

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

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23 **Abstract:**

24 In view of the low initial abundance of ^{146}Sm , ^{142}Nd anomalies are expected to be
25 extremely small (less than 40 ppm), and their detection requires ultra-precise
26 $^{142}\text{Nd}/^{144}\text{Nd}$ measurements. A rapid solid-phase micro-extraction (SPME) technique,
27 using HEHEHP resin as sorbent, is established to completely separate Ce from rare
28 earth elements (REEs) mixtures. This technique is applied to ultra-high-precision
29 $^{142}\text{Nd}/^{144}\text{Nd}$ measurements in geological materials. In contrast to the traditional
30 liquid–liquid micro-extraction (LLME) technique, the benefits of SPME tandem
31 column are high Nd recovery, low residual Ce ($\text{Ce}/\text{Nd} < 10^{-6}$), and easy operability. In
32 addition, a single HEHEHP resin column, replacing the traditional two-column
33 scheme (AG 50W + HDEHP resins), is used to further purify Nd by removing Na salt
34 and Sm isobaric interferences. All mean values of $^{140}\text{Ce}/^{144}\text{Nd}$ of geological samples
35 after separation never exceed 0.000010 even though the Ce/Nd ratio of geological
36 materials is > 3.0 . Thus, ^{142}Ce interferences on ^{142}Nd never exceed 1.3 ppm.
37 Ultra-high-precision thermal ionization mass spectrometry analyses of silicate
38 standards show that the internal precision of all runs are better than 4 ppm (2 RSE) for
39 $^{142}\text{Nd}/^{144}\text{Nd}$ values. $^{142}\text{Nd}/^{144}\text{Nd}$ values for JNdi-1, JR-3, and BCR-2 have external
40 precisions of ± 4.8 , ± 4.4 , and ± 3.9 ppm (2 RSD), respectively. The external
41 reproducibility is sufficient to distinguish and resolve 5 ppm anomalies in $^{142}\text{Nd}/^{144}\text{Nd}$
42 values.

43

44 **Keywords:** $^{142}\text{Nd}/^{144}\text{Nd}$; Solid-phase micro-extraction; HEHEHP resin; TIMS

45 **1. Introduction**

46 Sm and Nd have two different radiogenic decay systems that can be useful in
47 evaluating the hypothesis that the Earth and chondrites have the same Sm/Nd ratios,
48 i.e., ^{146}Sm decays to ^{142}Nd ($T_{1/2} = 68 \text{ Ma}$)¹ and ^{147}Sm decays to ^{143}Nd ($T_{1/2} = 106$
49 Ga).¹⁻³ In particular, short-lived ^{146}Sm – ^{142}Nd radioactive nuclides are ideal tools for
50 constraining the early silicate differentiation of planetary bodies and the early history
51 of the Earth's mantle.²⁻⁸ Because of its low initial abundance, ^{146}Sm is effectively
52 extinct after 4–5 half-lives, so that $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies can be solely related to the
53 differentiation of silicate reservoirs during the first few hundred million years of the
54 Earth. However, their detection requires ultra-precise $^{142}\text{Nd}/^{144}\text{Nd}$ ratio measurements
55 because the variation range is very small ($< 50 \text{ ppm}$).² New generation mass
56 spectrometers (TIMS) has been successfully used to perform this challenging work
57 and published reproducibilities of $^{142}\text{Nd}/^{144}\text{Nd}$ are around 5 to 7 ppm (2 RSD),²⁻¹⁵ the
58 best reproducibility of $^{142}\text{Nd}/^{144}\text{Nd}$ is published by Caro et al. (2006) at 2 ppm.³ For
59 ultra-high-precision $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic measurements, a good separation scheme is
60 indispensable. The high-purity separation of Nd from the matrix and isobaric
61 interfering elements is important. In particular, Ce and Sm are the most strongly
62 interfering elements and must be completely separated. During TIMS analysis,
63 $^{140}\text{Ce}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios must be lower than 0.000010.

