Technical Note

High-precision simultaneous determination of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios in Sm–Nd mixtures using multi-collector inductively coupled plasma mass spectrometry and its comparison to isotope dilution analysis

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ABSTRACT

This work demonstrates, for the first time, the feasibility and capability of the high-precision simultaneous determination of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios in Sm–Nd mixtures using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) without Nd and Sm separation and without the use of costly enriched spikes. Mass discrimination was exponentially corrected by applying the natural constant of ^{146}Nd/^{144}Nd ratio as an internal standard, after correction of the isobaric interference of ^{144}Sm on ^{144}Nd using interference-free ^{147}Sm/^{149}Sm ratio for Sm mass fractionation, without assuming identical mass bias of Nd and Sm. The accuracy and precision of the present protocol, obtained from replicate analyses of various types of Sm–Nd mixtures encompassing a wide range of Sm/Nd (*ca.* 0.1–1.0) or ^{147}Sm/^{144}Nd ratios (*ca.* 0.06–0.62) was found to be comparable to the classic isotope dilution (ID) method. The present method is characterized by a higher sample throughput compared to the ID method, and shows great potential for the simultaneous determination of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios in real geological samples.

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1. Introduction

It is well-known that both the determination of isotope ratios of radiogenic daughter elements and the ratios of parent to daughter elements are required when applying radiogenic isotopes in the fields of geochemistry and cosmochemistry [1]. In terms of Sm–Nd system, the precise and accurate determination of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios in rocks and minerals is essential in geochemical tracer and geochronology experiments, *e.g.*, in geological and planetary sciences. Generally, ^{147}Sm/^{144}Nd ratio can be determined by isotope dilution (ID) analysis, which is a widely used technique for its excellent precision and accuracy when properly applied. The ID technique requires the use of artificial and costly enriched spikes (*e.g.*, commonly-used ^{149}Sm and ^{150}Nd spikes) [1]. As for ^{143}Nd/^{144}Nd ratio measurements, owing to its inherent high precision, multi-collector thermal ionization mass spectrometry (TIMS) is still regarded as a benchmark for Nd isotope analysis, despite the fact that it is time-consuming and requires a strict analytical procedure and extensive source filament preparation [2–5].

Recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a routine technique for ^{143}Nd/^{144}Nd ratio measurements with high sample throughput and precision comparable to that offered by TIMS [6–14]. MC-ICP-MS has potential for the direct determination of isotope ratios of different elements, provided that isobaric interference is accurately corrected [6–14]. It is also possible to directly determine Nd isotopic compositions of relatively enriched Nd accessory minerals (*e.g.*, allanite, apatite, bastnaesite, calzirtite, eudialyte, loparite, monazite, perovskite, titanite, zirconolite) with high spatial resolution on sub-grain scale by complementing the measurement with a laser ablation system (LA) [15–26].

Previous efforts have been described for the determination of ^{147}Sm/^{144}Nd (Sm/Nd) ratio in geological materials using a quadruple ICP-MS [27,28]. However, as pointed out in the pertinent literature, these methods cannot match the ID method in term of precision and accuracy. Meantime, reliable ^{143}Nd/^{144}Nd data were reported in Nd standard solutions by MC-ICP-MS, using Sm as dopant [7,9,15–18,26]. Although ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd data of enriched Nd accessory minerals can be simultaneously obtained during LA-MC-ICP-MS analyses, the accuracy is inferior to the classic ID analysis because of the difficulties in correcting the spectral interference and the corrections for inter element ratio (Sm/Nd) [15–25].

The main objective of this work is to investigate the feasibility of MC-ICP-MS for the simultaneous determination of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios in Sm–Nd mixtures with an internal mass bias correction and proper isobaric interferences corrections. The present approach relies on the mathematical correction of isobaric interferences, eliminates the need of Nd and Sm isolation and the costly enriched spike consumption, thus allowing a simple, fast and inexpensive sample preparation.

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2. Experimental

2.1. Instrumentation

A Thermo Fisher Scientific (Bremen, Germany) Neptune MC-ICP-MS was used for all measurements. The external precision of measurements is further improved by utilizing a rotating amplifier concept, in which all Faraday cups are sequentially connected to all amplifiers, canceling out any gain calibration errors [29–31].

2.2. Chemical reagents and materials

Milli-Q H_2O is 18.2 MΩ at 25 °C from Millipore (Elix-Millipore, USA). HCl and HNO_3 from Beijing Institute of Chemical Reagent were purified by the Savillex™ DST-1000 sub-boiling distillation system (Minnetonka, USA) and diluted acids were prepared by dilution with Milli-Q water.

