

# Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICPMS measurements

Carsten Münker, Stefan Weyer, Erik Scherer, and Klaus Mezger

Zentrallabor für Geochronologie, Mineralogisches Institut, Universität Münster, Corrensstr. 24, 48149 Münster, Germany (muenker@nwz.uni-muenster.de; weyer@ThermoFinniganMAT.de; escherer@nwz.uni-muenster.de; klaush@nwz.uni-muenster.de)

[1] **Abstract:** The application of multiple collector inductively coupled plasma source mass spectrometry (MC-ICPMS) to  $^{176}\text{Lu}$ - $^{176}\text{Hf}$  and  $^{92}\text{Nb}$ - $^{92}\text{Zr}$  chronometry has been hampered by complex Zr-Hf purification procedures that involve multiple ion exchange column steps. This study presents a single-column separation procedure for purification of Hf and Lu by ion exchange using Eichrom<sup>®</sup> Ln-Spec resin. The sample is loaded in pure HCl, and element yields are not dependent on the sample matrix. For  $^{92}\text{Nb}$ - $^{92}\text{Zr}$  chronometry, a one-column procedure for purification of Zr using Biorad<sup>®</sup> AG-1- $\times$  8 resin is described. Titanium and Mo are completely removed from the Zr, thus enabling accurate  $^{92}\text{Zr}$  measurements. Zirconium and Nb are quantitatively separated from rock samples using Eichrom Ln-Spec resin, allowing measurements of Zr/Nb with a precision of better than  $\pm 5\%$  ( $2\sigma$ ). The Ln-Spec and anion resin procedures may be combined into a three-column method for separation of Zr-Nb, Hf, Ta, and Lu from rock samples. For the first time, this procedure permits combined isotope dilution measurements of Nb-Ta, Zr/Hf, and Lu/Hf using a mixed  $^{94}\text{Zr}$ - $^{176}\text{Lu}$ - $^{180}\text{Hf}$ - $^{180}\text{Ta}$  tracer. Analytical protocols for Zr and Hf isotope measurements using the Micromass Isoprobe, a second generation, single-focusing MC-ICPMS, are reported. Using the Isoprobe at Münster,  $2\sigma$  external precisions of  $\pm 0.5\epsilon$  units for Hf and Zr isotope measurements are achieved using as little as 5 ng (Hf) to 10 ng (Zr) of the element. The  $^{176}\text{Hf}/^{177}\text{Hf}$  and Lu/Hf for rock reference materials agree well with other published MC-ICPMS and thermal ionization mass spectrometry (TIMS) data.

**Keywords:** Separation; Ln Spec; zirconium; hafnium; niobium; tantalum.

**Index terms:** Isotopic composition/chemistry; instruments and techniques; trace elements; geochronology.

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## 1. Introduction

[2] The advent of multiple collector inductively coupled plasma source mass spectrometry (MC-ICPMS) has facilitated high-precision isotope

ratio measurements of the high field strength elements (HFSE:Zr-Hf-Nb-Ta) [e.g., *Blichert-Toft et al.*, 1997; *Münker et al.*, 2000; *Sanloup et al.*, 2000; *Hirata*, 2001]. In contrast to thermal ionization mass spectrometry (TIMS), where



the high first ionization potentials of HFSE necessitate the use of a large amount of sample material (typically  $>1\mu\text{g}$  of the element), the plasma source of MC-ICPMS instruments ionizes the HFSE with greater efficiency, so that external precisions of approximately  $\pm 0.5$  epsilon units can be achieved for less than 100 ng of the element.

[3] Zirconium and Hf are particularly interesting because they include the radiogenic daughters of the  $^{176}\text{Lu}$ - $^{176}\text{Hf}$  (half-life = 37.17 Ga [Scherer *et al.*, 2001]) and  $^{92}\text{Nb}$ - $^{92}\text{Zr}$  chronometers (half-life = 36 Ma [Nethaway *et al.*, 1978]). Accurate  $^{176}\text{Hf}$  and  $^{92}\text{Zr}$  measurements require removal of the interfering  $^{176}\text{Yb}$ ,  $^{176}\text{Lu}$ , and  $^{92}\text{Mo}$ . Moreover, the separation from whole rock matrices is necessary because the precision of MC-ICPMS data is adversely affected by (1) formation of interfering polyatomic species in the plasma and (2) matrix-dependent change of mass bias behavior. The influence of Ti on mass fractionation processes during Hf and Zr isotope ratio measurements, first noticed for Hf by Blichert-Toft *et al.* [1997], is shown in Figure 1. Owing to its high abundance in silicate rocks relative to Zr and Hf, Ti may cause significant shifts in measured Zr and Hf isotope ratios. Titanium behaves like Zr and Hf during cation and anion separations [Korkisch, 1989]; thus additional purification of Zr and Hf is required.

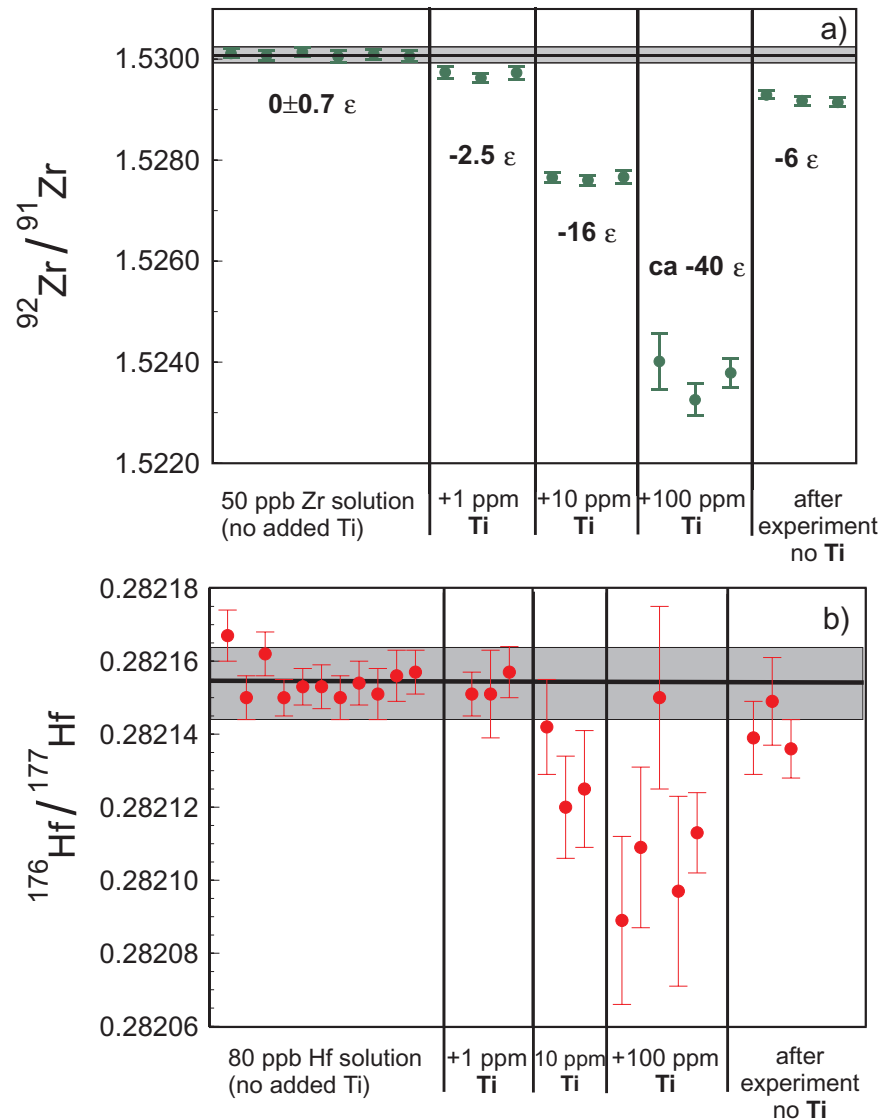
[4] Isotope dilution enables the precise measurement of Zr/Hf and Nb/Ta ratios, which in most terrestrial rocks apparently scatter by about  $\pm 30\%$  around the chondritic ratios of  $\sim 34.5$  and  $\sim 17.6$ , respectively [e.g., Eggins *et al.*, 1997; Jochum *et al.*, 1996; Münker, 1998; Niu and Batiza, 1997; Plank and White, 1995; Stolz *et al.*, 1996; Weyer *et al.*, 2001]. Such small natural ranges preclude measurements of Zr/Hf and Nb/Ta at sufficient resolution using externally calibrated methods such as quadrupole ICPMS, X-Ray Fluorescence

(XRF), or Instrumental Neutron Activation Analysis (INAA), which have typical external precisions and accuracies for these ratios of no better than  $\pm 10\%$ . Measurement of Zr/Hf and Nb/Ta by isotope dilution is therefore the most promising method for resolving natural variations of Zr/Hf and Nb/Ta. Although Nb is mono-isotopic and cannot be measured by isotope dilution, a  $^{180}\text{Ta}$  tracer [Weyer *et al.*, 2001] now permits much more precise Nb/Ta measurements. The approximately  $\pm 5\%$  accuracies of the first Zr/Hf isotope dilution measurements by ICPMS [David *et al.*, 1999; Reid *et al.*, 1999; Xie and Kerrich, 1995] were limited by the accuracy of spike calibration, mode of mass bias correction, and instrument sensitivity. These uncertainties can be reduced to better than  $\pm 1\%$  by removing the sample matrix and improving the spike calibrations.

