¹ Single Column REE Separation and Radiogenic ¹⁴³Nd/¹⁴⁴Nd

2 Analysis Without Sm Elimination

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17 <u>This is a non-peer reviewed preprint submitted to Geochemical Journal for formal peer</u>

18

review

19 Abstract

A single column separation method has been developed for the determination of radiogenic 20 ¹⁴³Nd/¹⁴⁴Nd for natural geological samples. Conventional radiogenic Nd isotope ratio 21 measurements require rigorous column chemistry involving multiple steps to extract a pure Nd 22 fraction. Elements that cause isobaric interference during analysis are removed using a multi-23 column separation method, which is often time consuming and/or expensive. In this work, we 24 use a single cation exchange column to extract a Nd fraction, and a novel method of mass 25 fractionation correction to circumvent the isobaric effect of Sm during analysis, allowing 26 accurate measurement of the ¹⁴³Nd/¹⁴⁴Nd ratio without the elimination of Sm. The ratio of two 27 non-radiogenic Nd isotopes with no natural isobars, ¹⁴⁵Nd/¹⁴⁶Nd, is used to correct for 28 instrumental mass fractionation on ¹⁴³Nd/¹⁴⁶Nd. The corrected ¹⁴³Nd/¹⁴⁶Nd can be converted to 29 the ¹⁴³Nd/¹⁴⁴Nd form using the conventionally used constant ratio of ¹⁴⁶Nd/¹⁴⁴Nd of 0.721900, 30 allowing direct comparison with published literature and databases. We have implemented this 31 sample preparation scheme to generate accurate and precise radiogenic ¹⁴³Nd/¹⁴⁴Nd ratios for 32 nine natural reference materials including basalts, granites, sediments and sedimentary rocks, 33 34 confirming the applicability and robustness of this technique.

35

Keywords: Nd isotope; single column separation; ¹⁴³Nd/¹⁴⁴Nd; isobaric interference; thermal
ionisation mass spectrometry

38 Introduction

¹⁴³Nd/¹⁴⁴Nd isotope geochemistry has been used to investigate chemical evolution of the Earth since the 1970s (DePaolo & Wasserburg, 1976a, 1976b; Notsu *et al.*, 1973; O'Nions *et al.*, 1979). Recently, radiogenic Nd isotope geochemistry has been used in various fields including, but not limited to, geochemistry, archaeology, anthropology, environmental sciences, and forensic analysis (De Bonis *et al.*, 2018; Lahd Geagea *et al.*, 2008; Martin & Haley, 2000; Tazoe *et al.*, 2021). Many of these fields require a large number of samples to be measured.

Nd isotope ratios are conventionally reported as normalised to ¹⁴⁴Nd which is an isobar of ¹⁴⁴Sm. 45 Any accurate determination of ¹⁴³Nd/¹⁴⁴Nd therefore requires either the total elimination of Sm 46 from the fraction being analysed or correction for any Sm present in the fraction. In most 47 laboratories, a Nd fraction is purified from the sample aliquot by rigorous column chemistry 48 using multiple ion exchange columns spanning 2-3 days (Caro et al., 2006; Hyung & Tissot, 49 2021; Kagami & Yokoyama, 2016; Pin et al., 2014; Shibata & Yoshikawa, 2004). This is not 50 only time consuming but also expensive. Trace amounts of Sm may be present in the sample 51 52 even after rigorous chemical separation due to various factors like incomplete oxidation of 53 fluorides, formation of organic complexes during column chemistry, column overloading etc (Dey et al., 2023; Yokoyama et al., 1999). Trace amounts of Sm present during thermal 54 ionisation mass spectrometry (TIMS), is usually corrected online, using interfering element 55 correction (IEC), by measuring the intensity of ¹⁴⁷Sm and assuming a constant ratio for 56 ¹⁴⁷Sm/¹⁴⁴Sm. The disadvantage of this method is that any instrumental mass fractionation on 57 Sm is not considered, and the error is propagated to the ¹⁴³Nd/¹⁴⁴Nd ratio. The maximum 58 tolerable ¹⁴⁷Sm/¹⁴⁶Nd, required for less than 5 ppm error in Nd isotopic measurement was 59 calculated to be 4.3×10^{-4} by Garcon *et al.* (2018). 60

Ln-Spec resin and DGA resin (Eichrom), which are commonly used for rare earth element (REE)
separation (Dey *et al.*, 2023; Pin & Gannoun, 2019; Tazoe *et al.*, 2021), are almost 20 times

63 more expensive than the cation exchange resin (AG50W-X8). The α -HIBA method is another 64 commonly used method that does not use expensive resins but requires careful control of pH 65 conditions and frequent calibration of the elution curve (Hyung & Tissot, 2021; Shibata & 66 Yoshikawa, 2004).

