

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

Type of Report: Annual

Reporting Period Start Date: August 1, 2000

Reporting Period End Date: July 31, 2001

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Date Report Issued: October 2001

DOE Award Number: DE-FG2698-FT40112

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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 minimizing the cost of any lamellar-hydroxide-based mineral carbonation sequestration process. This report covers the third year progress of this grant, as well as providing an integrated overview of the progress in years 1-3, as we have been granted a one-year no-cost extension to wrap up a few studies and publications to optimize project impact.

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, which may be able to enhance carbonation reactivity.* We also initiated studies to probe dehydroxylation/carbonation reaction mechanisms via C and H elemental analysis, optical microscopy and SIMS.

In the second year, we expanded our studies to better understand the mechanisms that govern Mg(OH)₂ carbonation reactivity. These investigations incorporated a range of techniques, including E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, XRD, and elemental analysis. In collaboration with DOE/NETL grant DE-FG26-99FT40580, we integrated advanced computational modeling studies with our experimental observations. *We found intermediate (e.g., oxyhydroxide) formation is a key component of both rehydroxylation-carbonation and dehydroxylation-carbonation processes, which, if controlled, can dramatically enhance carbonation reactivity, even at ambient temperature and CO₂ pressure.* Critical to optimizing this enhanced reactivity is the ability of Mg(OH)₂ to form nanostructured materials during controlled dehydroxylation, providing access to high surface area, carbonation reactive intermediate materials. Mechanisms that can inhibit carbonation include passivating carbonate layer formation and MgO crystal growth during dehydroxylation. These mechanisms combine

with delamination, cracking and nanostructured materials formation to control carbonation reactivity.

In the third year of the project, we primarily focused on developing a deeper understanding of nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated Mg(OH)_2 under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery of rapid Mg diffusion during dehydroxylated- Mg(OH)_2 rehydroxylation, via *in situ* atomic-level E-cell DHRTEM, which appears to be key to the above enhanced carbonation reactivity; and (iii) developing an integrated overview of the impact of Mg(OH)_2 cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

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EXECUTIVE SUMMARY

OBJECTIVE

The objective of this project is to develop an atomic-level understanding of the mechanisms that govern the carbonation kinetics of the prototypical Mg-rich lamellar-hydroxide-based mineral $Mg(OH)_2$, to facilitate engineering of improved carbonation materials and processes for CO_2 disposal. The chemical and structural simplicity of $Mg(OH)_2$ provides a model system to develop a deeper fundamental understanding of Mg-rich lamellar-hydroxide-based mineral carbonation reaction mechanisms. The potential for these mineral carbonation processes to be economically viable has helped generate substantial interest in CO_2 mineral sequestration as a possible carbon management option (e.g., carbonation of the chemically and structurally more complex Mg-rich lamellar hydroxide serpentine-based minerals). Environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM) is used to probe the associated reaction processes down to the atomic level. A battery of complementary techniques is used to further elucidate key reaction mechanisms at the macroscopic and microscopic levels (via *in-situ* and *ex-situ* studies). As carbonation involves dehydroxylation, carbonation and potential competition between them, this project focuses on developing an atomic-level understanding of dehydroxylation and carbonation reaction mechanisms and their impact on carbonation reactivity. Particular emphasis is placed on the mechanisms that have the greatest impact on carbonation reactivity.

ACCOMPLISHMENTS TO DATE

In year 3 we have continued to extend our studies beyond E-cell DHRTEM to develop a better understanding of the $Mg(OH)_2$ reaction mechanisms associated with carbonation processes. We have again expanded our *in situ/ex situ* mechanistic studies of dehydroxylation/rehydroxylation-carbonation reaction processes to include optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Integrating these investigations with advanced computational modeling {together 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)} has produced an enhanced atomic-level understanding of key reaction mechanisms.

We have discovered $Mg(OH)_2$ dehydroxylation is governed by a lamellar nucleation and growth process, which can result in intermediate lamellar oxyhydroxide formation. Slow nucleation/rapid growth and rapid nucleation/slow growth favor oxyhydroxide and $MgO + Mg(OH)_2$ intermediate formation, respectively. This process can also result in extensive nanoscale crystal fracture, resulting in a morphological evolution of the reaction matrix involving internal blister formation, lattice cracking and morphological reconstruction, which has the ability to form nanoporous materials. Blister formation occurs internally, before lattice cracking can connect these regions with the exterior reaction atmosphere. Matrix cracking proceeds inward from the lamellar crystal edge and basal plane surfaces, connecting with the internal blisters that have formed to create high-surface-area intermediate materials with enhanced carbonation reactivity. Together with the potential to form carbonation reactive oxyhydroxide

intermediate materials, these mechanisms provide exciting potential for engineering feedstock materials and processes with enhanced carbonation reactivity.

Although, the high-surface-area materials that result from low-temperature dehydroxylation were found to have a limited number of carbonation reactive sites, their controlled rehydroxylation can create/expose many more reactive sites resulting in *a dramatic increase in carbonation reactivity at ambient temperature*. *In situ* E-cell DHRTEM combined with parallel electron energy loss spectroscopy has shown an amorphous magnesium carbonate containing material is formed in the process. Analogous atomic-level observations of the rehydroxylation process have discovered dramatic Mg mobility leads to the reformation of Mg(OH)₂. Such high Mg mobility is apparently key to the greatly enhanced carbonation reactivity of dehydroxylated Mg(OH)₂ observed under humid conditions.

The Mg(OH)₂ dehydroxylation mechanisms discussed above and their ability to create nanoporous reaction matrices also impacts direct gas-phase Mg(OH)₂ carbonation, including providing mechanistic avenues that can bypass passivating carbonate layer formation and enhance carbonation reactivity. They are also associated with the novel observation that Mg(OH)₂ carbonation reaction rates *increase* with *decreasing* CO₂(g) pressure above the critical pressure needed for carbonate formation. Hence, direct gas-phase Mg(OH)₂ carbonation reactivity can be optimized at the lowest CO₂ pressure at which MgCO₃ is stable. Higher CO₂ pressures further inhibit H₂O(g) diffusion out of and CO₂(g) diffusion into the nanoporous reaction matrix that forms, slowing both dehydroxylation and carbonation. Investigations of the role of Fe impurities during dehydroxylation/carbonation suggest they can segregate into Fe-rich regions during dehydroxylation, possibly reducing their impact on carbonation reactivity in the process. Similar mechanisms may be more broadly applicable to Mg/Ca-rich lamellar-hydroxide-based mineral (e.g., serpentine) carbonation processes, offering substantial potential for reducing CO₂ mineral sequestration process costs.

The detailed discussion of our accomplishments that follows integrates an overview of our aggregate progress in developing an atomic-level understanding of the mechanisms that govern Mg(OH)₂ carbonation reactivity, with a more detailed summary of our third year progress.

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 coal 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's Office of Fossil 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 improvement via materials and process engineering.

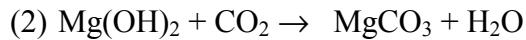
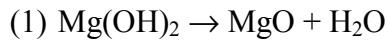
Mg-Rich Lamellar-Hydroxide-Based Minerals: Candidate Feedstock Materials for Cost Competitive CO₂ Mineral Sequestration

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. Increasing 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 low-cost 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 (reaction 1), is intimately associated with carbonation (reaction 2),



its mechanisms are of direct interest in understanding and optimizing the carbonation process. Although Mg(OH)₂ dehydroxylation has been extensively studied, relatively little was known about the atomic-level nature of the process, especially in the early stages of dehydroxylation, prior to this investigation. 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 our second year report, we described our studies that 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. In this, our third year report, we extend this understanding to direct atomic level observations of dehydroxylated Mg(OH)₂ rehydroxylation. These studies have discovered very high Mg mobility during gas-phase rehydroxylation, which leads to rapid Mg(OH)₂ crystal growth. Such Mg mobility is very likely key to the dramatically enhanced carbonation reactivity observed for dehydroxylated Mg(OH)₂ at ambient temperature under the humid conditions discussed below.

Mg(OH)₂ Dehydroxylation/Rehydroxylation-Carbonation Processes

In the first year 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.

