Precise determination of Sm, Nd concentrations and Nd isotopic compositions at the nanogram level in geological samples by thermal ionization mass spectrometry

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In this paper, a high sensitivity method for measurements of Nd isotopes as NdO^+, on a TIMS using a single W filament with TaF_5 as an ion emitter is presented. Although analyzing Nd isotopes as oxides (NdO^+) is a well known technique, this is the first report to analyze Nd isotopic compositions as oxides using W filaments and the TaF_5 emitter. When 0.5–1 ng loads of a Neodymium isotopic reference reagent, JNdi-1, were measured using this method, the ion yields were found to be mostly in excess of 15% and could be as high as 32%. Internal precision on $^{143}Nd/^{144}Nd$ could be better than 10 ppm (2SE) for 1 ng JNdi-1 loads and better than 15 ppm (2SE) for 0.5 ng JNdi-1 loads; thirteen replicates of 0.5–1 ng JNdi-1 loads yielded a $^{143}Nd/^{144}Nd$ value of 0.512112 ± 0.000028 (2SD). Compared with the previously reported NdO^+ measurement method using the Re (or W) filaments + Silica-gel + H_3PO_4 loading techniques, this method has advantages including higher sensitivity, a more stable ion beam, and no need for oxygen gas to be bled into the ion source chamber. Sm isotopes were analyzed as Sm^+ using the W filaments and the TaF_5 emitter, and high sensitivity and good ion beam stability were also obtained. Several international rock reference materials, including an ultramafic rock reference material USGS PCC-1 that contains very low amounts of Sm and Nd, were analyzed with full column chemistry and the TaF_5 method, and the results of Sm, Nd concentrations and Nd isotopic data are in good agreement with the reported values. Combined with a highly efficient and low-blank column chemistry to separate Nd from Sm, Ce, and Pr, this method holds potential to analyze Sm, Nd concentrations and Nd isotopic compositions of highly depleted peridotites; very small aliquots of minerals such as garnets; extra-terrestrial materials of limited sample size; and environmental samples that contain very low quantities of Sm and Nd.

1. Introduction

The ^{147}Sm-^{144}Nd system has been widely used in geochemistry and cosmochemistry. As known, it is becoming increasingly important to determine Sm, Nd concentrations and Nd isotopic compositions on very small amounts of Sm and Nd. For example, Sharma et al.[1,2] have determined Sm-Nd isotopes in highly depleted peridotites which contain extremely low amounts of Sm and Nd. Ducea et al.[3] have determined Sm-Nd isotopes in micro-drilled domains of garnet single crystals. Amelin[4] was the first to analyze Sm-Nd isotopic compositions in single grain zircons. Amelin[5] has also ever conducted Sm-Nd isotope measurements in single titanite grains. Recently, Harvey and Baxter[6] have performed high precision Sm-Nd isotopic analysis of very small garnet samples and consequently obtained highly precise garnet Sm-Nd ages. In addition, Amelin et al.[7] have conducted Sm-Nd isotope measurements on small amounts of phosphate and chondrule fragments separated from ordinary chondrites and carbonaceous chondrite. Borg et al.[8] have determined Sm-Nd isotopes in limited amounts of minerals such

as olivine and pyroxene separated from Martian meteorites ALH77005 and LEW88516, which contain very low amounts of Sm and Nd.

High precision measurements for Nd isotopic compositions can be mainly achieved using multi-collector thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). In particular, MC-ICP-MS has demonstrated high efficiency for precise Nd isotopic measurements.[9–11] Furthermore, high precision Nd isotopic measurements by MC-ICP-MS can even be realized by directly measuring Nd isotopes in a Sm-Nd mixture without Sm-Nd separation.[10,11] It is also possible to directly analyze Nd isotopic compositions in minerals such as apatite, monazite, perovskite etc., which contain high concentrations of Nd, using a MC-ICP-MS combined with a laser ablation system (i.e. LA-MC-ICP-MS).[12,13] Generally, however, TIMS has a higher ion yield than MC-ICP-MS for elements such as Rb, Sr, Sm, Nd and Pb[14] ("ion yield" is the number of ions registered by the collectors divided by the number of atoms used for analysis; the combination of ionization–transmission–detection efficiency). In addition, analytical disadvantages of ICP-MS (e.g., larger instrumental mass fractionation, memory effects that cannot be neglected and more complicated isobaric interferences due to oxides and/or argides) suggest that isotopic analysis by TIMS is likely to produce more precise results.[15] Therefore, TIMS is still

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regarded as the most powerful analytical technique for isotopic analysis of small amounts of Nd.

It has been reported that high precision determination of Nd isotopes as Nd^+ by TIMS is difficult to be achieved at levels of several tens of nanograms of Nd (*e.g.* ref. 16). It is well known/ reported that Nd can be ionized more efficiently as NdO^+ than as Nd^+ on TIMS (*e.g.* ref. 6, 16–20). Although there are some disadvantages of the NdO^+ technique, which include uncertainty resulted from oxygen corrections (*i.e.*, reductions of NdO isotopic ratios to Nd isotopic ratios) and the need for an efficient chromatographic separation of Nd from not only Sm but also Ce and Pr due to isobaric interferences of CeO^+ and PrO^+ (on NdO^+), the NdO^+ method is preferred when sample sizes and/or Nd concentrations are small.

Normally, it is necessary to use an ionization enhancer to determine Nd isotopes as oxides by TIMS. The traditional method for NdO^+ measurement by TIMS is loading the sample on Re filaments and using Silica gel and H_3PO_4 as an ionization enhancer (a kind of emitter more commonly used for Pb isotope analysis by TIMS),[21,22] whilst bleeding a flow of oxygen into the ion source chamber during mass spectrometric measurements (*e.g.* ref. 17). Griselin *et al.*[20] have reported a high sensitivity method to measure Nd isotopes as NdO^+ by using W filaments with TaCl as an ion emitter. Recently, Li *et al.*[16,19] have performed precise Nd isotope analyses on sub-nanograms of Nd as NdO^+ by using single W filaments with Silica gel and H_3PO_4 as an ionization enhancer. More recently, Harvey and Baxter[6] have used Re filaments with tantalum oxide (Ta_2O_5)-phosphoric acid slurry as an activator to measure Nd isotopes as NdO^+, and achieved sub-10 ppm internal precision and 10–20 ppm long term external precision on 4 ng Nd loads.

In this work, we developed a method using single W filaments with TaF_5 as an ion emitter for sensitive Nd isotopic measurement as NdO^+ by TIMS. TaF_5 emitter is a solution containing Ta, HF, H_3PO_4 and HNO_3, also named Ta-HF or Ta–HF– H_3PO_4 activator in the literature. The Ta-HF emitter was firstly introduced by Birck[23] to analyze Sr isotopes. Since that study, TaF_5 has been widely used as an ionization enhancer for Sr isotopic measurements on TIMS (*e.g.* ref. 24). Recently, Charlier *et al.*[25] and Li QL *et al.*[26–28] have performed very sensitive Sr isotope ratio measurement using TaF_5 emitter. Yokoyama *et al.*[15] have used TaF_5 emitter to analyze Ra isotopic compositions with high sensitivity. In this study, we attempted to be the first to use W filaments with TaF_5 as an ion emitter to measure Nd isotopes as NdO^+. The results showed that the technique can be used to determine Nd isotopic compositions of sub-nanogram amounts of Nd with high precision. Compared with the traditional Re (or W) filaments + Silica-gel + H_3PO_4 loading techniques, this method has advantages including higher sensitivity, a more stable ion beam, and no requirement of oxygen to be bled into the ion source chamber. Compared with the method using Re filaments with Ta_2O_5 slurry as an ion emitter, which also showed high ionization efficiency, as Harvey and Baxter[6] recently reported, our method should be less analytical experience dependent.

