

# Solubility of zircon in $\text{H}_2\text{O}-\text{Na}_2\text{Si}_3\text{O}_7$ solutions determined using a confocal setup for micro-XRF experiments with diamond-anvil cells

C. Schmidt, M. Wilke, K. Appel<sup>1</sup>, M. Borchert<sup>2</sup>, and L. Vincze<sup>3</sup>

Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum (GFZ), Section 3.3 Chemistry and Physics of Earth  
Materials, Telegrafenberg, 14473 Potsdam, Germany

<sup>1</sup>HASYLAB/DESY, Notkestr. 85, 22607 Hamburg, Germany

<sup>2</sup>Institut für Geowissenschaften, Universität Potsdam, Karl-Liebknecht-Str. 24/25, 14476 Potsdam-Golm, Germany

<sup>3</sup>Department of Analytical Chemistry, Ghent University, Krijgslaan 281, 9000 Gent, Belgium

The concentrations of high-field-strength elements (Ti, Zr, Hf, Nb, Ta) in natural magmatic rocks are important petrogenetic indicators in studies of the evolution of the Earth's crust and upper mantle. Zirconium and hafnium are predominantly hosted by the accessory mineral zircon ( $\text{Zr,HfSiO}_4$ ), the solubility of which in aqueous fluids and melts therefore strongly controls the mobility of Zr and Hf in geological processes (e.g., [1]). However, very little is known on the solubility of zircon in aqueous systems at high pressures and temperatures [2-4]. Particularly the influence of dissolved silicate components has not been studied, but can be expected to enhance Zr concentrations in the fluid by orders of magnitude in comparison to that in pure water, based on the considerable solubility of Zr in silicate melts (e.g., [5,6]).

The experiments were conducted using modified hydrothermal diamond-anvil cells (HDACs) as described in detail in refs. [7] and [8]. A zircon crystal was loaded into the sample chamber of the HDAC together with a piece of  $\text{Na}_2\text{Si}_3\text{O}_7$  glass and water. The weight fraction of glass relative to water was calculated from sample chamber volume, water density, and size and density of the prepared glass chip. The concentration of dissolved Zr in the fluid was then analyzed at various  $P$ - $T$  conditions in the one-phase fluid field using time-resolved SR-XRF analyses until the system had equilibrated. The XRF spectra were acquired at beamline L at HASYLAB using a high bandwidth multilayer (Ni/C) monochromator, an excitation energy of 20 keV, and a single-bounce capillary to focus the beam to a spot in the fluid of about 11 microns in diameter [4]. In addition, a glass polycapillary (XOS<sup>®</sup>) providing a focal spot of ca. 150  $\mu\text{m}$  (at 16.6 keV) at a focal distance of 50 mm was placed in front of the energy dispersive Vortex<sup>®</sup> Si drift-chamber solid-state detector (Fig. 1). This permitted confocal measurements, with several advantages for multiphase experiments using diamond-anvil cells. Collection of unwanted XRF signal is significantly suppressed, e.g., from co-excitation of the mineral by scattering in the upstream diamond anvil or from contamination outside the HDAC sample chamber (Fig. 1). This significantly facilitates the experiments, particularly because the actual location of the mineral relative to the recess in the sample chamber of the HDAC is less crucial. Moreover, the background intensity from Compton scattering along the path of the incident beam through the diamond anvil is much lower in the XRF spectra acquired using the confocal setup. Comparison of XRF spectra of a standard solution containing 1300 ppm Zr showed that this results in a slight decrease in the lower limit of detection for Zr to  $\sim 1$  ppm, although the total intensity is reduced by a factor of 3.4 for Zr  $K\alpha$  in the spectrum acquired with the detector capillary (Fig. 1).

Figure 2 shows the determined zirconium concentrations in the fluid upon equilibration of zircon in  $\text{H}_2\text{O}+\text{Na}_2\text{Si}_3\text{O}_7$  mixtures as a function of pressure for several temperatures. At constant temperature, the Zr solubility decreases slightly with pressure. This points to a significant dependence of the speciation in the fluid on pressure. The overriding effect, however, is the strong increase in the Zr solubility with  $\text{Na}_2\text{Si}_3\text{O}_7$  concentration, which signifies that aqueous sodium silicate fluids are efficient means for transport of Zr (and other HFSE) via formation of Na-Si complexes.

