

Determination of high-precision Zr/Hf ratios in bulk meteorites using LA-ICP-MS. A. Patzer¹, A. Pack¹ and A. Gerdes², ¹Geowissenschaftliches Zentrum, Abteilung Isotopengeologie, Universität Göttingen, D-37077 Göttingen, Germany, apatzer@uni-goettingen.de, ²Institut für Geowissenschaften, Senckenberganlage 28, D-60054 Frankfurt am Main, Germany.

Introduction: Zirconium (Zr) and hafnium (Hf) are incompatible, lithophile, and refractory trace elements. In general, trace element distribution and relative abundances may provide very valuable information of geological processes. With respect to meteorites, Zr/Hf ratios may help decipher condensation conditions and sequences during the early stages of solar system formation.

With analytical technology being continuously improved, the relative chondritic abundance of Zr and Hf was recently corrected to $Zr/Hf = 34.2 \pm 0.3$ [1] and 34.3 ± 0.3 (2σ) [2]. The former accepted value was 36.3 with an uncertainty of approx. 10% (for the CI1 chondrite Orgueil, [3]).

As opposed to [1] and [2] who used an isotope dilution method coupled with a multiple collector ICP-MS, our first objective was to verify the accuracy and precision of a relatively fast and inexpensive sample preparation method combined with expeditious laser ablation ICP-MS techniques.

Secondly, we intend to identify possible systematic fine-scale Zr/Hf variations within bulk meteoritic matter of different classes.

Sample preparation: As a first step, we analyzed 8 different standard reference materials (SRMs) including 7 terrestrial rock samples and the synthetic soda-lime glass NIST614 (Tab. 1). The natural SRMs were processed as follows: Individual aliquots of approximately 10 mg powder were transferred into a graphite crucible and melted using a CO₂ laser. The resulting, approx. 1 mm-sized spherules were placed on top of the gas stream of an aerodynamic levitation device for complete homogenization. Subsequently, they were quenched and embedded in resin. Four aliquots were prepared of each SRM and fused between one and four times. For further details on sample preparation see [4].

Almost all samples exhibited a glassy to finely crystallized texture after quenching. Only RGM-1 aliquots that were fused multiple times displayed more progressive recrystallization.

Instrumentation: Zr-Hf analyses were carried out by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Frankfurt University using a Thermo-Finnigan Element II sector field ICP-MS system coupled to a New Wave Research UP213 (213 nm) ultraviolet laser system [5]. Each analysis consisted of 25 s background acquisition followed by

approx. 60 s data acquisition. The laser was set to a beam diameter of 120 μ m and fired in line-scan mode.

Isotopes measured include ⁹⁰Zr, ⁹¹Zr, ¹⁷⁸Hf, ¹⁸⁰Hf, and ⁴⁴Ca as internal standard.

Table 1. List of examined standard reference materials (SRM) with Zr/Hf count ratios (weighted means, 1σ) and relative sensitivity factors (RSF, 1σ).

SRM	⁹⁰ Zr/ ¹⁸⁰ Hf count ratios	⁹⁰ Zr/ ¹⁷⁸ Hf count ratios
AGV-2	37.20 ± 1.15	48.10 ± 1.25
BCR-2	31.49 ± 0.30	41.15 ± 0.33
BHVO-2	31.52 ± 0.48	40.91 ± 0.39
BIR-1	20.29 ± 0.45	26.16 ± 0.42
GSP-2	33.03 ± 0.29	43.03 ± 0.45
RGM-1	31.60 ± 0.55	41.20 ± 0.65
W-2a	31.10 ± 0.70	40.50 ± 1.10
NIST614	0.967 ± 0.006	1.270 ± 0.007
RSF	0.838 ± 0.011	1.088 ± 0.016

Results: Fig. 1 shows ⁹⁰Zr/¹⁸⁰Hf count ratios as a function of recommended Zr/Hf mass ratios from the literature [6]. Zr/Hf count ratios of each standard material are plotted as weighted mean of multiple analyses (minimum of 4). While analytical uncertainties (standard error of counting rates) are generally below 1%, the relative sensitivity factor obtained exhibits an uncertainty of 1.3% (1σ).

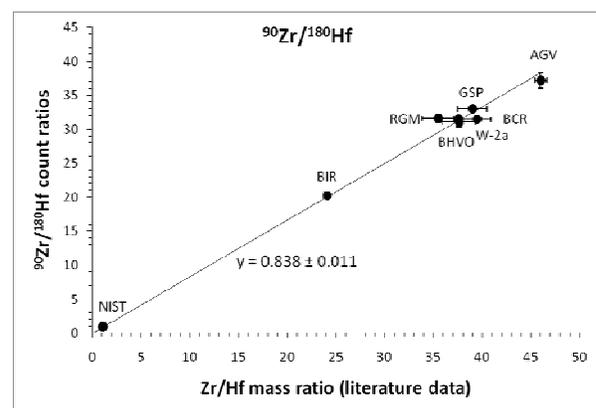


Figure 1. ⁹⁰Zr/¹⁸⁰Hf calibration curve obtained from 8 standard reference materials including 7 natural terrestrial rocks and the synthetic soda-lime glass NIST614.