64 Currently, ion exchange resin techniques^{2-12, 14-16, 18-27} are widely used to separate
65 Nd from REEs. It is mature to completely separate Sm from Nd using Ln Spec
66 (HDEHP, di(2-ethylhexyl) orthophosphoric acid) resin or HEHEHP (2-ethylhexyl

67 phosphoric mono-2-ethylhexyl ester) resin. In previous studies, the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is
68 usually never higher than 0.000005 using Ln Spec resin or HEHEHP resin.²⁻²⁶ In
69 contrast to eliminating Sm, complete separation of Ce from Nd is highly difficult.
70 Separation of Ce and Nd is usually performed from high purity REE fractions that are
71 obtained using column chromatographic techniques, such as AG 50W^{4, 5, 18-27} or
72 TRU-Spec^{2, 3, 7, 10, 11, 14} resins. Previously reported procedures of Nd extraction from
73 REEs fractions of rock samples for $^{142}\text{Nd}/^{144}\text{Nd}$ measurements include the
74 α -hydroxyiso-butyric acid chromatographic technique (HIBA)^{4, 7, 14, 16} and the
75 liquid-liquid micro-extraction (LLME)^{3, 10, 11, 17, 18} techniques. The HIBA technique
76 needs a good control of the pH value of the eluent solution^{4, 7, 14, 16} and is better
77 performed in an acid-free environment. Hence, the pH value of HIBA solution has to
78 be calibrated immediately before performing every experiment. In addition, a narrow
79 and long column (0.2×20 cm)^{4, 5} allows for good sample purity, which gives rise to
80 low eluting speed and very long separation time. Usually, three repetitions of HIBA
81 chemistry are necessary to reduce ^{142}Ce isobaric interference on ^{142}Nd . The
82 $^{142}\text{Ce}/^{142}\text{Nd}$ was always below 0.000004 after performing HIBA chemistry separation
83 thrice.^{4, 5} The LLME technique was presented by Rehkämper et al. (1996)¹⁷, and it
84 proved to be the most effective method to eliminate Ce from REEs. The LLME
85 technique is based on the distribution of the species of interest between two
86 immiscible phases, namely the aqueous and organic phases. This LLME technique
87 involves the oxidation of Ce^{3+} into its tetravalent state by a strong oxidizing agent
88 (NaBrO_3 in 10 M HNO_3) and preferential complexation of Ce^{4+} by an organic

89 extractant (HDEHP).¹⁷ This method combined with cation exchange resin technique
90 was further improved by Caro et al. (2006)³ and Ali et al.(2011)¹⁸ so that the
91 $^{142}\text{Ce}/^{142}\text{Nd}$ is always below 0.000003. However, concerning the LLME technique,
92 good technical skill is needed for extracting Nd because the volumes of organic
93 extractant phase containing Ce^{4+} and the aqueous solution containing Nd^{3+} are very
94 small (0.5 mL). This HDEHP organic extractant is pipetted away and discarded,
95 leaving behind the Ce-free aqueous phase solution. Generally, the HDEHP extraction
96 is repeated thrice to eliminate any residual HDEHP organic phase from the Nd and Na
97 enriched phase using n-heptane.^{3, 18} Imperfect LLME operation will directly lead to
98 low recovery of Nd or incomplete Ce elimination. For most geologists, achieving high
99 recovery (> 90 %) and high purity for Nd without Ce ($\text{Ce}/\text{Nd} < 0.1 \%$) during the
100 LLME step is greatly challenging. In addition, separating Na using a cation resin
101 column is indispensable because a lot of Na salt impinges on the ionization efficiency
102 of Nd during TIMS measurements.^{3, 18} This causes a severe suppression in signal
103 intensity, unstable ion beam emission, and an abnormal isotopic fractionation process.
104 Generally speaking, LLME and the Na eliminating procedure give rise to the
105 relatively low recovery (~ 80 %) of Nd and tedious operation steps.^{3, 18}

