**ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL:
OPTIMIZING REACTION PROCESS DESIGN**

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ABSTRACT

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Permanent and safe methods for CO₂ capture and disposal/storage need to be developed. Mineralization of stationary-source CO₂ emissions as carbonates can provide such safe capture and long-term sequestration. Mg-rich lamellar-hydroxide based minerals (e.g., brucite and serpentine) offer a class of widely available, low-cost materials, with intriguing mineral carbonation potential. Carbonation of such materials inherently involves dehydroxylation, which can disrupt the material down to the atomic level. As such, controlled dehydroxylation before and/or during carbonation may provide an important parameter for enhancing carbonation reaction processes. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity, (ii) interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component, and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine-based minerals) whose carbonation reaction processes are being explored due to their low-cost CO₂ sequestration potential. Fundamental understanding of the mechanisms that govern dehydroxylation/carbonation processes is essential for cost optimization of any lamellar-hydroxide-based mineral carbonation sequestration process.

In the first project year, we used environmental-cell (E-cell), dynamic high-resolution transmission electron microscopy (DHRTEM) to directly observe the Mg(OH)₂ dehydroxylation process at the atomic-level for the first time. We also carried out exploratory semi-empirical modeling studies of the intermediate materials formed. Dehydroxylation was discovered to be a lamellar nucleation and growth process, which includes intermediate lamellar oxyhydroxide formation. These intermediates offer a series of new carbonation reaction pathways, with the potential to enhance carbonation reactivity. We also initiated studies to probe dehydroxylation/carbonation reaction mechanisms, using elemental analysis, SIMS and optical microscopy.

In the second year, a wide range of studies has substantially enhanced our understanding of the reaction mechanisms associated with Mg(OH)₂ carbonation reactivity. These include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. Detailed advanced modeling studies were carried out in collaboration with DOE/NETL grant DE-FG26-99FT40580. *We have discovered intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation/carbonation and dehydroxylation/carbonation processes, which can be controlled to dramatically enhance carbonation reactivity at ambient temperature and CO₂ pressure.* The ability of Mg(OH)₂ to form nanostructured materials during controlled dehydroxylation is another key component governing carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal growth during dehydroxylation can also inhibit carbonation. Initial studies indicate that Fe impurities can phase separate during dehydroxylation, but, at low concentrations, do not initially appear to substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity.

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EXECUTIVE SUMMARY

OBJECTIVE

The goal of this project is to develop an atomic-level understanding of the mechanisms that govern the kinetics of the complex $\text{Mg}(\text{OH})_2$ carbonation process to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. $\text{Mg}(\text{OH})_2$ carbonation serves as a model system for developing a better fundamental understanding of Mg-rich lamellar-hydroxide-based mineral carbonation processes. These processes are of current interest due to their cost-effective CO_2 mineral sequestration potential. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM), including parallel electron energy loss spectroscopy (PEELS) is used to probe dehydroxylation/rehydroxylation-carbonation reaction processes down to and at the atomic level. A battery of complementary techniques is incorporated to further elucidate these processes at the macroscopic and microscopic level (i.e., *in-situ* and *ex-situ* studies). As the dehydroxylation-carbonation process involves dehydroxylation, carbonation and potential competition between them, developing an atomic-level understanding of the dehydroxylation process is first targeted to provide a foundation from which to explore the overall carbonation process. Initially, the primary focus has been on high purity $\text{Mg}(\text{OH})_2$ single crystal fragments to elucidate basic reaction processes for highly crystalline material. Investigations of the effects of material reconstruction, crystalline defects, and impurities (e.g., Fe, Ca) on dehydroxylation/carbonation processes are targeted to better understand their impact on carbonation reactivity.

ACCOMPLISHMENTS TO DATE

We have broadened our studies beyond our core atomic-level E-cell DHRTEM studies to better understand $\text{Mg}(\text{OH})_2$ dehydroxylation/carbonation mechanisms at the macroscopic, microscopic, and atomic level. Our studies have also been expanded to include rehydroxylation/carbonation processes to better understand the role of oxyhydroxide intermediate formation in carbonation reactivity. We have carried out integrated studies of partially dehydroxylated/carbonated powders and single crystal fragments using optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. These studies are being integrated with advanced computational modeling studies in collaboration with the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant # DE-FG26-99FT40580).

$\text{Mg}(\text{OH})_2$ dehydroxylation proceeds as a lamellar nucleation and growth process. Initially, lamellar oxide nuclei form (e.g., $\cdots\text{OH}/\text{Mg}/\text{OH}/\text{OH}/\text{Mg}/\text{OH}\cdots \rightarrow \cdots\text{OH}/\text{Mg}/\text{O}/\text{Mg}/\text{OH}\cdots + \text{H}_2\text{O}$) within the hydroxide matrix. Growth occurs with the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the $\text{Mg}(\text{OH})_2$ lamella. This process can take on lamellar solid solution (oxyhydroxide) or two-phase [$\text{Mg}(\text{OH})_2 + \text{MgO}$] character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. The free energies (400 °C) of the entire solid solution series of oxyhydroxide intermediates is within 2 kcal/mol of stoichiometrically equivalent $\text{Mg}(\text{OH})_2 + \text{MgO}$ mixtures, indicating the entire series can be accessible during carbonation. Importantly, dehydroxylation is reversible, via oxide/oxyhydroxide nanostructure formation. This creates a

broad range of new intermediate oxyhydroxide carbonation pathways via dehydroxylation or rehydroxylation.

