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Atomic Spectroscopy

HIGH-PRECISION MEASUREMENTS OF THE ^{143}ND/^{144}ND ISOTOPE RATIO IN CERTIFIED REFERENCE MATERIALS WITHOUT ND AND SM SEPARATION BY MULTIPLE COLLECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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We present a precise and accurate method for the determination of $^{143}Nd/^{144}Nd$ isotope ratio without Nd and Sm separation by multiple collector inductively coupled plasma mass spectrometry. We corrected instrumental mass discrimination by applying the natural constant $^{146}Nd/^{144}Nd$ ratio as an internal standard after isobaric interference correction of ^{144}Sm on ^{144}Nd using interference-free $^{147}Sm/^{149}Sm$ ratio for Sm mass fractionation. The present method was validated by duplicate analyses of several certified reference materials after dissolution and cation-exchange resin purification. The precision (2σ) of the $^{143}Nd/^{144}Nd$ ratio is less than 10 ppm (internal) and 20 ppm (external), respectively.

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INTRODUCTION

Neodymium isotope composition is an important geochemical tracer in solid earth sciences. The natural variation in the ^{143}Nd/^{144}Nd isotope ratio is derived from the radioactive α decay of ^{147}Sm to ^{143}Nd (half life = 106 billion years). Neodymium isotope composition has been widely used in geological, mantle process and the dating systems of Sm-Nd (Faure and Mensing 2005). Classical thermal ionization mass spectrometry (TIMS) is the common method for the precise measurement of Nd isotope ratio. Recently, multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a routine technique for Nd isotope measurement with

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higher sample throughput and comparable precision to classical TIMS (Walder, Platzner, and Freedman 1993; Halliday et al. 1995; Luais, Telouk, and Albarede 1997; Vance and Thirlwall 2002; Liang et al. 2003; Foster and Vance 2006; McFarlane and McCulloch 2007; Yang et al. 2007). However, these methods require an efficient chemical procedure to separate Nd from other rare earth elements (REEs).

Previous studies also reported reliable Nd data by measurement of Nd standard solutions spiked with pure Sm standard (Walder, Platzner, and Freedman 1993; Halliday et al. 1995; Liang et al. 2003; Foster and Vance 2006; McFarlane and McCulloch 2007). However, it is well-known that the mixture of pure standard Nd and Sm solutions is much different from the actual sample passed through cation-exchange resin. Luais, Telouk, and Albarede (1997) also obtained successfully Nd data using the Plasma 54 MC-ICP-MS for basalt samples after digestion and one-step cation resin purification. Unfortunately, they employed the ^{146}Nd/^{145}Nd ratio instead of ^{146}Nd/^{144}Nd ratio, which is commonly adopted in geochemistry and geochronology, to correct instrumental mass discrimination, in order to avoid the isobaric interference of ^{144}Sm on ^{144}Nd.

In this paper, we demonstrate that precise and accurate measurement of ^{143}Nd/^{144}Nd isotope ratio without Nd and Sm separation can be achieved using Neptune MC-ICP-MS for actual samples. Instrumental mass discrimination is corrected by the use of the natural constant ^{146}Nd/^{144}Nd ratio as an internal standard after isobaric interference correction of ^{144}Sm on ^{144}Nd using interference-free ^{147}Sm/^{149}Sm ratio for mass fractionation. Multiple replicate analyses of several international certified reference materials (CRMs) were conducted following the proposed procedure. The results show that reproducible ^{143}Nd/^{144}Nd isotope ratios with high precision can be obtained without Nd and Sm separation thus allowing for a simple and fast sample preparation procedure.

EXPERIMENTAL

Instrumentation

A Thermo Fisher Scientific Neptune MC-ICP-MS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing, China was employed in the static mode for isotope compositions of Nd determinations. Detailed descriptions for this instrument can be found elsewhere (Weyer and Schwieters 2003; Wu et al. 2006).

Standard and Reagent

All solutions were prepared using ultra-pure water with a resistivity of $18.2\,M\Omega\,cm^{-1}$ obtained from Milli-Q water purification system (Millipore, Bedford, MA, USA) and twice-distilled ultra-pure grade reagents were used in this study. Hydrochloric acid (GR grade) was prepared by sub-boiling distillation in a quartz still. Concentrated nitric and hydrofluoric acid (GR grade) were purified by sub-boiling distillation in a Teflon still. Concentrated perchloric acid (GR grade) was purified by decompressed distillation in a quartz distiller.

