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Accurate and precise determination of Lu and Hf contents and Hf isotopic composition at the sub-nanogram level in geological samples using MC-ICP-MS

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We describe protocols for highly reproducible analysis of Lu and Hf contents and Hf isotopic composition at sub-nanogram levels in geological samples by MC-ICP-MS. Powdered samples were spiked with a ¹⁷⁶Lu–¹⁸⁰Hf enriched tracer and completely digested using conventional HF, HNO₃ and HClO₄ acid dissolution protocols. Fluoride salts were dissolved during a final H₃BO₃ digestion and chemical purification was performed using a single Eichrom Technologies Ln resin. All measurements were carried out on a Neptune Plus MC-ICP-MS employing an Aridus II desolvator. In order to demonstrate the robustness of the proposed protocol, six rock reference materials (RMs) were analysed, spanning various rock types with very low Lu and Hf contents (from nanogram to sub ng g⁻¹ levels). The results are in good agreement within uncertainty with published values for the analysed RMs. Relative to other approaches and low-blank levels, this protocol has great potential for Lu–Hf analysis of low volume (100–500 mg) samples in geochemistry, cosmochemistry and environmental sciences (e.g., peridotite, garnet, meteorites, dust, etc.).

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1. Introduction

The rapid development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the mid-1990s has enabled precise Lu–Hf isotope ratio measurement, resulting in widespread applications of the ¹⁷⁶Lu–¹⁷⁶Hf radiogenic isotope system in geochemistry, cosmochemistry and environmental sciences.^{1,2} Compared to the sample preparation needed for conventional thermal ionization mass spectrometry (TIMS)³ and hot-secondary ionization mass spectrometry (SIMS)⁴ techniques, Lu and Hf chemical purification for MC-ICP-MS measurements can be greatly simplified, facilitating a much higher sample throughput and smaller sample size.^{4–14} Therefore, MC-ICP-MS has become a technique of choice for routine analysis of Lu and Hf contents and Hf isotopic composition at sub-microgram levels in geological samples (Hf > 0.1 μg g⁻¹).^{15–17} ¹⁷⁶Lu–¹⁷⁶Hf is an important tracer of geological

petrogenesis, and it is becoming increasingly important to measure this isotopic signature in samples that generally contain very low Lu and Hf contents (Hf < 0.1 μg g⁻¹) (e.g., peridotite, garnet, meteorites, dust, etc.).^{18–21}

It is very difficult to accurately and precisely measure nanogram or sub-nanogram levels of Lu and/or Hf using MC-ICP-MS for the following reasons: (1) if the concentration of Lu and Hf is extremely low (normally <0.1 μg g⁻¹ to several ng g⁻¹), as it is very difficult to separate sufficient Lu and Hf from the samples for highly precise mass spectrometric measurement, particularly if sample volume is limited;^{19,20,22} (2) Lu and Hf are strongly trapped into residual fluorides (mainly MgF₂) produced during acid dissolution (HF + HNO₃ + HClO₄). Ultramafic rocks contain abundant MgO (>35% m m⁻¹), resulting in low analyte yields, and making highly precise measurement of Hf isotopic signatures more challenging;^{6,11,18,19} (3) analyses are often compromised by problems that arise during ion exchange chemistry, including high Lu and Yb blanks, resulting in imprecise interference corrections on ¹⁷⁶Hf, and inefficient removal of Ti, leading to reduced Hf transmission in the mass spectrometer.^{10,13,16,17,23}

Given these challenges, few publications present Lu–Hf isotopic data for highly Hf-depleted geological samples, despite the capacity of this system to potentially elucidate some important geochemical processes.^{18–20} For the same reasons, there is limited Hf isotopic data for rock reference materials

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(RMs) containing $<0.1 \mu\text{g g}^{-1}$ Hf,²⁴ except for $^{176}\text{Hf}/^{177}\text{Hf}$ ratios determined using a pre-amplifier and a 10^{12} ohm resistor.^{19,25–27} The motivation of this work is to establish a rapid and simple analytical protocol for determining Lu and Hf concentrations and Hf isotopic compositions in depleted geological samples using MC-ICP-MS.

