



	Experiment title: A High-energy resolution XAS/XES spectroscopy study of the chemical state of Hf and Zr in chloride-rich hydrothermal fluids	Experiment number: ES 534
Beamline: BM20	Date of experiment: from: 02.11. 2016 to: 08.11. 2016	Date of report: 26.02.2017
Shifts: 18	Local contact(s): Kristina Kvashnina	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

- ***Kristina Kvashnina**, ESRF, Grenoble
- ***Alexander Trigub**, NRC “Kurchatov Institute”, Moscow, Russia
- ***Maximilian Nickolsky**, ***Olga Filimonova**, ***Boris Tagirov**, Institute of Geology of Ore Deposits RAS, Moscow, Russia

Experimental. Zirconium K-edge XANES/EXAFS spectra (17.998 keV), and spectra of Hf L₃- and L₁ (XANES only) edges (9.561 keV and 11.271 keV, respectively) were recorded *in situ* for a series of hydrothermal chloride solutions. For these experiments a silica glass capillary (Polymicro TechnologiesTM, 250 μm ID, 600 μm OD, 15 mm length) was loaded with experimental solution together with a small piece of natural baddeleyite (ZrO₂) or synthetic hafnium oxide (HfO₂) and hermetically sealed. The capillaries were placed into a microtomography furnace available at ESRF (Bellet et al., 2003). In order to eliminate temperature gradient inside the furnace the capillary was located between two plates of Ag (5 mm height, 0.6 mm thick). Temperature readings were calibrated before the experiment at an accuracy of ±5 °C using a K-type thermocouple placed instead of capillary. Results of the experiment showed that for one capillary EXAFS spectra can be recorded during ~12-16 hours, including heating/cooling and equilibration of the experimental system. For Hf, due to very slow dissolution kinetics, three shifts were necessary for one experiment. Therefore, only one Hf capillary was studied. The spectra of baddeleyite, HfO₂, zircon (Zr,Hf)SiO₄, and zirconium oxychloride were used as the reference ones.

Results. Our experiments showed that Zr and Hf form strong (hydroxide)-chloride complexes in acidic chloride fluids. The temperature effect on the absorption edge height suggests that these complexes are most stable at ~350 °C. Since the concentration of chlorides in natural hydrothermal fluids are ~100÷1000 times higher than the concentration of fluoride salts, chloride complexes of Zr and Hf, along with fluoride ones, can effectively transport these metals in medium-temperature acidic fluids (300 – 600 °C). Cesium has no effect on the spectra and, therefore, formation of complexes with alkaline metals in the second coordination shell is ruled out. This conclusion is important for hydrothermal chemistry of Zr and Hf as formally their solubility is best described by negatively charged complexes whose formation is unusual for acidic high-temperature fluids, but is confirmed by our experimental data. Two types of XANES spectra with different white line shapes depending on the total chloride concentration were detected. This implies that at least two types of complexes of different composition presented in the experimental solutions. The Zr K- and Hf L₁-edge XANES spectra recorded for 7.7m HCl solution are identical and, therefore, the composition and geometry of complexes are identical as well.

Lack of time did not allow us to collect Hf HERFD XAS/XES spectra. Experimental results showed that XES spectra can be recorded only for the most concentrated fluid (6m HCl + 5m Na(Cs)Cl) with the highest metal concentration. Record of spectra for chloride melts, initially planned in the project, was not possible because no metal was detected in the “dry” water-free system.

The EXAFS spectra collected during the experiment are shown in Fig. 1. An example of the experimental spectra fitting, performed with the aid of Monte-Carlo method, is presented in Fig. 2. The best agreement of experimental and calculated spectra is achieved for complex which contains 6 Cl and 1 O atoms (in the form of OH and/or H₂O ligands). The radial density functions are characterized by several diffuse peaks which imply distorted character of the central metal coordination shell. Further treatment of the experimental data will include XANES spectra modeling using complex geometries generated via the Monte-

Carlo method, and comparison of the experimental XANES/EXAFS spectra with results of *ab initio* molecular dynamics simulations in order to unambiguously determine the composition of complexes and their charge.

