

Tipping Point for Expansion of Layered Aluminosilicates in Weakly Polar Solvents: Supercritical CO₂

Herbert T. Schaefer^{1*}, Narasimhan Loganathan², Geoffrey M. Bowers³, R. James Kirkpatrick², A. Ozgur Yazaydin^{2,4}, Sarah D. Burton⁵, David W. Hoyt⁵, K. Sahan Thanthiriwatte⁶, David A. Dixon⁶, B. Peter McGrail¹, Kevin M. Rosso¹, Eugene S. Ilton^{1*}, John S. Loring^{1*}

¹Pacific Northwest National Laboratory, Richland WA 99356

²College of Natural Science, Michigan State University, East Lansing, MI, 48824

³Department of Chemistry and Biochemistry, St. Mary's College of Maryland, St. Mary's City, MD 20686

⁴Department of Chemical Engineering, University College London, London, WC1E 7JE, United Kingdom

⁵William R. Wiley Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99356

⁶Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487

KEYWORDS: carbon dioxide; montmorillonite; intercalation; Molecular dynamics; interlayer expansion.

ABSTRACT: Layered aluminosilicates play a dominant role in the mechanical and gas storage properties of the subsurface, are used in diverse industrial applications, and serve as model materials for understanding solvent-ion-support systems. Although expansion in the presence of H₂O is well known to be systematically correlated with the hydration free energy of the interlayer cation, in environments dominated by non-polar solvents (i.e. CO₂), uptake into the interlayer is not well-understood. Using novel high pressure capabilities, we investigated the interaction of dry supercritical CO₂ with Na⁺-, NH₄⁺-, and Cs⁺-saturated montmorillonite, comparing results with predictions from molecular dynamics simulations. Despite the known trend in H₂O, and that cation solvation energies in CO₂ suggest a stronger interaction with Na⁺, both the NH₄⁺- and Cs⁺-clays readily absorbed CO₂ and expanded while the Na⁺-clay did not. The apparent inertness of the Na⁺-clay was not due to kinetics, as experiments seeking a stable expanded state showed that none exists. Molecular dynamics simulations revealed a large endothermicity to CO₂ intercalation in the Na⁺-clay, but little or no energy barrier for the NH₄⁺- and Cs⁺-clays. Indeed, the combination of experiment and theory clearly demonstrate that CO₂ intercalation of Na-montmorillonite clays is prohibited in the absence of H₂O. Consequently, we have shown for the first time that in the presence of a low dielectric constant gas swelling depends more on the strength of the interaction between interlayer cation and aluminosilicate sheets and less on that with solvent. The finding suggests a distinct regime in layered aluminosilicates swelling behavior triggered by low solvent polarizability, with important implications in geomechanics, storage and retention of volatile gases, and across industrial uses in gelling, decoloring, heterogeneous catalysis, and semi-permeable reactive barriers.

INTRODUCTION

Layered aluminosilicates have unique properties that emerge from their quasi-2D structure, composition, permanent layer charge, and charge-balancing interlayer cations. As a primary source of nanoporosity^{1,2} gas absorptivity^{3,4}, and ductility⁵ in sedimentary rocks, their specific behavior, even in small concentrations, can control the geomechanical response of caprocks that seal reservoir formations⁶ or the extraction of natural gas from organic rich shales that are the source rocks driving the present fracking boom.⁷ They are also used widely in industrial applications that range from catalytic substrates⁸ to metal and gas sorbents^{9,10} to reactive barrier materials.¹¹

A key characteristic is their ability to expand or contract by absorbing or ejecting solvent and ions in response to changing fluid chemistry.¹² Layered aluminosilicates known as smectites are of particular interest, because they can swell substantially in the presence of certain volatiles¹³⁻¹⁴ due to incorporation of these species in their interlayer galleries. The extent to which swelling will be significantly altered when exposed to fracking fluids during gas extraction from shales and supercritical CO₂ (scCO₂) during and after injection of CO₂ into geologic reservoirs is often a crucial unknown.¹⁵ Unlike swelling performance requirements for clay based barriers in nuclear repositories¹⁶, geologic exploration operations using non-aqueous based technologies (i.e. scCO₂) are

designed to avoid clay swelling¹⁷ to minimize threats to formation permeability.

