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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

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ABSTRACT

A combined procedure for separating Lu, Hf, Rb, Sr, Sm and Nd from a single sample digestion is presented in this paper. The procedure consists of the following four steps: (1) sample dissolution in a mixture of concentrated HF–HNO_3–$HClO_4$; (2) Lu and Hf separation from the Rb, Sr, LMREE and other matrix elements by HF-free extraction chromatography; (3) Rb, Sr and LMREE separation from other matrix elements using a cation-exchange resin; (4) Sm and Nd separation from others LMREE by extraction chromatography. Analytical feasibility, flexibility and reproducibility of Rb–Sr, Sm–Nd and Lu–Hf isotope systems are demonstrated for international standard solutions and Certified Reference Materials (CRMs). Results show good agreement with previously reported values by isotope dilution methods, indicating the technique has fewer problems in respect to well-known sample inhomogeneity of natural geological materials and demonstrating its potential application to the study of limited and precious terrestrial rocks or minerals (like peridotite, kimberlite and xenoliths) and extra-terrestrial samples (like lunar rock and meteorites).

1. Introduction

Compared with the classical ^{87}Rb–^{87}Sr and ^{147}Sm–^{143}Nd radiogenic isotope systems, the ^{176}Lu–^{176}Hf radiogenic isotope system was not generally adopted in solid earth sciences until the advent of Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) in the mid-1990s [1], mainly because of the poor ionization efficiency of hafnium by conventional Thermal Ionization Mass Spectrometry (TIMS) [2]. However, with the rapid development of the MC-ICP-MS, the widespread application of Lu–Hf isotope system in the fields of geochemistry and geochronology has become more popular [1]. Based on the first Lu–Hf separation method using TIMS, as reported by Patchett and Tatsumoto [3], several other procedures were subsequently developed by combining cation- and anion-exchange chromatography [4–6]. In general, the method developed specifically for TIMS was labor-intensive and time-consuming. However, for MC-ICP-MS, chemical separations can be greatly simplified, which provides for a much higher sample throughput and smaller sample size compared to previous TIMS methods [1]. Subsequently, relatively simple Hf separation schemes for various kinds of samples have been further developed [7–17].

As suggested by Le Fe‘vre and Pin [10], in most cases, the chemical separation schemes are designed specifically for either Sm–Nd or Lu–Hf isotope analyses, but not for both at the same time. It is well known that the purification of Rb, Sr, Sm and Nd prior to mass spectrometric measurement is usually accomplished by two-column chromatography after a single sample digestion [18]. Because of the well-known inhomogeneity of most natural geological samples, and the need for rapid and efficient throughput, most recently, combined Sm–Nd and Lu–Hf separation schemes on the same rock powder have also been developed, using either fusion ($LiBO_2$ or $Li_2B_4O_7$) [10,14] or sintering (Na_2O_2) [8]. However, to the best of our knowledge, up to now there is no analytical protocol reported in the literature for concomitant separation of Lu–Hf, Rb–Sr and Sm–Nd isotope systems from a single sample digest.

Bearing in mind this consideration, the motivation of this work is to establish a simplified analytical procedure to obtain the maximum amount of radiogenic isotopic information from the same rock powder aliquot. This is especially important since the com-

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mercially available MC-ICP-MS machines from the mid-1990s, has mean that the combination of Rb–Sr, Sm–Nd and Lu–Hf isotope systems has become a more powerful tool for understanding fundamental Earth processes, especially in the fields of isotopic geochemistry and geochronology. Here we describe the development of a relatively simple rock digest and subsequent separation scheme for concomitant Lu, Hf, Rb, Sr, Sm and Nd. Samples are dissolved in an $HF–HNO_3–HClO_4$ mixture and separated using a combination of extraction and ion-exchange chromatography. The feasibility, flexibility and reproducibility of this scheme were validated by replicate analyses of international Certified Reference Materials (CRMs). This procedure makes the following three improvements or modifications, compared with the earlier published protocols in the literature: (1) by using mostly hydrochloric acid, with lesser amounts of H_2O_2 and HF, as the eluting solution rather than complex solutions like ascorbic, citric and nitric acid, or even hydrochloric acid on its own [7]; (2) by simplifying or shortening the chemical purification steps for three instead of two radiogenic systems from a single sample powder aliquot [8,10]. This decreases problems related to well-known inhomogeneity of natural geological materials and provides greater potential application to the analysis of limited and precious terrestrial rocks (like peridotite, kimberlite and xenoliths) and extra-terrestrial samples (including lunar rock and meteorites); (3) by increasing the flexibly to separate only those isotopes required for a particular experiment and making analysis feasible in most geochemical laboratories around the world, without the need for special equipment such as induction or muffle furnaces [8,10,11,14].

Table 1

Three-column procedure for combined separation of Lu, Hf, Rb, Sr, Sm and Nd concomitantly.

