Hf-Zr fractionation during dissolution of zircon and hafnon in H_2O-$Na_2Si_3O_7$ solutions

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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 $(Zr,Hf)SiO_4$, 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 solutions at high pressures and temperatures [2-4]. In this we focus on the influence of dissolved silicate components, which to enhance Zr concentrations in the fluid by orders of magnitude in comparison to that in pure water ([5]). Here, we present results of experiments on the simultaneous dissolution of zircon and hafnon (Hf end-member of zircon) in order to asses the chemical fractionation of these two elements.

The experiments were conducted using modified hydrothermal diamond-anvil cells (HDACs) as described in detail in refs. [4] and [6]. A zircon and a hafnon crystal were loaded into the sample chamber of the HDAC together with a piece of $Na_2Si_3O_7$ 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 pre-prepared glass chip. The concentration of dissolved Zr and Hf 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 21 keV for Zr and 11 keV for Hf. 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 was placed in front of the energy dispersive Vortex© Si drift-chamber solid-state detector. This permitted confocal measurements, which substantially improves the fluorescence to background ratio ([7]).

Figure 1 shows the determined hafnium and zirconium concentrations in the fluid upon equilibration of hafnon or hafnon & zircon with $H_2O+Na_2Si_3O_7$ mixtures as a function of pressure and temperatures. The data were acquired approximately along isochores. The highest Hf concentrations were achieved for the run with only hafnon and a fluid with 31 wt% $Na_2Si_3O_7$ (300-350 ppm). This is consistent with earlier results on the enhancement of zircon solubility in fluids containing sodium-silicate component [5]. Hf concentrations are substantially lower (ca. factor 2) in the run equilibrated with both hafnon and zircon although the difference in $Na_2Si_3O_7$ content is not significant. Zr concentrations in the same run are only between 30-40 ppm. The molar Hf/Zr ratio for this run is shown in Fig. 2 and lies between 2.6 and 2.7 for the conditions investigated. This implies that equilibration of natural zircon-hafnon solid solutions with alkaline silicate-bearing fluids will lead to substantial fractionation of these two elements.

A single measurement of the Zr concentration measured in a fluid containing 6 wt% of $NaAlSi_3O_8$ (Albite) glass yielded about 1 ppm. This date highlights the strong effect of the Na-Al ratio of the fluid on the zircon solubility, which was observed similarly for rutile [8].

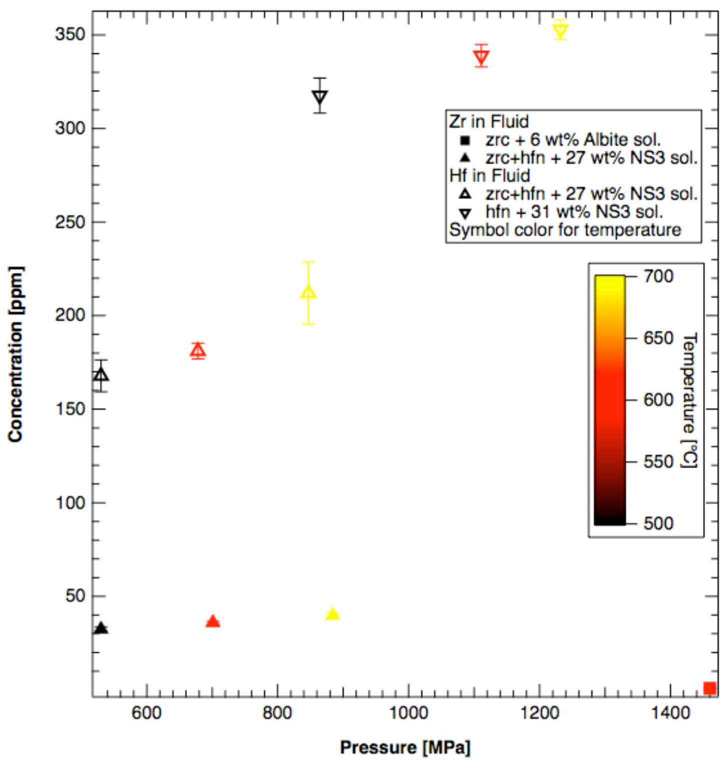

Figure 1: Zr and Hf concentrations in aqueous fluids containing silicate components euilibrated with zircon, zircon+hafnon or hafnon as indicated.

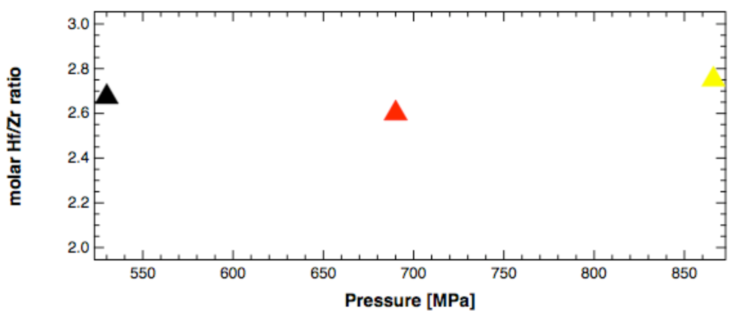

Figure 2: Molar Hf/Zr ratio in aqueous fluids equilibrated with both zircon and hafnon shown in Fig. 1

References

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