UNDERSTANDING OLIVINE CO$_2$ MINERAL SEQUESTRATION MECHANISMS AT THE ATOMIC LEVEL: OPTIMIZING REACTION PROCESS DESIGN

Type of Report: Final

Reporting Period Start Date: September 20, 2001

Reporting Period End Date: May 19, 2003

Principal Authors: M.J. McKelvy,* H. Béarat, A.V.G. Chizmeshya, R. Nunez, and R.W. Carpenter.

Date Report Issued: August 2003

DOE Award Number: DE-FG26-01NT41282

Submitting Organization: Arizona State University
                               Center for Solid State Science and
                               Science and Engineering of Materials Graduate Program
                               Tempe, AZ 85287-1704
                               * Phone: (480) 965-4535; FAX: (480) 965-9004;
                               E-mail: mckelvy@asu.edu

DISCLAIMER

ABSTRACT

Carbonation of Mg-rich minerals offers an intriguing candidate carbon sequestration process technology, which can provide large-scale CO_2 disposal. Such disposal bypasses many long-term storage problems by (i) providing containment in the form of mineral carbonates that have proven stable over geological time, (ii) generating only environmentally benign materials, and (iii) essentially eliminating the need for continuous site monitoring. The primary challenge for viable process development is reducing process cost. This is the primary focus of the CO_2 Mineral Sequestration Working Group managed by Fossil Energy at DOE, which includes members from the Albany Research Center, Los Alamos National Laboratory, the National Energy Technology Laboratory, Penn State University, Science Applications International Corporation, and the University of Utah, as well as from our research group at Arizona State University.

Carbonation of the widely occurring mineral olivine (e.g., forsterite, Mg_2SiO_4) is a leading process candidate, which converts CO_2 into the mineral magnesite ($MgCO_3$). As olivine carbonation is exothermic, it offers intriguing low-cost potential. Recent studies at the Albany Research Center have found aqueous-solution carbonation is a promising approach. Cost-effectively enhancing carbonation reactivity is central to reducing process cost. Many of the mechanisms that impact reactivity occur at the solid/solution interface. Understanding these mechanisms is central to the ability to engineer new and modified processes to enhance carbonation reactivity and lower cost. Herein, we report the results of our UCR I project, which focused on exploring the reaction mechanisms that govern aqueous-solution olivine carbonation using model olivine feedstock materials. Carbonation was found to be a complex process associated with passivating silica layer formation, which includes the trapping of magnesite nanocrystals within the passivating silica layers, cracking and exfoliation of the layers, silica surface migration, olivine etch pit formation, transfer of the Mg and Fe in the olivine into the product carbonate, and the nucleation and growth of magnesite crystals on/in the silica/olivine reaction matrix. These phenomena occur in concert with the large solid volume changes that accompany the carbonation process, which can substantially impact carbonation reactivity. Passivating silica layer formation appears to play a major role in inhibiting carbonation reactivity. New approaches that can mitigate the effectiveness of passivating layer formation may offer intriguing potential to enhance carbonation reactivity and lower process cost.

TABLE OF CONTENTS

INTRODUCTION

Fossil fuels, especially coal, can support global energy demands for centuries to come, if the environmental problems associated with CO_2 emissions can be overcome. Mineralization of stationary-source CO_2 emissions as carbonates offers intriguing process potential, as the minerals that form are inherently environmentally benign and have proven stable over geological time.[1,2] The primary challenge remaining for CO_2 mineral sequestration is economically viable process development. Aqueous carbonation of widely available Mg-rich minerals, such as olivine, is a leading process candidate, which generates the stable, naturally occurring mineral magnesite ($MgCO_3$).[3,4] Enhancing the carbonation reaction rate and its degree of completion are key to developing an economically viable process. Many of the mechanisms that impact reactivity occur at the solid/solution interface. The objective of this project is to use advanced analytical techniques, to identify key reaction interface mechanisms that govern aqueous solution, mineral carbonation reaction kinetics. The project goal is to develop the necessary understanding to engineer enhanced carbonation materials/processes for CO_2 disposal. The majority of the progress made during this project is described in the attached article: "Investigations of the Mechanisms that Govern Carbon Dioxide Sequestration via Aqueous Olivine Mineral Carbonation," Hamdallah Béarat, Michael J. McKelvy, Andrew V.G. Chizmeshya, Ryan Nunez, and R.W. Carpenter, *Proc. 28th International Technical Conference on Coal Utilization & Fuel Systems* (2003) 307-318. The progress described therein is summarized along with a description of the results not discussed in the above publication below.

