Interaction of Carbon Dioxide with Na-exchanged Montmorillonite at Pressures to 640 Bars:

Implications for CO₂ Sequestration

Paul Giesting¹

Stephen Guggenheim¹

August F. Koster van Groos¹

Andreas Busch²

1 - Department of Earth and Environmental Sciences

University of Illinois at Chicago

845 W. Taylor St., Chicago, IL 60607 USA

2 - Shell Global Solutions International

Kessler Park 1

2288GS Rijswijk, Netherlands

Abstract

Na-exchanged montmorillonite swells upon interacting with CO₂ under the conditions $P(CO_2) \le$ 50 bars, T = 22-47°C, as shown by experiments in high-pressure environmental chambers using powder X-ray diffraction techniques. The amount of swelling depends on the initial H₂O content of the montmorillonite. Maximum expansion, to 12.3 Å, occurred in a sample with an initial d(001) of 11.3 Å at $P(CO_2) = 57$ bars. Thus, montmorillonite can expand by 9% in contact with CO₂ where small amounts of H₂O are present in the interlayer. Little to no expansion occurs for samples with an initial $d(001) \le 10.0$ Å or d(001) = 12.3 to 12.5 Å. The reaction with CO₂ is complete by ~50 bars; increasing $P(CO_2)$ from 50 to 640 bars did not result in any significant further increase of d(001). This work shows that a smectite-rich cap rock above a carbon sequestration reservoir may be significantly altered by reacting with CO₂.

Keywords: geological sequestration; montmorillonite; smectite clay; X-ray diffraction; pressure

Introduction

Sequestration of anthropogenic CO_2 in deep sedimentary strata is a widely considered option for reducing greenhouse gas emissions. The challenge of injecting CO_2 into sedimentary rocks is to reliably predict the long-term behavior of the CO_2 ; this knowledge is essential for both the commercial and political viability of this carbon storage methodology. In particular, the long-term efficacy of the impermeable cap rock in sealing the reservoir against leakage of the injected CO_2 requires evaluation. This cap rock is generally a shale or mudstone rich in clay minerals, often including swelling clays (Abdou and Ahmaed, 2010) such as the smectite mineral montmorillonite.

Swelling clays occur as platy particles composed of silicate layers separated by interlayer material, including cations and H_2O molecules. The interlayer materials of a swelling clay are easily interchanged with the external environment, which distinguishes these minerals from other clays and micas. The term "swelling clay" derives from the ability of the particles to expand or contract based on the migration of H_2O molecules into and out of the interlayers.

A swelling clay particle bathed in supercritical CO_2 could experience changes to its interlayer contents and therefore possibly also to its molar volume. The particle could expand due to the incorporation of CO_2 directly, or it could dehydrate and contract if the supercritical CO_2 has a greater affinity for water molecules than the clay. CO_2 could also act as a delivery fluid (Serhatkulu et al. 2006) to assist in the intercalation of other chemical species in the clay.

Krooss et al. (2002, 2003) considered CO_2 adsorption and diffusion for coal, sandstone, and shale and found that shales can retain CO_2 , although the mechanisms involved are not clear. Nuttall et al. (2005, 2009) evaluated CH_4 and CO_2 sorption by black shales in Kentucky and nearby regions. They correlated the gas sorption capacity with the shale organic matter content, although their defined trend showed significant outliers for CO_2 . This suggests that other factors need to be considered in evaluating CO₂ sorption capacity, such as clay mineralogy. Using triaxial flow and manometric sorption experiments, Busch et al. (2008) examined sorption and diffusion of CO₂ in samples from the Muderong Shale, Australia, and in other selected clay samples. They determined the sealing performance and storage potential for CO₂ of this media at temperatures of 45-50°C and elevated pressures (< 20 MPa), conditions of pressure (*P*) and temperature (*T*) common for deep sedimentary strata. They found that CO₂ sorption on clay surfaces is variable (< 1 mmol/g for Muderong Shale, < 1.6 mmol/g for smectite, but lower for illite and kaolinite). Busch et al. (2008) suggested that the CO₂ retention in these samples is related to CO₂ dissolution in water and sorption onto clay and that alteration reactions at high pressures affect the specific surface area of the constituent particles, which would change over time with repeated exposure to CO₂. Wollenweber et al. (2010) found similar results for carbonate rocks, with sorption capacities up to 0.3 mmol/g for marlstone and less than 0.2 mmol/g for relatively pure limestone.

In the past, several groups studied the sorption and desorption of CO₂ by montmorillonite at low pressure and low temperature, beginning with Thomas and Bohor (1968) and Aylmore et al. (1970). These authors disputed whether CO₂ could enter the interlayers of montmorillonite, or whether it was sorbed only to external crystallite surfaces. Intercalation was more conclusively shown by Fripiat et al. (1974). Montmorillonite samples exchanged with one of several different cations were exposed to CO₂ at pressures <1 bar and at temperatures between -70 and 25°C. X-ray diffraction was used to confirm that at low temperature, some of the montmorillonite swelled by about 2.5 Å in the *c* direction. Infrared spectroscopy confirmed that CO₂ was present in an oriented form in these samples. These authors concluded that at low temperature, in addition to sorption in pore spaces between particles, CO₂ also intercalates into the interlayers and causes structural swelling.

