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Silicate Carbonation in Supercritical CO₂ Containing Dissolved H₂O: An *in situ* High Pressure X-Ray Diffraction and Infrared Spectroscopy Study

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Abstract

Technological advances have been significant in recent years for managing environmentally harmful emissions (mostly CO₂) resulting from combustion of fossil fuels. Deep underground geologic formations are viewed as reasonable options for long-term storage of CO₂, but mechanisms controlling the stability of rocks and minerals in contact with injected supercritical fluids containing water are relatively unknown. In this paper, we discuss mineral transformation reactions occurring between supercritical CO₂ containing water and the silicate minerals forsterite (Mg₂SiO₄), wollastonite (CaSiO₃), and enstatite (MgSiO₃). We utilized newly developed *in situ* high pressure x-ray diffraction (HXRDX) and *in situ* infrared (IR) spectroscopic capabilities to examine the mineral transformation reactions. Forsterite and enstatite were selected as they are important minerals present in igneous and mafic rocks. Wollastonite, classified as a pyroxenoid (similar to a pyroxene), was chosen as a suitably fast-reacting proxy for examining silicate carbonation processes. The experiments were conducted under modest pressures (90 to 160 bar), temperatures between 35° to 70° C, and varying concentrations of water dissolved in the scCO₂. Under these conditions, scCO₂ contains up to 3,500 ppm dissolved water. Forsterite carbonation products identified by *in situ* HXRDX included nesquehonite and magnesite. Wollastonite produced calcite and no detectable crystalline hydrated carbonates. In contrast, enstatite was the least reactive, based on *in situ* HXRDX data that contained no detectable crystalline carbonation. Based on *in situ* IR spectroscopic measurements, mineral surface hydration processes are critical for these reactions. Thicker water films were associated with forsterite and wollastonite compared to enstatite. Carbonation was evidenced by the appearance and growth of asymmetric C-O stretching bands of carbonate precipitates (1400 to 1550 cm⁻¹), and carbonation extents were correlated to water-film thicknesses. Overall, these fundamental studies are beginning to illustrate processes controlling carbonation rates and potentials of silicate minerals.

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1. Introduction

Understanding chemical reactions between supercritical CO₂ (scCO₂), native pore fluids, and rocks is a challenging aspect of predicting caprock integrity and overall reservoir permanence for geologic carbon sequestration (GCS). Caprock failure due to leakage along faults or fractures depends in part on possible mineral transformations and their gradual effects on capillarity and permeability. The vast majority of previous research has focused on mineral dissolution and precipitation reactions in aqueous solutions equilibrated with CO₂ from a co-existing scCO₂ phase. However, the partner water-bearing scCO₂ phase is also highly reactive and capable of causing either mineral carbonation or mineral dehydration that would impact seal performance. Additionally, mineral carbonation by reaction with wet scCO₂ remains unaccounted for in numerical simulations of geologically stored scCO₂. In this paper, we present experimental results from a unique suite of *in situ* probes that elucidate the role of water and demonstrate water-concentration thresholds for catalyzing mineralization.

2. Experimental Section

Synthetic forsterite used in this study, previously described by Schaefer et al. [1], has a surface area of 31.3 m²/g and is pure Mg₂SiO₄. Naturally occurring wollastonite (CaSiO₃), obtained from NYCO Minerals Inc. (Willsboro, NY) and characterized by Miller et al. [2] contains a minor amount of aragonite (~1 wt%) and has a measured surface area of 2.1 m²/g. The *in situ* high-pressure XRD technique [3-5] utilizes a small amount of sample (2-20 mg) that is packed into a pocket, pressed by a glass slide, and then placed inside a high-pressure reactor constructed of beryllium. Analyses were conducted at 50 °C, and 90 bar on a D8 Discover XRD unit equipped with a copper rotating anode (1.54 Å), and a GADDS[®] area detector system positioned at 26.0 °2θ with a measured distance from the sample of 15 cm. Pressurized infrared spectroscopic (IR) experiments [6, 7] were conducted by circulating a thermostated stream of wet scCO₂ through a high-pressure flow cell containing a thin mineral overlayer coated on a ZnSe window. Spectra were measured with a Perkin Elmer Spectrum One FTIR spectrometer equipped with a DTGS detector and an air-cooled source. Each spectrum was an average of 128 scans that were recorded over the range 4000-700 cm⁻¹ with a resolution of 4 cm⁻¹.

