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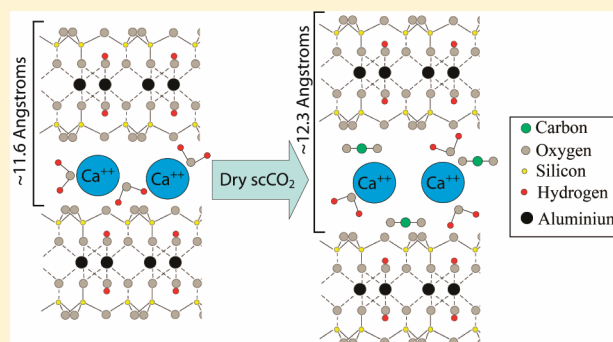
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# In Situ Molecular Spectroscopic Evidence for CO<sub>2</sub> Intercalation into Montmorillonite in Supercritical Carbon Dioxide

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**ABSTRACT:** The interaction of anhydrous supercritical CO<sub>2</sub> (scCO<sub>2</sub>) with both kaolinite and ~1W (i.e., close to but less than one layer of hydration) calcium-saturated montmorillonite was investigated under conditions relevant to geologic carbon sequestration (50 °C and 90 bar). The CO<sub>2</sub> molecular environment was probed *in situ* using a combination of three novel high-pressure techniques: X-ray diffraction, magic angle spinning nuclear magnetic resonance spectroscopy, and attenuated total reflection infrared spectroscopy. We report the first direct evidence that the expansion of montmorillonite under scCO<sub>2</sub> conditions is due to CO<sub>2</sub> migration into the interlayer. Intercalated CO<sub>2</sub> molecules are rotationally constrained and do not appear to react with waters to form bicarbonate or carbonic acid. In contrast, CO<sub>2</sub> does not intercalate into kaolinite. The findings show that predicting the seal integrity of caprock will have complex dependence on clay mineralogy and hydration state.



## INTRODUCTION

Geologic storage of carbon dioxide depends on low permeability caprocks to prevent upward migration of buoyant supercritical CO<sub>2</sub> (scCO<sub>2</sub>). Injection of scCO<sub>2</sub> will displace formation water, and the pore space adjacent to overlying caprocks could eventually be dominated by dry to water-saturated scCO<sub>2</sub>.<sup>1,2</sup> Water-bearing scCO<sub>2</sub> is capable of carbonating and hydrating certain minerals, whereas anhydrous scCO<sub>2</sub> can dehydrate water-containing minerals.<sup>3–8</sup> Because these geochemical processes affect solid volume and thus porosity and permeability, such changes may affect the long-term integrity of the caprock seal. Caprock formations often contain high concentrations of clay minerals,<sup>9</sup> including illite, montmorillonite, chlorite, kaolinite, and glauconite. Expandable (i.e., smectitic) clays sorb ions and molecules into their interlayer spaces by a process called intercalation. If water is present, smectitic clays will intercalate water and expand to a nominally high-volume state, thereby possibly lowering the permeability of a clay-rich caprock. However, the behavior of expandable clays under the low-water conditions of an scCO<sub>2</sub>-dominated fluid is much less predictable. Hence, especially in the context of the geologic sequestration of carbon dioxide, it is important to understand the intercalation reactions of clay minerals exposed to dry to water-saturated scCO<sub>2</sub>.

Recent *in situ* X-ray diffraction (XRD) studies have focused on the interaction of scCO<sub>2</sub> with montmorillonite, a 2:1 expandable phyllosilicate clay with low layer charge.<sup>3,7,10,11</sup> Schaef et al.<sup>7</sup> found that the *d*<sub>001</sub> spacing of Ca-saturated montmorillonite (Ca-STX-1) containing close to but less than

one layer of hydration (designated here as ~1W) expanded by ~0.8 Å during exposure to anhydrous scCO<sub>2</sub> at 50 °C and 90 to 180 bar. However, the ~1W Ca-STX-1 did not expand (or contract) during exposure to dry N<sub>2</sub> at the same pressure and temperature. Similarly, Giesting et al.<sup>10</sup> showed that the *d*<sub>001</sub> spacing of ~1W Na-montmorillonite (SWy-2) swelled by up to ~1.0 Å during exposure to CO<sub>2</sub> at temperatures between 22 and 47 °C and pressures of up to 50 bar. Further, Hemmen et al.<sup>11</sup> reported expansion of a synthetic montmorillonite exposed to CO<sub>2</sub> at –20 °C and 15 bar, but clay swelling was not observed under the same conditions with N<sub>2</sub>. All of these *in situ* XRD studies attributed expansion of the montmorillonite structure to intercalation of CO<sub>2</sub> but without direct evidence.

