

Precise Determination of Sm and Nd Concentrations and Nd Isotopic Compositions in Highly Depleted Ultramafic Reference Materials

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In this study, a high-precision method for the determination of Sm and Nd concentrations and Nd isotopic composition in highly depleted ultramafic rocks without a preconcentration step is presented. The samples were first digested using the conventional HF + HNO₃ + HClO₄ method, followed by the complete digestion of chromite in the samples using HClO₄ at 190–200 °C and then complete dissolution of fluoride formed during the HF decomposition step using H₃BO₃. These steps ensured the complete digestion of the ultramafic rocks. The rare earth elements (REEs) were separated from the sample matrix using conventional cation-exchange chromatography; subsequently, Sm and Nd were separated using the LN columns. Neodymium isotopes were determined as NdO⁺, whereas Sm isotopes were measured as Sm⁺, both with very high sensitivity using single W filaments with TaF₅ as an ion emitter. Several highly depleted ultramafic rock reference materials including USGS DTS-1, DTS-2, DTS-2b, PCC-1 and GSJ JP-1, which contain extremely low amounts of Sm and Nd (down to sub ng g⁻¹ level), were analysed, and high-precision Sm and Nd concentration and Nd isotope data were obtained. This is the first report of the Sm-Nd isotopic compositions of these ultramafic rock reference materials except for PCC-1.

Keywords: ultramafic rocks, sample digestion, isotope dilution thermal ionisation mass spectrometry, isotope ratios, reference materials.

Dans cette étude, une méthode de haute précision pour la détermination des concentrations en Sm et Nd et des compositions isotopiques du Nd, sans étape de pré-concentration préalable, dans les roches ultramafiques fortement appauvries est présentée. Les échantillons sont d'abord digérés avec le procédé classique associant HF + HNO₃ + HClO₄, suivie de la digestion complète de la chromite des échantillons en utilisant HClO₄ à 190–200 °C, puis de la dissolution complète du fluorure formé au cours de l'étape de décomposition au HF et ceci à l'aide de H₃BO₃. Ces étapes ont permis la digestion complète des roches ultramafiques. Les terres rares (REE) ont été séparées de la matrice de l'échantillon en utilisant la chromatographie classique d'échange de cations; ensuite, Sm et Nd ont été séparés en utilisant les colonnes LN. Les isotopes du néodyme ont été déterminés comme NdO⁺ alors que les isotopes du Sm ont été mesurés comme Sm⁺, tous les deux avec une très grande sensibilité à l'aide de simples filaments au tungstène et avec TaF₅ comme émetteur d'ions. Plusieurs roches ultramafiques de référence fortement appauvries dont USGS DTS-1, DTS-2, DTS-2b, PCC-1 et GSJ JP-1, qui contiennent des quantités extrêmement faibles de Sm et Nd (jusqu'à des teneurs de l'ordre du ng g⁻¹), ont été analysées, et des concentrations en Sm et Nd ainsi que des données isotopiques du Nd de haute précision ont été obtenues. Il s'agit des premiers résultats concernant les compositions isotopiques en Sm-Nd de ces roches ultramafiques de référence à l'exception de PCC-1.

Mots-clés : roches ultramafiques, digestion d'échantillon, spectrométrie de masse à ionisation thermique et dilution, isotopique, rapports isotopiques, matériaux de référence.

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Ultramafic rocks such as peridotite occur in ophiolite complexes, massif peridotites and abyssal peridotites and are present in mantle xenoliths and extraterrestrial materials.

It is well known that Sm and Nd isotopes are very important tracers in constraining the origin and petrogenesis of highly depleted ultramafic rocks (Sharma *et al.* 1995, Sharma and

Wasserburg 1996, Griselin *et al.* 2001). However, precise determination of Sm and Nd concentrations and Nd isotopic compositions from such rocks is very difficult for the following reasons: (1) the concentration of Sm and Nd in these materials is commonly extremely low (normally $< 1 \mu\text{g g}^{-1}$ to several ng g^{-1}) (Sharma *et al.* 1995, Sharma and Wasserburg 1996, Griselin *et al.* 2001, Amelin and Rotenberg 2004), rendering it very difficult to separate sufficient Sm and Nd from samples for highly precise mass spectrometric measurements; (2) Sm and Nd are strongly partitioned into fluorides (mainly MgF_2) produced by $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ decomposition of abundant MgO ($> 35\%$ m/m) in ultramafic rocks, resulting in low recovery yields for these elements (Sharma *et al.* 1995, Sharma and Wasserburg 1996, Yokoyama *et al.* 1999, Shibata and Yoshikawa 2004, Qi *et al.* 2005, Sun *et al.* 2013), and making highly precise measurement of Nd isotopes more challenging. Additionally, the fluoride gels that are formed often clog the cation-exchange columns used for the separation of rare earth elements from the sample matrix; (3) some accessory minerals such as chromite found in some ultramafic rocks are difficult to completely digest using $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ (Jain *et al.* 2000, Nakamura and Chang 2007, Sun *et al.* 2013). As a result of these analytical difficulties, there are very few publications dealing with Sm-Nd isotopes in ultramafic rocks, although they are vitally important in understanding mantle processes (Griselin *et al.* 2001). For the same reason, there are only very rare reports on Sm and Nd isotopes in highly depleted ultramafic rock reference materials.

To achieve high-precision measurement of Nd isotopes in highly depleted ultramafic rocks, the following two aspects are required: (1) a high-sensitivity mass spectrometric method to realise highly precise isotopic measurements on extremely low amounts of Nd and Sm and (2) a highly efficient and low-blank chemical procedure to completely decompose ultramafic rocks with high Sm and Nd recovery yields.

It has been widely reported that measuring Nd isotopes as NdO has high sensitivity (Wasserburg *et al.* 1981, Thirlwall 1991, Griselin *et al.* 2001, Li *et al.* 2007, Chu *et al.* 2009, Harvey and Baxter 2009). In our previous work (Chu *et al.* 2009), we established an extremely-high-sensitivity TIMS method for the measurement of Nd isotopes as NdO^+ using a single tungsten filament with TaF_5 as an ion emitter. With this method, the ion yield (defined as ions detected by collectors/atoms loaded on the filament) of NdO could be as high as 30% and thus measurement reproducibility ("external precision") of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio on amounts of Nd as little as 1 ng could be better than 50 ppm (2 RSD).

With respect to the chemical procedure, currently, one of the most efficient methods to preconcentrate Sm and Nd in ultramafic rocks for isotopic determination involves coprecipitation with ferric hydroxide, as reported by Sharma *et al.* (1995) and Sharma and Wasserburg (1996). This method has been used to efficiently collect Sm and Nd in about 2–4 g of highly depleted ultramafic rock. In combination with a high-sensitivity NdO mass spectrometric technique, this method has been used to precisely determine Nd isotopes in highly depleted ultramafic rock containing as little as 10 ng g^{-1} of Nd. However, this method is time-consuming and complex as pH needs to be held at 9.0 to precipitate $\text{Fe}(\text{OH})_3$ whilst leaving Mg in solution. Shibata and Yoshikawa (2004), on the other hand, used 6 mol l^{-1} HCl alone to repeatedly leach ultramafic rock at 110°C to dissolve olivine and then decomposed the remaining residue by the conventional $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ method. Since Mg is mainly leached out by the 6 mol l^{-1} HCl before HF is added, the formation of a large amount of MgF_2 is avoided. However, olivine is difficult to dissolve efficiently with 6 mol l^{-1} HCl.