2. Experimental

All chemical separations and mass spectrometry were performed at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. The chemical procedure is performed in a class 100 laminar flow hood in a class 10 000 clean room environment. A flow chart of the complete experimental procedure is given in Fig. 1. The following subsections include details of reagents and materials, sample digestion, column chemistry and mass spectrometry.

2.1. Reagents and materials

Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C) from a Millipore water purification system (Elix-Millipore, USA) was used for all sample chemical preparations in this work. A pre-packed extraction chromatography material (Ln Spec, 100–150 μm particle size, 2 mL) was purchased from Eichrom Industries (Darien, IL, USA).

Concentrated hydrochloric, nitric and hydrofluoric acids (BV-III grade, from Beijing Institute of Chemical Reagents) were twice purified using a Savillex™ DST-1000 Teflon sub-boiling distillation system (Minnetonka, MN, USA). 70% m m^{-1} HClO_4 (Acros, Geel, Belgium), high purity H_3BO_3 (Acros, Geel, Belgium) and 30% m m^{-1} H_2O_2 (extra-pure grade, from Beijing Institute of Chemical Reagents) were directly used without additional purification. H_3BO_3 (3% H_3BO_3 in 3 M HCl) was prepared as follows: 12 g high purity H_3BO_3 was weighed into a clean Teflon beaker, and dissolved with 300 mL Milli-Q water. Then 100 mL of Teflon distilled 12 M HCl was added into the solution.

Standard solutions of 1000 ng g^{-1} Lu (Stock no. 35765) and $10\,000 \text{ ng g}^{-1}$ Hf (Stock no. 14374) purchased from Alfa Aesar (Johnson Matthey Company) (plasma standard solution, Spec-pure) were used to gravimetrically prepare standard solutions, diluted with 2% HNO_3 + trace HF for mass spectrometric measurements. As in-house standards, 5 ng g^{-1} of Alfa Lu and 20 ng g^{-1} of Alfa Hf solution were prepared and used during the actual measurement. Additionally, 20 ng g^{-1} of JMC 475 Hf was used for quality control of instrumental performance.

International rock reference materials (RMs) with 0.005 ppm $<$ Hf con. $<$ 0.15 ppm, produced by the United States Geological Survey (USGS DTS-2b), Association Nationale de la Recherche Technique, Paris (ANRT UB-N), the Geological Survey of Japan (GSJ JP-1), and International Association of Geoanalysts (IAG MUH-1 and HARZ01), Council for Mineral Technology, South Africa (MINTEK NIM-D) were used to evaluate and validate the present procedure.

2.2. Sample digestion

About 100–500 mg of powdered rock RM (UB-N, HARZ01) and ^{176}Lu – ^{180}Hf spike were weighed (both to 0.1 mg precision) into 7 or 15 mL Savillex PFA vials. The samples were dissolved on a hot plate at 100 – 120°C for one week using an acid mixture of 2 mL 22 M HF, 1 mL 14 M HNO_3 and 0.2 mL 70% m m^{-1} HClO_4 . After cooling, the capsule was opened, gently heated to dryness, and evaporated to fuming HClO_4 . Then 3 mL of 6 M HCl were added to the residue and dried, and this procedure was repeated. After the samples were dried again, the residues were completely dissolved in 3 to 5 mL 3 M HCl + 3% m/v H_3BO_3 mixtures at 100°C on a hot plate overnight. The amount of the latter solution was in proportion to the sample mass. After cooling, the residue was re-dissolved in 5 mL of 3 M HCl + 3% m/v H_3BO_3 . The capsule was resealed and placed on a hot plate at $\sim 100^\circ\text{C}$ overnight in preparation for chemical purification.

