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Ce–Nd separation by solid-phase micro-extraction and its application to high-precision $^{142}Nd/^{144}Nd$ measurements using TIMS in geological materials

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Abstract:

In view of the low initial abundance of ^{146}Sm, ^{142}Nd anomalies are expected to be extremely small (less than 40 ppm), and their detection requires ultra-precise ^{142}Nd/^{144}Nd measurements. A rapid solid-phase micro-extraction (SPME) technique, using HEHEHP resin as sorbent, is established to completely separate Ce from rare earth elements (REEs) mixtures. This technique is applied to ultra-high-precision ^{142}Nd/^{144}Nd measurements in geological materials. In contrast to the traditional liquid–liquid micro-extraction (LLME) technique, the benefits of SPME tandem column are high Nd recovery, low residual Ce (Ce/Nd $< 10^{-6}$), and easy operability. In addition, a single HEHEHP resin column, replacing the traditional two-column scheme (AG 50W + HDEHP resins), is used to further purify Nd by removing Na salt and Sm isobaric interferences. All mean values of ^{140}Ce/^{144}Nd of geological samples after separation never exceed 0.000010 even though the Ce/Nd ratio of geological materials is > 3.0, Thus, ^{142}Ce interferences on ^{142}Nd never exceed 1.3 ppm. Ultra-high-precision thermal ionization mass spectrometry analyses of silicate standards show that the internal precision of all runs are better than 4 ppm (2 RSE) for ^{142}Nd/^{144}Nd values. ^{142}Nd/^{144}Nd values for JNdi-1, JR-3, and BCR-2 have external precisions of ± 4.8, ± 4.4, and ± 3.9 ppm (2 RSD), respectively. The external reproducibility is sufficient to distinguish and resolve 5 ppm anomalies in ^{142}Nd/^{144}Nd values.

Keywords: ^{142}Nd/^{144}Nd; Solid-phase micro-extraction; HEHEHP resin; TIMS

1. Introduction

Sm and Nd have two different radiogenic decay systems that can be useful in evaluating the hypothesis that the Earth and chondrites have the same Sm/Nd ratios, i.e., ^{146}Sm decays to ^{142}Nd ($T_{1/2}$ = 68 Ma)[1] and ^{147}Sm decays to ^{143}Nd ($T_{1/2}$ = 106 Ga).[1-3] In particular, short-lived ^{146}Sm–^{142}Nd radioactive nuclides are ideal tools for constraining the early silicate differentiation of planetary bodies and the early history of the Earth's mantle.[2-8] Because of its low initial abundance, ^{146}Sm is effectively extinct after 4–5 half-lives, so that ^{142}Nd/^{144}Nd anomalies can be solely related to the differentiation of silicate reservoirs during the first few hundred million years of the Earth. However, their detection requires ultra-precise ^{142}Nd/^{144}Nd ratio measurements because the variation range is very small (< 50 ppm).[2] New generation mass spectrometers (TIMS) has been successfully used to perform this challenging work and published reproducibilities of ^{142}Nd/^{144}Nd are around 5 to 7 ppm (2 RSD),[2-15] the best reproducibility of ^{142}Nd/^{144}Nd is published by Caro et al. (2006) at 2 ppm.[3] For ultra-high-precision ^{142}Nd/^{144}Nd isotopic measurements, a good separation scheme is indispensable. The high-purity separation of Nd from the matrix and isobaric interfering elements is important. In particular, Ce and Sm are the most strongly interfering elements and must be completely separated. During TIMS analysis, ^{140}Ce/^{144}Nd and ^{147}Sm/^{144}Nd ratios must be lower than 0.000010.

