Insights from X-ray absorption/fluorescence spectroscopy and ab-initio molecular dynamics on concentration and complexation of Zr and Hf in aqueous fluids at high pressure and temperature

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Abstract. High-field-strength elements such as Zr and Hf are important geochemical indicators for processes in the deep Earth. Aqueous fluids play a significant role in the transport of heat and matter in these systems. However, concentrations and complexation of Zr and Hf in these fluids at high pressure (P) and temperature (T) conditions are largely unknown. Zr/Hf contents were determined in-situ at P and T in aqueous fluids containing NaOH, HCl or Na-Al silicate components in equilibrium with zircon or baddeleyite. Concentrations are strongly enhanced in comparison to pure H2O. The variation of Zr/Hf contents with fluid composition and their respective variation with P and T point to differences in the Zr/Hf complexation. High-resolution Zr K-edge XANES spectra were collected in-situ at P and T as well as Hf L3-edge XANES spectra. Analysis of spectra evidences considerable differences in the coordination of Zr and Hf as a function of fluid composition. [7]Zr is found in NaOH solution. [7]Zr is also found in HCl solution, however, coordinated by both chlorine and oxygen. In fluids with Na-silicate components, Zr and Hf are 6-fold coordinated in zircono-silicate complexes, likely complexed with Na and Si. Further insight into the speciation was obtained by ab-initio molecular dynamics simulations of Zr monomers in H2O-NaOH and H2O-HCl. In basic solutions, Zr is five-fold coordinated by oxygen, whereas in acidic solutions, mixed oxychloride complexes are formed. The oxychloride complexes also seem to be present in experimental fluids, whereas the Zr coordination in basic fluids is underestimated by the simulations. The most likely explanation for this discrepancy is the formation of Zr oligomers in the fluid.

1. Introduction

High-field-strength elements (e.g. Ti, Zr, Hf, Nb, Ta) in natural rocks are important petrogenetic indicators for the geochemical evolution of the Earth’s crust and upper mantle. Zr and Hf are predominantly hosted by the accessory mineral zircon (Zr,Hf)SiO4, which occurs in nature as a Zr-rich solid solution between the end-members zircon and hafnon. Dissolution and re-crystallization of zircon therefore strongly controls the mobility of Zr and Hf in processes of the deep Earth (e.g., [1]). How-
ever, very little is known about the solubility of zircon in aqueous solutions at high pressures and temperatures as well as the incorporation mechanism of Zr and Hf in aqueous fluids.

In this study, we used a hydrothermal diamond cell (HDAC) to determine Zr and Hf contents in aqueous fluids in-situ at high P and T by X-ray fluorescence (XRF) spectroscopy. We particularly focused on the influence of Na-Al silicate components dissolved in the aqueous solution. With the same apparatus, the complexation of Zr and Hf in fluids was constrained by in-situ XANES measurements at the Zr K and Hf L3-edges, performed on the fluids in equilibrium with zircon or hafnon. Finally, the complexation of these two elements was investigated using ab-initio molecular dynamics (MD) simulations.

2. Experimental

2.1. Diamond anvil cell and sample composition

In-situ high T and high P experiments were performed using a modified Bassett-type HDAC ([2]). This cell has a recess with a diameter of 200 µm and a depth of up to 80 µm in the culet face of the lower anvil. This modification allows acquisition of the fluorescence signal from the fluid in the recess at 90° to the incident beam. Synthetic zircon or hafnon crystals, a silicate glass chip and distilled water were loaded into the HDAC. In case of HCl or NaOH-solutions, only a crystal and the solution were loaded. The glass compositions ranged from Na2Si3O7, Na2Si3O7 + 5 wt% Al2O3, to NaAlSi3O8. At run conditions the glass chip had dissolved in the aqueous fluid to form a homogeneous fluid. The pressure at the desired experimental T was estimated from the equation of state of water [3] and the vapor-liquid homogenization temperature.

2.2. X-ray fluorescence and absorption spectroscopy

For the zircon solubility study, XRF spectra were collected at beamline L, HASYLAB, using a high bandwidth multilayer (Ni/C) monochromator, and an excitation energy of 21 keV. A single-bounce capillary was used to focus the beam to a spot of about 11 µm in diameter [2]. In addition, a polycapillary was placed in front of the Si drift-chamber solid-state detector. This permitted confocal measurement of the XRF, which substantially improves the fluorescence to background ratio by reducing the signal from inelastic scattering (Fig. 1, [4]).

Figure 1: (left) Photograph showing a top view of the confocal arrangement at beamline L, HASYLAB. (right) Comparison of XRF spectra obtained with and without detector polycapillary.

Hafnium L3-edge XANES spectra were collected at beamline ID24, ESRF. Details on the dispersive optical scheme are described in ref. [5]. The optics is based on a vertically and a horizontally focusing mirror in Kirkpatrick-Baez geometry and a horizontally bent Si (111) Laue polychromator crystal. The focal spot size achieved with this setup was < 5 µm FWHM. XANES spectra in fluorescence mode were recorded by a stepwise scan of a 100 µm slit, positioned just downstream of the polychromator. A Si-drift detector together with a polycapillary half-lens was used to record the fluorescence signal in a confocal arrangement (see above). XRF spectra were also used to determine the solubility of hafnon.