Macroscopic and microscopic studies of gas-phase dehydroxylation-carbonation processes indicate dehydroxylation generally precedes carbonation locally, consistent with the creation of dehydroxylation intermediates with higher carbonation reactivity. Simultaneous rehydroxylation of partially dehydroxylated material was found to greatly enhance its gas-phase carbonation reactivity *at ambient temperature*, further underscoring the importance of transitory intermediate formation. In addition to forming lamellar oxyhydroxide intermediates, dehydroxylation can also result in substantial delamination, intralamellar cracking, and surface reconstruction to form nanostructured materials, due to the strain associated with $\text{Mg}(\text{OH})_2/\text{MgO}$ layer bending. These phenomena provide important pathways, which can be used to combat the formation of near surface carbonate passivation, as observed by SIMS. These highly porous structures can also lead to novel phenomena, such as $\text{Mg}(\text{OH})_2$ carbonation reactivity decreasing during dehydroxylation-carbonation with increasing CO_2 gas pressure (water vapor evolution during dehydroxylation inhibits CO_2 diffusion to available carbonation sites more effectively at higher gas pressures). Overall, these intermediate materials offer broad potential for enhancing carbonation reactivity. Their formation and the interplay of the cumulative factors that govern carbonation reactivity is only just now beginning to be understood, underscoring the potential for substantial improvements in carbonation reactivity via materials and process engineering. Furthermore, the close structural and chemical similarity between $\text{Mg}(\text{OH})_2$ and the Mg-rich, lamellar-hydroxide-based serpentine minerals, suggest these materials also possess large untapped potential for (i) enhanced carbonation reactivity and (ii) substantially lower mineral sequestration process costs.

INTRODUCTION

Mineral Carbonation: An Attractive Candidate Process for CO₂ Sequestration

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration. The resulting carbonates (e.g., magnesium and calcium carbonate, MgCO₃ and CaCO₃) occur in nature in quantities that far exceed those that could result from carbonating the world's known fossil fuel reserves. Furthermore, they have already proven stable over geological time, eliminating the safety and cost concerns associated with long-term storage of CO₂ in compressed form. Conversion of CO₂ into Mg/CaCO₃ effectively disposes of CO₂ by accelerating the natural processes that already occur in nature.

Mg-rich minerals and mineral derivatives are being investigated as low-cost mineral carbonation feedstock materials by the CO₂ Mineral Sequestration Working Group (comprised of members from the Albany Research Center, our CO₂ Mineral Sequestration Research Group at Arizona State University, Los Alamos National Laboratory, the National Energy Technology Laboratory and Science Applications International Corporation).¹ The primary focus of the Working Group, which is managed by the Department of Energy, is to evaluate the economic viability of mineral carbonation processes as long-term options for reducing atmospheric CO₂ emissions. A major challenge in cost-competitive process development is to accelerate these carbonation reaction(s) to a high degree of completion on an industrial time scale. The associated reaction rates depend on many materials and process parameters, providing substantial potential for rate enhancement. However, the effects of many of these parameters are poorly understood, especially at the atomic level, severely limiting their effective use. A fundamental understanding of the mechanisms that govern key carbonation processes is needed to create the foundation for reaction process optimization via materials and process engineering.

Mg-Rich Lamellar-Hydroxide-Based Minerals: Candidate Feedstock Materials for Cost Competitive CO₂ Mineral Sequestration

Carbonation of Mg-rich lamellar-hydroxide-based minerals (e.g., the serpentine-based minerals and brucite: Mg(OH)₂) is a leading CO₂-mineral-sequestration, process candidate. Optimizing the carbonation reaction rate and its degree of completion is key to lowering process cost. Mg(OH)₂ was chosen as the model material for investigating lamellar hydroxide mineral dehydroxylation/carbonation mechanisms due to (i) its structural and chemical simplicity,² (ii) the interest in Mg(OH)₂ gas-solid carbonation as a potentially cost-effective CO₂ mineral sequestration process component,³⁻⁵ and (iii) its structural and chemical similarity to other lamellar-hydroxide-based minerals (e.g., serpentine, see Figure 1), whose carbonation reaction processes are being explored due to their CO₂ sequestration potential.¹ This project focuses on developing an atomic-level understanding of the reaction mechanisms that govern dehydroxylation/rehydroxylation-carbonation processes for this model lamellar hydroxide feedstock material. The long-term goal is to develop the necessary atomic-level mechanistic

understanding to engineer improved carbonation materials and processes for Mg-rich lamellar-hydroxide-based minerals.

Mg(OH)₂ Dehydroxylation: The First Step in Carbonation

As Mg(OH)₂ dehydroxylation, depicted in reaction (2), is intimately associated with the carbonation process, its mechanisms are of direct interest in understanding and optimizing the carbonation process. Although Mg(OH)₂ dehydroxylation has been extensively studied, relatively little is known about the atomic-level nature of the process, especially in the early stages of dehydroxylation. The early stages of the process are of particular interest, since carbon dioxide may react to form magnesite (MgCO₃) locally as soon as dehydroxylation begins in that region. In our first year progress report, we reported our discovery that Mg(OH)₂ dehydroxylation is governed by a lamellar nucleation and growth process. Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) was used to directly observe the *in-situ* process at the atomic-level for the first time. These observations were combined with preliminary advanced computational modeling studies using a non-empirical density functional theory (DFT) approach to better elucidate the atomic-level dehydroxylation process. In this second year report, we describe our studies that have lead to a deeper understanding of the lamellar nucleation and growth process, including (i) analysis of the interrelationship between oxyhydroxide intermediate and nanostructure formation and (ii) advanced modeling studies of the oxyhydroxide intermediate materials formed in collaboration with DOE/NETL grant DE-FG26-99FT40580.

Mg(OH)₂ Dehydroxylation/Rehydroxylation-Carbonation Processes

In last year's report, we described combining the first-year dehydroxylation studies with preliminary dehydroxylation/carbonation studies of single crystal Mg(OH)₂ fragments to better elucidate dehydroxylation/carbonation reaction mechanisms. We found dehydroxylation generally occurred in advance of carbonation during Mg(OH)₂ carbonation, suggesting intermediate formation may be important to carbonation reactivity during simultaneous dehydroxylation-carbonation. We also discovered initial evidence for passivating carbonate layer formation and substantial delamination and cracking of the Mg(OH)₂ feedstock material during dehydroxylation-carbonation.

