

A straightforward separation scheme for the concomitant isolation of Lu, Hf, Sm, and Nd prior to isotope ratio and isotope dilution measurements following sample decomposition by Lithium metaborate fusion or Hydrofluoric acid dissolution

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A robust method is described allowing the sequential separation of Hf and the lanthanides from matrix elements of silicate rocks or minerals. This is based on a single chromatographic column filled with the conventional cation-exchange DowexAG50W-X8 resin, and hydrochloric, nitric and sulfuric acids as eluting agents. Samples can be processed following the same column protocol, irrespective whether they were decomposed by high temperature fusion with LiBO₂ (ensuring a thorough sample/tracer isotopic equilibration in the molten glass, in case the isotope dilution method is used), or by hydrofluoric acid dissolution. The hafnium fraction separated in this way is ready for isotope ratio measurements by MC-ICP-MS, while the REEs are further processed by extraction chromatography for isolating Nd, Sm, and Lu, in view of TIMS and MC-ICP-MS analyses. The precision and accuracy of the method were evaluated by repeat analyses of four geological Reference Materials covering a range of silicate rock compositions.

Keywords: chromatography, Lu-Hf, Sm-Nd, isotope dilution-mass spectrometry, silicates

INTRODUCTION

By virtue of their involvement in three long-lived, natural radioactive decay systems, namely ¹⁴⁷Sm-¹⁴⁴Nd, ¹³⁸La-¹³⁸Ce, and ¹⁷⁶Lu-¹⁷⁷Hf, the Lanthanide Elements and Hafnium provide valuable tools in Earth and Planetary Sciences, for both radiometric dating and isotopic tracing purposes (e.g., Dickin, 2005; Faure and Mering, 2012). Although less commonly used than other classical systems such as U-Th-Pb or Rb-Sr, they can also provide useful constraints in environmental studies (Baskaran, 2011). For these reasons, there has been a great interest in their chemical separation from geological and environmental samples, as required prior to mass spectrometric measurements of the isotope composition of the elements possessing the daughter isotopes (Nd, Ce, Hf), and the corresponding parent/daughter elemental ratios by using the isotope dilution method.

From the mid 1970's to the early 1990's, the separation of these trace elements from matrix elements has been

accomplished by means of cation-exchange chromatography, and the subsequent isotope ratio analyses made by using Thermal Ionization Mass Spectrometry (TIMS), which is now complemented by Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), especially for Hf isotope ratios, by virtue of a much greater ionization efficiency (Halliday *et al.*, 1995).

During the last two decades, extraction chromatography (EXC) has played an increasing role, by virtue of its inherently better selectivity, which triggered the production and commercialization of a range of element specific "resins", initially developed in the scope of nuclear wastes processing projects (Horwitz *et al.*, 1992). These allowed considerable down-scaling, and an overall improvement of geochemical separation procedures to be achieved (e.g., Pin and Rodriguez, 2014 and references therein). Albeit having brought a major breakthrough, the EXC technique is not free of some disadvantages, namely, the elevated cost of EXC materials and, from a practical point of view, the difficult reduction of memory effects to negligible levels. Indeed, persistent memory effects appear to be an almost unavoidable counterpart of the very high elemental selectivity of the extracting agents used on the one hand, and of the tortuous porous network—

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particularly the presence of “dead end” pores—of the polymer beads used as inert supporting materials for the organic extractants on the other (Pin and Rodriguez, 2014).

As a consequence of the huge improvement of ionization efficiency and sample throughput permitted by MC-ICP-MS instruments, the interest on Hf isotopes analysis has increased drastically. This has triggered the development of a wealth of methods aiming to achieve the isolation of an Hf fraction, based on different approaches for both sample decomposition (acid dissolution versus melting with an alkaline flux) and chemical separation (ion-exchange or extraction chromatography or a combination thereof (e.g., Scherer *et al.*, 1997; Blichert-Toft *et al.*, 1997; Yang and Pin, 1999; Le Fèvre and Pin, 2001, 2005; Münker *et al.*, 2001; Ulfbeck *et al.*, 2003; Lapen *et al.*, 2004; Connelly, 2006; Connelly *et al.*, 2006; Yang *et al.*, 2010; Li *et al.*, 2014; Bast *et al.*, 2015; Frisby *et al.*, 2016; Pin and Gannoun, 2017). In this work, we describe a robust method allowing the sequential separation of Hf and the whole REE from each-other and from matrix elements, by using a single chromatographic column filled with the conventional cation-exchange Dowex AG50W-X8 resin and different inorganic acids as eluting agents. This separation method can be applied to silicate rocks and minerals which have been decomposed either by fusion with a lithium metaborate flux or, optionally, by dissolution with hydrofluoric acid. This flexibility is advantageous when both easy-to-dissolve (e.g., basalts) and refractory-mineral bearing samples (e.g., granitoids) are to be processed on a routine basis. While an Hf fraction ready for MC-ICP-MS analysis is obtained in a single stage, Nd, Sm and Lu need to be further isolated from the other REE with a second column of the well-established HDEHP-based extraction chromatography material (Ln-Spec resin).

EXPERIMENTAL

Chemicals

Water with a resistivity higher than 18 M Ω cm was used throughout. This was prepared from tap water first by reverse osmosis by using an Elix (Merck Millipore, USA) device, and then further de-ionized with an Easypure II (Thermo Fisher Barnstead, USA) equipment. Nitric acid (HNO₃, 69.8%), and hydrochloric acid (HCl, 37%) of Pro Analyti grade (Merck, Germany) were purified by sub-boiling distillation in a Teflon acid purification system (Berghof, Germany). Hydrofluoric acid (HF, 50.2%) of Pro Analyti (Merck, Germany) quality was purified by subboiling distillation (Mattinson, 1972) in a PFA (Savillex Corp., USA) jar assembly. Perchloric acid (HClO₄, 70–72%), of Pro Analyti (Merck, Germany) quality was used without further purification. Sulfuric acid

(98%, ULTREX) was purchased from Baker (France) and used as received. The high purity LiBO₂ (Analysis Grade Ultra Pure) used as a flux was obtained from Corporation Scientifique Claisse (Canada) and the solution used as a non-wetting agent of the melt in Pt crucibles was prepared by dilution of LiBr (Merck Suprapur Germany) to 50% vol. with ultrapure water.

Extraction chromatography (EXC) material Ln-Spec (50–100 μ m particle size), manufactured by Eichrom Industries (USA) was purchased from Triskem International (France), while the conventional cation-exchange resin AG50W-X8, 200–400 mesh size, was obtained from Fluka Analytical (Switzerland).

Tracers

Isotopically-enriched tracers used in this work were obtained from Oak Ridge National Laboratory (USA). The ¹⁷⁶Lu-¹⁷⁹Hf tracer solution was calibrated by reverse isotope dilution against two mixed gravimetric normal solutions, prepared from 1000 \pm 2 mg l⁻¹ single element solutions purchased from Fluka (Switzerland) for Lu and Merck (Germany) for Hf. Before measurements by MC-ICP-MS, Lu and Hf in the tracer-normal mixtures were separated from each other by the procedure described hereafter, in order to avoid isobaric interference of ¹⁷⁶Hf on ¹⁷⁶Lu. The Lu/Hf ratio in the tracer was high enough (about 6) to be used on a wide range of samples, ranging from subchondritic rock ratios (Lu/Hf \approx 0.2) to garnet samples (Lu/Hf up to 30). Hf is the most sensitive element in the tracer/sample ratio. Indeed, when the ¹⁷⁶Hf/¹⁷⁷Hf ratio is to be measured on the totally spiked sample, it is necessary to reduce the magnitude of the correction of the spike contribution, while allowing a ¹⁷⁹Hf/¹⁷⁷Hf ratio of about 1 to be measured, in order to keep the measurement uncertainty magnification of isotope dilution calculations (Webster, 1960) to a minimum. The ¹⁴⁹Sm-¹⁵⁰Nd tracer is the solution used routinely in our laboratory, which was calibrated against a mixed solution prepared from high purity metal ingots supplied by the Ames Laboratory (USA). Unfortunately, this solution is too dilute for an optimal use of the fusion method described hereafter, in which an as small as possible volume of mixed tracer solution should preferably be added to the sample powder plus flux mixture, resulting in significant underspiking of the samples processed in this work. The characteristics of the mixed Lu-Hf and Sm-Nd tracers are given in Supplementary.

Instrumentation and labware

All the chemical treatments (dissolution-evaporation, chromatography, etc.) have been done in protected areas under laminar flow conditions and inside total exhaust acid-resistant workstations made of polypropylene (LFE-1500BT, Salare Inc., USA). The cabins are located in a

room with an over-pressure of filtered air (1:10,000 class clean room). Teflon® PFA containers of 15 ml (Savillex®) were used during the chemical treatment of the samples. Whenever possible, previously cleaned (with HNO₃ and deionized H₂O) disposable materials were used.

Quadrupole-based ICP-MS instruments [PQII+, VG-Instruments (Clermont-Ferrand), and XSeries 2, Thermo-Fisher Scientific (Bilbao)] with enhanced sensitivity through a dual pumping system were used in the semi-quantitative mode for setting up the method, and in the quantitative mode for measuring blanks. The Lu and Hf isotope ratios analyses were done in the static mode in Bilbao with a Neptune MC-ICP-MS (Thermo-Fisher Scientific) upgraded with a large dry interface pump and specific cones (so-called Jet interface). The sample was introduced with a high sample transport efficiency system (Apex IR, Elemental Scientific, USA) comprising a PFA micro-flow nebulizer, a heated cyclonic spray chamber, and a low-volume three-stage, thermo-electrically cooled (Peltier effect) condenser. An upgraded Finnigan MAT262 TIMS was used for isotope ratio measurements of Nd and Sm, in static multi-collection mode.

