

Linking CaCO₃ Dissolution Mechanisms in Seawater vs. Freshwater via Atomic Force Microscopy (AFM) and Implications for CaCO₃ Dissolution in Paleo-ocean

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Although the dissolution/precipitation of CaCO₃ that help regulate atmospheric CO₂ on millennial timescales occur primarily in seawater, almost all previous mechanistic studies on CaCO₃ dissolution were conducted in simple solutions of low ionic strength. Using a ¹³C labeling technique to determine bulk dissolution rates much more precisely near equilibrium, our group has recently shown that calcite dissolution responds to the saturation state (Omega) much differently in seawater than in freshwater. Here we present a new AFM study that compares and links microscale dissolution mechanisms of calcite in seawater vs. freshwater. We find that bulk dissolution rates and step retreat velocities in seawater are slower than in freshwater at high and mid Omega, and become comparable at low Omega. The onset of defect-assisted etch pit formation in seawater is at $W \sim 0.85$, higher than in freshwater (Omega ~ 0.54). The abrupt increase in etch pit density, indicating the transition from defect-assisted dissolution to homogeneous dissolution, also happens much closer to equilibrium in seawater (Omega ~ 0.7) than in freshwater (Omega ~ 0.1). The step retreat velocity does not scale linearly with W in seawater, potentially indicating a high order correlation between kink rate and W for non-Kossel crystals, or surface complexation processes. Combined with bulk calcite dissolution rate measurements with different sulfate concentrations in artificial seawater, we couple the effect of W with the speciation of the solution and mineral surface, and successfully describe calcite dissolution rates via defect-assisted etch pit formation in seawater. These mechanistic analyses serve as fundamentals to further understand CaCO₃ dissolution rates in paleo ocean when ion concentrations (i.e. [SO₄²⁻]) were highly variable through time.