During the second project year we have extended these studies. First, they were expanded to include rehydroxylation-carbonation, as well as dehydroxylation-carbonation. A wide range of investigations were undertaken and have substantially enhanced our understanding of the reaction mechanisms associated with Mg(OH)₂ carbonation reactivity. These include E-cell DHRTEM (including parallel electron energy loss spectroscopy – PEELS), optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. Detailed advanced modeling studies of carbonation processes were also carried out in collaboration with DOE/NETL grant DE-FG26-99FT40580. We have discovered dehydroxylation/rehydroxylation intermediate (e.g., oxyhydroxide) formation is a key component of both

dehydroxylation/carbonation and rehydroxylation/carbonation processes, with essentially the entire lamellar oxyhydroxide solid solution series ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) accessible during $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation. The ability of $\text{Mg}(\text{OH})_2$ to form nanostructured materials during controlled dehydroxylation is another key component affecting carbonation reactivity. Together with delamination and cracking, these factors enhance carbonation by increasing the reactive carbonation surface area. On the other hand, carbonation can slow high-surface-area reactive intermediate formation via the formation of passivating carbonate layers. MgO crystal growth during dehydroxylation can also inhibit carbonation. In addition, $\text{Mg}(\text{OH})_2$ feedstock impurities may also play important roles in carbonation reactivity. Although initial studies indicate Fe impurities can phase separate during $\text{Mg}(\text{OH})_2$ dehydroxylation at low concentrations, they do not appear to substantially inhibit carbonation, at least locally. All of the above factors must be adroitly balanced to enhance carbonation reactivity. Our initial efforts to combine oxyhydroxide intermediate formation with controlled nanostructure formation to probe their ability to enhance carbonation reactivity have proven quite promising, as we have already *achieved carbonation reaction rates at ambient temperature and CO_2 pressure that are similar to those previously reported for optimum ambient CO_2 pressure $\text{Mg}(\text{OH})_2$ carbonation (at 375 °C).*

EXPERIMENTAL

MATERIALS: Natural single crystal brucite from Delora, Canada was used as the starting material. Elemental analysis by proton-induced X-ray emission and total carbon analysis showed the material to contain 0.16% Mn, 0.06% C, 0.01% Cl and 0.01% Si by weight. X-ray powder diffraction was used to structurally characterize the starting material [$a=3.147(1)$ Å and $c=4.765(1)$ Å], in good agreement with the known parameters for brucite [$a=3.147$ Å and $c=4.769$ Å].² E-cell DHRTEM samples were prepared in a He glovebox by either cold crushing at -196°C or scraping the crystal with a razor blade. Crystals were then dry loaded on to holey-carbon-coated copper grids for DHRTEM analysis. Single crystal fragments for carbonation studies were cleaved from the crystal matrix. High pressure carbonation/dehydroxylation reactions were carried out in a sealed autoclave. The samples were introduced to the autoclave in vitreous silica boats. The autoclave was sealed, dry CO_2 introduced, and the autoclave brought quickly to reaction temperature. *In situ* $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation-carbonation reaction processes were investigated using a Setaram TGS2 thermogravimetric analysis system, with 1 µ sensitivity.

E-Cell DHRTEM: The *in-situ* studies of $\text{Mg}(\text{OH})_2$ dehydroxylation/rehydroxylation/carbonation were performed using a Philips 430 HRTEM (300 kV; 2.3 Å pt. to pt. resolution) equipped with a Gatan Imaging energy Filter (GIF) and a 0-5 torr E-cell. Dehydroxylation was induced by electron beam heating and resistive heating using the sample holder, both with and without the presence of water vapor. Direct imaging of the reaction was recorded on videotape in real time (30 frame/sec). Water vapor (e.g., ~ 1 torr) was required to slow the dehydroxylation process sufficiently for direct imaging. Digital Micrograph was used to analyze the interlamellar spacings in four-frame time-averaged images of the dehydroxylation process parallel to the brucite layers. Selected area diffraction of the reaction process was recorded as a function of

time using internal gold island diffraction standards and photographic plates. *In situ* rehydroxylation-carbonation processes were followed by direct imaging, SAD and PEELS. $\text{Mg}(\text{OH})_2$ was first dehydroxylated *in situ* via resistive heating, followed by reaction at ambient temperature with ~ 800 mtorr of humid CO_2 .

GENERAL FACILITIES: The SIMS system used was a Cameca IMS 3f ion microscope. Base pressure in the sample chamber is 10^{-7} torr. Depth resolution can be better than 10 nm. Lateral resolution is $\sim 5\text{-}20\ \mu\text{m}$ in point analysis mode and lateral image resolution is $\sim 1\ \mu\text{m}$. The digital optical microscope system used was a Mitutoyo Ultraplan FS-110, with bright and dark field, polarized light, Nomarski, and reflected and transmitted illumination capabilities together with extra-long working distance objectives and fraction of a micron resolution. X-ray powder diffraction (XPD) studies were carried out using a RigakuD/MAX-IIIB X-ray diffractometer with $\text{CuK}\alpha$ radiation, line focus, and graphite monochromator. Ion beam analyses of partially carbonated $\text{Mg}(\text{OH})_2$ single crystal samples were performed using a 1.7 MV General Ionex Tandetron system. Mg was analyzed via Rutherford backscattering spectroscopy (RBS) analysis using 2 MeV He^{++} ions. Carbon analysis used a $\text{C}(\alpha, \alpha)\text{C}$ reaction occurring at 4.63 MeV. Oxygen analysis used a similar reaction at 3.05 MeV. H analysis was performed by forward scattering using 2.8 MeV He^{++} ions. Total hydroxide, oxide and carbonate contents for the partially dehydroxylated/carbonated single crystal fragments were determined using a Perkin Elmer PE 2400 Series CHNS analysis system. Careful use of standards before and after sample analysis showed an absolute error of ± 0.2 wt%. The field emission scanning electron microscope (FESEM) system used was a Hitachi S-4100 equipped with an Oxford Instruments ISIS energy dispersive spectrometer.

MODELING: *Ab initio* density functional theory calculations and non-empirical electron-gas modeling based on the VIB method⁶ were used to investigate the relative stability, elastic behavior and structural trends of the intermediate oxyhydroxides as a function of composition. The methods used are described in detail in the attached manuscript submitted for publication in *Chemistry of Materials*. Similar methods were used for the carbonation modeling studies. These are described in detail in the annual report for the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO_2 Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant #DE-FG26-99FT40580), which is fully collaborating with the project described herein.