Sample decomposition

Alternative digestion methods were used depending on the aim of the measurement. Accessory minerals such as zircon (to a lesser degree, rutile) hosts major amounts of Hf, but their refractory character makes them difficult to decompose by conventional acid dissolution. In this study, decomposition by alkaline fusion was selected when the complete destruction of refractory minerals was required to ensure a quantitative recovery of the Hf contained in the bulk sample. If, instead, the aim was to determine the Hf isotope composition of a selected mineral (typically garnet, because of its high Lu/Hf ratio) a mild acid dissolution procedure was preferred. This is because garnets often contain inclusions of refractory minerals hosting large quantities of Hf and this procedure enables to leave the potentially troublesome inclusions undissolved.

Fusion with LiBO₂. An electrical Joule-effect automatic fusion machine (Katanax, K1 Prime Fluxer, Canada) was used for sample decomposition by fusion adapting the procedure from Le Fèvre and Pin (2002). The platinum crucibles are cleaned in dilute HNO₃ in an ultrasonic bath.

Sample powder (50–100 mg) is weighed into a crucible with flat bottom. The weighed quantity depends on the Hf concentration of the sample, and is chosen to permit the extraction of at least 40 ng of hafnium. The LiBO₂ flux is added to the sample, with a final flux to sample ratio of 5:1. This relatively high ratio was found to be the minimum required to allow the melt to be poured out of the crucible easily. At lower ratios, it was observed an inefficient pouring of the melt from the crucible. After

addition and weighing of the mixed ¹⁷⁶Lu-¹⁷⁹Hf and ¹⁴⁹Sm-¹⁵⁰Nd tracer solutions, the crucible is manually agitated to achieve a homogeneous mixture, which is then nearly dried at room temperature. The spiked mixture is placed in the furnace for 10 minutes at a temperature of 1200°C, as recommended by the manufacturer.

The resulting melt is poured and quenched in a pre-cleaned disposable 30 ml polystyrene beaker containing 10 ml of 2 mol l⁻¹HCl - 0.15% H₂O₂ continuously stirred with a magnetic bar. Hydrogen peroxide is added to prevent, or at least slow down the hydrolysis of the HFSE (Fritz and Dahmer, 1965). Complete dissolution and cooling are achieved within 10–15 minutes.

Dissolution by HF. Besides Hf-rich accessory phases, the selected silicate minerals to be analysed (mainly garnets for geochronological purposes due to their high Lu/Hf and Sm/Nd ratio) may contain inclusions of REE-rich phosphates (such as apatite, monazite or xenotime) which can bias the Sm-Nd and Lu-Hf systematics. To circumvent this problem, such phosphates were removed prior to silicate decomposition by using the sulfuric acid (H₂SO₄) selective dissolution procedure (Anczkiewicz and Thirlwall, 2003).

Another problem inherent to the HF dissolution method is that Hf forms very strong complexes with fluorine. These complexes are not retained by the cation-exchange resin used for the separation of Hf. In order to reduce fluorine to a sufficiently low level, the solutions were brought to strong fumes of perchloric acid (HClO₄), as described by Pin and Joannon (2002). To prevent hydrolysis problems, hydrogen peroxide was used, and the solutions were handled promptly. The detailed protocol is as follows:

An appropriate amount of the separated minerals is ground in an agate mortar and cleaned with acetone and water. After drying, the coarse powder is transferred to a Teflon PFA (Savillex®) container. 0.5 to 1 ml of concentrated (18 mol l⁻¹) sulfuric acid is added (depending on the sample size) and the vial is heated at 180°C for 24 hours (sulfuric acid leaching). The leachate, which contains the chemical elements from the selectively dissolved phosphates, is discarded, and the sample is rinsed several times with H₂O in order to remove quantitatively the sulfuric acid and the dissolved elements therein, and thus prevent the formation of insoluble calcium sulfates. The sample is then transferred with a drop of water into a new vial, dried and weighed. The evaporation should be done slowly and at low temperature, otherwise samples will tend to ‘jump’ out from the beaker due to electrostatic forces. Before the acid attack of the sample, both Lu-Hf and Sm-Nd tracers are added, by weight. Two ml of 14 mol l⁻¹HNO₃, 1 ml of 29 mol l⁻¹ HF and 0.5 ml of 11.8 mol l⁻¹ HClO₄ are added, and the beaker is closed and heated overnight at about 75°C. After opening the vial,

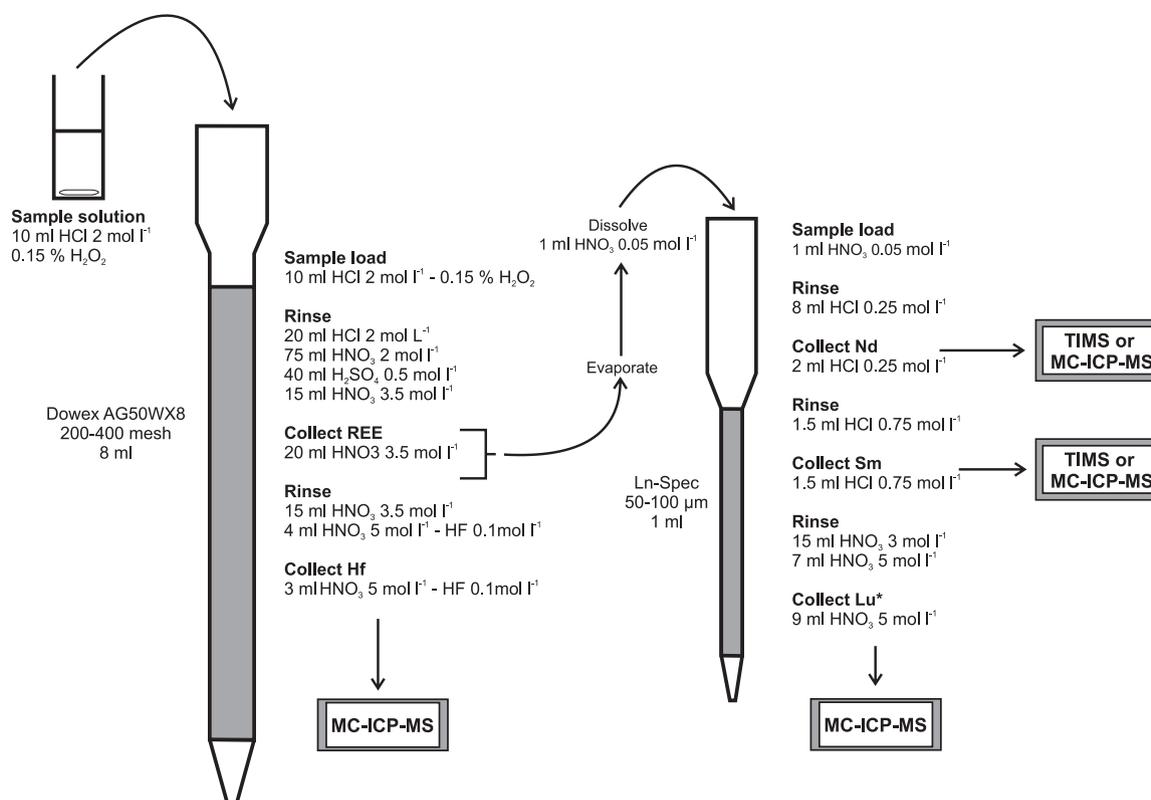


Fig. 1. Diagram of the separation procedure of the analytes of interest. Lu* refers to the fraction of Lu containing ca. 10% of Yb. See text for further explanations.

the excess of hydrofluoric and nitric acids is evaporated, together with volatile SiF₄. During evaporation, four ml of 11.8 mol l⁻¹ HClO₄ are added and the solution is brought to strong fumes of perchloric acid under an infra-red heater, taking care not to 'overcook' the mixture, which must remain in the liquid state, in order to prevent the formation of insoluble Ti compounds (e.g., Unruh *et al.*, 1983). The condensates that form on the walls of the beaker are rinsed with H₂O. The fuming step is stopped before evaporation goes to completion, leaving about 0.5–1 ml of liquid. Five ml of 6 mol l⁻¹ HCl are added and the sample solution is transferred to a centrifuge tube to isolate undissolved minerals (mainly zircon and rutile). The supernatant solution is returned to the dissolution PFA vial, and again evaporated until 1 ml is left.

Just prior to column work, the 1 ml sample solution is diluted with 9 ml of 2 mol l⁻¹ HCl - 0.15% H₂O₂. The sample is therefore in a medium and a volume roughly similar to that of the samples prepared by fusion (10 ml of 2 mol l⁻¹ HCl - 0.15% H₂O₂), which allows a single separation scheme to be used for the two methods of sample decomposition.

Separation of the analytes

Before isotope ratio measurements by TIMS and/or

MC-ICP-MS, it is necessary to isolate the elements of interest in an as pure as possible chemical form, not only to eliminate isobaric interferences (¹⁷⁶Yb, ¹⁷⁶Lu for ¹⁷⁶Hf and ¹⁴⁴Sm for ¹⁴⁴Nd), but also to reduce as much as possible any potential cause of matrix effects, particularly those which might jeopardize the correction for instrumental mass bias. A single cation-exchange column proved to be sufficient to get Hf in a suitable form for MC-ICP-MS measurements, while a second extraction chromatographic column based on the conventional HDEHP extracting agent was used for separating Nd, Sm, and Lu prior to measurements (Figs. 1, 2 and 3).