[5] Here we report ion exchange separation procedures for the HFSE and protocols for Zr and Hf measurements by MC-ICPMS that are used at Münster. A new, one-column method for rapid separation of Lu and Hf from whole rock matrices is introduced. This procedure also permits separation of Hf from almost any matrix, including peridotites, garnets, and phosphates. With previous hydrofluoric acid-based techniques, separation of Hf (and Zr) from peridotites and phosphates was extremely difficult owing to (1) coprecipitation of HFSE with Ca-Mg fluorides [Blichert-Toft, 2001] and (2) the large amount of sample required (up to several grams). We also report a new one-column procedure for separating Zr from rock matrices, Ti, and the interfering Mo.

## 2. Previous Separation Techniques

[6] The first routine Lu-Hf separation method designed specifically for geologic samples was introduced by Patchett and Tatsumoto [1980], who combined elements of earlier separation schemes [e.g., Benedict *et al.*, 1954; Faris,



**Figure 1.** The internally corrected (a)  $^{92}\text{Zr}/^{91}\text{Zr}$  and (b)  $^{176}\text{Hf}/^{177}\text{Hf}$  obtained for Zr-Hf standard solutions (50 ppb) at different Ti abundances. Ti/Zr and Ti/Hf of greater than 10 in the analyte cause a bias of internally corrected isotope ratios relative to those of the pure standard solutions. Likewise, pure standard solutions that were measured immediately after the Ti-rich solutions gave systematically wrong values. This offset is most likely caused by a change in mass fractionation processes during build-up of Ti in the cone-orifice region of the MC-ICPMS.

1960] into a three-column procedure (cation and anion resins). Other procedures based on various combinations of cation and anion exchange steps (three to four columns) were subsequently developed [e.g., *Salters and Hart*, 1991; *Salters*, 1994; *Barovich et al.*, 1995;

*Scherer et al.*, 1995; *Blichert-Toft et al.*, 1997; *Blichert-Toft and Arndt*, 1999; *Kleinhanns et al.*, 2000; *Blichert-Toft*, 2001]. The pre-1997 methods were designed for TIMS or hot SIMS analyses and thus required (1) handling of large samples (up to several grams of rock) and (2)



efficient Ti-Zr separation from Hf to maximize ionization efficiency. In some methods, the amount of sample matrix to be processed is reduced by first leaching the digested rock sample in HF to separate an HFSE-rich supernatant from the precipitated REE-bearing bulk matrix [Salter and Hart, 1991; Salter, 1994; Barovich et al., 1995; Scherer et al., 1995; Blichert-Toft et al., 1997]. For some rock matrices, such leaching decreases Hf yields dramatically (Hf is coprecipitated with Ca-Mg fluorides), but leaching can be replaced by an additional cation column step [Blichert-Toft, 2001]. Efficient Ti-Zr-Hf separation was achieved using H<sub>2</sub>SO<sub>4</sub> [Barovich et al., 1995; Scherer et al., 1995], in which distribution coefficients between Ti-Zr-Hf differ significantly [Danielson, 1965; Hague and Machlan, 1961; Strelow and Bothma, 1967]. In principle, chemical separations for MC-ICPMS can be simplified over previous methods because the high ionization efficiency of the plasma source (1) allows smaller samples to be run and (2) eliminates the need for efficient Zr-Hf separation. In practice, however, extreme care must still be taken to avoid significant isobaric interferences (e.g., <sup>176</sup>Yb and <sup>176</sup>Lu on <sup>176</sup>Hf) and matrix effects (Figure 1). Recently, simple, one-column Hf separation schemes based on Eichrom TEVA Spec have been developed [Yang and Pin, 1999; Le Fèvre and Pin, 2001]. Although they permit the direct separation of Hf from the bulk sample matrix, neither method provides a Lu fraction for ID analysis.

### 3. New Separation Procedures

#### 3.1. Reagents and Digestion Procedure

[7] Once-distilled HF, HCl, and HNO<sub>3</sub> were used throughout. Reagent grade acetic acid, citric acid, and H<sub>2</sub>O<sub>2</sub> were used; their contributions to HFSE blanks were negligible. Procedural blanks are <10 pg for Lu, <1 ng for Zr, <100 pg for Hf, <100 pg for Nb, and <100 pg

for Ta. For demanding, low-blank applications, blanks can be reduced to ~10 pg for Hf and ~300 pg for Zr by using HF and HCl that have been distilled a second time in Teflon.

[8] Rock samples were digested in ~1:1 HF-HNO<sub>3</sub>. Except for basalts (120°C tabletop digestions), all samples were digested at 180°C in Savillex<sup>®</sup> vials placed inside Parr<sup>®</sup> bombs. Zircon-bearing samples were fused with five parts Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, dissolved in HCl, and redigested in HF-HNO<sub>3</sub> to achieve full sample-spike equilibration for the HFSE. After evaporation, the samples were dried down 3 times in 2 mL of concentrated HNO<sub>3</sub>-trace HF (<0.05 M). The samples were then completely dissolved in 8–10 mL 6 M HCl-trace HF. No precipitates were observed. Combining strong HNO<sub>3</sub> or HCl with trace HF ensures sample-spike equilibration. (Using only trace HF stabilizes HFSE in solution without precipitating Lu-fluorides.) The external reproducibility of Lu/Hf ratios was better than ±1% (2σ) for multiple replicate rock digestions.

#### 3.2. One-Column Zr Separation by Anion Exchange

[9] The one-column procedure for Zr separation (Table 1, Figure 2) is based on anion-exchange chromatography using BIORAD AG-1-X8 resin (100–200 mesh, Cl<sup>-</sup> form). The Zr-Hf distribution coefficients in HCl-HF on anion resin depend little on HF molarity below 5 M [Faris, 1960; Kim et al., 1973], but they are extremely sensitive to the HCl molarity (>10 in molarities lower than 2 M HCl [Kim et al., 1973; Nelson et al., 1960; Wish, 1959]). The column is therefore preconditioned in ~2 column volumes (v) of 0.5 M HCl-0.5 M HF. After centrifuging, the sample is loaded in ~1 M HCl-0.5 M HF without a precipitation step, thus avoiding coprecipitation of Zr with fluorides. Typically, 100 mg of digested sample are first dissolved in ~1.5 mL 3 M HCl and then diluted

**Table 1.** Column Dimensions and Single-Column Separation Procedures for Zr, Lu-Hf<sup>a</sup>

One Column Lu-Hf	EICHROM Ln Spec (1 mL, ca. 3.8×0.6 cm) <sup>c</sup>		One Column Zr	BIORAD AG-1-X8 (4 mL, ca. 8.7×0.8 cm)	
Step	Column Volumes	Acid	Step	Column Volumes	Acid
Load sample	5 v	3M HCl (+ 0.1M ascorbic acid)	load sample	1.25 v	0.5 M HCl-0.5 M HF
Rinse matrix	10 v	3 M HCl	rinse matrix	2.5 v	0.5 M HCl-0.5 M HF
HREE (Lu-Yb) <sup>d</sup>	10 v	6 M HCl	rinse matrix	0.5 + 0.5 + 0.5 v	0.5 mM HCl-0.5 mM HF
Washout HCl	2 + 2 v	H <sub>2</sub> O	Ti	2.5 – 15 v	3.6 M HAc-8 mM HNO <sub>3</sub> -1% H <sub>2</sub> O <sub>2</sub>
Ti	variable	0.09 HCit-0.4N HNO <sub>3</sub> -1 wt% H <sub>2</sub> O <sub>2</sub>	washout H <sub>2</sub> O <sub>2</sub>	1.5 v	9 M HAc
Washout H <sub>2</sub> O <sub>2</sub>	5 v	0.09 HCit-0.4N HNO <sub>3</sub>	Zr(+Hf) <sup>b</sup>	2.5 v	6 M HCl-0.06 M HF
Zr	50 v	6 M HCl-0.06 M HF	Mo-Nb (optional)	5 v	6 M HNO <sub>3</sub> -0.2 M HF
Hf <sup>b</sup>	12 v	6 M HCl-0.2 M HF	cleaning	5 v	6 M HNO <sub>3</sub> -0.2 M HF-1 wt % H <sub>2</sub> O <sub>2</sub>
Cleaning	10 v	6 M HCl		5 v	1 M HCl-1 mM DTPA
	10 v	2 M HF (alternating)			

<sup>a</sup>Here v refers to resin volumes. Note that all solutions containing H<sub>2</sub>O<sub>2</sub> need to be freshly prepared.

