

Calcification by Amorphous Pathways: Revisiting mineralization process(es) and controls on compositional signatures

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Carbonate biominerals contain impurities and other composition information that may be used to infer past environments. Molluscs, which occur in coastal habitats worldwide over spans of geologic time, offer remarkable opportunities to decipher shifts in environmental conditions. Early studies are founded on the assumption that composition and isotopic signatures reflect partitioning between mineral and local environment during growth by an ion-by-ion attachment process. Realization that some biominerals begin from amorphous phases raises questions of where and how signatures are determined during the path to crystal products.

This presentation highlights findings from our recent studies of the amorphous calcium carbonate (ACC) to calcite and aragonite transformation to quantify controls of solution chemistry and physical agitation on the Mg content of calcite that forms by a nonclassical mineralization process. Insights are based upon experiments designed to use characterized solutions in a flow-through environment where chemistry was maintained constant [1]. Added experiments used stable isotopic tracers.

Higher pH and higher carbonate activities slow the rate of ACC to calcite transformation to favor higher Mg contents [2]. Thus, conditions provide a proxy for solution composition, but relationships indicate an apparent effect through slower kinetics. Isotopic labeling experiments suggest the extent of mixing between the initial ACC and labeled solution agrees well with a dissolution/reprecipitation pathway and indicates calcites record local environment at the time of transformation [3]. Very high Mg ACC is produced by regulating inorganic chemistry through a systematic relationship to local pH and total carbonate concentration at the time of formation. These high Mg ACC transform to a reduced Mg calcite, whereas low Mg ACC transforms to calcite of similar composition. Agitation affects polymorph selection with monohydrocalcite and calcite forming in stirred and unstirred environments, respectively. The interplay of factors reiterate the dependence of rate and composition on local environment and demonstrates plausible origins of vital effects in carbonates that form by an ACC pathway.

[1] Blue *et al* (2013) *Methods in Enzymology*, **532**, 259-308 [2] Blue *et al* in review. [3] Giuffre *et al* in prep.