

## X-ray spectroscopic constraints on complexing of high-field-strength elements in subduction zone aqueous fluids

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Magmatic rocks related to subduction zones commonly display element patterns characterized by depletion of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta). The depletion may be due to low solubility in the aqueous fluids that are involved in the processes at subduction zones. The geochemical budget of HFSE is largely controlled by accessory phases such as zircon. Therefore, knowledge is needed on solubility and stability of these phases. Fluid composition should be one of the most important parameters because it can strongly affect complexing of HFSE in aqueous fluids. Complexing with alkalis and silica dissolved in the fluid has been suggested as an efficient mechanism to promote HFSE mobility [1,2]. However, direct evidence on the HFSE speciation in fluids at subduction zone conditions is lacking.

Experimental information on HFSE complexation was obtained for aqueous fluids with HCl, NaOH, Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> (NS3), or Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> + 1 or 5 wt% Al<sub>2</sub>O<sub>3</sub>, equilibrated with zircon or hafnon in hydrothermal diamond-anvil cells at *T* up to 750 °C and *P* up to 1 GPa. On these fluids, XANES and EXAFS spectra were collected *in situ* at *P* and *T* at beamlines ID 24 and ID 26 (ESRF). For NS3 ± Al<sub>2</sub>O<sub>3</sub> solutions, measured XANES and EXAFS at the Zr-K and Hf-L<sub>3</sub> edges indicated complexes with 6 oxygens in the first shell. The XANES simulated with FEFF9 [3] based on a Na<sub>2</sub>ZrSi<sub>4</sub>O<sub>11</sub> cluster (as in vlasovite) is in good qualitative agreement with measured spectra. In contrast, 7 oxygens are indicated in the NaOH solution. For HCl solutions, a spectrum simulated for a (Zr,Hf)O<sub>4</sub>Cl<sub>3</sub> cluster reproduced qualitatively the features of the experimental spectra. Our results confirm that alkalis and silica dissolved in aqueous fluids may efficiently transport HFSE in the fluids emanating from the subducting slab.

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

## High pressure geochemistry in laser-heated diamond anvil cells with synchrotron light

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A major goal in the geosciences is to understand (and predict) how the Earth works, which requires a detailed knowledge of how the mineral phases which make up the Earth behave under high pressure and high temperature conditions. Geochemistry of deep Earth interiors is particularly concern with phase transitions and crystalchemistry of silicates and oxides, oxidation and electronic state of elements (first of all iron), and elements partitioning between major lower mantle phases. We demonstrate that combination of laser-heated diamond anvil cell technique and modern synchrotron facilities (high resolution angle dispersive X-ray diffraction, XANES, nuclear inelastic scattering (NIS), and nuclear forward scattering(NFS)) make possible *in situ* studies pressure and temperature dependence of chemical and physical properties of minerals. Particularly, accurate single crystal diffraction studies of iron bearing silicate perovskite and ferropericlase extended to 100 GPa and over 2500 K and, together with NFS, NIS, and XANES data reveal crystalchemistry of iron at conditions of Earth lower mantle.