



Rapid and precise determination of Sr and Nd isotopic ratios in geological samples from the same filament loading by thermal ionization mass spectrometry employing a single-step separation scheme

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ABSTRACT

Thermal ionization mass spectrometry (TIMS) offers the excellent precision and accuracy of the Sr and Nd isotopic ratio analysis for geological samples, but this method is labour intensive, expensive and time-consuming. In this study, a new analytical protocol by TIMS is presented that aims at improving analytical efficiency and cutting down experimental cost. Using the single-step cation exchange resin technique, mixed Sr and rare earth elements (REEs) fractions were separated from matrix and evaporated to dryness. Afterwards, mixed Sr + REEs fractions were dissolved and loaded onto the same Re filament using 1 μ L of 2 M HCl. Then, Sr and Nd were sequentially measured without venting using TIMS. In contrast to conventional TIMS methods, the merits of this analytical protocol are its cost- and time-saving adaptations. The applicability of our method is evaluated by replicated measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ for nine international silicate rock reference materials, spanning a wide range of bulk compositions. The typical internal precision in this study is ca. 0.001% (RSE) for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$; the analytical results obtained for these standard rocks show a good agreement with reported values, indicating the effectiveness of the proposed method.

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1. Introduction

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values, which show variations by the radioactive decay of long half-life isotopes of ^{87}Rb and ^{147}Sm , respectively, are routinely used for geochemical tracing and petrogenesis research [1,2]. Thermal ionization mass spectrometry (TIMS), with its excellent accuracy, high sensitivity, and low memory, has been widely used to determine Sr and Nd isotopic ratios [3–22]. However, the TIMS technique is time-consuming and laborious in terms of its complex operation procedure and rigorous sample preparation. Firstly, before the TIMS measurements, the Sr and Nd elements should be separated from sample matrices and be as clean a salt as possible using ion-exchange chromatographic methods [3–20]. Traditionally, the purification of Sr and Nd is accomplished by a two-step chromatography method. The first step involves separating Sr and the rare earth elements (REEs) group from the matrix elements [4–10,13,16–20]. Cation exchange resin such as AG50W or Dowex50 is the resin typically employed.

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The second step involves separating the Nd fraction from the REEs group to minimize the isobaric interference of Sm by the reverse-phase chromatographic technique or the high-performance liquid chromatography (HPLC) technique [4–10,13,16–20]. The HDEHP resin [4–13,16,17,20,25,26], HEHEHP resin [18], and Aminex A25 anion resin [19] are the resins typically used. Classical two-step separation methods are laborious and involve many collecting and evaporating steps and vessel and reagent preparation, thereby limiting the sample throughputs. Secondly, the main demerits regarding TIMS instruments are they are time-consuming and have high running costs. The sample magazine chamber of TIMS must be maintained at high vacuum to conduct measurements. However, the capability of the sample chamber in TIMS is limited to a certain number of sample holders (13–21), depending on the actual TIMS instruments, that are designed to use single-, double- or triple-filament geometries [3–22]. Limited sample capability confined the sample throughput, because the sample chamber must be vented to the atmosphere before being replaced with a new sample magazine. Afterwards, 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. The typical waiting time to achieve a working vacuum is approximately 2–3 h. In addition, the sample loading materials are high-purity filament such as Ta, Re and W, which are one-off and expensive. Thirdly, a

series of operation procedures in TIMS, including sample loading, sample mounting, filament welding, and filament degassing, are laborious and time-consuming. Traditionally, each purified Sr and Nd fraction is dissolved and evaporated on a thin degassed filament, respectively. Then, sample inserts should be carefully installed on the sample magazine one by one, after having checked the filament position using a multi-meter. To sum up, tedious sample loading, rigorous sample preparation, and limited sample numbers on a magazine greatly hinder the analytical efficiency in TIMS.

Recently, Li et al. [22] reported a novel method that directly determines Nd isotopic ratio from REEs by TIMS. The method significantly improved the determination efficiency for the Nd isotopic ratio. However, in many actual applications, both Sr and Nd are often required simultaneously for geological and environmental tracers [1,2]. The purpose of this article is to establish a rapid and precise analytical protocol for the Sr and Nd isotopic ratio using TIMS. A single-step separation scheme for Sr–Nd, combined with a sequential measurement of Sr–Nd on the same filament without venting using TIMS, yields a significant improvement in analytical efficiency and greatly reduces experimental costs. The feasibility and reproducibility of this scheme were validated by replicate analyses of international Certified Reference Materials (CRMs), encompassing a range of matrix composition and analyte concentrations.

2. Experimental

2.1. Reagents and materials

Re ribbon: 0.035 mm thick, 0.77 mm wide and 99.98% pure, H.Cross Company, USA.

