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Precise isotopic measurements of sub-nanogram Nd of standard reference material by thermal ionization mass spectrometry using the NdO^+ technique

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Abstract

The Sm–Nd isotopic system, one of the important techniques for dating and geochemical tracing, has been widely used in geosciences. Precise and accurate measurements of Nd isotopic ratios are more difficult to achieve for microsamples that contain less than 50 ng Nd, when routine Nd^+ technique is applied on thermal ionization mass spectrometer (TIMS). Compared to Nd^+ technique, the NdO^+ technique, owing to more efficient ionization, is a better choice for high precision measurements of Nd isotopic ratios of micro- or low-content samples. This study presents measurement results of sub-nanogram size samples of standard reference solution and rock-powder using NdO^+ technique on the latest TIMS (GV product IsoProbe-T). Sixteen rock-powder references and four reference solutions were measured both by NdO^+ and Nd^+ techniques for an evaluation of accuracy and precision of measurements obtained by the NdO^+ technique. Results show that analytical precision and reproducibility of NdO^+ measurements of sub-nanogram Nd is comparable with those obtained by the Nd^+ measurements of samples containing 200 ng Nd. Internal precision of the $^{143}Nd/^{144}Nd$ ratios achieved with both techniques is better than 0.003%. Our results show that the microsample NdO^+ technique is a very promising method for high resolution Sm–Nd geochronology and isotopic tracing.

Keywords: NdO^+ technique; Chromatography; Sub-nanogram sample; Isobaric interference

1. Introduction

The Sm–Nd isotopic system, owing to the chemical similarity of the two rare earth elements, exhibits potential applications in dating and especially in tracing geological and environmental processes. Due to the long half-life of ^{147}Sm (i.e., 106 billion years) the radioactive decay commonly leads to very slow increase of radiogenic ^{143}Nd and hence comparatively small change in $^{143}Nd/^{144}Nd$ ratios in most geological samples. Therefore, it is vital to achieve highly precise and accurate $^{143}Nd/^{144}Nd$ ratios to better distinguish variation in isotopic composition among geological samples. In the past decades, the analytical techniques for Nd isotopic measurement have been significantly improved. Measurements of Nd isotopic ratios with high precision and accuracy are mainly depended both on development of thermal ionization mass spectrometry (TIMS) and high efficient chromatographic technique. The TIMS has evolved into the most powerful analytical technique for precise and accurate measurement of Nd isotopic abundance, which is hardly accessible by using other means. Commonly, the Nd^+ technique is applied for samples that contain more than 50 ng Nd when measured by TIMS. Nevertheless, this technique cannot provide an analytical precision better than 0.01% for samples containing less than 50 ng Nd. To overcome this analytical problem, the NdO^+ technique was developed in the 1970s and was initially used to measure Nd isotopic composition of extraterrestrial material [1–3]. This technique is based on a more efficient ionization of NdO^+ compared to that of Nd^+. In view of imprecise oxygen correction and the immature TIMS technique, the NdO^+ technique has not been widely employed before the 1990s.

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In recent years, with the development of multicollector configuration of TIMS, Thirlwall has successfully measured 30 ng Nd sample size using the NdO^+ technique and made it practicable for geological purposes [4]. Griselin et al. [5] further developed the technique to precisely determine Nd isotopic ratios of clinopyroxene minerals and foraminifera, using samples containing only 1–5 ng Nd.

Nevertheless, precise measurements of Nd isotopic ratios by TIMS require an efficient chemical procedure to separate Nd from other rare earth elements (REE) as completely as possible. This separation is particularly important for measurements using the NdO^+ technique in order to minimize isobaric interferences such as LaO^+, CeO^+, PrO^+ and SmO^+. Previously reported procedures of Nd extraction from rock samples for NdO^+ measurements include high-pressure liquid chromatographic technique (HPLC) and α-hydroxyiso-butyric acid chromatographic technique (HIBA). Both techniques can achieve highly efficient separation of the REE, but are inconvenient for practical application and need special devices and rigorous experimental conditions. The HPLC technique requires a pressure controlling device and a special eluent that is composed of a mixed solution of acetic acid, methanol and HNO_3 [5]. Compared to HCl and HNO_3 acids, acetic acid and methanol are difficult to be purified. Methanol as a major component (69.30 wt.%) of the eluent solution is especially volatile and poisonous. The HIBA technique needs a good control of the pH value of the eluent solution and has to be performed in an acid-free environment [6,7]. The HIBA solution hence has to be calibrated immediately before every experiment. This technique is time-consuming and inconvenient.