Solvent selectivity in smectite swelling is not comprehensively well understood; while their swelling behavior when exposed to H₂O is well known¹⁸⁻²⁰, in multiphase and non-aqueous fluids questions remain regarding the underlying forces that lead to solvent uptake and expansion of the interlayer region. With respect to H₂O, the degree of H₂O intercalation and induced swelling largely depends on the hydration free energy of the interlayer cation.²¹⁻²² This is best demonstrated by comparing swelling behaviors of Na⁺ montmorillonites¹⁹, which maintain two layers of hydration (2W) to the identical clay containing Cs⁺, a so-called swelling hindrance interlayer cation, that restrict hydration to a 1W state.²¹ With respect to weakly polar solvents such as CO₂, recent laboratory studies have clearly demonstrated reversible volumetric transformations of smectite minerals due to exposure to gaseous CO₂ (CO_{2(g)}) or scCO₂.^{13, 23-30} For example, a number of studies^{13, 28} have reported increased basal spacings when montmorillonite with less than a full layer of H₂O molecules (sub 1W) was exposed to scCO₂, evidence that CO₂ enters the interlayer at least under relatively low H₂O chemical potentials. A striking observation was that H₂O and CO₂ intercalation was both synergistic and competitive: fully collapsed Na-montmorillonite neither expanded nor sorbed CO₂ into the interlayer region when exposed to dry scCO₂.^{26, 31-33} However, small additions of H₂O to scCO₂ promoted CO₂ intercalation up to a critical H₂O concentration beyond which H₂O expelled CO₂ from the interlayer region. An intuitive explanation is that because the free energy of solvation for H₂O-Na⁺ in the interlayer is expectedly larger than that for Na-CO₂, even at relatively low H₂O concentrations hydrated or partially hydrated Na⁺ essentially props the interlayers open, allowing CO₂ to enter as secondary outcome. Indeed, calculated solvation energies for Na⁺ in bulk water and scCO₂³⁴ show that the solvation energies for Na⁺ in scCO₂ are ~50% less than for Na⁺ in water. What is missing from such observations is a fundamental understanding of the behavior of the system in the complete absence of water. In other words, can nonpolar solvents, which do not have as strong an interaction with interlayer cations, drive open the interlayer space and, if so, why and under what conditions? A cation solvation-based interpretation alone ignores the importance of cation interaction with the aluminosilicate framework.

Probing the interactions of CO₂, interlayer cations, and the aluminosilicate structural units within nano-crystallites, a common size range for these minerals, is challenging. Confinement in the nanometer-scale interlayer space may alter the equilibrium configurations of relevant species. Theoretical studies have provided some insight into energetic barriers to intercalation, solvation of interlayer cations by CO₂, as well as the thermomechanical properties of clays.³⁵⁻⁴² Calculations by Makaremi et al.⁴⁰, in the absence of H₂O, suggest a large energy barrier for CO₂ intercalation into a fully collapsed Na-montmorillonite at both supercritical and non-supercritical conditions. The results also show that an expanded state near $d(001) \approx 12.3$ Å is metastable. The presence of an energy barrier to CO₂ intercalation is consistent with the experiments discussed above. Whether a stable expanded state for Na-montmorillonite/CO₂ exists or not has never been determined experimentally.

Enabled by novel *in situ* capabilities, here we explore the balance between cation-aluminosilicate and cation-CO₂ interactions with respect to CO₂ intercalation and swelling. We vary interlayer monovalent cation radius by using Na⁺, NH₄⁺, and Cs⁺ to systematically tune the strength of the interaction with the aluminosilicate sheet and their solvation free energies with CO₂. Similar to H₂O-cation interactions, classical molecular dynamics (MD)³⁴ and

high-level *ab initio* calculations (**Figure 1**) suggest that CO₂-cation solvation energies decrease in magnitude with increasing cation size (or charge density) from Na⁺ → Cs⁺. However, the solvation energies for CO₂-cation are on the order of 50% lower than for H₂O. Consequently, we hypothesize that the relatively low CO₂-cation solvation energies will highlight the interaction of the interlayer cation with the aluminosilicate structural units. Three dry montmorillonites (Na⁺, NH₄⁺, or Cs⁺ saturated SWy-2) were reacted with anhydrous scCO₂ and characterized in detail *in situ*. If the clays with the larger cations (NH₄⁺ or Cs⁺) expand but Na-clay does not, then the expansion cannot be attributed to the strength of the solvent interaction with the interlayer cation but rather the strength of the cation interaction with aluminosilicate sheet surfaces. However, this observation would not unambiguously identify the cause of CO₂ intercalation per se, because the propping effect of larger cations conceptually can enhance CO₂ diffusivity and uptake.⁴⁵ We directly test this by performing experiments that evaluate if the clay remains expanded or collapses once the “props” are removed, thus constraining the possible existence of a stable expanded state for the Na-montmorillonite/CO₂ system. Modifications to the clay structure were probed with x-ray diffraction (XRD), while changes in the CO₂ chemical environment were analyzed using infrared (IR) spectroscopy. Perturbations in the CO₂ molecules in the interlayer, including information on CO₂-cation interaction, were analyzed by magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. All measurements were performed on the fluid/clay system *in situ* under controlled pressurized conditions. Molecular dynamics simulations at the same conditions using the Grand Canonical ensemble (GCMC) were used to map the free energy landscape as a function of CO₂ intercalation and interlayer spacing for model Na⁺, NH₄⁺, and Cs⁺ clay structures. Collectively, in contrast to swelling behavior in H₂O systems, our findings demonstrate that cation-clay interactions play the commanding role relative to solvation of interlayer cations for clay expansion in weakly to non-polar solvents such as CO₂.