Montmorillonite interaction with scCO<sub>2</sub> has also been studied using molecular simulations.<sup>12–14</sup> On the basis of simulations run at 75 °C and both 25 and 125 bar, Botan et al.<sup>12</sup> predicted that CO<sub>2</sub> should intercalate 1W and 2W Na-saturated montmorillonites. The CO<sub>2</sub> molecules were predicted to occupy the center of the interlayers with the O–C–O axis oriented parallel to the basal surface for the 1W clay, but closer to the interlayer surface in the 2W clay. Interestingly, their calculations predict no swelling of the montmorillonite upon CO<sub>2</sub> intercalation. Yang and Yang<sup>13</sup> also carried out simulations, but they studied the interactions of CO<sub>2</sub> with 0W Na-saturated montmorillonite at 45 °C and either

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atmospheric pressure or 100 bar. Their calculations predict that the clay should not swell at atmospheric pressure, but should expand at 100 bar with intercalated CO<sub>2</sub> molecules associated with both the sodium cations and the interlayer surface.

In this study, we report the first *in situ* direct molecular-level evidence of CO<sub>2</sub> intercalation into a clay mineral under conditions relevant to geologic carbon sequestration (50 °C and 90 bar). We use both *in situ* magic angle spinning nuclear magnetic resonance (MAS NMR) and *in situ* attenuated total reflection infrared (ATR-IR) spectroscopies along with *in situ* XRD to investigate the interactions of ~1W Ca-saturated montmorillonite (~1W Ca-STX-1) and kaolinite (KGA-2) with anhydrous scCO<sub>2</sub>. ~1W Ca-STX-1 was chosen because previous XRD studies suggested that CO<sub>2</sub> intercalates this clay at the chosen temperature and pressure. KGA-2 was selected because it is a 1:1 phyllosilicate clay that is typically regarded as nonexpandable, thus serving as a control mineral lacking an accessible interlayer region.

## EXPERIMENTAL SECTION

The kaolinite (KGA-2) and montmorillonite (STX-1) used in this study are natural samples obtained from the clay mineral society (Columbia, MO).<sup>15,16</sup> The KGA-2 sample for NMR spectroscopic experiments was the dry clay as received, while KGA-2 samples for IR spectroscopic and XRD experiments were prepared from a 100 g/L suspension of the clay in deionized (DI) water. The STX-1 was processed according to the procedures in Schaefer, Ilton et al. (2012) to obtain the <2 μm fraction and remove any naturally occurring metal carbonate solids. Calcium saturated STX-1 (Ca-STX-1) was prepared by suspending the clay in 5 M CaCl<sub>2</sub> solution for two weeks. Afterward, the excess salt was removed by dialysis in DI water. The resulting Ca-STX-1 suspension was 50 g/L and was used to prepare samples for IR spectroscopic and XRD experiments. The Ca-STX-1 sample for NMR spectroscopic experiments was prepared by freeze-drying the concentrated suspension.

The *in situ* high-pressure X-ray diffraction (HXRD) technique and experimental procedure has been previously described in detail.<sup>3,7</sup> Briefly, an aliquot of Ca-STX-1 or KGA-2 suspension was pipetted onto a sample post and allowed to air-dry prior to positioning in the reaction chamber. Following alignment, the reactor was heated to 50 °C while under vacuum (approximately 1 × 10<sup>-3</sup> Torr) for 24 h before pressurization with CO<sub>2</sub> (90 bar). Diffraction patterns, processed with JADE XRD software, were collected throughout the experiment to monitor shifts and overall peak shapes in the *d*<sub>001</sub> basal reflections.

