LETTER

Transformation process of amorphous magnesium carbonate in aqueous solution

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Amorphous magnesium carbonate (AMC) is an important phase in the early formation stage of magnesium carbonate. In this study, precipitation experiments were conducted to clarify the formation and transformation process of AMC in aqueous solution. Fine AMC particles precipitated, immediately after mixing of Na_2CO_3 and MgCl_2 solutions. Chemical composition of the AMC was determined to be approximately $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$ although two hydration states were expected to exist for AMCs. Subsequently, the AMC transformed in aqueous solutions into needle-like crystals of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), eventually to tiny polycrystalline particles of dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$] via a solvent-mediated processes.

Keywords: Amorphous, Magnesium carbonate, Hydration

INTRODUCTION

Crystal formation of carbonate minerals from aqueous solution via amorphous precursor is often reported (Ogino et al., 1987; Kawano et al., 2002) and has recently attracted more research interest in various fields such as biomineralization (Addadi et al., 2003; Von Euw et al., 2017) and the design of new materials (Oaki et al., 2008; Matsunuma et al., 2014). Although a large number of studies have been performed, this crystallization mechanism is poorly understood. To probe this problem, we examined the model system of $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$. In this system, magnesite (MgCO_3) is the most stable phase. Modern magnesite is considered to have precipitated under atmospheric pressure and temperature in nature, however it cannot be synthesized from aqueous solutions at ambient conditions (so-called ‘the magnesite problem’; Deelman, 2011). Instead, various hydrated magnesium carbonates such as nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], and dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$] have been reported to precipitate from solution in the laboratory (Canterford and Tsambourakis, 1984; Hänchen et al., 2008). However, little is known concern-

ing the relation between the properties of AMC and the final crystalline magnesium carbonate hydrates.

Recently amorphous magnesium carbonate (AMC) was reported to precipitate from supersaturated solution (Radha et al., 2012). Montes-Hernandez and Renard (2016) suggested that AMC transformed into nesquehonite, eventually dypingite while Fukushima et al. (2017) reported hydromagnesite precipitated from AMC in the presence of monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) in the aqueous system of $\text{CaO}-\text{MgO}-\text{CO}_2$. The detail transformation mechanism, for example, change of hydration state or molecular behavior during this process, is still unclear. AMC may play a significant role in magnesium carbonate formation, thus understanding the hydration/dehydration process of AMC may lead to revealing the magnesite formation. The goal of this study is to explore this issue by examining the transformation process of AMC in aqueous solution.

EXPERIMENTAL PROCEDURE

Precipitation experiment

Precipitation experiments were conducted by mixing of 25 ml of 0.2 M Na_2CO_3 and 25 ml of 0.2 M MgCl_2 solutions in a PTFE (polytetrafluoroethylene) beaker in a

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closed system sealed with a rubber stopper. After rapid mixing, the solution was stirred magnetically in the thermostat bath at 15 °C. Solution pH was monitored by means of pH electrode (Metrohm No. 6.0258.100) calibrated with standard buffers (pH 7.00 and 9.00). In addition, the solutions and precipitates were monitored by an optical microscopy every 1000 s to 10000 s and every 100000 s to 1800000 s throughout the experiments.

Sample analysis

For phase identification, precipitates were collected and filtrated through a 0.2 µm membrane filter. After drying in a desiccator evacuated with a diaphragm pump (~0.1 MPa) overnight, the powder samples were harvested for additional analyses. Powder X-ray diffraction (XRD; CuKα, 40 kV, 30 mA) pattern of the samples were acquired using MAC Science MX-Labo in the range $2\theta = 2-70^\circ$. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 operated at 200 kV to obtain electron diffraction. A scanning electron microscope (SEM; JEOL JCM-500 NeoScope) was used to observe their morphologies. Infrared absorbance spectra of the powder samples were measured by a Fourier Transform Infrared (FT-IR) spectrometer (JASCO FT/IR 6100) equipped with an attenuated total reflection (ATR) stage at resolution of 2 cm^{-1} and accumulation of 100 scans. In addition, thermogravimetry-differential thermal analysis (TG-DTA, Rigaku Thermo plus EVO TG 8120) was performed by heating the samples on an alumina pan in flowing N₂ gas (100 ml/min) with alumina powder as a standard material to determine the concentrations of CO₂ and H₂O constituents in the samples. The heating conditions were followed the scheme suggested by Lin et al. (2015): raising T at 10 °C/min to 100 °C, keeping T at 100 °C for 20 minutes; and raising T again at 10 °C/min to 1400 °C.

