The Transformation of Nesquehonite to Hydromagnesite in the System CaO-MgO-H₂O-CO₂: An Experimental FT-Raman Spectroscopic Study

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ABSTRACT

This study reports the nature of the nesquehonite-to-hydromagnesite transition at 52°C in an aqueous medium hosting magnesian calcite and nesquehonite. The latter mineral occurs with abundant calcite at the floor of the experimental chamber [substrate] and as a film of needles at the interface between the mother liquor and atmosphere [surface film]. The experimental vessel was held at 52°C for 336 h and at 60°C for a further 192 h. Precipitates were analyzed by Fourier transform (FT)–Raman, augmented by FT-infrared and x-ray diffraction. At 52°C, hydromagnesite and dypingite occur with abundant quantities of a hitherto unreported transitory magnesium hydrate carbonate (TMHC), together with huntite, magnesian calcite, and traces of nesquehonite and monohydrocalcite. The FT-Raman spectra of the first-formed hydromagnesite crystals contain the Raman forbidden $v_2$ mode, interpreted to indicate a relaxation in selection rules, caused by rapid precipitation. Hydromagnesite growth at the expense of TMHC was more advanced in the substrate than in the coexisting surface film. Additional heating at 60°C resulted in the loss of TMHC and emergence of a dypingite- and hydromagnesite-rich assemblage, with associated strengthening of selection rules. Transitory magnesium hydrate and hydroxyl carbonates and huntite formed during CO₂ degassing, fueled by the thermally driven decrease in solubility of CO₂ in water and the progressive dissolution of metastable phases. Advancement of the N→HM transition in the substrate most likely reflects greater Ca²⁺(aq) availability to promote acid generation through calcite precipitation, thereby accelerating transitory-phase dissolution.

Introduction

Hydromagnesite is an abundant naturally occurring magnesium hydroxyl carbonate that constitutes a large and potentially reactive sink for C [e.g., Walling et al. 1995]. The mineral is of significant importance in sedimentary geology and planetology [e.g., Königsberger et al. 1999; Russell et al. 1999; Edwards et al. 2005b]. Accordingly, understanding possible biogenic and abiotic origins of the mineral is of consequence. Allied to this is the recognized need for Raman spectroscopic studies of mixed calcium and magnesium carbonate assemblages as databases for extraterrestrial planetary exploration [Edwards et al. 2005a].

The magnesium trihydrate carbonate nesquehonite readily precipitates from solutions of magnesium bicarbonate at room temperature. It is metastable and loses its CO₂ slowly at near-surface ambient temperatures in the air and under water and converts readily to hydromagnesite [e.g., Kazakov et al. 1959]. This process is accelerated significantly at higher temperatures, with transformation to hydromagnesite occurring in an aqueous medium by dissolution-precipitation step[s] at reported temperatures of 52°–65°C [Langmuir 1965; Davies and Bubela 1973, Botha and Strydom 2001]. The precise details of the transformation process and the character of the transitory mineral and/or mineraloid phase[s] remain unclear [fig. 1], although it seems certain that at least some naturally occurring hydromagnesite originates from the instability of the nesquehonite-to-hydromagnesite transformation (Davies and Bubela 1973).

Naturally occurring magnesium-enriched aqueous solutions overwhelmingly contain at least
some calcium. The nucleation and growth rate of CaCO₃ is strongly affected by the presence of Mg²⁺, while lattice strain due to the incorporation of magnesium ions increases the solubility of calcite (e.g., Aikin and Lagerwerff 1965; Folk 1974; Berner 1975; Reddy and Wang 1980; Mucci and Morse 1983; Compton and Brown 1994; Pokrovsky 1998; Chen et al. 2006). The quantity of Mg²⁺ incorporated into the calcite is also affected by the precipitation rate (e.g., Garrels and Wollast 1978). High magnesium concentrations in aqueous solutions can also potentially inhibit calcite formation, preferentially allowing monohydralcite or aragonite to precipitate (Lippmann 1973).

When thermally unstable nesquehonite exists in an aqueous system close to supersaturation with CaCO₃, the rise in pH promoted by nesquehonite dissolution can potentially promote calcite precipitation, the ensuing fall in pH accelerating continued nesquehonite dissolution (Davies et al. 1977). This means that the progress of the nesquehonite-hydromagnesite transformation [N→HM] may be influenced by calcium carbonate dissolution-precipitation kinetics and that, conversely, the progress of the N→HM transition may influence calcium carbonate mineralogy and mineral chemistry. Here we report an experiment devised to evaluate the nature of the material products of the N→HM transition in the system CaO-MgO-H₂O-CO₂.

