



A straightforward protocol for Hf purification by single step anion-exchange chromatography and isotopic analysis by MC-ICP-MS applied to geological reference materials and zircon standards

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ABSTRACT

A straightforward one-step Hf purification protocol for geological samples using common anion-exchange chromatography and isotopic measurements by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is described in this paper. The sample is dissolved in concentrated HF–HNO₃ mixtures with round-bottom Savillex™ Teflon screw-top capsules or high-pressure stainless steel jacketed Teflon bombs. After complete dissolution, the chemical separation between Hf and isobarically interfering elements such as Lu, Yb, and matrix elements like Ti, is performed and achieved simultaneously using a common one-step anion exchange resin (AG1-X8). The Hf yields are >90% and total procedural blanks are lower than 20 pg. This protocol not only avoids using multiple-stage ion exchange resins, but also eliminates perchloric acid to break down fluorides after HF treatment of the sample. In addition to whole rock, this protocol is also practical for zircon and baddeleyite Hf purification prior to isotopic measurement. New Hf isotopic data for zircon 91500, Temora, CN92-1 and FM0411, together with Phalaborwa baddeleyite are presented for this method. Multiple analyses of the international geological reference materials and standard zircon and baddeleyite used in U–Pb geochronology demonstrate that this method is simple, economic, efficient and reproducible.

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1. Introduction

Since the increase in commercial availability of multiple collector inductively coupled plasma mass spectrometers (MC-ICP-MS) in the mid 1990s, the isotopic composition of high first ionization potential elements (e.g., Hf, W) has been measured relatively easily and rapidly [1,2]. In contrast to traditional thermal ionization mass spectrometry (TIMS), where the high first ionization potential necessitates typically more than 1 µg of the element and the mass spectrometric measurement lasts several hours, commonly with unsatisfactory precision, the MC-ICP-MS instrument ionizes the high first ionization potential elements with greater efficiency and high precision data can be readily obtained with much smaller sample size and higher sample throughput [3,4].

In addition, the stringent requirements for Hf purification, which are a necessary prerequisite for TIMS or hot-SIMS (secondary ionization mass spectrometry) analyses [5,6], have been significantly relaxed and simplified, since Zr and Hf fractions can be measured satisfactorily without further chemical separation

using MC-ICP-MS [3]. Subsequently, relatively simpler Hf separation schemes for a great variety of samples have been developed [7–16]. Nevertheless, isolating Zr and Hf fractions from isobarically interfering elements such as Yb, Lu and matrix elements like Ti prior to MC-ICP-MS analyses remains a tedious, lengthy and labor-intensive task. Rather complicated, two-step procedures are still widely used, because several major elements (e.g., P, Ti, Al and Fe) accompany the analyte when conventional ion-exchange chromatography techniques are used [9,10,17–19].

Although a single column procedure, based on extraction chromatography in Ln, UTEVA and TODGA resin has been recently developed and described [7,8,13–15,19], these special resins have a high cost and are extremely sensitive to residual HF left after sample dissolution and have to be discarded after only a few extractions. Also, the use of fairly concentrated HF is not very attractive. Sometimes, perchloric acid (HClO₄) fuming steps have been used to break down fluoride complexes, otherwise the Hf recovery may be very low [7,8,12]. Alternatively, either fusion (LiBO₂ or Li₂B₄O₇) or sintering (Na₂O₂) instead of HF has to be adopted and used to attack and decompose the sample, which results in high procedural blanks [9–14].

The main purpose of this study is to establish a rapid, straightforward protocol, based on conventional anion chromatography,

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which will enable the separation of Zr and Hf fractions from other interference (Yb and Lu) and matrix elements (Ti) so as to achieve a one-step chemical purification method and thus provide a viable alternative to complicated multiple-stage ion exchange chromatographic methods [9–11,17,18]. The anion AG1-X8 resin was first introduced to provide Zr isotope purification [8]. In this study, we attempted to be the first to achieve Hf purification using this common resin prior to MC-ICP-MS mass spectrometric measurement. The results showed that this resin can be used to perform Hf chemical separation for geological samples. The feasibility, capability, reproducibility and compatibility of this protocol is demonstrated and validated by replicate measurements of ¹⁷⁶Hf/¹⁷⁷Hf ratios on several international geological reference materials of silicate rocks and standards used for U–Pb dating of zircon and baddeleyite. In addition, we present new Hf isotopic analyses for zircon 91500, Temora, CN92-1 and FM0411, together with Phalaborwa baddeleyite by this new solution method, which is comparable to common cation-exchange chromatographic procedures using a standard resin (AG50W-X8 or 12) [20–26].