CIT Sm–Nd mixture standard solution was from California Institute and Technology (CIT) [32]. IGG Nd and Sm solution from National Research Centre for Certified Reference Materials (NRC, CRM) were used as in-house standards in our laboratory [6,13,26].

Ln resin from Eichronm Technologies (USA) was ca. 4 cm long×8 mm with a 20 mL extension reservoir, pre-packed by with ~2 mL resin (100–150 μm particle size) [6,33].

2.3. Sample preparation

Sample preparation was conducted in class 100 horizontal laminar airflow hoods inside a class 1000 over-pressured clean laboratory. Seven aliquots of IGG Nd were placed in pre-clean 15 mL plastic vials and doped with variable amounts of IGG Sm (Sm/Nd ratio of ca. 0.1–1.0 or $^{147}Sm/^{144}Nd$ ratio of ca. 0.06–0.62). After mixing and equilibration, most aliquots of these synthetic Sm–Nd mixtures were directly measured for $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios, simultaneously.

In order to obtain accurate $^{147}Sm/^{144}Nd$ ratios of seven synthetic IGG Sm–Nd mixtures, aliquots of these synthetic Sm–Nd mixtures were weighed into a 7 mL round bottom Savillex™ Teflon screw-top capsule and spiked with appropriate amount of mixed ^{149}Sm–^{150}Nd spike. After addition of 2 mL of concentrated HCl-HNO_3 (1:1) solution, the capsule was capped and heated on a hotplate at about 100 °C for five days. After sample-spike equilibration, the capsule was opened and the solution was evaporated gently. The content was treated with 1 mL of 6 M HCl to completely convert it into chloride form. This step was repeated twice. Finally the remaining was dissolved in 0.5 mL of 0.25 M HCl prior to Sm and Nd isolation using Ln resin [2,3,6,33,34]. The collected Sm and Nd fractions were dried down and then re-dissolved with 2–5 mL of 2% HNO_3 prior to Neptune analysis.

2.4. Mass spectrometric measurements

Sample introduction was accomplished with a self-aspirating ca. 50 μl min^{-1} PFA concentric nebulizer. After every standard measurement, the sample introduction system was rinsed with 2% HNO_3 for 5 min in order to minimize memory effect. $^{147}Sm^+$ and $^{149}Sm^+$ were monitored to assess potential isobaric interferences from $^{144}Sm^+$, $^{148}Sm^+$ and $^{150}Sm^+$ on $^{144}Nd^+$, $^{148}Nd^+$ and $^{150}Nd^+$, respectively. Typical operating conditions for Neptune, data acquisition parameters and cup configuration for Sm–Nd mixtures are summarized in Table 1. The Nd isotope analyses consist of 9 blocks, 6 cycles per block, with an integration time of 8 s per cycle. For synthetic Sm–Nd mixtures analysis, a CIT Sm–Nd mixture was repeatedly measured for every five samples for the external calibration of $^{147}Sm/^{144}Nd$ ratio.

2.5. Data reduction protocol

The empirical correction protocol, such as the Russell's exponential law [35], was initially developed for TIMS, and has been widely used for MC-ICP-MS [12–14]. In this study, the Russell's exponential law was used to evaluate the instrumental mass bias. For synthetic IGG Sm–Nd mixtures analysis, the raw data were exported and reduced offline in order to correct for instrumental mass bias and isobaric interference. The data reduction was performed using a Microsoft Excel macro written in Visual Basic for Applications (VBA), within which the interference corrections is made, followed by a mass fractionation correction using the exponential law.

The calculation protocol of $^{143}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$, $^{148}Nd/^{144}Nd$, $^{150}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ data (Table 2) for Sm–Nd mixtures proceeds in the following order:

i) The required "true" values used are $R^{Sm}_{147/149} = 1.08680$ [37,38] and $R^{Nd}_{146/144} = 0.7219$ [36]. $r^{Sm}_{147/149}$ and $r^{Nd}_{146/144}$ are the measured $^{147}Sm/^{149}Sm$ and $^{146}Nd/^{144}Nd$ ratios, respectively. The symbols $^{147}Sm_m$, $^{149}Sm_m$, $^{146}Nd_m$ and $^{144}Nd_m$ represent the measured isotope ion signals, while the terms M^{Sm}_{147}, M^{Sm}_{149}, M^{Nd}_{146} and M^{Nd}_{144} represent the atomic masses of the indicated isotope [39].