In this study, the commercial Ln Spec (HDEHP-based) column separation scheme was used for the Nd extraction from other REEs [8]. The Ln Spec column is very suitable for Sm–Nd analysis. It can provide efficient separation of Nd from La, Ce and Sm, but has a shortcoming in Pr-Nd separation compared with separation schemes reported previously [5,7]. Using the Ln Spec columns, measured $^{141}Pr^{16}O^+/^{144}Nd^{16}O^+$ ratios of the samples can be as high as 0.1–0.5 when using TIMS. This is much higher than the recommended threshold value of 0.02 [4]. Nevertheless, results of systematic determination on five standard rock powder samples and one laboratory internal reference in this study demonstrate that the influence of $^{141}PrO^+$ isobaric interference on the accuracy of $^{143}Nd/^{144}Nd$ ratio is negligible after careful subtraction of isobaric interference, even when the $^{141}Pr^{16}O^+/^{144}Nd^{16}O^+$ ratio is closely to 0.5. Similar results have been obtained for sub-nanogram size standard solution and standard rock powder samples that contain less than 1 ng Nd. All analyses performed by the NdO^+ technique yield internal precision better than 0.003% that is comparable with results achieved on samples of more than 200 ng Nd measured in Nd^+ mode. This study aims simplifying the analytical procedure to broaden the application of the NdO^+ technique by a combination of the Ln Spec column for chemical separation and oxygen bleeding with constant pressure in the ion source of the TIMS during isotopic measurement. This combination makes the NdO^+ analytical technique different from the previous procedure in following aspects: (1) Using hydrochloric acid as elute solution rather than complex elute solution and special experimental device. (2) Redefining the threshold value of the Pr/Nd ratio of measurements related to isobaric interference of ^{141}Pr on ^{143}Nd. (3) Employing a multi-collector static measurement mode rather than multi-collector dynamic measurement mode to reduce uncertainty in subtraction of isobaric interferences.

2. Analytical procedure

2.1. Regents and resins

Water used in chemical procedures was deionized using a Milli-Q Element system (Millipore; resistance >18 MΩ). All acids (HCl, HF, HNO_3) were purified using sub-boiling distillation in PTFE distillers. $HClO_4$ is purified using decompress distillation in a quartz distiller. Phosphate acid was purified using chromatographic methods. The strongly acid cation resin AG50x12 (200 mesh particle size) manufactured by Bio-Rad company and the Ln Spec resin (50–100 mesh particle size) produced by Eichrom company were used for chromatographic extraction. The Ln Spec resin, conventional used for Sm–Nd separation is based on di-(2-ethylhexyl)-phosphoric acid (HDEHP) loaded on polymeric adsorbent.

2.2. Rock powder and solution references

Dissolved material from three international reference standards (Ames, JMC, Jndi-1) and a laboratory internal standard solution (LRIG-Nd) were used in this study. Reference solutions were prepared in four different concentrations (200 ppm, 1000 ppb, 500 ppb and 250 ppb). Decomposition of rock powder was performed using a solution of HF and $HClO_4$. About 100–200 mg of rock powder was used for each digestion in order to avoid inhomogeneity of the samples. For complete decomposition, samples were heated at 120 °C for 1 week. Then, the sample solution was evaporated at 120 °C and completely retransferred into solution using 6 M HCl. Sixteen international standard samples of rock powder, recommended by the Geological Survey of Japan (GSJ) and the Geological Survey of the United States (USGS), were decomposed following the above-mentioned procedure. After decomposition each sample solution was split into two aliquots. One aliquot, 90% in volume, was used for Nd isotopic measurements using the Nd^+ technique, while another aliquot of 10% in volume was firstly diluted to 700 ppb before measurements according to the NdO^+ technique were performed. Dilution volumes were calculated according to Nd-contents of the reference standards as previously reported [8–11].

2.3. Chemical separation procedures

The analytical procedure for Nd extraction consisted of two steps (Table 1) and both AG50Wx12 resin and LN column (HDEHP) were employed with HCl as eluent. In a first step, the REE fraction was separated from the bulk matrix using cationic resin AG50Wx12 (Bio-Rad) 100–200 mesh column [12,13]. The REE fraction extracted from the cationic resin AG50Wx12 was

