

Molecular modeling of geochemical reactions at mineral-water interfaces

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Geochemical reactions such as adsorption and redox reactions at mineral-water interfaces play an important role in many environmental processes, including transport of contaminants and geochemical cycling of elements. Molecular modeling techniques are capable to translate the molecular-scale descriptions of the complex mineral surface reactions to thermodynamic quantities that are useful for the purpose of linking with macroscopic models. The thermodynamic properties can be used in predictive models such as toxic contaminants transport in the subsurface environment. The mechanisms allow for the thermodynamic properties to be extrapolated beyond the conditions at which the thermodynamic properties are determined. By linking molecular scale mechanisms of the reactions to their thermodynamic properties at the interfaces, geochemical processes can be better predicted.

Among many interfacial geochemical reactions, water exchange reaction at mineral surfaces has been recognized to be one of the key factors controlling the surface reactions. However, experimental determination of the rates has been possible only for most aqueous ions and a few simplest polynuclear ion clusters, and much is unknown for water exchange reaction at mineral surfaces. An unanswered question remains: how can water exchange rates and chemical reactivities of aqueous ions in solution be used to understand those at nanoparticles and mineral surfaces? Using a series of realistic molecular structures of aluminum-bearing aqueous ion, ion clusters, nanoparticles, and bulk mineral surfaces as models, kinetic rates of aqueous ion adsorptions are calculated and a linear correlation of the rate as a function of particle size and bond length are established. The results show that the reaction barrier height, the phenomenological activation enthalpy, and logarithm reaction rate scale linearly with the bond distance between water and Al in the structures. With this correlation, well-known solution chemistry such as water exchange is translated to ion clusters, nanoparticles, and extended structure of the mineral surfaces. This contribution illustrates how molecular simulations of interfacial reactions can be used to link molecular scale descriptions to thermodynamic properties of geochemical reactions across the length scale: the solute-to-solid continuum.