In our second year, we 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 ($Mg_{x+y}O_x(OH)_{2y}$) accessible during $Mg(OH)_2$ dehydroxylation/rehydroxylation. The ability of $Mg(OH)_2$ 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, $Mg(OH)_2$ feedstock impurities may also play important roles in carbonation reactivity. Although initial studies indicate Fe impurities can phase separate during $Mg(OH)_2$ 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 efforts to combine oxyhydroxide intermediate formation with controlled nanostructure formation to probe their ability to enhance carbonation reactivity proved quite promising, as we *achieved carbonation reaction rates at ambient temperature and CO_2 pressure similar to those previously reported for optimum ambient CO_2 pressure $Mg(OH)_2$ carbonation (at 375 °C)*.

In the third year of the project, we primarily focused on developing a deeper understanding of the reaction matrix morphology, nanostructure and oxyhydroxide formation and their impact on carbonation reactivity, due to their dramatic ability to enhance carbonation reaction rates and potential application to other Mg-rich lamellar hydroxide minerals of interest (e.g., serpentine-based minerals). These investigations include E-cell DHRTEM, optical microscopy, FESEM, ion beam analysis, SIMS, TGA, Raman, XRD, and elemental analysis. Highlights include: 1) *in situ* atomic-level observations of the dramatically enhanced ambient-temperature carbonation reactivity of dehydroxylated $Mg(OH)_2$ under humid conditions, which produces an amorphous hydroxycarbonate; 2) the discovery (via *in situ* atomic-level E-cell DHRTEM) of dramatically enhanced Mg diffusion during dehydroxylated- $Mg(OH)_2$ rehydroxylation, which appears to be a key mechanistic tool for enhancing carbonation reactivity; and (iii) developing an integrated overview of the impact of $Mg(OH)_2$ cracking, delamination, nanoreconstruction, oxide crystal growth, and passivating carbonate layer formation on carbonation intermediate formation and carbonation reactivity based on macroscopic, microscopic, and nanoscopic dehydroxylation/rehydroxylation/carbonation mechanistic observations.

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].⁶ 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 CO₂ introduced, and the autoclave brought quickly to reaction temperature. *In situ* Mg(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 Mg(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. Mg(OH)₂ was first dehydroxylated *in situ* via resistive heating, followed by reaction at ambient temperature with ~800 mtorr of humid CO₂.

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 ~5-20 μ m in point analysis mode and lateral image resolution is ~1 μ m. The digital optical microscope system used was a Mititoyo 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 CuK α radiation, line focus, and graphite monochromator. Ion beam analyses of partially carbonated Mg(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 C(alpha, alpha)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 \pm 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.

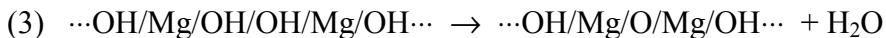
MODELING: *Ab initio* density functional theory calculations and non-empirical electron-gas modeling based on the VIB method⁶ were used to investigate the relative stability, elastic behavior and structural trends of the intermediate oxyhydroxides as a function of composition. The methods used are described in detail in the attached reprint published in *Chemistry of Materials*.⁶ Similar methods were used for the carbonation modeling studies. These are

described in detail in the 2000 annual report for the DOE UCR Innovative Concepts project “Atomic-Level Modeling of CO₂ Disposal as a Carbonate Mineral: a Synergetic Approach to Optimizing Reaction Process Design,” (grant #DE-FG26-99FT40580), which fully collaborated with the project described herein.

RESULTS AND DISCUSSION

Mg(OH)₂ DEHYDROXYLATION

Our DHRTEM observations parallel to the Mg(OH)₂ lamella during dehydroxylation discovered the general lamellar nature of the process (see appended copy of *Chem. Mater.* **13** (3), 921-6 (2001)).⁶ *In situ* selected area diffraction (SAD) studies confirmed Mg(OH)₂ dehydroxylation is best described as a lamellar nucleation and growth process. After initial oxide layer nucleation, as described in equation 3, 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 Mg(OH)₂ matrix. Advanced computational modeling, in collaboration with the above UCR Innovative Concepts project (grant #DE-FG26-99FT40580), has provided a deeper understanding of the nature of the intermediate oxyhydroxides (see appended copy of *Mater. Chem. and Phys.*, (2001), in press).⁷ We have found that essentially the entire oxyhydroxide solid solution series is accessible during dehydroxylation/rehydroxylation-carbonation, opening the door to a broad new range of intermediate carbonation reaction pathways, with potentially enhanced carbonation reactivity (Figure 2).⁶⁻⁸

Slow nucleation/rapid growth and rapid nucleation/slow growth processes generally favor lamellar oxyhydroxide (Mg_{x+y}O_x(OH)_{2y}) intermediate formation and two-phase (e.g., MgO + Mg(OH)₂) intermediate behavior, respectively (Figure 3). Host-layer bending during lamellar nucleation and growth also induces substantial local elastic strain. Such strain likely induces cracking, delamination and reconstruction, which can lead to the formation of nanostructured materials during dehydroxylation. This offers the exciting possibility of providing some control over nanostructure intermediate 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 as a function of reaction progression.⁹ Dehydroxylation of Mg(OH)₂ to form MgO is accompanied by a large volume decrease, which results from an ~50% collapse of the interlayer distance (Figure 2). It is also accompanied by an ~5% decrease in the in-plane packing distance, as confirmed by macroscopic observations of single crystal fragments during dehydroxylation (Figure 4). This induces substantial interlamellar and intralamellar strain at the nanoscale during dehydroxylation, as discussed above.⁶ Early in the dehydroxylation process, blisters are observed to form in the Mg(OH)₂ crystal interior, as shown in Figure 5. These regions can be associated with the onset of dehydroxylation internally, with blisters forming in the lamellar interior of the crystal via

equation (1). The external onset of dehydroxylation is characterized by translamellar and lamellar cracking, which are commonly observed as water escapes from the Mg(OH)₂ crystallite matrix during dehydroxylation.¹⁰ As seen in Figure 6, external dehydroxylation is often initiated at the edges of freshly-cleaved, Mg(OH)₂ single-crystal fragments. As dehydroxylation continues, new cracks branch away from the primary cracks, with overall crack propagation continuing inward from the crystal edge. Crack nucleation centers can also form independently in the central region of the basal surface (Figure 6e), indicating crack formation can nucleate at basal surface sites (e.g., defect sites), as well as at edge sites. Basal plane nucleation typically results in the formation of crack centers that nucleate and grow on the basal plane surface, as shown in Figure 7. At lower temperatures basal plane cracks initially nucleate as linear cracks on the basal plane surface (Figure 7a), followed by crack center formation (Figure 6e). At higher temperatures, basal-plane crack centers can form early in the dehydroxylation process. The upward bending of the basal planes in Figures 7b and 7c indicate that water evolution exerts strong local pressure perpendicular to the basal plane surface during crack center formation.

The onset of crack formation at the crystal edge or step surface is often associated with the formation of planar cracks that intersect at 120° angles, as seen in Figures 6b, 6c, 8a and 8b. Laue X-ray diffraction analysis of the crystal orientation prior to dehydroxylation shows the crack propagation occurs along the 11-20 direction, indicating these surfaces can be selectively exposed during dehydroxylation. Hence, their gas-phase carbonation reactivity is of particular interest and will be the subject of future advanced computational modeling studies. Although crystal cracking along crystallographic directions was observed routinely, primary and secondary cracking and the formation of crack centers were more commonly observed (Figures 8c-e). The formation of basal-plane crack centers can be correlated with basal-plane surface defects, as seen in Figure 8d and e. Thus, crack propagation and dehydroxylation is promoted by roughening the basal plane surfaces of the brucite crystal fragments.

As crack propagation continues beyond the nucleation and initial growth stage, externally nucleated cracks, including basal-plane nucleated crack centers and edge-nucleated cracks, intersect internal blisters leading to the formation of a highly porous reaction matrix. Extensive dehydroxylation ultimately disrupts the material down to the sub-micron/nanoscale. Such extensive low-temperature dehydroxylation can also lead to morphological reconstruction to form well-known nanostructured materials, which typically consist of intergrown cubic MgO nanocrystals, with edge dimensions as low as ~1 nanometer, depending on the dehydroxylation conditions.^{11,12} Figure 9 shows the larger intergrown MgO nanocrystals that can form via moderate temperature (580 °C) dehydroxylation. The combination of the high-surface-area materials that can be generated via the above crack propagation processes and nanoreconstruction, with the ability to form highly carbonation reactive intermediate materials during dehydroxylation/rehydroxylation, can dramatically impact carbonation reactivity.

