EXPLORING THE LIMITS OF Hf ISOTOPIC ANALYSIS BY SINGLE-COLLECTOR, SECTOR FIELD ICP-MS

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The Lu-Hf decay system has been used in planetary science as both a geochemical tracer and for geochronology. Phosphate minerals preferentially incorporate rare-earth elements such as Lu, while excluding Hf, making them excellent target minerals for Lu-Hf isotopic dating [1]. However, measurement of Hf isotopic compositions remains a challenge for conventional MC-ICPMS analysis due to low total Hf concentrations. Because of this, Hf isotope composition measurements of phosphate minerals separated from meteorites are rare [2].

We have developed an ICP-MS technique for determination of $^{176}Hf/^{177}Hf$ ratios in phosphates having low Hf concentrations (<< 1 ng/g). Because of its high sensitivity and rapid scanning abilities we have used a Thermo-Fisher Element-XR, single-collector, sector-field ICP-MS. The Element-XR was fitted with a 'H' skimmer cone (Ni) and Jet sampler cone to enhance instrument sensitivity. Samples were introduced into the mass spectrometer using a Nu Instruments DSN-100 desolvating nebulizer at a rate of ~100 µl/min. The addition of the Jet sampler cone and desolvating nebulizer resulted in > 40x signal enhancement for all isotopes measured. In order to reduce background counts on all isotopes a 2% HNO_3 + 0.05M HF solution was aspirated overnight, prior to each analytical session. Typical blank count rates were less than 1000 cps for the most abundant isotope, ^{180}Hf. This corresponds to ~50 fg/g Hf blank. The future challenge is to develop miniature column chemistry technique to reduce total Hf procedure blank to levels of <50 fg/g. Measurements were made in fast, Escan mode with a dwell time of 25 ms for ^{172}Yb, $^{174}(Yb+Hf)$, ^{175}Lu, ^{178}Hf, and ^{180}Hf and a dwell time of 100 ms for $^{176}(Yb+Lu+Hf)$, ^{177}Hf and ^{179}Hf for a total time of 425 ms/sweep. Each analysis consisted of 500 sweeps for a total time of approximately 3.5 minutes. Ion intensities were ~20,000 cps/ppt for ^{180}Hf. Raw data was processed off-line. All raw signals are blank corrected using the mean count rates for the blank measured between each standard and unknown analysis. Yb and (Yb+Lu) interference corrections were made for ^{174}Hf and ^{176}Hf, respectively. Hf mass bias factor (β_{Hf}) was calculated using the exponential law and $^{179}Hf/^{177}Hf = 0.7325$ [3]. Hf isotope ratios are calculated and corrected for instrumental mass bias using β_{Hf} and then normalized to the average Hf isotopic composition for the JMC 475 standards run before and after each unknown.

The average $^{176}Hf/^{177}Hf$ for 100 pg/g Hf JMC 475 solutions run to date on the Element-XR is 0.2822 ± 0.0008 (2SD, n = 8), similar to results for a 100pg/g Hf JMC 475 solution analyzed on the Neptune MC-ICPMS in our lab (0.2820 ± 0.0011, 2SD, n = 4), and within error or the reference value of 0.28216 [2]. The average $^{176}Hf/^{177}Hf$ for 10 pg/g Hf JMC475 solutions run to date on the Element-XR is 0.2820 ± 0.0007 (2SD, n = 10). The average $^{176}Hf/^{177}Hf$ for a 10 pg/g Hf BCR2 solution is 0.2828 ± 0.0011 (2SD, n = 3). We will apply the ICPMS technique to measure Hf isotopic compositions of phosphate mineral separates from well-preserved, low-shock, rapidly cooled meteorites.

References: [1] Barfod G.H. et al. 2003. *Chem Geol* 200: 241-253. [2] Amelin Y. 2005. *Science* 310:839–841. [3] Blichert-Toft J. et al. 1997. *Contrib Mineral Petrol* 127:238-260.