2. Experimental

2.1. Chemical materials and reagents

Milli-Q water (18.2 MΩ cm⁻¹) from Millipore (Elix-Millipore, USA) and twice-distilled extra-pure grade reagents were used in this study. Concentrated hydrochloric, nitric and hydrofluoric acids were purified using the Savillex™ DST-1000 sub-boiling distillation system (Minnetonka, USA).

Alfa Lu, Yb, Ti and Zr purchased from Alfa Aesar of the Johnson Matthey Company (Stock Nos. 35765, 13819, 35768 and 13875, plasma standard solution, Specpure) were gravimetrically diluted with 2% HNO₃.

Hf standard solution: JMC 475 Hf international standard solution, donated by Dr. P.J. Patchett and JMC 475 solution of 200 µg/L was used. Alfa Hf, an in-house Hf standard solution, purchased from Alfa Aesar of the Johnson Matthey Company (Stock No. 14374, plasma standard solution, Specpure) was gravimetrically diluted with 2% HNO₃ + trace HF during the actual sample preparation.

H₃BO₃ (3% H₃BO₃ in 2.5 M HCl): 12 g of high purity H₃BO₃ was weighed into a clean Teflon beaker and dissolved with 300 mL of Milli-Q water. The resulting solution was passed through a Bio-Rad AG50W-X12 cation exchange column to remove rare earth elements (REEs). Then 100 mL of Teflon distilled 10 M HCl was added to the solution. Acetic acid (36%, HAc) and hydrogen peroxide (30%, H₂O₂) of analytical grade were obtained commercially from the Beijing Institute of Chemical Reagent.

The commercially available cation (AG50W-X12, H⁺ form, 200–400 mesh size) and anion (AG1-X8, Cl⁻ form, 200–400 mesh size) exchange resins and polypropylene 2 mL resin bed (0.8 cm × 4 cm), including an integral 10 mL reservoir, were obtained from Bio-Rad (Richmond, USA).

International rock powder geological reference materials, recommended by the United States Geological Survey (USGS), and an in-house basalt sample, were used to validate and evaluate the present protocol. In addition, aliquots of standard zircon 91500, Temora, CN92-1 and FM0411, together with Phalaborwa baddeleyite, were used to evaluate the Zr and Hf fractions separated from the REEs.

2.2. Sample decomposition

All chemical preparations were performed on special class 100 work benches inside a class 1000 clean laboratory. About 100 mg of reference material rock powder were weighed into a 7 mL round-

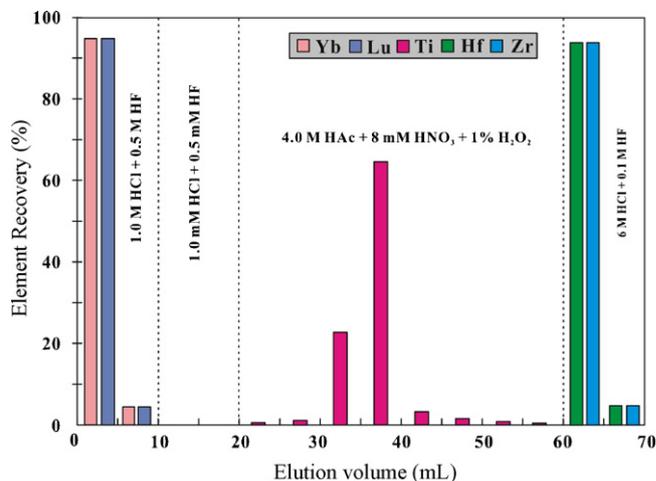


Fig. 1. Typical elution curves for interesting elements on a 2 mL (0.8 cm × 4 cm) AG1-X8 common anion resin (200–400 mesh particle size). The concentration of the load solution is fixed at 5 mL of 1 M HCl + 0.5 M HF, with recovery normalized to the total amounts loaded.

