

**Complexation of high-field-strength elements in aqueous fluids at high pressure and temperature****Experiment number:**
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18**Local contact(s):**
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Report:

The aim of the experiment is to study 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 Zr in the fluid. Temperature and pressure conditions are achieved by using hydrothermal diamond anvil cells.

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 $< 20 \mu\text{m}$. At these conditions an energy range of more 1000 eV was usable in transmission mode. The XAFS spectra at high P & T were taken in fluorescence mode due to the low concentrations of Zr in the fluids. The energy range that was feasible to be used in fluorescence with these samples was about 400 eV. The fluorescence yield was collected using a Si drift-chamber detector (Vortex). Contributions by elastic and inelastic scattering were reduced using an Y filter ($\Delta\mu = 3$). The XAFS spectra were acquired by scanning a slit through the fan after the polychromator (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 Zr contents as a function of the Al content of the fluid. Contents range between 100 and 700 ppm. These match solubilities calculated from linear interpolation of the maximum solubility in pure H₂O (from the detection limit) and the solubility in the most alkaline high-silica melts reported by Ellison and Hess [1]. These data clearly demonstrate the enhancement of zircon solubility by addition of silicate components to the fluid.

Fig. 2 shows the comparison of XANES spectra of Zr in various fluids at high P & T. These XANES spectra significantly differ from the one collected for Zr in a Zr-bearing standard solution. Spectra of solutions containing Al show some slight difference in pre-edge region compared to the one with Na₂Si₂O₅ only. The resolution of the XANES spectra is probably limited by the low resolution of the Laue polychromator and inhibits more detailed analysis. All spectra taken on the fluids at P & T look quite similar to the spectrum taken on Zr in Na₂Si₂O₅ glass. Qualitatively, this points to a similar local environment of Zr for the silicate-bearing fluid and the glass (see also [2]).

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.

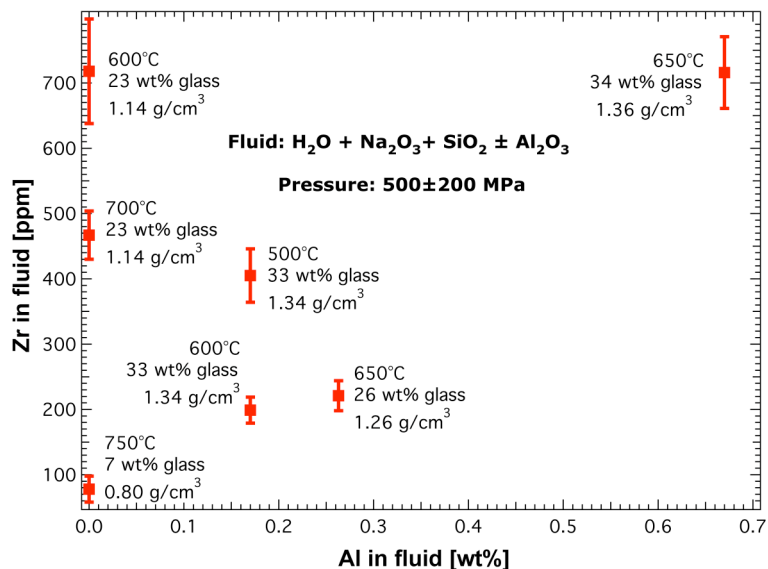


Fig. 1: Zr contents of fluids equilibrated with zircon at conditions indicated.

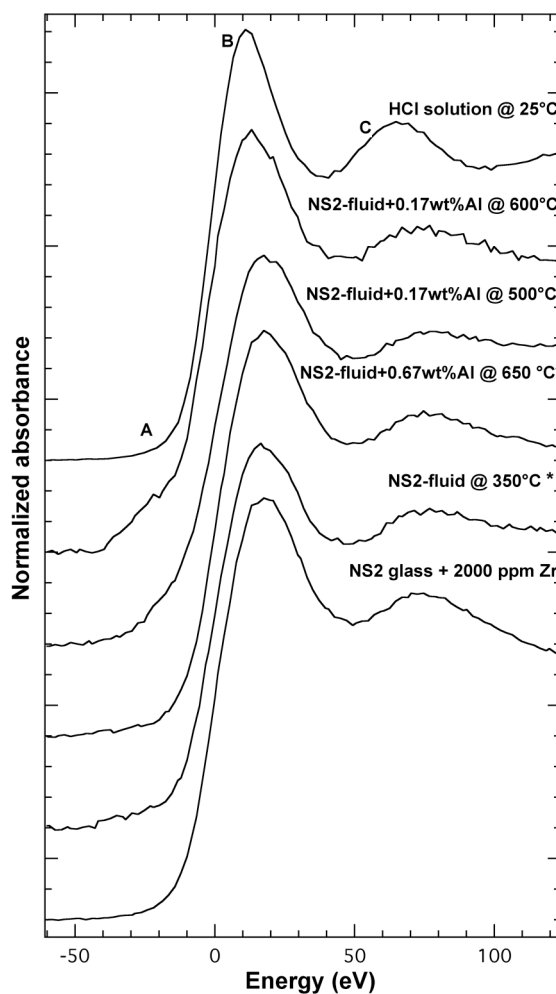


Fig. 1: XANES spectra of Zr in aqueous solutions containing $\text{Na}_2\text{Si}_2\text{O}_5$ at conditions indicated. In addition, a spectrum of Zr in a standard solution as well as in a $\text{Na}_2\text{Si}_2\text{O}_5$ glass is shown. Energy scale is relative to edge position of spectra.

References:

- [1] Ellison AJ, Hess PC (1986) *Contrib. Mineral. Petrol.* **94** 343
- [2] Stechern A, Wilke M, Schmidt C, Pascarelli S, Manning CE, Rickers K (in press) *Journal of Physics: Conf. Series.*

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