Crystal structure of nesquehonite, MgCO₃·3H(D)₂O by neutron diffraction and effect of pH on structural formulas of nesquehonite

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Neutron diffraction, Raman spectroscopy, and thermal analysis were performed to investigate the composition, structure, and formation conditions of the magnesium carbonate hydrate nesquehonite. The crystal structure of deuterated nesquehonite was analyzed by Rietveld refinement of the time-of-flight neutron powder diffraction pattern. The crystal structure possessed the monoclinic space group P2₁/n with lattice parameters of a = 7.72100(12) Å, b = 5.37518(7) Å, c = 12.1430(3) Å, β = 90.165(4)°, and V = 503.956(13) Å³. The refinement with a final crystal structure model of deuterated nesquehonite converged to wRp = 4.22% and Rp = 3.50%. The result of structure refinement showed that two deuterium atoms are coordinated to the O1, O2, and O6 atoms as a water molecule in the nesquehonite. The fact that the three water molecules were included in the structure suggests the structural formula of the nesquehonite obtained in the study should be written as MgCO₃·3H₂O not Mg(HCO₃)(OH)·2H₂O.

Keywords: Nesequehonite, Magnesium carbonate hydrate, Neutron diffraction, Hydrogen-bonding network

INTRODUCTION

The mineral carbonation of CO₂ is one of the promising technology for reducing the amount of carbon dioxide in the atmosphere (e.g., Oelkers et al., 2008; Matter and Kelemen, 2009; Sanna et al., 2014). Numerous approaches to CO₂ sequestration have extensively been studied (Park and Fan, 2004; Rendek et al., 2006; Kelemen and Matter, 2008; Assayag et al., 2009; Montes-Hernandez et al., 2009; Felmy et al., 2012; Farhang et al., 2016; Noiriel and Daval, 2017). Magnesium carbonates, therefore, offer attractive possibilities for the permanent and safe geological storage of CO₂ (Hänchen et al., 2008; Ferrini et al., 2009; Ballirano et al., 2010; Harrison et al., 2019). In the MgO–CO₂–H₂O system at temperatures ranging from 0 to 60 °C, the thermodynamically stable phases are brucite Mg(OH)₂ and magnesite MgCO₃ (Königsberger et al., 1999). The aqueous phase reaction, nevertheless, yields exclusively hydrated magnesium carbonates. The inhibition of magnesite formation has been ascribed to the strong hydration status of Mg²⁺ ions (e.g., Hänchen et al., 2008). Instead of magnesite, a variety of magnesium carbonate hydrates are formed depending on the temperature, the partial pressure of CO₂, and pH (Perchiazzi and Merlino, 2006; Back and Mandarino, 2008; Frost et al., 2008; Hänchen et al., 2008; Beinlich and Austrheim, 2012; Kristova et al., 2014). A large number of magnesium carbonate hydrates are known in the Mg–CO₂–H₂O system (Fig. 1). They can be classified into three types: the nesquehonite group (MgCO₃·nH₂O), the hydromagnesite group [Mg₅(CO₃)₄(OH)₂·nH₂O], and the artinite group [Mg₃CO₃(OH)₂·nH₂O]. Nesquehonite is precipitated in the temperature range from room temperature to 55 °C and at a partial pressure of CO₂ close to or below ambient pressure (Zhang et al., 2006; Morgan et al., 2015). It subsequently transforms to hydromagnesite at moderate
temperatures and \( \text{CO}_2 \) pressures depending on the reaction time (Davies and Bubela, 1973; Zhang et al., 2006; Hopkinson et al., 2008). Nesquehonite, therefore, acts as a precursor for hydromagnesite, which is by far the most common naturally occurring magnesium carbonate hydrate mineral at atmospheric \( \text{CO}_2 \) pressure within the temperature interval typical of most surface environments (Langmuir, 1965; Hopkinson et al., 2012).