bottom Savillex™ Teflon screw-top capsule. 2 mL of concentrated HF plus 1 mL of concentrated HNO₃ were added and left sealed on a hot plate at about 120 °C for a week. Chips of zircon and baddeleyite were crushed to a fine power using an agate pestle and mortar. Small aliquots (ca. 0.5 mg) were weighted and soaked in an ultrasonic bath with Milli-Q water and dilute nitric acid to clean them and then they were dissolved in a concentrated mixture of HF–HNO₃ acids using stainless steel jacketed Teflon bombs that were placed in an oven for 48 h at 180 °C. After complete dissolution, the capsule was opened and evaporated to dryness. Then the residue was dissolved with 5 mL of 2.5 M HCl and saturated H₃BO₃ solution at 80 °C on a hotplate overnight. After the H₃BO₃ dissolution step, the fluoride gels formed during decomposition of mafic and ultramafic rocks were completely dissolved [15,25,27]. 1 mL of 6 M HCl was then added to the residue and evaporated to dryness. This procedure was repeated, allowing for the conversion of fluorides to chlorides which is important for facilitating clean separation of Hf from the REEs. When cool, the residue was dissolved in 1.5 mL of 3 M HCl. The capsule was then sealed and placed on an 80 °C hot plate overnight prior to chemical separation.

2.3. Chemical separation

Purification of Hf was accomplished in a single step through common anion-exchange chromatography [8]. The chemical separation scheme is illustrated in Fig. 1. Prior to chemical separation, 3 mL of Mill-Q H₂O was added to the 1.5 mL 3 M HCl sample solution and then 0.5 mL 6 M HF was added. Finally, the sample solution is mixed with 5 mL 1 M HCl + 0.5 M HF. The sample solution was then centrifuged and loaded onto cleaned and pre-conditioned anion resin with 6 M HCl and 1 M HCl + 0.5 M HF (Table 1). Firstly, the most major elements, including REEs, were eluted five times with 2 mL of

Table 1
One-step purification protocol for Hf using common anion exchange resin (AG1-X8, 200–400 mesh particle size, 2 mL resin bed).

Steps	Acids	Column volumes
Precondition	6 M HCl	10 mL × 3 times
Balance	1 M HCl + 0.5 M HF	3 mL × 3 times
Loading sample	1 M HCl + 0.5 M HF	1 mL × 5 times
Eluting matrix	1 M HCl + 0.5 M HF	2 mL × 5 times
Eluting matrix	1.0 mM HCl + 0.5 mM HF	2 mL × 5 times
Eluting Ti	4 M HAc + 8 mM HNO ₃ + 1% H ₂ O ₂	10 mL × 4 times
Collecting Hf(Zr)	6 M HCl + 0.1 M HF	10 mL × 1 times

Table 2
Typical operating parameters for Hf measurement using Neptune.

Neptune MC-ICP-MS	Setting
RF forward power	1300 W
Cooling gas	15.2 L/min
Auxiliary gas	0.6 L/min
Sample gas	~1.05 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 μ L/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
Integration time	4 s
Analytical time	500 s
Baseline	ca. 1 min on peak in 2% HNO_3

1 M HCl + 0.5 M HF. Before eluting Ti, the column was cleaned with 2 mL of 1.0 mM HCl + 0.5 mM HF. Secondly, Ti was eluted from the Zr and Hf fractions using a 4 M HAc + 8 mM HNO_3 + 1% H_2O_2 mixture. Finally, Hf and Zr fractions were eluted and extracted from the column with 6 M HCl + 0.1 M HF, collected in a 15 mL PFA beaker, and gently evaporated to dryness. This fraction was taken up with trace 2 M HF, diluted to 1 mL with 2% HNO_3 , and was then ready for Hf isotopic measurement.