106 In this study, a solid-phase micro-extraction tandem column technique using
107 HEHEHP resin as absorbent was developed to eliminate Ce. Using our method, yield
108 of 97.3 % are achieved for Nd and very minor Ce ($\text{Ce}/\text{Nd} < 10^{-6}$) was detected in the
109 Nd fraction. In addition, Nd with high purity can be quickly separated from the mixed
110 resulting Na + REEs solution using a short HEHEHP resin column rather than the

111 traditional two-column (AG 50W + HDEHP)^{2, 3, 7, 8, 10, 11, 14, 15, 18} technique, which
112 significantly improves separation speed (two working days). In contrast to traditional
113 methods,²⁻¹⁸ our method greatly cut down separation time and the overall Nd yield was
114 significant improved to ~ 92 %. The accuracy of ¹⁴²Nd/¹⁴⁴Nd results achieved using
115 the proposed protocol was validated through TIMS measurements of nine certified
116 reference materials (CRMs) of silicate rocks with a wide range of Sm/Nd, Ce/Nd and
117 bulk compositions.

118

119 **2. Experimental**

120 **2.1 Reagents and Materials**

121 All analytical reagent grade acids (hydrochloric acid, nitric acid and hydrofluoric
122 acid) were purified using SavillexTM DST-1000 sub-boiling distillation system
123 (Minnetonka, USA). Ultra-pure water with resistivity of 18.2 MΩ.cm⁻¹ was used
124 (Milli-Q). Sodium bromate (NaBrO₃) with high purity (> 99 %) was purchased from
125 Alfa Aesar. The employed cation exchange column is 7 cm long and has a 6 mm
126 inside diameter with a 30 mL reservoir, packed with 2 mL Bio-Rad AG 50W-X12
127 resin (200-400 mesh). The solid-phase micro-extraction mini-column is 2 cm long and
128 has a 3 mm i.d and a 0.4 mL reservoir. It is packed with 0.08 mL of HEHEHP resin.
129 The HEHEHP column is 6 cm long and has a 4 mm inside diameter, packed with 0.55
130 mL HEHEHP resin. The HEHEHP resin, manufactured by the Beijing Research
131 Institute of Chemical Engineering and Metallurgy and conventional for Sm-Nd
132 separation,¹⁹ was based on 2-ethylhexyl phosphoric mono-2-ethylhexyl ester

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

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

140

141 **2.2 Sample digestion**

142 All chemical preparations were conducted on special class 100 workbenches
143 inside a class 1000 clean laboratory. Approximately 100 to 110 mg of rock powder
144 were weighed into a steel-jacketed acid-washed high-pressure PTFE bomb. The
145 samples were dissolved on a hotplate at 190 °C using an acid mixture of 3 mL of 29 M
146 HF, 0.3 mL of 14 M HNO₃, and 0.3 mL of 11.8 M HClO₄ for four days. Digested
147 samples were dried on a hotplate overnight at ~ 120 °C and then reconstituted in 3 mL
148 of 6 M HCl. This solution was again dried at ~ 160 °C. Finally, the samples were
149 re-dissolved with 1.1 mL of 2.5 M HCl on a 100 °C hotplate overnight before
150 commencing ion exchange chemistry.