Currently, ion exchange resin techniques[2-12, 14-16, 18-27] are widely used to separate Nd from REEs. It is mature to completely separate Sm from Nd using Ln Spec (HDEHP, di(2-ethylhexyl) orthophosphoric acid) resin or HEHEHP (2-ethylhexyl phosphoric mono-2-ethyhexyl ester) resin. In previous studies, the $^{147}Sm/^{144}Nd$ ratio is usually never higher than 0.000005 using Ln Spec resin or HEHEHP resin.[2-26] In contrast to eliminating Sm, complete separation of Ce from Nd is highly difficult. Separation of Ce and Nd is usually performed from high purity REE fractions that are obtained using column chromatographic techniques, such as AG 50W[4, 5, 18-27] or TRU-Spec[2, 3, 7, 10, 11,14] resins. Previously reported procedures of Nd extraction from REEs fractions of rock samples for $^{142}Nd/^{144}Nd$ measurements include the α-hydroxyiso-butyric acid chromatographic technique (HIBA) [4, 7, 14, 16] and the liquid-liquid micro-extraction (LLME)[3, 10, 11, 17, 18] techniques. The HIBA technique needs a good control of the pH value of the eluent solution [4, 7, 14, 16] and is better performed in an acid-free environment. Hence, the pH value of HIBA solution has to be calibrated immediately before performing every experiment. In addition, a narrow and long column (0.2 × 20 cm)[4, 5] allows for good sample purity, which gives rise to low eluting speed and very long separation time. Usually, three repetitions of HIBA chemistry are necessary to reduce ^{142}Ce isobaric interference on ^{142}Nd. The $^{142}Ce/^{142}Nd$ was always below 0.000004 after performing HIBA chemistry separation thrice.[4, 5] The LLME technique was presented by Rehkämper et al. (1996) [17], and it proved to be the most effective method to eliminate Ce from REEs. The LLME technique is based on the distribution of the species of interest between two immiscible phases, namely the aqueous and organic phases. This LLME technique involves the oxidation of Ce^{3+} into its tetravalent state by a strong oxidizing agent ($NaBrO_3$ in 10 M HNO_3) and preferential complexation of Ce^{4+} by an organic extractant (HDEHP).[17] This method combined with cation exchange resin technique was further improved by Caro et al. (2006)[3] and Ali et al.(2011)[18] so that the $^{142}Ce/^{142}Nd$ is always below 0.000003. However, concerning the LLME technique, good technical skill is needed for extracting Nd because the volumes of organic extractant phase containing Ce^{4+} and the aqueous solution containing Nd^{3+} are very small (0.5 mL). This HDEHP organic extractant is pipetted away and discarded, leaving behind the Ce-free aqueous phase solution. Generally, the HDEHP extraction is repeated thrice to eliminate any residual HDEHP organic phase from the Nd and Na enriched phase using n-heptane.[3, 18] Imperfect LLME operation will directly lead to low recovery of Nd or incomplete Ce elimination. For most geologists, achieving high recovery (> 90 %) and high purity for Nd without Ce (Ce/Nd < 0.1 %) during the LLME step is greatly challenging. In addition, separating Na using a cation resin column is indispensable because a lot of Na salt impinges on the ionization efficiency of Nd during TIMS measurements.[3, 18] This causes a severe suppression in signal intensity, unstable ion beam emission, and an abnormal isotopic fractionation process. Generally speaking, LLME and the Na eliminating procedure give rise to the relatively low recovery (~ 80 %) of Nd and tedious operation steps.[3, 18]

In this study, a solid-phase micro-extraction tandem column technique using HEHEHP resin as absorbent was developed to eliminate Ce. Using our method, yield of 97.3 % are achieved for Nd and very minor Ce ($Ce/Nd < 10^{-6}$) was detected in the Nd fraction. In addition, Nd with high purity can be quickly separated from the mixed resulting Na + REEs solution using a short HEHEHP resin column rather than the traditional two-column (AG 50W + HDEHP)[2, 3, 7, 8, 10, 11, 14, 15, 18] technique, which significantly improves separation speed (two working days). In contrast to traditional methods,[2-18] our method greatly cut down separation time and the overall Nd yield was significant improved to ~ 92 %. The accuracy of ^{142}Nd/^{144}Nd results achieved using the proposed protocol was validated through TIMS measurements of nine certified reference materials (CRMs) of silicate rocks with a wide range of Sm/Nd, Ce/Nd and bulk compositions.

2. Experimental

2.1 Reagents and Materials

All analytical reagent grade acids (hydrochloric acid, nitric acid and hydrofluoric acid) were purified using Savillex^{TM} DST-1000 sub-boiling distillation system (Minnetonka, USA). Ultra-pure water with resistivity of 18.2 MΩ.cm^{-1} was used (Milli-Q). Sodium bromate ($NaBrO_3$) with high purity (> 99 %) was purchased from Alfa Aesar. The employed cation exchange column is 7 cm long and has a 6 mm inside diameter with a 30 mL reservoir, packed with 2 mL Bio-Rad AG 50W-X12 resin (200-400 mesh). The solid-phase micro-extraction mini-column is 2 cm long and has a 3 mm i.d and a 0.4 mL reservoir. It is packed with 0.08 mL of HEHEHP resin. The HEHEHP column is 6 cm long and has a 4 mm inside diameter, packed with 0.55 mL HEHEHP resin. The HEHEHP resin, manufactured by the Beijing Research Institute of Chemical Engineering and Metallurgy and conventional for Sm-Nd separation,[19] was based on 2-ethylhexyl phosphoric mono-2-ethyhexyl ester

(HEHEHP) coated on Teflon powder in fine-grained form (75-100 µm).