**Material and Methods**

**Experimental Procedure.** Pulverized Mg(OH)₂ (2.90 g, 0.05 mol) and CaCl₂·2H₂O (1.47 g, 0.01 mol) were suspended in water (150 mL). The suspension was stirred at room temperature (Mg²⁺(aq) = Ca²⁺(aq) = 5:1), and CO₂ was bubbled through it for 12 h at 25°C. During this period, the pH dropped from 10.5 to 6.6. The addition of CO₂ was continued until the slurry pH stabilized. At this point the CO₂ flow was stopped. The suspension was filtered and the residue allowed to dry in air. The vibrational spectrum was measured. The residue was resuspended in the filtrate and heated at 35°C for 12 h. After filtration and air drying, the vibrational spectrum was remeasured. This procedure was continued, heating at 44°C, with the experimental cell covered to prevent reequilibration of the system with atmospheric CO₂. Precipitates in association with the mother liquor were held at 52°C for 336 h and then at 60°C for a further 192 h. At 52°C and 60°C a continuous crust of precipitated crystals (surface film) formed at the interface between the mother liquor and the atmosphere, in addition to precipitates lining the floor of the experimental vessel (substrate). Accordingly, analyses were undertaken for both substrate and film precipitates.

**Analytical Methods.** Identification of minerals was performed on powders of the synthesized precipitates. All powders were lightly ground and air dried at 25°C for 24 h. Techniques employed were Fourier-transform mid-infrared (FT-IR), FT-Raman, and x-ray diffraction (XRD). All analyses were conducted at 25°C. Raman analyses were undertaken (with a 1064-nm NdYAG laser source) in the range 150–2000 cm⁻¹ using a Nicolet Nexus FT-Raman module. Sharp bands are probably accurate to within 2 cm⁻¹. Infrared analyses were performed in the range 600–4000 cm⁻¹ using a Nicolet Avatar 320 FT-IR spectrometer fitted with a diamond attenuated total reflectance accessory. Electron microscopic analyses were conducted with a Jeol JSM6310 scanning electron microscope (SEM) with an Oxford Instruments ISIS energy dispersive spectrometer. FT-Raman, FT-IR, and SEM analyses were conducted at the University of Brighton.
pH measurements were undertaken at 25°C with a Mettler Toledo MP220 meter. The readings are accurate to 0.01 pH.

The XRD analyses were undertaken with a position-sensitive detector (PSD) at the Natural History Museum, London. X-ray powder diffraction data were collected using a Nonius PDS120 Powder Diffraction System with an INEL curved PSD. This detector has an output array of 4096 digital channels representing an arc of 120° 2θ and permits the simultaneous measurement of diffracted x-ray intensities at all angles of 2θ across 120° with a static beam-sample-detector geometry. Copper Kα radiation was selected from the primary beam using a germanium [111] single-crystal monochromator, and horizontal and vertical slits were used to restrict the beam to 0.24 × 5.0 mm. For these samples, measurements were made in reflection geometry with the powder sample surface at a fixed angle of 10° to the incident beam, to ensure good peak resolution. Data collection times were 40 min for each sample. The angular range recorded was 10°–120° 2θ. National Institute of Standards silicon powder SRM640, silver behenate, and Y₂O₃ were used as external 2θ calibration standards, and the 2θ linearization of the detector was performed using a least squares cubic spline function.

Raman Spectroscopic Study of Calcium and Magnesium Carbonates

The Raman spectroscopic signatures of magnesium and calcium carbonates are found in three wave-number regions: 1500–1000, 1000–500, and 500–100 cm⁻¹ (e.g., Scheetz and White 1977; Edwards et al. 2005a). In general, bands at frequencies above 500 cm⁻¹ are due to the internal motions of the molecular carbonate ion (internal modes), and those below 500 cm⁻¹ are due to motions involving the entire lattice cell (lattice modes). Within the 1500–1000 cm⁻¹ region, the symmetrical stretching mode ν₁ of the CO₃²⁻ ion is the strongest band observed in the Raman spectrum of the carbonates. The antisymmetric stretching ν₃ Raman band of CO₃²⁻ is of lower intensity than ν₁ but usually occurs near 1400 cm⁻¹. The antisymmetric bending vibration ν₄ occurs near 700 cm⁻¹. Lattice external modes occur in the low-wavenumber region (100–500 cm⁻¹). Because the ν₁ Raman stretching wavenumbers are higher for the magnesium carbonates than for their calcium analogues, the ν₁ stretching vibration in isolation can be used to differentiate between groups of either calcium or magnesium carbonates. However, the ν₁ mode in isolation is not sufficient for the unequivocal identification of individual calcium or magnesium carbonates in each group (Edwards et al. 2005a). Identification of mineral phases in mixed calcium-magnesium carbonate assemblages requires corroboration with other characteristic bands and, where appropriate, employment of complementary analytical techniques.