151

152 **2.3 Column chemistry**

153 As shown in Fig 1 and Table 1, our separation method is composed of three steps.

154 First, the solutions obtained after sample digestion were centrifuged at 5000 rpm for

155 8 min. Before sample loading for the separation of REEs from the sample matrix, the
156 resin column was pre-washed with 30 mL of 6 M HCl and 3 mL of H₂O in turn. Then,
157 as shown in Table 1a, 1 mL of the supernatant was loaded onto the pre-conditioned
158 cation columns containing 2 mL of AG50W-X12 (200–400 mesh) resin for separation
159 of REEs from the sample matrix. After rinsing for 4 times with 0.5 mL of 2.5 M HCl,
160 the column was washed with 9.5 mL of 5 M HCl to remove the matrix elements. Then,
161 16.5 mL of 4 M HCl was used to strip Nd and efficiently remove Ba, La, and some Ce.
162 In this step, all matrix elements (K, Na, Ca, Mg, Al, Fe, Ti), ~ 70 % of La, ~ 75 % of
163 Ba and ~ 65 % of Ce were eliminated and LREEs fractions enriched in Nd (~ 98.2 %)
164 and Sm were obtained. Second, the eluted fraction enriched in Nd was evaporated to
165 dryness and re-dissolved in 0.4 ml of an oxidizing solution of 10 mM NaBrO₃ in 10
166 M HNO₃. During this step, all Ce³⁺ was oxidized to Ce⁴⁺. As shown in Table 1b, a
167 tandem micro-column containing 0.16 ml of HEHEHP resin, each single
168 micro-column was packaged with 0.08 ml of HEHEHP resin, was pre-washed with
169 0.4 mL of 10 M HNO₃ and 0.8 ml of 10 mM NaBrO₃ in 10 M HNO₃ in turn for
170 preparation of column condition. The dissolved REEs fraction was loaded on the mini
171 HEHEHP resin column and collected, 0.2 mL of 10 mM NaBrO₃ in 10 M HNO₃ was
172 used to elute the residual minor Nd on the column. During this step, all Ce⁴⁺ (>
173 99.999%) is strongly sorbed to the HEHEHP resin. The Ce–Nd separation coefficient
174 for this step exceeded 10⁶, due to the employed tandem column, two complete
175 extractions were performed. During this step, all Na, Ba and 97.3 % of Nd+Sm were
176 eluted. Finally, the enriched Na, Nd and Sm fraction without Ce was dried and

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

183

184 **2.4 TIMS Measurement**

185 The Nd isotopic ratios were measured using a Triton Plus TIMS instrument
186 (ThermoFisher) at the Institute of Geology and Geophysics, Chinese Academy of
187 Sciences (IGGCAS) in Beijing, China. Nd was measured as Nd⁺ using a double Re
188 filaments configuration. 0.5 µl of 0.1 M phosphoric acid was first loaded on a
189 degassed Re filament and dried at 0.8 A. Nd samples then were dissolved and loaded
190 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
191 was loaded and dried, the filaments were heated to a dull red glow at c.a 2.2 A for 3
192 seconds. Previous researches demonstrated that a multi-dynamic measurement
193 approach could obtain the best external reproducibility of ¹⁴²Nd/¹⁴⁴Nd (2~6 ppm).^{2, 3,}
194 ⁹⁻¹¹ Hence, we also employed a multi-dynamic measurement approach. Two
195 quadrupole lenses in the Triton Plus were used to adjust the dispersion of the ion
196 beams so that good peak overlaps were obtained during multi-dynamic data
197 acquisition. During measurements, the intensity of the ¹⁴²Nd signal typically ranged
198 between 2.7 and 4.5 V. Each measurement corresponded to 24 blocks of 26 ratios (8 s