A stock solution of 500 ppm JNdi-1 Nd standard was gravimetrically prepared to examine the reproducibility of Nd isotopic ratios by a Triton Plus TIMS instrument. Nine rock powders of CRMs were obtained from the United States Geological Survey (USGS) and Geological Survey of Japan (GSJ). These CRMs include USGS BCR-2 (basalt), BHVO-2 (basalt), W-2 (diabase), AGV-2 (andesite), RGM-2 (rhyolite), GSP-2(granodiorite) GSJ JR-3(rhyolite), JG-1a (granodiorite), and JA-3 (andesite).

2.2 Sample digestion

All chemical preparations were conducted on special class 100 workbenches inside a class 1000 clean laboratory. Approximately 100 to 110 mg of rock powder were weighed into a steel-jacketed acid-washed high-pressure PTFE bomb. The samples were dissolved on a hotplate at 190 ^{o}C using an acid mixture of 3 mL of 29 M HF, 0.3 mL of 14 M HNO_3, and 0.3 mL of 11.8 M $HClO_4$ for four days. Digested samples were dried on a hotplate overnight at ~ 120 ^{o}C and then reconstituted in 3 mL of 6 M HCl. This solution was again dried at ~ 160 ^{o}C. Finally, the samples were re-dissolved with 1.1 mL of 2.5 M HCl on a 100 ^{o}C hotplate overnight before commencing ion exchange chemistry.

2.3 Column chemistry

As shown in Fig 1 and Table 1, our separation method is composed of three steps. First, the solutions obtained after sample digestion were centrifuged at 5000 rpm for

8 min. Before sample loading for the separation of REEs from the sample matrix, the resin column was pre-washed with 30 mL of 6 M HCl and 3 mL of H_2O in turn. Then, as shown in Table 1a, 1 mL of the supernatant was loaded onto the pre-conditioned cation columns containing 2 mL of AG50W-X12 (200–400 mesh) resin for separation of REEs from the sample matrix. After rinsing for 4 times with 0.5 mL of 2.5 M HCl, the column was washed with 9.5 mL of 5 M HCl to remove the matrix elements. Then, 16.5 mL of 4 M HCl was used to strip Nd and efficiently remove Ba, La, and some Ce. In this step, all matrix elements (K, Na, Ca, Mg, Al, Fe, Ti), ~ 70 % of La, ~ 75 % of Ba and ~ 65 % of Ce were eliminated and LREEs fractions enriched in Nd (~ 98.2 %) and Sm were obtained. Second, the eluted fraction enriched in Nd was evaporated to dryness and re-dissolved in 0.4 ml of an oxidizing solution of 10 mM $NaBrO_3$ in 10 M HNO_3. During this step, all Ce^{3+} was oxidized to Ce^{4+}. As shown in Table 1b, a tandem micro-column containing 0.16 ml of HEHEHP resin, each single micro-column was packaged with 0.08 ml of HEHEHP resin, was pre-washed with 0.4 mL of 10 M HNO_3 and 0.8 ml of 10 mM $NaBrO_3$ in 10 M HNO_3 in turn for preparation of column condition. The dissolved REEs fraction was loaded on the mini HEHEHP resin column and collected, 0.2 mL of 10 mM $NaBrO_3$ in 10 M HNO_3 was used to elute the residual minor Nd on the column. During this step, all Ce^{4+} (> 99.999%) is strongly sorbed to the HEHEHP resin. The Ce–Nd separation coefficient for this step exceeded 10^6, due to the employed tandem column, two complete extractions were performed. During this step, all Na, Ba and 97.3 % of Nd+Sm were eluted. Finally, the enriched Na, Nd and Sm fraction without Ce was dried and

re-dissolved using 0.2 ml of 0.1 M HCl. As shown in Table 1c, Sm and Nd separation was conducted using a small column containing 0.55 mL of HEHEHP resin. During this step, most Nd (~ 96.5 %) with high purity was separated from the mixed solution (Na + Sm + Nd). All Na was washed before collecting Nd. In final, total procedural blanks were 65–90 pg for Nd and the yield of Nd was higher than 92 %. Procedural blanks were thus negligible, since the ratio of Nd sample/blank was larger than 3300.

