Single Column REE Separation and Radiogenic ¹⁴³Nd/¹⁴⁴Nd Analysis in TIMS

Bidisha **Dey***^{1, 2}

Email: bidisha-dey@hiroshima-u.ac.jp

Tomoyuki **Shibata**^{1, 2}

Email: tomo33hk@hiroshima-u.ac.jp

Masako Yoshikawa^{1, 2}

Email: masako@hiroshima-u.ac.jp

Higashi-Hiroshima City, Hiroshima, 739-8526, Japan

Ph: +81-082-424-7305

1 Kagamiyama, Higashi-Hiroshima City, Hiroshima, 739-8526, Japan

Ph: +81-082-424-7305

This is a non peer reviewed manuscript submitted to Talanta for peer review

^{*} corresponding author

¹ Earth and planetary systems science program, Hiroshima University, 1-3-1 Kagamiyama,

² Hiroshima Institute of Plate Convergence Region Research, Hiroshima University, 1-3-

Abstract

We use 145Nd/146Nd for instrumental mass fractionation correction to accurately

determine radiogenic ¹⁴³Nd/¹⁴⁴Nd for natural samples without requiring Sm elimination

from Nd fraction. Conventionally, radiogenic Nd isotope ratios are expressed relative to

the non-radiogenic ¹⁴⁴Nd which is an isobar of ¹⁴⁴Sm. To mitigate this problem, traditional

analysis methods eliminate Sm entirely from the sample aliquot using multi-column

separation process. In this work, we explore a correction method that enables accurate

measurement of ¹⁴³Nd/¹⁴⁴Nd ratio without the elimination of Sm, and thus reducing time

and cost of measurement. We use the ratio of two non-radiogenic isotopes of Nd without

any natural isobars, ¹⁴⁵Nd/¹⁴⁶Nd, to correct instrumental mass fractionation on

¹⁴³Nd/¹⁴⁶Nd. The corrected ¹⁴³Nd/¹⁴⁶Nd is then converted to the ¹⁴³Nd/¹⁴⁴Nd form using

the constant ratio of ¹⁴⁶Nd/¹⁴⁴Nd of 0.7219 in order to allow direct comparison with

published literature and databases. We have implemented this correction method

combined with a fast single column separation scheme to generate accurate and precise

radiogenic ¹⁴³Nd/¹⁴⁴Nd 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; ¹⁴³Nd/¹⁴⁴Nd; Isobaric interference;

TIMS

1. Introduction

Rare earth element (REE) geochemistry is a robust tool for research in the natural sciences due to their chemical similarity and low mobility in surface processes. Among these, a particular parent-daughter pair, ¹⁴⁷Sm - ¹⁴³Nd has been used to investigate radiogenic isotope geochemistry of the Earth since the 1970s [1-4]. However, isobaric interference of Sm on many of the Nd isotopes (i.e., 144, 148, 150) have always been a problem in accurate determination of radiogenic Nd isotope ratios. Although this problem was solved by rigorous column chemistry, the process made Nd isotope geochemistry an expensive and time-consuming effort. Recently, radiogenic Nd isotope geochemistry is being used in various fields including but not limited to geochemistry, archaeology, anthropology, environmental sciences, forensic analysis etc [5-8]. Many of these fields require a large number of samples to be measured. The conventional REE separation method, which often takes days and involve expensive and/or hard to control reagents [9] makes the number of samples for radiogenic Nd isotope chemistry to be constrained by time and resources available to the lab. However, if a faster analytical method which does not require inter-REE separation is established, the scope and applicability of Nd isotope chemistry can be increased by many folds.