In addition, this study has also shown that Sm can be analyzed as both Sm^+ and SmO^+ ions using W filaments with TaF_5 as an ion emitter with very high sensitivity. Compared with traditional methods which use Re filaments analyzing Sm as metal ions, both the TaF_5-Sm^+ and TaF_5-SmO^+ methods have a much higher ion yield. In this study, we analyzed Sm isotopes as Sm^+.

For comparison, the minimum quantity of Nd required for high precision Nd isotopic measurements as Nd^+ by using triple Re filaments was also tested in this study, and was evaluated to be about 10 ng.

Lastly, in order to demonstrate the reliability of the TaF_5 NdO^+ and Sm^+ measurement methods, several rock reference materials, including an ultra-mafic rock reference material, USGS PCC-1, which contains very low amounts of Sm and Nd, were analyzed with full column chemistry and the TaF_5 method. Except for the ultramafic rock, the sample load sizes of the Sm and Nd separated from the rock reference materials were only about 0.2 ng and 1 ng, respectively. The analytical results of Sm, Nd concentrations and Nd isotope ratios of these reference materials are in good agreement with the published values.

2. Experimental

2.1. Reagents and materials

W ribbon: 0.03 mm thick, 0.72 mm wide and 99.95% pure, H. Cross Company.

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

Milli-Q H_2O: 18.2 MΩ at 25 °C.

HCl, HF, $HClO_4$: Purified by sub-boiling distillation using Teflon apparatus.

H_3PO_4: Purified using cation exchange chromatographic methods.

H_3BO_3 (3% H_3BO_3 in 2.5 M HCl): 12 g high purity H_3BO_3 was weighed into a clean Teflon beaker, and dissolved with 300 mL Milli-Q water. The resulting solution was passed through a Bio-rad AG50W × 12 (200–400 mesh) cation exchange column to remove rare earth elements (REE). Then 100 mL of Teflon distilled 10 M HCl was added into the solution.

TaF_5 emitter: The Ta–HF–H_3PO_4 activator solution was prepared and purified using the method outlined by Charlier *et al.*[25] The Nd blank in 1 μL TaF_5 emitter was found to be lower than 0.1 pg.

Silica gel emitter: The Silica-gel + H_3PO_4 ionization enhancer was prepared using the method described by Gerstenberger and Haase.[22]

JNdi-1: Neodymium isotopic reference reagent;[29] JNdi-1 solutions of 100 ppm, 10 ppm, 1 ppm and 0.5 ppm were used.

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.

HEHEHP chromatographic column: 16 cm long × 5 mm *i.d.* with a 40 mL reservoir, packed with HEHEHP resin, ∼3 mL of resin bed volume; HEHEHP resin: particle size 120–200 mesh (75–125 μm), consisted of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) coated Teflon powder, made by Beijing Research Institute of Chemical Engineering and Metallurgy.

Rock powder reference materials: USGS BCR-2 (basalt), BHVO-2 (basalt), W-2a (diabase), BIR-1a (basalt), AGV-2 (andesite), GSP-2 (granodiorite), PCC-1 (peridotite); GSJ JA-2 (andesite), JB-3 (basalt).

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2.2. Sample digestion and column chemistry

2.2.1. Sample digestion. 30–50 mg of basaltic to granodioritic rock reference materials and 200 mg of ultramafic rock reference materials were weighed (to 0.01 mg precision) into Savillex Teflon-PFA vials, and spiked with appropriate amounts of mixed ^{149}Sm-^{150}Nd tracer solution (to 0.01 mg precision). The analytical uncertainty on Sm and Nd concentrations resulted from the weighing of the sample and the spike was smaller than 0.3% (2RSD) for a conservative estimate based on error propagation calculations. The added amounts of the spike were evaluated according to the previously reported Sm, Nd concentrations[30–35] in these reference materials, such that the resulting mixed ratios were around 4–8 for $^{149}Sm/^{147}Sm$ and around 0.4–0.6 for $^{150}Nd/^{144}Nd$. Consequently, the error magnification factor on isotope dilution calculations was <1.5 for Sm and <2.5 for Nd, respectively. The mixed ^{149}Sm-^{150}Nd spike solution was frequently calibrated using the CIT Sm-Nd solution standard[17] and USGS BCR-2 standard in our laboratory; the calibration error on Sm and Nd concentrations of the spike was evaluated to be smaller than 0.2% (2RSD).

The samples were dissolved on a hotplate at 100–120 °C using a mixed acid of 2 mL 22 M HF and 0.2 mL 70% $HClO_4$ for one week; the added amounts of these acids are excessive for the digestion of 200–300 mg of silicate rock samples. The dissolved sample solution was then evaporated to dryness and treated overnight with 4 mL of 6 M HCl at *ca.* 100 °C. Then, the solution was dried down again. The next step was different for andesitic-granodioritic rocks and mafic-ultramafic rocks. For andesitic to granodioritic rocks, the residues were dissolved with 2 mL of 2.5 M HCl on a 90 °C hotplate overnight. For Ca–Mg rich mafic to ultramafic rocks, the residues were dissolved with 2 mL of the 3% H_3BO_3 in 2.5 M HCl solution on a 90 °C hotplate overnight.[30,36] After the H_3BO_3 dissolution step, the fluoride gels formed during decomposition of mafic and ultramafic rocks were dissolved completely.

2.2.2. Column chemistry. The resulting solutions obtained from the former steps were centrifuged at 4000 rpm for 10 min and then the supernatant was loaded onto the pre-conditioned AG 50W × 12 columns for separation of REE from sample matrix. After rinsing four times with 0.5 mL of 2.5 M HCl, the column was washed with 9 mL of 5 M HCl. The REE was then stripped with 9 mL of 6 M HCl. Some heavy REE (HREE) was removed from Sm and Nd during this step, and the Sm, Nd recovery yields of this step were close to 100%.

The Ce, Pr, Nd, Sm separations were conducted using the HEHEHP chromatographic columns.[37] The column was pre-cleaned with Milli-Q H_2O, 30 mL 3 M HCl and 30 mL Mill-Q H_2O, and then conditioned with 2 mL of 0.07 M HCl. The REE fraction obtained from the cation exchange column was dried down, then taken up with 0.2 mL of 0.07 M HCl and loaded onto the HEHEHP columns. After rinsing four times with 0.2 mL of 0.07 M HCl, the La, Ce and 80% of Pr were eluted with 35 mL of 0.07 M HCl. The Nd was stripped with 12 mL of 0.14 M HCl. The fraction of Nd also contained *ca.* 20% Pr, less than 1% Ce and no detectable Sm. The recovery yield of Nd was higher than 90%. The Sm was then stripped with 8 mL of 0.4 M HCl. The recovery yield of Sm was higher than 95%.

For the basaltic to granodioritic rocks, the collections of Sm and Nd from the HEHEHP columns were dried down, and then re-dissolved with 2.5 M HCl to get a final solutions of about 0.2 ppm for Sm and 1 ppm for Nd to be ready for TIMS analysis. Dilution volumes were calculated according to Sm and Nd contents of the reference standards as previously reported.[30–35] For the ultramafic sample USGS PCC-1, the collections of Sm and Nd obtained from the HEHEHP columns were dried down and then ready for TIMS analysis.

2.3. Mass spectrometry

Isotopic measurements were performed on an IsoProbe-T thermal ionization mass spectrometer (GV instruments, England), installed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The instrument is equipped with nine Faraday cups, seven Channeltron ion counters, one Daly detector and one ETP multiplier.

