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Wollastonite Carbonation in Water-Bearing Supercritical CO₂: Effects of Particle Size

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Abstract

The performance of geologic CO₂ sequestration (GCS) can be affected by CO₂ mineralization and changes in the permeability of geologic formations resulting from interactions between water-bearing supercritical CO₂ (scCO₂) and silicates in reservoir rocks. However, without an understanding of the size effects, the findings in previous studies using nanometer- or micrometer-size particles cannot be applied to the bulk rock in field sites. In this study, we report the effects of particle sizes on the carbonation of wollastonite (CaSiO₃) at 60 °C and 100 bar in water-bearing scCO₂. After normalization by the surface area, the thickness of the reacted wollastonite layer on the surfaces was independent of particle sizes. After 20 h, the reaction was not controlled by the kinetics of surface reactions but by the diffusion of water-bearing scCO₂ across the product layer on wollastonite surfaces. Among the products of reaction, amorphous silica, rather than calcite, covered the wollastonite surface and acted as a diffusion barrier to water-bearing scCO₂. The product layer was not highly porous, with a specific surface area 10 times smaller than that of the altered amorphous silica formed at the wollastonite surface in aqueous solution. These findings can help us evaluate the impacts of mineral carbonation in water-bearing scCO₂.

Introduction

To mitigate adverse impacts of global climate change, anthropogenic CO₂ can be captured from point sources and sequestered in subsurface environments, such as deep saline aquifers or depleted oil and gas reservoirs.(1) The safety and efficiency of CO₂ trapping in these storage sites

are related to interactions among supercritical CO₂ (scCO₂), water, and rock. (2, 3) For example, the carbonation of silicates can trap CO₂ in mineral phases and cause changes in the wettability and porosity of reservoir rocks, which can, in turn, alter their permeability. Furthermore, a change of permeability in geologic formations can influence the transport of CO₂ and potentially affect CO₂ leakage. For similar reasons, scCO₂-water-rock interactions can be important in other subsurface CO₂ injection processes, including scCO₂-enhanced oil recovery and scCO₂-energized hydraulic fracturing. (4-8)

While most previous studies on scCO₂-water-rock chemical interactions focused on mineral dissolution and precipitation in the presence of the bulk aqueous phase, (2, 3) recent studies have revealed the following importance of interactions between scCO₂ and minerals in the absence of aqueous solutions. (9-11) First, because injected scCO₂ will displace brine, most of the contact areas between scCO₂ and caprocks and a certain portion of the contact areas between scCO₂ and formation rocks are in the absence of bulk aqueous solution. (12) Second, scCO₂ has higher diffusivity and lower viscosity and, thus, lower capillary entry pressure than aqueous-phase fluid (i.e., CO₂-dissolved brine). (13) Therefore, scCO₂ can enter smaller pore throats that brine cannot enter. Third, recent studies reported that water dissolved in scCO₂ has higher reactivity on mineral surfaces than that of water in the aqueous phase. (9, 13, 14) Based on these considerations, the reactions of minerals with water-bearing scCO₂ are at least equally, if not more, important than reactions of mineral with aqueous solutions. (13, 15)

Our current understanding of water-bearing scCO₂-mineral interactions focuses on the carbonation of various Ca-, Mg-, or Fe-bearing minerals, including wollastonite, (16-19) forsterite, (12, 15, 20-23) fayalite, (24) dolomite, (25) and phlogopite. (9) While these studies investigated the effects of the water saturation percentage of CO₂, (15, 19, 20, 22, 26) temperature, (18, 19, 21, 24) and organic ligands (23) on carbonation reactions, we need a better understanding of the dependency of water-bearing scCO₂-silicate reactions on particle sizes. There are several knowledge gaps. First, previous studies mostly used micrometer- or even nanometer-size particles, (15-24) a far cry from the bulk rock in field sites. Without understanding the effects of particle sizes, we cannot know whether the outcomes obtained with small particles are applicable to bulk rock in field sites. Second, findings from different studies are not directly comparable due to the different particle sizes used. Thus, results from previous studies on water-bearing scCO₂-silicate reactions cannot be combined. Third, investigating the effects of particle sizes can reveal the mechanisms of mineral carbonation reactions. For example, a recent study of metal oxide carbonation (i.e., CaO) in dry CO₂ found that the reacted fraction is constant for different particle sizes and concluded that the reaction extent of CaO carbonation is determined by the porosity of CaO particles. (27) Similarly, investigating the effects of particle sizes on silicate carbonation in water-bearing scCO₂ can inform us about

whether the reaction is controlled by the porosity of silicates or other limiting factors, such as the kinetics of silicate dissolution in water films. However, to the best of the authors' knowledge, there have been no studies on the effects of particle sizes on water-bearing scCO₂-silicate interactions.