199 integration time) using amplifier rotation. Measurements including filament warm are
200 typically 7~8 hours long. All raw data were corrected for mass fractionation using the
201 exponential law and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ following the off-line method reported by
202 Caro et al. (2006)³ and Upadhyay et al.(2008).⁹ The $^{142}\text{Nd}^+$ signals are corrected for
203 $^{142}\text{Ce}^+$ interference using a $^{142}\text{Ce}/^{140}\text{Ce}$ value of 0.125653.¹⁸ The $^{144}\text{Nd}^+$ signals are
204 corrected for $^{144}\text{Sm}^+$ interference using a $^{144}\text{Sm}/^{147}\text{Sm}$ value of 0.204803.¹⁸ The $^{148}\text{Nd}^+$
205 and $^{150}\text{Nd}^+$ signals are corrected for $^{148}\text{Sm}^+$ and $^{150}\text{Sm}^+$ interference using a
206 $^{148}\text{Sm}/^{147}\text{Sm}$ value of 0.749833 and a $^{150}\text{Sm}/^{147}\text{Sm}$ value of 0.492328.¹⁸ Further details
207 of collector array and the run conditions were listed in Table 2. JNdi-1 Nd standards
208 were analyzed during the sample measurement period to monitor instrument status.
209 The repeated analyses of JNdi-1 Nd standards yielded highly reliable and reproducible
210 results over a long period of time (~2 years). All JNdi-1 data overlap within errors
211 with recently reported results. The JNdi-1 average value of $^{142}\text{Nd}/^{144}\text{Nd}$ and
212 $^{143}\text{Nd}/^{144}\text{Nd}$ was 1.1418367 ± 0.0000055 (2 SD, n = 37) and 0.5121009 ± 0.0000036
213 (2 SD, n = 37), respectively (Table S-1), in good agreement with recently reported
214 $^{142}\text{Nd}/^{144}\text{Nd}$ (Table 3)^{7, 10-12, 15, 27} and $^{143}\text{Nd}/^{144}\text{Nd}$ ^{15, 19, 20, 22-28} values.

215

216 **3. Results and discussion**

217 **3.1 Merit of solid-phase micro-extraction using HEHEHP resin**

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

221 +10 M HNO₃ solution) were passed through the tandem micro-column containing
222 0.16 ml of HEHEHP resin. No Ce was detected using ICP-MS, ~ 97.3 % of Nd and all
223 other REEs and Na were collected in Nd analyte object. To check the residual Ce
224 during TIMS measurements, six mixed standards (Ce + Nd) with the ratios of Ce/Nd
225 = 2.0, 3.0 and 4.0 (with 5 µg of Nd) were separated using the SPME technique. Then,
226 because a large amount of Na salt affects the stability of the ion beam, one-third of
227 those samples were loaded and determined using TIMS. As indicated in Table 4, all
228 ¹⁴⁰Ce/¹⁴⁴Nd ratios were lower than 0.000015. This means that ¹⁴²Ce interferences on
229 ¹⁴²Nd even for those tests with Ce/Nd = 4.0 are always lower than 2 ppm after
230 performing the SPME separation. Usually, the yield of Nd is about 70~90 % using the
231 traditional LLME technique corresponding to a separation coefficient of 10³ for Ce
232 and Nd.^{3, 18} In contrast to the LLME technique, the recovery of Nd was stable and
233 high (~ 97.3 %), whereas the separation coefficient of Ce and Nd using the SPME
234 technique exceeded 10⁶, which is significantly higher than 10³ using the LLME
235 technique.^{2, 3, 10, 11, 15, 17, 18} However, the HEHEHP resin in the tandem micro-column
236 cannot be recycled because the HEHEHP resin had been oxidized and had absorbed a
237 lot of Ce.

238

239 **3.2 Elimination of Na and Sm interferences**

240 High-purity of Nd was obtained following the procedure detailed in Table 1c. To
241 examine the separation efficiency of Na and Sm, a mixed standard containing 5 µg of
242 REEs and 150 µg of Na, 10 µg of Ba was dried and performed separated using the

243 procedure of Table 1c. Table-5 showed that all Na, Ba and most of La (~ 98.5 %) and
244 Ce (~ 97.6 %) were washed out before collecting Nd. All Sm and MREEs + HREEs
245 were washed out after collecting Nd. Sm-Nd separation using a short HEHEHP resin
246 column resulted in $^{144}\text{Sm}/^{144}\text{Nd}$, $^{148}\text{Sm}/^{148}\text{Nd}$ and $^{150}\text{Sm}/^{150}\text{Nd}$ ratios usually less than
247 1 ppm, thus, performing Sm isobaric interference correction was not necessary.
248 During this step, ~ 96.5 % Nd was collected. In contrast to previous studies, the
249 two-column method was simplified to one column, and the preparation of a cation AG
250 50W resin column to eliminate Na salt before performing the Sm-Nd separation was
251 not needed.