Therefore, the current method is developed using a single cation exchange column and a novel correction method for interfering Sm, in order to reduce the time and cost of a multi-column separation process. A faster analytical method, that does not require inter-REE separation, will increase the scope and applicability of Nd isotope chemistry many fold.

71

72 Experimental

73 Reagents and instruments

74 Electronic grade HCl and HNO₃, ultrapure grade HClO₄ (Kanto Chemicals), AA-10 grade HF and H₂O₂ (Tamapure) was used for rock powder digestion and column chemistry. Milli Q water 75 $(>18.2 \text{ M}\Omega \text{ cm})$ was used for reagent dilution and washing. Cation exchange resin AG50W-X8 76 77 from BioRad was used to extract the REE fractions from the rock powders. An ICP-MS (X-2 78 series) from Thermo Scientific installed at the Hiroshima University was used to determine elution curves and recovery of elements. TIMS from Thermo Scientific (MAT-262) installed at 79 the Hiroshima University was used to measure Nd isotope ratios. The instrument is equipped 80 with one fixed and eight movable Faraday cups with $10^{11} \Omega$ amplifiers with a dynamic range of 81 10 V, and one secondary electron multiplier with $10^7 \Omega$ amplifier. La Jolla Nd standard solution 82 was used to determine the accuracy and precision of the correction method. Nine geological 83 reference materials, including JB-2, JG-1a, JG-2, JG-3, JSl-1, JSd-1 and JLk-1 from GSJ and 84 85 BCR-2 and SDO-1 from USGS, were used to determine accuracy and precision of correction method in natural samples. 86

88 Sample preparation

Seven aliquots of 20 mg fractions of JB-2 and single aliquots of the other reference materials were digested with HF-HClO₄ (Yokoyama *et al.*, 1999) and finally dissolved in 1 mL 2.5 M HCl and loaded onto a washed 1 mL AG50W-X8 resin column. The column chemistry was developed by modifying the Ba elution method of Lin *et al.* (2020). The major elements were rinsed with 8 mL of 2.5 M HCl and Ba was removed using 7 mL 1.7 M HNO₃. Nd fraction was collected with 4 mL 3 M HCl. The collected Nd fraction was dried and redissolved with 2-3 drops of concentrated HNO₃ and HF to digest any organic material leached from the resin.

96

97 Isotope ratio analysis

Nd fractions were loaded onto degassed Re double filaments using dilute HNO₃. Measurements 98 were done in Nd⁺ mode. The ionisation filament was slowly heated with 4.5 A current while the 99 evaporation filament was heated up to ~1.8 A current until a stable Nd beam was found. The 100 ion beam was focused using the intensity at mass 146. Gain correction was performed once per 101 day prior to measurement and all ratios were analysed in static multicollection mode using 102 Faraday cups. Data were collected for 10 to 30 blocks with 10 ratios per block. Each ratio was 103 104 collected for an integration time of 8s with a half-mass baseline measurement of 16s between the blocks. IMF was corrected using $^{145}Nd/^{146}Nd = 0.482636$. The total time for each run in the 105 proposed method was 30 to 80 minutes depending on the number of blocks. Each run was 106 followed by another analysis in conventional method using ${}^{146}Nd/{}^{144}Nd = 0.721900$ for IMF 107 correction and 144 Sm/ 147 Sm = 0.2069 for interfering element correction (IEC). 108