The goal of this study is, therefore, to understand the effects of particle size on the carbonation of wollastonite in water-bearing scCO₂. We chose wollastonite because it has been frequently used as a representative of silicates in previous studies on silicate reaction in scCO₂ and in aqueous solutions.(18, 19, 28, 29) We hypothesize that the reaction is controlled by the kinetics of wollastonite hydrolysis. If the anisotropic reactivity of different crystal faces is not significant, the reaction extent of different size particles should be similar after normalization to surface area. To test this working hypothesis, particles with five different size ranges were reacted at 60 °C and 100 bar, conditions closely relevant to geologic CO₂ sequestration (GCS). The information provided can contribute to a better understanding of the water-bearing scCO₂-silicate reactions and the scaling-up of findings in laboratory studies using small-size mineral particles to the larger-scale bulk rock formations.

Experimental Methods

Minerals

Natural wollastonite particles with five different size ranges were purchased from NYCO Company (Willsboro, NY). By using X-ray powder diffraction (XRPD, Bruker D8), its structure was identified to be wollastonite-1A, the most common polymorph in the natural environment.(30) The size distribution and shape for each size range were determined by laser diffraction and image analysis (Microtrac Inc.) performed by NYCO Company. Most particles were in a cylindrical shape (Figure S1). The spherical equivalent volumetric mean diameters were 3.8, 5.2, 11.1, 17.8, and 82.0 μm, and the respective typical aspect ratios were 3:1, 3:1, 3:1, 4:1, and 15:1. The detailed size distribution is available in Figure S1. These size ranges were chosen because they can provide detectable and significantly different reaction extents. Using N₂ as adsorbate and 11 points on the isotherm in the BET method (AX1C-MP-LP, Quantachrome Instruments), the specific surface areas were determined to be 4.46 ± 0.01 , 3.61 ± 0.01 , 1.95 ± 0.01 , 1.45 ± 0.01 , and 0.54 ± 0.01 m²/g, respectively, for 3.8, 5.2, 11.1, 17.8, and 82.0 μm particles. The error ranges are based on duplicate measurements. X-ray fluorescence (Table S1) showed that the Ca-to-Si ratio was 0.959. Thermogravimetric analysis (TGA, Q5000IR, TA Instruments) showed a 0.45% mass loss between 150–780 °C. As shown by the XRD patterns in Figure S5, the unreacted sample contains aragonite, which is estimated to be 1 wt %, determined based on 0.45% mass loss in TGA. No further treatment was performed after the wollastonite were obtained from the vendor.

Carbonation in Water-Bearing scCO₂ at Simulated GCS Conditions

Carbonation experiments were conducted in a 300 mL high-pressure and high-temperature reactor (Parr Instruments, Moline, IL) modified from the reactor used in our previous studies.(31-35) A schematic diagram of the reaction system setup is available in Figure S2. The conditions (60 °C and 100 bar CO₂) are similar to typical conditions at GCS sites: 65 °C and 150 bar in the Frio formation,(36) 37 °C and 100 bar at the Sleipner site,(37) and 63 °C and 140 bar at the Weyburn field site.(38) To investigate carbonation of wollastonite in the absence of an aqueous phase, wollastonite particles were placed in 10 mL Teflon tubes, while ultrapurified deionized water (Barnstead, > 18.2 MΩ·cm) was added outside the tubes. After scCO₂ was injected into the vessel, water dissolved in the scCO₂ and generated water-bearing scCO₂. A total of five polytetrafluoroethylene (PTFE) tubes were placed in the reactor during each test. Considering the volume taken up by tubes and liners in the reactor, the volume of CO₂ during the experiment was 201 mL. The tubes were capped but have small holes that allow contact between the wollastonite and water-bearing scCO₂. The solubility of water in CO₂ was predicted using Spycher's model.(39) At 35 and 60 °C, the mole fraction of 100% saturated water in 100 bar CO₂ is 0.41 and 0.49%, which indicates 234 and 117 μL water in the 201 mL of scCO₂. The solubility of water in scCO₂ is affected by the salinity of water. As a starting point, ultrapurified water was used for simplicity. This result can serve as an important underpinning for understanding the effects of salinity on silicate carbonation in the future. Each sample contained 0.3 g of particles. To check the possible influence of particle stacking inside the tubes on the reaction, results were compared with samples using 0.05 g of particles. Selected samples were analyzed using X-ray powder diffraction (XRPD). In this study, no attempt of XRPD quantitative analysis was made. Instead, the reaction extent was determined by thermogravimetric analysis (TGA). A previous study has shown that the results from XRPD quantitative analysis are comparable with the results from TGA.(19)