Table 1
Chemical procedures for Nd separation and purification

Procedure	Eluting reagent	Eluting volume (ml)
Step 1		
Loading sample	2.5 M HCl	1.0
Rinse	2.5 M HCl	2.0 (0.5 × 4)
Rinse	5 M HCl	10.0
Eluting REE	6 M HCl	5.0
Step 2		
Loading sample	0.2 M HCl	0.2
Rinse	0.2 M HCl	1.0 (0.25 × 4)
Rinse	0.25 M HCl	5.5
Eluting Nd	0.25 M HCl	6.0

dried at 80 °C on a hot plate and then dissolved again in 0.2 ml 0.2 M HCl. In a second step, the REE fraction was loaded onto the Ln resin. The Ln column (column size 5A) was pre-eluted with 10 ml 6 M HCl and 10 ml deionised water. From our experience, it is noteworthy to mention that the 10 ml volume of deionised water should be strictly limited for the LN column in order to avoid loss of the HDEHP material, which will eventually lead to instability of the chemical procedure. Separation of individual light lanthanides from La to Nd was performed using 0.25 M HCl as eluent. Experiments have shown that the first 6.5 ml solution can elute about 99.5% La, 97% Ce, 75% Pr, and 25% Nd from the column. The main Nd fraction was collected in the next 6 ml solution that contains about 75% Nd, less than 2% Ce and 25% Pr; no Sm was detected in this fraction. About 90% and 75% of the total Nd can be acquired using AG50Wx12 and LN resin, respectively. REE concentrations were quantitatively measured using an ICP-MS (VG Plasmaquad PQII). The LN column exhibits excellent performance for extraction of Nd and effectively eliminates La, Ce, and most heavy REE elements, which can significantly influence the measurement of Nd isotopic ratios by the NdO^+ technique. However, the LN resin has a drawback in effective separation of Pr from Nd. Total procedural Nd blanks measured by the isotope dilution method were 10–20 pg ($n = 5$).

2.4. Sample loading methods

Prior to sample measurement, different loading techniques have been tested for NdO^+ measurement. Results have shown that a combination of Si-gel and H_3PO_4 solution is the best emitter for the NdO^+ technique on tungsten metal filaments. This emitter can yield stable ion beams of high intensity. Sandwich loading (loading sequence: emitter, sample, emitter) is particular suited for sub-nanogram samples. For this purpose, a 5-μl Si-gel and H_3PO_4 mixture solution was loaded on a degassed tungsten filament and dried at low temperature in a clean bench; the Nd sample was dissolved in 2-μl 2 M HCl and subsequently loaded and dried, before a 5-μl Si-gel and H_3PO_4 mixture solution was loaded again. After final drying, the filament was heated up slowly until glowing dull red for about three seconds. For Nd^+ measurement, 2-μl H_3PO_4 and the Nd sample dissolved in 2 M HCl were loaded on a degassed rhenium filament and dried in a clean bench at low temperature. The filament then was heated up very slowly until glowing dull red for about 3 s.

2.5. Mass spectrometry

An IsoProbe-T mass spectrometer manufactured by GV Company, and a Finnigan MAT-262 mass spectrometer were used for Nd measurements in order to compare analytical reproducibility both for the Nd^+ and the NdO^+ technique. We are fully aware that for close comparison of analytical data the same instrument should by used to rule out the instrument systematic errors. However, the IsoProbe-T in Beijing is generally used for Os isotopic measurements. Nd^+ measurements are normally performed using rhenium filaments, which can cause high Re blank which, in turn, would affect Os isotope measurements [14]. Consequently, Nd^+ measurements were performed on the MAT-262 mass spectrometer and the IsoProbe-T mass spectrometer was used only for NdO^+ measurements. Repeated measurements on the Ames Nd reference solution, performed in the MAT-262 mass spectrometer during the years 2005–2006, yield a mean $^{143}Nd/^{144}Nd$ ratio of 0.512141 ± 0.000019 (2S.D., $n = 100$). During NdO^+ analysis on the IsoProbe-T mass spectrometer pure oxygen gas was introduced into the ion source chamber via a needle valve in the source gas bleeding system. Oxygen pressure was constantly held between 5×10^{-7} and 5.2×10^{-7} mbar during pre-heating and measurement. Collector arrays of both mass spectrometers are given in Table 2.

3. Results and discussion

Calculation of Nd isotopic ratios using the NdO^+ technique involves subtraction of isobaric interferences, oxygen correction, and calibration of mass fractionation. These factors substantially influence accuracy and precision of $^{143}Nd/^{144}Nd$ ratios and therefore are crucial for the application of the NdO^+ technique.