Experimental Results

Synthesized Precipitates, 25°C–44°C (12 h). The Raman spectrum of the precipitates formed as the pH dropped from 10.5 to 6.6 with CO₂ addition at 25°C is presented in fig. 2A. The three polymorphs of CaCO₃ (aragonite, calcite, and vaterite) show strong overlap in the 1085–1088-cm⁻¹ region. Moreover, the ν₁ mode of calcite, together with various other internal and lattice modes, range in frequency and band width as a function of MgCO₃ content (Bischoff et al. 1985). The presence of a band centred at ~1010 cm⁻¹ [a prototypical feature of vaterite], together with several lattice vibrations that can be assigned to calcite and/or vaterite, indicates a mixture of the two polymorphs. Vaterite is frequently formed in laboratory settings when CaCO₃ is precipitated rapidly. The polymorph is unstable with respect to calcite and can rapidly transform to the stable polymorph calcite through dissolution-precipitation reactions, the Mg²⁺ ion accelerating the crystal transformation process (Chen et al. 2006; Han et al. 2006).

The absence of resolvable bands at 1904, 1574, 1462, and 704 cm⁻¹ and of several lattice modes associated with aragonite suggests that the polymorph is not present, at least in any great abundance. Aragonite is frequently reported to form instead of calcite in magnesium-rich aqueous solutions (e.g., Lippmann 1973). The apparent absence of the polymorph may result from the low temperature of calcium carbonate precipitation (e.g., Han et al. 2006). Further, synthetic magnesian calcites in the <15-mol% range show products with ion activity lower than that of the equilibrium solubility product of aragonite (Bischoff et al. 1987).

The Raman spectrum of the precipitates formed after the residue was resuspended in the filtrate and heated at 35°C shows Raman-active bands for calcite and vaterite. Also present is a high-intensity band at 1099 cm⁻¹, which together with bands at 187, 228, and 703 cm⁻¹ indicate the presence of nesquehonite (fig. 2B). The pH of the 35°C mother liquor was measured at 7.08. The intensity of the 1099-cm⁻¹ ν₁ band of nesquehonite relative to background increases between 35° and 44°C (fig. 2C), with a discontinuous film of acicular nesquehonite crystals apparent at the surface of the mother liquor by 44°C. The pH of the solution...
was 7.45 close to the surface of the mother liquor, compared to 7.33 close to the calcite-bearing substrate, consistent with progressive CO₂ degassing of the mother liquor.

**Synthesized Precipitates, 52°C (336 h), FT-Raman Analysis.** At the transition temperature, the surface film of precipitates was sufficiently developed for sampling. The pH of the mother liquor was measured at 7.50 directly below the surface film and at 7.53 just above the substrate. The Raman spectrum of the substrate shows that calcite is the dominant phase (fig. 3A). A subordinate band at 1121 cm⁻¹ is broadly coincident with the ν₁ internal mode of the unidentified amorphous compound (UIC) of Lanas and Alvarez (2004). This mineraloid was produced over short experimental durations during heating of dried nesquehonite at >115°C. The 1121-cm⁻¹ band is also broadly coincident with the ν₁ band of hydromagnesite, which has been reported at frequencies ranging from 1117 to 1120 cm⁻¹ (e.g., White 1974; Edwards et al. 2005a), and huntite, reported at 1123 cm⁻¹ (Scheetz and White 1977).

Various lattice bands in the spectrum can be assigned to calcite, hydromagnesite, and dypingite. An additional medium-intensity band centered at ~800 cm⁻¹ is present. This band is barely resolvable in the surface film spectrum (fig. 3B). The 800-cm⁻¹ band is coincident with the infrared-active Raman-forbidden ν₂ carbonate bending vibration of hydromagnesite and occurs in conjunction with Raman-active hydromagnesite bands at 183, 202, 726, and 1450 cm⁻¹ (fig. 3A). To clarify the nature of the Raman-active 800-cm⁻¹ band, a subsample of the substrate was held in the presence of the mother liquor for an additional 168 h at 52°C (for a total of 504 h). The Raman spectrum shows a dramatic increase in the intensity of the 800-cm⁻¹ band relative to the substrate at 336 h. The intensity of the 800-cm⁻¹ band exactly equals that of the 1121-cm⁻¹ band. The ν₁ calcite band is subordinate in intensity. The Raman-active hydromagnesite bands, particularly the 726-cm⁻¹ band, are higher in intensity than those from the 336-h experiment. The evident growth of the 800-cm⁻¹ band at the N→HM transition and its coincidence with the infrared-active Raman-forbidden carbonate bending band of hydromagnesite suggest a relaxation of

![Figure 2](image-url)

Figure 2. Raman spectra of 25°C (12 h, A), 35°C (12 h, B), and 44°C (12 h, C) precipitates. C = calcite, N = nesquehonite, and V = vaterite.
selection rules, which can occur when distorted crystal structures are generated by rapid precipitation [e.g., White 1974]. Rapid synthesis of crystals at low temperatures means that mineral structures frequently do not reequilibrate readily into a well-ordered form [e.g., Scheetz and White 1977].

