

Pressure-induced phase transitions of vaterite, a metastable phase of calcium carbonate

MARUYAMA, Koji^{1*}; KOMATSU, Kazuki¹; KAGI, Hiroyuki¹; YOSHINO, Toru²; NAKANO, Satoshi³

¹Geochemical Research Center, Univ. Tokyo, ²TIRI, ³National Institute for Materials Science

1. Introduction

Calcium carbonate is one of the most common and ubiquitous minerals on the Earth's surface and plays an important role in global carbon cycle. There are many studies about high-pressure behavior of calcite and aragonite. At ambient temperature, calcite transforms to calcite II at about 1.5 GPa and to calcite III at about 2.0 GPa. The transition from aragonite to post-aragonite phase was observed at about 40 GPa. In contrast, no study has been reported on the high-pressure behavior of vaterite, which is a metastable phase of CaCO₃, and is known as a precursor material of more stable CaCO₃ polymorphs, calcite and aragonite. In this study, the high-pressure behavior of vaterite was investigated by in situ synchrotron X-ray diffraction (XRD) experiments using a diamond anvil cell.

2. Experimental method

In this study, vaterite was synthesized by mixing two aqueous solutions, 60 mM CaCl₂ aq. and 60 mM NaHCO₃ aq., kept at 30 degree C. The mixed solution was sealed in a plastic bottle and stirred for 10 min at 30 degree C, and then filtered using an aspirator, washed by pure water, and dried at about 130oC. The obtained white powder was identified as pure vaterite using powder XRD method.

High-pressure experiments were carried out using a diamond anvil cell (DAC). The synthesized vaterite and several tiny ruby crystals were loaded into a gasket hole together with helium as a pressure transmitting medium. The pressure was changed between 0-14 GPa, which was measured by the ruby fluorescence method. XRD patterns were measured at each pressure at room temperature. X-ray diffraction observations were carried out at room temperature using the synchrotron beam line of BL18C in the Photon Factory, Japan.

3. Results and discussion

XRD patterns recorded at pressures lower than 4.7 GPa indicated that the sample consists of vaterite only. At 4.7 GPa, main three peaks of vaterite were split and a peak assignable to calcite III appeared. The discontinuous changes in axial lengths were observed by refinement of lattice constants using a crystal structure model proposed by Le Bail et al. (2011). This change suggests a pressure-induced phase transition from vaterite to a high-pressure form (hereafter vaterite II). Change in the diffraction intensities suggested that vaterite II transformed to calcite III with increasing pressure up to about 9 GPa. At 12.9 GPa, new diffraction spots were observed. These spots were not explainable with the diffraction peaks from any polymorphs of CaCO₃. This implies that the new spots are derived from another high-pressure phase of vaterite (vaterite III). After decompression, the recovered sample was identified as a mixture of calcite and vaterite. These results indicate that the transition from vaterite II to calcite III is irreversible. In this study, new high-pressure phases of CaCO₃ (vaterite II and III) were discovered by high-pressure experiments of vaterite at ambient temperature.

Keywords: vaterite, phase transition, high-pressure