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Sub-Micron Heterogeneity In Biominerals: What Is the Role Of Organic-Mineral Interactions?

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From the pace of the ice ages to how the carbon cycle has changed through time, much of what we know about earth history and climate dynamics is based on chemical signatures locked within mineral archives. When viewed at the sub-micron to nano-scale however, chemical composition rarely follows a simple relationship with environmental conditions. This is especially true for the preserved $CaCO_3$ skeletons of marine organisms, which often exhibit systematic patterns of high magnitude chemical variability at the sub-micron scale. While this biologically-driven variability can complicate the interpretation of climate records, it also represents a rich and largely untapped signal – a window into the mechanisms controlling biomineral growth and the possible basis for new paleoproxies.

A possible explanation for some of this small-scale variability is organic-mineral interactions. We have been quantifying the geochemical impacts of organic-mineral interactions in several climatically relevant biomineral systems using a suite of high spatial resolution tools like NanoSIMS, ToF-SIMS, Atom Probe Tomography (APT), and near-field IR mapping, together with stable isotope labels and biomineral culture techniques. Using APT, we mapped the chemistry of an embedded organic template structure within the test of a simple spherical foraminifera at the atomic scale. We then linked this structure to sub-micron sodium banding, explaining a component of small-scale proxy heterogeneity. Armed with this understanding of sodium anomalies, we then mapped the location of organic layers in more complex foraminifera, allowing us to reconstruct the process of test formation. In complementary experiments using cultured coral, we have been quantifying the impact of exogenous organic compounds on the rate of skeletal nucleation and on the composition of these nuclei. While there is a long history of invoking organic-mineral interactions to explain biomineral heterogeneity, our work aims to put quantitative bounds on what this class of interactions can and cannot explain with regards to geochemistry. Collectively, the mechanistic understanding of biomineralization developed in these experiments can help us explain small-scale proxy heterogeneity, upscale this variability to bulk composition, and more accurately resolve specific environmental signals from the geochemical record.