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In Situ Measurement of Magnesium Carbonate Formation from CO₂ Using Static High-Pressure and -Temperature ¹³C NMR

J. Andrew Surface,[†] Philip Skemer,[‡] Sophia E. Hayes,^{*,†} and Mark S. Conradi^{*,§}

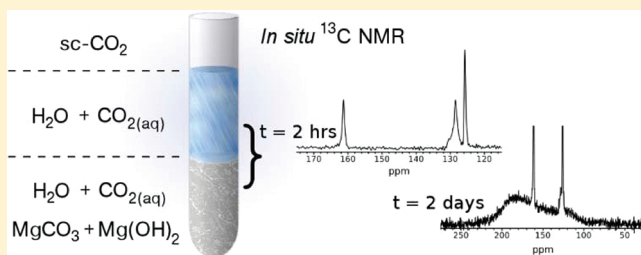
[†]Department of Chemistry, Washington University, 1 Brookings Drive, St. Louis, Missouri 63130, United States

[‡]Department of Earth and Planetary Sciences, Washington University, 1 Brookings Drive, St. Louis, Missouri 63130, United States

[§]Department of Physics, Washington University, 1 Brookings Drive, St. Louis, Missouri 63130, United States

S Supporting Information

ABSTRACT: We explore a new in situ NMR spectroscopy method that possesses the ability to monitor the chemical evolution of supercritical CO₂ in relevant conditions for geological CO₂ sequestration. As a model, we use the fast reaction of the mineral brucite, Mg(OH)₂, with supercritical CO₂ (88 bar) in aqueous conditions at 80 °C. The in situ conversion of CO₂ into metastable and stable carbonates is observed throughout the reaction. After more than 58 h of reaction, the sample was depressurized and analyzed using in situ Raman spectroscopy, where the laser was focused on the undisturbed products through the glass reaction tube. Postreaction, ex situ analysis was performed on the extracted and dried products using Raman spectroscopy, powder X-ray diffraction, and magic-angle spinning ¹H-decoupled ¹³C NMR. These separate methods of analysis confirmed a spatial dependence of products, possibly caused by a gradient of reactant availability, pH, and/or a reaction mechanism that involves first forming hydroxy-hydrated (basic, hydrated) carbonates that convert to the end-product, anhydrous magnesite. This carbonation reaction illustrates the importance of static (unmixed) reaction systems at sequestration-like conditions.



I. INTRODUCTION

Due to rising carbon levels in the atmosphere, there is much interest in the chemical and physical implications of carbon sequestration, a process by which CO₂ generated as a byproduct of energy production (or other industrial processes, such as cement production) is captured and stored instead of being released into the atmosphere. While many different storage mechanisms have been and continue to be considered,^{1–3} one of the most promising is geological sequestration, where the captured CO₂ is pressurized and pumped deep underground into geological formations. It is so promising because of the massive containment volume that this method offers (~100 trillion tons of CO₂ globally, assuming complete mineralization).^{4,5}

CO₂ geological storage is accomplished through one or more entrapment mechanisms:^{5,6} stratigraphic (physically trapped CO₂), solubility (CO₂ dissolved in the geological brine), hydrodynamic (dissolved CO₂ trapped due to slow flow of geological brine), residual (CO₂ trapped in pore spaces by capillary pressure), and chemical (CO₂ reacts with a divalent metal, such as Mg²⁺, Ca²⁺, or Fe²⁺, to form highly stable solid carbonates). Chemical trapping, or mineralization, is widely considered to be the most secure form of geological entrapment since the CO₂ has been converted into an immobile, more chemically stable state and is not merely physically trapped.^{5–7} Here we focus on mineralization reactions of CO₂.

Solid carbonates are formed when a divalent cation reacts with the anionic carbonate species (CO₃^{2–}).^{2,4–6} Successful formation of the carbonates therefore depends on the concentration and availability of the metal cation and the carbonate anion in the solution, in addition to favorable conditions for precipitation and crystallization. In geological CO₂ sequestration, sites are selected that contain significant quantities of these cations in the brine solution and in the minerals present, which are released when the pH of the brine dissolves the mineral into its constituent ionic species.^{2,4–6} The carbonate anion comes from the reaction of CO₂ with water.