252

253 **3.3 Validation of the method and final results**

254 To assess the analytical reproducibility and feasibility of our chemical procedure
255 for silicate samples, nine CRMs were selected to encompass a wide range of matrix
256 compositions (from mafic to felsic) and Ce/Nd were determined. As shown in Table 6,
257 the $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of all analyzed USGS and GSJ
258 reference materials were obtained with an internal precision (2 SE) better than
259 0.000005 and 0.000002, respectively. The $^{143}\text{Nd}/^{144}\text{Nd}$ data presented in Table 6 agree
260 well with previously published data obtained through TIMS or MC-ICP-MS.^{19-26, 29-30}
261 Few $^{142}\text{Nd}/^{144}\text{Nd}$ data except for BCR-2³¹ were reported for those standards in previous
262 studies. Hence, it is difficult to compare the actual difference of $^{142}\text{Nd}/^{144}\text{Nd}$ data in
263 this study and previous investigations. As indicated in Table 6 and Fig 2, no ^{142}Nd
264 anomaly in the geological standard samples was found in this study.

265 The reproducibility of our procedure was demonstrated by nine different
266 dissolutions of BCR-2 and JR-3 powder materials. As shown in Table 6, replicate
267 measurements (n = 9) of BCR-2 yielded a $^{142}\text{Nd}/^{144}\text{Nd}$ value of $1.14183491 \pm$
268 0.0000044 and a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.5126205 ± 0.0000032 (2 SD). Replicate
269 measurements (n = 9) of JR-3 yielded a $^{142}\text{Nd}/^{144}\text{Nd}$ value of 1.1418339 ± 0.0000050
270 and a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.5126666 ± 0.0000016 (2 SD). The $^{142}\text{Nd}/^{144}\text{Nd}$ external
271 reproducibility of both BCR-2 and JR-3 were better than 5 ppm (2 SD). Notable is the
272 fact that JR-3 has a high ratio of Ce/Nd (3.13)³² and a high content of Ce (319 ppm)³²;
273 ~110 mg of JR-3 yields ~35.1 μg of Ce. Thus, to completely separate Ce from JR-3 is
274 the biggest challenge for our method, even though all $^{140}\text{Ce}/^{144}\text{Nd}$ values for JR-3 are
275 never higher than 0.0000009 during TIMS measurements. The maximum ^{142}Ce
276 interference is ~ 1.1 ppm on the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio. The ^{142}Ce interference is lower than
277 0.6 ppm for most silicate samples. This suggests our method is perfect for Ce and Nd
278 separation.

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

282

283 **4. Conclusions**

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

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

295

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365 **Figure captions**

- 366 Figure 1. Our separation protocol compared with traditional methods^{3, 10, 11, 18}
- 367 Figure 2. $^{142}\text{Nd}/^{144}\text{Nd}$ data for CRMs samples are plotted as deviations in ppm ($\mu^{142}\text{Nd}$)
368 from the JNdi-1 standard relative to the terrestrial Nd standard JNdi-1. $\mu^{142}\text{Nd} =$
369 $((^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{142}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}} - 1) \times 10^6$, where $^{142}\text{Nd}/^{144}\text{Nd}$ value of JNdi-1 is
370 the average value in this study (1.1418367 ± 0.0000055 , 2 SD, $n = 37$). The dashed
371 line area defines the external error of 5 ppm (2 RSD) of the repeated measurements of
372 JNdi-1 standard ($n = 37$). Error bars are 2 SE errors of individual measurements.

