XAFS measurements on Zr in aqueous fluids at high pressures and temperatures using a modified hydrothermal diamond-anvil cell

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Abstract. Aqueous fluids play a significant role in the transport of heat and matter in the Earth's crust and the upper mantle, and high-field-strength elements such as Zr are important geochemical tracers for these processes. However, the dissolution mechanism and complexation of Zr in the fluids at high pressure and temperature are unknown, in part because very low concentrations present severe experimental challenges. Here, we present an experimental setup for in-situ investigation of the coordination environment of elements at low concentrations in aqueous fluids up to 800 °C and 1.5 GPa using XAFS. Experiments were carried out in a modified hydrothermal diamond-anvil cell optimised for the detection of the fluorescence signal. We have investigated the effects of silicate components dissolved in aqueous fluids on the Zr solubility and complexation at high pressure and temperature. The observed Zr concentrations in fluids containing 7-33 wt% $Na_2Si_2O_5$ and variable Al contents were between 75 and 720 ppm at 500 to 750°C and ~300 MPa to ~700 MPa. Initial XAFS results show clear differences between spectra of Zr in an HCl solution and in an H_2O-$Na_2Si_2O_5$ aqueous fluid, implying considerable differences in the Zr complexation.

1. Introduction

The geochemical behavior of high-field-strength elements (HFSE), like Zr, Hf, Ti and Nb, in aqueous fluids at high pressure (*P*) and temperature (*T*) is fundamentally important to understand geological settings such as subduction zones, where processes of magma evolution and element transport are complex and poorly known. The possibility of *in-situ* experiments at high *P* & *T* is a strength of synchrotron-radiation based analytical methods. Therefore, synchrotron radiation X-ray micro-fluorescence (SR-μXRF) as well as X-ray absorption micro-spectroscopy (μ-XAS) have gained importance for earth and planetary sciences over the last years, particularly for the investigation of fluids under *in-situ* conditions [1] [2]. For this purpose, pressure devices, like the hydrothermal diamond-anvil cell (HDAC), have been modified for X-ray spectrometric measurements [3][4]. With the setup used here, fluids can be studied at conditions ranging up to a temperature of 800 °C and

pressures of 1.5 GPa. These techniques offer novel opportunities for the in-situ study of key elemental tracers, such as the HFSE.

Standard μ-XAS beamlines operate with scanning monochromators. The major challenge for these setups is the angular stability of the beam after the monochromator, and as a consequence the stability of the focal spot position in the scanned energy range. In contrast, an energy dispersive XAS beamline, which is optimized for both transmission and fluorescence detection, features a rigorously stable focal spot, in both position and shape, and offers the possibility of a rapid acquisition time for the spectra [5]. Here, we present results on Zirconium in aqueous fluids collected at the K-edge using the energy-dispersive XAS beamline ID24 at the ESRF, Grenoble, France.

2. Experimental

### 2.1. Diamond anvil cell and sample composition

In-situ high-temperature and high-pressure experiments were performed using a modified Bassett-type HDAC. This cell has a focused-ion-beam milled recess with a diameter of 200 μm and a depth of 80 μm in the culet face of the lower anvil. This modification allows acquisition of the fluorescence signal from the sample in the recess at 90° to the incident beam. This assembly has the advantage that even XAS spectra in very dilute samples can be acquired in fluorescence mode. Use of a recess avoids possible contributions from phases in other areas of the sample chamber to the XRF signal.

The sample chamber of the cell consists of the recess in the culet face of the diamond anvil and a cylindrical hole in a polished Re gasket, which seals the cell and separates the two diamond anvils from each other. The gaskets had an initial inner-hole diameter of 510 μm and a thickness of 120 μm. A synthetic zircon, a silicate glass chip and distilled water were loaded into the gasket hole. The glass compositions ranged from $Na_2Si_2O_5$ to $Na_2Si_2O_5$ + X wt% Al, where X varied between 0.5 and 5 wt%. These compositions were used because the Na/Al ratio of silicate components dissolved in fluids at high P & T may play an important role for the zircon solubility and Zr complexation [6]. In one run, no zircon was added and H_2O and a piece of glass doped with 2000 ppm Zr were loaded. The bulk density of the sample was calculated from the sample chamber volume, the size and density of the glass chip, and the water density.

The cell was heated by NiCr-coils around the tungsten carbide seats of the diamonds. Two K-type thermocouples, attached to each diamond, were used to measure the temperature. During heating, all phase transitions were recorded using an optical microscope that was positioned downstream of the cell. From the H_2O liquid/vapor homogenization temperature, measured during the heating, the pressure at the desired experimental temperature can be estimated from the equation of state of water [7]. The experimental conditions were reached after the glass chip has melted and had dissolved in the aqueous fluid to form a homogeneous fluid in the sample chamber.