Determination of the Reaction Extent

The reacted fraction of wollastonite was determined based on TGA results. After the sample was recovered from the reactor, the samples were stored at atmospheric pressure and analyzed within 24 h. The powder sample was briefly mixed using a plastic spatula, and approximately 10 mg was used for each TGA analysis. A minimum of duplicate samples were analyzed. Samples were heated to 900 °C with a ramp of 20 °C/min under N₂ flow (25 mL/min). Wollastonite and amorphous silica were stable below 900 °C, while calcium carbonate completely decomposed into CaO and CO₂.(19) The amount of CO₂ was measured by the mass loss between 150 and 780 °C during TGA (Figure 1B). Given the amount of CO₂, the reacted fraction of the original wollastonite was derived using this equation:

$$F = \frac{\text{mass of reacted wollastonite}}{\text{mass of original wollastonite}} = \frac{m_L \times \frac{M_{\text{CaSiO}_3}}{M_{\text{CO}_2}}}{m_o - m_L} \quad (1)$$

where m_L is the mass loss during TGA, which is the mass of CO_2 from CaCO_3 decomposition. According to eq 2, the mass loss is equal to the mass of CO_2 consumed during reaction with water-bearing scCO_2 , so the mass of wollastonite consumed as reactant can be calculated using m_L and the molecular weight of CO_2 and wollastonite; m_o is the mass of the sample reacted with water-bearing scCO_2 , which includes the mass of the original wollastonite (wollastonite before reaction with CO_2) and the mass of sorbed CO_2 on wollastonite (equal to m_L); and M is the molecular weight of different species. Given the 0.45% mass loss in unreacted wollastonite, the detection limit of this method is estimated to be 1%. The reacted fraction of the largest particle size used (82 μm) is 7.8%, so the uncertainty of the reaction extent determined using this method is no more than 15%.

Figure 1. (A,B) XRPD pattern and TGA analysis of wollastonite particles reacted for 40 h with 45 times more water than needed for saturation ($45 \times S_w$, where S_w represents the solubility of water in CO_2) at 60 °C and 100 bar CO_2 . (C) Mass loss of two duplicate samples of wollastonite particles reacted for 40 h at $45 \times S_w$ at 60 °C and 100 bar CO_2 during dissolution in nitric acid and TGA. (D) Reacted fraction of wollastonite particles with volumetric mean diameters of 3.8 and 17.8 μm , reacted for 20 h with the addition of different amounts of water. Both sizes showed no dependency on the amount of water at $45 \times S_w$.

Calculation of the Reacted Thicknesses of Wollastonite Samples

Based on the reacted fraction, we calculated the thicknesses of the reacted layer by using a shrinking core model. The schematic diagram in Figure 2A

shows the geometry. Before the reaction, each particle was assumed to be cylindrical in shape, with aspect ratio R and diameter D , calculated using eq 3 based on the spherical equivalent diameter (D_{eq}) measured by laser diffraction by the NYCO Company. During the reaction, a shell with thickness L was consumed as the reactant, and according to the model, the wollastonite particle shrank to a cylindrical shape core with a diameter of $D - 2L$. The volume fraction of the shell is the reacted fraction of the particle. By integrating all the size intervals shown in the size distribution (Figure S1), the reacted fraction of each size range was calculated. The reacted thickness L was obtained by solving eq 4, which equated the calculated reacted fraction and the reacted fraction determined by TGA:

$$D = D_{eq} \times \sqrt{\frac{2}{3 \times R}} \quad (3)$$

$$F = \frac{\sum_{D_{min}}^{D_{max}} \left\{ \frac{\pi D^2}{4} \times 2L + \left[\frac{\pi \times D^2}{4} - \frac{\pi \times (D - 2L)^2}{4} \right] \times (RD - 2L) \right\}}{\sum_{D_{min}}^{D_{max}} \left\{ \frac{\pi \times D^2}{4} RD \right\}} \quad (4)$$

In eqs 3 and 4, L is the thickness of the reacted layer, F is the reacted fraction, D_{eq} is the spherical equivalent diameter of each size range from laser diffraction results provided by NYCO Company, D is the cylindrical equivalent diameter of each size range, and R is the aspect ratio. L was obtained by solving this equation. For small particle size ranges, in which $(R \times D - 2 \times L) < 0$, the volume measured by laser diffraction was used to replace the calculated value because these particles are so small that the reacted fraction is 100%. From eq 3, F is strongly correlated to L/D . Therefore, if L is constant, F will change significantly with D . However, if L is proportional to D , F will not be correlated with D .

Figure 2. (A) Diagram of the shrinking core model used to calculate reacted thickness. The orange part is the unreacted core of wollastonite. The green part represents the wollastonite consumed during the reaction with water-bearing scCO_2 . L is the reacted thickness, D is the diameter of the particle, and R is the aspect ratio of cylindrical shape particle. (B) Reacted fraction of wollastonite particles with a volumetric mean diameter of 3.8 μm after 40 h at $45 \times S_w$ at 60 $^\circ\text{C}$ and 100 bar CO_2 . Samples containing 0.3 and 0.05 g of particles showed the same reacted fraction. (C) Reacted fraction of wollastonite particles with volumetric mean diameters of 3.8, 5.2, 11.2, 17.8, and 81.0 μm reacted for 5, 10, 20, 30, and 40 h with $45 \times S_w$ at 60 $^\circ\text{C}$ and 100 bar CO_2 . Error bars are the differences among three replicates. (D) The thickness of the reacted wollastonite layer calculated based on the reacted fraction. The thickness of the reacted surface layer is similar for different particle sizes, 177 ± 11 nm. (E) Reacted thicknesses of wollastonite particles with volumetric mean diameters of 3.8 and 17.8 μm at different water saturation percentages.