RESULTS AND DISCUSSION

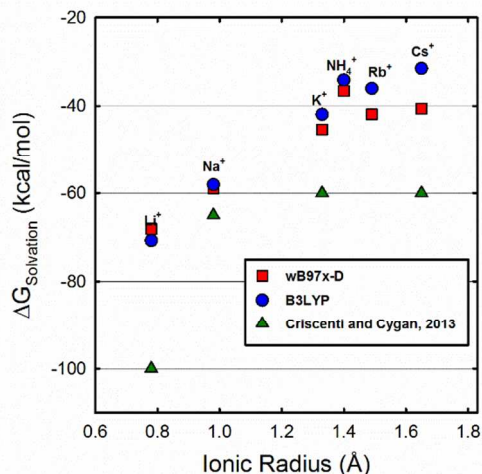


Figure 1. Free energy of solvation by CO₂ versus ionic radius⁴³⁻⁴⁴ for alkali cations and the ammonium cation calculated using electronic structure calculations (see supplemental information). Also shown are values calculated by Criscenti and Cygan et al.,³⁴ using classical molecular dynamics simulations.

Pressurized X-ray Diffraction

The $d(001)$ values of SWy-2 (Na^+ , Cs^+ , and NH_4^+) were determined by XRD at atmospheric (24°C and ~35% RH) and vacuum ($\sim 10^{-3}$ Torr, 50°C) conditions, and during exposure to CO_2 at 90 bar (50°C). The measured peak centroids of the $d(001)$ basal reflections are listed in **Table 1** (see **Figure S1** for the XRD tracings). The range of values for $d(001)$ under atmospheric conditions (~35% RH) are consistent with those reported in the literature for nominally the same clays and similar conditions.^{18, 46-48}

The $d(001)$ values for all the clays decreased when exposed to vacuum (10^{-3} Torr, 50°C), indicating the removal of interlayer water. The $d(001)$ value (9.75 Å) for Na-SWy-2 is slightly larger than the reported value (9.66 Å) for a completely dehydrated Na-SWy-1;¹⁹ where the Na^+ cations are coordinated by six basal oxygen atoms.^{46, 49} The larger $d(001)$ value (11.13 Å) for Cs-SWy-2 correlates with the relatively larger size of the Cs^+ cation (Cs: 1.69 Å, Na: 0.95 Å, and NH_4 : 1.43 Å)⁵⁰⁻⁵¹. Calculated and experimental $d(001)$ values from the literature show a significant range for dehydrated Cs-montmorillonite. For example, Bérend et al.,¹⁸ cite values from 10.7 to 11.35 Å; their own experimental work on Cs-SWy-1 yielded $d(001) = 11.08$ Å (exposed to vacuum at 100 °C for 4-24 hours). Simulations of anhydrous Cs^+ smectites consistently yield smaller $d(001)$ values compared to experiment, with spacings ranging from 10.50 to 10.70 Å.^{48, 52-53} The $d(001)$ values for NH_4 -SWy-2 reported here are intermediate (10.39-10.49 Å) with respect to the Na^+ and Cs^+ clays. Gautier et al.⁴⁷ also analyzed an anhydrous NH_4 -SWy-2 sample and reported $d(001) = \sim 10.4$ Å, consistent with the present study.⁵⁴

Both Cs^+ and NH_4^+ montmorillonite expanded during exposure to scCO_2 , but Na^+ montmorillonite did not (**Table 1**). Other than peak intensity attenuation from the dense CO_2 fluid, the patterns for Na^+ montmorillonite were essentially identical under vacuum and exposure to scCO_2 (see **Figure S1-S3**). When the pressurized experiments were opened to the vacuum for a few minutes, the Cs^+ and NH_4^+ clays collapsed back to their original vacuum basal spacing with no sign of alteration or secondary phase formation.

Table 1. Measured and [calculated] $d(001)$ basal spacing (Å) for cation saturated SWy-2 clays while exposed to atmospheric conditions (24°C), vacuum (10^{-3} Torr, 50°C), and CO_2 (90 bar, 50°C).

Clay	Cation	atmosphere	Vacuum	CO_2
		1.0 bar	(10^{-3} Torr)	90 bar
SWy-2	Cs	12.30	11.13	12.03
	NH_4	12.10	10.39	11.50
	Na	12.10	9.75	9.75

Pressurized MAS NMR

^{13}C

The ^{13}C MAS NMR resonances for the pure scCO_2 and scCO_2 plus Na^+ montmorillonite systems (**Figure 2**) are characterized by narrow center bands at ~124 ppm with full widths at half height (FWHH) of ~0.11 ppm. These narrow peaks reflect rapid, isotropic tumbling of CO_2 molecules in the supercritical fluid. There are also pairs of small spinning sidebands (SSBs). For pure scCO_2 , these SSBs are likely associated with CO_2 either adsorbed to or being compressed on the rotor wall due to the centrifugal forces caused by the rotor rotation at ~3 kHz.