Many studies^{6,8–10} have focused on the carbonation of the magnesium-containing mineral olivine, Mg_xFe_{2–x}SiO₄, because it has the highest magnesium fraction among rock-forming minerals present in candidate sequestration sites. Olivine is also the singly most abundant mineral in the earth's upper mantle and has the fastest carbonation rate of the naturally occurring minerals.¹¹ Olivine that contains no iron is called forsterite, Mg₂SiO₄, and is the primary constituent in naturally occurring olivine, Mg_{1.8}Fe_{0.2}SiO₄.

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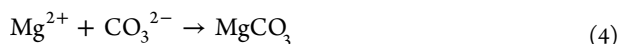
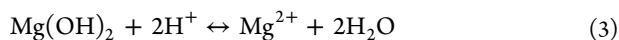
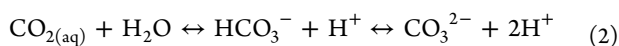
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As forsterite contains two units of MgO and one of SiO₂ (quartz), reacting carbonation systems of Mg₂SiO₄ are often addressed in terms of a simplified MgO–CO₂–H₂O phase diagram,¹² since MgO is the constituent of interest. Every chemical intermediate in that ternary system corresponds to different stoichiometric amounts of the three constituents MgO, CO₂, and H₂O, with the exception of SiO₂. SiO₂ dissolves and reprecipitates during the reaction, and is thus not a chemical participant in the reaction as long as there is an abundance of water.^{5,10,13,14} We have selected the magnesium-containing species brucite, Mg(OH)₂, as a model system where carbonate formation can be studied in a straightforward manner. Though brucite is not present geologically in quantities significant enough for use in sequestration, studies of such a mineral as a model system allows the carbonation of magnesium to be elucidated, without complications from the parallel process of dissolution and precipitation of SiO₂. In addition to sequestration applications, minerals such as brucite (or periclase, MgO) also have potential applications as CO₂ scrubbers in an industrial setting.¹⁵

The mineralization processes in sequestration reactions are kinetically hindered and depend on the rates of several sequential reaction steps.⁶ These steps are summarized in the following four chemical equations:



Equation 1 describes the dissolution of CO₂ into the geological brine. Equation 2 describes the two-step reaction of CO₂ with water to form bicarbonate and carbonate ions. Equation 3 describes the dissolution of a nearby mineral, in this case brucite [Mg(OH)₂], and finally Equation 4 describes the formation of MgCO₃ product by precipitation.

Here we report on the development of a new static, in situ, noninvasive ¹³C NMR spectroscopy under high pressure and temperature conditions that possesses the ability to monitor the chemical evolution of supercritical (sc) CO₂ in unmixed, sequestration-like conditions. While others have completed related high-pressure ¹³C NMR experiments,^{16,17} our method distinguishes itself by both monitoring mineralization in an unmixed, nonspinning system and using a solid mineral as a reactant. A static, unmixed system is significant in that this technique enables the observation of spatially dependent reaction products in the heterogeneous reaction mixture due to reactant gradients that are more reflective of true sequestration conditions.

II. EXPERIMENTAL SECTION

Ninety-nine percent ¹³C-labeled ¹³CO₂ gas from Sigma Aldrich was used in the reactions reported here. Brucite (0.761 g), Mg(OH)₂, with purity exceeding 98% was used as-received from Alpha Aesar and mixed with 2.7 mL of distilled water to form a heterogeneous mixture with an excess of water (molar ratio of mineral/water was 8.7%). The less than 2% impurities in the brucite are soluble salts left over from the manufacturing process.

For NMR experiments, the T₁ spin–lattice relaxation time of ¹³C of CO₂ (aq) in this system is ~7 s at 80 °C and 88 bar and ~35 s at room temperature (22 °C). The relaxation time of ¹³C of HCO₃[−] (aq) is ~1 s, and the magnesium carbonate products' are ~7 s at room temperature, shorter for both species at higher temperatures. Because of these long spin–lattice relaxation times, $\pi/4$ excitation pulses were used to enhance signal-to-noise ratios at shorter recycle delays.