2.3.1. Sample loading

2.3.1.1. NdO⁺ loading method. Firstly, 1 µL of Ta-HF activator was loaded onto the center of an out-gassed single tungsten filament and heated to near dryness with a filament current of 2 A. Secondly, 1 µL of Nd analyte (JNdi-1 standard solutions, or Nd solutions obtained from rock reference materials as described in section 2.2; for USGS PCC-1, dissolved with 1 µL 2.5 M HCl) was loaded onto the filament exactly on the top of the activator and then dried down with a filament current of 2 A. Once the sample was dry, the filament current was increased to 5 A, and then immediately turned down. To enhance ionization efficiency, the sample should be loaded onto as small an area as possible on the filament (about 1 mm × 0.7 mm square).

The sample loading on Re or W filaments with Silica-gel + H_3PO_4 emitter followed the method described by Li *et al.*[16] (only JNdi-1 standard was loaded).

2.3.1.2. Nd⁺ loading method. A triple Re filament configuration was used. All the three Re filaments were previously degassed. 1 µL of the JNdi-1 standard solutions was loaded onto as small an area as possible on one of the side Re filaments (about 1 mm × 0.7 mm square).

2.3.1.3. Sm loading. 1 µL of Sm analyte (Sm solutions obtained from rock reference materials as described in section 2.2; for PCC-1, dissolved with 1 µL 2.5 M HCl) was loaded onto an out-gassed single W filament, using the same method as that for NdO⁺.

2.3.2. Mass spectrometric measurements

2.3.2.1. NdO⁺ measurement method. The NdO⁺ method was conducted using a static collection of nine Faraday cups involving measurements of all Nd isotopes as NdO⁺. The cup configuration for NdO⁺ measurement is shown in Table 1. The peaks of masses 156 and 157 were measured to allow for corrections of CeO⁺ and PrO⁺ interferences (on NdO⁺). Mass 170 ($^{154}Sm^{16}O$) was monitored prior to data acquisition to confirm there were no SmO⁺ interferences.

Mass spectrometric measurement for NdO⁺ was conducted without oxygen being bled into the ion source chamber as oxygen bleeding had no effect on the NdO⁺ sensitivity.

Table 1 Faraday cup configuration for IsoProbe-T mass spectrometer

Faraday cup	L2	AX	H1	H2	H3	H4	H5	H6	H7
NdO$^+$ measurement									
Mass	156	157	158	159	160	161	162	164	166
Major isotopes	$^{140}Ce^{16}O$	$^{141}Pr^{16}O$	$^{142}Nd^{16}O$	$^{143}Nd^{16}O$	$^{144}Nd^{16}O$	$^{145}Nd^{16}O$	$^{146}Nd^{16}O$	$^{148}Nd^{16}O$	$^{150}Nd^{16}O$
Nd$^+$ measurement									
Mass	140	142	143	144	145	146	147	148	150
Major isotopes	^{140}Ce	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Nd	^{148}Nd	^{150}Nd
Sm measurement									
Mass	144	146	147	148	149	150	152	154	155
Major isotopes	$^{144}Sm + {}^{144}Nd$	^{146}Nd	^{147}Sm	$^{148}Nd + {}^{148}Sm$	^{149}Sm	$^{150}Nd + {}^{150}Sm$	^{152}Sm	^{154}Sm	^{155}Gd

When the ion source vacuum was better than 1×10^{-7} mbar, the measurement of NdO$^+$ ion beams could be started. Firstly, a warm-up program of about 5–10 min was run to raise the filament temperature gradually to about 1100 °C. Then, the filament current was raised very carefully ($\sim$0.001 A/sec) and an auto-focus routine was fully run to find and optimize the ion beam of $^{144}Nd^{16}O^+$. When a stable ion beam of $^{144}Nd^{16}O^+$ was reached as expected with a filament temperature of about 1150–1300 °C, the data acquisition was started. Normally, the $^{144}Nd^{16}O^+$ ion beam could reach 0.4–0.5 V for 0.5 ng Nd loads and 0.8–1 V for 1 ng Nd loads.

The measurement run consisted of 6 blocks of data with 20 cycles per block. The integration time per cycle was 8 seconds. Prior to data acquisition of each block, a peak-center routine was run, and then the baseline was measured at half masses with an integration time of 15 seconds. An auto-focus routine was run every three blocks to re-focus the ion beam.

Calculation of Nd isotopic ratios by the NdO$^+$ method involves corrections for isobaric interferences (*e.g.*, $^{141}Pr^{18}O$ on $^{143}Nd^{16}O$), reductions of NdO isotopic ratios to Nd isotopic ratios (*i.e.*, oxygen corrections), and mass fractionation corrections.[17] For spiked Nd samples, a further calculation for subtracting the contributions of the spike on the sample is needed.[17,38] Because the ^{143}Nd, ^{144}Nd, ^{146}Nd abundance in the highly-enriched ^{150}Nd spike (^{150}Nd, 97.8%) that we used are very low and, as mentioned above, the $^{150}Nd/^{144}Nd$ of the sample-spike mixture was limited to around 0.4–0.6, the uncertainty on $^{143}Nd/^{144}Nd$ resulted from spike subtractions was confirmed to be negligible.[17] The data reduction was performed by an off-line computer using a self-written EXCEL VBA (Visual Basic for Applications) macro program, within which interference corrections, oxygen corrections, spike subtractions, and lastly mass fractionation corrections using exponential law[17] with $^{146}Nd/^{144}Nd = 0.7219$ as a reference value[39,40] were performed cycle by cycle.

Oxygen isotopic compositions were measured using a high purity Pr ICP standard solution.[6,16,18,20] 1 ng Pr was loaded on W filaments for PrO$^+$ measurement using the same method as that for NdO$^+$. The cup configuration for the PrO$^+$ measurement was also the same as that for NdO$^+$. CeO and NdO interferences (on PrO) were monitored on masses 156 ($^{140}Ce^{16}O$) and 160 ($^{144}Nd^{16}O$) during the PrO$^+$ mass spectrometric measurements, and were confirmed to be insignificant. During the PrO$^+$ measurements, the $^{141}Pr^{16}O^+$ ion beam was maintained at 8–9 V to get about 3 mV $^{141}Pr^{17}O^+$ and 18 mV $^{141}Pr^{18}O^+$ ion beams, at filament temperature similar to that for NdO$^+$ measurement.

Each measurement run consisted of 120 cycles of data. The measured oxygen isotopic compositions are $^{17}O/^{16}O = 0.000365 \pm 0.000006$ (2SD, n = 10) and $^{18}O/^{16}O = 0.002056 \pm 0.000008$ (2SD, n = 10). These measured values were used to do oxygen corrections for all samples.

2.3.2.2. Nd$^+$ measurement method. The cup configuration for the Nd$^+$ measurement is shown in Table 1. Mass 147 was measured to monitor the interferences of Sm (on Nd).

For the Nd$^+$ measurement, the center filament current was raised to 4.2–4.5 A to get a filament temperature of about 1800 °C and then the current of the side filaments was raised to 1.0 A. Once this warm-up was completed, the current on the side filaments was raised very carefully ($\sim$0.001 A/sec) and an auto-focus routine was repeatedly run to find and optimize the ion beam of ^{144}Nd. When the ^{144}Nd ion beam reached a signal size as expected, the data acquisition was started. Normally, the ^{144}Nd ion beam could be higher than 0.5 V for 10 ng Nd loads.

The data acquisition process for Nd$^+$ was similar to that for NdO$^+$. Only JNdi-1 standard was measured by the Nd$^+$ method, mass fractionation corrections using exponential law[17] with $^{146}Nd/^{144}Nd = 0.7219$[39,40] as a reference value were performed cycle by cycle on-line.