2.4. Mass spectrometry

Hf isotopic compositions were measured on the Thermo-Finnigan Neptune MC-ICP-MS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing (IGG, CAS). Detailed descriptions for this instrument can be found elsewhere [28]. Analyses were made in the static mode using 9 Faraday cups and the typical instrument operating parameters and cup configurations are presented in Tables 2 and 3. Besides 176 , 177 , 178 , 179 , ^{180}Hf isotopes, signals corresponding to masses 173, 175, 181 and 183 were measured in order to monitor any isobaric interference of Lu and Yb (on mass 176) and Ta and W (on mass 180 (Table 3)). The JMC 475 Hf standard solution of 200 $\mu\text{g/L}$ was used for evaluating the reproducibility and accuracy of the instrument during analytical sessions. One sample run of Hf isotope analyses by standard solution consists of a baseline measurement at half mass positions and 90 cycles of sample signal collection, which were divided into 9 blocks so as to complete the 9 rotations of the amplifiers connected to the Faraday cups, in order to eliminate amplifier gain errors between different amplifiers [29]. The integration time of the signals for one cycle was set at a value of 4 s and the total time of one measurement lasted about 10 min and consumed about 100 ng of sample for each measurement. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratio data were directly normalized to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ for mass bias using the exponential law (Table 3). Samples in this study were interspersed with analyses of an in-house Alfa Hf 14374 standard solution which had been cross-calibrated by reference to $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$ for JMC475 [17,26]. Over the past two years, 140 analyses of JMC

475 yielded a $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282158 ± 18 (2SD), identical to the recommended value of Blichert-Toft et al. [17], within uncertainties. In addition, 167 analyses of Alfa Hf 14374 gave a $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282189 ± 19 (2SD) [26], also identical within error to the value of 0.282192 ± 6 (2σ , $n = 12$) obtained by other colleagues [16].

3. Results and discussion

3.1. Sample dissolution

As is well-known, hydrofluoric acid (HF) is commonly used to digest silicates and eliminate silicon as volatile SiF_4 during the sample dissolution process. High-purity HF can be easily obtained using sub-boiling distillation, which helps to control the blank at a low level [9–11,15]. However, most ion exchange resins, especially costly extraction resins (like Ln and TODGA resin), are extremely sensitive to residual HF left after sample dissolution and have to be discarded after only a few uses [8,13,14,19]. Furthermore, for mafic and ultramafic rocks, a great deal of Ca-, Mg- and REE-fluorides are often precipitated and absorb Hf after HF attack of the sample, which compromises the precision and accuracy of the measurements and gives a poor Hf yield [3,17]. Therefore, the use of fairly concentrated HF is not very attractive. Previously, perchloric acid (HClO_4) has been used to deal with residual HF and break down fluoride precipitations by fuming at high temperatures. In this study, considering that the strong tendency for B to complex with F^- ensures the efficient dissolution of Ca-fluorides that precipitate during the initial post-dissolution drying, we used saturated H_3BO_3 solution to break down the various fluoride precipitations [15,25,27]. After the H_3BO_3 dissolution step, the fluoride gels formed during decomposition of mafic and ultramafic rocks were dissolved completely. Therefore, in our work we not only used Hf to attack the silicates, but we also used H_3BO_3 to complex residual HF and break down the fluorides, instead of using perchloric acid.

3.2. Column chemistry

A one-step protocol is adopted in our work where the major elements, including REEs, are firstly separated and then Hf and Zr fractions are subsequently purified from the matrix elements, including Ti (Fig. 1 and Table 1). It is widely appreciated that REEs have to be completely separated from Hf fractions, given the isobaric interference of $^{160}\text{Gd}^{160}\text{O}$, $^{160}\text{Dy}^{160}\text{O}$, ^{176}Yb and ^{176}Lu on ^{176}Hf (Fig. 2a and b). As cations, REEs cannot be absorbed on anion exchange resin and pass through quickly, thus avoiding any potential interference in the subsequent Hf analyses. In general, the signal intensity of ^{173}Yb and ^{175}Lu was less than ca. 10^{-5} V during our Hf MC-ICP-MS analyses, which is the same signal intensity as that of the standard JMC475 and in-house Alfa Hf, and thus results in an inaccuracy on the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of ca. 15×10^{-5} . Therefore, the contribution of residual ^{176}Yb and ^{176}Lu on ^{176}Hf is very small to negligible.

As shown in Fig. 2a and b, when the isobaric interference of ^{176}Yb and ^{176}Lu on ^{176}Hf are corrected for mass discrimination by the exponential law and assuming the Yb and Lu mass discrimination is the same as that of Hf, the residual Yb and Lu in the final Hf and

Table 3
Faraday cup configuration for Hf isotope measurement using Neptune.