Step	Column volumes	Acid
Column I (Ln Spec 2 mL ca. 0.8 cm × 4 cm)		
Preparation	20 mL × 3 times	6 M HCl + 0.2 M HF
Preconditioning	7 mL × 3 times	3 M HCl
Loading sample[a]	5 mL	3 M HCl
Eluting matrix[a]	5 mL × 2 times	3 M HCl
Eluting matrix[a]	5 mL × 2 times	4 M HCl
Collecting Yb–Lu	5 mL	4 M HCl
Eluting residual Yb, Lu	5 mL × 4 times	6 M HCl
Eluting Ti	Variable (50–70 mL for basalts)	4 M HCl + 0.5% H_2O_2
Collecting Zr–Hf	5 mL	2 M HF
Column II (AG50W-X12 2 mL ca. 0.5 cm × 10 cm)		
Preparation	5 mL + 20 mL	6 M HCl
Eluting	5 mL	Mill-Q-H_2O
Preconditioning	2 mL × 2 times	2.5 M HCl
Loading sample	1.5 mL	2.5 M HCl
Eluting	0.5 mL × 4 times	2.5 M HCl
Eluting	2.5 mL	5 M HCl
Collecting Rb	1.5 mL	5 M HCl
Eluting	4 mL	5 M HCl
Collecting Sr	3 mL	5 M HCl
Collecting LMREE[b]	6 mL	6 M HCl
Column III (Ln Spec = as Column I)		
Preparation	5 mL × 2 times	6 M HCl
Eluting	5 mL × 3 times	Mill-Q-H_2O
Preconditioning	2 mL × 2 times	0.25 M HCl
Loading sample	0.5 mL	0.25 M HCl
Eluting La and Ce	6 mL	0.25 M HCl
Collecting Nd	6 mL	0.25 M HCl
Collecting Sm	10 mL	0.40 M HCl

[a] These eluted portions were collected for Rb, Sr and LMREE purification in the column II step.

[b] These eluted portions were collected for Sm and Nd purification in the column III step.

2. Experimental

2.1. Chemicals and materials

Milli-Q water ($18.2\,\mathrm{M\Omega\,cm^{-1}}$) from Millipore (Elix-Millipore, USA) and twice-distilled extra-pure grade reagents were used in this study. Hydrochloric acid (6 M) was prepared by sub-boiling distillation in a quartz still. Concentrated nitric and hydrofluoric acid were purified by sub-boiling distillation in a Teflon still. Concentrated perchloric acid was purified by decompressed distillation in a quartz distiller.

An international standard solution of *ca.* $200\,\mu\mathrm{g\,L^{-1}}$ JMC475 Hf was used for monitoring conditions during the analytical sessions. Standard solutions of $1000\,\mu\mathrm{g\,mL^{-1}}$ Lu (Stock No. 35765) and $10{,}000\,\mu\mathrm{g\,mL^{-1}}$ Hf (Stock No. 14374) purchased from Alfa Aesar of Johnson Matthey Company (plasma standard solution, Specpure) were used to gravimetrically prepare standard solutions with known concentrations. These solutions were used to calibrate the spike solution using MC-ICP-MS measurements of spiked standard solutions. For Rb, Sr, Sm and Nd tracers, the solutions were calibrated by reverse isotope dilution against gravimetric standards that were precisely prepared from pure metals obtained from Ames Laboratory [19].

Pre-packed extraction chromatography material (Ln Spec, 100–150 μm particle size, 2 mL) was purchased from Eichrom Industires (Darien IL, USA), while the conventional cation-exchange resin (AG50W-X12, 200–400 mesh size), was obtained from Bio-Rad (Richmond, CA, USA). International CRMs rock powders, recommended by the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ), were used to evaluate and validate the present procedure.

2.2. Step 1: Sample digestion

All chemical preparations were conducted on special class 100 work benches inside a class 1000 clean laboratory. About 100 mg of rock powder was weighted into a 7 mL round-bottom Savillex^{TM} Teflon screw-top capsule. Weighed portions of the mixed $^{176}Lu–^{180}Hf$, $^{87}Rb–^{84}Sr$ and $^{149}Sm–^{150}Nd$ isotopically enriched tracer were added and gently evaporated to dryness. The mixed concentrate $HF–HNO_3–HClO_4$ (2 mL–1 mL–0.2 mL) was added to the samples and the capsule capped and then heated on a hotplate at about 120 °C for 1 week. After cooling, the capsule was opened and evaporated to fume $HClO_4$. 1 mL of 6 M HCl was added to the residue and dried, and this procedure was then repeated. When it had cooled down, the residue was dissolved in 5 mL of 3 M HCl. The capsule was again sealed and placed on a hot plate at ∼100 °C overnight prior to chemical separation.