The structural formula of nesquehonite has been long recognized as \( \text{MgCO}_3 \cdot 3\text{H}_2\text{O} \), which has been approved by the International Mineralogical Association, Commission on Minerals and Mineral Names (IMA–CNMMN) (Genth and Penfield, 1890; Giester et al., 2000). However, recent studies using IR spectroscopy (Frost and Palmer, 2011; Hopkinson et al., 2012), infrared emission spectroscopy (Frost and Palmer, 2011), and Raman spectroscopy (Hales et al., 2008; Hopkinson et al., 2012) have strongly suggested that bicarbonate (\( \text{HCO}_3^- \)) and hydroxyl (\( \text{OH}^- \)) groups exist in the structure. These results enable the interpretation accurately the behavior of nesquehonite in an aqueous solution, it is critically important to clarify the difference between \( \text{MgCO}_3 \cdot 3\text{H}_2\text{O} \) and \( \text{Mg(HCO}_3^-)(\text{OH})^- \cdot 2\text{H}_2\text{O} \). In previous studies (Stephan and MacGillavry, 1972; Giester et al., 2000), the crystal structure of nesquehonite was examined using an X-ray diffraction technique. As a result, six hydrogen positions were determined by difference electron density syntheses (Giester et al., 2000). The structural factors measured by neutron diffraction are heavily weighted by the contribution from the hydrogen (or deuterium) atoms. We, therefore, investigated the crystal structure of deuterated nesquehonite by a neutron diffraction technique. It was further characterized by Raman spectroscopy and thermal analysis. In this paper, we discuss the structural formula of nesquehonite and the possibility that nesquehonite can possess two structural formulas depending on the pH in a solution.

**EXPERIMENTAL METHODS**

Commercially available \( \text{MgCl}_2 \) (Wako Pure Chemicals Co., Inc., purity, \( \geq 97.0\% \)) and \( \text{Na}_2\text{CO}_3 \) (Wako Pure Chemicals Co., Inc., purity, \( \geq 99.5\% \)) were used as starting materials for nesquehonite. For the deuterated nesquehonite, solutions containing 20 ml of 0.5 M \( \text{MgCl}_2 \) and 20 ml of 0.5 M \( \text{Na}_2\text{CO}_3 \) were first prepared with distilled water. A white slurry immediately appeared when the solutions were mixed in a 1:1 molar proportion. The solution was then stirred at room temperature under vigorous magnetic stirring for 3 h in a closed system while sealed with a paraffin film. The pH value in the solution was ultimately stabilized at 10.9. The precipitate was subsequently filtered and washed on the filter with distilled water. The precipitate was collected and dried in the air overnight. The deuterated nesquehonite was also prepared for neutron diffraction measurements by dissolving the \( \text{MgCl}_2 \) and \( \text{Na}_2\text{CO}_3 \) in deuterium oxide (\( \text{D}_2\text{O} \)) (Wako Pure Chemicals Co., Inc., purity, \( \geq 99.9\% \)). The subsequent steps were the same as those described above. The precipitate was filtered and washed with deuterium oxide.

In order to identify the precipitates resulting from mixing \( \text{MgCl}_2 \) and \( \text{Na}_2\text{CO}_3 \) in water, X-ray diffraction measurements were performed by powder X-ray diffraction (Bruker AXS GmbH, D8 Advance TSM) equipped with a \( \text{CuK} \alpha \) rotating-anode generator operated at 40 kV and 40 mA. Powder samples were mounted on a non-reflective silicon plate. Data were collected in step-scan mode in the region of 10° ≤ 2θ ≤ 70° with a step size of 0.02° and a counting time of 0.1 s per step.

Raman spectra of undeuterated and deuterated nesquehonites were recorded by a micro-Raman spectrometer (NRS–5100, Japan Spectroscopic Co., Japan) equipped with a grating of 1800 lines/mm and a high sensitivity cooled CCD detector. Samples were excited with a green laser operating at 532.12 nm. The incident laser power was kept at less than 5.4 mW to prevent dehydration of nesquehonite. A 100× objective lens was used to focus the laser beam onto a 1-μm area. Raman spectra were collected with an integration time of 1 min, and the two accumulations were averaged. The resolution of the spectra was below 4.1 cm\(^{-1}\). The spectra were corrected by the emission lines of a neon lamp. The laser beam produced no visible damage on the surface of the samples in the measurements. The least-squares peak-fitting soft-
were Peak-Fit (AISN Software Inc., Chicago) was used to perform the analysis of the Raman spectra data. Data smoothing and baseline fitting were conducted using a Savitzky–Golay method and hyperbolic model, respectively. Band positions were determined by fitting the Raman peaks with a Lorentzian peak shape function.

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed to characterize the thermal behavior using a thermal analyzer (TG/DTA-7300, Seiko Instruments Inc., Japan). Approximately 10 mg of undeuterated nesquehonite and α-alumina used as a reference were placed in Al pans. They were subsequently heated over a 60–550 °C temperature range with a heating rate of 5 °C min⁻¹ in argon flowing at 200 mL min⁻¹.