2.3.2.3. Sm isotopic measurements. It was found that Sm could be ionized both as Sm$^+$ and SmO$^+$ with the W + TaF$_5$ loading method, with an Sm$^+$/SmO$^+$ of about 1.5–2 at the normal filament temperature for the NdO$^+$ analysis. Sm isotopic compositions were measured as Sm$^+$ in this study, as there are more isobaric interferences with SmO$^+$ method (*e.g.*, HREE, NdO on SmO) and the Sm$^+$ mode shows a higher sensitivity. The Faraday cup configuration for Sm$^+$ measurement is also shown in Table 1.

The Sm$^+$ warm-up was conducted in the same way as that for NdO$^+$ to find and optimize the ion beam of $^{147}Sm^+$. After a stable ion beam of $^{147}Sm^+$ was reached as expected, the data acquisition was started. Normally, the $^{147}Sm^+$ ion beam could reach 30–80 mV for 0.2 ng Sm loads.

The measurement run for Sm$^+$ consisted of 2 blocks of data with 15 cycles per block. The integration time per cycle was 8 seconds. Similarly, before each block, a peak center routine was run, and the baseline was measured at half masses with an integration time of 15 seconds. The isotope fractionation effect of $^{149}Sm/^{147}Sm$ was corrected cycle by cycle using $^{152}Sm/^{147}Sm = 0.56081$[39] as a reference value off-line as follows:[17] (1) the

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contribution of ^{152}Sm and ^{147}Sm of the spike on Sm samples was subtracted based on the measured ^{149}Sm/^{147}Sm ratios; (2) the spike-subtracted ^{152}Sm/^{147}Sm was used for isotope fractionation correction of ^{149}Sm/^{147}Sm. Because the ^{152}Sm and ^{147}Sm abundance in the highly-enriched ^{149}Sm spike (^{149}Sm, 97.7%) are very low, and the ^{149}Sm/^{147}Sm of the sample-spike mixture was limited to around 4–8, the error on ^{152}Sm/^{147}Sm resulted from spike subtraction is insignificant.[17] Consequently, better than 0.2% external precision (2RSD) on ^{149}Sm/^{147}Sm could be achieved.

3. Results

3.1. Nd Isotope measurement of trace amount of JNdi-1

In order to demonstrate the measurement efficiency and accuracy of the W + TaF$_5$ NdO$^+$ mass spectrometric analytical method, 0.5–1 ng of JNdi-1 Neodymium, was loaded for Nd isotopic measurement.

Normally, with 1 ng loads of JNdi-1, the ^{144}Nd^{16}O$^+$ ion beam could reach 0.8–1 V after the filament current was carefully raised and the ion beam was fully focused, and could last for more than 50 minutes. With 0.5 ng loads of JNdi-1, again after carefully increasing the filament current and fully focusing, the ^{144}Nd^{16}O$^+$ ion beam could normally reach 0.4–0.5 V and last for more than 50 minutes. The ion yield (number of ions of ^{144}Nd^{16}O$^+$ registered by the collector divided by the number of atoms of ^{144}Nd loaded on the filament)[1,4,14,15] of the TaF$_5$–NdO$^+$ method was evaluated to be mostly in excess of 15% and could be as high as 32%. Both sample loading techniques and filament conditions (e.g., filament shape, the resistance between the filament supports and the sample turret) used for each analysis could possibly influence the NdO$^+$ ionization efficiency. As summarized in Table 2, compared with previously reported NdO$^+$ measurement method, our method shows greater ionization efficiency.

The measured ^{143}Nd/^{144}Nd values for 0.5–1 ng JNdi-1 loads by the W + TaF$_5$ method are shown in Fig. 1a. Six 0.5 ng JNdi-1 loads and seven 1 ng JNdi-1 loads yielded ^{143}Nd/^{144}Nd values of 0.512112 ± 0.000034 (2SD) and 0.512112 ± 0.000026 (2SD), respectively, and the results were in good agreement with the reference value, 0.512116.[29] Internal precision on ^{143}Nd/^{144}Nd varied from 7 ppm to 13 ppm (2SE) for 1 ng JNdi-1 loads and from 9 ppm to 17 ppm (2SE) for 0.5 ng JNdi-1 loads. It could be concluded that the analytical reproducibility and accuracy of isotopic measurement on sub-nanogram amounts of Nd using the W + TaF$_5$ NdO$^+$ method are not compromised by the small sample size (Table 2).

The precision and reproducibility on sub-nanograms of Nd achieved by Li et al.[16] are comparable to the precision and reproducibility of our W + TaF$_5$ method. However, our W + TaF$_5$ method showed improvements on ionization efficiencies over the W + Si-gel method, which achieved a 2.0 V ^{142}Nd^{16}O$^+$ (~1.75 V ^{144}Nd^{16}O$^+$) beam lasting for 90 min on a 5 ng load of Nd standard[19] (Table 2). For comparison, we also measured Nd isotopes as NdO$^+$ using the Re (and W) + Si-gel loading method as previously reported[16] in this study. During the Re (and W) + Si-gel measurement runs, no oxygen was bled into the source, as we had not found the effect of oxygen flow on the intensity of the

Table 2 Comparison of NdO$^+$ isotopic measurement method using different sample loading techniques[a]

Reference	Sample	Method	Sample sizes (ng)	^{144}Nd ion beam	Ion yield (%)	Measured value	Internal Precision (2SE, ppm)	External precision (2SD, ppm)	Reference Value
This study	JNdi-1	W + TaF$_5$, NdO$^+$	1	0.8–1 V, 40–80 min	10–32	0.512112	7–13	26 (n = 7)	0.512116[29]
	JNdi-1	W + TaF$_5$, NdO$^+$	0.5	0.4–0.5 V, 40–80 min	10–30	0.512112	9–17	34 (n = 6)	
Li et al.[16,19]	JNdi-1	Triple Re, Nd$^+$	20–100	0.7–1.3 V	—	0.512120	9–15	27 (n = 8)	
	JNdi-1	W + Si-gel, NdO$^+$ oxygen flow to source	1	1.75 V on 5 ng Nd load, 90 min	~12	0.512123	15	26 (n = 5)	
Griselin et al.[20]	La Jolla	Re + Si-gel, NdO$^+$	5	0.5 V	—	0.511833	—	23 (n = ?)	0.511855[39]
	La Jolla	W + TaCl, NdO$^+$	5	0.9–1.4 V, 90 min	~8	0.511864	—	20 (n = 10)	
	La Jolla	Nd$^+$	100	—	—	0.511850	—	22 (n = 43)	
Amelin[4]	La Jolla	Re + Si-gel, NdO$^+$	0.3	—	4–18.7	0.511874	20–46	45 (n = 6)	
Harvey and Baxter[6]	Ames	Re + Ta$_2$O$_5$, NdO$^+$	4	1.8–2.2 V, ~40–>120 min	—	0.512132	4–11	20 (n = 83)	0.512138[16]

[a] All literature ion beam data are converted to ^{144}Nd. Some Nd$^+$ data are listed for comparison of the analytical reproducibility.