RESULTS AND DISCUSSION

Mg(OH)₂ DEHYDROXYLATION

During the first year of this project, DHRTEM observations parallel to the $\text{Mg}(\text{OH})_2$ lamella during dehydroxylation were found to show the general lamellar nature of the process. *In situ* selected area diffraction (SAD) studies confirmed a lamellar nucleation and growth process governed $\text{Mg}(\text{OH})_2$ dehydroxylation. After initial oxide layer nucleation, as described in equation 1, growth occurs via the formation of additional partial/full oxide layers nearby, creating lamellar oxyhydroxide regions, which can grow parallel and perpendicular to the lamella

in the $\text{Mg}(\text{OH})_2$ matrix. Preliminary advanced modeling of the lamellar oxyhydroxide $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ reaction intermediates was reported last year. During the second year of this project, detailed advanced modeling studies have provided a much better understanding of the nature of the intermediate oxyhydroxides, as highlighted in Figures 2 and 3. Both thermodynamic stability and elastic behavior appear key to the intermediate oxyhydroxide formation, as shown in Figure 2. Oxyhydroxides containing low or high concentrations of oxide lamella are more stable, but not dramatically so, as all compositions are thermodynamically accessible by 500 °C. The oxyhydroxide bulk moduli reveal a dramatic increase in material stiffness early during dehydroxylation, substantially increasing the host-layer bending (deformation) energy needed for dehydroxylation. This significantly slows dehydroxylation for all but low oxide layer concentrations. The greater lamellar flexibility present during initial dehydroxylation combines with the lower stability of intermediate composition oxyhydroxides to promote relatively rapid dehydroxylation to higher oxide layer concentrations. This explains the high concentration of oxide lamella initially found in the oxyhydroxide regions observed by electron diffraction and the enhanced resistance of these regions to further dehydroxylation.

The presence of lamellar oxyhydroxide solid solution behavior during dehydroxylation is confirmed by the in-plane structural behavior of the $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ oxyhydroxide solid solution series determined by VIB-based non-empirical electron gas modeling. Figure 3 shows that two-dimensional Vegard's-law-like behavior is predicted for the oxyhydroxides,⁷ as proposed based on the above SAD studies (see attached copy of manuscript submitted to *Chemistry of Materials*). As a result, determination of the in-plane packing distance during dehydroxylation allows direct evaluation of the composition of the lamellar oxyhydroxide regions *in situ*. Table 1 shows the range of oxyhydroxide compositions observed based the present investigation and re-evaluation of previous *in situ* SAD observations of the dehydroxylation process.^{8,9} In each study, the in-plane packing distance (e.g., Mg-Mg distance) and composition of the host $\text{Mg}(\text{OH})_2$ matrix remains unchanged during dehydroxylation and is largely unaffected by oxyhydroxide nucleation and growth. However, essentially the full range of packing distances and compositions has been observed during nucleation and growth of the lamellar oxyhydroxide solid solution series, indicating these new lamellar materials are broadly accessible, at least locally. Thus, essentially the entire oxyhydroxide solid solution series is accessible during dehydroxylation-carbonation, opening the door to a broad new range of intermediate carbonation reaction pathways, with potentially enhanced carbonation reactivity.

Slow nucleation/rapid growth and rapid nucleation/slow growth processes generally favor lamellar oxyhydroxide ($\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$) intermediate formation and two-phase (e.g., $\text{MgO} + \text{Mg}(\text{OH})_2$) intermediate behavior, respectively (Figure 4). Host-layer bending during lamellar nucleation and growth also induces substantial local elastic strain. Such strain likely induces cracking, delamination and reconstruction to form nanostructured materials, during dehydroxylation. This offers the exciting possibility of controlling nanostructure formation by controlling the relative rates of lamellar nucleation and growth during dehydroxylation.

Optical microscopy observation of the dehydroxylation process has provided substantial insight into the microscopic effects of the lamellar nucleation and growth process. Figures 5 and 6 show the progression of dehydroxylation for a single crystal brucite fragment observed perpendicular to its upper basal plane at different times during the dehydroxylation process. Figure 5 shows typical observations of blisters, likely associated with delamination, that occur early in the dehydroxylation process. Figure 6 shows images taken as a function of time for dehydroxylation of a single crystal fragment at 380 °C, a temperature at which nano-reconstruction routinely occurs. Initial dehydroxylation is associated with blister formation, quickly followed by crack formation onset. Major crack nucleation centers soon develop, with extensive cracking extending to the submicron level after two hours. Thermogravimetric analysis of similar low-temperature dehydroxylation processes indicate that dehydroxylation is only ~93% complete under these conditions, indicating the resulting material contains ~7% residual oxyhydroxide/hydroxide. Such low-temperature dehydroxylated materials have also undergone nano-reconstruction.¹⁰ Thus, low-temperature dehydroxylation forms high-surface-area materials via delamination and cracking of $\text{Mg}(\text{OH})_2$ crystallites to micron/sub-micron dimensions, which simultaneously surface reconstruct to form nano-structured materials. Combining the formation of these high-surface-area materials with dehydroxylation/rehydroxylation intermediate (e.g., lamellar oxyhydroxide) formation has been found to greatly enhance their carbonation reactivity, as discussed in the subsequent section “Enhancing the Carbonation Reaction Process.”

Mg(OH)₂ DEHYDROXYLATION/CARBONATION

As discussed above, our $\text{Mg}(\text{OH})_2$ dehydroxylation studies have identified the formation of a solid solution series of lamellar oxyhydroxide intermediate materials, which form at least locally, en route to MgO formation. These materials are of particular interest as they offer a range of potential new carbonation reaction pathways. A major focus of our dehydroxylation/rehydroxylation-carbonation studies described below, is to better understand the role of such intermediate materials in carbonation and their potential to enhance carbonation reactivity.