<sup>b</sup>These particular element-cuts are collected for further analysis (as discussed in text).

<sup>c</sup>Note that separation efficiency and yields decrease after the resin has been used about 15 times.

<sup>d</sup>At high Lu/Hf, more 6 M HCl is required to remove all Lu.

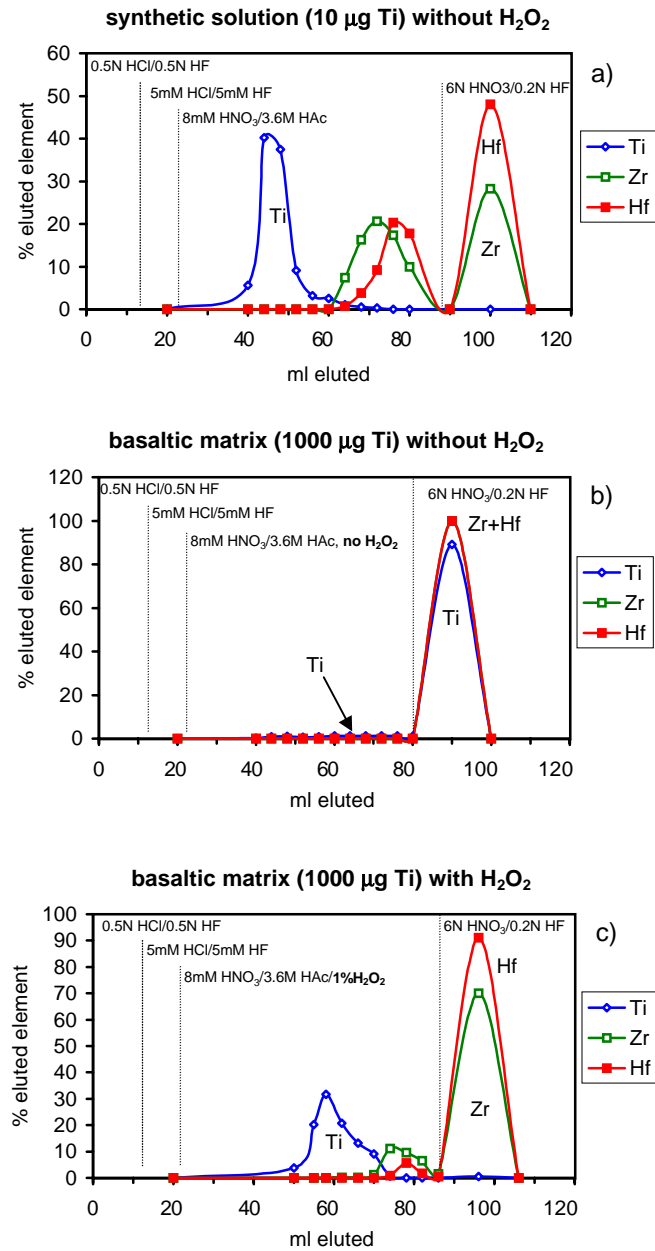
to ~4.5 mL with H<sub>2</sub>O. Upon complete dissolution, ~0.5 mL of 6 M HF are added to achieve a final concentration of ~1 M HCl-0.5 M HF. Higher loading volumes (5 mL or more), especially for peridotites, are required to keep larger samples in solution. Loading ~100 mg of basaltic sample matrix in up to 40 mL of 1 M HCl-0.5 M HF gave >90% Zr yields. For >200 mg peridotite samples, coprecipitation of Zr with Ca-Mg-fluoride reduced the yields.

[10] After loading, the bulk matrix is eluted with 0.5 M HCl-0.5 M HF, while the HFSE, Mo, and W stay on the column [Kim *et al.*, 1973]. Titanium is eluted with a mixture of acetic acid (HAc), HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> because the distribution coefficients for Ti in acetic acid are much lower (~1) than those for other HFSE (>100 [van den Winkel *et al.*, 1971]). Optimum separation of Ti is achieved in a mixture of 3.6 M HAc-8 mM HNO<sub>3</sub> (Figure 2). Higher HNO<sub>3</sub> (and HCl) molarities (i.e., a decrease in pH) lower the partition coefficients in acetic acid,

causing early elution of all HFSE at HNO<sub>3</sub> (and HCl) molarities >0.1 [Kim *et al.*, 1973]. For this reason, 1.5 v of 0.5 mM HCl-0.5 mM HF are passed before Ti is eluted.

[11] The Ti-Zr separation is less efficient at lower HAc molarities (<2 M), but it is relatively insensitive to the length of the resin bed (4–23 cm) and the amount of resin used (3–8 mL). If >50 µg of Ti are loaded on the column, H<sub>2</sub>O<sub>2</sub> is added to the HAc-HNO<sub>3</sub> mixtures (Figure 2b–2c) to prevent hydrolysis of Ti on the column. For mafic samples (~1000 µg Ti per 100 mg sample), ~80% of the Ti would otherwise be eluted with the Zr, resulting in unacceptably high Ti/Zr in the Zr cut.

[12] After Ti elution, the column is equilibrated with ~1.5 v of H<sub>2</sub>O<sub>2</sub>-free 9 M HAc to prevent elution of the remaining HFSE in H<sub>2</sub>O<sub>2</sub>-HCl-HNO<sub>3</sub> mixtures. To minimize the isobaric interference of <sup>92</sup>Mo on <sup>92</sup>Zr, Zr-Mo separation is achieved in 6 M HCl-0.06 M HF [Sahoo and



**Figure 2.** Elution schemes for Zr separation from a synthetic solution and a basaltic matrix using our anion exchange chemistry. For high-Ti samples, the use of H<sub>2</sub>O<sub>2</sub> together with acetic acid (HAc) - nitric acid is required to remove the Ti efficiently.



Masuda, 1997; Wish, 1959], where a Mo-free Zr-Hf (+some Nb) fraction is eluted in 2.5 v. The Ti/Zr of the Zr-Hf fraction is typically  $\sim 1$  (Ti minerals, basalts) or lower (Ti-poor samples), allowing sufficiently accurate Zr isotope measurements (Figure 1). The Mo/Zr of the Zr cuts were always  $< 0.001$ . If needed, Mo and some of the Nb can be eluted after Zr with 6 M HNO<sub>3</sub>-0.2 M HF [Huff, 1964]. Cleaning the column with a sequence of 6 M HNO<sub>3</sub>-0.2 M HF-1% H<sub>2</sub>O<sub>2</sub>, 1 mM DTPA-1 M HCl, and 3 M HNO<sub>3</sub> (4 v each) removes all remaining HFSE, allowing multiple use of the resin. Complexes of HFSE with F<sup>-</sup> or DTPA (Diethylene-triamine-pentaacetic acid) are efficiently eluted from anion resin at low pH [Faris, 1960, and this study].

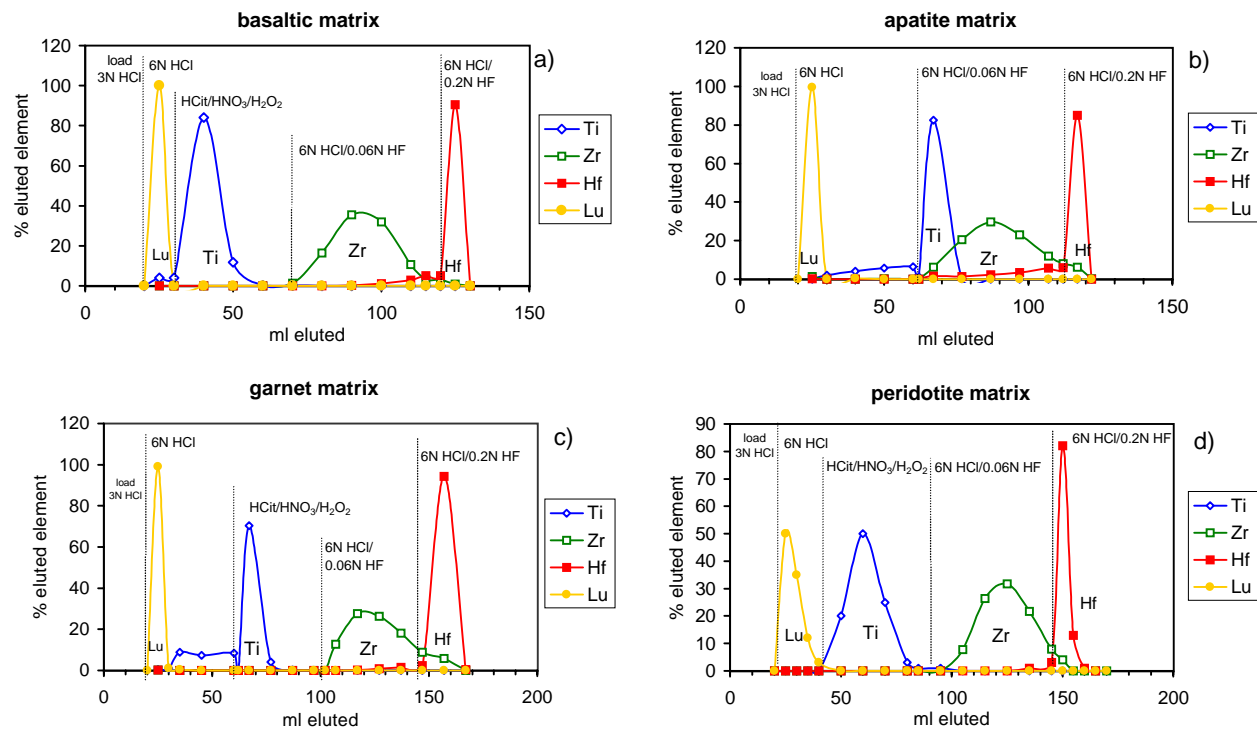
### 3.3. One-Column Lu-Hf Separation Using EICHRM<sup>®</sup> Ln-Spec