Neutron diffraction measurements were conducted using a time-of-flight neutron diffractometer at the BL11 beamline PLANET (Hattori et al., 2015) in the Materials and Life Science Experimental Facility (MLF) of J-PARC, Japan. The deuterated nesquehonite synthesized was loaded into a cylindrical vanadium can with 3.0 mm outer diameter and 0.1 mm wall thickness. The incident beam size was adjusted by slits to approximately 5 mm in the horizontal direction and 10 mm in the vertical direction. To obtain data of sufficient statistical quality for Rietveld structure refinement, the sample was exposed to the neutron beam for 2 h at an accelerator power of approximately 500 kW. The data for the vanadium rod, empty vanadium container, and instrumental background were also separately measured for intensity corrections.

The crystal structure of nesquehonite was investigated by the Rietveld structure refinement analysis using the General Structure Analysis System (GSAS) package (Larson and Von Dreele, 2004) with the EXPGUI interface (Toby 2001). The lattice parameters, atomic positional parameters, isotropic displacement parameters, profile function, background function, and scale factor were refined using TOF data in the 3.786–40.000 ms range, corresponding to d-spacings of 0.400 < d < 4.227 Å. Regarding site occupancy, all sites were assumed to be fully occupied. In the analysis, the peak profile was modeled with an exponential pseudo-Voigt function (Larson and Von Dreele, 2004). The peak cut-off was set to 0.1% of the intensity of the strongest reflection of nesquehonite, and the background was fitted with an 18-term Chebyshev polynomial (Larson and Von Dreele, 2004). No constraints on bond lengths and angles were applied in the refinements.

RESULTS AND DISCUSSION

Characteristics of synthesized nesquehonite

Figure 2 shows the X-ray diffraction patterns of the precipitates obtained in the study. The peak positions of the precipitates collected from the distilled water were in approximate agreement with that of nesquehonite. Although there is a small peak shift due to the isotope effect, the XRD patterns of the precipitates collected from the deuterium oxide were entirely consistent with that of precipitates obtained in the distilled water. Therefore, it appears that undeuterated and deuterated nesquehonite were successively synthesized. The XRD measurements, however, showed a small amount of impurity that could not be identified.

Figure 3 shows the Raman spectra of the undeuterated and deuterated nesquehonite. Compared with the OH stretching vibration modes in the undeuterated nesquehonite, the OD stretching vibration modes in the deuterated nesquehonite were significantly shifted to the lower wavenumber region due to the isotope effect (Fig. 3). In the deuterated nesquehonite, weak OH stretching vibrations were observed in the range from 3000 to 3700 cm⁻¹ (Fig. 3d), indicating slight atmospheric hydrogen contamination.

Figure 4 shows TG, DTG, and DTA curves for the undeuterated nesquehonite. We could clearly observe three endothermic peaks below 300 °C (i.e., 105, 144, and 195 °C) and two endothermic peaks between 300 and 550 °C (i.e., 435 and 478 °C). The thermogravimetric data for the undeuterated nesquehonite are given in Table 1. The total mass loss of 36.4% experimentally determined between 60 and 320 °C was slightly smaller than the theoretical value of 39.1% that corresponds to the elimination of 3 mol H₂O from nesquehonite. On the other hand, the peak positions, the peak areas, and the peak shapes of the deuterated nesquehonite were significantly shifted to the lower wavenumber region due to the isotope effect.
er hand, a total mass loss of 34.1% between 320 and 550 °C was higher than the theoretical value of 31.8% that corresponds to 1 mol CO₂ of nesquehonite. The total mass loss of 70.5% observed by the thermal analysis was close to the theoretical mass loss of 70.9%.

Table 1. Thermogravimetric data for undeuterated nesquehonite

| T (°C)   | Mass loss (%) |
|---------|---------------|
| 60–134  | 17.3          |
| 134–179 | 8.76          |
| 179–320 | 10.3          |
| Σ       | 39.1          |
| 320–464 | 30.8          |
| 464–550 | 3.33          |
| Σ       | 31.8          |
| Total   | 70.9          |

Table 2. Data collection parameters, refinement details, crystal structural data, and atomic coordinates and displacement parameters (Å²) for deuterated nesquehonite