2.3. Column chemistry

The sample solution was centrifuged and then loaded onto pre-conditioned 2 mL Ln Spec resin for separation of Lu and Hf from the sample matrix.^{10,28} First, matrix elements (including light rare earth elements) were eluted with 3 M and 4 M HCl sequentially. The Lu (+Yb) fraction was eluted with 4 M HCl, and evaporated to dryness, and then diluted to 1 mL with 2% HNO_3 prior to mass spectrometry measurements. In order to minimize the isobaric interference of ^{176}Lu and ^{176}Yb

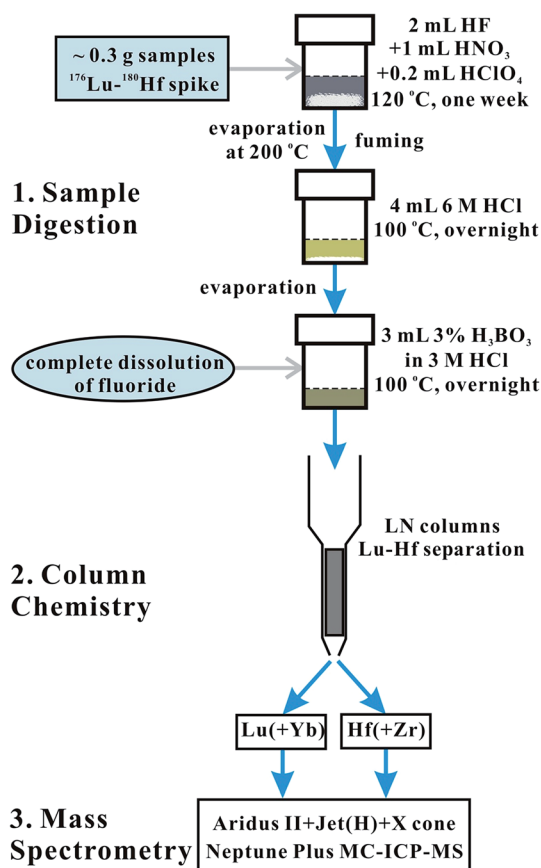


Fig. 1 Outline of the procedure for Lu–Hf isotopic determination of highly depleted ultramafic rocks.

on ^{176}Hf , the column was rinsed with ~ 40 mL of 6 M HCl to effectively remove Lu and Yb residues before collecting the Hf (+Zr) fraction. Titanium was separated from Hf using a 4 M HCl + 0.5% H_2O_2 mixture. Finally, Hf-Zr fractions were extracted from the column with 5 mL 2 M HF, collected in a 7 mL PFA beaker, and gently evaporated to dryness (Table 1). This fraction was taken up in 2 M HF, diluted to 1 mL with 2% HNO_3 , and was then ready for Hf isotopic analysis. The recovery yields of Lu and Hf were greater than 50% and 90%, respectively.

2.4. Mass spectrometry

A Thermo Fisher Scientific Neptune Plus (Bremen, Germany) MC-ICP-MS, housed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), equipped with nine Faraday cups was used for all isotope ratio measurements. The Neptune Plus comprises a high sensitivity option that uses a larger interface pump and an X skimmer cone configuration. All detectors used normal pre-amplifiers with a 10^{11} ohm resistor. The plug-in quartz torch with a quartz injector was fitted with a platinum guard electrode. Instrument optimization was performed following standard procedures outlined in the manufacturer's manual. In brief, the instrument was tuned to achieve the highest sensitivity while maintaining low oxides, flat-top peaks and stable signals.

