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Simultaneous Determination of ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd Ratios and Sm−Nd Contents from the Same Filament Loaded with Purified Sm−Nd Aliquot from Geological Samples by Isotope Dilution Thermal Ionization Mass Spectrometry

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Ⓢ Supporting Information

ABSTRACT: Isotope dilution thermal ionization mass spectrometry (ID-TIMS) is the standard technique used to achieve precise ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd isotope ratios and accurate elemental concentrations of Sm−Nd. However, in previous studies, purified Sm and Nd fractions must be individually loaded onto different filaments for their accurate determination using TIMS because of severe isobaric interferences. Thus, the classical ID-TIMS technique is time consuming and laborious. In this study, a new method is proposed, which is able to acquire both ratios of ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd and concentrations of Sm−Nd simultaneously on the same filament arrangement. The measurement time and filament consumption are reduced by 50% with the current method, and therefore, the operation cost of TIMS is significantly reduced. A mixed ^{152}Sm−^{148}Nd spike was employed to achieve accurate results after spike subtraction and isobaric interference corrections. Results obtained from a series of standard rock samples are in good agreement with recommended values, within ±0.003% for the ^{143}Nd/^{144}Nd ratio and ±1% for the ^{147}Sm/^{144}Nd ratio.
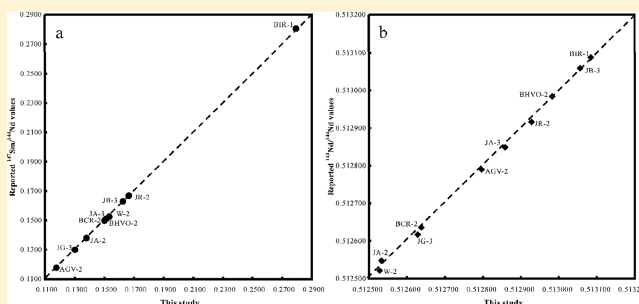
The classical ^{147}Sm−^{143}Nd radiogenic isotopic system has been extensively used in geochemistry and cosmochemistry as a powerful geochemical tracer or chronometer since the 1970s.[1,2] High precision ratios of ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd are prerequisites for dating and tracing purposes. Usually, reproducibility of ≤0.003% for ^{143}Nd/^{144}Nd ratio and ≤1% for ^{147}Sm/^{144}Nd ratio is required in geochronological and geochemical studies. Isotope dilution mass spectrometry (IDMS) technique is considered to be a primary method that can produce excellent accuracy and precision.[3,4] Isotope dilution thermal ionization mass spectrometry (ID-TIMS) technique[5−11] and isotope dilution multiple-collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) technique[12−15] have been used for achieving accurate and precise results for Sm−Nd.

MC-ICP-MS offers high efficiency for precise isotopic ratio measurements with high sample throughputs.[12−16] When a laser ablation is coupled with MC-ICP-MS, in situ analysis of tiny mineral grains with high concentrations of Sm−Nd (>200 ppm at least), such as apatite, monazite, and perovskite can be done.[17−20] However, compared to TIMS, the cost of the MC-ICP-MS instrument and operation is higher. In addition, MC-ICP-MS suffers much larger mass bias and more complicated

isobaric interferences of oxides and/or argides.[21] On the other hand, TIMS generally offers better sensitivity and precision for Sm−Nd measurements. For example, the external precision of ^{143}Nd/^{144}Nd in a Nd standard (Ames) reached the level of ±2 ppm using TIMS.[22] The excellent precision in Sm−Nd data was obtained using TIMS even at very small sample size down to 1 ng.[10,11,23] Hence, both Sm−Nd isotopic compositions and elemental contents are traditionally performed by TIMS, considered as the benchmark technique.[10,22,24]

To achieve accurate Sm and Nd isotopic data in geological samples, all isobaric interferences (^{144}Sm on ^{144}Nd, ^{148}Sm on ^{148}Nd, and ^{150}Sm on ^{150}Nd) need to be eliminated. Traditionally, after sample digestion and sample-spike (^{149}Sm−^{150}Nd) equilibration, Sm and Nd fractions are completely separated from the matrix solutions using the classical two-step cation exchange chromatography technique before TIMS measurements.[5−10,14,15,22−29] After the solution dried, the purified Sm and Nd fractions from spiked samples are loaded onto different

filaments, respectively, for the determination of Sm^+ and Nd^+ by TIMS. Both ratios of $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ and concentrations of Sm and Nd are calculated using the well-known equations of isotope dilution method.[3−5,10,11] Despite the achieved excellent Sm−Nd isotopic data, the main drawback of this ID-TIMS technique is its low sample throughput and high experimental cost. For example, low analytical efficiency mainly originates from two aspects. First, the capability of the TIMS sample chamber is limited to a certain number of sample holders (13−21).[5−11,22−29] Limited sample capability greatly constrains the sample throughput because the sample chamber must be vented to the atmosphere before being replaced with a new sample magazine. Afterward, the sample chamber must be evacuated to achieve a satisfactory vacuum pressure ($\leq 2.5 \times 10^{-7}$ mbar in ion source) before the next sample magazine analysis is conducted. Typical waiting time to achieve a working vacuum is approximately 3 h. Second, a series of operation procedures employed using TIMS, such as filament cleaning, filament welding, filament degassing, and sample loading, are laborious and time consuming. In addition, the experimental cost is high because the sample carriers are high-purity filaments, such as Ta, Re, W, and so on, which are expensive and one-off. For the measurements of Sm and Nd, at least four filaments are commonly consumed for each analysis. Thus, tedious sample loading, extensive filament preparation and consumption, and limited sample locations greatly hinder the analytical efficiency and increase experimental cost.