Static in Situ ¹³C NMR. A typical $\pi/2$ pulse length is approximately 30 μs for this probe. NMR experiments were conducted using Bloch decay pulse sequences with $\pi/4$ pulses and recycle delays of 10 s at an observe frequency of 89.07 MHz for ¹³C, without ¹H decoupling. The high-pressure sample tube (with loaded sample, described below) was placed under modest vacuum (0.1 bar) before connecting to the ¹³CO₂ source in order to remove most of the O₂ and N₂ gases from the apparatus without dehydrating the sample. Chemical shift referencing was completed by using the highly stable ¹³CO₂ (aq) peak at 126.0 ppm.^{16,18,19} It was found that the CO₂ peak's chemical shift does not change within experimental error at the reaction conditions considered in this paper, and therefore could serve as an internal reference.

Raman Spectroscopy. Raman was performed both “in situ” on the depressurized, but otherwise untouched, high-pressure sample tube, as well as ex situ on powders collected from the tube. The in situ Raman was performed by focusing the laser through the walls of the glass tube on the material inside. The glass produced small background fluorescence but did not inhibit observation of the reaction products. This method enabled spatial observation without disturbing the product morphology. Both Raman experiments were performed using a HoloLab Series 5000 Laser Raman Microprobe (Kaiser Optical). The microprobe delivered a 532-nm laser beam from a frequency-doubled Nd:YAG laser through a 20× (except where noted) long-working-distance objective with a 0.4 numerical aperture. This configuration delivered a maximum of 11 mW of laser power onto the sample; each spectrum had a resolution of about 3 cm^{−1} and was recorded from 100 to 4000 cm^{−1} with a reproducibility of 0.1 cm^{−1}. The sampled regions were about 5 μm in diameter with a penetration depth of a similar magnitude due to the highly scattering nature of the product crystals. Multiple spectra were obtained from the sample, even though not all are shown, to support conclusions and ensure that the microprobe was providing spectra indicative of the entire sample.

Powder X-ray Diffraction (pXRD). pXRD analysis was performed on a well-ground and mixed portion of the product sample to ensure that the pXRD results were a net average of the products made. The pXRD spectrum was obtained using a Rigaku Geigerflex D-MAX/A diffractometer with Cu–K α radiation at 35 kV and 35 mA. The instrument was calibrated using the silicon (111) reflection at 28.443 degrees (2 θ). The pXRD pattern was obtained at room temperature from 10 to 65 degrees (2 θ). Analysis of spectra, including background removal, was completed using Jade Plus software. The PDF-4 and American Mineralogist powder diffraction databases were used for the matching of different reference patterns (amcsd 0009586, PDF 01-075-8824, 00-023-1218, 00-007-0239).

Ex Situ ¹³C{¹H} MAS NMR. ¹H-decoupled ¹³C MAS NMR experiments were performed using a 4-mm Varian HXMAS NMR probe on solids collected from the high-pressure sample tube after completion of all reactions, with a ¹³C observe

frequency of 74.02 MHz and ^1H decoupling frequency of 294.38 MHz, at a MAS rotational frequency of 5 kHz. Typical experimental parameters include a $\pi/4$ pulse that was 1.5 μs with a recycle delay of 5 s, recording 256 scans. Samples were externally referenced to adamantane's $-\text{CH}$ carbon at 28.680 ppm, which is a secondary reference based on ^{13}C of tetramethylsilane at 0 ppm.

III. RESULTS AND DISCUSSION

A. In Situ ^{13}C NMR. The reactions were carried out in a home-built high-pressure and -temperature solid-state NMR probe in which all of the static solid-state ^{13}C NMR spectra were obtained. Thus, the NMR was performed on the reacting system (i.e., in situ NMR, as opposed to ex situ NMR after the reaction has been quenched and subsequently sampled). This combination NMR probe plus reactor enabled monitoring of the uptake of CO_2 and the precipitation of various carbonate products during the reaction.

