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Presence of amorphous calcium carbonate in coral skeletons and tissue

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Calcium carbonate ($CaCO_3$) biomineralization is a naturally occurring phenomenon many organisms, including corals, use to form crystalline skeletal structures.[1] Coral biomineralization allows us to better understand how corals adapted to dramatic environmental changes[2], their contribution to ecological systems, and how they will respond to future environmental changes.[2,3]

Using PhotoEmission Electron spectroMicroscopy (PEEM) and X-ray Absorption Near-Edge Structure (XANES) spectroscopy, we discovered direct evidence of the existence of hydrated and anhydrous amorphous calcium carbonate (ACC) precursors in *Stylophora pistillata* corals. We mapped the position of these precursors using “component maps”, created by fitting the Ca L-edge spectrum from each pixel with the best-fitting linear combination of known Ca component spectra, or simply “components”. These are hydrated and anhydrous ACC, aragonite, and poorly crystalline aragonite. Each component is assigned a color (RGBY). Then, each pixel is assigned a specific color resulting from the additive color mixing of the components the best fit contains.[4]

Component mapping confirms the presence of amorphous precursors in coral skeletons. Most importantly, all the amorphous pixels were localized by the surface of the coral skeleton, that is, where the minerals were most recently deposited by the living animal.

Polarization-dependent imaging contrast (PIC) mapping, a method developed by us[5], also using PEEM, measures the orientation of the *c*-axes of carbonate crystals and displays their 3D orientation in 2D maps using colors, including in-plane and off-plane angles, displayed as hue and brightness, respectively. If PIC maps show black pixels (no polarization dependence, lack of crystallinity) in the same pixels where the amorphous precursors were found by component mapping, then the agreement of the two techniques supports the conclusion that the precursors are amorphous, and lack crystallinity.

The recent observation of these amorphous precursor phases in multiple reef-building coral skeletons means that they are not deposited one ion at a time from solution, but one particle at a time by an active biological mineralization process. This implies that the skeleton formation occurs in a closed system, isolated from seawater, and is important because it predicts that coral biomineralization may continue, even in acidifying oceans.

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