Precise determination of isotope ratios requires effective elimination of isobaric effects. However, most mass spectrometers used for high-precision isotope analysis, e.g., Multi collector Inductively coupled plasma mass spectrometer (MC-ICP-MS), or Thermal ionization mass spectrometer (TIMS) cannot discriminate between isobars during measurement without sacrificing sensitivity and precision of data. Therefore, analysis of isotope ratios from rare earth elements (REE) requires proficient chemical separation to

extract a single-element fraction free of isobaric interference. The fact that most REEs are very similar in chemical characteristics to each other, makes the process even more difficult. Nd isotope ratios are conventionally reported as normalized to ¹⁴⁴Nd. This isotope is an isobar of ¹⁴⁴Sm. So, any accurate determination of ¹⁴³Nd/¹⁴⁴Nd either requires total elimination of Sm from the analysed fraction or needs calculation for any existing Sm in the fraction. In most laboratories producing high precision Nd isotopic data, a Nd fraction is purified from the sample aliquot by rigorous column chemistry involving multiple ion exchange columns [10-14]. This is not only time consuming but also expensive. Trace level 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 chemistry, column overloading etc [9,15]. Trace level of Sm present during TIMS analysis is usually corrected online by measuring the intensity of ¹⁴⁷Sm and assuming a constant ratio for ¹⁴⁷Sm/¹⁴⁴Sm. The drawback of this method is that any instrumental mass fractionation on Sm is unaccounted for, and the error is propagated to the ¹⁴³Nd/¹⁴⁴Nd ratio. The maximum tolerable ¹⁴⁷Sm/¹⁴⁶Nd, required for less than 5 ppm error in Nd isotopic measurement was calculated to be 4.3×10^{-4} [16]. An approach to determine precise and accurate Nd isotope ratios without REE separation has been adopted by Li et al. (2011) [17] in which they measure ¹⁴⁷Sm and ¹⁴⁹Sm along with Nd isotopes to first determine instrumental mass fractionation for Sm. The raw ¹⁴⁴Sm intensity is then calculated and subtracted from the total intensity on mass 144 to determine ¹⁴⁴Nd. This yields accurate isotope ratios, provided that the Sm fractionation is accurately determined and 144Nd is accurately corrected for. However, any error in determination of fractionation factor of Sm during routine analysis will be propagated to

the ¹⁴⁴Nd intensity and prevent accurate fractionation calculation of Nd using the conventional ¹⁴⁶Nd/¹⁴⁴Nd ratio. Moreover, at least 5 masses (143, 144, 146, 147, 149) need to be measured accurately and simultaneously to determine ¹⁴³Nd/¹⁴⁴Nd and the detection errors will be propagated to the final ¹⁴³Nd/¹⁴⁴Nd ratio.

We propose a different approach to solve this problem which does not require the accurate correction of ¹⁴⁴Nd intensity. 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 which is considered constant at a value of 0.7219 [18,19] is conventionally used to correct mass dependent fractionation during measurement [9,10,20,21,11-14,16-19]. However, ¹⁴⁵Nd/¹⁴⁴Nd 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 [12,19,21]. This is because ¹⁴⁴Nd and ¹⁴⁵Nd are non-radiogenic in geological time frame and show constant abundances in nature. Therefore, we can use the ratio of ¹⁴⁵Nd/¹⁴⁶Nd, which is theoretically constant, to correct instrumental mass fractionation (IMF) on ¹⁴³Nd/¹⁴⁶Nd ratio. As most Nd isotopic data present in literature is reported with 144Nd as the denominator, we convert the calculated ¹⁴³Nd/¹⁴⁶Nd to ¹⁴³Nd/¹⁴⁴Nd by multiplying the ratio with the constant value of ¹⁴⁶Nd/¹⁴⁴Nd for terrestrial silicate rocks which is equal to 0.7219. We have used this correction method to correct IMF for La Jolla Nd standard and nine geological reference materials, including basalts, granites, sediments, and sedimentary rocks from Geological survey of Japan (GSJ) and United States Geological Survey (USGS) using a single column Nd separation using cation exchange resin (AG50W-X8), to check the accuracy and external reproducibility of this method.