2.4 TIMS Measurement

The Nd isotopic ratios were measured using a Triton Plus TIMS instrument (ThermoFisher) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) in Beijing, China. Nd was measured as Nd^+ using a double Re filaments configuration. 0.5 μl of 0.1 M phosphoric acid was first loaded on a degassed Re filament and dried at 0.8 A. Nd samples then were dissolved and loaded in 1 μl of 2 M of HCl and dried at 0.8 A. Finally, after 0.5 μl of 0.1 M phosphoric acid was loaded and dried, the filaments were heated to a dull red glow at c.a 2.2 A for 3 seconds. Previous researches demonstrated that a multi-dynamic measurement approach could obtain the best external reproducibility of $^{142}Nd/^{144}Nd$ (2~6 ppm).[2, 3, 9-11] Hence, we also employed a multi-dynamic measurement approach. Two quadrupole lenses in the Triton Plus were used to adjust the dispersion of the ion beams so that good peak overlaps were obtained during multi-dynamic data acquisition. During measurements, the intensity of the ^{142}Nd signal typically ranged between 2.7 and 4.5 V. Each measurement corresponded to 24 blocks of 26 ratios (8 s integration time) using amplifier rotation. Measurements including filament warm are typically 7~8 hours long. All raw data were corrected for mass fractionation using the exponential law and $^{146}Nd/^{144}Nd = 0.7219$ following the off-line method reported by Caro et al. (2006)[3] and Upadhyay et al.(2008).[9] The $^{142}Nd^+$ signals are corrected for $^{142}Ce^+$ interference using a $^{142}Ce/^{140}Ce$ value of 0.125653.[18] The $^{144}Nd^+$ signals are corrected for $^{144}Sm^+$ interference using a $^{144}Sm/^{147}Sm$ value of 0.204803.[18] The $^{148}Nd^+$ and $^{150}Nd^+$ signals are corrected for $^{148}Sm^+$ and $^{150}Sm^+$ interference using a $^{148}Sm/^{147}Sm$ value of 0.749833 and a $^{150}Sm/^{147}Sm$ value of 0.492328.[18] Further details of collector array and the run conditions were listed in Table 2. JNdi-1 Nd standards were analyzed during the sample measurement period to monitor instrument status. The repeated analyses of JNdi-1 Nd standards yielded highly reliable and reproducible results over a long period of time (~2 years). All JNdi-1 data overlap within errors with recently reported results. The JNdi-1 average value of $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ was 1.1418367 ± 0.0000055 (2 SD, n = 37) and 0.5121009 ± 0.0000036 (2 SD, n = 37), respectively (Table S-1), in good agreement with recently reported $^{142}Nd/^{144}Nd$ (Table 3)[7, 10-12, 15, 27] and $^{143}Nd/^{144}Nd$[15, 19, 20, 22-28] values.

3. Results and discussion

3.1 Merit of solid-phase micro-extraction using HEHEHP resin

In ultra-high-precision $^{142}Nd/^{144}Nd$ measurements, the biggest separation challenge is to completely eliminate Ce from Nd. To test the separation efficiency of Ce from Nd, serial solutions of mixed REEs standards (oxided by the mixed $NaBrO_3$

+10 M HNO_3 solution) were passed through the tandem micro-column containing 0.16 ml of HEHEHP resin. No Ce was detected using ICP-MS, ~ 97.3 % of Nd and all other REEs and Na were collected in Nd analyte object. To check the residual Ce during TIMS measurements, six mixed standards (Ce + Nd) with the ratios of Ce/Nd = 2.0, 3.0 and 4.0 (with 5 μg of Nd) were separated using the SPME technique. Then, because a large amount of Na salt affects the stability of the ion beam, one-third of those samples were loaded and determined using TIMS. As indicated in Table 4, all $^{140}Ce/^{144}Nd$ ratios were lower than 0.000015. This means that ^{142}Ce interferences on ^{142}Nd even for those tests with Ce/Nd = 4.0 are always lower than 2 ppm after performing the SPME separation. Usually, the yield of Nd is about 70~90 % using the traditional LLME technique corresponding to a separation coefficient of 10^3 for Ce and Nd.[3, 18] In contrast to the LLME technique, the recovery of Nd was stable and high (~ 97.3 %), whereas the separation coefficient of Ce and Nd using the SPME technique exceeded 10^6, which is significantly higher than 10^3 using the LLME technique.[2, 3, 10, 11, 15, 17, 18] However, the HEHEHP resin in the tandem micro-column cannot be recycled because the HEHEHP resin had been oxided and had absorbed a lot of Ce.

3.2 Elimination of Na and Sm interferences

High-purity of Nd was obtained following the procedure detailed in Table 1c. To examine the separation efficiency of Na and Sm, a mixed standard containing 5 μg of REEs and 150 μg of Na, 10 μg of Ba was dried and performed separated using the procedure of Table 1c. Table-5 showed that all Na, Ba and most of La(~ 98.5 %) and Ce (~ 97.6 %) were washed out before collecting Nd. All Sm and MREEs + HREEs were washed out after collecting Nd. Sm-Nd separation using a short HEHEHP resin column resulted in ^{144}Sm/^{144}Nd, ^{148}Sm/^{148}Nd and ^{150}Sm/^{150}Nd ratios usually less than 1 ppm, thus, performing Sm isobaric interference correction was not necessary. During this step, ~ 96.5 % Nd was collected. In contrast to previous studies, the two-column method was simplified to one column, and the preparation of a cation AG 50W resin column to eliminate Na salt before performing the Sm-Nd separation was not needed.

