



High-field strength elements complexing in aqueous fluids at subduction zone P-T conditions

Julien Dubrail (1), Max Wilke (1), Christian Schmidt (1), Karen Appel (2), Sakura Pascarelli (3), Kristina Kvashnina (3), and Craig Manning (4)

(1) Deutsches GeoForschungszentrum (GFZ), Section 3.3 Chemistry and Physics of Earth Materials, Potsdam, Germany (julien@gfz-potsdam.de), (2) DESY, ein Forschungszentrum der Helmholtzgemeinschaft, Hamburg, Germany, (3) ESRF, European Synchrotron Radiation Facility, Grenoble, France, (4) Department of Earth and Space Science, University of California Los Angeles, Los Angeles, CA, USA

One of the characteristic geochemical features of subduction zones is the depletion of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta) relative to large ion lithophile elements (LILE, i.e., Rb, Sr, Cs, Ba, Pb, U and Th) in primitive arc magmas compared to the HFSE and LILE concentrations in mid-ocean ridge basalts. The mechanism that causes the HFSE depletion is still not completely understood. One of the reasons is that the knowledge on the HFSE speciation in fluids at subduction zone conditions is only fragmentary. Complexing of HFSE with alkalis and silica dissolved in aqueous fluids has been suggested as an efficient mechanism to promote HFSE mobility during fluid-rock interaction in the lower crust and upper mantle [1-2].

Here, we obtained data on the solubility of Zr and Hf in aqueous fluids containing $\text{Na}_2\text{Si}_3\text{O}_7$ (NS3), $\text{Na}_2\text{Si}_3\text{O}_7 + 1 \text{ wt\% Al}_2\text{O}_3$, $\text{Na}_2\text{Si}_3\text{O}_7 + 5 \text{ wt\% Al}_2\text{O}_3$, NaOH, or HCl. For this, these fluids were equilibrated with zircon or hafnion in hydrothermal diamond-anvil cells at temperatures up to 750 °C and pressures up to ~1 GPa and analysed in-situ using synchrotron radiation micro-XRF and XAFS at beamline L HASYLAB, DESY and at the ESRF beamlines ID 24 and ID26.

The Zr and Hf concentrations in the fluids are highest in aqueous NS3 solutions and decrease with addition of alumina. Determined Zr and Hf concentrations in NS3 + 5 wt% Al_2O_3 fluids were about the same or somewhat higher than those in NaOH and HCl solutions. The enhanced Zr and Hf solubilities in NS3 fluids point to the formation of (Zr,Hf)-O complexes involving Na and/or Si, i.e., they signify the importance of dissolved alkalis and silica for the transport of HFSE in subduction-zone fluids.

Moreover, we performed XANES measurements at the Zr-K and Hf- L_3 edges to obtain more detailed information on the HFSE complexes in aqueous fluids at high pressures and temperatures. Theoretical ab-initio XANES spectra were calculated using the FEFF9 code [3] to extract structural data from the experimental spectra. The simulated XANES spectra of clusters based on the structure of vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) are in good qualitative agreement with the Zr-K and Hf- L_3 XANES spectra in NS3 solutions. This indicates Zr and Hf complexes with 6 oxygens in the first coordination shell with additional Si and Na neighbours in further shells. Experimental XANES spectra from Zr and Hf in HCl and NaOH solutions differ significantly from those of fluids with dissolved silicate.

In the case of aqueous HCl solutions, a (Zr,Hf) O_4Cl_3 cluster with a 7-fold first coordination shell reproduced qualitatively the features of the experimental spectra. Comparison of the experimental spectra on Zr in NaOH solutions showed good agreement with experimental and calculated spectra of baddeleyite (ZrO_2) model compound, which points to complexes with 7 oxygens in the first coordination shell.

References:

- [1] Manning, C. E. (2004), *Earth Planet. Sci. Lett.* 223, 1-16
- [2] Manning, C.E. et al. (2008), *Earth Planet. Sci. Lett.* 272, 730-737
- [3] Rehr, J.J., Albers, R.C. (2000), *Reviews of Modern Physics.* 72, 621-654