

Precise and accurate determination of Sm, Nd concentrations and Nd isotopic compositions in geological samples by MC-ICP-MS

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In this work, we established a highly reproducible analysis of Sm, Nd concentrations and Nd isotopic compositions in geological samples by isotope dilution analysis with MC-ICP-MS. This technique is superior in terms of the analytical reproducibility or rapidity of analysis compared with quadrupole ICP-MS or with thermal ionization mass spectrometry (TIMS) isotope dilution techniques. Samples were spiked with ^{149}Sm – ^{150}Nd enriched tracer and then digested by a commonly used HF, HNO_3 and HClO_4 acid protocol. The bulk rare earth elements (REEs) were separated from the sample on a standard cation exchange resin, and further purified on Eichrom Technologies Ln Resin, to obtain Sm and Nd fractions prior to mass spectrometric measurements. Replicate analyses of international certified reference materials (CRMs) demonstrate that our obtained $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios are in good agreement with previously published values from isotope dilution methods. In addition to determining the concentrations of Sm and Nd, the Nd isotopic composition can be measured simultaneously during Nd isotope dilution run. Additionally, a mineral Sm-Nd isochronal age that is identical to, within error, a U-Th-Pb zircon age for the same rock is further measured and validates the robustness of the present protocol. Therefore, the high actual sample throughput inherent to the MC-ICP-MS can be fully exploited for the determination of Sm and Nd concentrations and Nd isotopic compositions.

1. Introduction

Owing to the similar chemical characters of the two rare earth elements, the classical ^{147}Sm – ^{143}Nd radiogenic isotopic system has been extensively used in geochemistry and cosmochemistry as a powerful geochemical tracer or chronometer. Besides, Nd isotopic composition of environmental samples (*e.g.*, detrital apatite, planktonic foraminifera, ferromanganese and fossil fish teeth) have also been widely used to trace the environmental provenance and process in paleogeography, paleoclimatology and paleoceanography.¹ Due to the long half-life of ^{147}Sm (106 billion years), the radiogenic variation of $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio is comparatively small in most geological samples. For $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio, multi-collector thermal ionization mass spectrometry (TIMS) is almost invariably used since the mid 1960s, owing to its inherent high precision. The classic TIMS technique is still regarded as the benchmark technique for Nd isotopic analysis,^{2–4} though this technique is tedious, time-consuming and requires strict analytical procedure and extensive

source filament preparation and loading and hours of mass spectrometric measurement.

However, since its commercial advent in the mid 1990s and more recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a routine and competitive technique for $^{143}\text{Nd}/^{144}\text{Nd}$ isotope measurement,^{5–16} offering relatively simplified chemical purification and high sample throughput with comparable precision to classic TIMS, though Nd can be ionized more efficiently as NdO^+ than as Nd^+ on TIMS, which is generally involved with uncertainty results from oxygen corrections and the need for a lengthy and efficient chromatographic purification of Nd and therefore preferred for sub-nanogram level sample.^{2,3,7} It is also possible to directly analyze Nd isotopic compositions of minerals enriched in Nd (*e.g.*, apatite, titanite, monazite, perovskite *etc.*) with high spatial resolution on sub-grain scale, using MC-ICP-MS coupled with a laser ablation system (LA).^{17–20}

Furthermore, since the ICP ion source is under atmospheric pressure liquid samples can be easily and sequentially introduced using standard nebulizer with only short (<5 min) washout times. High precision Nd isotopic measurements of geological samples by MC-ICP-MS can even be realized in a Sm-Nd mixture without Sm-Nd separation,^{5,8,16} which shortens sample preparation time and avoids more potential contamination. Recently, Baker *et al.*²¹ demonstrated precise rare earth elements (REEs)

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analyses of six international rock standard materials after a simplified one-step chemical separation procedure using isotope dilution (ID) MC-ICP-MS. More recently, Kent *et al.*²² have reported precise REEs analyses of eleven international geochemical reference materials, including NIST glass and USGS rock standards, using this method. Unfortunately, they reported Sm and Nd concentrations without simultaneous Nd isotopic composition.

The motivation of this work is to establish a simple, rapid and practical analytical protocol for Sm and Nd concentrations with Nd isotopic compositions from natural geological samples using ID-MC-ICP-MS, without comprising the precision and accuracy of the measurements. We further exemplify a mineral Sm-Nd isochronal age, which is identical to, within error, a U-Th-Pb zircon age for the same rock and illustrate the usefulness and applicability of present protocol.

2. Experimental

2.1. Chemical materials and reagents

Milli-Q H₂O: 18.2 MΩ at 25 °C from Millipore (Elix-Millipore, USA).

HCl, HF and HNO₃: from Beijing Institute of Chemical Reagent and purified by the Savillex™ DST-1000 sub-boiling distillation system (Minnetonka, USA) and diluted acids were prepared by dilution with Milli-Q water. Twice-distilled extra-pure grade reagents were used in this study.

HClO₄: 70% from Acros Organics Belgium.

CIT natural Sm Nd mixture solution: from California Institute and Technology.

Neodymium isotopic reference reagents: JNdi-1²³ solution of 200 μg L⁻¹ was used for actual analytical session. 200 μg L⁻¹ of Merck Nd from Thermo Fisher Scientific and La Jolla Nd were also measured. IGG Nd solution of 200 μg L⁻¹ from National Research Centre for Certified Reference Materials, China was used as an in-house standard in our laboratory.

