Competitive Sorption of CO₂ and H₂O in 2:1 Layer Phyllosilicates

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ABSTRACT

Expandable clays such as montmorillonite have interlayer exchange sites whose hydration state can be systematically varied from near anhydrous to almost bulk-like water conditions. This phenomenon has new significance with the simultaneous implementation of geological sequestration and secondary utilization of CO₂ to both mitigate climate warming and enhance extraction of methane from hydrated clay-rich formations. In this study, the partitioning of CO₂ and H₂O between Na-, Ca-, and Mg-exchanged montmorillonite and variably hydrated supercritical CO₂ (scCO₂) was investigated using *in situ* X-ray diffraction (HXRD), infrared (IR) spectroscopic titrations, and quartz crystal microbalance (QCM) measurements. Density functional theory calculations provided mechanistic insights. Structural volumetric changes were correlated to quantified changes in sorbed H₂O and CO₂ concentrations as a function of percent H₂O saturation in scCO₂. Intercalation of CO₂ is inhibited when the clay is fully collapsed (dehydrated interlayer), peaks sharply with the introduction of some H₂O and partial expansion of the interlayer region, and then decreases systematically with further hydration of the clay. This behavior is discussed in the context of recent theoretical calculations of the montmorillonite H₂O-CO₂ system.

INTRODUCTION

Low permeable shale formations with high clay content have become increasingly important for long-term geologic storage of CO₂. In parallel, supercritical CO₂ (scCO₂) is used as a working fluid for enhancing CH₄ production from nearly depleted shale gas reservoirs. For example, in geologic carbon sequestration (GCS), supercritical carbon dioxide (scCO₂) is injected into the subsurface as a strategy for reducing emissions of anthropogenic CO₂ into the atmosphere (Bachu et al., 1994; Benson and Surles, 2006; IPCC, 2007). The success of this endeavor initially depends on physical confinement of buoyant CO₂ by overlying caprock formations,

(Gaus, 2010) which are typically composed of shales with high contents of clay minerals (phyllosilicates). Additionally, shales and tight sand formations host significant quantities of natural gas that are now being tapped through unconventional production methods. In North America, increases in reservoir transmissivity by horizontal drilling and single or multiple fracture stages followed by completion and stimulation treatments enabled these formations to deliver ~23 % of total gas production in 2010, and this is predicted to increase to 49% by 2035 (EIA, 2012). Historically, shale gas plays produce nearly 24% of the total gas recovered during the first 12 to 18 months of operation (Baihly et al., 2010). Estimating ultimate recoveries independently of immobile gas fractions is difficult and requires advanced knowledge of reservoir characteristics and favorable economics.

These simultaneous developments in carbon management and unconventional resource extraction are potentially creating future conflicts. Comparison of shale gas producing regions in North America with deep saline aquifers suitable for subsurface CO₂ storage indicates significant overlap (Elliot and Celia, 2012). Reservoir permeability, enhanced through intense fracturing, potentially compromises the sealing properties of shale formations as barriers to injected CO₂. Furthermore, economic drivers to lower energy penalties associated with carbon capture and sequestration (CCS) operations have stimulated a more comprehensive carbon storage strategy in the U.S. with a focus on CO₂ utilization. The potential for shale formations to serve as storage facilities for carbon projects with the added benefit of producing unrecoverable natural gas have been proposed (Busch et al., 2008; Chareonsuppanimit et al., 2012; Kang et al., 2011).

Gas adsorption processes on shales and their clay constituents are complex, making it difficult to design ideal conditions for enhanced gas recovery and GCS operations. Moreover, a broad range of mutual CO₂- H₂O solubilities may occur as injected CO₂ contacts formation waters (Spycher et al., 2003). It is therefore essential to investigate the physicochemical interactions of key shale components, such as the smectite mineral montmorillonite, with variably hydrated scCO₂. Montmorillonite is a 2:1 layered phyllosilicate that can swell and shrink by movement of molecules (principally H₂O) in and out of the mineral's interlayer (Cases et al., 1992; Ferrage et al., 2005; Norrish, 1954). Volume changes associated with this intercalation process could have a significant impact on CO₂ storage capacities as well as the porosity and permeability of caprocks.

Previously, we used a combination of specialized *in situ* experimental techniques to indirectly (structural data from XRD and neutron diffraction) and directly (spectroscopic data from IR and NMR, and coherent scattering contrast from neutron diffraction) to demonstrate that CO₂ can intercalate the interlayer region of montmorillonite at supercritical conditions (Ilton et al., 2012; Loring et al., 2014; Loring et al., 2012; Rother et al., 2013; Schaef et al., 2012). Giesting et al. (2012a) and Hemmen et al. (2012) also proposed CO₂ intercalation of montmorillonite under supercritical as well as sub-critical conditions based on *in situ* XRD experiments. More recently, swelling strain experiments with nearly dry montmorillonites produced volume changes in the presence of scCO₂ leading to possible implications about reservoir permeability (de Jong et al., 2014). Loring et al., (2014) used a combination of ATR-IR and transmission-IR to show that the extent of CO₂ intercalation in a sodium-saturated montmorillonite exposed to variably wet scCO₂ was dependent on the sorbed H₂O concentration. The spectroscopic data was tightly correlated to *in situ* XRD data showing that CO₂ intercalation peaked at *d*(001) values corresponding to a one water of hydration (1W) state (i.e., 12.3 to 12.6 Å).

