

# Single column REE separation and radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ analysis without Sm elimination

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## Abstract

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

## Keywords

Nd isotope, single column separation,  $^{143}\text{Nd}/^{144}\text{Nd}$ , isobaric interference, thermal ionisation mass spectrometry

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## Introduction

$^{143}\text{Nd}/^{144}\text{Nd}$  isotope geochemistry has been used to investigate chemical evolution of the Earth since the 1970s (DePaolo and 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 and 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 nor-

malised to  $^{144}\text{Nd}$  which is an isobar of  $^{144}\text{Sm}$ . Any accurate determination of  $^{143}\text{Nd}/^{144}\text{Nd}$  therefore requires either the total elimination of Sm from the fraction being analysed or correction for any Sm present in the fraction. In most laboratories, a Nd fraction is purified from the sample aliquot by rigorous column chemistry using multiple ion exchange columns spanning 2–3 days (Caro *et al.*, 2006; Hyung and Tissot, 2021; Kagami and Yokoyama, 2016; Pin *et al.*, 2014; Shibata and Yoshikawa, 2004). This is not only time consuming but also expensive. Trace amounts of Sm may be present in the sample even after rigorous chemical separation due to various factors like incomplete oxidation of fluorides, formation of organic complexes during column chemis-



try, column overloading etc (Dey *et al.*, 2023; Yokoyama *et al.*, 1999). Trace amounts of Sm present during thermal ionisation mass spectrometry (TIMS), is usually corrected online, using interfering element correction (IEC), by measuring the intensity of  $^{147}\text{Sm}$  and assuming a constant ratio for  $^{147}\text{Sm}/^{144}\text{Sm}$ . The disadvantage of this method is that any instrumental mass fractionation (IMF) on Sm is not considered, and the error is propagated to the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio. The maximum tolerable  $^{147}\text{Sm}/^{146}\text{Nd}$ , required for less than 5 ppm error in Nd isotopic measurement was calculated to be  $4.3 \times 10^{-4}$  by Garçon *et al.* (2018).

Ln-Spec resin and DGA resin (Eichrom), which are commonly used for rare earth element (REE) separation (Dey *et al.*, 2023; Pin and Gannoun, 2019; Tazoe *et al.*, 2021), are almost 20 times more expensive than the cation exchange resin (AG50W-X8). The  $\alpha$ -HIBA method is another commonly used method that does not use expensive resins but requires careful control of pH conditions and frequent calibration of the elution curve (Hyung and Tissot, 2021; Shibata and Yoshikawa, 2004).

Therefore, the current method is developed to allow sample preparation within a few hours using a single cation exchange column. A novel correction method is also developed to correct for interfering Sm during TIMS measurement. A faster analytical method, that does not require inter-REE separation, will significantly increase the scope and applicability of Nd isotope chemistry.

## Experimental

### Reagents and instruments

Electronic grade HCl and HNO<sub>3</sub>, ultrapure grade HClO<sub>4</sub> (Kanto Chemicals), AA-10 grade HF and H<sub>2</sub>O<sub>2</sub> (Tamapure) was used for rock powder digestion and column chemistry. Milli Q water (>18.2 M $\Omega$  cm) was used for reagent dilution and washing. Cation exchange resin AG50W-X8 from BioRad was used to extract the REE fractions from the rock powders. An ICP-MS (X-2 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 the Hiroshima University was used to measure Nd isotope ratios. The instrument is equipped with one fixed and eight movable Faraday cups with 10<sup>11</sup>  $\Omega$  amplifiers with a dynamic range of 10 V, and one secondary electron multiplier with 10<sup>7</sup>  $\Omega$  amplifier. La Jolla Nd standard solution was used to determine the accuracy and precision of the correction method. Nine geological reference materials, including JB-2, JG-1a, JG-2, JG-3, JSI-1, JSd-1 and Jlk-1 from GSJ, and BCR-2 and SDO-1 from USGS, were used to determine accuracy and precision of correction method in natural samples.

### Sample preparation

Seven aliquots of 20 mg fractions of JB-2 and single aliquots of the other reference materials were digested with HF-HClO<sub>4</sub> (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 HNO<sub>3</sub>. Nd fraction was collected with 4 mL 3 M HCl. The collected Nd fraction was dried and redissolved with 2–3 drops of concentrated HNO<sub>3</sub> and HF to digest any organic material leached from the resin.