3.1. Oxygen isotopic ratios and interference correction

For isobaric interference correction, oxygen isotopic ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) were statically measured in this study by using a ^{150}Nd spike solution (loaded with Si-gel and 1% H_3PO_4 on a tungsten filament) between 1150 and 1180 °C, similar to the conditions applied for measurements of NdO^+. In order to reduce influence of minor ^{150}Sm, the ^{150}Nd spike solution was purified with the Ln resin prior to analyses. Replicate analysis yielded mean $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios of 0.002059 ± 0.000006 and 0.0003896 ± 0.000004 (1S.D.), respectively. This shows that more reproducible results (about 2% variation) can be obtained by this technique using tungsten filaments. Mass fractionation of oxygen isotopes was independent from intensities of the ion beam during the measurement. The oxygen pressure in the ion source, the loading technique and the heating temperature of the filament have the highest influence on mass fractionation. Hence, these conditions should be kept constant for each analyses in order to avoid uncertainties

Table 2
Array of collectors of the IsoProbe-T and MAT-262 mass spectrometers

IsoProbe-T	L2	AX	H1	H2	H3	H4	H5	H6	H7
NdO^+	^{140}Ce ^{6}O	^{141}Pr ^{16}O	^{142}Nd ^{16}O	^{143}Nd ^{16}O	^{144}Nd ^{16}O	^{145}Nd ^{16}O	^{146}Nd ^{16}O	^{150}Nd ^{16}O	^{154}Sm ^{16}O
MAT-262									Nd^+
C2									^{143}Nd
C3									^{144}Nd
C4									^{146}Nd
C5									^{149}Sm
C6									^{150}Nd

of mass fractionation of oxygen isotopes, which can extremely influence the precision of $^{143}Nd/^{144}Nd$ ratio.

When comparing the results of oxygen isotope measurements of this study with those from literature [5,14–20,22,29], it can be observed that a wide range of up to 7% variation exists. Obviously, oxygen isotopic composition determined in different laboratories is not in accordance with each other. This variation strongly indicates that many factors can significantly influence oxygen isotopic ratios, such as filament material, heating temperature of the filament, sample loading technique, the purity of the oxygen gas used as well as the stability of the oxygen pressure in the ion sources [5,19]. Hence, precise measurement of oxygen isotopic ratios is essential for accurate determination of Nd isotopic ratios.

3.2. Potential isobaric interferences

Possible interferences of $REEO^+$, fluoride ions, and $HREE^+$ during NdO^+ measurement were examined and a correction method has been already proposed [4]. The major isobars are CeO^+, PrO^+, LaO^+, BaO^+, SmO^+, BaF^+, Tb^+, Er^+, Gd^+, and Dy^+. Following the proposed method [4], potential isobaric interferences of $REEO^+$, fluoride ions and $HREE^+$ were surveyed. Only CeO^+ and PrO^+ could be significantly observed during the measurement runs. The measured $^{140}CeO^+/^{144}NdO^+$ ratio was normally lower than the recommended value of 0.00035, but the measured $^{141}PrO^+/^{144}NdO^+$ ratio was higher than the recommended value of 0.02, owing to imperfect chemical separation of Pr from Nd. Calibration of mass fractionation was performed by using the exponential law and the $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$.

In an attempt to minimize isobaric interference of PrO^+ on NdO^+ isotopic ratios, more elaborate analyses were performed on five rock-powder standard references (BCR-1, BIR-1, JB-3, JGb-1, and JGb-2) and an internal laboratory standard solution (LRIG-Nd) that was artificially made from a mixture containing La, Pr, Ce, Sm and Nd. Results are graphically shown in Fig. 1. Samples containing about 5 ng Nd amount were chemically separated and purified by using the above-mentioned procedures. Repeated measurements were performed for each sample to eliminate uncertainty caused by single analysis. To reduce isobaric interferences, the samples were pre-heated for 15 min at 1050 and 1100 °C before data acquisition. During pre-heating, masses of 154, 155 and 170 (^{154}M, ^{155}M and ^{170}M) were hardly detected in the Faraday cups, suggesting less interferences of Ba, La, Sm, and Gd. Mass ^{156}M ($^{140}Ce + ^{16}O$) was detected in the beginning of warm-up at 1050 °C, but rapidly decreased with increasing temperature of the warm-up. During data acquisition, the $^{156}M/^{160}M$ ratio ($^{140}Ce^{16}O/^{144}Nd^{16}O$) was constantly lower than the recommended value of 0.00035 [4,5]. Variable intensities of mass ^{157}M ($^{141}Pr + ^{16}O$) were observed during the pre-heating and data acquisition processes due to the impure chemical separation procedure. At low heating temperature (<1050 °C), intensity of ^{157}M can more rapidly increase than that of ^{160}M ($^{144}Nd + ^{16}O$) due to significantly different emitting temperatures of NdO^+ and PrO^+. Nevertheless, ^{157}M ($^{141}Pr + ^{16}O$) can be effectively evaporated at heating temperature above 1150 °C that are suitable for the NdO^+ emission.