Simulation and modeling studies have also been conducted on mica and clay-CO₂ systems.

Primarily by using computer modeling and diffuse-reflectance infrared spectroscopy, Romanov et al. (2010) tentatively concluded that CO_2 may intercalate in the interlayer of smectite. Botan et al. (2010) performed molecular simulation studies of CO_2 intercalation into Na-exchanged montmorillonite and found that CO_2 was stable in the interlayers, but they did not find either expansion or contraction of the interlayers as a result of CO_2 intercalation. These and other modeling studies (Yang and Zhang, 2005; Peng et al., 2007; Cole et al., 2010), while differing significantly in their model formulations, agree that CO_2 molecules can exist in the interlayers of clays.

Whereas there are both modeling and experimental studies describing CO₂ intercalation, no experimental work has been conducted at pressures or temperatures relevant to geological carbon sequestration. Smectite intercalation reactions at non-ambient conditions often reverse when the experimental charges are returned to room temperature and pressure. Fripiat et al. (1974), for example, showed that the sorption and intercalation of CO₂ at low temperatures in montmorillonite are quickly reversed upon warming to room temperature. Thus, structure-related experimental data using diffraction (or spectroscopic) techniques are more informative when the experiments are done at the PT conditions of interest. To obtain reliable structure information on materials at the high-pressure conditions relevant to geological questions such as carbon sequestration, high-pressure environmental chambers were developed to study mineral interactions with gases at elevated pressure, using X-ray diffraction (XRD) as the analytical tool (Koster van Groos et al., 2003; Koster van Groos and Guggenheim, 2009). The focus of the study presented here was to investigate the reaction of montmorillonite containing varying amounts of interlayer H₂O with CO₂ gas and supercritical fluid to evaluate whether CO₂ can enter the interlayers of swelling clays under subsurface conditions likely to exist in carbon sequestration reservoirs.

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Experimental methods

High-pressure environmental chambers (HPECs)

HPECs of two different designs have been constructed and used in our laboratory. The reflection-mode chamber (RHPEC; Koster van Groos et al., 2003) is mounted on a Siemens D5000 θ - θ powder diffractometer. This chamber is built to handle conditions up to 100 bars and to 100°C. Owing to the long X-ray path length within the RHPEC (nearly 2 cm), the X-ray intensity exiting the chamber drops rapidly with pressure. The attenuation depends on the density of the gas/fluid used to pressurize the chamber; for CO₂, the RHPEC cannot be effectively used at pressures above about 40-50 bars.

A second chamber was developed to study the interaction of minerals with a variety of fluids, including gases, supercritical fluids, and liquids, *e.g.*, brines; it can also analyze bulk solid samples. This chamber may be used to 1000 bars and 200°C. The chamber has a transmission-mode X-ray geometry (THPEC). The THPEC used here mounts on a Bruker D8 three-circle diffractometer, with X-rays transmitted through 1-mm thick diamond windows with O-ring pressure seals. Both entry and exit windows are adjustable to alter the irradiated volume of the sample. In the present experiments, 10 to 12 mg samples of smectite were placed between the diamond windows, which were then adjusted to hold the sample at the center of the chamber with window-to-window distances of 0.25 - 0.5 mm.

Starting material

A Na-rich montmorillonite (Clay Minerals Society Source Clay SWy-2, Costanza and Guggenheim, 2001 and papers therein) was used as starting material. To remove soluble salts that affect grain-size separation, aliquots of SWy-2 were sonified in distilled water and centrifuged to recover the clay. This washing was repeated until the addition of AgNO₃ to the supernatant showed no precipitation of AgCl. Next, the aliquots were grain-size separated to retain the $< 2 \mu m$ fraction following Moore and

Reynolds (1997, pp. 211-213), which removes all or most of the non-clay material. Next, this fraction was cation exchanged by adding 1 M NaCl solution to the clay aliquots, agitating the mixture with a sonicator, centrifuging the resulting suspension to recover the clay, pouring off the supernatant, then repeating the process two additional times. After the final cation exchange, the aliquots were washed until addition of AgNO₃ to the supernatant showed no precipitation of AgCl. The samples, hereafter referred to as NaSWy2, were combined and stored in sealed glass bottles.

All experiments used "bone dry" grade CO_2 from Airgas, which was either used at tank pressure or pressurized using an external pump before being introduced into the respective HPEC.

Sample preparation - THPEC

A 2 g batch of NaSWy2 was dried at 200°C in a muffle furnace in air for 2 days. Aliquots of clay were subjected to different treatments to change their hydration state. Sample TAc was cooled in air and then loaded immediately into the THPEC. Sample TDc was cooled in a desiccator. Sample TGc was crushed in a mortar in air, allowing it to sorb more H₂O from the atmosphere than sample TAc. Finally, sample THe/T33 was held above a saturated solution of MgCl₂ (relative humidity 33% at room temperature) for several days before analysis. This resulted in the clays having varying amounts of interlayer water in the order TDc < TAc < TGc < THe/T33.

