Ca-carbonate nucleation in aqueous solution and its implication for biomineralization

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It still puzzles us that only metastable aragonite precipitated naturally from supersaturated modern seawater, while marine organisms can build their skeletons using either calcite (e.g. mollusks) or aragonite (e.g. corals). Several hypotheses have been proposed to unravel this mystery. Among them, the Mg/Ca ratio of seawater has been suggested to play a significant role. In this study, we systematically investigate how solution chemistry (including Mg/Ca, salinity) affects the nucleation dynamics of Ca-carbonates.

Experiments were conducted to precipitate calcite and aragonite over a range of saturation states, (Ca + Mg)/CO_3^{2-} and Mg/Ca activity ratios between 20-25 ^{o}C. In each experiment, a total of ~3 ml $CaCl_2$, $MgCl_2$, $NaHCO_3$, and NaOH solutions with known concentrations were mixed in a ~3.5 ml polystyrene cuvette (1 cm optical path). Solutions were oversaturated relative to both calcite and aragonite. The turbidity and pH value of the solution were continuously monitored using a fiber optic spectrometer coupled with a CCD detector (measured between 450-900 nm), and a pH micro-probe, respectively. During an experiment, solutions were sampled for observation using phase contrast microscopy and cryogenic transmission electron microscopy at ASRC, CUNY. Induction time in each experiment was deduced from the turbidity variation with time. The saturation state of the solution and ion speciation were calculated using PHREEQC program and the measured pH values. From these data, the interfacial energy between carbonates and aqueous solution can be extracted from the correlation between induction time and saturation states.

Our results show analyses based on turbidity measurements provide a more accurate estimate of the induction-time compared with those based on pH data. The precipitation experiments with similar metal (Ca or Mg)/CO_3^{2-} activity ratios are consistent with classical nucleation theory (CNT), while the interfacial energy, derived from the turbidity data and CNT, systematically increases with decreasing Mg/Ca, and varies with mineral phases.