2.3. Step 2: Lu and Hf purification

The 3 M HCl sample solution was centrifuged and then loaded onto pre-conditioned 2 mL Ln Spec resin (modified after Münker et al. [7]) (Table 1). Firstly, the matrix elements including Light and Middle Rare Earth Elements (LMREE) were eluted with 3 M and 4 M HCl sequentially, which was collected in a 30 mL PFA beaker for further purification in the following step 3. The Lu (+Yb) fraction was then eluted with 4 M HCl, and evaporated to dryness, ready for mass spectrometry. In order to minimize the isobaric interference of ^{176}Lu and ^{176}Yb on ^{176}Hf, the column was rinsed with 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) was extracted from the column with 5 mL 2 M HF, collected in a 10 mL PFA beaker, and gently evaporated to dryness. This fraction was taken up in trace 2 M HF, diluted to 1 mL with 2% HNO_3, and was then ready for Hf analysis.

2.4. Step 3: Rb, Sr and LMREE separation

The solution collected from step 2, consisting of matrix elements, including the LMREE, was gently evaporated to dryness and diluted with 1.5 mL 2.5 M HCl prior to the second-column purification (Table 1). After centrifuging, the solution was loaded into a quartz column packed with AG50W-X12, which has preconditioned with 2 mL of 2.5 M HCl. The resin was then washed with a further 2 mL of 2.5 M HCl, followed by 2.5 mL of 5 M HCl to remove the unwanted elements. Then, the Rb was eluted with 1.5 mL of 5 M HCl for ID analyses using the MAT 262. In order to minimize the isobaric interference of ^{87}Rb on ^{87}Sr, the resin was rinsed with 4 mL of 5 M HCl to remove residual Rb. Finally, the Sr fraction was eluted using 3 mL of 5 M HCl for analyses using the MAT 262, whereas the LMREE fraction was eluted with 6 mL of 6 M HCl in readiness for step 4.

2.5. Step 4: Sm and Nd purification

The separation of Nd and Sm was achieved using another commercial Ln Spec resin column (modified after Pin and Santos-Zalduegui [20]) (Table 1). The LMREE fraction collected in step 3 was gently evaporated to dryness, taken up with 0.5 mL of 0.25 M HCl and loaded onto Ln Spec resin. La, Ce and Pr were removed with 6 mL of 0.25 M HCl wash. Then the fraction containing Nd was eluted with 6 mL of 0.25 M HCl for ID analyes using the MAT 262 (no Sm was detected in this fraction during mass spectrometric measurement). Finally, the Sm fraction was stripped with 10 mL of 0.4 M HCl for ID analyses using the MAT 262.

2.6. Mass spectrometry

Determination of Lu and Hf isotope ratios were carried out in static mode on Faraday cups on the Thermo Fisher Scientific Neptune MC-ICP-MS at the Institute of Geology and Geophysics (IGG), Chinese Academy of Sciences (CAS), Beijing. The typical instrument parameters and cup configuration are summarized in Tables 2 and 3. Free sample aspiration was performed with a 50 μl/mL standard PFA nebulizer (Table 2). The Lu fraction from the first column was redissolved in 0.5 mL of 2% HNO_3 and the mass bias behavior of Lu was assumed to follow that of Yb and calculated by ^{172}Yb/^{173}Yb = 1.35272 and ^{176}Yb/^{172}Yb = 0.5887 for the interference correction of ^{176}Yb on ^{176}Lu using the exponential law, following the protocols of Vervoort et al. [21] (Table 3).

The Hf fraction was taken up with trace HF and 1 mL of 2% HNO_3. In general, the signal intensity of ^{176}Yb and ^{176}Lu by monitoring ^{173}Yb and ^{175}Lu is less than 5×10^{-5} V after the chemical purification described above, resulting in an inaccuracy of about 1×10^{-5} on the ^{176}Hf/^{177}Hf ratios, which is almost equal to the typical internal precision. In addition, signals corresponding to masses 181 and 183 were also measured to monitor any isobaric interference from ^{180}Ta and ^{180}W on ^{180}Hf, considering that enriched an ^{180}Hf tracer was used in this study. However, the levels of W and Ta were found to be very low in every case (Table 3). The signal intensities of ^{181}Ta and ^{183}W were usually less than 1×10^{-3} V after chemical separation. The relative efficiencies of the Faraday cups and amplifiers were calibrated using virtual amplifier rotation techniques [22]. Hf isotope analyses consist of 9 blocks of 10 cycles per block with an integration time of 4 s per cycle (Table 2). Over the past 2-year period, 140 analyses of JMC 475 yielded a ^{176}Hf/^{177}Hf value of 0.282158 ± 18 (2SD) [22], identical to the result recommended by Blichert-Toft et al. [6], within uncertainties. Meanwhile, 167 analyses of Alfa Hf gave a ^{176}Hf/^{177}Hf value of 0.282189 ± 19 (2SD) [22], identical to 0.282192 ± 06 (2σ, $n = 12$) by Lu et al. [17], within error. In terms of Hf ID analyses, the data were exported and reduced offline in order to correct for instrumental mass bias and tracer contribution with normalization to ^{179}Hf/^{177}Hf = 0.7325 using the exponential law. Hf concentrations were calculated from the corrected ^{180}Hf/^{177}Hf mixture ratio, using the isotope dilution equation.