The Raman spectrum of the 336-h surface film shows a high-intensity band coincident with the intense $v_1$ vibration mode of huntite and broadly coincident with the $v_1$ band of hydromagnesite and the UIC (fig. 3B). No other bands could be assigned to huntite. However, it is interesting to note that the resolution of Raman-active bands from natural samples of huntite is variable and includes samples in which the $v_1$ mode is the only resolvable band (Scheetz and White 1977). Three low-intensity shoulders on the 1123-cm$^{-1}$ band are assigned to calcite, monohydrocalcite (tentatively), and dypingite. Low-intensity bands at 769 cm$^{-1}$ and just over 1500 cm$^{-1}$ suggest residual traces of nesquehonite. Barely resolvable bands at 800 and 726 cm$^{-1}$ suggest traces of hydromagnesite in the surface film, although it is evident that hydromagnesite precipitation is less advanced than in the associated 336-h substrate, in which Raman-active lattice modes of hydromagnesite are clearly resolved alongside the Raman-forbidden $v_2$ mode of hydromagnesite. Accordingly, XRD and FT-IR analyses were performed on the surface film to further characterize the nature of the transitory phase(s) present immediately before the onset of widespread hydromagnesite precipitation.

Surface Film Precipitates, 52°C (336 h), XRD Analysis.
The diffraction pattern indicates the presence of nesquehonite, dypingite, and huntite (fig. 4). However, peaks at $d = 22.28$ and 11.14 Å indicate that the main phase present is not a recognized magnesium hydroxyl or hydrate carbonate but probably has a layered structure, because its low-angle reflections can be indexed as first and second order, that is, 001 and 002, with $d(001) = 22.28$ Å. These peaks are not apparent in the XRD analysis of "protohydromagnesite" presented by Davies and Bubela [1973]. Protohydromagnesite (for which no vibrational spectra have been published) is extensively similar in chemical composition to barring-
tonite (fig. 1). In our work, XRD indicates the existence of an \( N \rightarrow HM \) transitory mineral phase in addition to dypingite and protohydromagnesite. Surface Film Precipitates, 52°C (336 h) FT-IR Analysis. The spectrum presented in fig. 5 shows that various bands that can be assigned to dypingite and/or hydromagnesite. It has previously been suggested that dypingite may be a transitory phase in the \( N \rightarrow HM \) transformation (Davies and Bubela 1973). Sharp bands at 1420 and 1476 cm\(^{-1}\) are consistent with the CO\(_3^{2-}\) \( v_3 \) stretching vibrations of both minerals and rule out the presence of the UIC. The spectrum also shows a broad band at \( \sim 1000 \) cm\(^{-1}\), consistent with dypingite (Raade 1970). However, the strong absorption band at 3650 cm\(^{-1}\), which results from OH\(^-\) groups in hydromagnesite and dypingite, is not resolved. Further, strong absorption at 1645 cm\(^{-1}\) (e.g., Raade 1970; White 1974; Lanas and Alvarez 2004) and the absence of a clearly resolved CO\(_3^{2-}\) bending band at 800 cm\(^{-1}\) are inconsistent with hydromagnesite and/or dypingite being the dominant constituents of the surface film. Hence, although the spectrum is composite in nature [because of the multimineral makeup of the surface film], FT-IR suggests that the layered main phase reported by XRD is a previously unidentified transitory magnesium hydrate carbonate (TMHC).

Extensive overlap exists between the infrared spectra of huntite and those of magnesium hydroxyl
and hydrate carbonates \(\text{e.g., Raade 1970; White 1974}\). Further, variability exists in the reported numbers and assigned frequencies of huntite infrared-active bands \(\text{e.g., Scheetz and White 1977; Kangal et al. 2005}\). The mid-infrared spectrum of the surface film shows a couplet of bands located at 851 cm\(^{-1}\) and a shoulder at 877 cm\(^{-1}\). The frequencies closely correspond to the huntite \(v_2\) bands reported, in two different studies, at 847 and 877 cm\(^{-1}\) \(\text{Böttcher et al. 1997}\) and 858 and 880 cm\(^{-1}\) \(\text{Scheetz and White 1977}\). Also present is a band at 1113 cm\(^{-1}\), broadly coincident with the huntite infrared-active \(v_1\) band variously reported at 1110, 1113, and 1105 cm\(^{-1}\) \(\text{Scheetz and White 1977; Böttcher et al. 1997}\). Several mid-infrared-active bands for huntite associated with splitting of \(v_3\) have been cited in the region 1450–1430 cm\(^{-1}\). Bands at 1539, 1508, and 1457 cm\(^{-1}\) \(\text{fig. 5}\) correspond to reported bands at 1535, 1510, and 1460 cm\(^{-1}\) \(\text{Scheetz and White 1977}\).