However, there is much that remains unknown, including a quantitative understanding of CO₂ and H₂O partitioning between expandable clays and variably hydrated scCO₂. In particular, Loring et al. (2014) described CO₂ sorption trends but were unable to quantify the concentration of sorbed CO₂ using only IR data. The objective of the current study is to address this knowledge gap and elucidate molecular-level mechanisms that control the partitioning. A unique combination of *in situ* techniques and theoretical simulations were applied. Structural transformations of the clays were characterized by pressurized X-ray diffraction measurements. Sorbed CO₂ and H₂O were quantified with high-pressure IR spectroscopy and quartz crystal microbalance (QCM) titration experiments. Data interpretation was aided by density functional theory calculations to obtain mechanistic descriptions of CO₂ and H₂O intercalation. Results from this work shed light on the mutual interactions of non polar CO₂ molecules and H₂O with inorganic cations and provides insight into processes occurring during geologic carbon storage and secondary natural gas production from shale gas reservoirs.

METHODS

Materials. Naturally occurring montmorillonites (SWy-2 and STx-1) were purchased from the Clay Mineral Repository and have been previously well characterized (Chipera and Bish, 2001; Jaynes and Bigham, 1986, 1987; Madejova and Komadel, 2001; Mermut and Cano, 2001; Mermut and Lagaly, 2001; Olphen and J. J. Fripiat, 1979). STx-1 contains up to 30 wt. % cristobalite which does not interfere with the clay $d(00l)$ reflection series. SWy-2 contains trace quartz which contributes a minor reflection at 3.34 Å. The structural formulae of as-received STx-1 and SWy-2 are $(\text{Ca}_{0.27}\text{Na}_{0.04}\text{K}_{0.01})(\text{Al}_{2.41}\text{Fe}^{3+}_{0.09}\text{Mn}_{\text{tr}}\text{Mg}_{0.71}\text{Ti}_{0.03})\text{Si}_4\text{O}_{10}(\text{OH})_2$ and $(\text{Ca}_{0.12}\text{Na}_{0.32}\text{K}_{0.05})(\text{Al}_{3.01}\text{Fe}^{3+}_{0.41}\text{Mn}_{0.01}\text{Mg}_{0.54}\text{Ti}_{0.02})(\text{Si}_{7.98}\text{Al}_{0.02})\text{O}_{10}(\text{OH})_2$, respectively (Van Olphen and Fripiat, 1979).

Clay samples were size fractionated to $<2\ \mu\text{m}$ following previously described methods (Ilton et al., 2012; Schaef et al., 2012). SWy-2 aliquots were saturated with Ca^{2+} , Na^+ , and Mg^{2+} and STx-1 with Ca^{2+} to produce homoionic samples referred to as Ca-SWy-2, Na-SWy-2, Mg-SWy-2, and Ca-STx-1, respectively. Saturation with ethylene glycol at ambient conditions yielded $d(001)$ values of 16.79-16.99 Å, typical values for these types of homoionic clays (Moore and Reynolds, 1989).

In situ XRD. The swelling properties of the clays were studied in a high pressure X-ray diffraction reactor (HXRD). Procedures for sample preparation, alignment, pattern collection and processing, and reactor pressurization have been described in detail previously (Miller et al., 2013; Schaef et al., 2012). Prior to sealing the clay in the reactor, variable amounts of water (0.0-3.0 μl) were pipetted into the HXRD (the water did not contact the clay). The system was then sealed and equilibrated at 50 °C prior to pressurization with CO_2 . Basal reflections were monitored during equilibration, and steady state was reached within 0.5 hours. To achieve initial 1W or 0W (for the Ca/Mg- and Na-saturated samples, respectively) hydration states, the clay was exposed to a vacuum at 50 °C while the $d(001)$ basal reflection was monitored to verify interlayer collapse.

The $d(00l)$ reflection series was monitored in order to track expansion or contraction of the interlayer region. Four potential hydration states are defined as dehydrated (0 W), monohydrated (1 W), bihydrated (2 W), and trihydrated (3 W), which correspond to intercalation of 0, 1, 2, or 3 planes of H_2O molecules, respectively (Ferrage et al., 2010). At ambient conditions ($\sim 27\ ^\circ\text{C}$ and

1.01 bar), commonly reported $d(001)$ values corresponding to these integral hydration states are 9.6–10.1 Å (0W), 12.3–12.7 Å (1W), 15.0–15.8 Å (2W), and 18.00–18.5 Å (3W) (Ferrage et al., 2005).