In this study, we describe a highly efficient and low-blank chemical procedure to completely decompose ultramafic rocks that yielded high Sm and Nd recovery involving HF digestion of silicate, HClO_4 decomposition of chromite (Nakamura and Chang 2007) and then H_3BO_3 dissolution of the formed fluorides. By combining this chemical procedure with the high-sensitivity TaF_5 TIMS NdO and Sm isotopic measurement method (Chu *et al.* 2009), precise measurement of Sm and Nd concentrations and Nd isotopic compositions in highly depleted ultramafic rocks was successfully realised, without the requirement of the complex $\text{Fe}(\text{OH})_3$ coprecipitation step. Several ultramafic rock reference materials, including USGS PCC-1, DTS-1, DTS-2, DTS-2b and GSJ JP-1, which contain extremely low amounts of Sm and Nd (Sm, $0.003\text{--}0.008 \mu\text{g g}^{-1}$; Nd, $\sim 0.01\text{--}0.03 \mu\text{g g}^{-1}$) (Govindaraju 1994, Jain *et al.* 2000, Dulski 2001, Raczek *et al.* 2001, Qi *et al.* 2005, Makishima and Nakamura 2006, Nakamura and Chang 2007, Sun *et al.* 2013, Ulrich *et al.* 2012), were measured, and high-precision Sm-Nd isotopic data were obtained. To the best of our knowledge, this is the first report of the Sm-Nd isotopic compositions of these ultramafic rock reference materials except for PCC-1.

Experimental

An outline of the complete experimental procedure is given in Figure 1. The following subsections include details of (1) the preparation of clean reagents and materials, (2) sample digestion and chemical separation and (3) mass spectrometry.

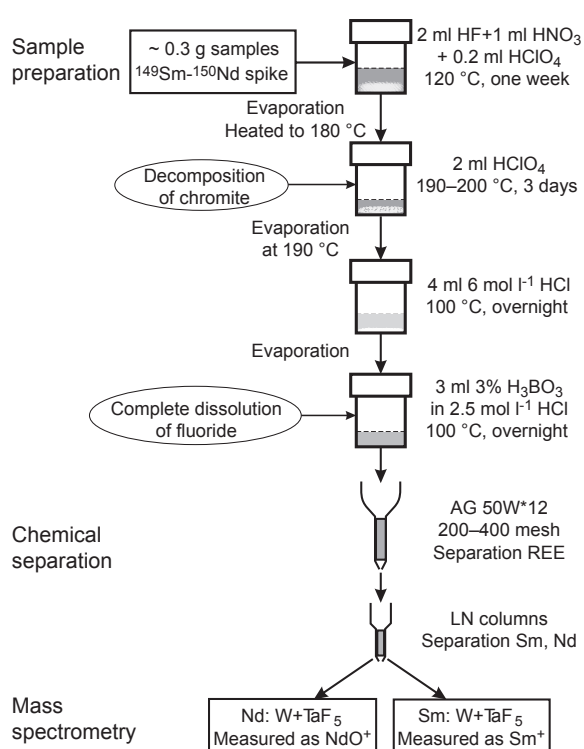


Figure 1. Outline for the procedure for Sm-Nd isotopic determination of highly depleted ultramafic rocks.

Reagents and materials

HCl, HF, HNO₃ (BV-III grade, all from Beijing Institute of Chemical Reagents) were further purified by sub-boiling distillation using a Savillex DTS-1000 Teflon apparatus; 70% m/m HClO₄ (Acros, Geel, Belgium) was used without additional purification. Water (18.2 MΩ cm at 25 °C) from a Millipore purification system was used. The H₃BO₃ solution (3% H₃BO₃ in 2.5 mol l⁻¹ HCl) was purified as described in detail by Chu *et al.* (2009).

TaF₅ emitter: Ta₂O₅ powder (500 mg) (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was weighed into a 30 ml Teflon PFA beaker and dissolved with 12 ml 22 mol l⁻¹ HF at 100 °C on a hot plate for one week. The solution was subsequently evaporated to dryness, and the residue was dissolved with 2 ml 22 mol l⁻¹ HF and diluted to 20 ml with Milli-Q H₂O. The resulting solution was passed through a Bio-rad AG 50W × 12 (200–400 mesh, 2 ml resin bed) cation-exchange column to remove REEs. The collected solution was evaporated to dryness again, and the residue was completely dissolved with 740 μl of purified 22 mol l⁻¹ HF. Finally, 540 μl 85% m/m H₃PO₄ (Merck, Darmstadt, Germany) and 945 μl purified 13.5 mol l⁻¹ HNO₃ were added to the solution. The solution was then diluted to 40 ml with Milli-Q water.

¹⁴⁹Sm-¹⁵⁰Nd spike: An enriched ¹⁴⁹Sm-¹⁵⁰Nd spike with 114.9 ± 0.3 pmol g⁻¹ (*n* = 3, 2s) ¹⁴⁹Sm (¹⁴⁹Sm, 97.71%) and 56.75 ± 0.13 (*n* = 3, 2s) pmol g⁻¹ ¹⁵⁰Nd (¹⁵⁰Nd, 97.83%) was used for isotope dilution concentration determination. The spike was calibrated using gravimetric standards for Sm and Nd during the analytical session.

Neodymium isotopic reference material JNdi-1: Neodymium isotopic reference material JNdi-1 (Tanaka *et al.* 2000) solutions of 10 μg g⁻¹ and 1 μg g⁻¹ were used to monitor the status of the mass spectrometer.

Cation exchange: Cation-exchange columns (6 mm i.d.) packed with 2 ml 200-400 mesh AG 50W X 12 resin were used to separate REE from sample matrix. Eichrom polypropylene columns (8 mm i.d.) packed with 0.5 ml 50–100 μm Eichrom-LN resin were used to separate Sm and Nd from REEs.

Sample digestion

About 300 mg of ultramafic rock reference materials and appropriate amounts of ¹⁴⁹Sm-¹⁵⁰Nd mixed spike solution were weighed (both to 0.1 mg precision) into 7 ml Savillex PFA vials. The added amounts of the spike were evaluated according to the previously reported Sm and Nd concentrations (Govindaraju 1994, Jain *et al.* 2000, Dulski 2001, Raczek *et al.* 2001, Qi *et al.* 2005, Makishima and Nakamura 2006, Nakamura and Chang 2007, Sun *et al.* 2013, Ulrich *et al.* 2012) in these reference materials.

