

論文の内容の要旨

Pressure-induced phase transitions of metastable phases of calcium carbonate

(炭酸カルシウム準安定相の圧力誘起相転移)

丸山 浩司

Chapter 1 describes the general introduction. Calcium carbonate, CaCO_3 , is a ubiquitous mineral on the Earth's surface. Calcium carbonate has three anhydrous polymorphs (calcite, aragonite, and vaterite) at ambient pressure. In addition to these crystalline phases, amorphous calcium carbonate (ACC: $\text{CaCO}_3 \cdot x\text{H}_2\text{O}$, $x \leq 1.5$) is known as a precursor of more stable crystalline phases in biomineralization and inorganic formation. In nature, ACC exists only in biominerals. Calcium carbonate crystals with complex morphology are formed via ACC in biomineralization. Therefore, the crystallization from ACC is an important process to understand biomineralization. It is already known that ACC crystallizes to calcite via anhydrous ACC by heating (e.g., Kojima et al., 1993). In a super-saturated solution, Rodriguez-Blanco et al. (2011) reported the crystallization from ACC to calcite via vaterite by time-resolved XRD measurements. Recently, Yoshino et al. (2012) presented a different type of crystallization process, pressure-induced crystallization from ACC at room temperature. The pressure-induced crystallization from ACC resulted in coexistence of calcite and vaterite, a metastable phase of calcium carbonate, occurred below 1 GPa. The crystallization mechanism of ACC is still unclear, because previous experiments were based on observations of recovered samples. Moreover, pressure responses of calcium carbonate polymorphs would provide useful information for the crystallization from ACC at high pressure. Many studies have investigated the high-pressure behavior of calcite and aragonite. On the other hand, no report described the pressure response of vaterite. In this study, to elucidate the mechanism of pressure-induced crystallization from ACC, I conducted in situ X-ray diffraction (XRD) observations on ACC and vaterite at high pressure.

Chapter 2 describes basic properties of ACC used in this study and pressure-induced crystallization from ACC based on observations of the recovered samples using a piston-cylinder. XRD patterns of synthesized ACCs with different water contents and its recovered samples from high pressure are presented in Fig. 1. ACC crystallized to calcite and vaterite by applying pressure (< 1 GPa) at room temperature. The vaterite/calcite ratios decreased with increase of applied pressure. ACC with lower H₂O content needed higher pressure for its crystallization than ACC with higher H₂O content did. Moreover, this crystallization was associated with dehydration. These results indicate that H₂O in ACC plays an important role in the crystallization process.

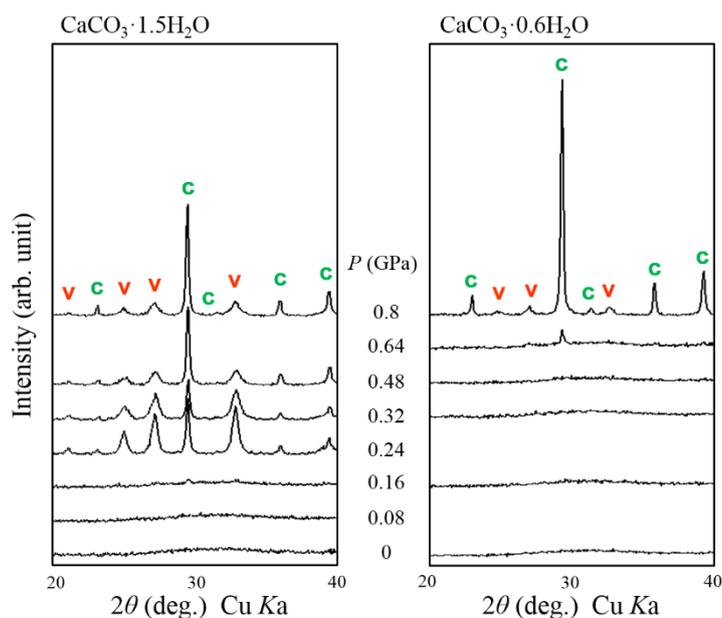


Fig. 1. XRD patterns of synthesized ACC ($\text{CaCO}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{CaCO}_3 \cdot 0.6\text{H}_2\text{O}$) and its recovered samples from high pressure: **c**, calcite; **v**, vaterite.

