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# Sm-Nd isotopic analysis of mixed standard solutions by multi-collector inductively coupled plasma mass spectrometry: evaluations on isobaric interference correction of Nd isotopic composition and external calibration of Sm/Nd ratio

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## Abstract

**Background:** The Sm-Nd isotope system has long been used to provide information on the age and geochemical evolution of terrestrial rocks and extraterrestrial objects. Traditional thermal ionization mass spectrometry requires a refined chemical separation of Sm and Nd. Here, we present multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) Sm-Nd isotopic results for a series of mixed standard solutions with different Sm/Nd ratios to test the validity of isobaric interference corrections of Nd isotopic composition and external calibration of Sm/Nd inter-elemental ratio.

**Findings:** Reliable  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{145}\text{Nd}/^{144}\text{Nd}$  ratios of the mixed solutions were obtained by using the exponential law and selected Sm isotopic compositions. The Sm/Nd ratios of the mixed solutions corrected by the standard bracketing method were consistent with the gravimetric values mostly within 1% difference.

**Conclusions:** This study provides a simple and high-throughput technique that can simultaneously measure Nd isotopic composition and Sm/Nd ratio without chemical separation between Sm and Nd.

**Keywords:** Sm-Nd, MC-ICP-MS, Isobaric interference, Isotopic composition, Inter-elemental ratio

## Introduction

Sm and Nd are rare earth elements presenting in only small amounts in most rock-forming minerals. Sm and Nd each have seven naturally occurring isotopes ( $^{144}\text{Sm}$ ,  $^{147}\text{Sm}$ ,  $^{148}\text{Sm}$ ,  $^{149}\text{Sm}$ ,  $^{150}\text{Sm}$ ,  $^{152}\text{Sm}$ ,  $^{154}\text{Sm}$ ;  $^{142}\text{Nd}$ ,  $^{143}\text{Nd}$ ,  $^{144}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{146}\text{Nd}$ ,  $^{148}\text{Nd}$ ,  $^{150}\text{Nd}$ ). One isotope of Sm ( $^{147}\text{Sm}$ ) decays by  $\alpha$ -emission to one isotope of Nd ( $^{143}\text{Nd}$ ) with a half-life of 106 Ga (Lugmair & Marti 1978; Begemann et al. 2001). The Sm-Nd decay system has been efficiently used for determining the timing of major events occurred during the chemical evolution of planets and probing into the earth's interior (DePaolo

1988). The application of this system demands highly accurate Sm-Nd isotope data because its half-life is very long and natural variations in Sm/Nd inter-elemental ratio are typically quite limited.

Although the traditional thermal ionization mass spectrometry (TIMS) is still regarded as the benchmark technique for Sm-Nd isotopic measurement (Chu et al. 2009; Harvey & Baxter 2009; Ali & Srinivasan 2011), more recent multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) has also become a routine technique with high sample throughput and comparable precision to TIMS (Walder et al. 1993; Vance & Thirlwall 2002; Yang et al. 2010; Yang et al. 2011). The classic Sm-Nd isotope analysis requires a separation of two elements from the sample matrix by refined chemical

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procedures. Recently, however, it was reported that the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of geological samples could be measured accurately by MC-ICP-MS without Sm and Nd separation (Yang et al. 2010). This study further evaluates the validity of Nd isotopic and Sm/Nd elemental ratio measurements for a series of Sm + Nd mixed standard solutions by MC-ICP-MS technique, and revisited various sets of reported Sm isotopic composition.

### Instrumentation

The Sm-Nd isotopic analysis of this study was conducted by using a Neptune MC-ICP-MS installed at the Korea Basic Science Institute (KBSI) in Ochang. This double focusing high-resolution ICP-MS is equipped with eight movable Faraday collectors and one fixed axial channel where the ion beam intensities can be measured with either a Faraday collector or an ion counting electron multiplier. The Faraday collectors were statically set to simultaneously detect the required isotopes:  $^{140}\text{Ce}$  (L4),  $^{142}\text{Nd}$  (L3),  $^{143}\text{Sm}$  (L2),  $^{144}(\text{Sm} + \text{Nd})$  (L1),  $^{145}\text{Nd}$  (axial),  $^{146}\text{Nd}$  (H1),  $^{147}\text{Sm}$  (H2),  $^{148}(\text{Sm} + \text{Nd})$  (H3), and  $^{149}\text{Sm}$  (H4). The sensitivity on  $^{145}\text{Nd}$  was typically around 5 V/Nd ppm ( $10^{11}\Omega$  resistors) in a low-resolution mode. Details of the other operational parameters are summarized in Table 1.