Determination of the Amounts of Structural Water in Reacted Samples

The mass loss determined by TGA can be affected by potentially existing structural water in reacted samples, which would lead to an overestimation of the reacted fraction. To check whether large amounts of structural water existed in reacted samples, 0.3 g of reacted sample (3.8 μm) were dissolved in 5 mL of 1 M nitric acid (BDH), and the dissolved solutions were weighed. The Ca concentration in dissolved solutions was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-OES; Figure S3), which confirmed that the particles were completely dissolved in solution. The mass change was compared to the mass loss predicted based on TGA. If the mass loss is similar to the prediction, then the amount of structural water is not significant enough to affect the reacted fraction determined by TGA.

Amorphous Silica Layer Formed in Aqueous Solution

When the researchers of recent studies on wollastonite carbonation in water-bearing scCO_2 discussed the amorphous silica formed, references to wollastonite dissolution in the aqueous phase were cited to support their points.(17, 19) However, it is unclear whether the amorphous silica layers formed in aqueous solution and in water-bearing scCO_2 are comparable. To compare the amorphous silica layers formed in an aqueous solution and in water-bearing scCO_2 , an amorphous silica layer was produced on wollastonite surface by a preferential dissolution of Ca in acidic solution. Specifically, 2 g of unreacted wollastonite (17.8 μm) was reacted in 200 mL of nitric acid solution with an initial pH of 1 for 1 h. A control sample was reacted with ultrapurified water. Liquid samples were filtered using 0.22 μm PTFE filters and analyzed using ICP-OES. Solid samples were washed with ultrapurified water, centrifuged at 5000 rpm for 30 min, dried in N_2 , and reacted with water-bearing scCO_2 . The reaction extents of the pretreated sample and control sample were compared to show differences between the amorphous silica layers formed in aqueous solution and in water-bearing scCO_2 .

SEM Imaging

To observe the cross-section of the surface product layer, wollastonite particles were embedded into a resin (Eponate 12) and sectioned using an ultramicrotome (Leica EM UC7). The cross-sections were analyzed using scanning electron microscopy (SEM, JEOL 7001LVF FE-SEM), coupled with energy dispersive X-ray spectrometry (EDS) to obtain the elemental composition. Both SEM and EDS were operated in low-vacuum mode (10 Pa), with an accelerating voltage of 10.00 kV and a probe current of 16 μA . The working distance was 10 mm.

Results and Discussion

Carbonation of Wollastonite in Water-Bearing scCO_2 and Formation of Calcite and Amorphous Silica Secondary Mineral Phases

Among the products of the reaction, calcite was the dominant crystalline phase identified by XRPD (Figures 1A and S6–S9). This observation is consistent with previous studies,(16–19) in which the carbonation of wollastonite was described as eq 2. The other product reported is amorphous silica, whose broad peak cannot be clearly shown in an XRPD pattern. Based on XRPD results, the amounts of aragonite and vaterite were not significant. Although the existence of amorphous calcium carbonate (ACC) is possible, it is likely that ACC transformed to more-stable phases during ex situ treatment. The difficulty in determining in situ phases of CaCO_3 does not affect the determination of reaction extent because the formations of ACC and calcite consumed the same amount of wollastonite.

To investigate the effects of particle size on wollastonite carbonation in water-bearing scCO_2 , we conducted experiments to ensure that the potential

existence of structural water in the reaction product did not affect the accuracy of the reacted fraction determined using TGA. It is important to check because ACC or amorphous silica contain structural water, which would enhance the mass loss and, therefore, lead to an overestimation of the reacted fraction. However, the TGA curve (Figure 1B) is smooth between 150 and 600 °C, indicating no significant amount of structural water in the reacted samples. To further investigate the potential influence of structural water on the accuracy of determined reacted fraction, the mass loss in TGA was compared to the mass loss when the reacted sample was dissolved in nitric acid, which is affected only by CO₂ (Figure 1C). The mass changes were similar, which suggests that no significant amounts of structural water existed in the reaction product. Even if a small amount of structural water existed, it was not enough to affect the accuracy of the reaction fraction of wollastonite determined using eq 1.