Details of instrument operating conditions, data acquisition and Faraday cup configuration are summarized in Tables 2 and 3. Sample solution was introduced with an Aridus II desolvator using a self-aspirating $50 \mu\text{L min}^{-1}$ PFA nebulizer. Sweep gas Ar and N_2 gas flow rates were finely tuned daily to get maximum intensity using 20 ng g^{-1} Alfa Hf 14374 standard solution, while 2% HNO_3 + 0.1% HF was used as carrier and washing solution. The 20 ng g^{-1} Alfa Hf or JMC475 was measured every ten samples to check instrument stability. The mass bias behavior of Lu was assumed to follow that of Yb for the interference correction of ^{176}Yb on ^{176}Lu using the exponential law.¹³ The Hf isotopic data were reduced off-line in order to correct for instrumental mass bias and tracer contribution with normalization to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ using the exponential law. Usually, it takes 5 ($\text{Hf} > 0.05 \mu\text{g}$

g^{-1}) or 10 ($\text{Hf} < 0.05 \mu\text{g g}^{-1}$) minutes for one run Hf isotopic measurement, while one Lu content measurement takes about 5 minutes in this work. All data for geological samples are reported relative to the JMC 475 reference value of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$.^{2,23,27,28}

3. Results and discussion

3.1. Hf isotopic measurement of trace amounts of Hf

In order to demonstrate the improved capability of the high-sensitivity Neptune Plus MC-ICP-MS coupled with a desolvator Aridus II over the standard wet inlet introduction system, JMC 475 Hf was repeatedly measured with different sample load sizes, decreasing from 10 to 1 ng Hf. Normally, a 4–5 volt signal intensity is obtained for ^{180}Hf in a 20 ng g^{-1} Hf solution, assuming that the sample gas and ion beam were carefully optimized. The current Hf sensitivity is about 10–15 times higher than that of the standard wet inlet introduction system.²⁸ The mean $^{176}\text{Hf}/^{177}\text{Hf}$ for 10 and 5 ng JMC 475 solutions (*i.e.*, 20 and 10 ng g^{-1} Hf) is 0.282163 ± 05 (2SD, $n = 12$) and 0.282162 ± 11 (2SD, $n = 12$), respectively (Fig. 2). Comparatively, the mean $^{176}\text{Hf}/^{177}\text{Hf}$ for 2 and 1 ng JMC 475 solutions (*i.e.*, 4 and 2 ng g^{-1} Hf) is 0.282159 ± 13 (2SD, $n = 18$) and 0.282162 ± 26 (2SD, $n = 12$), respectively, which are in good agreement with the reference value of 0.282160.^{2,3} The internal $^{176}\text{Hf}/^{177}\text{Hf}$ precision

Table 2 Typical operating parameters for Lu and Hf isotopic measurement using the Neptune Plus MC-ICP-MS + Aridus

| Instrumentation | Setting |
|--|---|
| Neptune Plus MC-ICP-MS | |
| RF forward power | 1300 W |
| Cooling gas | 16 L min^{-1} |
| Auxiliary gas | 0.8 L min^{-1} |
| Sample gas | $\sim 1.00 \text{ L min}^{-1}$ (optimized daily) |
| Extraction | -2000 V |
| Focus | -645 V |
| Detection system | Nine Faraday collectors |
| Acceleration voltage | 10 kV |
| Interface cones | X cone + H cone |
| Nebulizer type | Micromist PFA nebulizer |
| Sample uptake rate | $50 \mu\text{L min}^{-1}$ |
| Uptake mode | Free aspiration |
| Instrument resolution | ~ 400 (low) |
| Typical sensitivity on ^{180}Hf | $\sim 160 \text{ V ppm}^{-1}$ ($10^{-11} \Omega$ resistors) |
| Sampling mode | 9 blocks of 6 cycles for Hf 1 block of 50 cycles for Lu |
| Integration time | 8 s for Hf and 4 s for Lu |
| Baseline/background determination | <i>ca.</i> 1 min on peak in 2% HNO_3 |
| Aridus II | |
| Sweep gas (Ar) | 7 to 10 L min^{-1} |
| Addition gas (N_2) | 2 to 4 L min^{-1} |
| Spray chamber temperature | $110 \text{ }^\circ\text{C}$ |
| Membrane temperature | $160 \text{ }^\circ\text{C}$ |