110 Results and Discussion

111 Column chemistry

The column process was optimised in order to reduce Ba and Ce in the measured fraction as 112 both Ba and Ce reduce ionisation efficiency of Nd. The elution curves for Ba, Ce, Nd and Sm 113 are illustrated in Fig. 1.1 mL fractions of eluted solution were collected and analysed in ICP-114 MS for Ba and light REE (LREE)s. The results show that most of the Ba ($\sim 90\%$) can be 115 removed by rinsing the column with 7 mL 1.7 M HNO₃ after loading (1 mL) and rinsing (8 116 mL) with 2.5 M HCl. Major elements, Pb and Sr are eluted during loading and rinsing the 117 column with 2.5 M HCl and can be collected and analysed for radiogenic isotope ratios (Dey 118 119 et al., 2023). Nd elution was tested using HCl at several concentrations and 3 M HCl was selected based on elution volume and degree of separation from Ce. Nd fraction is collected 120 using 4 mL of 3 M HCl with a recovery yield > 80%. This fraction contains $\sim 50\%$ of the 121 total Ce. The column chemistry can be repeated if lower Ba and Ce is required for analysis. 122 Total blank for this process is less than 50 pg, as measured in Dey et al. (2023). The column 123 chemistry can be completed within 2-3 hrs including initial cleaning of resin. Use of AG50W-124 X8 in a single column not only reduces sample preparation time compared to conventional 125 methods (2 to 3 column steps, >2 days), but also significantly reduces the cost of resins and 126 127 reagents.

128

129 Mass fractionation correction

130 Calculation and theoretical basis of the mass fractionation correction method is described in131 this section.

Three isotopes of Nd, i.e., ¹⁴⁶Nd, ¹⁴⁵Nd and ¹⁴³Nd do not have any natural isobars. Of these,
¹⁴³Nd is the radiogenic daughter of ¹⁴⁷Sm and the target isotope in radiogenic isotope
geochemistry. The other two are stable and considered non radiogenic in geological timescales.

¹⁴⁶Nd/¹⁴⁴Nd ratio is considered constant at a value of 0.7219 (Depaolo, 1988) and 135 conventionally used to correct mass dependent fractionation during measurement (Caro et al., 136 2006; Depaolo, 1988; Dey et al., 2023; Garçon et al., 2018; Hyung & Tissot, 2021; Kagami & 137 Yokoyama, 2016; Li et al., 2016; Li et al., 2011; Pin et al., 2014; Saji et al., 2016; Shibata et 138 al., 2003; Shibata & Yoshikawa, 2004). However, ¹⁴⁵Nd/¹⁴⁴Nd is also constant at the limit of 139 reproducibility of TIMS for terrestrial silicate rocks and has been demonstrated by the repeated 140 analysis of several natural reference materials (Li et al., 2016; Pin et al., 2014; Saji et al., 2016). 141 Saji et al. (2016) determined variations in ¹⁴⁶Nd/¹⁴⁴Nd and ¹⁴⁵Nd/¹⁴⁴Nd for terrestrial rocks 142 relative to JNdi-1 (Nd isotopic standard from GSJ), by normalizing against ¹⁴⁸Nd/¹⁴⁴Nd = 143 0.241578 to correct instrumental mass fractionation. They show an average of 0.4 ± 1.6 for 144 μ^{146} Nd (ppm variations in 146 Nd/ 144 Nd) and -2.4 ± 1.9 for μ^{145} Nd (ppm variations in 145 Nd/ 144 Nd) 145 which suggests that very little variability exists within the terrestrial reservoirs in terms of 146 ¹⁴⁶Nd/¹⁴⁴Nd and ¹⁴⁵Nd/¹⁴⁴Nd. This uniformity is expected as ¹⁴⁴Nd, ¹⁴⁵Nd and ¹⁴⁶Nd are non-147 radiogenic in geological time frame and show constant abundances in nature. Therefore, we can 148 use the ratio of ¹⁴⁵Nd/¹⁴⁶Nd, which is constant at the limit of reproducibility, to correct IMF on 149 ¹⁴³Nd/¹⁴⁶Nd ratio. 150

Each measured ¹⁴³Nd/¹⁴⁶Nd ratio was corrected according to Eq. (1) following Rayleigh
fractionation law.