For Na-SWy-2- scCO_2 , they are likely to arise from similar effects, given that their intensities are similar to those for scCO_2 . Although they may also be associated with a small fraction of CO_2 weakly adsorbed to the exterior surfaces of clay particles.⁵⁵

The center bands for the NH_4 - and Cs-SWy-2 are also at ~124 ppm, demonstrating that the resonance comes from CO_2 . However, the increased peak widths (FWHMs: ~0.31 ppm) indicate greater interaction of the CO_2 with solid surfaces and are consistent with greater restriction of CO_2 mobility. The SSB patterns are similar for the NH_4 - and Cs-SWy-2 samples and are more intense with greater basal widths than for Na-SWy-2, showing four well resolved SSBs. The spans of the chemical shift anisotropy (CSA) for the NH_4 - and Cs-SWy-2 are at least 160 ppm with a negative skew in each case. As discussed by Bowers et al.,³² the SSBs are assigned to interlayer CO_2 molecules adsorbed in a 1WL-type (~12.5 Å) interlayer with the O-C-O molecular axes oriented parallel to the basal clay surface on average and experiencing rapid ($>10^5$ Hz) reorientation about an axis normal to the

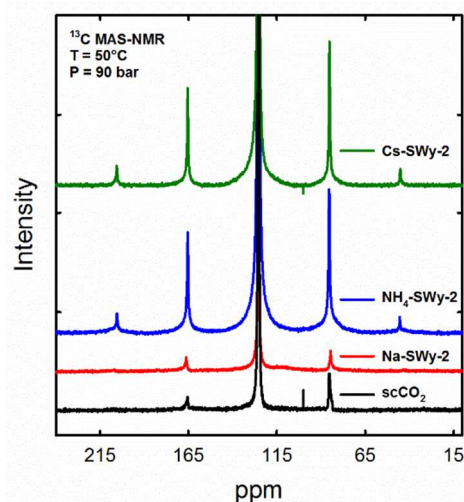


Figure 2. ^{13}C MAS NMR spectra of neat scCO_2 , Na-SWy-2- scCO_2 , NH_4 -SWy-2- scCO_2 , Cs-SWy-2- scCO_2 vertically expanded to highlight the spinning sideband patterns. Note that the Cs^+ - and the NH_4^+ - clays show evidence of interlayer-adsorbed CO_2 in the SSB patterns, whereas the Na^+ saturated clay shows no evidence of interlayer CO_2 .

clay basal surface.⁵⁵

^{133}Cs

The ^{133}Cs NMR spectrum of Cs-SWy-2 at 50°C and 1 bar N_2 contains a broad center band at ~43 ppm and a well-developed SSB pattern (**Figure 3**). The broad peaks and broad spinning sideband manifold arise from strong paramagnetic coupling between $^{133}\text{Cs}^+$ and structural Fe in SWy-2,⁵⁶ consistent with the Cs^+ being close to the basal surfaces in collapsed interlayers.⁵³ These results are similar to those reported by Weiss et al.,⁵⁷ and others.^{49, 52}

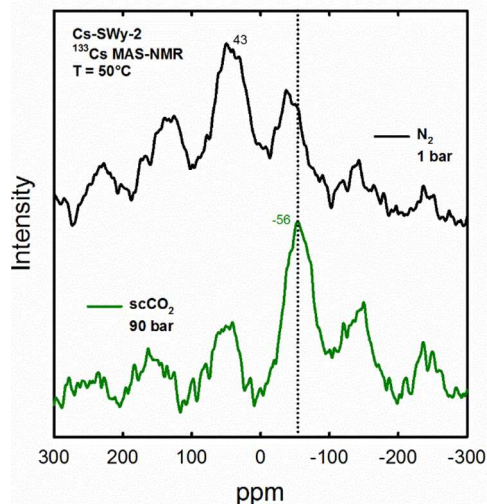


Figure 3. ^{133}Cs MAS NMR spectra of Cs-SWy-2 (top) and Cs-SWy-2- scCO_2 (bottom). Note the increase in area of the central peak due to CO_2 -coordinated interlayer Cs^+ (-56 ppm).

Following exposure to scCO_2 , the ^{133}Cs centerband for Cs-SWy-2 shifts to -56 ppm but the strong SSB pattern remains. The full widths at half maximum of the centerband and spinning sidebands are very similar for both conditions (16 ± 9 ppm pre- CO_2 and 13 ± 5 ppm post- CO_2). However, the baseline flattens and the standard deviations of the FWHH decrease for the sample exposed to scCO_2 . We interpret these changes to be due to reduced paramagnetic interaction with structural Fe in the clay as the distance between Cs and Fe increases with interlayer expansion. It is more difficult to comment on changes in the peak area since the magnitude of the quadrupolar coupling and paramagnetic coupling are both changing as the coordination environment changes. The large change in the position of the ^{133}Cs center band is well correlated to the XRD data (Table 1) and previous studies of Cs-hectorite³², and reflects a change in the coordination environment of Cs^+ due to some combination of interlayer expansion and Cs^+ solvation by CO_2 .