Besides determining the reacted fraction, we investigated the effects of the amount of water added in our system. The model we used to calculate the solubility of water in scCO₂ did not consider the presence of minerals.⁽³⁹⁾ In addition, some water will adsorb on the mineral surfaces. Consequently, even though the same amount of water was added, different sizes of particles could possibly experience a different extent of water saturation. To ensure that different particle sizes were reacted under the exact same conditions, we studied the dependencies of the reacted fraction on the amount of water added to the reactor (Figure 1D). Our data suggested that the reacted fraction increased with the amount of water and is more-dependent on water saturation for small particle sizes. However, for different particle sizes, plateaus were reached with 20 times more water than needed for saturation in CO₂ (For simplicity, $20 \times S_w$, where S_w represents the solubility of water in CO₂). When the value was higher than $20 \times S_w$, the reacted fractions of different size particles do not have a strong dependency on water saturation. Therefore, to elucidate the effects of particle sizes, $45 \times S_w$ was chosen as the main condition used.

Next, the potential influence of CO₂ diffusion through interparticle spaces was investigated. Experiments using 0.3 and 0.05 g of particles (i.e., different packing heights and thus different path lengths) showed the same reacted fraction (Figure 2B). The top part and bottom part of the sample also showed the same reacted fraction (Figure S4). This finding indicates that water-bearing scCO₂ easily reached the bottom of the tube, even though particles were packed inside the tubes, and each particle experienced exactly the same reaction condition. This observation also suggests that the ratio between mineral and water-bearing scCO₂ fluid will not affect the extent of reaction in the range of the experimental conditions. In our system, the small amount of water adsorbed on the mineral surface cannot change the water saturation percentage in CO₂ fluid because $45 \times S_w$ was added. If a certain amount of water originally dissolved in CO₂ was adsorbed on the mineral surface, the loss of water in CO₂ fluid could be compensated quickly

by the $45\times S_w$ added. However, it is worthwhile to note that in field sites, low water saturation conditions can exist. The adsorption of water on the mineral surface may change the water saturation percentage in CO_2 and therefore affect the carbonation of silicates.

Reacted Fractions of Wollastonite and Decrease with Larger Particle Sizes

The reacted fractions of wollastonite were measured after 5, 10, 20, 30, and 40 h of reaction at 60 °C and 100 bar with $45\times S_w$. The reacted fractions did not keep increasing with time but fluctuated in certain error ranges (Figure 2C). This observation shows that the reaction extent reached a plateau. To explain this trend, several limiting factors of mineral carbonation were considered.

First, a recent study using wollastonite suggested that the plateau results from the limited availability of water.(18) In our system, $45\times S_w$ was added. Thus, the plateau is not due to limited water availability during the reaction. As we have shown above, no significant amount of structural water existed in the reaction products, so the reaction did not consume large amounts of water. The water acted more likely as a catalyst for the overall reaction. After the reaction, there were significant amounts of water left in the aqueous phase, although the amount was not quantified.

Second, besides the availability of water, other controlling mechanisms for mineral carbonation have also been suggested. For example, a recent study of CaO carbonation in dry CO_2 found that the reacted fraction is independent of particle sizes and concluded that carbonation of CaO is not limited by reaction at the surface but happens throughout the entire particle.(27) We show, however, that the reacted fraction of wollastonite decreased significantly with larger particle sizes (Figure 2B). From the SEM images (Figure 3C,D), larger particles have much larger unreacted cores than do smaller particles, in contrast to keeping a constant reacted fraction. This finding confirms that carbonation of wollastonite in water-bearing CO_2 is substantially different from carbonation of CaO in CO_2 . The wollastonite carbonation is limited to the surface.

Figure 3. SEM images of wollastonite particle cross-sections. (A) Unreacted wollastonite particles with a volumetric mean diameter of 17.8 μm . (B) Unreacted wollastonite particles with a volumetric mean diameter of 3.8 μm . (C) Wollastonite particles with a volumetric mean diameter of 17.8 μm reacted for 40 h with $45\times S_w$ at 60 $^{\circ}\text{C}$ and 100 bar CO_2 . (D) Wollastonite particles with a volumetric mean diameter of 3.8 μm reacted for 40 h with $45\times S_w$ at 60 $^{\circ}\text{C}$ and 100 bar CO_2 . The thickness of product layer is similar to that of the 17.8 μm size particles. The red bars are 300 nm. (E) Wollastonite particles with a volumetric mean diameter of 17.8 μm reacted for 40 h with $45\times S_w$ at 35 $^{\circ}\text{C}$ and 100 bar CO_2 . The unreacted wollastonite, with $\text{Ca/Si} = 0.86$ as determined by EDS, is surrounded by a darker layer, with $\text{Ca/Si} = 0.12$, which was attributed to amorphous silica. Outside the amorphous silica layer, discrete calcite, $\text{Ca/Si} = 5.33$, can be observed. (F) Wollastonite particles with a volumetric mean diameter of 17.8 μm pretreated with nitric acid.