2. Experimental

2.1. Reagents and instruments

Electronic grade HCl and HNO₃, Ultrapure grade HClO₄ (Kanto Chemicals), AA-10 grade HF and H₂O₂ (Tamapure) was used to digest rock powder and for column chemistry. Milli Q water (>18.5 M Ω cm) was used to dilute reagents and for washing purpose. Cation exchange resin AG50W-X8 from BioRad was used to extract REE fractions from rock powder. An Inductively Coupled Plasma Mass Spectrometer (X SERIES II) from Thermo Scientific installed at the Hiroshima University was used to determine elution curve and recovery of Ba and light rare earth elements (LREEs). Thermal Ionization Mass Spectrometer (TIMS) from Thermo Fisher (Finnigan MAT-262) situated at the Hiroshima University was used to measure Nd isotope ratios. The instrument is equipped with nine movable Faraday cups with 10^{11} Ω amplifiers and a dynamic range of 10 V and one Secondary electron multiplier with 10^7 Ω amplifier. La Jolla Nd standard was used to determine accuracy and precision of correction method. Nine geological reference materials, including JB-2, JG-1a, JG-2, JG-3, JSl-1, JSd-1 and JLk-1 from GSJ and BCR-2 and SDO-1 from USGS, were used to determine accuracy of correction method in natural samples.

2.2. <u>Sample preparation</u>

Nine aliquots of 20-40 mg fractions of JB-2 and single aliquots of the other reference materials were digested with HF-HClO₄ [15] and finally dissolved in 1 mL 2.5 M HCl and loaded on to a washed 1 mL AG50W-X8 resin column. Column chemistry was modified after Lin *et al.* (2020) [22]. Major elements were rinsed with 8 mL of 2.5 M

HCl, and Ba was removed using 7 mL 1.7 M HNO₃. LREE fraction was collected with 4 mL 3 M HCl. Six of the JB-2 aliquots were prepared for conventional measurement according to the column chemistry of Dey *et al.* (2023) [9] using AG50W-X8 resin for major element removal and Ln-spec resin for Sm, Ce and Ba removal from Nd fraction.

2.3. Isotope ratio analysis

LREE fractions were loaded onto degassed Re double filaments using dilute HNO₃. Measurement was done in Nd⁺ mode. Ionization filament was slowly heated with 4.5 A current while the evaporation filament was heated up to \sim 1.8 A current until a stable Nd beam was found. Data was collected for 10 to 30 blocks with 10 ratios per block. Instrumental mass fractionation (IMF) was corrected using ¹⁴⁵Nd/¹⁴⁶Nd = 0.482636. Total time for each run was 30 to 80 minutes depending on the number of blocks. Each run was followed by another analysis in conventional method using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 for IMF correction and ¹⁴⁴Sm/¹⁴⁷Sm = 0.2069 for interfering element correction (IEC).

3. Calculation

Calculation and theoretical basis of this method is described in this section. Each ¹⁴³Nd/¹⁴⁶Nd ratio was corrected according to eq. (1) following Rayleigh correction method.

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

Where (143Nd/146Nd)Meas and (145Nd/146Nd)Meas are the measured isotope ratios and (143Nd/146Nd)Corr is the IMF 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 15 measurements of JB-2 in conventional method.

The corrected ¹⁴³Nd/¹⁴⁶Nd was then converted to ¹⁴³Nd/¹⁴⁴Nd according to eq. (2) for comparison with published data.

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

Where $(^{146}\text{Nd}/^{144}\text{Nd})^{Nat}$ is the ratio in nature with the value of 0.7219. Standard error of measurement (σ_m) was propagated from the TIMS output $^{143}\text{Nd}/^{146}\text{Nd}$ to calculated $^{143}\text{Nd}/^{144}\text{Nd}$.

4. Results and Discussion

4.1. Column chemistry

The column process was modified after Lin *et al.* (2020) [22] in order to reduce Ba and Ce in the measured fraction as both Ba and Ce reduce ionization efficiency of Nd [9]. The elution curve for Ba, Ce, Nd and Sm is illustrated in Figure 1. Each fraction of 1 mL was collected and analysed in ICP-MS for Ba and LREEs.