Ultrapure (Milli-Q) H₂O: 18.2 MΩ cm⁻¹ at 25 °C.

HCl, HF, HNO₃, and HClO₄: Purified via sub-boiling distillation using Savillex Teflon distillers.

H₃PO₄: Purified using cation-exchange chromatographic methods.

JNdi-1: Neodymium international reference (Nd₂O₃) and 99.999% pure; JNdi-1 solutions of 200 ppm.

NIST NBS-987: Sr international reference (SrCO₃) and 99.999% pure; NBS-987 solutions of 200 ppm.

Cation-exchange column: 7 cm long × 6 mm i.d. with a 30 mL reservoir, packed with Bio-Rad AG50W × 12 resin (200–400 mesh), 2 mL of resin bed volume.

Rock powder certificate reference materials (CRMs) from United States Geological Survey (USGS) and Geological Survey of Japan (GSJ): USGS BCR-2 (basalt), BHVO-2 (basalt), W-2 (diabase), BIR-1(basalt), GSP-2 (granodiorite), RGM-2 (rhyolite); GSJ JA-3 (andesite), JR-2 (rhyolite), and JB-3 (basalt).

2.2. Sample digestion and column chemistry

2.2.1. Sample digestion

To achieve excellent low blank levels for the geological rock sample applications, all chemistry were performed inside better than Class 100 chemical workstations located inside a suite of Class 1000 over-pressured clean rooms. Labware included 15 mL and 7.5 mL PFA Teflon beakers with screw-top lids (Savillex Corporation, USA), which were used for all sample digestions, solution collection and evaporations and were cleaned before use with a degreasing agent followed by sequential washing in AR grade HNO₃, HCl, and Milli-Q H₂O. Pre-cleaned PFA beakers used during sample processing were prepared by refluxing with 2 mL of ultrapure, concentrated 6 M HCl for 60 min and refluxing again with 2 mL of Milli-Q H₂O for 60 min.

Table 1
Chemical procedures for Sr and REEs separation.

Procedure	Eluting reagent	Eluting volume (mL)	Eluting fraction
Loading sample	2.5 M HCl	1.0	1
Rinsing	2.5 M HCl	2.0 (0.5 × 4)	1
Rinsing	5.0 M HCl	7.0	1
Eluting Sr	5.0 M HCl	3.5	2
Eluting REEs	4.0 M HCl	14.0	2
Washing column	6.0 M HCl	10.0	3

Approximately 110 mg of rock reference materials were weighed (to 0.1 mg precision) into Savillex 7.5 mL Teflon-PFA vials. The samples were dissolved on a hotplate at about 120 °C using a mixed acid of 2.5 mL 22 M HF + 0.3 mL 14 M HNO₃ + 0.2 mL 12.5 M HClO₄ for five days. The sample dissolution was further promoted by evaporating to dryness twice with 2 mL of 6 M HCl at ca. 100 °C. Finally, the samples were dissolved with 1.1 mL of 2.5 M HCl on a 90 °C hotplate overnight.

2.2.2. Column chemistry

The resulting sample solutions obtained from the previous steps were centrifuged at 5000 rpm for 8 min. Then, 1 mL of the supernatant was loaded onto the pre-conditioned resin column with 2 mL of AG50W × 12 (200–400 mesh) for the separation of Sr and REEs from the sample matrix. The chemistry procedure for Sr and REEs extraction was carried out following Table 1. After rinsing four times with 0.5 mL of 2.5 M HCl, the column was washed with 7 mL of 5 M HCl. Afterwards, the mixed Sr and REEs fractions were stripped with 3.5 mL of 5 M HCl plus 14.0 mL of 4 M HCl. The recovery of Sr and Nd was approximately 77% and 93%, respectively. Finally, the mixed Sr and Nd fractions were evaporated to dryness. Detailed column condition experiments are discussed in Section 3.1. The whole procedure blank for Nd and Sr is lower than 50 pg and 150 pg respectively, rendering the blank corrections insignificant.

2.3. Determination of Sr and Nd isotopes by TIMS

2.3.1. Loading method

Re filaments were degassed in vacuum before use. Approximately 0.5 μL of 0.15 M H₃PO₄ was dried on ~1 mm spot in the middle of the Re filament at 0.8 A. Mixed Sr and REEs analytes were dissolved with 1 μL of 2.5 M HCl, then loaded on the spot and dried at 0.8 A. The sample size of Sr and Nd showed a large variation (0.7–31 μg for Sr; 0.2–20 μg for Nd), depending on the actual silicate samples. The spot was then covered with 0.5 μL of 0.15 M H₃PO₄ and evaporated at 0.8 A. Once the load was completely dry, the filament was heated and kept at dull glow for 4–6 s. Mixed standard materials (NBS-987 + JNdi-1) were employed to monitor the instrument state. Each loading size was 200 ng for the mixed standard following the loading procedure just mentioned.

