

Kinetics of Water Exchange and Ion Detachment at Obtuse Kink Sites on Calcite (104)

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Mineral dissolution rates are often correlated with the kinetics of water exchange surrounding their constituent ions in solution. These reactivity trends suggest that the ligand exchange reactions that drive ion detachment at the mineral-water interface are activated by mechanisms similar to those that drive water exchange. For this reason, cation hydration and dehydration are considered to be important if not dominant factors moderating dissolution and growth. However, dissimilarities between interfacial and solution-borne reactions are also widely recognized. Whereas water exchange reactions are elementary processes consisting of a single reaction step in which a coordinating ligand is replaced by an equivalent ligand, ion detachment reactions are complex chain reactions that involve the dissociation of multiple metal-oxygen bonds and the exchange of both surface and solvent associated ligands.

This research aims to use molecular dynamics simulations of water exchange and ion detachment to clarify the role of ion hydration in moderating the kinetics of calcite dissolution. Consistent with previous studies, simulations of water exchange on calcium in bulk solution indicate that the exchange mechanism is associative in character. Similar results were obtained from simulations of water exchange on calcium at kink sites along the obtuse step edge on the (104) surface. However, the modeled exchange rate was significantly reduced at the kink site compared to solution. The Forward Flux Sampling method was used to calculate calcium ion detachment rates from the kink site and to harvest reactive trajectories. As observed for water exchange, an analysis of the detachment trajectories indicated that calcium detachment is preceded by an increase in the water coordination number at the kink. However, in contrast to water exchange, dissociation of calcium from the kink was also facilitated by a concomitant and transient increase in the number of coordinating surface ligands. This result reinforces the view that ion hydration is a critical component of the ion detachment process; however, it also reveals that surficial ligands are equally important facilitators of ion detachment.