The home-built solid-state NMR probe is able to achieve reaction conditions (i.e., temperatures up to 250 $^\circ\text{C}$, pressures up to 300 bar) similar to those found in geological sequestration environments^{6,20,21} by using a zirconia high-pressure sample tube (dimensions: 15.24 mm outer diameter, 10.03 mm inner diameter, 73.66 mm length, and closed at one end) contained within a well-insulated zone heated by flowing temperature-regulated air. A glass liner was placed inside the high-pressure vessel to allow easy removal of reaction products and to prevent carbonate from crystallizing on the zirconia tube itself (which proved difficult to remove). The radio frequency NMR coil is situated outside the high-pressure zirconia vessel and is of an Alderman–Grant design.²² A $^{13}\text{CO}_2$ source was cryogenically pressurized for both reactions studied here and was delivered into the high-pressure vessel in the liquid state. Supercritical (sc) conditions were achieved by warming the heating zone around the vessel. Figure 1 is a schematic of the reaction setup in the high-pressure tube, with sc- CO_2 in the headspace over water-soaked mineral powder. The coil was placed around the high-pressure vessel in such a way that the vessel could be moved up and down, allowing ^{13}C NMR

spectra to be collected specifically on the solution above the powder, within the powder, or centered at the interface between the two.

The heating zone's temperature (and subsequent reaction temperature) was measured by a type E thermocouple placed next to the high-pressure vessel, in the heated zone. The internal temperature of the high-pressure vessel was calibrated from a previous experiment during which an additional type E thermocouple was placed at different positions in a water solution within the length of the high-pressure vessel. The entire NMR coil region as well as areas directly above and below within the high-pressure vessel assumed the same temperature as the heated zone around it with a small lag time during warming and cooling events. This test ensured that the probe did not induce a temperature gradient across the sample during high-pressure and -temperature experiments.

Solid Carbonate Formation. Conversion of CO_2 into magnesium carbonates can be monitored by NMR as shown in Figures 2 and 3. Solid brucite powder was added to the

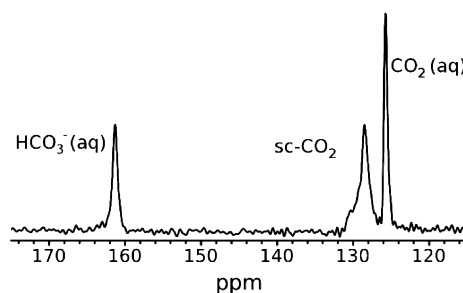


Figure 2. ^{13}C static NMR of reaction mixture of CO_2 and a slurry of water and brucite, $\text{Mg}(\text{OH})_2$, recorded 2 h into the reaction before any mineralization had been detected. Conditions were 80 $^\circ\text{C}$ and 91.8 bar. The aqueous CO_2 and supercritical CO_2 have slightly different resonance frequencies because of magnetic susceptibility effects.

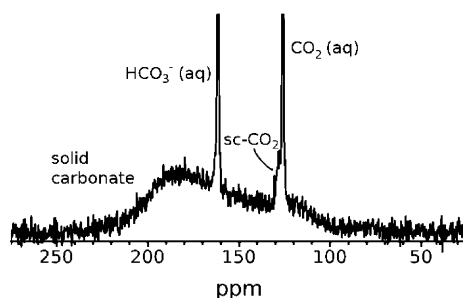


Figure 3. ^{13}C static NMR of CO_2 and a slurry of water and brucite, recorded 58 h into the reaction at 80 $^\circ\text{C}$ and 88.5 bar. The broad feature underlying the sharp resonances is the powder pattern indicative of a solid carbonate species. The HCO_3^- and CO_2 peaks are truncated (off-scale) so that the powder pattern is clearly evident.