The international standard, La Jolla Nd, solution of $200\,\mu g\,L^{-1}$, was employed to evaluate instrument performance during analytical session. Eight international CRMs of rock powder, recommended by the United States Geological Survey

(USGS), and the Geological Survey of Japan (GSJ), were also used to validate the present method.

The conventional cation-exchange resin AG50 W-X12, 200–400 mesh size, was   75
obtained from Bio-Rad (Richmond, CA, USA).

Sample Preparation

About 100 mg of CRMs rock powder was weighed into a 7 mL round-bottom Savillex^{TM} Teflon screw-cap capsule. Two mL of concentrated HF plus 0.2 mL of concentrated HClO$_4$ were added and left sealed on a hot plate for a week. After com-   80
plete dissolution, the capsule was opened and evaporated to fumes at ca. 180°C. A 1 mL of 6 M HCl was added to the residue and dried. This procedure was repeated. The treatment with 6 M HCl completely converts fluorides into chlorides. When cool, the residue was dissolved in 1 mL of 2.5 M HCl. The capsule was sealed on a hot plate for overnight prior to chemical separation.   85

In order to evaluate the feasibility of isobaric interference correction of our Neptune, CRMs were purified deliberately on traditional cation-exchange resin without further Nd and Sm separation. The sample solution was taken up in 2.5 M HCl, centrifuged for 10 minutes at 5000 rpm, and loaded on a quartz column packed with a 2 mL resin bed of AG50 W-X12 (200–400 mesh) pre-conditioned with 2 mL of   90
2.5 M HCl. The column was washed with 2 mL of 2.5 M HCl, followed by 10 mL of 5 M HCl to remove the bulk matrix elements (major element, Rb and Sr). Finally, the REE fraction was eluted with 6 mL of 6 M HCl (Li, Chen, and Li 2007). The REEs were gently evaporated and taken up with 2% HNO$_3$ for Nd isotope analyses by MC-ICP-MS. Further dilution just prior to analyses was adjusted in order to   95
obtain appropriate beam intensity during mass spectrometric measurement. The full procedural blanks for this technique were <30 pg of Nd.

Mass Spectrometry

Nd isotope composition analyses were carried out on a Neptune MC-ICP-MS. A summary of typical instrument operating parameters is presented in Table 1. The   100
Nd isotopic data were acquired in static, multi-collector mode with low resolution. The Faraday cup configuration array is shown in Table 2. An aliquot of international standard solution of 200 μg L^{-1} La Jolla Nd was used regularly for optimizing the operation parameters and evaluating the reproducibility and accuracy of the instru-ment during the actual Nd isotope analytical session. Ion-lens settings were optimized   105
daily for maximum sensitivity and optimal peak shape. The REEs fractions taken up with 2% HNO$_3$ were aspirated into the ICP source using a Micromist PFA nebulizer in a free aspiration mode.

Before the measurement, the Neptune MC-ICP-MS was allowed to stabilize for at least one hour under normal conditions. The signal intensity of ^{146}Nd for   110
200 μg L^{-1} standard solutions was typically 1.5 volts. The sample solution was aspirated for 15 seconds to obtain stable signal before starting data acquisition. One run of the Nd isotopic ratio measurement consists of a baseline measurement at On Peak Zero (OPZ) for 60 seconds and 90 cycles of sample signal collection. The 90 cycles of signals are divided into 9 blocks to complete the 9 rotations of   115

Table 1. Typical instrument operating parameters

Thermo Finnigan Neptune MC-ICP-MS	
RF forward power	1304 W
Cooling gas	15.2 L/min
Auxiliary gas	0.8 L/min
Sample gas	0.7 L/min
Interface cone	Nickel
Mass resolution	400 (Low)
Acceleration voltage	10 kV
Sample uptake rate	50 μL/min
Uptake mode	Free aspiration
Spray chamber	Glass cyclonic
Sensitivity on ^{146}Nd	8 V/ppm
Sampling mode	ca. 15 min (9 blocks × 10 cycle)
Integration time	8 Sec/cycle
Baseline determination	ca. 1 min on peak in 2% HNO_3

the amplifiers connected to the Faraday cups in order to eliminate amplifier gain errors between different amplifiers (Weyer and Schwieters 2003; Chu, Yang, and Qiao 2006). For Nd measurement, the signal integration time for one cycle was 8 seconds.

