

Water structure and dynamics on aqueous barium ion and the {001} barite surface

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Water structure and exchange kinetics are important to a number of fundamental geochemical processes. For example, the rate of dissolution of isostructural materials often correlates with the rate of water exchange on the aqueous cation. However, thus far most computational studies have focused on structure of the mineral surface. Water structure and kinetics are less often studied, yet are necessary to understand such basic properties of the interface such as adsorption energy. In this work, we use an existing molecular dynamics potential model [1] to estimate the water structure and exchange kinetics of aqueous barium ion the barite {001} surface.

Water exchange kinetics were using a correlation function as well as the potential of mean force and a reactive flux. The latter methods involve calculating a transition state theory rate constant through integrating a free energy of activation estimated from a radial distribution function and a transmission coefficient estimated via a reactive flux. It was found that using only the barium-oxygen distance to constrain the reaction coordinate resulted in unphysical results and a solvent organization parameter is necessary. Using these methods, water structure and exchange kinetics surrounding aqueous barium ion fall within the range of experimental estimates.[2] Water-barium distances for the surface ions on the {001} barite surface are very close to those of the aqueous ion, yet the rate constant is significantly faster. This increase in exchange rate is attributed to a relatively hydrophobic, high energy interface.

The calculated water structure of the overall interface is relatively complicated, with up to five distinguishable oxygen positions interacting with both surface sulfates and bariums. This complex structure contrasts to the fit of experimental X-ray reflectivity data, which can only justifiably include a single ordered layer of water that matches unsaturated barium-oxygen bonds.[3] It is unclear at this point how to reconcile of this discrepancy, but there are substantial uncertainties in both the experimental and computational water structures.

This study is the first time the kinetics of water exchange on aqueous barium ion and barite surfaces have been examined using a reactive flux method and as such, represent a significant expansion of this new and hitherto relatively unexplored method to systems of geochemical interest.

References

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Continental erosion averaged over space and time

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Matching rates of denudation at all temporal scales have been used to infer erosional steady state in various mountain belts. What variation in erosion rates is significant or expected from one temporal and spatial scale to another and over a range of tectonic regimes?

Under ideal conditions, the cosmogenic nuclide flux out of a basin can be used to measure the denudation rates that average over millennia for the entire drainage area. Erosion rates measured over shorter timescales (e.g. sediment yield, reservoir infill) show greater variance due to the stochastic nature of erosion and surface process interactions. Short-term measurements miss rare events in a predictable way and because of this property, rates of surficial processes measured over increasingly longer time intervals can incorporate longer intervals of process inactivity, thus producing a different apparent rate of deposition and erosion (Sadler, 1981; Gardner *et al.*, 1987).

We use a new (available from the author) compilation of all previously published and new cosmogenic nuclide-derived denudation rates and sediment-flux measurements for the same basins to evaluate this variability. Despite anthropogenic effects, the majority of sediment fluxes are less than long-term rates of erosion, contrary to that predicted by Gardner *et al.* (1987).

References

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