Samarium isotopic reference reagent: Alfa Sm from Alfa Aesar of Johnson Matthey Company (Stock No. 13854, plasma standard solution, Specpure) was used for actual sample measurement as external calibration.

Cerium reference reagent: from National Research Centre for Certified Reference Materials, China was used to evaluate whether or not Ce has a significant effect on the ¹⁴³Nd/¹⁴⁴Nd isotopic measurement (¹⁴²Ce on ¹⁴²Nd).

Cation resin column: 10 cm long × 5 mm (internal diameter) with a 25 mL reservoir (quartz construction), filled with ~2.0 mL of Bio-Rad (Richmond, USA) AG50W-X12 resin (200–400 mesh size).

Ln resin column: 4 cm long × 8 mm (internal diameter) with a 20 mL extension reservoir, pre-packed by Eichrom Technologies (Darien IL, USA) with ~2 mL Ln resin (100–150 μm particle size di(2-ethylhexyl) orthophosphoric acid extraction chromatography material).

Certified reference materials (CRMs) from the United States Geological Survey (USGS): BCR-2 (Basalt), BHVO-2 (Basalt), BIR-1 (Basalt), AGV-2 (Andesite), W-2 (Diabase) and DNC-1 (Dolerite).

2.2. Sample digestion

All chemical preparations were conducted on class 100 work benches within a class 1000 clean laboratory. About 100 mg of rock powder was weighted into a 7 mL round bottom Savillex™ Teflon/PFA screw-top capsule. Weighed aliquots of the mixed ¹⁴⁹Sm–¹⁵⁰Nd isotopically enriched tracer were added to the samples and then gently evaporated to dryness. The mixed ¹⁴⁹Sm–¹⁵⁰Nd spike solution was frequently calibrated using the CIT Sm–Nd solution standard in our laboratory.^{24,25} The added amounts of the spike were evaluated according to the previously reported Sm, Nd concentrations in these reference materials, such that the resulting mixed ratios were around 4–8 for ¹⁴⁹Sm/¹⁴⁷Sm and around 0.4–0.6 for ¹⁵⁰Nd/¹⁴⁴Nd. Consequently, the error magnification factor on isotope dilution calculations was <1.5 for Sm and <2.5 for Nd, respectively. Concentrated HF, HNO₃ and HClO₄ acids (2 mL, 1 mL, 0.2 mL) were added to the samples, the capsules capped and then heated on a hotplate at about 120 °C for 1 week. The added amounts of these acids are excessive for the digestion of 200–300 mg of silicate rock samples. After cooling, the capsule was opened and then heated to evaporate HClO₄. 1 mL of 6 M HCl was added to the residue and then evaporated, this procedure was then repeated. After cooling, the residue was dissolved in 1.5 mL of 2.5 M HCl. The capsule was again sealed and placed on a hot plate at ~100 °C overnight to dissolve the solid residues prior to chemical separation.²⁵

2.3. Column chemistry

The bulk REEs, as a group, were separated from the sample on a standard cation exchange resin, and then further purified on a Ln resin to collect a mixed Sm and Nd fraction prior to mass spectrometric measurement. The separation protocol is detailed as follows. After centrifuging, the sample solution was loaded into a quartz column packed with AG50W-X12 pre-conditioned with 2 mL of 2.5 M HCl. The resin was washed with 2 mL of 2.5 M HCl, followed by 2.5 mL of 5 M HCl to remove the majority of the matrix elements. Then the Rb and Sr fractions were eluted with 8 mL of 5 M HCl. Finally, the REEs fraction was eluted with 6 mL of 6 M HCl for the further purification.

The separation of Nd and Sm was achieved using the commercial Ln Resin column (modified after Pin and Santos-Zaldugui²⁶). The REEs fraction collected from the cation exchange resin was gently evaporated to dryness, taken up with 0.5 mL of 0.25 M HCl and loaded onto Ln Spec resin. La, Ce and Pr were removed with 6 mL of 0.25 M HCl wash. Then the fraction containing Nd was eluted with 6 mL of 0.25 M HCl for ID analysis. The recovery yield for Nd was higher than 90%, and no Sm was detected in this fraction during mass spectrometric measurement. Finally, the Sm fraction was stripped with 10 mL of 0.4 M HCl for ID analysis, the recovery yield of Sm was higher than 95%.

2.4. Mass spectrometry

Sm and Nd isotopic measurements were performed on a Thermo Scientific (Bremen, Germany) Neptune MC-ICP-MS, located at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG, CAS). The instrument is equipped with eight motorized Faraday cups and one fixed central channel where the

beam can be switched between a Faraday cup and a secondary electron multiplier (SEM). A detailed description of this instrument can be found elsewhere.^{18,27}

At the start of each analytical session the instrument was tuned for maximum sensitivity and optimal peak shape using an in-house standard (IGG Nd or Alfa Sm solution) and the mass calibration was updated by peak-centering on the centre-cup mass (¹⁴⁶Nd or ¹⁴⁹Sm). Sample introduction was *via* a self-aspirating 50 μL min⁻¹ PFA concentric nebulizer and quartz spray chamber. After every sample or standard measurement, 2% HNO₃ wash was aspirated for 3 to 5 min until the major isotope signals reduced to 0.1 mV. The typical instrument parameters and the cup configurations are summarized in Table 1 and 2. The purified Sm and Nd fractions from the Ln column were firstly taken up with several drops of concentration HNO₃ and then gently evaporated to dryness. Then 1 mL of 2% HNO₃ was added to dissolve the residue, before further dilutions in order to obtain appropriate beam intensity during the mass spectrometry measurements.