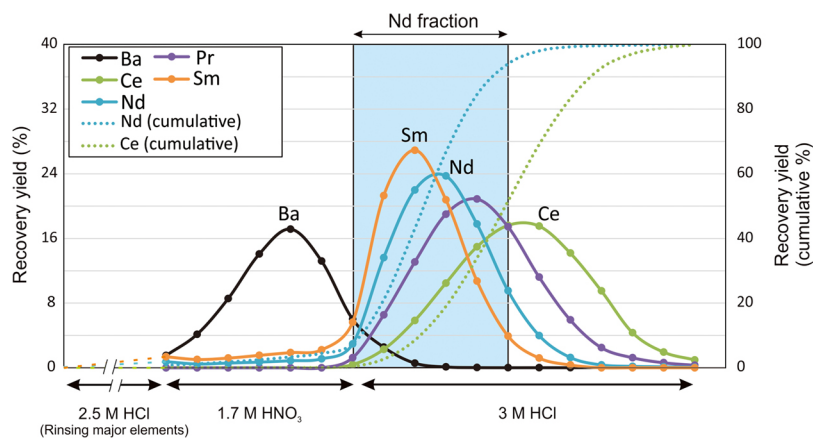
### Isotope ratio analysis

Nd fractions were loaded onto degassed Rhenium double filaments using dilute HNO<sub>3</sub>. Measurements were done in Nd<sup>+</sup> mode. The ionisation filament was slowly heated with 4.5 A current while the evaporation filament was heated up to ~1.8 A current until a stable Nd beam was found. The ion beam was focused using the intensity at mass 146. Gain correction was performed once per day prior to measurement and all ratios were analysed in static multicollection mode using Faraday cups. Data were collected for 10 to 30 blocks with 10 ratios per block. Each ratio was collected for an integration time of 8 s with a half-mass baseline measurement of 16 s between the blocks. IMF was corrected using  $^{145}\text{Nd}/^{146}\text{Nd} = 0.482636$ . The total time for each run in the proposed method was 30 to 80 minutes depending on the number of blocks. Each run was followed by another analysis in conventional method using  $^{146}\text{Nd}/^{144}\text{Nd} = 0.721900$  for IMF correction and  $^{144}\text{Sm}/^{147}\text{Sm} = 0.2069$  for interfering element correction (IEC).

## Results and Discussion

### Column chemistry

The column process was optimised in order to reduce Ba and Ce in the measured fraction as both Ba and Ce reduce ionisation efficiency of Nd. The elution curves for Ba, Ce, Nd and Sm are illustrated in Fig. 1. 1 mL fractions of eluted solution were collected and analysed in ICP-MS for Ba and light REEs (LREEs). The results show that most of the Ba (~90%) can be removed by rinsing the column with 7 mL 1.7 M HNO<sub>3</sub> after loading (1 mL) and rinsing (8 mL) with 2.5 M HCl. Major elements, Pb and Sr are eluted during loading and rinsing the column with 2.5 M HCl and can be collected and analysed for radiogenic isotope ratios (Dey *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 using 4 mL of 3 M HCl with a recovery yield >80%. This fraction contains ~50% of the total Ce. The column



**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 HNO<sub>3</sub> and 3 M HCl is 1 mL.

chemistry can be repeated if lower Ba and Ce is required for analysis. Total blank for this process is less than 50 pg, as measured in Dey *et al.* (2023). The column chemistry can be completed within 2–3 hrs including initial cleaning of resin. Use of AG50W-X8 in a single column not only reduces sample preparation time compared to conventional methods (2 to 3 column steps, >2 days), but also significantly reduces the cost of resins and reagents.