Table 1 Lu-Hf chemical purification procedure using Ln resin

| Step | Column volumes | Acid |
|---|------------------------|---|
| Ln Spec 2 mL <i>ca.</i> $0.8 \times 4 \text{ cm}$ | | |
| Preparation | 20 mL \times 3 times | 6 M HCl + 0.2 M HF |
| Preconditioning | 7 mL \times 3 times | 3 M HCl |
| Loading sample | 5 mL | 3 M HCl + 3% m/v H_3BO_3 |
| Eluting matrix | 5 mL \times 2 times | 3 M HCl |
| Eluting matrix | 5 mL \times 2 times | 4 M HCl |
| Collecting Yb and Lu | 2.5 mL | 4 M HCl |
| Eluting residual Yb and Lu | 5 mL \times 8 times | 6 M HCl |
| Eluting Ti | 5 mL \times 4 time | 4 M HCl + 0.5% H_2O_2 |
| Collecting Zr and Hf | 5 mL | 2 M HF |

Table 3 Faraday cup configurations for Lu and Hf isotopic measurement by Neptune Plus MC-ICP-MS

| Element | L4 | L3 | L2 | L1 | C | H1 | H2 | H3 | H4 |
|---------|--------------------------|--------------------------|-------------------------------|-------------------|-------------------|--------------------------|------------------------------|-------------------------------|-------------------|
| Lu | $^{168}\text{[Er + Yb]}$ | $^{170}\text{[Er + Yb]}$ | ^{171}Yb | ^{172}Yb | ^{173}Yb | $^{174}\text{[Yb + Hf]}$ | ^{175}Lu | $^{176}\text{[Lu + Yb + Hf]}$ | ^{178}Hf |
| Hf | ^{173}Yb | ^{175}Lu | $^{176}\text{[Hf + Yb + Lu]}$ | ^{177}Hf | ^{178}Hf | ^{179}Hf | $^{180}\text{[Hf + Ta + W]}$ | ^{181}Ta | ^{186}W |

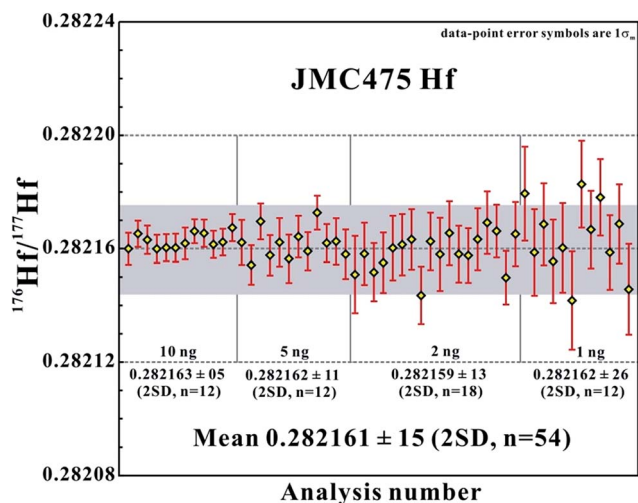


Fig. 2 $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for different load sizes of JMC 475 measured using a Neptune Plus MC-ICP-MS fitted with an Aridus II and X-skimmer cone. The error bars for each measurement are 1SE. Dashed line in the middle and shaded area represent the mean and 2SD of all measurements, respectively.

varied from 15 to 20 ppm (2SE) for 2 ng Hf and from 35 ppm to 40 ppm (2SE) for 1 ng Hf. These results are in excellent agreement with those previously obtained using a MC-ICP-MS with a wet-method spray chamber and PFA self-aspirating nebulizer (>100 ng Hf).

