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Kinetics and thermodynamics of Sr and Mg interactions with calcite during growth: Deciphering mineralization processes

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The problem

Over the last 50 years, Earth scientists have noted systems where biologically-produced minerals contain compositional signatures reflecting the organisms environment. Reliable interpretation of paleoenvironments from proxies require sorting desired environmental signals from vital effects. Ongoing questions surround the nature of Sr and Mg interactions with calcite to affect growth rate, polymorph of the biogenic carbonate that forms and the relative contributions of vital effects versus environment to compositional signatures. We examine nanoscale effects of key proxy elements, Mg and Sr, on calcite formation in the absence of vital effects to investigate relations between growth conditions and composition.

Approach

Nanoscale effects of Sr and Mg on calcite growth were determined under carefully controlled solution chemistry and growth mechanism. By *in situ* atomic force microscopy, we directly measured rates of monomolecular (3.1A) step flow and growth hillock properties that yield the surface thermodynamics for each condition. Experiments were designed with Sr/Ca and Mg/Ca ratios comparable to some intracellular fluids associated with controlled mineralization.

Mg and Sr cause element-specific effects on growth

Though geochemically similar, Mg and Sr have sharply dissimilar effects on growth kinetics and step structure. Increasing Mg concentrations cause monotonic decreases in step velocities as previously documented by our group. In contrast, low levels of Sr *increase* step flow rates. As Sr levels are increased to approximate those found in modern seawater, Sr pins step edges to halt further growth. Our finding that Sr acts as a growth promoter when present at low concentrations may be surprising in the context of crystal growth models, but the data show that the faster rates are a kinetic effect manifest as an increasing kinetic coefficient.

Although low levels of Sr enhance growth, both Mg and higher Sr levels can *inhibit* calcite growth to stabilize the higher energy polymorph, aragonite, by different processes: Higher Mg levels inhibit growth by resulting in the more soluble Mg-calcites, thus lowering driving forces for growth. In contrast, higher Sr concentrations abruptly poison calcite growth. Perhaps by regulating Sr levels, organisms can exert nanoscale control on the CaCO₃ polymorph that forms.

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Sensitivity of calcite growth rate to solution Mg/Ca increases with increasing temperature

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Biological processes control many aspects of biomineral formation. At a fundamental level, however, mineral growth is subject to thermodynamic and kinetic constraints imposed by the conditions of formation. Crystal growth rates, in particular, are sensitive to subtle changes in temperature or chemical composition of the growth medium. These factors could influence biomineral size, morphological fidelity, time for an organism to reach maturity, and, possibly, trace element composition. Some highly abundant calcite producers, such as the coccolithophorid algae, are found over a wide range of temperatures; it is important to understand how major controls on biomineralization processes vary with environmental conditions.

We have quantified growth rates for calcite, in the form of monomolecular step speeds, as a function of temperature (15°-30°C), degree of supersaturation, and fluid [Mg]/[Ca], by atomic force microscopy. Our experiments were conducted in the inorganic system; thus we have examined only thermodynamic and kinetic effects on growth. Real-time, *in situ* measurement ensures that growth occurred by the layer growth mechanism. We find that growth rate has substantially higher sensitivity to solution chemistry at higher temperatures. Multiple linear regression of our step speed data enables comparison of the relative contributions of temperature and solution chemistry to crystal growth rate. For example, at 12°C, a typical temperature for coccolithophores in the Baltic Sea, assuming certain starting conditions, calcite growth rate doubles as fluid [Mg]/[Ca] is decreased by 40%. By contrast, at a temperature of 25°C, such as algae experience in the Gulf Stream, an equivalent change in step speed can be achieved with a 19% decrease in [Mg]/[Ca]. Thus, aside from effects imposed by nutrient limitations or enzymatic factors, organisms in warmer waters will have mineral growth rates more sensitive to subtle changes in fluid chemistry. If regulating growth rate is important for biological success, more strict regulation of fluid compositions, including [Mg]/[Ca], is required.

The next crucial step is to determine how crystal growth rates affect Mg partitioning into calcite. Studies in the literature disagree on whether there is such an effect; determining this is critical to interpreting paleoproxies in natural carbonates.