Other studies also suggested that hydrolysis of the mineral can be the controlling step.(20, 26)Water adsorbs on the mineral surface and forms a thin film. Hydrolysis of silicates within the water film releases cations, such as Ca^{2+} and Mg^{2+} , which form carbonate later with the CO_2 dissolved in the water films. We hypothesize that this mechanism is applicable to our system: the extent of reaction is limited by the slow kinetics of wollastonite

hydrolysis. This hypothesis is consistent with our observations of the reacted fraction: smaller particles have larger surface area, which enhanced the kinetics of wollastonite hydrolysis and thus led to larger reacted fractions.

Constant Reacted Thickness for Various Particle Sizes

If the dissolution rate of the mineral phase is the limiting factor, it should be possible to observe differences in the thickness of the reacted wollastonite layer because particles with different sizes may have different combinations of crystal surfaces, which can have different dissolution rates. To compare the thicknesses of the reacted layer on different particle sizes, we applied eq 4 and calculated the reacted thicknesses. Interestingly, the reacted thickness was constant for different particle sizes (Figure 2C). Because five different size ranges have been used, the constant thickness from these samples is not a coincidence. We admit that the model used to calculate the thickness has simplifications: ideal cylindrical shapes of particles are assumed, and the heterogeneity in shape and surface roughness of actual particles have been omitted. However, the thickness obtained with this model is a statistically averaged result, and thus, it is not significantly affected by heterogeneity in shape and surface roughness. More specifically, the size used in the calculations is a volumetric equivalent and, hence, already considers the heterogeneity in shape and surface roughness.

Because the reacted layers from different size samples have a constant thickness, the thickness of the product layer should also be constant: the particles share the same chemical phase and should produce the same products. This conclusion is proven by the similar thickness of the product layer observed in Figure 3C,D. Thus, we suggest that the thickness of the reacted layers should be used to represent the extent of reaction, rather than the reacted fraction of samples, or the weight fraction of CO_2 and carbonate in the samples after reaction. Because the thickness of the reacted layer is independent of particle size, such a replacement of the term can make the results obtained with different particle sizes directly comparable.

We also found that after converting the reacted fraction into the reacted thickness, the reacted thickness of different particle sizes showed the same dependency on the water saturation percentage (Figure 2D). Therefore, besides the value of $45 \times S_w$ used above, at various water-saturation conditions, the reacted thickness is independent of particle size. If the reacted fraction or other size-dependent indexes are used to represent reaction extent, smaller particles tend to have larger apparent dependency on the water-saturation percentage (Figure 1D). However, using the reacted thickness, the reaction extents of various particle sizes have the same actual dependency on the water-saturation percentage.

Furthermore, the constant reacted layer thickness suggests that particle size has no significant effects on the reaction extent if normalized by its surface area. These results show that the anisotropic reactivities of different crystal

faces may not be significant. Another possibility is that the reactivity of wollastonite does not affect the reaction extent in water-bearing scCO_2 -silicate reaction after 20 h. The reaction is not controlled by the kinetics of mineral hydrolysis but by the diffusion of water-bearing scCO_2 across the surface product layer. We observed that the product layer containing amorphous silica and calcite covered the surface of the wollastonite and thus could act as a diffusion barrier to water-bearing scCO_2 . This mechanism explained why the reaction reached a plateau, which cannot be explained by mineral hydrolysis alone. The constant thickness of the product layer is strong evidence to support this mechanism. Although the reactivities of different crystal surfaces and different surface sites varied, various surfaces and particles tend to form a product layer with the same thickness. In addition to the conditions affecting the diffusivity of water-bearing scCO_2 , such as temperature and pressure, the thickness and the permeability of the product layer are controlling factors for silicate carbonation in water-bearing scCO_2 .

Earlier, we described that the reaction reached a plateau after 20 h (Figure 2C). For all particle sizes, the pseudo-equilibrium reacted thickness was 177 ± 11 nm with $45 \times S_w$ at 60°C and 100 bar CO_2 . These results can be directly applied to bulk rocks at field sites. Provided a sufficiently long reaction time, other silicates may follow the same mechanism, although their kinetics of hydrolysis can be much slower than for wollastonite. It could take longer than 20–40 h before the reaction becomes diffusion-controlled. Thus, within the time scale of days or weeks in laboratory experiments, other silicates may not reach plateau, and wollastonite can be a good model for investigating the long-term state of silicate carbonation in water-bearing scCO_2 .