### Measurement of Nd standard solutions

The basic performance of KBSI Neptune was tested by using the JNdi standard solution with Nd concentration of 100  $\mu\text{g/L}$ . The mass bias was exponentially normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . One measurement consists of 9 blocks of 10 cycles with an integration time of 4.194 s. The average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio was  $0.512100 \pm 0.000004$  ( $n = 10$ ,  $2\sigma$  S.E.), in reasonable agreement with the recommended value ( $0.512115 \pm 0.000007$ ) (Tanaka et al. 2000).

**Table 1 Instrumental setting and operational parameters**

RF forward power	1200 W
RF reflected power	< 2 W
Cooling gas	15 L/min
Auxiliary gas	0.75 - 0.80 L/min
Sample gas	0.985 - 0.990 L/min
Extraction	-2 kV
Focus	-0.654 kV
Acceleration voltage	10 kV
Interface cones	Nickel
Spray chamber	Quartz dual cyclonic
Nebulizer	ESI PFA MicroFlow
Sample uptake rate	100 $\mu\text{L}/\text{min}$
Instrumental resolution	ca. 400
Mass analyzer pressure	$2.9 \times 10^{-9}$ mbar

The in-house Nd standard solution of 100  $\mu\text{g/L}$  was prepared from the AccuTrace™ Nd Reference Standard (lot no. B9035110, plasma emission standard). It yielded an average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.512204 \pm 0.000005$  ( $n = 9$ ,  $2\sigma$  S.E.) with the same analytical design as above (9 blocks of 10 cycles with an integration time of 4.194 s). Two diluted in-house Nd solutions of 50 and 10  $\mu\text{g/L}$  also yielded comparable results of  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512212 \pm 0.000006$  ( $n = 5$ ,  $2\sigma$  S.E.) and  $0.512207 \pm 0.000004$  ( $n = 5$ ,  $2\sigma$  S.E.), respectively.

### Isobaric interference correction

The contribution of  $^{144}\text{Sm}$  imposed on the  $^{144}\text{Nd}$  peak should be carefully corrected for accurate determination of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio. The first step of correction in this study was to calculate the Sm mass bias factor,  $\beta(\text{Sm})$ , for which the exponential law (Russel et al. 1978) was applied as the following.

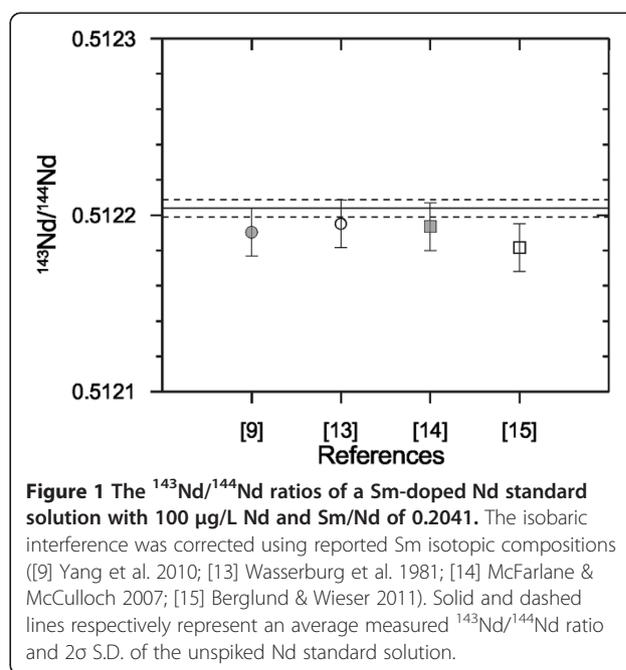
$$\beta(\text{Sm}) = \ln \left[ \frac{(^{147}\text{Sm}/^{149}\text{Sm})_{\text{true}}}{(^{147}\text{Sm}/^{149}\text{Sm})_{\text{measured}}} \right] \div \ln (M_{147}/M_{149}), \quad (1)$$

where  $M$  denotes the mass of the isotope.