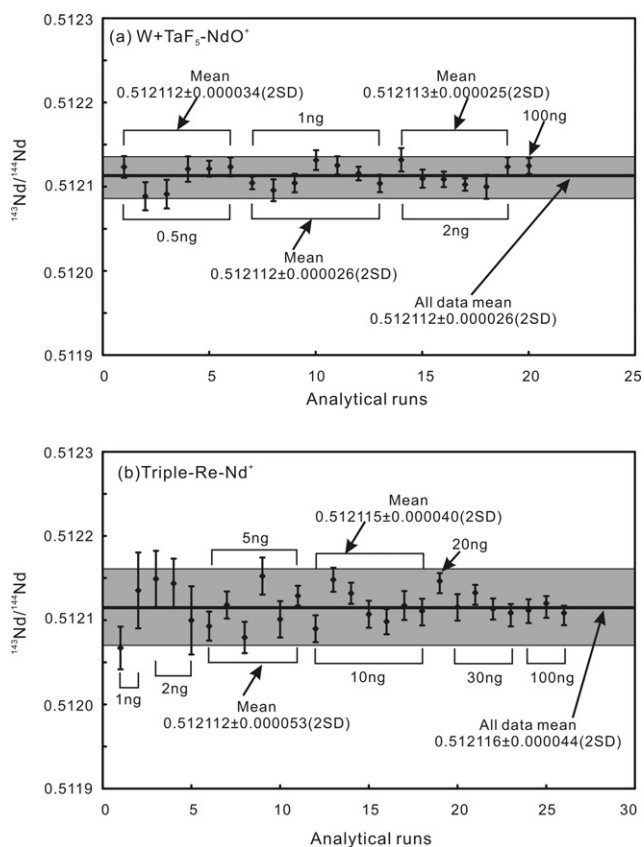**Fig. 1** $^{143}Nd/^{144}Nd$ results of JNdi-1 measured with the W + TaF5–NdO$^+$ (a) and Triple–Re–Nd$^+$ (b) methods. The error bars in each measurement method is given in 2SE. Solid horizontal line and shaded area represent mean and 2SD of all measurements, respectively.

NdO$^+$ ion beams. Consistent with the comparison result in Table 2, it was found that the ionization efficiency of Re (and W) + Si-gel methods was commonly lower than that of the TaF$_5$ method, with NdO$^+$ ion yields of mostly around 8–18%. Moreover, although more work is needed to be done for the comparisons, in general, it was found that our TaF$_5$ method showed an increased ion beam stability compared to the Si-gel methods.

For comparison, the minimum required amount of Nd for high precision isotopic measurement as Nd$^+$ by the Isoprobe-T mass spectrometer with a triple Re filament configuration was also tested in this study. The analytical results of JNdi-1 by Nd$^+$ method are shown in Fig. 1b. Although Shibata et al.[41] have reported that it is possible to obtain precise Nd isotopic data using Nd$^+$ measurement method on 2 ng loads of La Jolla Nd standard, in this study, it was found that it is difficult to obtain highly precise Nd isotopic data using the Nd$^+$ method on 1–5 ng of Nd loads. Six 5 ng JNdi-1 loads and seven 10 ng JNdi-1 loads yielded $^{143}Nd/^{144}Nd$ values of 0.512112 ± 0.000053 (2SD) and 0.512115 ± 0.000040 (2SD), respectively. The internal run precision on $^{143}Nd/^{144}Nd$ varied from 12 ppm to 22 ppm (2SE) on 5 ng Nd loads and from 13 ppm to 17 ppm (2SE) on 10 ng loads. It could be concluded that the minimum quantity of Nd for a high precision isotopic measurement by the Isoprobe-T TIMS was about 10 ng. Therefore, the sensitivity of the Nd$^+$ method was evaluated to be about 10–20 times lower than that of the TaF$_5$–NdO$^+$ method.

3.2. Sm-Nd isotope analyses of international rock reference materials

Eight international mafic to granodioritic rock reference materials of silicate rocks, selected to encompass a wide range of major element composition and analyte concentration, were analyzed. For Sm, Nd separates from these mafic to granodioritic rock reference materials, only about 1 ng of Nd and 0.2 ng of Sm were loaded for individual analysis. As shown in Table 3, the analytical results of the Sm, Nd concentrations and the Nd isotopic compositions mostly are in good agreement with the published values (Sm, Nd concentrations agree within 1%; $^{143}Nd/^{144}Nd$ values agree within 50 ppm). Some Sm and Nd concentration results (e.g., BHVO-2, GSP-2) have relative differences of about 2–3% compared to the literature data (Sm/Nd ratios still agree within 0.5% of the published data). The reason for these discrepancies is unclear, possibly related to sample heterogeneity because only 30–50 mg of the sample powders was digested. The internal run precision of $^{143}Nd/^{144}Nd$ on 1 ng loads of Nd separates from these reference materials was better than 15 ppm (2SD) (Table 3).

The analytical reproducibility for Sm, Nd concentrations and $^{143}Nd/^{144}Nd$ ratios on replicate 0.2 ng loads of Sm and 1 ng loads of Nd for a rock sample was evaluated using the USGS reference material BCR-2. As shown in Table 3, seven replicate measurements of 1 ng loads of Nd from a spiked BCR-2 sample yielded a $^{143}Nd/^{144}Nd$ value of 0.512641 ± 0.000018 (2SD) and a Nd concentration of 28.60 ± 0.01 ppm (2SD); two loads of 0.2 ng Sm from the same sample yielded a Sm concentration of 6.543 ± 0.001 ppm (2SD).

It can be concluded that, combined with a sufficiently low blank column chemistry procedure, it is possible to determine Sm, Nd concentrations and Nd isotopic compositions of samples containing sub-nanograms of Sm and Nd by using the W + TaF$_5$ NdO$^+$ and Sm$^+$ method, with analytical precision and accuracy comparable to those routinely obtained for larger sample sizes.

The Sm and Nd concentrations and Nd isotopes of an ultra-mafic rock reference material, PCC-1, were also measured using the W + TaF$_5$ NdO$^+$ and Sm$^+$ method. The amount of Nd and Sm separated from the 200 mg of PCC-1 was about 4.5 ng and 0.9 ng, respectively, as the recovery yield of our whole chemical procedure was about 90%. All the 0.9 ng of Sm and 4.5 ng of Nd individually separated from 200 mg of PCC-1 were loaded for each mass spectrometric measurement run. As shown in Table 3, two replicate analyses of 200 mg of PCC-1 yielded reproducible Sm, Nd concentration and $^{143}Nd/^{144}Nd$ values. Internal precision on $^{143}Nd/^{144}Nd$ of each analysis was better than 11 ppm (2SD), and the $^{143}Nd/^{144}Nd$ results agreed within analytical error with the results reported by Shibata et al.[41] The Sm, Nd concentration results showed relatively larger differences with previously reported values (Table 3), possibly due to powder heterogeneity of this peridotite standard or incomplete digestion of this sample in this study. We have not attempted to analyze less than 1 ng load of Nd from the peridotite standard with our TaF$_5$ method at the preliminary stage of this study, and further work needs to be done.