3.2. Sample decomposition

HF + HNO₃, HF + HClO₄ or similar acid mixtures are commonly used to dissolve silicates in geological samples. Utilizing clean HF and HNO₃ leads to lower blanks. These acids can be easily purchased in a highly pure form or produced by repeated distillation of lower purity acids, which is the method we adopted here.^{19,28} However, in HF-assisted digestion, the resulting insoluble Mg-fluoride (mainly MgF₂) is undesirable as its formation significantly reduces Lu and Hf recovery. As typical peridotites have MgO > 35 wt%, such samples are highly prone to formation of insoluble fluorides. H₃BO₃ completely dissolves these salts and solutions with no residue were obtained for the RMs analyzed in this study. This ensured complete sample digestion and high Lu and Hf recovery yields.^{14,15,18,29,30}

3.3. Chemical purification

Commercial Ln resin is widely used to concentrate Lu and Hf in a single purification step.¹⁰ We used an improved mixture, dominated by hydrochloric acid with lower amounts of H₂O₂

and HF, as the elution solution, simplifying the chemical procedure. Our experience indicates that residual Yb and Lu are evident in the Hf fraction, particularly in Hf-depleted samples. Instead of elution with 20 mL of 6 M HCl which resulted in residual Yb and Lu, 40 mL was used. The final Hf content and isotopic ratio were identical to the recommended values of the Alfa Hf solution, indicating complete separation of Yb and Lu from Hf and negligible isobaric interference correction of ^{176}Lu and ^{176}Lu for ^{176}Hf .

3.4. Total procedural Lu and Hf blanks

Using sub-boiling distilled HCl, HF, and HNO₃, typical total procedural blank values (including sample decomposition, H₃BO₃ dissolution step, column chemistry, and mass spectrometry) for Lu and Hf were mostly lower than 5 pg and 10 pg, respectively. Thus, Hf sample/blank ratios were more than 300 for most geological RMs and 200 for DTS-2b. The blank effect on the Hf isotopes and Lu/Hf ratio is insignificant.

3.5. Lu–Hf isotopic analysis of RMs

Lu and Hf concentrations and Hf isotope data (duplicate or triplicate determinations) for six geological RMs are summarized in Table 4.^{31–40} There was an insignificant difference between the Hf isotope ratios obtained with or without the Hf spike. DTS-2b (~4 ng g⁻¹ Hf) was measured as an alternative to peridotite PCC-1 (5 ng g⁻¹ Hf) considering that the latter is in

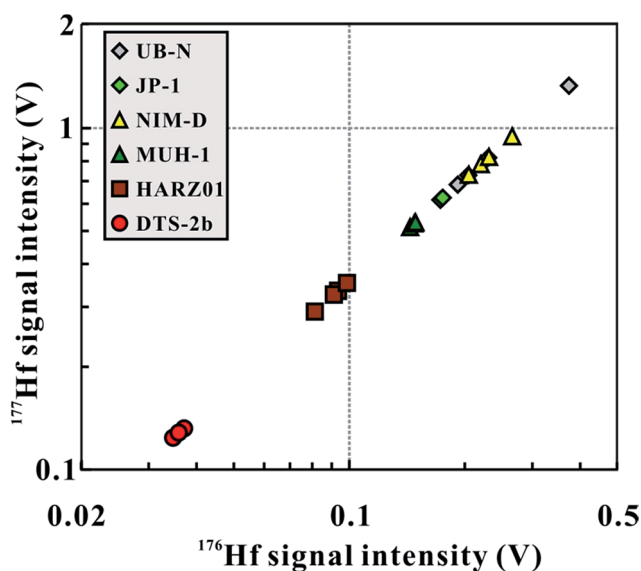


Fig. 3 The ^{176}Hf vs. ^{177}Hf signal intensity (V) of the actual samples investigated in this work, indicating our high Hf recovery and corresponding data precision during mass spectrometric measurement.

limited supply.¹⁹ The duplicate analysis of DTS-2b yielded reproducible Lu and Hf concentrations and $^{176}\text{Hf}/^{177}\text{Hf}$ values. Internal precision of $^{176}\text{Hf}/^{177}\text{Hf}$ of each analysis was better than 40 ppm, and the $^{176}\text{Hf}/^{177}\text{Hf}$ results agreed with each other within analytical error (Fig. 3).