RESULTS AND DISCUSSION

Amorphous magnesium carbonate

Upon quickly mixing of the pre-prepared salt solutions, a white slurry of fine precipitates was observed in a few seconds. Powder XRD pattern of the precipitates collected immediately after did not show any apparent peaks, indicating that the early formed precipitate was amorphous phase. The lack of crystallinity was further confirmed by TEM, which revealed a halo pattern under selected area electron diffraction (SAED) on the fine precipitated nano-particles (Fig. 1). The infrared absorption bands corresponding to H₂O (1654 and 3354 cm^{-1}) and CO₃ vibration (858, 1098, and 1456 cm^{-1}) were observed, indicat-

Figure 1. TEM image and electron diffraction of AMC (inset: SAED).

Figure 2. FT-IR spectrum of AMC.

ing that hydrous status of the precipitated AMC (Fig. 2).

TG-DTA was performed up to the temperature the powder AMC was decomposed into periclase (MgO) in order to determine the composition of AMC (Fig. 3). We found that endothermic reaction of decomposition of AMC proceeded via three weight losses thought of as two dehydration (<100 °C and 100–200 °C) and one decarbonation (>200 °C) reactions. There seemed to be a few endothermic peaks in DTA profile over 500 °C, tiny amount (negligible weight losses) of sodium salts. It is possible that the second weight loss was caused by the following dehydroxylation reaction: $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$. However, if the present AMC has such hydroxyl groups, the charge balance of the AMC can not be maintained. Thus, the AMC should not contain $\text{Mg}(\text{OH})_2$. From this result, it was calculated that the weight losses for two dehydration reactions were 17.5 and 12.4 wt% and it for the decarbonation reaction was 36.4 wt%, respectively. Thus, the chemical composition of AMC was

Figure 3. TG-DTA curves of AMC. TG weight, DTA, and temperature profiles were shown as the bold, dotted and fine line, respectively. Black arrows indicate three weight losses corresponding to dehydration and decarbonation reactions of AMC.

determined to be about $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$. This AMC contained more water than AMC previously reported in Lin et al. (2015) ($\text{MgCO}_3 \cdot 0.91\text{H}_2\text{O}$) and Radha et al. (2012) ($\text{MgCO}_3 \cdot 1.28\text{H}_2\text{O}$). Furthermore, the detection of two weight losses below 100 °C and from 100 to 200 °C suggested the existence of two types of hydration waters, consistent with the measurement by Lin et al. (2015), corresponding to a loosely bound water stable at $T < 100$ °C and a tightly bound water stable in the temperature range of 100 to 200 °C. This concept was based on Schmidt et al. (2014), who showed the weight loss below 100 °C of amorphous calcium carbonate was due to the dehydration of not only physisorbed water but also structural water. AMC obtained in the present study thermally decomposed in the same way as Lin et al. (2015), thought to contain loosely bound water (58%) and tightly bound water (42%). Whether this AMC has the same structure as the one reported in previous studies remains to be investigated, however, it appears safe to conclude that AMCs may have various water contents and perhaps different hydration states.

Transformation into nesquehonite

Measured pH near the time of initial AMC formation was around 10, but gradually decreased slightly to 9.95 in 3000 s (stage I in Fig. 4). After that, AMC began to dissolve with increasing pH (stage II). At the same time, well-defined needle crystals of several tens micrometers were observed under optical and SEM microscope (Fig. 5A). AMC were still existed separately, suggesting that the transformation of AMC by a solvent-mediated mechanism. XRD pattern of the precipitates indicated that the needle crystals were nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), one

Figure 4. The change of solution pH with time. This pH change can be divided into 5 stages. The early stage of the measurement is shown in the inset.

