

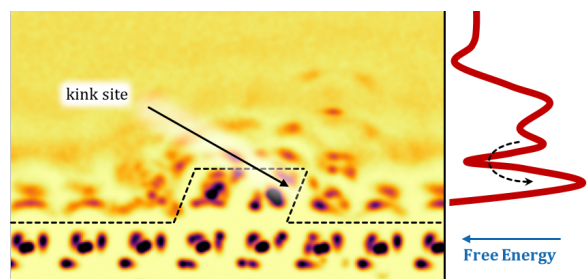
## Molecular simulations of kinetic Ca isotope fractionation at the calcite-water interface

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Kinetic stable isotope fractionation is ubiquitous during mineral growth and can be used as a powerful tracer of subsurface geochemical processes. Even for the very well-studied process of calcite growth from aqueous solution, the mechanisms of kinetic stable Ca isotope fractionation are poorly understood. In principal, these effects arise from the mass-dependence of solvation shell dynamics and ion diffusivities at the mineral-aqueous interface, but a detailed picture of the key rate-limiting phenomena is still under development. We use Umbrella Sampling with Molecular Dynamics to probe the energy barriers of Ca ion attachment and detachment at active growth sites (kink sites) at the calcite-water interface (Fig. 1). A detailed analysis of the potential energy profile in the direction normal to the surface allows us to identify the energies of formation of inner- and outer-sphere complexes. We determine characteristic frequencies at the potential energy minima and use these, together with barrier heights, to estimate the forward and backward reaction rates using Transition State Theory. The applied methodology enables determination of the Ca isotope fractionation factors as a function of temperature. We find that rate-limiting step for calcium ion attachment is partial desolvation from an inner-sphere complex, characterized by a barrier of ~26 kJ/mol, which corresponds to removal of on average 2.2 water molecules from the  $\text{Ca}^{2+}$  solvation shell. These findings validate the long-standing hypothesis that Ca desolvation is the rate-limiting step during calcite growth.



**Figure 1.** Density profiles of calcite-water interface. Free energy barrier for  $\text{Ca}^{2+}$  adsorbed at the kink site.