First column: Separation of Hf + REE by cation-exchange. The separation of Hf and REE from matrix elements is achieved by using a 1 cm i.d. silica glass column containing 8 ml of Dowex AG50W-X8 (200–400 mesh) cationic resin. Prior to use, the column is thoroughly cleaned with several rinses of 6 mol l⁻¹ HCl and 5 mol l⁻¹ HNO₃ - 0.1 mol l⁻¹ HF, and finally left to drain overnight with 100 ml of H₂O. Prior to sample loading, the column is preconditioned with 10 ml 2 mol l⁻¹ HCl. The sample is then loaded onto the column. During the elution, other elements of radiogenic isotope interest are separated, and although not used in this work, they will be mentioned.

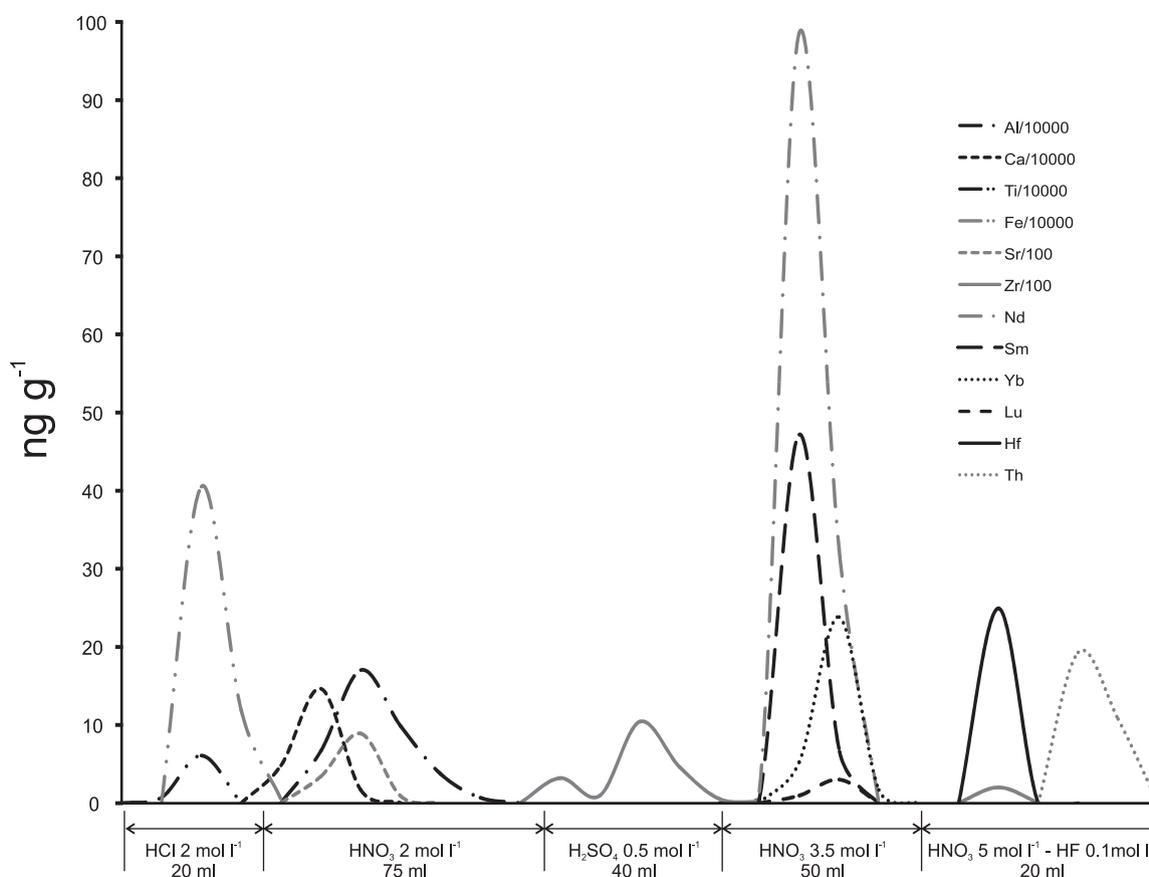


Fig. 2. Typical elution curves for some of the major elements as well as for the elements of interest on Dowex AG50W-X8 cation-exchange resin.

In the first step, the column is rinsed with 20 ml of 2 mol l⁻¹ HCl, removing Si and Li and B from the flux, when the fusion method was used. Many other elements (Na, Mg, Ti, Fe, Mn, Cu, Zn and about half of Co and Ni) are also eluted at that stage. Then, 20 ml of 2 mol l⁻¹ HNO₃ are loaded onto the column, removing K, about two-thirds of Al, half of Ca and Cr, and the rest of Co and Ni. This fraction also contains U and Rb which might be collected and further purified if required. With further 30 ml of the same acid, Sr could be collected. However, it is accompanied by large quantities of Al and Ca, and would need to be further purified by extraction chromatography by using the Sr-Spec resin (Pin and Bassin, 1992). Another fraction of 25 ml of 2 mol l⁻¹ HNO₃ ensures the elution of Ba, which is discarded. Then, 40 ml of 0.5 mol l⁻¹ H₂SO₄ allows removal of most (80–85%) of the Zr present in the sample.

The eluting medium is returned to HNO₃, but 3.5 mol l⁻¹ in that case. Fifteen ml of that acid are first discarded allowing reduction of the amount of Zr left in the Hf fraction and getting rid of interstitial sulfuric acid. Then, the REE (Sm, Nd, Lu for our purpose) are collected in the

next 20 ml. Fifteen further milliliters are passed through the column in order to elute the tails of the La, Ce, Pr and Y peaks. Finally, the eluting medium is switched to a mixture of 5 mol l⁻¹ HNO₃ - 0.1 mol l⁻¹ HF. The first 3.5 ml (free of any element but some residual La) are discarded before Hf is collected in a further fraction of 3.5 ml. The Hf separated in this way contains less than 10% of the Zr initially present in the sample, and is ready for Hf isotopic analyses by MC-ICP-MS. Peters *et al.* (2015) reported that at Zr/Hf > 10 there is an observable bias on ¹⁷⁶Hf/¹⁷⁷Hf when using X skimmer- and Jet sample cones on a Neptune MC-ICP-MS. If one is interested in collecting Th, it can be recovered in an additional fraction of 13 ml of 5 mol l⁻¹ HNO₃ - 0.1 mol l⁻¹ HF. The column work takes about 10 hours (plus one hour for the cleaning steps). From a practical point of view, the dilute (0.1 mol l⁻¹, that is <0.2%) HF-bearing solutions used to strip Hf and then Th did not produce any noticeable attack of our fused silica glass columns. This is in line with etching rates < 0.1 μm/hour in 10 wt% HF at 25°C reported for fused silica glass (Tosoh Corp., 2013) and also with the presence of 2% (1.2 mol l⁻¹) HF in the mixture recommended

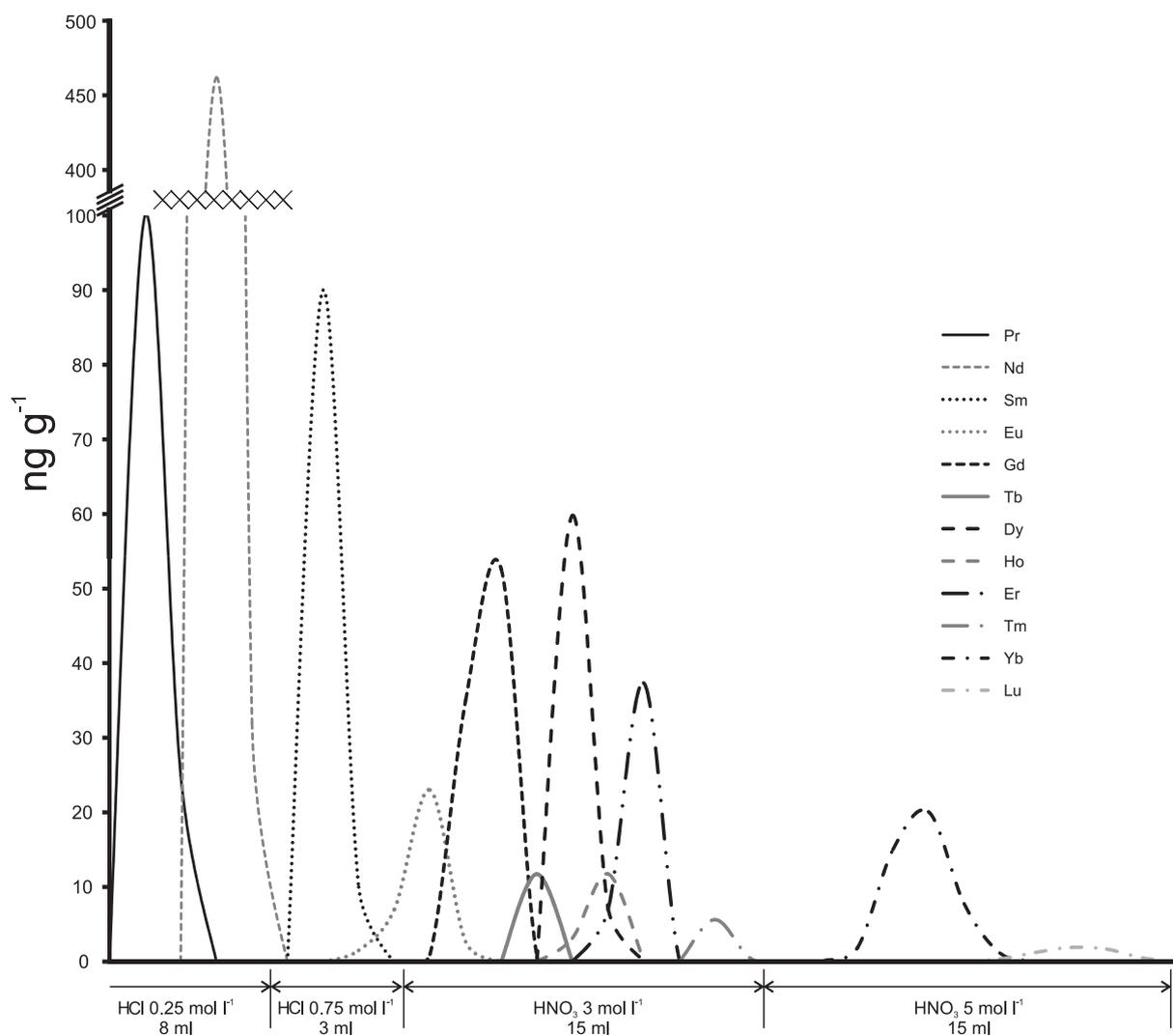


Fig. 3. Typical elution curves for REEs on Ln-Spec extraction-resin.

by the manufacturer to clean Quartex silica glass sub-boiling stills.