3.3 Validation of the method and final results

To assess the analytical reproducibility and feasibility of our chemical procedure for silicate samples, nine CRMs were selected to encompass a wide range of matrix compositions (from mafic to felsic) and Ce/Nd were determined. As shown in Table 6, the ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd isotopic ratios of all analyzed USGS and GSJ reference materials were obtained with an internal precision (2 SE) better than 0.000005 and 0.000002, respectively. The ^{143}Nd/^{144}Nd data presented in Table 6 agree well with previously published data obtained through TIMS or MC-ICP-MS.[19-26, 29-30] Few ^{142}Nd/^{144}Nd data except for BCR-2[31] were reported for those standards in previous studies. Hence, it is difficult to compare the actual difference of ^{142}Nd/^{144}Nd data in this study and previous investigations. As indicated in Table 6 and Fig 2, no ^{142}Nd anomaly in the geological standard samples was found in this study.

The reproducibility of our procedure was demonstrated by nine different dissolutions of BCR-2 and JR-3 powder materials. As shown in Table 6, replicate measurements (n = 9) of BCR-2 yielded a ^{142}Nd/^{144}Nd value of 1.14183491 ± 0.0000044 and a ^{143}Nd/^{144}Nd value of 0.5126205 ± 0.0000032 (2 SD). Replicate measurements (n = 9) of JR-3 yielded a ^{142}Nd/^{144}Nd value of 1.1418339 ± 0.0000050 and a ^{143}Nd/^{144}Nd value of 0.5126666 ± 0.0000016 (2 SD). The ^{142}Nd/^{144}Nd external reproducibility of both BCR-2 and JR-3 were better than 5 ppm (2 SD). Notable is the fact that JR-3 has a high ratio of Ce/Nd (3.13) [32] and a high content of Ce (319 ppm)[32]; ~110 mg of JR-3 yields ~35.1 µg of Ce. Thus, to completely separate Ce from JR-3 is the biggest challenge for our method, even though all ^{140}Ce/^{144}Nd values for JR-3 are never higher than 0.0000009 during TIMS measurements. The maximum ^{142}Ce interference is ~ 1.1 ppm on the ^{142}Nd/^{144}Nd ratio. The ^{142}Ce interference is lower than 0.6 ppm for most silicate samples. This suggests our method is perfect for Ce and Nd separation.

The reproducibility and precision of ^{142}Nd/^{144}Nd data obtained for silicate samples using the presented novel methods are satisfactory and completely fit the demands for the application of the ^{146}Sm-^{142}Nd isotope system.

4. Conclusions

A rapid and robust SPME method using HEHEHP resin as sorbent was developed to eliminate Ce from REEs. Removal of up to 99.999 % of Ce was achieved with a tandem micro-column. Base on the SPME method, using a short

HEHEP resin column, Ce was further removed to 97.6 %, and 96.5 % of Nd with high purity was obtained. Thus, the separation factor between Ce and Nd exceeded 10^8 in final. During this step, all Na and Sm were also completely eliminated. Therefore, the traditional two-column separation procedure to separate Nd from Na and Sm was further simplified to one-column. In contrast to the traditional methods, the proposed separation procedure achieved the satisfactory and rapid separation of Nd-Ce-Sm, thereby offering significant advantages over existing methods in terms of simplicity, Nd recovery, miniaturization, and waste reduction.

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Figure captions

Figure 1. Our separation protocol compared with traditional methods[3, 10, 11, 18]

Figure 2. ^{142}Nd/^{144}Nd data for CRMs samples are plotted as deviations in ppm (μ^{142}Nd) from the JNdi-1 standard relative to the terrestrial Nd standard JNdi-1. $\mu^{142}\text{Nd} = ((^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}}/(^{142}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}-1)\times10^6$, where ^{142}Nd/^{144}Nd value of JNdi-1 is the average value in this study (1.1418367 ± 0.0000055, 2 SD, n = 37). The dashed line area defines the external error of 5 ppm (2 RSD) of the repeated measurements of JNdi-1 standard (n = 37). Error bars are 2 SE errors of individual measurements.

