

Unexpected phases and phase transitions in biomineral aragonite

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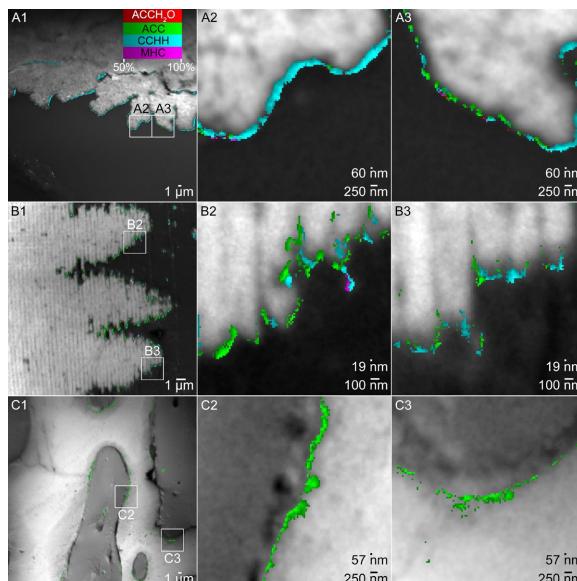
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Analyzing 200 million spectra with Myriad Mapping (MM) of nanoscale mineral phases we found expected and unexpected precursors on the surface of freshly deposited coral skeleton and nacre, but not on sea urchin spines. The expected phases, found on all biominerals (1-11), were amorphous calcium carbonate hydrated ($\text{ACC}\text{-H}_2\text{O}$) and anhydrous (ACC). The unexpected crystalline precursors were calcium carbonate hemihydrate ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, CCHH) and monohydrocalcite ($\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$, MHC)(12). These results demonstrated that biomimetic pathways are more complex and diverse than previously understood, opening new questions on the effect of multiple metastable precursor phases on isotopic and trace element compositions that are commonly used as proxies for paleo-environmental reconstructions.

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Figure 1. Metastable transient precursors to coral skeleton and nacre formation. These Myriad Maps (MMs) show that amorphous and crystalline precursors are both present, but only on the forming surface of fresh, forming aragonite (CaCO_3) biominerals, including coral skeletons (A1, A2, A3) and abalone nacre (B1, B2, B3). Calcite biominerals, including sea urchin spines (C1, C2, C3) only have amorphous precursors. Legend: red is amorphous calcium carbonate hydrated (ACC-H₂O), green is amorphous calcium carbonate dehydrated (ACC), cyan is calcium carbonate hemihydrate (CCHH), and magenta is monohydrocalcite (MHC). Data from (12).



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