In general, the signal intensity for ¹⁴⁶Nd was about 2 volts for 200 μg L⁻¹ Nd standard solution. The relative efficiencies of the Faraday cup amplifiers were cancelled using the virtual amplifier rotation technique.^{27,28} The Nd isotope analyses consist of 9 blocks of 6 cycles per block with an integration time of 8 s per cycle (Table 1). The Nd standard solution was corrected for mass bias by measuring ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219²⁹ and using the exponential law.³⁰

In terms of Nd ID analyses, the raw data were exported and reduced offline in order to correct for instrumental mass bias and tracer contribution. Nd concentrations were calculated from the corrected ¹⁵⁰Nd/¹⁴⁴Nd mixture ratio, using the isotope dilution equation. The data reduction was performed by a computer using a self-written Excel VBA (Visual Basic for Applications) macro program, within which interference corrections and spike subtractions are made, followed by a mass fractionation correction using the exponential law³⁰ (¹⁴⁶Nd/¹⁴⁴Nd = 0.7219), these calculations are performed cycle by cycle.³¹

Table 1 Typical instrumental operating conditions and data acquisition parameters for Sm and Nd measurements

Thermo Finnigan Neptune MC-ICP-MS	
RF forward power	1300 W
Cooling gas	15.2 L min ⁻¹
Auxiliary gas	0.8 L min ⁻¹
Sample gas	~1.05 L min ⁻¹ (optimized daily)
Extraction	-2000 V
Focus	-630 V
Detection system	Nine Faraday collectors
Interface cone	Nickel
Mass resolution	400 (Low)
Acceleration voltage	10 kV
Spray chamber	Glass cyclonic
Nebulizer type	PFA nebulizer
Sample uptake rate	50 μL min ⁻¹
Uptake mode	Free aspiration
Sensitivity on ¹⁴⁶ Nd	8 V/ppm (10 ⁻¹¹ Ω resistors)
Sampling mode	9 blocks of 6 cycles for Nd 1 block of 40 cycles for Sm
Integration time	8 s for Nd and 4 s for Sm
Baseline determination	<i>ca.</i> 1 min on peak in 2% HNO ₃

In the case of the Sm isotopic measurements, the analyses consist of 1 block of 40 4-second cycles (Table 1 and 2). The ¹⁴⁷Sm/¹⁴⁹Sm ratio for the spiked samples was externally corrected for mass bias by measuring Alfa Sm standard solution after every five sample (¹⁴⁷Sm/¹⁴⁹Sm = 1.08680^{32,33}). Then the Sm concentration of the actual sample is calculated from the corrected ¹⁴⁷Sm/¹⁴⁹Sm ratio, using the isotope dilution equation.

3. Results and discussion

3.1. Nd isotopic composition of standard solutions

Four standard solutions of Merck, Lo Jolla, JNdi-1 and IGG Nd were used for evaluating the precision and accuracy of Nd isotope measurement methodology (Fig. 1). As shown in Fig. 1, our long-term replicate analyses of Merck, Lo Jolla and JNdi-1 Nd reference materials yielded mean ¹⁴³Nd/¹⁴⁴Nd ratio of 0.511725 ± 14 (2SD, *n* = 38), 0.511849 ± 14 (2SD, *n* = 68) and 0.512110 ± 10 (2SD, *n* = 54), respectively, which are in good agreement with other previously published values by TIMS^{2,3,10,23} or MC-ICP-MS.^{5,8,10,11} Likewise, our replicate analyses of an in-house IGG Nd standard resulted in a mean ¹⁴³Nd/¹⁴⁴Nd ratio of 0.511604 ± 18 (2SD, *n* = 69).^{14,16} As a whole, our obtained standard Nd isotopic data are compatible and consistent with previously published values, indicating the good performance of our methodology and the Thermo Scientific Neptune MC-ICP-MS.

3.2. Spiked Nd measurement by MC-ICP-MS

Because the ¹⁵⁰Nd abundance of available commercial ¹⁵⁰Nd spike is about 97.8% in this work, the ¹⁵⁰Nd spike contains relative low amounts of ¹⁴³Nd, ¹⁴⁴Nd, ¹⁴⁵Nd, ¹⁴⁶Nd and ¹⁴⁸Nd. Therefore, although only a little amount of ¹⁵⁰Nd spike should be added to the sample to obtain an appropriated ¹⁵⁰Nd/¹⁴⁴Nd mixed ratio due to the very low (about 5.64%) abundance of ¹⁵⁰Nd in natural Nd sample, ¹⁴³Nd/¹⁴⁴Nd, ¹⁴⁵Nd/¹⁴⁴Nd, ¹⁴⁶Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd could still be significantly altered by the added ¹⁵⁰Nd spike. It is well known to correct mass fractionation and subtract spike contribution for classic TIMS technique.³¹ However, the mass bias for MC-ICP-MS is about one order of magnitude greater than that of TIMS. Consequently, it is very important to use an appropriate method to correct the mass fractionation for spiked Nd isotope analysis.