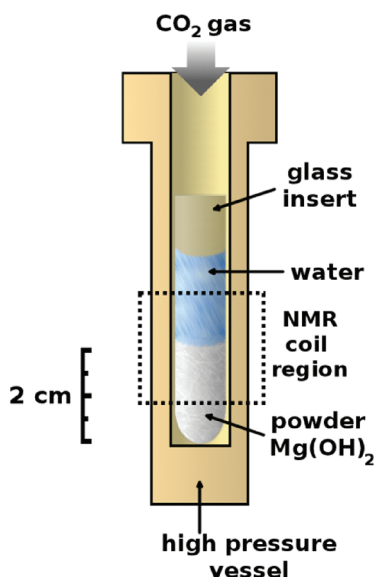


Figure 1. Cross-section of the zirconia high-pressure vessel for in situ NMR.

distilled water to create a heterogeneous mixture. Brucite was chosen to demonstrate the feasibility of this method because it quickly reacts with CO_2 when exposed to sequestration-like conditions.^{7,15}

The brucite and water mixture was allowed to sit overnight so that the solid phase settled, making two distinct layers: liquid on top and water-saturated brucite powder on the bottom. The mixture was heated to 80 $^\circ\text{C}$ upon introduction of $^{13}\text{CO}_2$ and pressurized to 93 bar, which slowly dropped to 88 bar as some of the CO_2 dissolved into the water and began to react.

Even though brucite is only sparingly soluble, its presence in the solution makes the solution basic, raising the pH and thereby shifting the $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ equilibrium (eq 2) considerably more to the right, increasing the relative HCO_3^- concentration. Two hours into the reaction, as shown in Figure 2, both aqueous and supercritical CO_2 are observed (see Figure S1 for justification of peak assignments), in addition to aqueous HCO_3^- . Since the ^{13}C NMR peak areas are quantitative indicators of the amount of each species, this early stage in the reaction shows that the HCO_3^- concentration is close to that of aqueous CO_2 .

After more than two days of reaction (58 h) at elevated temperature and pressure, a ^{13}C solid-state carbonate powder pattern emerged (Figure 3), indicating solid carbonate precipitation. The solid-state signals are broad because of the absence of reorientational motions, which narrow the resonances in fluid phases. With the absence of motion, the chemical shift is dependent upon the orientation of the ^{13}C nucleus' environment relative to the magnetic field (chemical shift anisotropy) and generates a "powder pattern" based on the fractional distribution of nuclei in each molecular orientation. The HCO_3^- and CO_2 (aq) peaks are off-scale in order to depict the shape and height of the carbonate powder pattern, which resembles that of well-studied calcium carbonate^{23,24} and is similar to the measured magnesium carbonate pattern but with some important differences that indicate that there are other carbonate phases contributing to the powder pattern (see Figure S2).

At 60 h of reaction, the temperature was lowered by blowing room-temperature air into the heating zone around the high-pressure vessel. After cooling to room temperature, the high-pressure vessel was depressurized slowly (over a 60-min period), to prevent $^{13}\text{CO}_2$ gas from bubbling out of the solution and forming a foam. The glass insert was then removed from the reaction vessel and capped so that spatially resolved Raman experiments could be run on the sample immediately. After the Raman experiments, the aqueous solution was pulled off of the solid sample using a pipette, and the remaining solid product was placed in a vacuum chamber overnight at room temperature to dry. A small amount of sample was removed from the dried product at both the top of the sample and deeper into the sample, was crushed and finely ground for proper pXRD analysis using an agate mortar and pestle, and ex situ analysis was performed.

Postreaction analysis of solid carbonate phases was accomplished through three complementary techniques: Raman spectroscopy, powder X-ray diffraction (pXRD), and ^{13}C MAS NMR, all of which provided additional information on the different carbonate phases that were formed during the reaction.

B. "In Situ" and ex Situ Raman. Figure 4 displays the in situ Raman spectra obtained by focusing the laser through the glass sample tube that was still wet and contained both solution and solid from the reaction. The tube and its contents had been depressurized only minutes before these spectra were obtained and had not been subjected to any other treatment. While the glass tube produced very little fluorescence, it was enough to prevent quantitative comparison between the different spectra. Instead, a relative comparison of the fraction of each peak area in each spectrum can be compared from one spectrum to another to see the spatial distribution of the products. It is important to note that all peaks observed in the Raman spectrum were analyzed and consistent with previously

