

Structural state of coprecipitated magnesium, copper, and strontium in calcium carbonate

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A formation of calcium carbonate polymorph is an important factor for biomineralization or the use of carbonate records as geochemical tools. Experimental investigations have pointed out that a coexisting divalent ion which smaller than Ca^{2+} gives an advantage for a formation of aragonite whereas a larger one does so for calcite [1]. However, the smaller ions themselves favor calcite structure (e.g., MgCO_3). A detailed mechanism for the formation of aragonite is poorly understood. In this study, we present an X-ray absorption fine structure (XAFS) analysis to investigate local structures of coprecipitated magnesium, copper, and strontium in calcium carbonate. Copper is a strong promoter for the formation of aragonite according to the inorganic experiment [2], whereas magnesium is an important factor in the ocean.

We conducted Mg, Cu and Sr K-edge XAFS measurements for synthetic calcite and aragonite. Natural samples (biominerals and abiotic minerals) were also measured only for magnesium.

Mg XANES spectra of biominerals show similar features with those of synthetic polymorphs. This result leads that the host phase of magnesium in the biogenic shells is calcium carbonate. EXAFS spectra of calcites indicate every divalent metal can substitute Ca^{2+} site in calcite. For aragonite, on the other hand, magnesium and copper do not show contributions of neighboring Ca^{2+} in their EXAFS spectra, though strontium shows it. There is no or pretty weak Mg- or Cu-EXAFS oscillation which is contributed by the second- or higher-order coordination shell in aragonite. These features are similar to those of copper in amorphous calcium carbonate and hydrated Cu^{2+} . Furthermore, the XANES spectrum shows that copper in aragonite is Jahn-Teller distorted octahedral. These results suggest smaller ions than Ca^{2+} tend to form six-fold coordinations when coprecipitated with aragonite. And the local environment around the small ions is disordered.

[1] Y. Kitano (1962a) Bull. Chem. Soc. J. 35 1973-1980.

[2] Y. Kitano and M. Okumura (1973) Geochem. J. 7 37-49.