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| | **Hf complexation in aqueous fluids at high pressure and high temperature** | **Experiment number**:<br>EC 1078 |
| **Beamline**:<br>ID24 | **Date of experiment**:<br>from: 28.11.12 to: 04.12.12 | **Date of report**:<br>26.2.13 |
| **Shifts:**<br>18 | **Local contact(s)**:<br>Sakura Pascarelli | *Received at ESRF:* |

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## Report:

The scope of the study is understanding the complexation of high-field-strength elements such as Hf and Zr in supercritical aqueous solutions. In this experiment we aimed at obtaining EXAFS measurements at high temperature and pressure to provide insight to the complexation of Hf in the fluid and obtain evidence for any changes occurring at high pressue and temperature. These data are of fundamental interest for understanding element transport by aqueous fluids in processes of the deep Earth. Temperature and pressure of interest were achieved by using hydrothermal diamond anvil cells.

For the measurements at the Hf $L_3$-edge, a horizontally bent Si (111) Bragg polychromator was used. The focal spot size achieved in combination with a vertically focussing mirror was 4 x 6 µm. At these conditions an energy range of ca. 1000 eV was usable at the Hf $L_3$-edge in transmission mode. Due to the low concentrations of Hf in the fluids, the EXAFS at high P & T was taken in fluorescence mode. The energy range after the edge that was feasible to be used with these samples was about 400 eV for solutions with ca. 9000 ppm Hf, which corresponds to $k = 10$ Å$^{-1}$. 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 with a photo diode.

Representative EXAFS spectra taken on Hf in HCl solutions are shown in Fig. 1. In that figure, we compare Hf in a solution that was produced by dissolution of $HfCl_4$ in HCl solution to Hf in a HCl solution in equilibrium with solid $HfO_2$. $HfCl_4$ in HCl at room temperature yields Hf in distorted 8-fold coordination by oxygen consistent with Hagfeld et al. 2004. Heating this solution results in immidiate precipitation of a very fine-grained Hf phase, likely $HfO_2$. Presence of this phase throughout the sample volume precluded any further measurements. The data obtained on HCl solutions in equilibrium with a single grain of solid $HfO_2$ indicate 8-fold oxygen coordination at room temperature and vapor pressure. At higher temperatures and pressures the EXAFS indicates a significant change in the Hf environment, which is particularly highlighted by the shift of the first maximum in the Fourier transform by ca. 0.2 Å to higher distances. Preliminary fits of the data indicate at least partial replacement of oxygen ligands by chlorine. Concomittant to the change in the EXAFS, the fluorescence yield obtained from the fluid decreases with temperature and pressure, consistent with a decrease in the solubility of $HfO_2$. All observations indicate that the Hf complexation found in HCl solution at room temperature cannot be stabilized at higher temperatures.

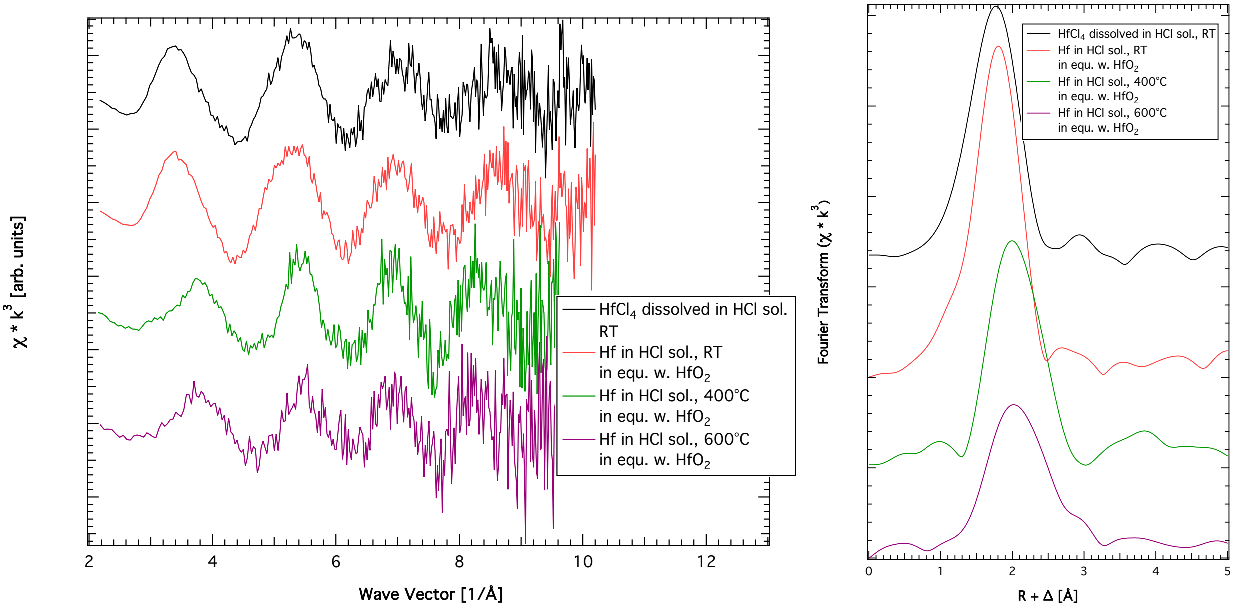

**Figure 1:** k$^3$-weigthed EXAFS obtained at the Hf L$_3$-edge on aqueous fluids as indicated (left), Fourier transform of the EXAFS.

## References:

Hagfeld et al. (2004) Dalton Trans., 2142-2151.
Wilke et al. (2010) J. Synchroton Rad., 17, 669-675.

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