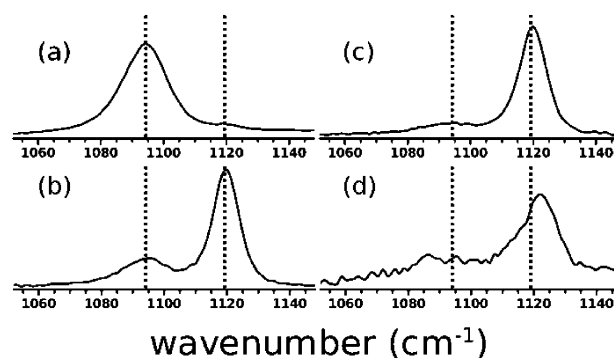


Figure 4. Raman spectra of the reaction products in the range of the characteristic CO_3^{2-} symmetric stretches, each taken at different points along the length of the sample tube: (a) at the solution/solid interface (0.0 cm), (b) 0.25 cm below the interface, (c) 0.5 cm, and (d) 0.6 cm. Spectra (b)–(d) were acquired at 5 \times magnification and thus have different arbitrary intensity scales than (a). In addition, the y-axis in spectrum (d) has been expanded so as to better see the peaks. The lines at 1094 and 1119 cm^{-1} are guides to the eye for the locations of the magnesite and hydromagnesite/dypingite peaks, respectively.

reported assignments, and only the symmetric CO_3^{2-} symmetric stretching frequencies are shown here. These stretching frequencies are considered to be very good indicators of the identities of some carbonate minerals^{25,26} and are unaffected by the change in carbon isotope (to 99% ^{13}C) because the carbon atom remains at rest in the symmetric stretching mode.

The peak at 1094 cm^{-1} is indicative of magnesite (MgCO_3),²⁵ while the peak at 1119 cm^{-1} is in the region of other hydroxy-hydrated metastable carbonate species, namely hydromagnesite and dypingite^{27,28} [$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, respectively].^{25,26,29} While both hydromagnesite and dypingite are difficult to differentiate using any method besides pXRD, literature suggests that dypingite has its symmetric stretch in the 1120–1124 cm^{-1} region,²⁹ slightly different from hydromagnesite's well-defined 1119 cm^{-1} stretch.²⁵ The trend in Figure 4 therefore suggests that the reaction is complete at the solution/solid interface end-state product (dominated by MgCO_3), and becomes less complete (more hydroxy-hydrated carbonate products) as one observes locations further down the length of the tube, with the hydromagnesite species being the dominant species at shallower regions, gradually transitioning to dypingite at the lowest, deepest regions. No carbonate signals could be observed at depths greater than 0.7 cm into the sample, and no Raman peaks for $^{13}\text{CO}_2$ were observed.

Previous research^{7,12,15,26,30,31} summarizes the extensive experimental and computational results from the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ system. It is clear from these results that temperature and partial pressure of CO_2 are both of primary importance in directing which mineral forms preferentially. The products are not always the most thermodynamically stable, as there are kinetic inhibitions in these reactions, which has been discussed in great detail by others.^{7,12,26,31,32} At room temperature and ambient to moderate CO_2 pressures, the basic carbonate mineral nesquehonite [$\text{Mg}(\text{OH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$] forms.⁷ At higher temperatures, above approximately 40 $^\circ\text{C}$, hydromagnesite becomes the primary carbonate product.²⁶ Anhydrous magnesite forms only at even higher temperatures (>60–100 $^\circ\text{C}$),^{12,33,34} and only if higher CO_2 pressures are present.^{6,26,32}

Dypingite, a lesser-known mineral, is very similar to hydromagnesite in composition but is less stable and can be considered an intermediate hydrate phase between nesquehonite and hydromagnesite.^{28,35} Its molecular formula has been reported with different numbers of waters throughout literature, but is generally thought of as a more-hydrated version of hydromagnesite. Its observation *ex situ* may also be a result of small amounts of mineralization during the cooling, depressurization, and drying process, even though great effort was made to make this process as fast as possible. Generally, dypingite is regarded to form at slightly higher temperatures than that of nesquehonite,³⁶ and some evidence exists that it is more likely to form under more basic conditions.³⁷ In addition, dypingite can be observed in nature, like magnesite and hydromagnesite, but is generally only found in cooler climates^{27–29,38} as warm temperatures will speed its conversion to hydromagnesite.