In Chapter 3, in situ time-resolved X-ray diffraction studies are presented to understand the mechanisms and kinetics of pressure-induced crystallization from ACC to calcite and vaterite. The SEM observations were also conducted to obtain more information of the crystallization mechanism. High pressure was generated using the cubic-type high-pressure apparatus (MAX80) at the Photon Factory–Advanced Ring (PF–AR), KEK. In order to control pressure precisely at a low-pressure range, below 1 GPa, a relatively large truncated edge length of 10 mm for the second stage anvil made by WC was used. Figure 2 shows time-resolved XRD patterns obtained for every 10 seconds. From the XRD results, degree of transformation is represented in Fig. 3a, suggesting that calcite and vaterite simultaneously crystallized from ACC. To understand the mechanism of pressure-induced crystallization from ACC, I introduced Avrami model (Fig. 3b). The n value in Avrami model is a constant dependent on the nucleation and crystal growth process at time. The obtained n values suggest that the formation of calcite is more controlled by the nucleation process than that of vaterite is. However, the grain sizes of calcite and vaterite observed from SEM images are about 100 to 200 nm; there is no

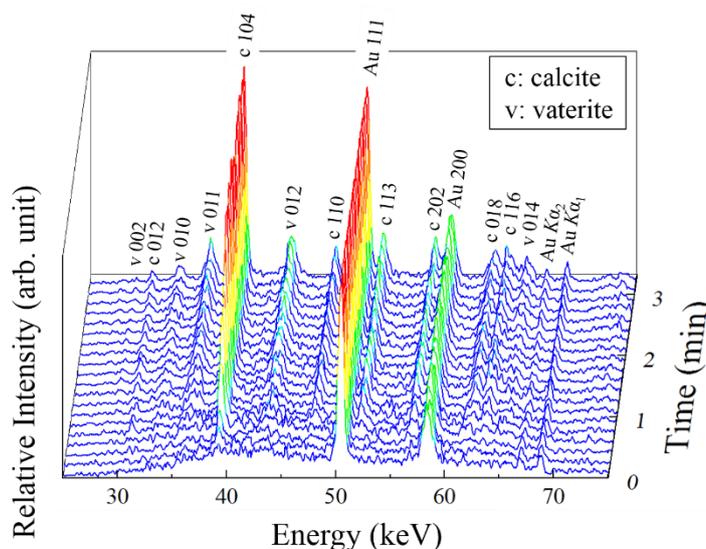


Fig. 2. Time-resolved X-ray diffraction patterns of ACC ($\text{CaCO}_3 \cdot 0.67\text{H}_2\text{O}$) with Au powder during compression. Intensity was normalized by the diffraction intensity from the 111 reflection of Au. Indices of vaterite were referred from the structure model proposed by Kamhi (1963).