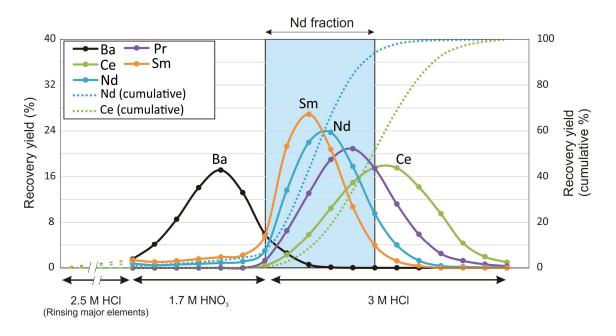


Figure 1. Elution curve for Ba and LREEs in 1 mL AG50W-X8 column. Data is plotted for fractions after loading and rinsing of major elements (9 mL 2.5 M HCl). Each fraction for 1.7 M HNO_3 and 3 M HCl is 1 mL.

The results show that most of the Ba (~90%) can be removed by rinsing the column with 7 mL 1.7 M HNO₃ after loading (1 mL) and rinsing of major elements (8 mL) with 2.5 M HCl. Nd fraction is then collected using 4 mL of 3 M HCl with a recovery yield >80%. This fraction contains ~ 50% of the total Ce. Loading and rinsing fraction do not contain measurable amount of Ba or LREEs [9,22]. Total blank for this process is less than 50 pg [9]. 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. Ln-Spec resin and DGA resin (Eichrom) which are commonly used for REE separation [8,9,23] are almost 20 times more expensive than the cation exchange resin (AG50W-X8). High purity acids are also very expensive, and use of a single-step separation reduces the volume of eluents used for cleaning and elution.

The α -HIBA method is another commonly used method [13,14] which does not use expensive resins but require careful control of pH conditions and frequent calibration of elution curve. The proposed method on the other hand provides an inexpensive yet simple sample preparation method which can be performed without expertise.

4.2. La Jolla Nd standard

5. Table 1. ¹⁴³Nd/¹⁴⁴Nd ratio determined in conventional method vs proposed method for La Jolla

	143 Nd/ 144 Nd	¹⁴³ Nd/ ¹⁴⁴ Nd
	conventional method	this method
1	0.511845 ± 0.000006	0.511863 ± 0.000020
2	0.511847 ± 0.000007	0.511861 ± 0.000021
3	0.511847 ± 0.000009	0.511872 ± 0.000018
4	0.511849 ± 0.000009	0.511850 ± 0.000019
5	0.511858 ± 0.000010	0.511877 ± 0.000024
6	0.511850 ± 0.000009	0.511855 ± 0.000021
7	0.511832 ± 0.000008	0.511830 ± 0.000027
8	0.511847 ± 0.000009	0.511844 ± 0.000032
9	0.511834 ± 0.000008	0.511844 ± 0.000020
10	0.511848 ± 0.000009	0.511840 ± 0.000026
11	0.511852 ± 0.000010	0.511864 ± 0.000021
Average	0.511846 ± 0.000014	0.511855 ± 0.000027
Ref. value [13]	0.511855 ± 0.000020	

Standard error of mean for each measurement and standard deviation for average is reported as error.

Nd isotope standard La Jolla was measured multiple times in conventional mode and raw data was copied from the output file of TIMS. Raw data was manually corrected using abovementioned calculation (Section 3) in excel for comparison between conventional and proposed IMF correction methods. Corrected data from 11 measurements of La Jolla show values (Table 1) with 143 Nd/ 144 Nd ratio of 0.511855 \pm 0.000027 (2 σ , n= 11) in this

method, compared to 0.511846 ± 0.000014 (2σ , n= 11) for the same measurements in the conventional method. La Jolla measurements using the proposed online IMF correction also agree to these values with 143 Nd/ 144 Nd = 0.511850 ± 21 ($2\sigma_m$). All measured data agree to previously reported value of 0.511855 ± 0.000020 [13].

5.1. Natural reference materials

Six aliquots of JB-2 prepared using Ln-spec resin chemistry (Sm removal) were measured in conventional method and show 143 Nd/ 144 Nd ratio of 0.513089 \pm 0.000018 (2 σ , n= 13) (Table 2). The raw data was manually corrected using proposed calculation and show 143 Nd/ 144 Nd ratio of 0.513091 \pm 0.000041 (2 σ , n= 13). Both data agree to the published value of 0.513097 \pm 0.000011 [20].