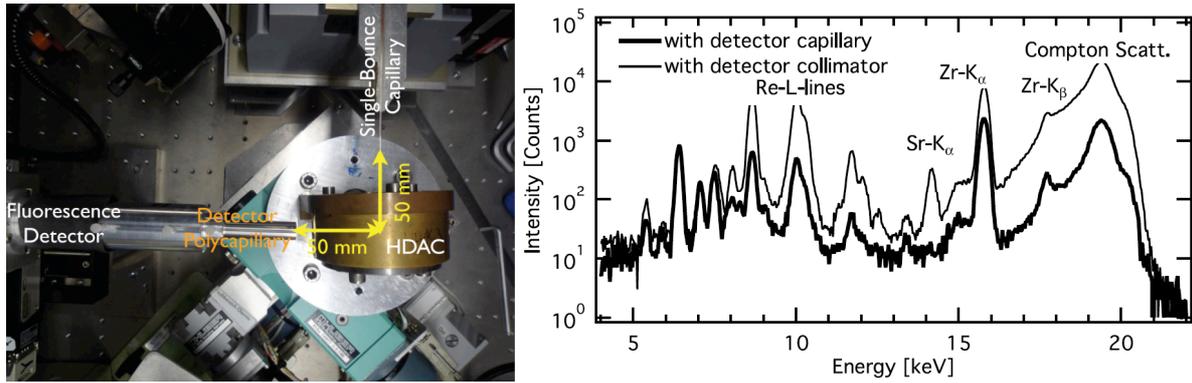


Figure 1: Left: top view of the experimental configuration at beamline L, HASYLAB. Right: comparison of XRF spectra of a standard solution containing 1300 ppm Zr in the HDAC. The spectrum collected with the collimator shows a Sr K<sub>α</sub> peak from a contamination outside the sample chamber, which is not present in the spectrum measured using the confocal setup with the detector capillary.

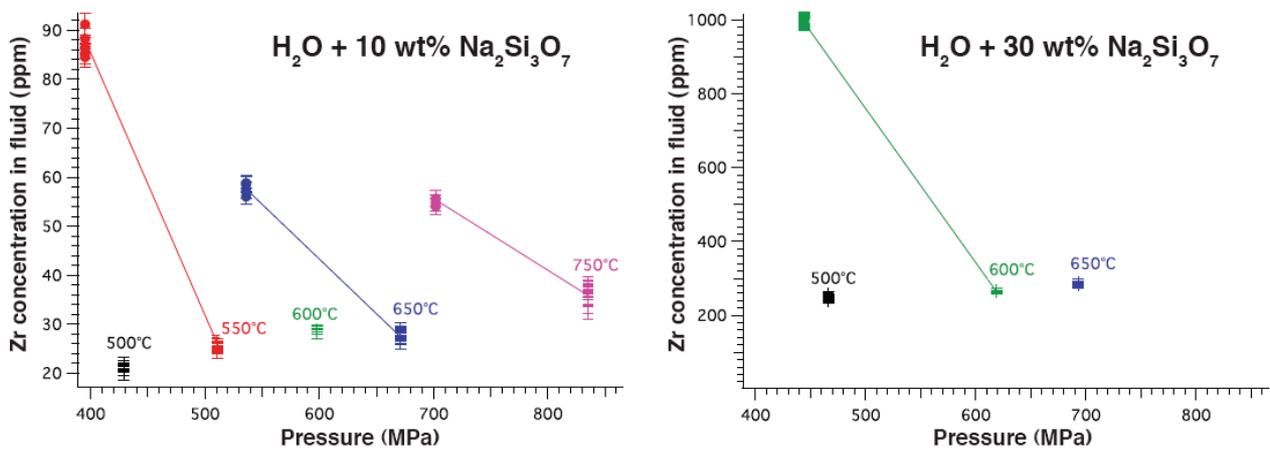


Figure 2: Determined Zr concentrations upon dissolution of zircon in aqueous sodium silicate fluids.

## References

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