Table 2
Typical operating parameters for Lu and Hf measurement.

Neptune MC-ICP-MS	Setting
RF forward power	1300 W
Cooling gas	15.2 l/min
Auxiliary gas	0.6 l/min
Sample gas	~1.10 l/min (optimized daily)
Extraction	−2000 V
Focus	−630 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Interface cones	Nickel
Spray chamber	Glass cyclonic
Nebulizer type	Micromist PFA nebulizer
Sample uptake rate	50 μl/min
Uptake mode	Free aspiration
Instrument resolution	~400 (low)
Typical sensitivity on ^{180}Hf	~16 V/ppm ($10^{-11}\,\Omega$ resistors)
Sampling mode	9 blocks of 10 cycles for Hf 1 block of 30 cycles for Lu
Integration time	4 s for Hf and 2 s for Lu
Baseline/background determination	*ca.*1 min on peak in 2% HNO_3

A Finnigan MAT 262 thermal ionization mass spectrometer in IGG, CAS was used for Rb–Sr and Sm–Nd isotopic analyses in static mode using Faraday cups [23]. Solution standards of SRM 987 for Sr and Ames for Nd were measured during the same TIMS runs as the samples. Prior to sample measurement, the Sr, Nd and Sm fractions were dissolved using 2 μL 2.5 M HCl and loaded with a 2 μL H_3PO_4 onto one side of the filaments (*ca.* 1 mm × 0.7 mm square) of a degassed double Re filament (0.035 mm thick, 0.77 mm wide) assembly and dried on a clean bench at low temperature and subsequently loaded and dried again. However, the Rb fraction was dissolved using fresh Milli-Q H_2O and loaded onto a previously degassed double Re filament (on similar dimensions). After final drying, the filament was heated up slowly until glowing dull red for about three seconds. The measured ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd ratios of SRM 987 and Ames Nd reference solution, during all analytical sessions of our data collection, were 0.710250 ± 16 (2SD, $n = 10$) and 0.512140 ± 12 (2SD, $n = 10$), respectively. All Sr and Nd isotope ratios were internally corrected for mass fractionation using a constant value of 0.1194 for ^{86}Sr/^{88}Sr and 0.7219 for ^{146}Nd/^{144}Nd by exponential law.

Table 3
Faraday cup configurations for Lu and Hf isotope analysis using Neptune MC-ICP-MS.

Faraday cup	L4	L3	L2	L1	Center	H1	H2	H3	H4
Lu									
Nominal mass	168	170	171	**172**	**173**	174	175	176	177
Measured element	Er + Yb	Er + Yb	Yb	**Yb**	**Yb**	Yb + Hf	Lu	Lu + Yb + Hf	Hf
Hf									
Nominal mass	173	175	176	**177**	178	**179**	180	181	183
Measured element	Yb	Lu	Hf + Yb + Lu	**Hf**	Hf	**Hf**	Hf + Ta + W	Ta	W

Bolded text indicates masses used to determine mass fractionation.

3. Results and discussion

3.1. Sample decomposition

Compared to previous methods for combination of Nd and Hf separation based on sodium peroxide (Na_2O_2) sintering [8] or lithium metaborate ($LiBO_2$) [10–12] and Lithium borate ($Li_2B_4O_7$) fluxing [14], our sample digestion offers some obvious advantages as follows. Hydrofluoric acid (HF) is commonly used to digest silicates and eliminate silicon as volatile SiF_4 in the process. High-purity HF and HNO_3 can be easily obtained using sub-boiling distillation, which helps to control the blank at a low level [8]. However, the sintering or fluxing reagent that contributes to the blank cannot be easily purified, although high-grade pure reagents are available, but at high cost. In addition, the purity of individual batches of sintering or fluxing reagent varies significantly in the levels of LMREE [12]. Finally, considering the relatively large amount of flux needed, which is from 2:1 [10,15] up to 6:1 [8] of total flux to sample, more matrix elements are added and can cause a column capacity issue. As for very resistant mineral phases such as zircon and garnet, a steel-jacketed bomb, which is extensively available for whole-rock trace element dissolution in most geochemical laboratories around the world, can be broadly adapted for complete decomposition. Therefore, in terms of simplicity, feasibility and sample throughput for concomitant separation of three radiogenic isotope systems, our sample digestion method has obvious advantages over previous techniques using flux fusions, as preferred in the literature.