Sample preparation - RHPEC

Thin, oriented aggregate mounts of NaSWy2 on glass slides (~13x18 mm) were prepared using the Method 2 procedure in Koster van Groos and Guggenheim (2009). One mount was prepared using the method of Moore and Reynolds (1997, pp. 214-5), which produces a thicker sample. The samples were either placed directly in a container at a controlled humidity above a saturated salt solution

(MgCl₂, 33%RH; or NaCl, 75%RH) or dried in an oven for several days at 115°C. One of the ovendried slides was later placed in an 11%RH atmosphere (over a saturated solution of LiCl), while the other was held in a desiccator. The samples were removed from the controlled humidity atmospheres and loaded quickly in the RHPEC.

The preparation methods for the THPEC and RHPEC samples are summarized in Table 1.

Experimental methods - THPEC

The THPEC is equipped with a jacket through which heated silicone oil from a NESLAB heater/circulator may flow to control temperature (see schematic, Figure 1). Temperature was measured with a type-K thermocouple located ~1 mm from the sample. The THPEC experiments were run at or near 45° C, although data collection was started at a lower temperature for some experiments. Pressure was monitored using an external Bourdon-tube style Heise gauge (range 0-1000 bar, believed accurate to $\pm 0.1\%$). The THPEC was not evacuated of air or flushed before experiments to avoid dehydrating the sample. CO₂ pressures to ~60 bars were obtained using bottle gas pressure and higher pressures were obtained using a SC Hydraulic Engineering Corporation pump. Samples were allowed to equilibrate with the CO₂ (gas or supercritical fluid, depending on pressure) for varying lengths of time before analysis (the NaSWy2-CO₂ reaction reached steady state within ~10 min as confirmed by repeated XRD analyses). For comparison, a series of experiments was conducted using He as well.

The THPEC was mounted on the Bruker D8 diffractometer with a Mo X-ray tube, which was operated at 45 kV and 25 mA. The diffractometer was equipped with a graphite monochromator, MonoCap (0.3° divergence) collimator, and APEX CCD area detector (1024 x 1024 pixels) at a distance of 120 mm from the sample center. All THPEC data frames were collected with the APEX detector centered on $2\theta = 0^\circ$, which produced a range in data of $2\theta = 1.5$ to 13.6° (d = 27.1 to 3.00 Å).

The THPEC frames were collected for times varying from 600 s (10 min) to 2400 s (40 min), with most frames collected for 1200s (20 min). Data collection used the Bruker application SMART (v. 5.6.635, 2010). A typical THPEC data frame is presented in Figure 2.

Experimental methods - RHPEC

The RHPEC samples were run at 25 ± 3 °C. Pressure conditions were obtained from a digital Heise gauge. The RHPEC was not evacuated or flushed before experiments to avoid changing the water content of the sample. After each pressure change, samples were equilibrated for a minimum of 10 min before analysis.

The RHPEC was mounted on the Siemens D5000 diffractometer with a Cu X-ray tube, which was operated at 40 kV and 25 mA. Each RHPEC scan used a 0.02 degree step size and 1.25 s dwell time. Data collection used the DataScan application (MDI, v. 4.3.355, 2005).

Data processing

The THPEC data were corrected for air scattering and other background. An empirical correction was applied using a frame collected from the THPEC packed with fluorite (CaF₂) with 0.5 mm spacing. Fluorite has no low-angle diffraction peaks, so the low-angle intensity in the fluorite frame was essentially from background scattering. Fluorite has a higher X-ray attenuation factor than montmorillonite; the resulting background intensity of the fluorite frame was lower than the data frame intensity for all experiments. This background frame was subtracted from the experimental data frame.

Background-corrected THPEC data were integrated over arcs of constant 2θ by the Bruker application GADDS (v. 4.1.14, 2003), using a bin size of 0.1° and an arc length of 50°, to generate intensity vs. 2 θ datasets. Given the geometry of the experiment and the pixel density of the area

detector, the statistical advantage of using smaller bin sizes was negligible. The RHPEC data are presented in raw form without background or other corrections.

Results

The (001) peak centers at half maximum for the THPEC and RHPEC data are listed in Tables 2 and 3, respectively. The (001) peak center (angle) corresponds to a d(001) value calculated from the Bragg equation (see, *e.g.*, Moore and Reynolds 1997, p. 69). This d(001) represents an averaged interlayer spacing or repeat distance ("d" in Figure 4) over all diffracting particles in the sample, but does not necessarily represent the (001) spacing of any individual pair of diffracting layers of atoms. Presenting clay diffraction data solely in the form of a table of peak centers eliminates valuable information contained in the peak width and shape, and we therefore present the diffraction patterns in figures as well.

Uncertainty in the tabulated d(001) values is not easily quantified. In relative terms, it is high for samples with broad, low peaks (*e.g.*, RHe) and low for samples with sharp, intense peaks (*e.g.*, R75th). We quote d(001) values to the nearest 0.1 Å, but the uncertainty on these values may be reasonably estimated as 0.3 to 0.5 Å in the most problematic cases.

