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Speciation of La^{3+} in Cl-bearing hydrothermal fluids: Development of a new polarizable force field

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The rare earth elements (REEs) are an important group of elements both geologically as well as economically. The ability of fluids to mobilize the REEs depends on the chemical composition and the presence of suitable ligands such as chloride and fluoride. *Ab initio* molecular dynamics simulations (AIMD) have been used to predict stability constants of various REE complexes under hydrothermal conditions [1]. However, AIMD simulations often suffer from significant finite time and size effects.

Due to their much higher efficiency, classical force fields can overcome some of the shortcomings of AIMD while providing sufficient geochemical insights into fluid properties at hydrothermal conditions. The accuracy of classical force fields for simulations of aqueous electrolytes depends on the representation of ionic charge and size and also on the polarization of the charge densities of solvent and solute. Different polarizable force fields have different representations of polarizability.

Here, we develop a new polarizable force field for La^{3+} in Cl-bearing hydrothermal fluids. The force field is fitted to snapshots of AIMD simulations of La^{3+} and Cl^- ions in water at hydrothermal conditions (773 K,5 kbar). We use maximally localized Wannier functions (MLWFs) along with force and dipole matching techniques to fit the parameters of the potential [2]. Experimental and AIMD data (wherever available) are used to test the validity of the new potential by comparing structural and thermodynamic properties. We also investigate the speciation of La^{3+} in highly concentrated hydrothermal brines for which no experimental/AIMD data exists. Finally, we present dissociation constants of La^{3+} complexes derived from MD simulations with the new potential and discuss their use for parameterizing species-based equations of state for hydrothermal fluids. The latter help us to understand better the role of such fluids in the transport of REEs from the magmatic source to the ore deposit.

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