We previously observed in project years 1 and 2, that partially dehydroxylated Mg(OH)₂ exhibits strongly enhanced carbonation reactivity under humid conditions.^{8,13} In order to better understand the mechanisms that lead to this enhanced carbonation reactivity, we have imaged the rehydroxylation of partially dehydroxylated Mg(OH)₂ down to the atomic level to elucidate the mechanism(s) whereby rehydroxylation can dramatically enhance carbonation reactivity. Figure

10 shows E-cell DHRTEM observations of the nucleation and growth of Mg(OH)₂ lamella during Mg(OH)₂ rehydroxylation after *in situ* dehydroxylation at 465 °C. Recrystallization shows very rapid Mg diffusion, as evidenced by rapid layer-by-layer Mg(OH)₂ crystal growth on the Mg(OH)₂ crystal surface. Rapid growth and movement of edge dislocations parallel to the lamella were also observed. In addition, edge dislocation motion was observed perpendicular to the lamella, with individual lamella breaking and reforming resulting in c-axis motion of the edge dislocations. All of the processes observed were highly dynamic. Such processes are likely to strongly contribute to the dramatically enhanced carbonation reactivity observed for low-temperature dehydroxylated Mg(OH)₂ under humid conditions, by providing access to fresh carbonation reactive reaction sites.

Mg(OH)₂ DEHYDROXYLATION/REHYDROXYLATION-CARBONATION

As discussed above, our Mg(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. Such intermediate formation can be combined with Mg(OH)₂ reaction matrix cracking and reconstruction down to the nanoscale, to form very high surface area intermediate materials. These high surface area materials are of particular interest as they can offer a range of potential new carbonation reaction pathways, as shown in Figure 2. The mechanisms associated with these materials provide exciting potential for engineering feedstock materials and processes with enhanced carbonation reactivity, as reported in our second year technical progress report and the referenced publications.^{6-9,13-15} Although, the high-surface-area materials that result from low-temperature dehydroxylation were found to have a limited number of carbonation reactive sites, their controlled rehydroxylation was found to create/expose many more reactive sites resulting in *a dramatic increase in carbonation reactivity at ambient temperature*.

ATOMIC-LEVEL OBSERVATIONS OF REHYDROXYLATION-CARBONATION PROCESSES

We have utilized *in situ* E-cell DHRTEM to observe the exceptional carbonation reactivity of low-temperature dehydroxylated Mg(OH)₂ during rehydroxylation-carbonation to better understand the mechanisms that govern this exciting rapid carbonation process. As described in last year's report, rehydroxylation-carbonation is quite rapid at ambient temperature and yields an amorphous carbonate that appears to contain some rehydroxylated material as well. E-cell DHRTEM imaging of the process revealed the onset of ambient temperature rehydroxylation-carbonation is instantaneous upon exposure of low-temperature dehydroxylated Mg(OH)₂ to even low pressures of humid CO₂ (Figure 11). The porous reaction matrix provided by low-temperature dehydroxylated Mg(OH)₂ appears to absorb CO₂ and H₂O into the reaction matrix as well as their reacting with the matrix surface causing the swelling and breathing motion observed during rehydroxylation-carbonation. The amorphous carbonate containing product is confirmed to contain carbonate via parallel electron energy loss spectroscopy and selected area electron diffraction.¹⁴ During rehydroxylation-carbonation we occasionally observe lamella in addition to the general amorphous carbonate and hydroxide containing material formed, as seen in Figure 12. These lamella often have the layer repeat expected for Mg(OH)₂ and sometimes a greater interlayer repeat. This is consistent with at least transitory rehydroxylation accompanying

carbonation at ambient temperature (as also evidenced by C and H elemental analysis), which, in turn, is likely associated with the formation of new oxyhydroxide-like intermediates that can dramatically enhance carbonation reactivity.

MICROSCOPIC OBSERVATIONS OF Mg(OH)₂ DEHYDROXYLATION/REHYDROXYLATION CARBONATION

As discussed in last year's report, dehydroxylation-carbonation reaction rates for Mg(OH)₂ single crystal fragments were generally observed to decrease over time consistent with passivating carbonate layer formation. In terms of its effect on carbonation reactivity, such carbonate passivating layer formation is countered by the Mg(OH)₂ cracking, delamination and nano-reconstruction processes associated with dehydroxylation.^{6-9,13-15} We have made extensive microscopic observations of these processes to better understand their role in carbonation reactivity. The importance of lattice cracking during dehydroxylation/rehydroxylation-carbonation is indicated in Figures 13 and 14 and compared with the extent of carbonation observed (Figure 15). At pressures below the critical carbonation pressure at 585 °C (~ 53.7 atm CO₂),⁸ the reacting crystals extensively dehydroxylate at 585 °C, followed by rapid rehydroxylation-carbonation on cooling, as discussed in last year's report. Above the critical carbonation pressure, carbonation occurs directly at 585 °C.^{8,9,14} The extent of crack formation, as observed via optical microscopy, is directly related to the extent of dehydroxylation in either process, as seen in Figures 13 and 14. This underscores the importance of matrix crack formation in enhancing H₂O and CO₂ diffusion out of and into the Mg(OH)₂ reaction matrix, respectively, which, in turn, generally enhances carbonation reactivity.

FIGURES

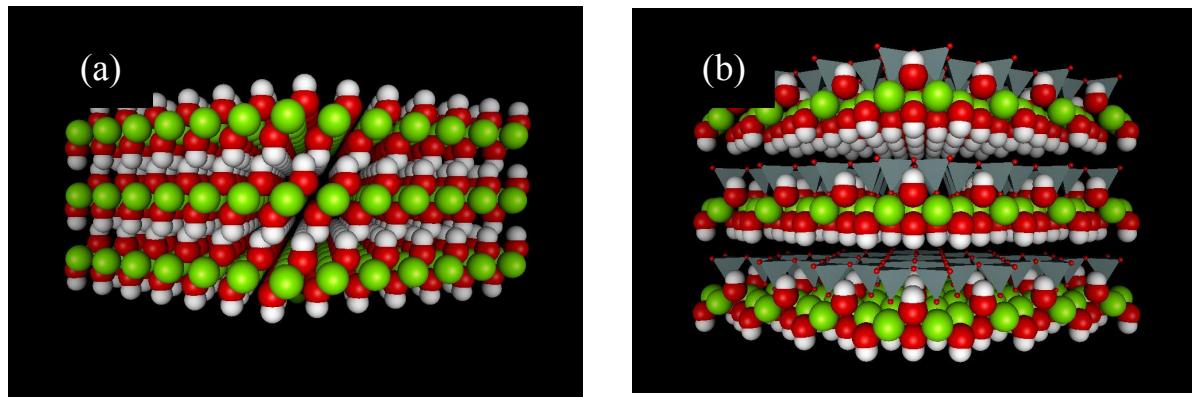


Figure 1. A lamellar view of the Mg-rich lamellar hydroxide minerals (a) brucite, $\text{Mg}(\text{OH})_2$, and (b) serpentine (lizardite). Note the close structural similarities, with both structures containing Mg lamella and hydroxide lamella. The green, red and white spheres correspond to the Mg, 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.

