

Deciphering Mg signatures of carbonates in the framework of biogenic versus inorganic pathways to mineralization

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The ability of organisms to mineralize tissues into skeletons and other functional structures is a crowning achievement of biology. High-resolution studies of biominerals are revealing that many calcifying organisms do not use the classical crystal growth process of step nucleation and propagation by the terrace-ledge kink model. Rather, diverse phyla deploy alternative strategies that involve accumulation of amorphous precursor phases that transform into a crystalline material in intimate association with proteins, polysaccharides and other macromolecules. Calcification involving amorphous intermediates could be widespread in some types of sedimentary environments as well as organisms.

This presentation will highlight findings from experimental and theoretical efforts to understand factors that regulate the growth of biominerals during calcification and resultant mineral compositions. I will begin with insights gained from our studies of calcite by the classical process of step propagation to establish the influence of biomolecules on kinetics and magnesium incorporation. The magnesium content, or signature, is of particular interest because it is a widely used proxy for reconstructing paleoenvironmental conditions. From this 'baseline' of behavior, I will then show that when calcification involves an amorphous calcium carbonate phase, there are again marked increases in the Mg/Ca ratio. The shifts are correlated with the chemistry of the biomolecule, and molecular dynamics simulations indicate this occurs through changes in cation solvation.

Insights from these studies suggest a number of long standing enigmas, including some vital effects, may be explained when viewed through the lens of calcification by different mineralization processes and the influence of local biomolecule chemistry. Established paradigms for controls on compositional and isotopic signatures in carbonate minerals may need to be revisited in light of pathway-specific influences on mineralization.

Constraining the duration and rate of garnet growth and dehydration during subduction, Sifnos, Greece

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Garnet-bearing blueschists from the island of Sifnos, Greece (located in the Attic-Cycladic Blueschist Belt) provide information on the timescales of dehydration during subduction (540-580°C and 2.0-1.8 GPa). Textural observations and thermodynamic modeling of a mafic blueschist in this unit indicate that garnet grew via reaction (s) of the form chloritoid + jadeite + epidote + quartz = garnet + glaucophane + paragonite + H₂O. If the stoichiometry of the garnet forming reaction is known, measurement of the garnet growth rate can be used to constrain the dehydration rate of the subducted lithology. Previous studies have constrained growth rates of large garnets by dating cores and rims. Here, two garnet grains, roughly 1.5cm each in diameter, were microdrilled based on major element zoning contours as determined by electron microprobe mapping. Three zones were sampled from each garnet for Sm-Nd geochronology using ID-TIMS. Very low Nd concentrations in acid-cleaned garnet (0.03 to 0.07 ppm) yielded very small sample sizes (~1 ng Nd) which were analyzed using a NdO⁺ with Ta₂O₅ activator method. Powdered residues rich in mineral inclusions from each garnet zone were also analyzed. The inclusions fall slightly off of the garnet-matrix isochron which could indicate inheritance in the inclusions. For one crystal, garnet-matrix isochron ages of 46.60 ± 0.92Ma for the core, 46.33 ± 0.55Ma for the intermediate zone, and 46.30 ± 0.59Ma for the rim were calculated, indicating a growth duration of 300kyr, with an upper bound (2 SD) on growth duration of 1.4Myr. Ages from the second garnet had larger uncertainties but do overlap with the first garnet. Using this upper bound for duration and garnet modal abundance (11 vol%), the calculated time-averaged rate of water release is >6.6 x 10⁻¹⁰ moles of water/cm³ of rock/year. This equates to a release of 2.3 vol% of water due to this reaction. Comparisons of this dehydration flux can be made with models that predict water contents for subducting lithologies at the pressures and temperatures similar to the peak P-T of this blueschist. In addition, relating the duration of garnet growth to predicted changes in P-T conditions during subduction can provide insight into the influence of kinetics in subduction zone metamorphism.