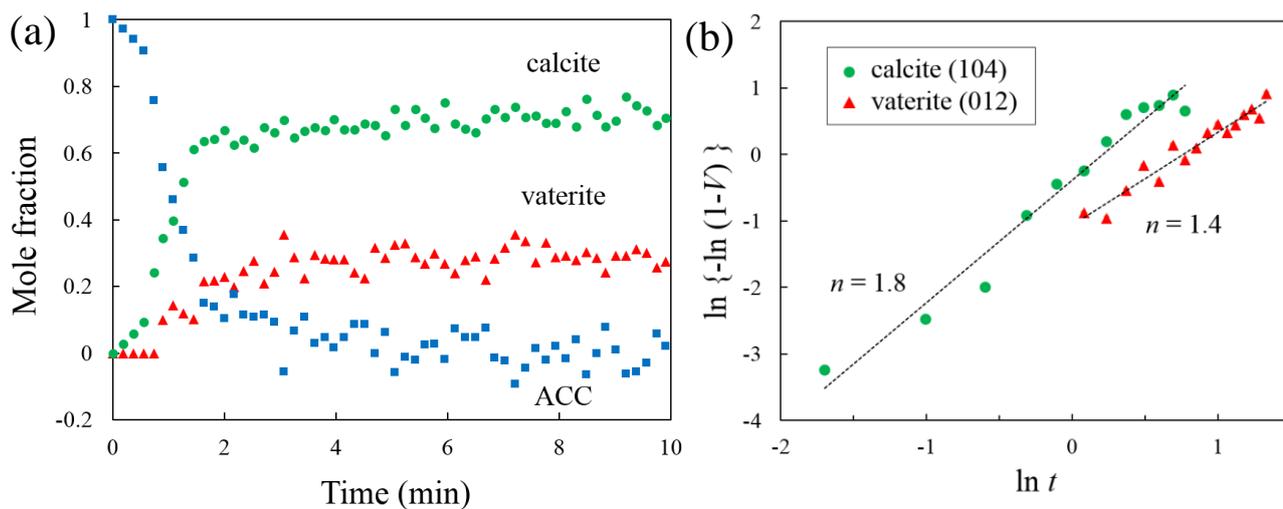


Fig. 3. (a) Degree of transformation determined from the intensities of vaterite 010 and calcite 104 reflections as a function of time. The vaterite/calcite ratio was calculated using the calibration line described in Chapter 2. The fraction of ACC was estimated from the balance of calcite and vaterite. (b) Plots of Avrami fitting for calcite (104 reflection) and vaterite (012 reflection) during crystallization from ACC.

significant difference in the grain size between calcite and vaterite (see Fig. 4a and 4b). Figure 4c shows the polymorph distributions in the recovered sample determined from Raman spectra. Vaterite mainly distributed around cavities, which would be filled with aqueous fluid dehydrated from ACC. This observation suggests that the formation of vaterite strongly connects to the existence of fluid. In contrast, calcite distributed throughout the sample. Moreover, calcite exhibited a spherical texture which is the pseudomorph of ACC, which suggests that calcite crystallized directly from ACC. These results indicate that the crystallization mechanisms from ACC to calcite and vaterite differ from each other, and this difference might result in the difference in the n values.

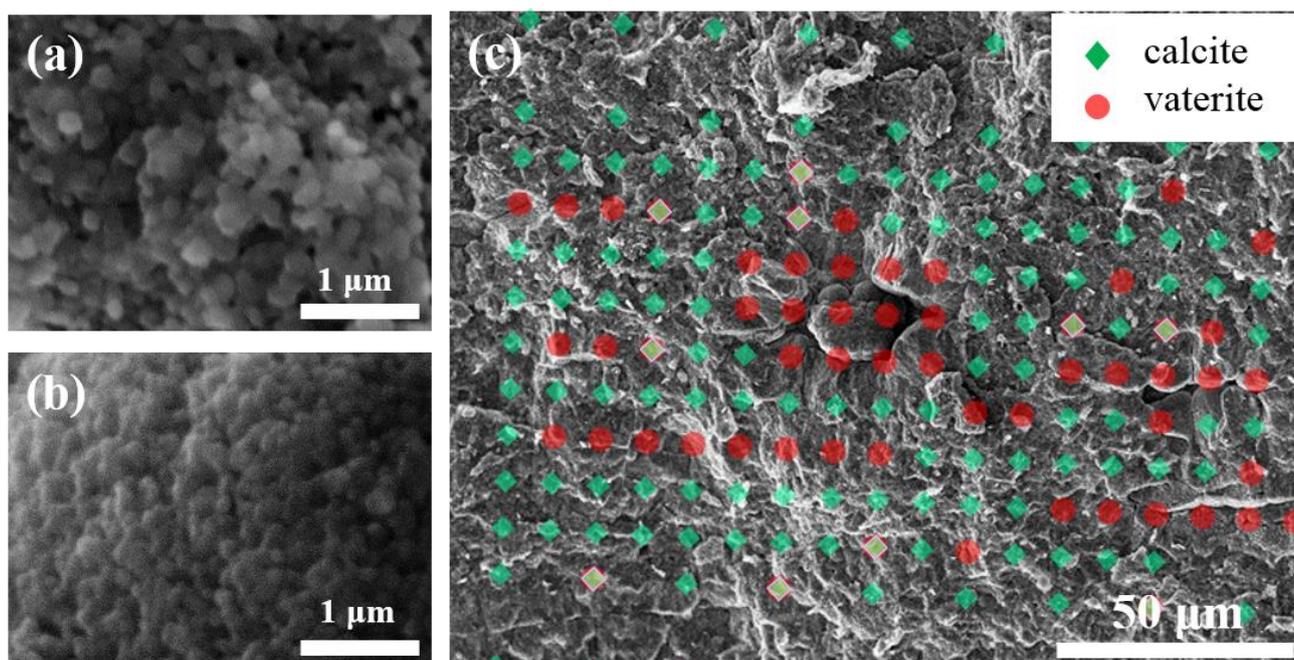


Fig. 4. SEM images of a recovered run product: (a) calcite, (b) vaterite, and (c) polymorph distribution on an SEM image determined with Raman mapping.