Second column: isolation of individual lanthanides by Extraction Chromatography. The isolation of Sm, Nd, and Lu is achieved following the method adapted from Le Fèvre and Pin (2005) by using 1 ml of the Ln-Spec extraction chromatography material, contained in a 5 mm i.d. silica glass column. Before loading the sample, the column is cleaned with 6 mol l⁻¹ HCl and the conditioning is done with 0.05 mol l⁻¹ HNO₃.

The 20 ml of 3.5 mol l⁻¹ HNO₃ containing the REE separated on the first column are evaporated to dryness overnight. The residue is taken up with 1 ml of 0.05 mol l⁻¹ HNO₃ and loaded onto the column. The Ln-Spec material allows the separation of all the REE, and the sequence of acids used in our case consists of 8 ml of 0.25 mol l⁻¹ HCl (La + Ce, and a great part of Pr), 2 ml of 0.25

mol l⁻¹ HCl (Nd plus the rest of Pr), 1.5 ml of 0.75 mol l⁻¹ HCl (discarded), another 1.5 ml of 0.75 mol l⁻¹ HCl (Sm plus <5% Eu), followed by 15 ml of 3 mol l⁻¹ HNO₃ (Gd-Tb-Dy-Ho-Er-Tm), 7 ml of 5 mol l⁻¹ HNO₃ (ca. 90% of Yb). Finally, the Lu fraction (containing ca. 10% of Yb) is collected with 8 ml of 5 mol l⁻¹ HNO₃ in a PFA vial. The Nd and Sm fractions are collected in single-use, polystyrene pots and evaporated to dryness before isotopic analyses by TIMS.

Isotope ratio analyses

The instrument parameters and cup configurations used for the Lu and Hf (MC-ICP-MS) and Sm and Nd (TIMS) isotope ratio determinations are listed in Tables 1, 2 and 3. The fractions of Lu and Hf are diluted or evaporated to increase their concentration, depending on the expected signal. Measurements were made in the static

Table 1. MC-ICP-MS parameters for isotopic Lu and Hf measurements

ICP Conditions	
RF power	1200 W
Sample gas flow	0.75–0.8 l min ⁻¹
Coolant gas flow	15 l min ⁻¹
Auxiliary gas flow	0.45 l min ⁻¹
Additional gas flow (N ₂)	0.28–0.35 l min ⁻¹ (optimized daily)
Sample uptake	100 μl min ⁻¹
Washing time	60 sec
Uptake time (wash)	120 sec
Sampling time	Lu - ca. 6 min (6 blocks of 10 cycles each) Hf - ca. 7 min (8 blocks of 10 cycles each)
Integration time	4.194 sec cycle ⁻¹
Idle time	3 sec
Interface	
Sample cone	Nickel
Skimmer cone	Nickel
Apex	
T spray chamber	140°C
T condenser	2°C

multi-collection mode.

Lutetium. The ICP-MS instrumental mass bias is corrected by using the neighbouring Yb with constant isotope composition (e.g., Chu *et al.*, 2002; Vervoort *et al.*, 2004) and this is why ca. 10% of the Yb was collected together with the Lu fraction. The ratio $^{171}\text{Yb}/^{173}\text{Yb} = 0.88296$ (Amelin and Davis, 2005) is used to correct the mass bias of Lu, whereas the interference of ^{176}Yb on ^{176}Lu is corrected based on $^{176}\text{Yb}/^{173}\text{Yb} = 0.7964$ (Amelin and Davis, 2005). Calibration of the measurements is made by reference to a commercial single element calibrator solution, doped with Yb to correct the mass bias, with a $^{176}\text{Lu}/^{175}\text{Lu}$ ratios of 0.02656 ± 0.00001 (2 SD, $n = 35$), in agreement with published values (Patchett and Tatsumoto, 1980; Blichert-Toft and Albarede, 1997; Scherer *et al.*, 2001).

Hafnium. Calibration of the measurements is made by reference to the JMC 475 Hafnium (Johnson Matthey) used as an isotopic calibrator which is regularly measured between samples in order to monitor any instrumental drift. Mass bias is corrected by using an exponential law and a reference value for $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ (Patchett and Tatsumoto, 1980). The $^{176}\text{Hf}/^{177}\text{Hf}$ ratio measured with our instrument is 0.282151 ± 6 (2 SD, $n = 92$), close to other results obtained elsewhere with the same model of MC-ICP-MS (e.g., Schmidt *et al.*, 2011; Cheng *et al.*, 2012). Combined isotopic composition-isotopic dilution (IC-ID) measurements on totally spiked samples with a ^{179}Hf -enriched tracer are made by using the same procedure, but the 'raw' measurements (that is, corrected only for interference on mass 176), are proc-

Table 2. Configuration of the collectors for Lu and Hf analysis by MC-ICP-MS

L4	L3	L2	L1	Center	H1	H2
171	173	175	176	177	178	179
Yb	Yb	Lu	Lu/Yb/Hf	Hf	Hf	Hf

Table 3. Configuration of the collectors for Sm and Nd analysis by TIMS

L3	L2	L1	Center	H1	H2	H3
144	147	148	149	150	152	154
Sm	Sm	Sm	Sm	Sm	Sm	Sm
143	144	145	146	147	148	150
Nd	Nd	Nd	Nd	Sm	Nd	Nd

essed off-line for mass bias correction and tracer contribution, by using an iterative procedure (Le Fèvre and Pin, 2005) following an algorithm written by Dr. J.-L. Birck. In this case, the ratio used for correcting mass bias is $^{178}\text{Hf}/^{177}\text{Hf} = 1.46711$, consistent with $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ used for normalizing isotope composition runs. The Hf analysis are done with 20 to 30 ppb solutions and each measurement consumed around 1 ml of sample (20–30 ng per analysis).

Samarium and Neodymium. Sm and Nd are measured by TIMS in the static multi-collection mode using standard techniques, with normalization to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (O'Nions *et al.*, 1977) and $^{152}\text{Sm}/^{147}\text{Sm} = 1.783079$ (Wasserburg *et al.*, 1981), respectively. The average value of the La Jolla Nd isotopic calibrator during this study is 0.511848 ± 9 (2 SD; $n = 3$).

RESULTS

Chemical yields

The chemical yields (as well as analytical purity) were monitored repeatedly for both HF dissolved and LiBO₂ fused samples, and were found to give similar results. Indeed, provided they occur as their cationic species in the solution to be processed, all the target elements of this study are much more strongly adsorbed by the AG50W resin than the elements occurring as major and minor components of silicate rocks, as indicated by a compilation of the relevant distribution coefficients (Table 4). In so far as hydrolytic problems which may affect many highly charged elements (including Ti, Zr, Hf) are circumvented by using not too dilute acids ($\geq 2\text{N}$) and a suitable complexing agent (H₂O₂), the solutions prepared by LiBO₂ fusion behave satisfactorily. However, Hf (and Zr) has a very strong affinity for fluorine, which is used as a major reagent when HF digestion is used. Therefore, it is a necessary prerequisite to break down the hafnium

Table 4. Distribution coefficients of elements on the AG50Wx8 cation exchange resin relevant to the separation protocol. (a) Strelow (1960); (b) Strelow *et al.* (1965); (b') interpolated from data in 3M and 4M acid.

Cation	2M HCl (a)	2M HNO ₃ (b)	0,5 M H ₂ SO ₄ (b)	3,5M HNO ₃ (b')
Li(I)	2.5	2.6	3	ca. 1.5
Na(I)	3.6	3.4	3.7	ca. 1.5
K(I)	7.4	5.7	7.4	ca. 3
Mg(II)	6.2	9.1	12	ca. 5
Ca(II)	12	9.7		ca. 3
Sr(II)	18	8.8		ca. 5
Ba(II)	36	13		ca. 5
Al(III)	13	17	28	ca. 6
Fe(III)	5.2	14		ca. 5
Ti(IV)	3.7	6.5	9	ca. 4
Ce(III)	48	44	320	ca. 12
Sm(III)		30	270	ca. 5
Yb(III)		41	250	ca. 12
Y(III)	30	36	250	ca. 12
Zr(IV)		650	4.6	ca. 200
Hf(IV)		165	12	ca. 40
Th(IV)		123	52	ca. 35

fluorides and expel the F left in the sample following acid decomposition, so as to achieve a nearly quantitative presence of Hf as a cationic species. Otherwise, extremely poor Hf yields would be obtained. Bearing in mind that using treatments with the high boiling point sulfuric acid would produce insoluble calcium sulfates, the less efficient (Šulcek and Povondra, 1989) method involving repeated fumings with perchloric acid was used, following the procedure described by Pin and Joannon (2002). By virtue of their high Ds with the AG50W resin over a large range of perchloric acid molarity (Nelson *et al.*, 1964; Strelow and Sondorp, 1972), the adsorption of the target elements is not impaired by the presence of HClO₄ left as a small volume of liquid by the end of the fuming steps.