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

377 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

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379 b. the second mini solid-phase micro-extraction tandem column containing 0.16 mL
 380 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

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382 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

383 Comment: The yield of Nd during the three-step separation procedure is about 98.2 %, 97.3 % and
 384 96.5%, respectively. In the final, the yield of Nd is about 92.2 % after performing three-step
 385 separation.

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389 **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

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391 **Run conditions:**

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

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

394 Amplifiers rotated left every block, baseline measured every block.

395 Peak center on ¹⁴⁵Nd, ¹⁴⁴Nd and ¹⁴³Nd and ion source lens focus on ¹⁴⁵Nd done every 4 block,
396 turret position optimized at start.397 Typical ¹⁴²Nd signal strength on 10¹¹Ω resistor was 3~4 V for most samples.

398 Magnet removed from the ion source.

399 Rejected ratios always less than 5 % of total.

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

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404 **Table 3. Published JNdi-1 ¹⁴²Nd/¹⁴⁴Nd values determined using Triton Plus**
405 **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	

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

Sample	$^{140}\text{Ce}/^{144}\text{Nd}$	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

417 Note: HEH-1 to HEH-6 are artificial mixed standard solution with the different Ce/Nd ratios.
 418 $^{140}\text{Ce}/^{144}\text{Nd}$ ratios mean the actual measurement values using TIMS after performing SPME
 419 separation.

421 **Table 5. Sample purity and the recovery of Nd in the third HEHEHP resin**
 422 **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
$\Sigma\text{HREE}+\text{MREE}$	0	0	0	100

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

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

CRMs	$^{142}\text{Nd}/^{144}\text{Nd}$ this study (± 2 SE)	$^{143}\text{Nd}/^{144}\text{Nd}$ this study (± 2 SE)	$^{143}\text{Nd}/^{144}\text{Nd}$ Refer Values	$^{145}\text{Nd}/^{144}\text{Nd}$ this study (± 2 SE)	$^{148}\text{Nd}/^{144}\text{Nd}$ this study (± 2 SE)	$^{150}\text{Nd}/^{144}\text{Nd}$ this study (± 2 SE)	$^{146}\text{Nd}/^{144}\text{Nd}_m$	$^{140}\text{Ce}/^{144}\text{Nd}$
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