[13] Most previous methods of Hf separation involve several column steps and are sensitive to the amount of sample loaded, the sample's bulk composition, and the anionic speciation of the solute [see Patchett and Tatsumoto, 1980; Blichert-Toft, 2001]. Our new, matrix-independent, one-column separation procedure for Lu and Hf (Figure 3, Table 1) is based on reversed phase cation-exchange chromatography using EICHRM Ln-Spec resin (100–150 μm, H<sup>+</sup> form). EICHRM Ln-Spec resin consists of an HDEHP (di (2-ethylhexyl) phosphoric acid) coating on an inert polymeric carrier (Amberchrom CG71). HDEHP has long been used in solvent/solvent extraction procedures between aqueous and organic phases, where HDEHP is dissolved in the organic phase (see Braun and Gheradini [1975] for a review). In contrast to HDEHP-coated Teflon (widely used for Sm-Nd separations [e.g., Richard et al., 1976]), the separation efficiency of Ln-Spec resin is relatively insensitive to different sample matrices, allowing direct loading of bulk digested samples in HCl. On Ln-Spec resin, HFSE have high distribution coefficients in strong ( $> 1$  M) HCl,

in marked contrast to most other major and trace elements [Braun and Gheradini, 1975; Vin and Khopkar, 1991; M. Langer, personal communication, 2000, and this study]. At HCl molarities  $< 4$ , Lu and Fe<sup>3+</sup> are co-adsorbed with the HFSE. However, Fe<sup>3+</sup> shows minimum adsorption at 3 M HCl [Braun and Gheradini, 1975], making this the ideal molarity for loading bulk rock samples without overloading the column with Fe.

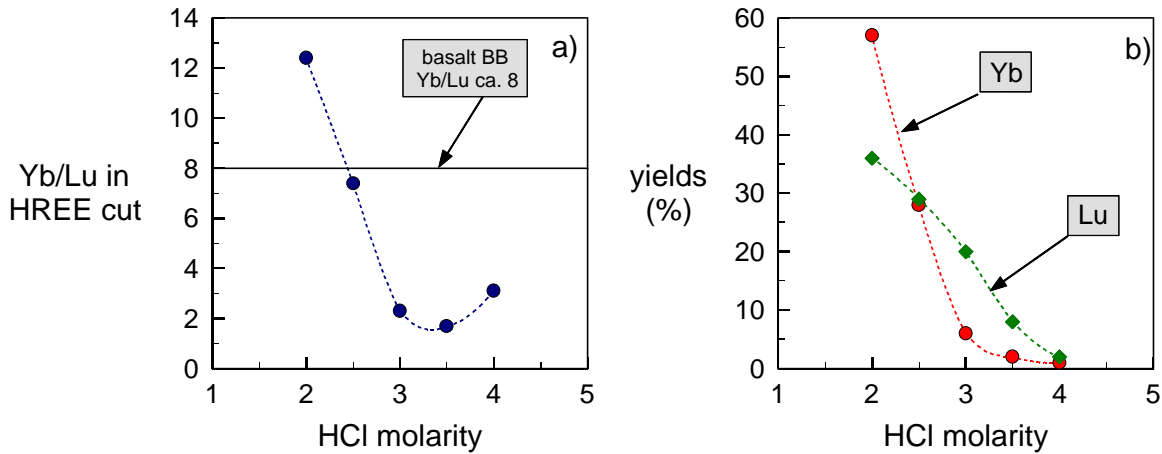
[14] For accurate Lu ID measurements, the large isobaric interference of <sup>176</sup>Yb on <sup>176</sup>Lu necessitates at least partial separation of Yb from Lu. This separation has been achieved using HDEHP [e.g., Braun and Gheradini, 1975; Lahiri et al., 1998] and can also be accomplished on Ln-Spec resin in 2–4 M HCl (Figure 4). With increasing HCl molarity, Lu yield decreases, but Yb-Lu separation increases. A good compromise between Lu recovery (20–30%) and Lu-Yb separation (i.e., a decrease of Yb/Lu by a factor of  $\sim 5$ ) occurs with 3 M HCl.

[15] High field strength elements have low distribution coefficients with Ln-Spec in 2 M HF [Vin and Khopkar, 1991; M. Langer, personal communication, 2000; and this study]. HF is therefore a suitable elution media for HFSE. HF also prevents the hydrolysis of HFSE on the column. In HCl-HF mixtures, adsorption behaviors differ among the HFSE. Salters [1994] separated Zr from Hf on HDEHP-coated Teflon with 6 M HCl-0.15 M HF. Our experiments with Ln-Spec showed that the separation factor is extremely sensitive to HF molarity but relatively insensitive to HCl molarity. Optimum Zr-Hf separation is achieved in 6 M HCl-0.06 M HF. No Zr or Hf is eluted at HF molarities below 0.03, thereby defining the maximum HF-tolerance level in sample loads. In 6 M HCl-0.2 M HF, Zr and Hf are completely eluted, while  $\sim 60$ –80% of the Ta is retained on the column.



**Figure 3.** One-column separation of Lu and Hf. Eichrom Ln-Spec elution profiles are shown for (a) a basalt sample, (b) a peridotite sample, (c) apatite, and (d) garnet. For apatite, the Ti elution step is unnecessary. Column yields and separation efficiencies are not dependent on the rock matrix.





**Figure 4.** Dependence of the Ln-Spec Yb-Lu separation on the HCl molarity that is used for loading of the sample. (a) Optimum separation is achieved at HCl molarities between 3 and 3.5. (b) Both Yb and Lu yields decrease with increasing HCl molarity. At 3 N HCl, the Lu yield is  $\sim 20\%$ , which, in most cases, is still sufficiently high for isotope dilution measurements.

[16] On the basis of *Patchett and Tatsumoto* [1980], we explored the partitioning behavior of Ti, Zr, and Hf on Ln-Spec resin in mixtures of  $\text{HNO}_3$ , citric acid (HCit), and  $\text{H}_2\text{O}_2$ . In contrast to their behavior on AG50W-X8 cation resin, all HFSE stick as citrate complexes to Ln-Spec resin in 0.09 M HCit and 0.45 M  $\text{HNO}_3$ . By adding  $\text{H}_2\text{O}_2$  to this mixture, Ti is selectively eluted as an orange peroxide complex, while Zr and Hf remain on the column. The amount of HCit- $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  that is needed (typically  $\sim 30$  v per mg Ti) increases with the amount of Ti present and decreases with  $\text{HNO}_3$  molarity (minimum at  $\sim 0.1$  M). With increasing  $\text{HNO}_3$  molarity, more Nb and Ta are co-eluted with Ti.

