

## Crystal dependent sodium partitioning into calcium carbonate and its soft X-ray absorption fine structure

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Carbonate structures formed by marine organisms such as corals and foraminifera are important geological archives to record the Quaternary marine environment. Although bivalves have hard shells of calcium carbonate, their trace element concentrations are markedly deficient due to the physiological control. Exceptionally, sodium is contained in marine carbonates at high concentration regardless of the species, and is considered to be an element which is not physiologically controlled. In this study, we investigate the influence of sodium on crystallization of marine species and elucidate the control mechanisms of elements by bivalves. In particular, to clarify the partitioning behavior of sodium in marine carbonates, two polymorphs of calcium carbonate, calcite and aragonite, were synthesized by carbon dioxide degassing method. Crystallographic arrangements of Na in synthesized calcium carbonates were studied by Na K-edge XANES.

The synthesis of calcite was carried out by the following procedure. Calcium carbonate powders were mixed with sodium chloride solution, and then carbon dioxide gas was passed. After the dissolution of carbonate powders, the water temperature was adjusted to the target temperature (10°C, 20°C, 30°C, 40°C). Then, after filtration, while keeping at the target temperature, the solvent was stirred for inducing CO<sub>2</sub> degassing. The produced powder sample was rinsed with ultrapure water and air-dried. The synthesis of aragonite was carried out following the procedure of calcite synthesis, excepting for the additions of magnesium hydroxide to obtain the Mg/Ca of 5 mol/mol, and acetic acid to adjust the water pH to around neutral. Na K-edge XANES measurements were performed at BL-10 in SR Center, Ritsumeikan University. Beryl was used as the monochromator crystal, and the partial fluorescence yield method was used for low concentration samples. Na containing reagents were analyzed with total electron yield method.

As a result, while the partition coefficient of sodium for calcite was slightly decreased as the water temperature increased, the partition coefficient for aragonite increased with temperature. In all cases, the partition coefficient of sodium for aragonite exceeded that for calcite.

For Na K-edge XANES of calcite, the pre-edge

peak was found at 1077 eV and the main peak was observed at 1080 eV. Although the XANES of aragonite also showed almost the same, the peak position was shifted to higher energy side by 0.5 eV. In calcite samples, a broad peak is observed at 1090 eV, whereas in aragonite, there is no peak on the high energy side. These characteristics are coincident with the bivalve shell samples (scallop middle layer and giant clam represent natural calcite and aragonite, respectively), suggesting that the different XANES is due to the different crystal structures of calcium carbonates.

Yoshimura et al. concluded that sodium is absorbed as sodium carbonate by replacing the calcium site by measuring Na K-edge XANES of various biogenic carbonates<sup>1</sup>. Although the spectral shape obtained in this study is almost similar to the results of Yoshimura et al., our observed peaks are shifted to high energy side, and are inconsistent with the spectra of sodium carbonate, sodium bicarbonate or sodium carbonate decahydrate. In comparison with the previously reported data, peak positions of calcite correspond to sodalite, while main peak of aragonite resembles to that of hauyne<sup>2</sup>. Both sodalite and hauyne are kinds of feldsparthoids showing a cubic system, in which sodium is bonded with three oxygen atoms and one chloride or sulfate. The Na-O distance of hauyne (2.526 Å) is longer than that of sodalite (2.358 Å), and the difference in the bonding distance corresponds well to the Ca-O distances of aragonite (2.411 to 2.655 Å) and calcite (2.360 Å). Because the bonding distance between hydrated sodium ion and water molecules is 2.40 to 2.43 Å at 25°C<sup>3</sup>, higher energy may be required for sodium partition in aragonite. The long bonding distance caused by thermal energy might explain the sodium partition coefficient for aragonite increasing with the water temperature.

### References

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