High-resolution XANES spectra at the Zr-K-edge were acquired at beamline ID26 using a high-resolution wavelength dispersive spectrometer in Rowland geometry [6] for fluorescence detection.
and a Si (111) double-crystal monochromator. The spot size was 80 x 120 µm². High-resolution X-ray emission detection was achieved with 4 spherically bent Ge crystals (bending radius 1004 mm) in (888) orientation and a Si drift detector. During XANES scans the emission spectrometer was tuned to the Kα emission line of Zr (15775.1 eV). The convoluted resolution of the monochromator and the emission spectrometer was 2.8 eV.

2.3. Ab-initio Molecular dynamics simulation and XANES calculation

Ab initio molecular dynamical simulations were performed using the Car–Parrinello molecular dynamics code CPMD [7] which implements the density functional theory (DFT) using a plane-wave basis set and pseudo potentials for the core electrons. The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerhof modification to the Generalized Gradient Approximation and Troullier-Martins-type pseudo potentials were used. Gas phase optimized clusters of [Zr(OH)₈]⁴⁺ and [Hf(OH)₈]⁴⁺ with n=1 to 8 were immersed in simulation boxes containing 32 water molecules at densities corresponding to a pressure range of 0.4 GPa to 2 GPa at 1000 K. XANES spectra were calculated using Feff 9.03 [8]. Input structures were either estimated from crystal structures or snapshots taking from the MD trajectories were used.

3. Results and Discussion

3.1. Zirconium and Hafnium concentrations in aqueous fluids

Zircon solubility is strongly enhanced by addition of Na₂Si₃O₇ (NS3) to H₂O (Fig. 2). The degree of enhancement increases with Na₂Si₃O₇ concentration. The Zr content of fluids containing 10 wt% Na₂Si₃O₇ reached up to 86±2 ppm Zr at 550°C and 400 MPa. At 30 wt% Na₂Si₃O₇, the maximum Zr concentration was 997±6 ppm at 600°C and 440 MPa. Zircon solubility in these fluids decreases considerably with pressure and increases slightly with temperature. Addition of Al₂O₃ decreases the zircon solubility. In H₂O-NaAlSi₃O₈ fluids, Zr concentrations are in the sub-ppm to ppm range. Zr concentrations in NaOH solutions in equilibrium with baddeleyite reached up to 390±2 ppm at 600°C and 930 MPa and increase with pressure and temperature (see also [9]). The solubility of hafnon shows quite similar systematics as zircon. However, the maximum absolute Hf concentrations in NS3-bearing fluids are much higher, by a factor of 1.5 on molar basis. The different dependence of the Zr and Hf contents on pressure and temperature in silicate-H₂O fluids and in NaOH-solutions points to different complexation of Zr and Hf. For Na-Al silicate-bearing fluids, Zr and Hf likely complex with silicate components in the fluid.

![Figure 2](image-url)

**Figure 2:** (left) solubility of zircon in aqueous fluid containing 18 wt% Na₂Si₃O₇ (NS3) as a function of pressure and temperature. Tags indicate Zr concentrations in the fluid and lines indicate isopleths of Zr content. (middle) solubility of monoclinic ZrO₂ in NaOH-solution. Tags and lines as before. (right) solubility of hafnon in aqueous fluids with dissolved NS3, NaOH, and HCl-solutions as indicated.

3.2. XANES at Zr K-edge and Hf L₃-edge – constraints on complexation in fluid

In-situ XANES spectra collected on Zr in H₂O-Na₂Si₃O₇, H₂O-Na₂Si₃O₇+Al₂O₃, H₂O-NaOH, and H₂O-HCl fluids in equilibrium with zircon provide evidence for strong differences in the Zr complexation between these fluids (Fig. 3). Comparison of XANES spectra to those of model compounds and ab-
initio simulation of XANES spectra revealed $^{18}$Zr for the standard solution and $^{7}$Zr for the NaOH solution. In the HCl-solution, Zr is coordinated by both O and Cl. $^{6}$Zr and $^{6}$Hf are found for the Na-Al-silicate-bearing solutions and formation of alkali zircono-silicate complexes is indicated by the similarity of XANES spectra to spectra simulated based on the local structure around Zr in the alkali zircono-silicates vlasovite and catapleite [8]. Alkali zircono-silicate complexes are responsible for the enhancement of Zr concentrations in Na-Al-silicate-bearing solutions.

Figure 3: (left) Experimental and calculated XANES spectra at the Zr K-edge of aqueous fluids at P and T for various compositions as indicated. (right) Experimental and calculated XANES spectra at the Hf L$_3$-edge of aqueous fluids at P and T for fluid compositions as indicated.

3.3. MD simulation of Zr-monomers in aqueous solution
For solutions with [Zr(OH)$_n$]$^{4-n}$ and with n=1 to 8, Zr and Hf is five to six-fold coordinated by oxygens (Fig. 4). XANES spectra calculated based on monomers of the MD results do not reproduce the experimental spectrum of Zr in NaOH solution. The experimental spectrum indicates further contributions by a higher coordination shell indicating polymerization of Zr with other components. In HCl-solutions mixed oxychloride complexes are formed in MD runs, which is consistent with the experimental results (Fig. 3).

Figure 4: (left) Zr coordination in fluids with [Zr(OH)$_n$]$^{4-n}$ with n=1 to 8. (middle) snapshot of MD runs for 4-fold and 5-fold coordinated Zr monomers. (right) XANES spectra calculated with Feff based on indicated MD simulations in comparison to Zr measured in NaOH solution.

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