Faraday cup	L4	L3	L2	L1	Center	H1	H2	H3	H4
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

Bold values indicate masses used to determine mass fractionation of Hf.

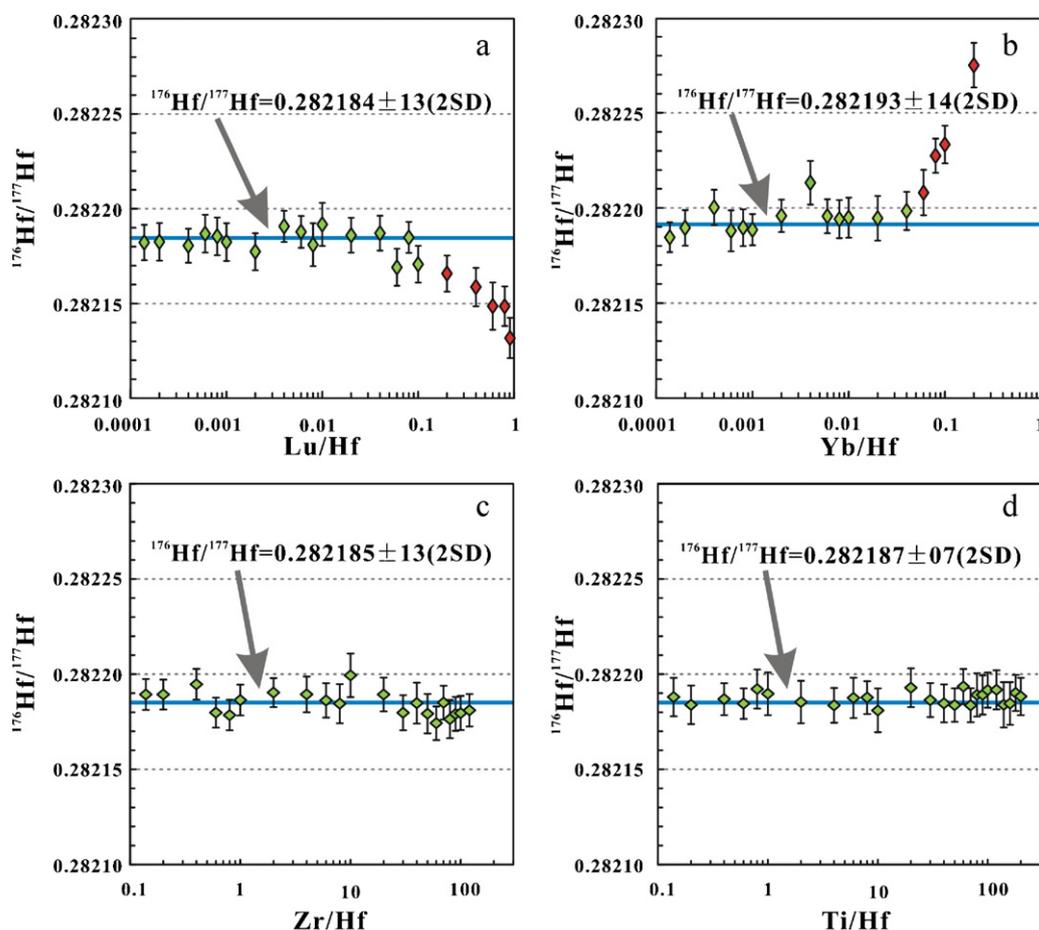


Fig. 2. $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios for in-house standard Alfa Hf (200 $\mu\text{g}/\text{L}$) doped with different and increasing amounts of Alfa Lu (a), Yb (b), Zr (c) and Ti (d). The isobaric interference of ^{176}Yb and ^{176}Lu on ^{176}Hf are corrected for mass discrimination by the exponential law and assuming the Yb and Lu mass discrimination is the same as that of Hf. The horizontal axes represent the sequence of measurements, typically about 10 min, between points. Other diamonds are used to calculate average values in each figure, while the last five (a) and four (b) diamonds are excluded data points.

Zr fraction can be effectively corrected for isobaric interference, even if Lu/Hf and Yb/Hf ratios are up to 0.1 and 0.04, respectively, indicating that the Neptune MC-ICP-MS effectively discriminates between these masses. In addition, the elution procedure described above allows for the complete separation between heavy REEs and the Hf fractions, so any potential mass interference of $^{160}\text{Gd}^{16}\text{O}$ and $^{160}\text{Dy}^{16}\text{O}$ on ^{176}Hf is considered unlikely. However, the extent of W and Ta interferences was monitored, and found to be very small in every case [19].