3.2. Separation chemistry

Our designed purifying protocol is depicted in Table 1. The major advantage of the first column is to separate Lu and Hf into different fractions ready for isotope analyses in a single step [7]. Several advancements have been made by using our new procedures. No further separation of Hf and Zr needed to be conducted, because there is insignificant influence on Hf isotope measurement by MC-ICP-MS when Zr exists in the Hf fractions. However, the presence of significant amounts of Ti in the Hf fraction significantly reduces the transmission of Hf during MC-ICP-MS measurement and causes systematic drift of the instrument [6]. Therefore, Ti was separated from Hf in the Ln resin using 4 M HCl + 0.5% H_2O_2 mixtures instead of using the complex HCit–HNO_3–H_2O_2 mixture, as previously reported [7], and eluted as an orange to orange-red complex until the eluted solution appeared colorless. It is shown that the relative proportions of Hf to Ti are reduced from Ti/Hf $\sim$4000 in normal geological samples to Ti/Hf < 0.04 in the Hf fraction in this study. Of course, all solutions containing H_2O_2 need to be freshly prepared in order to achieve efficient separation of Ti and Hf. Finally, compared with previous studies, we used a mixture dominated by hydrochloric acid, with lesser amounts of H_2O_2 and HF as the elute solution, rather than complex elute solutions like ascorbic, citric and nitric acid, and even hydrochloric acid [7,8,10], which simplifies and shortens the chemical procedure.

In addition, the matrix elements, including LMREE, are not retained in the Ln Spec resin in a 4 M HCl medium. Therefore, the loading and rinsing solutions were collected before eluting the Lu fraction, and further processed to isolate Rb, Sr, Sm and Nd. This is one of our major considerations and achievements, since the process is highly efficient and allows rapid throughput, coupled with the fact that three sets of radiogenic isotopic data can be obtained from the one sample powder aliquot, thus greatly eliminating the effect of well-known natural geological material inhomogeneity and decreasing sample preparation times and consumptions of reagents.

3.3. Analyte recoveries and blanks

The Hf yield is more than 90% and the Lu recovery was deliberately set at about 30% to ensure only a small amount of Yb in the Lu fraction for Lu mass bias correction. The recoveries of Rb, Sr, Sm and Nd are also higher than 90%. The total procedural blanks measured for Lu, Hf, Rb, Sr, Sm and Nd were less than 10 pg, 50 pg, 50 pg, 100 pg, 50 pg and 50 pg, respectively, which are at the lower end of recently-published results for both the flux fusion [8,10–12,14] and acid-based dissolutions [1,6,16,17]. For example, the procedure of Lu–Hf and Sm–Nd separation from a single rock digest, recently developed by Kleinhanns et al. [8], is associated with higher Hf procedural blanks (>300 pg), which make this procedure inappropriate and inapplicable for most terrestrial and extra-terrestrial samples (Hf concentration < 0.5 $\mu g\, g^{-1}$). Therefore, the total procedure blank contribution in this work is negligible and requires no correction of the measured isotopic ratios.

3.4. Reproducibility of international CRMs

In order to evaluate and validate the present procedure, replicate analyses of six CRMs from USGS and GSJ were conducted for Lu–Hf, Rb–Sr and Sm–Nd isotope systems on a Neptune MC-ICP-MS and MAT 262 TIMS. Approximately 100 mg aliquots of CRMs were digested with mixed concentrated HF–HNO_3–$HClO_4$. Separation of Lu, Hf, Rb, Sr, Sm and Nd for all sample solutions was carried out using the chemical separation procedure described above. Two or three aliquots of CRMs rock powder went through the chemical procedure here, considering the well-known sample heterogeneity of natural geological samples. The results for the reference material together with data cited in the literature are summarized in Tables 4–6.

Our replicate Rb and Sr concentration data are internally consistent (0.01% < R.S.D. < 0.52%) with the exception of BCR-2 (1.13%), which could be due to operating errors in sample digestion (Table 4). Our replicate Sm and Nd concentration data are also internally consistent (0.03% < R.S.D. < 0.33%) (Table 5), while the reproducibility of Lu and Hf concentration measurements is 0.03–0.50%, except for one analysis of W-2 (R.S.D. 0.95%), which is systematically lower by 1.50% than the other two analyses (Table 6). It is likely that some sample or solution was lost during the pre-spiking stage of digestion of this sample. Specifically, our concentration data of CRMs from USGS agree well with previously published ID-TIMS or ID-MC-ICP-MS data [20,24] and high-precision ICP-MS analyses [32]. For the three international CRMs from GSJ, the Sm and Nd concentration of JB-2 and JB-3 also agree well with the published ID-TIMS data of Pin and Santos-Zalduegui [20]. The differences are all within 1%. The previous ICP-MS data of Dulski [28] for JA-2, JB-2 and JB-3 are somewhat lower than our data and those of others studies [20,27,30,32]. Additionally, our Hf concentration data all agree within 1% of the published ID-MC-ICP-MS data of Lu et al. [17,34]. As shown in Tables 4–6, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ ratios determined for replicate analyses of the basaltic and andesite reference materials are all within analytical uncertainty. These $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ ratios of CRMs are well within the range of values measured previously and reported in the literature.