Recently, Luias et al.[12] and Yang et al.[30] have presented a rapid and precise method to determine the $^{143}Nd/^{144}Nd$ ratios in rock samples without further Sm−Nd separation from sample matrix using MC-ICP-MS. The traditional two-step matrix separation procedure[5−10,14,15,22−29] was simplified to one-step due to efficient isobaric interference correction in mass spectrometry analysis. More recently, Li et al.[31] have successfully applied this one-step procedure in a TIMS instrument. The $^{143}Nd/^{144}Nd$ ratios in actual silicate samples were measured with TIMS with a satisfactory precision (<0.003%, 2 RSE).[31] The external precision of 10−12 ppm for $^{143}Nd/^{144}Nd$ was reported by Li et al.,[31] which is better than the 20−30 ppm published by Luias et al[12] and Yang et al.[30] These methods significantly improved the analytical efficiency of Nd isotopic ratio for unspiked samples.[12,30,31] However, both $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios are required for tracing or dating purposes.[1,2] Thus, previous methods[12,30,31] are only suitable for tracing the provenance of those relatively young samples because the $^{147}Sm/^{144}Nd$ ratio cannot be obtained simultaneously.

The motivation of this study is to establish a rapid and precise analytical protocol to simultaneously determine $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios from a same filament loading using TIMS. In this study, the mixed $^{152}Sm−^{148}Nd$ spike rather than the traditional $^{149}Sm−^{150}Nd$ spike was used to measure both Sm and Nd contents and $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios from the same filament arrangement. The proposed method greatly cuts down the experimental cost and improves analytical efficiency. The accuracy of results achieved using the proposed protocol was validated through TIMS measurements of 10 Certified Reference Materials (CRMs) of silicate rocks with a wide range of Sm/Nd and bulk compositions.

■ EXPERIMENTAL SECTION

Reagent and Materials. Ultrapure water with resistivity of 18.2 MΩ.cm^{-1} was used (Milli-Q). The HCl, HF, HNO$_3$, and HClO$_4$ were purified via sub-boiling distillation using Savillex Teflon distillers. The cation exchange column was 7 cm long and had a 6 mm inside diameter with a 30 mL reservoir packed with Bio-Rad AG50W × 12 resin (200−400 mesh) and 2 mL of resin bed volume. The Ln column was 6 cm long and had a 5 mm inside diameter packed with Ln Spec resin and 2 mL of resin bed volume. The Ln Spec resin, manufactured by Eichrom Industries and conventional for Sm−Nd separation, was based on di-(2-ethylhexyl)-phosphoric acid (HDEHP) loaded on polymeric adsorbent in fine-grained form (100−150 μm).

Ten international standard rock samples (BCR-2, BHVO-2, BIR-1, W-2, AGV-2, JA-2, JA-3, JR-2, JG-3, and JB-3), recommended by the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ), were employed to examine the capabilities of the method.

Preparation of $^{152}Sm−^{148}Nd$ Spike and Mixed JNdi-1 Standard. The isotopically enriched tracers included ^{152}Sm (99.45%) and ^{148}Nd (95.24%) were purchased from Oak Ridge National Laboratory (U.S.A). Single-element powder of these tracers were weighed (to 0.01 mg precision) and dissolved in 2 M HCl for Sm and Nd. Portions of these solutions were mixed appropriately to prepare mixed tracers of $^{152}Sm+^{148}Nd$. The mixed isotopic tracer solution was calibrated using reverse isotope dilution against two mixed gravimetrically prepared standards following the method reported by Wasserburg et al.[5] and Le et al.[14] The composition and content of the $^{152}Sm+^{148}Nd$ tracer are summarized in Table S-1 of the Supporting Information.

Two mixed JNdi-1 standards (Mix-A and Mix-B) with different Sm/Nd (0.2029 and 1.1503) concentrations are employed to examine the accuracy and reproducibility of the $^{152}Sm−^{148}Nd$ spike combination. With respect to the preparation of the mixed standard solution, Sm$_2$O$_3$ (99.99%) powder was dissolved using 2 M HCl, diluted to 500 ppm, and then added into the JNdi-1 standard solution.

Sample Decomposition. The sample preparation was undertaken in a class-1000 clean room. Approximately 110−120 mg of powdered rock samples were weighed (to 0.01 mg precision) and spiked with a mixed $^{152}Sm+^{148}Nd$ tracer into screw-top PFA vials (Savillex). The added spike amounts (35−220 mg) were evaluated according to the previously reported Sm and Nd concentrations for these CRMs, resulting mixture ratios were around 3−6 for $^{152}Sm/^{147}Sm$ and around 0.35−0.6 for $^{148}Nd/^{144}Nd$. After addition of 0.5 mL 14 M HNO$_3$, 0.3 mL 70% HClO$_4$, and 2.5 mL 29 M HF to the sample, the container was tightly capped and then heated on a hot plate at 120 °C for 5 days. During this period, the PFA vials were placed in an ultrasonic bath for 15 min daily in order to disaggregate granular material and render it more susceptible to acid attack. Then, the vials were opened, and the resulting solution was evaporated to dryness at temperatures from 140 to 190 °C. The residues were subsequently dried down twice with 1 mL of 6 M HCl to break down insoluble fluoride compounds. Finally, the samples were taken up in 1.1 mL of 2.5 M HCl and transferred into PFA vials. Clear solutions of all sample fractions were obtained with exception of W-2. All vials were tightly capped again and then heated on a hot plate at 80 °C for 2 h to obtain sample-spike equilibration. As for W-2, a small amount of gelatinous fluoride precipitate was observed at the bottom of