3. Results and Discussion

We studied the rate and extent of carbonation of minerals important to currently scheduled pilot studies (FutureGen, Wallulla Basalt, and Carbfix) in wet scCO₂. These studies involve precisely controlled amounts of dissolved water in the scCO₂, geologically relevant pressure and temperatures (90 bar and 50° to 75° C), and time-dependent tracking of amorphous and crystalline carbonation products *in situ*. Carbonation products were found to be strongly dependent on the water concentration. For example, in the presence of excess water, carbonation is at a maximum when forsterite was reacted at 50 °C and 100 bar for 72 hours. As shown in Figure 1, only reflections corresponding to forsterite are visible immediately following pressurization (Time = 0). However, after a few hours of exposure, a set of reflections that correspond to a hydrated magnesium carbonate,

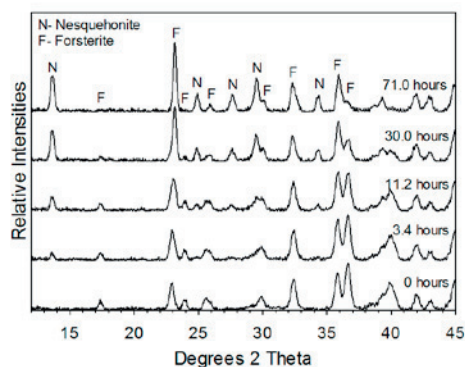


Figure 1 X-ray diffraction tracings of forsterite carbonation in the presence of water bearing scCO₂ (90 bar, 50°C).

nesquehonite, ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), begin to appear. These reflections increase in intensity with time (71 hours). Not obvious from these *in situ* patterns is the presence of magnesite (MgCO_3), which is obscured by the more intense forsterite reflection at $32.316^\circ 2\theta$ (primary reflection for magnesite is at $32.631^\circ 2\theta$). Pattern processing with Rietveld refinements indicated nearly 20 wt% magnesite compared to 50 wt% nesquehonite. Similar experiments conducted at 35°C for 7 days produced a larger percentage of magnesite [8]. There are only a few reports in the literature of magnesite precipitation at temperatures below 80°C . Decreases in water concentrations to below what is required to saturate scCO_2 significantly reduced carbonate formation and limited the reaction products to nesquehonite. When forsterite was reacted with scCO_2 at 82% and 67% water saturation, only ~18 wt% and ~6 wt%, respectively, of the forsterite was converted to nesquehonite.

In comparison, experiments with wollastonite indicate similar degrees of carbonation when the mineral was exposed to scCO_2 in contact with a free water phase. Likewise, decreasing concentrations of water in the scCO_2 to near 100% saturation produced ~40 wt% calcite. Reactions occurring in these water-rich fluids produce cores of unreacted wollastonite surrounded by a thin layer of amorphous silica in a matrix of calcite, as shown in the polished cross section of reacted grains (Figure 2). These images indicate passivating layers of silica are partially controlling the extent of carbonation observed under these experimental conditions. However, experiments conducted under limiting water conditions show a different mechanism restricting carbonation. As observed with *in situ* HXRD, carbonation rates were reduced to 5 wt% when the dissolved water concentrations were near 70% (70°C , 160 bar). Hence, there is a critical water threshold (CWT) that must be exceeded in order for the carbonation kinetics to be significant.

