± 0.07	−2.25 ± 0.47	2
JG-2	Granite	0.01 ± 0.16	0.16 ± 0.10	0.25 ± 0.09	0.25 ± 0.23	2
G-2	Granite	0.32 ± 0.15	−0.25 ± 0.14	−0.50 ± 0.09	−0.96 ± 0.23	2
JG-1a	Granodiorite	−1.93 ± 0.18	1.13 ± 0.10	2.12 ± 0.27	4.26 ± 0.13	3
GSP-2	Granodiorite	0.85 ± 0.10	−0.42 ± 0.08	−0.71 ± 0.09	−1.72 ± 0.17	2
SDC-1	Mica schist	0.79 ± 0.13	−0.34 ± 0.13	−0.71 ± 0.10	−1.45 ± 0.17	3
JSD-1	Stream sediment	2.85	−1.28	−2.65	−5.09	1
GBW07315	Marine sediment	0.50	−0.68	−0.44	−1.10	1
GBW07246	Polymetallic nodule	−0.12 ± 0.15	0.33 ± 0.10	0.26 ± 0.13	0.51 ± 0.10	2
GBW07295	Polymetallic nodule	−0.00 ± 0.17	0.06 ± 0.14	0.21 ± 0.12	0.33 ± 0.12	2
GBW07296	Polymetallic nodule	0.11 ± 0.15	−0.05 ± 0.14	−0.08 ± 0.14	−0.33 ± 0.18	2

[a] The analysis numbers for the pure Nd standard refer to the separated measurement of different aliquots in different measuring session, and those for rock samples are separated aliquots after full chemical treatments. [b] The errors are the standard deviation (1 SD) of the replicated measurements. For the rock samples only measured once, the errors are not presented. [c] The reference values for La Jolla are from ref. 16.

standards, and avoids possible influences from mis-match. Meanwhile, the signal-to-noise ratio for each measurement is >6000. Thus, the influence of the background is negligible and no on-peak-zero correction is needed.

The measurement was carried out in the sequence of JNdi-1–sample–JNdi-1. The stable Nd isotope ε^{x}Nd values were calculated from the measured Nd isotope ratios of the sample and the averages of the bracketing JNdi-1 as follows:

$$\varepsilon^{x}\mathrm{Nd} = \left(\frac{2 \times {}^{x}\mathrm{Nd}/{}^{144}\mathrm{Nd}_{\mathrm{sample}}}{{}^{x}\mathrm{Nd}/{}^{144}\mathrm{Nd}_{\mathrm{JNdi\text{-}1A}} + {}^{x}\mathrm{Nd}/{}^{144}\mathrm{Nd}_{\mathrm{JNdi\text{-}1B}}} - 1 \right) \times 10\,000$$

where JNdi-1A and JNdi-1B refer to the JNdi-1 standard measured after and before the sample, respectively. The ^{x}Nd/^{144}Nd ratios adopted in these calculations are all the originally measured ratios without any mass bias correction.

Each data acquisition contains 10 blocks with each block containing 10 cycles. The integration time for each cycle is 4.194 s, and the total 100 scans take about 8 min, yielding an internal precision of about ($\pm$5–8) $\times$ 10^{-6}, ($\pm$2–3) $\times$ 10^{-6}, ($\pm$4–5) $\times$ 10^{-6} and ($\pm$3–4) $\times$ 10^{-6} for the ^{142}Nd/^{144}Nd, ^{145}Nd/^{144}Nd, ^{146}Nd/^{144}Nd and ^{148}Nd/^{144}Nd, respectively. Such internal precision corresponds to an uncertainty of around $\pm$0.1 for ε^{142}Nd, ε^{145}Nd and ε^{146}Nd, and of around $\pm$0.2 for ε^{148}Nd estimated by a Gaussian error propagation equation with the measured errors of both the sample and the bracketing standards being considered.

Instrumental mass discrimination stability

Short-term drift in mass bias on MC-ICP-MS between samples and the bracketed standards is believed to affect the precision of the isotopic ratios measured using the direct SSB protocol. Maintaining constant time intervals between each measurement, such as keeping a constant washing time and constant parameters of the instrument after optimization may help to decrease the short-term drift in mass bias of the machine. Fig. 2 shows the results of ε^{142}Nd, ε^{145}Nd, ε^{146}Nd and ε^{148}Nd of the $\sim$10 h continuous measurements of JNdi-1. The external precision for ε^{142}Nd and ε^{145}Nd is of around $\pm$0.1 (1 SD), and of around $\pm$0.15 (1 SD) and $\pm$0.18 (1 SD) for ε^{146}Nd and ε^{148}Nd, respectively. Such a high external precision indicates an excellent stability of the instrumental mass discrimination on our machine. Therefore, high precision stable Nd isotopes could be obtained by using the SSB measuring protocol on our machine.