EXPERIMENTAL

Feedstock Characterization: A variety of olivine, $(Mg_xFe_{1-x})_2SiO_4$, materials from different sources were structurally and compositionally characterized (e.g., via X-ray powder diffraction, field-emission scanning electron and optical microscopy, and electron microprobe and particle induced X-ray emission elemental analysis) to identify model materials with high phase and compositional purity. Two olivine materials, which primarily differ in their iron content, from San Carlos, Arizona, were selected as the model materials for investigation. One is light green (LG), while the other is gray green (GG). Their elemental compositions were determined to be LG: $(Mg_{0.92}Fe_{0.08})_2SiO_4$ and GG: $(Mg_{0.83}Fe_{0.17})_2SiO_4$ by electron microprobe and particle induced X-ray emission analysis. Energy dispersive X-ray spectroscopy (EDS) was coupled with field-emission scanning electron microscopy to probe the olivine compositions at the microscale, as shown for the LG olivine in Figure 1. X-ray powder diffraction (XPD) was used to structurally characterize the starting materials. Both materials are phase pure, as seen in Figure 2. The lattice constants are in good agreement with those observed for olivine LG (a = 4.763 Å, b = 10.223 Å, c = 5.993 Å) and GG (a = 4.766 Å, b = 10.243 Å, c = 5.999 Å).[5,6] Each of the trace impurities observed for both materials were well below 1%, with Ca being the principle trace impurity. Single crystals, single crystal fragments, and, occasionally, polycrystalline materials were investigated. The studies described herein primarily focused on the LG olivine to facilitate comparison with the Twin Sisters olivine being investigated at the Albany Research Center (ARC), which has a similar composition, and maximize project impact.[3,4]
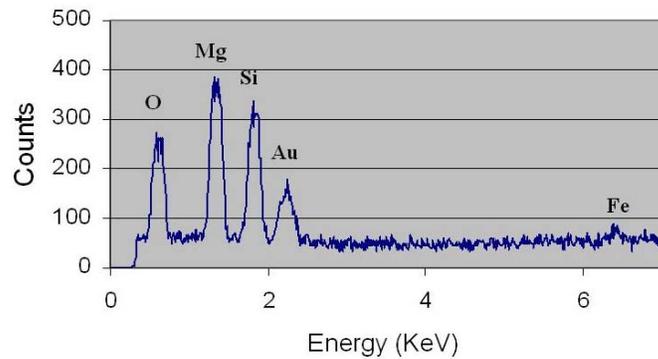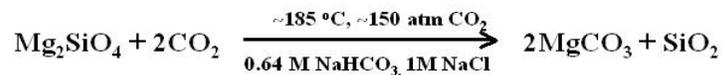
Figure 1. Typical energy dispersive X-ray spectrum for the LG olivine feedstock showing the low-level of Fe present. The gold peak results from gold coating the sample to minimize charging in the FESEM.
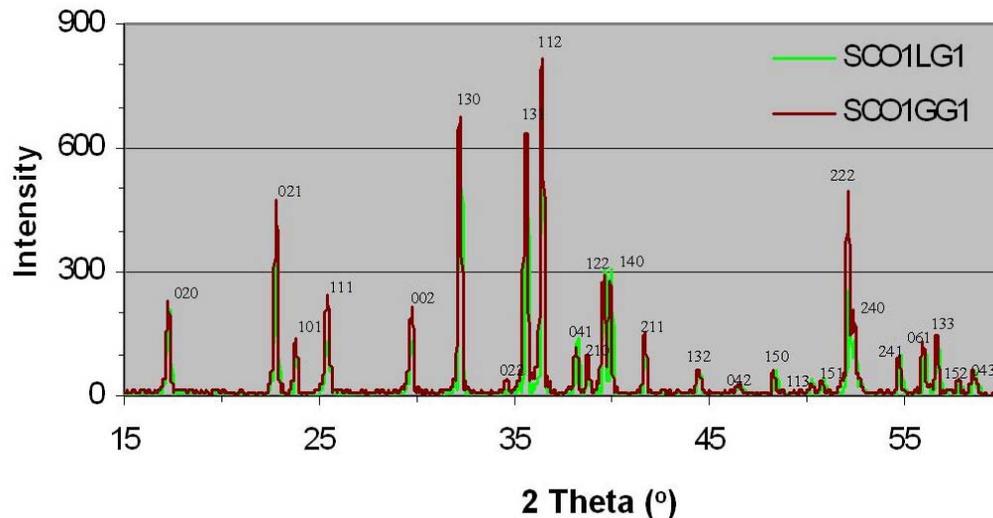
Figure 2. X-ray powder diffraction patterns for the model olivine feedstock materials. Both materials are from San Carlos, Arizona. The green pattern corresponds to the LG olivine (SCO1LG1) and the red-brown pattern to the GG olivine (SCO1GG1). The reflections are indexed as shown. Note the slight shift of gray green reflections to lower angles, consistent with the slight increase in cell parameters expected for higher Fe concentrations in olivine.

The reaction conditions employed are the same as those used in the ARC process, as summarized below for forsterite, to facilitate direct integration of the mechanistic studies herein with the

$$Mg_2SiO_4 + 2CO_2 \xrightarrow[\text{0.64 M NaHCO}_3, \text{1M NaCl}]{\sim 185\ ^\circ C,\ \sim 150\ \text{atm CO}_2} 2MgCO_3 + SiO_2$$

process development research being carried out at the ARC.[4] The reactions were carried out for a variety of particle sizes and reaction times to probe the intermediate reaction materials that form. Aggressive stirring was generally employed (1,000 to 2,000 rpm) to further replicate the actual ARC process. The carbonation feedstock typically contained equal amounts by weight of largely single crystal LG olivine fragments in the size ranges -37μ and 37 to 200 μ. Larger single

6

crystal fragments were occasionally reacted to investigate the intermediate materials that form over larger regions. Select samples for cross-section transmission electron microscopy analysis of the surface reaction interface region were subjected to carbonation reaction conditions identical to those above, but without stirring. These runs were employed to better preserve the reaction interface region by avoiding any mechanical surface abrasion that may occur during stirring. The mineral carbonation system employed was an Autoclave Engineers EZE-Seal Hastelloy C-276 reaction system. The system employs essentially the same design as the reactor being used at the Albany Research Center. The principle difference is the reaction volume. The ASU system incorporates a substantially smaller volume (100ml vs. 2 liters at the ARC), to better accommodate the smaller sample sizes used herein. Comparative carbonation runs in both systems using the same Twin Sisters olivine feedstock[7] gives essentially the same extent of carbonation (36 ± 3%), which indicates similar reaction conditions are present in both systems using the standard conditions above.