Besides isobaric interference elements, other matrix elements have to be separated completely from the Hf fractions. For Zr, it is necessary to undertake tedious chemical procedures for both TIMS [5] and hot-SIMS [6], but it is not necessary for MC-ICP-MS Hf analyses. As also pointed out by others [22–25], the addition of Alfa Zr in the Alfa Hf of 200 $\mu\text{g}/\text{L}$, even up to 120 of Zr/Hf in our mimic experiments on the Neptune does not seem to affect significantly the measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of our in-house standard (Fig. 2c). Therefore, we did not perform any separation of Zr and Hf. However, as a major element, Ti behaves similarly to Zr and Hf when passed through ion-exchange resin and has been shown to be responsible for significant Hf isotopic variation during MC-ICP-MS analyses [8,11,17]. As shown in Fig. 2d, the $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio for in-house standard Alfa Hf (200 $\mu\text{g}/\text{L}$) doped with different but increasing amount of Alfa Ti, even at Ti/Hf ratios up 200, shows no significantly variability during measurement, indicating the Neptune's good tolerance for Ti. This is why Hf isotope analysis of rutile (TiO_2) can be determined by Laser Ablation MC-ICP-MS (LA-MC-ICP-MS), as shown in other studies [30,31]. In our work, Ti

was eluted effectively with a 4 M HAc + 8 mM HNO_3 + 1% H_2O_2 mixture. Finally, Hf and Zr as F^- complexes were eluted with 6 mol L^{-1} HCl + 0.1 mol L^{-1} HF, prior to MC-ICP-MS analysis. Usually in our work, the Ti/Hf ratio in the final Hf and Zr fractions was less than 0.1, indicating the efficiency of the chemical purification.

In summary, after complete dissolution, the chemical separation between Hf and isobaric elements such as Lu, Yb and matrix materials like Ti can be performed and achieved simultaneously using the common one-step anion exchange resin procedure described here.

3.3. Analyte recoveries and blanks

As for recovery of Hf, a comparison of Hf concentrations in the geological reference materials with the sample weight revealed the chemical recovery of Hf using our procedure was more than 90%. Full procedural blanks for Hf in this work were <20 pg, which is at the lower end of recently-published results for both the flux fusion [7,9,14] and acid-based dissolution [3,8,15,18] methods. Therefore, the total procedure blank contribution is negligible and requires no correction of the measured isotopic ratios.

3.4. Hf isotope analyses of international geological reference materials

Several international geological reference materials from the USGS and an in-house basalt rock powder were used to validate and evaluate the present protocol. Hf isotope ratios were determined

Table 4

Comparison of results of $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios of CRMs using the one-step common anion exchange resin technique (this study) with previously published data by multi-step ion exchange or special extraction chromatography resin.

CRMs	Aliquot	$^{176}\text{Hf}/^{177}\text{Hf}$ ($\pm 2\sigma$)	$^{176}\text{Hf}/^{177}\text{Hf}$
		This study	Recommended value
BCR-1	1	0.282875(10)	0.282879 [3]; 0.282913 [5]
Basalt	2	0.282862(08)	0.282817 [7]; 0.282892 [8]
USGS	3	0.282870(10)	0.282875 [10]; 0.282867 [11]
	4	0.282880(08)	0.282860 [18]
W-2	1	0.282709(09)	0.282715 [7]; 0.282718 [13]
Diabase	2	0.282714(10)	0.282724 [19]
USGS	3	0.282719(09)	
	4	0.282716(09)	
		0.282715(08) [†]	
BHVO-2	1	0.283094(07)	0.283116 [10]; 0.283099 [13]
Basalt	2	0.283096(07)	0.283106 [14]; 0.283096 [32]
USGS	3	0.283088(08)	
	4	0.283098(06)	
		0.283094(08) [†]	
GSR-3	1	0.282992(08)	0.282983 [13]
Basalt	2	0.282984(06)	
In-house	3	0.282979(06)	
		0.282985(14) [†]	

[†]Means the averaged value.

