

## How do corals precipitate aragonite?

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Atmospheric CO<sub>2</sub> levels are rising rapidly, resulting in a decrease in both oceanic pH, and the carbonate saturation state ( $\Omega$ ). It has been hypothesized that calcifying marine organisms, including reef-building corals, will be affected by the decline of the carbonate saturation state. However, the lack of a mechanistic understanding of processes that lead to and control calcification limits our ability to predict the response of corals to increasing atmospheric CO<sub>2</sub>.

For many years, it has been hypothesized that the biological precipitation of carbonates is catalyzed by and organized on an extracellular organic matrix containing a suite of proteins, lipids and polysaccharides. The structures of these molecules, their evolutionary history, and the biophysical mechanisms responsible for calcification remain enigmatic. Although it has long been recognized that mineralized tissues contain proteins that are unusually rich in aspartic and glutamic acids, their sequence and the precise role of these acidic amino acids in the precipitation of carbonates has remained elusive.

We identified, cloned, and characterized four highly acidic proteins, derived from expression of genes obtained from the common stony coral, *Stylophora pistillata*. Each of these four proteins spontaneously can catalyze the precipitation of calcium carbonate from unamended sea water *in vitro*. Our results demonstrate that coral acid-rich proteins (CARPs) not only bind Ca<sup>2+</sup> stoichiometrically but also precipitate aragonite at pH 8.2 and 7.6 *via* an electrostatic interaction with protons on bicarbonate anions. Similar, highly acidic, proteins appear to have evolved several times independently in metazoans through convergence to catalyze the precipitation of calcium carbonate *via* ionic interactions.

Based purely on thermodynamic grounds, the predicted change in surface ocean pH over the next several decades would appear to have minimal effect on the capacity of these acid-rich proteins to precipitate carbonates.