Table 1. Three-step Nd purification scheme using columns of AG 50W-X12 resin, solid-phase micro-extraction, and HEHEHP resin, sequentially.

a. the first column containing 2 mL of AG50W-12 resin

Procedure	Eluting reagent		Eluting volume (mL)
Cleaning column	6.0 M	HCl	30.0
Cleaning column	Milli-Q	Water	3.0
Loading sample	2.5 M	HCl	1.0
Rinsing	2.5 M	HCl	2.0
Rinsing	5.0 M	HCl	9.5
Eluting LREEs	4.0 M	HCl	16.5

b. the second mini solid-phase micro-extraction tandem column containing 0.16 mL of HEHEHP resin

Procedure	Eluting reagent	Eluting volume (mL)
Cleaning column	10 M HNO_3	0.4
Cleaning column	10 mmol $NaBrO_3$ in 10 M HNO_3	0.8
Loading and collecting Nd	10 mmol $NaBrO_3$ in 10 M HNO_3	0.4
Collecting Nd	10 mmol $NaBrO_3$ in 10 M HNO_3	0.2

c. the third column containing 0.55 mL of HEHEHP resin

Procedure	Eluting reagent		Eluting volume (mL)	Fractions
Cleaning column	3 M	HCl	10.0	
Cleaning column	Milli-Q	Water	2.0	
Loading sample	0.1 M	HCl	0.2	F 1
Rinsing	0.1 M	HCl	0.4 (0.1 x 4)	F 1
Rinsing Na, Ba, La, Ce, Pr	0.2 M	HCl	3.0	F 2
Eluting Nd	0.2 M	HCl	1.5	F 3
Rinsing Sm+MREEs+HREEs	6.0 M	HCl	3.0	F 4

Comment: The yield of Nd during the three-step separation procedure is about 98.2 %, 97.3 % and 96.5%, respectively. In the final, the yield of Nd is about 92.2 % after performing three-step separation.

Table-2 Cup setting of dynamic multi-collector mode

Cup	L3	L2	L1	CC	H1	H2	H3	H4	Foucs（V）	Disp（V）
S1	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{150}Nd	0	0
S2		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm	0	5.0
S3	^{140}Ce		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	0	10.0

Run conditions:

Ionization filament heated to 4.6A (1680~1720℃), evaporation filament heated to 1.6-1.9 A.

Typically, a block consisted of 26 cycles each with 3 sequences of 8 seconds integration.

Amplifers rotated left every block, baseline measured every block.

Peak center on ^{145}Nd, ^{144}Nd and ^{143}Nd and ion source lens focus on ^{145}Nd done every 4 block, turret position optimized at start.

Typical ^{142}Nd signal strength on $10^{11}\Omega$ resistor was 3~4 V for most samples.

Magnet removed from the ion source.

Rejected ratios always less than 5 % of total.

Zoom system was employed to improve peak shape. It included Focus quadrupole and Dispersion quadrupole lens.

Table 3. Published JNdi-1 $^{142}Nd/^{144}Nd$ values determined using Triton Plus TIMS

Reference	Reference Value	External precision (2 SD)	Measurement Mode
Gannoun A et al.(2011)[12]	1.1418331	0.0000066 (n=18)	Static
Li et al.(2010)[27]	1.1418353	0.0000074 (n=12)	Static
Rizo et al.(2012)[7]	1.1418400	0.0000030 (n=50)	Dynamic
Roth A.S.G et al.(2014)[10]	1.1418370	0.0000049 (n=13)	Dynamic
Roth A.S.G et al.(2013)[11]	1.1418351	0.0000042 (n=30)	Dynamic
Jackson M.G et al.(2012)[15]	1.1418383	0.0000063 (n=12)	Dynamic
Li et al.(2010)[27]	1.1418348	0.0000044 (n=12)	Dynamic
Mean	1.1418362	0.0000046	

Table 4. Evaluation of residual Ce in the mixed standards after SPME separation

Sample	^{140}Ce/^{144}Nd	Ce/Nd
HEH-1	0.000010	2.0
HEH-2	0.000002	2.0
HEH-3	0.000002	3.0
HEH-4	0.000002	3.0
HEH-5	0.000015	4.0
HEH-6	0.000012	4.0

Note: HEH-1 to HEH-6 are artificial mixed standard solution with the different Ce/Nd ratios. ^{140}Ce/^{144}Nd ratios mean the actual measurement values using TIMS after performing SPME separation.

Table 5. Sample purity and the recovery of Nd in the third HEHEHP resin column

Elements	Fraction 1(%)	Fraction 2(%)	Fraction 3(%)	Fraction 4(%)
Na	92.5	7.5	0	0
Ba	86.3	13.7	0	0
La	28.2	70.2	1.5	0
Ce	2.4	95.2	2.4	0
Pr	0	84.8	14.5	0.7
Nd	0	2.3	96.5	1.2
Sm	0	0	0	100
ΣHREE+MREE	0	0	0	100

Note: The sample purity in different fractions is corresponding to fractions defined in Table 1c

Table 6. Results for Nd isotopic ratios in international CRMs determined using Triton Plus TIMS