During the second project year, we have substantially expanded our preliminary studies of dehydroxylation/carbonation reactions for $\text{Mg}(\text{OH})_2$ single crystal fragments. Table 2 shows the compositional analysis of a series of partially dehydroxylated and carbonated $\text{Mg}(\text{OH})_2$ single crystal fragments as a function of CO_2 pressure at 585 ± 5 °C. The observed values for the carbonate and hydroxide compositions are derived from analysis of the total H and C present in each sample. Based on agreement with known standards run immediately before and after the sample runs, the error in MgCO_3 and $\text{Mg}(\text{OH})_2/\text{MgO}$ compositions are estimated to be $\pm 2\%$ and $\pm 6\%$, respectively. The reactions were carried out in a sealed autoclave under dry CO_2 , without added water. Hence, the only water vapor present evolved from $\text{Mg}(\text{OH})_2$ dehydroxylation. The extent of dehydroxylation was always observed to be substantially greater than the extent of carbonation, suggesting carbonation primarily occurs via intermediate (e.g., oxyhydroxide/oxide) formation. Thus, dehydroxylation and carbonation do not occur as a simple exchange reaction (i.e., carbon dioxide directly displacing two hydroxyl groups, with water evolution). Instead, dehydroxylation and carbonation appear to be concurrent individual processes, with

dehydroxylation intermediate formation providing a key step in the carbonation process. The range and type of intermediate oxyhydroxides/oxides that can form in advance of carbonation should provide a degree of control over both the intermediate materials formed and their potential carbonation reactivity.

The extent of dehydroxylation and carbonation shows intriguing behavior as a function of pressure, as seen in Figures 7 and 8. Whereas, the extent of dehydroxylation generally decreases with increasing CO₂ pressure, the extent of carbonation increases, then decreases as the pressure is increased. These observations are consistent with highly-porous oxyhydroxide/oxide matrix formation and its partial carbonation during the dehydroxylation-carbonation process. The decrease in dehydroxylation observed with increasing pressure follows from the decreasing rate of water diffusion out of the porous hydroxide/oxyhydroxide/oxide/carbonate matrix expected with increasing CO₂ pressure. Locally higher partial pressures of H₂O(g) develop at higher CO₂ pressures, inhibiting the dehydroxylation process. The extent of carbonation shows even more intriguing behavior as a function of CO₂ pressure. A peak in % carbonation is observed near the decomposition pressure expected for MgCO₃ at 585 °C.

Above the MgCO₃ decomposition pressure, *increasing the reactant CO₂ pressure resulted in a dramatic decrease in carbonation reactivity.* This observation is critical for mineral carbonation process engineering, as it is generally assumed increasing the reactant CO₂ activity should increase the extent of carbonation. The overall dehydroxylation-carbonation process is best understood at the nanoscale. As discussed above, dehydroxylation is inhibited by increasing CO₂ pressures. This results in higher local H₂O(g) pressures, inhibition of carbonation reactive intermediate formation via dehydroxylation and slower CO₂(g) diffusion to the dehydroxylating matrix. All of these factors serve to inhibit carbonation, as observed by the decrease in extent of carbonation with increasing CO₂ reaction pressure in the high-pressure region of Figure 7.

Equally intriguing behavior was observed below the pressure at which MgCO₃ becomes unstable with respect to MgO and CO₂. Since, at these low pressures MgCO₃ cannot form at 585 °C, substantial carbonation must be occurring during the sample heat up or cool down cycles. These cycles were carried out under carbon dioxide pressure and lasted ~ 30-40 minutes. To determine the effect of the cool down process on the extent of dehydroxylation and carbonation, samples were quenched from 585 °C to ambient temperature, with simultaneous evacuation of the carbon dioxide present. Figures 7 and 8 include the data from two quenched runs, one above and one below the MgCO₃ decomposition pressure. Whereas, the run above the decomposition pressure agrees well with the unquenched runs, the run below the decomposition pressure shows essentially no carbonation within experimental error ($\pm 2\%$), while exhibiting extensive dehydroxylation consistent with the unquenched samples. This indicates that substantial carbonation can occur relatively quickly during cool down for extensively dehydroxylated Mg(OH)₂.

Dehydroxylation-carbonation studies as a function of temperature at 370 psi of CO₂ further underscore the relationship between simultaneous dehydroxylation and carbonation processes, as shown in Figure 9. Both the extent of dehydroxylation and carbonation increases with increasing temperature until the critical temperature for MgCO₃ formation is reached (the temperature above which MgCO₃ becomes unstable with respect to MgO and CO₂). The relatively small

amount of carbonate formation observed for the sample above this temperature is likely associated with carbonation of extensively dehydroxylated material during the cool down process, as observed for the above pressure dependent dehydroxylation-carbonation studies at 585 °C. *In situ* thermogravimetric analysis studies were combined with elemental analysis to further explore the carbonation reactivity of such highly dehydroxylated intermediate materials as a function of temperature and the presence of H₂O(g), as discussed below.

ENHANCING THE CARBONATION REACTION PROCESS

Combined thermogravimetric and elemental analysis studies of *in situ* Mg(OH)₂ carbonation processes involving dehydroxylation and rehydroxylation suggest intermediate oxyhydroxide formation can play a major role in enhancing carbonation reaction rates (Figure 10 and Table 3). 5 mg single crystal Mg(OH)₂ fragments were used as the starting material to reduce the effect of structural defects (surface and internal), particle size, and surface impurities (e.g., MgO or MgCO₃). Samples were initially dehydroxylated by heating under dry He at 2 °C/min to 375 °C and holding them isothermal for two hours, resulting in high-surface-area materials that are ~93% dehydroxylated. The reaction gas was then changed to dry or humid (bubbled through a degassed, distilled water bubbler at 20 °C) CO₂. Both processes resulted in relatively rapid carbonation of 1% of the sample, after which no further carbonation occurred (similar runs changing from dry to humid He at 375 °C exhibited no change in weight, indicating the weight gain for humid CO₂ results from carbonation. Slight weight losses between positions 2 and 3 are similarly assigned to dehydroxylation). Cooling to ambient temperature (23 °C) under dry CO₂ results in little reaction, whereas the same process using humid CO₂ results in relatively rapid rehydroxylation and carbonation, indicating that simultaneous rehydroxylation substantially enhances the carbonation reaction rate.

