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The Dissolution Rate of Calcium Carbonate in Seawater

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The dissolution of $CaCO_3$ in the marine water column and surface sediments plays a key role in the alkalinity balance of the ocean as marine biota produce more carbonate than must be buried to balance alkalinity from rivers. In addition, carbonate dissolution at the sea floor will be the main natural buffer for anthropogenic CO_2 emissions. The mechanistic understanding of how this dissolution process works at the solid solution interface requires a deeper understanding than just making the rate proportional to the mineral under saturation raised to some arbitrary power. While the freshwater dissolution rate of calcite is well understood to be controlled by three aqueous elementary reactions, seawater dissolution does not follow the same trend with saturation state.

We have developed a new isotope labeling approach to measure dissolution rates in the lab that is ~200x more sensitive than direct alkalinity or pH measurement. The rate of calcite dissolution is strongly curved relative to the degree of undersaturation. This curvature arises from three distinct surface driven mechanisms that follow the energy available for dissolution; from step edge retreat near equilibrium, to defect assisted and then homogeneous etch pit formation farther from equilibrium. However the surface theory used successfully for quartz dissolution, and aspects of calcite dissolution in freshwater, does not fully explain our data. Both the catalysis by carbonic anhydrase and the temperature dependence show deviations from classic nucleation theory. The complicated physical chemical medium that is seawater provides an important test bed for the development of a full kinetic ‘rate law’. Our work to date shows that the surface driven processes seen in lab experiments are important in the marine water column and that acceleration of CO_2 driven $CaCO_3$ dissolution might be a feasible mechanism to cheaply and effectively store anthropogenic CO_2 on human relevant time scales.

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