With these provisos, no significant difference of elution behaviour was observed between samples prepared by HF dissolution and by fusion. The relatively large cation-exchange column used in this work enables excellent recoveries of REE and Hf to be achieved. This was checked by semi-quantitative ICP-QMS analyses of fractions recovered on both sides of the REE and Hf fractions. Based on repeated analyses, REE yields of about 95% were achieved on the cation-exchange column, although the most retained La and Ce were not completely recovered, while the Hf recovery was nearly quantitative. Likewise, the separation on the Ln-Spec column allows ca.99% of Nd, Sm and Lu to be recovered. The resulting overall yield for all the elements is therefore estimated to be at least 95%.

It may be noted that we have been using these columns for over 5 years (broadly 10 uses per year) without any evidence of resin degradation.

Table 5. (a) Column blanks (in pg), measured on three separate, already used columns. (b) Total procedural blanks (in pg), measured for Lu and Hf on three separate runs.

(a)	Sr	Nd	Hf	Th	(b)	Hf	Lu
Col. A	74	53	18	283	Col. A	37	12
Col. B	57	141	10	375	Col. B	36	23
Col. C	80	135	25	335	Col. C	48	23
Mean	70	110	18	331	Mean	40	19
RSD	17%	45%	42%	14%	RSD	17%	33%

Purity of the analytes

The protocol achieves a very good separation of the analytes from major elements, including Ti which is reduced to less than 0.1% of its initial amount (Fig. 2). The Hf fraction also contains 5–10% of the Zr, up to 3% of the Ta, and about 1% of Nb and La present in the sample. Tungsten, which would interfere Hf at *m/z* 180 (not used in this work), is stripped during the early steps of the separation. Lanthanum is the most strongly held lanthanide by AG50W and, not unexpectedly, it occurs as the tail of the peak eluted in 3.5 mol l⁻¹ HNO₃. In contrast, the presence of Nb and Ta is at odd with their anticipated behaviour on a cation-exchanger, and the small amounts found in the Hf fraction are interpreted to reflect the presence in the loaded solutions of hydrolytic compounds which are passively retained onto the resin beads before being eventually dissolved by the HF-bearing solution used to strip Hf. None of these accompanying elements produced troublesome effects during MC-ICP-MS analyses. Only Sc was observed in the lanthanides + Y fraction, in line

Table 6. Results obtained for international reference materials by the IC-ID method set up in this study. Comparison with the reference values: (a) Brandl *et al.* (2015); (b) GEOREM preferred value (Jochum *et al.*, 2016). It should be noted that each pair of values (A-B, C-D and E-F) are two measurements of the same solution.

Standard	$^{176}\text{Hf}/^{177}\text{Hf}$			Hf concentration($\mu\text{g g}^{-1}$)			Lu concentration($\mu\text{g g}^{-1}$)			$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2\text{SD}$
	Reference	Measured	$\pm 2 \text{ S.E.}$	Reference	Measured	$\pm 2\text{SD}$	Reference	Measured	$\pm 2\text{SD}$		
BHVO-2-A		0.283095	4.00E-06		4.32	0.03		0.294	0.002	0.00965	0.002
BHVO-2-B		0.283094	7.00E-06		4.32	0.03		0.294	0.002	0.00965	0.002
BHVO-2-C	0.283099 ± 4	0.283093	9.00E-06	4.47 \pm 0.03 (95% CL)	4.33	0.03	0.275 \pm 0.002 (95% CL)	0.287	0.002	0.00947	0.002
BHVO-2-D	(2SD) (a)	0.283085	7.00E-06	(b)	4.33	0.03	(b)	0.291	0.002	0.00954	0.002
BHVO-2-E		0.283099	9.00E-06		4.34	0.03		0.289	0.002	0.00947	0.002
BHVO-2-F		0.283097	8.00E-06		4.33	0.03		0.290	0.002	0.00953	0.002
Mean		0.283094 \pm 6			4.33 \pm 0.01			0.291 \pm 0.002		0.00955 \pm 1	
RSD		0.002%			0.23%			0.91%		0.85%	
W-2-A		0.282711	9.00E-06		2.48	0.02		0.314	0.002	0.01799	0.004
W-2-B		0.282724	9.00E-06		2.48	0.02		0.314	0.002	0.01799	0.004
W-2-C	0.282730 ± 16	0.282732	8.00E-06	2.44 \pm 0.04 (95% CL)	2.47	0.02	0.309 \pm 0.003 (95% CL)	0.318	0.002	0.01809	0.004
W-2-D	(SD) (b)	0.282728	9.00E-06	(b)	2.47	0.02	(b)	0.318	0.002	0.01804	0.004
W-2-E		0.282722	1.00E-05		2.46	0.02		0.313	0.002	0.01809	0.004
W-2-F		0.282702	1.00E-05		2.46	0.02		0.313	0.002	0.01809	0.004
Mean		0.282720 \pm 8			2.47 \pm 0.01			0.315 \pm 0.003		0.01805 \pm 1	
RSD		0.003%			0.40%			0.84%		0.27%	
AGV-2-A		0.282996	4.00E-06		4.95	0.04		0.225	0.001	0.00646	0.001
AGV-2-B		0.283000	8.00E-06		4.95	0.04		0.225	0.001	0.00646	0.001
AGV-2-C	0.282973 ± 10	0.282987	1.00E-05	5.14 \pm 0.06 (95% CL)	5.2	0.04	0.251 \pm 0.003 (95% CL)	0.262	0.002	0.00715	0.001
AGV-2-D	(SD) (b)	0.282973	1.00E-05	(b)	5.22	0.04	(b)	0.263	0.002	0.00715	0.001
AGV-2-E		0.282977	1.00E-05		5.19	0.04		0.266	0.002	0.00728	0.001
AGV-2-F		0.282972	5.00E-06		5.19	0.04		0.266	0.002	0.00728	0.001
Mean*		0.282984 (0.282977 \pm 6)			5.12 (5.20 \pm 0.01)			0.251 (0.264 \pm 0.003)		0.00696 (0.0722 \pm 1)	
RSD*		0.005%(0.002%)			2.8% (0.27%)			9.0%(1.1%)		5.66% (1.04%)	
G-2-A		0.282527	4.00E-06		7.75	0.06		0.110	0.001	0.00202	0.0004
G-2-B		0.282533	4.00E-06		7.75	0.06		0.110	0.001	0.00202	0.0004
G-2-C	0.282516 ± 7	0.282528	1.00E-05	7.78 \pm 0.22 (95% CL)	7.68	0.06	0.102 \pm 0.004 (95% CL)	0.107	0.001	0.00197	0.0004
G-2-D	(SD) (b)	0.282518	9.00E-06	(b)	7.68	0.06	(b)	0.107	0.001	0.00199	0.0004
G-2-E		0.282515	1.00E-05		7.78	0.06		0.108	0.001	0.00198	0.0004
G-2-F		0.282527	1.00E-05		7.78	0.06		0.108	0.001	0.00198	0.0004
Mean		0.282525 \pm 6			7.74 \pm 0.05			0.108 \pm 0.001		0.00199 \pm 1	
RSD		0.002%			0.66%			1.40%		1.08%	

*Values in parentheses correspond to the mean and RSD of the C to F analysis.

with its overall affinity with the REE and its distribution coefficient on AG50W in nitric acid medium (Strelow *et al.*, 1965) which is only slightly lower than those of the heavy lanthanides.

The extraction chromatographic Ln resin allows a clean extraction of the different Rare Earths, obtaining pure analytes except for significant Pr in the Nd cut. The Lu fraction contains a subordinate (ca. 10%) part of the Yb which is intently left for external correction of the $^{175}\text{Lu}/^{176}\text{Lu}$ ratio from instrumental mass bias.

In every case, stable ion beams were obtained during mass spectrometric analyses, and within-run precisions were similar to those obtained when analysing single el-

ement calibrator solutions, demonstrating that adequate degrees of purification of the target elements were achieved.

Procedural blanks

The contamination introduced by the proposed method was assessed by measuring different blank samples associated with the procedure. First, the main reagents used during the process were checked, and then column blanks were measured for the elements Sr, Hf, Nd, and Th which are investigated for their isotope composition. Finally, three total procedural blanks throughout the full procedure were determined.

Table 7. Results obtained for international reference materials by the IC-ID-TIMS method. Comparison with the reference values. (a) Sánchez-Lorda et al. (2013); (b) Pin et al. (1995); (c) Weis et al. (2006); (d) Pin et al. (1994).

Standard	$^{147}\text{Sm}/^{144}\text{Nd}$		$^{143}\text{Nd}/^{144}\text{Nd}$	
	Reference	Measured	Reference	Measured
AGV-2-A	0.1091 (a)	0.1088	0.512765 ± 6 (a)	0.512759 ± 6
AGV-2-B		0.1088		0.512755 ± 6
BHVO-2-A	0.1500* (b)	0.1499	0.512981 ± 10 (c)	0.512951 ± 6
BHVO-2-B		0.1508		0.512954 ± 6
G-2-A	0.0811 (b)	0.0810	0.512192 ± 12 (d)	0.512187 ± 6
G-2-B		0.0808		0.512194 ± 6
W-2-A	0.1525 (a)	0.1517	0.512490 ± 5 (a)	0.512481 ± 7
W-2-B		0.1519		0.512481 ± 5
	Sm concentration ($\mu\text{g g}^{-1}$)		Nd concentration ($\mu\text{g g}^{-1}$)	
	Reference	Measured	Reference	Measured
W-2-A	3.27 (b)	3.35	12.9 (b)	13.3
W-2-B		3.06		12.2

Note that analysis A corresponds to Lu-Hf analysis A, while analysis B corresponds to Lu-Hf analysis C.
*No BHVO-2 values were found in the literature, and for comparative purposes, BHVO-1 was used.