In situ IR. *In situ* high-pressure titrations with IR detection were performed at 50 °C and 90 bar using a fully automated scCO₂ generation and delivery apparatus coupled to a high-pressure IR cell with both transmission and attenuated total reflection (ATR) IR optics. Details of the apparatus, cell, and the method for performing titrations of clay samples are reported elsewhere (Loring et al., 2014; Thompson et al., 2014). The high-pressure cell containing the clay was washed with scCO₂ at 50 °C and 90 bar and then evacuated to approximately 500 mTorr. The procedure was repeated three times. However, ATR IR still detected H₂O associated with the clay. In order to determine this initial sorbed H₂O concentration, an independent experiment was performed where a known mass of the CO₂ washed clay was titrated with formamide in scCO₂ at 50 °C and 90 bar. Formamide has a higher dielectric constant than H₂O, promoting desorption of H₂O into the scCO₂ where the H₂O was quantified by transmission IR. ATR IR spectra were collected after each addition of formamide, and when the HOH bending mode of sorbed H₂O was no longer detected, a transmission IR spectrum was collected. The integrated absorbance of the HOH bending mode of H₂O in the scCO₂ from this transmission IR spectrum was used along with a calibration curve and the volume of the cell to determine the number of moles of H₂O sorbed per gram of CO₂ washed clay.

Quartz crystal microbalance (QCM). Micro gravimetric measurements from the QCM followed a procedure recently described by Schaef et al., (2014). 7–30 µg of clay were deposited on the active area of one or both sides of the quartz crystal and dried at 50°C. The system was evacuated to $\sim 1 \times 10^{-3}$ Torr) at 50°C, and the clays dehydrated to a sub-1W (Ca-SWy-2) or 0W (Na-SWy-2) hydration state. The clay was then exposed to N₂ or CO₂ at ~ 5 –8 bar increments, and the crystal frequencies were recorded after stabilizing. Pressurization typically occurred over a 2 to 8 hour period, followed by evacuation to check if crystal frequencies were consistent with pre-pressurization values. Corrections for pressure (Cassiede et al., 2010), fluid viscosity (Rechendorff et al., 2007), and surface roughness (Rechendorff et al., 2007) were applied to obtain a delta frequency representative of a mass change of the crystal (g) per active surface area (cm²). Root-mean-square (rms) roughness values for each clay-coated crystal were estimated

from the N₂ run where 1 monolayer of N₂ sorbed to the active crystal surface area (0.42 cm⁻²) and mineral.

Theoretical Simulations. We employed density functional theory (DFT) based molecular simulations utilizing a Ca-rich montmorillonite analogue developed by Lee et al. (2014). The simulations were done within the generalized gradient approximation (GGA) with the exchange correlation functional of Perdew, Burke and Ernzerhoff (PBE) (Perdew et al., 1996) as implemented in the CP2K package (1994; VandeVondele et al., 2005). Dispersion corrections were taken into account using Grimme's et al. third-generation corrections (DFT-D3) (Grimme et al., 2012). This general approach has been found to yield accurate energies for adsorption on ionic surfaces (Ehrlich et al., 2011). The core electrons in our systems were described by norm-conserving pseudopotentials (Goedecker et al., 1996; Krack, 2005), while the valence wave function was expanded in terms of double-zeta quality basis sets optimized for condensed systems to minimize linear dependencies and superposition errors (VandeVondele and Hutter, 2007). An additional auxiliary plane-wave basis set with a 400-Ry cutoff was used for the calculation of the electrostatic terms (Lippert et al., 1997). The Γ -point approximation employed for the Brillouin zone integration was deemed appropriate because of the significant size of the supercell.

Three types of DFT calculations were performed for this work: (1) CO₂ adsorption energies on external surfaces, (2) interlayer spacing calculations at variable CO₂:H₂O concentrations matching experimental conditions, and (3) energetics of CO₂ intercalation. Our computational models were based on a Ca-montmorillonite developed by Viani et al. (2002) to study the disorder of X-ray powder patterns with unit cell Al₄Si₈O₂₄Ca₂. For the simulations, we used a modified 2x1x1 supercell containing 2Ca²⁺ in the interlayer regions and 4H⁺ in the octahedral unit, corresponding to an overall neutral simulation cell [Al₈Si₁₆O₄₄(OH)₄·2Ca] with initial lattice parameters of $a=10.48$ Å, $b=9.03$ Å, $c=10.06$ Å, $\alpha=90.9^\circ$, $\beta=99.3^\circ$ and $\gamma=90^\circ$. The resulting layer charge, which originates from deprotonated hydroxyls in the octahedral layer, is close to that of a mica. As discussed in the text, this will inhibit expansion to some degree for any given concentration of interlayer molecule. However, the focus is on trends, and the model yields a systematic response to both H₂O and CO₂ intercalation that is generally consistent with experimental observations. A series of full cell optimizations at external pressure $P=90$ bar

were conducted with variable numbers of H₂O and CO₂ molecules in the interlayer region to determine corresponding $d(001)$ values (see Table S1). Configurational sampling of the systems representing sub-1W, 1W, and 2W states, was mitigated through the choice of different starting configurations, some based on structures captured from *ab initio* MD simulations reported by Lee et al (2014).