$$\beta_{Sm} = \frac{\ln\left(\frac{R^{Sm}_{147/149}}{r^{Sm}_{147/149}}\right)}{\ln\left(\frac{M^{Sm}_{147}}{M^{Sm}_{149}}\right)} = \frac{\ln\left(\frac{R^{Sm}_{147/149}}{^{147}Sm_m/^{149}Sm_m}\right)}{\ln\left(\frac{M^{Sm}_{147}}{M^{Sm}_{149}}\right)} \quad (1)$$

$$\beta_{Nd} = \frac{\ln\left(\frac{R^{Nd}_{146/144}}{r^{Nd}_{146/144}}\right)}{\ln\left(\frac{M^{Nd}_{146}}{M^{Nd}_{144}}\right)} = \frac{\ln\left(\frac{R^{Nd}_{146/144}}{^{146}Nd_m/^{144}Nd_m}\right)}{\ln\left(\frac{M^{Nd}_{146}}{M^{Nd}_{144}}\right)} \quad (2)$$

Table 1
Typical operating conditions, data acquisition parameters and cup configuration.

Instrumental settings and data acquisition parameters								
RF power	1300 W			Nebulizer type				Micromist PFA
Cooling gas flow rate	15.2 L/min			Sample uptake rate				50 μl/min
Auxiliary gas flow rate	0.8 L/min			Sampling cone				Ni, aperture 1.0 mm
Nebulizer gas flow rate	1.05 L/min			Skimmer cone				Ni, aperture 0.8 mm
Extraction voltage	−2000 V			Integration time				8 sec.
Focus voltage	−645 V			Number of cycles				6 per block
Acceleration voltage	10 kV			Number of blocks				9
Spray chamber	Glass cyclonic			Measurement time				~600 s

Nd cup configuration									
Cup	L4	L3	L2	L1	Center	H1	H2	H3	H4
Mass	142	143	144	145	146	147	148	149	150
Nd	$^{142}Nd^+$	$^{143}Nd^+$	**$^{144}Nd^+$**	$^{145}Nd^+$	**$^{146}Nd^+$**		$^{148}Nd^+$		$^{150}Nd^+$
Ce or Sm	$^{142}Ce^+$		$^{144}Sm^+$			$^{147}Sm^+$	$^{148}Sm^+$	**$^{149}Sm^+$**	$^{150}Sm^+$

Bold text indicates masses used to determine mass fractionation.

Table 2
Results of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios of IGG Sm–Nd mixtures measured simultaneously using present protocol and the comparison of ^{147}Sm/^{144}Nd ratios between the present protocol and ID analysis in different analytical sessions.