2.2. X-ray absorption spectroscopy

Zirconium K-edge X-ray absorption spectra were collected at beamline ID24 at the ESRF. Details on the optical scheme of the beamline are described by [5] and are just shortly reviewed (Fig. 1). The optics are based on a vertically and a horizontally focusing mirror in Kirkpatrick-Baez geometry and a horizontally bent Si (111) Laue polychromator crystal. A second vertically focusing mirror is positioned downstream of the polychromator to refocus the beam on the sample. The focal spot size achieved with this setup was <20 μm FWHM. The maximum energy range achieved was about 1200 eV at the Zr K-edge. The incident photon flux, I_0, was monitored using a Si diode collecting the scattered radiation by a Kapton foil. XAS spectra in fluorescence mode were recorded by a stepwise scan of a 100 μm slit, positioned just downstream of the polychromator (Turbo-XAS [8]). The slit selects a monochromatic beam from the polychromatic fan. A Vortex Si-drift detector was used to record the signal. A typical spectrum consisted of 200 steps with a scan-time of up to 10 seconds per step. Depending on the signal five to ten scans were summed to one spectrum. To calibrate the energy of the absorption spectra, a Zirconium foil was measured in transmission mode and the position of
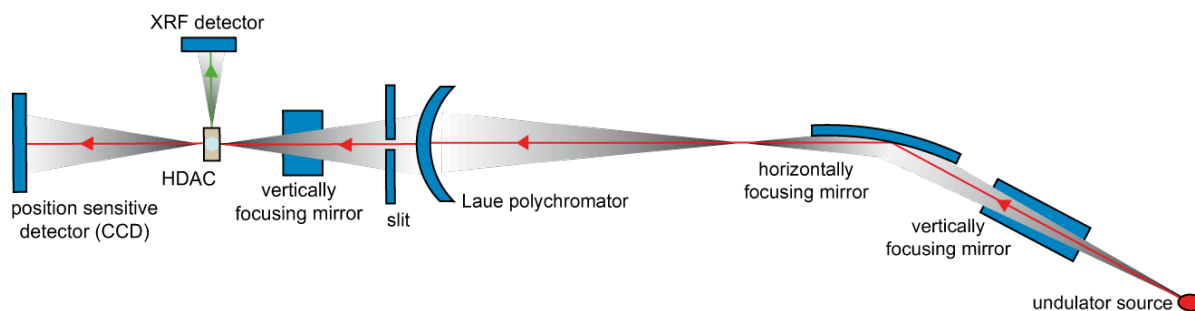
Figure 1. Optical scheme of ID24, modified after Pascarelli et al. 2006 [5].

spectral features on the pixels of the CCD were matched with a spectrum of known energy. The position of the slit was then calibrated against the position on the CCD. Before the acquisition of spectra, the cell was adjusted to the focal spot of the optics and oriented in such a way that no Bragg peaks are present in the energy region of interest. The stability of the optics was repeatedly checked by measurements on a Zr foil.

2.3. X-ray fluorescence spectroscopy

In addition to the XAS measurements, fluorescence spectra were collected at a fixed energy for the determination of the Zr content in the aqueous fluid at experimental *P-T* conditions. XRF spectra with counting times of 100 seconds were taken after equilibration of the sample. XRF signals were calibrated by measuring a Zr standard solution in 7 wt% HCl matrix loaded into the sample chamber. Net fluorescence intensities were determined by fitting the spectra with PyMCA [9]. Intensities were corrected for density, absorption in the fluid and normalized to the intensity of the incoming beam.