on replicate digestions of sample of in-house basalt GSR-3 and on international standards BCR-1, W-2 and BHVO-2 and the results, together with data cited in the literature, are summarized in Table 4. Here, Hf isotopic compositions of in-house basalt and international geological reference materials are shown to be reproducible within the analytical error of individual analyses. Three replicate analyses of GSR-3 yield an average $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282985 ± 14 (2SD), which agrees well with the value of 0.282983 recently published for the fusion ($\text{Li}_2\text{B}_4\text{O}_7$) technique [13]. Similarly, BCR-1 analyses yield a mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282872 ± 16 (2SD), which compares well with other data obtained by either TIMS or MC-ICP-MS [3,5,7,8,10,11,18]. W-2 analyses yield a mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282715 ± 08 (2SD). This value is identical to the value obtained by Le Fèvre and Pin [7] and within error of the value of 0.282718

obtained by Li et al. [13] and 0.282724 determined during our earlier study [19]. BHVO-2 analyses yield a mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.283094 ± 08 (2SD), which is within error of other published data by MC-ICP-MS [10,13,32], although our data do appear to be consistently slightly lower (Table 4).

On the basis of these data, it is considered that our new procedure brings a significant improvement in Hf isotopic analysis by solution MC-ICP-MS, because of its ability to greatly reduce sample preparation time without compromising the precision and accuracy of the measurements. This enables the high analytical throughput inherent to MC-ICP-MS to be fully exploited.

3.5. Hf isotope measurement of standard zircon and baddeleyite

It has been recognized that the zircon (ZrSiO_4) and baddeleyite (ZrO_2) Lu–Hf isotopic systems are an important and powerful tracer in deciphering crust and mantle evolution because of their high Hf concentration and extremely low Lu/Hf ratios; these data can also be integrated with U–Pb geochronology on the same minerals [26]. However, different protocols are adopted for the isobaric interference correction of ^{176}Yb and ^{176}Lu on ^{176}Hf by various laboratories during *in situ* Lu–Hf isotopic analyses of zircon and baddeleyite by LA-MC-ICP-MS [26]. Therefore, the solution method of analysis after chemical purification is the most reliable way to obtain the correct Hf isotopic composition of the standard zircons and baddeleyites and the benchmark technique to validate the accuracy of laser ablation data, because it is free of isobaric interference. There have been a number of studies on Hf purification of standard zircons, in which common cation-exchange chromatography (AG50W-X8 or 12) is always used for chemical purification after complete dissolution [20–26]. However, there is no report of zircon Hf purification using anion exchange chromatography.

Here, in order to further evaluate the feasibility of the present Hf purification protocol, replicate analyses of several well-known standard zircons (including 91500, Temora, CN92-1 and FM0411) and Phalaborwa baddeleyite, all commonly used in U–Pb geochronology, were carried out. After complete dissolution, the subsequent procedure followed the above-mentioned protocol.

Table 5

Comparison of the results of $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios of standard zircon and baddeleyite using common anion exchange resin (this study) with previous data using common cation exchange resin (AG50W-X8 or 12).

Zircon or baddeleyite	Aliquot	$^{176}\text{Hf}/^{177}\text{Hf}$ ($\pm 2\sigma$)	$^{176}\text{Hf}/^{177}\text{Hf}$
		This study	Recommended value
91500	1	0.282290(07); 0.282292(08) [*]	0.282302 [20]; 0.282320 [21]; 0.282302 [22]
Zircon	2	0.282305(07); 0.282299(06) [*]	0.282306 [23]; 0.282310 [24]; 0.282300 [26]
	3	0.282308(05); 0.282312(06) [*]	0.282305 [33]; 0.282298 [34]; 0.282289 [35]
		0.282301(18) ^{**}	0.282304 [36];
Temora	1	0.282685(08); 0.282688(09) [*]	0.282686 [23]; 0.282706 [24]; 0.282685 [26]
Zircon	2	0.282677(09); 0.282682(10) [*]	
	3	0.282680(04); 0.282685(06) [*]	
		0.282683(08) [*]	
CN92-1	1	0.282171(04); 0.282166(04) [*]	0.282172 [26]
Zircon	2	0.282169(10); 0.282163(11) [*]	
	3	0.282178(10); 0.282176(08) [*]	
		0.282170(11) [*]	
FM0411	1	0.282984(12); 0.282986(11) [*]	0.282984 [26]
Zircon	2	0.282980(10); 0.282981(11) [*]	
		0.282983(05) ^{**}	
Phalaborwa-1	1	0.281237(10); 0.281239(08) [*]	0.281229 [26]
Baddeleyite	2	0.281230(12); 0.281235(10) [*]	
	3	0.281241(08); 0.281243(09) [*]	
		0.281237(09) ^{**}	
Phalaborwa-2	1	0.281202(13); 0.281195(14) [*]	0.281206 [26]; 0.281187 [37]
Baddeleyite	2	0.281198(12); 0.281201(10) [*]	
	3	0.281202(08); 0.281192(11) [*]	
		0.281198(08) ^{**}	