To examine CO₂ adsorption on Ca-montmorillonite, molecular models of 2x2x2 supercells were used. In these, the interlayer space was kept at the fixed distance of 12.5 Å, corresponding to the $d(001)$ values for ~1W state with intercalated CO₂, including a fixed number of 6 H₂O and 4 CO₂ (see SI, Figure S1). A vacuum of 15.4 Å was used in the (001) direction (on top of the second mineral layer) to minimize the interaction between adsorbed species and the periodic image of the surface. We then systematically added two CO₂ molecules on the surface up to a total of 16 to cover the range of experimental CO₂ densities encountered in the experiments, and roughly corresponding to an increase of 0.05 g/cm³ in the CO₂ density at a time. Each system was equilibrated for a short time (~5 ps) at temperatures similar to the experiment and then slowly annealed and optimized to obtain the final energy. We optimized several different geometries with 1 and 2 adsorbed CO₂ molecules to determine the most favorable binding sites. Finally, a simulation with just CO₂ at experimental conditions (supercritical, 50 °C, 90 bar) was performed, followed by annealing and optimization to extract an average energy for the scCO₂(1) system, $E[(sc)CO_2(l)]$. The intercalation/adsorption energies used in Figure 6 and Figure 7 at given hydration states were calculated as energy differences (Glezakou et al., 2009) based on a chemical equilibrium of the general form:

$$\Delta E_{\text{rxn}} = [E[\text{Clay}/(\text{H}_2\text{O})_n/(\text{CO}_2)_m] - E[\text{Clay}/(\text{H}_2\text{O})_n/(\text{CO}_2)_{m-q}] - q \times E[(\text{sc})\text{CO}_2(l)]]/q$$

where for the intercalation model $n=2-16$, $m=0$, and $q=1-6$, and for the adsorption model, $n=6$, $m=4$ representing intercalated species in the interlayer space at ~1W of the mineral, and $q=1-16$ for CO₂ adsorbed on the external surface.

RESULTS AND DISCUSSION

Structural Changes. Conditions and $d(001)$ values for HXRD experiments are listed in **Table S2**. The measured final $d(001)$ values represent a mixture of both H₂O and CO₂, which cannot be

determined by HXRD; so the % H₂O saturation values are likely overestimates and do not take into account partitioning of H₂O between the clay and the scCO₂. In **Figure 1**, the closed circles represent $d(001)$ values at 50 °C prior to exposure of Na-SWy-2 to scCO₂. Open squares indicate $d(001)$ after equilibration with scCO₂. Arrows illustrate the positive, negative, and combination volume changes resulting from scCO₂ exposure. The $d(001)$ values for the corresponding 1W, 2W, and 3W hydration states are marked by gray shading (Ferrage et al., 2005). Changes in % H₂O saturation yielded a stepwise $d(001)$ profile, as a function of %H₂O saturation, after exposure to scCO₂ (**Figure 1**), where a decrease in $d(001)$ values can occur even in the presence of free water. Subjecting Na-SWy-2 to a vacuum at 50°C removed all measurable H₂O from the interlayer and collapsed the basal spacing from 12.62 Å (1W) to 9.96 Å (0W) (Berghout et al., 2010; Ferrage et al., 2005). A poorly formed $d(002)$ reflection, visible only in the 0W state, is positioned at 4.86 Å (**Figure S2**). With near equal intensity, the $d(003)$ maximum at 3.21 Å (vacuum) replaces the less intense $d(004)$ reflection (3.159 Å) observed under atmospheric conditions. Pressurization with anhydrous scCO₂ has negligible impact on $d(00l)$ series peak positions (**Figure 1 and Figure S2**), indicating that CO₂ cannot access adsorption sites in the interlayer if the clay is initially in a 0W state.

Ca-SWy-2 exhibited stepwise hydration/dehydration behavior as a function of %H₂O saturation in scCO₂ at 50°C and 90 bar (**Figure 2**). Exposure of an initially sub-1W sample to anhydrous scCO₂ increased $d(001)$ by ~0.5 Å. In contrast, $d(001)$ values decreased slightly for clays in an initial ~2W hydration state. Sub 3W Ca-SWy-2 dehydrated to 2W unless scCO₂ was oversaturated with respect to H₂O. Interestingly, both 2W and ~3W hydration states were detected near H₂O saturation in scCO₂ (**Table S2 and Figure 2**). The bimodal reflection was also observed for the Ca-STx-1 (**Figure S3**) as well as Na-STx-1 (Ilton et al., 2012). Comparable trends were observed for Ca-STx-1, Na-SWy-2, and Mg-SWy-2 (**Table S2, Figure 1, and Figure S3**). As expected (Ferrage et al., 2005), montmorillonite containing divalent interlayer cations (i.e. Ca, Mg) required less %H₂O saturation to achieve the same $d(001)$ values compared to those containing monovalent cations (i.e. Na).