IGG Sm–Nd mixtures	Sm [μg g^{-1}]	Nd [μg g^{-1}]	^{147}Sm/^{144}Nd [ID]	^{147}Sm/^{144}Nd [this study]	Differ. [%]	^{143}Nd/^{144}Nd (2σ) [This study]	^{145}Nd/^{144}Nd (2σ) [This study]	^{148}Nd/^{144}Nd (2σ) [This study]	^{150}Nd/^{144}Nd (2σ) [This study]	Remarks
Mix. 0.1R	0.0222	0.2165	0.0620	0.0618	−0.27	0.511 601 (12)	0.348 411 (08)	0.241 530 (08)	0.236 366 (13)	2010.05.25
				0.0621	+0.18	0.511 608 (09)	0.348 423 (06)	0.241 540 (09)	0.236 389 (11)	2011.01.31
				0.0621	+0.17	0.511 600 (10)	0.348 420 (07)	0.241 541 (08)	0.236 388 (10)	2011.02.09
Mix. 0.2R	0.0489	0.2409	0.1228	0.1224	−0.31	0.511 596 (11)	0.348 409 (07)	0.241 536 (09)	0.236 367 (11)	2010.05.25
				0.1229	+0.13	0.511 598 (10)	0.348 416 (07)	0.241 554 (09)	0.236 404 (12)	2011.01.31
				0.1226	−0.09	0.511 600 (09)	0.348 417 (06)	0.241 542 (08)	0.236 394 (11)	2011.02.09
Mix. 0.4R	0.1618	0.3994	0.2449	0.2443	−0.26	0.511 603 (08)	0.348 413 (04)	0.241 541 (06)	0.236 379 (08)	2010.05.25
				0.2452	+0.12	0.511 603 (10)	0.348 415 (07)	0.241 542 (09)	0.236 399 (11)	2011.01.31
				0.2451	+0.08	0.511 606 (12)	0.348 411 (06)	0.241 558 (11)	0.236 419 (13)	2011.02.09
Mix. 0.5R	0.1984	0.3957	0.3030	0.3018	−0.38	0.511 598 (09)	0.348 405 (05)	0.241 534 (06)	0.236 368 (09)	2010.05.25
				0.3024	−0.19	0.511 602 (13)	0.348 405 (09)	0.241 547 (12)	0.236 411 (14)	2011.01.31
				0.3026	−0.12	0.511 600 (10)	0.348 414 (06)	0.241 547 (08)	0.236 411 (08)	2011.02.09
Mix. 0.6R	0.3710	0.6058	0.3701	0.3688	−0.36	0.511 601 (07)	0.348 417 (04)	0.241 541 (06)	0.236 382 (08)	2010.05.25
				0.3706	+0.13	0.511 597 (11)	0.348 417 (08)	0.241 559 (12)	0.236 425 (12)	2011.01.31
				0.3707	+0.15	0.511 606 (12)	0.348 417 (07)	0.241 563 (11)	0.236 420 (11)	2011.02.09
Mix. 0.8R	0.4736	0.5874	0.4873	0.4867	−0.12	0.511 596 (07)	0.348 406 (04)	0.241 548 (06)	0.236 403 (08)	2010.05.25
				0.4879	+0.12	0.511 594 (10)	0.348 417 (07)	0.241 567 (12)	0.236 448 (13)	2011.01.31
				0.4878	+0.11	0.511 605 (10)	0.348 423 (07)	0.241 558 (11)	0.236 429 (11)	2011.02.09
Mix. 1.0R	0.2166	0.2101	0.6230	0.6232	+0.03	0.511 597 (11)	0.348 402 (06)	0.241 542 (11)	0.236 402 (13)	2010.05.25
				0.6238	+0.12	0.511 598 (10)	0.348 412 (05)	0.241 561 (12)	0.236 457 (13)	2011.01.31
				0.6243	+0.21	0.511 605 (12)	0.348 424 (07)	0.241 560 (13)	0.236 453 (11)	2011.02.09
Mean						0.511 601 (08)	0.348 414 (13)	0.241 548 (21)	0.236 405 (54)	
IGG Nd						0.511 602 (14)	0.348 416 (06)	0.241 539 (06)	0.236 387 (14)	n = 10

Differ. $= [(^{147}Sm/^{144}Nd)_{This\ study} - (^{147}Sm/^{144}Nd)_{ID}]/(^{147}Sm/^{144}Nd)_{ID} \times 100\%$.

ii) Using the measured ^{147}Sm/^{149}Sm ratio value and Eq. (1), calculate β_{Sm}.

iii) Using the value of β_{Sm} from ii) and Eqs. (3)–(8) below, calculate the values of the mass biased signals of $^{144}Sm_m$. $^{148}Sm_m$ and $^{150}Sm_m$.

$$R^{Sm}_{147/144} = r^{Sm}_{147/144} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{144}}\right)^{\beta_{Sm}} = \frac{^{147}Sm_m}{^{144}Sm_m} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{144}}\right)^{\beta_{Sm}} \quad (3)$$

$$^{144}Sm_m = \frac{^{147}Sm_m}{R^{Sm}_{147/144}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{144}}\right)^{\beta_{Sm}} \quad (4)$$

$$R^{Sm}_{147/148} = r^{Sm}_{147/148} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{148}}\right)^{\beta_{Sm}} = \frac{^{147}Sm_m}{^{148}Sm_m} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{148}}\right)^{\beta_{Sm}} \quad (5)$$

$$^{148}Sm_m = \frac{^{147}Sm_m}{R^{Sm}_{147/148}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{148}}\right)^{\beta_{Sm}} \quad (6)$$

$$R^{Sm}_{147/150} = r^{Sm}_{147/150} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{150}}\right)^{\beta_{Sm}} = \frac{^{147}Sm_m}{^{150}Sm_m} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{150}}\right)^{\beta_{Sm}} \quad (7)$$

$$^{150}Sm_m = \frac{^{147}Sm_m}{R^{Sm}_{147/150}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{150}}\right)^{\beta_{Sm}} \quad (8)$$

iv) Using the values of $^{144}Sm_m$, $^{148}Sm_m$ and $^{150}Sm_m$ from iii) and Eqs. (9)–(11) below, calculate the values of the mass biased signals of $^{144}Nd_m$, $^{148}Nd_m$ and $^{150}Nd_m$.