THPEC data

THPEC samples are bulk powders, and the diffraction patterns obtained from them are different from those obtained from oriented clay samples. The integrated diffraction patterns for these samples show two prominent peaks in the low-angle region visible at a detector angle of $0^{\circ} 2\theta$ (Figure 3). The (001) peak shifts with changing interlayer spacing and contents. The (02;11) peak, a diffraction band

indicating turbostratic layering (Moore and Reynolds, 1997, p. 338), retains its position and asymmetric shape even as the (001) peak changes. No impurity phases were detected in the THPEC samples.

Sample TAc. At 0 bars, the sample has a d(001) of 10.4 Å; increasing $P(CO_2)$ to 52 bars results in an increase in d(001) to 11.2 Å. When $P(CO_2)$ was gradually reduced to 21 bars, d(001) decreased to 11.0 Å (Figure 5a).

Sample TDc. In this experiment, the sample was taken from the desiccator without apparent change by ambient humidity. Increasing $P(CO_2)$ to 52 bars did not result in an increase in d(001) (Figure 5b).

Sample THe/T33. This sample was stored at RH = 33%. After exposure to P(He) = 59 bars, d(001) changed little between scans over 12.5 h (frames THe0 - THe60c, Figure 5c and Table 2). Next, the He was vented and the chamber was pressurized with 57 of CO₂ resulting in an increase in d(001) to 12.2 Å (frames T33-0 – T33-60a, Table 2).

Sample TGc. Pressurizing the chamber to 48 bars of CO₂ resulted in a sharpening of the peak and a shift to a higher d(001) from 11.4 to 12.2 Å. Further increase in pressure to 640 bars resulted in little change of d(001) (Frame TGc7 – TGc14, Table 2). A decrease of $P(CO_2)$ to 53 bars increased d(001) to 12.4 Å. Finally, a gradual reduction of pressure from 53 bars to 1 bar resulted in a considerable decrease in d(001) to 10.4 Å (Figure 5d), which is significantly lower than the original value of 11.4 Å. The relationship between $P(CO_2)$ and d(001) for this sample is shown in Figure 6.

RHPEC data

The RHPEC samples show only (00*l*) peaks owing to the orientation of the sample mounts. The higher order (002), (003), and (004) peaks are apparent for scans with a sharp (001) peak. No impurity

phases were detected in the RHPEC samples.

Sample Rov. The diffraction patterns for this sample (Figure 7a) do not change or change slightly between 0 and 10 bars. At higher pressures (21 - 31 bars), the intensity of the (001) peak diminishes and the peak occurs at higher d(001), although the precise location is uncertain owing to the reduction of peak size. The final scan, at 2 bars, is similar to the earlier scan at 2 bars.

Sample RHe. In this sequence of scans with He pressure, the peaks are not well developed. There is a small and irregular increase in d(001) with pressure (Figure 7b).

Sample R11. From 0 – 10 bars, d(001) remains at 10.0 – 10.1 Å. At higher CO₂ pressures (16 – 31 bars), d(001) increases with pressure (to 10.5 Å). The increase continues (to 10.7 Å) as pressure drops to 6 bars. As pressure is reduced further, d(001) decreases until the pressure reaches 1 bar (10.4 Å) (Figure 7c). Note in Figure 6 that the *d* values do not return to the original spacing.

Sample R33. The d(001) remained near 12.5 Å for this sample over the pressure range of $P(CO_2) = 0 - 33$ bars (Figure 7d).

Sample R75. This sample (Figure 7e) showed an initial decrease in d(001) (12.9 Å) at $P(CO_2) = 0$ to 12.5 Å at 1 bar. At higher pressures, d(001) appears to gradually increase to ~13.0 Å at 31 bars, larger than its original starting value.

Sample R75th. As in sample R33, $a \le 0.1$ Å change in d(001) was observed for this sample between $P(CO_2) = 0 - 41$ bars (Figure 7f). Repeated experiments with longer hold times (up to 16 h) did not produce significantly different results.

Discussion

Initial material

The structures of montmorillonite-H₂O complexes have been well studied. The hydration of

montmorillonite interlayers involves discrete numbers of H₂O groups. Individual interlayers assume one of a series of characteristic spacings (MacEwan and Wilson, 1984). The silicate (2:1) layer (Figure 4) is little affected by H₂O sorption; the different (001) spacings are caused by the presence of different numbers of H₂O planes within the interlayer. A montmorillonite interlayer with no H₂O has an (001) layer-to-layer spacing of about 9.6 Å. Such an interlayer is designated 0W in the notation of Ferrage et al. (2005). An interlayer with one plane of H₂O groups (notated 1W) has an (001) spacing near 12.5 Å. The series continues with ~15.5 Å (2W) and larger spacings.

Bulk montmorillonite often shows broad, asymmetric, low intensity diffraction peaks that are not centered at positions indicating one of the above layer spacings. Such samples contain populations of interlayers with different spacings arranged in random sequence within the individual clay particles. Segregation of spacings into large contiguous groups results in the presence of multiple distinct peaks; Fripiat et al. (1974) observed this behavior. In still other situations, ordering of layers into a repeating sequence (*e.g.*, ABAB...) can result in the production of superstructure peaks at locations corresponding to the sum of the spacings of the repeating layer types.