153
$$\left(\frac{^{143}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Corr}} = \frac{\left(\frac{^{143}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Meas}}}{\left[\left(\frac{^{145}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Meas}} / \left(\frac{^{145}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Nat}}\right]^{\left(\frac{1-\sqrt{\frac{146}{143}}}{1-\sqrt{\frac{146}{145}}}\right)}$$
(Eq. 1)

Where (¹⁴³Nd/¹⁴⁶Nd)^{Meas} and (¹⁴⁵Nd/¹⁴⁶Nd)^{Meas} are the measured isotope ratios and (¹⁴³Nd/¹⁴⁶Nd)^{Corr} is the corrected ratio. (¹⁴⁵Nd/¹⁴⁶Nd)^{Nat} used in this calculation was 0.482636.
The value of (¹⁴⁵Nd/¹⁴⁶Nd)^{Nat} was determined from average of 33 measurements of La Jolla and

157 15 measurements of JB-2 in conventional method. The corrected ¹⁴³Nd/¹⁴⁶Nd was then
 158 converted to ¹⁴³Nd/¹⁴⁴Nd according to eq. (2) for comparison with published data.

159
$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)^{\text{Corr}} = \left(\frac{^{143}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Corr}} \times \left(\frac{^{146}\text{Nd}}{^{144}\text{Nd}}\right)^{\text{Nat}}$$
 (Eq 2)

160 Where $({}^{146}Nd/{}^{144}Nd)^{Nat}$ is the ratio in nature with the value of 0.721900 (Saji *et al.*, 2016). 161 Standard error of measurement (σ_m) was propagated from the TIMS output ${}^{143}Nd/{}^{146}Nd$ to the 162 calculated ${}^{143}Nd/{}^{144}Nd$.

163

164 Accuracy and precision of measured ratios

165 Nd isotope standard La Jolla was measured multiple times in the proposed method and in 166 conventional mode to compare the accuracy and precision of the two approaches. 167 Measurements in the proposed method yielded an average of 0.511852 ± 0.000021 (2σ , n= 15; 168 Table 1) which is consistent with measured values in the conventional method $0.511846 \pm$ 169 0.000014 (2σ , n= 11). Internal reproducibility range between 10 to 25 ppm for data acquired in 170 10 to 30 blocks in the proposed method as represented in Table 1. All data agree to previously 171 reported value of 0.511855 ± 0.000020 (Shibata & Yoshikawa, 2004).

The accuracy and precision of the measured data were determined using the basaltic rock 172 standard JB-2, prepared following Dey et al. (2023) (Sm removal) and the single column 173 method developed in this work. Isotope ratios measured in conventional mode for Sm free Nd 174 fractions show ¹⁴³Nd/¹⁴⁴Nd ratio of 0.513089 ± 0.000018 (2 σ , n= 13) (Table 2) in agreement 175 with published values. The raw ratios from these measurements were manually corrected using 176 the proposed calculations (Eqs. 1 and 2), in order to compare the accuracy and precision of the 177 two methods. The thirteen measurements provide a 143 Nd/ 144 Nd ratio of 0.513091 ± 0.000041 178 $(2\sigma, n= 13; Table 2)$ which also agrees with the published value of 0.513097 \pm 0.000011 179 (Shibata *et al.*, 2003). 180

Three aliquots of JB-2 prepared using the proposed single column method (without Sm removal) 181 were measured five times using the proposed online correction and the conventional interfering 182 element correction method. An average ¹⁴³Nd/¹⁴⁴Nd ratio of 0.513096 ± 0.000039 (2 σ , n = 5; 183 sample nos. 7 -9 in Table 2) was obtained which is also in agreement with published values. 184 ¹⁴⁷Sm/¹⁴⁶Nd ratios varied during each measurement and ranged between 0.152 and 0.313 at the 185 beginning of measurement for each sample (sample nos. 7 -9 in Table 2). It should be noted that 186 this ratio does not reflect the actual ¹⁴⁷Sm/¹⁴⁶Nd of the measured sample and is dependent on 187 the ionisation efficiency and isotopic fractionation of Sm and Nd during the measurement. The 188 conventional interfering element corrected values range between 0.513137 and 0.513610, all of 189 which overestimate the effect of ¹⁴⁴Sm on the ¹⁴³Nd/¹⁴⁴Nd ratio in the sample and are 190 significantly higher than the reference values. The ¹⁴³Nd/¹⁴⁴Nd ratios obtained using IEC and 191 the proposed method are plotted against the ¹⁴⁷Sm/¹⁴⁶Nd ratios obtained during the 192 measurement in Fig. 2. It can be seen from the plot that the ¹⁴³Nd/¹⁴⁴Nd ratios increase with 193 increasing ¹⁴⁷Sm/¹⁴⁶Nd. The observation suggests that the ¹⁴³Nd/¹⁴⁴Nd ratios with IEC are the 194 result of overestimating the effect of ¹⁴⁴Sm. Although all the data obtained using the proposed 195 method in these 9 samples (Table 2, sample nos. 1-9) agree within error to reference values, the 196 internal and external precisions are worse ($2\sigma > 25$ ppm) than in conventional measurements. 197 198 However, as both sets of data, i.e., with and without Sm separation, show worse precisions, we speculate that this is an artefact of the calculation process rather than an interference from 199 matrix elements. This is expected as the proposed method uses ¹⁴⁵Nd in the equations, which is 200 lower in abundance than ¹⁴⁴Nd. The lower abundance leads to higher relative error in the 201 detected ion intensities which is propagated to the final ¹⁴³Nd/¹⁴⁴Nd ratio. Therefore, in order 202 to increase the precision in final ¹⁴³Nd/¹⁴⁴Nd ratio, we have attempted to reduce the error on 203 ¹⁴⁵Nd ion intensity. One way to achieve this is to analyse the samples at a higher ion intensity. 204 Another would be to increase the number of ratios in order to reduce the standard error of mean. 205