2.3.2. Determination method for Sr and Nd isotopes

The isotopic composition of Sr and Nd was performed by TIMS using a Triton instrument (ThermoFisher), operating in the positive ionization mode with a 10 kV acceleration voltage and 10¹¹ Ω for the Faraday cups. This instrument was equipped with nine Faraday collectors. A double Re filament geometry was used to obtain Sr⁺ and Nd⁺ ion beams.

All data were acquired by static multi-collection with the collector array illustrated in Table 2. Owing to TIMS devices that allow the selective ionization of a specific element species in different temperature conditions, Sr and Nd can be measured in sequence from the same Re filament. The ideal ionization temperature of Sr is approximately 1200 °C and it is significantly lower than that of Nd (~1750 °C). Hence, Sr was measured before Nd. First, the ionization filament was heated at a rate of 450 mA min⁻¹ to 3.5 A which

Table 2
Cup setting of static multi-collector mode.

Element	L4	L3	L2	L1	CC	H1	H2
Sr			⁸⁴ Sr	⁸⁵ Rb	⁸⁶ Sr	⁸⁷ Sr	⁸⁸ Sr
Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁹ Sm	

corresponds to a temperature of $\sim 1200^\circ\text{C}$. The evaporation filament was then heated at 300 mA min^{-1} until a signal of ⁸⁸Sr reached 30 mV. The beam was centered and roughly focused, and the evaporation filament was slowly heated to obtain a 3–4 V for ⁸⁸Sr. Data acquisition was started when the signal intensity of ⁸⁸Sr had reached $\sim 5\text{ V}$. Before data acquisition of each block, a peak-centre routine was run, and then the baseline was measured at half-mass with an integration time of 33 s by deflecting the beams using the x-symmetry lens. An auto-focus routine was run every three blocks to re-focus the ion beam. The measurement run consisted of 9–12 blocks of data with 15 cycles per block. The integration time per cycle was 4 s.

Before mass fractionation correction, the ⁸⁷Sr signal intensity was corrected for the potential bias caused by the remaining isobaric overlap of ⁸⁷Rb on ⁸⁷Sr using an ⁸⁷Rb/⁸⁵Rb value of 0.385041 [15]. Then, corrected ⁸⁷Sr/⁸⁶Sr values were normalized to ⁸⁸Sr/⁸⁶Sr = 8.375209 using the classical exponential law [3,5–15]. Typical internal precision of ⁸⁷Sr/⁸⁶Sr were better than $\pm 0.001\%$ (1 RSE) for most samples after isobaric interference and mass fractionation correction. Replicate analyses of the Sr reference material NBS-987 yielded the ⁸⁷Sr/⁸⁶Sr values of 0.710256 ± 16 (2 SD; $n = 5$), showing good agreement with published data [5–15,23–26].

After having finished all the Sr measurements in a whole set of turret samples, the collector array of Sr was switched to the Nd Faraday cup configuration by operating software. Minor tunes were required to overlap the mass peak shapes. This configuration for advanced Triton TIMS can be finished easily and quickly (ca. 10 min). Then, Nd analysis was started. Similar to the Sr measurements, the ionization filament was first heated at a rate of 450 mA min^{-1} with a temperature of $\sim 1750^\circ\text{C}$. The evaporation filament was then heated at 300 mA min^{-1} until a signal of ¹⁴⁶Nd reached 20 mV. Afterwards, the beam was centred and roughly focused, and the evaporation filament was slowly heated to obtain a 1–1.3 V intensity of ¹⁴⁶Nd. Data acquisition was started once the intensity of ¹⁴⁶Nd had reached $\sim 1.6\text{ V}$. Before the commencement of the analysis, a peak-centre routine was run, and then, the baseline was measured at half-mass with an integration time of 33 s by deflecting the beams using the x-symmetry lens. An auto-focus routine was run every three blocks to re-focus the ion beam. Data were collected for 10–12 blocks with each block containing 15 cycles, which, in turn, consisted of 4 s of integration time. The typical intensity of ¹⁴⁷Sm was about 0.3–0.5 V during the period of data acquisition. Isobaric interference from ¹⁴⁴Sm can be accurately subtracted following our latest research [22]. Most of the data were acquired and yielded an internal precision of $\pm 0.001\%$ (1 RSE), which was corrected using our off-line programme. The detailed correction method can be found elsewhere [22]. Replicate analyses of the JNdi-1 reference material gave an ¹⁴³Nd/¹⁴⁴Nd value of 0.512113 ± 0.000012 (2 SD; $n = 5$), illustrating good agreement with published data [9,18,20–22,25–27].