Our initial diffraction data (before exposure to CO_2) for each sample (Figures 5 and 7) fit this hydration model and indicate disordered layering for all samples with multiple interlayer types. Sample TDc, which was thoroughly dried, had dominantly 0W interlayers, resulting in a relatively sharp and intense (001) peak centered at 9.9 Å. Sample Rov, also dried in an oven, appears to have adsorbed a small number of H₂O during handling, resulting in a diffraction peak centered near 10 Å, with most interlayers of the 0W type, but showing a tail of diffracted intensity at lower angles indicating the presence of 1W interlayers. Other THPEC samples (TAc, TGc, THe/T33) and sample R11 show broad, asymmetric, low-intensity peaks at *d*(001) values of 10.4 – 12.4 Å, which indicate that both 0W and 1W interlayers are present. Sample R33, a thin mount on a glass slide, equilibrated more fully with the atmosphere inside the aging container and was more hydrated than the corresponding bulk THPEC sample THe/T33; it was dominated by 1W interlayers. R75th was similar, and may not have reached complete equilibrium at 75% RH. R75 had mostly 1W interlayers and a few interlayers with 2W spacings. In general, the initial diffraction data agree with those of Ferrage et al. (2005) for Na-exchanged montmorillonite at similar relative humidities.

Effect of CO₂ exposure

Figure 8 shows the maximum d(001) value for each sample as a function of the initial d(001) value. The initial H₂O content of the montmorillonite is measured by the d(001) value at the outset of the experiment, as discussed above. The straight line represents no interlayer expansion.

Significant expansion in the presence of CO_2 occurs when the initial d(001) values are between 10.0 and 11.5 Å; little expansion is observed below this range, and no expansion is observed above it. The expansion of NaSWy2 in CO₂ strongly depends on the internal H₂O content of the clay at the beginning of the experiment. NaSWy2 samples with all 0W or all 1W interlayers do not expand. Only samples containing a mixture of the two interlayer types show expansion under the conditions studied.

Fripiat et al. (1974) report interlayer expansion even for completely dehydrated montmorillonite--*i.e.*, montmorillonite dominated by 0W interlayers. In their case, the initial ~10.0 Å (001) peak continued to be visible but was accompanied by a lower-angle peak at ~12.3 Å in the presence of cold CO₂ (-48 and -62°C) at 700 torr (0.9 bar) pressure. They looked for the presence of linear CO₂ groups in the interlayer by monitoring the intensity of the infrared stretching band near 2550 cm⁻¹ for well-oriented samples at differing beam-to-sample angles and found evidence that such groups were present.

Chemical simulations have examined the possibility of linear CO₂ groups intercalating into clay

interlayers, and seem agreed that this is plausible. Since Fripiat et al. (1974) were able to find experimental conditions where this occurred, it is not surprising that modeling such behavior can produce stable results. However, simulation studies such as Botan et al. (2010) have not considered the possibility of other C-bearing species forming in the interlayer; their calculations are performed using constraints that include conservation of linear CO_2 groups. Their results cannot be used to comment on the possibility that CO_2 could react with some component of the system (such as the interlayer walls or H₂O groups) and form a nonlinear surface complex or carbonate group.

On the other hand, Poppa and Elliot (1971) considered CO_2 sorption to cleaved mica surfaces at room temperature and concluded that H_2O was probably necessary to form these surface complexes. Later workers suggested that CO_2 sorption to mica or clay surfaces depends on the formation of carbonate complexes by reaction with either mica/clay hydroxyls or H_2O . See Bhattacharyya (1989) for a reference list. More recently, Christenson (1993), Ostendorf et al. (2008), and Cole et al. (2010) have continued to attribute CO_2 sorption on phyllosilicate surfaces to the formation of carbonate surface complexes. Cole et al. (2010), after simulating the structure of muscovite with intercalated linear CO_2 , observed, "Additionally, when discussing realistic geological systems, it is necessary to take into account water and other chemical paths leading to carbonates." Fripiat et al. (1974), studying the montmorillonite- CO_2 system at very different *PT* conditions than those examined here, and using a different montmorillonite than SWy2, may have observed CO_2 intercalation via a different mechanism (incorporation of linear CO_2 groups) than that pertaining to the higher *P* and *T* states we examined.

 CO_2 reacts with H₂O groups to form carbonate species such as H₂CO₃ and HCO₃⁻. We suggest that under the conditions we studied, H₂O groups are scavenged from 1W interlayers in mixed 0W-1W montmorillonite samples, as well as from external clay surfaces, the experimental chamber walls, and the ambient air in the chamber at the outset of the experiment. The carbonate complexes may interact via hydrogen bonding with the adjacent basal oxygen planes and via electrostatic attraction to the interlayer Na cations. This model explains why at very small initial H_2O contents, little expansion occurs, because the small quantity of H_2O groups in the system limits the ability of CO_2 to form these complexes. As initial H_2O content increases, a greater number of these complexes can form.