In this work, four JNdi-1 Nd standard solutions doped with different amounts of ¹⁵⁰Nd spike (containing about 97.8% of ¹⁵⁰Nd), were measured by Neptune MC-ICP-MS with static mode using the cup configuration as shown in Table 2, to validate the usefulness of our calculation method.³¹ The measured results calculated with our method are shown in Table 3. Our obtained ¹⁴³Nd/¹⁴⁴Nd ratio of JNdi-1 Nd was in excellent agreement with the recommended value of 0.512115 when the ¹⁵⁰Nd/¹⁴⁴Nd mixed ratio is less than about 1. As mentioned above, our ¹⁵⁰Nd/¹⁴⁴Nd mixed ratio of actual sample is usually around 0.4 to 0.6. It could be concluded that, our calculation method for spiked Nd isotopic analyses by MC-ICP-MS is reliable and feasible.

Table 2 Faraday cup configuration for Sm and Nd isotopic measurement^a

Faraday cup	L4	L3	L2	L1	Center	H1	H2	H3	H4
<i>Sm</i>									
Measured element	¹⁴⁴ Sm ⁺	¹⁴⁶ Nd ⁺	¹⁴⁷Sm⁺	¹⁴⁸ Sm ⁺	¹⁴⁹Sm⁺	¹⁵⁰ Sm ⁺	¹⁵² Sm ⁺	¹⁵⁴ Sm ⁺	¹⁵⁵ Gd ⁺
Interference element	¹⁴⁴ Nd ⁺			¹⁴⁸ Nd ⁺		¹⁵⁰ Nd ⁺	¹⁵² Gd ⁺	¹⁵⁴ Gd ⁺	
<i>Nd</i>									
Measured element	¹⁴² Nd ⁺	¹⁴³ Nd ⁺	¹⁴⁴Nd⁺	¹⁴⁵ Nd ⁺	¹⁴⁶Nd⁺		¹⁴⁸ Nd ⁺		¹⁵⁰ Nd ⁺
Interference element	¹⁴² Ce ⁺		¹⁴⁴ Sm ⁺			¹⁴⁷ Sm ⁺	¹⁴⁸ Sm ⁺	¹⁴⁹ Sm ⁺	¹⁵⁰ Sm ⁺

^a **Bold** text indicates masses used to determine mass fractionation.