### Mass fractionation correction

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

Three isotopes of Nd, i.e., <sup>146</sup>Nd, <sup>145</sup>Nd and <sup>143</sup>Nd do not have any natural isobars. Of these, <sup>143</sup>Nd is the radiogenic daughter of <sup>147</sup>Sm and the target isotope in radiogenic isotope geochemistry. The other two are stable and considered non radiogenic in geological timescales. <sup>146</sup>Nd/<sup>144</sup>Nd ratio is considered constant at a value of 0.7219 (DePaolo, 1988) and conventionally used to correct mass dependent fractionation during measurement (Caro *et al.*, 2006; DePaolo, 1988; Dey *et al.*, 2023; Garçon *et al.*, 2018; Hyung and Tissot, 2021; Kagami and Yokoyama, 2016; Li *et al.*, 2016; Li *et al.*, 2011; Pin *et al.*, 2014; Saji *et al.*, 2016; Shibata *et al.*, 2003; Shibata and Yoshikawa, 2004). However, <sup>145</sup>Nd/<sup>144</sup>Nd is also constant at the limit of reproducibility of TIMS for terrestrial silicate rocks and has been demonstrated by the repeated analysis of several natural reference materials (Li *et al.*, 2016; Pin *et al.*, 2014; Saji *et al.*, 2016). Saji *et al.* (2016) determined variations in <sup>146</sup>Nd/<sup>144</sup>Nd and <sup>145</sup>Nd/<sup>144</sup>Nd for terrestrial rocks relative to JNdI-1 (Nd isotopic standard from GSJ), by normalizing against <sup>148</sup>Nd/<sup>144</sup>Nd = 0.241578 to correct instrumental mass fractionation. They show an average of 0.4 ± 1.6 for μ<sup>146</sup>Nd (ppm variations in <sup>146</sup>Nd/<sup>144</sup>Nd) and -2.4 ± 1.9 for μ<sup>145</sup>Nd (ppm variations in <sup>145</sup>Nd/<sup>144</sup>Nd) which suggests that very little variability exists within the terrestrial reservoirs in terms of <sup>146</sup>Nd/<sup>144</sup>Nd and <sup>145</sup>Nd/<sup>144</sup>Nd. This uni-

formity is expected as <sup>144</sup>Nd, <sup>145</sup>Nd and <sup>146</sup>Nd are non-radiogenic in geological time frame and show constant abundances in nature. Therefore, we can use the ratio of <sup>145</sup>Nd/<sup>146</sup>Nd, which is constant at the limit of reproducibility, to correct IMF on <sup>143</sup>Nd/<sup>146</sup>Nd ratio.

Each measured <sup>143</sup>Nd/<sup>146</sup>Nd ratio was corrected according to Eq. 1 following Rayleigh fractionation law.

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

Where  $\left(\frac{^{143}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Meas}}$  and  $\left(\frac{^{145}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Meas}}$  are the measured isotope ratios and  $\left(\frac{^{143}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Corr}}$  is the corrected ratio.  $\left(\frac{^{145}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Nat}}$  used in this calculation was 0.482636. The value of  $\left(\frac{^{145}\text{Nd}}{^{146}\text{Nd}}\right)^{\text{Nat}}$  was determined from average of 33 measurements of La Jolla and 15 measurements of JB-2 in conventional method. The corrected <sup>143</sup>Nd/<sup>146</sup>Nd was then converted to <sup>143</sup>Nd/<sup>144</sup>Nd according to Eq. 2 for comparison with published data.

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

Where  $\left(\frac{^{146}\text{Nd}}{^{144}\text{Nd}}\right)^{\text{Nat}}$  is the ratio in nature with the value of 0.721900 (Saji *et al.*, 2016). Standard error of measurement ( $\sigma_m$ ) was propagated from the TIMS output <sup>143</sup>Nd/<sup>146</sup>Nd to the calculated <sup>143</sup>Nd/<sup>144</sup>Nd.

### Accuracy and precision of measured ratios

Nd isotope standard La Jolla was measured multiple times in the proposed method and in conventional mode to compare the accuracy and precision of the two approaches. Measurements in the proposed method yielded an average of 0.511852 ± 0.000021 (2σ, n = 15; **Table 1**) which is consistent with measured values in the conventional method 0.511846 ± 0.000014 (2σ, n = 11).

**Table 1.**  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio determined proposed method for La Jolla Nd standard

Sample No.	$^{143}\text{Nd}/^{144}\text{Nd}$	$2\sigma_m$
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

Error for each measurement is standard error of mean and for average is standard deviation. Reference value is from Shibata and Yoshikawa (2004).

