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Experimental investigation of the partitioning of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} between aragonite and seawater at 5 to 45 °C

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The Sr/Ca and Mg/Ca ratios of the carbonate skeletons of many marine organisms vary with seawater temperature and, therefore, provide useful tools for deciphering the history of temperature changes in the ancient oceans. Despite the widespread use of skeletal chemistry as an indicator of environmental conditions, there is little consistency among the proxy sea surface temperature (SST) estimates for crucial periods of Earths' climate history. The lack of agreement amongst SST estimates reflect, in part, our limited understanding of the factors that control how trace elements are partitioned between seawater and the growing carbonate skeleton. We carried out experiments to determine the partitioning behavior of divalent cations with respect to inorganically precipitated aragonite and natural seawater to provide a framework for understanding the factors that control the compositions of marine invertebrate skeletons.

Experiments were carried out by slow (~1 ml/min) addition of dilute aqueous Na_2CO_3 solution to Vineyard Sound seawater held in a PTFE beaker. The seawater was continuously stirred, and temperature was controlled using an isothermal bath. The minor and trace element content of individual crystals was determined by ion microprobe, and their Ca content by electron microprobe. The composition of the fluid from each experiment was determined by ICPMS.

The temperature-dependence of the Sr/Ca ratio of aragonite determined in our experiments agrees well with the results of [1]. The Mg/Ca ratio displays a negative dependence on temperature, counter to the positive trend observed in coral skeletons. The Ba/Ca ratio of aragonite, which is typically used as an indicator of nutrient supply in biological systems, also shows a pronounced negative temperature dependence, in agreement with the findings of [2]. Weight-ratio partition coefficients calculated for each experiment demonstrate that the relative partitioning of Mg, Ca, Sr, and Ba between aragonite and seawater is consistent with the lattice strain model of [3]. Further, the variations in Sr/Ca, Mg/Ca, and Ba/Ca ratios of the aragonite reflect an increase in the compatibility of Ca in aragonite relative to seawater with increasing temperature, coupled with a decrease in the compatibilities of Mg, Sr, and Ca.

References

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Tracing 20 years of U, Sr and Mg into *Porites* coral from the Elat reef

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Uranium, Sr and Mg are used as paleo-environmental proxies (e.g. SST, pH, salinity), however, the mode of co-precipitation, Kd (distribution coefficient) and effects of subtle early diagenesis (in marine environments) are still open questions (e.g. the large number of paleo–SST equations in the literature). We investigated the incorporation of these trace elements into a live *Porites* coral-head growing in the Nature Reserve Reef (NRR), off the Marine Biology Laboratory, Elat. We drilled the coral and sampled porewater from the drill-hole. Profiles of strontium, U, Mg and Ca were determined in the core. The Sr/Ca and U/Ca stratigraphy (calibrated against the past 15 y instrumental SST record) suggests that reef eutrophication decrease corals calcification rate as shown by direct community metabolism studies. The Mg/Ca signal was not only seasonal.

The Kd's of U and Sr were determined in primary and secondary aragonite in the live coral and in aragonite precipitated chemically on coral fragments. The secondary aragonite contains significantly higher U and Sr and lower Mg than the biogenic aragonite. This difference reflects the close system incorporation of uranyl tris-carbonate or Sr^{+2} into the biogenic aragonite with bulk Kd close to unity, versus the open system incorporation into secondary aragonite with $Kd_{U,Sr} >1$. In addition, we calculated the effect of pH and/or carbonate ion on Kd_U relative to the effect of temperature.