[17] For the single-column Lu-Hf chemistry (Figure 3 and Table 1), a typical 100 mg sample is loaded in  $\sim 5$  mL of 3 M HCl. The sample must be essentially HF-free (i.e., HF molarity of  $< 0.03$ ). Fe-rich samples are loaded in  $\sim 3$  M HCl-0.1 M ascorbic acid, in which Fe is reduced to  $\text{Fe}^{2+}$  and passes through the column. Peridotite samples are typically loaded in 10–20 mL 2 M HCl-0.05 M ascorbic acid, where, in contrast to 3 M HCl, sufficient Lu is retained

on the column. Rinsing with  $\sim 10$  v of 3 M HCl removes most matrix elements while leaving behind a HREE fraction (Lu + Yb  $\pm$  Tm). This fraction is eluted in 6 M HCl. Titanium is then eluted with 10–50 v of 0.09 M HCit-0.45 M  $\text{HNO}_3$ -1 wt.%  $\text{H}_2\text{O}_2$ . To avoid partial loss of the HFSE in HCl- $\text{H}_2\text{O}_2$  mixtures, the column is rinsed with  $\text{H}_2\text{O}$  before the Ti elution and with  $\text{H}_2\text{O}_2$ -free 0.09 M HCit-0.45 M  $\text{HNO}_3$  after the Ti elution. Next, Nb and most of the Zr are eluted in  $\sim 50$  v of 6 M HCl-0.06 M HF and Hf is subsequently eluted in 6 M HCl-0.2 M HF. The Zr/Hf in the Hf cut is decreased from  $\sim 35$  to  $\sim 1$ . Hafnium yields are typically  $> 95\%$  and are largely independent of the bulk matrix composition (Figure 3). Individual elution schemes for phosphates, garnets, and peridotites are shown in Figure 3.

### 3.4. Combined Separation of Lu, Zr-Nb, Hf, and Ta

[18] The Lu, Zr-Nb, Hf and Ta separation scheme (Table 2) combines our procedures for the Zr and Hf separations. Because no isotopic tracer for Nb exists, Nb and Zr (+Ti) are quantitatively recovered from the sample.

**Table 2.** Three-Column Separation Procedure for Combined Separation of Lu, Hf, Ta, and a Quantitatively Recovered Zr-Nb Fraction<sup>a</sup>

Three column Lu-HFSE	Ln Spec (1mL, ca. 3.8×0.6 cm) AG-1-X8 (4 mL, ca. 8.7×0.8 cm)	
Step	Column Volumes	Acid
	<i>Column I (Ln Spec)</i>	
Load sample	5 v	3 M HCl
Rinse matrix	10 v	3 M HCl
HREE (Lu-Yb) <sup>b</sup>	10 v	6 M HCl
Ti-Zr-Hf-Nb-Ta <sup>b, c</sup>	12 v	2 M HF
	<i>Column II (AG-1-× 8)</i>	
Load Ti-Zr-Hf-Nb-Ta cut	2.5 v	2 M HF
Rinse	2.5 v	2 M HF
Ti-Zr-Hf (Nb) <sup>b</sup>	1+1+1 v	6 M HNO <sub>3</sub> -0.2 M HF
Rinse remaining Hf	4 v	6 M HNO <sub>3</sub> -0.2 M HF
Ta <sup>b</sup>	1.5+1.5 v	6 M HNO <sub>3</sub> -0.2 M HF-1 wt % H <sub>2</sub> O <sub>2</sub>
	<i>Column III (Ln Spec = Column I)</i>	
Load Ti-Zr-Hf (Nb)	5 v	3 M HCl
Rinse	10 v	6 M HCl
Washout HCl	2+2 v	H <sub>2</sub> O
Ti	Variable	0.09 HCit-0.4N HNO <sub>3</sub> -1wt % H <sub>2</sub> O <sub>2</sub>
Rinse H <sub>2</sub> O <sub>2</sub>	5 v	0.09 HCit-0.4N HNO <sub>3</sub>
Zr	50 v	6 M HCl-0.06 M HF
Hf <sup>b</sup>	12 v	2 M HF

<sup>a</sup>Here v refers to resin volumes. Note that all solutions containing H<sub>2</sub>O<sub>2</sub> need to be freshly prepared.

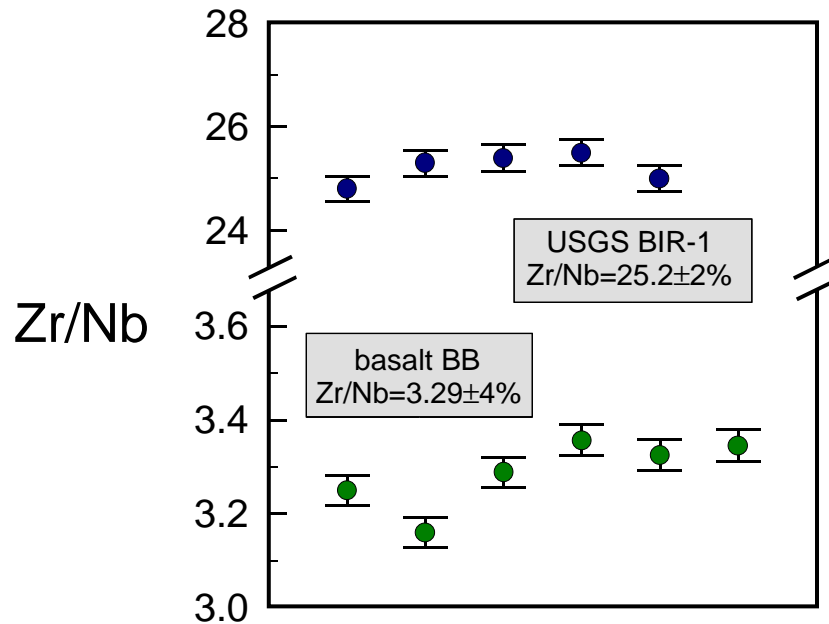
<sup>b</sup>These particular element-cuts are collected for further analysis (as discussed in text).

<sup>c</sup>2 mL Zr/Nb aliquot, 10 mL are directly loaded onto column II.

The absence of Cr in the Ti-Zr-Nb cuts rules out any systematic error caused by the possible <sup>53</sup>Cr/<sup>40</sup>Ar interference on <sup>93</sup>Nb; so Nb can be measured as Zr/Nb, using the Zr concentration obtained by isotope dilution. In contrast to earlier anion exchange methods, where some Zr is coprecipitated during the HF-based loading procedure, a fully quantitative Zr-Nb recovery is achieved using Ln-Spec. To correct for the <sup>180</sup>Hf interference on <sup>180</sup>Ta, which only has a natural abundance of 120 ppm relative to <sup>181</sup>Ta, a virtually complete separation of Hf from Ta is needed. This is particularly important if a combined <sup>180</sup>Ta-<sup>180</sup>Hf tracer is used.

[19] Three column steps are required for the combined separation procedure (Table 2). Column I and III are identical to the Ln-Spec Hf column and column II is an anion column.

After loading the sample and rinsing in 3 M HCl, Lu is eluted in 6N HCl. A complete HFSE fraction (Ti-Zr-Nb-Hf-Ta) is then eluted with 12 v of 2 M HF. This cut contains virtually all of the Zr and Nb in the sample, thus permitting direct measurements of Zr/Nb. After the optional removal of a 10–20% aliquot from the HFSE fraction for Zr/Nb measurements, the remaining solution is loaded directly onto column II (BIORAD AG-1-X8). In 2 M HF, all HFSE are retained on the column [Faris, 1960]. A fraction containing Ti-Zr-Nb-Hf is subsequently eluted with 12 v 6 M HNO<sub>3</sub>-0.2 M HF while Ta remains on the column [Huff, 1964]. Complete Hf-Ta separation is accomplished by repeated rinsing with 6 M HNO<sub>3</sub>-0.2 M HF (Table 2). The Ta fraction is best eluted with 12 mL of 6 M HNO<sub>3</sub>-0.2 M HF-1 wt.% H<sub>2</sub>O<sub>2</sub>. After the Ti-Zr-Nb-Hf cut from column



**Figure 5.** Zr/Nb obtained for different digestions of the rock standards USGS BIR-1 (14 ppm Zr, 0.55 ppm Nb) and BB (in-house standard; 192 ppm Zr, 58 ppm Nb) after separation of a Ti-Zr-Nb cut using Ln-Spec resin. Zr/Nb can be measured at an external precision of better than  $\pm 5\%$  ( $2\sigma$ ) against a Zr/Nb standard that was prepared from 99.9% pure AMES metals.

II is evaporated down, it is dissolved in 3 M HCl and loaded onto column III (identical to Ln-Spec column I). Titanium is again eluted as an orange peroxide complex in 0.09 M HCl-0.45 M HNO<sub>3</sub>-1 wt.% H<sub>2</sub>O<sub>2</sub>. Following Zr-Nb elution in 50 v of 6 M HCl-0.06 M HF, a clean Hf fraction is recovered in 2M HF.