In summary and in accord with previously cited experimental work (Giesting et al., 2012a; Ilton et al., 2012; Loring et al., 2012; Schaef et al., 2012), scCO₂ can either diffuse into or extract H₂O from the interlayer region of montmorillonites to produce volumetric changes. If the initial

hydration state of the clay is low (sub 1W), yet high enough to allow interlayer access, CO₂ intercalation induces a positive volume change manifested by 0.5-0.8 Å increases in *d*(001). Higher hydration states ($\geq 2W$) presumably released some interlayer H₂O to scCO₂, and *d*(001) values decreased. However, when scCO₂ is oversaturated with respect to H₂O, the montmorillonite structure expands from a sub-3W to a full 3W after exposure to scCO₂ (Schaefer et al., 2012). At this point, it is not clear whether this small expansion is caused by intercalation of CO₂ or H₂O.

Quantification of CO₂ Sorption. CO₂ sorption isotherms for sub-1W Ca-SWy-2 and 0W Na-SWy-2 were generated using QCM at 50°C and 5-125 bar (see **Table S3** for experimental conditions). 0W Na-SWy-2 recorded only external CO₂ adsorption whereas sub-1W Ca-SWy-2 sorbed CO₂ on external surfaces and in the interlayer region. The concentration of interlayer CO₂ is estimated from the difference in sorption between the two clays. Although using a fully collapsed Ca-clay would have been optimal for estimating external sorption of CO₂, harsher measures are required with potential attendant artifacts

There is a distinct difference in behavior between the two clays (**Figure 3** and **Table 1**): Ca-SWy-2 sorbed ~0.45 mmol of CO₂/g clay at only 5-8 bar, and the sorption profile is nearly linear where the rate of sorption decreased with increasing pressure throughout the subcritical CO₂ regime. Supercritical conditions are marked by a transition to a higher rate of sorption until a maximum is reached at ~90 bar. Additional pressurization leads to a decrease in sorbed CO₂ concentrations, similar to that reported for kaolinite (Schaefer et al., 2014). In contrast, Na-SWy-2 sorbs minimal CO₂ at low CO₂ pressure (0.02 mmol CO₂/g), likely reflecting restricted access of CO₂ to the clay interlayer space, and the sorption profile indicates a marginal increase in sorption rate with increasing pressure until a maximum average CO₂ concentration of ~0.45 mmol CO₂/g clay is reached at ~90 bar. Although not as pronounced as for Ca-SWy-2, desorption occurs above this maximum until the ending pressure. The net effect is that the difference in sorption between the two clays decreases with increasing pressure until ~60 bar; from ~60 to 125 bar the difference in sorption is nearly constant.

The results suggest that given an accessible interlayer, intercalation of CO₂ is the dominant process at low pressure. This is consistent with HXRD studies that recorded positive and no

interlayer expansion for sub 1W Ca-SWy-2 and 0W Na-SWy-2, respectively, at low CO₂ pressures (Giosting et al., 2012b). At ~5-8 bars ~0.43 mmol of CO₂/g sorbed in the interlayer region of Ca-SWy-2 and only 0.02 mmol CO₂/g on the external surfaces (**Figure 3**). The interlayer CO₂ concentration varies throughout the pressure range, approaching a maximum concentration of ~0.81 mmol CO₂/g at ~90 bars. Although the total internal interlayer region has appreciably more surface area than the external basal surfaces, the fact that the ratio of interlayer/external CO₂ decreases from ~22 to ~1.8 from low pressure to 90 bars signals that adsorption of CO₂ to the external basal plane is becoming more favorable. This is consistent with calculations presented later.

Spectroscopic characterization and quantification of CO₂ and H₂O intercalation. High-pressure ATR-IR and transmission-IR were used to directly measure H₂O and CO₂ partitioning between Ca-SWy-2 and scCO₂. Sorbed H₂O concentrations and *d*(001) values for Ca-SWy-2 are plotted versus %H₂O saturation in **Figure 4**. Mg-SWy-2 displayed similar behavior (**Figure S6**). The smooth increase in sorbed H₂O seems inconsistent with the stepwise increase in *d*(001) values. While sorption to the external clay surfaces and into inter-particle pore space contributes to total sorbed H₂O (Cases et al., 1992; Ferrage et al., 2005; Johnston et al., 1992; Xu et al., 2000), H₂O sorption is likely dominated by uptake in the interlayer space below about 70% H₂O saturation (Ferrage et al., 2010; Ferrage et al., 2005; Loring et al., 2014). Two conceptual models have been proposed to reconcile the sorbed H₂O and *d*(001) trends (Loring et al., 2014). The space-filling model assumes that the clay sample is homogeneous with respect to the hydration state at any given %H₂O saturation (Cases et al., 1992; Cases et al., 1997; Hatch et al., 2012). Only a minimum amount of H₂O is required to expand the clay from one hydration state to another which creates void space. Once this expansion occurs, however, void space can continue to intercalate H₂O with increasing %H₂O saturation without further swelling. On the other hand, the hydration-heterogeneity model (Cases et al., 1992; Ferrage et al., 2010; Ferrage et al., 2005; Hatch et al., 2012) posits that the clay is heterogeneously hydrated; *d*(001) only appears to change in stepwise fashion because *d*(001) values at the peak maximum were plotted. In contrast, interpretation of careful XRD profile modeling (Ferrage et al., 2005) has suggested that an expandable clay might exist as a distribution of integral hydrations states (i.e., 0W, 1W

and 2W) at a given %H₂O saturation. Our data is not sufficiently resolved, due to technical constraints, to evaluate this possibility.