Figure 5. SEM image of precipitates (A) 5000 s and (B) 1800000 s after mixing.

of the hydrated magnesium carbonates. Sharp XRD peaks of nesquehonite imply a good crystallinity (Fig. 6A). However, electron diffraction could not be obtained for nesquehonite because nesquehonite crystals immediately transformed into amorphous phase by electron beam damage during the TEM observation.

Nesquehonite may have started forming in stage I and the rise of pH in stage II may be caused by the dissolution of AMC exceeding the formation of nesquehonite, which means the following reaction could have occurred:

When the formation reaction of nesquehonite became predominant, the slope of pH change turned from positive to negative at 10.8.

Transformation into dypingite

After 240000 s of pH drop (stage III), solution pH was stable at around 10.4, indicating that nesquehonite was in quasi-equilibrium with solution (stage IV in Fig. 4). pH started decreasing again at 750000 s (stage V), indicating that a less soluble phase started precipitating, following the dissolution of nesquehonite. It is thought that the dissolution of atmospheric CO_2 does not greatly affect this pH change because the amount of CO_2 is much smaller than carbonate ions in the closed beaker. A lot of newly formed tiny particles and shortened nesquehonite needle crystals were observed in the precipitates formed in this period as seen under optical microscope. This result indicates the solvent-mediated transformation from nesquehonite to another phase occurred. From powder XRD pattern (Fig. 6B), the new phase was identified as dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$], another phase of hydrated magnesium carbonates. To the best of our knowledge, there has been no reports about detail crystal structure of dypingite but is believed to be a similar structure of hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] (Hopkinson et al., 2012). Raade (1970) pointed out that these two phases have similar XRD patterns, however dypingite has a characteristic peak at $2\theta = 8.3^\circ$, so can be distinguished from hydromagnesite. Solubility of dypingite has not been reported either, however the structural similarity to hydromagnesite suggests that it is also similar to that of hydromagnesite [the solubility product of hydromagnesite, $K_{\text{sp-hydromagnesite}} = 10^{-36.77}$, for the following equilibrium: $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow 5\text{Mg}^{2+} + 4\text{CO}_3^{2-} + 2\text{OH}^- + 4\text{H}_2\text{O}$, calculated using Königsberger et al., 1999] which is lower than nesquehonite ($K_{\text{sp-nesquehonite}} = 10^{-5.31}$, in the form of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$, calcu-

Figure 6. Powder XRD patterns of precipitates (A) 5000 s and (B) 1800000 s after mixing. (A) All peaks are agreement with the pattern of nesquehonite (Stephan and MacGillavry, 1972). (B) Almost all of peaks correspond to X-ray powder data reported by Raade (1970) in the range $2\theta = 5.8\text{--}60.9^\circ$.

lated using Königsberger et al., 1999). Broad XRD peaks, SEM images and SAED of the powder sample indicated that the precipitated dypingite was fine polycrystalline particles with low crystallinity (Figs. 5B and 6B). It should be noted that, in this transformation, crystals with well developed morphology and high crystallinity transformed into irregular shaped tiny crystals with low crystallinity increasing the surface energy, possibly affected by the stabilities of nesquehonite and dypingite. The reason for this transformation is unknown, however, the driving force for this transformation could be due to the difference of the K_{sp} between these two phases. The solution in stage IV would be saturated with respect to nesquehonite but supersaturated with dypingite.

To conclude, we showed in this study the formation of AMC immediately after mixing of 0.2 M MgCl_2 and Na_2CO_3 solutions. This AMC had an approximated chemical formula $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$ and contained two types

(loosely and tightly bounded) of waters. It transformed into well-developed needle crystals of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) during the mixing solution in dozens of minutes; after that, nesquehonite transformed into irregular shaped tiny crystals of dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$]. Both transformations were solvent-mediated. Considering hydration/dehydration behavior, water content increased in the former transformation, and Mg/ CO_3 ratio of the solid phases deviated from 1 in the latter. Both processes are opposite trends to the direct route for the formation of the most stable phase, magnesite, which is anhydrous and $\text{Mg}/\text{CO}_3 = 1$.

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