

First results of phase transformation from vaterite to calcite observed by Ca K-edge XAFS and XRD.

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Insoluble calcium carbonate can be synthesized by mixing two aqueous solutions for calcium source and carbonate source, and calcium carbonate is precipitated under a condition of supersaturation (**FIG.1**) [1]. The initial precipitation is vaterite, and it will be transformed into more stable phase like calcite. We are interested in the mechanism of phase transformation, and X-ray absorption spectroscopy is utilized to obtain local structural information around Ca in an aqueous environment.

The supersaturation was realized by mixing solutions of CaCl_2 and NaHCO_3 , and the typical

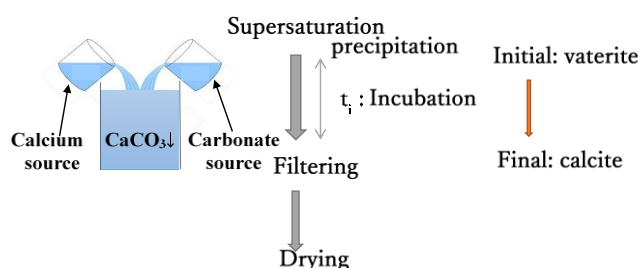


FIGURE 1. A schematic synthesis process of calcium carbonate.

concentration of the solution was from 30 mM to 300 mM. Selective synthesis of the phase was carried out by changing the incubation time, t_i , before filtering the precipitation with a membrane filter (pore size $0.45\ \mu\text{m}$). The obtained calcium carbonate was identified by powder X-ray diffraction measurements (XRD). **FIG. 2** shows XRD patterns obtained from reagent (pure) calcite, pure vaterite

($t_i=16$ mins for 30 mM solutions [1]), and the mixture of them as a function of the incubation time. The fraction of vaterite in a mixed sample can be determined by using normalized peak intensity with that of pure phase. The fraction of vaterite, f_v was estimated by the following equation by using the normalized peak intensities of 112 reflection of vaterite and 104 reflection of calcite.

$$f_v = V_{112n}/(V_{112n} + C_{104n}) \quad (1)$$

XAFS (X-ray absorption fine structure) measurements were carried out by using a transmission mode, and a sample was attached to a Scotch tape and was placed in a helium filled chamber.

XAFS data were processed with Athena and Artemis, and extracted EXAFS oscillations, $\chi(k)$ and Fourier transform of them were shown in **FIG. 3**, and the obtained data were almost identical to those reported previously [2]. It was also confirmed that the XAFS spectrum from a sample with t_i of 520 mins was identical to that of reagent calcite. FT spectra showed main peak corresponding to neighboring oxygens (Ca-O). Moreover, new peaks corresponding to Ca-Ca might be obtained. They were not observed when EXAFS spectra of calcium acetate in an aqueous solution were investigated [3]. Possibilities of observing the phase transformation in the aqueous solution will be discussed in this presentation.

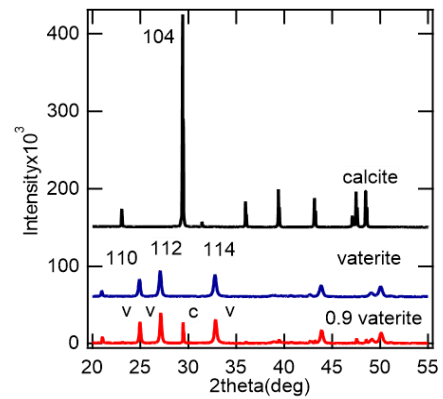


FIGURE 2. XRD patterns of calcium carbonates. Reagent calcite (black), synthesized vaterite (blue) and a mixture of them $t_i=16$ mins for 90 mM solutions, $f_v=0.9$.

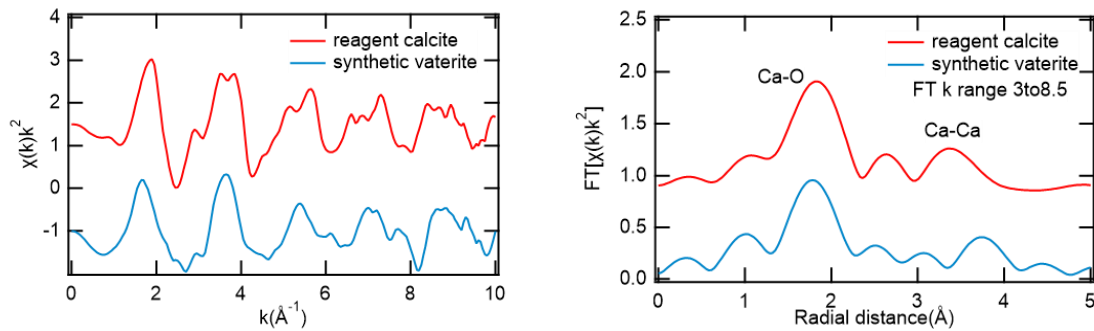


FIGURE 3. $\chi(k)$ spectra and their Fourier transform of $\chi(k)$, FT k range was 3 to 8.5. Reagent calcite (red line) and vaterite (blue line) Red line was reagent calcite, blue line was synthetic vaterite.

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