The partially carbonated reaction products were analyzed structurally, morphologically and analytically to probe the mechanisms that govern the mineral carbonation reaction process. X-ray powder diffraction patterns were obtained for the carbonation products using a Rigaku D/MAX-IIB X-ray diffractometer with $CuK\alpha$ radiation. Scans were taken over different 2θ ranges between 10º and 70º, with steps of 0.01º/s. Partially carbonated reaction products were imaged using a Hitachi 4700 field-emission scanning electron microscope (FESEM). Elemental analysis of individual reaction product particles was accomplished via energy dispersive X-ray spectroscopy (EDS) using a EDAX Phoenix system coupled with the Hitachi 4700. Cross-sectioned samples of the reaction interface were imaged by transmission electron microscopy, using a FEI CM200-FEG. The extent of carbonation and nature of the silica-rich by-product (e.g., is the silica formed primarily SiO_2 or is it partially hydroxylated) that forms during carbonation were assessed using a Perkin Elmer Series II CHNS Analyzer. Comparative standards gave total carbon and hydrogen accuracies of ± 0.3 wt%.

## RESULTS AND DISCUSSION

The objective of this IC1 project was to conduct the first high-resolution studies of solid/solution CO_2 mineral carbonation reaction processes to investigate the mechanisms that govern olivine carbonation reactivity. As many of the factors that impact olivine carbonation reactivity are found at the solid/solution reaction interface, these studies primarily focus on exploring the mechanisms that operate in the interface region. Single crystal and polycrystalline olivine were used as model materials for these exploratory studies.

During this project, we developed a miniature, but otherwise identical, version (100 ml reaction volume) of the ARC aqueous carbonation reactor (2 liter reaction volume).[3,4] Both systems yield essentially the same extents of carbonation and product materials for the standard ARC reaction conditions discussed above, facilitating direct comparison of the fundamental mechanistic studies carried out at ASU with the process development research conducted at the ARC.

Mechanistic Observations: Aqueous-solution olivine carbonation was discovered to be a complex process associated with passivating silica layer formation, cracking and exfoliation of the silica-rich passivating layers that form, silica migration, and nucleation and growth of magnesite crystals in the silica/olivine reaction matrix. In addition to the nucleation and growth of magnesite in the reaction matrix, substantial numbers of magnesite nanocrystals were discovered to form and apparently become entrapped in the passivating silica layers that form. It is important to note that these phenomena occur in concert with the large solid volume changes that accompany the carbonation process, which can substantially impact carbonation reactivity. For example, for Mg_2SiO_4 carbonation the product carbonate ($2MgCO_3$) expands to ~130% of the original feedstock volume, while the SiO_2 generated contracts to ~62% of the initial volume. This results in substantial expansive and compressive forces, which can disrupt the olivine reaction matrix, and, in particular, the silica-rich passivating layers that are observed to form during carbonation.

X-ray powder diffraction (XPD) indicates the only crystalline product that forms is magnesite, as shown in Figure 3. This suggests the silica-containing reaction products must be essentially amorphous in character. The cell parameters observed for the product magnesite are slightly
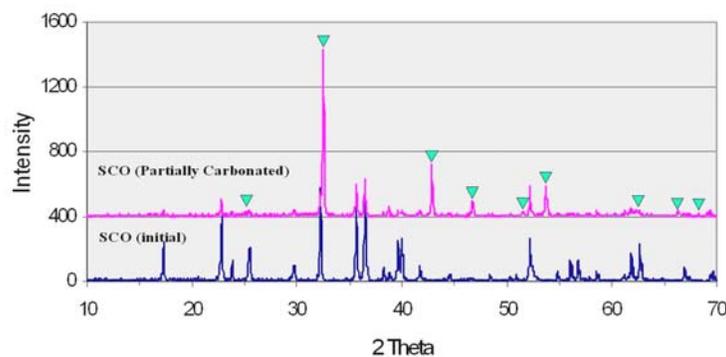
Figure 3. X-ray powder diffraction analysis showing the only crystalline product formed during olivine carbonation is magnesite. A slight increase in the cell parameters above those for $MgCO_3$ (i.e., a=4.63 and c=15.15Å) is generally observed suggesting some Fe is transferred from olivine to the product magnesite during the carbonation process. The major product magnesite peaks are identified by the green triangles.

greater than those observed for pure $MgCO_3$, suggesting that the magnesite may contain ~10% Fe substitution for Mg based on Vegard's Law.[8] As the original olivine feedstock material contains 8% Fe substitution for Mg, this level is consistent with both Mg and Fe being transferred into the product magnesite during the mineral carbonation process. Figure 4 shows an FESEM image and EDS analysis of the carbonation product materials. The products generally consist of crystals intergrown with an irregularly shaped product matrix. Energy dispersive X-ray spectroscopy (EDS) for Mg, Si, and O (up to 5 keV) shows the crystals exhibit the strong Mg and O signals expected for magnesite, while the irregularly shaped matrix materials that have formed