As expected, the most important contributor among the reagents is the LiBO_2 used in the fusion step. Four different fluxes available in our laboratory were measured to select the cleanest one. It was found that the ultrapure LiBO_2 (Corporation Scientifique Claisse) contained at most 15 pg g^{-1} of Hf, whereas individual REE contents were below 10 pg g^{-1} , with a highest value of 9 pg g^{-1} for Ce. Similar results for decomposition by fusion have been reported elsewhere for an in-house prepared LiBO_2 (Le Fèvre and Pin, 2001). The other reagents, including the acids, proved to contain negligible amounts of target elements.

Column blanks were measured on three already used columns. The results are given in Table 5a. The mean values show that the contamination associated with the separation protocol is not of significant concern for Hf ($m = 18 \text{ pg}$, $\text{RSD} = 42\%$) and Nd ($m = 110 \text{ pg}$, $\text{RSD} = 45\%$). The column blank for Sr ($m = 70 \text{ pg}$, $\text{RSD} = 17\%$) is also negligible. It can be seen, however, that the Th column blank is much higher ($m = 330 \text{ pg}$, $\text{RSD} = 14\%$). This is not unexpected bearing in mind the extremely strong affinity of AG50W for this element. Clearly, a more efficient cleaning procedure (e.g., with oxalic acid as a complexing agent) would be required if Th was to be separated in view of $^{230}\text{Th}/^{232}\text{Th}$ measurements on the same aliquot as that used for the other radiogenic isotopes.

The total procedural blanks were determined by

processing through the Dowex and Ln-Spec resins 500 mg of LiBO_2 melted without any sample, in order to quantify the contamination associated with the sample decomposition and all the forthcoming separation chemistry steps. This includes any potential memory effect of the crucibles and resin, because employed columns were already used several times. The blanks measured in this way were ca. 20 pg Lu and 40 pg Hf (Table 5b). The whole procedure blanks were $<400 \text{ pg}$ and $<100 \text{ pg}$ for Nd and Sm, respectively (J. Rodriguez Aller, personal communication). These values correspond to less than 0.1% of the minimum amount of element processed, and are not a source of significant concern.

Analyses of international geological reference materials

In order to validate the method, four international reference materials covering a wide range of major element compositions, from basalt through andesite to granite, have been analysed in triplicate for $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and Hf and Lu concentrations, and in duplicate for $^{143}\text{Nd}/^{144}\text{Nd}$ and Nd and Sm contents. In all cases, the samples were decomposed by fusion with LiBO_2 , our preferred method for whole-rocks. Each of the separated fractions of Hf and Lu was measured twice by MC-ICP-MS, during two analytical sessions separated by about one week, while Sm-Nd measurements by TIMS were made only once. The results are listed in Tables 6 and 7 and compared with

literature values. In the case of Lu-Hf, GEOREM preferred values (Jochum *et al.*, 2016) whenever possible. For Sm-Nd, reference values obtained by TIMS and MC-ICP-MS have been used for assessing our results.

¹⁷⁶Hf/¹⁷⁷Hf isotope ratios. The two measurements of the same solutions of Hf (combined IC/ID runs) and Lu (ID) made at one week interval overlap within their repeatability precision, suggesting that the MC-ICP-MS procedures are reproducible from one session to the other. Besides this purely instrumental aspect, it can be seen that the overall measurement repeatability of the results of three independent analyses is good, as expressed by RSDs comprised between 0.002% and 0.005%. This demonstrates the robustness of the whole procedure, from the decomposition step to the final isotope ratio measurements and data reduction steps. Finally, our results are within errors with available published data, which comprise ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios obtained on hafnium that was isolated by a range of different chemical separation schemes. Also, the agreement of our data with reference values that were measured on un-spiked hafnium, validates the correction of the spike contribution, and lends support to the overall small bias of our procedures.

Hf concentrations. The Hf concentration data obtained by isotope dilution display a good intermediate precision, with RSDs calculated from the three independent determinations ranging from 0.23% for BHVO-2 (a basalt) and 0.40% for W-2 (a dolerite), to 0.66% for G-2 (a granite). A higher degree of scatter is not unexpected in powders prepared from coarse-grained granitic rocks, in which most of the Hf occurs in an accessory mineral (zircon) and is therefore prone to the so-called “nugget effect”. These data are within the relatively large range of literature values. However, the data for AGV-2 are more dispersed (RSD = 2.8%) because the first value (4.95 $\mu\text{g g}^{-1}$) is anomalously low compared to the two others (5.19 and 5.21 $\mu\text{g g}^{-1}$, respectively) and the reference value of $5.14 \pm 0.06 \mu\text{g g}^{-1}$ (95% confidence interval, Jochum *et al.*, 2016).

Lu concentrations. The Lu concentrations have RSDs close to 1% in the two basaltic reference materials, and 1.4% in G-2. These figures are not as good as those achieved for Hf, mainly as a reflection of much lower concentration levels, namely 0.1–0.3 $\mu\text{g g}^{-1}$ against 2–8 $\mu\text{g g}^{-1}$. As observed for Hf, the first aliquot of AGV-2 gives an anomalously low concentration of 0.225 $\mu\text{g g}^{-1}$ against 0.263 and 0.266 $\mu\text{g g}^{-1}$ in the two others, reflected by an overall RSD of 9%. The discrepant Lu and Hf concentrations measured on the first powder aliquot cannot merely reflect a weighing uncertainty of spike or tracer because the ¹⁷⁶Lu/¹⁷⁷Hf ratio is also anomalously low (0.0065 against 0.0072). Indeed, this ratio is immune to such kind of uncertainty because a mixed tracer was used, so that any weighing uncertainty would cancel out dur-

ing calculation of the Lu/Hf ratio. Likewise, these odd data cannot merely reflect dilution by an enhanced proportion in this powder aliquot of a mineral depleted in Hf and Lu such as plagioclase, which occurs in the AGV-2 andesite. We are left with the possibility that this sample was contaminated at some stage (presumably, sample fusion) of the analytical protocol by a component with lower Hf and Lu concentrations and more radiogenic Hf than AGV-2 itself.

Sm-Nd system. As already stated, the concentration of the mixed ¹⁴⁹Sm-¹⁵⁰Nd tracer used is far from optimal. Specifically, in order to keep the sample powder + flux mixture as little wet as possible, the quantity of tracer solution should be small (<100 μl). In this study, a too dilute tracer solution (prepared for routine analyses of samples decomposed by HF dissolution) was used, and accordingly most samples were largely underspiked. For this reason, concentration data are quoted only for W-2, with the lowest contents of Nd and Sm among the studied reference materials.

The measurement repeatability of the ¹⁴³Nd/¹⁴⁴Nd isotope ratios is good as exemplified by the duplicate analyses, and within analytical uncertainty, our results are within the range of literature values, although the analysis of BHVO-2 is slightly less radiogenic. However, ¹⁴³Nd/¹⁴⁴Nd as low as ours have been reported (e.g., Heyworth *et al.*, 2007; Chu *et al.*, 2007). The precision achieved for the ¹⁴⁷Sm/¹⁴⁴Nd ratio is better than 0.5% RSD, demonstrating that a fair degree of reproducibility can be reached by using the fusion technique of sample digestion.

DISCUSSION

All the elements of interest in this study (Zr, Hf, Th, REE) are strongly adsorbed by cation-exchange resins from dilute aqueous solutions of mineral acids, enabling them to be separated from less retained matrix elements, provided that a column of sufficient capacity is used. Based on distribution data available for hydrochloric (Strelow, 1960), nitric and sulfuric (Strelow *et al.*, 1965) acid media, summarized in Table 4, the following elution sequence has been selected:

1) First, 2 mol l⁻¹ HCl - 0.15% H₂O₂ is used to remove the less retained cationic major elements, especially Fe(III) with D ca. 5. Most of the titanium is eluted at that stage as its peroxo complex. When the sample was decomposed by fusion, B is readily eliminated as a negative species, and Li is very weakly retained by virtue of its low D of 2.5. Al and Ca (with Ds ca. 12) are also partly displaced at that stage.

2) After having stripped Fe(III) with HCl, the elution is continued with 2 mol l⁻¹ HNO₃ which allows to strip the alkaline earths Ca, Sr, Ba, thereby preventing the risk

of precipitating insoluble sulfates on the column, as required by the further use of sulfuric acid to remove most of Zr.

3) In $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, the elements of interest still adsorbed on the resin have very high distribution coefficients with the notable exception of Zr(IV) with D ca. 5 (Strelow *et al.*, 1965). It is therefore possible to get rid of a large proportion (typically, 80–85%) of the Zr, and thus to reduce the Zr/Hf ratio in the Hf fraction eluted subsequently.

4) The REE are then eluted by using $3.5 \text{ mol l}^{-1} \text{ HNO}_3$, after discarding the early fraction in order to avoid the presence of sulfuric acid in the REE eluate, and eliminate any tail of Yb and Lu.

5) Finally, Hf is collected as a sharp (3.5 ml) fraction by $5 \text{ mol l}^{-1} \text{ HNO}_3 - 0.1 \text{ mol l}^{-1} \text{ HF}$. Thorium, the last retained element, could be obtained with a further volume of the same medium.

The advantages of this procedure can be summarized as follows:

1) It offers the possibility to obtain, with high yields and suitable blank levels, an Hf fraction ready for MC-ICP-MS measurement by using a single column and not the mere separation of all the HFSE (including Ti) plus P, etc. that would require further separation steps. In this work, the REE fraction was further processed by using EXC techniques in order to isolate Nd and Sm as required for ID-TIMS measurements. But it might be possible to measure without further separation both the $^{143}\text{Nd}/^{144}\text{Nd}$ and the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios by using the MC-ICP-MS approach described by Sanchez-Lorda *et al.* (2013), enabling a better sample throughput to be achieved. In another simple separation scheme (Li *et al.*, 2014), based on a single column combining an upper bed of AG50-x12 resin and a lower bed of Ln extraction chromatography material, Hf + Zr, and bulk REE cuts are obtained, suitable for measuring $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of unspiked samples. In our protocol, the “parent” elements are also isolated enabling the analyst to determine not only $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, but also the $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios by using the isotope dilution method. This makes the procedure suitable for dating and tracing the origin of ancient rocks.