The samples were first dissolved on a hot plate at 100–120 °C using a mixed acid of 2 ml 22 mol l⁻¹ HF, 1 ml 13.5 mol l⁻¹ HNO₃ and 0.2 ml 70% m/v HClO₄ for 1 w. The samples were then evaporated to dryness, followed by a further digestion with 2 ml 70% m/m HClO₄ on a hot plate at 190–200 °C for 3 d. Subsequently, the beaker was opened to dry at 190 °C to remove the HF, followed by treatment with 4 ml 6 mol l⁻¹ HCl at about 100 °C overnight. After the samples were dried again, the residues were then completely dissolved in a 3-ml 2.5 mol l⁻¹ HCl–3% m/v H₃BO₃ mixture at 100 °C on a hot plate overnight. The amount of the latter solution used for an ultramafic rock sample was in proportion to the sample size. For 300 mg of ultramafic rock, about 3 ml 3% m/v H₃BO₃ solution was enough to completely dissolve the formed fluorides.

Column chemistry

The resulting sample solutions obtained from the previous step were loaded onto preconditioned BioRad-AG

50W × 12 columns for separation of REE from the sample matrix as described in detail by Li *et al.* (2007), Chu *et al.* (2009) and Yang *et al.* (2010).

Cerium, Pr, Nd and Sm were separated by the Eichrom-LN chromatographic columns (Pin and Santos Zalduegui 1997). The columns were precleaned with 10 ml Milli-Q H₂O, 15 ml 6 mol l⁻¹ HCl and 10 ml Milli-Q H₂O and then conditioned with 5 ml 0.18 mol l⁻¹ HCl. The REE fractions obtained from the cation-exchange column step were dried, taken up with 0.4 ml 0.18 mol l⁻¹ HCl and then loaded onto the LN columns. After rinsing four times with 0.5 ml 0.18 mol l⁻¹ HCl, the La, Ce and about 70% of Pr were eluted with 18 ml 0.18 mol l⁻¹ HCl. Subsequently, the Nd was eluted with 3 ml 0.3 mol l⁻¹ HCl. The fraction of Nd also contained ca. 30% of Pr, less than 1% of Ce and no detectable Sm. The Sm was then eluted with 3 ml 0.6 mol l⁻¹ HCl. The recovery yields of Nd and Sm during this step were greater than 80% and 95%, respectively.

Instrumentation

An IsoProbe-T thermal ionisation mass spectrometer (Isotopx company, formerly GV Instruments, England), installed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), was used in this study.

A tungsten ribbon (0.03 mm thick, 0.72 mm wide and 99.95% pure, H. Cross Company) was used for the Nd and Sm isotopic determinations. All the filaments were predegassed in a degassing machine prior to sample loading.

Nd isotopic measurements

Neodymium isotopes were determined as NdO⁺ using a single tungsten filament and using TaF₅ as an ionisation activator, as described in detail by Chu *et al.* (2009).

The cup configuration employed for NdO⁺ measurement is shown in Table 1. The peaks of masses 156, 157 and 170 were measured to monitor and correct the CeO⁺, PrO⁺ and SmO⁺ interferences (on NdO⁺). ¹⁴⁵Nd¹⁶O was not measured in this study; instead, ¹⁴⁵Nd/¹⁴⁴Nd = 0.3484 was used for oxygen correction calculations (Harvey and Baxter 2009). This is reasonable for the following reasons: (1) the only interfering effect of ¹⁴⁵Nd is the very small ¹⁴⁵Nd¹⁷O interference on ¹⁴⁶Nd¹⁶O; (2) for spiked Nd samples, the small amounts of ¹⁴⁵Nd in the highly enriched ¹⁵⁰Nd spike caused only very small changes in the ¹⁴⁵Nd/¹⁴⁴Nd ratio.

The data reductions included corrections of isobaric interferences (e.g., ¹⁴¹Pr¹⁸O on ¹⁴³Nd¹⁶O), oxygen corrections (i.e., reduction of NdO isotopic ratios to Nd isotopic ratios), spike subtractions and finally corrections for mass fractionation using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The data reductions were performed online using a self-written embedded program cycle by cycle. The oxygen isotopic ratios used for the data reduction were ¹⁷O/¹⁶O = 0.000383 and ¹⁸O/¹⁶O = 0.002072, which were based on the measurements of high-purity Pr as PrO during the analytical period of this study.

During the period of data collection, the measured values for the reference material JNdi-1 were ¹⁴³Nd/¹⁴⁴Nd = 0.512117 ± 10 (2s, n = 8), consistent with the published value (0.512115 ± 7 (1s), Tanaka *et al.* 2000).

Sm isotopic measurements

Samarium isotopes were determined as Sm⁺, also using a single W filament with TaF₅ as an ion emitter, as described by Chu *et al.* (2009). The cup configuration for Sm⁺ measurement is also shown in Table 1. The method has

Table 1.
Cup configuration for NdO and Sm isotopic measurements

	L2	Ax	H1	H2	H3	H4	H5	H6	H7
NdO⁺ measurements									
Mass	156	157	158	159	160	162	164	166	170
Major isotopes	¹⁴⁰ Ce ¹⁶ O	¹⁴¹ Pr ¹⁶ O	¹⁴² Nd ¹⁶ O	¹⁴³ Nd ¹⁶ O	¹⁴⁴ Nd ¹⁶ O	¹⁴⁶ Nd ¹⁶ O	¹⁴⁸ Nd ¹⁶ O	¹⁵⁰ Nd ¹⁶ O	¹⁵⁴ Sm ¹⁶ O
Major interferences		¹³⁸ Ba ¹⁹ F	¹⁴² Ce ¹⁶ O	¹⁴² Nd ¹⁷ O	¹⁴² Nd ¹⁸ O	¹⁴⁴ Nd ¹⁸ O	¹⁴⁶ Nd ¹⁸ O	¹⁴⁸ Nd ¹⁸ O	
			¹⁴¹ Pr ¹⁷ O	¹⁴¹ Pr ¹⁸ O	¹⁴³ Nd ¹⁷ O	¹⁴⁵ Nd ¹⁷ O			
Sm measurements									
Mass	144	146	147	148	149	150	152	154	155
Major isotopes	¹⁴⁴ Sm	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁸ Sm	¹⁴⁹ Sm	¹⁵⁰ Sm	¹⁵² Sm	¹⁵⁴ Sm	¹⁵⁵ Gd
Potential interferences					¹³⁰ Bd ¹⁹ F		¹³⁶ Ce ¹⁶ O		
							¹³⁶ Ba ¹⁶ O		
							¹⁵² Gd		

also very high sensitivity and can determine Sm isotopic compositions down to $< 10^{-11}$ g with high precision (2 RSD $< 0.1\%$). Measured $^{149}\text{Sm}/^{147}\text{Sm}$ ratios were corrected for mass fractionation using a value for $^{152}\text{Sm}/^{147}\text{Sm}$ of 0.56081 (Chu *et al.* 2009).

Results and discussion

Total procedural blanks

A very low total procedural blank level is the prerequisite for reliable Sm-Nd isotopic determinations from highly depleted ultramafic rocks containing extremely low amount of Sm and Nd. When Teflon sub-boiling distilled HF, HNO₃, HCl and Acros HClO₄ were used, and the procedure described in the Experimental section was used to purify the H₃BO₃ solution and the TaF₅ emitter, typical total procedural blank values of Sm and Nd, including sample decomposition, HClO₄ decomposition step, H₃BO₃ dissolution step, column chemistry and mass spectrometry, were found to be mostly lower than 5 pg and 1.5 pg, respectively. The total Sm and Nd amounts in the ultramafic rock reference materials analysed here were higher than 0.9 ng for Sm and 3.6 ng for Nd, respectively. The blank contributions on Sm and Nd for these samples were thus less than 0.5%. Consequently, the blank effect on Sm and Nd concentration and Nd isotope determination of these highly depleted ultramafic rocks should be insignificant.