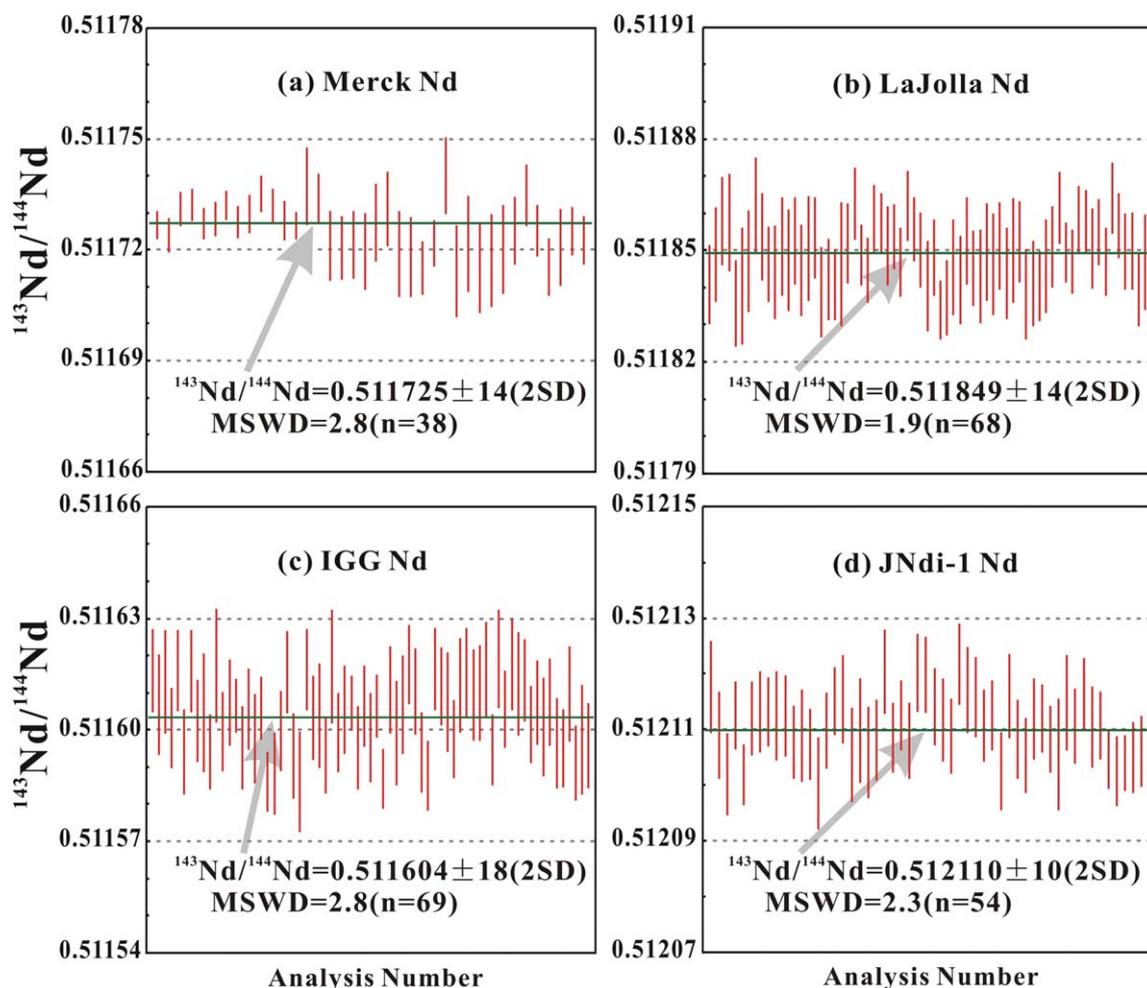


Fig. 1 Measured ¹⁴³Nd/¹⁴⁴Nd ratios of four standard Nd solutions for Merck Nd (a), La Jolla Nd (b), IGG Nd (c) and Jndi-1 Nd (d), normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 for mass discrimination using exponential law. Error bars for individual analyses are 2 S.E. (2σ_m, in-run standard error). Mean values of measured ¹⁴³Nd/¹⁴⁴Nd ratios are represented by solid horizontal lines with ±2SD (2σ) errors represented by dashed horizontal lines. The MSWD means the Mean Square of Weighted Deviates. Results indicate that highly accurate and reproducible Nd isotopes ratios can be obtained using our methodology and the Thermo Scientific Neptune MC-ICP-MS.

3.3. Isobaric interferences

3.3.1. Ce interference. As summarized in Table 2, there is an isobaric interference of ¹⁴²Ce on ¹⁴²Nd, although this is not of interest for the radiogenic ¹⁴³Nd. Usually it is impossible to completely separate Ce and Nd when using ion exchange chromatography because of their almost identical chemical character.^{11,14,26} In order to evaluate residual Ce in the Nd fraction we

carried out isotopic measurement of IGG Nd synthetic mixture solution doped with different amounts of Ce. As seen in Fig. 2, there is no significant influence on the ¹⁴³Nd/¹⁴⁴Nd analysis even with Ce/Nd ratios up to 3, which is maximal for most natural geological samples. Therefore, the impact of ¹⁴²Ce isobaric interferences on the precision and accuracy of the ¹⁴³Nd/¹⁴⁴Nd ratio of interest is negligible using the Neptune MC-ICP-MS, and residual Ce in the Nd fraction is not an issue. This conclusion

Table 3 Calculated results for JNdi-1 Nd standard materials spiked with different amounts of ^{150}Nd enriched tracer isotope analyses by Neptune MC-ICP-MS

Sample	$(^{150}\text{Nd}/^{144}\text{Nd})_{\text{meas.}}$	$(^{150}\text{Nd}/^{144}\text{Nd})_{\text{norm.}}$	$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{norm.}} (\pm 2\sigma)$
Refer. Value		0.236446 ²⁴	0.512115 ²³
JNdi-1 Mix. 0 ^a	0.254672	0.236422	0.512113 (11)
JNdi-1 Mix. 1 ^b	0.682759	0.634056	0.512120 (11)
JNdi-1 Mix. 2 ^b	0.847839	0.787326	0.512117 (10)
JNdi-1 Mix. 3 ^b	1.106994	1.027865	0.512117 (12)
JNdi-1 Mix. 4 ^b	2.145052	1.991266	0.512146 (15)

^a Un-spiked with ^{150}Nd enriched tracer. ^b Spiked with different amounts of ^{150}Nd enriched tracer.

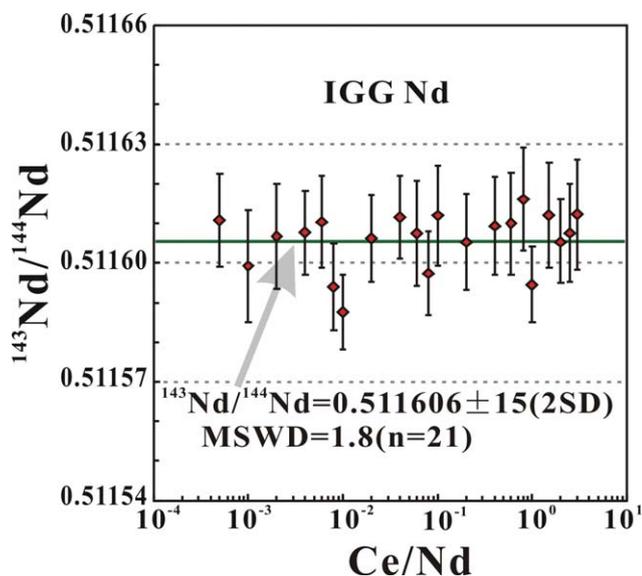


Fig. 2 $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios for in-house standard IGG Nd ($200 \mu\text{g L}^{-1}$) doped with different and increasing amounts of Ce. Error bars for individual analyses are 2 S.E. ($2\sigma_{\text{m}}$, in-run standard error). The isobaric interference of ^{142}Ce on ^{142}Nd is not significant to the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of our interest. The horizontal axes represent the sequence of measurements, typically about 10 min, between points. Gray diamonds are used to calculate average values of $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio. The MSWD means the Mean Square of Weighted Deviates. Result indicates that there are no significant spectral interferences on the mass bias corrected $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio for Ce/Nd ratio up to 3, which is the maximum ratio found in most natural geological samples.

