ESRF	**HFSE complexation in aqueous fluids at high temperature and pressure**	**Experiment number**: EC 477
Beamline: ID24	**Date of experiment**: from: 10.11.09 to: 16.11.09	**Date of report**: 2.9.10
Shifts: 18	**Local contact(s)**: Sakura Pascarelli	*Received at ESRF:*

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Report:

The aim of the experiment is to study the complexation of high-field-strength elements (HFSE) in aqueous fluids containing dissolved silicate components at conditions of the deep Earth. XANES measurements at high temperature and pressure are used to provide further insight to the nearest and next-nearest neighbor elements surrounding HFSE in the fluid. Temperature and pressure conditions are achieved by using hydrothermal diamond anvil cells. Due to the outcome of EC-388 the original idea of dissolving Nb-bearing rutile was dropped. Instead, the zircon analogue hafnon and the hafnium complexation in the fluid was studied.

For the measurements on Hf, a horizontally bent Si (111) Bragg polychromator was used. The focal spot size achieved in combination with the vertically focussing mirror was 5 x 7 µm. At these conditions an energy range of ca. 1000 eV was usable at the Hf L_3-edge in transmission mode. The XAFS spectra at high P & T were taken in fluorescence mode due to the low concentrations of Hf in the fluids. The energy range that was feasible to be used in fluorescence mode with these samples was about 250 to 350 eV depending on concentration. The fluorescence yield was collected using a Si drift-chamber detector (Vortex). Contributions by elastic and inelastic scattering were excluded by using a confocal setup, i.e. a focussing polycapillary half-lens was inserted between diamond-anvil cell and detector (Wilke et al. 2010). The XAFS spectra were acquired by scanning a slit through the fan after the polycromator (Turbo XAFS mode). The intensity of the incoming beam was monitored by measuring the scattered signal of a Kapton foil using a photo diode.

Shown in Fig. 1 are Hf contents as a function of pressure and temperature for fluids in equilibrium with hafnon. All fluids show enhanced concentrations of Hf. Contents range between <100 and ca. 2900 ppm. Highest concentrations are found for fluids containing 28 wt% $Na_2Si_3O_7$ component. Adding Al_2O_3 significantly lowers the Hf content.

Fig. 2 shows a comparison of XANES spectra of Hf in various fluids at high P & T. Spectra of solutions containing silicate components differ from those found for NaOH or HCl-solutions. Qualitatively, this points to a local environment of Hf for the silicate-bearing fluid that involves Si and possibly Na. These hypotheses are being tested using ab-initio code to simulate spectra of potential model structures.

Acquisition of longer EXAFS spectra was limited by the relatively low signal on one hand. Furthermore, Bragg peaks from the diamond represent a severe problem at this high energy and often limit the possible range for energy scans or they may produce spurious features in the spectra that cannot be corrected.

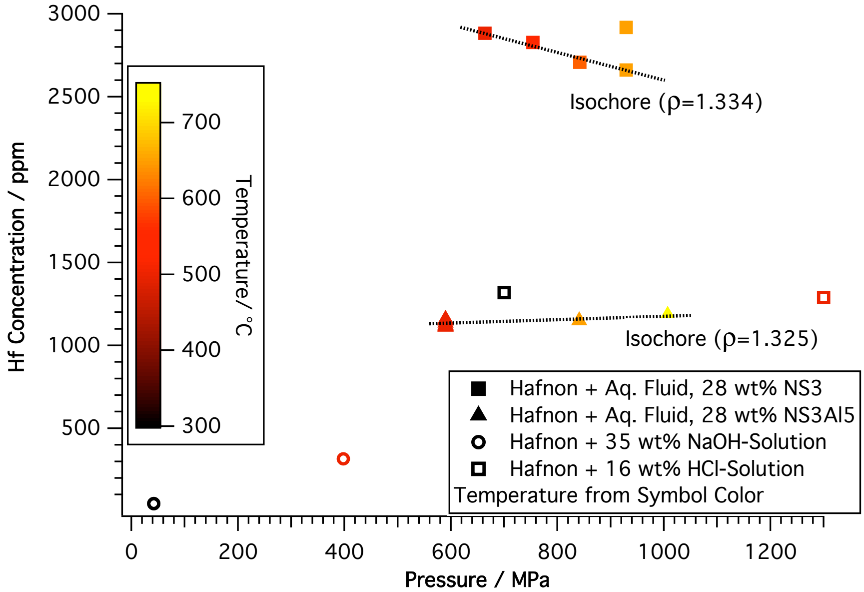

Fig. 1: Hf contents of fluids equilibrated with hafnon at conditions indicated. Color of symbol indicates temperature.

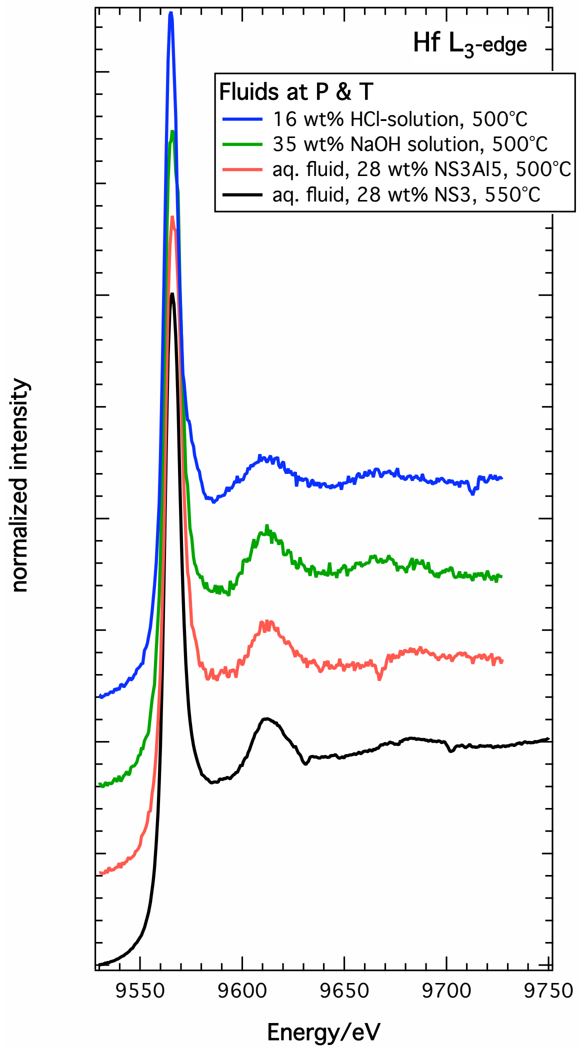

Fig. 2: XANES spectra of Hf in aqueous solutions containing $Na_2Si_3O_7$ at conditions indicated.

References:

Wilke M., Appel K., Vincze L., Schmidt C., Borchert M., Pascarelli S. (2010)j. Synchrotron Rad, 17, 669-675.

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