Synthesized Precipitates, 336 h at 52°C and 192 h at 60°C. The Raman spectra of the substrate and surface film both show a high-intensity band at 1121 cm\(^{-1}\) that, with several weaker bands, is assigned to hydromagnesite \(\text{fig. 6}\). A subordinate band at 995 cm\(^{-1}\) is assigned to dypingite. The intensity of this band in the substrate and film is far greater than that recorded at 52°C. No 800-cm\(^{-1}\) band is unambiguously resolved in either spectrum. The presence of a shoulder at 1069 cm\(^{-1}\) in both spectra may suggest the presence of traces of monohydrocalcite.

The FT-IR spectrum of the surface film shows an absorption band resulting from \(\text{OH}^-\) groups at 3650 cm\(^{-1}\) and the \(\text{CO}_2^-\) bending band at 800 cm\(^{-1}\) \(\text{fig. 7}\). Various other bands can similarly be assigned to dypingite and/or hydromagnesite. UIC is not detected. Huntite is not clearly resolved in the spectrum. However, line overlap of huntite with hydromagnesite and dypingite is extensive, and the relative strength of absorption bands at 850 and 880 cm\(^{-1}\), together with strong absorption at 1115 cm\(^{-1}\), suggests that huntite may be present.

SEM Analysis. The \(\text{52°C (336 h)}\) surface film is characterized by abundant platy aggregates of magnesium carbonates \(\text{fig. 8A}\). The aggregates are texturally distinct from accounts of natural occurring dypingite or barringtonite but are texturally similar to synthesized protohydromagnesite and some natural and synthesized hydromagnesite. However, it should be noted that radiating globular aggregates of natural dypingite may result from transformation of nesquehonite in the dry state. In addition, the dry-state N→HM transformation occurs without apparent change in crystal morphology \(\text{Dell and Weller 1959; Davies and Bubela 1973}\).

Huntite crystals occur with platy rhomboidal habits, aggregated into compact masses a few microns in diameter and hosted by the platy magnesium hydrate carbonates \(\text{fig. 8B}\). The textural occurrence and size ranges of the crystals are comparable to those of natural huntite \(\text{e.g., Dollase and Reeder 1986}\). Also present in the surface film are small quantities of acicular magnesium carbonates \(\text{fig. 8C}\). They are texturally comparable to nesquehonite synthesized in the early stages of the experiments and to synthesized nesquehonite in previous reports \(\text{e.g., Davies and Bubela 1973}\).

Nesquehonite aggregates host small rounded or dumbbell-shaped magnesium-bearing calcite crystals. The surfaces of the crystals are pitted and irregular \(\text{fig. 8D}\). The \(\text{Mg}^2+\) ion is known to influence calcite crystal morphology: the ion adsorbs on the surface of calcite, causing an increase in surface roughness and distortion of crystals \(\text{Chen et al. 2006}\). Analysis of the substrate revealed the same textural variability. All calcite crystals inspected were magnesium bearing. The magnesian calcite crystals range in size from a few microns up to \(\sim\)100 \(\mu\)m and show variable MgCO\(_3\) content. Magnesian calcites with up to 20 mol\% MgCO\(_3\) content have been reported from a number of low-temperature natural and experimental environments \(\text{e.g., Lippmann 1973; Bischoff et al. 1987}\).

The \(\text{60°C surface film contains platy aggregates of magnesium carbonate texturally comparable to natural and some synthesized hydromagnesite (documented in, e.g., fig. 8E)}\). The surfaces of the magnesium hydroxyl carbonates are variably overgrown with huntite \(\text{fig. 8F}\). No textures comparable to nesquehonite were detected, although rare magnesium-bearing calcite crystals showing morphologies extensively similar to those of the \(\text{52°C surface film precipitates were detected. Analysis of the substrate revealed the same textural variability with abundant magnesian calcite. No well-developed rhombohedral calcite crystals were encountered. Generally high Mg\(^{2+}_{(aq)}/\text{Ca}^{2+}_{(aq)}\) activity in pore waters accounts for calcite crystal morphologies and the low total numbers of calcite in the surface films, because increasing the Mg\(^{2+}_{(aq)}/\text{Ca}^{2+}_{(aq)}\) ratio in the mother liquor can promote a decrease in abundance of CaCO\(_3\) crystals (Chen et al. 2006).}

Discussion

Nesquehonite Formation. Presented in figure 9, plotted against temperature, are the pH readings and intensities of the \(v_1\) bands of calcite, nesque-
honite, and dypingite (measured as a ratio relative to background), along with those of the band situated approximately equidistant between the $v_1$ bands of huntite, hydromagnesite, and most likely TMHC (variably recorded between 1120 and 1123 cm$^{-1}$). The majority of CaCO$_3$ was precipitated as substrate at 25°C. A reduction at 35°C coincides with the appearance of nesquehonite and an increase in pH (fig. 9). A decrease in pH at 44°C is coincident with an increase in the intensity of the $v_1$ band of calcite and continued increase in the intensity of the $v_1$ mode of nesquehonite. At this stage, a surface tension-mediated discontinuous film of acicular nesquehonite crystals developed at the surface of the mother liquor, conditions being tangibly more acidic in the static pore waters close to the magnesian calcite enriched substrate.