PrO interferences and oxygen corrections during NdO measurement

When the NdO⁺ method is used for Nd isotopic measurement, it is necessary to correct for REE¹⁸O⁺ and REE¹⁷O⁺ interferences (Table 1) and possibly the SmO⁺, NdF⁺ and HREE (Gd, Tb, Dy, Er) interferences on the measured NdO⁺ abundances (Li *et al.* 2007, Chu *et al.* 2009). By using the chemical purification method as described in the Experimental section, Sm and HREEs were separated completely from Nd and only less than 1% of Ce remained in the Nd fraction. Thus SmO and HREE interferences were negligible and CeO had a significant interference on ¹⁴²NdO only. Furthermore, since no detectable signal could be found at mass 169 (¹⁵⁰Nd¹⁹F) when a ¹⁵⁰Nd spike was measured with the W + TaF₅ sample loading method, the formation of NdF⁺ was judged to be negligible. However, about 30% of Pr remained in the Nd fraction when Nd recovery was 80% during the LN column separation step in this study. Therefore, accurate correction of ¹⁴¹Pr¹⁸O interference (on ¹⁴³Nd¹⁶O) is very important. Additionally, the oxide interferences between NdO isotopes (e.g., ¹⁴²Nd¹⁸O interference on ¹⁴⁴Nd¹⁶O) are also significant.

The oxygen isotope ratios, ¹⁸O/¹⁶O and ¹⁷O/¹⁶O, are used for isobaric corrections between Nd oxide masses (oxygen corrections) and the ¹⁴¹Pr¹⁸O interference correction (on ¹⁴³Nd¹⁶O), so the reliability and accuracy for Nd isotopic determination as NdO⁺ are highly dependent on the values of ¹⁸O/¹⁶O and ¹⁷O/¹⁶O that are used for oxygen and PrO corrections. In the literature, ¹⁸O/¹⁶O ratios vary by up to 6.85% (Griselin *et al.* 2001, Li *et al.* 2007, Chu *et al.* 2009, Harvey and Baxter 2009), depending on the oxygen reservoir used for analysis and the analytical method. The observed scattering in the oxygen isotope data is big enough to significantly influence the oxygen and PrO corrections. Since oxygen isotopic composition is variable in nature as well as in the laboratory during the sample treatment, the ideal isobaric interference correction should be done using oxygen isotopic ratios measured in run during the sample measurement (Luguet *et al.* 2008). However, high-precision measurement of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O in run during NdO measurement is very difficult to achieve. Alternatively, Liu *et al.* (2000) report a method involving the introduction of ¹⁶O-enriched oxygen into the ion source chamber during NdO measurement. Nevertheless, it is possible that the oxygen forming the oxide species may come from the oxygen-bearing compounds loaded on the filament and it is difficult to ultimately remove the natural oxygen remaining in the ion source.

Here, we discuss in detail the impact of PrO interferences and oxygen corrections on the precision and accuracy of the ¹⁴³Nd/¹⁴⁴Nd ratio. First, due to some Pr remaining in the Nd analyte, the ¹⁴¹Pr¹⁶O/¹⁴⁴Nd¹⁶O ratios were as high as ca. 0.2–0.5 during our NdO mass spectrometric measurement (Tables 2 and 3). This PrO interference level would shift ¹⁴³Nd¹⁶O/¹⁴⁴Nd¹⁶O about +400 ppm to +1000 ppm due to the interference of ¹⁴¹Pr¹⁸O (on ¹⁴³Nd¹⁶O). Accordingly, 1% variation of ¹⁸O/¹⁶O will lead to a 4–10 ppm variation on the final PrO-corrected ¹⁴³Nd/¹⁴⁴Nd values (the ¹³⁸Ba¹⁹F interference on ¹⁴¹Pr¹⁶O was found to be insignificant). For oxide isobaric interferences between Nd oxide isotopes (Table 1), the ¹⁴²Nd¹⁸O and ¹⁴³Nd¹⁷O interferences (on ¹⁴⁴Nd¹⁶O), the ¹⁴²Nd¹⁷O interference (on ¹⁴³Nd¹⁶O) and the ¹⁴⁴Nd¹⁸O and ¹⁴⁵Nd¹⁷O interferences (on ¹⁴⁶Nd¹⁶O) will totally shift ¹⁴³Nd¹⁶O/¹⁴⁴Nd¹⁶O and ¹⁴⁶Nd¹⁶O/¹⁴⁴Nd¹⁶O about -874 ppm and +355 ppm, respectively. By uncertainty magnification calculation based on oxygen correction equations, a 1% variation in ¹⁸O/¹⁶O and a 2% variation in ¹⁷O/¹⁶O will cause uncertainties in the final fractionation-corrected ¹⁴³Nd/¹⁴⁴Nd ratio of about 12 ppm (2s) and 7 ppm (2s), respectively.

It should be pointed out that, when the W + TaF₅ sample loading method is used, the NdO measurement is

Table 2.
Sm and Nd isotopic results for USGS BCR-2 and BHVO-2

	Analysis No. ^a	¹⁴¹ Pr/ ¹⁶ O/ ¹⁴⁴ Nd/ ¹⁶ O	Sm (µg g ⁻¹)	Nd (µg g ⁻¹)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2SE ^b
BCR-2	1	0.3	6.560	28.74	0.1380	0.512649	0.000009
	2	0.2	6.559	28.76	0.1378	0.512629	0.000008
	3	0.4	6.555	28.73	0.1380	0.512664	0.000005
	4	0.3	6.563	28.69	0.1382	0.512631	0.000008
	5	0.14	6.566	28.78	0.1379	0.512634	0.000007
	Mean ± 2s ^c		6.561 ± 0.008	28.74 ± 0.07	0.1380 ± 0.0003	0.512641 ± 0.000030	
(A)			6.57	28.7			
(B)						0.512637 ± 0.000012 (2s ^c)	
BHVO-2	1	0.5	6.074	24.56	0.1496	0.513002	0.00001
	2	0.4	6.077	24.57	0.1495	0.512969	0.000006
	Mean ± 2s ^c		6.075 ± 0.004	24.56 ± 0.01	0.1495 ± 0.0001	0.512986 ± 0.000047	
(A)			6.07	24.5			
(B)						0.512984 ± 0.000011 (2s ^c)	

^a Each analysis means that a different ~ 50 mg aliquot of BCR-2 or BHVO-2 powder was analysed. ^b 2SE is the absolute error value of the individual sample analyses and is reported as times 10⁶. ^c 2s is the 2 standard deviation value of the individual reference material analyses and reported as times 10⁶. (A) Data from Raczek *et al.* (2001), (B) Data from Weis *et al.* (2006).