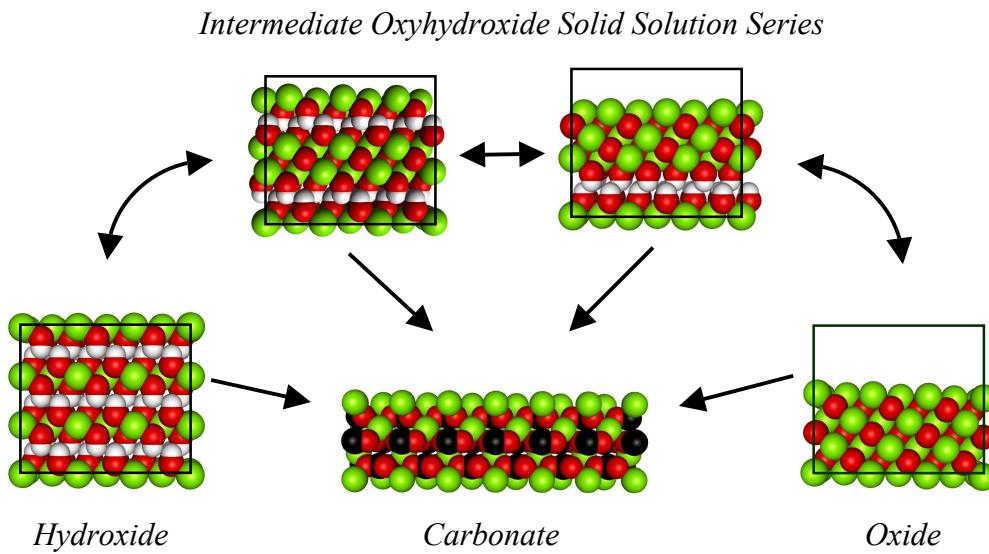


Figure 2. Possible $\text{Mg}(\text{OH})_2$ carbonation reaction pathways during dehydroxylation and/or rehydroxylation. The intermediate lamellar oxyhydroxide solid solution series, $\text{Mg}_{x+y}\text{O}_x(\text{OH})_{2y}$, is represented by nominal compositions of $\text{Mg}_3\text{O}(\text{OH})_4$ and $\text{Mg}_3\text{O}_2(\text{OH})_2$.⁶⁻⁸ 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).

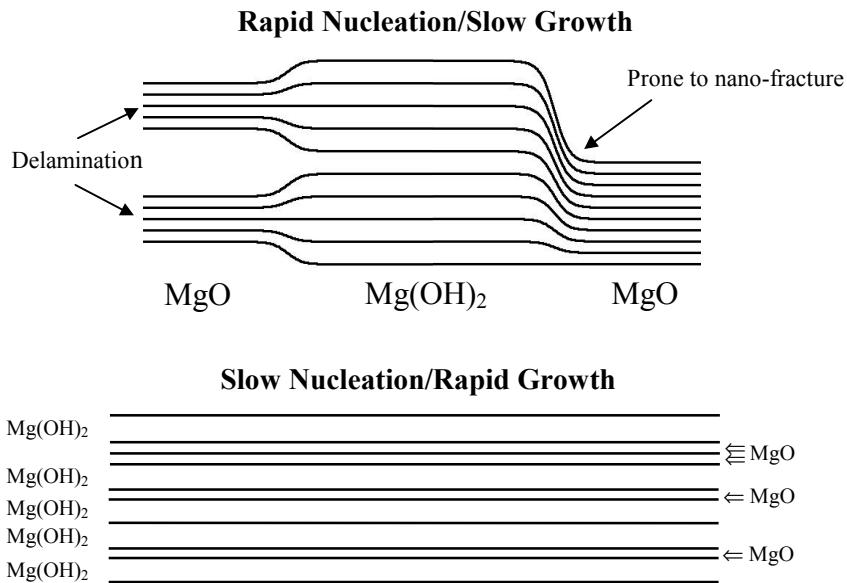


Figure 3. Models of relatively rapid nucleation/slow growth and slow nucleation/rapid growth lamellar nucleation and growth processes. The two-phase ($\text{Mg}(\text{OH})_2 + \text{MgO}$) and homogeneous lamellar oxyhydroxide character of these processes is consistent with previous low-magnification TEM SAD observations of $\text{Mg}(\text{OH})_2$ dehydroxylation.^{10,11}

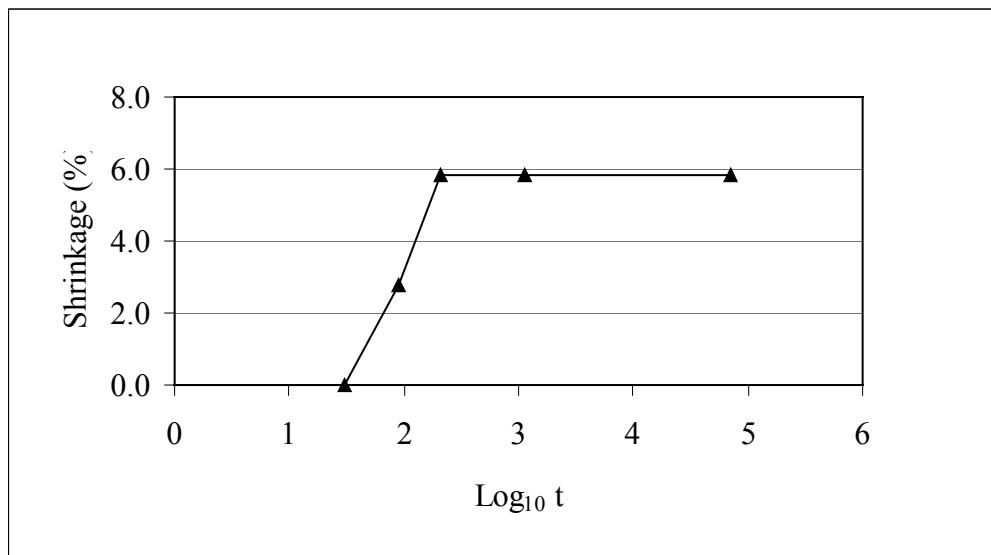


Figure 4. Macroscopic observations of in-plane, basal-plane shrinkage during the dehydroxylation of a brucite single crystal fragment. Dehydroxylation was carried out as a function of heating time (minutes) at 475°C in air. t is expressed in minutes.

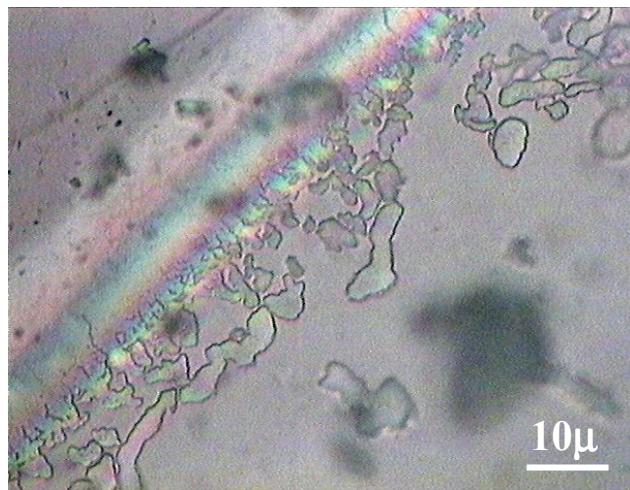


Figure 5. Optical micrograph showing blister formation during dehydroxylation for 1 min in air at 580°C. Optical axis is perpendicular to the basal plane layers.