Table 1. Cup Setting of Static Multi-Collector Mode

element	L4	L3	L2	L1	CC	H1	H2	H3	H4
Nd+Sm	^{143}Nd	^{144}(Nd+Sm)	^{145}Nd	^{146}Nd	^{147}Sm	^{148}(Sm+Nd)	^{149}Sm	^{150}(Sm+Nd)	^{152}Sm
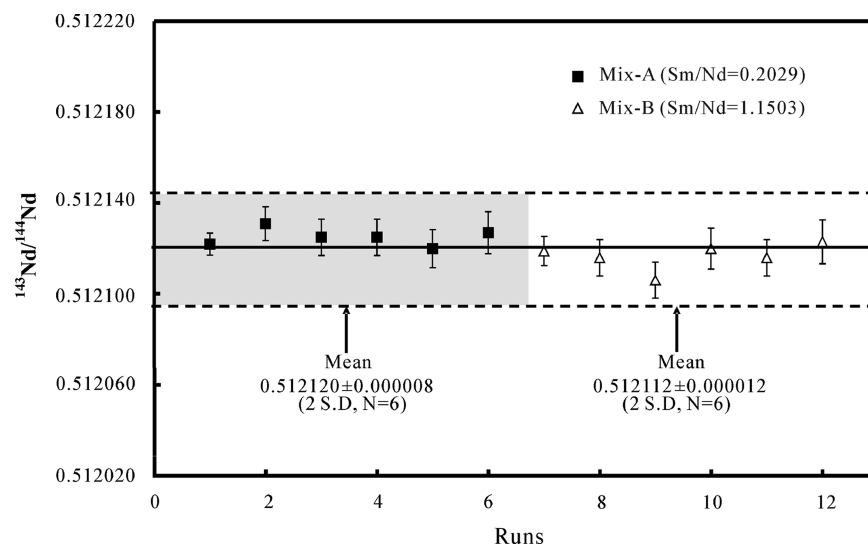
Figure 1. Corrected ^{143}Nd/^{144}Nd ratios for spiked Mix-A and Mix-B samples.

the centrifuge tube. The residues were isolated and dissolved with 1.5 mL 29 M HF, 0.5 mL $HClO_4$, and 0.2 mL 14 M HNO_3 in small Teflon PTFE bombs at 200 °C for two days. The resulting solution was treated as described above and mixed with the bulk solution.

Chemical Separation. As indicated in Table S-2 of the Supporting Information, the matrix separation procedure consisted of two-step separations. The resulting solutions obtained from the former steps were centrifuged at 5000 rpm for 8 min, and 1 mL of the supernatant was then loaded onto the preconditioned AG50W columns for separation of REEs from the sample matrix. After rinsing for 4 times with 0.5 mL of 2.5 M HCl, the column was washed with 9.5 mL of 5 M HCl to remove the matrix elements. Four M HCl, instead of 6 M HCl, was employed to efficiently remove Ba, La, and Ce. The REEs were stripped using 15 mL of 4 M HCl. Some heavy REEs (HREEs) and most Ba (∼90%), La (∼85%), Ce (∼80%), and a portion of Gd (∼35%) were removed from Sm and Nd during this step. Recoveries for Sm−Nd were higher than 95%.

The separations of Ba, Ce, Pr, Nd, Sm, and Gd were conducted using the Ln columns. The columns were precleaned using 15 mL of 5 M HCl and 5 mL of Mill-Q H_2O. The REEs fraction obtained from the AG50W column was dried then taken up with 0.1 mL of 0.1 M HCl and loaded onto the Ln columns. After rinsing for 4 times with 0.1 mL of 0.1 M HCl, all Ba and most La (∼99.5%), Ce (∼98%), and Pr (∼70%) elements, and ∼25% of Nd were washed with 8.5 mL of 0.25 M HCl. The Nd+Sm fraction was stripped with 7.0 mL of 0.25 M HCl plus 10.5 mL of 0.4 M HCl. The Nd+Sm fraction also contained approximately 30% Pr, less than 2% Ce, and no detectable Ba and Gd. The recovery yields of Nd and Sm during this step were approximately 75% and 94%, respectively. Thus, the final recoveries of Nd and Sm were about 70% and 90%, respectively. Approximately 0.4% of Ce was detected in the mixed Nd+Sm fraction after using the aforementioned two-step chromatographic column method.

TIMS Measurement. The Sm−Nd isotopic measurements were performed on a Thermo Fisher Scientific Triton TIMS at the Tianjin Institute of Geology and Mineral Resources. The instrument was equipped with nine Faraday collectors with a dynamic range of 50 V and a 21-sample turret. A double Re filament configuration was used. All the Re filaments were previously degassed. To enhance ionization efficiency, the sample was loaded into as small an area as possible on the filament. 0.5 μL of 0.13 M phosphoric acid was loaded on an outgassed Re filament and dried at 0.8 A. Next, the mixed Sm +Nd samples were dissolved in 1 μL of 2.5 M HCl, loaded on the Re filament, and then dried by heating with 0.8 A current. Finally, 0.5 μL of 0.13 M phosphoric acid was loaded and dried, and the filaments were then heated to glow to a dull red at approximately 2 A for ∼4s.