3.6. Protocol advantages

To date, there are few papers reporting sub-nanogram Lu and Hf measurements in real geological samples.^{18,19} The protocol described herein avoids two- or three-stage chemical separation involving complex reagents and instruments equipped with 10^{12} ohm resistors,^{19,22,25–27} and instead utilizes extremely simple and rapid digestion and separation to facilitate the analysis of low Lu and Hf signals ($0.005 \mu\text{g g}^{-1} < \text{Hf} < 0.1 \mu\text{g g}^{-1}$). Sample-spike equilibration is readily achieved, even for large mass samples, as illustrated by the highly reproducible Lu–Hf isotopic data and low blanks for RMs (Table 4). Moreover, this procedure provides flexibility to change the analyte of interest (*e.g.*, Lu–Hf, Rb–Sr, or Sm–Nd), and chemical purification can easily be tailored and performed routinely in most geochemical laboratories. As we previously mentioned,²⁸ if only Lu–Hf

isotopic data are required, the first column step is enough and adequate for their purification. Likewise, if Rb–Sr and/or Sm–Nd isotopic data are also of interest as well, their purification by collecting first elution solutions can be further achieved and accomplished using only the second standard cation exchange resin and third Ln columns.^{17,18,28,40}

3.7. Potential applications

This analytical protocol will offer potential applications in the following geochemistry fields. (1) The method is suited to Lu–Hf isotopic measurements in highly Hf depleted ultramafic rocks (*e.g.*, peridotite, serpentinite, dunite, harzburgite, *etc.*);^{18–20} (2) very small aliquots (10 mg) of minerals or materials (*e.g.*, apatite, garnet or clinopyroxene with $\text{Hf} < 0.1 \mu\text{g g}^{-1}$, or even below $0.01 \mu\text{g g}^{-1}$) can be utilized for Lu–Hf geochronometry. Recent work showed that micro-zones in a single garnet crystal can be analyzed for high-precision Lu–Hf and Sm–Nd geochronology,^{40,42} an application that is well-suited to this simplified analytical approach; (3) precious and small mass samples of extraterrestrial materials (*e.g.*, meteorites, chondrites, asteroidal dust) with very low Lu and Hf contents can be

Table 4 Analytical results of Lu–Hf isotopic composition for highly Hf-depleted geological RMs^a