The above reaction processes are consistent with the formation of high-surface-area material, which is 93% dehydroxylated. Initial exposure to CO₂, under dry or humid conditions, results in only 1% carbonation, after which the reactive carbonation sites have been consumed. On cooling to room temperature under humid CO₂, substantial carbonation and rehydroxylation occur. This indicates the rehydroxylation process greatly enhances carbonation reactivity. This observation is similar to the above studies of the simultaneous dehydroxylation-carbonation process, which indicate enhancing dehydroxylation under controlled conditions directly enhances carbonation. Thus, it appears the carbonation process is dramatically enhanced by the formation of transitory intermediate materials, such as the Mg_{x+y}O_x(OH)_{2y} lamellar oxyhydroxides, during dehydroxylation/rehydroxylation processes.

ATOMIC-LEVEL OBSERVATIONS OF REHYDROXYLATION-CARBONATION PROCESSES

For the model Mg-rich lamellar hydroxide, Mg(OH)₂, heat activation (dehydroxylation) can disrupt macroscopic single crystals into micron-size fragments comprised of intergrown oxide/oxyhydroxide nanocrystals. As discussed above, these materials have high gas-phase carbonation reactivity during rehydroxylation. XPD analysis of the resulting carbonated material shows no peaks characteristic of magnesite or any other carbonate, indicating the carbonated material is highly disordered (e.g., amorphous), which is not unexpected for an ambient

temperature gas phase carbonation process. Direct high temperature carbonation of $\text{Mg}(\text{OH})_2$ routinely produced crystalline magnesite, as evidenced by XPD. We have successfully used parallel electron energy loss spectroscopy (PEELS) to directly observe the rehydroxylation carbonation process in our E-cell DHRTEM reaction system. Direct imaging of the process supports the formation of highly disordered material, as suggested by the above XPD studies. The carbon and oxygen K-edges observed during *in situ* carbonation of two separate samples are shown in Figure 11.

The C K-edge spectra clearly show carbonate formation has occurred. The absence/weak presence of the third peak in the magnesite spectra (~ 319 eV) in the *in situ* carbonated spectra is consistent with the formation of an amorphous carbonate during *in situ* carbonation. The O K-edge spectra of the *in situ* carbonated samples indicate substantial oxide-rich material is present together with the carbonate (e.g., the pre-edge feature at ~ 522 eV for the carbonate is only weakly apparent for the *in situ* carbonated sample). This indicates that only a small fraction of the sample has carbonated so far. This level of reaction control should facilitate future *in situ* PEELS observation of the complete carbonation process. These studies will include detailed advanced modeling analysis of the spectra, via collaboration with DOE/NETL grant DE-FG26-99FT40580, to better characterize the amorphous carbonate materials that form.

ON THE COMPETITION BETWEEN $\text{Mg}(\text{OH})_2$ DELAMINATION, CRACKING AND NANOSTRUCTURE FORMATION AND PASSIVATING CARBONATE LAYER FORMATION

Dehydroxylation-carbonation reaction rates for $\text{Mg}(\text{OH})_2$ single crystal fragments were generally observed to decrease over time consistent with passivating carbonate layer formation. This is consistent with the observation of carbonate surface layer formation, as observed by near-surface SIMS studies and reported in our first year technical progress report. In terms of its effect on carbonation reactivity, such carbonate passivating layer formation is countered by the $\text{Mg}(\text{OH})_2$ cracking, delamination and nano-reconstruction processes associated with dehydroxylation (see attached manuscripts submitted to *Chemistry of Materials* and the 17th International Pittsburgh Coal Conference and our 25th International Technical Conference on Coal Utilization & Fuel Systems Proceedings article, (2000) pp. 897-908). We have made and are in the process of making extensive optical microscopy and FESEM observations of these processes to better understand their role in carbonation reactivity. The aggregate insight these observations provide into carbonation reactivity will be described in next year's report. Overall, these factors have the potential to counter the carbonation inhibiting effects of passivating layer formation by disrupting the solid state structure down to the atomic level and creating high surface area reaction intermediates.

Ion beam analysis of partially dehydroxylated and carbonated single crystal samples has provided new insight into the dehydroxylation-carbonation reaction interface as a function of depth from the crystal surface, as shown in Table 4. As expected, the extent of carbonate formation and dehydroxylation decreases with increasing sample depth. Of particular interest, is the increase in carbonate to oxide ratio with increasing reaction depth, which increased from 2:1 at the crystal surface to 4:1 approximately 0.2 mm below the surface. This is likely associated with slower dehydroxylation rates and higher $\text{H}_2\text{O}(\text{g})$ partial pressures deeper in the crystal during the dehydroxylation-carbonation reaction. This suggests one can substantially improve the

MgCO₃/MgO product ratio by controlling the rate of dehydroxylation during dehydroxylation-carbonation processes.

INITIAL OBSERVATIONS OF IMPURITY EFFECTS

FESEM studies of partially dehydroxylated/carbonated samples perpendicular to the host Mg(OH)₂ single crystal lamella revealed occasional formation of triangular/hexagonal features. These features were often associated with trace Fe impurity segregation/concentration, with local concentrations as high as 5% being observed, as seen in Figure 12. Preliminary studies indicate these features do not appear to significantly affect the extent of carbonation present locally, as the extent of carbonation across them and into the neighboring Fe-deficient matrix material was essentially unchanged.

TABLES

Table 1. In-Plane Packing Distances Observed by SAD for the Oxyhydroxide, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, Regions and the $\text{Mg}(\text{OH})_2$ Matrix during *In Situ* Dehydroxylation. The Composition Range is Determined by Comparison with Figure 3.