[20] Accuracy and precision of the Zr/Nb ratios were tested by replicate digestions and Zr/Nb analyses of reference materials (Figure 5). Zr/Nb was measured at a typical internal precision of  $\pm 0.1\%$  ( $2\sigma$ ) by MC-ICPMS against a standard prepared from 99.9% pure AMES Zr and Nb metals. Better than  $\pm 5\%$  ( $2\sigma$ ) external precision was obtained for multiple digestions of peridotite and basalt samples. To measure HFSE yields, low-HFSE samples (e.g., peridotites) were doped with our mixed AMES HFSE standard (Zr-Nb-Hf-Ta) so that their HFSE

concentrations were known to better than  $\pm 1\%$ . The Ti-Zr-Nb cuts from these samples were spiked with the mixed HFSE tracer, and Zr-Nb concentrations were measured as described. Zirconium and Nb yields were  $>98\%$  for basalts (100 mg samples) and  $>90\%$  for peridotites (1 g samples) (Table 3), demonstrating nearly quantitative recovery for Zr and Nb.

#### 4. Zr and Hf Isotope Measurements by MC-ICPMS

[21] The Micromass Isoprobe at Münster is a new, second generation ICP-source magnetic sector mass spectrometer with a multiple collector configuration (nine Faraday collectors, four channeltron ion counters, and a Daly ion counter, Table 4). Elements having high first

**Table 3.** Recovery of HFSE for a Doped Basalt, a Doped Peridotite Matrix, and Pure AMES Metal Standard Using Eichrom Ln-Spec<sup>a</sup>

	Basalt BIR-1 (100 mg, Doped)	Peridotite BP7-Pe (1 g, Doped)	Mixed Shelf
Yields in percent			
Zr	98	93	-
Hf	91	80	-
Nb	101	89	-
Ta	91	84	-
Deviation in percent			
Zr/Nb	-3	+4	+1

<sup>a</sup>Concentrations of HFSE in the doped samples were known to better than  $\pm 1\%$ .

ionization potentials, such as Zr and Hf, are ionized at much higher efficiencies than with thermal ionization mass spectrometers (TIMS). In contrast to all other MC-ICPMS instruments, which require an electrostatic analyzer before the magnetic sector, the Isoprobe is a single-focusing mass spectrometer, wherein a hexapole collision cell reduces the energy spread of the extracted ions from  $\sim 20\text{--}30$  V to  $\sim 1$  V. Argon ( $\sim 1.2$  mL/min) is typically used as the collision gas for masses  $>40$ . A Cetac MCN-6000 desolvating nebulizer yields higher sensitivities than those achieved with conventional glassware systems. Isotope composition measurements can be routinely performed on as little as 5 ng (200 amu mass range) to 10 ng (100 amu mass range) of the element with typical external precisions of better than 50 ppm.

[22] During the measurement period (late 1999–2001), the Isoprobe has operated at an abundance sensitivity of 10–15 ppm (U), corresponding to an analyzer vacuum of  $\sim 2 \times 10^{-8}$  mbar. Peak tails on  $^{181}\text{Ta}$  were  $\sim 50\text{--}70$  ppm at mass 180.5 and  $16 \pm 2$  ppm for 181.5. For Hf measurements, this abundance sensitivity level precludes baseline measurements at half masses between peaks, which would result in  $\sim 100\text{--}200$  ppm shifts for measured Hf isotope ratios (Table 5). Hence baselines were measured at half masses below the Hf isotope array (i.e., at masses 168.5–172.5 for masses 176–180). Baseline tests at other half mass arrays located both below and above the Hf array gave Hf isotope compositions that are indistinguishable from the “off-array” values (Table 5). Owing to the wider distance between the Zr peaks (masses 90–96), Zr baselines at

**Table 4.** Cup Configurations for Zr and Hf Isotope Measurements Using the Micromass Isoprobe in Münster

Configuration	L3	L2	(L1)Ax	H1	H2	H3	H4	H5	H6
Zr-1	87 Sr (Rb)	88 Sr	90 Zr	91 Zr	92 Zr (Mo)	93 Nb	94 Zr (Mo)	95 Mo	96 Zr (Mo, Ru)
Zr-2	90 Zr	91 Zr	92 Zr (Mo)	93 Nb	94 Zr (Mo)	95 Mo	96 Zr (Mo, Ru)	97 Mo	99 Ru
Hf	173 Yb	175 Lu	176 Hf (Yb, Lu)	177 Hf	178 Hf	179 Hf	180 Hf (Ta, W)	181 Ta	182 W



**Table 5.** Isotopic Compositions Obtained for Zr (AMES Metal) and Hf (AMES Metal, Isotopically Indistinguishable From JMC-475) Compared to Literature Values<sup>a</sup>

Method	Author(s)	<sup>91</sup> Zr/ <sup>90</sup> Zr	<sup>92</sup> Zr/ <sup>90</sup> Zr	<sup>96</sup> Zr/ <sup>90</sup> Zr
TIMS	<i>Minster and Allègre</i> [1982]	0.21799	0.33338	0.054390
	<i>Nomura et al.</i> [1983]	0.21819	0.33339	0.054474
	<i>Harper</i> [1996]	0.21797	0.33337	0.054381
	<i>Sahoo and Masuda</i> [1997]	0.21798	0.33336	0.054386
MC-ICPMS	<i>Hirata</i> [2001]	0.21797	0.33341	0.054373
	<i>Sanloup et al.</i> [2000]	0.21798	0.33341	0.054333
	<i>Yin et al.</i> [2000]	0.21800	0.33338	0.054376
	<i>Rehkämper et al.</i> [2001] this study	- 0.21795	0.33338 0.33339	- 0.054347

Method	Author(s)	<sup>176</sup> Hf/ <sup>177</sup> Hf	<sup>178</sup> Hf/ <sup>177</sup> Hf	<sup>180</sup> Hf/ <sup>177</sup> Hf
TIMS	<i>Patchett and Tatsumoto</i> [1980]	0.282195	-	1.88651
	<i>Patchett</i> [1983a, 1983b]	0.282142	1.46710	1.88651
	<i>Nowell et al.</i> [1998]	0.282155	-	-
	<i>Scherer et al.</i> [2000]	0.282165	1.46717	1.88679
Hot-SIMS	<i>Salter</i> [1994]	0.282207-37	1.46714	-
MC-ICPMS	<i>Blichert-Toft et al.</i> [1997]	0.282160	1.46717	1.88667
	<i>Halliday et al.</i> [2000]	0.282161	-	-
	this study (half mass baseline) this study (off array baseline)	0.282126 0.282151	1.46743 1.46718	1.88699 1.88652

<sup>a</sup>Hf isotope values obtained using the Isoprobe (cup efficiencies set to unity) agree well with literature values if baselines are measured outside the Hf array. All Zr isotope ratios (including values from other laboratories) are normalized to <sup>94</sup>Zr/<sup>90</sup>Zr = 0.3381 [*Minster and Allègre*, 1982], Hf isotope values are normalized to <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325. Note that *Blichert-Toft et al.* [1997] and *Sanloup et al.* [2000] report TIMS averages reproduced within error by MC-ICPMS. Zr isotope ratios obtained in Münster relative to <sup>90</sup>Zr/<sup>91</sup>Zr of 4.584 [*Nomura et al.*, 1983] are <sup>90</sup>Zr/<sup>91</sup>Zr = 1.53110, <sup>94</sup>Zr/<sup>91</sup>Zr = 1.55528, and <sup>96</sup>Zr/<sup>91</sup>Zr = 0.25047.

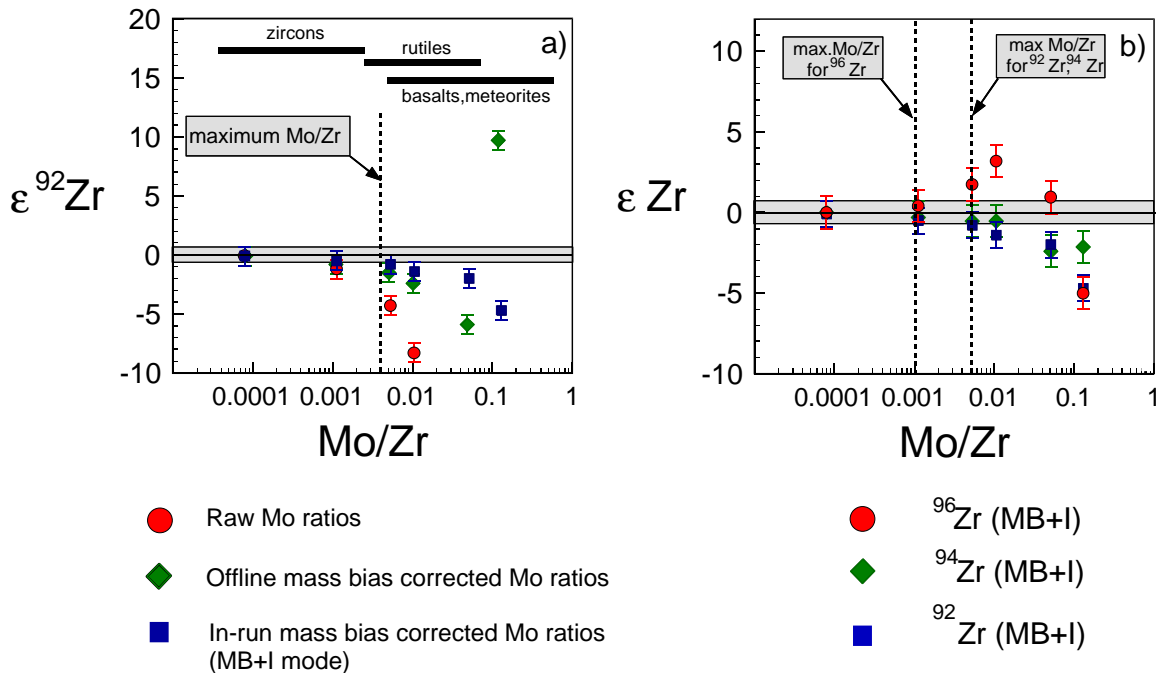
half masses are not significantly affected by tails. The most critical interferences for Zr and Hf isotope measurements are listed in Table 6. Because the mass bias of the Isoprobe MC-ICPMS (~0.5% at >200 amu and ~2.5% at 100 amu) is typically 10 times higher than that of

