The dehydration kinetics of hydromagnetite and nesquehonite at high pressure and high temperature / The dehydration kinetics of hydromagnetite and nesquehonite at high pressure and high temperature

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1. Introduction

Mechanisms of carbonate mineral formation and its phase change in geological system have been studied for many years because of their abundance and wide distribution over the Earth's crust. Magnesite ($MgCO_3$), calcite ($CaCO_3$), and dolomite [$CaMg(CO_3)_2$] are the stable phases at ambient conditions. Petrologic observations, laboratory experiments, and theoretical investigations on stability and breakdown kinetics of the carbonates have clarified that magnesite is the most stable carbonate phase throughout most of the mantle and can be subduct to the deep mantle due to its higher melting temperature. At ambient pressure and temperature, however, magnesite precipitation is virtually inhibited because of the strong hydration of magnesium ions (Mg^{2+}) in solution. Instead of precipitation of magnesite, a variety of metastable magnesium carbonate hydrates are mineralized in the $MgO–CO_2–H_2O$ system depending on the temperature, partial pressure of CO_2, and pH. In an aqueous solution at room temperature to 55 °C and partial pressure of CO_2 close to ambient pressure or below, nesquehonite is precipitated. Since nesquehonite is however unstable at near surface ambient conditions, it subsequently transforms to hydromagnesite at moderate temperature and CO_2 pressure depending on the reaction time. This is achieved through one or more dissolution–precipitation steps, giving rise to a variety of short-lived metastable intermediates such as dypingite-type phase. Hence, nesquehonite acts as a precursor for hydromagnesite, which is by far the most common naturally occurring magnesium carbonate hydrates minerals at atmospheric CO_2 pressure within the temperature interval typical of most surface environment. With a further increase of the hydrothermal reaction temperature ranging from 120 °C to 185 °C, hydromagnesite transforms to magnesite via the dissolution–precipitation mechanism.

Here, we investigated the effects of pressure and temperature on hydromagnesite by using high-pressure and high-temperature neutron diffraction technique. In the report, we report the thermal and compression behaviors of hydromagnesite and new magnesite formation mechanism that proceeds under high-pressure and high-temperature conditions.

2. Experiment

In-situ high-pressure and high-temperature neutron diffraction patterns were obtained using the multi-anvil apparatus with six independently acting 500 t rams, 6-axis press called ATSUHIME, installed in the PLANET diffractometer, located at the beamline BL11 in the Materials and Life Science Experimental Facility of J-PARC, Japan. A multi-anvil 6-6 type (MA6-6) assembly was adopted in the study. The second-stage anvils were made of tungsten carbide with a truncated edge length of 10 mm. The deuterated hydromagnesite sample was transferred into a Teflon container of 5.5 mm diameter and 8 mm length with glycerol used as a hydrostatic pressure medium. It was inserted into a graphite tube heater embedded in the pressure transmitting medium of MgO. The sample temperature was estimated in advance from the relation between the generated temperature and input electric power calibrated with a thermocouple. The sample pressure was estimated from the load-pressure calibration curve determined in advance. The typical exposure time for collecting a diffraction pattern was 1 h. The accelerator power was approximately 200 kW during this experiment.

3. Results

Figure 1 displays variation of in-situ high-pressure and high-temperature neutron powder diffraction pattern in the temperature range from 25 °C to 200 °C at 1.2 GPa. At 150 °C, small peaks corresponding to magnesite appeared, and then the peaks became shaper at 175 °C. Magnesite coexisted with hydromagnesite in the temperature range from 150 °C to 175 °C. Furthermore, peaks corresponding to brucite appeared at 200 °C, while those corresponding to hydromagnesite completely disappeared. Hydromagnesite therefore changed directly into magnesite and brucite without the intermediate phase of poor crystalline magnesium carbonate hydrate. Under high-pressure and high-temperature condition (high-temperature in closed environment), the decomposition of hydromagnesite occurs as follows; $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \rightarrow 4MgCO_3 + Mg(OH)_2 + 4H_2O$. The similar result was obtained at 5.0 GPa. The SEM image revealed that the after the high-pressure and high-temperature measurement up to 200 °C at 1.2 GPa some single crystals clearly showed well-developed rhombohedral shape consistent with the typical euhedral morphology of magnesite. Thus, hydromagnesite was dissolved by the dehydrated water from itself, and subsequently magnesite and brucite were hydrothermally grown in the solution. That is, with increasing temperature in closed environment, dehydration of hydromagnesite leads to the dissolution and precipitation reaction that results in the formation of magnesite and brucite. Recently, kinetics of transformation of hydromagnesite into magnesite was investigated at 120 °C, 150 °C, and 180 °C with different heating times. This experiment was performed by using $MgCl_2$ solution and Na_2CO_3 solution as starting materials. As a result, hydromagnesite was precipitated as an initial precipitate at each temperature, but the transformation times at 120 °C, 150 °C, and 180 °C were approximately 10, 2, and 1 day. In this experiment, no mineral other than hydromagnesite and brucite were detected. Compared with the previous study, it is particularly noteworthy that the transformation of hydromagnesite into magnesite (the dissolution and precipitation reaction) more readily occurs with the dehydrated water from itself than in the aqueous solution. Figure 2 shows the variation of unit cell and unit cell volume of hydromagnesite in the temperature range from 25 °C to 150 °C at 1.2 GPa. Hydromagnesite exhibited on isotropic expansion along all directions. This thermal behavior under high-pressure, especially the behavior for *b*-axis, is appreciably different from that under ambient pressure. This is because in hydromagnesite the *b*-axis is the most highly compressible compared with the *a*- and *c*-axes. Consequently, since the unit cell is already contracted at 1.2 GPa, it can be expanded isotropically with temperature.

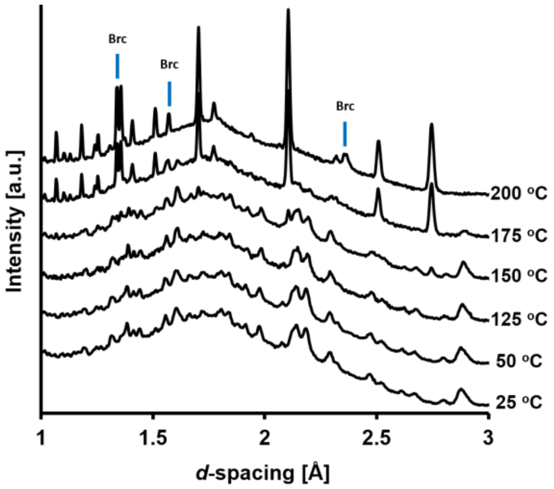

Figure 1. Variation of neutron powder diffraction pattern. Peaks of brucite are labeled with Brc.

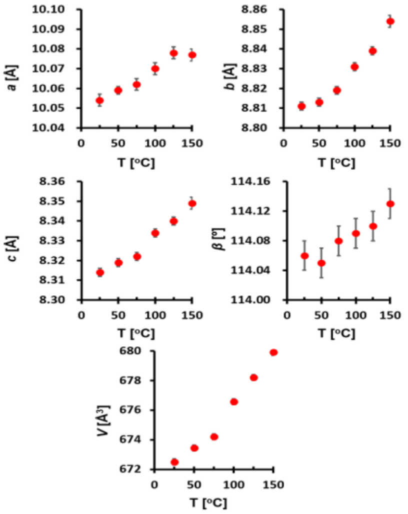

Figure 2. The variation of unit cell parameters of hydromagnesite from 25 to 150 °C at 1.2 GPa.