CRMs	^{142}Nd/^{144}Nd this study (± 2 SE)	^{143}Nd/^{144}Nd this study (± 2 SE)	^{143}Nd/^{144}Nd Refer Values	^{145}Nd/^{144}Nd this study (± 2 SE)	^{148}Nd/^{144}Nd this study (± 2 SE)	^{150}Nd/^{144}Nd this study (± 2 SE)	^{146}Nd/^{144}Nd$_m$	^{140}Ce/^{144}Nd
JR-3	1.1418321(41)	0.5126655(14)	0.512679[24]	0.3484047(9)	0.2415759(13)	0.2364463(15)	0.720838	0.000004
JR-3	1.1418370(41)	0.5126669(13)		0.3484051(9)	0.2415758(13)	0.2364449(14)	0.721626	0.000006
JR-3	1.1418340(39)	0.5126665(17)		0.3484048(12)	0.2415775(17)	0.2364419(17)	0.723291	0.000003
JR-3	1.1418316(40)	0.5126667(13)		0.3484055(9)	0.2415734(13)	0.2364436(14)	0.721024	0.000006
JR-3	1.1418322(42)	0.5126657(15)		0.3484049(10)	0.2415773(15)	0.2364483(15)	0.721186	0.000005
JR-3	1.1418369(41)	0.5126678(13)		0.3484031(9)	0.2415787(12)	0.2364475(13)	0.722543	0.000002
JR-3	1.1418343(41)	0.5126673(14)		0.3484048(9)	0.2415770(13)	0.2364466(14)	0.721904	0.000002
JR-3	1.1418370(38)	0.5126673(14)		0.3484033(10)	0.2415782(12)	0.2364467(14)	0.722885	0.000003
JR-3	1.1418305(38)	0.5126658(13)		0.3484043(9)	0.2415786(13)	0.2364473(13)	0.720606	0.000004
Mean	1.1418339	0.5126666		0.3484045	0.2415769	0.2364459		
2 SD	0.0000050	0.0000016		0.0000016	0.000003	0.000004		
2 RSD (%)	0.00044	0.00031		0.00046	0.00140	0.00176		
BCR-2	1.1418364(42)	0.5126203(15)	0.512641[19]; 0.512636[24]	0.3484045(11)	0.2415784(16)	0.2364496(17)	0.720932	0.000002
BCR-2	1.1418343(42)	0.5126183(14)	0.512634[29]; 0.512640[30]	0.3484041(11)	0.2415766(15)	0.2364529(15)	0.722074	0.000002
BCR-2	1.1418342(36)	0.5126232(15)		0.3484058(10)	0.2415781(13)	0.2364459(14)	0.722042	0.000007
BCR-2	1.1418374(40)	0.5126217(14)		0.3484032(11)	0.2415758(14)	0.2364510(15)	0.721615	0.000005
BCR-2	1.1418355(39)	0.5126203(13)		0.3484046(10)	0.2415768(12)	0.2364457(13)	0.721406	0.000002
BCR-2	1.1418319(41)	0.5126203(13)		0.3484050(9)	0.2415759(13)	0.2364453(14)	0.721549	0.000003
BCR-2	1.1418323(37)	0.5126184(13)		0.3484047(9)	0.2415769(13)	0.2364454(14)	0.720699	0.000009

BCR-2	1.1418387(38)	0.5126221(12)		0.3484038(9)	0.2415772(12)	0.2364465(13)	0.722028	0.000002
BCR-2	1.1418338(36)	0.5126197(13)		0.3484042(8)	0.2415770(12)	0.2364477(13)	0.721543	0.000004
Mean	1.1418349	0.5126205		0.3484044	0.2415770	0.2364478		
2 SD	0.0000044	0.0000032		0.0000015	0.0000017	0.0000055		
2 RSD (%)	0.00039	0.00062		0.00043	0.00072	0.00234		
AGV-2	1.1418360(40)	0.5127763(14)	0.512790[29]; 0.512781[30]	0.3484050(10)	0.2415770(14)	0.2364462(15)	0.721697	0.000008
JA-3	1.1418314(43)	0.5128387(15)	0.512859[22]; 0.512850[24]	0.3484043(10)	0.2415781(14)	0.2364437(16)	0.723033	0.000010
W-2	1.1418347(44)	0.5125067(16)	0.512512[24]; 0.512516[30]	0.3484034(11)	0.2415835(15)	0.2364497(16)	0.722207	0.000010
BHVO-2	1.1418353(39)	0.5129682(14)	0.512983[25]; 0.512981[29]	0.3484045(10)	0.2415800(13)	0.2364598(15)	0.721719	0.000002
JG-1a	1.1418382(43)	0.5123705(15)	0.512365[21]; 0.512383[22]	0.3484032(11)	0.2415755(15)	0.2364476(16)	0.721063	0.000006
RGM-2	1.1418338(42)	0.5127815(13)	0.512803[26]	0.3484045(9)	0.2415821(14)	0.2364519(14)	0.722395	0.000002
GSP-2	1.1418351(41)	0.5113480(14)	0.511368[24]; 0.511369[29]	0.3484053(10)	0.2415758(14)	0.2364483(15)	0.720373	0.000008

Note: The measured average value for ^{146}Nd/^{144}Nd$_m$ in sequence S2 is shown for reference. Few ^{142}Nd/^{144}Nd data in silicate standards are reported except for BCR-2, which average value is 1.1418327 (n = 2) reported by Roth et al. (2014)[31].