2) Besides its overall robustness, ensured by the use of a most conventional, affordable, cation-exchange resin and simple mineral acids, our separation method can be used without changes for processing samples decomposed either by fusion with LiBO_2 (a major advantage when dealing with most continental materials containing the refractory mineral zircon) or by dissolution with HF (when total sample decomposition is not a satisfactory option due to the presence of troublesome inclusions of refractory minerals which should preferably be left un-attacked). As far as we are aware, no other published scheme

allows for this flexibility. In the scope of isotope dilution analyses, the very high temperature reached during the fusion step also ensures a very good sample-tracers isotopic equilibration for both Hf and Lu. This is a non-trivial issue when dealing with elements that have contrasting solution chemistry behavior when HF dissolution is used.

3) Albeit considerably slower due to the tedious HClO_4 fuming step the alternative sample decomposition procedure based on HF dissolution can be used when easy-to-dissolve samples (e.g., basaltic rocks) are dealt with, or for analysis of low-concentration samples, because HF and HClO_4 are easier to obtain in a highly pure form than LiBO_2 . Also, it is more appropriate when separated minerals (e.g., garnet) containing zircon inclusions are to be analysed, because an HF decomposition under mild conditions offers the major advantage to dissolve selectively the host mineral, while leaving the inclusions of more refractory zircon or rutile undissolved.

4) When HF dissolution is used, Rb and Sr could also be recovered, thereby enabling to combine three radiogenic isotope systems and affording a more complete sample characterization. Nevertheless, it is preferable to further clean-up the Sr fraction by using a very small column of Sr-Spec to remove accompanying Ca and Al. Thorium might also be included in the separation scheme, in so far as column blanks better than those measured in this work can be achieved.

5) Finally, the concomitant analysis of major and trace elements could be made by ICP-AES and ICP-MS, respectively, on suitably diluted small aliquots of the same solution. This would afford the significant reduction in overall sample preparation time and related costs.

The main disadvantages of the method are the relatively long duration of the chemical separation, a full working day, and the use of large volumes of reagents, compared to those typical for miniaturized methods based on extraction chromatography. Indeed, since the AG50W resin retains (to different degrees) all cationic species of the loaded solution, the sample size which can be processed is limited by the resin volume. This method was developed mainly for analysing crustal whole-rocks or minerals containing sufficient Nd and Hf in sample aliquots of 100 to 200 mg. Should much larger samples being processed, an appropriate up-scaling of the separation scheme would be required.

Conversely, the elution volumes could be decreased by using narrower bore columns if the size of the bulk sample to be processed can be reduced (e.g., when dealing with samples that are comparatively rich in LREE and Hf). But the column length of ca. 10 cm should be kept unchanged, so that the elution time would remain essentially similar, thus making automation the only way to save analyst time. It is emphasized however, than in our preferred version based on sample decomposition by

fusion with LiBO₂, the *overall* method is quite rapid compared to those based on HF dissolution which requires time-consuming, alternating steps of digestion and evaporation (and high-pressure vessels when refractory minerals such as zircon are present).

CONCLUSION

Fractions containing Hf and total REE (plus, potentially, Rb, Sr, and Th) are separated from matrix elements by using a single conventional column filled with the cation-exchange resin AG50W-X8 and three common mineral acids (HCl, HNO₃, H₂SO₄) as eluting agents. The individual lanthanides of interest (Nd, Sm, Lu) are further isolated with a Ln Spec column used in tandem configuration, without intervening evaporation. Samples decomposed either by fusion with lithium metaborate or, optionally, by hydrofluoric acid dissolution can be processed with the same column protocol. When the LiBO₂ fusion method is used, refractory minerals rich in REE and/or Hf are efficiently and rapidly decomposed, and a solution ready for column separation is promptly obtained. Moreover, a thorough isotope equilibration of the sample-tracer mixture is achieved in the high temperature melt, a critical feature for successful isotope dilution analyses. Since no fluorine is involved in the decomposition process, the risk of poor chemical recoveries due to the formation of insoluble fluoride compounds before the separation step is cancelled, and a fluorine-free starting solution makes it easy to take full advantage of the strong affinity of Hf(IV) for cation-exchange resins. The variant based on dissolution with HF was implemented to cope with the specific problem posed by garnets containing zircon inclusions, demonstrating that our separation method is compatible with this alternative procedure of sample decomposition, but this requires a complete elimination of residual fluorine through tedious fumings with perchloric acid.

Although the method cannot compete with extraction chromatographic procedures in terms of miniaturization and ultimate analytical purity, it may offer a robust alternative which does not imply using expensive materials, provided that high purity acids can be prepared in-house from low-cost starting reagents.

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REFERENCES

- Amelin, Y. and Davis, W. J. (2005) Geochemical test for branching decay of ¹⁷⁶Lu. *Geochim. Cosmochim. Acta* **69**, 465–473; doi:10.1016/j.gca.2004.04.028.
- Anczkiewicz, R. and Thirlwall, M. F. (2003) Improving precision of Sm-Nd garnet dating by H₂SO₄ leaching—a simple solution to phosphate inclusions problem. *Geochronology: Linking the Isotopic Record with Petrology and Textures* (Vance, D., Mueller, W. and Villa, I. M., eds.), 83–91, *Geological Society London Special Publications* **220**, London; doi:10.1144/GSL.SP.2003.220.01.05.
- Baskaran, M. (2011) *Handbook of Environmental Isotope Geochemistry*. Springer, Berlin, 951 pp.
- Bast, R., Scherer, E. E., Sprung, P., Fischer-Gödde, M., Strackea, A. and Mezgerd, K. (2015) A rapid and efficient ion-exchange chromatography for Lu-Hf, Sm-Nd, and Rb-Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS. *J. Anal. Atom. Spectrom.* **30**, 2323; doi:10.1039/c5ja00283d.
- Blichert-Toft, J. and Albarède, F. (1997) The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system. *Earth Planet. Sci. Lett.* **148**, 243–258; doi:10.1016/S0012-821X(97)00040-X.
- Blichert-Toft, J., Chauvel, C. and Albarède, F. (1997) Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS. *Contrib. Mineral. Petrol.* **127**, 248–260; doi:10.1007/s004100050278.
- Brandl, P. A., Genske, F. S., Beier, C., Haase, K. M., Sprung, P. and Krumm, S. (2015) Magmatic evidence for carbonate metasomatism in the lithospheric mantle underneath the Ohře (Eger) rift. *J. Petrol.* **56**, 1743–1774; doi:10.1093/petrology/egv052.
- Cheng, H., Zhang, C., Vervoort, J. D., Li, X., Li, Q., Wu, Y. and Zheng, S. (2012) Timing of the eclogite facies metamorphism in the North Qinling by U-Pb and Lu-Hf geochronology. *Lithos* **136–139**, 45–59; doi:10.1016/j.lithos.2011.06.003.
- Chu, N. C., Taylor, R., Chavagnac, V., Nesbitt, R., Boella, R., Milton, J., German, C., Bayon, G. and Burton, K. (2002) Hf isotope ratio analysis using multi-collector inductively coupled plasma mass spectrometry: An evaluation of isobaric interference corrections. *J. Anal. Atom. Spectrom.* **17**, 1567–1574; doi:10.1039/B206707B.
- Chu, Z., Chen, F., Yang, Y. H. and Guo, J. (2007) Precise determination of Sm, Nd concentrations and Nd isotopic compositions at the nanogram level in geological samples by thermal ionization mass spectrometry. *J. Anal. Atom. Spectrom.* **24**, 1534–1544; doi:10.1039/B904047A.
- Connelly, J. N. (2006) Improved dissolution and chemical separation methods for Lu-Hf garnet chronometry. *Geochem. Geophys. Geosyst.* **7**, Q04005; doi:10.1029/2005GC001082.
- Connelly, J. N., Ulfbeck, D. G., Thrane, K., Bizzarro, M. and Housh, T. (2006) A method for purifying Lu and Hf for analyses by MC-ICP-MS using TODGA resin. *Chem. Geol.* **233**, 126–136; doi:10.1016/j.chemgeo.2006.02.020.
- Dickinson, A. P. (2005) *Radiogenic Isotope Geology*. 2nd ed., Cambridge University Press, Cambridge, 492 pp.