$$^{144}Nd_m = {}^{144}(Nd+Sm)_m - {}^{144}Sm_m = {}^{144}(Nd+Sm)_m - \frac{^{147}Sm_m}{R^{Sm}_{147/144}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{144}}\right)^{\beta_{Sm}} \quad (9)$$

$$^{148}Nd_m = {}^{148}(Nd+Sm)_m - {}^{148}Sm_m = {}^{148}(Nd+Sm)_m - \frac{^{147}Sm_m}{R^{Sm}_{147/148}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{148}}\right)^{\beta_{Sm}} \quad (10)$$

$$^{150}Nd_m = {}^{150}(Nd+Sm)_m - {}^{150}Sm_m = {}^{150}(Nd+Sm)_m - \frac{^{147}Sm_m}{R^{Sm}_{147/150}} \times \left(\frac{M^{Sm}_{147}}{M^{Sm}_{150}}\right)^{\beta_{Sm}} \quad (11)$$

v) Using the value of $^{144}Nd_m$, from step iv), the measured $^{146}Nd_m$ signal and Eq. (2), calculate β_{Nd}.

vi) Using Eqs. (12)–(15), the values of $^{144}Nd_m$, $^{148}Nd_m$ and $^{150}Nd_m$ from step iv) and the β_{Nd} from v), calculate the desired ^{143}Nd/^{144}Nd, ^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd ratios.

$$R^{Nd}_{143/144} = r^{Nd}_{143/144} \times \left(\frac{M^{Nd}_{143}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} = \frac{^{143}Nd_m}{^{144}Nd_m} \times \left(\frac{M^{Nd}_{143}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} \quad (12)$$

$$R^{Nd}_{145/144} = r^{Nd}_{145/144} \times \left(\frac{M^{Nd}_{145}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} = \frac{^{145}Nd_m}{^{144}Nd_m} \times \left(\frac{M^{Nd}_{145}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} \quad (13)$$

$$R^{Nd}_{148/144} = r^{Nd}_{148/144} \times \left(\frac{M^{Nd}_{148}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} = \frac{^{148}Nd_m}{^{144}Nd_m} \times \left(\frac{M^{Nd}_{148}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} \quad (14)$$

$$R^{Nd}_{150/144} = r^{Nd}_{150/144} \times \left(\frac{M^{Nd}_{150}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} = \frac{^{150}Nd_m}{^{144}Nd_m} \times \left(\frac{M^{Nd}_{150}}{M^{Nd}_{144}}\right)^{\beta_{Nd}} \quad (15)$$

vii) Using Eq. (16), the value of $^{144}Nd_m$ from Eq. (9) in step iv) and β_{Sm} from ii), calculate the true ^{147}Sm/^{144}Nd ratio.

$$R^{Sm/Nd}_{147Sm/144Nd} = r^{Sm/Nd}_{147Sm/144Nd} \times \left(\frac{M^{Sm}_{147}}{M^{Nd}_{144}}\right)^{\beta_{Sm}} = \frac{^{147}Sm_m}{^{144}Nd_m} \times \left(\frac{M^{Sm}_{147}}{M^{Nd}_{144}}\right)^{\beta_{Sm}} \quad (16)$$

viii) Finally, external correction was applied to ^{147}Sm/^{144}Nd data in Sm–Nd mixtures by using the correction factor obtained from the bracketing CIT Sm–Nd standard. Specifically, the bracketing CIT Sm–Nd $R_{Sm/Nd}$ values were averaged (after correction of mass bias and spectral interferences) and the correction factor ($R_{Sm/Nd}/0.19665$) was applied to the

unknowns in the interval between the standards by dividing the observed values of $R_{Sm/Nd}$ in the unknowns by the correction factor.

For purified IGG Nd and Sm fractions for ID analysis, the Nd and Sm concentrations of synthetic IGG Sm–Nd mixtures were calculated using the standard isotope dilution equation. Details of data processing can be found elsewhere [6].