Four separate aliquots of JB-2 were used to test this hypothesis and the results indicate that 145 Nd ion intensity > 400 mV can produce high precision ($2\sigma_m < 25$ ppm) 143 Nd/ 144 Nd ratios within 10 to 30 blocks of data (Table 2, sample 10-13). The data also confirms that a higher ion intensity leads to a better precision on 143 Nd/ 144 Nd ratios. The ion intensities during the measurement and the run times (number of blocks) are described in Table 2 for each measurement.

Single aliquots of eight other silicate reference materials with a wide variation in matrix 212 (sediments, sedimentary rocks and mafic- felsic igneous rocks), reported ¹⁴³Nd/¹⁴⁴Nd ratios 213 (0.5121 - 0.5131), and Sm/Nd ratios (0.20 - 0.36), were prepared using the single column 214 215 method and analysed using the proposed online IMF correction method and the conventional IEC method. Data from all analyses are described in Table 3 and plotted against reference values 216 in Fig. 3. The ¹⁴³Nd/¹⁴⁴Nd isotope ratios agree with the reference values with sufficient precision 217 for geochemical purposes ($2\sigma < 25$ ppm), demonstrating that this correction method can be 218 successfully applied to natural samples regardless of the sample type or Sm/Nd ratios. Online 219 IEC, using a constant value of 144 Sm $^{/147}$ Sm = 0.2069, was performed by determining 144 Nd from 220 the total intensity at mass 144 (¹⁴⁴Nd + ¹⁴⁴Sm), and ¹⁴³Nd/¹⁴⁴Nd were determined during 221 conventional analysis. This is a standard correction applied to all measurements to correct trace 222 223 amounts of interfering elements. However, this correction was unable to provide accurate isotope ratios for samples without Sm separation as shown in Table 3 and Fig. 3. 224

An approach to determine accurate and precise Nd isotope ratios without REE separation was adopted by Li *et al.* (2011) where they measure ¹⁴⁷Sm and ¹⁴⁹Sm along with Nd isotopes to first determine the instrumental mass fractionation for Sm. The raw ¹⁴⁴Sm intensity is then calculated and subtracted from the total intensity at mass 144 to determine ¹⁴⁴Nd. This yields accurate isotope ratios, provided the Sm fractionation is accurately determined and ¹⁴⁴Nd is accurately corrected for. However, we noticed that the Sm/Nd ratio is constantly changing during analysis

as Nd and Sm evaporate from the filament at different rates. Therefore, any error in 231 determination of the fractionation factor of Sm during routine analyses will propagate to the 232 ¹⁴⁴Nd intensity and prevent accurate calculation of fractionation factor in Nd, using the 233 conventional ¹⁴⁶Nd/¹⁴⁴Nd ratio. In addition, at least 5 masses (143, 144, 146, 147, 149) must be 234 accurately and simultaneously measured to determine ¹⁴³Nd/¹⁴⁴Nd and the detection errors will 235 propagate to the final ¹⁴³Nd/¹⁴⁴Nd ratio. Thus, we suggest that the use of ¹⁴⁵Nd/¹⁴⁶Nd ratios to 236 correct mass fractionation is a more reliable method compared to recalculating ¹⁴⁴Nd intensities 237 for each ratio. 238