TIMS (~0.1%), we apply a mass bias correction to the interference correction ratios (see Figure 6, Zr). In contrast to instruments equipped with an electrostatic analyzer, mass bias in the Isoprobe not only depends on the cone interface but also varies with hexapole parameters and

**Table 6.** Important Interferences on Zr and Hf Isotope Measurements<sup>a</sup>

Zr-Isotope Measurements		Hf-Isotope Measurements	
Isotope	Interference	Isotope	Interference
<sup>90</sup> Zr	<sup>50</sup> Ti <sup>40</sup> Ar, <sup>180</sup> Hf <sup>++</sup> , <sup>56</sup> Fe <sup>35</sup> Cl, <sup>40</sup> Ar <sup>35</sup> Cl <sup>16</sup> O,	<sup>173</sup> Yb	<sup>157</sup> Gd <sup>16</sup> O
<sup>91</sup> Zr	<sup>182</sup> W <sup>++</sup>	<sup>175</sup> Lu	<sup>159</sup> Tb <sup>16</sup> O <sup>176</sup> Yb, <sup>176</sup> Lu, <sup>144</sup> Nd <sup>16</sup> O <sub>2</sub> ,
<sup>92</sup> Zr	<sup>92</sup> Mo, <sup>52</sup> Cr <sup>40</sup> Ar, <sup>184</sup> W <sup>++</sup>	<sup>176</sup> Hf	<sup>160</sup> Gd <sup>16</sup> O
<sup>93</sup> Nb	<sup>53</sup> Cr <sup>40</sup> Ar, <sup>186</sup> W <sup>++</sup>	<sup>177</sup> Hf	<sup>161</sup> Dy <sup>16</sup> O
<sup>94</sup> Zr	<sup>94</sup> Mo, <sup>40</sup> Ar <sub>2</sub> <sup>14</sup> N	<sup>178</sup> Hf	<sup>162</sup> Dy <sup>16</sup> O
<sup>95</sup> Mo	<sup>79</sup> Br <sup>16</sup> O	<sup>179</sup> Hf	<sup>163</sup> Dy <sup>16</sup> O
<sup>96</sup> Zr	<sup>96</sup> Mo, <sup>96</sup> Ru, <sup>40</sup> Ar <sub>2</sub> <sup>16</sup> O	<sup>180</sup> Hf	<sup>180</sup> W, <sup>180</sup> Ta
<sup>97</sup> Mo	<sup>81</sup> Br <sup>16</sup> O		

<sup>a</sup>Using the separation procedures as described and clean acids, these interferences are absent or typically less than 0.1% of the interfered isotope (Mo on Zr, Figure 6).



**Figure 6.** Zr isotope compositions obtained for AMES metal Zr solutions that were doped with variable amounts of Mo. Results are reported in  $\epsilon$ -units relative to a Mo-free AMES Zr solution. (a) The most accurate  $^{92}\text{Mo}$  interference correction is achieved by in-run correction of each measured ratio, where a mass bias correction is also applied to the interference correction itself (see text). (b) An accurate Mo correction for  $^{92}\text{Zr}$  and  $^{94}\text{Zr}$  is possible up to Mo/Zr of  $\sim 1 \times 10^{-2}$ , whereas for  $^{96}\text{Zr}$  an accurate correction is only possible up to Mo/Zr of  $\sim 1 \times 10^{-3}$ . These Mo/Zr ratios are far below typical values in basalts, meteorites, and Ti minerals (0.01–1), thus requiring the separation of Mo from Zr by ion exchange chromatography as described in the text.

the collision cell gas flow rate. From 1999 to 2001, uncorrected  $^{90}\text{Zr}/^{91}\text{Zr}$  and  $^{179}\text{Hf}/^{177}\text{Hf}$  ranged from 4.452 to 4.481 (2.3–2.9% mass bias per amu) and from 0.7344 to 0.7475 (0.15–1% mass bias per amu), respectively. Typical drifts in mass bias were  $\sim 500$  ppm over one measurement session. No dependence of exponential law-normalized isotope ratios on changing mass bias was observed.

#### 4.1. Zirconium Isotope Measurements

[23] Zirconium isotope ratios were normalized to both  $^{90}\text{Zr}/^{91}\text{Zr} = 4.584$  and  $^{94}\text{Zr}/^{90}\text{Zr} = 0.3378$  [Nomura et al., 1983] using the exponential law. The  $^{90}\text{Zr}/^{91}\text{Zr}$  value was confirmed

by our measurements of  $^{90}\text{Zr}/^{91}\text{Zr}$  normalized to the  $^{87}\text{Sr}/^{88}\text{Sr}$  of NBS 987 ( $4.584 \pm 4$  ( $2\sigma$ ), 15 measurement sessions, Zr cup configuration 1, Table 4). Normalizing Zr isotope ratios to both  $^{90}\text{Zr}/^{91}\text{Zr}$  and  $^{94}\text{Zr}/^{90}\text{Zr}$  ensures identification of interferences on  $^{94}\text{Zr}$  and  $^{91}\text{Zr}$ . A normalization solely to  $^{94}\text{Zr}/^{90}\text{Zr}$ , as previously used by TIMS workers [Harper, 1996; Minster and Allègre, 1982; Sahoo and Masuda, 1997], might be severely affected by (1) an inaccurate  $^{94}\text{Mo}$  interference correction and (2)  $^{40}\text{Ar}_2^{14}\text{N}^+$  interferences generated in the plasma (Table 6). Important potential interferences on  $^{91}\text{Zr}$  include  $^{56}\text{Fe}^{35}\text{Cl}^+$  and  $^{40}\text{Ar}^{35}\text{Cl}^{16}\text{O}^+$ . Iron is usually removed during our separation procedure described above, and ArOCl interferences



were negligible in most cases (ArCl levels at mass 75 were monitored).

[24] Long-term values of  $^{92}\text{Zr}/^{91}\text{Zr} = 1.53110 \pm 15$  and  $^{92}\text{Zr}/^{90}\text{Zr} = 0.33324 \pm 3$  ( $2\sigma$ ,  $n = 20$  averages of measurement sessions) were obtained for AMES Zr. Typical external precisions for  $n > 10$  measurements during one measurement session were  $\pm 0.6\epsilon$  ( $2\sigma$ ) for  $^{92}\text{Zr}/^{91}\text{Zr}$  and  $\pm 0.4\epsilon$  ( $2\sigma$ ) for  $^{94}\text{Zr}/^{90}\text{Zr}$ . The external reproducibility for samples was determined with 20 measurements of the zircon NZ-159, which was processed through chemistry. These measurements gave values of  $-0.1 \pm 0.7\epsilon$  ( $2\sigma$ ) for  $^{92}\text{Zr}/^{91}\text{Zr}$  and  $0.0 \pm 0.5\epsilon$  ( $2\sigma$ ) for  $^{94}\text{Zr}/^{90}\text{Zr}$  relative to AMES Zr, reflecting the true external reproducibility rather than just the daily within-run reproducibility of the AMES solution.

