Dissolution Kinetics of Calcium Carbonate Minerals

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We present a novel measurement of the dissolution kinetics of calcium carbonate minerals in seawater. These experiments significantly impact our understanding of calcium carbonate response to ocean acidification, water column dissolution, and near-equilibrium mineral-water interactions at \textit{in situ} ocean conditions.

Carbonates labeled with $^{13}$C are placed in undersaturated seawater in a closed system. The time-evolving seawater $\delta^{13}$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\% $\delta^{13}$C per 1 $\mu$eq/kg alkalinity increase. Signal to noise ratios of $\delta^{13}$C on a Picarro CRDS or traditional gas-source IRMS are roughly 200:1 and 700:1, respectively. We measure seawater $\Omega$ 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 are highly non-linear as a function of $1-\Omega$, suggesting the possible influence of two separate dissolution mechanisms. Geometric surface area, not BET surface area, is shown to be the correct normalization factor for explaining grain size differences among inorganic calcites. Dissolution rates of benthic foraminifera are very similar to those observed in \textit{in situ} ocean experiments.

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