Internal reproducibility range between 10 to 25 ppm for data acquired in 10 to 30 blocks in the proposed method as represented in **Table 1**. All data agree to previously reported value of  $0.511855 \pm 0.000020$  (Shibata and Yoshikawa, 2004).

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

Three aliquots of JB-2 prepared using the proposed single column method (without Sm removal) were measured five times using the proposed online correction and the conventional interfering element correction method. An average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.513096 \pm 0.000039$  ( $2\sigma$ ,  $n = 5$ ; sample nos. 7–9 in **Table 2**) was obtained which is also in agreement with published values.  $^{147}\text{Sm}/^{146}\text{Nd}$  ratios varied during each measurement and ranged between 0.152 and 0.313 at the beginning of measurement for each sample (sample nos. 7–9 in **Table 2**). It

should be noted that this ratio does not reflect the actual  $^{147}\text{Sm}/^{146}\text{Nd}$  of the measured sample and is dependent on the ionisation efficiency and isotopic fractionation of Sm and Nd during the measurement. The conventional interfering element corrected values range between 0.513137 and 0.513610, all of which overestimate the effect of  $^{144}\text{Sm}$  on the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio in the sample and are significantly higher than the reference values. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios obtained using IEC and the proposed method are plotted against the  $^{147}\text{Sm}/^{146}\text{Nd}$  ratios obtained during the measurement in **Fig. 2**. It can be seen from the plot that the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios increase with increasing  $^{147}\text{Sm}/^{146}\text{Nd}$ . The observation suggests that the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios with IEC are the result of overestimating the effect of  $^{144}\text{Sm}$ . Although all the data obtained using the proposed method in these 9 samples (**Table 2**, sample nos. 1–9) agree within error to reference values, the internal and external precisions are worse ( $2\sigma > 25$  ppm) than in conventional measurements. 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 matrix elements. This is expected as the proposed method uses  $^{145}\text{Nd}$  in the equations, which is lower in abundance than  $^{144}\text{Nd}$ . The lower abundance leads to higher relative error in the detected ion intensities which is propagated to the final  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio. Therefore, in order to increase the precision in final  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio, we have attempted to reduce the error on  $^{145}\text{Nd}$  ion intensity. One way to achieve this is to analyse the samples at a higher ion intensity. Another would be to increase the number of ratios in order to reduce the standard error of mean. Four separate aliquots of JB-2 were used to test this hypothesis and the results indicate that  $^{145}\text{Nd}$  ion intensity  $>400$  mV can produce high precision ( $2\sigma_m < 25$  ppm)  $^{143}\text{Nd}/^{144}\text{Nd}$  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  $^{143}\text{Nd}/^{144}\text{Nd}$  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 (sediments, sedimentary rocks and mafic-felsic igneous rocks), reported  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios (0.5121–0.5131), and Sm/Nd ratios (0.20–0.36), were prepared using the single column 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 in **Fig. 3**. The  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratios agree with the reference values with sufficient precision for geochemical purposes ( $2\sigma < 25$  ppm), demonstrating that this correction method can be successfully applied to natural samples regardless of the sample type or Sm/Nd ratios. Online IEC, using a constant value of

**Table 2.**  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio determined in conventional method vs proposed method for JB-2