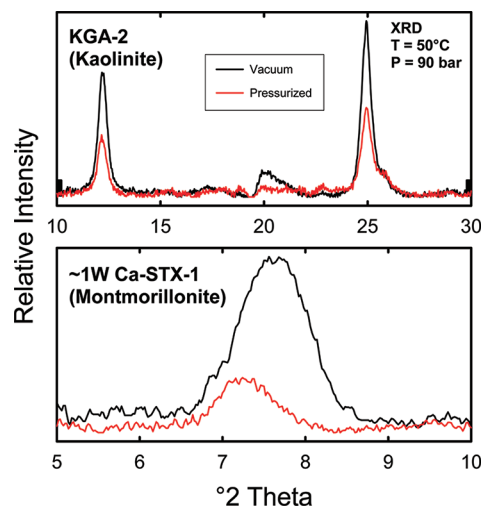
The *in situ* high-pressure MAS NMR technique has also been described in detail previously.<sup>17</sup> An empty high-pressure MAS rotor was used for the spectrum of bulk scCO<sub>2</sub> at 50 °C and 90 bar, while a dry clay was loaded into the rotor for the spectra of scCO<sub>2</sub> exposed to Ca-STX-1 or KGA-2. The unsealed rotor was placed into a reaction vessel and heated at 50 °C for 18 h under vacuum (approximately 1 × 10<sup>-3</sup> Torr) before pressurization with CO<sub>2</sub> at 90 bar. The rotor was then sealed under pressure, removed from the reaction vessel, and transferred to an Agilent-Varian VNMRS spectrometer equipped with an 89 mm bore 7.05 T magnet. During the transfer and subsequent data acquisition, the temperature of the rotor was maintained at 50 °C and its pressure was held by design at 90 bar. <sup>13</sup>C NMR spectra were collected at a Larmor frequency of 75.43 MHz using a 7.5 mm MAS probe capable of 7.0 kHz maximum spinning frequency, in conjunction with a commercially available variable temperature (VT) stack. Spectra of bulk scCO<sub>2</sub>, KGA-2, and Ca-STX-1 were collected at 2.3, 2.5, and 2.7 kHz spinning rates and were an average of 120, 1120, and 4580 scans, respectively. All experiments employed a pulse width of 1.5 μs (30° flip angle) and a relaxation delay of 2 s were used, and a Lorentz line broadening of 8 Hz was applied before Fourier transformation.

*In situ* high-pressure ATR-IR spectra were measured using a Bruker Vertex 80v spectrometer equipped with a DTGS detector, a water-

cooled Globar source, and a custom-built high-pressure ATR cell. The ATR cell used a 45° single-reflection internal reflection element (IRE) made of ZnSe. The IRE was sealed against a stainless-steel high-pressure vessel by a Viton O-ring. The vessel was jacketed and heated using a water bath and pressurized with supercritical-fluid grade CO<sub>2</sub> (Oxarc, Pasco, WA) using a syringe pump (Teledyne Isco Inc.). Temperature was measured using a type-K thermocouple that was located inside the vessel, and pressure was monitored using a transducer that was in-line with the vessel. All background and sample single-channel spectra were an average of 1024 scans. For the spectrum of bulk scCO<sub>2</sub> at 50 °C and 90 bar, a background single-channel spectrum was collected of the evacuated (approximately 1 × 10<sup>-3</sup> Torr) ATR cell thermostatted at 50 °C. Then, a sample absorbance spectrum of bulk scCO<sub>2</sub> was collected after pressurizing the cell with CO<sub>2</sub> to 90 bar. For the spectra of scCO<sub>2</sub> exposed to Ca-STX-1 or KGA-2, first 0.2 mL of a concentrated (50 and 100 g/L, respectively; see above) suspension of a clay was pipetted onto the IRE and allowed to dry under vacuum at 50 °C for at least 12 h. After a background spectrum was collected, the cell was pressurized with CO<sub>2</sub> to 90 bar, and a sample absorbance spectrum was acquired of the scCO<sub>2</sub> in contact with the clay. On the basis of the masses and densities of the clays, as well as the surface area of the IRE, we calculated that the thickness of the clay films on the IRE were greater than 30 μm, which is larger than the effective path length of the infrared radiation (less than 6 μm between 2200 and 2400 cm<sup>-1</sup>).<sup>18</sup>

## RESULTS AND DISCUSSION

In Figure 1, XRD patterns are shown for KGA-2 and Ca-STX-1 at 50 °C, either under vacuum or exposed to scCO<sub>2</sub> at 90 bar.

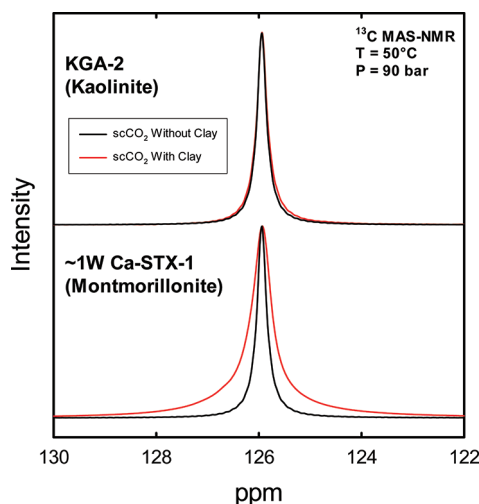


**Figure 1.** *In situ* high-pressure XRD tracings collected at 50 °C (top) of Kaolinite (KGA-2) under vacuum (black) and in contact with scCO<sub>2</sub> (red), and (bottom) ~1W Ca-saturated Montmorillonite (~1W Ca-STX-1) under vacuum (black) and in contact with scCO<sub>2</sub> (red).

