

Speciations of copper coprecipitated in calcite and aragonite: an analog study for magnesium in aragonite

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Calcium carbonate has two common polymorphs which are easily found in the natural environment. Calcite is a stable phase of calcium carbonate, whereas aragonite crystallizes from high Mg/Ca ratio solution instead of calcite [1]. It seems that the presence of magnesium ion affects polymorph selection of calcium carbonate. X-ray absorption fine structure (XAFS) has been applied to speciation of magnesium coprecipitated in calcium carbonate. However, it is difficult to obtain a wide energy range of spectrum at Mg K-edge (1303 eV) because of interference from Al K-edge (1559 eV). Therefore, we investigated copper as an analog for magnesium. Copper also promotes crystallization of aragonite [2]. It is expected that copper similarly behaves with magnesium in carbonate due to their similar ion sizes.

We synthesized Cu-doped calcite and aragonite by controlling magnesium ion concentration of the parent solution. To keep the pH of parent solutions roughly, we added sodium hydrogen carbonate to the parent solution (from 7.5 to 8.5). The spectra of Cu K-edge XAFS were collected at BL-12C of Photon Factory (Tsukuba, Japan).

Synthesized aragonite contained slightly lower amount of copper than calcite. This is consistent with the fact that smaller ion favors the site with low coordination number. The colors of synthesized calcite and aragonite were white and sky blue, respectively. Generally, Jahn-Teller distorted Cu²⁺ shows blue in various copper compounds. Although Jahn-Teller distorted Cu²⁺ has a shoulder in the main peak in XANES, Cu²⁺ in calcite did not show the shoulder in its spectrum. It is suggested that Jahn-Teller distortion of Cu²⁺ is suppressed by its substitution into Ca²⁺ site in calcite. Aragonite, while calcite indicated the suppression of Jahn-Teller distortion, showed a shoulder peak in its XANES spectrum. EXAFS spectrum of aragonite was similar to that of aqueous Cu²⁺. These results suggest that copper coprecipitated in aragonite preserves 6-coordinated and Jahn-Teller distorted octahedral, though Ca²⁺ has 9 coordination in aragonite. It is also suggested that magnesium, which is too small to have 9 coordination, has 6 coordination in aragonite.

[1] Y. Kitano *et al.* (1962) *J. Geophys. Res.* **67** 4873-4874.

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