3.3. Total procedural blanks

Besides high analytical sensitivities, a low total procedural blank level is another prerequisite for the reliable Sm-Nd isotopic

Table 3 Analytical results of Sm, Nd concentrations and Nd isotopic ratios of international rock reference materials[a]

Sample	Sample weight (mg)	Separates Sm (ng)	Separates Nd (ng)	Loads Sm (ng)	Loads Nd (ng)	$^{140}Ce^{16}O/^{144}Nd^{16}O$	$^{141}Pr^{16}O/^{144}Nd^{16}O$	Sm (ppm) This study	Sm (ppm) Reference values	Nd (ppm) This study	Nd (ppm) Reference values	$^{143}Nd/^{144}Nd$ This study (±2SE)	$^{143}Nd/^{144}Nd$ Reference values
Basaltic-granodioritic rocks													
BCR-2 (Basalt)	54.26	321	1396	0.2	1	0.005	0.24	6.543		28.59		0.512642 ± 11	
				0.2	1	0.004	0.21	6.544		28.60		0.512635 ± 11	
					1	0.004	0.23			28.59		0.512655 ± 9	
					1	0.005	0.28			28.60		0.512634 ± 9	
					1	0.006	0.24			28.60		0.512632 ± 12	
					1	0.005	0.24			28.59		0.512638 ± 9	
					1	0.005	0.23			28.59		0.512652 ± 10	
Mean of BCR-2						0.005	0.24	6.543 ± 0.001 (2SD)	6.57[31]	28.60 ± 0.01 (2SD)	28.7[31]	0.512641 ± 18 (2SD)	0.512632 ± 12 (2SD, n = 3)[16]; 0.512633 ± 16 (2SD, n = 5)[42]; 0.512637 ± 12 (2SD, n = 11)[43]
BHVO-2 (Basalt)	54.87	291	1171	0.2	1	0.002	0.22	5.894	6.07[31]; 6.030[32]	23.72	24.5[31]; 24.39[32]	0.512951 ± 10	0.512994 ± 18 (2SD, n = 3)[16]; 0.512957 ± 11 (2SD, n = 3)[42]
BIR-1a (Basalt)	47.85	47	99	0.2	1	0.001	0.14	1.086	1.1[30]; 1.148[33]	2.310	2.38[30]; 2.490[33]	0.513107 ± 14	0.512984 ± 11 (2SD, n = 13)[43]; 0.513064 ± 18 (2SD, n = 3)[16]; 0.513094 ± 7 (2SE)[30]; 0.513113 ± 12 (2SE)[33]
W-2a (Diabase)	49.45	143	567	0.2	1	0.004	0.21	3.205	3.28[30]; 3.234[32]	12.75	13.0[30]; 12.71[32]	0.512537 ± 12	0.512516 ± 9 (2SE)[30]
GSP-2 (Granodiorite)	27.60	664	5231	0.2	1	0.012	0.28	26.73	26.2[31]	210.6	207[31]	0.511389 ± 12	0.511353 ± 5 (2SE)[42]; 0.511374 ± 3 (2SD, n = 5)[43]
AGV-2 (Andesite)	50.38	250	1382	0.2	1	<0.001	0.30	5.502	5.49[31]; 5.46[32]	30.47	30.5[31]; 30.45[32]	0.512811 ± 15	0.512755 ± 6 (2SE)[42]; 0.512791 ± 13 (2SD, n = 8)[43]
JA-2 (Andesite)	50.10	136	638	0.2	1	0.003	0.21	3.027	3.0[34]	14.14	14.2[34]	0.512576 ± 12	0.512544 ± 42 (2SD, n = 3)[16]
JB-3 (Basalt)	50.65	193	712	0.2	1	0.004	0.12	4.205	4.25[30]; 4.17[34]	15.63	15.8[30]; 15.9[34]	0.513089 ± 15	0.513057 ± 19 (2SD, n = 3)[16]; 0.513055 ± 7 (2SE)[30]; 0.513089 ± 20 (2SD, n = 4)[44]
Ultramafic rocks (Peridotite)													
PCC-1	202.79	0.9	4.8	0.9	4.5	0.012	0.38	0.00519	0.00551[41]; 0.0053[34]; 0.0050[35]	0.0265	0.0278[41]; 0.0282[34]; 0.0262[35]	0.512237 ± 9	0.512232 ± 26 (2SD, n = 10)[41]
PCC-1-duplicate	199.56	0.9	4.8	0.9	4.5	0.013	0.52	0.00523		0.0267		0.512221 ± 11	

[a] Sm and Nd separates obtained from column chemistry: (Mass of dissolved sample) × (Sm, Nd concentration) × recovery yield (~90%). Loads: sample load sizes for mass spectrometric measurements. The analytical precision on Sm, Nd concentrations is better than 1% (2RSD) for a conservative estimate. $^{143}Nd/^{144}Nd$ values were normalized to $^{146}Nd/^{144}Nd = 0.7219$ using exponential law. $^{143}Nd/^{144}Nd$ values are reported as times 10^6. 2SD means external precision, reported as times 10^6. 2SE means internal precision of individual analysis, reported as times 10^6.

analyses of samples containing extremely low amounts of Sm and Nd.

When Teflon sub-boiling distilled HCl, HF, and HClO$_4$ were used, and the procedure described in section 2.1 was used to purify the H$_3$BO$_3$ solution, typical total procedural blank values of Sm and Nd, including sample decomposition, H$_3$BO$_3$ dissolution step, column chemistry, and mass spectrometry, were found to be mostly lower than 3 pg and 10 pg, respectively. For this Nd blank level, at least 1 ng of Nd is required to be contained in a sample to suppress the blank effect to <1%.

4. Discussion

4.1. Oxygen corrections

The oxygen isotopic compositions must be determined accurately for the NdO$^+$ method to allow for precise oxygen corrections (i.e., reduction of NdO isotopic ratios to Nd isotopic ratios) and isobaric interference corrections such as PrO$^+$ on NdO$^+$. The oxygen ratios published in the literature vary up to a 7%.[6,20] The observed scatter in the data is big enough to significantly influence the oxygen correction on NdO$^+$ isotope ratios and, therefore, the accuracy and precision of the ^{143}Nd/^{144}Nd values.[6,17] For example, if oxygen isotopic ratios vary by 1% for ^{17}O/^{16}O and 2% for ^{18}O/^{16}O, the variation on the ^{143}Nd/^{144}Nd ratio resulted from oxygen correction is up to 18 ppm.

The variation in the oxygen isotope ratios is mainly due to the oxygen isotope fractionation effect relative to different loading techniques.[20] The oxygen pressure in the ion source, the type of ionization filament and the nature of the chemical emitter are all parameters that will influence the measured oxygen isotope ratios. For example, Griselin et al.[20] reported a 0.7% variation between ^{18}O/^{16}O measured on Re and W filaments. Liu et al.[45] showed that the oxygen isotope composition could vary significantly during a single analysis or between analyses, as a function of the oxygen pressure in the ion source chamber. Recently, Luguet et al.[46] reported that oxygen isotopic composition should be determined in-run for extremely high precision Os isotopic measurement by TIMS (measured as OsO$_3$$^-$).

The oxygen isotopic composition can be measured using a high purity Pr standard or highly enriched ^{150}Nd spike (e.g. ref. 6, 16, 17, 18, 20). Griselin et al.[20] reported that measuring oxygen isotopes using the ^{150}Nd method might produce more accurate results, possibly due to Ce, Nd impurities in the Pr solution. However, Harvey and Baxter[6] demonstrated that the offset of measured oxygen isotope ratios between Pr and ^{150}Nd method is insignificant.

As described in the section 2.3.2.1, the oxygen isotopes were measured using a high purity ICP Pr standard in this study. During a PrO measurement run, up to a 0.3% fractionation of the oxygen isotopes was found, however, the impact of this small variation in oxygen isotope ratio on the precision and accuracy of Nd isotopic ratios is insignificant[6,17] (<3 ppm). Better than 10 ppm (2SD) internal run precision on ^{143}Nd/^{144}Nd could be achieved on 1 ng of Nd loads (Table 2), also confirming that the effect of the oxygen isotope fractionation during a NdO measurement run is insignificant. According to the external precision obtained on oxygen isotope measurements in this study, the typical error on ^{143}Nd/^{144}Nd associated with oxygen corrections was evaluated to be smaller than 7 ppm (2SD), being much less than the long term precision. Finally, as stated above, precise and accurate ^{143}Nd/^{144}Nd data for both JNdi-1 and the rock reference materials could be obtained (Fig. 1a, Table 3), confirming that the measured oxygen isotopic ratios in this study are reliable.

