

## NANOSCALE MECHANISM OF MINOR AND TRACE ELEMENT COMPOSITIONS IN CARBONATE BIOMINERALS: ESTABLISHING ORIGINS OF VITAL EFFECTS

STEPHENSON, Allison E., Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The chemical composition of biominerals can reflect the conditions of the environment in which they form. Many studies have positively correlated Mg content in biogenic carbonates with temperature, but it is difficult to differentiate the effect of temperature from other environmental factors such as precipitation rate, salinity, pH, and ion concentration. It is also difficult to distinguish environmental signature from the ‘vital effect,’ or the elemental signature superimposed by the organism. In addition to recording surrounding chemical and physical conditions, minor and trace elements affect the growth kinetics and crystal morphology in distinct ways. In order to construct viable paleoenvironmental proxies from biomineral compositions, we must first sort out the underlying thermodynamic and kinetic mechanisms for inorganic incorporation of trace elements from the vital effects’ of the organism.

Recent findings from our group showed that acidic biomacromolecules, such as those commonly isolated from sites of biomineralization, greatly enhance the kinetics of calcite growth in a predictable manner (Elhadj et al., *PNAS*, 2006). This enhancement likely arises from their influence on the structure of water near calcite surfaces by processes that lower the energy barrier to dehydration of calcium into the crystal structure (Elhadj et al., *CGD*, 2006).

Dehydration of the cation is generally agreed to be the rate limiting step in the growth of sparingly soluble crystalline materials. Because Mg and Sr contents in calcite are known to increase with an increasing rate of growth and because Mg is a strongly hydrated cation, we hypothesized that biomolecules may increase the impurity contents. This could come about by increasing the rate of growth through influence on calcium ion or by the combined effect of also lowering the barrier to dehydrating and incorporating Mg.

To test this idea, we used *in situ* AFM to measure the growth rate of calcite at the nanoscale under controlled solution compositions and at characterized chemical driving force.

The relationship between the presence of carboxyl-rich peptides in solution during growth and the magnesium content in the calcite overgrowths is quantified using time-of-flight SIMS. This new work with ToF-SIMS has validated previous compositional maps of Mg distributions collected by electron microprobe, and has yielded new insights into controls on impurity content.

The presence of polypeptide causes increases in Mg content, with greatest enhancement on the positive step directions, where Mg contents are increased up to 2-fold.