conducted without the requirement of extra introduction of oxygen into the ion source (Chu *et al.* 2009). Therefore, the oxygen-bearing compounds in the TaF₅ emitter are probably the main source of oxygen forming the NdO⁺ ions. Consequently, for a batch of TaF₅ emitter, the measured ¹⁸O/¹⁶O and ¹⁷O/¹⁶O values are kept in relative constancy for a long period. The oxygen isotopic ratios were measured using a high-purity Pr ICP standard solution in this study and the values of measured oxygen isotopic ratios were normally: ¹⁸O/¹⁶O = 0.002072 and ¹⁷O/¹⁶O = 0.000383. Although similar to the results of Harvey and Baxter (2009), a slight drift (normally < 1.0%) of the oxygen isotope ratios with time during a PrO measurement run was commonly observed due to the isotope fractionation effect, the long-term measurement reproducibility (external precision) of ¹⁸O/¹⁶O and ¹⁷O/¹⁶O measured by the PrO method in this study was normally found to be better than 1.0% (2 RSD) and 2.0% (2 RSD), respectively. At this ¹⁸O/¹⁶O and ¹⁷O/¹⁶O precision level, the uncertainty on the final ¹⁴³Nd/¹⁴⁴Nd ratio should be less than 10 ppm (2s) resulting from the PrO correction when ¹⁴¹Pr/¹⁴⁴Nd < 0.5 and 14 ppm (2s) resulting from oxygen corrections, based on uncertainty propagation; both are less than the long-term precision on ¹⁴³Nd/¹⁴⁴Nd (< 50 ppm 2 RSD for < 10 ng sample size). Accordingly, with respect to the PrO interference, and similar to previous reports (Li *et al.* 2007, 2011, Chu *et al.* 2009), the small amount of Pr remaining in the Nd fraction had an insignificant effect on Nd isotopic measurements. In fact, although normally the Pr/Nd ratio decreased gradually during a Nd sample analysis run, no obvious correlation between the PrO interference-

corrected ¹⁴³Nd/¹⁴⁴Nd and the Pr/Nd ratios could be found, also indicating that the PrO interference correction is generally robust when the W filament + TaF₅ sample loading method is used.

In this study, USGS BCR-2 and BHVO-2 were analysed to further check the reliability of the whole chemical procedure and the mass spectrometry. As shown in Table 2, the NdO measurement method gave Nd isotopic results with high precision and accuracy even when the ¹⁴¹Pr/¹⁶O/¹⁴⁴Nd/¹⁶O ratio was as high as 0.5, further confirming that the PrO and oxygen corrections in this study are reliable.

Isobaric interferences for Sm measurement

As described in the Experimental section, with the Sm⁺ method, ¹⁵²Sm/¹⁴⁷Sm ratio was used for the isotope fractionation correction and ¹⁴⁹Sm/¹⁴⁷Sm was used for the isotope dilution calculation. ¹⁵²Gd, ¹³⁶Ba/¹⁶O and ¹³⁶Ce/¹⁶O could possibly affect ¹⁵²Sm (Table 1). Amongst these, Gd should have been almost completely removed by the two stage column chemistry. Furthermore, Gd was found to be mainly ionised as oxide ions with the W + TaF₅ loading method. In addition, the abundance of ¹⁵²Gd was very low (only 0.2%). Therefore, the potential isobaric interference of ¹⁵²Gd (on ¹⁵²Sm) was negligible. With respect to the CeO interferences, it was found that minor Ce might remain in the Sm fraction, but normally the ¹⁴⁰Ce/¹⁶O signal was low (¹⁴⁰Ce/¹⁶O/¹⁵²Sm < 0.1). Since the abundance of ¹³⁶Ce was very low (only 0.185%), the ¹³⁶Ce/¹⁶O

Table 3.
Analytical results of Sm-Nd isotopic compositions for highly depleted ultramafic rock reference materials

Sample	Analysis No.	Sample mass (g)	Mass Sm (ng) ^a	Mass Nd (ng) ^a	$^{144}\text{Nd}/^{144}\text{Nd}$ (V)	$^{141}\text{Pr}^{16}\text{O}/^{144}\text{Nd}^{16}\text{O}$	Sm ($\mu\text{g g}^{-1}$)	Nd ($\mu\text{g g}^{-1}$)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE ^b
JP-1	1	0.30189	2	6	0.8	0.2	0.00784	0.0308	0.154	0.512648	0.000011
	2	0.30173	2	6	0.6	0.3	0.00794	0.0309	0.156	0.512639	0.000012
	3	0.30108	2	6	0.7	0.3	0.00807	0.0320	0.153	0.512621	0.000009
	4	0.30202	2	6	0.8	0.4	0.00781	0.0306	0.154	0.512659	0.000011
	5	0.30224	2	6	0.6	0.3	0.00814	0.0319	0.155	0.51262	0.000012
	Mean $\pm 2s^c$						0.00796 \pm 0.00029	0.0312 \pm 0.0012	0.154 \pm 0.002	0.512637 \pm 0.000034	
	Ref.						A: 0.009; B: 0.00769; A: 0.033; C: 0.0084; B: 0.0297; D: 0.00827; C: 0.0318; E: 0.00776; D: 0.0317; E: 0.0347				
DTS-1	1	0.30128	1	4.5	0.5	0.2	0.00412	0.0220	0.113	0.512039	0.000014
	2	0.30003	1	4.5	0.6	0.3	0.00431	0.0226	0.115	0.51207	0.000013
	3	0.30358	1	4.5	0.4	0.3	0.00418	0.0224	0.113	0.512082	0.000016
	Mean $\pm 2s^c$						0.00421 \pm 0.00021	0.0223 \pm 0.0006	0.114 \pm 0.002	0.512064 \pm 0.000044	
	Ref.						C: 0.0042; D: 0.00446; C: 0.0215; D: 0.0229; F: 0.0045; G: 0.0041; F: 0.024; G: 0.0231; H: 0.00444; H: 0.0246				
DTS-2	1	0.29984	0.8	3	0.8	0.3	0.00305	0.0136	0.136	0.51256	0.000014
	2	0.30183	0.8	3	0.6	0.3	0.00291	0.0125	0.140	0.512601	0.000012
	3	0.30059	0.8	3	0.7	0.2	0.00297	0.0127	0.141	0.512598	0.000012
	Mean $\pm 2s^c$						0.00298 \pm 0.00014	0.0129 \pm 0.0012	0.139 \pm 0.005	0.512586 \pm 0.000046	
	Ref.						D: 0.00332; H: 0.0136; H: 0.0131; I: 0.00302; I: 0.0027				
DTS-2b	1	0.30162	0.8	3	0.5	0.2	0.00296	0.0128	0.140	0.512571	0.000015
	2	0.3017	0.8	3	0.5	0.2	0.00303	0.0135	0.136	0.512507	0.000015
	3	0.30036	0.8	3	0.4	0.4	0.00294	0.0131	0.136	0.512547	0.000018
	4	0.30051	0.8	3	0.8	0.4	0.0031	0.0138	0.136	0.512517	0.000012
	5	0.30032	0.8	3	0.5	0.2	0.00295	0.0129	0.138	0.512569	0.000013
	Mean $\pm 2s^c$						0.00300 \pm 0.00014	0.0132 \pm 0.0008	0.137 \pm 0.004	0.512542 \pm 0.000059	
	Ref.						0.00543	0.0291	0.113	0.512189	0.000012
PCC-1	1	0.30249	1.2	6	0.8	0.3	0.00543	0.0291	0.112	0.512223	0.00001
	2	0.30058	1.2	6	0.9	0.4	0.00542	0.0293	0.112	0.512223	0.00001
	Mean $\pm 2s^c$						0.00543 \pm 0.00001	0.0292 \pm 0.0003	0.113 \pm 0.001	0.512206 \pm 0.000048	