| Sample (Rock type) | MgO (%) | Lu (ng g ⁻¹) | Hf (ng g ⁻¹) | $^{176}\text{Lu}/^{177}\text{Hf}$ | $^{176}\text{Hf}/^{177}\text{Hf}$ ($\pm 2\text{SE}^b$) | $^{176}\text{Hf}/^{177}\text{Hf}^c$ ($\pm 2\text{SE}^b$) |
|--|---------|--|--|-----------------------------------|--|--|
| UB-N (serpentinite) | 35.21 | 45.6 | 126.2 | 0.0513 | 0.283237(07) | 0.283248(08) |
| | | 45.3 | 123.8 | 0.0520 | 0.283246(10) | |
| | | 45.7 | 126.5 | 0.0514 | 0.283250(10) | |
| | | 45.5[0.4] | 125.5[3.0] | 0.0516[08] | 0.283245[11] | |
| JP-1 (peridotite) | 44.72 | 4.05 | 119.8 | 0.00480 | 0.282314(08) | 0.282303(09) |
| | | 4.10 | 119.9 | 0.00485 | 0.282309(10) | |
| | | 4.01 | 117.7 | 0.00484 | 0.282311(09) | |
| | | 4.05[0.09] | 119.1[2.5] | 0.00483[05] | 0.282308[11] | |
| NIM-D (dunite) | 43.51 | 4.0, ³⁴ 4.6 ³⁴ | 121, ³⁴ 101 ³³ | | 0.282304[18] ²² | 0.282725(08) |
| | | 4.2 ³⁵ | 124 ²² | | 0.282309[26] ²⁵ | |
| | | 3.93[0.15] ²⁵ | 116.0[3.0] ²⁵ | 0.00456[15] ²⁵ | | |
| | | 8.47 | 56.6 | 0.0213 | 0.282736(09) | |
| MUH-1 (harzburgite) | 38.25 | 8.53 | 57.1 | 0.0212 | 0.282713(09) | 0.283574(11) |
| | | 8.74 | 57.0 | 0.0218 | 0.282731(10) | |
| | | 8.58[0.28] | 56.9[0.5] | 0.0214[06] | 0.282726[20] | |
| | | 8.9, ³¹ 9.49 ³⁴ | 28.6 | 0.0891 | 0.283557(11) | |
| HARZ01 (harzburgite) | 45.84 | 17.9 | 28.0 | 0.0908 | 0.283569(13) | 0.282352(13) |
| | | 18.2 | 29.2 | 0.0885 | 0.283580(12) | |
| | | 18.0[0.3] | 28.6[1.2] | 0.0895[24] | 0.283570[20] | |
| | | 3.08[0.14] | 14.2[0.6] | 0.0307[15] | 0.282369(14) | |
| DTS-2b (dunite) | 49.58 | 3.7 ³⁵ | 18 ³⁵ | | 0.282370(15) | 0.283088(28) |
| | | 3.02 | 14.3 | 0.0299 | 0.282374(16) | |
| | | 2.18 | 4.49 | 0.0690 | 0.283093(38) | |
| | | 2.16 | 4.39 | 0.0699 | 0.283069(36) | |
| Mean [$\pm 2\text{SD}$] ^d | | 2.17[0.03] | 4.44[0.14] | 0.0695[13] | 0.283083[25] | |
| | | 2.01, ³⁸ 1.99 ³⁹ | 5.55, ³⁸ 8.39 ³⁹ | | | |

^a Approximately 0.1 g of rock powder was digested for UB-N and JP-1, respectively, corresponding to *ca.* 10 ng of Hf. Approximately 0.2 g of NIM-D and MUH-1 were weighed for digestion, corresponding to about 10 ng and 5 ng of Hf respectively, while 0.3 g and 0.5 g of rock powder were digested for the HARZ01 and DTS-2b, which corresponded to *ca.* 3 ng and 2 ng of Hf respectively. The MgO (%) data are from GeoReM (<http://georem.mpch-mainz.gwdg.de/>) or corresponding certificate data. ^b Analytical uncertainty in the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio (2SE) quoted in the last two decimal places. ^c Unspiked data. ^d The standard deviation (SD) quoted in the last two decimal places.

analysed;^{2,11,40–44} (4) the radiogenic Hf composition of aerosols can potentially be used to trace mineral dust to source sites^{40,45} and Hf isotopic signatures have been widely used as tracers of global geochemical cycles. The analytical approach described will facilitate reduced sample consumption and high spatial resolution research.²¹

4. Conclusions

A highly reproducible analytical protocol for the determination of Lu and Hf concentrations and Hf isotopic compositions at sub-nanogram levels in geological samples using MC-ICP-MS is described in this work. The six highly Hf-depleted RMs analysed contain ng g^{-1} levels of Lu and Hf and yielded high-precision Lu and Hf contents and Hf isotopic data consistent with reported or unspiked values, demonstrating that the procedures are robust. Given the successful column chemistry and sufficiently low blanks, this high sensitivity analytical protocol will offer more opportunities in a wide range of research fields including geochemistry, cosmochemistry, and environmental sciences.

Conflicts of interest

There are no conflicts to declare.

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