3. Results and discussion

3.1. Results

Seven IGG Sm–Nd mixtures with various Sm/Nd ratios encompassing a wide range (*ca.* 0.1–1.0), or $^{147}Sm/^{144}Nd$ ratios (*ca.* 0.06–0.62), were measured at different analytical sessions. The results are illustrated in Fig. 1 and summarized in Table 2. The obtained Nd isotopic compositions of seven IGG Sm–Nd mixtures using the present protocol were clearly in good agreement with values obtained in previous studies [6,13], thus confirming the accuracy of the technique and the effectiveness the proposed methods for isobaric interference corrections. Moreover, the simultaneously obtained $^{147}Sm/^{144}Nd$ data of these IGG Sm–Nd mixtures are in agreement with the ID method within 0.12–0.38 %, indicating the feasibility and the capability of simultaneous determination (Fig. 2). From these observations, it is clear that the simultaneous measurement of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios of Sm–Nd mixtures is

feasible using MC-ICP-MS after proper mathematical correction of isobaric interferences.

3.2. $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ simultaneous measurement

In order to obtain accurate $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios in Sm–Nd mixtures based on simultaneous measurements, great care must be taken to properly correct the contribution of the isobaric interference of ^{144}Sm on the ^{144}Nd signal. In this work, an approach similar to that described by McFarlane & McCulloch [16] was implemented, using recently revised Sm isotopic abundance ($^{144}Sm/^{149}Sm = 0.22332$). The measured $^{147}Sm/^{149}Sm$ ratio was used to obtain β_{Sm} and then the $^{147}Sm/^{144}Sm$ ratio was used to calculate the measured ^{144}Sm value by considering the higher ^{147}Sm natural abundance compared to ^{149}Sm. Finally, the interferences corrected $^{146}Nd/^{144}Nd$ ratio was used to calculate β_{Nd}, which was used to correct $^{143}Nd/^{144}Nd$ and $^{145}Nd/^{144}Nd$ ratios using the exponential law. The obtained $^{145}Nd/^{144}Nd$ ratio (Fig. 1b), after isobaric interference correction, agrees well with the recommended value of 0.348415 obtained by TIMS [32]. It should be noted that Fisher et al. [17] recently adopted our revised values of Sm isotope ratios, further confirming the correctness of the present protocol.

In addition, other non-radiogenic ratios (*i.e.*, $^{148}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) can be used to further demonstrate the robustness of the present protocol. Results obtained for $^{148}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$ shown in Fig. 1c & d were slightly higher than the TIMS values. This can be