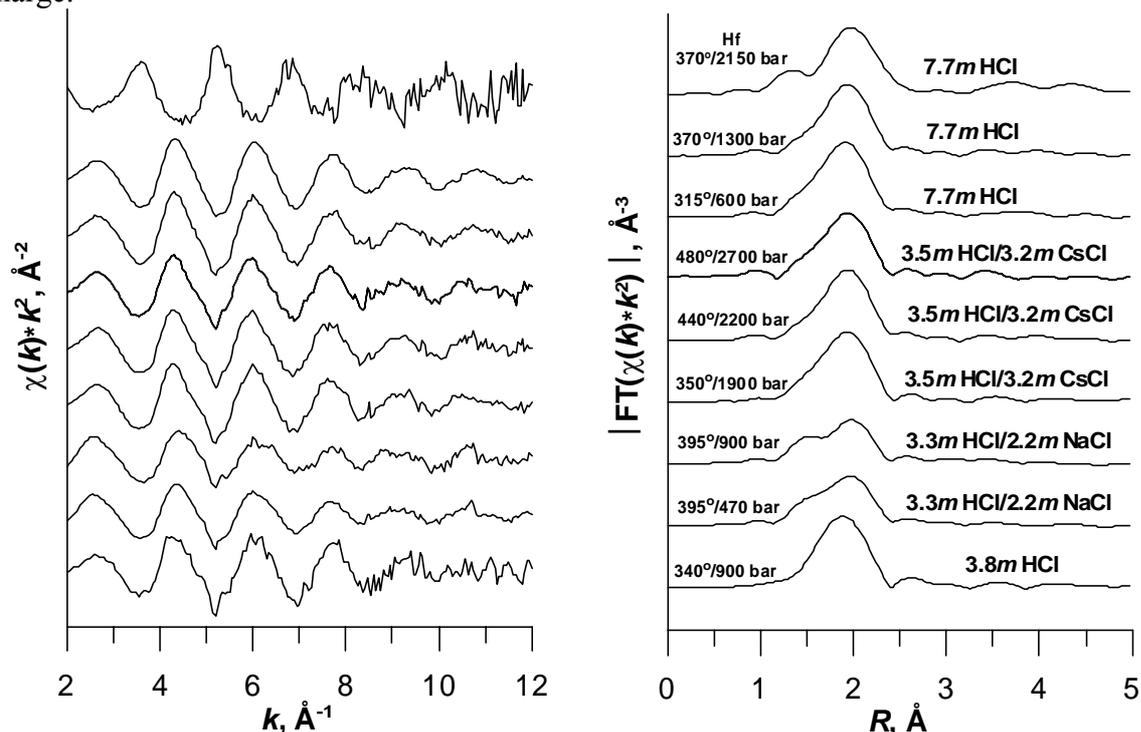


Figure 1. Zirconium K-edge and Hf L₃-edge spectra recorded at high *TP* –parameters. *Left*: k^2 -weighted background-subtracted EXAFS spectra, *right*: Fourier transform (not corrected for phase shift).

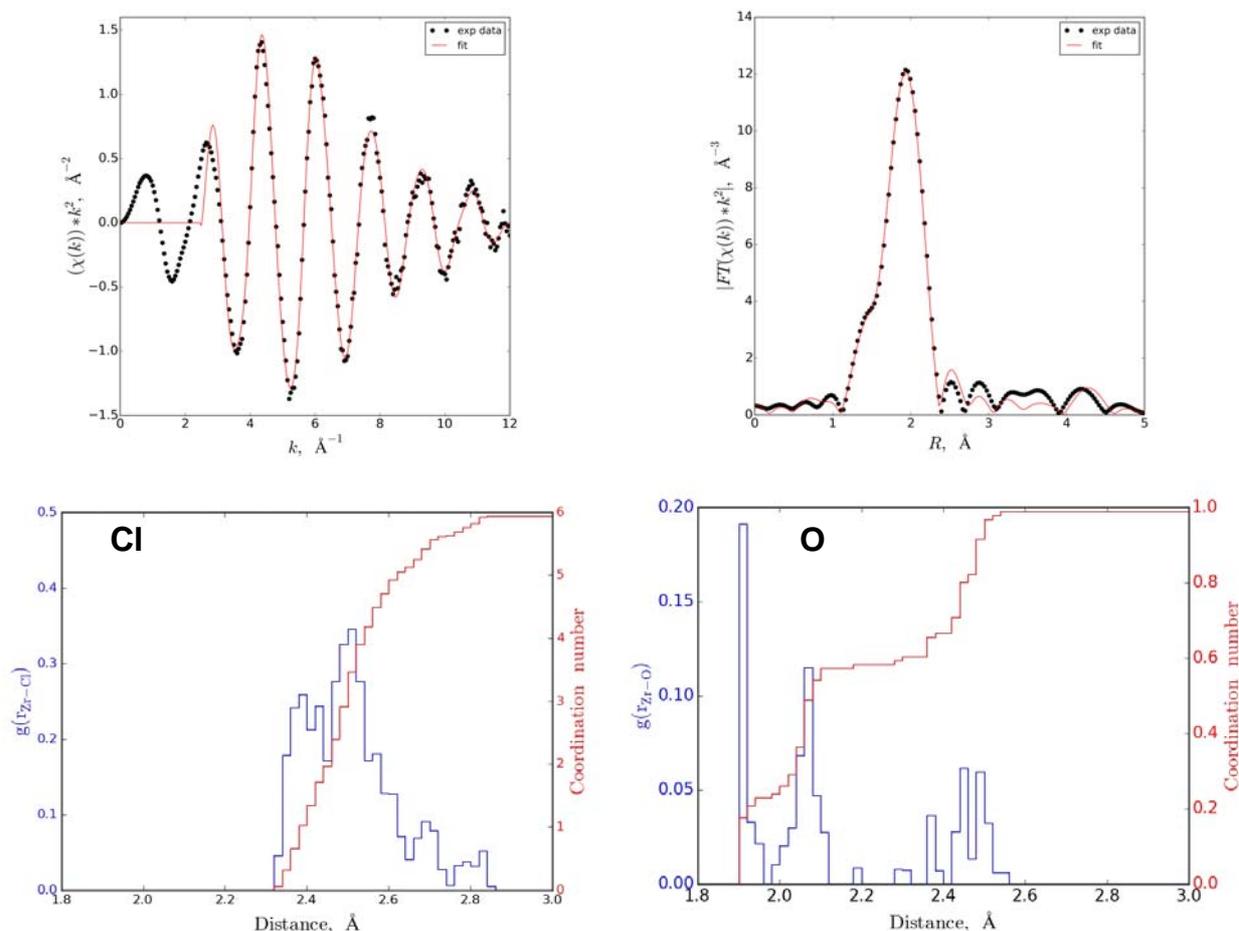


Figure 2. Zirconium K-edge EXAFS spectra for 7.7m HCl solution at 370 °C, 1300 bar. *Top*: k^2 -weighted background-subtracted EXAFS spectra and its Fourier transform (not corrected for phase shift). Points – experiment, red lines – fit results. *Bottom*: Radial densities (blue) and coordination numbers (red) of Cl and O atoms located around Zr.