Experimental results link nesquehonite formation to the decrease in solubility of CO$_2$ gas in water with increasing temperature (e.g., Pierantozzi 1993; Botha and Strydom 2001). Magnesium bicarbonate solutions deposit nesquehonite depending on the concentration of dissolved carbon dioxide: at concentrations of 2–19 g dm$^{-2}$ at 20°C, nesquehonite forms; at lower concentrations, 0.27–2 g dm$^{-2}$, artinite forms (Kazakov et al. 1959). The formation of nesquehonite during CO$_2$($aq$) degassing takes place in two steps (Menzel and Brückner 1930). Implicit in this is that the escape of carbon dioxide leads to the continued hydrolysis of the bicarbonate ion into carbonate (e.g., Deelman 2005):

$$\begin{align*}
\text{Mg}^{2+} + 2\text{HCO}_3^- + 3\text{H}_2\text{O} &\rightarrow \text{Mg}^{2+} + \text{H}_2\text{CO}_3 + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \\
&\rightarrow \text{MgCO}_3 \cdot 3\text{H}_2\text{O}_{(s)} + \text{H}_2\text{O} + \text{CO}_2_{(g)}.
\end{align*}$$

**The Nesquehonite $\rightarrow$ Hydromagnesite Transition.**

At temperatures greater than 50°C, nesquehonite readily converts to hydromagnesite (e.g., Davis and Bubela 1973). The decomposition of nesquehonite in an aqueous medium involves hydroxyl formation and the continuous addition of dissolved carbon dioxide to the mother liquor, with transitory

Figure 6. Raman spectra of 60°C precipitates substrate \(\{A\}\) and surface film \(\{B\}\). \(C = \text{calcite, } D = \text{dypingite, } H = \text{huntite, and } HM = \text{hydromagnesite.}\) The likely sources of unassigned peaks are discussed in “Synthesized Precipitates, 336 h at 52°C and 192 h at 60°C.”
phase(s) forming over a narrow thermal interval from the dissociation products (Davies et al. 1977):

\[
\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{HCO}_3^- + \text{OH}^- + \text{H}_2\text{O}.
\]

\[\text{(2)}\]

The simplest approximation of the chemical formula for protohydromagnesite is \(\text{MgCO}_3 \cdot 2\text{H}_2\text{O}\). Its growth at the expense of nesquehonite represents water loss (Davies and Bubela 1973). The time frame for production of TMHC was double that for protohydromagnesite, and therefore TMHC most likely represents water loss relative to the dihydrate. Accordingly, TMHC may approximate to a monohydrate. Although magnesium monohydrate carbonate has not yet been found in nature, it has been synthesized during the dry thermal decomposition of nesquehonite (e.g., Menzel and Brückner 1930; Dell and Weller 1959) and may be an extremely short-lived transitory phase during the N→HM transition in an aqueous medium.

At the transition temperature, \(\text{CO}_2\) addition to the mother liquor would be ongoing, as a consequence of dissolution of metastable carbonate phases and the effect of temperature on the solubility of \(\text{CO}_2\) in water. Accordingly, transitory magnesium hydrate and hydroxyl carbonates may have formed consecutively in a sequence of dewatering dissolution-precipitation steps, accompanying \(\text{CO}_2\) degassing. The proportionality of \(\text{CO}_2\) fixed in mineral phases, relative to \(\text{CO}_2\) gas escape, is not known, but it may approximate the following equations:

\[
\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{OH}^- + \text{H}_2\text{O}
\rightarrow
\text{Mg}^{2+} + \text{CO}_3^{2-} + 2\text{H}_2\text{O} + \text{OH}^- + \text{H}_2\text{CO}_3
\]

\[\text{(3)}\]

\[
\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{OH}^-
\rightarrow
\text{Mg}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{CO}_3 + \text{OH}^-
\]

\[\text{(4)}\]

\[
5\text{Mg}^{2+} + 8\text{HCO}_3^- + 2\text{OH}^- + \text{H}_2\text{O}
\rightarrow
5\text{Mg}^{2+} + 4\text{CO}_3^{2-} + 4\text{H}_2\text{CO}_3 + 4\text{OH}^- + \text{H}_2\text{O}
\]

\[\text{(5)}\]