^{15}N

The ^{15}N MAS NMR spectra of NH_4 -SWy-2 show an appreciable increase in intensity, a small change in chemical shift, and little change in peak width after exposure to scCO_2 (6.0 ± 0.4 ppm without vs. 6.3 ± 0.6 ppm with) (Figure 4). With and without CO_2 the spectra contain one center band and four SSBs distributed symmetrically about the center band. In the presence of scCO_2 , the central peak shifts from -13.1 ± 0.1 ppm to -14.5 ± 0.1 ppm, and the intensities of the central peak and SSBs increase dramatically, with the absolute intensity of the center band increasing by more than a factor of three during exposure to scCO_2 . The increase in intensity reflects greater dynamic motion of the NH_4^+ cations due to interlayer expansion as CO_2 intercalates the clay, likely the result of more rapid NH_4^+ reorientation about the axes of molecular symmetry. As for the Cs-clay, we attribute the changes in the ^{15}N MAS NMR signal, which parallel the XRD results, to a combination of interlayer expansion and CO_2 solvation.

^{23}Na

The ^{23}Na MAS NMR spectrum of Na-SWy-2 at one bar (N_2) is dominated by a broad central peak and broad SSBs, consistent with Na^+ experiencing paramagnetic coupling to structural Fe (Figure 5).⁵⁶ In contrast to the Cs- and NH_4 - samples, there is no significant change in the ^{23}Na signal after exposure to scCO_2 ,

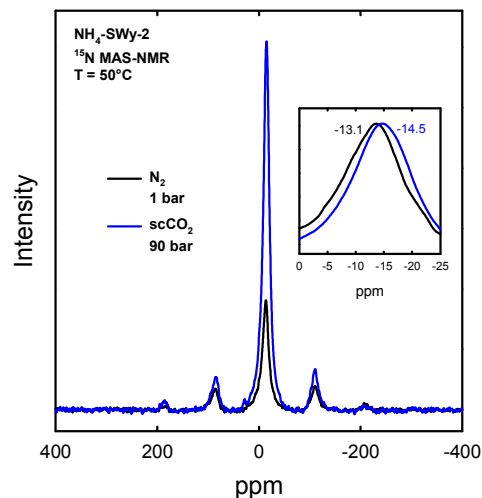


Figure 4. ^{15}N MAS NMR spectra of NH_4 -SWy-2 before (bottom) and during (top) exposure to scCO_2 , plotted on the same absolute intensity scale.

paralleling the XRD and ^{13}C NMR results that also show no changes during exposure to scCO_2 . The better signal/noise ratio for the sample exposed to scCO_2 simply reflects longer acquisition times. Consequently, the ^{23}Na NMR spectrum clearly indicates that CO_2 does not intercalate dry Na-SWy-2. Accounting for the field-dependent quadrupolar shift of ^{23}Na , these results are very similar to those for dry Na-montmorillonite⁵⁸ and dry Na-hectorite.^{59,60}

Molecular Dynamics Simulations

Molecular dynamics simulations were conducted in the grand canonical ensemble⁶¹ for model Na^+ , Cs^+ , NH_4^+ -montmorillonite (SWy-2) with imposed basal spacings using the RASPA software package.⁶² The computed interlayer CO_2 contents and associated immersion energies of the SWy-2 clay systems vary significantly depending on the exchangeable cation (Figure 6). For Na-SWy-2, interlayer adsorption of CO_2 molecules begins only after the $d(00l)$ basal spacing is substantially increased from the collapsed state at 9.5 ± 0.1 Å (vertical black

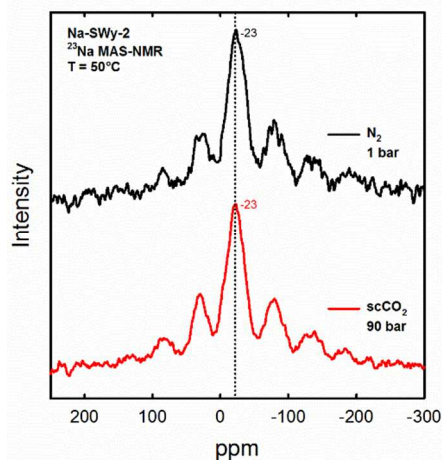


Figure 5. ^{23}Na MAS NMR of Na-SWy-2 (top) and Na-SWy-2- scCO_2 (bottom). Note the absence of any change in position or intensity of the central peak at -23 ppm in the presence of scCO_2 .

line in Figure 6)^{46, 48} to >10.7 Å. Consequently, the immersion energy increases from $d(001) = 9.5$ Å to 10.7 Å, predicting that the

collapsed state is stable relative to the 1WL state and that there is a significant energetic barrier to CO₂ intercalation. This conclusion is consistent with previous molecular simulations by Makaremi et al.⁴⁰ Consequently, the modeling results are in accord with the experiments that showed no change in the basal spacing (**Table 1**) or ²³Na NMR signal upon exposure to scCO₂.