ATR IR spectra of Ca- and Mg-SWy-2 are shown in **Figures S7 and S8**. At low sorbed H₂O, wavenumbers for the OH stretching and HOH bending modes are indicative of H₂O coordinated to interlayer cations (Johnston et al., 1992; Xu et al., 2000). With increasing sorbed H₂O, the frequency of the OH stretching and HOH bending bands shift towards the wavenumber for bulk water (Johnston et al., 1992; Xu et al., 2000). The bulk scCO₂ signal (no clay) was subtracted from the spectrum of scCO₂ in the presence of clay (Loring et al., 2014), isolating an asymmetric CO stretching band at about 2343 cm⁻¹ (Loring et al., 2014). The shoulder near ~2356 cm⁻¹ is related to a “mirage-like” optical distortion caused by the presence of the clay overlayer, as identified by Loring et al (Loring et al., 2014). The shapes and positions of the difference spectra (**Figures S9 and S10**) are similar to those of CO₂ dissolved in bulk water, which might be due to CO₂ associated with H₂O in the interlayer region (Loring et al., 2014). In particular, the shift in the CO stretching band predicted by CO₂ solvation of the interlayer cation at low H₂O cannot be resolved in the present spectra (Criscenti and Cygan, 2013; Lee et al., 2014; Myshakin et al., 2013).

In order to quantify CO₂ adsorption with ATR-IR, the area under the asymmetric CO stretching band (Figure S9) for sub-1W Ca-SWy-2 at ~0% H₂O saturation was normalized to the total CO₂ concentration (~1.3 mmol/g) derived from the QCM measurement (**Figure 3**). Total sorbed CO₂ concentrations at higher %H₂O were then anchored to this point. The results are given by the solid red circles in **Figure 5**. A similar, but qualitative plot for Mg-SWy-2 is shown in **Figure S11**. Total sorbed CO₂ decreases from ~0 to ~100% H₂O saturation but appears to temporarily plateau between 20 and 25% H₂O saturation; this plateau did not occur with any other clay and is not discussed further. Desorption of CO₂ begins to plateau again around 12 mmol/g sorbed H₂O (**Figure 5 and S11**). The analysis can be taken a step further: Given the assumption that CO₂ desorbs from both the external surfaces and interlayer region proportionally as H₂O is titrated into the system, then the concentrations of externally adsorbed (open circles in **Figure 5**) and intercalated CO₂ (half open/solid circles in **Figure 5**) can be calculated across the entire %H₂O saturation range. The estimated intercalated H₂O:CO₂ ratios are ~1.2 and ~40 at ~0 and ~70% H₂O saturation in scCO₂, respectively.

The ratio of intercalated CO₂ and H₂O to one interlayer Ca²⁺ can be estimated for the equivalent 1W state at nominal 0% H₂O saturation using 0.382 mmol Ca²⁺/g of Ca-SWy-2 (Rutherford et al., 1997). Designation of Ca-SWy-2 as an equivalent 1W clay is based on the 12.4 Å *d*(001) value obtained when the sub 1W clay with *d*(001) = 11.78 Å was exposed to anhydrous scCO₂ (**Figure 2**). Intercalated H₂O and CO₂ concentrations were 0.971 and 0.81 mmol/g clay, respectively, which translates to 2.6 H₂O and 2.17 CO₂ per Ca²⁺. Therefore, the estimated (CO₂+H₂O)/Ca ratio is 4.8. Given that a sub 1W Ca montmorillonite has 4.28 H₂O per interlayer cation (Ferrage et al., 2005), the data are consistent with intercalation of CO₂ expanding the sub-1W clay to the equivalent 1W state. We note that our value for total intercalated H₂O + CO₂ is low relative to Ferrage's estimated H₂O concentration for a *d*(001) value of 12.65 Å. This apparent discrepancy is likely due in part to the fact that we ascribed the *d*(001) value to the maximum peak height and did not model the peak, as done in Ferrage et al. (2005), to draw out the percentage of 0W layers.