In summary, the Lu, Hf, Rb, Sr, Sm and Nd concentration and isotopic data presented here show good agreement with published data on international CRMs using the MC-ICP-MS or TIMS techniques. These results demonstrate the overall validity of our procedure. Based on these data, our method is suitable and feasible for Rb–Sr, Sm–Nd and Lu–Hf isotope geochemistrical tracer and geochronological dating studies.

Table 4
Rb–Sr concentration and isotope data obtained on international CRMs.

CRMs	Rb (μg g^{-1})		Sr (μg g^{-1})		^{87}Sr/^{86}Sr	
	This study	Rec. value	This study	Rec. value	This study (±2σ)	Rec. value
BCR-2	45.97	46.9 [24]	340.9	340 [24]	0.705023(13)	0.705003 [25]
Basalt	46.72		341.0		0.705022(13)	0.705013 [26]
USGS	46.35[a]	1.13%[b]	340.9[a]	0.01%[b]	0.705023(01)[a]	
AGV-2	65.01	66.3 [24]	655.6	661 [24]	0.703976(13)	0.703976 [25]
Andesite	64.45		652.0		0.703995(12)	0.703981 [26]
USGS	64.59		651.9		0.703963(14)	
	64.68[a]	0.35%[b]	653.2[a]	0.32%[b]	0.703978(19)[a]	
W-2	19.02	20 [27]	195.0	194 [27]	0.706952(14)	0.70695 [24]
Diabase	19.11	19.8 [28]	196.4	196 [28]	0.706997(10)	
USGS	19.00		195.0		0.706950(13)	
	19.04[a]	0.31%[b]	195.5[a]	0.41%[b]	0.706966(31)[a]	
JA-2	68.96	68 [27]	246.2	252 [27]	0.706353(11)	0.706338 [29]
Andesite	69.18	69 [28]	247.6	246 [28]	0.706346(11)	
GSJ	69.20[c]	72.9 [30]	247.4[c]	248 [30]	0.706342(11)[c]	
	69.11[a]	0.19%[b]	247.1[a]	0.30%[b]	0.706347(06)[a]	
JB-2	6.04	6.2 [27]	178.0	178 [27]	0.703673(13)	0.703703 [29]
Basalt	6.03	6.3 [28]	178.2	179 [28]	0.703655(13)	0.703709 [31]
GSJ	5.98	7.37 [30]	176.9	178 [30]	0.703685(15)	
	6.02[a]	0.52%[b]	177.7[a]	0.40%[b]	0.703671(17)[a]	
JB-3	13.70	13 [27]	408.0	395 [27]	0.703417(14)	0.703446 [29]
Basalt	13.83	14.3 [28]	406.6	414 [28]	0.703387(15)	0.703432 [31]
GSJ	13.75	15.1 [30]	406.8	403 [30]	0.703385(14)	
	13.76[a]	0.46%[b]	407.2[a]	0.18%[b]	0.703396(21)[a]	

[a] The average value.
[b] The R.S.D. of the average value in this study.
[c] Marked values were measured for Sr and Nd after dissolution, but with the first column stage skipped and conducted directly on the second and third stage of purification.

3.5. Comparison with previous procedures

Chemical separation procedures for Lu–Hf isotope system by MC-ICP-MS are relatively simple compared to the protocols for classical TIMS [1]. After the pioneering work by Blichert-Toft et al. [6] demonstrated a simple procedure for Lu and Hf separation for the Plasma 54 MC-ICP-MS, subsequent research has developed increasingly simple Lu and Hf separation schemes for a great vari-

Table 5
Sm–Nd concentration and isotope data obtained on international CRMs.