Study	$\text{Mg}(\text{OH})_2$ Matrix (packing distance)	$\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ (packing distance)	$\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$ composition (% $\text{Mg}(\text{OH})_2$)
Gordon & Kingery ⁸	3.15 Å	3.14 → 2.98 Å	94% → 0%
Kim, et al. ⁹	3.15 Å	3.00 → 2.98 Å	12% → 0%
Present Study	3.15 Å	3.04 → 2.98 Å	35% → 0%

Table 2. Phase Analysis of Samples Dehydroxylated/Carbonated for 16 hours at 585 °C as a Function of CO_2 Pressure.*

Sample	Time (hr)	P_{CO_2} (psi)	Temp. (°C)	MgCO_3 wt. %	MgO wt. %	$\text{Mg}(\text{OH})_2$ wt. %
HB23.1	16	20	588	5.10	88.39	6.51
HB22.1	16	80	586	7.32	82.55	10.14
HB20.1	16	150	588	7.03	81.69	11.28
HB24.1	16	200	587	5.61	87.39	7.00
HB25.1	16	240	588	6.76	81.76	11.49
HB26.1	16	300	586	10.71	77.09	12.20
HB15.1	16	300	588	20.51	63.94	15.55
HB14.1	16	310	588	21.55	62.48	15.97
HB27.1	16	400	589	26.09	55.26	18.64
HB28.1	16	640	588	26.04	57.93	16.03
HB32.1	16	800	583	16.47	20.19	63.34
HB16.1	16	940	589	11.20	24.72	64.09
HB29.1	16	1560	580	4.08	15.44	80.48
HB31.1	16	2070	581	1.76	7.01	91.23
HB17.1	16	2700	588	1.44	14.69	83.88
HB55.1	16	150	588	1.37	95.75	2.88
HB56.1	16	1080	580	8.25	44.58	47.17

* The MgCO_3 and $\text{Mg}(\text{OH})_2$ compositions are determined by carbon and hydrogen elemental analysis, respectively. The MgO composition is determined by difference, assuming the remainder of the sample is MgO . These analyses offer bulk phase composition and do not discriminate between the presence of mixed $\text{MgO} + \text{Mg}(\text{OH})_2$ materials and lamellar oxyhydroxide materials. Runs HB55.1 and HB56.1 were simultaneously quenched to 20 °C and evacuated at the end of 16 hrs. All other runs were cooled under CO_2 in 30-40 minutes.

Table 3: Sample Compositions for Reaction Positions in Figure 10*

Reaction	Humid CO ₂			Dry CO ₂		
Position	%MgCO ₃	%MgO	%Mg(OH) ₂	%MgCO ₃	%MgO	%Mg(OH) ₂
1	0.0	93.0	7.0	0.0	93.6	6.4
2	1.1	91.9	7.0	0.9	92.7	6.4
3	1.1	92.5	6.4	0.9	92.9	6.2
4**	8.1	76.6	15.3	1.4	92.4	6.2

* Compositions are given in mol% and determined by weight change for positions 1-3, as described in the text.

** The final compositions for humid and dry CO₂ are determined by total C & H analysis and TGA assuming only carbonation occurs, respectively. The humid compositions agree well with the final weight gain observed on cooling (between position 3 and 4; 7.8% TGA vs. 8.0% estimated from C & H elemental analysis). The dry compositions agree well with those from C & H analysis (1.2 % MgCO₃, 95.3% MgO, 3.5% Mg(OH)₂). The slight increase in %MgCO₃/%Mg(OH)₂ may be associated with traces of H₂O left in the TGA system from dehydroxylation.

Table 4: Ion Beam Mg(OH)₂, MgCO₃, and MgO Composition Analysis as a Function of Depth from the Basal Plane (0001) of a Brucite Single Crystal Reacted for 16 hours at 589 °C under 940 psi of CO₂.

Depth	%Mg(OH) ₂	%MgCO ₃	%MgO	MgCO ₃ /MgO
Surface	27.1	50	22.9	2.2
0.1 mm	50	40	10	4.0
0.2 mm	70	24	6	4.0

FIGURES

Figure 1. A lamellar view of the Mg-rich lamellar hydroxide minerals (a) brucite, $\text{Mg}(\text{OH})_2$, and (b) serpentine (lizardite). Note the close structural similarities, with both structures containing Mg lamella and hydroxide lamella. The green, red and white spheres correspond to the Mg, O, and H atom positions, respectively. The grey tetrahedra with small red spheres at the corners correspond to the silica (SiO_4) groups connected in lamellar sheets, which also contain hydroxyl groups.

Figure 2 Free energies (red) and enthalpies (green) for representative lamellar oxyhydroxide intermediate materials (x oxide layers for every y hydroxide layers) relative to stoichiometrically equivalent amounts of MgO and $\text{Mg}(\text{OH})_2$. The bulk moduli of the intermediates are shown in blue. The inset shows the structure of the $\text{Mg}_2\text{O}(\text{OH})_2$ oxyhydroxide intermediate, which contains equal numbers of oxide and double hydroxide layers, viewed parallel to the layers. The green, red, and white spheres represent the Mg, O and H atom positions, respectively.

Figure 3 In-plane (e.g., Mg-Mg) packing distances for the intermediate lamellar oxyhydroxides, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, as a function of hydroxide layer composition. A small systematic overestimate of 0.02 Å in all the computed distances, determined by VIB-based non-empirical electron gas modeling, is inferred by comparison with the known values for MgO and $\text{Mg}(\text{OH})_2$. The computed values shown are shifted to allow for the overestimate. The line extrapolates between the experimentally observed (XPD) in-plane packing distances for MgO and $\text{Mg}(\text{OH})_2$.

Figure 4. Models of relatively rapid nucleation/slow growth and slow nucleation/rapid growth lamellar nucleation and growth processes. The two-phase ($\text{Mg}(\text{OH})_2 + \text{MgO}$) and homogeneous lamellar oxyhydroxide character of these processes is consistent with previous low-magnification TEM SAD observations of $\text{Mg}(\text{OH})_2$ dehydroxylation (see Table 1).^{8,9}

Figure 5. The onset of low-temperature dehydroxylation is frequently associated with delamination “blister” formation. The above bright field optical microscopy images are taken perpendicular to the $\text{Mg}(\text{OH})_2$ single crystal basal planes just after the onset of low-temperature dehydroxylation.