has significant implications for *in situ* Nd measurement by LA-MC-ICP-MS.^{19,20} In contrast, there was evidently a negative linear relationship between Ce/Nd ratio and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio for the GV Instruments (formerly Manchester, UK) Isoprobe MC-ICP-MS when Ce/Nd ratio is more than 0.1.¹¹ The real reason for these discrepancies is still unclear, possibly related to spectral interferences generated by the hexapole collision cell, which served to reduce certain isobaric interferences as well as the kinetic energy spread of the ions. Presumably one or more of the Nd or Sm signals, used for interference and mass bias corrections and/or the ratio of interest, were affected by either scattered ions, polyatomic interferences, and/or baseline issues. The Thermo Scientific Neptune MC-ICP-MS uses a double focusing geometry and does not suffer from these issues; an

electrostatic analyzer serves to correct for the kinetic energy spread of the ions.²⁷ This observation is also strongly supported by Scher and Delaney⁹ that potential matrix effects due to the presence of Ce in the Nd fractions had a negligible impact on measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios.

3.3.2. Sm interference. Unlike the ^{142}Ce interference on ^{142}Nd , the radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio of interest has a significant isobaric interference of ^{144}Sm on ^{144}Nd (Table 2) and precise measurements of Nd isotopic ratios of geological samples require an efficient chemical procedure to separate Nd from Sm. The common method used for Nd and Sm separation of geological sample is HDEHP coated Teflon powder resin or the Eichrom Ln column with HCl as eluent.^{2-4,11,24,25} In this work, the Ln chromatographic method as described in section 2.3 was used to separate Nd from Sm.²⁵ It was observed during mass spectrometric measurement that the signal intensity of interference-free ^{147}Sm and ^{149}Sm for the samples is less than 10^{-5} voltage, which was identical to that of the standard Nd solutions, indicating that Sm was completely removed from the Nd fraction by the column chemistry described above. Therefore, it can be concluded that the Ln column described in this study is suitable to separate Nd from other light REEs (LREEs) for high precision Nd isotopic measurement by MC-ICP-MS. Furthermore, the results in Table 4 and 5 also show that this interference was negligible, yielding accurate $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and Nd concentration data for the international rock CRMs.

3.4. Recovery and total procedural blanks

As for recovery of analyte, a comparison of Nd and Sm concentrations in the geological CRMs with the sample weight reveal the chemical recovery of Nd and Sm using our procedure was higher than 90%. Besides high yield of analyte, a low total procedural blank level is another prerequisite for the reliable Sm-Nd isotopic data. A Teflon SavillexTM DST-1000 sub-boiling distillation system was used to double the HCl, HF and HNO_3 reagents used in this work, and the sample preparation was conducted within a Class 100 environment. The typical total procedural blank values of Sm and Nd, including sample digestion, column chemistry and mass spectrometric measurement were less than 10 pg and 20 pg, respectively, which are at the lower end of recently-published results.^{2-4,11,26,34} The total procedure blank contribution in this work is negligible and requires no correction of the measured isotopic ratios.

Table 4 Sm, Nd concentrations and $^{147}\text{Sm}/^{144}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of international CRMs measured in this study and literature values

CRMs	$\text{Sm}/\mu\text{g g}^{-1}$		$\text{Nd}/\mu\text{g g}^{-1}$		$^{147}\text{Sm}/^{144}\text{Nd}$		$^{143}\text{Nd}/^{144}\text{Nd}$	
	This Study	Refer. Value	This Study	Refer. Value	This Study	Refer. Value	This Study ($\pm 2\sigma$)	Refer. Value
BCR-2	6.512	6.543, ³ 6.534, ²¹	28.43	28.60, ³ 28.71, ²¹	0.1385	0.1383, ³ 0.1376, ²¹	0.512637 (07)	0.512632, ² 0.512641, ³
Basalt	6.508	6.612, ²⁵ 6.570, ³⁵	28.44	28.97, ²⁵ 28.70, ³⁵	0.1384	0.1380, ²⁵ 0.1384, ³⁵	0.512645 (07)	0.512624, ⁴ 0.512639, ⁹
	6.503		28.45		0.1382		0.512656 (08)	0.512638, ¹⁶ 0.512640, ²⁵
	6.504		28.46		0.1382		0.512631 (11)	0.512633, ³⁶ 0.512637, ³⁷
BHVO-2	6.113	5.984, ³ 6.03, ²²	24.69	23.72, ³ 24.39, ²²	0.1497	0.1502, ³ 0.1495, ²²	0.512994 (14)	0.512989, ² 0.512951, ³
Basalt	6.111	6.07, ³⁵	24.69	24.5, ³⁵	0.1496	0.1498, ³⁵	0.512999 (14)	0.512992, ⁹ 0.512979, ¹⁶
	5.986		24.10		0.1502		0.512991 (10)	0.512957, ³⁶ 0.512984, ³⁷
BIR-1	1.108	1.086, ³ 1.090, ²¹	2.412	2.310, ³ 2.380, ²¹	0.2778	0.2843, ³ 0.2774, ²¹	0.513102 (11)	0.513107, ³ 0.513079, ⁴
Basalt	1.124	1.100, ²⁶ 1.148, ³⁴	2.452	2.380, ²⁶ 2.490, ³⁴	0.2773	0.2794, ²⁶ 0.2787, ³⁴	0.513105 (14)	0.513085, ²⁶ 0.513108, ³⁴
	1.110		2.423		0.2769		0.513109 (15)	
AGV-2	5.493	5.502, ³ 5.460, ²²	30.25	30.47, ³ 30.42, ²²	0.1098	0.1092, ³ 0.1085, ²²	0.512789 (06)	0.512811, ³ 0.512776, ¹⁶
Andesite	5.383	5.514, ²⁵ 5.490, ³⁵	29.71	30.69, ²⁵ 30.50, ³⁵	0.1095	0.1086, ²⁵ 0.1088, ³⁵	0.512797 (05)	0.512781, ²⁵ 0.512755, ³⁶
W-2	3.192	3.205, ³ 3.234, ²²	12.74	12.75, ³ 12.71, ²²	0.1514	0.1520, ³ 0.1538, ²²	0.512522 (10)	0.512537, ³⁰ 0.512516, ²⁵
Diabase		3.290, ²⁵ 3.285, ²⁶		13.08, ²⁵ 13.00, ²⁶		0.1521, ²⁵ 0.1528, ²⁶		0.512510, ²⁶
DNC-1	1.444	1.44, ³⁸ 1.43, ^a	4.998	5.01, ³⁸ 5.02, ^a	0.1746	0.1722, ³⁸ 0.1738, ^a	0.512464 (10)	0.512466, ^a 0.512455, ^b
Dolerite								