CRMs	Sm (μg g^{-1})		Nd (μg g^{-1})		^{143}Nd/^{144}Nd	
	This study	Rec. value	This study	Rec. value	This study (±2σ)	Rec. value
BCR-2	6.599	6.57 [24]	28.90	28.7 [24]	0.512644(12)	0.512632 [23]
Basalt	6.625		29.04		0.512636(13)	0.512633 [25]
USGS	6.612[a]	0.28%[b]	28.97[a]	0.33%[b]	0.512640(08)[a]	0.512637 [26]
AGV-2	5.507	5.49 [24]	30.65	30.5 [24]	0.512777(10)	0.512755 [25]
Andesite	5.519		30.71		0.512793(10)	0.512791 [26]
USGS	5.516		30.70		0.512772(13)	
	5.514[a]	0.11%[b]	30.69[a]	0.10%[b]	0.512781(13)[a]	
W-2	3.289	3.29 [20]	13.07	13.00 [20]	0.512507(12)	0.512516 [18]
Diabase	3.291	3.22 [28]	13.08	12.70 [28]	0.512538(10)	0.512510 [20]
USGS	3.290	3.31 [32]	13.08	12.95 [32]	0.512503(12)	
	3.290[a]	0.03%[b]	13.08[a]	0.04%[b]	0.512516(22)[a]	
JA-2	3.099	3.11 [27]	14.56	13.9 [27]	0.512547(14)	0.512531 [23]
Andesite	3.103	2.9 [28]	14.61	13.9 [28]	0.512552(14)	0.512558 [29]
GSJ	3.101[c]		14.58[c]		0.512556(13)[c]	
	3.101[a]	0.07%[b]	14.58[a]	0.17%[b]	0.512552(05)[a]	
JB-2	2.259	2.26 [20]	6.338	6.30 [20]	0.513100(12)	0.513089 [20]
Basalt	2.265	2.11 [28]	6.357	6.10 [28]	0.513099(13)	0.513087 [23]
GSJ	2.261	2.31 [30]	6.341	6.63 [30]	0.513106(16)	0.513097 [29]
	2.261[a]	0.15%[b]	6.345[a]	0.16%[b]	0.513102(04)[a]	0.513085 [31]
JB-3	4.254	4.25 [20]	15.82	15.8 [20]	0.513055(09)	0.513049 [20]
Basalt	4.251	4.08 [28]	15.82	15.1 [28]	0.513085(13)	0.513062 [23]
GSJ	4.245	4.27 [30]	15.81	15.6 [30]	0.513052(12)	0.513048 [29]
	4.250[a]	0.11%[b]	15.82[a]	0.04%[b]	0.513064(21)[a]	0.513056 [31]

[a] The average value.
[b] The R.S.D. of the average value in this study.
[c] Marked values were measured for Sr and Nd data after dissolution, but with the first column stage skipped and conducted directly on the second and third stage of purification.

Table 6
Lu–Hf concentration and isotope data obtained on international CRMs.

CRMs	Lu ($\mu g\,g^{-1}$)		Hf ($\mu g\,g^{-1}$)		$^{176}Hf/^{177}Hf$	
	This study	Rec. value	This study	Rec. value	This study ($\pm 2\sigma$)	Rec. value
BCR-2	0.5109	0.499 [11]	4.923	4.97 [11]	0.282876(05)	0.282884 [9]
Basalt	0.5114	0.504 [16]	4.923	4.99 [16]	0.282875(06)	0.282875 [11]
USGS	0.5116[a]	0.519 [24]	4.946[a]		0.282880(09)[a]	0.282869 [12]
	0.5113[b]	0.07%[c]	4.931[b]	0.27%[c]	0.282877(03)[b]	0.282862 [21]
						0.282870 [33]
AGV-2	0.2496	0.247 [24]	5.151	5.10 [17]	0.282967(06)	
Andesite	0.2495		5.152	5.10 [34]	0.282963(06)	0.282969 [17]
USGS	0.2494		5.154		0.282967(08)	0.282984 [33]
	0.2495[b]	0.05%[c]	5.152[b]	0.03%[c]	0.282966(03)[b]	
W-2	0.3076	0.33 [27]	2.384	2.56 [9]	0.282730(10)	0.702715 [9]
Diabase	0.3075	0.32 [28]	2.420	2.41 [28]	0.282724(11)	0.702718 [14]
USGS	0.3080		2.427	2.56 [27]	0.282718(08)	
	0.3077[b]	0.09%[c]	2.410[b]	0.95%[c]	0.282724(07)[b]	
JA-2	0.2527	0.27 [30]	2.945	2.96 [17], 2.86 [30]	0.282872(07)	0.282874 [15]
Andesite	0.2553	0.25 [28]	2.954	3.1 [28]	0.282863(07)	0.282873 [17]
GSJ	0.2540[a]		2.937[a]	2.92 [34]	0.282866(09)[a]	
	0.2540[b]	0.50%[c]	2.946[b]	0.29%[c]	0.282867(05)[b]	
JB-2	0.3914	0.40 [30]	1.462	1.49 [30]	0.283229(11)	0.283283 [15]
Basalt	0.3917	0.38 [28]	1.465	1.80 [28], 1.47 [17]	0.283253(10)	0.283243 [17]
GSJ	0.3916		1.463	1.45 [34]	0.283257(11)	
	0.3916[b]	0.04%[c]	1.463[b]	0.12%[c]	0.283246(17)[b]	
JB-3	0.3795	0.39 [30]	2.686	2.68 [17], 2.67 [30]	0.283228(08)	0.283228 [14]
Basalt	0.3793	0.366 [28]	2.683	3.0 [28]	0.283223(07)	0.283245 [15]
GSJ	0.3796		2.675	2.66 [34]	0.283216(08)	0.283222 [17]
	0.3795[b]	0.04%[c]	2.681[b]	0.22%[c]	0.283222(07)[b]	