8
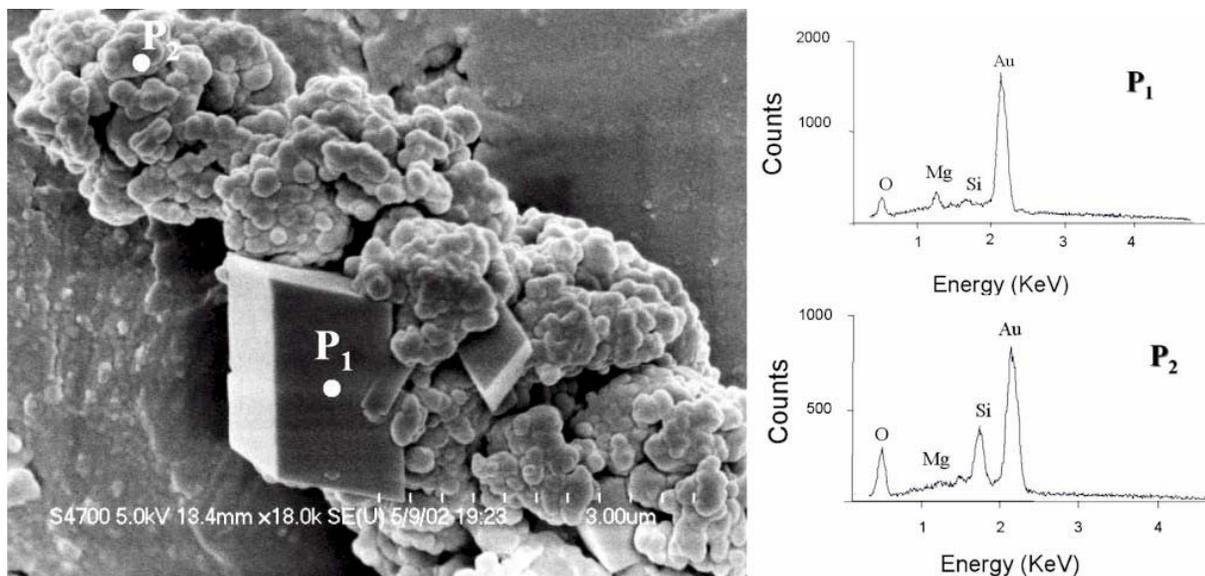
Figure 4. FESEM image and energy dispersive X-ray spectroscopy (EDS) of the olivine carbonation reaction products. A strong Mg and O signal is associated with the product crystals (P_1), whereas a strong Si and O signal is associated with the irregular habited product material (P_2). Note: due to the small size of the particles observed, there is a slight overlap of the EDS scattering volume between the irregularly shaped and crystalline particles. The gold peak observed is due to gold coating of the sample to minimize charging.

exhibit the strong Si and O signals expected for silica, consistent with reaction (1). Higher energy EDS analysis confirmed that Fe is carried into the magnesite during carbonation, leaving the product silica essentially Fe free. C and H elemental analysis of the reaction products shows they are H free within experimental error ($\pm$ 0.3 wt%), indicating the silica formed is primarily amorphous SiO_2. However, the analytical error associated with the low weight of H is relatively large, resulting in an assessment of the product silica as containing $\sim 90^+$ % silica. More accurate H analyses (e.g., via secondary ion mass spectrometry -SIMS) are required to ascertain if lower levels of H are incorporated in the silica-rich product material during the carbonation process. SIMS studies are currently underway as a follow-on to this project to further explore the level of H present. The goal is to provide additional insight into the role that proton exchange may play in Mg dissolution/carbonation.

In order to explore the intact olivine reaction surface that forms during carbonation, samples were prepared without stirring, but under otherwise identical reaction conditions. This approach was used to avoid potential particle-particle and particle-wall collisions that can damage and potentially abrade the olivine reaction surface. Figure 5 shows the passivating silica layers that form after one hour. Clearly, these layers can be very effective locally at reaction passivation (Figure 5b), as the reaction layer is only observed to penetrate $\sim$ 40nm into the olivine surface in an hour. However, the volume contraction associated with silica formation can also disrupt/crack the silica layer surface (Figure 5a) facilitating carbonation deeper into the olivine/silica reaction matrix. Such silica layer cracking is key for enhancing olivine carbonation reactivity as the passivating layer regions between the cracks (Figure 5b) can be very long lived.

9
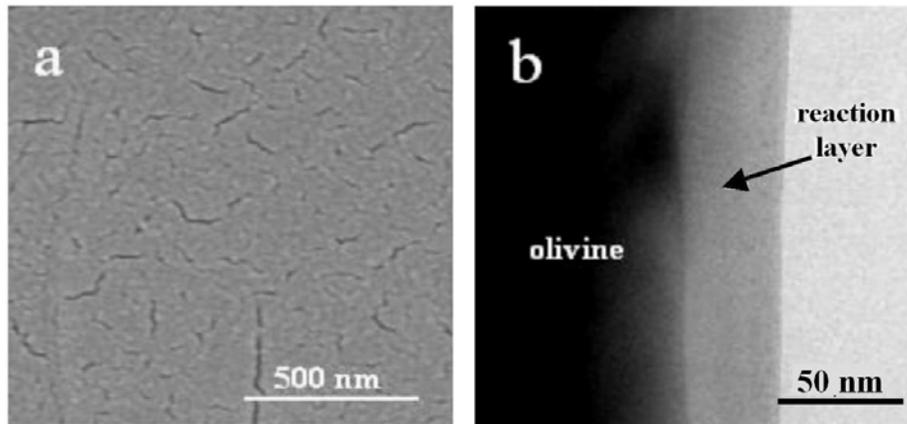
Figure 5. a) a FESEM image of passivating silica layer formation on a (001)-olivine single crystal surface during olivine carbonation. b) a cross-section HRTEM image of the same silica reaction layer in between the cracks induced by the layer contraction associated with silica formation. The silica reaction layers formed in between the cracks can be very slow growing, effectively passivating the carbonation process locally.
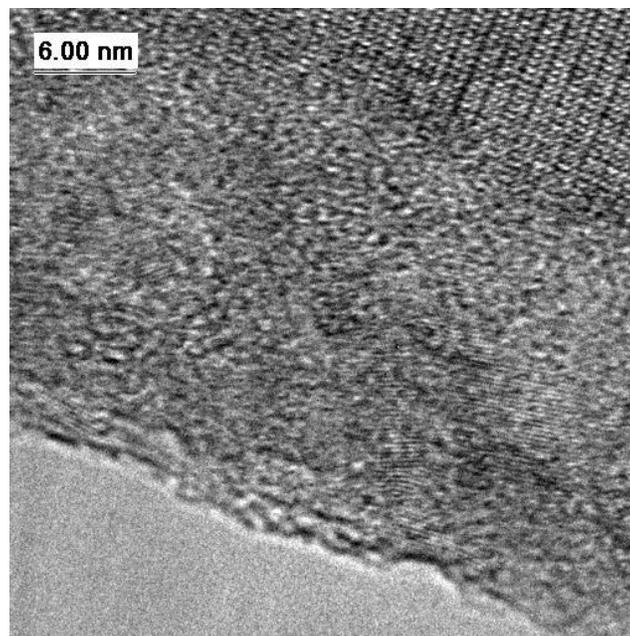

