Hafnium isotope analysis of Yb-doped zircon and JMC475 reference materials by MC-ICP-MS: Protocols and pitfalls

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The Hf isotopic composition of zircon is a powerful proxy for the reconstruction of magmatic processes. Because both Hf and trace elements are often measurede in one sample, analyses are conducted without the time consuming Hf chemical purification using conventional MC-ICP-MS.

We tested new analytical approaches to eliminate inaccuracies due to $^{176}\mathrm{Yb}$ isobar on $^{176}\mathrm{Hf},$ matrix effects and imprecise mass bias coefficient ($\beta\mathrm{Hf}$ and $\beta\mathrm{Yb})$ determination.

Firstly, JMC475 Hf standard and Plešovice zircon [1] were Yb-doped so that Yb/Hf ranges up to 0.5. The ¹⁷⁶Yb isobar was removed using in-run optimization of the 176Yb/173Yb value that is matrix dependent and varied within 0.8% of natural abundancies from Thirwall and Anczkiewicz [2]. The overall external reproducibility was better than $\pm 1.0~\epsilon_{Hf}$ (2SD, n>30). Then, JMC475 was doped with Zr, U, Th and REEs. The major cause of inaccuracy was the addition of Gd, which shifted the ε_{Hf} by ~+4 due to Gd-oxide generation in the ICP, creating isobars on Yb and Hf masses [3]. This effect can be reduced by using matrix matched reference material for data normalization. Finally, Plešovice zircon was used as a bracketing standard to determine βHf and βYb for low Yb and/or Hf analytes. Diluted Plešovice zircons (~3ppb Hf) were found accurate to within 2.1 EHf (2SD) of the reference value. The reproducibility was improved by a factor of >2 when using standard bracketing instead of internal β calculation.

These experiments suggest that Hf isotope measurements of samples with variable matrices by solution MC-ICP-MS can be improved by employing matrix matched reference materials for data reduction and that accurate measurements of very small samples can be conducted if standard bracketing is used for external determination of mass bias coefficients.

[1].Sláma, J., et al. (2008) *Chemical Geology.***249**, 1-35.[2].Thirlwall, M.F., et al. (2004) *Int. J. Mass Spectrom.***235**, 59-81.[3].Fisher, C.M., et al. (2014) *Chemical Geology.***363**, 125-133.