3. Results and discussion

3.1. Purity and recovery of Sr and Nd

In practice, purity and recovery are crucial to Sr and Nd isotopic analysis. Especially, purity of the sample might impinge on the ionization efficiency of the analyte in TIMS, potentially causing a severe suppression in signal intensity and unstable ion beam

Table 3
Sample purity and recovery of Sr and Nd.

Elements	Fraction 1 (%)	Fraction 2 (%)	Fraction 3 (%)
K	99.9	0.1	0
Na	99.0	1.0	0
Ca	99.3	0.7	0
Mg	100.0	0	0
Al	100.0	0	0
Fe	100.0	0	0
Ti	99.3	0.7	0
Mn	100.0	0	0
Cr	100.0	0	0
Rb	99.9	0.1	0
Sr	22.8	77.2	0
Y	43.9	56.1	0
Cs	100.0	0	0
Ba	4.0	3.3	92.7
La	15.8	7.1	77.1
Ce	5.2	15.3	79.5
Pr	5.6	45.4	49.0
Nd	5.0	93.2	1.8
Sm	4.6	95.0	0.4
Eu	4.0	89.0	7.0
Gd	4.6	64.4	31.0
Tb	5.3	89.5	5.3
Dy	8.7	91.3	0
Ho	25.4	74.6	0
Er	49.8	48.3	2.0
Tm	81.3	18.8	0
Yb	83.3	16.7	0
Lu	90.3	9.7	0
Hf	98.8	1.2	0

Fraction 1: 3 mL 2.5 M HCl (1 mL loading + 2 mL rinsing) + 7 mL 5.0 M HCl (rinsing).

Fraction 2: 3.5 mL 5.0 M HCl + 14 mL 4.0 M HCl (collecting Sr and Nd).

Fraction 3: 10 mL 6.0 M HCl (rinsing).

emission [11–14]. Hence, purity of the samples should be carefully examined, because previous research suggested that the ionization efficiency of Sr and Nd were prohibited by Ba, Fe, and Ca. In this study, column condition experiments have been optimized and recalibrated in order to reduce possible potential matrix prohibition. Elements assays and semi-quantitative analyses were carried out using a Thermo Fisher Element-XR ICP-MS instrument.

As shown in Table 3, most matrix elements (Fe, K, Na, Mg, Ca, Ti, Al, Mn, Cr) and Rb had been rinsed in fraction 1 before the collection of Sr and REEs fractions. More than 80% of Tm, Yb, Lu and Hf are also found in fraction 1. Most Sr, Nd, Pr, Sm and HREEs were eluted and partly Ba (3.3%), La (7.1%), and Ce (15.3%) coexisted in fraction 2. The Sr and Nd yield were more than 75% and 90%, respectively, in fraction 2. The Nd yield was excellent, whereas the Sr yield was slightly low. Most Ce, La and Ba were rinsed in fraction 3. Few matrix elements were found in the mixed Sr + REEs fractions. The inter-effect extent from Sr and REEs during the course of data acquisition is discussed in Section 3.3.

For bulk analysis, usually, 100–150 mg of rock powder was digested. Hence, a sufficient amount of Sr and Nd ($\geq 100\text{ ng}$) was easy to be obtained by the chemical procedure just mentioned. In actual works, for those samples with the Rb/Sr ratios higher than 50, such as granites and rhyolite, it is possible for very small amounts of Rb to pour into Sr fraction. Therefore, we partly sacrifice the Sr yield to obtain a high purity of Sr. However, it is still difficult to completely separate Sr and Rb for those special minerals with high ratios of Rb/Sr using the traditional AG50W resin. With regard to those samples with high Rb/Sr ratios, a purification procedure performed twice is necessary to eliminate Rb isobaric interference or using Sr specTM resin to make further purification.

Table 4
Analytical results of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for CRMs determined by TIMS.