[25] Molybdenum interferences on  $^{92}\text{Zr}$  and  $^{96}\text{Zr}$  were corrected using  $^{95}\text{Mo}$  as an interference monitor (Table 6) and the Mo abundances of *Lee and Halliday* [1995]. Since  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$  are both free of monatomic isobaric interferences, it is possible to check for polyatomic peaks at mass 95 by monitoring  $^{95}\text{Mo}/^{97}\text{Mo}$  ( $\sim 1.66$ ). The  $^{79}\text{Br}^{16}\text{O}$  and  $^{81}\text{Br}^{16}\text{O}$  interferences may occur on masses 95 and 97 (Table 6) but in a ratio of  $\sim 1$ . Oxide rates and bromine levels (masses 79 and 81) were therefore checked before each measurement. The  $^{96}\text{Ru}$  interferences on  $^{96}\text{Zr}$  were corrected using  $^{99}\text{Ru}$  as an interference monitor and the Ru abundances of *de Bièvre and Taylor* [1993]. As determined by measurements of Mo-doped Zr standards (Figure 6), accurate  $^{92}\text{Zr}$  measurements are possible at Mo/Zr below  $10^{-2}$ . Likewise, Mo/Zr below  $1 \times 10^{-3}$  and Ru/Zr below  $1 \times 10^{-2}$  are required for accurate  $^{96}\text{Zr}$  measurements.

#### 4.2. Hf and Lu Measurements

[26] Measured Hf isotope values were corrected for mass bias relative to  $^{179}\text{Hf}/^{177}\text{Hf} =$

$0.7325$  [*Patchett and Tatsumoto*, 1980] using the exponential law. A long-term  $^{176}\text{Hf}/^{177}\text{Hf}$  value of  $0.282151 \pm 13$  ( $2\sigma$ , off-array baseline, Table 5) was obtained for our AMES Hf, which is isotopically indistinguishable from the JMC-475 standard. The  $^{176}\text{Yb}$  and  $^{176}\text{Lu}$  interferences on  $^{176}\text{Hf}$  were corrected using  $^{173}\text{Yb}$  and  $^{175}\text{Lu}$  as interference monitors (Table 4) and the isotope compositions of *Blichert-Toft et al.* [1997] (Lu) and of *Scherer et al.* [1999; unpublished data, 2001] ( $^{176}\text{Yb}/^{173}\text{Yb} = 0.7939$ ). Typically, no detectable amounts of sample rare earth elements (REE) were observed in the Hf cuts. Isobaric  $^{180}\text{Ta}$  and  $^{180}\text{W}$  interferences on  $^{180}\text{Hf}$  were corrected using  $^{181}\text{Ta}$  and  $^{182}\text{W}$  as interference monitors (Table 4) and the isotope compositions of *Lee and Halliday* [1995] (W) and *Weyer et al.* [2001] ( $^{180}\text{Ta}/^{181}\text{Ta}$ ,  $0.0001198 \pm 6$ ). The  $^{176}\text{Hf}/^{177}\text{Hf}$  and Lu/Hf for international reference materials (Table 7) show good agreement with literature data. Lu/Hf ratios obtained for JB-1 and the Allende meteorite agree with those reported by *Patchett and Tatsumoto* [1980] and *Blichert-Toft et al.* [1997] within  $\pm 1\%$  (present  $2\sigma$  error), demonstrating interlaboratory consistency of spike calibrations. Lu-Hf concentrations were determined using a mixed  $^{176}\text{Lu}$ - $^{180}\text{Hf}$  tracer that has been calibrated against pure (99.9%) AMES metal standards.

[27] Although previous MC-ICPMS procedures for Lu measurement by isotope dilution require a large correction for the isobaric interference of  $^{176}\text{Yb}$  on  $^{176}\text{Lu}$ , a precision of  $\pm 1\%$  has been achieved by normalization to naturally occurring Yb in the Lu cut [*Blichert-Toft et al.*, 1997]. This precision is sufficient for most applications, including calculation of initial  $^{176}\text{Hf}/^{177}\text{Hf}$  for low-Lu/Hf samples. In Münster, Lu ID measurements are made using the method of *Scherer et al.* [1999], where  $^{176}\text{Lu}/^{175}\text{Lu}$  is normalized to the  $^{187}\text{Re}/^{185}\text{Re}$  [*de Bièvre and Taylor*, 1993] of



**Table 7.** The  $^{176}\text{Hf}/^{177}\text{Hf}$  and Lu/Hf Obtained for International Rock Reference Samples<sup>a</sup>

Sample	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon\text{Hf}$	ppm Hf	ppm Lu	$^{176}\text{Lu}/^{177}\text{Hf}$	Reference
JB-1	0.282946 ± 10	6.2	3.536	0.308	0.0124	this study
	0.282966 ± 7	6.9	-	-	-	this study
	0.282941 ± 7	6.0	-	-	-	this study
	0.282904 ± 75	4.7	3.612	0.313	0.0123	<i>Patchett and Tatsumoto</i> [1980] average
BCR-1	0.282933 ± 44	5.7	3.559	0.303	0.0121	<i>Patchett</i> [1983b]
	0.282892 ± 6	4.2	4.993	-	-	this study
BIR-1	0.282879 ± 8	3.8	-	-	-	<i>Blichert-Toft</i> [2001]
	0.283255 ± 9	17.1	0.572	0.244	0.0604	this study
BE-N	0.283248 ± 8	16.8	-	-	-	this study
	0.283266	17.5	-	-	-	<i>Blichert-Toft</i> [2001] average
	0.282939 ± 4	5.9	5.812	-	-	this study
	0.282923 ± 9	5.3	5.808	0.246	0.00600	this study
AUG-7	0.282921 ± 6	5.3	-	-	-	this study
	0.282921 ± 5	5.3	-	-	-	<i>Blichert-Toft</i> [2001]
	0.283223 ± 11	15.9	2.511	0.340	0.0192	this study
	0.283227 ± 6	16.1	-	-	-	this study
KIL-19	0.283219 ± 12	15.8	-	-	-	this study
	0.283219	15.8	-	-	-	<i>Salters</i> [1994] average
	0.283200	15.1	-	-	-	<i>Blichert-Toft et al.</i> [1997] average
DR-N	0.283096 ± 7	11.5	4.514	0.279	0.00875	this study
	0.283116 ± 4	12.2	-	-	-	<i>Blichert-Toft et al.</i> [1999]
Allende-MS	0.282752 ± 7	-0.7	3.203	0.379	0.0168	this study
	0.282761 ± 6	-0.4	-	-	-	this study
	0.282860 ± 6	3.1	-	-	-	<i>Blichert-Toft</i> [2001]
Allende (Cph)	0.282855 ± 14	2.9	0.1970	0.0468	0.0337	this study
Allende (SI)	0.282776 ± 15	0.1	0.2109	0.0498	0.0335	<i>Blichert-Toft and Albarède</i> [1997]
	0.282825 ± 11	1.9	0.1920	0.0461	0.0341	<i>Blichert-Toft and Albarède</i> [1997]

<sup>a</sup>All  $^{176}\text{Hf}/^{177}\text{Hf}$  data are reported relative to 0.282160 for JMC-475. Note that DR-N (zircon-rich) was digested by flux fusion (see text), possibly explaining the deviation from the data of *Blichert-Toft* [2001] (acid digestion).

admixed Re. For applications that require Lu/Hf precisions better than 1%, the large Yb interference correction is eliminated by processing the sample through alpha-hydroxyisobutyric acid ( $\alpha\text{HIBA}$ ) chemistry [*Gruau et al.*, 1988] to remove Yb. This additional step lowers the Lu/Hf uncertainties to  $\pm 0.2\%$  ( $2\sigma$  external reproducibility [*Scherer et al.*, 2001]). The isotope compositions used for the interference corrections of  $^{176}\text{Hf}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Lu}$  are  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28216$  [*Blichert-Toft et al.*, 1997] and  $^{176}\text{Yb}/^{173}\text{Yb} = 0.7939$  [*Scherer et al.*, 1999; unpublished data, 2001]. Like our  $^{176}\text{Lu}/^{175}\text{Lu}$  measurements, this Yb isotope composition was corrected for mass bias using admixed Re, thus

providing an internally consistent interference correction.

## 5. Conclusions

[28] Our new HFSE separation procedures enable precise measurements of Nb/Ta and Zr/Hf by isotope dilution, using a mixed  $^{94}\text{Zr}$ - $^{176}\text{Lu}$ - $^{180}\text{Hf}$ - $^{180}\text{Ta}$  tracer. Lu-Hf separations can be performed on a single column. This procedure facilitates separation of Hf from peridotites, garnets, and phosphates, opening fundamentally new perspectives in Lu-Hf geochronology. Using the Isoprobe MC-ICPMS, it is possible to perform Hf isotope measurements





on as little as 5 ng of Hf, thus permitting  $^{176}\text{Hf}/^{177}\text{Hf}$  measurements on small amounts of low-abundance samples. Using a combined anion resin and Ln-Spec procedure, it is possible to recover both a clean Zr cut and a quantitative Zr-Nb cut from a single sample. Even without a Nb tracer, a precision of  $\pm 5\%$  ( $2\sigma$ ) is achieved for Zr/Nb, thus enabling the routine application of  $^{92}\text{Nb}$ - $^{92}\text{Zr}$  chronometry to meteorite samples that contain as little as 10 ng Zr.

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