In contrast to Ca- and Mg-SWy-2, which could not be dehydrated much below the 1W state (excluding draconian measures), previous work using Na-SWy-2 initially in the 0W state clearly showed that sorbed CO₂ sharply increased as the clay transitioned from 0W to 1W (Loring et al., 2014). This result was deemed consistent with the space-filling model discussed above; i.e. CO₂ fills interlayer void space that is created when the clay is propped open after a minimum concentration of H₂O hydrates the interlayer cations. However, a similar spike in the CO₂ concentration would be expected if new void space is exposed during the transition from the 1W to the 2W hydration state (Loring et al., 2014). Consequently, the space-filling model fails to explain the continuous decrease in sorbed CO₂ during the 1W to 2W transition for all three clays. Instead, we suggest that the trends in sorbed CO₂ concentrations are more comprehensively explained by the hydration-heterogeneity model, which posits that ~integral hydration states contain fixed but different CO₂ concentrations (Loring et al., 2014). If interlayer CO₂ concentrations are zero, relatively high, and relatively low for the 0W, 1W and 2W states, respectively, then varying linear combinations of integral hydrations states could explain the CO₂ sorption trends with increasing % H₂O saturation in scCO₂.

Nonetheless, both models are conceptual, with no hard independent data to distinguish them. Taken at its extreme, the space-filling model does not require any attraction between the clay and

CO₂. However, theory (see below) suggests that CO₂ can partially solvate interlayer cations. In this regard, density functional theory was used in the following section to evaluate the energies for CO₂ intercalation at different H₂O and CO₂ concentrations. Theory was also used to calculate CO₂ surface adsorption energies and the response of *d*(001) values to varying intercalation of H₂O and CO₂.

Computational modeling. Molecular simulations provided mechanistic insight into the sorption behavior of CO₂ on the external surfaces of Ca-SWy-2. As illustrated in **Figure 6**, the overall interaction energy between the surface and adsorbed CO₂ is more favorable than the average CO₂-CO₂ interaction in bulk scCO₂ (-0.2 eV/CO₂, green line) from ~0.15 to ~0.32 g/cm³. The adsorption curve implies the formation of a CO₂ film marked by adsorption energies less than -0.2 eV/CO₂, which is the average CO₂ interaction in the bulk at similar conditions. It reaches a maximum (minimum in adsorption E) at ~0.28 g/cm³ and for densities... greater than ~0.32 g/cm³, the CO₂ layer becomes increasingly 'bulk-like' and desorbs. Consequently, the simulations are consistent with the the QCM data for Na-SWy-2 (**Figure 3**) and indicate that Na-SWy-2 is a good analogue for the Ca-SWy-2 external surface, at least in terms of trends, which supports our approach to distinguishing intercalated and externally adsorbed CO₂.

A series of full simulation cell optimizations for the Ca montmorillonite analogue (Lee et al., 2014) were performed over a range of intercalated H₂O and CO₂ concentrations. For 1-3 H₂O (corresponding to ~2.4 to ~4 mmol H₂O/gram clay) per 8 Si (1/2 our simulation cell), calculated *d*(001) values ranged from 10.25 to 11.29 Å, all within the sub 1W state. For reference, simulated XRD profiles of Ca-SWy-1 by Ferrage et al., (2005) yielded *d*(100) = 11.65 Å for ~1.5 H₂O per 8 Si. The lower calculated *d*(001) values reflect, in part, the higher layer charge of the model clay relative to the natural material. Nonetheless, intercalation of 0.5-3 CO₂ to the 1-3 H₂O hydrated clay model, yields 3-12% increases in *d*(001) values. These relative expansions bracket the experimentally observed ~5 % increase in *d*(001) when the sub 1W clay (11.78 Å) was exposed to scCO₂ and expanded to an equivalent 1W state. With increasing H₂O, theory describes a transition between 1W and 2W states (i.e., 1 layer versus 2 layers of H₂O) from 3 to 4 H₂O. A 2 layer hydrate was stable from 5 to 8 H₂O (~6.6 to 10 mmol H₂O/g clay), the highest H₂O concentration considered, where the corresponding calculated *d*(001) values range from 14.2 to 14.6 Å. Experimentally determined *d*(001) values for Ca-montmorillonite are consistently

larger (15.1 - 15.51 Å) at only 6.6 H₂O per unit cell (Ferrage et al., 2005), which again is due to the greater layer charge of the clay model.