Table 3 (continued).
Analytical results of Sm-Nd isotopic compositions for highly depleted ultramafic rock reference materials

Sample	Analysis No.	Sample mass (g)	Mass Sm (ng) ^a	Mass Nd (ng) ^a	¹⁴⁴ Nd/ ¹⁴⁴ Nd ^a	¹⁴¹ Pr/ ¹⁶ O/ ¹⁴⁴ Nd/ ¹⁶ O (V)	Sm (μg g ⁻¹)	Nd (μg g ⁻¹)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2SE ^b
Chu <i>et al.</i> (2009) ^c							0.00521	0.0266	0.118	0.512229 ± 0.000023	(2s) ^d
Shibata and Yoshikawa (2004)							0.00551	0.0278	0.12	0.512226 ± 0.000026	(2s) ^d

A: 0.006; B: 0.00596; A: 0.027; B: 0.0321;
C: 0.0053; C: 0.0282;
D: 0.00525; E: D: 0.0266; E: 0.028;
0.00539; F: 0.0049; F: 0.026; G: 0.032
G: 0.007

^a (Mass of dissolved sample) × (Sm or Nd concentration) × (Sm or Nd recovery). Approximately, this entire amount was loaded to the mass spectrometer for analysis. ^b 2SE is the absolute error value of the individual sample analyses and is reported as times 10⁶. ^c 2s is the 2 standard deviation value of the individual reference material analyses and reported as times 10⁶. A: Dulski (2001); B: Qi *et al.* (2005); C: Makishima and Nakamura (2006); D: Nakamura and Chang (2007); E: Sun *et al.* (2013); F: Jain *et al.* (2000); G: Olive *et al.* (2001); H: Raczek *et al.* (2001); I: Ulrich *et al.* (2012).

interference (on ¹⁵²Sm) was also negligible. For the BaO interferences, minor Ba might also remain in the Sm fraction, since a ¹³⁸Ba signal could sometimes be found during Sm measurements (Ba may also have been derived from the tungsten filament). However, the ¹³⁶Ba¹⁶O interference (on ¹⁵²Sm) could also be ignored since it was found that the Ba was ionised dominantly as Ba⁺ with the W + TaF₅ sample loading method, whilst the production of BaO⁺ was negligible. Thus the BaO interference (on ¹⁵²Sm) was also insignificant. ¹³⁰Ba¹⁹F could possibly affect ¹⁴⁹Sm; however, since the production of BaF⁺ during Sm determination was found to be insignificant and at the same time the abundance of ¹³⁰Ba was very low (only 0.106%), the ¹³⁰Ba¹⁹F interference (on ¹⁴⁹Sm) was also negligible. The Sm analytical results for BCR-2 and BHVO-2 are consistent with published data (Table 2), confirming that our Sm measurement method is reliable.

Analytical results for Sm-Nd isotopes from highly depleted ultramafic rock reference materials

As emphasised above, due to the high MgO content and the presence of some refractory minerals such as chromite in ultramafic rocks, it is difficult to completely digest these rocks to achieve high recovery yields of Sm and Nd. Nonetheless, it has been reported that chromite can be efficiently dissolved by HClO₄ at 190–200 °C over several days (Nakamura and Chang 2007) and fluoride (mainly MgF₂) formed during the HF dissolution step can be efficiently dissolved by H₃BO₃ (Pin and Santos Zalduegui 1997, Chu *et al.* 2009, Sun *et al.* 2013). Accordingly, by applying the HClO₄ treatment step and using H₃BO₃ to completely dissolve the fluorides formed (Figure 1), very clear sample solutions lacking residues were obtained for all the highly depleted ultramafic rock reference samples analysed in this study. This very probably ensured complete sample digestion and thus high Sm and Nd recovery yields. Consequently, by combining the complete sample dissolution, high-efficiency column chemistry and the high-sensitivity NdO and Sm mass spectrometric measurement method (Chu *et al.* 2009), high-precision Sm-Nd isotopic data of highly depleted ultramafic rock reference materials which contain extremely low amount of Sm and Nd (down to sub ng g⁻¹), such as JP-1, DTS-1, DTS-2, DTS-2b and PCC-1, were obtained (Table 3).

As shown in Table 3 and Figure 2, the analytical results for Sm and Nd are different from previously reported values far beyond analytical uncertainty. In general, the high-sensitivity Sm-Nd ID-TIMS method in this study resulted in more precise Sm and Nd concentration data (Table 3, Figure 2). Despite this, the differences of Sm and Nd

concentrations in these ultramafic rock reference materials for duplicate analyses are sometimes well beyond analytical uncertainty of about 1% for the ID-TIMS method (Raczek *et al.* 2001) (Table 3, Figure 2). In particular, the maximum differences of duplicate analyses were up to 4% for JP-1 and 8% for DTS-2b. These differences are probably due to the inhomogeneity of the low levels of REEs in these rocks (Sun *et al.* 2013).

The Sm and Nd concentrations obtained in this study for PCC-1 (here referred to split 2) were slightly higher than those measured by Chu *et al.* (2009) (here referred to split 1) (Table 3, Figure 2). Because splits 1 and 2 were from different batches of PCC-1, it is possible also that the differences in their Sm and Nd concentrations are due to sample heterogeneity.

Consistent with previous reports (Raczek *et al.* 2001, Nakamura and Chang 2007), DTS-2 gave much lower Sm and Nd concentrations than DTS-1 (Table 3, Figure 2). It is found in this study that they also differed in Nd isotopic composition (Table 3, Figure 3). However, DTS-2b showed similar Sm and Nd concentrations and Nd isotopic composition to DTS-2 (Figures 2 and 3, Table 3). In addition, the measurement reproducibility for Nd isotopes from DST-2 and DTS-2b from duplicate analyses was relatively large (2

RSD > 100 ppm), well beyond the general reproducibility for $^{143}\text{Nd}/^{144}\text{Nd}$ on < 10 ng Nd found in this study (about 50 ppm, 2 RSD) (Figure 3). Furthermore, there is a rough positive correlation between the Sm/Nd and Nd isotopic compositions (Figure 4). These lines of evidence taken together also probably indicate sample heterogeneity in reference materials DTS-2 and DTS-2b.