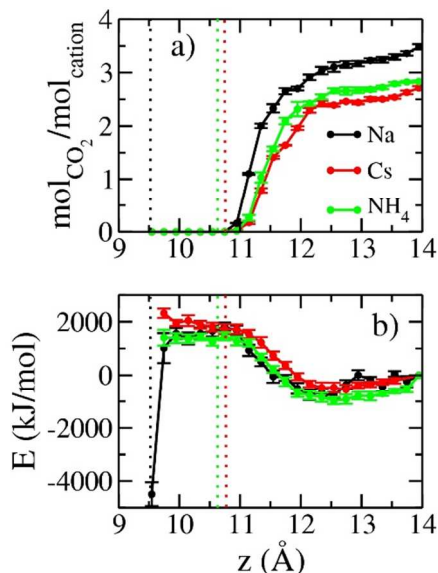


Figure 6. CO₂ content (a) and immersion energy of the system (b) as a function of basal spacing for SWy-2. The solid line at 9.5Å, 10.6Å, and 10.7Å indicate the collapsed basal spacing of Na⁺ (black), NH₄⁺ (green), and Cs⁺ (red) clays, respectively. The error bars show the 95% confidence level. The reference state for the immersion energies is the 14.0Å basal spacing.

The computed $d(001)$ value for fully collapsed Cs-SWy-2 (10.7 ± 0.2 Å; red vertical dotted line in **Figure 6a and b**) is similar to previous calculated values^{48, 52-53}, but slightly less than experimental values (**Table 1** and cited literature^{18, 47-48}). The calculated $d(001)$ value for fully collapsed NH₄-SWy-2 (10.6 ± 0.2 Å; delineated by the green vertical dotted lines in **Figure 6a and b**) is slightly larger than the experimentally determined value (10.39 Å). For both the Cs- and NH₄-systems the immersion energies of 1WL states (~ 12.5 Å) are significantly less than collapsed states, and there is no energy barrier to CO₂ intercalation (**Figure 6a**). For instance, the immersion energy decreases from ~ 1700 kJ/mol (10.7Å) to ~ 500 kJ/mol (12.5Å) for Cs-SWy-2, while, the energy decreases from ~ 1400 kJ/mol (10.6Å) to ~ 800 kJ/mol (12.5Å) with NH₄-SWy-2. Consequently, and in contrast to Na-SWy-2, the simulations indicate that CO₂ should readily enter the interlayer galleries of NH₄- and Cs-montmorillonites and form a stable expanded state (~ 12.5 Å), in agreement with the XRD and NMR results.

The computed basal spacings of the 1WL states of NH₄- and Cs-SWy-2 at $d(001) \sim 12.5$ -12.6 Å are larger than the corresponding experimental values of 11.50 and 12.03 Å (**Table 1**). The models and experiments also showed somewhat different $d(001)$ values for the fully collapsed clays (**Table 1**). In this regard, the calculated energy wells for the stable expanded states (around ~ 12.5 Å) are broad and, consequently, the minimum energy $d(001)$ values are not precisely known. Likewise, the simulations yielded energy plateaus for NH₄- and Cs-SWy-2 around the stable collapsed spacings (10.6Å – NH₄ and 10.7Å – Cs-SWy-2) and it is difficult to precisely determine the minimum energy $d(001)$ in this region. In addition, the immersion energies show very little difference in

magnitude (~ 1600 kJ/mol) between their collapsed state and at distances when CO₂ intercalation begins with Cs- and NH₄- SWy-2 (~ 10.9 Å). It is also possible that the experiments did not reach equilibrium and record metastable states beyond the resolution of the simulations. We did not investigate energy versus $d(001)$ behavior below 9.6 Å for the Na⁺ clay.

Simulations indicate an equilibrium 1 WL (~ 12.5 Å) interlayer CO₂ content for NH₄-SWy-2 (2.61 mol CO₂/mol NH₄⁺) that is slightly greater than for Cs-SWy-2 (2.40 mol CO₂/mol Cs⁺) (**Figure 6a**) and that both are less than the value for the metastable 1WL state of the Na⁺ clay (2.99 mol CO₂/mol Na⁺). Recall, however, that CO₂ is not thermodynamically favored to intercalate the dry Na⁺ clay; in this case, small concentrations of interlayer H₂O are required for CO₂ intercalation.^{26, 30}

The energetic contribution from different interacting pairs involved during CO₂ intercalation with all 3 SWy-2 were examined to better understand the reason for the different behaviors of these clays. Figure 7 clearly illustrates that the primary cause for the large intercalation energy barrier for CO₂ with and the high stability of the collapsed state for Na-SWy-2 arises from the strong interaction of Na with the clay in contrast to the NH₄ and Cs-models. In particular, the difference in the Na/clay interaction energies between the collapsed state (9.5Å) and at the transition state for CO₂ intercalation (~ 10.8 Å) is ~ 125 kJ/mol (Figure 7a). In contrast, the difference in interaction energies for NH₄/clay and Cs/Clay between their collapsed states (10.6Å - NH₄, 10.7Å - Cs) and their transition states for CO₂ intercalation (~ 10.9 Å) is negli-