In Chapter 4, the pressure responses of vaterite were studied using diamond anvil cells (DACs). Representative XRD patterns obtained on a synchrotron beamline at PF are shown in Fig. 5. At 4.7 GPa, several peaks of vaterite were split and new peak attributable to calcite III appeared. The unit-cell parameters refined using a crystal structure model proposed by Le Bail et al. (2011) suggested that vaterite (vaterite I) transformed to a high-pressure phase (vaterite II) at 4.7 GPa. Vaterite II was more compressible than vaterite I was. At 8.7 GPa, another phase transition was observed with discontinuous changes of $2\theta \approx 8.3^\circ$. This change suggested that vaterite II transformed to a new phase, vaterite III. These phase transitions were also suggested by Raman spectra. At 13.1 GPa, new diffraction spots were observed around 20° in 2θ . These spots were not explainable with any polymorphs of calcium carbonate. This implies that these spots are derived from another high-pressure phase of vaterite (vaterite IV). At ambient pressure after decompression, the recovered sample was identified as a mixture of calcite I and vaterite. This observation suggests that vaterite II transformed to calcite III irreversibly.

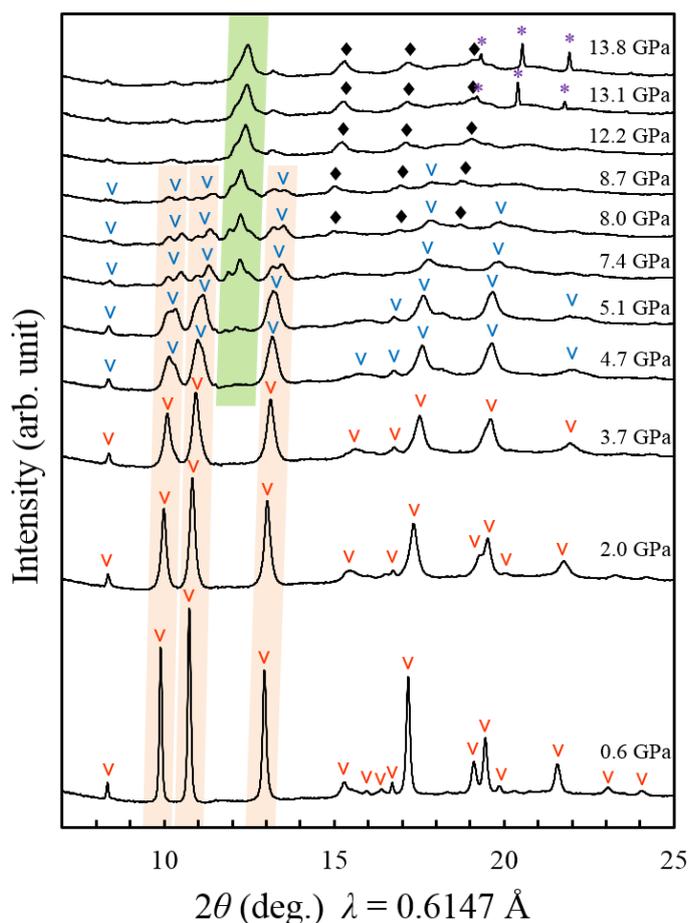


Fig. 5. Representative XRD patterns at high pressure with compression. The intensity has been normalized to the same measurement time. **v**, vaterite I; **v**, vaterite II; **♦**, vaterite III; *****, vaterite IV. The orange- and green-shaded regions indicate the highest intensity peaks of vaterite and calcite III, respectively.

For summary of this study, in situ observations of ACC and vaterite at high pressure provided us the information of crystallization mechanism from ACC at high pressure. The crystallization from ACC to calcite and vaterite proceeded by different mechanisms. ACC transformed to calcite directly by solid-to-solid phase transition accompanied by dehydration, which differs from the mechanism of calcite formation via vaterite in a super-saturated solution. The high-pressure experiments on vaterite, which clarified that vaterite does not transformed to calcite at pressures lower than 1 GPa, supports the direct formation of calcite from ACC at high pressure. In contrast, ACC transformed to vaterite in dehydrated fluid, for example, a dissolution-precipitation process.