Conclusions

In this study, methods were developed to determine precisely Sm and Nd concentrations and Nd isotopic compositions in highly depleted ultramafic rocks. Ultramafic rock samples were first digested using the conventional HF + HNO₃ + HClO₄ method, followed by complete digestion of chromite in the samples using HClO₄ at 190–200 °C and then complete dissolution of fluoride formed during the HF decomposition using H₃BO₃. By using these digestion steps, very clear sample solutions without visible residues were finally obtained, and thus high Sm and Nd recovery yields were achieved. By combining this chemical procedure with the high-sensitivity NdO and Sm isotopic determination method, using a tungsten filament with TaF₅ as an ion emitter, high-precision Sm-Nd isotopic determination in highly depleted ultramafic rocks was successfully achieved, without the requirement of the complex Fe(OH)₃

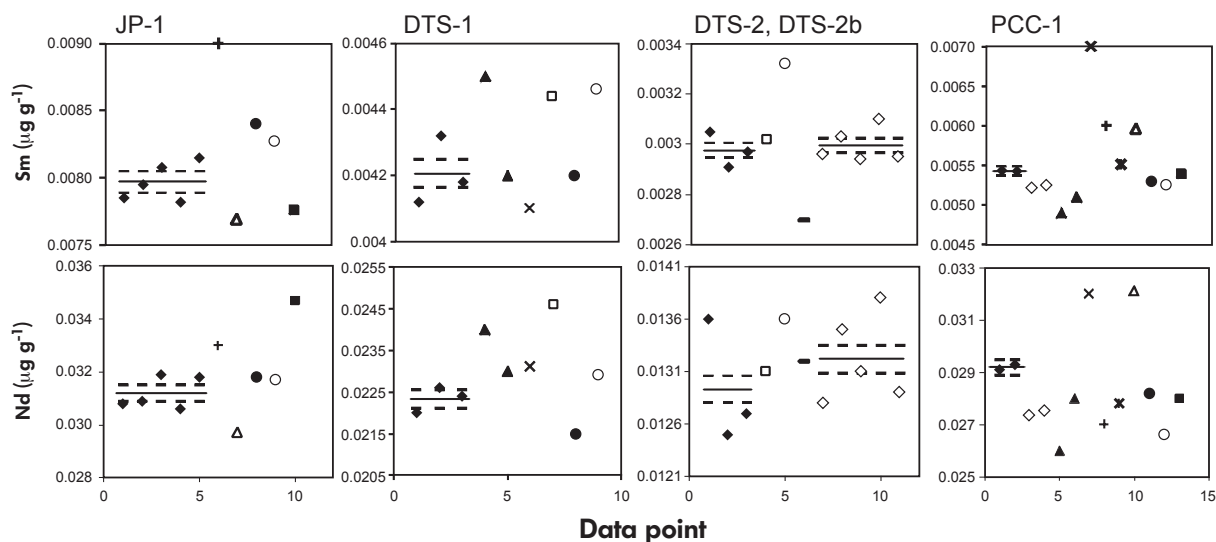


Figure 2. Sm and Nd concentrations in highly depleted ultramafic reference materials. Solid diamonds (♦) represent data obtained in this study for JP-1, DTS-1, DTS-2 and PCC-1-split 2. Open diamonds (◇) represent data for DTS-2b obtained in this study and for PCC-1-split 1 from Chu *et al.* (2009). Other data source: ▲, Jain *et al.* 2000; ×, Olive *et al.* 2001; +, Dulski 2001; □, Raczek *et al.* 2001; *, Shibata and Yoshikawa 2004; △, Qi *et al.* 2005; ●, Makishima and Nakamura 2006; ○, Nakamura and Chang 2007; –, Ulrich *et al.* 2012; ■, Sun *et al.* 2013. Solid horizontal lines represent mean value of data in this study for each reference material. The dotted lines define the range of generally accepted reproducibility (2 RSD, 1%) for ID-TIMS analyses.

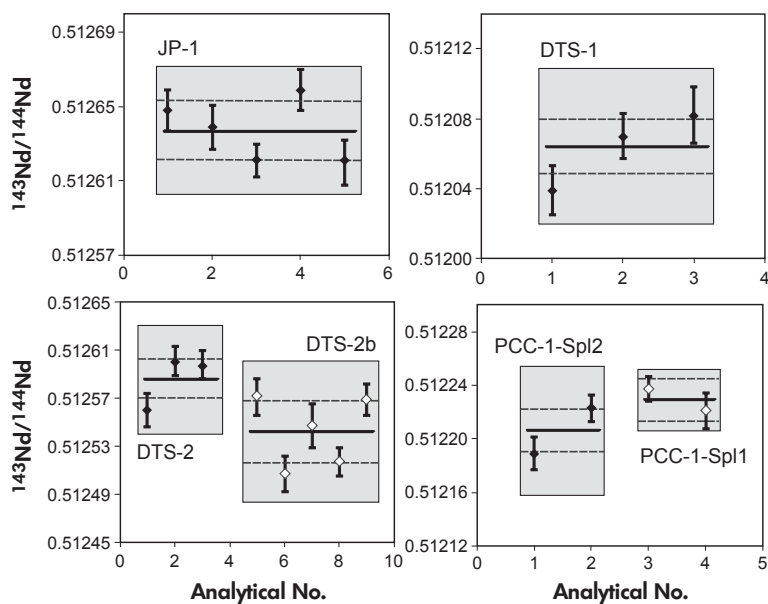


Figure 3. Analytical results for Nd isotopes in highly depleted ultramafic reference materials. Solid horizontal lines represent the mean value for each reference material. The bars give the in-run uncertainties. The shaded bands represent the uncertainty estimated as 2s. The dotted lines define the range of generally accepted reproducibility (2 RSD, 50 ppm) for Nd isotopic determinations on < 10 ng sample size.

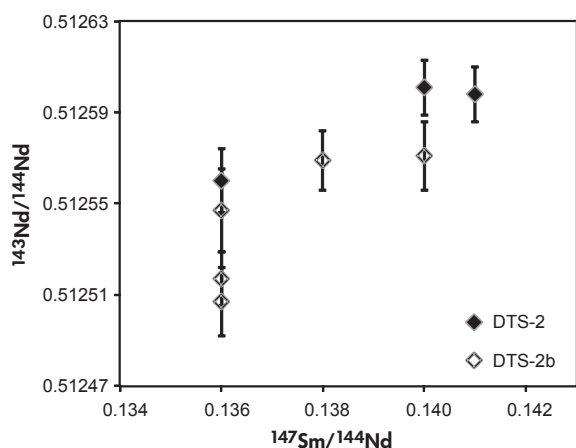


Figure 4. Sm/Nd vs. Nd isotopic compositions for DTS-2 and DTS-2b. The bars represent the in-run uncertainties.

coprecipitation preconcentration step. The ultramafic rock reference materials USGS PCC-1, DTS-1, DTS-2, DTS-2b and GSJ JP-1, which contain extremely low amount of Sm and Nd (down to sub ng g⁻¹), were analysed, and high-precision Sm-Nd isotopic data were obtained. The basalt reference materials USGS BCR-2 and BHVO-2 were analysed together with the ultramafic rock reference materials and

high-precision Sm and Nd concentration and Nd isotopic data consistent with reported values were obtained, indicating that the whole chemistry procedure and mass spectrometry method are reliable. This is the first report of Sm-Nd isotope data in these ultramafic reference materials, except for PCC-1. It is possible that the trace amounts of Sm and Nd are distributed inhomogeneously in some ultramafic rock reference materials.