Figure 6. The microscopic progression of low-temperature dehydroxylation (380 °C): (a) blister formation after one minute; (b) the onset of cracking perpendicular to the host lamella after two minutes; (c) formation and growth of cracking nucleation centers after 30 minutes; (d) extensive cracking down to the micron/sub-micron level after two hours. The images are shown in grey scale to emphasize crack growth and propagation.

Figure 7. Percent carbonate formed vs. CO₂ pressure for brucite single crystals reacted at 585°C (±5°C) for 16 hours (±15min). The triangles represent samples cooled down under CO₂ in 30-40 minutes. The squares represent samples that were quenched to ambient temperature from 585 °C and simultaneously evacuated.

Figure 8. Percent dehydroxylation vs. CO₂ pressure for brucite single crystals reacted at 585°C (±5°C) for 16 hours (±15min). The triangles represent samples cooled down in CO₂ in 30-40 minutes. The squares represent samples that were quenched to ambient temperature from 585 °C and simultaneously evacuated.

Figure 9. MgO, MgCO₃, and Mg(OH)₂ compositional analysis for partially dehydroxylated/carbonated brucite single crystal fragments as a function of reaction temperature for 4 hours at 370 psi CO₂.

Figure 10. *In situ* thermogravimetric analysis studies of carbonation of low-temperature (375 °C) calcined $\text{Mg}(\text{OH})_2$. After stabilizing at $\sim 93\%$ dehydroxylation (position 1), the atmosphere was changed from dry He to humid ($\sim 70\%$ humidity) and dry CO_2 for the separate runs at 375 °C, as shown. Slight carbonation ($\sim 1\%$) occurs initially (by position 2), but does not continue (position 3). Cooling to ambient temperature (position 4) results in little reaction under dry CO_2 , whereas humid CO_2 shows strong carbonation and rehydroxylation behavior, as confirmed by carbon and hydrogen elemental analysis. The slight dip between position 3 and 4 is associated with instrumental/buoyancy effects.

Figure 11. Electron loss near edge structure spectra observed during *in situ* carbonation of partially dehydroxylated $\text{Mg}(\text{OH})_2$. The spectra are expected to change slightly via further background subtraction refinement. The orange curves are theoretical *ab initio* C K-edge spectra for magnesite (left) and O K-edge spectra for magnesite (upper right) and MgO (lower right).

Figure 12. Field emission scanning electron microscopy (FESEM) analysis of triangular surface features that form during dehydroxylation-carbonation processes. Fe impurities segregate into the above triangular regions during dehydroxylation/carbonation, but seem to have little effect on carbonation reactivity at these low concentrations, as discussed in the text.

Figure 13. Possible $\text{Mg}(\text{OH})_2$ carbonation reaction pathways during dehydroxylation and/or rehydroxylation. The intermediate lamellar oxyhydroxide solid solution series, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, is represented by nominal compositions of $\text{Mg}_3\text{O}(\text{OH})_4$ and $\text{Mg}_3\text{O}_2(\text{OH})_2$. The green, red, white, and black spheres correspond to the Mg, O, H, and C atom positions, respectively. Whereas MgO and $\text{Mg}(\text{OH})_2$ can form by dehydroxylation and rehydroxylation, respectively (potentially cycling back and forth at low temperatures), carbonate formation is thermodynamically dictated as a one way reaction (below the MgCO_3 decomposition temperature).

CONCLUSIONS

Mg(OH)₂ dehydroxylation proceeds as a lamellar nucleation and growth process. Lamellar oxide nuclei nucleate within the brucite matrix, followed the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions. These regions can grow both parallel and perpendicular to the Mg(OH)₂ lamella within the brucite matrix, leaving the matrix structure largely undisturbed until it is consumed. This process can take on lamellar solid solution (oxyhydroxide) or two-phase [Mg(OH)₂ + MgO] character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. Lamellar nucleation and growth also induces substantial local elastic strain that likely leads to the widely observed cracking, delamination and nano-reconstruction of the host matrix. Locally this strain will depend on the slow nucleation/rapid growth vs. rapid nucleation/slow growth character of the dehydroxylation process. As a result, it may be possible to control the nano-reconstruction process by controlling the lamellar nucleation and growth process.

The free energies (400 °C) of the entire solid solution series of oxyhydroxide intermediates is within 2 kcal/mol of stoichiometrically equivalent Mg(OH)₂ + MgO mixtures, indicating the entire series is theoretically accessible during dehydroxylation/carbonation. Compositional analysis based on *in situ* SAD measurements indicates that essentially the entire solid solution series has been observed as intermediates during the dehydroxylation process. Importantly, low-temperature Mg(OH)₂ dehydroxylation is reversible, via oxide/oxyhydroxide nanostructure formation. This opens the door to a wide range of potential new intermediate oxyhydroxide carbonation pathways via dehydroxylation or rehydroxylation, as shown in Figure 13.

Macroscopic and microscopic studies of gas-phase carbonation indicate dehydroxylation generally precedes carbonation locally, consistent with the creation of dehydroxylation intermediates with higher carbonation reactivity. Simultaneous rehydroxylation of partially dehydroxylated material was found to greatly enhance its gas-phase carbonation reactivity *at ambient temperature*, further underscoring the importance of transitory intermediate formation. This observation, which includes substantial carbonation reaction rates at ambient temperature and CO₂ pressure, may open the door to new CO₂ mineral sequestration processes under ambient conditions, with broader applications and the potential for substantially reducing process cost. In addition to forming lamellar oxyhydroxide intermediates, dehydroxylation can also result in substantial delamination, intralamellar cracking, and surface reconstruction to form nanostructured materials, as discussed above. These phenomena can be used to combat the formation of near surface carbonate passivating layers, which likely inhibit carbonation. The highly porous structures that result from dehydroxylation and form during dehydroxylation/carbonation can also lead to novel phenomena, such as Mg(OH)₂ carbonation reactivity increasing with decreasing CO₂ gas pressure.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

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