CRM	Analysis number	$^{87}\text{Sr}/^{86}\text{Sr}(\pm \text{S.E.})$	Reported values	Reported Rb/Sr ratio	$^{85}\text{Rb}/^{86}\text{Sr}$	Mean of $^{88}\text{Sr}/^{86}\text{Sr}$
BCR-2	a	0.705029(7)	0.705019 ⁶ ; 0.705023 ²⁵	0.1360 ²⁵	0.000014	8.296884
	b	0.705023(6)			0.000004	8.299462
	Mean	0.705026				
BHVO-2	a	0.703483(5)	0.703487 ⁶	0.0229 ²⁹	0.000008	8.308243
	b	0.703474(6)			0.000008	8.309857
	Mean	0.703479				
JA-3	a	0.704172(6)	0.704183 ⁸ ; 0.704160 ⁹	0.1232 ²⁸	0.000109	8.318484
	b	0.704182(6)			0.000016	8.323274
	Mean	0.704177				
JB-3	a	0.703429(3)	0.703432 ⁷ ; 0.703446 ⁸	0.0345 ²⁸	0.000015	8.302531
	b	0.703451(6)			0.000012	8.304169
	Mean	0.703440				
RGM-2	a	0.704188(5)	No data		0.000035	8.296685
	b	0.704179(5)			0.000009	8.292511
	Mean	0.704184				
W-2	a	0.706983(3)	0.706960 ¹¹	0.1010 ²⁸	0.000108	8.309635
	b	0.706962(6)			0.000002	8.307829
	Mean	0.706973				
GSP-2	a	0.765182(7)	0.765151 ⁶	1.017 ²⁹	0.000091	8.323042
	b	0.765175(7)			0.000099	8.326779
	Mean	0.765177				
JR-2	a	0.705453(7)	0.705482 ⁸ ; 0.705451 ⁹ ;	36.63 ²⁸	0.000078	8.330579
	b	0.705466(7)			0.000041	8.348598
	c	0.705467(6)			0.000006	8.325764
	d	0.705475(5)			0.000006	8.344231
	e	0.705446(6)			0.000055	8.338289
	f	0.705465(7)			0.000014	8.351493
	Mean \pm 2SD	0.705462(21)				
BIR-1	a	0.703105(6)	0.703130 ¹²	0.0033 ²⁸	0.000011	8.289934
	b	0.703105(5)			0.000007	8.293950
	c	0.703111(6)			0.000016	8.295856
	d	0.703089(6)			0.000015	8.300420
	e	0.703108(5)			0.000007	8.301783
	f	0.703105(6)			0.000010	8.305927
	Mean \pm 2SD	0.703104(15)				

Table 5
Analytical results of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for CRMs determined by TIMS.

CRM	Analysis number	$^{143}\text{Nd}/^{144}\text{Nd}(\pm \text{S.E.})$	Reported values	Reported Sm/Nd value	$^{145}\text{Nd}/^{144}\text{Nd}(\pm \text{S.E.})$	Mean of $^{146}\text{Nd}/^{144}\text{Nd}$
BCR-2	a	0.512627(4)	0.512634 ⁵ ; 0.512640 ¹⁸	0.2282 ²⁵	0.348407(3)	0.719534
	b	0.512644(3)			0.348415(2)	0.720039
	Mean	0.512636			0.348411	
BHVO-2	a	0.512987(3)	0.512981 ⁶ ; 0.512994 ²⁶	0.2478 ²⁹	0.348417(2)	0.719691
	b	0.512989(2)			0.348419(1)	0.720641
	Mean	0.512988			0.348418	
JA-3	a	0.512854(4)	0.512859 ⁸ ; 0.512859 ⁹	0.2479 ²⁸	0.348418(2)	0.720618
	b	0.512850(3)			0.348417(2)	0.722233
	Mean	0.512852			0.348418	
JB-3	a	0.513042(3)	0.513048 ⁸ ; 0.513037 ⁹	0.2702 ²⁸	0.348411(2)	0.720018
	b	0.513054(2)			0.348415(1)	0.721749
	Mean	0.513048			0.348413	
RGM-2	a	0.512799(6)	No data		0.348414(4)	0.719870
	b	0.512806(4)			0.348421(3)	0.720794
	Mean	0.512803			0.348418	
W-2	a	0.512516(4)	0.512510 ¹³ ; 0.512513 ²²	0.2535 ²⁸	0.348419(3)	0.719585
	b	0.512520(3)			0.348419(2)	0.720071
	Mean	0.512518			0.348419	
GSP-2	a	0.511353(4)	0.511369 ⁶ ; 0.511359 ²²	0.1266 ²⁹	0.348407(3)	0.719334
	b	0.511347(4)			0.348409(3)	0.719752
	Mean	0.511350			0.348408	
JR-2	a	0.512913(6)	0.512919 ⁸ ; 0.512913 ⁹	0.2751 ²⁸	0.348419(3)	0.719518
	b	0.512920(4)			0.348418(2)	0.720001
	c	0.512907(3)			0.348415(2)	0.720643
	d	0.512912(3)			0.348417(2)	0.721616
	e	0.512907(5)			0.348413(3)	0.719729
	f	0.512911(4)			0.348419(3)	0.720951
	Mean \pm 2SD	0.512911(10)			0.348417(5)	
BIR-1	a	0.513099(5)	0.513080 ¹² ; 0.513105 ²⁶	0.4596 ²⁸	0.348414(3)	0.720158
	b	0.513094(3)			0.348412(2)	0.721642
	c	0.513094(5)			0.348412(6)	0.721690
	d	0.513094(5)			0.348419(3)	0.723848
	e	0.513088(3)			0.348419(2)	0.722067
	f	0.513081(4)			0.348418(3)	0.723902
	Mean \pm 2SD	0.513091(13)			0.348416(7)	