^{*}Means re-analysis of the same aliquot.

^{**}Means the averaged value.

The only difference between the chemical separation of zircon and baddeleyite and whole-rock powder is that no further Ti and Hf fraction separation was undertaken, given that Ti content in zircon is low. The results for standard zircon and baddeleyite, together with data cited in the literature, are summarized in Table 5.

Zircon 91500, one of the most widely distributed standards, has been extensively used for U–Pb age, trace element and Hf isotopic analyses by various laboratories all over the world [26]. Our six analyses of three aliquots yielded a mean $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282301 ± 18 (2SD), which is identical, within error, to the values reported previously using cation exchange resin purification techniques [22–26,33–36]. For Temora zircon, it is important to note that our present six analyses of three aliquots gave a mean of 0.282683 ± 8 (2SD) for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, which agrees well with the value of 0.282685 ± 11 obtained during our previous cation purification [26] and with other published values [23,24]. Similarly, our current solution analyses of zircon CN92-1 yielded a mean $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282170 ± 11 (2SD) for six runs of three aliquots, which agree well with our previously obtained value of 0.282172 ± 11 (2SD) by common cation-exchange chromatography purification [26]. FM0411, a euhedral zircon megacryst measuring 6 by 8 mm, collected from Cenozoic basalt at Mingxi in southeastern China, was run as an in-house Hf standard in our laboratory [26]. Our previous ten runs of five aliquots by solution analysis recorded a value of 0.282984 ± 14 (2SD) for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, identical to the present result of 0.282983 ± 5 (2SD) from four runs of two aliquots.

Besides zircon, baddeleyite is also a suitable mineral for *in situ* Hf analyses due to its extremely high Hf contents [36,37]. Baddeleyite from the Phalaborwa carbonatite of South Africa has been commonly used as a standard. However, only a few Hf analytical results have been published. Scherer et al. [37] obtained $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.281187 ± 17 using the TIMS method. Our Phalaborwa baddeleyite was provided by the Mineralogical Research Company. Previously, seventeen runs of 4 aliquots using the solution method yielded a $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.281229 ± 11 (2SD), which agrees well with the present result of 0.281237 ± 11 (2SD) for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. In addition, 20 measurements of 4 aliquots of this standard donated by Scherer using a previous solution recorded a value of 0.281206 ± 19 for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, which is also compatible with the value by Scherer et al. [37] using the same solution. Moreover, our present purification yielded 0.281198 ± 9 (2SD) for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, which also further confirms the accuracy of the results.

In summary, the Hf isotopic data of several standard zircon and Phalaborwa baddeleyite presented here show good agreement with published data using cation purification methods. These results demonstrate the overall validity of the present protocol and our method is comparable to those using cation purification.

4. Conclusions

We have established a straightforward protocol for Hf purification of geological samples prior to MC-ICP-MS solution measurement using common anion-exchange chromatography. After complete sample dissolution with HF–HNO₃, chemical separation of the analyte between interference and matrix elements was accomplished and achieved easily in a one-step protocol with high recoveries and satisfactory procedural blanks. In addition, our present protocol is also comparable to that of standard cation exchange resin techniques, which are currently widely adopted for Hf purification of zircon and baddeleyite. Multiple replicate analyses of the geological reference materials and standard zircons and baddeleyite demonstrate that our present protocol is a

simple, economic, efficient method, able to deliver high precision isotopic measurements. The high analytical throughput inherent to the MC-ICP-MS can thus be fully exploited.

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