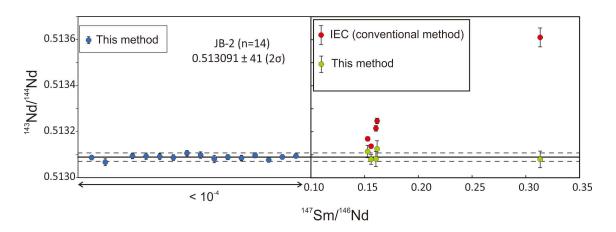


Figure 2. Corrected ¹⁴³Nd/¹⁴⁴Nd from JB-2. Solid and dashed lines represent average and 2 standard deviations of fourteen measurements for sample preparation and IMF correction in conventional method. Blue points represent IMF correction in proposed method for the same fourteen measurements. Green and red points represent sample preparation in proposed method. Horizontal axis represents ¹⁴⁷Sm/¹⁴⁶Nd at the start of measurement. Green and red points show IMF correction in proposed method and conventional method using interfering element correction (IEC) respectively.

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

Sample no.	¹⁴³ Nd/ ¹⁴⁴ Nd conventional method	¹⁴³ Nd/ ¹⁴⁴ Nd this method	¹⁴⁷ Sm/ ¹⁴⁶ Nd
1	$\begin{array}{c} 0.513087 \pm 0.000010 \\ 0.513067 \pm 0.000015 \end{array}$	0.513090 ± 0.000035 0.513096 ± 0.000039	
2	$\begin{array}{c} 0.513094 \pm 0.000012 \\ 0.513093 \pm 0.000015 \end{array}$	$\begin{array}{c} 0.513129 \pm 0.000032 \\ 0.513062 \pm 0.000037 \end{array}$	
3	$\begin{array}{c} 0.513092 \pm 0.000013 \\ 0.513087 \pm 0.000012 \end{array}$	0.513099 ± 0.000040 0.513113 ± 0.000031	
4	0.513106 ± 0.000012	0.513097 ± 0.000028	<10 ⁻⁴
5	0.513089 ± 0.000011 0.513085 ± 0.000012 0.513097 ± 0.000011	$\begin{array}{c} 0.513103 \pm 0.000032 \\ 0.513055 \pm 0.000028 \\ 0.513072 \pm 0.000036 \end{array}$	
6	$\begin{array}{c} 0.513077 \pm 0.000010 \\ 0.513090 \pm 0.000010 \\ 0.513094 \pm 0.000010 \end{array}$	$\begin{array}{c} 0.513067 \pm 0.000028 \\ 0.513101 \pm 0.000031 \\ 0.513094 \pm 0.000029 \end{array}$	
Average	0.513089 ± 0.000018	0.513091 ± 0.000041	
7	$\begin{array}{c} 0.513247 \pm 0.000012 \\ 0.513215 \pm 0.000012 \end{array}$	$0.513125 \pm 0.000035 \\ 0.513081 \pm 0.000033$	0.162 0.160
8	$\begin{array}{c} 0.513137 \pm 0.000008 \\ 0.513169 \pm 0.000009 \end{array}$	$\begin{array}{c} 0.513080 \pm 0.000021 \\ 0.513114 \pm 0.000027 \end{array}$	0.156 0.153
9	0.513610 ± 0.000041	0.513080 ± 0.000036	0.313
Average	0.513276 ± 0.000343	0.513096 ± 0.000039	
Ref. value [20]	0.513097 ± 0.000011		

Standard error of mean for each measurement and standard deviation for average is reported as error. Ratio of first block is reported as ¹⁴⁷Sm/¹⁴⁶Nd.