239

240 Conclusion

A new method for the analysis of ¹⁴³Nd/¹⁴⁴Nd ratio was developed using a single column 241 separation scheme. A single cation exchange column was used for fast sample processing (2-3 242 hrs) which reduces the time as well as cost of sample preparation. All major elements as well 243 as ~90% of Ba and ~50% Ce was eliminated from the Nd fraction before analysis. A novel 244 correction method was developed to circumnavigate the isobaric effect of ¹⁴⁴Sm which remains 245 in the Nd fraction. This method uses the two non-radiogenic and non-isobaric isotopes of Nd, 246 i.e., ¹⁴⁵Nd and ¹⁴⁶Nd for mass fractionation correction and does not require elimination of Sm 247 248 from analysed fraction. The method was applied for Nd standard solution La Jolla and nine natural rock reference materials which yield concordant values to published ¹⁴³Nd/¹⁴⁴Nd ratios. 249 As this method is not dependent on elemental abundance of Sm or the mass 144 which includes 250 isobaric effect of ¹⁴⁴Sm, it can be applied to any sample irrespective of the Sm/Nd ratio. This 251 process can be used for fast analysis of a large number of samples and does not require high 252 skill in column chemistry for the analyst. 253

254

256 Acknowledgment

257 We thank the two anonymous reviewers for the helpful comments in improving the manuscript.

258 This work was partially supported by HiPeR, which is selected and supported by Hiroshima

- 259 University. We thank the Hiroshima University for providing the research facilities.
- 260

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339 **Table 1.**

Sample No.	¹⁴³ Nd/ ¹⁴⁴ Nd	$2\sigma_m$
1	0.511859	0.000013
2	0.511834	0.000011
3	0.511844	0.000011
4	0.511839	0.000012
5	0.511847	0.000012
6	0.511850	0.000021
7	0.511855	0.000022
8	0.511863	0.000020
9	0.511861	0.000021
10	0.511872	0.000018
11	0.511850	0.000019
12	0.511855	0.000021
13	0.511844	0.000020
14	0.511840	0.000026
15	0.511864	0.000021
Average	0.511852	0.000021
Ref. value	0.511855	0.000020

340 ¹⁴³Nd/¹⁴⁴Nd ratio determined proposed method for La Jolla Nd standard

Reference value is from Shibata and Yoshikawa (2004).

³⁴¹ Error for each measurement is standard error of mean and for average is standard deviation.

343 **Table 2.**

Samula na	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁷ Sm/	Run time
Sample no.	conventional method	this method	¹⁴⁶ Nd	
1	0.513087 ± 0.000010	0.513090 ± 0.000035		
	0.513067 ± 0.000015	0.513096 ± 0.000039		
2	0.513094 ± 0.000012	0.513129 ± 0.000032		
	0.513093 ± 0.000015	0.513062 ± 0.000037		
3	0.513092 ± 0.000013	0.513099 ± 0.000040		
	0.513087 ± 0.000012	0.513113 ± 0.000031		
4	0.513106 ± 0.000012	0.513097 ± 0.000028	<10-4	10 blocks
5	0.513089 ± 0.000011	0.513103 ± 0.000032		
	0.513085 ± 0.000012	0.513055 ± 0.000028		
	0.513097 ± 0.000011	0.513072 ± 0.000036		
6	0.513077 ± 0.000010	0.513067 ± 0.000028		
	0.513090 ± 0.000010	0.513101 ± 0.000031		
	0.513094 ± 0.000010	0.513094 ± 0.000029		
Average	0.513089 ± 0.000018	0.513091 ± 0.000041		
7	0.513247 ± 0.000012	0.513125 ± 0.000035	0.162	
	0.513215 ± 0.000012	0.513081 ± 0.000033	0.160	
8	0.513137 ± 0.000008	0.513080 ± 0.000021	0.156	10 blocks
	0.513169 ± 0.000009	0.513114 ± 0.000027	0.153	
9	0.513610 ± 0.000041	0.513080 ± 0.000036	0.313	
Average	0.513276 ± 0.000343	0.513096 ± 0.000039		
10	n.d.	0.513095 ± 0.000023	0.101	29 blocks
	n.d.	0.513100 ± 0.000023	0.090	14 blocks
11	n.d.	0.513117 ± 0.000016	0.330	10 blocks
12	n.d.	0.513084 ± 0.000012	0.310	29 blocks
13	n.d.	0.513102 ± 0.000014	0.205	30 blocks
	n.d.	0.513084 ± 0.000020	0.105	18 blocks
Average		0.513097 ± 0.000023		
Ref. value	0.513097 ± 0.000011			