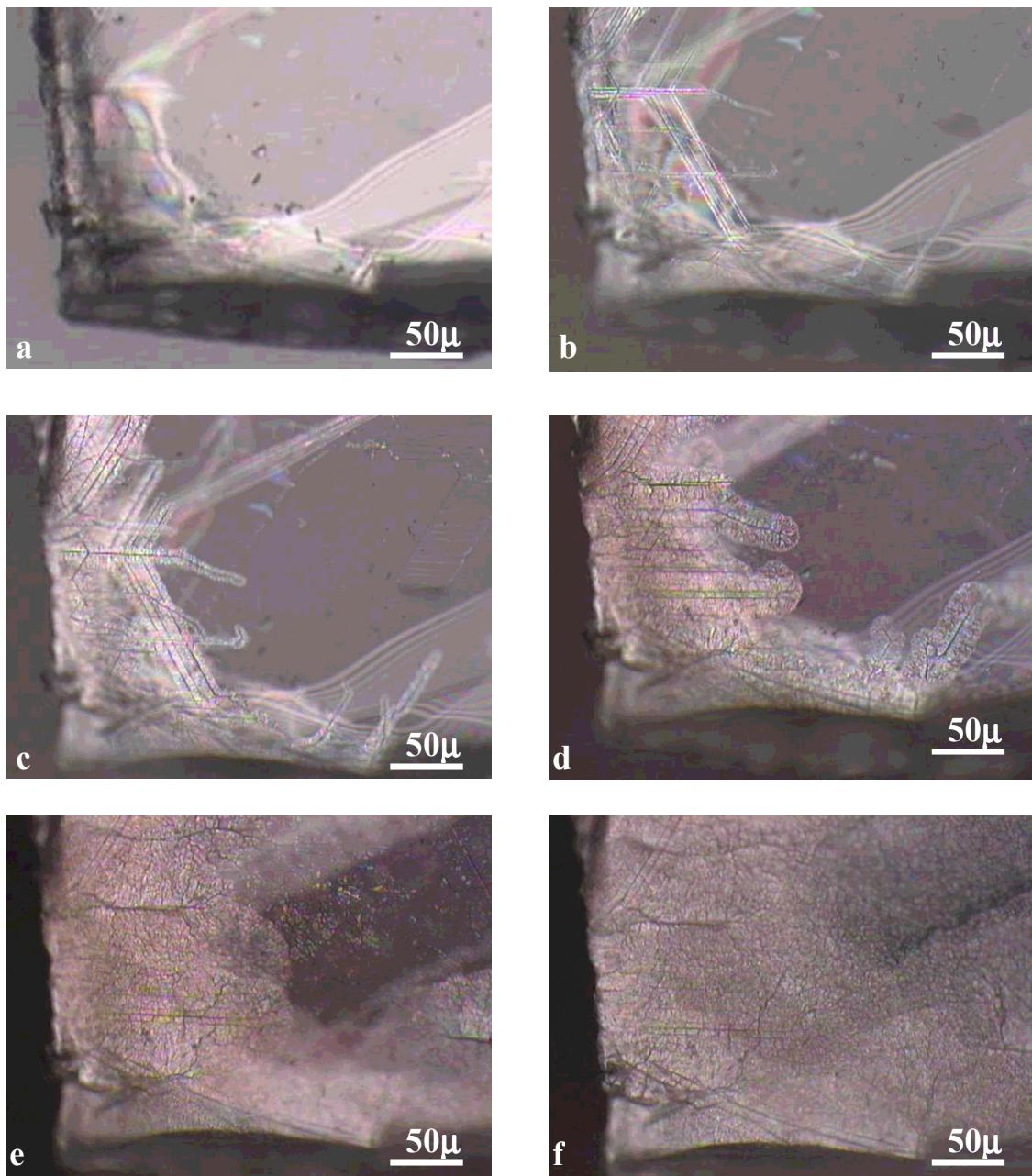


Figure 6. Lattice cracking observed perpendicular to the layers during $\text{Mg}(\text{OH})_2$ dehydroxylation in static air at 375 °C; a) freshly cleaved crystal fragment (strain fields indicate some delamination occurred due to cleaving); b-f) crack propagation observed after 1, 2, 6, 15, and 30 hours, respectively.

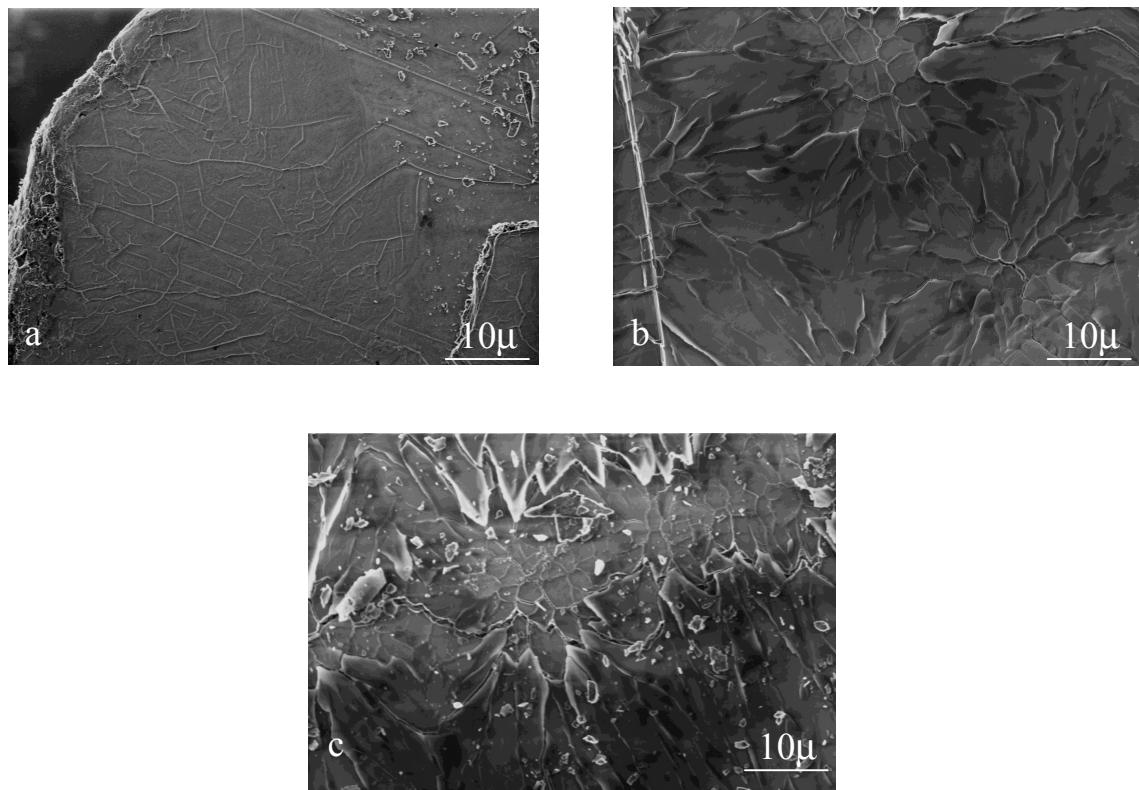


Figure 7. FESEM micrographs showing basal-plane crack nucleation/growth, including the formation of crack centers. The images were taken after heating in air for 5 min, as a function of temperature: (a) 380°C, (b) 480°C, and (c) 580°C.

