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Complexation of Zr and Hf in subduction zone fluids: Insights from ab initio molecular dynamics and x-ray absorption spectroscopy

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Trace element patterns of subduction related igneous rocks display negative anomalies for high field strength elements (HFSE, i.e. Ti, Zr, Hf, Nb, Ta), which is usually explained by retention of these elements in accessory phases like rutile or zircon during fluid-rock interactions at some step of the process at depth. Both phases are known to be quite insoluble in aqueous fluids. Still there is ample evidence in nature that this is not always the case. The solubility of HFSE-bearing minerals and hence the HFSE concentration in the fluid is controlled by the solute speciation in the fluid. The speciation strongly depends on the chemical composition of the involved phases, pH, temperature and pressure. While Zr and Hf are almost insoluble in pure water, the solubility increases in strongly basic or acidic environment. Very high concentrations have also been measured when the fluid contains alkali silicate components (Wilke et al., 2011). To understand the molecular origin of HFSE mobilization, we have started a systematic computational and experimental investigation of the Zr and Hf speciation under various geologically relevant conditions. Here, we present first results on the complexation of Zr and Hf monomers in H_2O-NaOH and H_2O-HCl solutions under subduction zone conditions ($P = 0.5 - 2.0$ GPa, $T = 1000$ K) obtained by ab initio molecular dynamics simulations. While for the basic solutions, Zr and Hf are essentially five- and six-fold coordinated by oxygens, mixed oxochloride complexes are formed at acidic conditions. Finally, the simulation results are compared to recent in-situ XANES data of fluids with similar compositions. While the oxochloride complexes seem to be present in the experimental samples as well, the Zr coordination in basic fluids is underestimated in the simulations. The most likely explanation for this discrepancy is the formation of oligomers in the fluid, which needs to be considered in future modeling.

Wilke et al. (2011) Mineral. Mag. 75, 2160.