The exponential law also yields an equation for  $(^{144}\text{Sm}/^{149}\text{Sm})_{\text{measured}}$ :

$$(^{144}\text{Sm}/^{149}\text{Sm})_{\text{measured}} = (^{144}\text{Sm}/^{149}\text{Sm})_{\text{true}} \times (M_{149}/M_{144})^{\beta(\text{Sm})} \quad (2)$$

The  $^{144}\text{Sm}$  intensity was calculated as multiplying Eq (2) by measured  $^{149}\text{Sm}$  intensity. Then,  $^{144}\text{Nd}$  intensity



**Figure 1** The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of a Sm-doped Nd standard solution with 100  $\mu\text{g/L}$  Nd and Sm/Nd of 0.2041. The isobaric interference was corrected using reported Sm isotopic compositions ([9] Yang et al. 2010; [13] Wasserburg et al. 1981; [14] McFarlane & McCulloch 2007; [15] Berglund & Wieser 2011). Solid and dashed lines respectively represent an average measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio and  $2\sigma$  S.D. of the unspiked Nd standard solution.

**Table 2 Nd isotope ratios of the Sm-doped Nd standard solutions with the Sm/Nd ratio of 0.2**

	Gravimetric Sm/Nd	$^{143}\text{Nd}/^{144}\text{Nd}$	$2\sigma$ S.E.	$^{145}\text{Nd}/^{144}\text{Nd}$	$2\sigma$ S.E.	n
100 $\mu\text{g/L}$ Nd	0.2041	0.512195	0.000011	0.348415	0.000005	140
200 $\mu\text{g/L}$ Nd	0.2022	0.512195	0.000022	0.348419	0.000010	20
50 $\mu\text{g/L}$ Nd	0.2036	0.512208	0.000038	0.348420	0.000031	20

was calculated by subtracting the  $^{144}\text{Sm}$  intensity from the intensity on mass 144 using the equation.

$$^{144}\text{Nd}_{\text{measured}} = ^{144}(\text{Sm} + \text{Nd})_{\text{measured}} - \left[ ^{149}\text{Sm}_{\text{measured}} \times \left( ^{144}\text{Sm}/^{149}\text{Sm} \right)_{\text{true}} \times (M_{149}/M_{144})^{\beta(\text{Sm})} \right] \quad (3)$$

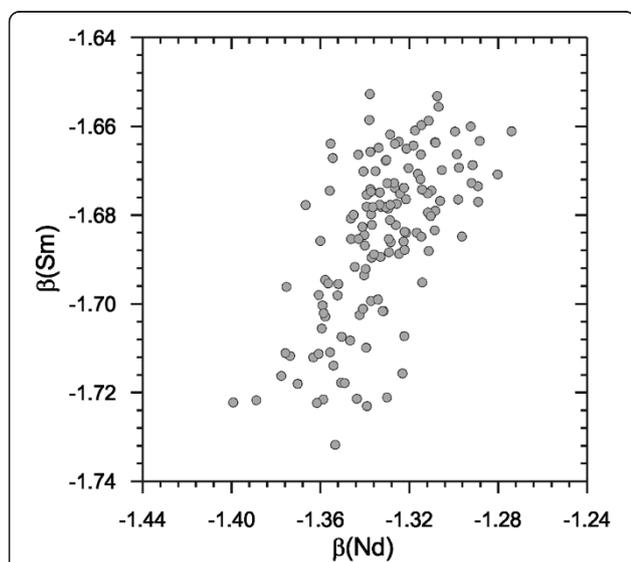
Finally, the  $^{144}\text{Sm}$ -corrected  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio was exponentially normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ .

The Sm isotope ratios ( $^{147}\text{Sm}/^{149}\text{Sm}$  and  $^{144}\text{Sm}/^{149}\text{Sm}$ ) have not been uniformly reported. The following sets of reported Sm isotopic composition were evaluated in this study.