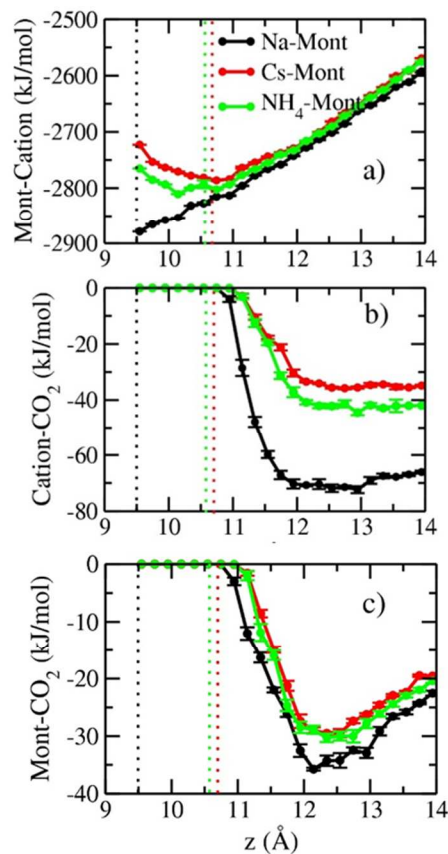


Figure 7. Variation in interaction energies between 3 different pairs. a) (SWy-2-Cation); b) Cation - CO₂; c) SWy-2-CO₂ as functions of interlayer spacing for Na-, Cs- and NH₄-SWy-2 at 323 K and 90 bar. Dotted vertical lines indicate respective collapsed interlayer distances for cations.

gible. At $d(001)$ values $> 10.7\text{\AA}$ the interaction energies for Na/CO₂ are significantly larger than for Cs/CO₂ and NH₄/CO₂, consistent with the solvation energy trends reported in Figure 1. Further, CO₂/clay interaction energies are relatively similar for all the cations (Figure 7c). The small, but significantly more favorable CO₂/clay interaction for Na-SWy-2 (Figure 7c) might reflect the stronger CO₂/Na interaction energy (Figure 7b). Lastly, the sum of CO₂/Na and CO₂/clay interaction energies is always less favorable than the Na/clay interaction energy from the collapsed state up to the metastable state. Thus, the simulations indicate that it is the strong interaction of Na⁺ with the clay that inhibits CO₂ intercalation and the relatively weak interaction of Cs and NH₄ with the clay that facilitates CO₂ intercalation, in accord with experiment.

Quartz crystal microbalance (QCM) gas sorption measurements and discrete IR measurements (see Supplemental Information for details) were used to quantify the amount of interlayer CO₂ under the experimental conditions to compare to the calculated concentrations. While these experimental techniques cannot distinguish external from intercalated CO₂, the measurements help to validate the simulation results. Indeed, the IR intensity associated with the asymmetrical CO₂ band (Figure 8) trends with the simulations if we use the experimental $d(001)$ values in Table 1 to calculate the sorbed CO₂ concentrations from the simulation results plotted in Figure 6a. Similarly, these computed concentrations of CO₂ (0.0 mol CO₂/mol Na⁺, 1.55 mol CO₂/mol NH₄⁺, and 1.99 mol CO₂/mol Cs⁺) trend well with our QCM measurements (0.5 mol CO₂/mol Na⁺, 1.74 mol CO₂/mol NH₄⁺, and 3.66 mol CO₂/mol Cs⁺). We suggest that the higher values for the QCM measured results are due to detection of both external and intercalated CO₂, whereas the simulations only quantify intercalated CO₂.

Is there a stable expanded state for Na-clay?

The immersion energy plots for Na-SWy-2 (Figure 6b) indicate that the collapsed basal spacing (9.5Å) is the most stable state, with energy minimum of ~ -4500 kJ/mol when compared to -700

systematically dehydrated the clay. The hydrated clay was first exposed to scCO₂ at 90 bars and 50°C and then cycled between 90 and 180 bars at constant temperature, where the fluid was leaked out of the cell on each down-pressure leg of the cycle and fresh CO₂ injected on every upward-pressure leg. The results show that as the clay dehydrated, eventually to the collapsed state (9.67 Å), intercalated CO₂ was systematically and nearly completely expelled from the interlayer region. We then performed a similar experiment except the clay was cycled between scCO₂ at 90 bars and 50°C, and liquid CO₂ at 90 bars and 25°C, with CO₂+H₂O leaked on the upward-temperature leg of the cycle and fresh ChyO₂ injected on every down-pressure leg. The results were the same: As the clay dehydrated, CO₂ was expelled from the interlayer region. Consequently, these experiments are in agreement with our GCMC calculations and the computed results of Makaremi et al.,⁴⁰ showing that the collapsed state of Na-montmorillonite is the stable state in equilibrium with dry scCO₂.