The Behavior of Magnesian Calcite. Reactions \[1\]–\[5\] indicate the transient production of \(\text{HCO}_3^-\). The apparent decline in the solution \(p\text{H}\) with calcite precipitation at 44°C implies temporal availability of \(\text{HCO}_3^-\) to react with \(\text{Ca}^{2+}\)\(_{\text{aq}}\) to form calcite, thereby depressing the \(p\text{H}\) by \(\text{H}^+\)\(_{\text{aq}}\) liberation (e.g., Jiménez-López et al. 2001). Transient increases in \(\text{H}^+\) also leads to an increase in \(\text{CO}_2\)\(_{\text{aq}}\) in solution, with the \(\text{CO}_2\) either gradually escaping or being fixed in precipitating phases. It also follows that acceleration of nesquehonite dissolution by calcite formation may be limited by the progressive rise in \(\text{Mg}^{2+}/\text{Ca}^{2+}\)\(_{\text{aq}}\) gradually inhibiting calcite precipitation.

The thermodynamic stability of magnesian calcites has been the subject of many studies (e.g., Bischoff et al. 1987; Königsberger and Gamsjäger 1992). Dissolution congruency may vary with time and composition and may lead to the precipitation of secondary low-magnesium calcites and \(\text{Mg}^{2+}\) enrichment in pore solutions (e.g., Bischoff et al. 1987; Busenberg and Plummer 1989). Hence, thermally driven dissolution of magnesian calcite would most likely impart isothermal temporal heterogeneity in pore solution chemistries. Further, compositional limitation of high-magnesium calcites may be caused by the formation of the more stable compound huntite, formation of the latter potentially preventing the formation or causing

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Figure 7. FT-IR spectrum of the 60°C surface film. The infrared spectra of dypingite and hydromagnesite are extensively similar (Raade 1970; White 1974). Absorption bands resulting from \(\text{OH}^-\) groups (3650 cm\(^{-1}\)) and water of crystallization (3510 and 3450 cm\(^{-1}\)) are identical for both, as are \(\text{CO}_2\)\(^{\text{3-}}\) stretching bands (1480, 1420, and 1120 cm\(^{-1}\)) and \(\text{CO}_2\)\(^{\text{3-}}\) bending bands (880 and 850 cm\(^{-1}\)).
the decomposition of higher magnesian calcites [Königsberger and Gamsjäger 1992].

The preferential development of monohydrocalcite over calcite in magnesium-rich aqueous solutions has been documented [e.g., Hull and Turnbull 1973; Lippmann 1973]. Evidently, its formation in the experiments documented here was occasionally kinetically favored with respect to calcite during the N→HM transition, presumable because of the lower activation energy for its formation with respect to calcite [Jiménez-López et al. 2001] and varying but generally high prevailing \[\text{Mg}^{2+}_{\text{aq}}/\text{Ca}^{2+}_{\text{aq}}\]. The presence of monohydrocalcite could indicate that its nucleation rate was faster than calcium dehydration kinetics. Alternately, if the \(\text{CaHCO}_3\)^+ ion pair was the main Ca-bearing complex in solution due to induction and growth of monohydrocalcite [e.g., Jiménez-López et al. 2001], then interaction with increasingly abundant OH⁻ groups, afforded by the N→HM transformation process to form \(\text{CaCO}_3 \cdot \text{H}_2\text{O}\) [e.g., Stipp 1999; Jiménez-López et al. 2001], may account for its presence. In either event, monohydrocalcite is metastable with respect to calcite [Hull and Turnbull 1973] and transforms to the latter through a sequence of dissolution-precipitation reactions [Jiménez-López et al. 2001]. Further, dissolution of monohydrocalcite where surrounded by unstable magnesium hydrate carbonates provides a source of calcium for huntite [Davies et al. 1977] and, potentially, elevated \[\text{Mg}^{2+}_{\text{aq}}/\text{Ca}^{2+}_{\text{aq}}\] ratios to suppress or cause the decomposition of higher magnesian calcite.

**Huntite Formation.** Huntite forms either by direct precipitation from aqueous solutions or as a result of interaction of such solutions with preexisting carbonates [Kinsman 1967; Dollase and Reeder 1986; Zachmann 1989; Calvo et al. 1995].
The mineral is scarce in the natural environment and the geological record. To some extent, this is because conditions for its formation may not be common (Walling et al. 1995). However, the mineral is frequently associated with destructive degradation cycles and where occurring in modern sediments is probably subject to progressive replacement during later diagenesis by an equilibrium assemblage such as magnesite-dolomite or dolomite-calcite (Kinsman 1967; Lippmann 1973; Stamatakis 1995). Attempts to measure the solubility of huntite have proven problematic. The reported range of Gibbs energies of formation correspond to a variation of about 7.4 orders of magnitude in the equilibrium solubility product at 25°C (Walling et al. 1995). Further, magnesian huntite with Mg\(^{2+}\)/Ca\(^{2+}\) ratios as high as 4 have been reported (Stanger and Neal 1994).