| Site   | x     | y     | z     | U₁₁₁ (Å²) |
|--------|-------|-------|-------|-----------|
| Mg     | 0.2433(15) | 0.0822(9) | 0.1466(5) | 0.00111(16) |
| C      | 0.2524(10) | 0.1381(10) | 0.4084(4) | 0.00147(12) |
| O1     | 0.5185(13) | 0.0890(17) | 0.1570(8) | 0.0019(3) |
| O2     | 0.9828(13) | 0.0946(17) | 0.1490(10) | 0.0034(3) |
| O3     | 0.2599(12) | 0.4011(10) | 0.0644(4) | 0.00147(14) |
| O4     | 0.2502(13) | 0.1974(10) | 0.3096(5) | 0.00135(16) |
| O5     | 0.2519(13) | 0.8069(10) | 0.0202(5) | 0.00171(15) |
| O6     | 0.2798(12) | 0.3516(14) | 0.8305(6) | 0.00162(2) |
| D1     | 0.586(11)  | 0.1569(14) | 0.0879(7) | 0.0042(3) |
| D2     | 0.5852(11) | 0.0464(15) | 0.1568(7) | 0.0051(3) |
| D3     | 0.9109(14) | 0.1472(16) | 0.0913(9) | 0.0039(3) |
| D4     | 0.9174(12) | 0.1197(20) | 0.2172(8) | 0.0077(3) |
| D5     | 0.1638(11) | 0.3108(16) | 0.8211(8) | 0.0065(4) |
| D6     | 0.2733(13) | 0.3739(13) | 0.9184(6) | 0.0049(2) |

**Neutron diffraction**

The crystal structure of the deuterated nesquehonite was determined by Rietveld analysis of the time-of-flight neutron powder diffraction pattern. The results of structural refinements and structural parameters are presented in Table 2. Selected interatomic distances and angles are listed in Table 3. Initial atomic positional parameters were taken from the data of Giester et al. (2000), in which the crystal structure of nesquehonite was defined as MgCO₃·3H₂O. In order to obtain information on the positions of deuterium (D) atoms, first, the crystal structure of deuterated nesquehonite was refined without deuterium (D) atoms. As mentioned above in the discussion of the Raman spectra, since the effect of the hydrogen contamination was negligible, all residuals were treated as deuterium atom positions. The three-dimensional difference-Fourier map of the residual nuclear scattering length density distribution was visualized by the VESTA program (Momma and Izumi, 2011) (Fig. 5), which shows residual densities near the O1, O2, and O6 atoms. Two deuterium (D) atoms were then placed near each of the...
oxygen atoms. As a result, all atomic positions and equivalent isotropic displacement parameters were converged to the residual factors of $wR_p = 4.22\%$ and $R_p = 3.50\%$ (Table 2). The neutron diffraction data were adequately fitted with the crystal structure model (Fig. 6).

Figure 7 shows the crystal structure of deuterated nesquehonite refined in the study, implying that deuterium (D) atoms are coordinated to O1, O2, and O6 atoms, forming a water molecule in the nesquehonite. In the crystal structure of nesquehonite, the infinite ribbons running along the $b$-axis consist of MgO$_6$ octahedra, in which each Mg atom is coordinated to two O atoms in water molecules and four O atoms in CO$_3$ groups. The ribbons are interconnected by the hydrogen bonding of water molecules between the ribbons (Fig. 7a).

The interatomic distances and angles refined in the study are in satisfactory agreement with those reported by Giester et al. (2000) (Table 3). The D3 and D4 atoms coordinated to O2 form a symmetric configuration with the water molecules, but the D1 and D2 atoms coordinated to O1 exhibit a highly asymmetric configuration, which may be ascribed to the asymmetric charge distribution on the water molecule. The O1–D2 distance has the shortest bond distance of 0.891(9) Å (Table 3). This shortest bond among all O–D bonds was observed in the previous study as well (Giester et al., 2000). The water molecules consisting of O6, D5, and D6 locate between the ribbons and are included in the hydrogen-bonding network (Fig. 7a). The hydrogen bonds range between 1.752(12) Å and 1.953(11) Å, except for the D5–O1 and D5–O2 bonds with distances of 2.346(14) Å and 2.483(13) Å, respectively. All hydrogen bonds were shorter than those determined by Giester et al. (2000), which is due to the longer O–D bonds. The water molecules coordinated to Mg atoms and located between ribbons form a three-dimensional hydrogen-bonding network (Fig. 7a). It is, therefore, concluded that three water molecules are included in the structural formula. Consequently, the structural formula of nesquehonite is clearly described as MgCO$_3$·3H$_2$O. Based on the empirical parameters of Brese and O’Keeffe (1991), the bond valence sums are listed in Table 4. The Mg and C atoms showed reasonable bond valence sums. Although the Mg–O$_3$ bond distance of 1.988(7) Å is considerably shorter than the average bond distance (Table 3), the bond valence sum of the O$_3$ atom gives a significantly lower bond valence than the ideal value of 2.0 (Table 4). This bond valence deficiency would be a structural feature of nesquehonite, and it sug-

| Table 3. Selected interatomic distances (Å) and angles (°) in nesquehonite |
|---------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Mg   – O1                             | 2.129(12)       | 1.988(7)       | 2.074(7)       | 2.136(6)       | 2.134(7)       | 2.079          | 2.076          |
| Mg   – O2                             | 2.012(12)       | 2.066(1)       | 2.009(1)       | 2.118(1)       | 2.148(1)       |                |                |
| Mg   – O3                             | 1.320(7)        | 1.269(1)       | 1.288(1)       | 1.291(1)       |                |                |                |
| C    – O3                             | 1.320(7)        | 1.269(1)       | 1.288(1)       | 1.291(1)       |                |                |                |
| Average                                   | 1.272           | 1.283          |                |                |                |                |                |

