

# ***In Situ* Mechanistic Observations of Serpentine Mineral Carbonation Reaction Processes: Facilitating the Engineering of Lower-cost Carbon Dioxide Sequestration Options**

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## **Introduction**

Unlike many other proposed CO<sub>2</sub> sequestration technologies that provide long-term storage, mineral carbonation instead disposes of CO<sub>2</sub> as environmentally benign and geologically stable mineral carbonates. Disposal bypasses many long-term storage problems, including the need to ensure permanent containment, avoid adverse environmental consequences, and provide continuous site monitoring. It substantially reduces the process cost by eliminating the ongoing costs associated with long-term storage. The primary goal for mineral carbonation is cost-competitive process development. Enhancing carbonation reaction rates is crucial to reducing cost. This is the primary focus of the CO<sub>2</sub> Mineral Sequestration Working Group managed by the U.S. Department of Energy's Office of Fossil Energy (DOE/Fossil Energy), which includes members from the Albany Research Center (ARC), Arizona State University (ASU), Los Alamos National Laboratory (LANL), National Energy Technology Laboratory (NETL), Penn State University, Science Applications International Corporation (SAIC), and the University of Utah.

Recently, the ARC made an exciting breakthrough, accelerating serpentine (e.g., lizardite, antigorite, and chrysotile) mineral carbonation, which naturally occurs in geologic time, to near completion in less than an hour via serpentine heat-activation [1]. Serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] carbonation is a particularly attractive sequestration technology candidate, because of serpentine's wide and low-cost availability [2, 3]. Mineral carbonation uses water/CO<sub>2</sub> fluid reaction media under relatively modest conditions (e.g., 155°C and 150 atm). Developing a fundamental understanding of the mechanisms that govern the mineral carbonation process is the key to further enhancing reaction rates and reducing the process cost. To further such understanding, we have developed the novel microreaction system shown in Fig. 1 to make the first *in situ* observations of the mineral carbonation reaction process described herein [4, 5].

## **Methods and Materials**

The microreaction system utilizes the recent development of moissanite as a high-pressure and

high-temperature window to enable *in situ* materials/process investigations [6]. The system, shown in Fig. 1, is suitable for a variety of x-ray synchrotron, visual, and spectroscopic investigations. It offers the ability to investigate both fluid-fluid and fluid-solid processes with pressure and temperature control from ambient conditions to 200 atm and 250°C. The windows are transparent to x-ray radiation at energies above 25 keV [6], facilitating x-ray synchrotron investigation. The core of the microreaction system, the microreactor, is attached to an external high-pressure CO<sub>2</sub> supply that provides pressure monitoring and control throughout the mineral carbonation process. Manual or programmed temperature control is provided through an external heating system that incorporates a thermocouple located very close to the sample in a thermocouple well in the microreactor core. Importantly, the combination of external pressure and temperature control also provides reactant activity control throughout the reaction processes under investigation. The relatively large reaction volume (~0.1 cm<sup>3</sup>) in comparison with diamond anvil cell technology allows microscopic observation of both the fluid-fluid and fluid-solid reaction regions, as shown in Fig. 1(d) [5].

Two serpentine samples collected from Globe, Arizona — lizardite and lizardite containing minor chrysotile inclusions — were used to generate the heat-activated meta-serpentine materials investigated. A series of meta-serpentine materials was generated for each feedstock material for heat activation temperatures ranging from 550° to 800°C. Samples were activated by heating at 2°C per minute under helium during combined thermogravimetric and differential thermal analysis and quenching from a select set of activation temperatures. With increasing activation temperature, the meta-serpentine materials generated a range — from well-crystallized serpentine materials exhibiting only minor dehydroxylation, to poorly ordered materials exhibiting extensive dehydroxylation (as seen in Fig. 2), to materials that are almost completely dehydroxylated (in which forsterite/enstatite have begun to nucleate and grow from the disordered meta-serpentine).

