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Mg/Ca partitioning between aqueous solution and aragonite mineral: a molecular dynamics study

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Calcium carbonate is one of the most abundant minerals. It is polymorphous and occurs naturally in three anhydrous crystalline forms—calcite, aragonite and vaterite. The first two are abundant in geological and biological systems, while vaterite is only meta-stable under ambient conditions. Although calcite is thermodynamically more stable than aragonite at low pressures and temperatures, aragonite is yet the major constituent of coral reefs, shells, pearls and other biominerals. The magnesium content in coral fossils has been proposed as a proxy for the reconstruction of past climates, based on correlations found between the Mg/Ca ratio and the sea surface temperature (SST) during biomineralization.[1] Magnesium is always present in corals, with typical Mg/Ca ratios of ∼4×10-3, well below the ratio Mg/Ca=5.14 in seawater. The variation found for the Mg/Ca ratio with SST is about four times that of the Sr/Ca ratio, which is the most widely used signature in paleothermometry, thus promising higher resolution in climate change reconstructions.[1] However, doubts remain regarding the reliability of the method due to the poor reproducibility of the correlations and uncertainties about the location of Mg in the coral skeleton.[2]

In order to shed light on the understanding of the chemical basis of Mg/Ca paleothermometry, we have investigated the equilibrium partitioning of Mg between aqueous solution and the bulk and surfaces of aragonite, using a combination of molecular dynamics simulations[3] and grand-canonical statistical mechanics[4]. Our calculations indicate that Mg will be incorporated in the surfaces, in particular in the (001) terraces, rather than in the bulk of aragonite particles. It is therefore expected that the Mg content of aragonite particles from corals will depend strongly on particle size and morphology, which determine the available surface area of the particle, thereby complicating the interpretation of the origin of the correlation between coral Mg content and temperature. Furthermore, the total Mg content in the bulk and surface of aragonite particles is found to be too small to account for the measured Mg/Ca ratios in corals. We therefore argue that most Mg in corals is either highly metastable in the aragonite lattice, or is located outside the aragonite phase of the coral skeleton. If the latter is the case, the Mg concentration in corals is a function of phase distribution, which can be affected by several uncontrollable factors, effectively randomising any dependence with temperature. Taken together with other experimental evidence, our results suggest that the Mg/Ca ratio in coral fossils is unlikely to constitute a reliable record of past temperatures at the sea surface.

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