Carbonate groups are assumed to lay flat within the interlayer to decrease volume and maximize hydrogen and van der Waals bonding opportunities with adjoining layer surfaces. The thickness of a flat-lying CO₃ complex is approximately equal to that of an O ion or an H₂O molecule, and thus a fully carbonated clay complex is likely to have layer-to-layer spacings equivalent to those of 1W interlayers. This model also explains why expansion does not proceed beyond a d(001) of ~12.5 Å and, therefore, the lack of expansion for the more hydrated RHPEC samples: the (001) spacing is the same for 1W and carbonated interlayers. Conversely, this model does not allow us to comment on the possibility that 1W interlayers may be carbonated upon exposure to CO₂. The carbonated interlayers thus formed would have essentially the same interlayer spacing as the original 1W interlayers and would be indistinguishable from them using powder XRD.

Montmorillonite, with its disordered, turbostratic structure, is not amenable to detailed structural determinations using diffraction data. Hence, we cannot directly confirm the presence of carbon in any form in the interlayer using XRD. The presence or absence of CO_2 and/or CO_3^{2-} groups in expanded clays could be evaluated using infrared or Raman spectroscopy, since the vibrational modes of the triangular CO_3^{2-} groups are clearly distinguishable from those observed for linear CO_2 groups. Spectroscopic methods may also be able to determine whether full 1W interlayers are carbonated by CO_2 exposure, the extent to which this process proceeds at differing pressures and temperatures, and whether any CO_2 and/or CO_3^{2-} groups remain in montmorillonite after the clay is removed from a CO_2 atmosphere.

Although we observed very little expansion of the fully dehydrated TDc sample, there was some expansion of the comparable Rov sample. The THPEC, using bulk samples, has a much higher ratio of clay to chamber volume than the RHPEC, so that the air and chamber surfaces could provide more H_2O per unit mass of clay in the RHPEC experiment, producing more expansion under CO_2 . This additional water seems to have remained in the RHPEC samples even after the end of the experiment, resulting in final d(001) values higher than the initial values (Figure 6).

The TGc sample, by contrast, had a final d(001) lower than the initial d(001). We suggest that the supercritical CO₂ in these experiments may have partially dehydrated the NaSWy2, but the effect is masked by carbonate intercalation while CO₂ pressure is high. When the CO₂ pressure is released and the carbonated interlayers revert to 0W and 1W states, the H₂O dissolved in the bulk CO₂ is lost. More work is required to evaluate this effect.

Control samples: Effect of pressure

Control experiments involving He were also conducted in this study. It is difficult to envision a mechanism for He to intercalate into montmorillonite, and so these control experiments were intended to probe the effect of increased pressure on montmorillonites independently of any possible intercalation reaction. In the THPEC series, He-exposed samples expanded from 11.0 to 11.2 Å, whereas in the RHPEC the samples expanded from 11.4 to 11.8 Å. The low diffracted intensity and broad peak widths in these data make these peak center positions uncertain. If the shifts are significant, this behavior may be due to the increase in overall pressure in the system, which could have shifted equilibria within the chamber, populating additional montmorillonite interlayers with H_2O groups at the expense of gas-phase H_2O due to the lower molar volume of H_2O in 1W interlayers compared to the vapor phase. The effect of He pressure on interlayer spacings in montmorillonite is smaller than the

effect of CO_2 pressure. Thus, the interpretation that a particular chemical mechanism is at work in causing the large degree of expansion observed in the CO_2 experiments, not the effect of pressure *per se*, is reinforced by these data.

Geologic considerations and further work

 CO_2 exposure can significantly affect the structure of Na-exchanged montmorillonite. The potential exists for CO_2 to cause swelling of the expanding clay fraction of the caprock of reservoirs used for carbon sequestration, which could then cause structural changes to the caprock, possibly swelling pores shut, but also potentially causing formation cracking. Further experimental work is needed to examine the existence and extent of this effect for smectites besides montmorillonite and interlayer cations other than Na.

The effect of CO_2 on montmorillonites with 2W and more hydrated interlayers also requires further study. The R75 data, which indicated the presence of some 2W interlayers in the initial material, do suggest that there may be an H₂O activity and CO₂ pressure range where dehydration is important. Thus, in a single reservoir, CO₂ may cause dehydration of clays in some regions, while in other regions it may cause swelling.

Dehydration of montmorillonite by CO_2 was not observed at low H_2O contents for static exposure to CO_2 . However, the TGc results suggest that a transient pulse of CO_2 could dehydrate the clay and cause its structure to partially collapse.

The range of pressures over which swelling occurs is also an important area for further research. At increasing pressures, the intercalation of CO_2 could be reversed, depending on the activities of H_2O and CO_2 and the molar volumes of the bulk fluid and clay phases. Uniaxial stress, which in a rock with depositional fabric has the potential to be oriented at a consistent angle relative to the clay particle lattices, could affect CO_2 intercalation, especially if the stress is directed normal to the layers. Thus, the relationship between the stress environment and CO_2 -induced swelling may require study before swelling effects can be incorporated into models to predict reservoir and caprock stability.

Our observation that H_2O is necessary for CO_2 -induced expansion suggests that carbonate species may intercalate into montmorillonite interlayers under the conditions we studied. As we have noted, existing computational studies assume the preservation of the linear CO_2 molecule within interlayers when considering the intercalation of CO_2 into clay or mica. Simulations with carbonate species in different geometrical configurations would be useful to assess their stability relative to each other and to models using linear CO_2 .