3. Results and Discussion

3.1. Zircon solubility

Zr concentrations in equilibrium with zircon are shown in Fig. 2 as a function of the total Al-content of the fluid for various amounts of dissolved silicate melt. Initial bulk densities are also indicated. The observed concentrations range from 75 to 720 ppm at temperatures from 500 to 750°C and do not show a systematic dependence on the Al-content. At this point, the effect of pressure cannot be clearly evaluated. After most runs, the homogeneous fluid phase did not separate back into an aqueous fluid and a melt/glass and no vapor bubble appeared. Instead, a water glass formed and was stable until room *T*. Therefore, the determination of *P* at high *T* was not possible and only the bulk density of the sample before the run is known accurately. Pressures were roughly estimated from the initial water density and the experimental temperature using an EOS of water [7]. These estimates ranged 330 to 630 MPa. For a given initial bulk density and Al-content, the Zr
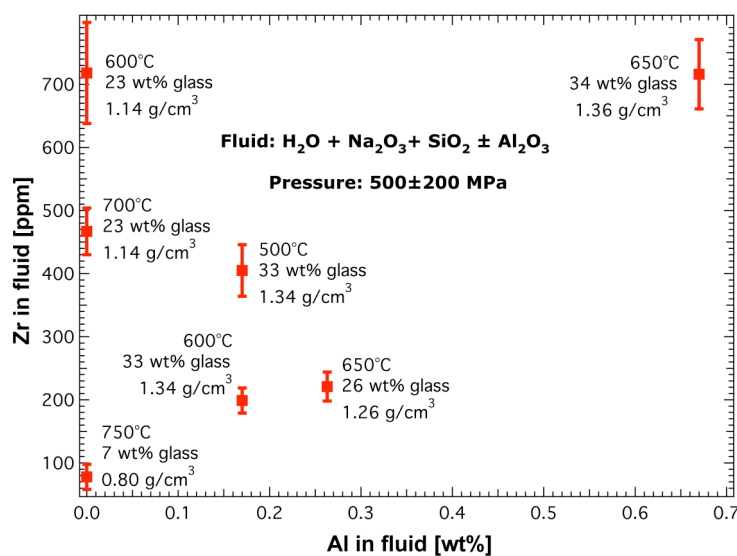
Figure 2. Zr concentrations in zircon-saturated fluids vs. Al content in the fluid. Temperature, glass content and initial bulk fluid density as indicated.

concentrations decrease with increasing T. The solubility values match solubilities calculated from linear interpolation of the maximum solubility in pure H_2O (from the detection limit) and the solubility in the most alkaline high-silica melts reported by Ellison and Hess [10]. Overall, these high Zr concentrations signify that aqueous fluids with alkali silicates are efficient means for HFSE transport.
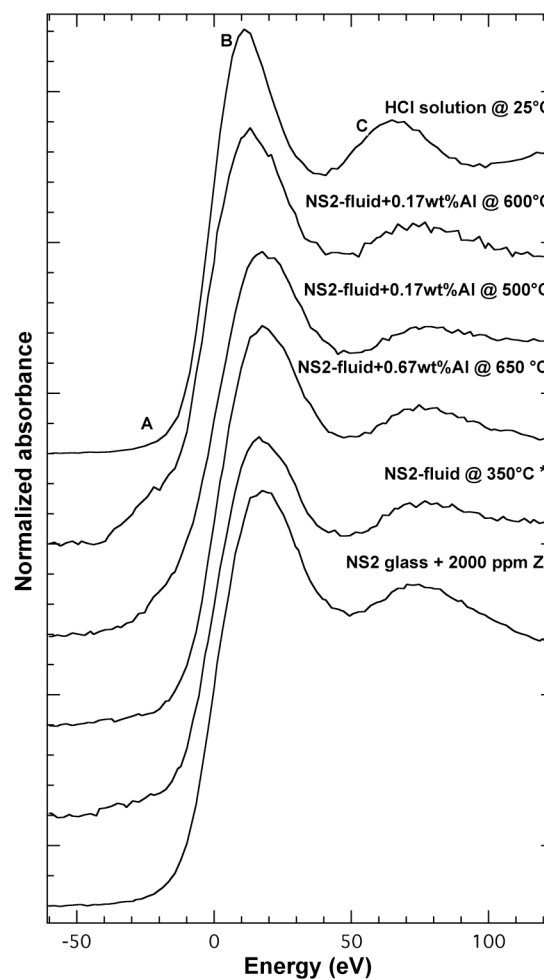
Previous similar work [2] has shown that the amount of Al in hydrous fluids has a strong effect on the rutile (TiO_2) solubility in such fluids. A clear effect of Al in the fluid cannot be observed in our data for zircon. However, most data points presented here cannot be directly compared due to differences in total melt content and bulk density. Effects of these parameters are certainly superimposed and might have a stronger influence on the zircon solubility.

3.2. Zr K-edge XANES

The high solubilty of Zr in alkali-silicate bearing fluids can be explained by complexation of HFSE with Si, Na, and perhaps also Al, via formation of polymerized solutes, as suggested by Manning [7]. To investigate this hypothesis, Zr K-edge XAS spectra were taken on the samples shown above at zircon saturation as well as for a sample below saturation level and are shown in Fig. 3. Spectra taken at high P & T on these fluids are compared to a spectrum taken on Zr in a 7 wt% HCl standard solution as well as to a spectrum taken on a glass at room T doped with 2000 ppm Zr. Clear differences can be observed between the HCl solution and the NS2-fluids. The distance between features B and C is significantly smaller for the HCl solution indicating considerably longer Zr-O distance [11]. No difference in the separation of these features is observed in the NS2-fluids. Spectra of Al-bearing fluids show a small extra feature at position A, which may indicate a difference in the Zr complex compared to that in the binary NS2+H_2O fluid.

Figure 3. K-edge XANES of Zr in aqueous fluids. All NS2-fluids except * are zircon saturated. A glass spectrum is shown for comparison.

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