Meta-serpentine samples were loaded into the sample holder in the microreactor cell (Fig. 1). The cell was then

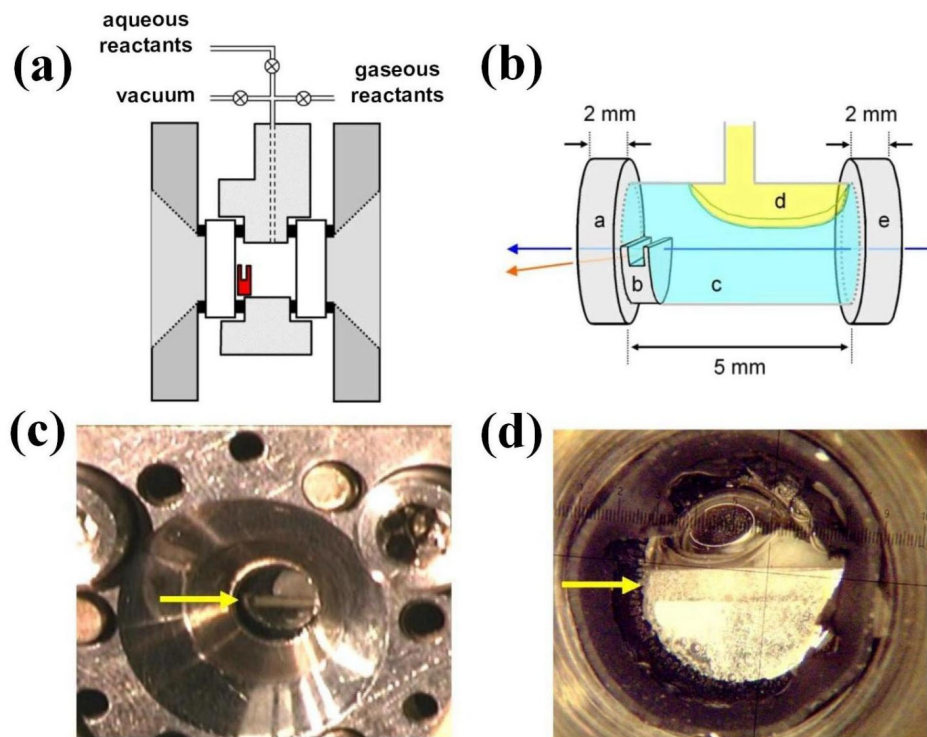


FIG. 1. A schematic diagram and photographs of the microreaction system. (a) Side view of the microreactor assembly: gaskets (black), moissanite windows (white), reactor core (light grey), reactor frame (dark grey), and moissanite sample holder (red). (b) Schematic of the sample chamber dimensions, configuration, and components including exit window, a; sample holder, b;  $\text{H}_2\text{O}$ -rich fluid, c;  $\text{CO}_2$ -rich fluid, d; and entrance window, e. The incident and scattered x-ray beams are drawn as blue and orange lines, respectively. (c) Photograph of the empty microreactor viewed from the exit window (detector side), in which the location of the sample trough (yellow arrow) can be seen in relation to exit window. (d) Close-up photograph of the microreactor exit window shown after sample loading, evacuation, injection of the aqueous reaction solution, and carbon dioxide pressurization. The yellow arrow indicates the sample trough. The  $\text{CO}_2$ -rich fluid phase can be clearly seen as a bubble above the sample trough. Figure was taken from Ref. 5.

sealed. The residual air was removed by evacuating to  $10^{-3}$  torr. The cell was then injected with just enough solution (0.64 M  $\text{NaHCO}_3$  + 1.0 M  $\text{NaCl}$ ) to immerse the sample (~60% full) and reproduce the ARC's reaction process conditions as closely as possible [1]. The cell was then pressurized to 150 atm  $\text{CO}_2$ , inducing strong mixing of the aqueous and  $\text{CO}_2$ -rich fluid phases. After time was allowed for equilibration, the microreactor was slowly heated. The ensuing reaction process was monitored via *in situ* synchrotron x-ray diffraction at GSECARS beamline 13-BM.

## Results and Discussion

The new microreaction system we designed and developed to provide full temperature and  $\text{CO}_2$  pressure control over the pressure and temperature range of interest for mineral carbonation (from ambient conditions to  $185^\circ\text{C}$  and 160 atm  $\text{CO}_2$ ) performed very well. We have continued to improve system performance, including

(1) enhancing its signal-to-noise ratio threefold by modifying the window and sample holder assemblies and (2) extending its temperature and pressure range to  $250^\circ\text{C}$  and 200 atm. The microreactor has generated substantial interest. As a result, we have submitted a Patent Cooperation Treat (PCT) patent application, which includes further improvements made in 2003, and are pursuing both U.S. and foreign patent rights accordingly [4].