During pre-heating, the ion beam intensity of ^{157}M ($^{141}Pr + ^{16}O$) was relatively stable, but $^{157}M/^{160}M$ ratios ($^{141}Pr^{16}O/^{144}Nd^{16}O$) fluctuated from 0.5 to 0.05 after a quick decrease of the ^{157}M ion beam intensity. Nevertheless, reasonable values of $^{143}Nd/^{144}Nd$ ratio can be still achieved even for $^{141}Pr^{16}O/^{144}Nd^{16}O$ ratios as high as 0.5 (Fig. 1). Most of the data (mean values of the measured $^{143}Nd/^{144}Nd$ ratio on five reference rock-powders and one laboratory internal reference) are plotted with ±20 ppm error bars. Thirty-five measurements on four rock powder references BIR-1, BCR-1, JGb-2 and JB-3 all gave mean $^{143}Nd/^{144}Nd$ ratios similar to their reference values within the error bars, even for variable $^{157}M/^{160}M$ ratios (ranging from 0.1 up to 0.6). Only 2 out of 13 runs performed on rock-powder reference JGb-1 yielded $^{143}Nd/^{144}Nd$ mean ratios outside the error bar limit of the certified value, similar to results of eleven measurements performed on the LRIG-Nd laboratory internal reference. Apparently, no clear relationship between the $^{143}Nd/^{144}Nd$ and $^{141}Pr/^{144}Nd$ ratios was observed after subtraction of isobaric interferences and mass fractionation correction when the measured $^{157}M/^{160}M$ or $^{141}Pr^{16}O/^{144}Nd^{16}O$ ratio was not higher than about 0.5. Consequently, it can be concluded that isobaric interference from ^{141}Pr on ^{143}Nd is negligible if the $^{157}M/^{160}M$ ratios are in the range between 0 and 0.5 for measurements using the NdO^+ technique.

3.3. Calibration of mass fractionation

Normalization of Nd isotopic ratios was performed after subtraction of isobaric interferences and correction of oxygen isotopic interferences. In this study, calibrations were done by