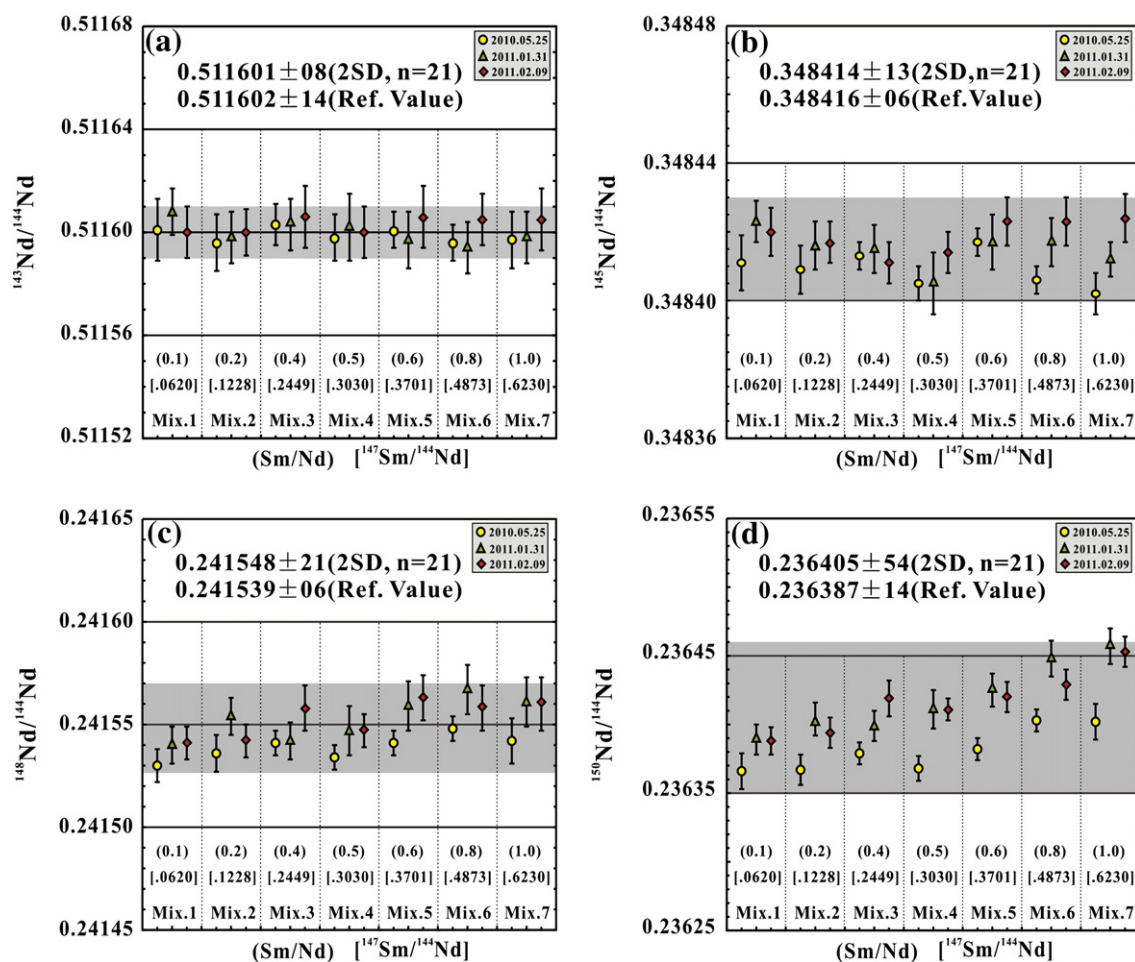**Fig. 1.** Results of Nd isotopic compositions of the various IGG Sm–Nd mixtures (Table 1). (a) $^{143}Nd/^{144}Nd$, (b) $^{145}Nd/^{144}Nd$, (c) $^{148}Nd/^{144}Nd$ and (d) $^{150}Nd/^{144}Nd$ ratios simultaneous determination using the present protocol in different analytical runs. Error bars for individual analyses are shown at 2SE (2 standard in-run errors). Gray fields represent the corresponding average value with 2SD (2 standard deviation).
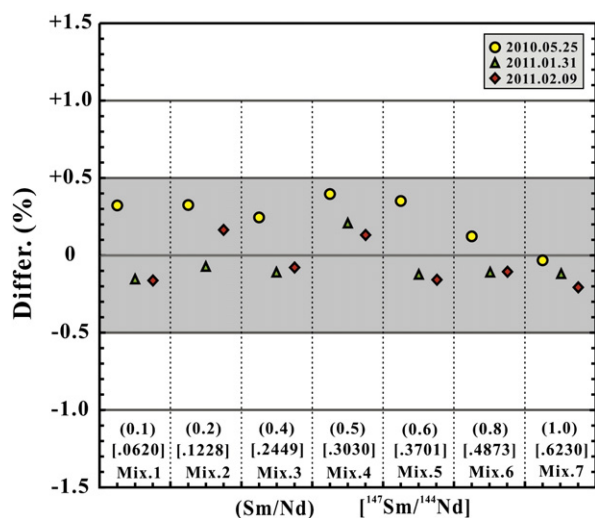
Fig. 2. Comparison of $^{147}Sm/^{144}Nd$ ratio of various IGG Sm–Nd mixtures simultaneously measured in this study in different analytical runs with the recommended values obtained by ID analysis. 2SE (2 standard in-run errors) error bars are significantly smaller than the symbols and not shown on this scale. The Difference (Differ. = $[(^{147}Sm/^{144}Nd)_{This\ study} - (^{147}Sm/^{144}Nd)_{ID}]/(^{147}Sm/^{144}Nd)_{ID} \times 100\%)$ of our obtained $^{147}Sm/^{144}Nd$ is significantly less than 0.5%, indicating the robustness of our present protocol.

Fig. 3. Relationship between the measured β_{Sm} and β_{Nd} for Sm–Nd mixtures materials analyzed in this study. Plots are the measured $\beta_{Sm\ (147/149)}$ and $\beta_{Nd\ (146/144)}$ of CIT and synthetic various IGG Sm–Nd mixture solutions in eight different analytical runs over a two-year period in this study. Error bars (internal precisions) are smaller than the size of the symbols in all cases and therefore are not shown.

attributed to the fact that mass discrimination in MC-ICP-MS is about one order of magnitude greater than that of TIMS. Mass bias may not be perfectly corrected by the empirical exponential law as the exponential mass discrimination only holds over limited mass ranges of Nd isotopes [10–12]. As noted in a number of studies, this is because the assumption made in empirical exponential law for MC-ICPMS is not valid, since mass bias is different even for different isotope pairs of the same element [10,14]. The corrections are, after all, empirical correction factors with a limited range of applicability, but nevertheless adequate to the task. $^{148}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$ data are another example of the above limitation. In addition to the $^{143}Nd/^{144}Nd$ ratio, the $^{147}Sm/^{144}Nd$ ratio is also an important parameter for classic Sm–Nd isotopic tracer or dating experiments in order to obtain the initial Nd (ε_{Nd}) composition of geological samples, particularly with relatively old age (e.g., Archean) samples characterized by an elevated $^{147}Sm/^{144}Nd$ ratio [18].