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

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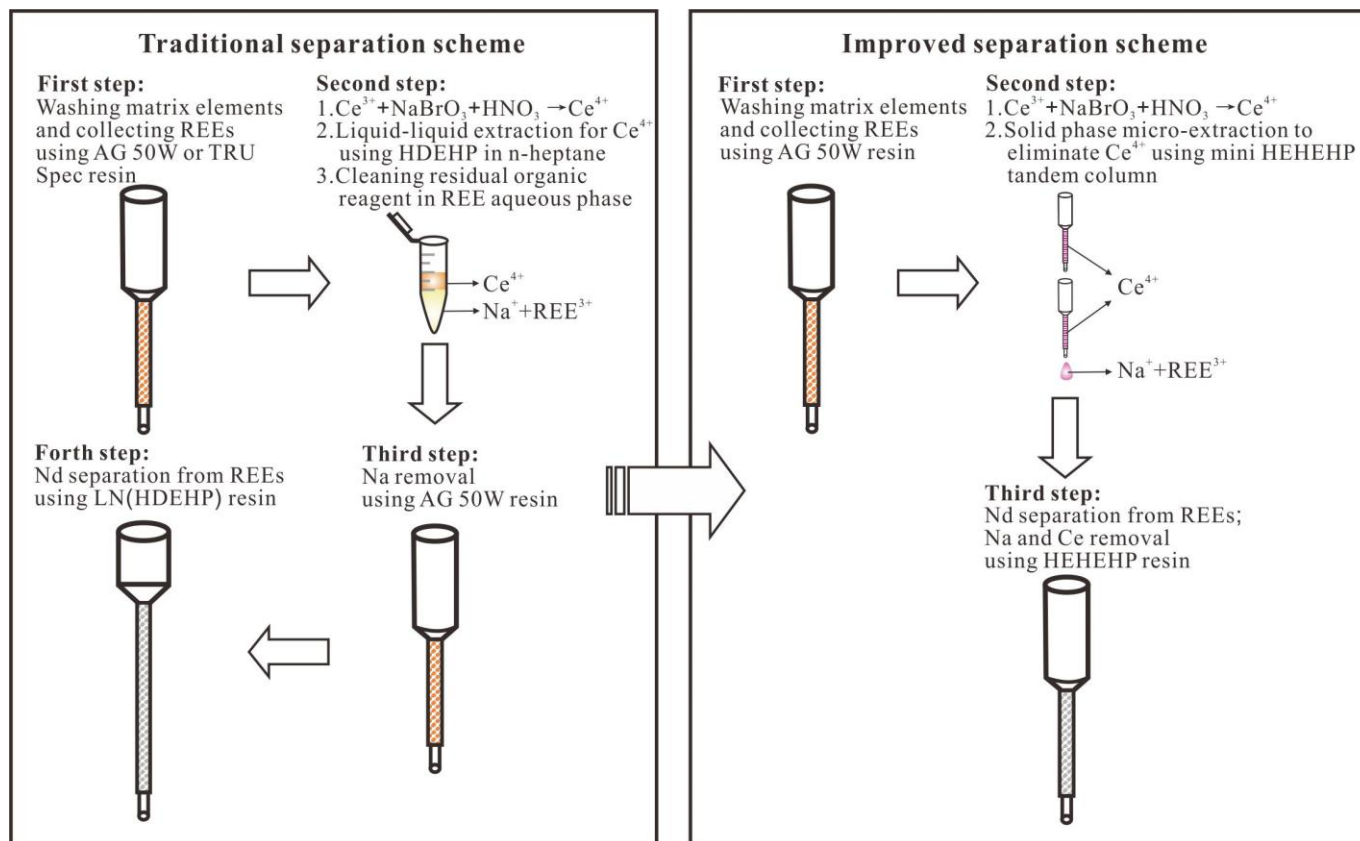
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442 **Figure captions**

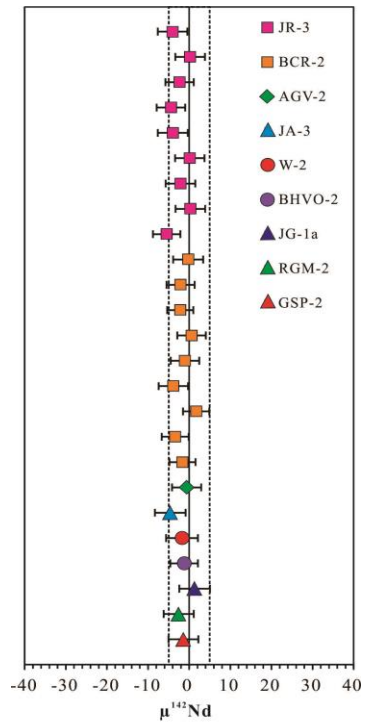
443 Figure 1. Our separation protocol compared with traditional methods



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446 Figure 2. $^{142}\text{Nd}/^{144}\text{Nd}$ data for CRMs samples are plotted as deviations in ppm ($\mu^{142}\text{Nd}$) from the JNdi-1 standard relative to the terrestrial Nd
 447 standard JNdi-1. $\mu^{142}\text{Nd} = ((^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{142}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}} - 1) \times 10^6$, where $^{142}\text{Nd}/^{144}\text{Nd}$ value of JNdi-1 is the average value in this study
 448 (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
 449 JNdi-1 standard ($n = 37$). Error bars are 2 SE errors of individual measurements.



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