DFT calculations were used to evaluate the energy (entropy not considered) change as CO₂ partitions between the supercritical fluid and the interlayer region as a function of H₂O concentrations in the clay as explained in the Theory section. The trend, shown in **Figure 7**, is broadly consistent with the experimentally observed decrease in CO₂ sorption with increasing sorbed H₂O (**Figure 5**) and points to a reactivity (i.e., binding) based driving force for CO₂ intercalation as opposed to a passive space filling mechanism. For example, at relatively low H₂O concentration, CO₂ intercalation is thought to be mainly stabilized by cation/CO₂ binding interactions (Criscenti and Cygan, 2013; Lee et al., 2014; Myshakin et al., 2013). However, it should be kept in mind that the ATR IR data did not isolate any features attributable to a CO₂-cation interaction.. The energy trends for the 1 and 2 (and 4 to a lesser extent) CO₂ per unit cell simulations indicate increased stabilization between 2 and 4 mmol/g sorbed H₂O in contrast to the experimentally observed decrease in CO₂ sorption (**Figure 7**). It is possible that the extra layer charge in the simulation cell relative to the naturally occurring clay requires more H₂O to expand the interlayer region to favor intercalation of CO₂. On the other hand, while the simulated data involves the 'idealized' situation of sparsely hydrated clay, in reality, our experimental measurements are subject to a more inhomogeneous environment (Ferrage et al., 2005) including localized H₂O clustering that could drive CO₂ off. Inhomogeneous hydration of the clay cannot be very well captured by periodic approximation of finite cells, which could account for the increased CO₂ stabilization predicted for 2-4 mmol/g adsorbed water. However, the more important point to make is that the estimated DFT-based energies of intercalation do indicate the propensity of the system to absorb CO₂ at these lowest hydration states. This tendency becomes increasingly less favorable, as indicated by the positive intercalation energies, as the system transitions to the 2W state. These trends, as captured by the simulations, are in qualitative agreement with the experimentally observed decrease in CO₂ sorption and support the concept of CO₂-cation interactions as the driving force for CO₂ intercalation under low water environments.

Conclusions

In situ XRD indicates that the swelling and contraction of montmorillonite under geologic sequestration conditions is sensitive to the %H₂O saturation in scCO₂. The magnitude of this behavior may be particularly relevant for caprocks that seal potential CO₂ storage formations but have been fractured for extraction of oil and gas, where the proppant changes the balance of lithostatic to hydrostatic pressure. Further, hydration of swelling clays can both facilitate and decrease CO₂ intercalation under reservoir conditions. For Na montmorillonite, CO₂ intercalation peaks from ~0W to 1W equivalent hydration states, and then decreases with further hydration (Loring et al., 2014). These observations were extended to Ca and Mg saturated montmorillonites in the present study, which puts an upper limit on the capacity of clays to sequester CO₂. Theoretical computations of very low H₂O systems demonstrate that CO₂ can solvate inorganic ions (Cygan et al., 2012; Lee et al., 2014; Myshakin et al., 2013). As H₂O and the H₂O/CO₂ ratio increase, H₂O displaces CO₂ from the cation solvation shell. Given that cation-H₂O interactions are on average ~30% stronger than cation-CO₂ interactions (Criscenti and Cygan, 2013), the displacement of CO₂ from the solvation shell of the interlayer cations reduces the enthalpic driving force for CO₂ intercalation and places a limit on how much CO₂ can actually intercalate montmorillonite. Theoretical studies (e.g., (Myshakin et al., 2013)) have also shown that artificially increasing interlayer CO₂ (i.e., the clay is not open to a reservoir) leads to segregation of CO₂ from H₂O. This lack of mixing would also favor CO₂ partitioning into the scCO₂ phase. The fact that such a state is never reached is supported by the ATR-IR data which, instead indicates that interlayer CO₂-H₂O interactions dominate over a broad range of sorbed water concentrations. Regardless, the processes described here will be at play during geologic carbon sequestration and its *doppelgänger*, secondary utilization of scCO₂ for extracting methane and oil from tight shale formations.

ASSOCIATED CONTENT

Supporting Information

Supporting Information includes (1) a table for optimized cell parameters and d₀₀₁ spacings as a function of number of H₂O with and without CO₂, (2) a table for *in situ* high-pressure X-ray diffraction parameters, (3) a table showing the measured frequencies for individual quartz crystals used in the quartz crystal microbalance, (4) a figure showing the computational model for CO₂ adsorption studies on Ca-montmorillonite, (5) a figure showing the X-ray diffraction patterns of

Ca- and Na-SWy-2 clays during exposure to vacuum and scCO₂, (6) a figure showing the *d*(001) basal spacing of the Ca-STx-1 and Mg-SWy-2 clays before and after exposure to scCO₂ and variable amounts of hydration, (7) two figures showing the integrated absorbance from transmission IR under the HOH bending mode of water dissolved in scCO₂ for the Ca- and Mg-SWy-2 clay, (8) a figure showing the integrated absorbance from transmission IR under the HOH bending mode of water dissolved in scCO₂ versus total water concentration for Mg-SWy-2 clay, (9) four figures showing ATR IR spectra of as a function of sorbed water concentration for Ca- and Mg-SWy-2 clays, and (10) a figure of the integrated absorbance of the asymmetric CO stretching band as a function of the sorbed water concentration for a titration of Mg-SWy-2 with water at 50 °C and 90 bar. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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Table 1

Table 1. CO₂ concentrations as determined by QCM for the Ca- and Na-SWy-2 at low (5-8) bar and high (90 bar) pressure (50°C).

	Hydration State	Sorbed CO ₂ ~5-8 bar (mmol/g)	Sorbed CO ₂ ~90 bar (mmol/g)
Ca-SWy-2	sub 1 W	0.45 ± 0.05	1.26 ± 0.03
Na-SWy-2	0W	0.02 ± 0.01	0.45 ± 0.09

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7