^a C. F. Li 2011. unpublished data using ID-TIMS. ^b Z. C. Liu 2011. unpublished data using Neptune MC-ICP-MS.

Table 5 Sm–Nd isotope data for garnets and orthopyroxene for the high-pressure mafic granulites from Manjinggou, Hebei Province^a

Sample	Fraction	Sm/ppm	Nd/ppm	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\sigma$)	Initial $^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\sigma$)	Isochron Age ($\pm 2\sigma$)
MJ36	Grt	3.943	3.305	0.7223	0.518653 (21)	0.510042 (18)	1809.4 (6.7) Ma
	Grt	3.850	3.264	0.7141	0.518520 (12)		
	Grt	3.816	3.303	0.6995	0.518377 (19)		
	Opx	0.2453	0.8191	0.1810	0.512196 (29)		

^a Decay constant used for ^{147}Sm is $6.54 \times 10^{-12} \text{ year}^{-1}$. Isochronal age was calculated using a model 1 fit of the Isoplot V.3.23 program. Errors calculated for ages are based solely on external reproducibility of spiked standards (errors for individual analyses are negligible): $^{147}\text{Sm}/^{144}\text{Nd} = 0.5\%$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.003\%$, error correlations = 0.6.

3.5. Reproducibility of international CRMs

In order to evaluate and verify the present method, replicate analyses of six international CRMs from USGS were conducted for Sm–Nd isotope systems on Neptune MC-ICP-MS. One to four aliquots of CRMs rock powder went through the chemical procedure here, considering possible heterogeneity of the natural geological samples. The results of our analyses of the CRMs, together with data cited in the literature, are summarized in Table 4 for comparison.

As shown in Table 4, the analytical results of the Sm, Nd concentration and the Nd isotopic composition are in good agreement with the previously published values using ID-TIMS^{2–4,25,26,34–37} or ID-MC-ICP-MS^{21,22} (Sm, Nd concentrations agree within 1%; $^{143}\text{Nd}/^{144}\text{Nd}$ values agree within 22 ppm, 2σ). Some of the Sm and Nd replicate concentration data (e.g., AGV-2) have differences of about 1.5%, which is possibly related to sample heterogeneity. However, the replicate $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for AGV-2 agreed within 0.5% of each other. The other Sm and Nd replicate concentration data (e.g., BCR-2, BHVO-2 and BIR-

1) were in excellent accord (0.1%–0.8%) with each other. The internal run precision of $^{143}\text{Nd}/^{144}\text{Nd}$ from these reference materials was better than 15 ppm (2σ). Additionally, our obtained concentration and isotopic data of W-2 (Diabase) also agreed well with our previous data using ID-TIMS.²⁵ Likewise, we firstly report the Sm and Nd concentration and Nd isotopic composition of DNC-1 (dolerite), which is almost identical to those values using ID-TIMS or MC-ICP-MS by our colleagues (Table 4). As given in Table 4, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios determined for replicate analyses of the basalt, andesite, diabase and dolerite of CRMs are all within analytical uncertainty. Based on these data, our methodology is suitable and feasible for not only Sm–Nd isotope geochemical tracer and geochronological dating studies, but also the environmental provenance and process studies.