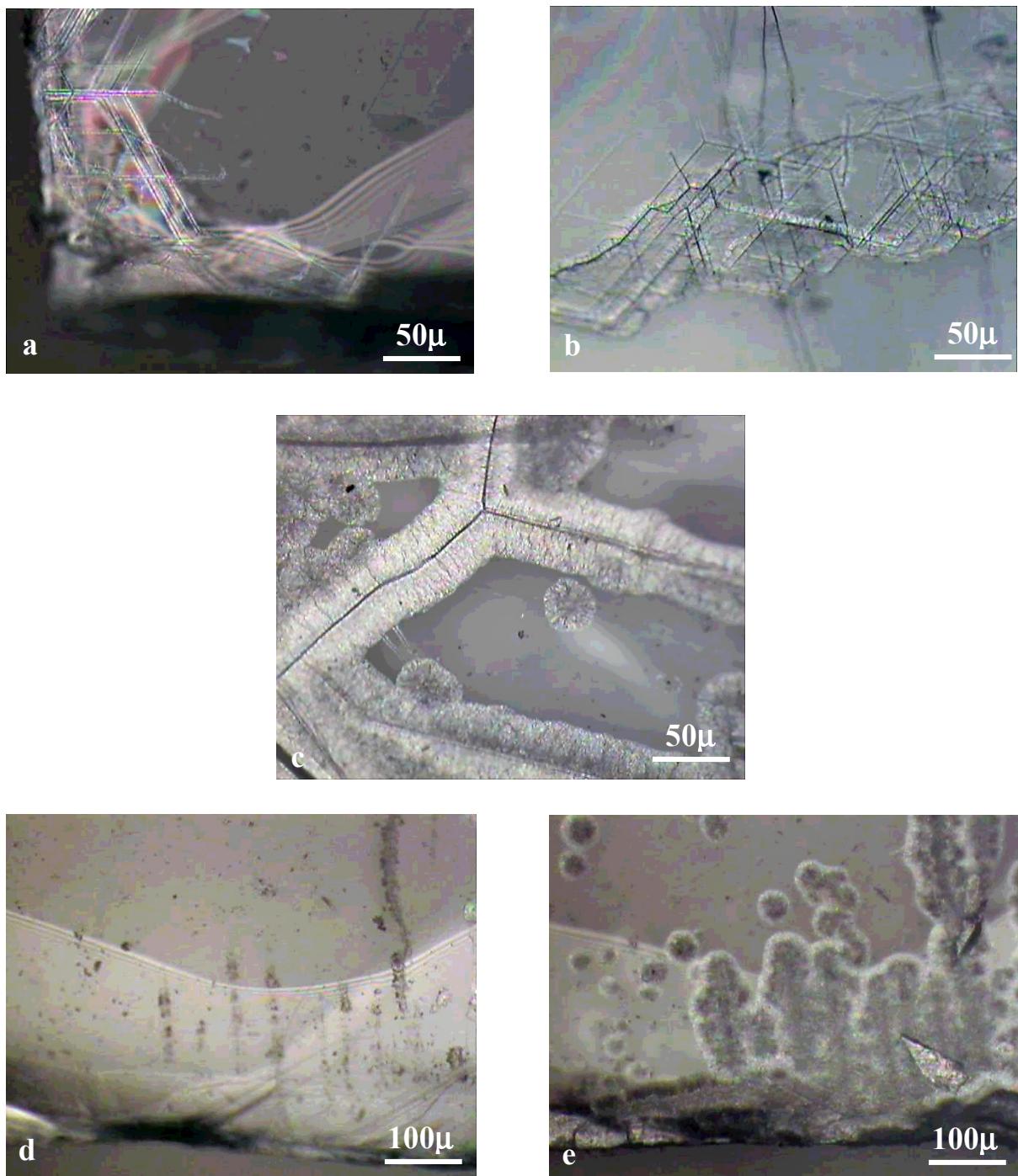


Figure 8. Optical micrographs viewed perpendicular to the brucite basal planes during dehydroxylation. Different nucleation locations for cracks during dehydroxylation (a) and (b) the onset of basal-plane cracking at 375 °C forming 120° crack angles at the crystal edge (a) and a basal plane step (b); (c) Primary and secondary cracking nucleated from the crystal edge together with crack center formation (after 2 minutes at 475°C); (d) surface defects on a freshly cleaved brucite basal plane prior to dehydroxylation onset; (e) onset of dehydroxylation with extensive crack center formation indicating basal plane crack centers often nucleate at defect sites (1 min at 475°C).

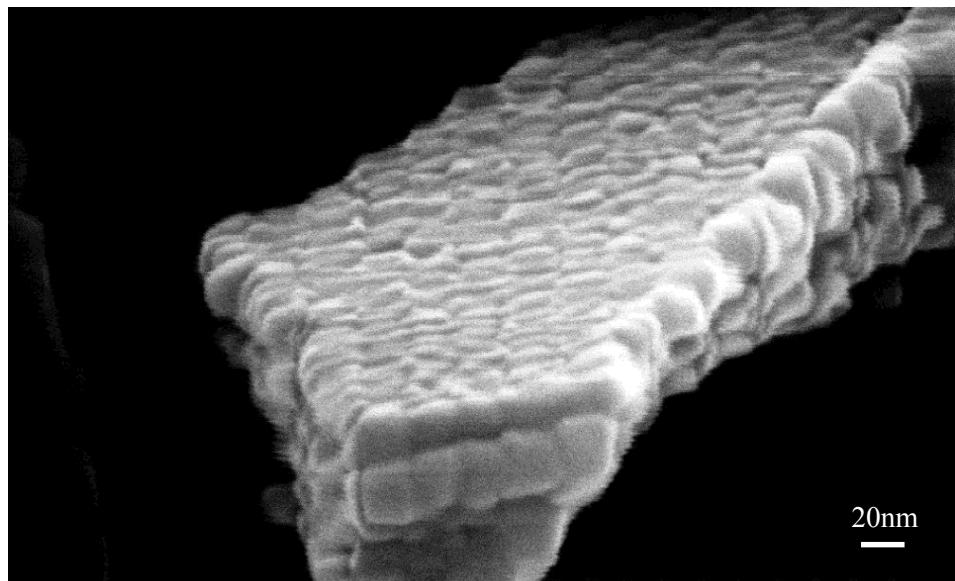


Figure 9. FESEM image of the intergrown MgO nanostructure formed via $\text{Mg}(\text{OH})_2$ dehydroxylation at 580°C for 2 hours. The sample is gold coated. The image was taken using a Hitachi S4700 FEG-SEM (at 25kV and a 12.5mm working distance).

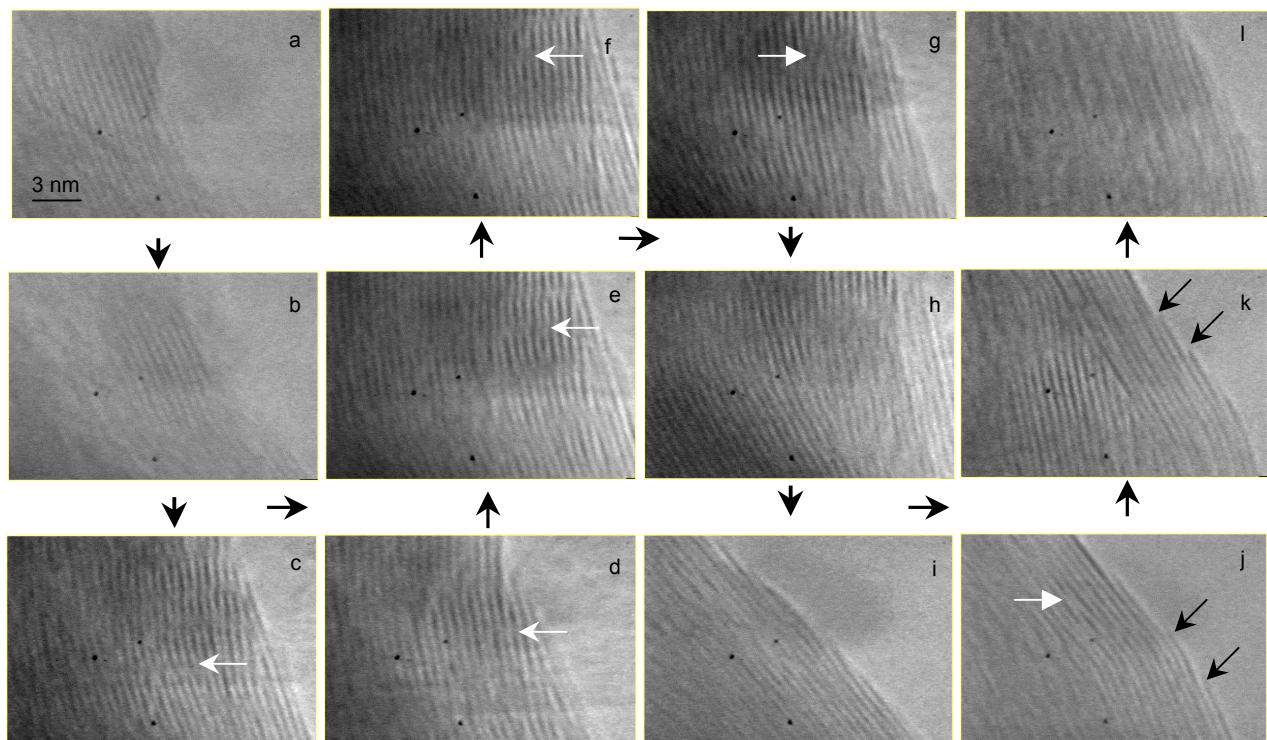


Figure 10. *In situ* HREM observations of rehydroxylation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment under ~ 1 torr H_2O (g). The $\text{Mg}(\text{OH})_2$ recrystallization process exhibits (1) the formation and annealing of defective $\text{Mg}(\text{OH})_2$ structures to form single crystal regions of $\text{Mg}(\text{OH})_2$ (the $\text{Mg}(\text{OH})_2$ crystallites formed in a and b, eventually grow together to form the defective region c), (2) rapid edge dislocation motion, parallel and perpendicular to the lamella (see white arrows), and (3) rapid layer by layer $\text{Mg}(\text{OH})_2$ crystal growth (e.g., black arrows in j and k show surface layer growth in less than a second) in this sequence.