Amorphous Silica As a Diffusion Barrier for Water-Bearing scCO_2

Furthermore, based on our understanding of the reacted layer, we can provide insight into the identity of the diffusion barrier of wollastonite reaction with water-bearing scCO_2 . A recent study on wollastonite carbonation in water-bearing scCO_2 claimed that the calcite formed on the surface of wollastonite acted as diffusion barrier because the amorphous silica looked highly porous.(16) Another study argued that the amorphous silica layer should be the diffusion barrier because in their SEM images, the calcite particles were discontinuous and did not substantially cover the surface of the wollastonite particles.(19) Both studies cited references reporting wollastonite dissolution in the bulk water phase to support their points. However, whether the amorphous silica layer formed during silicate dissolution in the bulk solution acts as a diffusion barrier is still controversial. (40, 41) Previous studies found that the structure and degree of polymerization of silica layers formed in aqueous solutions are affected by the substrate, and the solution chemistry, thus, can be either passivating or nonpassivating.(42-45) Schott et al. found that for wollastonite, the amorphous silica layer is not a diffusion barrier for aqueous species.(40)

Even if we know the answer in the presence of the bulk solution, there is still no evidence to show that the amorphous silica layer formed in exposure to water-bearing scCO_2 can be analogous to the amorphous silica layer formed in bulk solution.

Based on this study, we suggest that the amorphous silica layer should be the diffusion barrier for water-bearing scCO_2 . The sample reacted at 35 °C was used to clearly show the relative distribution of calcite and amorphous silica (Figure 3E), and it has a much thicker product layer than the 60 °C samples that allowed us to do more-accurate EDS analysis. We assumed that the distribution of calcite and amorphous silica was the same at 35 and 60 °C. From the SEM results (Figure 3E), we learned that the calcite presents as discrete particles or aggregates, which did not fully cover the surface of wollastonite. Thus, it is less likely that calcite can be the diffusion barrier. However, the amorphous silica layer substantially covered the surface of the unaltered core of wollastonite. This observation is consistent with the findings in the study of Miller et al.(19) In contrast, Daval et al. observed alternating layers of amorphous silica and calcite on wollastonite surfaces. (17) We suggest that the 60 °C and 100 bar conditions used in our study are similar to the 50–70 °C and 90–160 bar used in Miller et al.'s study(19) and lower than the 90 °C and 250 bar used in Daval et al.'s work.(17) In addition, Daval et al. conducted water-saturated CO_2 experiments together with a bulk aqueous-phase experiment in one reactor.(17) An unlimited amount of water was in their system and could potentially migrate to the wollastonite surface, which may explain the different observations in their work and in this study. In addition, analysis using the Brunauer-Emmett-Teller (BET) method indicated that the particles after reaction have a smaller specific surface area of $1.02 \pm 0.08 \text{ m}^2/\text{g}$ compared to $1.57 \pm 0.13 \text{ m}^2/\text{g}$ for the unreacted sample. The decrease in surface area suggests that the average particle size may become larger and the amorphous silica layer may not be highly porous. Therefore, we concluded that the amorphous silica layer forms a diffusion barrier in our experimental systems.

To demonstrate the differences between the amorphous silica layer formed in the bulk aqueous phase and that formed in water-bearing scCO_2 (Figure 4), we conducted the following experiments. As a control sample, wollastonite particles with a volumetric mean diameter of 17.8 μm were reacted for 40 h with water-bearing scCO_2 with $45 \times S_w$ at 60 °C and 100 bar. Based on TGA results, 17% of the raw wollastonite was consumed in the reaction with water-bearing scCO_2 , which corresponds to a layer of wollastonite with a thickness of 199 nm, determined based on eq 4. The products were calcite and amorphous silica, which formed a layer on the unaltered wollastonite core. According to the stoichiometry of the reaction (eq 2), the thickness of the product layer was calculated to be 270 nm (Figure 4C), based on the reported densities of quartz, wollastonite, and calcite, i.e., 2.65, 2.90, and 2.71 g/cm^3 , respectively.(46) We used the density of quartz for the vitreous amorphous silica, because the apparent

density of vitreous amorphous silica depends on its porosity, which can vary significantly for different samples. The thickness of the product layer obtained is not the actual thickness, and is used only to compare the amount of surface layer on different samples. The details on the calculation of product layer thickness are shown in section S2 in the Supporting Information.

Figure 4. Schematic diagram of surface layers on a control and a sample pretreated with nitric acid. (A–C) Wollastonite particles reacted for 40 h with $45\times S_w$ at $60\text{ }^{\circ}\text{C}$ and 100 bar CO_2 . According to the measured reacted fraction, (B) a 199 nm thick layer of wollastonite on the surface was reacted (dotted layer). (C) A 270 nm product layer formed by calcite and amorphous silica. (D–F) The sample pretreated in nitric acid has (D) a 274 nm highly porous amorphous silica layer on its surface, based on calculations using ICP results. (E) A 202 nm thick layer of wollastonite was reacted after 40 h with $45\times S_w$ at $60\text{ }^{\circ}\text{C}$ and 100 bar CO_2 . Compared to the 199 nm layer of the control sample, the same amount of wollastonite reacted, indicating that the porous amorphous silica layer formed in the aqueous phase cannot act as a diffusion barrier for water-bearing scCO_2 .

