

The role of sulfate on calcite dissolution kinetics in seawater

**HOLLY BARNHART¹, JESS F ADKINS¹, JOHN
NAVIAUX¹, WILLIAM M BERELSON² AND NICK
ROLLINS²**

¹California Institute of Technology

²University of Southern California

Presenting Author: hbarnhart@caltech.edu

The composition of seawater controls the dissolution rate of calcite via changes in saturation state, in part due to aqueous complexation and ionic strength effects. The composition of fluids in contact with the mineral surface can also influence dissolution rates via changes to surface speciation and changes to surface energetic processes (e.g. the rate of step retreat and the nucleation frequency of etch pits). In order to fully describe the mechanistic basis for the dissolution kinetics of calcite in seawater (and in complex solutions, generally) both surface energetic and speciation controls on dissolution rate must be well characterized. Changes in seawater sulfate concentration and undersaturation allow us to probe the effects of both speciation and energetic processes on calcite dissolution rates. Preliminary experiments of calcite dissolution rates in seawater with 24mM sulfate (modern seawater) and 0mM seawater reveal varying impacts on dissolution kinetics depending on the saturation state. Near equilibrium, dissolution rates slow in the absence of sulfate, but far from equilibrium (very undersaturated), dissolution rates are faster in the absence of sulfate. Early interpretations of these results point to surface speciation control on gross fluxes on and off the mineral surface influencing net dissolution rates. Close to equilibrium, the Ca sites on the calcite surface are dominated by carbonate and sulfate complexation. In the absence of aqueous sulfate, more of the mineral surface is complexed with the more stable carbonate complexes, inhibiting dissolution. Far from equilibrium, where aqueous carbonate concentrations are low, the Ca sites on the mineral surface are either complexed with sulfate or are not complexed and considered “free” sites. In the absence of aqueous sulfate, the surface is dominated by the more reactive “free” sites, promoting faster dissolution. Surface and aqueous speciation models can refine these interpretations when coupled to high-resolution data around critical undersaturation values. The implications of sulfate controls on dissolution rates are of particular interest for understanding the preservation of carbonate minerals in reducing environments (e.g. anoxic porewaters) and under past ocean conditions with sulfate concentrations different from modern seawater.