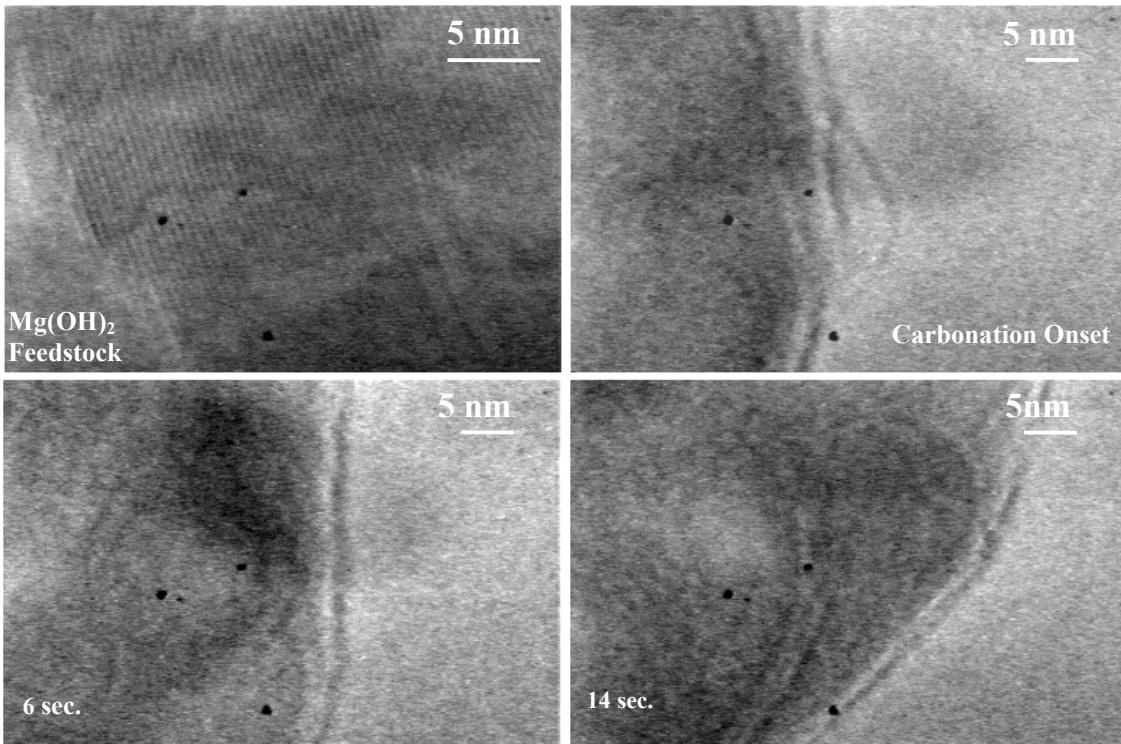


Figure 11. *In situ* E-cell DHRTEM observations of the ambient temperature rehydroxylation-carbonation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment under 400 mtorr $\text{CO}_2 + \text{H}_2\text{O}$; (a) the $\text{Mg}(\text{OH})_2$ feedstock viewed parallel to the layers prior to dehydroxylation under the microscope vacuum at 465 °C; (b) initial exposure of dehydroxylated $\text{Mg}(\text{OH})_2$ to $\text{CO}_2 + \text{H}_2\text{O(g)}$ initiates rehydroxylation-carbonation instantly; (c and d) rehydroxylation-carbonation continues rapidly, with the host matrix generally swelling as the reaction continues superimposed with intermittent breathing-like expansion/contraction behavior.

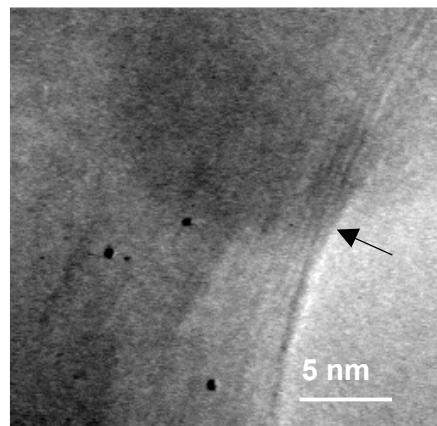


Figure 12. *In situ* E-cell DHRTEM observation of the ambient temperature rehydroxylation-carbonation process, showing the intermittent appearance and disappearance of $\text{Mg}(\text{OH})_2$ -like lamella during rehydroxylation-carbonation of an extensively dehydroxylated $\text{Mg}(\text{OH})_2$ fragment.

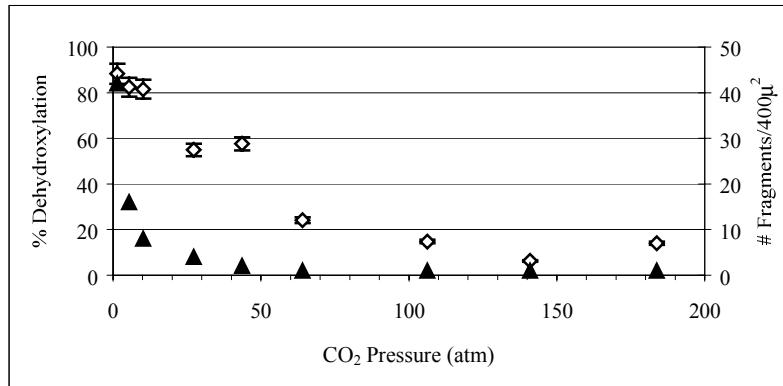


Figure 13. A comparison of the extent of $\text{Mg}(\text{OH})_2$ reaction matrix cracking (expressed as the number of fragments formed per $400 \mu\text{m}^2$ of the basal plane surface) with the extent of dehydroxylation during dehydroxylation-carbonation as a function of CO_2 pressure after 16hrs at 585°C . Below the critical pressure for MgCO_3 formation, ~ 53.7 atm CO_2 at 585°C , carbonation occurs on cooling to ambient temperature, once the temperature drops below the critical temperature for MgCO_3 formation at 53.7 atm. The solid triangles represent the fragment density, while the diamonds represent the extent of dehydroxylation.

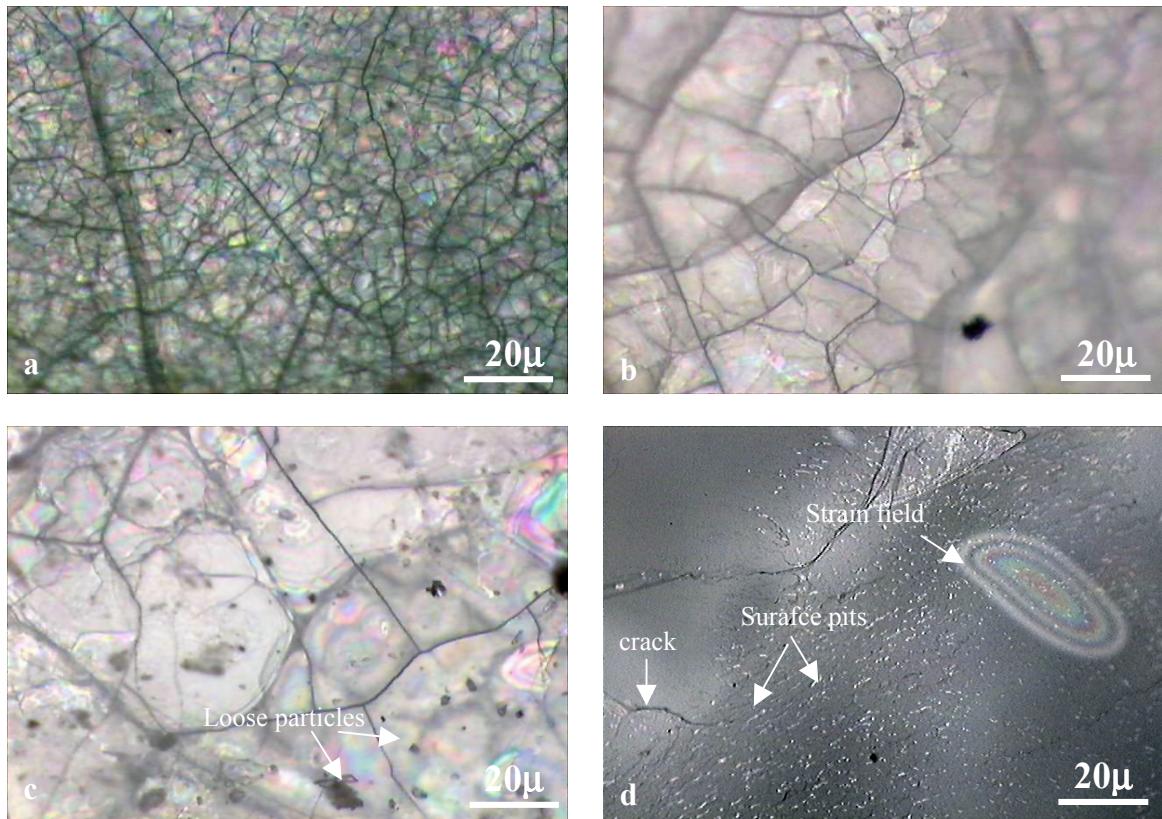


Figure 14. Cracking of the brucite single crystal surface for select samples in Figure 13. Samples a through d are for samples reacted at 1.4, 10.2, 43.6, and 183.7 atm. Note, the first three samples dehydroxylated at 585°C and carbonated on cooling to ambient temperature, while the fourth sample carbonated directly at 585°C .