The Sm−Nd isotopic data were acquired in the static collection mode, and the configuration of the Faraday cups is shown in Table 1. First, the current of the ionization filament was slowly increased until a temperature of ∼1700 °C was reached. Then, the evaporation filament was heated at 300 mA/min until the ^{146}Nd signal reached 0.02 V. The beam was roughly focused, and the evaporation filament was slowly heated to obtain a ^{146}Nd signal of ∼1.2 V. At this point, the intensity of the ^{147}Sm signal was approximately 0.3 V. Data acquisition started when the signal intensity of ^{146}Nd had reached ∼1.5 V. Typically, the measurement routine lasts for approximately 40 min and comprises 10−12 "blocks" of 15 "scans". Each scan represents a 4 s measurement of the ion currents with masses of Sm and Nd collected simultaneously in the Faraday cups.

Data reduction was performed "offline," which included spike subtraction corrections, isobaric interference corrections, mass fractionation corrections, and elemental content calculations. All detailed calculation equations are listed in Table S-3 of the Supporting Information. In brief, Sm spike subtraction corrections were conducted following eqs 1−4 to obtain the $(^{147}Sm/^{149}Sm)_c$ ratio. Then, the mass fractionation factor of Sm

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(β_{Sm}) was obtained using the $^{147}Sm/^{149}Sm$ ratio of 1.08583[32] following eq 5. A series of isobaric interference corrections were carried out following eqs 6−9. The isobaric interference corrections of ^{144}Sm on ^{144}Nd and ^{148}Sm on ^{148}Nd were calculated using the $^{147}Sm/^{144}Sm$ ratio of 4.87090[32] and $^{147}Sm/^{148}Sm$ ratio of 1.33437.[32] Thus, accurate ion beam intensities of ^{144}Nd and ^{148}Nd were achieved. The intensities of ^{143}Nd, ^{145}Nd, and ^{146}Nd isotopes were considered to be the interference-free isotopes. Thus, isobaric corrections of these isotopes were not necessary. Afterward, the corresponding measured ratios, $(^{143}Nd/^{144}Nd)_{mix}$, $(^{145}Nd/^{144}Nd)_{mix}$, $(^{146}Nd/^{144}Nd)_{mix}$, and $(^{148}Nd/^{144}Nd)_{mix}$, were obtained on the basis of based on eqs 10−13. Then, the mass fractionation factor of Nd (β_{Nd}) was obtained following eqs 14−16. Subsequently, the corrected measured ratios, $(^{143}Nd/^{144}Nd)_{cor\ mix}$, $(^{145}Nd/^{144}Nd)_{cor\ mix}$, and $(^{148}Nd/^{144}Nd)_{cor\ mix}$, were obtained according to eqs 17−19. Finally, the corrected Nd isotopic ratios after spike subtractions, $(^{143}Nd/^{144}Nd)_{c}$ and $(^{145}Nd/^{144}Nd)_{c}$, were obtained according to eqs 20 and 21. The Sm and Nd contents were calculated using the classical isotope dilution principle following eqs 22−29. The average atomic weights of Sm and Nd were 150.3628[32] and 144.2409,[33] respectively. The $^{147}Sm/^{144}Nd$ ratio was calculated following eq 30. Correction for instrumental mass fractionation was performed using the exponential law[5,10,22,25] with normalizing values of $[^{147}Sm/^{149}Sm]_{t}$ = 1.08583[32] and $[^{146}Nd/^{144}Nd]_{t}$ = 0.7219.[6−11,14,15,17−20,22−31]

The international standard JNdi-1 was employed to evaluate the instrument stability during the analytical session. During the data collection period, the measured average value of the JNdi-1 was 0.512120 ± 9 (2 SD, N = 8) for $^{143}Nd/^{144}Nd$, in good agreement with the reported value of 0.512115 ± 15.[10,11,15,23,24,30,31,34]

RESULTS AND DISCUSSION

Purity of Sm+Nd Fractions, Recovery, And Blank. Efficient separation of analyte from sample matrix is crucial to achieve high-precision Sm−Nd isotope compositions. In this study, a two-step chemical procedure was employed to achieve highly purified analyte. First, matrix elements were completely eliminated, and the corresponding REEs were also obtained using the first AG50W column. Then, the mixed Sm+Nd fraction was eluted by dilute HCl acid using the second Ln column.

Isobaric or polyatomic interferences arising from Gd and Ce are potential interferences on analyte isotopes. The intensity of ^{152}Sm is needed in order to perform all corrections. In addition, the ^{152}Sm spike is employed to calculate the content of Sm. Furthermore, the accuracy of β_{Sm} mainly depends on the accuracy of the ^{147}Sm, ^{149}Sm, and ^{152}Sm signals. Hence, Gd must be completely removed from the mixed Sm+Nd fraction because the main isobaric interference isotope is the ^{152}Gd, which directly affects on the ^{152}Sm. In previous studies,[8,35] Ln Spec resin was used for efficient separating of Sm from Gd. In this study, Gd was not detected in the mixed Sm+Nd fraction after column separation. Ce has to be removed as completely as possible because $^{136}Ce^{16}O^{+}$ is a potential polyatomic interference on $^{152}Sm^{+}$. Only ~0.4% of Ce was found in the mixed Sm+Nd fraction. Thus, it is negligible, because the abundance of ^{136}Ce is low (~0.2%).

Contamination of Sm and Nd during the total sample preparation procedure including sample dissolution, separation steps, and column memory effects could affect the quality of the final results of Sm−Nd. The extent of effect depends on the concentrations and isotopic compositions of Sm and Nd between the blank and the sample. In this study, the whole procedure blank for Nd and Sm was lower than 80 and 30 pg, respectively. For conventional Sm−Nd isotopic analysis, a 100−120 mg sample used for most samples is sufficient (>100 ng) for Sm and Nd. The ratio of most samples over the blank is higher than the recommended value of 1000 easily.[6] Thus, the blank effect can be neglected in this study.