Sample no.	$^{143}\text{Nd}/^{144}\text{Nd}$ conventional method	$^{143}\text{Nd}/^{144}\text{Nd}$ this method	$^{147}\text{Sm}/^{146}\text{Nd}$	Run time
1	$0.513087 \pm 0.000010$	$0.513090 \pm 0.000035$	<10 <sup>-4</sup>	10 blocks
	$0.513067 \pm 0.000015$	$0.513096 \pm 0.000039$		
2	$0.513094 \pm 0.000012$	$0.513129 \pm 0.000032$		
	$0.513093 \pm 0.000015$	$0.513062 \pm 0.000037$		
3	$0.513092 \pm 0.000013$	$0.513099 \pm 0.000040$		
	$0.513087 \pm 0.000012$	$0.513113 \pm 0.000031$		
4	$0.513106 \pm 0.000012$	$0.513097 \pm 0.000028$		
	$0.513089 \pm 0.000011$	$0.513103 \pm 0.000032$		
5	$0.513085 \pm 0.000012$	$0.513055 \pm 0.000028$		
	$0.513097 \pm 0.000011$	$0.513072 \pm 0.000036$		
	$0.513077 \pm 0.000010$	$0.513067 \pm 0.000028$		
6	$0.513090 \pm 0.000010$	$0.513101 \pm 0.000031$		
	$0.513094 \pm 0.000010$	$0.513094 \pm 0.000029$		
Average	$0.513089 \pm 0.000018$	$0.513091 \pm 0.000041$		
7	$0.513247 \pm 0.000012$	$0.513125 \pm 0.000035$	0.162	10 blocks
	$0.513215 \pm 0.000012$	$0.513081 \pm 0.000033$	0.160	
8	$0.513137 \pm 0.000008$	$0.513080 \pm 0.000021$	0.156	
	$0.513169 \pm 0.000009$	$0.513114 \pm 0.000027$	0.153	
9	$0.513613 \pm 0.000041$	$0.513080 \pm 0.000036$	0.313	
Average	$0.513276 \pm 0.000343$	$0.513096 \pm 0.000039$		
10	n.d.	$0.513095 \pm 0.000023$	0.101	29 blocks
	n.d.	$0.513100 \pm 0.000023$	0.090	14 blocks
11	n.d.	$0.513117 \pm 0.000016$	0.330	10 blocks
12	n.d.	$0.513084 \pm 0.000012$	0.310	29 blocks
13	n.d.	$0.513102 \pm 0.000014$	0.205	30 blocks
	n.d.	$0.513084 \pm 0.000020$	0.105	18 blocks
Average		$0.513097 \pm 0.000023$		
Ref. value	$0.513097 \pm 0.000011$			

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.  $^{147}\text{Sm}/^{146}\text{Nd}$  are reported for the first block of measurement.

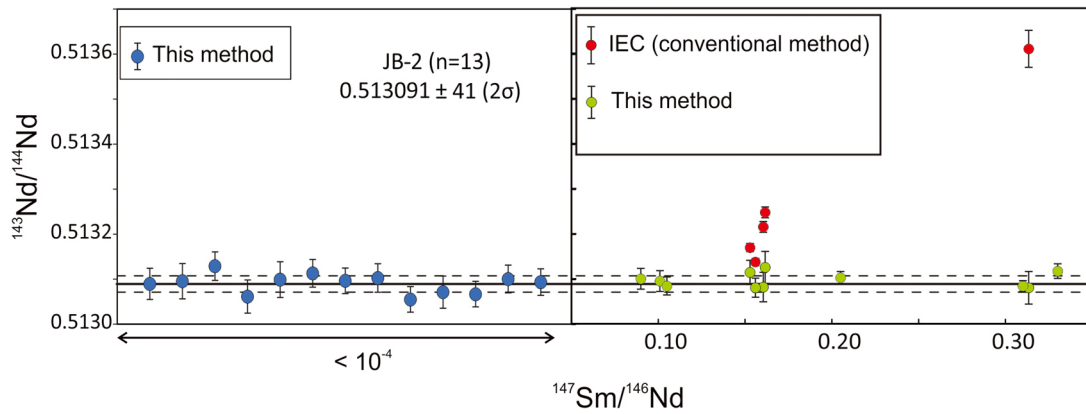
$^{144}\text{Sm}/^{147}\text{Sm} = 0.2069$ , was performed by determining  $^{144}\text{Nd}$  from the total intensity at mass 144 ( $^{144}\text{Nd} + ^{144}\text{Sm}$ ), and  $^{143}\text{Nd}/^{144}\text{Nd}$  were determined during conventional analysis. This is a standard correction applied to all measurements to correct trace 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**.