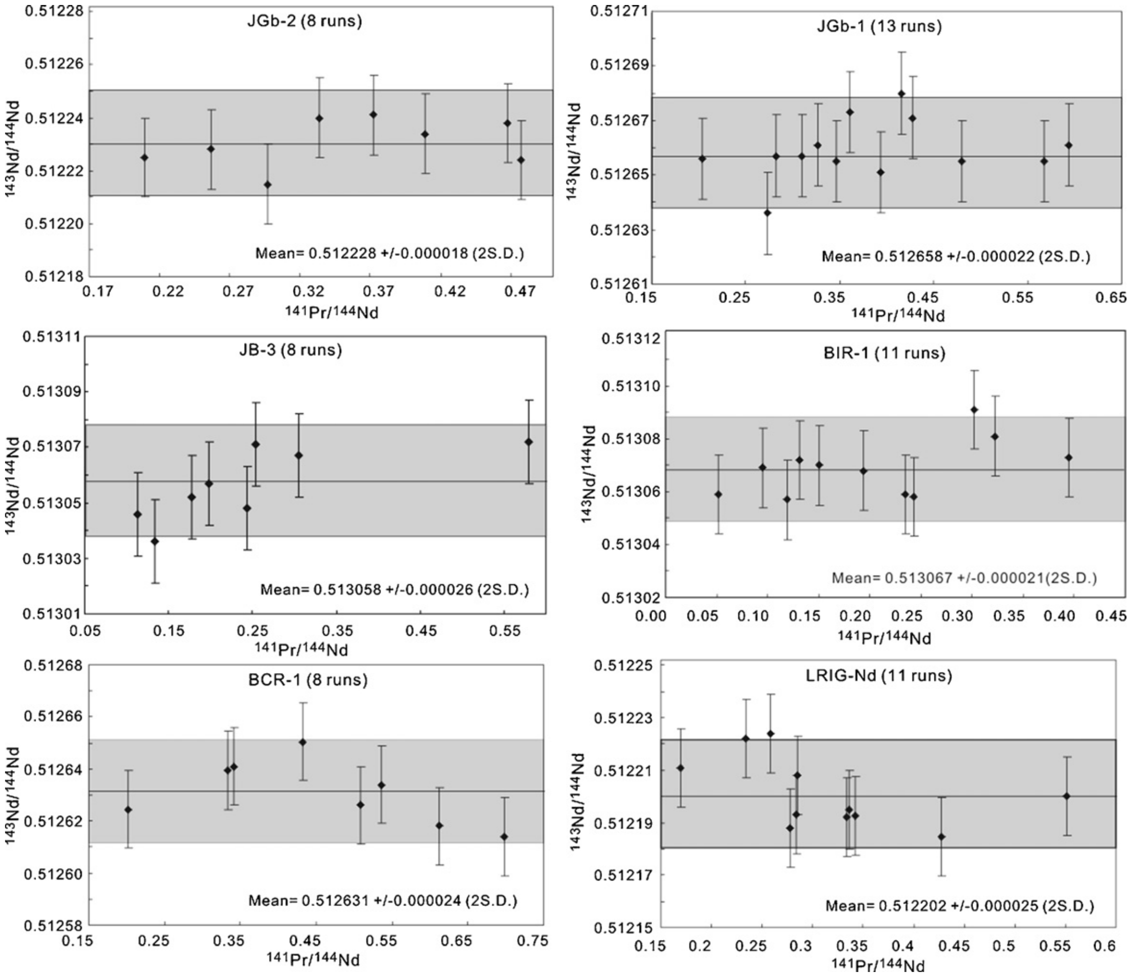

Fig. 1. Analytical results on rock-powder references BIR-1, BCR-1, JGb-1, JGb-2, JB-3, and LRIG-Nd (internal reference) measured by the NdO$^+$ technique.

using four different methods, i.e., linear, Rayleigh, exponential, and power laws on the measured results of twenty analyses on the reference solution Jndi-1 for a systematical comparison. All data of Nd isotopic ratios were normalized to ^{146}Nd/^{144}Nd of 0.7219. Results of the calculation show that the exponential and linear fractionation laws seem to be more suitable for calibration than the Rayleigh and power laws. Values of ^{143}Nd/^{144}Nd ratios obtained from the exponential and linear fractionation laws vary about ±15 ppm around a recommended value of 0.512115 for Jndi-1 [21]. Mean ^{143}Nd/^{144}Nd ratios obtained from twenty analyses are 0.512117 and 0.512119 calculated from the linear and exponential laws, respectively. Considering the quick decrease of ion beam intensity especially during the end of the measurements on the sub-nanogram Nd samples, mass fractionation likely did not show a linear trend, therefore, the exponential law should be the most suitable calibration method for the NdO$^+$ technique. This conclusion is also supported by the suggestions of Thirlwall [4] and Wasserburg et al. [16].

3.4. Reproducibility of measurements

External precision or reproducibility of a measurement as specified by instrument manufacturers is usually obtained over a short time period (e.g., during the instrument installation time). Thirlwall has pointed out that external precision cannot reflect any time-related changes in machine performance, perhaps resulting from minor change in ion optics, nor does it reflect any inter-operator bias [22]. Only long-term monitoring over months or years by using the same loading technique can reflect the true accuracy of the TIMS. In this study, repeated measurements ($n = 100$) of the Ames reference solution performed on the MAT-262 mass spectrometer over a period of 9 months yielded a mean ^{143}Nd/^{144}Nd ratio of 0.512141 ± 0.000019 (2S.D., $n = 100$), similar to the recommended values previously reported [23,28]. This indicates that actual accuracy of the ^{143}Nd/^{144}Nd ratio obtained by the Nd$^+$ technique using a multi-collection static mode on the MAT-262 fluctuates ±0.004% around the mean value in spite of internal precision of better than 0.003% (or <15 ppm) for each measurement run. The reproducibility of the ^{143}Nd/^{144}Nd ratio achieved during this study (±0.000012 to ±0.000026, 2S.D.) is similar to previously reported data [8,24–27]. Thirlwall has demonstrated that the multi-collection dynamic mode (MDM) can achieve much higher external precision than the multi-collection static mode (MSM) [4]. Thirlwall also achieved excellent reproducibility (±0.000008) with the MDM, which is substantial better than

Table 3
Analytical results of the standard solutions

Standard reference	Sample size (ng)	Measurement method	Analytical runs	$^{143}Nd/^{144}Nd$	Error (2S.D.)
JMC	200	Nd^+	20	0.511979	±0.000026
LRIG-Nd	500	Nd^+	12	0.512197	±0.000012
Ames	200	NdO^+	10	0.512138	±0.000020
Jndi-1	200	NdO^+	5	0.512113	±0.000024
Jndi-1	1	NdO^+	5	0.512123	±0.000026
Jndi-1	0.5	NdO^+	5	0.512122	±0.000013
Jndi-1	0.25	NdO^+	5	0.512121	±0.000020
Mean		NdO^+	20	0.512120	±0.000022
JMC	1	NdO^+	5	0.511992	±0.000026
JMC	0.5	NdO^+	5	0.511984	±0.000025
JMC	0.25	NdO^+	5	0.511986	±0.000022
Mean		NdO^+	15	0.511986	±0.000024
LRIG-Nd	1	NdO^+	5	0.512210	±0.000018
LRIG-Nd	0.5	NdO^+	5	0.512202	±0.000017
LRIG-Nd	0.25 ng	NdO^+	5	0.512189	±0.000012
Mean		NdO^+	15	0.512203	±0.000022