Spike Subtraction and Isobaric Interference Correction. Selection of the suitable mixed tracer is very important to determine precisely the $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios and Sm and Nd concentrations in geological samples. Traditionally, the mixed $^{149}Sm−^{150}Nd$ spike is used for determination of the elemental content and isotope ratios of Sm and Nd.[5−12,14,15] However, in our method, obtaining an accurate $^{147}Sm/^{149}Sm$ ratio is a prerequisite in calculating β_{Sm} and subtracting accurately the isobaric interferences. Adopting the ^{149}Sm spike will lead to a large uncertainty in calculating β_{Sm} and to uncorrected $^{143}Nd/^{144}Nd$ ratio. Hence, the conventional $^{149}Sm−^{150}Nd$ spike is not suitable for our method. Thus, the mixed $^{152}Sm−^{148}Nd$ spike was chosen to perform all measurements in this study.

Before verification of our method, concentrations of Sm−Nd and $^{147}Sm/^{144}Nd$ ratios for Mix-A and Mix-B were precisely determined using the conventional $^{149}Sm−^{150}Nd$ method.[5−12,14,15] Mix-A and Mix-B solutions were precisely weighed to PFA vials and spiked with appropriate amounts of mixed $^{152}Sm−^{148}Nd$ spike solution. To minimize the uncertainty of the spike subtraction, the $^{148}Nd/^{144}Nd$ and $^{152}Sm/^{147}Sm$ ratios in the sample-spike mixture were limited to around 0.35−0.6 and 3−6, respectively. To obtain sample-spike equilibration, all vials were tightly capped and then heated on a hot plate at 80 °C for 2 h. Subsequently, the mixed solution was dried and redissolved using 1 μL of 2.5 M HCl. Then, the sample was directly loaded onto the Re filament. Afterward, replicate measurements (N = 6) for Mix-A and Mix-B were performed using our aforementioned method.

Both measured results using the present method and classical $^{149}Sm−^{150}Nd$ method are listed in Table S-4 of the Supporting Information. In contrast to the classical $^{149}Sm−^{150}Nd$ method, the reproducibility of the $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios and the Sm−Nd contents show good agreement. As shown in Figure 1 and Table S-4 of the Supporting Information, our obtained $^{143}Nd/^{144}Nd$ ratios of Mix-A and Mix-B are in excellent agreement with the reported values of 0.512115 ± 0.000015 measured using MC-ICP-MS and TIMS.[10,11,15,23,24,30,31,34] The obtained average values of $^{143}Nd/^{144}Nd$ are 0.512120 ± 0.000008 (2 SD, N = 6) for the Mix-A and 0.512112 ± 0.000012 (2 SD, N = 6) for the Mix-B, respectively, after isobaric interference and spike corrections. The reproducibility of the $^{143}Nd/^{144}Nd$ ratio for spiked Mix-A and Mix-B is as good as that of the unspiked JNdi-1. With regard to the high-purity spiked Sm+Nd fraction, the good result can be achieved after "off-line" corrections even if the Sm/Nd value of the analyte reaches 1.15. In fact, few rock samples in nature have ratios larger than 1.0. Likewise, the reproducibility of the Sm and Nd contents of for Mix-A and Mix-B (N = 6) is 0.08−0.26%. The reproducibility of the $^{147}Sm/^{144}Nd$ ratio is approximately 0.02%. Clearly, the proposed method is capable of producing precise

Table 2. Results for Sm, Nd Concentrations and $^{147}Sm/^{144}Nd$, $^{143}Nd/^{144}Nd$ Isotopic Ratios in International CRMs