By utilizing beamline 13-BM, we successfully made the first *in situ* observations of  $\text{CO}_2$  sequestration via mineral carbonation [5]. Our initial studies focused on the optimal ARC process to date, in which the 0.64 M  $\text{NaHCO}_3$  + 1.0 M  $\text{NaCl}$  aqueous solution reacts with the heat-activated meta-serpentine feedstock under supercritical  $\text{CO}_2$  at moderate temperatures and pressures (e.g., 150 atm  $\text{CO}_2$  and  $180^\circ\text{C}$ ) [1]. Lowering the reaction temperature and pressure while maintaining carbonation reactivity offers an intriguing potential for reducing the

process cost. Hence, the range of temperatures and pressures from ambient to the current reaction conditions are of particular interest. Two fluids are present under these conditions: CO<sub>2</sub>-rich and aqueous-rich. The meta-serpentine reactant is immersed in the more reactive aqueous-rich phase, while fluid-fluid contact is maintained with the CO<sub>2</sub>-rich phase to facilitate CO<sub>2</sub> transport and mimic mineral carbonation process conditions, as seen in Fig. 1(d).

Fig. 2 shows the reaction products observed for the poorly ordered meta-serpentine generated via 640°C heat activation of lizardite containing minor chrysotile inclusions. The reaction temperature was gradually raised under 150 atm CO<sub>2</sub> until carbonation was observed at 150°C, as seen in Fig. 2. Further heating to 180°C enhanced the extent of carbonation. All of the diffraction lines observed correspond to magnesite, indicating (1) magnesite forms directly without observable intermediate formation and (2) the silica-like products that form possess an amorphous structure. In experiments using the meta-serpentine materials generated from

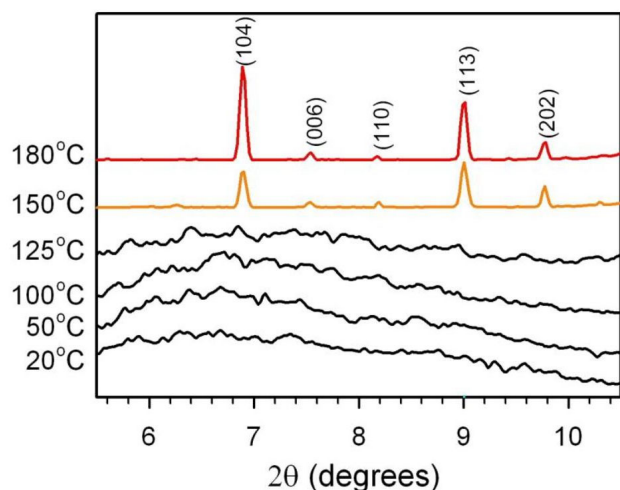


FIG. 2. Sequence of x-ray diffraction patterns observed as a function of temperature for the in situ mineral carbonation of meta-serpentine under 150 atm CO<sub>2</sub>. Little change is observed until the reaction onset at 150°C, when the (104), (006), (110), (113), and (202) magnesite reflections are observed to form (yellowish orange curve) at 2.75, 2.51, 2.31, 2.10, 1.93 Å, respectively. Heating to 180°C resulted in further carbonation and confirmed the stability of the magnesite formed (orangish red). The lower temperature spectra (black curves) are all 5-minute scans while the 150°C and 180°C spectra were obtained over 20 minutes. The latter intensities were normalized for the purpose of comparison. Each scan was taken under isothermal conditions ( $\pm 1^\circ\text{C}$ ) by using an x-ray wavelength of 0.3311 Å. Figure was taken from Ref. 5.

lizardite, we have observed mineral carbonation onset temperatures as low as 100°C for the most carbonation-reactive meta-serpentine materials studied to date. By comparison, unactivated lizardite did not react up to 185°C and 160 atm CO<sub>2</sub>.

The most reactive meta-serpentine materials discovered are being extensively investigated by using a battery of high-resolution analytical techniques, together with advanced computational modeling, in order to better identify the characteristics that are most effective in enhancing carbonation reactivity. In particular, the extent of structural disorder present in the meta-serpentine appears to be strongly correlated with enhanced carbonation reactivity.

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