

TOWARD A MECHANISTIC UNDERSTANDING OF CALCITE MINERALIZATION IN SEAWATER

WATERS, Jason F., Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The earth science community is widely using minor and trace elements contents in carbonate minerals as indicators of paleoenvironmental conditions. Researchers in paleothermometry have found, however, that ratios of Mg/Ca and Sr/Ca in marine calcium carbonates do not always faithfully preserve the environment of formation through these ‘signatures’. Rather, these ratios can be influenced by the organism during mineralization by phenomena broadly known as ‘vital effects’. To better interpret past environmental conditions from these compositional signatures, there is a significant need to understand fundamental growth processes and the corresponding factors that control trace and minor element contents.

To date, considerable insights into controls on compositional signatures have been gained from *in situ* studies of calcite growth. Using Atomic Force Microscopy (AFM), these experimental efforts have provided a direct means for determining fundamental physical controls of carbonate signatures. In studies that used carefully controlled growth solutions with a background salt of 0.10 M NaCl, research in our group has given an explanation of:

- The processes by which Mg influences step dynamics and hillock morphology on the faces of an anisotropic mineral surface
- The kinetic effects that cause greater uptake of Mg²⁺ in calcite crystal surfaces than is predicted by equilibrium partitioning models
- The different interactions of Sr²⁺ and Mg²⁺ with growing calcite surfaces
- The relationship between Sr²⁺ concentration and calcite growth rates

While these findings provide an important baseline of understanding into the controls on elemental signatures, they are nonetheless limited in their application to marine environments. Seawater, with an ionic strength of approximately 0.69 M, has a very high salinity compared to the 0.1 M solutions studied to date. The high concentrations of ions, particularly NaCl, in these solutions complicate the chemistry of these waters and call for a group of experiments to validate that growth and impurity behaviors determined in the 0.1 M NaCl solutions are also applicable to the higher salinity seawater.

Toward that goal, this study investigated the relationship between calcite growth kinetics and ionic strength. Measurements of calcite growth kinetics were conducted using fluid cell AFM in solutions with carefully controlled chemical compositions that held the background concentration = 0.7 M. Solutions constrained the pH = 8.5, the saturation state with respect to calcite = 1.6, and the ratio of $a_{\text{Ca}^{2+}} : a_{\text{CO}_3^{2-}} = 1$. Experimental results show the effect of increasing ionic strength on calcite step growth rates when saturation state, the chemical driving force, is held constant. Experiments also showed that this rate of growth at an ionic strength of 0.70 M is constant over the duration of long term growth experiments. We also found that Mg modifies growth kinetics by the same trends seen in the 0.1 M NaCl experiments. These findings indicate it is possible to conduct *in situ* calcite growth experiments in solutions that model the ionic strengths of natural marine environments and give early evidence that the basic principles established in 0.10 M NaCl may also be applicable to the higher salinity of seawater.