Presumably, the phosphoric acid in the TaF$_5$ emitter is the main source of oxygen to form the NdO$^+$ ions with our method, because oxygen pressure in the ion source had no effect on the intensity of the NdO$^+$ ion beams. The same batch of the TaF$_5$ emitter was used for all the Nd isotopic measurements in this study. Care should be taken if a new batch of phosphoric acid is used to make the TaF$_5$ emitter.

4.2. Isobaric interferences on NdO$^+$

When measuring a mixed REE solution using the W filament + TaF$_5$ emitter sample loading method, it was found that Ce and Pr could also be ionized as CeO$^+$ and PrO$^+$ very efficiently. 1 ng loads of Pr could easily produce an up to 9 V ^{141}Pr^{16}O$^+$ ion beam with no sign of decay after 40 min, also suggesting Pr could be ionized as PrO$^+$ with very high efficiency. The evaporation temperature of CeO$^+$ and PrO$^+$ was found to be lower than that of NdO$^+$. Typically, for a rock sample, the ^{141}Pr^{16}O/^{144}Nd^{16}O and ^{140}Ce^{16}O/^{144}Nd^{16}O ratios decreased gradually with time before they reached a relatively stable level. Therefore, a pre-heating procedure is useful to get lower CeO/NdO and PrO/NdO ratios for a given sample.

Due to the isobaric interferences of CeO$^+$ and PrO$^+$ (on NdO$^+$) (for example, ^{141}Pr^{18}O$^+$ on ^{143}Nd^{16}O$^+$), precise measurements of Nd isotopic ratios using the NdO$^+$ technique for geological samples require an efficient chemical procedure to separate Nd from not only Sm, but also Ce and Pr, as completely as possible.[18,20] Currently, it is especially difficult to separate Nd from Pr completely. Cation exchange resin with α-hydroxyisobutyric acid (HIBA) as an eluent can achieve efficient separation of the REE (e.g. ref. 2, 6, 41, 47). However, the HIBA technique requires good control of the pH value of the eluent solution and has to be performed in an acid-free environment. Griselin et al.[20] have used anion-exchange chromatography and a special eluent composed of a mixed solution of acetic acid, methanol and HNO$_3$ to efficiently separate the Nd from other REE (including Pr). However, this method requires a pressure controlling device, and methanol, the major component of the eluent solution, is especially poisonous. The common method used for Sm-Nd separation of geological samples is HDEHP coated Teflon powder resin or Eichrom LN column with HCl as eluent (e.g. ref. 3, 4, 16, 30, 37). However, although Eichrom LN column or HDEHP coated Teflon powder resin is very efficient for Sm-Nd separation, it is not very efficient for Ce–Nd and Pr–Nd separation (especially Pr–Nd). Fortunately, Amelin et al.[7] reported that the impact of PrO$^+$ isobaric interferences on precision and accuracy of ^{143}Nd/^{144}Nd is very small when ^{141}Pr^{16}O$^+$/^{144}Nd^{16}O$^+$ is at level of about 0.1. More recently, Li et al.[16] reported that the influence of PrO$^+$ isobaric interferences on the accuracy of ^{143}Nd/^{144}Nd ratio is negligible after careful subtraction of isobaric interferences, even when the ^{141}Pr^{16}O$^+$/^{144}Nd^{16}O$^+$ ratio is close to 0.5.

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In this study, the HEHEHP chromatographic method as described in section 2.2 was used to separate Nd from Ce, Pr, and Sm. As shown in Table 3, the $^{140}Ce^{16}O^+/^{144}Nd^{16}O^+$ and $^{141}Pr^{16}O^+/^{144}Nd^{16}O^+$ ratios were mostly lower than 0.01 and 0.3, respectively. Although some Pr remained in the Nd samples, highly precise and accurate $^{143}Nd/^{144}Nd$ results were obtained for the rock reference materials. It could be concluded that the HEHEHP columns described in this study are suitable to separate Nd from other light REE (LREE) for high precision Nd isotopic measurement as NdO$^+$. Meantime, the results (Table 3) also showed that the interference corrections of PrO on NdO isotopes are robust, yielding the correct $^{143}Nd/^{144}Nd$ value for the rock reference materials even when $^{141}Pr^{16}O^+/^{144}Nd^{16}O^+$ is as high as 0.5.

Potential isobaric interferences such as BaF$^+$, LaO$^+$ (on $^{140}Ce^{16}O$ and $^{141}Pr^{16}O$, consequently on NdO), HREE (Gd, Tb, Dy, Er; on NdO) could be ignored because Ba, La, HREE are easy to be completely removed from Nd fraction by using the HEHEHP columns. Because the nine Faraday cups equipped on our IsoProbe-T mass spectrometer are not enough to measure all the NdO isotopes (for oxygen corrections) and monitor CeO, PrO, SmO interferences in one static collection (Table 1), potential isobaric interferences of SmO have not been monitored in this study. During the course of our NdO$^+$ analyses, no SmO$^+$ ion beam were found before and after the data acquisition of NdO$^+$. It implied that Sm was completely removed from the Nd fraction by the column chemistry. However, although it is easy to completely separate Nd from Sm by using the HEHEHP columns, it is a little dangerous to measure Nd isotopes without Sm interferences monitoring. An alternative method (e.g. ref. 6, 16) is to measure $^{154}Sm^{16}O$ (mass 170) for monitoring Sm interference, whereas not to measure $^{145}Nd^{16}O$ or $^{148}Nd^{16}O$; instead, using $^{145}Nd/^{144}Nd = 0.348$ or $^{148}Nd/^{144}Nd = 0.242$ for oxygen correction calculations. The method is reasonable due to the following reasons: (1) the only interfering effect of ^{145}Nd and ^{148}Nd is the very small $^{145}Nd^{17}O$ interference on $^{146}Nd^{16}O$ and the very small $^{148}Nd^{18}O$ interference on $^{150}Nd^{16}O$, respectively; (2) for spiked Nd samples, the small amounts of the ^{145}Nd and ^{148}Nd present in the highly enriched ^{150}Nd spike cause only very small changes in the $^{145}Nd/^{144}Nd$ and $^{148}Nd/^{144}Nd$ ratios.

$^{141}Pr^{16}O^+/^{144}Nd^{16}O^+$ values of 0.1–0.3 (Table 3) would shift $^{143}Nd^{16}O^+/^{144}Nd^{16}O^+$ from + 200 ppm to + 600 ppm; at this PrO interference level, the additional uncertainty to $^{143}Nd/^{144}Nd$, introduced by the PrO correction is less than 6 ppm if the precision of $^{18}O/^{16}O$ is better than 1%. As described in section 2.3.2.1, typical precision of $^{18}O/^{16}O$ was better than 0.5% (2RSD). Consequently, typical error on $^{143}Nd/^{144}Nd$ resulted from PrO correction should be smaller than 3 ppm, which is also much less than the long term precision.

CeO$^+$ isobaric interferences only have strong impact on $^{142}Nd/^{144}Nd$. $^{140}Ce^{16}O^+/^{144}Nd^{16}O^+$ of 0.01 would only generate a <1 ppm shift on $^{143}Nd^{16}O^+/^{144}Nd^{16}O^+$ and a <2 ppm shift on $^{146}Nd^{16}O^+/^{144}Nd^{16}O^+$. Therefore, the impact of CeO$^+$ isobaric interferences on the precision and accuracy of $^{143}Nd/^{144}Nd$ is negligible in this study.