Figure 6. A cross-section HRTEM image showing the mineral carbonation reaction product layer that forms during unstirred carbonation on the (001) olivine surface. Note the intergrowth of several nanocrystals in the amorphous reaction surface layer (bottom). Combined imaging and EDS analysis of the region indicates that magnesium carbonate nanocrystals form and are trapped in the primarily amorphous silica reaction layer that forms on the (001) surface as the reaction progresses. The olivine host crystal is at the top of the image.

Figure 6 shows a high-resolution transmission electron microscope (HRTEM) image of a cross-section of the silica-rich passivating layer that slowly forms on the (001) olivine surface during carbonation. Single-crystal (001) olivine surfaces were initially prepared for reaction by orienting, cutting and polishing San Carlos olivine single crystals (8% Fe). The sample

containing the reaction product layer shown in Figure 6 was prepared by cross sectioning and thinning a partially reacted crystal. Careful structural examination and EDS analysis reveals multiple magnesite nanocrystals are trapped in the thin amorphous silica-rich passivating layer that forms during carbonation. Low-energy, cryogenic, argon ion-milled sample thinning and low-beam-dose sample observation under cryogenic temperatures were required to observe the magnesite nanocrystals under high resolution. Even then, some MgO nanocrystals were observed in the reaction layer due to $MgCO_3$ decomposition to $MgO + CO_2$ (g) during sample thinning and/or electron-beam observation. This follows from the high sensitivity of $MgCO_3$ to decomposition via electron and ion beam exposure,[9] as demonstrated for single crystal $MgCO_3$ reference materials herein, especially when the carbonate is in nanocrystalline form. These studies indicate the silica-rich passivating layers that form during carbonation can effectively trap magnesite nuclei that form during carbonation. If left intact, these layers can present a substantial barrier to carbonation.

The progression of the reaction interface during stirred (1,500 rpm) carbonation was further investigated via quenched, partially carbonated samples. Silica-rich layers were found to frequently envelope nearly entire olivine particles, for example see Figure 7a. Layer cracking was found to lead to exfoliation of layer fragments, leaving behind fracture surface morphologies that are reminiscent of broken glass (Figure 7b). As the passivating layers are abraded and the fragments exfoliate, fresh olivine is exposed, greatly enhancing local carbonation reactivity.
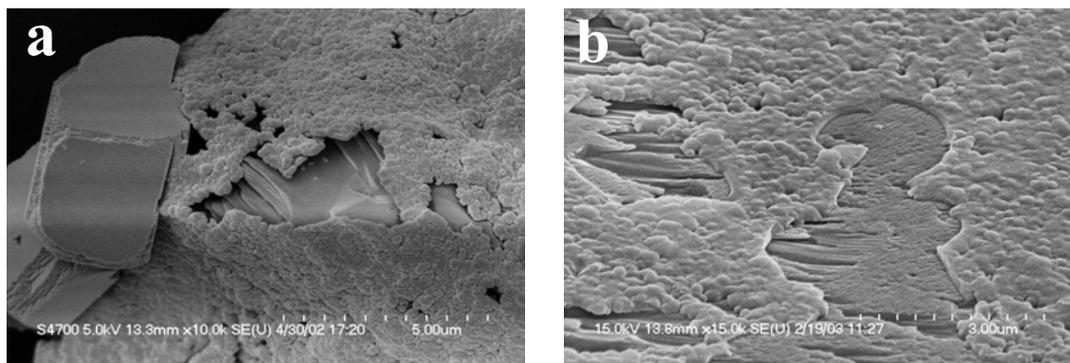
Figure 7. a) FESEM image of the silica-rich passivating layer enveloping an olivine particle during carbonation. Note the rounded outer corners of the intergrown magnesite crystal indicating the particle experienced substantial particle-particle/particle-wall abrasion during carbonation; b) fracture and exfoliation of passivating-layer fragments. Note the early-stage regrowth of a new passivating layer where a layer fragment previously exfoliated.

