Nucleation of Ca and Mg carbonates from aqueous solution

ZELING LONG[1,2], AL KATZ[3], CHEN ZHU[4], LIANG ZHAO[4], ZHENGRONG WANG[2,*]

[1]State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Beijing 100083, China
[2]Department of Earth and Atmospheric Sciences, CCNY, CUNY, New York, NY 10583, USA
[3]Department of Physics, CCNY, CUNY, New York, NY 10583, USA
[4]Key Laboratory of Surficial Geochemistry, Nanjing University, Nanjing 210093, P.R. China

Naturally-occurring carbonates represent an essential sink in global carbon cycle. They are also an archive of geochemical proxies which are frequently used to infer environmental histories and biomineralization processes. Studying factors controlling carbonate precipitation can potentially improve our capability to solve geological problems involving carbonates.

More than 200 experiments were conducted to understand the effect of solution chemistry on the nucleation of Ca- and Mg-bearing carbonates. In each experiment, about 3.0 ml of solution was mixed in a 3.5 ml semi-micro polystyrene cuvette from $CaCl_2$/$MgCl_2$, $NaHCO_3$, and NaOH with known concentrations. Solutions were oversaturated relative to calcite/nesquehonite. Experiments were carried out over a range of saturation states and cation (Ca or Mg)/CO_3^{2-} ratios between 15 and 40 ^{o}C, and the turbidity and pH of the solution were continuously monitored using a fiber optic spectrometers coupled with a CCD detector (measured at 700 nm wavelength), and a pH micro-probe, respectively. 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 measured pH values.

Our experimental results show analyses based on turbidity results provide a more accurate estimate of the induction-time compared with those based on pH data. Our precipitation experiments with similar metal (Ca or Mg)/CO_3^{2-} activity ratios are consistent with classical nucleation theory (CNT), while the surface energy derived from CNT varies with metal (Ca or Mg)/CO_3^{2-} activity ratios. Although the induction time decreases with increasing temperature, the surface energy has a rather low temperature sensitivity. A quantitative model is presented to explain these results.