CRMs	$^{143}Nd/^{144}Nd$ this study (±2 SE)	$^{143}Nd/^{144}Nd$ refer. values	$^{147}Sm/^{144}Nd$ this study	$^{147}Sm/^{144}Nd$ refer. values	$^{145}Nd/^{144}Nd$ this study (±2 SE)	$^{145}Nd/^{144}Nd$ refer. values	Nd [ppm] this study	Nd [ppm] refer. values	Sm [ppm] this study	Sm [ppm] refer. values
rhyolite										
JR-2	0.512935(6)	0.512917;[11] 0.512910[23]	0.1667	0.1670;[11] 0.1671[36]	0.348423(3)		19.45	19.5;[11] 20.4[36]	5.354	5.38;[11] 5.63[36]
	0.512921(8)	0.512913;[28] 0.512923[31]	0.1664	0.1665[39]	0.348413(5)		19.32	18.9[39]	5.309	5.20[39]
mean	0.512928	0.512916	0.1665	0.1669	0.348418		19.38	19.6	5.331	5.40
granite										
JG-3	0.512628(7)	0.512620;[11] 0.512624[23]	0.1171	0.1165;[11] 0.1193[36]	0.348422(4)		17.00	17.1;[11] 17.2[36]	3.288	3.28;[11] 3.39[36]
	0.512629(8)	0.512606;[26] 0.512617[28]	0.1182	0.1222;[37] 0.1126[39]	0.348423(5)		16.91	16.5;[37] 17.2[39]	3.301	3.33;[37] 3.2[39]
mean	0.512629	0.512617	0.1177	0.1177	0.348423		16.95	17.00	3.295	3.30
andesite										
JA-3	0.512860(8)	0.512852;[11] 0.512835[23]	0.1511	0.1505;[11] 0.1501[36]	0.348422(5)		12.22	12.2;[11] 12.3[36]	3.049	3.02;[11] 3.05[36]
	0.512857(7)	0.512859;[28] 0.512850[31]	0.1513	0.1533;[37] 0.1501[39]	0.348421(5)		12.18	12.2;[37] 12.1[39]	3.041	3.09;[37] 3.00[39]
mean	0.512859	0.512849	0.1512	0.1510	0.348422		12.20	12.2	3.045	3.04
JA-2	0.512528(7)	0.512576;[10] 0.512552[15]	0.1302	0.1296;[10] 0.1287[15]	0.348414(4)		13.83	14.14;[10] 14.58[15]	2.976	3.027;[10] 3.101[15]
	0.512537(8)	0.512531;[23] 0.512530;[28] 0.512550[30]	0.1302	0.1354;[36] 0.1263[39]	0.348412(5)		13.70	13.9;[36] 13.9[39]	2.945	3.11;[36] 2.90[39]
mean	0.512533	0.512548	0.1302	0.1300	0.348413		13.77	14.10	2.960	3.03
AGV-2	0.512793(9)	0.512811;[10] 0.512781[15]	0.1093	0.1093;[10] 0.1086[15]	0.348414(5)		30.13	30.47;[10] 30.69[15]	5.441	5.502;[10] 5.514[15]
	0.512801(8)	0.512790;[29] 0.512776[30]	0.1103	0.1090;[38] 0.1086[40]	0.348413(6)		30.22	30.5;[38] 30.42[40]	5.507	5.49;[38] 5.46[40]
mean	0.512797	0.512790	0.1098	0.1089	0.348413		30.18	30.52	5.474	5.49
diabase										
W-2	0.512536(8)	0.512510;[7] 0.512537;[10] 0.512537[11]	0.1531	0.1530;[7] 0.1522[10]	0.348421(6)		13.15	13.00;[7] 12.75[10]	3.324	3.285;[7] 3.205[10]
	0.512510(10)	0.512516;[15] 0.512511;[30] 0.512512[31]	0.1534	0.1525;[11] 0.1523[15]	0.348414(7)		13.40	13.30;[11] 13.08[15]	3.393	3.350;[11] 3.290[15]
mean	0.512528	0.512521	0.1532	0.1525	0.348418		13.27	13.03	3.359	3.28
basalt										
BHVO-2	0.512984(7)	0.512985;[11] 0.512989[23]	0.1503	0.1500;[38] 0.1497[39]	0.348417(4)		24.73	24.5;[38] 24.39[39]	6.136	6.07;[38] 6.03[39]
	0.512981(7)	0.512981;[29] 0.512979[30]	0.1499	0.1492;[41] 0.1505[42]	0.348418(4)		24.53	24.5;[41] 24.7[42]	6.071	6.04;[41] 6.14[42]
mean	0.512983	0.512984	0.1501	0.1499	0.348418		24.63	24.52	6.104	6.07
JB-3	0.513053(7)	0.513049;[7] 0.513089;[10] 0.513064[15]	0.1626	0.1628;[7] 0.1629[10]	0.348415(4)		15.66	15.8;[7] 15.63[10]	4.203	4.25;[7] 4.205[10]
	0.513059(9)	0.513062;[23] 0.513037;[28] 0.513055[30]	0.1626	0.1626;[15] 0.1636[39]	0.348412(6)		15.59	15.82;[15] 15.1[39]	4.185	4.250;[15] 4.08[39]
mean	0.513056	0.513059	0.1626	0.1630	0.348414		15.62	15.59	4.194	4.20
BCR-2	0.512628(7)	0.512641;[10] 0.512630[11]	0.1380	0.1384;[10] 0.1381[11]	0.348413(5)		28.63	28.60;[10] 28.8[11]	6.524	6.543;[10] 6.57;[11]
	0.512630(5)	0.512640;[15] 0.512632[23]	0.1377	0.1378;[13] 0.1382[15]	0.348415(3)		28.68	28.71;[13] 28.97[15]	6.524	6.534;[13] 6.612[15]
	0.512640(5)	0.512634;[29] 0.512638[30]	0.1381	0.1383;[38] 0.1357[41]	0.348422(3)		28.53	28.7;[38] 28.6[41]	6.505	6.57;[38] 6.41[41]
	0.512642(6)	0.512636[31]	0.1380	0.1396;[42] 0.1382[43]	0.348421(4)		28.64	29.1;[42] 28.9[43]	6.531	6.71;[42] 6.60[43]
	0.512636(6)		0.1379		0.348405(3)		28.56		6.503	