Three aliquots of JB-2 prepared in single column method (LREE fraction) were measured five times using proposed online correction (Table 2). 143 Nd/ 144 Nd ratio of 0.513096 \pm 0.000039 (2 σ) was obtained which also agrees to published data. 147 Sm/ 146 Nd ratios varied during each measurement. The ratio for the five measurements ranged between 0.152 and 0.313 at the beginning of measurement. It is to note that this ratio does not reflect the actual 147 Sm/ 146 Nd of the measured sample and is dependent on the ionization efficiency of Sm and Nd during measurement. Online interfering element correction using a constant value of 144 Sm/ 147 Sm = 0.2069 was done by determination of 144 Nd from the total intensity at mass 144 (144 Nd + 144 Sm). This is a standard correction done for all

measurements to correct trace amounts of interfering elements. However, this correction was not able to provide an accurate ratio for samples without Sm separation (Figure 2). The data also reflects that deviation of measured ¹⁴³Nd/¹⁴⁴Nd in IEC method from reference value, is roughly proportional to ¹⁴⁷Sm/¹⁴⁶Nd during measurement.

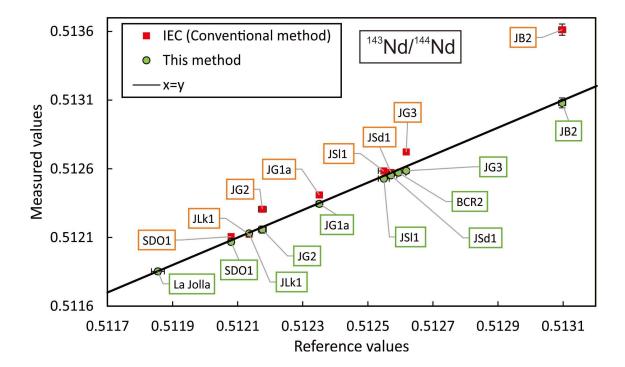


Figure 3. Corrected 143 Nd/ 144 Nd ratios for LREE fraction from ten reference materials in the proposed IMF correction method (green circles) and conventional interfering element correction method (red square). Diagonal line represents X=Y, distance of plot points from this line represents deviation from reference values. Data for all reference materials in proposed IMF correction method is conformable to reference values. Error bars represent 2 standard error of mean.

Single aliquots of eight other reference materials were prepared using single column and analysed using proposed online IMF correction method and conventional method. All samples show ¹⁴³Nd/¹⁴⁴Nd isotope ratios (Table 3) conformable to reference values (Figure 3), proving that this correction method can be successfully applied to natural samples irrespective of the sample type or Sm/Nd ratio. The results also show that the

conventional method with interfering element correction can provide reliable data when 147 Sm/ 146 Nd is low (< 0.1) but cannot be used when 147 Sm/ 146 Nd is higher.

Table 3 143 Nd/ 144 Nd ratio determined in conventional method vs proposed method for ten reference materials

Reference material	This method	Conventional method (interfering element correction)	Reference values	147Sm/146Nd 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
BCR2	0.512572 ± 0.000019	-	0.512594 ± 0.000023 [9]	0.001- 0.015
JG1a	0.512345 ± 0.000014	0.512410 ± 0.000018	0.512351 ± 0.000010 [9]	0.118- 0.040
JG2	0.512158 ± 0.000026	0.512306 ± 0.000010	0.512176 ± 0.000012 [9]	0.012- 0.152
JG3	0.512586 ± 0.000011	0.512723 ± 0.000007	0.512618 ± 0.000008 [20]	0.098- 0.131
JLk1	0.512130 ± 0.000013	0.512124 ± 0.000007	0.512135 ± 0.000006 [24]	0.105- 0.092
JSd1	0.512553 ± 0.000015	0.512574 ± 0.000011	0.512571 ± 0.000018 [25]	0.006- 0.022
JS11	0.512529 ± 0.000016	0.512585 ± 0.000008	0.512549 ± 0.000017 [9]	0.049- 0.120
SDO1	0.512067 ± 0.000012	0.512107 ± 0.000005	0.512080 ± 0.000008 [9]	0.060- 0.088
JB2	0.513080 ± 0.000036	0.513613 ± 0.000041	0.513097 ± 0.000011 [20]	0.402- 0.002
La Jolla	0.511850 ± 0.000021	NA	0.511855 ± 0.000020 [13]	0.0000

 $^{^{147}\}mathrm{Sm}/^{146}\mathrm{Nd}$ ratio represents variation between first and last block of measurement during run in proposed method.