3.6. Comparison with other techniques

Since its advent in the early 1980s, ICP-MS has begun to be widely used for accurate concentration analysis of geological,

environmental and biological samples owing to ID-ICP-MS's inherent high sample throughput.¹ However, the principal limitation of this technique generally is being unable to obtain simultaneously high precision isotope ratios because of its inherent poor Gauss peak shape in quadrupole ICP-MS. As mentioned above, the classic ID-TIMS technique is still regarded as the benchmark technique for Sm and Nd concentration and Nd isotope composition analysis.^{2–4} Nevertheless, it well recognized that after tedious and lengthy chemical purification the purified Sm or Nd fractions must be loaded onto single or triple pre-degassed filaments for classic TIMS analysis, which usually requires several hours (typically 1 h) of analytical time. In addition, TIMS usually takes several hours (typically 4–5 h) to evacuate the thermal ionization source following exchange of the sample magazine. The relatively low efficiency can not meet the developing increasing demand in widespread applications of geochemistry and environmental sciences of Sm–Nd isotopic system.

Compared to quadrupole ICP-MS or TIMS, the main characteristics of MC-ICP-MS is its combination of magnetic sector multi-collector Faraday cup array and high efficient ICP ion source, which make it possibility for high precision isotope measurement as well as high sample throughput.^{5,6,12,15,17} As for relatively low content samples, it is well-known that Nd can be ionized more efficiently as NdO^+ than as Nd^+ on TIMS, which is generally involved with uncertainty results from oxygen corrections (*i.e.*, reductions of NdO isotopic ratios to Nd isotopic ratios) and the need for a lengthy and efficient chromatographic separation of Nd from not only Sm but also Ce and Pr due to isobaric interference of CeO^+ and PrO^+ on NdO^+ and therefore preferred for sub-nanogram level sample.^{2,3,7} Considering combination new generation of sample inlet system (*e.g.*, Aridus II or Apex) with MC-ICP-MS (*e.g.*, Neptune Plus, Nu Instrument), it will be becoming feasible for low concentration in the near future. Therefore, in terms of simplicity, feasibility and sample throughput for routine Nd isotope analysis, MC-ICP-MS has obvious advantages over previous techniques.

3.7. Application

The Sm–Nd isotopic system has been extensively used in the field of geochemical tracer and chronometer studies. In order to further validate and demonstrate the effectiveness and robustness of our present protocol, we exemplify the practical Sm–Nd dating application of garnet and orthopyroxene isochrons from the high-pressure mafic granulites of Manjinggou (MJ36), Hebei Province.³⁹ These samples were fully dissolved and separated using the previously described protocols. As shown in Table 5 and Fig. 3, using our established procedure, with *ca.* 100–150 mg separated mineral yielded Sm–Nd mineral isochron ages of 1809.4 ± 6.7 Ma, which is consistent within error of a zircon U–Th–Pb age of 1817 ± 12 Ma,^{39,40} confirming the accuracy of our methodology. This practical dating example has demonstrated the applicability and prospect of our methodology. Similarly, our current procedure is also suitable and feasible for extraterrestrial materials (*e.g.*, lunar rocks and meteorites) used in cosmochemistry research.

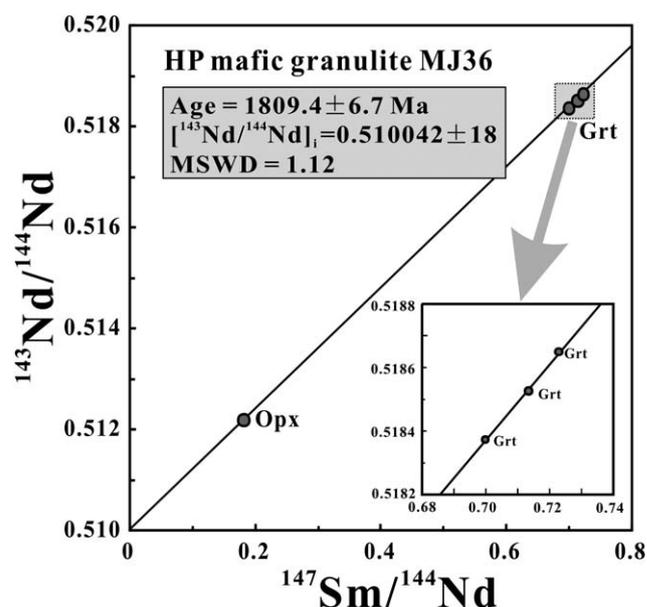


Fig. 3 Sm–Nd garnet and orthopyroxene isochrons of the high-pressure mafic granulites of Manjinggou, Hebei Province. Age errors are 2σ of a model 1 fit in the Isoplot program.⁴⁰ Individual errors are smaller than the size of the symbols. The MSWD means the Mean Square of Weighted Deviates.

4. Conclusions

We developed a simple, rapid and practical analytical method of highly reproducible analysis of Sm, Nd concentrations and Nd isotopic compositions in geological samples by ID-MC-ICP-MS, without comprising the precision and accuracy of the measurements in this paper. This technique is superior in terms of the analytical reproducibility or rapidity of analysis compared with quadrupole ID-ICP-MS or ID-TIMS techniques. Using this methodology, replicate analyses of international rock CRMs demonstrate that Sm and Nd concentrations can be reproduced to less than 1% and our $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is in good agreement with published values using isotope dilution methods. In addition to determining the concentrations of Sm and Nd by isotope dilution analysis, the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition can be accurately determined simultaneously. Therefore, the high actual sample throughput inherent to the MC-ICP-MS can be fully exploited for classic Sm–Nd isotopic system.

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