RESULTS AND DISCUSSION

Mass Fractionation Correction

For radiogenic isotope systems, like Rb-Sr, Sm-Nd and Lu-Hf, the use of internal normalization for mass discrimination correction is a common practice in TIMS and MC-ICP-MS. In this study, the exponential law was used to assess the instrumental mass discrimination (Russell, Papanastassiou, and Tombrello 1978):

$$R_t = R_m(M_2/M_1)^\beta \tag{1}$$

Where R_t and R_m denote the true and the measured ratios of an isotope of exact mass M_2 to an isotope of exact mass M_1. Hence, β is the mass fractionation coefficient.

$$\beta = \ln(R_t/R_m)/\ln(M_2/M_1) \tag{2}$$

Table 2. Faraday cup configuration and potential isobaric interference

Faraday cups	L4	L3	L2	L1	Center	H1	H2	H3	H4
Nominal mass	142	143	144	145	146	147	149		
Measured elements	Nd	Nd	Nd	Nd	Nd				
Natural abundance (%)	27.13	12.18	23.80	8.30	17.19				
Interfering elements	Ce		Sm			Sm	Sm		
Natural abundance in (%)	11.08		3.1			15.0	13.8		

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β is calculated using an invariant isotope ratio with accepted values. In terms of Nd isotopes, $R_t = {}^{146}Nd/{}^{144}Nd = 0.7219$ (Wasserburg et al. 1981). Other measured Nd isotope ratios are corrected for mass bias using the β determined for ${}^{146}Nd/{}^{144}Nd$ (Chu et al. 2002).   135

Interference Correction

Usually, the isobaric and molecular interferences are main and potential interference on mass spectrometric measurement of Nd isotope by MC-ICP-MS. We found the Ba oxide and REE hydride (i.e., ${}^{130}Ba{}^{16}O$ and ${}^{142}Ce{}^{1}H$) interferences described by Luais, Telouk, and Albarede (1997) were negligible. As was noted by   140
Foster and Vance (2006), Nd isotopes interference problems are principally caused by Ce (${}^{142}Ce$ on ${}^{142}Nd$) and Sm (${}^{144}Sm$ on ${}^{144}Nd$, ${}^{148}Sm$ on ${}^{148}Nd$ and ${}^{150}Sm$ on ${}^{150}Nd$) (Table 2).

Cerium Interference. The interference of ${}^{142}Ce$ on ${}^{142}Nd$ is small in the La Jolla Nd standard and in separated samples from which the matrix was removed   145
(Pin and Zalduegui 1997); however, it is highly significant in REEs fraction for actual samples. Our previous work indicates that the influence of Ce on Nd isotope analyses is insignificant even for Ce/Nd ratio up to 3, which is typical in the natural geological materials (Yang et al. 2007). Therefore, it is unnecessary to make interference of ${}^{142}Ce$ on ${}^{142}Nd$ correction in this study, considering the radiogenic ${}^{143}Nd/{}^{144}Nd$ isotope   150
ratio of interest.

Samarium Interference. In this study the dissolved CRMs are purified using a one-column technique. The REEs fraction contains all REEs including Sm making the correction for ${}^{144}Sm$ on ${}^{144}Nd$ vitally important in order to obtain high quality ${}^{143}Nd/{}^{144}Nd$ data. Generally, the mass 144 subtraction equation of isobaric   155
interference of ${}^{144}Sm$ on ${}^{144}Nd$ can be expressed as:

$$({}^{144}Nd)_m = ({}^{144}Nd + {}^{144}Sm)_m - ({}^{147}Sm)_m$$
$$/({}^{147}Sm/{}^{144}Sm)_t \times (M_{147}/M_{144})^{\beta Sm} \qquad (3)$$

In the aforementioned equation, "m" and "t" mean measured and true value, respectively. Measuring the mass discrimination of Sm (βSm) for each sample is   160
essential for an accurate correction.

In previous study, McFarlane and McCulloch (2007) independently measured ${}^{147}Sm/{}^{149}Sm$ ratio of 1.06119 and ${}^{144}Sm/{}^{149}Sm$ ratio of 0.2103 by repeated analysis of a pure Sm standard solution and normalize to mean value for to correct for mass discrimination (βSm). They also pointed out that these values are $\sim 2\%$ lower than   165
TIMS values owing to the larger mass discrimination inherent to plasma-source mass spectrometers.