At the pressure and temperature conditions reported here (80 °C and 88 bar), any or all magnesite, hydromagnesite, and dypingite could exist.

After drying the sample and removing it from the tube, a small sample from the middle portion of the tube was removed and examined via *ex situ* Raman (see Figure S3). Well-defined coexistent peaks indicate the presence of both magnesite and hydromagnesite/dypingite, and no Raman peaks for ¹³CO₂ were seen in the analysis. The increased breadth of the magnesite peak (as compared to our magnesite standard and the hydromagnesite/dypingite peak) in both *in situ* and *ex situ* experiments indicates that other hydrated phases of magnesium carbonate might be present, coexisting with the magnesite, and/or that the magnesite phase is composed of extremely small crystallites.

C. *Ex situ* X-ray Powder Diffraction. Figure 5 shows the diffraction pattern and analysis. The pattern confirms the

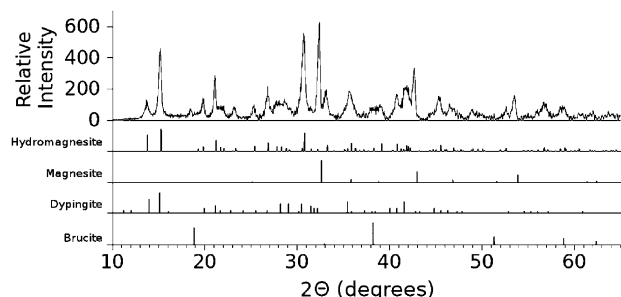


Figure 5. X-ray diffraction pattern from the reaction product. The magnesite peaks are shifted by $\sim 1^\circ$ from the reference magnesite spectrum, suggesting that the unit cell is expanded.

coexistence of dypingite, hydromagnesite, and magnesite, with little or no remaining brucite. These results are consistent with our findings from Raman spectroscopy.

As XRD is a time- and space-averaged measurement,³⁹ the smaller 2θ values ($\sim 1^\circ$ left-shifted) indicate that some of the MgCO₃ unit cells have expanded. The unit cell expansion is likely due to incomplete removal of water during the hydromagnesite-to-magnesite transition²⁶ leading to partial hydration. It is also important to note that nesquehonite [Mg(HCO₃)(OH)·2H₂O] was not observed in the reaction products, probably because the reaction temperature was too high.³⁵

D. *Ex situ* ¹³C{¹H} MAS. Proton-decoupled ¹³C solid-state magic-angle spinning (MAS) NMR on the powder collected

from the top portion of the sample from the high-pressure sample tube shows multiple solid carbonate species present in the reaction product (Figure 6). A resonance at 169.2 ppm

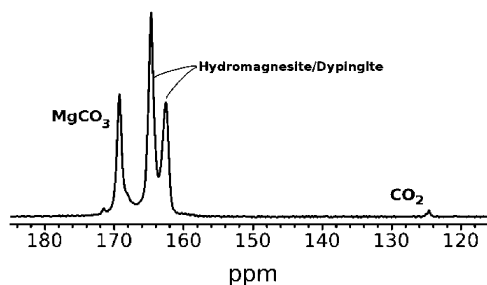


Figure 6. *Ex situ* ¹³C MAS NMR spectrum (with ¹H decoupling) of the upper reaction product. The CO₂ peak is residual CO₂, most likely physically trapped in the solid phase.

confirmed the existence of magnesite, MgCO₃.⁴⁰ Two other peaks, at 164.7 and 162.6 ppm, are suggestive of the coexistence of hydromagnesite and dypingite^{27,28} in agreement with the pXRD data. Recent research proposes assignments for hydromagnesite and dypingite, each with two resonances that are very close to one another.¹⁴ Hydromagnesite has been assigned to two peaks of equal area at 166.4 and 164.1 ppm (further substantiated by its single-crystal XRD structure showing two inequivalent carbons⁴¹), while dypingite has been assigned to two peaks of unequal area at 165.7 and 163.4 ppm.¹⁴ The differences between our reported chemical shift values for these species and the recent research can be explained by the error between the two different chemical shift referencing techniques used in the two studies. As our reported peaks at 164.7 and 162.6 ppm (Figure 6) have unequal areas, this implies a possible mixture of hydromagnesite and dypingite.