Alternatively, the relative sensitivity factor can be calculated from $^{90}\text{Zr}/^{178}\text{Hf}$ ratios. The Hf isotope 178 is less abundant than 180 (27.28% vs. 35.08%). Counting statistics for ^{178}Hf are therefore somewhat less precise than those for ^{180}Hf . However, as opposed to ^{180}Hf , ^{178}Hf is free of isobaric interferences (see below). Our data on SRMs suggest that attainable 1σ -errors are equal (1.3% vs. 1.4%, Tab. 1, Fig. 2).

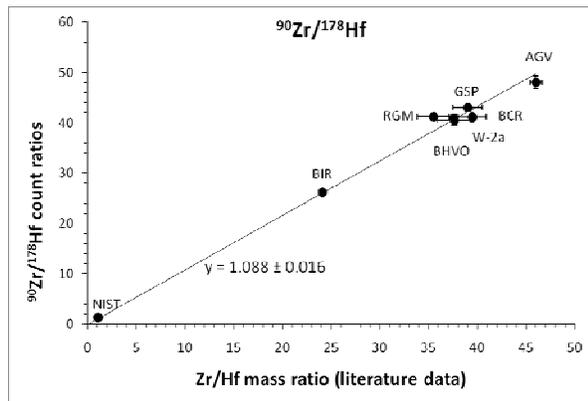


Figure 2. $^{90}\text{Zr}/^{178}\text{Hf}$ calibration curve obtained from 8 standard reference materials including 7 natural terrestrial rocks and the synthetic soda-lime glass NIST614.

Discussion: In comparison to isotope dilution techniques, the preparatory and analytical procedure applied here offers the following advantages: Sample preparation requires only small amounts of meteorite material (approx. 10 mg) and is relatively fast (approx. 5 min per sample fusion/homogenization). Laser ablation ICP-MS analyses, too, are significantly less time-consuming (approx. 90 s per analysis).

Zr/Hf ratios published in [2] yield an uncertainty of $\pm 0.4\%$ (1σ , weighted mean of 25 analyses). The final precision of our method is yet undetermined. However, the precision of count rates of individual isotopes as well as isotope ratios (better than 1% [1σ] standard error for single analyses) and the uncertainty of the relative sensitivity factor ($\pm 1.3\%$, 1σ , Fig. 1) have proven satisfactory.

Outlook: We will now examine the Zr-Hf inventory of 34 meteorites with an emphasis on chondritic rocks. Replicate analyses of Orgueil (CI1) and other carbonaceous chondrites will be compared to data of [1] and [2] and used as an internal reference point. This particular approach ensures minimization of matrix effects as Orgueil and our suite of chondritic and achondritic meteorites display similar matrices. Resulting relative Zr/Hf ratios are expected to yield a precision of $\pm 1 - 2\%$.

Regarding isobaric interferences, we will investigate the significance of a possible W interference on

^{180}Hf . Our data on SRMs show that ^{178}Hf offers to be a good alternative (Fig. 2). Its abundance is lower than that of ^{180}Hf but no isobaric interferences exist.

In their work, [1] indicate that Zr/Hf ratios of different chondrites and achondrites (eucrites) as well as of individual aliquots of the same sample fluctuate within 3%. They exclude any systematic deviations between chondritic groups based on the assumption that condensation temperatures of Zr and Hf are very similar. Consequently, they conclude that the average Zr/Hf ratio of many chondritic analyses yielded the most representative value for the solar system.

Recent condensation calculations [8], however, suggest that Zr and Hf exhibit significantly different 50%-condensation temperatures. Bulk chondrite Y/Ho [4] and REE (La-Lu) [7] data show considerable variation for different types of chondrites. The observed patterns were partly explained in terms of differences in volatility and demonstrate that fractional condensation operated on a large scale. Likewise, we believe that different groups of chondrites may yield distinctive Zr/Hf ratios. If this hypothesis proves true, our data may further contribute to understanding the extent of large-scale fractional condensation in the early solar nebula.

Our goal is not to determine absolute Zr/Hf values but rather resolve small but significant variations among different chondrite classes. Selected samples include 8 carbonaceous, 9 H-, 4 L-, 3 LL-, 4 EL6, and 1 EH3 chondrite, 3 eucrites, and 2 additional achondrites. In contrast, meteorite types investigated by [1] and [2] were mostly carbonaceous chondrites and eucrites. The better balanced diversity of meteorite classes in this study may be the key to seeing the expected heterogeneousness.

References:

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