However, in this study, prior to Nd normalization using ${}^{146}Nd/{}^{144}Nd$ ratio of 0.7219 (Wasserburg et al. 1981), the interference-free ${}^{147}Sm/{}^{149}Sm$ ratio of 1.08680 (Dubois, Retali, and Cesario 1992) on the sample itself was measured to   170
determine Sm mass discrimination (βSm). Using a theoretical ${}^{144}Sm/{}^{149}Sm$ ratio of 0.22332 (Isnard et al. 2005) determined by MC-ICP-MS, the isobaric correction of ${}^{144}Sm$ on ${}^{144}Nd$ was then calculated. In the following paragraphs, our CRMs
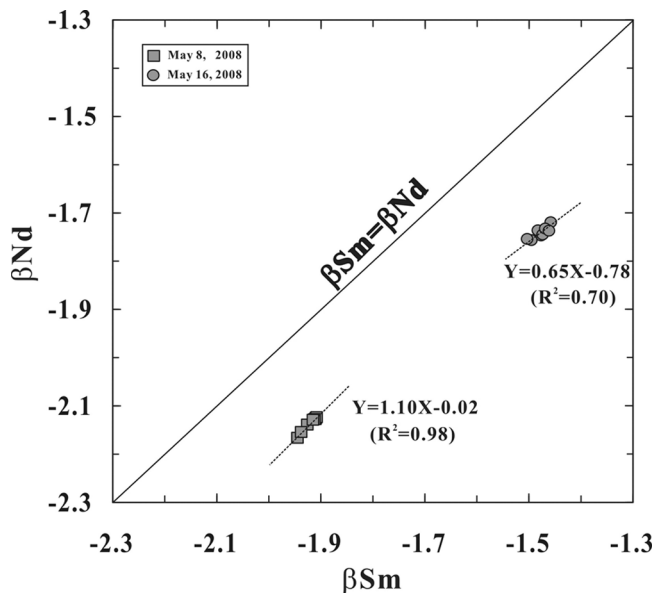
Figure 1. Variations of mass bias between Sm and Nd in different analytical session.

measurements indicate that mass discrimination of Sm and Nd (βSm and βNd) are not equal (Fig. 1). What is more, the βSm and βNd change during an analytical session (Table 3).

We employed the stable ^{145}Nd/^{144}Nd ratio as internal invariant and canonical value to evaluate the feasibility of our method (Foster and Vance 2006; McFarlane and McCulloch 2007). In the following sections, we show that our normalized ^{145}Nd/^{144}Nd ratios, after isobaric interference correction, agree well with the recommended value, within error, of 0.348415 obtained by TIMS (Wasserburg et al. 1981) (Table 3).

Isotope Analysis of La Jolla Nd

An international standard La Jolla Nd of $200\,\mu g\,L^{-1}$ was used for evaluating the reproducibility and accuracy of Neptune MC-ICP-MS for solution Nd isotope measurement. Over a two-year period, duplicate analyses of this standard obtain ^{143}Nd/^{144}Nd $= 0.511849 \pm 0.000014$ (2SD, N $= 68$) was normalized to ^{146}Nd/^{144}Nd $= 0.7219$ using exponential law for mass discrimination correction (Yang et al. 2007). This value is, within error, identical to the recommended results of $0.511856 \sim 0.511858$ by MC-ICP-MS (Vance and Thirlwall 2002).

Isotope Measurements of RCMs

In order to test the accuracy of this correction method, we performed ^{143}Nd/^{144}Nd isotope ratios analyses of CRMs from USGS and GSJ purified using the cation-exchange resin without further Sm and Nd separation thus retaining all its REEs. As can be seen from Figure 2 and Table 3, when Sm is corrected using

Table 3. Comparison results of ^{143}Nd/^{144}Nd isotope ratios: CRMs using MC-ICP-MS without Nd and Sm separation (this study) with published TIMS analyses of purified Nd fractions