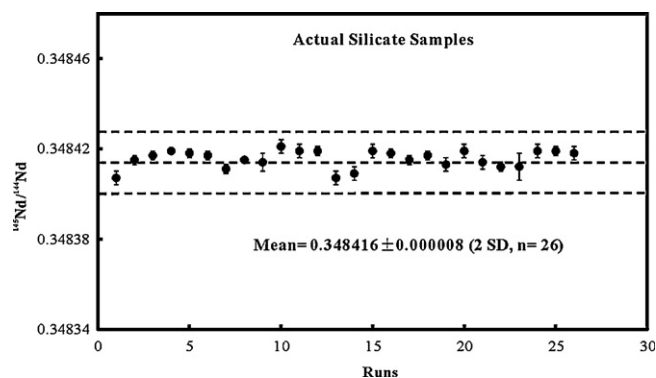


Fig. 1. Corrected $^{145}\text{Nd}/^{144}\text{Nd}$ ratios for each actual silicate rock from USGS and GSJ.

3.2. Isobaric interference correction of Sr and Nd

Isobaric interference correction is the key issue to accurately determine the Sr and Nd isotopic ratios. The main isobaric interference comes from ^{87}Rb and ^{144}Sm regarding $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ measurements. With regard to the ^{144}Sm isobaric interference on ^{144}Nd , we have reported the detailed correction method elsewhere [22]. The basic correction principle is based on the β_{Sm} (the mass fractionation factor of Sm) value, which can be directly obtained from the $^{147}\text{Sm}/^{149}\text{Sm}$ in the sample itself [22]. Then, it is applied to the isobaric interference correction of ^{144}Sm on ^{144}Nd [22,24]. Hence, it is not necessary to conduct the separation of Sm and Nd. In addition, the mass-bias corrected value for $^{145}\text{Nd}/^{144}\text{Nd}$ is a good indicator of checking whether ^{144}Sm can be accurately subtracted from a mixed intensity of $^{144}\text{Sm} + ^{144}\text{Nd}$. As shown in Fig. 1 and Tables 4 and 5, corrected $^{145}\text{Nd}/^{144}\text{Nd}$ value is 0.348416 ± 0.000008 (2 SD; $n = 26$) in the actual silicate reference rock samples from USGS and GSJ, agreeing well with reported values [4,16,22,24].

As for ^{87}Rb interference on ^{87}Sr , depending on the initial Rb/Sr value in the samples and the efficiency of the separation in the columns, the $^{85}\text{Rb}/^{86}\text{Sr}$ ratios in the final samples varied between 10^{-4} and 10^{-5} and can be accepted [23]. As shown in Table 3, only ~0.1% of Rb is detected in the Sr and REEs fractions. Such a small Rb is easy to burn off before the measurement of Sr. In this study, $^{85}\text{Rb}/^{86}\text{Sr}$ ratios for all the Sr samples are lower than 1.1×10^{-4} even for JR-2 with a high Rb/Sr ratio (~37) [28], thus demonstrating negligible isobaric interference from ^{87}Rb .

3.3. Whether inter-restraint from Sr and REEs existed in the same filament

In previous studies, it was unclear whether Sr and REEs were inter-inhibits in the same filament. Hence, it is important to examine whether this problem existed and affected final accuracy of Sr and Nd isotopic ratios. We investigate this issue from two aspects. Firstly, a 100 ppm of mixed standard solution (JNdi-1 + NBS-987) was prepared. Each loading size was 200 ng. As for this mixed standard solution, in every case, very strong and stable ion beam can be achieved, thus giving excellent data accuracy and precision. Replicate analyses of the mixed reference material gave the $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.710256 ± 16 (2 SD; $n = 5$) and the $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512113 ± 0.000012 (2 SD; $n = 5$), illustrating good agreement with published data [5–15,22–27]. Hence, few inter-restraint from Sr and Nd existed in the same filament is found in this study. Secondly, the purity of our actual samples is worse than that of mixed standard solution (NBS-987 + JNdi-1). As shown in Table 3, the main unwanted elements come from REEs. Hence, inter-restraint from Sr and REEs should be further examined. Natural silicate samples,

spanning a wide range of Ba, Sr and REEs contents, and bulk composition, are ideal and sensitive indicators that test the potential problems just mentioned. As for TIMS measurements, ion beam intensity and signal stability are the prerequisites to achieve excellent data accuracy and precision. In every case, stable, strong, and long-lasting ion beam intensity of Sr^+ and Nd^+ can be obtained during the period of data acquisition. The intensity of ^{88}Sr and ^{146}Nd was maintained at a satisfied level for each sample which was never lower than 5 V and 1.5 V so that high precision can be achieved. Especially, GSP-2 and RGM-2 amongst these samples, with a high content of Sr and REEs, may exist in the most serious inter-restraint issue. A very strong and long-lasting ion beam of Sr^+ and Nd^+ can be obtained even for GSP-2 and RGM-2 and excellent data precision also can be achieved. Clearly, REEs have a negligible suppression effect on the emission of Sr^+ and Nd^+ .