[a] Marked values were measured on the Neptune for Lu and Hf data only after the first stage of purification.
[b] The average value.
[c] The R.S.D. of the average value in this study.

ety of geological samples [7–17]. Generally speaking, the principal limitation of these methods is the need to undertake two sample digestions in order to obtain three data series for Lu–Hf, Rb–Sr and Sm–Nd isotope systems. That is to say, currently one sample digestion is commonly adopted for Rb–Sr and Sm–Nd isotope systems, whereas another is required to perform Lu–Hf and/or Sm–Nd isotope analysis [1–17]. Our procedure has obvious advantages over those requiring two digestions in terms of saving time and eliminating the need to prepare multiple samples from rock powder, thereby reducing the potential for error.

Moreover, our procedure provides flexibility according to the analyses of interest. For example, if only Lu–Hf isotopic data are required, the first column step is enough and adequate for their purification (*e.g.* BCR-2 and JA-2 in Table 6). Likewise, if only Rb–Sr and Sm–Nd isotopic data are of interest, their purification can be achieved by skipping the first column stage and accomplished using only the second and third columns with 1.5 mL of 2.5 M HCl instead of 5 mL of 3 M HCl taken with sample solutions, after complete dissolution (*e.g.* JA-2 in Tables 4 and 5). Therefore, chemical separation can be easily tailored to the analyses of interest and performed routinely in most geochemical laboratories around the world.

In summary, the technique developed here for dissolution and chemical purification of samples for Lu–Hf, Rb–Sr and Sm–Nd isotopic analysis allows extremely effective sample dissolution and chemical purification of these three radiogenic components in just three working days, as illustrated by the highly reproducible ratio data determinations of CRMs and the low blank levels (Tables 4–6).

3.6. Application

As is well-known, the coupling or decoupling relationship of Sr and Nd isotopes ($I_{Sr} - \varepsilon_{Nd}$) or Nd and Hf isotopes ($\varepsilon_{Nd} - \varepsilon_{Hf}$) is extensively used, discussed and argued in classical isotopic geochemical tracer and Sm–Nd and Lu–Hf isotope studies. For example, it has been applied to the coupled dating of garnet-bearing rocks, such as eclogite [1]. In order to further validate and demonstrate the effectness and robustness of our procedure, we have applied samples of kimberlite [35], mantel peridotite and xenoliths [36,37], which are rare, precious and of limited sample size. For example, perovskite ($CaTiO_3$) is a groundmass mineral in kimberlite of early magmatic crystallization and has the potential to record the primary geochemical and isotopic signature of the magma, prior to any contamination and/or weathering. From only *ca.* 5 mg of perovskite separate, Sr, Nd and Hf isotope data can be obtained to check and validate laser ablation analysis, using our established procedure [35]. Similarly, mantle peridotite and xenoliths are important indicators and windows into the deep mantle, and of limited sample size [36]. From *ca.* 150 mg samples, some peridotite xenoliths from the Penglai suite in Shandong province yielded Proterozoic Lu–Hf clinopyroxene mineral isochron ages of 1259 ± 22 Ma, which is consistent with its Os model age [37]. For the studies of Lu–Hf and Sm–Nd coupled dating of garnet-bearing rocks are currently being undertaken. In addition, our current procedure is also suitable and feasible for extra-terrestrial material (such as lunar samples and meteorites) in cosmochemistry research. These practical examples further exemplify the usefulness and applicability of this new method.

4. Conclusions

We have developed a three-column separation procedure for the concomitant extraction of Lu–Hf, Rb–Sr and Sm–Nd radiogenic isotopes from a single sample digestion prior to MC-ICP-MS and TIMS measurement. Using this procedure, Lu, Hf, Rb, Sr, Sm and Nd fractions can be prepared with a high degree of purity and satisfactory recovery. The technique has the following advantages or improvements over existing methods:

(1) The simplified chemical separation using mainly HCl as the eluting reagent results in rapid purification in just three working days, which will facilitate more widespread application of the three isotopic systems in the fields of geochemistry and geochronology.
(2) Only one sample digestion is needed for separating all three isotope systems at one time and with low blank levels, reducing sample preparation time and reagent consumption without compromising the precision and accuracy of the measurements and the problems associated with well-known sample heterogeneity of natural geological materials. In particular, it has great potential application where limited or precious terrestrial rocks (like kimberlite, peridotite and mantel xenoliths) and extra-terrestrial samples (like lunar rock and meteorites) are involved. Therefore, the high analytical throughput inherent to the MC-ICP-MS can be fully exploited.
(3) The technique allows flexibility in the chemical separation scheme, dependent on the isotopic system of interest, which can be tailored and carried out routinely in most geochemical laboratories around the world, without the need for special equipment such as induction or muffle furnaces.

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