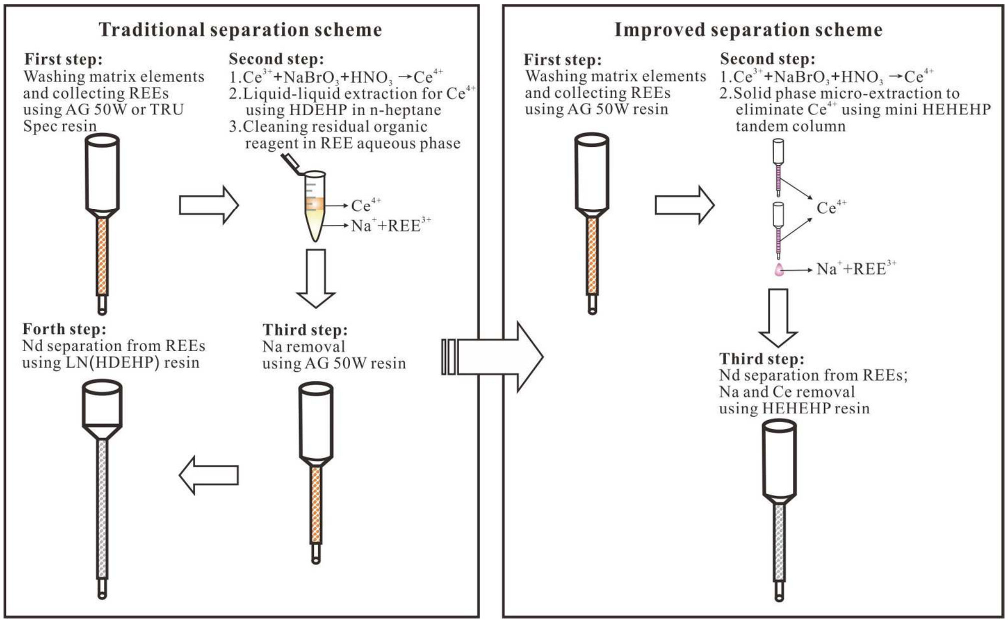

Figure 1
193x119mm (300 x 300 DPI)

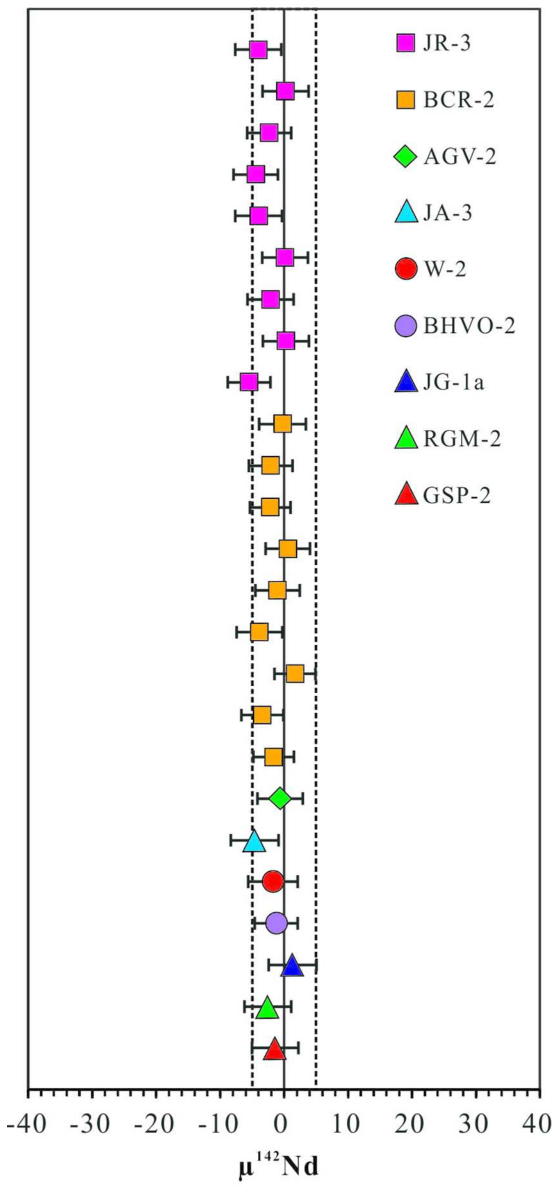

Figure 2
67x148mm (300 x 300 DPI)