Under vacuum, preferentially oriented grains of KGA-2 produce intense *d*<sub>001</sub> basal reflections positioned at 7.16 Å (12.181°2θ) and 3.58 Å (24.979°2θ) typical for kaolinite<sup>19</sup> (Figure 1). Following pressurization with CO<sub>2</sub> to 90 bar, the intensities of the *d*<sub>001</sub> basal reflections decreased due to beam attenuation by the supercritical fluid, but the positions of these reflections remained constant. Hence, there is no indication of KGA-2 expansion. For Ca-STX-1 under vacuum, the *d*<sub>001</sub> basal reflection was positioned at 11.59 Å (7.621°2θ), which indicates a sub-1W hydration state for Ca<sup>2+</sup> saturated montmorillonite<sup>20</sup> (i.e., ~1W Ca-STX-1). Following exposure of ~1W Ca-STX-1 to scCO<sub>2</sub>, the *d*<sub>001</sub> basal reflection decreased

in intensity and expanded to  $12.23 \text{ \AA}$  ( $7.220^\circ 2\theta$ ). Consequently, in contrast to KGA-2, XRD provides indirect evidence that  $\text{CO}_2$  intercalates  $\sim 1\text{W}$  Ca-STX-1.

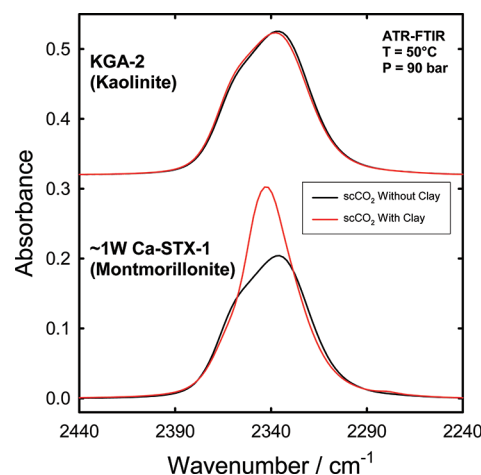
Figure 2 compares  $^{13}\text{C}$  MAS NMR spectra for bulk  $\text{scCO}_2$  and  $\text{scCO}_2$  in the presence of KGA-2 or  $\sim 1\text{W}$  Ca-STX-1 at 50



**Figure 2.** *In situ*  $^{13}\text{C}$  high-pressure MAS NMR of  $\text{scCO}_2$  in the presence of Kaolinite (KGA-2, red upper spectrum) and  $\sim 1\text{W}$  Ca-saturated Montmorillonite ( $\sim 1\text{W}$  Ca-STX-1, red lower spectrum) at 90 bar and  $50^\circ\text{C}$ . Also shown for comparison is the spectrum of bulk  $\text{scCO}_2$  under the same conditions (black upper and lower spectra).

$^\circ\text{C}$  and 90 bar. The spectra of bulk  $\text{scCO}_2$  and  $\text{scCO}_2$  in contact with KGA-2 show relatively narrow and symmetric peaks centered at  $125.9 \text{ ppm}$  that have nearly the same shape. Hence, there is no evidence from NMR of significant  $\text{CO}_2$  interactions with kaolinite. In contrast, the spectrum of  $\text{scCO}_2$  in contact with  $\sim 1\text{W}$  Ca-STX-1 has a width that is nearly twice that of the bulk  $\text{scCO}_2$ . This broadening could be explained by two different mechanisms. On one hand, the increased width could indicate inhomogeneous broadening due to multiple types of  $\text{CO}_2$ –clay interactions that give rise to a series of peaks that resonate at a spread of different frequencies. These interactions could include  $\text{CO}_2$  perturbed by the interlayer surface,  $\text{CO}_2$  interacting with  $\text{Ca}^{2+}$  or water in the interlayer, and  $\text{CO}_2$  bound to the external surface of the clay. Furthermore, a particular  $\text{CO}_2$ –clay interaction could involve an ensemble of different binding sites and coordination modes, which could also cause a broadened line shape. Another possibility is that the broadening is caused primarily by the low rotational and translational mobility of the  $\text{CO}_2$  molecules that are interacting with the clay. This would especially be the case for  $\text{CO}_2$  trapped in the interlayer. Reduced molecular mobility could lead to shorter longitudinal relaxation times ( $T_1$ ) and broader NMR peaks.<sup>21</sup>