The range of pressures (0 - 50 bars) over which CO₂-related expansion was observed is also relevant to planetary atmospheres. Although current Earth and Mars have too little CO₂ in their atmospheres, historic Earth and Mars may have had atmospheres with sufficient CO₂ for smectites to swell from CO₂-related expansion.

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Sample	Preparation		
TAc	Oven dried at 200°C, cooled in air		
TDc	Oven dried at 200°C, cooled in desiccator		
TGc	As TDc, then crushed in air		
THe*/T33	As TGc, then held at 33%RH for 9 days		
Rov	Oven dried at 115°C		
R11	Oven dried at 115°C, held at 11%RH		
RHe*	Oven dried at 115°C, held at 11%RH		
R33	Held at 33%RH		
R75	Held at 75%RH		
R75th	Thick mount, held at 75% RH		

Table 1. Sample preparation summaries. Asterisks denote samples exposed to He instead of CO₂.

Frame	P(CO ₂ or He)	Center (°)	<i>d</i> (001) (Å)
TAc0	0 bars	3.93	10.4
TAc1	52 bars	3.64	11.2
TAc2	44 bars	3.64	11.2
TAc3	36 bars	3.66	11.1
TAc4	29 bars	3.68	11.1
TAc5	21 bars	3.71	11.0
TDc1	0 bar	4.03	10.1
TDc3	5 bars	4.01	10.2
TDc4	13 bars	4.02	10.1
TDc5	21 bars	4.01	10.2
TDc6	41 bars	3.98	10.2
TDc7	36 bars	4.01	10.2
THe0	0 bar	3.70	11.0
THe60	59 bars	3.70	11.0
THe60a	59 bars	3.68	11.1
THe60b	59 bars	3.66	11.1
THe60c	59 bars	3.63	11.2
T33-0	1 bar	3.62	11.3
T33-60	57 bar + <i>1 bar</i>	3.32	12.3
T33-60a	57 bar + <i>1 bar</i>	3.34	12.2
TGc1	0 bar	3.58	11.4
TGc7	48 bars	3.35	12.2
TGc11	60 bars	3.34	12.2
TGc80a	80 bars	3.38	12.1
TGc80c	65 bars	3.38	12.1
TGc100b	105 bars	3.38	12.1
TGc200c	204 bars	3.38	12.1
TGc400b	414 bars	3.32	12.3
TGc14	640 bars	3.36	12.1
TGc50D	53 bars	3.28	12.4
TGc40D	41 bars	3.31	12.3
TGc30D	32 bars	3.36	12.1
TGc20D	21 bars	3.40	12.0

Table 2. Experimental conditions for THPEC data collection and resulting (001) peak center positions and d(001) values. Experiments were conducted at low supercritical temperatures for CO₂ (40-45°C). Pressures in italics denote *P*(He) instead of *P*(CO₂).

TGc15	16 bars	3.44	11.9
TGc16	11 bars	3.48	11.7
TGc17	6 bars	3.52	11.6
TGc18	3.5 bars	3.62	11.3
TGc19	1 bar	3.93	10.4

Table 3. Experimental conditions for RHPEC data collection and peak center results. Experiments were conducted at ambient laboratory temperature (~25°C). Pressures in italics denote P(He) instead of $P(\text{CO}_2)$.

Scan	P(CO ₂ or He)	Center (°)	d(001) (Å)
Rov1	0 bar	8.94	9.9
Rov2	1 bar	8.92	9.9
Rov3	2 bar	8.88	10.0
Rov4	5 bar	8.94	9.9
Rov5	10 bar	8.88	10.0
Rov6	21 bar	8.78	10.1
Rov7	31 bar	8.62	10.3
Rov8	2 bar	8.78	10.1
RHe1	0 bar	7.74	11.4
RHe2	1 bar	7.62	11.6
RHe3	2 bar	7.70	11.5
RHe4	3 bar	7.66	11.6
RHe5	4 bar	7.60	11.6
RHe6	5 bar	7.66	11.6
RHe7	10 bar	7.50	11.8
RHe8	21 bar	7.60	11.6
RHe9	31 bar	7.58	11.7
RHe10	41 bar	7.58	11.7
RHe11	52 bar	7.52	11.8
R11-1	0 bar	8.88	10.0
R11-2	1 bar	8.86	10.0
R11-3	2 bar	8.88	10.0
R11-4	3 bar	8.80	10.1
R11-5	8 bar	8.80	10.1
R11-6	10 bar	8.78	10.1
R11-7	16 bar	8.58	10.3
R11-8	21 bar	8.50	10.4
R11-9	31 bar	8.40	10.5
R11-10	14 bar	8.32	10.6
R11-11	11 bar	8.24	10.7
R11-12	8 bar	8.28	10.7
R11-13	6 bar	8.24	10.7
R11-14	4 bar	8.26	10.7
R11-15	3 bar	8.36	10.6
R11-16	2 bar	8.36	10.6
R11-17	1 bar	8.48	10.4
R33-1	0 bar	7.06	12.5
R33-2	1 bar	7.06	12.5
R33-3	2 bar	7.06	12.5

