Computational molecular modeling of ions in aqueous solutions

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Nearly all geochemical processes in the Earth's crust involve the complexation of ions in aqueous fluids. Complexation by ligands such as Cl- and HS- is responsible for the extraction of metals from primary rocks and the formation of ore deposits. Complexation of metals by mineral surfaces limits the aqueous concentrations of biolimiting micronutrients and controls the mobility of toxic metals and radionuclides in soil and groundwater. For the past 50 years, geochemists have sought to develop thermodynamic models of the speciation of ions in complex aqueous solutions. Stability constants and mineral solubilities measured at low P and T can be extrapolated to high PT using models based on the Born theory of ion solvation. However, it is often ambiguous which complexes are necessary to account for measured mineral solubilities. There are a number of reasons why the Born model of aqueous solvation may be unreliable. We now have the ability to explore aqueous solutions at a molecular level using computational quantum chemistry (based on density functional theory) and atomistic simulations (based on classical interatomic potentials) Several examples will be given to illustrate the range of possibilities achievable with a small parallel computing cluster (< 20 nodes). Static calculations on large atomic clusters can be used to predict the structures and energetics of metal complexes on mineral surfaces. Insights from these calculations are used to develop surface complexation models to fit sorption isotherms. Examples include the sorption of As, Cu, U on FeOOH and kaolinite. Ab initio molecular dynamics simulations (100's of atoms, t < 10 ps) can be used to predict the speciation of metals such as Cu and Sn in hydrothermal fluids as a function of pressure and temperature. Classical molecular dynamics calculations allow very large simulations (1000's of atoms, t > 100 ps) that can predict phase separation and equations of state of NaCl-H_2O mixtures. For practical geochemical applications, we need to be able to predict the activities of aqueous species. Direct calculations of ion chemical potentials are possible but at much greater computational expense. It is anticipated, however, that such calculations will become increasingly practical and routine as computational technology develops.

Ab initio molecular dynamics of clay mineral surfaces and interfaces

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Sorption/desorption processes on surfaces or in interlayer spaces of clay minerals play an important role both in natural environments as well as in industrial production. Owing to the structural complexity of clay mineral surfaces it is often difficult to explain in detail the molecular mechanisms of these processes in spite of the application of various experimental techniques. In this situation, computer simulation methods provide a very powerful tool to model particular scenarios and to study surface complexes at molecular level for providing a detailed insight into the adsorption processes.

In this work we discuss ab initio molecular dynamics simulations of interactions between selected clay minerals (namely kaolinite and montmorillonite) and several polar molecules (water, acetic acid and phenoxyacetic-acid derivatives). These interactions are studied with either isolated molecules or entire molecular layers adsorbed on the surfaces or embedded in the interlayer space. Solvent effects are considered by including water molecules explicitly in the simulation. Structural, energetic and dynamic properties are evaluated. The most improtant phenomena in forming the surface complexes with the polar molecules are hydrogen bonds. The kaolinite surface formed from hydroxyl groups is chemically very active and hydroxyl groups are able to act as proton donors or acceptors. On the other hand, the kaolinite surface formed from basal oxygen atoms form only weak hydrogen bonds with polar molecules. In case of a water layer on this surface hydrogen bonds formed among water molecules prevail over hydrogen bonds formed with this surface. In contrast to kaolinite, the surface of the montmorillonite layer is formed only from basal oxygen atoms. Moreover, this layer also posesses an excess negative charge due to isomorphic substitutions within the layer. The models used here are more complex than in the previous cases since the sorption of polar or ionic species can proceed via a cation bridge mechanism. This situation was investigeted and it was found that in the presence of water molecules the surface cation bridge complexes are less stable than the clay+cation complexes in the solution.