Yttrium speciation in Cl- and F-bearing aqueous fluids - an ab initio molecular dynamics study

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Aqueous fluids are considered important carriers for rare earth elements (REE) in a variety of geological environments including settings associated with hydrothermal ore deposits or subduction zones. The capacity to mobilize REE strongly depends on the chemical compositions of the fluid and the presence of suitable ligands such as fluoride, chloride, sulfate or carbonate ions. Especially the role of fluoride in the transport of REE in aqueous fluids is still controversial (e.g. [1]). Here, we choose yttrium as a representative of the heavy REE and study its complexation with chloride and fluoride in aqueous fluids between 1.3 GPa to 4.5 GPa and temperatures up to 800 °C using ab initio molecular dynamics (AIMD) simulations. The model systems with approximately 260 atoms describe a two molal NaCl brine with dissolved YCl_n or YF_n (n=1-3) complexes. Some changes in the Y speciation are observed directly on the AIMD time scale of a few tens of picoseconds. To obtain a quantitative understanding of the thermodynamic stability of different yttrium fluoride and chloride complexes, we used the potential of mean force approach to predict the free energy change of dissociation reactions. The interpretation of the simulation results is complicated by hydrolysis events, which leads to the formation of HF and hydroxide ions that also act as ligands for the yttrium cations. Nevertheless, we find a decreasing stability of Y-Cl complexes with increasing pressure and an increasing appearance of $Y\text{-}OH^-$ association. Furthermore, at low pressure the stability of Y-F complexes partly depends on the HF formation. The possible effect of increasing $Y\text{-}OH^-$ association on the Y/Ho fractionation observed in geological aqueous systems (e.g. [2]) is discussed.

[1] Migdisov & Williams-Jones (2014) *Miner. Depos.* 49, 987-997; Xing et al. (2019) *Chem. Geol.* 504, 158-176.
[2] Bau et al. (1995) *Contrib. Mineral. Petrol.* 119, 213-223.