Figure 8 shows the typical inward reaction progression from the olivine surface that is found for stirred (1,500 rpm) carbonation. Importantly, the structural disruption that occurs in association with reaction layer formation is observed to further penetrate into the unreacted olivine region of the particle in the "structural interface" region in Figure 8. This suggests that the strain associated with reaction layer formation and the concurrent particle-particle and/or particle-wall collisions that occur during carbonation can combine to extend the structurally disrupted surface region into the unreacted olivine region of the particle. As the associated structural disruption penetrates into the unreacted olivine core, it can facilitate carbonation by bypassing any

passivating layers that have formed in the process. This underscores the key role that structural disruption plays in enhancing carbonation reactivity, especially given how effective silica-layer formation can be at passivating the carbonation reaction process.
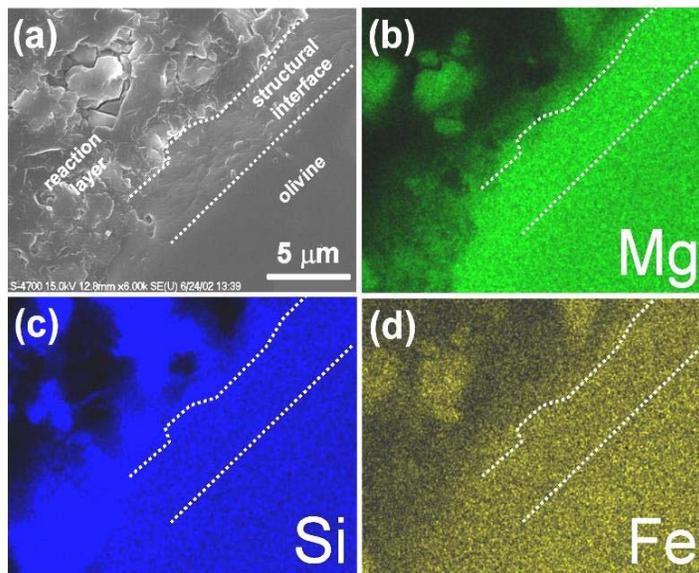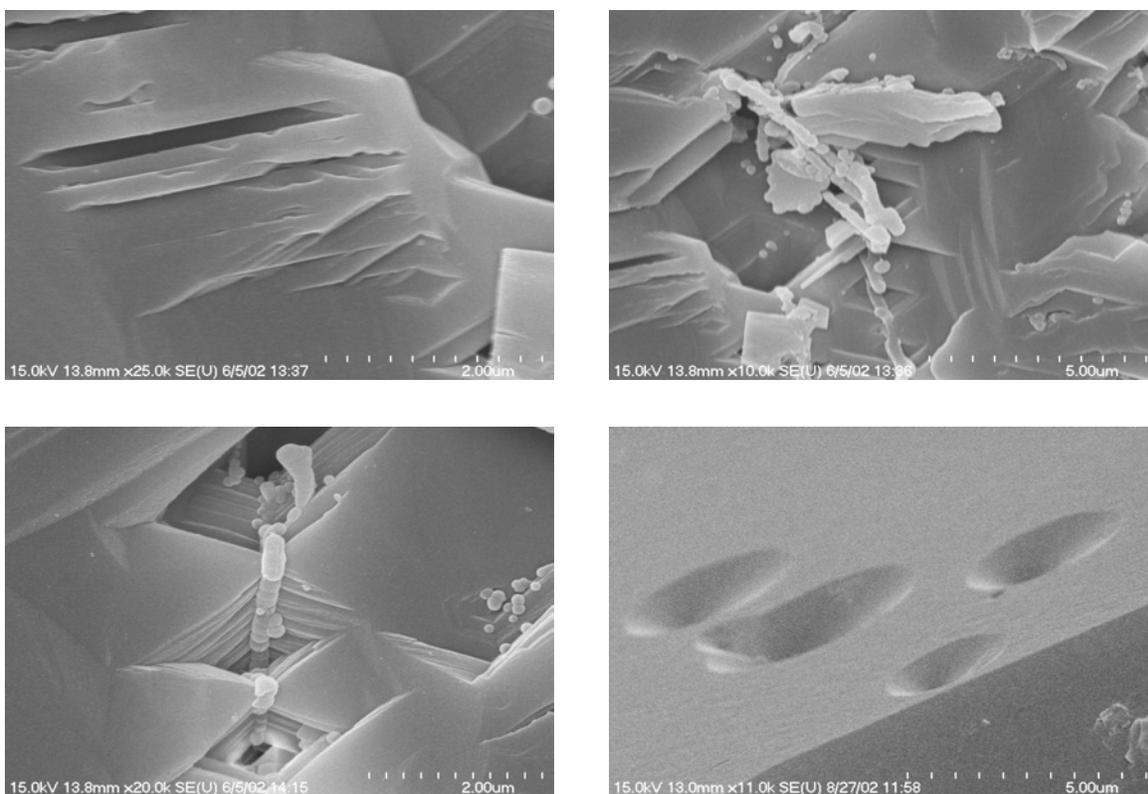

Figure 8. a) FESEM secondary electron image of a cross-section of a partially carbonated olivine single crystal showing the structural disruption that accompanies the mineral carbonation process as the reaction front penetrates to the crystal interior. The crystal surface is in the upper left corner. b-d) Mg, Si, and Fe EDS maps of the reaction interface cross section that indicate the chemical reaction has not yet penetrated into the structural interface region.

Intergrowth of silica and magnesite is clearly seen in the reaction layer via the Si and Mg EDS maps. The Mg and Fe maps also demonstrate a strong correlation between the Mg and Fe in the olivine feedstock and that found in the product magnesite. The silica-rich regions are largely Fe free, confirming Fe is transported into the magnesite with Mg. As magnesite nucleates and continues to grow in the reaction layer, its relatively large molar volume can effectively disrupt passivating silica layer formation, as discussed above, resulting in the commonly observed intergrown magnesite and silica reaction products shown in Figure 9.
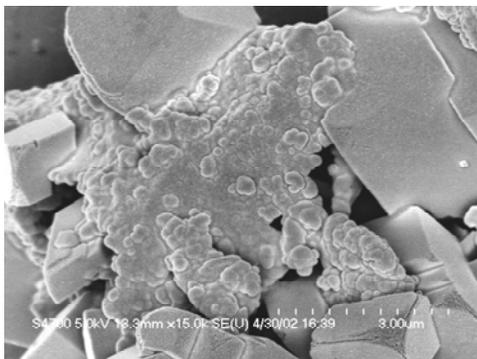

Figure 9. A FESEM secondary electron image of the intergrowth of magnesite and silica on the surface of the olivine reaction matrix. Note only the outer edges of the magnesite crystals are abraded, confirming the reaction matrix formed during *in situ* carbonation and not via particle settling after reaction completion.