In addition, both $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ ratios are also sensitive indicators that are used to monitor the mass fractionation state during the course of data acquisition. We can not only monitor the changing trends of $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$, but also know the extent of effect from matrix and other complicated unknown factors. Regarding TIMS instruments, it is typical that the continual process of mass fractionation starts to 'use up' the lighter isotope on the filament so that the isotopic composition of the sample becomes progressively heavier. Usually, the $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ ratios will increase little by little in each cycle. As shown in Tables 4 and 5, all average values of $^{88}\text{Sr}/^{86}\text{Sr}$ are lower than 8.375209, and most average values of $^{146}\text{Nd}/^{144}\text{Nd}$ are lower than 0.7219. This suggested that mass fractionation was still at an early stage, even though all measurements for most samples had been finished, thus indicating that much Sr and Nd still remained on the filaments. Therefore, little inter-restraint effect from Sr and REEs was found in this study.

3.4. Reproducibility and precision of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$

In order to evaluate and validate this method, nine CRMs from USGS and GSJ were conducted for Sr and Nd isotopic ratios by a Triton TIMS. These CRMs encompassed samples with a wide range of matrix composition and diversified Rb/Sr and Sm/Nd ratios. As shown in Tables 4 and 5, the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for all the analysed USGS and GSJ reference materials were obtained with an internal precision better than 10 ppm. The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ data presented here show good agreement with previously published data by TIMS and MC-ICP-MS techniques [5–13,18,20,22,24–26]. The reference values of RGM-2 cannot be found, and to the best of our knowledge, the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ of RGM-2 are to be published for the first time.

The analytical reproducibility for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ was evaluated using reference materials BIR-1 and JR-2, with a relatively low Nd and Sr content in the usual standard reference materials. In addition, both BIR-1 and JR-2 have a high Sm/Nd with 0.4596 [28] and a high Rb/Sr with 36.63 [28], thus exhibiting the biggest challenge for our method. Hence, BIR-1 and JR-2 are ideal proxies to check the reliability of our method. As shown in Tables 4 and 5, six replicated measurements of BIR-1 yielded $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.513091 ± 0.000013 (2 SD) and $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.703104 ± 0.000015 (2 SD). Six replicated measurements of JR-2 yielded $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512911 ± 0.000010 (2 SD) and $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.705462 ± 0.000021 (2 SD). Both JR-2 and BIR-1 analysis data were well consistent with the reported values [8,9,12,20,22,26,28]. The reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ from JR-2 and BIR-1 is approximately 0.002–0.003% (2 RSD). In general, data reproducibility and precision are satisfactory and completely fit the demand in geoscience.