In Figure 3, the ATR-IR spectrum in the asymmetric CO stretching region of bulk  $\text{scCO}_2$  is compared to that of  $\text{scCO}_2$  in the presence of KGA-2 or  $\sim 1\text{W}$  Ca-STX-1 at  $50^\circ\text{C}$  and 90 bar. For bulk  $\text{scCO}_2$ , the asymmetric CO stretching band has a peak maximum at  $2336 \text{ cm}^{-1}$ ; however, the line shape of this band is not symmetric, and there is a shoulder located at roughly  $2360 \text{ cm}^{-1}$ . The irregular line shape is a result of rotational fine structure. Rotational–vibrational peaks are well-known in the IR spectra of molecules in the gas phase at low pressures, where individual P- and R-branch bands can be resolved with sufficiently high instrument resolution. Rotational



**Figure 3.** *In situ* high-pressure ATR-IR spectra of  $\text{scCO}_2$  in the presence of Kaolinite (KGA-2, red upper spectrum) and  $\sim 1\text{W}$  Ca-saturated Montmorillonite ( $\sim 1\text{W}$  Ca-STX-1, red lower spectrum) at 90 bar and  $50^\circ\text{C}$ . Also shown for comparison is the spectrum of bulk  $\text{scCO}_2$  under the same conditions (black upper and lower spectra).

fine structure is also present at the pressures of  $\text{scCO}_2$ . However, at higher pressures, molecular collisions are more frequent. These collisions cause rotational relaxation that leads to broadened and coalesced P- and R-branch peaks, as well as collapse of the rotational fine structure into the Q-branch peak.<sup>22</sup> This yields nonsymmetric and complex line shapes, as seen for the asymmetric CO stretching band of bulk  $\text{scCO}_2$ . The intensity, position, and shape of the asymmetric CO stretching band of  $\text{scCO}_2$  in contact with KGA-2 are nearly the same as for bulk  $\text{scCO}_2$ . Thus, there is no indication from these infrared data of significant rotational perturbations to  $\text{CO}_2$  by interactions with kaolinite. On the other hand, the asymmetric CO stretching band of  $\text{scCO}_2$  in contact with  $\sim 1\text{W}$  Ca-STX-1 is more intense, symmetric, and narrow than for bulk  $\text{scCO}_2$ . These differences indicate that the rotational fine structure of the  $\text{CO}_2$  molecules interacting with  $\sim 1\text{W}$  Ca-STX-1 has collapsed even further than for bulk  $\text{scCO}_2$  (and  $\text{scCO}_2$  interacting with kaolinite), consistent with rotationally constrained  $\text{CO}_2$  trapped in the interlayer region of montmorillonite.

The NMR and IR spectroscopic data reported here are thus consistent and show the first direct evidence of  $\text{CO}_2$  intercalation into montmorillonite exposed to  $\text{scCO}_2$ . This supports the hypothesis, based on *in situ* XRD, that intercalation of  $\text{CO}_2$  into the interlayer region of  $\sim 1\text{W}$  montmorillonite during exposure to  $\text{scCO}_2$  is the cause of  $d_{001}$  spacing expansion.

This combination of structural and molecular characterization provides powerful insight into the mechanism of  $\text{CO}_2$  interaction with montmorillonite. In this regard, Giesting et al.<sup>10</sup> speculated that  $\text{CO}_2$  in the interlayer region of Na-saturated montmorillonite (SWy-2) exposed to  $\text{CO}_2(\text{g})$  and  $\text{scCO}_2$  can react with  $\text{H}_2\text{O}$  to form bicarbonate ( $\text{HCO}_3^-$ ) or carbonic acid ( $\text{H}_2\text{CO}_3$ ) in the interlayer region. Consequently, we looked for carbonate species, where  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$  have NMR  $^{13}\text{C}$  peaks at  $161.5$  and  $162.9 \text{ ppm}$ ,<sup>17,23</sup> respectively, and CO stretching and HCO bending bands between  $1250$  and  $1750 \text{ cm}^{-1}$ .<sup>24,25</sup> However, no such signals were detected. Instead, both techniques identified linear  $\text{CO}_2$  molecules that were rotationally constrained by possibly more than one preferential interlayer surface, cation, or water binding mode.



More fundamental insight is now possible using structural and molecular level characterization techniques combined as was done in this study, in particular, to test whether clay composition, including H<sub>2</sub>O content, can influence the mode of CO<sub>2</sub> interaction with expandable clays under conditions expected for geologic sequestration of CO<sub>2</sub>.

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### Notes

The authors declare no competing financial interest.

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