Etch pits were occasionally observed to form on olivine surfaces during carbonation, as seen in Figure 10. These pits are likely associated with the presence of defect(s) in the original olivine crystal (e.g., dislocations, impurities, etc.), which can greatly enhance olivine dissolution in their vicinity. These observations suggest such defects offer the potential to dramatically enhance mineral carbonation locally, making low-cost means of inducing them of particular interest for enhancing carbonation reactivity. The typical etch-pit morphologies observed are shown in Figure 10. The pits observed were occasionally found in association with silica-rich reaction products, as observed in the lower left panel. That silica can be found in association with and inside such etch pits, indicates that silica can migrate during carbonation, as well as be associated with passivating layer formation. That most etch pits are not found in association with either silica-rich material or magnesite, further indicates that olivine dissolution can be substantially enhanced in the presence of such crystal defects.


Figure 10. FESEM secondary electron images of the etch pits that are observed to form during stirred single crystal olivine carbonation. Note the relatively deep etch pits in the lower left crystal surface. These pits are associated with irregular silica particles/particle chains within and near the pits, which indicates etch pit dissolution can be associated with silica migration as well as dissolution.

Magnesite crystals were occasionally observed to intergrow with the olivine/silica reaction matrix, as shown in Figure 11, suggesting that magnesite may be able to grow into, as well as away from, the matrix surface. Such a process may be associated with near surface CO_2(aq) diffusion into a growth zone at the base of the magnesite crystal and the relatively high concentration of CO_2(aq) present under reaction conditions (see attached).[10]
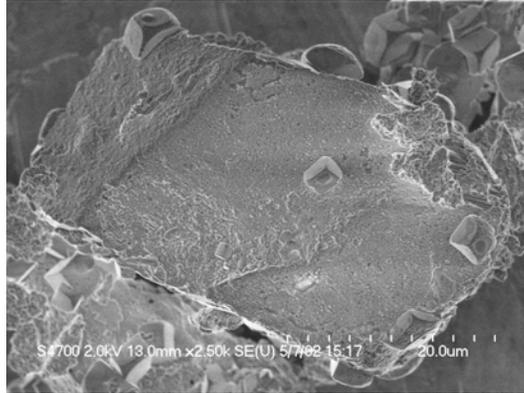
Figure 11. A FESEM image showing the intergrowth of magnesite crystals with the olivine/silica mineral carbonation reaction matrix. Note, in particular, the magnesite crystal in the upper left, which is clearly rooted in the olivine rich region of the reaction matrix, suggesting it was growing into, as well as away from, the olivine/silica reaction matrix surface during mineral carbonation.

Passivating layer formation can greatly inhibit carbonation, as seen in Figures 5 and 6. To explore the ability of particle-particle collisions to erode the passivating layers as they form and enhance reactivity, as suggested by Figure 7b above, we investigated the extent of carbonation observed as a function of the wt.% solids present in the reaction charge for typical ARC operating conditions (1,500 rpm; 180 ^{o}C; 2,200 psi CO_2; 1hr). Figure 12 shows the extent of carbonation exhibits a maximum near 15% and decreases for both decreasing and increasing solid concentrations. The decrease below 15% is likely associated with a decrease in particle-particle collisions/abrasion for decreasing particle concentrations. This is consistent with initial FESEM observations of a substantial decrease in the abrasive wear of the reaction products with decreasing particle concentrations below 15%. The abrupt drop in extent of carbonation above 15% appears to be associated with particle agglomeration, consistent with initial FESEM observations, which can shield much of the coalesced particles from abrasion. Incomplete particle dispersion at high particle concentrations may also reduce the extent of carbonation. This possibility will be the subject of a future investigation.
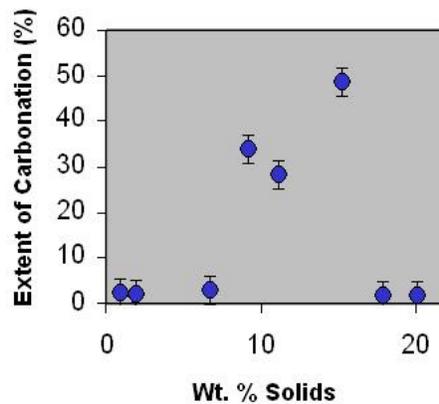
Figure 12. A plot of the extent of carbonation observed as a function of weight % solids during olivine mineral carbonation at 1,500 rpm (180 ^{o}C; 2,200 psi CO_2; 1hr). The error bars show the error associated with the product carbonate analysis.