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suggests that the O3 atom can act as a tridentate ligand linking three different atoms to form the bicarbonate (HCO₃⁻) species. That is, the O3 atom can potentially be coordinated not only to Mg and C atoms but also to the H atom. Consequently, nesquehonite could have the structural formula of Mg(HCO₃)(OH)·2H₂O due to this bond valence deficiency. The larger bond valence sums of the O₁ and D₂ atoms are due to the short O₁–D₂ bond, whereas the lower bond valence sums of D₁ and D₆ atoms are ascribed to the longer O₁–D₁ and O₆–D₆ bonds. These deviations from the ideal values are likely caused by the highly asymmetric configuration, which may be ascribed to the asymmetric charge distribution on the water molecule (Soper, 2005), but further study is required to understand the details.

### Structural formula of nesquehonite

The structural formula of nesquehonite has been long recognized as MgCO₃·3H₂O (Genth and Penfield, 1890; Giester et al., 2000), but recent studies have strongly suggested that its structural formula should be redefined as Mg(HCO₃)(OH)·2H₂O (Hales et al., 2008; Frost and Palmer, 2011; Hopkinson et al., 2012). This controversy may be resolved by accounting for differences in formation conditions. In this study, we applied an alkali metal carbonate as a starting material, which was the same method as that of Coleyshaw et al. (2003) and Jauffret et al. (2015). However, the pH of alkali metal carbonate solutions, such as Na₂CO₃ and K₂CO₃, completely differed from that in Hales et al. (2008) and Hopkinson et al. (2012). The pH value can be considered as a critical factor in the formation of magnesium carbonate hydrates because these minerals exhibit wide chemical variability depending on the temperature, the partial pressure of CO₂, and pH (Perchiazzi and Merlino, 2006; Back and Mandarino, 2008; Frost et al., 2008; Häńchen et al., 2008; Beinlich and Austrheim, 2012; Kristova et al., 2014).

It is well known that the relative proportions of car-
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Bon ion species (CO$_2$, HCO$_3^-$, and CO$_3^{2-}$) depend on the alkalinity (Fig. 8). Thus, bicarbonate ion (HCO$_3^-$) is the dominant species between pH 6.35 and 10.33 at 25 °C. In the studies of Hales et al. (2008) and Hopkinson et al. (2012), nesquehonite was synthesized at a pH below 8. It is, therefore, quite reasonable that nesquehonite with the structural formula of Mg(HCO$_3$)(OH)·2H$_2$O would be crystallized in a solution with a pH below 8.1. In the present study, on the other hand, nesquehonite was prepared from MgCl$_2$ and Na$_2$CO$_3$ solutions, which led to a high pH value (pH = 10.9). The solution prepared in the study was dominated by the carbonate ion (CO$_3^{2-}$). As a result, nesquehonite with the structural formula of MgCO$_3$·3H$_2$O would be crystallized in the solution. It has already been reported that nesquehonite of MgCO$_3$·XH$_2$O phases occurred at pH values between 8.5 and 12.5 (Zhang et al., 2006), whereas the Mg(HCO$_3$)(OH)·2H$_2$O phase was formed at a pH below 8 (Hopkinson et al., 2012). Consequently, the pH value seems to determine which carbon ion species are incorporated into the nesquehonite structure. There would, therefore, be two structural formulas of nesquehonite, MgCO$_3$·3H$_2$O and Mg(HCO$_3$)(OH)·2H$_2$O, which are formed separately depending on the pH value in an aqueous solution.

ACKNOWLEDGMENTS

The authors must acknowledge and appreciate two anonymous reviewers for their constructive comments and insightful suggestions to improve the original manuscript. The neutron diffraction experiment was approved by the Neutron Science Proposal Review Committee of J-PARC MLF (proposal no. 2018B0038). This work was partially supported by JSPS KAKENHI Grant Number JP17K05702.

SUPPLEMENTARY MATERIAL

Color version of Figure 5 is available online from https://doi.org/10.2465/jmps.200117.

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