6. Conclusion

A new method for the analysis of ¹⁴³Nd/¹⁴⁴Nd ratio was developed without requiring Sm separation from the Nd fraction. This method uses the two non-radiogenic and non-isobaric isotopes of Nd, i.e., ¹⁴⁵Nd and ¹⁴⁶Nd for mass fractionation correction and does not require elimination of Sm from analysed fraction. A single column Nd separation

method was developed for fast sample processing (2-3 hrs) which reduces the time as well as cost of sample preparation. The method was applied for Nd standard solution La Jolla and nine natural reference materials which yields accurate and reproducible values. As this method is not dependent on elemental abundance of Sm or the mass 144 which includes isobaric effect of ¹⁴⁴Sm, it can be applied to any sample irrespective of the Sm/Nd ratio. This process can be used for fast analysis of large number of samples and does not require high skill in column chemistry for the analyst.

7. Acknowledgment

This work was partially supported by HiPeR, which is selected and supported by Hiroshima University. We thank the Hiroshima University for providing the research facilities.

References

- 1. O'Nions, R. K., Carter, S. R., Evensen, N. M. & Hamilton, P. J. Geochemical and cosmochemical applications of Nd isotope analysis. *Annu. Rev. Earth Planet. Sci.* 7, 11–38 (1979).
- 2. Notsu, K., Mabuchi, H., Yoshioka, O., Matsuda, J. & Ozima, M. Evidence of the extinct nuclide 146Sm in "Juvinas" achondrite. *Earth Planet. Sci. Lett.* **19**, 29–36 (1973). https://doi.org/10.1016/0012-821X(73)90175-1
- 3. DePaolo, D. J. & Wasserburg, G. J. Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.* **3**, 249–252 (1976). https://doi.org/10.1029/GL003i005p00249
- 4. DePaolo, D. J. & Wasserburg, G. J. Inferences about magma sources and mantle structure from variations of 143Nd/144Nd. *Geophys. Res. Lett.* **3**, 743–746 (1976). https://doi.org/10.1029/GL003i012p00743

- 5. De Bonis, A. *et al.* Sr-Nd isotopic fingerprinting as a tool for ceramic provenance: Its application on raw materials, ceramic replicas and ancient pottery. *J. Archaeol. Sci.* **94**, 51–59 (2018). https://doi.org/10.1016/j.jas.2018.04.002
- 6. Geagea, M. L., Stille, P., Gauthier-Lafaye, F. & Millet, M. Tracing of industrial aerosol sources in an urban environment using Pb, Sr, and Nd isotopes. *Environ. Sci. Technol.* **42**, 692–698 (2008). https://doi.org/10.1021/es071704c
- 7. Martin, E. E. & Haley, B. A. Fossil fish teeth as proxies for seawater Sr and Nd isotopes. *Geochim. Cosmochim. Acta* **64**, 835–847 (2000). https://doi.org/10.1016/S0016-7037(99)00376-2
- 8. Tazoe, H. *et al.* Determination of Nd isotopic composition in seawater using newly developed solid phase extraction and MC-ICP-MS. *Talanta* **232**, 122435 (2021). https://doi.org/10.1016/j.talanta.2021.122435
- 9. Dey, B., Shibata, T. & Yoshikawa, M. Sequential Pb-Sr-LREE separation from silicates for isotopic analysis. *Geochem. J.* GJ23006 (2023) https://doi.org/10.2343/geochemj.GJ23006.
- 10. Kagami, S. & Yokoyama, T. Chemical separation of Nd from geological samples for chronological studies using 146Sm-142Nd and 147Sm-143Nd systematics. *Anal. Chim. Acta* **937**, 151–159 (2016). https://doi.org/10.1016/j.aca.2016.07.004
- 11. Caro, G., Bourdon, B., Birck, J.-L. & Moorbath, S. High-precision Nd measurements in terrestrial rocks: Constraints on the early differentiation of the Earth's mantle. *Geochim. Cosmochim. Acta* **70**, 164–191 (2006). https://doi.org/10.1016/j.gca.2005.08.015
- 12. Pin, C., Gannoun, A. & Dupont, A. Rapid, simultaneous separation of Sr, Pb, and Nd by extraction chromatography prior to isotope ratios determination by TIMS and MC-ICP-MS. *J. Anal. At. Spectrom.* (2014) https://doi.org/10.1039/C4JA00169A.
- 13. Shibata, T. & Yoshikawa, M. Precise Isotope Determination of Trace Amounts of Nd in Magnesium-rich Samples. *J. Mass Spectrom. Soc. Jpn.* **52**, 317–324 (2004). https://doi.org/10.5702/massspec.52.317
- 14. Hyung, E. & Tissot, F. L. H. Routine high-precision Nd isotope analyses: An optimized chromatographic purification scheme. *J. Anal. At. Spectrom.* **36**, 1946–1959 (2021). https://doi.org/10.1039/D1JA00169H
- 15. Yokoyama, T., Makishima, A. & Nakamura, E. Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. *Chem. Geol.* **157**, 175–187 (1999). https://doi.org/10.1016/S0009-