CONCLUSIONS

The aqueous solution carbonation of olivine can be impacted by a variety of mechanisms at the solution/solid reaction interface. Overall, the process is quite complex, involving silica-rich passivating-layer formation, which can entrap magnesite nanocrystals during the formation process. These layers are prone to cracking, due to the large volume changes associated with carbonation, with the silica and magnesite formed having substantially lower and higher molar volumes than the host olivine, respectively. In particular, the silica regions can form under substantial stress, as their volumes decrease in comparison with olivine via the removal of magnesium. Although the presence of magnesite nanocrystals in the silica passivating layers can compensate for the reduction in volume associated with silica formation, the volume fraction observed herein was relatively small, consistent with an overall decrease in passivating layer volume and the layer cracking observed. The particle collisions (e.g., inter-particle and particle-wall) associated with stirred reactions can further enhance particle cracking. The passivating layers that form during stirred carbonation were also found to be prone to exfoliation, which can expose fresh olivine surfaces and enhance carbonation reactivity. Reaction interface regions have been observed to form during stirred carbonation with a structurally disrupted reaction front that precedes mineral carbonation penetration, further indicating the importance of olivine structural disruption in enhancing carbonation reactivity. Overall, passivating layer (e.g., silica) formation and reactant particle abrasion may play substantial roles hindering and enhancing carbonation reactivity, respectively. New approaches that mitigate the effectiveness of passivating layer formation may offer intriguing potential to enhance carbonation reactivity and lower process cost.

It is important to note the olivine feedstock particles investigated herein were largely small single crystals. The impact of passivating surface layer formation and particle abrasion on carbonation reactivity may differ substantially for olivine particles that contain significantly higher numbers of crystal defects. The observation of olivine etch pits with relatively high dissolution rates, which are likely associated with crystal defects, suggests such defected regions exhibit much higher carbonation reactivity. This is consistent with the strong increase carbonation reactivity that accompanies the introduction of high concentrations of structural defects via mechanical olivine activation, as observed by the ARC.[4] Other processes that were observed and can significantly contribute to olivine's carbonation reactivity include silica surface migration, which occurs in addition to passivating layer formation and dissolution, and transfer of the Mg and Fe in the olivine into the product carbonate.

REFERENCES

1) Seifritz, W. *Nature* 345, 486 (1990).
2) Lackner, K.; Wendt, C.; Butt, D.; Joyce Jr., E.; Sharp, D.; *Energy* 20, 1153-70 (1995).
3) O'Connor, W.; Dahlin, D.; Nilsen, D.; Walters, R.; Turner, P. *Proc. 25th Int. Tech. Conf. Coal Util. & Fuel Syst.* pp. 153-64 (2000).
4) O'Connor, W.K.; Dahlin, D.C.; Nilsen, D.N.; Gerdemann, S.J.; Rush, G.E.; Walters, R.P.; Turner, P.C. *Proc. 27th Int. Tech. Conf. Coal Util. & Fuel Syst.* pp. 819-30 (2002).
5) Ottonello, G.; Princivalle, F.; Della Giusta, A.; *Phys. Chem. Miner.* 17, 301 (1990).
6) Yu, S.C.; Proc. Nat. Sci. Counc. A. ROC, 21, 173 (1997).
7) Sample provided by D. Dahlin and W. O'Connor, Albany Research Center, Albany, Oregon.
8) Wells, A.F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press, Oxford, 1984; p. 1293.
9) Kim, M. G.; Dahmen, U.; Searcy, A. W. *J. Am. Ceram. Soc.* **1987**, *70*, 146.
10) Chizmeshya, Andrew V.G.; McKelvy, Michael J.; Wolf, George H.; Kocher, Michael; Gormley, Deirdre *Proc. 28th International Technical Conference on Coal Utilization & Fuel Systems* (2003) 319-330 (see attached).

APPENDIX I: ARTICLES AND PRESENTATIONS

Articles

- "Investigations of the Mechanisms that Govern Carbon Dioxide Sequestration via Aqueous Olivine Mineral Carbonation," Hamdallah Béarat, Michael J. McKelvy, Andrew V.G. Chizmeshya, Ryan Nunez, and R.W. Carpenter, *Proc. 28th International Technical Conference on Coal Utilization & Fuel Systems* (2003) 307-318 (see attached).

- "Quantum Simulation Studies of Olivine Mineral Carbonation," Andrew V.G. Chizmeshya, Michael J. McKelvy, George H. Wolf, Michael Kocher, and Deirdre Gormley, *Proc. 28th International Technical Conference on Coal Utilization & Fuel Systems* (2003) 319-330 (see attached). Note: due to a transcription error, this article inadvertently acknowledged DE-FG26-98FT40112; as in the attached copy, DE-FG26-01NT41282 should be acknowledged instead).

Conference Presentations

- "Understanding Olivine CO_2 Mineral Sequestration Mechanisms at the Atomic Level: Optimizing Reaction Process Design," M.J. McKelvy, R.W. Carpenter, H. Béarat, G. Wolf, and R. Sharma *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, June 4-5, 2002.

- "Developing an Atomic Level Understanding of Olivine Mineral Carbonation Mechanisms," Michael J. McKelvy, Andrew V.G. Chizmeshya, Hamdallah Béarat, Ryan Nunez, Michael Kocher, and R.W. Carpenter, an invited presentation at the at the Eighth Carbon Dioxide Mineral Sequestration Forum at the Albany Research Center, Albany, Oregon, September 10-11, 2002.

Conference Presentations Continued

- "Investigations of the Mechanisms that Govern Carbon Dioxide Sequestration via Aqueous Olivine Mineral Carbonation," Hamdallah Béarat, Michael J. McKelvy, Andrew V.G. Chizmeshya, Ryan Nunez, and R.W. Carpenter, presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, March 9-13, 2003.

- "Quantum Simulation Studies of Olivine Mineral Carbonation," Andrew V.G. Chizmeshya, Michael J. McKelvy, George H. Wolf, Michael Kocher, and Deirdre Gormley, presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, March 9-13, 2003.