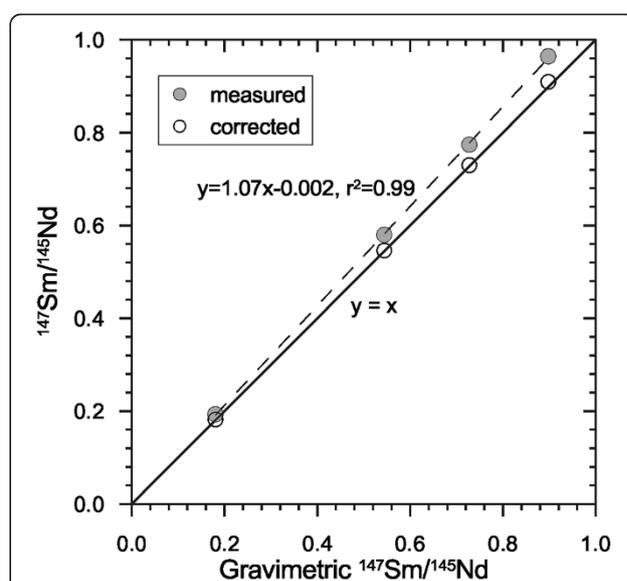
$$^{147}\text{Sm}/^{149}\text{Sm} = 1.0868 \text{ (Yang et al. 2010),} \\ 1.0851 \text{ (Wasserburg et al. 1981),} \\ 1.06119 \text{ (McFarlane McCulloch 2007),} \\ 1.0847 \text{ (Berglund Wieser 2011)} \quad (4)$$

$$^{144}\text{Sm}/^{149}\text{Sm} = 0.22332 \text{ (Yang et al. 2010),} \\ 0.22249 \text{ (Wasserburg et al. 1981),} \\ 0.2103 \text{ (McFarlane McCulloch 2007),} \\ 0.22214 \text{ (Berglund Wieser 2011),} \quad (5)$$

To evaluate these Sm isotopic compositions, the in-house Nd standard solution of 100  $\mu\text{g/L}$  was doped with AccuTrace<sup>TM</sup> Sm Reference Standard (lot no. B8085072, plasma emission standard), in which the concentration ratio of Sm to Nd was 0.2041. As depicted in Figure 1, analytical results (7 measurements, 1 block of 20 cycles with an integration time of 4.194 s) of this solution were different according to the employed Sm isotopic compositions (Yang et al. 2010; Wasserburg et al. 1981; McFarlane & McCulloch 2007; Berglund & Wieser 2011). Sm isotopic compositions reported in (Yang et al. 2010; Wasserburg et al. 1981; McFarlane & McCulloch 2007) yielded the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios comparable with the unspiked value, which were  $0.512190 \pm 0.000014$  ( $2\sigma$  S.E.),  $0.512195 \pm 0.000014$  ( $2\sigma$  S.E.), and  $0.512194 \pm 0.000014$  ( $2\sigma$  S.E.), respectively.



**Figure 2** The correlation between the Sm and Nd mass bias factors ( $\beta(\text{Sm})$  and  $\beta(\text{Nd})$ ) measured for Sm-doped Nd standard solutions with the Sm/Nd ratio of 0.2041.



**Figure 3** Comparisons of the measured and corrected  $^{147}\text{Sm}/^{145}\text{Nd}$  ratios with gravimetric values.

**Table 3 Sm-Nd isotopic data of the Sm-doped Nd standard solutions of 100 µg/L Nd**

<sup>143</sup> Nd/ <sup>144</sup> Nd	2σ S.E.	n	<sup>147</sup> Sm/ <sup>145</sup> Nd			Nd (µg/L)	
			Gravimetric	Measured	Corrected	Gravimetric	Calculated
0.512185	0.000022	20	0.1805	0.1934	0.1818	100	101
0.512191	0.000026	20	0.5441	0.5796	0.5457	100	103
0.512214	0.000028	20	0.7275	0.7744	0.7302	100	103
0.512223	0.000026	20	0.8978	0.9641	0.9091	101	103

Sm isotopic compositions were iteratively solved to minimize the residual sum of squares between corrected <sup>143</sup>Nd/<sup>144</sup>Nd ratio of Sm-doped Nd standard solution and the unspiked value using the Excel Solver. The result suggests that the ratios of <sup>147</sup>Sm to <sup>149</sup>Sm and <sup>144</sup>Sm to <sup>149</sup>Sm would be 1.0844 and 0.22233, respectively. Because these values are the closest to the recommended values in (Wasserburg et al. 1981), we hereafter use 1.0851 and 0.22249 as the (<sup>147</sup>Sm/<sup>149</sup>Sm)<sub>true</sub> and (<sup>144</sup>Sm/<sup>149</sup>Sm)<sub>true</sub> ratios for correcting mass fractionation of Sm and calculating its isobaric contribution to <sup>144</sup>Nd.