R33-4	6 bar	7.04	12.6
R33-5	10 bar	7.06	12.5
R33-6	22 bar	7.04	12.6
R33-7	33 bar	7.04	12.6
R33-8	14 bar	7.06	12.5
R33-9	11 bar	7.08	12.5
R33-10	6 bar	7.08	12.5
R33-11	3 bar	7.08	12.5
R33-12	2 bar	7.08	12.5
R33-13	1 bar	7.10	12.5
R33-14	1 bar	7.10	12.5
R75-1	0 bar	6.88	12.9
R75-2	0 bar	6.88	12.9
R75-3	1 bar	7.12	12.4
R75-4	2 bar	7.12	12.4
R75-5	3 bar	7.06	12.5
R75-6	4 bar	7.10	12.5
R75-7	5 bar	7.06	12.5
R75-8	6 bar	6.98	12.7
R75-9	7 bar	6.98	12.7
R75-10	8 bar	6.94	12.8
R75-11	9 bar	6.96	12.7
R75-12	10 bar	6.96	12.7
R75-13	11 bar	6.96	12.7
R75-14	12 bar	6.94	12.8
R75-15	13 bar	6.98	12.7
R75-16	14 bar	6.98	12.7
R75-17	15 bar	6.92	12.8
R75-18	16 bar	6.94	12.8
R75-19	17 bar	6.96	12.7
R75-20	18 bar	6.92	12.8
R75-21	20 bar	6.86	12.9
R75-22	21 bar	6.88	12.9
R75-23	22 bar	6.88	12.9
R75-24	23 bar	6.92	12.8
R75-25	24 bar	6.90	12.8
R75-26	25 bar	6.88	12.9
R75-27	26 bar	6.90	12.8
R75-28	29 bar	6.82	13.0
R75-29	31 bar	6.80	13.0
R75th1	0 bar	7.04	12.6
R75th2	0 bar	7.04	12.6
R75th3	1 bar	7.06	12.5

R75th4	1 bar	7.04	12.6
R75th5	2 bar	7.04	12.6
R75th6	2 bar	7.06	12.5
R75th7	2 bar	7.06	12.5
R75th8	3 bar	7.06	12.5
R75th9	3 bar	7.04	12.6
R75th10	4 bar	7.06	12.5
R75th11	6 bar	7.06	12.5
R75th12	10 bar	7.04	12.6
R75th13	26 bar	7.02	12.6
R75th14	31 bar	7.06	12.5
R75th15	41 bar	7.02	12.6
R75th16	19 bar	7.08	12.5
R75th17	11 bar	7.06	12.5
R75th18	7 bar	7.06	12.5
R75th19	5 bar	7.06	12.5
R75th20	3 bar	7.08	12.5
R75th21	2 bar	7.06	12.5
R75th22	1 bar	7.08	12.5
R75th23	1 bar	7.06	12.5

Figure 1. Simplified schematic of the THPEC.

Figure 2. Raw data from the THPEC (frame TAc0) showing the integration area (the wedge left of the beam-stop shadow). Integration of this frame resulted in the plot shown in Figure 3.

Figure 3. Diffraction patterns of typical starting material (samples TAc and R75th). The THPEC data have been integrated, but no background correction has been applied. THPEC samples are random mounts and show the prominent, asymmetric (02;11) turbostratic band as well as the (001) interlayer peak. RHPEC samples are oriented aggregates on glass slides and show only (00*l*) series peaks. No impurity peaks are visible.

Figure 4. Structure of Na-exchanged montmorillonite (after Cygan et al. 2004). Area "a" is the interlayer, including interlayer Na⁺ (spheres) and H₂O groups, whereas "b" shows the silicate sheet. Region "a" is expandable, whereas region "b" is essentially rigid. "d" shows the d(001) layer repeat distance, which is about 12.1 Å in this figure.

Figure 5. THPEC data, collected using Mo radiation, integrated and background corrected, showing the migration of the (001) peak as a function of CO_2 (or He) partial pressure. Intensities are normalized by exposure time. Data are shown in chronological order from bottom to top. See Table 1 for sample preparation details. (a) Sample TAc. (b) Sample TDc. (c) Sample THe/T33. (d) Sample TGc.

Figure 6. Center of the (001) peak plotted against partial pressure of CO_2 for samples TGc (diamonds) and R11 (triangles). Solid symbols indicate that data were collected while the pressure was being increased, and open symbols indicate that data were collected as the pressure was lowered. Arrows indicate the chronological progress of the experiment; dashed arrows indicate a pressure range that was passed over with no data frames collected.

Figure 7. RHPEC data, collected using Cu X-rays, showing the migration of the (001) peak as a function of CO_2 (or He) partial pressure. Data are shown in chronological order from bottom to top. See Table 1 for sample preparation details. (a) Sample Rov. (b) Sample RHe. (c) Sample R11. (d) Sample R33. (e) Sample R75. (f) Sample R75th.

Figure 8. Maximum value of the (001) spacing under CO_2 or He pressure as a function of the initial (001) spacing (affected by H₂O content). Boxes signify THPEC samples and triangles signify RHPEC samples. Filled symbols show the results of CO_2 experiments and open symbols signify He experiments.

Figure 1.







Figure 3.



Figure 4.



















