Me/Ca Proxies and Foram Biomineralization: The Role of Cation Transport

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The Mg/Ca paleothermometer is a widely used technique and a powerful tool to reconstruct past sea surface temperatures from the tests of planktic foraminifera. However, the presence of unexplained diurnal Mg/Ca bands in these same tests [1] stands as a reminder of how little we know regarding the mechanistic details of biomineralization. During skeletal growth Mg/Ca and other proxies are controlled by a host of biological and physical factors including ion transport, aquatic speciation, surface chemistry, thermodynamic partitioning, crystal growth kinetics, and mineralization pathways. To build accurate environmental reconstructions we need to separate the impact of each parameter and use these data to build a chemical-scale understanding of biomineralization. In this study we isolate and characterize cation transport in cultured planktic foraminifera using stable isotope spikes and microanalysis. We then test if ion transport can explain diurnal Mg/Ca banding and develop a general model for the impact of ion dynamics on skeletal composition.

Living planktic foraminifera (*O. universa*) were placed in seawater enriched with stable isotopes of Mg, Ca, and Li. After 48 hours the forams were returned to natural abundance seawater. Imaged using NanoSIMS, the skeletal records of isotope uptake and efflux during this experiment reflect ion transport rates. We found that the calcium pool used for skeletal growth exchanges with the surrounding seawater with a turnover time of less than two hours. Furthermore, we observed no evidence for distinct day or night cation pools. Finally, magnesium, calcium, and lithium all showed identical dynamics suggesting direct and rapid seawater transport to the site of calcification rather than ion specific pathways. Thus selective calcium or magnesium pumping into the site of calcification cannot be used to explain diurnal Mg/Ca banding. Specific pumping of magnesium out from the site of calcification is still consistent with our data, however, and may explain banding. Combining ion transport rates and skeletal growth rate measurements from the same forams, we build a general analytical model to quantify the impact of ion dynamics on test composition. This transport model complements ongoing work on mineral growth rate effects in calcite and contributes towards a holistic and chemical-scale understanding of proxy behavior in foraminifera.

[1] Eggins, Sadekov, & De Decker (2004) *EPSL* **255**, 411-419.

Toward a quantitative model of metamorphic nucleation

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Mineral reactions in rocks take place as the result of a complex interplay between various atomic scale processes including dissolution, chemical diffusion, nucleation, and crystal growth. It is generally assumed that the product of a mineral reaction forms if the formation of that phase lowers the Gibbs free energy of the effective chemical system. However, even when that phase is part of the thermodynamically stable mineral assemblage, it may not necessarily nucleate. A certain departure from equilibrium is required to gain energy for the formation of the interface between reactants and products. This energy is referred to as interfacial energy, and only little is known about its magnitude during rock formation. In addition to this energy that has to be provided to initiate crystallization in rocks, chemical elements have to be transported between the sites of reactant dissolution and product nucleation, and attachment and detachment processes at the interfaces have to be efficient for crystallization to proceed. Knowledge of chemical transport and interface reaction rates in rocks are scarce but it is known that their interplay controls the microstructure and texture of rocks with important implications for the derivation of the conditions of rock formation relevant for the interpretation of past and future tectonic processes of Earth.

In this talk, a simple numerical model will be presented that accounts for the departure from equilibrium required for interface-controlled mineral nucleation [1]. The model simulates interface processes during metamorphic mineral reactions by which nuclei and crystals form on a molecular level based on classical nucleation and reaction rate theory and Gibbs free energy dissipation in a multi-component model system. Modeling results will be shown that allow to explore the interplay of several key parameters that impact on crystallization kinetics during petrogenesis such as the relative influences of interfacial energy and interface mobility on mineral content, mineral chemistry, and texture of rocks accounting for different rates of pressure – temperature changes during crystallization.

The comparison of nucleation simulations of contact-metamorphic garnet with analytical data obtained through XR-CT and EPMA provides first estimates of the order of magnitude of interfacial energies during metamorphic crystallization. It suggests furthermore that the interfacial energy has a first-order control on the departure from equilibrium required for mineral reactions if attachment and detachment processes at the surface of the product phase limit the overall crystallization rate. The influence of the heating rate on thermal overstepping is found to be negligible. A significant feedback is predicted between chemical fractionation associated with garnet formation and the kinetics of nucleation and crystal growth of garnet giving rise to its commonly lognormal – shaped crystal size distribution.

[1] Gaidies *et al.* (2011) CMP **155**, 657-671.