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Soft X-ray absorption fine structure of sodium incorporated into synthesized calcium carbonates

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Substantial amount of sodium can incorporate into calcium carbonates. We synthesized calcium carbonates at different temperatures (10, 20, 30 and 40 °C) to determine the partitioning behavior of Na and to understand its properties during the calcification of marine organisms. We also examined the role of organic ligands in the solvent because calcification fluids in marine organisms contain some carboxylates[1,2], and also organic ligands affect significantly on partitioning behavior of trace elements[3].

For calcite synthesis in the organic-free solvent, NaCl was dissolved in 500 mL of Milli-Q water to achieve approximately equal concentration to seawater (0.47 mol/L). For calcite synthesis in the solvent containing carboxylic acid, some portion of NaCl were replaced by NaOH to achieve total Na concentration of 0.47 mol/L. After the addition of acetic acid, the pH was adjusted to that in the organic-free solvent. Then, $CaCO_3$ powder was added to the solvent to achieve three different Ca concentrations of 5.0, 10, and 15 mmol/L, respectively. For aragonite synthesis in the organic-free solvent, $MgCl_2$ was added to the solvent to obtain five times of Ca (mol/mol). For the case of aragonite synthesis in the solvent containing carboxylic acid, instead of the $MgCl_2$, $Mg(OH)_2$ and acetic acid were added to the solvent. The solvent was then bubbled with 40 L of CO_2 gas. After the solvent temperature was set to 10, 20, 30, or 40 °C, 100 mL of this solvent was stirred on a cool/hot plate at the required temperatures to obtain carbonate precipitates.

Sodium K-edge X-ray absorption near edge structure (XANES) was analyzed at the beam line of BL-10 of the synchrotron (AURORA, Sumitomo Heavy Industries, Ltd.) at the SR center of Ritsumeikan University. The dispersive crystal was beryl ($10\bar{1}0$ crystal surface), and the absolute energy position was corrected by the main peak of halite (1076.60 ± 0.05 eV, 2σ).

The signal of Na in calcite crystals showed first and main peaks at 1077 eV and 1080 eV, respectively. The spectrum shape for aragonite well resembles that of calcite, while the peak position shifted 0.5 eV to higher energy (Fig. 1). Importantly, the fine structure of Na is consistent regardless of acetic acid was contained or not contained in the solvent that means Na^+ does not occurred as organic complex. Because of the good reproducibility in XANES spectra of calcite or aragonite specimens synthesized at the different chemical conditions, the energy shift of 0.5 eV is significant and is likely to be originated from the crystal structure.

Comparing with reference materials, we found that the feldspathoids are potential candidates to explain the Na geometry in $CaCO_3$ crystals. Especially, sodalite is characteristic with the main peak at 1080 eV and a broad high-energy peak at 1090 eV, which well resembles that of Na in calcite. On the other hand, the main peak of hauyne is slightly higher than that of sodalite without the higher energy peak at 1090 eV, relatively consistent with the spectrum of Na in aragonite specimens. Feldspathoids having a cubic system well explain high symmetry in $CaCO_3$ crystals, suggesting the Na^+ substitution for Ca^{2+} site.

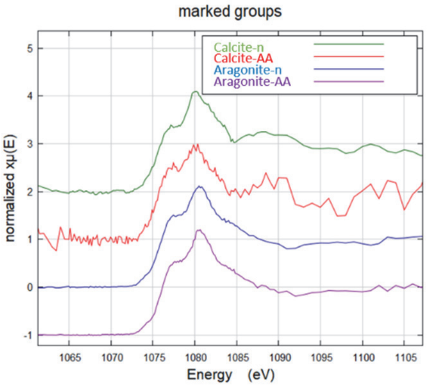

Fig. 1 Na K-edge XANES spectra near 1080 eV of synthesized calcite and aragonite specimens. “n” represents the solvent not containing organic ligand, while “AA” represents that containing acetic acid.

References

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