In contrast, another sample with the same particle size was prereacted with nitric acid solution (initial pH of 1) to generate amorphous silica layer on the surface of the wollastonite. Based on the Ca and Si concentrations measured by ICP-OES, the thickness of this amorphous silica layer was calculated to be 274 nm (Figure 4D), assuming that the density of amorphous silica is 2.65 g/cm^3 . Such a thickness is comparable with the thickness of the product layer formed on the control sample after reaction in water-bearing scCO_2 . Therefore, if amorphous silica formed in the aqueous phase could act as

diffusion barrier, the sample pretreated with nitric acid should not further react with water-bearing scCO_2 due to diffusion-limited reaction. However, when pretreated wollastonite was reacted with water-bearing scCO_2 under the same conditions as the control sample, 21% of the sample had reacted, and the thickness of the reacted wollastonite layer was calculated to be 202 nm (Figure 4E). Such a small enhancement in the reacted fraction (17% to 21%) is due to the shrinkage of the particle during the reaction with nitric acid, and is consistent with the calculation using our shrinking core model (eq 4). The similar reacted thicknesses (199 and 202 nm) show that the amorphous silica formed during the aqueous-phase dissolution of wollastonite does not act as a diffusion barrier for water-bearing scCO_2 at all, while the amorphous silica layer formed in water-bearing scCO_2 can be a diffusion barrier. The specific surface areas of samples pretreated with nitric acid after reaction with nitric acid and after additional reaction with water-bearing scCO_2 were 14.16 ± 0.80 and $13.87 \pm 1.20 \text{ m}^2/\text{g}$, respectively. These values are much larger than $1.572 \pm 0.126 \text{ m}^2/\text{g}$ for the original wollastonite sample. This observation indicates that the amorphous silica layer formed in the aqueous phase is highly porous (Figure 3F) compared to that formed in water-bearing scCO_2 (Figure 3C), which is further confirmed by SEM images. It shows that the amorphous silica layer formed in water-bearing scCO_2 , and those formed in the aqueous phase may have substantially different porosities, which is likely due to the different chemistries in the thin water film. The low-porosity amorphous silica layer formed during water-bearing scCO_2 -mineral interaction can act as diffusion barrier for water-bearing scCO_2 .

Environmental Implications

We found that the amorphous silica layers formed in water-bearing scCO_2 and those formed in solutions have different morphologies. Specifically, the altered amorphous silica layers formed in aqueous solutions had 10 to 100 times larger BET surface areas than those formed in water-bearing scCO_2 . These new findings help to understand the differences between silicate reactions in water-bearing scCO_2 and in solutions. They also provide insights into the role of water on the silicate carbonation in water-bearing scCO_2 . In addition, our observations suggest that the carbonation of wollastonite in water-bearing scCO_2 was limited by the diffusion barrier of the amorphous silica layer. The thickness of the reacted wollastonite layer was determined to be $177 \pm 11 \text{ nm}$ with $45\times S_w$ at 60°C and 100 bar CO_2 . This thickness was found to be independent of the particle sizes used. Therefore, the reacted thickness should be used to represent the extent of reaction instead of any other parameter that changes with particle size. These findings allow us to compare the results of previous studies using different particle sizes directly after normalization by surface area. Moreover, the work can be a good first step to fill the knowledge gap between small size particles used in the laboratory and the bulk rock in real GCS systems. Because we have shown that the equilibrium reacted thickness does not change with particle size, the

thickness measured using small particles can be applicable to larger sizes of rocks.

Other Mg- or Fe-containing silicates also produce corresponding carbonate and amorphous silica during their reactions with water-bearing scCO_2 . We suggest that the low porosity of amorphous silica layers formed in water-bearing scCO_2 is due to an insufficient amount of water compared to aqueous solutions. Thus, it is likely that the amorphous silica layers formed on other minerals in water-bearing scCO_2 are also diffusion barriers. Hence, the results obtained using wollastonite can be potentially applicable to other silicates. However, there is a caveat that the substrate chemistry may affect the structure of silica layers. In addition, the plateau we observed in this study is not the real equilibrium. Provided a sufficiently long reaction time, the crystallization of amorphous silica in water-bearing scCO_2 can possibly change the permeability of the amorphous silica layer. This process can determine the reaction extent on a geologic time scale.

The carbonation of silicates can lead to a change of wettability because the silicates are usually more hydrophilic than carbonate.⁽⁴⁷⁾ It can also result in volume change because the densities of reaction products are different from the original silicates. The carbonation can also contribute to CO_2 mineralization, which is the most-permanent way to trap CO_2 . With these considerations, the reacted thickness can be the most important factor in understanding water-bearing scCO_2 -mineral reactions. In short, the new insights provided in this work can help us predict both the stability of silicate in water-bearing scCO_2 and the impact of water-bearing scCO_2 -silicate reactions on subsurface scCO_2 injections. Furthermore, the water-bearing scCO_2 -silicate reaction can potentially be applicable to CO_2 capture and ex situ mineralization. The results of this work can benefit the understanding of all of these environmental processes.

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