In this study, huntite occurs as late-stage primary precipitate, associated with transitory magnesium carbonates. The requisite conditions for huntite formation include a high Mg\(^{2+}\)\(_{(aq)}\)/Ca\(^{2+}\)\(_{(aq)}\) ratio, high CO\(_3^{2-}\) concentrations (e.g., Stanger and Neal 1994; Walling et al. 1995), and a sufficient induction period for nucleation and growth. The conditions were evidently met during the N→HM transition. The textural occurrence of huntite is accounted for by the progressive depression of the Mg\(^{2+}\)\(_{(aq)}\)/Ca\(^{2+}\)\(_{(aq)}\) ratio with transitory magnesium carbonate formation sourced by the N→HM transitory steps, in a high-CO\(_3^{2-}\) environment with Ca\(^{2+}\)\(_{(aq)}\) derived from monohydrocalcite and magnesian calcite dissolution:

\[
\text{Ca}^{2+} + 3\text{Mg}^{2+} + 8\text{HCO}_3^- \rightarrow \text{Ca}^{2+} + 3\text{Mg}^{2+} + 4\text{CO}_3^{2-} + 4\text{H}_2\text{CO}_3 \quad \text{(6)}
\]

\[
\text{CaMg}_3(\text{CO}_3)_4(\text{s}) + 4\text{H}_2\text{O} + 4\text{CO}_2(\text{g})
\]

**Metastable Mineral Phases and the Ostwald Step Rule.** A feature of the 52°C precipitates is the presence of four metastable magnesium carbonates in conjunction with at least three metastable calcium-bearing carbonates. In many low-temperature systems, mineral precipitation follows the Ostwald step rule, in which metastable phases nucleate and are progressively replaced by more stable phases (e.g., Morse and Casey 1988; Deelman 1999; Jiménez-López et al. 2001). However, apparent mineral stabilities are affected by factors such as surface area/solution volume ratio, the solid/solution ratio, particle size, and precipitation of phases within the pore solution network (e.g., Bischoff et al. 1987). The high solids-to-liquid ratios in the experiment documented here also means that pore-scale chemical changes, notably in CO\(_2(\text{gas})\), HCO\(_3^-\) and CO\(_3^{2-}\) concentrations, pH, and Mg\(^{2+}\)\(_{(aq)}\)/Ca\(^{2+}\)\(_{(aq)}\) ratio, would exist. In such a setting, stability of metastable phases may not depend as much on averaged values described in the macroscopic parameters as on local crossings of the supersaturation limit (e.g., Deelman 1999).
Experimental results indicate preferential advancement of the N→HM transition in the magnesian calcite–enriched substrate relative to coexisting surface film. The latter represents the air-solution interface and a porous membrane to escaping CO₂. However, the surface film remained largely saturated at all times, and the evolution of the calcium-bearing carbonate mineralogy at the N→HM transition is common to both film and substrate. Hence, differences in availability of Ca²⁺(aq) to influence pH through calcite precipitation may account for the apparent disparity in the progress of the N→HM transition. Given this, it follows that pore-scale periodical fluctuations of variable magnitude in pH, dissolved CO₂, and Mg²⁺(aq)/Ca²⁺(aq) are attributes of the transformation process, arising in the absence of externally imposed periodic events.

Conclusions

The material products of the N→HM transition are strongly controlled by experiment duration. A hitherto undocumented short-lived TMHC develops immediately before the onset of hydromagnesite precipitation. The TMHC may well grow at the expense of protohydromagnesite. While the complete Raman spectroscopic signature of both minerals remains to be established, the v₁ mode of the TMHC closely coincides with the v₁ modes of huntite and hydromagnesite, producing a complicating factor in interpretation of Raman data. The growth of hydromagnesite at the expense of TMHC is sufficiently rapid for relaxation in Raman selection rules to occur. The absence of the hydromagnesite v₂ band in the Raman spectra of the 60°C sample implies that subsequent dissolution-crystallization steps strengthen selection rules. The coexistence of dypingite with hydromagnesite indicates that the former mineral is a transitory phase in the N→HM and suggests that pore-scale variability in structural ordering and water content persisted above the transition temperature. The formation of huntite and transitory magnesium hydrate and hydroxyl carbonates can be explained by CO₂ degassing reactions. However, the instability of the transitory phases to transformation also means that huntite may form autonomously in consecutive pulses at the end of each episode of transitory-phase precipitation. Nonuniformity in the progress of the N→HM transition is tied to pore-scale processes, associated variability in aqueous solution chemistries, and local crossings of supersaturation limits. Geochemical feedback between calcium carbonate and transitory phases, through dissolution-precipitation steps, serves to accelerate the N→HM transition.

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Queries

1. In the sentence beginning “Infrared analyses,” the abbreviation ATR has been deleted because it is not used again in the article.