The <sup>143</sup>Nd/<sup>144</sup>Nd ratios of the Sm-doped Nd standard solutions with similar Sm/Nd ratio of around 0.20 but different Nd concentrations (200 and 50 µg/L) were 0.512195 ± 0.000022 and 0.512208 ± 0.000038, respectively, corroborating the validity of this correction design (Table 2). Furthermore, the corrected <sup>143</sup>Nd/<sup>144</sup>Nd ratios of the mixed solutions were well consistent with a constant value of 0.348417 obtained by TIMS (Wasserburg et al. 1981). The correlation between β(Sm) and β(Nd) values indicates that the two factors are not identical and are roughly positively correlated with each other (β(Sm) = 0.516 × β(Nd) - 0.997) (Figure 2).

We further analyzed a series of Sm-doped Nd standard solutions of 100 µg/L Nd with different Sm/Nd ratios (Sm/Nd = ca. 0.1, 0.3, 0.4, and 0.5) to test the validity of correction scheme described above. The results show that the correction protocol is reasonable (Table 3). However, there is a systematic increasing trend in the corrected <sup>143</sup>Nd/<sup>144</sup>Nd ratio with increasing Sm/Nd ratios, implying that the mass bias may not be perfectly corrected by the exponential law for high-Sm/Nd (> 0.5) samples.

### Calibration of Sm/Nd ratio

The instrumental mass bias on isotope measurements could be corrected by using either double-spike or standard bracketing methods. The latter method consists in interpolating the mass bias of an unknown sample between the biases inferred from two standard runs, one preceding and one following the sample analysis (Albarede & Beard 2004).

In order to correct the inter-elemental mass bias on the measurement, this study considered the Sm-doped

Nd standard solution with the Sm/Nd of 0.2 as the bracketing standard and various mixed solutions with different Sm/Nd values (Sm/Nd = ca. 0.1, 0.3, 0.4, and 0.5) as unknown samples. During the measurements, the average correlation factor in the instrumental mass bias inferred from the standard runs was 0.943 ± 0.002 (n = 7, 2σ S.E.), which yielded consistent Sm/Nd ratios with gravimetric Sm/Nd values mostly within 1% difference (Table 3; Figure 3). This result indicates that the mass bias in the measurement of the Sm/Nd ratio can be reasonably corrected by the standard bracketing method.

The Nd concentrations of the mixed solutions were calculated based on the intensity of the bracketing standard of 100-101 µg/L. Calculated Nd concentrations were consistent with gravimetric values within 3% difference (Table 3).

### Conclusions

We evaluated the capability of a Neptune MC-ICP-MS to obtain accurate Nd isotopic composition and Sm/Nd elemental ratio using a series of Sm + Nd mixed standard solutions with different Sm/Nd ratios. The isobaric interference correction using the exponential law and selected Sm isotopic composition yielded accurate <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>145</sup>Nd/<sup>144</sup>Nd ratios for the mixed solutions, although there is a systematic increasing trend in the corrected <sup>143</sup>Nd/<sup>144</sup>Nd ratios with increasing Sm/Nd ratios. The Sm/Nd ratios of the Sm-doped Nd standard solutions could be reliably calibrated by the standard bracketing method mostly within 1% difference from the gravimetric values. These results indicate that accurate Nd isotopic composition and Sm/Nd ratio can be simultaneously measured by a simple and high-throughput technique without chemical separation of Sm and Nd.

### Competing interests

The authors declare that they have no competing interests.

### Authors' contributions

CSC, JSR and YJJ designed the study. JSR and MSC made the sample solutions and carried out isotope measurements. CSC and JSR drafted the manuscript. All authors read and approved the final manuscript.

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