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Trace element “vital effects” in corals: A new tool for probing biomineralization chemistry

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The strong linear co-fractionation of carbon and oxygen isotopes in the skeletons of tropical and deep-sea aragonitic corals has been used to study biomineralization processes. Several possible mechanisms have been debated recently, but resolving these requires additional information.

Recently, laser-ablation ICP-MS analysis of the skeletons of aragonitic corals has revealed strong linear correlations between the trace elements Mg, U, B and Sr. These correlations are present at seasonal scales, indicating a link with water temperature. The same correlations are also present in large, high-resolution (daily – weekly) variations in the coral. The amplitude of the fine-scale variations precludes daily temperature fluctuations, and the correlations are believed to be caused by a chemical process occurring during biomineralization. This process is sensitive to temperature, but also short-term physiological variability such as diurnal fluctuations in calcification rate.

The major calcification model, developed to explain C and O isotope variations, proposes that corals precipitate their skeletons freely from a membrane-isolated seawater solution which has been modified by exchanging 2H^+ for Ca^{2+} using the ion pump enzyme Ca-ATPase. Raising the pH of the calcifying fluid results in diffusion of CO_2 into the fluid, resulting in a significant increase in the supersaturation of CaCO_3 and spontaneous precipitation of aragonite.

Under this model, rapid calcification (such as occurs during the day in tropical corals) would be associated with elevated pH, Ca^{2+} and CO_3^{2-} concentrations in the calcifying fluid. This would significantly dilute trace cation substituents (such as Sr) or anion substituents (such as B and U), resulting in a positive correlation between these elements in the skeleton (with higher calcification rates being correlated with lower TE concentrations).

Combined equilibrium and kinetic models of the calcifying fluid have been set up to test if calcification rate can explain the correlations. These reproduce the positive correlations between B Sr and U. Mg, however, is negatively correlated with the other trace elements, and cannot be explained by mutual dilution at high calcification rates. It is possible that Mg does not substitute directly for Ca^{2+} or CO_3^{2-} in the aragonite, and is instead bound to lattice defects, which would be expected to increase as calcification rates rise.

The models suggest that pHs in the calcifying fluid probably average around 8.5, and do not fluctuate more than 0.2 pH units. This is inconsistent with equilibrium models of C and O isotope fractionation, which require high pHs.

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The skeletal chemistry of scleractinian corals: A window on biomineralization

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The aragonite skeleton of scleractinian corals is constructed of bundles of micron-sized, needle-shaped crystals that radiate out in three-dimensions from a calcification center. Crystallographic features of the coral sclerodermites – including morphology, orientation and banding – are characteristic of abiotic aragonite spherulites precipitated rapidly from supersaturated solutions in both laboratory and natural settings. In contrast to abiotic systems however, the biomineralization of coral skeleton occurs in an environment that is created through selective uptake or excretion of elements by a living organism. Therefore, analysis of the chemical composition of the coral skeleton sheds light on the nature and degree to which the organism controls the mineralization process.

I used SIMS ion microprobe to track microscale changes in the trace element chemistry of the sclerodermite from the nucleation site to the tip of the fasciculus, a distance of 50 - 100 μm . The chemical composition of seed crystals within the calcification centers is similar to that of aragonitic spherulites precipitated experimentally from a supersaturated seawater solution. This indicates that the initial phase of the daily cycle of crystal growth occurs from seawater trapped within cavities that form above the tips of the skeletal spines. The chemical composition of the sclerodermite changes significantly as it grows out from the calcification center to fill the cavity formed between the uplifted tissue and the skeletal surface. The amplitude, direction and rate of change in Sr/Ca, Mg/Ca and Ba/Ca ratios along the length of the aragonitic fibre bundles suggests a semi-closed system in which seawater is replenished at the start of each day and its composition modified by the light-driven and carrier-mediated transport of Ca^{2+} into the calcifying space.