Speciation of metal ions in aqueous fluids from ab initio molecular dynamics simulations

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Aqueous fluids are important agents in metasomatic, magmatic and hydrothermal processes in the interior and at the surface of the Earth. They do not only change the physical properties of rocks but they are also able to dissolve and transport mineral components. Therefore, they play a key role in accumulating efficiently rare elements such as Be [1] to form significant amounts of respective minerals in magmatic and metasomatic systems. The content of, e.g., rare Earth elements in high grade metamorphic rocks [2] is strongly affected by the occurrence of aqueous fluid.

A starting point for understanding the role of fluids in fluid-rock interactions is to investigate their molecular structure, especially the formation of various solute species, at relevant thermodynamic conditions. Here, we use constrained *ab initio* molecular dynamics simulations in combination with thermodynamic integration [3-5] to investigate the complexation of two metal ions, Be^{2+} and Y^{3+}, in aqueous solutions in a range of temperatures (T) and pressures (P).

In the simulations, we are able to reproduce experimental stability constants of Be-F aqueous complexes at T = 300 K [6] and to make predictions of thermodynamic data in the high T/P range that deviate from earlier extrapolations. We conclude that at high fluoride activity BeF_2(aq) and BeF_4^{2-} are the majority species in late magmatic fluids. This outcome correlates with field observations in Be-rich pegmatites [7]. Further, we compute stability constants of Y species in highly saline solutions as they occur, e.g., in the Earth's deep crust. At ambient conditions our simulation predict $YCl(H_2O)_7^{2+}$ and $YCl_2(H_2O)_6^{+}$ as the only stable species, which is in agreement with experimental data [8]. The speciation changes under high T/P conditions, e.g. of a subducted slab, where we find five different stable aqueous Y-Cl complexes.

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