There are three other resonances of note in Figure 6: a peak at 124.7 ppm, which is likely ¹³CO₂ trapped in the precipitated crystal product; an unidentified small peak at 171.5; and an unidentified small shoulder on the magnesite peak at ~ 168 ppm. The two unidentified peaks could be other morphologically distinct phases of MgCO₃, such as singly hydrated MgCO₃. It is known that singly hydrated calcite (CaCO₃·H₂O) has a slightly higher-frequency ¹³C chemical shift relative to its anhydrous counterpart (CaCO₃), changing from 168.21 to 171.10 ppm,⁴² supporting this preliminary interpretation. While the areas of the MgCO₃ peaks (171.5, 169.1, and 168 ppm) cannot be precisely compared due to potential differences in their T₁ relaxation times, the spectrum suggests that there is vastly more MgCO₃ as compared to its morphologically distinct counterparts at 171.5 and 168 ppm. Further, ¹³C MAS NMR demonstrates that MgCO₃ (magnesite) and hydroxy-hydrated forms (like dypingite and hydromagnesite) are the major reaction products.

Figure 7 is a spectrum obtained from a lower portion of the sample, further confirming the spatial dependence of the products that were formed. Recorded in the same manner as the spectrum in Figure 6, it is evident that there are no MgCO₃ phases, with only the two peaks characteristic of hydromagnesite and dypingite present. Their increased breadth indicates a less-crystalline phase, and the reduced signal-to-noise ratio of the spectrum indicates less total carbonate product. Furthermore, no residual CO₂ was detected.

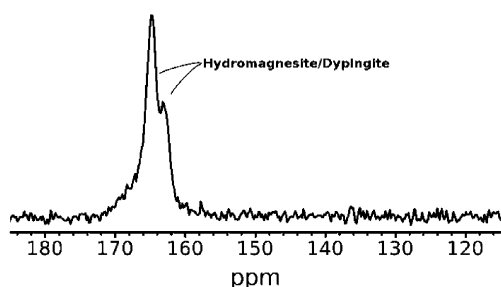


Figure 7. Ex situ ^{13}C MAS NMR spectrum (with ^1H decoupling) of the lower reaction product. There are two prominent peaks located at 162.8 and 164.8 ppm.

Precise determination of the relative amounts of the different solid-state products was not possible in these experiments, although the chemical identities found using MAS NMR confirm results from Raman and pXRD experiments. Raman (Figure 4) and ^{13}C MAS NMR results (Figures 6 and 7) suggest, however, that the relative amount of each possible product varies by depth into the sample. Magnesite exists only in the layers closest to the solution/solid interface, with increasing amounts of coexisting dypingite and hydromagnesite deeper into the sample. The pXRD pattern (Figure 5) fortifies our ^{13}C NMR and Raman results by further confirming the existence of these phases in our sample.

The spatial dependence of the products demonstrates the importance of a static reacting system when studying sequestration reactions. This experiment has the advantages of incorporating both the chemistry and physics of sequestration reactions. We surmise that the physical barrier that a solid imposes on the pivotal reactant CO_2 (aq) restricts its diffusion and therefore makes a spatial dependence of products based on the local pH and carbon concentration gradient.

While the results presented in this paper demonstrate the new ability to monitor sequestration reactions in situ, subsequent work will also expand the reactions to additional mineral and rock systems, as well as different pressures and systems, as well as different pressures and temperatures. We also intend to further investigate the cause of the spatial dependency of the products in these reacting systems.

■ ASSOCIATED CONTENT

Supporting Information

Additional spectra and simulations. This information is available free of charge via the Internet at <http://pubs.acs.org/>

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hayes@wustl.edu; tel.: (314) 935-4624; fax: (314) 935-4481 (S.E.H.); e-mail: msc@wustl.edu; tel.: (314) 935-6418; fax: (314) 935-6219 (M.S.C.).

Notes

The authors declare no competing financial interest.

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