Table 2. continued

CRMs	$^{143}Nd/^{144}Nd$ this study (±2 SE)	$^{143}Nd/^{144}Nd$ refer. values	$^{147}Sm/^{144}Nd$ this study	$^{147}Sm/^{144}Nd$ refer. values	$^{145}Nd/^{144}Nd$ this study (±2 SE)	$^{145}Nd/^{144}Nd$ refer. values	Nd [ppm] this study	Nd [ppm] refer. values	Sm [ppm] this study	Sm [ppm] refer. values
	0.512635(6)		0.1379		0.348405(3)		28.79		6.554	
	0.512645(8)		0.1380		0.348411(5)		28.70		6.539	
	0.512648(8)		0.1381		0.348410(5)		28.42		6.483	
mean ± SD	0.512638 ± 0.000007	0.512636 ± 0.000004	0.1379 ± 0.0001	0.1380 ± 0.0011	0.348413 ± 0.000013		28.62 ± 0.11	28.80 ± 0.18	6.520 ± 0.022	6.569 ± 0.084
RSD (%)	0.0014	0.0008	0.07	0.79	0.0037		0.38	0.63	0.34	1.3
BIR-1	0.513088(12)	0.513085;[7] 0.513107[10]	0.2790	0.2798;[7] 0.2846[10]	0.348421(9)		2.430	2.38;[7] 2.31[10]	1.120	1.10;[7] 1.086[10]
	0.513075(12)	0.513093;[11] 0.513108[14]	0.2780	0.2764;[11] 0.2798[13]	0.348412(7)		2.440	2.42;[11] 2.38[13]	1.120	1.11;[11] 1.10[13]
	0.513085(8)	0.513064;[23] 0.513088[31]	0.2802	0.2787;[14] 0.2784[41]	0.348418(5)		2.410	2.49;[14] 2.37[41]	1.115	1.148;[14] 1.09[41]
	0.513090(11)		0.2797	0.2852;[42] 0.2828[43]	0.348411(7)		2.446	2.42;[42] 2.44[43]	1.130	1.14;[42] 1.14[43]
	0.513093(10)		0.2810		0.348412(7)		2.438		1.131	
	0.513079(10)		0.2792		0.348421(8)		2.404		1.108	
	0.513080(12)		0.2796		0.348419(7)		2.428		1.121	
	0.513079(12)		0.2791		0.348422(9)		2.414		1.112	
mean ± SD	0.513084 ± 0.000006	0.513091 ± 0.000016	0.2795 ± 0.0009	0.2807 ± 0.0031	0.348417 ± 0.000009		2.426 ± 0.015	2.401 ± 0.054	1.120 ± 0.008	1.114 ± 0.0247
RSD (%)	0.0013	0.0031	0.31	1.1	0.0026		0.62	2.2	0.71	2.2

$^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios in the mixed Sm+Nd fraction after corrections.

Accuracy and Precision. In order to check the feasibility of our method, 10 CRMs selected to encompass a wide range of matrix composition, analyte concentrations, and diverse Sm/Nd ratios were measured. The sample size of Sm and Nd in the filament varied significantly 0.13−0.66 μg for Sm and 0.30−3.62 μg for Nd, depending on the actual silicate samples in ~120 mg of these CRMs samples. In this study, the $^{143}Nd/^{144}Nd$ ratios in most spiked CRMs were obtained with a typical internal precision (≤0.002%, 2 RSE), well within the range of values measured previously for nonspiked samples of the same CRMs.[6,23,26−31] As shown in Table 2 and Figure 2 (a) and (b), the Sm−Nd contents and $^{147}Sm/^{144}Nd$ data for all CRMs, except for JA-2 and W-2, show good agreement with previously published data within ±1.5% uncertainty.[7,10,11,14,15,36−43] With regard to JA-2 and W-2, the Sm and Nd concentration results showed relatively larger differences (~2.3%) compared with previously reported values ($^{147}Sm/^{144}Nd$ ratios still agree within 0.5% of the published data), possibly due to powder heterogeneity or incomplete digestion in this study.

The reproducibility of $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios in the silicate samples were further evaluated using BCR-2 and BIR-1. As shown in Table 2, eight replicated measurements for BCR-2 yielded a $^{143}Nd/^{144}Nd$ value of 0.512638 ± 0.000014 (2 SD) and a $^{147}Sm/^{144}Nd$ value of 0.1379 ± 0.0001. In addition, the Sm and Nd contents (ppm) for BCR-2 yielded a value of 6.520 ± 0.022 and 28.62 ± 0.11, respectively, in good agreement with reported values for BCR-2.[10,11,13−15,23,38,41−43] Eight replicated measurements for BIR-1 yielded a $^{143}Nd/^{144}Nd$ value of 0.513084 ± 0.000012 (2 SD) and a $^{147}Sm/^{144}Nd$ value of 0.2795 ± 0.0009. Further, the Sm and Nd contents (ppm) for BIR-1 yielded a value of 1.120 ± 0.008 and 2.426 ± 0.015, respectively. BIR-1 has the highest ratio of Sm/Nd (0.46) and relatively low Sm−Nd content among the previously published ~100 natural CRMs.[13,36−41] Thus, the biggest challenge to our method is precisely determining $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios for BIR-1, although both precision and reproducibility of BIR-1 showed good consistency with reported values.[7,10,11,14,23,31]

In general, the data reproducibility and precision are satisfactory and completely fit the demand in geoscience. These practical examples further exemplify the usefulness and applicability of this new method.

Stability of $^{145}Nd/^{144}Nd$ Ratio. In previous investigations, the $^{145}Nd/^{144}Nd$ value was regarded as constant in solar system.[2,12,22,30,31] The corrected $^{145}Nd/^{144}Nd$ of any solar system sample should be identical to primordial compositions when results are normalized with the $^{146}Nd/^{144}Nd$ ratio of 0.7219. Hence, the $^{145}Nd/^{144}Nd$ is a good indicator for checking whether ^{144}Sm can be accurately subtracted from the mixed intensity of 144 ($^{144}Sm+^{144}Nd$). With regard to the unspiked samples, the stability and accuracy of the $^{145}Nd/^{144}Nd$ had been systematically examined and showed satisfactory effect using TIMS and MC-ICP-MS.[12,30,31] However, it is unclear for samples doped with the mixed $^{152}Sm-^{148}Nd$ spike whether accurate $^{145}Nd/^{144}Nd$ values can be obtained after spike subtractions. Thus, in this study, the $^{145}Nd/^{144}Nd$ value is employed as internal invariant value to evaluate the feasibility of our method.