Measurements by using the Nd^+ and NdO^+ techniques were performed on a MAT-262 mass spectrometer and an IsoProbe-T mass spectrometer, respectively.

other reported data [22]. Compared to MSM, the MDM can yield much higher external precision owing to effective elimination of different collector efficiencies, but it is time-consuming and unbeneficial for measurements of sample quantities in the sub-nanogram range. Considering that reproducibility of 15–25 ppm for $^{143}Nd/^{144}Nd$ ratio are generally accepted during conventional Nd isotopic analyses in multi-collection static mode (MSM) on long-term scale, an error bar of ±0.004% or 20 ppm was defined as a criterion to be fulfilled for NdO^+ analyses in this study.

Four Nd isotopic reference solutions (Ames, Jndi-1, JMC and LRIG-Nd) were repeatedly measured with different sample sizes of 0.25, 0.5, 1, 200 and 500 ng by using the NdO^+ and Nd^+ techniques. Results given in Table 3 indicate variations of reproducibility ranging from 12 to 26 ppm. Mean values of the analytical results obtained in this study on the Ames and Jndi-1 solutions are similar to the previously published data of 0.512115 for the Jndi-1 [21] and 0.512124–0.512147 for the Ames [28–30]. Due to different production batches, different values are reported for the JMC Nd reference standard in previous reports. Therefore, analytical data of the JMC reference solution as well as the LRIG-Nd internal reference solution measured by using the Nd^+ and NdO^+ techniques are used for comparison. Results shown in Table 3 clearly display that the differences between $^{143}Nd/^{144}Nd$ ratios obtained by both techniques are smaller than 10 ppm, indicating reliability of the NdO^+ technique on sub-nanogram sample sizes. Further examination was done by measurements using the NdO^+ technique on 16 rock-powder references standards recommended by the USGS and the GSJ. Analytical results of the references and data cited from previous reports are given in Table 4. Samples of all measurement runs contained less than 1 ng Nd. $^{141}Pr/^{144}Nd$ ratios detected in all samples varied from 0.1 to 0.5 during the measurements. For comparison, results of the 16 reference samples obtained by the Nd^+ technique are also given in Table 4. Analytical data demonstrate that most of the samples, except JGb-2 and JR-1 reference samples, give results for NdO^+ measurements which are in good agreement with data previously reported for the Nd^+ technique (less than 15 ppm deviation). For samples JGb-2 and JR-1 25 ppm and 21 ppm deviation between the data obtained by the NdO^+ and Nd^+ techniques were observed and the reason for this remains unknown.

3.5. *Prospect of geochemical applications*

The combination of chemical extraction using the Ln Spec column and NdO^+ TIMS measurement, as outlined above, can provide highly precise $^{143}Nd/^{144}Nd$ ratios on sub-nanogram or microsamples. Compared to the conventional Nd^+ technique, this combination will offer more opportunities in many research fields in a wide range of earth sciences, such as geochemistry, geochronology, and environmental sciences. In marine geochemistry, planktonic and benthic foraminifera are usually considered as ideal research objects that potentially record isotopic composition of water masses in which they live and consequently, can provide high-resolution records of change of continental erosion and evolution of oceanic circulation [27], while Nd isotopic composition of seawater can further reflect mixing of water masses [41,42] and Nd exchange between dissolved and particulate phases [43–46]. Nevertheless, Nd-contents of both seawater and oceanic fauna/flora are low, usually less than 1 ppm. This requires an efficient analytical technique for highly precise measurements on such research objects of low Nd-contents. Another example of application is the geochronology of microsample which attracts increas-

