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Ligand-Exchange Mechanisms and Solvation Dynamics Related to Ion Attachment and Detachment at the Calcite-Water Interface

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The kinetics of water exchange surrounding a mineral's constituent ions in solution are often correlated with dissolution rates, suggesting that the ligand exchange reactions driving ion detachment at the mineral-water interface are activated by mechanisms similar to those that drive water exchange. This tendency to view mineral surface reactions through the lens of ions in solution sometimes diminishes the potentially important roles of surface ligands and interfacial water dynamics in mediating reaction rates. With advances in molecular dynamics simulation protocols for rare events has emerged the ability to test classical hypotheses related to the role of ion solvation dynamics in mediating the kinetics of ion attachment and detachment.

In this research, we have utilized classical molecular dynamics simulations to investigate the kinetics of ion attachment and detachment at obtuse kink sites on the calcite (104) surface. The free energy landscapes for both calcium and carbonate attachment / detachment were computed via Well-Tempered Metadynamics using a set of collective variables that account for interfacial water dynamics and the coordination of the ions by surfacial ligands. The calculated energy landscapes reveal the presence of multiple locally stable states adjacent to the kink site for both calcium and carbonate. Forward Flux Sampling simulations were performed to obtain the forward and reverse rate constants for transitions between each of the free energy basins. The model results indicate that for obtuse kink sites, the first bond breaking event for calcium detachment is the rate limiting step for dissolution, and that carbonate attachment is the rate limiting step for growth. The solvent dynamics at the kink site are influential for both processes. For calcium detachment, over-coordination of the ion by water enables dissociation of a surface ligand. Where carbonate attachment is physically impeded due to the presence of water in the kink site.