As shown in Figure 3, our corrected $^{145}Nd/^{144}Nd$ value after isobaric interference correction is 0.348413 ± 0.000012 (2 SD,
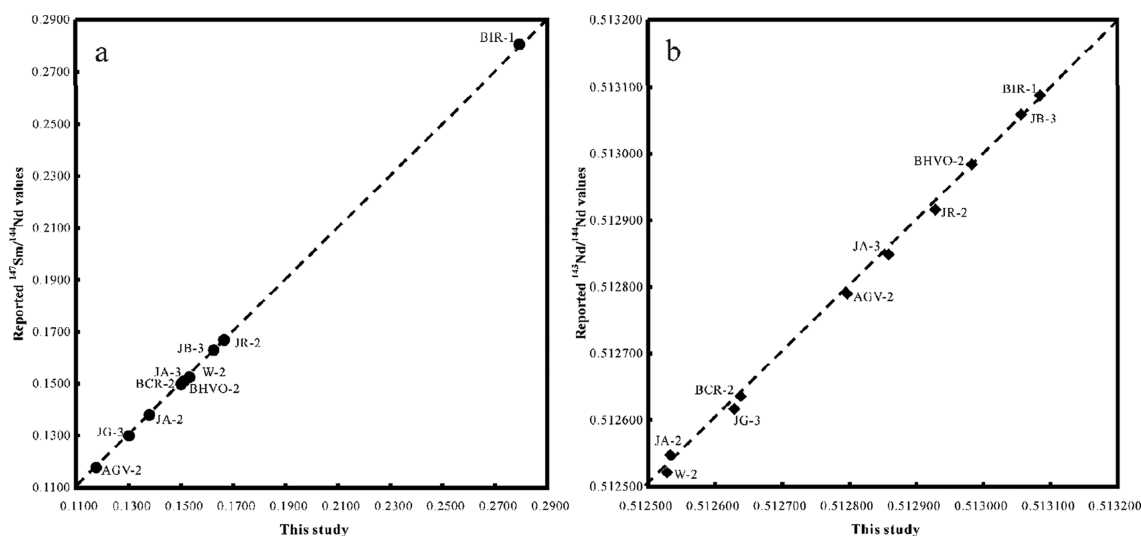
Figure 2. Comparison results of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios: average values in previous investigations in Table 2 and in this study. Error bars are significantly smaller than the symbols and not shown on this scale. (a) $^{147}Sm/^{144}Nd$ data. (b) $^{143}Nd/^{144}Nd$ data.
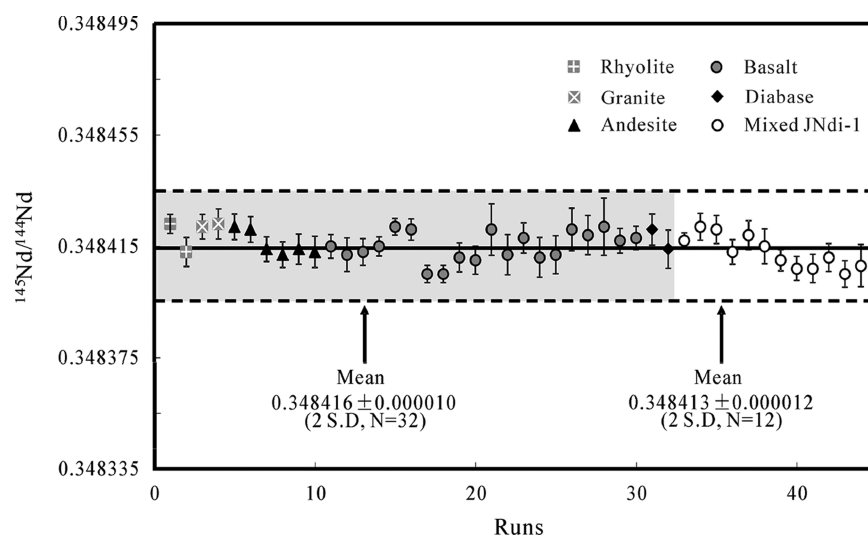

Figure 3. Corrected $^{145}Nd/^{144}Nd$ ratios for each spiked samples.

$N = 12$) in the artificial mixed standard JNdi-1, in agreement with the reported value of 0.348415 ± 0.000015 obtained by MC-ICP-MS and TIMS.[5,12,22,29−31] Likewise, the corrected $^{145}Nd/^{144}Nd$ value of 0.348416 ± 0.000010 (2 SD, $N = 32$) in the actual silicate rock samples from the USGS and GSJ agreed well with the reported values.[5,12,22,29−31] This observation confirms that results obtained using the proposed method are accurate.

◼ CONCLUSIONS

The accurate results for the ratios of $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ and contents of Sm−Nd in silicate samples can be obtained by simultaneous measurements from a same filament loading using TIMS. The novel mixed $^{152}Sm-^{148}Nd$ spike was employed to enhance the analytical efficiency of Sm and Nd isotopic compositions in the silicate samples using TIMS. The applicability of this method was demonstrated for different international standard rock samples, showing excellent reproducibility and precision for the ratios of $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ and contents of Sm−Nd. Compared to previous

methods, the proposed method greatly reduces experimental costs and laboratory time without compromising accuracy or precision of final results. Sample throughput for Sm−Nd measurements by TIMS is improved by one-fold. In addition, time for filament welding, filament degassing, and sample loading is reduced by one-fold. In addition, filament consumption is reduced by one-fold in this study.

◼ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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