Table 4
Analytical data on the USGS and GJS rock-powder standard references

Sample	^{143}Nd/^{144}Nd NdO$^+$ (0.7 ng)	^{143}Nd/^{144}Nd Nd$^+$ (200 ng)	Reference values [cited reference]
JB-2 Basalt	0.513062 (±12) 0.513076 (±16) 0.513088 (±15)	0.513087 (±12)	0.513085 [33]; 0.513090 [32] 0.513078–0.513100 [8] 0.513078–0.513055 [31] 0.513090 [35]; 0.513085 [34]
JB-3 Basalt	0.513067 (±15) 0.513057 (±14) 0.513048 (±12)	0.513062 (±10)	0.513054 [37]; 0.513046 [31] 0.513042 [8]; 0.513055 [8] 0.513035 [38]; 0.513037 [35]
JA-2 Andesite	0.512568 (±14) 0.512533 (±13) 0.512531 (±15)	0.512531 (±13)	0.512519[a]; 0.512550 [31] 0.512530 [33]
JA-3 Andesite	0.512848 (±12) 0.512829 (±12)	0.512835 (±10)	0.512843[a] 0.512859 [33]
JG-2 Granite	0.512210 (±14) 0.512217 (±15) 0.512240 (± 9)	0.512240 (±10)	0.512212 [33] 0.512219 [31]
JG-3 Granodiorite	0.512612 (±15) 0.512644 (±13)	0.512624 (±12)	0.512600[a]; 0.512617 [33] 0.512606 [31]
JG-1a Granodiorite	0.512334 (±16) 0.512331 (±14) 0.512350 (±13)	0.512354 (±12)	0.512345 [38]; 0.512365 [34] 0.512361[a]; 0.512383 [33] 0.512368 [8]; 0.512380 [8] 0.512377 [36]; 0.512378 [8]
JGb-1 Gabbro	0.512657 (±15) 0.512661 (±13) 0.512655 (±10)	0.512672 (±10)	0.512624 [31]; 0.512647 [34] 0.512635 [8]; 0.512653 [8] 0.512648 [33]
JGb-2 Gabbro	0.512240 (±14) 0.512227 (±15) 0.512239 (±13)	0.512210 (±8)	
JR-1 Rhyolite	0.512879 (±14) 0.512895 (±15) 0.512891 (±13)	0.512909 (±8)	0.512908 [33]; 0.512893 [31] 0.512896[a]
JR-2 Rhyolite	0.512918 (±12) 0.512917 (± 9)	0.512910 (±8)	0.512913 [35]; 0.512900[a]
JR-3 Rhyolite	0.512666 (±15) 0.512677 (±14)	0.512685 (±8)	0.512659[a]
BIR-1 Basalt	0.513069 (±15) 0.513054 (±16) 0.513070 (±15)	0.513064 (±9)	0.513069 [39]; 0.513088 [39] 0.513075 [8]; 0.513094 [8]
BHVO-2 Basalt	0.512984 (±11) 0.513002 (±14) 0.512996 (±12)	0.512989 (±9)	0.512957 [40]
BCR-1 Basalt	0.512654 (± 9) 0.512625 (±10) 0.512650 (±11)	0.512642 (±9)	0.512629 [40] 0.512645 [29]
BCR-2 Basalt	0.512614 (± 9) 0.512611 (±10) 0.512622 (±10)	0.512632 (±8)	0.512624 [40]

[a] O. Okano, personal communication.

ing interest in petrogenetic studies. A Rb–Sr isochron technique on single mica grains by means of a microsampler and low-blank chromatography has been reported [47,48]. This technique bears significant potential for in-situ geochronological studies. Compared to the Rb–Sr dating technique, the Sm–Nd isotopic system has been barely applied for geochronology of microsamples. Ducea et al. have firstly reported successful application of this technique on single minerals [49]. They separated and analyzed the Sm–Nd isotopic composition of core and rim fractions of garnet grains from high-grade metamorphic rocks and obtained different Sm–Nd ages corresponding to cooling rates of the geological terrain.

4. Conclusions

Precise Nd isotope measurements of microsamples in static multi-collection mode according to the NdO^+ technique can be achieved by employing improved analytical techniques such as oxygen bleeding into ion source of mass spectrometer and a special sample loading method. The quality of sub-nanogram Nd measurement of reference solution and rock-powder benefited from low-blank chromatography using the Ln resin column technique. Pre-heating of the samples before data acquisition can efficiently remove most of the isobaric interferences that are especially crucial for precise measurement by using the NdO^+ technique. Pr and Nd cannot be completely separated from each other with the Ln resin chromatography, nevertheless, systematic investigation using international rock-powder references has shown that isobaric interference of PrO^+ on NdO^+ can be efficiently subtracted if the $^{157}M/^{160}M$ ($^{141}Pr^{16}O/^{144}Nd^{16}O$) ratio is not higher than 0.5. Maintaining stable oxygen pressure of about 5×10^{-7} mbar in the ion source chamber during each sample run is crucial for the achievement of high-precision Nd isotopic ratios. The oxygen pressure influences not only the stability of ion beam but also the accuracy of the oxygen isotopic composition and hence the correction of isobaric interferences. Compared to previous methods, the analytical method presented in this study, i.e., combining Ln chromatography and the NdO^+ technique, offers the opportunity to precisely measure Nd isotopic ratios of samples containing less than 1 ng Nd. The achieved external precision (±0.000020) for sub-nanogram Nd samples is comparable to that obtained for sample loads >100 ng Nd using the Nd^+ technique.

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