Influence of Ce on ε^{142}Nd

Because significant Nd isotope fractionation occurs during the ion-exchange chromatography treatments,[16] the loss of Nd during this procedure may significantly bias the stable Nd isotopes. Thus, maintaining nearly 100% recovery of Nd is very important for stable Nd isotope analysis. As mentioned above, our ion-exchange chromatographic procedure can maintain a very high Nd recovery (>96%), and remove all the Sm to avoid isobaric interference of ^{144}Sm and ^{148}Sm on ^{144}Nd and ^{148}Nd, respectively. However, Ce could not be removed entirely when a high Nd recovery is needed. The influence of ^{142}Ce isobaric interference on ^{142}Nd to the ε^{142}Nd value should be evaluated.

Such an influence was tested by adding pure Ce into the JNdi-1 standard to make different Ce/Nd ratios in the solution, and then they were measured as samples. The ratio of ^{140}Ce/^{145}Nd was monitored instantaneously, and the results are shown in Fig. 3. The measured ε^{142}Nd values are all within the range of 0.00 $\pm$ 0.20, the 2 SD range of the short-term variability of the JNdi-1 as shown in Fig. 2 when ^{140}Ce/^{145}Nd is less than 0.2. When the ^{140}Ce/^{145}Nd ratio is larger than 0.2, the measured ε^{142}Nd values increase rapidly, and bias significantly away from the zero value. The $\sim$0.2 ^{140}Ce/^{145}Nd ratio corresponds to about 0.7% contribution of ^{142}Ce to the total signal of m/z 142. For most of the rock samples with Ce/Nd ranging from 1.5 to 5, nearly all the Ce could be removed after the duplicated ion-exchange procedure of column 2, and the ^{142}Ce contribution to the total signal of m/z 142 is generally less than 0.2%. Thus, the Nd elution after such a purification procedure could provide reliable ε^{142}Nd results.

In order to further assess the influence of the chemical treatments on the stable Nd isotopic compositions, pure Ce solution was first added into the JNdi-1 standard to make Ce/Nd ratios ranging from 1.5 to 5. Those Ce-spiked JNdi-1 standards were then treated through the full ion-exchange chromatographic procedure as described above, and measured as samples. The mean, stable Nd isotopic compositions are -0.03 $\pm$ 0.22, 0.00 $\pm$ 0.10, 0.05 $\pm$ 0.18 and 0.06 $\pm$ 0.54 (n = 4, and the errors are 1 SD) for ε^{142}Nd, ε^{145}Nd, ε^{146}Nd, and ε^{148}Nd, respectively. These values are identical to zero within analytical errors. This indicates that the chemical procedure we have developed here is robust for separating Ce from Nd to provide reliable Nd isotopic compositions.

Results and discussion

The ε^{142}Nd, ε^{145}Nd, ε^{146}Nd and ε^{148}Nd results of the pure Nd standards and the rock samples are summarized in Table 3. Each measurement of the pure Nd standards was taken on different aliquots in different measuring sessions, and for the rock samples, each analysis was taken on an individual sample with full chemical treatment. The errors are the standard deviation (1 SD) of the replicated measurements. As shown in Table 3, the external precision for ε^{142}Nd, ε^{145}Nd and ε^{146}Nd is generally better than $\pm$0.25, and better than $\pm$0.5 for ε^{148}Nd. This precision is comparable to that from double-spike methods.[16]

The stable Nd isotopic compositions for La Jolla were previously reported by using the double-spike methods.[16] We also included these results in Table 3 for comparison. Our measured results for La Jolla are identical with these published values within the range of analytical error. It is therefore that our method can measure stable Nd isotopic compositions with both precision and accuracy.

Being a brand new isotopic system, the stable Nd isotopes may potentially be applied in geological studies. Firstly, they could be used to test whether there are stable Nd isotope fractionations during some special geological processes, such as chemical weathering, then to evaluate how the fractionation occurs and to investigate its mechanism. Secondly, the high precision ε^{142}Nd could be useful for investigating the early

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differentiation of the Earth.[17–19] And thirdly, they may have great implications on evaluating the influence of changing $^{146}Nd/^{144}Nd$ on the traditional $^{143}Nd/^{144}Nd$ ratio calibrated by a constant $^{146}Nd/^{144}Nd$ value. As changing $^{88}Sr/^{86}Sr$ can cause significant bias of $^{87}Sr/^{86}Sr$ when it is calibrated by a constant $^{88}Sr/^{86}Sr$ value,[22] a similar situation may possibly occur for the radiogenic Nd isotopic ratio $^{143}Nd/^{144}Nd$. Thus, how such influence takes effect, and to what extent the $^{143}Nd/^{144}Nd$ bias away from its real value should be, are important affairs for Nd isotopic systematics.

Conclusion

We have developed a new method to measure stable Nd isotopic compositions of various geological samples. By using a two-column ion-exchange chromatographic procedure, Nd in geological samples could be effectively pre-concentrated with the isobaric interference materials, such as Ce and Sm, being effectively removed. The stable Nd isotopic compositions $\varepsilon^{142}Nd$, $\varepsilon^{145}Nd$, $\varepsilon^{146}Nd$ and $\varepsilon^{148}Nd$ of the chemically-treated Nd could be precisely measured by MC-ICP-MS by using an SSB mode. The precision and accuracy of our results are in accordance with those from double-spike methods, but our method is more efficient. With no spike being used, our method can provide precise and accurate data on stable Nd isotopic compositions for various geological materials.

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