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References

- Amelin Y. and Rotenberg E. (2004) Sm-Nd systematics of chondrites. *Earth and Planetary Science Letters*, **223**, 267–282.
- Chu Z.Y., Chen F.K., Yang Y.H. and Guo J.H. (2009) Precise determination of Sm, Nd concentrations and Nd isotopic compositions at the nanogram level in geological samples by thermal ionization mass spectrometry. *Journal of Analytical Atomic Spectrometry*, **24**, 1534–1544.

references

Dulski P. (2001)

Reference materials for geochemical studies: New analytical data by ICP-MS and critical discussion of reference values. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 25, 87–125.

Govindaraju K. (1994)

1994 compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, 18 (Special Issue), 158pp.

Griselin M., van Belle J.C., Pomies C., Vroon P.Z., van Soest M.C. and Davies G.R. (2001)

An improved chromatographic separation of Nd with application to NdO⁺ isotope analysis. *Chemical Geology*, 172, 347–359.

Harvey J. and Baxter E.F. (2009)

An improved method for TIMS high precision neodymium isotope analysis of very small aliquots (1–10 ng). *Chemical Geology*, 258, 251–257.

Jain J.C., Field M.P. and Neal C.R. (2000)

Determination of the REE in geological reference materials DTS-1 (dunite) PCC-1 (peridotite) by ultrasonic and micro-concentric desolvating nebulisation ICP-MS. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 24, 65–72.

Li C.F., Chen F.K. and Li X.H. (2007)

Precise isotopic measurements of sub-nanogram Nd of standard reference material by thermal ionization mass spectrometry using the NdO⁺ technique. *International Journal of Mass Spectrometry*, 226, 34–41.

Li C.F., Li X.H., Li Q.L., Guo J.H., Li X.H. and Liu T. (2011)

An evaluation of a single-step extraction chromatography separation method for Sm-Nd isotope analysis of micro-samples of silicate rocks by high-sensitivity thermal ionization mass spectrometry. *Analytica Chimica Acta*, 706, 297–304.

Liu Y.Z., Masuda A. and Inoue M. (2000)

Measurement of isotopes of light rare earth elements in the form of oxide ions: A new development in thermal ionization mass spectrometry. *Analytical Chemistry*, 72, 3001–3005.

Luguet A., Nowell G.M. and Pearson D.G. (2008)

¹⁸⁴Os/¹⁸⁸Os and ¹⁸⁶Os/¹⁸⁸Os measurements by negative thermal ionisation mass spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision. *Chemical Geology*, 248, 342–362.

Makishima A. and Nakamura E. (2006)

Determination of major, minor and trace elements in silicate samples by ICP-QMS and ICP-SFMS applying isotope dilution-internal standardisation (ID-IS) and multi-stage internal standardisation. *Geostandards and Geoanalytical Research*, 30, 245–271.

Nakamura K. and Chang Q. (2007)

Precise determination of ultra-low (sub-ng g⁻¹) level rare earth elements in ultramafic rocks by quadrupole ICP-MS.

Geostandards and Geoanalytical Research, 31, 185–197.

Olive V., Ellam R.M. and Wilson L. (2001)

A protocol for the determination of the rare earth elements at picomole level in rock by ICP-MS: Results on geological reference materials USGS PCC-1 and DTS-1. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 25, 219–228.

Pin C. and Santos Zalduegui J.F. (1997)

Sequential separation of light-rare-earth elements, thorium and uranium by miniaturization extraction chromatography: Application to isotopic analyses of silicate rocks. *Analytica Chimica Acta*, 339, 79–89.

Qi L., Zhou M.-F., Malpas J. and Sun M. (2005)

Determination of rare earth elements and Y in ultramafic rocks by ICP-MS after preconcentration using Fe(OH)₃ and Mg(OH)₂ coprecipitation. *Geostandards and Geoanalytical Research*, 29, 131–141.

Raczek I., Stoll B., Hofmann A.W. and Jochum K.P. (2001)

High-precision trace element data for the USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-2, AGV-1, DTS-1, DTS-2, GSP-1 and GSP-2 by ID-TIMS and MIC-SSMS. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 25, 77–86.

Sharma M. and Wasserburg G.J. (1996)

The neodymium isotopic compositions and rare-earth patterns in highly depleted ultramafic rocks. *Geochimica et Cosmochimica Acta*, 60, 4537–4550.

Sharma M., Wasserburg G.J., Papanastassiou D.A., Quick J.E., Sharkov E.V. and Laz'ko E.E. (1995)

High ¹⁴³Nd/¹⁴⁴Nd in extremely depleted mantle rocks. *Earth and Planetary Science Letters*, 135, 101–114.

Shibata T. and Yoshikawa M.J. (2004)

Precise isotope determination of trace amounts of Nd in magnesium-rich samples. *Journal of Mass Spectrometry Society of Japan*, 52, 317–324.

Sun Y.L., Sun S.L., Wang C.Y. and Xu P. (2013)

Determination of rare earth elements and thorium at nanogram levels in ultramafic samples by inductively coupled plasma-mass spectrometry combined with chemical separation and pre-concentration. *Geostandards and Geoanalytical Research*, 37, 65–76.

Tanaka T., Togashi S., Kamioka H., Amakawa H., Kagami H., Hamamoto T., Yuhara M., Orihashi Y., Yoneda S., Shimizu H., Kunimaru T., Takahashi K., Yanagi T., Nakano T., Fujimaki H., Shinjo R., Asahara Y., Tanimizu M. and Dragusanu C. (2000)

JNdi-1: A neodymium isotopic reference in consistency with LaJolla neodymium. *Chemical Geology*, 168, 279–281.



references

Thirlwall M.F. (1991)

High-precision multicollector isotopic analysis of low levels of Nd as oxide. *Chemical Geology*, 94, 13–22.

Ulrich M., Bureau S., Chauvel C. and Picard C. (2012)

Accurate measurement of rare earth elements by ICP-MS after ion-exchange separation: Application to ultradepleted samples. *Geostandards and Geoanalytical Research*, 36, 7–20.

Wasserburg G.J., Jacobsen S.B., DePaolo D.J., McCulloch M.T. and Wen T. (1981)

Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta*, 45, 2311–2323.

Weis D., Kieffer B., Maerschalk C., Barling J., De Jong J., Williams G., Hanano D., Pretorius W., Mattielli N., Scoates J.S., Goolaerts A., Friedman R. and Mahoney J.B. (2006)

High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. *Geochemistry Geophysics Geosystems*, 7, Q08006, doi: 10.1029/2006GC001283.

Yang Y.H., Zhang H.F., Chu Z.Y., Xie L.W. and Wu F.Y. (2010)

Combined chemical separation of Lu, Hf, Rb, Sr, Sm and Nd from a single rock digest and precise and accurate isotope determinations of Lu-Hf, Rb-Sr and Sm-Nd isotope systems using multi-collector ICP-MS and TIMS. *International Journal of Mass Spectrometry*, 290, 120–126.

Yokoyama T., Makishima A. and Nakamura E. (1999)

Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. *Chemical Geology*, 157, 175–187.