4.3. Advantages of TaF$_5$-Sm$^+$ method

As mentioned above, Sm could be ionized both as Sm$^+$ and SmO$^+$ with the W + TaF$_5$ loading method, with an Sm$^+$/SmO$^+$ of about

1.5–2. It was found that, both the W + TaF$_5$ Sm$^+$ and SmO$^+$ methods showed much higher ionization efficiencies and an increased ion beam stability over the traditional methods that analyze Sm isotopes as Sm$^+$ using Re or Ta filaments (e.g., ref. 17), or as SmO$^+$ with Re + Si-gel loading technique (e.g. ref. 1, 2, 7). With 0.2 ng of Sm loads, the $^{147}Sm^+$ and $^{147}Sm^{16}O^+$ ion beam could easily reach 30–80 mV and 20–40 mV, respectively.

The Sm$^+$ method has advantages over the SmO$^+$ method because there are more isobaric interferences on SmO isotopes (e.g., HREE, NdO and GdO). With the Sm$^+$ method, $^{152}Sm/^{147}Sm$ could be used for isotope fractionation correction. Gd could affect Sm isotopes. Although large fraction of Gd should have been removed by the two stage column chemistry, minor Gd might remain in the Sm fraction. However, it was found that Gd was mainly ionized as oxide ions with the W + TaF$_5$ loading method at normal filament temperature for Sm$^+$ analysis. Meantime, the abundance of ^{152}Gd is very low (only 0.2%). Collectively, the potential isobaric interference of ^{152}Gd on ^{152}Sm was confirmed to be negligible. The $^{136}Ba^{16}O$ interference on ^{152}Sm could also be ignored as no Ba remained in the Sm fraction with the HEHEHP columns.

4.4. Sm-Nd determination for ultramafic rocks

Highly precise $^{143}Nd/^{144}Nd$ data of ultramafic rocks have been hard to obtain compared with other rock samples.[1,2,20,41] Firstly, rock powders are decomposed generally by a mixture of HF + HNO$_3$ or HF + HNO$_3$ + HClO$_4$ acids. Highly concentrated MgO (>35 wt %) in ultramafic rocks make large amounts of fluorides during decomposition, and Sm and Nd are strongly partitioned to the fluorides, resulting in low recovery yields of these elements.[41] Secondly, ultramafic rocks are depleted in trace elements (normally Nd < 100 ppb). Thus, it is hard to separate from ultramafic rocks an amount of Nd to generate an ion beam sufficient for precise isotopic measurements. On the other hand, the formed fluoride gel during decomposition of ultramafic rock often clogs the cation exchange column used for separation of REE from the sample matrix. Therefore, in the case of ultramafic rocks, it is very important to completely dissolve the fluorides formed during decomposition to increase the recovery yield of Sm and Nd. Normally, some techniques such as repeating fume treatments with HClO$_4$ have been proposed to decompose the fluorides;[48] however, decomposition takes a relatively long time and fluorides cannot be decomposed completely. It has been reported that breaking down fluorides with H$_3$BO$_3$ is a better choice to improve the recovery yields of the Sm and Nd during digestion of ultramafic rocks.[30,36]

In this study, boric acid was used to dissolve the fluorides formed during decomposition of ultramafic rocks. It was found that the amount of 3% H$_3$BO$_3$ solution used for an ultramafic rock was in proportion to the sample size, e.g., for 200 mg of ultramafic rock, about 2 mL of 3% H$_3$BO$_3$ solution should be used to dissolve the formed fluorides completely.

By using H$_3$BO$_3$ to dissolve the fluorides, precise Sm, Nd concentrations and Nd isotope ratios for 200 mg of ultramafic rock reference material PCC-1 containing only 0.0266 ppm of Nd were obtained (Table 3). It could be concluded that it is possible to obtain high precision data of Sm, Nd concentrations and Nd isotope ratios of highly depleted ultramafic rocks by combining

the H_3BO_3 assistant dissolution step and the TaF_5 NdO^+ and Sm^+ mass spectrometric measurement method.

4.5. Potential applications

The high sensitivity TaF_5 TIMS NdO^+ and Sm^+ measurement method, combined with a highly efficient and low blank column chemistry procedure, as outlined above, will offer more opportunities in many research fields in a wide range of earth sciences, such as geochemistry, geochronology, cosmochemistry, and environmental sciences.

Firstly, as mentioned above, the method can be used to analyze Sm-Nd isotopes of highly depleted ultramafic rocks. Ultramafic rocks occur in peridotite and ophiolite complexes or are obtained as mantle xenoliths on the Earth's surface or as extraterrestrial materials. The Sm-Nd isotope system of ultramafic rocks is an important tracer in geochemistry.[1,2,20,41] Due to the difficulties of Sm-Nd isotope analysis of ultramafic rocks, rare work has been done on Sm-Nd isotope systematics of ultramafic rocks. Our method will show advances for applications in this research field.

The second application field is to analyze Sm, Nd concentrations and Nd isotopes of very small aliquots of minerals, such as garnets or clinopyroxenes. For example, as Harvey and Baxter[6] recently reported, it is very important to obtain high precision Sm-Nd data on very small garnet samples, even micro-zones of a garnet single crystal, for high precision garnet Sm-Nd geochronology purpose. Meantime, Nd concentrations in garnet can be extremely low; frequently below 1 ppm, or even below 0.1 ppm, especially when partial dissolution methods are employed to completely remove REE rich inclusions (very important for high precision garnet Sm-Nd dating) (*e.g.* ref. 6, 49). Collectively, a low-blank, high sensitivity Sm-Nd isotope analytical method is very important for high precision garnet Sm-Nd geochronology. The TaF_5–NdO^+ and Sm^+ method should hold potential for applications in such research field.

The third application field of the method is to measure the Sm, Nd concentrations and Nd isotopic compositions of extra-terrestrial material of limited sample size. For example, as reported by Borg *et al.*,[8,50] the pyroxene, olivine and whole rock separated from Martian meteorites normally contain very low amount of Sm and Nd; meantime, only very limited sample size (*e.g.*, 10–30 mg) of the mineral and whole rock separates could be obtained; collectively, it is difficult to measure Sm, Nd isotopes in the mineral and whole rock separated from Martian meteorites for precise dating and cosmochemical research purpose (*e.g.* ref. 8, 50). The TaF_5–NdO^+ and Sm^+ method may hold potential for applications in this research field.

The fourth application field of the method is to measure the Sm, Nd concentrations and Nd isotopic compositions in environmental samples which contain low amounts of Sm and Nd. For example, planktonic foraminifera potentially record isotope composition of the water masses they lived in and consequently may provide a high resolution record of changing continental erosion and ocean circulation (*e.g.* ref. 51, 52); whereas Nd isotopic composition of modern surface seawater can reflect input of different water masses and Nd exchange between dissolved and particulate phases (*e.g.* ref. 53). Nevertheless, Nd contents in both foraminifera and seawater are very low. The TaF_5–NdO^+ method should show advantages on such research objects of low Nd quantities.

5. Conclusions

A high sensitivity method for measurements of Nd isotopes as NdO^+, and Sm isotopes as Sm^+ on TIMS using single W filaments with TaF_5 as an ion emitter has been developed. The method presented here can be used to measure isotopic compositions of sub-nanogram levels of Nd with high precision. It is the first report of using W filaments with TaF_5 as an emitter to analyze Nd isotopic compositions as oxides. Compared with the conventional method using the Re (or W) filaments with Silica-gel and H_3PO_4 as an emitter, the method shows advantages including higher sensitivity, a more stable ion beam, and no need for oxygen to be bled into the ion source chamber.

Given successful column chemistry, and sufficiently low blanks, the TaF_5 method holds potential for Sm-Nd isotopic analyses of highly depleted peridotites, very small aliquots of minerals such as garnets and clinopyroxenes, extra-terrestrial materials of limited sample size and environmental samples containing extremely low content of Sm and Nd.

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