	Complexation of high-field-strength elements in aqueous fluids at highpressure and temperature	**Experiment number**: EC 236
Beamline: ID24	**Date of experiment**: from: 20.2.08 to: 22.2.08 from: 01.3.08 to: 4.3.08	**Date of report**: 14.3.08
Shifts: 15	**Local contact(s)**: Sakura Pascarelli	*Received at ESRF:*

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Report:

The aim of the experiment is to study Ti and Zr complexation 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 Ti and Zr in the fluid. Temperature and pressure conditions are achieved by using hydrothermal diamond anvil cells. Spectra have to be recorded in fluorescence mode due to the low concentrations of Ti and Zr in the solutions.

The review panel alloted beamtime for feasibility experiments for this project. Since the two elements require completely different setups of the beamline optics, one set of shifts was used to test the possibility of acquiring XANES data at the Ti K-edge. In a second set of shifts test experiments at the Zr K-edge were performed. At the end of the second set, these test experiments turned out to be very promising for future work. However, only at the last day it was realized that the used fluorescence detector (Vortex Si-drift detector from detector pool) was not properly working (only about 1% of nominal efficiency).

Ti K-edge:

For the measurements on Ti, a horizontally bent Si (111) Bragg polychromator was used. The focal spot size achieved in combination with the vertically focussing mirror was about 5 µm. The maximum energy range achieved at this Bragg angle is about 110 eV. Thus, only the XANES region is accessible. Spectra could be acquired in fluorescence mode on pieces of silicate glass, which were doped with ca. 500 ppm Ti (Fig. 1). XANES in fluorescence mode is measured by scanning a slit through the fan of the incoming beam after the polychromator. The resulting spectra show that the photon flux and energy dispersion provided by the optical setup is suitable to perform Ti XANES measurements at ID24 even at quite low concentrations. We tried to acquire, as well, a XANES of Ti in a solution that was loaded into a diamond anvil cell. In this case, no Ti fluorescence could be detected. However, this was certainly in part due to the defective fluorescence detector, so that this experiment might still be practible.

Zr K-edge:

For the measurements on Zr, a horizontally bent Si (111) Laue polychromator was used. The focal spot size achieved in combination with the vertically focussing mirror was < 20 µm. The maximum energy range achieved was about 400 eV in fluorescence mode. A larger range should be possible by use of a better suited polychromator crystal. Since we could replace the fluorescence detector on the last day, spectra could be acquired on Zr in several different aqueous solutions (Fig. 2) at high temperatures and pressures. Lowest concentration measured was ca. 500 ppm Zr using acquisition times of 8 - 10 s per point.

In conclusion, these first results indicate that the chosen method is well suited to study the speciation of elements in aqueous solutions at high temperatures and pressures, i.e. conditions of the deep Earth.

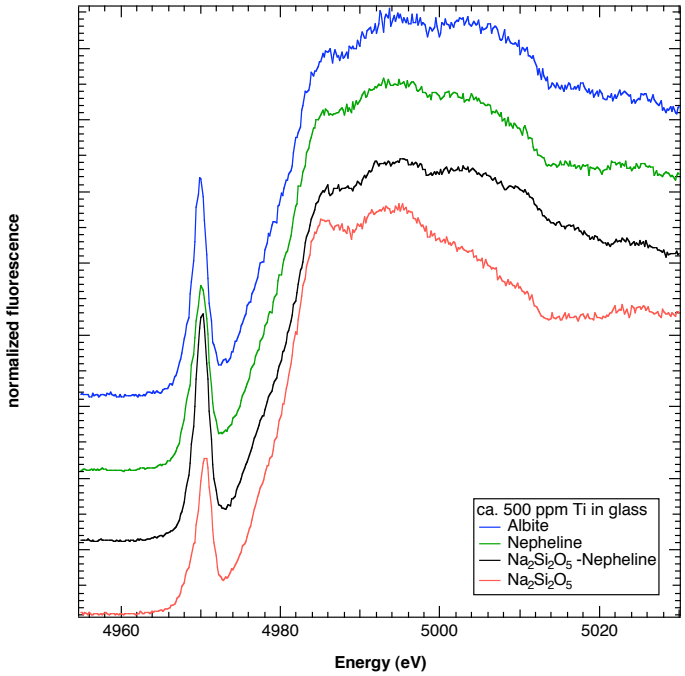

Fig. 1: XANES spectra of Ti in silicate and alumino-silicate glasses. Acquisition time for spectra was 4s/pt.

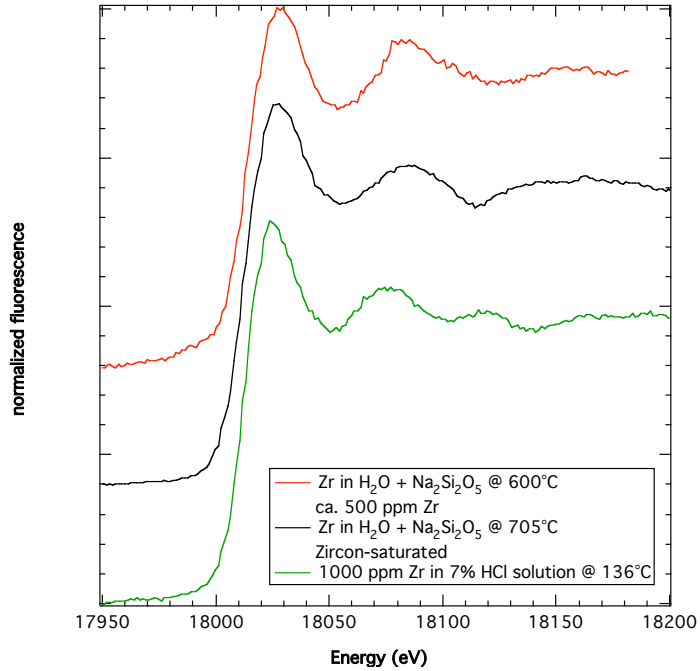

Fig. 1: XANES spectra of Zr in aqueous solutions at conditions indicated. Spectra were collected using a hydrothermal diamond anivil cell.

Acknowledgements:
The great help and support of Sakura Pascarelli, Sebastian Pasternak, Florian Perrin, Manuel Munoz, John Morse and Remi Tucoulou is highly appreciated.