

Dissolution Kinetics of Calcium Carbonate Minerals

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We present a novel method of measuring the dissolution kinetics of calcium carbonate minerals in seawater. Carbonates labeled with ^{13}C are placed in undersaturated seawater in a closed system. The time-evolving seawater $\delta^{13}\text{C}$ is then a direct tracer of mass loss. By using 100% labeled materials, we can measure instantaneous dissolution rates without significantly changing the mass of material or the seawater carbonate system parameters. Our sensitivity is 20‰ $\delta^{13}\text{C}$ per 1 $\mu\text{eq/kg}$ alkalinity increase. Signal to noise ratios of $\delta^{13}\text{C}$ on a Picarro CRDS or traditional gas-source IRMS are roughly 200:1 and 700:1, respectively. We measure seawater Ω to a relative precision of a few percent by alkalinity titration, which is negligible relative to uncertainty in the thermodynamic constants.

Inorganic calcite dissolution rates normalized to BET surface area are highly non-linear as a function of $1-\Omega$, suggesting the possible influence of two separate dissolution mechanisms. Experiments with synthetically grown calcite of multiple grain sizes demonstrate no grain size effect on surface area-normalized dissolution rates. Our rates are also at least an order of magnitude slower than those previously measured.

We are extending our analytical capabilities to more relevant ocean conditions. We have cultured several marine calcifiers in $\delta^{13}\text{C}$ -rich seawater, including benthic and planktic foraminifera and high-Mg calcite soft corals, which we plan on using to investigate biomineral dissolution rates. We have built and tested a pressure chamber to measure dissolution rates at *in situ* ocean pressures, and a modified Niskin water sampling device to perform dissolution experiments at sea.

These results significantly impact our understanding of calcium carbonate response to ocean acidification, water column dissolution, and near-equilibrium mineral-water interactions at *in situ* ocean conditions.