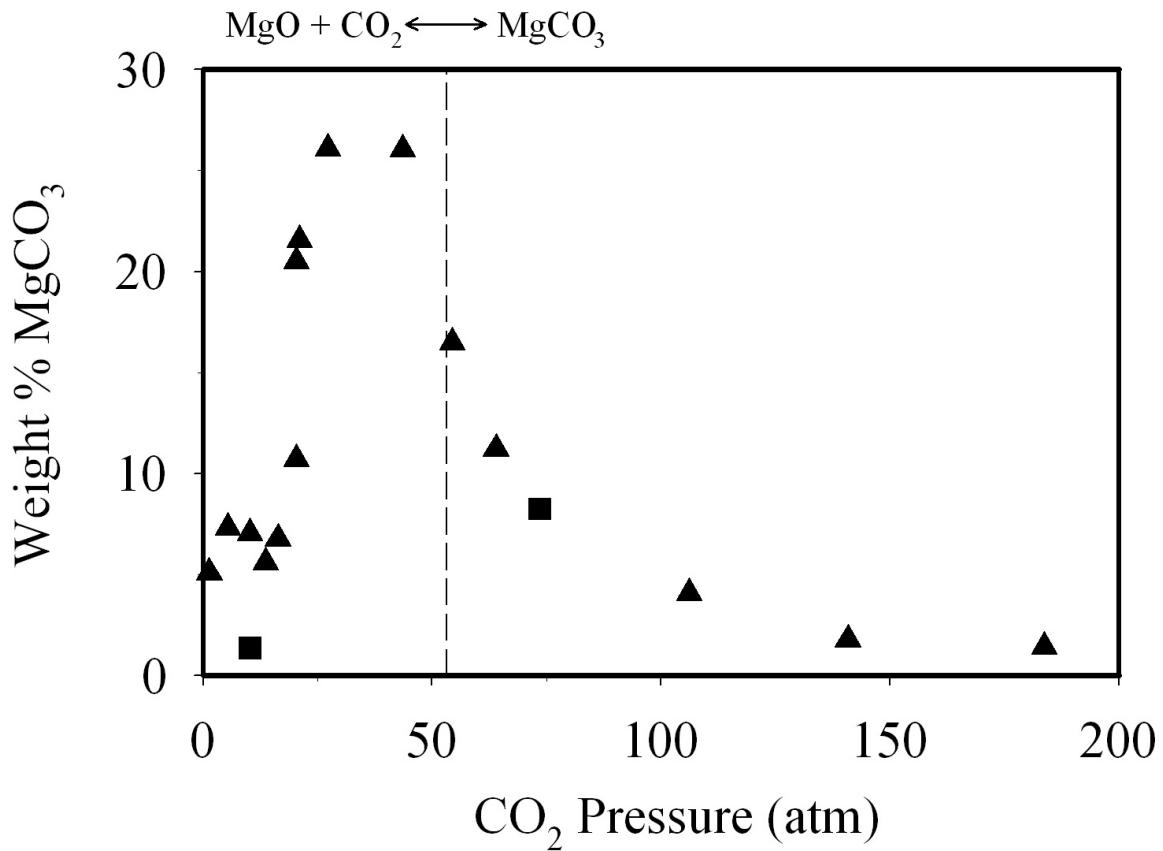


Figure 15. Wt % MgCO_3 formed vs. CO_2 pressure for similarly-sized Mg(OH)_2 single crystal fragments reacted at 585°C ($\pm 5^\circ\text{C}$) for 16 hours. Triangles represent reactions in which the autoclave was air-cooled (~30 min, while the sample was still under CO_2) to ambient temperature at the end of each run. Squares represent reactions in which the autoclave was water quenched, immediately followed by CO_2 evacuation at the end of each run. The critical carbon dioxide pressure for MgCO_3 formation at 585°C (~53.7 atm) is shown.^{8,9,14} The very low extent of carbonation observed for the sample quenched from below the critical carbon dioxide pressure confirms that carbonation occurs on cooling (or at ambient temperature) for samples reacted below the critical carbon dioxide pressure.

CONCLUSIONS

Mg(OH)_2 gas-phase carbonation reactivity is intimately associated with dehydroxylation/rehydroxylation processes. The extent of dehydroxylation is consistently observed to exceed the extent of carbonation for direct Mg(OH)_2 carbonation reactions, indicating that dehydroxylation and carbonation are separate but intimately interrelated reaction processes. Mg(OH)_2 dehydroxylation is a more complicated process than the simple two-phase process previously assumed and is best described as a lamellar nucleation and growth process that can lead to a solid solution series of lamellar oxyhydroxide intermediate materials with potentially enhanced carbonation reactivity, as shown in Figure 2. These intermediates may also form during rehydroxylation, providing similar new reaction pathways for rehydroxylation-carbonation. Relatively low-temperature dehydroxylation also induces a range of morphological changes that can serve to enhance carbonation reactivity, including translamellar cracking, delamination, and morphological reconstruction into nanostructured materials. Importantly, these phenomena can mitigate the ability of passivating carbonate layer formation to slow carbonation reaction rates.

The above mechanistic understanding leads to general approaches to enhance carbonation reaction rates. Highlights include, first, reaction rates for direct Mg(OH)_2 carbonation are optimized at CO_2 reaction pressures that just exceed the minimum pressure needed to stabilize MgCO_3 formation. Progressively higher reaction pressures increasingly inhibit dehydroxylation and carbonation by slowing H_2O diffusion away from and CO_2 diffusion to the reaction sites, respectively. Second, dramatically enhanced carbonation reactivity can be achieved via rehydroxylation-carbonation for low-temperature dehydroxylated Mg(OH)_2 , even at ambient temperature. We have observed this process at the atomic-level/nanoscale via DHRTEM and parallel energy loss spectroscopy for the first time. Advanced computational modeling corroborates that the ambient temperature carbonation process yields an amorphous carbonate containing material during rehydroxylation-carbonation. We have also observed the rehydroxylation of partially dehydroxylated Mg(OH)_2 via E-cell DHRTEM and found Mg(OH)_2 recrystallization exhibits rapid Mg diffusion, which likely contributes to the dramatic increase in carbonation reactivity observed during rehydroxylation-carbonation. As Mg(OH)_2 is a prototypical Mg-rich lamellar hydroxide based mineral, some of the above reaction mechanisms may also apply more generally (in whole or in part) to Mg-rich lamellar hydroxide based mineral (e.g., serpentine) dehydroxylation/rehydroxylation-carbonation reaction processes.

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ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Articles

- “Developing a Mechanistic Understanding of Lamellar Hydroxide Mineral Carbonation Reaction Processes to Reduce CO₂ Mineral Sequestration Process Cost,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Béarat, Renu Sharma, and R.W. Carpenter, *Proceedings of the First National Conference on Carbon Sequestration* (2001) 6C, 1-13.
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Conference Presentations

- “Atomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Bearat, Renu Sharma, and R.W. Carpenter, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, June 5-6, 2001.
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- Kenneth Streib, graduate (Ph.D.) student in the Science and Engineering of Materials Ph.D. Program, Arizona State University