In our experience, the first-stage obtained $^{147}Sm/^{144}Nd$ data from Eq. (16) is always 3–5% higher than the ID data, which is mostly attributed to the space charge effect in the interface of the ICP ion source [41–43]. Sample matrix may preferentially suppress Nd or enhance Sm ionization in the plasma [40,44,45]. These effects can be empirically corrected for by the external calibration procedure using Sm–Nd mixtures with known $^{147}Sm/^{144}Nd$ ratios (e.g., CIT Sm–Nd). In addition, this empirical correction factor is very stable during an analytical run. Therefore, empirical external calibration with a known $^{147}Sm/^{144}Nd$ ratio determined by ID analysis can be used to accurately correct the $^{147}Sm/^{144}Nd$ ratio in samples after isobaric interfering corrections. Compared to previous studies, it was found that this empirical correction scheme is capable of generating reliable data (Table 2).

3.3. Sm and Nd mass bias

The measured β_{Sm} and β_{Nd} for all Sm–Nd mixtures materials analyzed in different analytical runs over two-year period are shown in Fig. 3. All Sm–Nd mixtures in the present study show a highly correlated β_{Sm}–β_{Nd} relationship. It is important to note that β_{Sm} is not equal to β_{Nd}, validating the approach of determining individual β coefficients in the present work. This relationship was also observed and demonstrated in the study of Fisher et al. [17], indicating robustness and fitness of the present protocol.
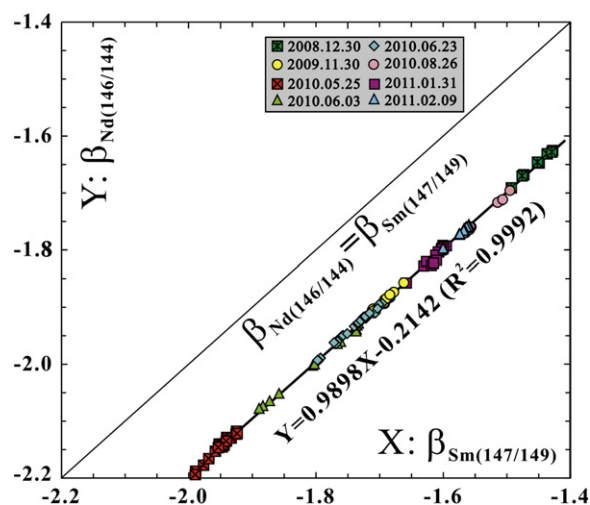
3.4. Merits of simultaneous determination

Compared to the ID method based on ICP-MS and TIMS detections, the present simultaneous determination protocol offers several advantages. First, Sm and Nd separation becomes unnecessary, thus greatly simplifying sample preparation while at the same time reducing the consumption of chemical reagents and materials. Second, the fact that the use of costly enriched tracers is not needed eliminates the complex spike calibration procedure for both concentration and isotopic composition prior to its usage [2–6,33], making the present protocol more environmental friendly [1–6]. Third, the present protocol for simultaneous determination of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios is highly efficient, requiring only 10 min of measurement time per sample [6].

4. Conclusions

An analytical protocol for high-precision simultaneous determination of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios in Sm–Nd mixtures using MC-ICP-MS is presented as a good alternative to the ID analysis. The present protocol is capable of producing $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios with an accuracy and precision comparable to that of the classic ID method, but at a fraction of the time and cost needed. In addition, it is characterized by a high sample throughput.

To the best of our knowledge, this study represents the first attempt of achieving a simultaneous determination of the $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios using MC-ICP-MS, without Nd and Sm separation and without the use of enriched spikes. The proposed protocol can potentially become an important alternative approach to the classic ID method for the Sm–Nd isotopic system.

Future studies will be aimed at developing a chemical purification procedure for Sm and Nd with 100 % recovery, aimed at the simultaneous determination of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios in real geological samples.

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