

Zr and Hf speciation in aqueous fluids at high P and T

SANDRO JAHN AND MAX WILKE

GFZ German Research Centre for Geosciences,

Telegrafenberg, 14473 Potsdam, Germany

e-mail: jahn@gfz-potsdam.de; max@gfz-potsdam.de

Transport properties of metal cations in hydrothermal and subduction zone environments are strongly related to the solubility of the metal-bearing minerals in co-existing aqueous fluids or silicate melts. The high-field strength elements (HFSE) Zr and Hf are usually considered relatively immobile due to their very low solubility in H₂O. However, recent studies (e.g. [1]) showed substantially increased Zr concentrations in alkali silicate or acidic aqueous fluids. To constrain better the conditions under which HFSEs are mobilized we need to understand their complexation and coordination in the fluid. *In-situ* x-ray absorption spectroscopy at high pressures, *P*, and temperatures, *T* [1,2] provides evidence for the formation of alkali zircono-silicate complexes in the silicate-bearing and oxo-chloridic complexes in Cl-bearing acidic fluids. So far, the interpretation of these experimental results was based on comparison to crystalline model compounds and on theoretical XANES spectra of simple clusters representing possible coordination environments.

Here, we develop more realistic structure models for Zr and Hf speciation in aqueous fluids at high *P* and *T* by performing *ab initio* molecular dynamics simulations. In this presentation, we mainly discuss monomeric species in HCl and NaOH solutions at *T*=1000 K and pressures of about 1 GPa. In all cases, both Zr and Hf are predominantly in octahedral coordination, i.e. surrounded by six nearest neighbor anions (O or Cl). The coordination number decreases somewhat towards a pure water solvent. *Ab initio* simulations and theoretical XANES spectra computed from snapshots of the molecular dynamics simulations indicate that the most probable complexes in chloridic solutions are [(Zr,Hf)Cl₄(Cl,OH)(H₂O)]⁻. The agreement of computed and experimental XANES spectra is less satisfactory for NaOH solutions, which suggests the formation of larger oligomeric Zr or Hf complexes in these fluids. Spectroscopic signatures obtained from some of these more complex molecular species will be presented and discussed.

[1] Wilke *et al* (2012) *Earth Planet. Sci. Lett.* **349-350**, 15-25

[2] Louvel *et al* (2013) *Geochim. Cosmochim. Acta* **104**, 281-299