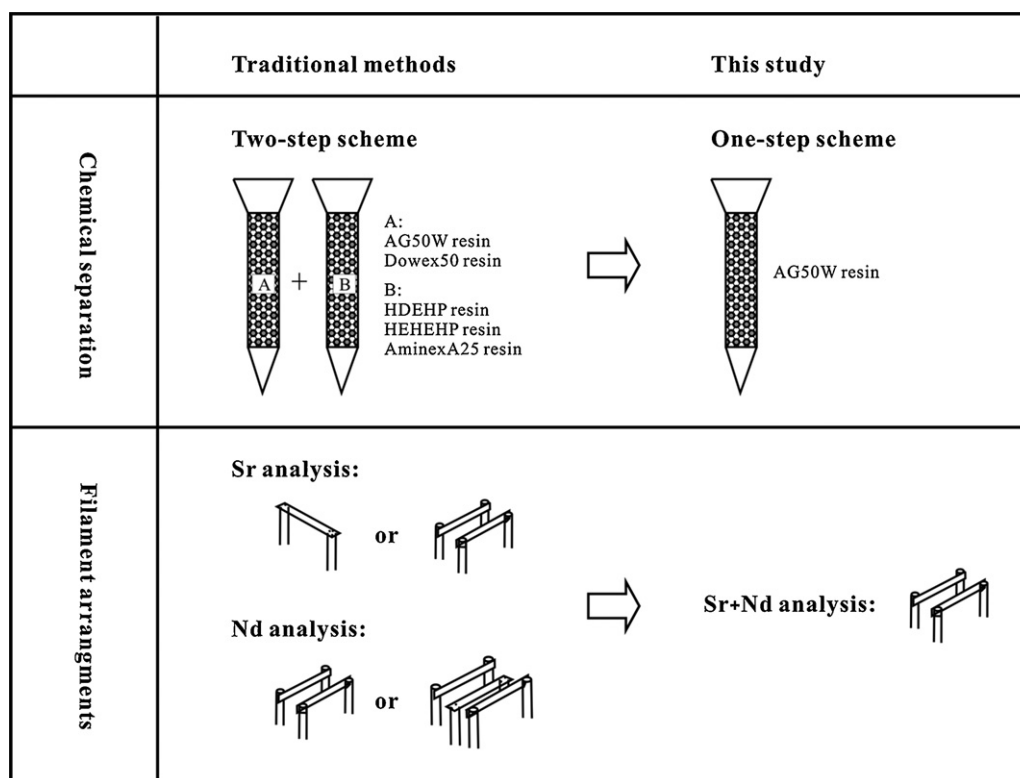


Fig. 2. Our analytical protocol compared with traditional methods.

3.5. Merits and limitations

As shown in Fig. 2, this method makes the following two improvements compared with the protocols published earlier in the literature [4–10,12,13,25]: Firstly, analytical efficiency is greatly prompted because the procedures of sample separation and sample loading are simplified to 50% of the original procedure. Mixed Sr and REEs can be purified by a single-step cation resin technique, and loaded onto the same filament, and measured in sequence without venting using TIMS. This improvement is time saving is as follows: (1) the two-step separation scheme is replaced by single-step separation to save 50% of the separation time. (2) the time of sample loading and sample installing is reduced by 50% due to the mixed Sr and REEs fractions that are permitted to load onto the same filament. In addition, many corresponding filament preparing works, including filament welding and filament degassing, are cut in half. Further, sample capability in the same sample magazine increases by one-fold, because the Sr and Nd can be sequentially measured without venting, resulting in a reduction in the waiting time in order to reach the working vacuum ($\leq 3 \times 10^{-7}$ mbar in ion source) in TIMS. Secondly, the running cost is significantly cut down. One of the main costs of TIMS comes from consuming expensive high-purity filament, such as Ta, Re and W. Sr and Nd fractions are loaded on the same filament to reduce 50% of the filament consumption. In addition, the one-step separation scheme saves a lot of chemical reagents and resin and reduces the corresponding experimental costs.

Moreover, if large numbers of samples are to be processed, then our method greatly reduces the operator errors existing in the requirement of sample loading, filament installation and sample separation.

Despite the suitability in application to most natural silicate rocks, this new method has several limitations. Firstly, it may be not suitable for samples with Rb/Sr values higher than 100, and Sm/Nd values higher than 1.0, such as mica, garnet and zircon. More

strict experiments should be performed to assess the feasibility of our method for the special minerals just mentioned. Secondly, our method is suitable for the precise determination of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ for un-spiked samples, but Rb, Sr, Sm, and Nd concentrations cannot be obtained in the same aliquot simultaneously. However, accurate $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ values are indispensable to date or for calculating $\varepsilon_{\text{Sr}}(t)$ and $\varepsilon_{\text{Nd}}(t)$, which are the most useful indicators for tracing researches. This limitation can be partly overcome by deploying quadrupole-based or sector-field ICP-MS for determining both Rb/Sr and Sm/Nd values [28–31]. Thirdly, this method cannot provide satisfactory precision for sample sizes smaller than 50 ng of Sr and Nd, such as ultramafic rocks. As for these special samples, traditional TIMS analytical methods [15,17–20] are exclusive even for 1 ng of Sr and Nd.

4. Conclusions

The single-step isolation procedure was employed to obtain a mixed Sr and REEs fraction. Mixed Sr+REEs fractions were loaded onto the same filament. Then, the Sr and Nd isotopic ratios were sequentially measured using TIMS without venting. Excellent precision $\leq \pm 0.000010$ of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios was achieved for a series of CRMs that completely fits the geochemical tracing need. In a direct comparison of the time and expenditure spent running columns and making the Sr and Nd isotope ratios using TIMS, our method provides a significant improvement. On the one hand, our method simplifies the separation procedure for the Sr and Nd. On the other hand, by taking the measurements of Sr and Nd from the same filament without venting, both experimental cost and time were saved. In addition, the corresponding filament installing, filament welding, filament degassing and sample loading in TIMS were reduced 50% of the original workload, thus greatly prompting analytical efficiency.

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