

The impact of crystal growth rate on element ratios in aragonite: an experimental approach to understanding vital effects

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The elemental composition of biogenic skeletons provide an increasingly significant proportion of the climate proxy data used to understand Earth's climate system [1]. However, the factors that control how elements are partitioned between seawater and a growing skeleton are not well understood, nor are the contributions of biological processes or "vital effects" to skeletal composition [2]. We employed an experimental approach to study the effects of crystal growth rate on the composition of aragonite grown from seawater. Because organisms modify conditions in the calcifying space, most biogenic aragonites grow at rates significantly higher than they would under ambient seawater conditions [3]. This study was designed to assess crystal growth rate as a potential source of "vital effects" on the composition of biogenic aragonites.

Aragonite crystals were grown from seawater at 25°C. The solution was subsampled during the experiment to determine changes in fluid composition. Linear growth rates of the crystals were constrained by addition of ⁸⁴Sr and ⁸⁶Sr spikes into the growth solution at different times during each experiment. Location of spikes within crystals was determined to ±5 μm by SIMS ion microprobe. Mg/Ca and Sr/Ca ratios of the crystals were measured at the same time. Analyses of Ca, Mg, and Sr in the solution were performed separately by ICP-MS.

Our data indicate that the Mg exchange coefficient ($K_d^{Mg} = [Mg/Ca]_{crystal} / [Mg/Ca]_{fluid}$) increased from $3 \cdot 10^{-4}$ to $12 \cdot 10^{-4}$ (i.e. $Mg/Ca_{crystal} = 2.2-9.3$ mmol/mol) as crystal growth rate increased from 2 to 135 μm/day. In contrast K_d^{Sr} was independent of crystal growth rate over the studied range ($K_d^{Sr} = 1.2 \pm 0.1$, i.e. $Sr/Ca_{crystal} = 8.7 \pm 0.1$ mmol/mol). Our data imply that Mg/Ca ratios of biogenic aragonites are highly sensitive to growth rate and should be interpreted with caution in paleotemperature reconstructions. Further, our data suggest that offsets in mean Sr/Ca ratios among corals inhabiting the same reef environment may be due to variations in the Sr/Ca ratio of the calcifying fluid (i.e., a true "vital effect") rather than to differences in growth rate.

References

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