- 2541(98)00206-X
- 16. Garçon, M. *et al.* Factors influencing the precision and accuracy of Nd isotope measurements by thermal ionization mass spectrometry. *Chem. Geol.* **476**, 493–514 (2018). https://doi.org/10.1016/j.chemgeo.2017.12.003
- 17. Li, C. F., Li, X. H., Li, Q. L., Guo, J. H. & Li, X. H. Directly determining 143Nd/144Nd isotope ratios using thermal ionization mass spectrometry for geological samples without separation of Sm-Nd. *J. Anal. At. Spectrom.* **26**, 2012–2022 (2011). https://doi.org/10.1039/C0JA00081G
- 18. Depaolo, D. J. *Neodymium Isotope Geochemistry: an introduction. Springer-Verlag* (1988). https://doi.org/10.1180/minmag.1990.054.376.21.
- 19. Saji, N. S., Wielandt, D., Paton, C. & Bizzarro, M. Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS. 1490–1504 (2016) https://doi.org/10.1039/c6ja00064a.
- 20. Shibata, T., Yoshikawa, M. & Tatsumi, Y. An analytical method for determining precise Sr and Nd isotopic compositions and results for thirteen rock standard materials. *Front. Res. Earth Evol.* **1**, 363–367 (2003).
- 21. Li, C.-F., Wang, X.-C., Guo, J.-H., Chu, Z.-Y. & Feng, L.-J. Rapid separation scheme of Sr, Nd, Pb, and Hf from a single rock digest using a tandem chromatography column prior to isotope ratio measurements by mass spectrometry. *J. Anal. At. Spectrom.* (2016) https://doi.org/10.1039/C5JA00477B.
- 22. Lin, Y.-B. *et al.* Accurate Determination of Barium Isotopic Compositions in Sequentially Leached Phases from Carbonates by Double Spike-Thermal Ionization Mass Spectrometry (DS-TIMS). *Anal. Chem.* **92**, 2417–2424 (2020). https://doi.org/10.1021/acs.analchem.9b03137
- 23. Pin, C. & Gannoun, A. A triple tandem columns extraction chromatography method for isolation of highly purified neodymium prior to 143Nd/144Nd and 142Nd/144Nd isotope ratios determinations. *J. Anal. At. Spectrom.* **34**, 310–318 (2019). https://doi.org/10.1039/C8JA00360B
- 24. Jo, H. J., Lee, H. M., Kim, G. E., Choi, W. M. & Kim, T. Determination of Sr–Nd–Pb isotopic ratios of rock reference materials using column separation techniques and TIMS. Separations 8, (2021). https://doi.org/10.3390/separations8110213
- 25. Nath, B. N., Makishima, A., Noordmann, J., Tanaka, R. & Nakamura, E. Comprehensive analysis for major, minor and trace element contents and Sr-Nd-Pb-Hf isotope ratios in sediment reference materials, JSd-1 and MAG-1. Geochem. J. 43, 207–216 (2009). https://doi.org/10.2343/geochemj.1.0018