¹⁴³Nd/¹⁴⁴Nd ratio determined in conventional method vs proposed method for JB-2

345

346 Error for each measurement is standard error of mean and for average is standard deviation.

Reference value is from Shibata et al. (2003). n.d. refers to not determined. ¹⁴⁷Sm/¹⁴⁶Nd are

348 reported for the first block of measurement.

349

351 **Table 3.**

352 ¹⁴³Nd/¹⁴⁴Nd ratio determined in conventional method vs proposed method for ten

353 reference materials

Reference material	This method	Conventional method (interfering element correction)	Reference values	¹⁴⁷ Sm/ ¹⁴⁶ Nd during
	$^{143}Nd/^{144}Nd\pm 2\sigma_m$	$^{143}Nd/^{144}Nd \pm 2\sigma_m$	$^{143}Nd/^{144}Nd \pm 2\sigma$	measurement
BCR 2	0.512572 ± 0.000019	-	0.512594 ± 0.000023^1	0.001-0.015
JG1a	0.512345 ± 0.000014	0.512410 ± 0.000018	0.512351 ± 0.000010^1	0.118- 0.040
JG2	0.512158 ± 0.000026	0.512306 ± 0.000010	0.512176 ± 0.000012^1	0.012-0.152
JG3	0.512586 ± 0.000011	0.512723 ± 0.000007	0.512618 ± 0.000008^2	0.098-0.131
JLk1	0.512130 ± 0.000013	0.512124 ± 0.000007	0.512135 ± 0.000006^3	0.105-0.092
JSd1	0.512553 ± 0.000015	0.512574 ± 0.000011	0.512571 ± 0.000018^4	0.006- 0.022
JS11	0.512529 ± 0.000016	0.512585 ± 0.000008	0.512549 ± 0.000017^1	0.049- 0.120
SDO1	0.512067 ± 0.000012	0.512107 ± 0.000005	0.512080 ± 0.000008^1	0.060- 0.088
JB2	0.513102 ± 0.000014	0.513613 ± 0.000041	0.513097 ± 0.000011^2	0.402-0.002
La Jolla	0.511850 ± 0.000021	NA	0.511855 ± 0.000020^5	0.0000

³⁵⁴ Reference values: ¹Dey et al. (2023); ²Shibata et al. (2003); ³Jo et al. (2021); ⁴Nath et al. (2009);

⁵Shibata and Yoshikawa 2004.

357

Fig. 1. Elution curve for Ba and LREEs for 1 mL AG50W-X8 column are shown. Data is plotted
for fractions after loading and rinsing of major elements (9 mL 2.5 M HCl). Each fraction for
1.7 M HNO3 and 3 M HCl is 1 mL.

361

Fig. 2. Measured ¹⁴³Nd/¹⁴⁴Nd ratios from JB-2 using the proposed corrected method from 362 samples separated by a single column, compared to the three-column separation method (Dey 363 et al. (2023). Horizontal axis represents ¹⁴⁷Sm/¹⁴⁶Nd at the start of measurement. Solid and 364 365 dashed lines represent average and 2σ of thirteen measurements in conventional method. Blue points represent data in proposed IMF correction using ¹⁴⁵Nd/¹⁴⁶Nd on the same thirteen 366 measurements. Green and red points represent sample preparation in the proposed single 367 column method. Data reduction in proposed method (green) and conventional method using 368 interfering element correction (red) are shown. 369

370

Fig. 3. Corrected ¹⁴³Nd/¹⁴⁴Nd ratios for ten reference materials using single column separation
(Sm present), in the proposed method (green circles) and conventional interfering element
correction method (red squire) compared to published reference values. Data for all reference
materials in proposed method is conformable to reference values. Error bars represent 2
standard error of mean.







Fig. 3