- Faure, G. and Mensing, T. M. (2012) *Isotopes: Principles and Applications*. 3rd ed., Wiley, New York, 897 pp.
- Frisby, C., Bizimis, M. and Mallick, S. (2016) Hf-Nd isotope decoupling in bulk abyssal peridotites due to serpentinization. *Chem. Geol.* **440**, 60–72.
- Fritz, J. S. and Dahmer, L. H. (1965) Cation exchange separation of Molybdenum, Tungsten, Niobium, and Tantalum from other metal ions. *Anal. Chem.* **37**, 1272–1274; doi:10.1021/ac60229a026.
- Halliday, A. N., Lee, D. C., Christensen, J. N., Walder, A. J., Freedman, P. A., Jones, C. E., Hall, C. M., Yi, W. and Teagle, D. (1995) Recent development in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spectrom. Ion Process* **146/147**, 21–33.
- Heyworth, Z., Turner, S. P., Schaefer, B., Wood, B., George, R., Berlo, K., Cunningham, H. S., Price, R. E., Cook, C. and Gamble, J. (2007) ^{238}U - ^{230}Th - ^{226}Rd - ^{210}Pb constrains the genesis of high Mg andesites at White Island, New Zealand. *Chem. Geol.* **243**, 105–121; doi:10.1016/j.chemgeo.2007.05.012.
- Horwitz, E. P., Dietz, M. L. and Chiarizia, R. (1992) The application of novel extraction chromatographic materials to the characterization of radioactive waste solutions. *J. Radioanal. Nucl. Chem.* **161**, 575–583; doi:10.1007/BF02040504.
- Jochum, K. P., Weis, U., Schwager, B., Stoll, B., Wilson, S. S., Haug, G. H., Andreae, M. O. and Enzweiler, J. (2016) Reference values following ISO guidelines for frequently requested rock reference materials. *Geostand. Geoanal. Res.* **40**, 333–350; doi:10.1111/j.1751-908X.2015.00392.x.
- Lapen, T. J., Mahlen, N. J., Johnson, C. M. and Beard, B. L. (2004) High precision Lu and Hf isotope analyses of both spiked and unspiked samples: a new approach. *Geochem. Geophys. Geosyst.* **5**, Q10009; doi:10.1029/2003GC000582.
- Le Fèvre, B. and Pin, C. (2001) An extraction chromatography method for Hf separation prior to isotopic analysis using multiple collection ICP-mass spectrometry. *Anal. Chem.* **73**, 2453–2460; doi:10.1021/ac001237g.
- Le Fèvre, B. and Pin, C. (2002) Determination of Zr, Hf, Th, and U by Isotope Dilution and ICP-Quadrupole Mass Spectrometry after concomitant separation using Extraction Chromatography. *Geostandard. Newslett.* **26**, 161–170; doi:10.1111/j.1751-908X.2002.tb00884.x.
- Le Fèvre, B. and Pin, C. (2005) A straightforward separation scheme for concomitant Lu-Hf and Sm-Nd isotope ratio and isotope dilution analysis. *Anal. Chim. Acta* **543**, 209–221; doi:10.1016/j.aca.2005.04.044.
- Li, C.-F., Guo, J.-H., Yang, Y.-H., Chu, Z.-Y. and Wang, X.-C. (2014) Single-step separation scheme and high-precision isotopic ratios analysis of Sr-Nd-Hf in silicate materials. *J. Anal. At. Spectrom.* **29**, 1467–1476; doi:10.1039/c3ja50384d.
- Mattinson, J. M. (1972) Preparation of hydrofluoric, hydrochloric and nitric at ultralow lead levels. *Anal. Chem.* **44**, 1715–1716; doi:10.1021/ac60317a032.
- Münker, C., Weyer, S., Scherer, E. and Mezger, K. (2001) Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICP-MS measurements. *Geochem. Geophys. Geosyst.* **2**, 1064; doi:10.1029/2001GC000183.
- Nelson, F., Murase, T. and Kraus, K. A. (1964) Ion exchange procedures. I. Cation exchange in concentrated HCl and HClO₄. *J. Chromatogr. A* **13**, 503–535; doi:10.1016/S0021-9673(01)95146-5.
- O’Nions, R. K., Hamilton, P. J. and Evensen, N. M. (1977) Variation in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in oceanic basalts. *Earth Planet. Sci. Lett.* **34**, 13–22; doi:10.1016/0012-821X(77)90100-5.
- Patchett, P. J. and Tatsumoto, M. (1980) A routine high-precision method for Lu-Hf isotope geochemistry and chronology. *Contrib. Mineral. Petrol.* **75**, 263–267; doi:10.1007/BF01166766.
- Peters, S. T. M., Münker, C., Wombacher, F. and Elfers, B.-M. (2015) Precise determination of low abundance isotopes (^{174}Hf , ^{180}W and ^{190}Pt) in terrestrial materials and meteorites using multiple collector ICP-MS equipped with $10^{12}\ \Omega$ Faraday amplifiers. *Chem. Geol.* **413**, 132–145; doi:10.1016/j.chemgeo.2015.08.018.
- Pin, C. and Bassin, C. (1992) Evaluation of a strontium-specific extraction chromatographic method for isotopic analysis in geological materials. *Anal. Chem.* **269**, 249–255; doi:10.1016/0003-2670(92)85409-Y.
- Pin, C. and Gannoun, A. (2017) Integrated extraction chromatographic separation of the lithophile elements involved in long-lived radiogenic isotope systems (Rb-Sr, U-Th-Pb, Sm-Nd, La-Ce, and Lu-Hf) useful in geochemical and environmental sciences. *Anal. Chem.* **89**, 2411–2417.
- Pin, C. and Joannon, S. (2002) Combined cation-exchange and extraction chromatography for the concomitant separation of Zr, Hf, Th, and the Lanthanides from geological materials. *Talanta* **57**, 393–403; doi:10.1016/S0039-9140(02)00040-1.
- Pin, C. and Rodriguez, J. (2014) Separation methods based on liquid-liquid extraction, extraction chromatography, and other miscellaneous solid phase extraction processes. *Treatise on Geochemistry 16* (Holland, H. D. and Turekian, K. K., eds.), 2nd ed., 147–170, Elsevier; doi:10.1016/B978-0-08-095975-7.01409-1.
- Pin, C., Briot, D., Bassin, Ch. and Poitrasson, F. (1994) Concomitant separation of strontium and samarium-neodymium for isotopic analysis in silicate samples, based on specific extraction chromatography. *Anal. Chim. Acta* **298**(2), 209–217; doi:10.1016/0003-2670(94)00274-6.
- Pin, C., Telouk, P. and Imbert, J. L. (1995) Direct determination of the Samarium: Neodymium ratio in geological materials by inductively coupled plasma quadrupole mass spectrometry with cryogenic desolvation. Comparison with isotope dilution thermal ionization mass spectrometry. *J. Anal. Atom. Spectrom.* **10**, 93–98; doi:10.1039/JA9951000093.
- Sánchez-Lorda, M. E., García de Madinabeitia, S., Pin, C. and Gil Ibarguchi, J. I. (2013) Concomitant measurement of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios without isotope dilution in geological samples: An assessment of MC-ICP-MS capabilities. *Int. J. Mass Spectrom.* **333**, 34–43; doi:10.1016/j.ijms.2012.08.038.
- Scherer, E. E., Cameron, K. L., Johnson, C. M., Beard, B. L.,

- Barovich, K. M. and Collerson, K. D. (1997) Lu-Hf geochronology applied to dating Cenozoic events affecting lower crustal xenoliths from Kilbourne Hole, New Mexico. *Chem. Geol.* **142**, 63–78; doi:10.1016/S0009-2541(97)00076-4.
- Scherer, E. E., Münker, C. and Mezger, K. (2001) Calibration of the Lutetium-Hafnium clock. *Science* **293**, 683–687; doi:10.1126/science.1061372.
- Schmidt, A., Mezger, K. and O'Brien, P. J. (2011) The time of eclogite formation in the ultrahigh pressure rocks of the Sulu terrane. Constraints from Lu-Hf garnet geochronology. *Lithos* **125**, 743–756; doi:10.1016/j.lithos.2011.04.004.
- Strelow, F. W. E. (1960) An ion exchange selectivity scale of cations based on equilibrium distribution coefficients. *Anal. Chem.* **32**, 1185–1188; doi:10.1021/ac60165a042.
- Strelow, F. W. E. and Sondorp, H. (1972) Distribution coefficients and cation-exchange selectivities of elements with AG50W-X8 resin in perchloric acid. *Talanta* **19**, 1113–1120; doi:10.1021/ac60220a027.
- Strelow, F. W. E., Rethemeyer, R. and Bothma, C. J. C. (1965) Ion exchange selectivity scale for cations in nitric acid and sulfuric acid media with a sulfonated polystyrene resin. *Anal. Chem.* **37**, 107–111; doi:10.1021/ac60220a027.
- Šulcek, Z. and Povondra, P. (1989) *Methods of Decomposition in Inorganic Analysis*. CRC Press, Boca Raton, Florida, 325 pp.
- Tosoh Corp. (2013) Fused silica glass Brochure (<https://www.tosoh.com/our-products/advanced-materials/silica-glass>).
- Ulfbeck, D., Baker, J., Waight, T. and Krogstad, E. (2003) Rapid sample digestion and chemical separation of Hf for isotopic analysis by MC-ICP-MS. *Talanta* **59**, 365–373; doi:10.1016/S0039-9140(02)00525-8.
- Unruh, D., Stille, P., Patchett, P. J. and Tatsumoto, M. (1983) Lu-Hf and Sm-Nd evolution in Lunar Mare Basalts. *J. Geophys. Res.* **89**(S02), B459–B477; doi:10.1029/JB089iS02p0B459.
- Vervoort, J. D., Patchett, P. J., Söderlund, U. and Baker, M. (2004) Isotopic composition of Yb and the determination of Lu concentrations and Lu/Hf ratios by isotope dilution using MC-ICP-MS. *Geochem. Geophys. Geosyst.* **5**, Q11002; doi:10.1029/2004GC000721.
- 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. *Geochim. Cosmochim. Acta* **45**, 2311–2323; doi:10.1016/0016-7037(81)90085-5.
- Webster, R. K. (1960) Mass spectrometric isotope dilution analysis. *Methods in Geochemistry* (Smales, A. A. and Wager, L. R., eds.), 202–246, Intersciences Publishers Inc., New York.
- 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. M. and Mahoney, J. B. (2006) High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. *Geochem. Geophys. Geosyst.* **7**, Q08006; doi:10.1029/2006GC001283H.
- 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. *Int. J. Mass Spectrom.* **290**, 120–126; doi:10.1016/j.ijms.2009.12.011.
- Yang, X.-J and Pin, C. (1999) Separation of hafnium and zirconium from Ti- and Fe-rich geological materials by extraction chromatography. *Anal. Chem.* **71**, 1706–1711.

SUPPLEMENTARY MATERIALS

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