Reactions of silicate minerals with scCO_2 containing varying amounts of water were also examined by *in situ* IR spectroscopy. A distinct strength of this technique is the ability to probe mineral surface hydration processes. For example, interactions between the water dissolved in scCO_2 and the enstatite surface are illustrated in Figure 3. A liquid-like, nanometer-thick water film formed on the mineral surface, as indicated by a broad O-H stretching band around 3380 cm^{-1} and a peak at 1640 cm^{-1} , which is from a bending mode of liquid water that was not subtracted away when the dissolved water contribution to the spectra was removed. The peak around 1500 cm^{-1} is due to an asymmetric C-O stretching band of a carbonate precipitate. Another interesting aspect of the enstatite data is the negative-going absorbance between $1250 - 770\text{ cm}^{-1}$. Bands in this region are due primarily to Si-O stretches of the enstatite reactant. That these bands are negative-going is an indication that the enstatite has dissolved. Loring et al. [6] conducted a comprehensive series of *in situ* experiments to show the thickest films occur on forsterite grains exposed to scCO_2 containing the highest concentrations of water (i.e., fully saturated). In comparison, IR spectra reported by Miller et al. [9] also provided evidence of thin water films in the reaction of wollastonite with wet scCO_2 at 50°C and 90 bar. However, the growth of these films correlated with an increase in carbonate and amorphous SiO_2 reaction products, likely because these precipitates had a much higher surface area than the original wollastonite. Lower water concentrations in the scCO_2 resulted in lower

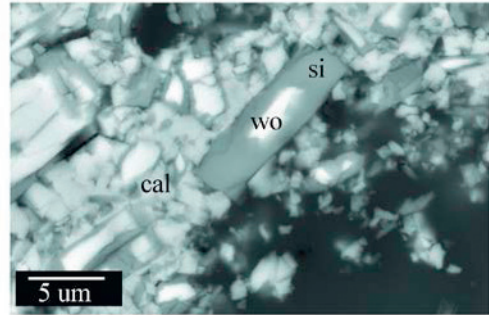


Figure 2. Polished cross section of reacted wollastonite grains (70°C , 160 bar, 100% saturated scCO_2).

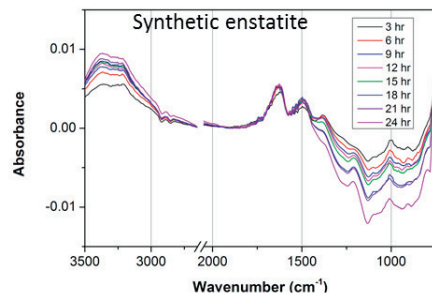


Figure 3. Infrared spectra as a function of time during the reaction of synthetic enstatite with wet scCO_2 at 50°C and 90 bar.

carbonation extents. The presence of water films appears to be critical for the mineral carbonation of silicates exposed to wet scCO₂.

Understanding interfacial processes that occur at the mineral surface is essential for discerning how carbonation proceeds in water-bearing supercritical fluids. Our prior studies [3, 7] with the mineral brucite [Mg(OH)₂] showed extensive carbonation in the absence of a condensed water layer on the mineral surface. In contrast, Thompson et al. [10], showed that water films containing dissolved bicarbonate formed on the surface of antigorite when the serpentine mineral was exposed to wet scCO₂. Relative to forsterite, antigorite's reactivity was low, and no carbonate precipitate was formed until water was removed from the scCO₂ at the end of the 24-hr reaction period. The differences in mechanisms, reaction rates, and products formed in these studies highlights the importance of fundamental investigations for understanding the long-term fate of geologically stored CO₂.

4. Conclusion

Significant insights about silicate mineral reactivity with water-bearing scCO₂ have been enabled by the unique *in situ* instrument suite developed at PNNL. Researchers are now able to examine the relevant chemistry that spans from the pore-scale down to the molecular-level. This path is providing a foundation for developing a comprehensive understanding of chemical reactions relevant to caprock integrity for both programmatic and industrial research. The instrument suite at PNNL is available to the external scientific community through a competitive user proposal process. We envision that this unique suite will enable more accurate representation of chemical mechanisms in reactive transport simulators, provide the data needed to improve relevant thermodynamics and kinetics databases, and ultimately help assess and assure prospective scCO₂ reservoir permanence.

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