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

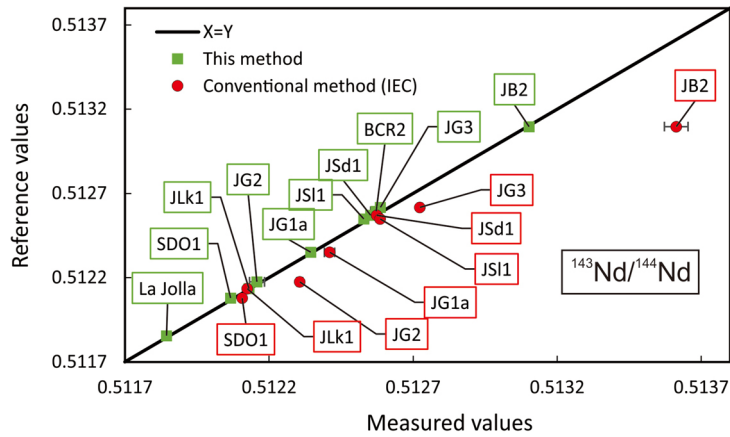
ing analysis as Nd and Sm evaporate from the filament at different rates. Therefore, any error in determination of the fractionation factor of Sm during routine analyses will propagate to the  $^{144}\text{Nd}$  intensity and prevent accurate calculation of fractionation factor in Nd, using the conventional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

## Conclusion

A new method for the analysis of the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio has been developed using a single column separation scheme. A single cation exchange column was used for



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



**Fig. 3.** Corrected  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios for ten reference materials using single column separation (Sm present), in the proposed method (green squares) and conventional interfering element correction method (red circles) 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.

**Table 3.**  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio determined in conventional method vs proposed method for ten reference materials

Reference material	This method	Conventional method (interfering element correction)	Reference values	$^{147}\text{Sm}/^{146}\text{Nd}$ during measurement
	$^{143}\text{Nd}/^{144}\text{Nd} \pm 2\sigma_m$	$^{143}\text{Nd}/^{144}\text{Nd} \pm 2\sigma_m$	$^{143}\text{Nd}/^{144}\text{Nd} \pm 2\sigma$	
BCR 2	$0.512572 \pm 0.000019$	—	$0.512594 \pm 0.000023^1$	0.001–0.015
JG1a	$0.512345 \pm 0.000014$	$0.512410 \pm 0.000018$	$0.512351 \pm 0.000010^1$	0.118–0.040
JG2	$0.512158 \pm 0.000026$	$0.512306 \pm 0.000010$	$0.512176 \pm 0.000012^1$	0.012–0.152
JG3	$0.512586 \pm 0.000011$	$0.512723 \pm 0.000007$	$0.512618 \pm 0.000008^2$	0.098–0.131
JLk1	$0.512130 \pm 0.000013$	$0.512124 \pm 0.000007$	$0.512135 \pm 0.000006^3$	0.105–0.092
JSd1	$0.512553 \pm 0.000015$	$0.512574 \pm 0.000011$	$0.512571 \pm 0.000018^4$	0.006–0.022
JSI1	$0.512529 \pm 0.000016$	$0.512585 \pm 0.000008$	$0.512549 \pm 0.000017^1$	0.049–0.120
SDO1	$0.512067 \pm 0.000012$	$0.512107 \pm 0.000005$	$0.512080 \pm 0.000008^1$	0.060–0.088
JB2	$0.513102 \pm 0.000014$	$0.513613 \pm 0.000041$	$0.513097 \pm 0.000011^2$	0.402–0.002
La Jolla	$0.511844 \pm 0.000011$	NA	$0.511855 \pm 0.000020^5$	0.0000

Reference values: <sup>1</sup>Dey *et al.* (2023); <sup>2</sup>Shibata *et al.* (2003); <sup>3</sup>Jo *et al.* (2021); <sup>4</sup>Nath *et al.* (2009); <sup>5</sup>Shibata and Yoshikawa (2004).

rapid sample processing (2–3 hrs) reducing both the time and cost of sample preparation. All major elements as well as ~90% of Ba and ~50% Ce were removed from the Nd fraction prior to analysis. A novel correction method was developed to circumnavigate the isobaric effect of  $^{144}\text{Sm}$  remaining in the Nd fraction. This method uses the two non-radiogenic and non-isobaric isotopes of Nd, i.e.,  $^{145}\text{Nd}$  and  $^{146}\text{Nd}$ , for mass fractionation correction and does not require the elimination of Sm from the analysed fraction. The method has been applied to the Nd standard solution La Jolla and nine natural rock reference materials which yield concordant values to published  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. As this method is independent of the elemental abundance of Sm or the mass 144 which includes isobaric effect of  $^{144}\text{Sm}$ , it can be applied to any sample irrespective of the Sm/Nd ratio. This method can be used for fast analysis of a large number of samples and does not require the analyst to be highly skilled in column chemistry.

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