CRMs	Fraction	βSm	βNd	^{143}Nd/^{144}Nd($\pm2\sigma$)	^{145}Nd/^{144}Nd($\pm2\sigma$)	Recommended Value[c] ^{143}Nd/^{144}Nd
AGV-2 (Andesite)	REE[a]	−1.93	−2.14	0.512773(10)	0.348417(06)	0.512755[d], 0.512791[e]
	REE[b]	−1.48	−1.75	0.512778(08)	0.348420(05)	
BCR-1 (Basalt)	REE[a]	−1.91	−2.12	0.512630(07)	0.348417(03)	0.512638[e], 0.512642[f], 0.512629[g], 0.512634[h]
	REE[b]	−1.49	−1.73	0.512634(06)	0.348413(04)	
BCR-2 (Basalt)	REE[a]	−1.95	−2.16	0.512641(04)	0.348413(02)	0.512633[d], 0.512637[e], 0.512632[f]
	REE[b]	−1.50	−1.75	0.512635(06)	0.348412(03)	
BHVO-2 (Basalt)	REE[a]	−1.91	−2.13	0.512984(06)	0.348416(04)	0.512957[d], 0.512984[e], 0.512989[f], 0.512983[i]
	REE[b]	−1.46	−1.72	0.512974(05)	0.348414(03)	
W-2 (Diabase)	REE[a]	−1.94	−2.15	0.512509(06)	0.348414(04)	0.512510[j], 0.512516[k]
	REE[b]	−1.51	−1.75	0.512513(08)	0.348413(05)	
JA-2 (Andesite)	REE[a]	−1.91	−2.12	0.512540(06)	0.348413(03)	0.512531[f], 0.512558[g], 0.512530[l]
	REE[b]	−1.48	−1.74	0.512560(09)	0.348413(04)	
JB-2 (Basalt)	REE[a]	−1.91	−2.13	0.513100(08)	0.348420(05)	0.513087[f], 0.513097[g], 0.513089[j], 0.513090[l]
	REE[b]	−1.47	−1.73	0.513102(10)	0.348416(06)	0.513110[m], 0.513085[n]
JB-3 (Basalt)	REE[a]	−1.92	−2.13	0.513045(07)	0.348418(04)	0.513062[f], 0.513048[g], 0.513049[j], 0.513092[l]
	REE[b]	−1.46	−1.74	0.513065(06)	0.348419(04)	0.513056[n]

[a]Measurement at May 8, 2008; [b]Measurement at May 16, 2008; [c]Determination purified Nd fraction by TIMS; [d]Raczek et al. 2003; [e]Weis et al. 2006; [f]Li et al. 2007; [g]Shibata et al. 2003; [h]Qi and Zhou 2008; [i]Weis et al. 2005; [j]Pin and Zaldegui 1997; [k]Pin et al. 1994; [l]Miyazaki and Shuto 1998; [m]Nohda and Wasserburg 1998; [n]Orihashi et al. 1998.
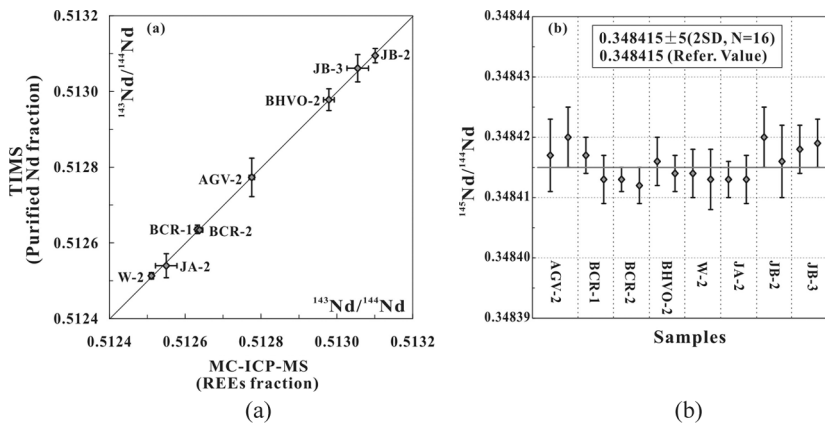
Figure 2. Comparison results of ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd isotope ratios of CRMs between recommended value and our data. The purified TIMS data is the average of the recommended value.

the described protocols, we can obtain accurate results for both stable $^{145}Nd/^{144}Nd$ and radiogenic $^{143}Nd/^{144}Nd$ isotope ratios which are in good agreement with those data of Sm purified Nd fractions measured previously by TIMS (Pin et al. 1994; Pin and Zalduegui 1997; Miyazaki and Shuto 1998; Nohda and Wasserburg 1981; Orihashi et al. 1998; Raczek, Jochum, and Hofmann 2003; Shibata, Yoshikawa, and Tatsumil 2003; Weis et al. 2005; 2006; Li, Chen, Li 2007; Qi and Zhou 2008). In addition, they show good overlap within error for different analytical sessions indicating our method robustness.

CONCLUSION

The performance of Neptune MC-ICP-MS for Nd isotope ratio measurement for CRMs without Nd and Sm separation is evaluated in this paper and shown to equal the precision and accuracy of those results obtained by classical TIMS. The $^{146}Nd/^{144}Nd$ internal standard corrects for mass discrimination, after isobaric interference correction of ^{144}Sm on ^{144}Nd using interference-free $^{147}Sm/^{149}Sm$ ratio for mass fractionation. Therefore, the Nd and Sm separation is not necessary, allowing for a simple and fast sample preparation procedure.

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