Towards δ^{11}B external reproductibility of 0.1‰ (2σ) for MC-ICP-MS measurements with direct injection as introduction system

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Recent development of the d-DIHEN [1] (demountable direct injection high efficiency nebulizer) has permitted faster and more precise determination of boron isotope ratio by MC-ICP-MS [2].

With direct injection, the whole volume of sample introduced through the d-DIHEN ends up in the plasma, thus theoretically increasing the sensitivity, compared to other classical introduction systems (spray chambers and desolvation systems such as APEX and Aridus). However, the ionisation yield is not as good as expected due to still large water droplet size. Direct injection systems are interesting for ‘sticky’ elements, for which wash times are hard to reduce with the classical introduction systems, and for volatile elements, whose sensitivity cannot be enhanced by desolvation. Boron belongs to both categories.

With d-DIHEN on a Neptune MC-ICP-MS, boron sensitivity reaches 10V/ppm for an uptake rate of 30 µl/min and wash times are of only 2 to 3 minutes. We are able to measure sample/standard every 6 to 7 minutes. The actual external reproducibility is 0.25‰ based on 3 to 5 replicate measurements of a sample solution, over different days. Using a bracketing sequence of 3 successive standard – sample measurements for each sample at a boron concentration of 200 ppb, we can achieve an external reproducibility of 0.15‰ (2σ) over the 11B/10B isotope ratio of most seawater and carbonate samples. Automation of the sample introduction (SC-DIN) is expected to enhance the reproducibility. The chemical separation might become a limitation for such precise determination.

[1] Westphal, Kahen, Rutkowski, Acon & Montaser (2004) *Spectrochimica Acta* **59**, 353–368. [2] Louvat, Bouchez & Paris (in press) *Geostandards & Geoanalytical Research*.

Zr mobilization and complexation in subduction zone fluids

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The distinctive depletion in HFSE observed in arc magmas has been a matter of debate in the study of trace-element recycling in subduction zones. Recently, several studies proposed that HFSE could be efficiently mobilized by alkali SiO_2-rich fluids and fluorine-rich melts [1, 2]. In order to investigate the behavior of HFSE in subduction zone fluids, the speciation and partitioning of Zr were determined *in situ* using X-ray Absorption Fine Structure (XAFS) and Synchrotron X-ray fluorescence (SXRF) spectroscopy up to 800 °C – 1.5 (1) GPa. Experiments were conducted in a hydrothermal diamond-anvil cell (HDAC)[3] at BM30B FAME beamline at the ESRF (Grenoble, France). Zr fluid-melt partition coefficients were determined in the haplogranite-H_2O system, while Zr speciation was investigated over a wide range of compositions, including 5000ppm Zr standard solutions (in 2.5 wt% HCl), $Na_2Si_2O_5$ and haplogranite glasses and melts, and alkali–SiO_2 aqueous fluids (20-30 wt% NS2). In addition, the influence of fluorine on Zr speciation and partition was also investigated.

The results of SXRF experiments show that Zr preferentially partitions into the melt phase at any investigated P-T. The partition coefficients $D_{Zr}^{fluid/melt}$ increase with increasing temperature and with the addition of fluorine, suggesting the efficient mobilization of Zr (and HFSE) by fluids enriched in alkali-Al-Si dissolved components, possibly due to changes in Zr complexation. High-resolution XANES spectra of Zr in glasses, melts and alkali-SiO_2 fluids display distinct features compared to Zr in HCl, but bear a strong resemblance to spectra in vlasovite ($Na_2ZrSi_4O_{11}$), providing evidence for octahedrally coordinated Zr [4]. However, the similarities observed between Zr XAFS spectra in F-free and F-bearing melts may indicate the absence of Zr-F complexation in hydrous silicate melts. Further modelling of XANES and EXAFS spectra is in progress to better constrain the complexation of Zr in subduction zone fluids. The implications of this results for Zr and HFSE recycling in subduction zones will be discussed.

[1] Manning *et al.* (2008) *Earth Planet. Sci. Lett.* **272**, 730–737. [2] Farges (1996) *Chem. Geol.* **127**, 253–268. [3] Bassett *et al.* (1993) *Rev. Sci. Inst.* **64**, 2340–2345. [4] Sokolova E. *et al.* (2006) *Can. Mineral.* **44**, 1349–1356.