CONCLUSION and IMPLICATIONS

Experiments and complementary GCMC simulations for Na-, NH₄- and Cs-SWy-2 exposed to dry scCO₂ at 50°C and 90 bars reveal that because this weakly polar solvent does not strongly solvate the interlayer cations the tendency to intercalate and swell is controlled instead by the strength of the cation interaction with the aluminosilicate sheets. The stable state of the Na-clay is the fully collapsed interlayer region with no intercalated CO₂. Further, the Na-clay exhibits a large energy barrier for CO₂ intercalation. In contrast, the stable state of the NH₄- and Cs-clay is an expanded, 1WL-like state, containing substantial interlayer CO₂, coupled with little to no energy barrier for CO₂ diffusion into the interlayer region. The combination of experiment and theory demonstrates, for the first time, that it is the cation-clay interaction that determines the extent of interlayer expansion and absorption of relatively low dielectric volatiles by swelling clays. This is in contrast to cation-H₂O interactions, where the hydration energy of the cation dominates interlayer expansion behavior. In addition to the cationic radius to charge characteristics, this also suggests that clay swelling in weakly polar solvents will be more sensitive to the layer charge and its distribution between tetrahedral and octahedral sites compared to H₂O-containing systems.

EXPERIMENTAL SECTION

The smectite used in our studies, Wyoming bentonite (SWy-2) was obtained from the Source Clays Repository of the Clay Mineral Society (Purdue University, www.agry.purdue.edu/cjohnston/sourceclays). The as-received SWy-2 clay was processed using the procedures of Loring et al.,²⁶ and saturated with Na⁺, NH₄⁺, or Cs⁺. For the XRD, dilute clay suspensions were prepared by suspending the cation saturated clays in water. NMR experiments required dry powders, which were obtained by drying clay suspensions on glass slides at room temperature. The resulting clay films were scraped off with a razor blade and placed into glass vials. The clays were characterized by XRD while either under vacuum or during exposure to CO₂ (3.45 or 90 bar) at 50°C using a high pressure and temperature X-ray diffraction technique described previously.^{13, 55} Initially, measured aliquots of dilute clay suspensions were pipetted onto a beryllium post, each occupying a circular area with an approximate diameter of 2-3 mm. Each clay mount was allowed to air dry to produce a thin preferentially oriented clay film. The alignment process consisted of placing the beryllium post onto the XYZ stage and with the aid of the laser alignment system, manipulating the stage to expose only one clay film at a time to the XRD beam. Once the coordinates were established, the pressurized reactor was assembled, mounted into the instrument, and heated to 50°C. Subsequent exposure to vacuum for 30 minutes removed most of the water from the clays. Pressurization with

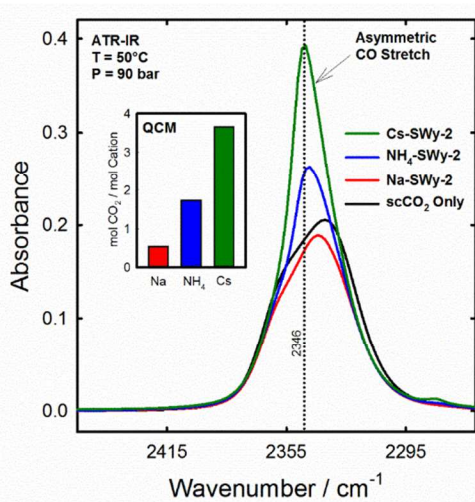


Figure 8. IR spectra in the asymmetric CO stretching of CO₂ in the presence of Na-, Cs-, and NH₄-SWy-2 at 90 bar and 50°C. Also shown for comparison is that spectrum of bulk scCO₂ under the same conditions.

kJ/mol hypothetical metastable state at ~ 12.5 Å, in agreement with Makaremi et al.,²⁰ and our own calculations. To verify the computational results, we performed a series of high pressure IR experiments using an initially hydrated 1WL Na-SWy-2, a composition known to facilitate CO₂ intercalation (see SI),²⁶ and then

CO₂ was accomplished through an ISCO pump connected directly to the reactor. Patterns were collected using a Bruker D8 Discover XRD instrument with a rotating Cu anode (CuK alpha = 1.5418 Å), programmable XYZ customized stage, and a Vantec 500 detector set at a sample-to-detector distance of 15 cm. This instrument, operated at 50 kV and 24 mA, is capable of producing an intensely focused 0.5 mm beam. The resulting XRD patterns had an acquisition time of 300 seconds, were integrated over a range of 4-45° 2θ, and subsequently analyzed with the MDI JADE[®] XRD software package (Materials Data Inc, Livermore, Ca, 64550) to obtain peak positions.

¹³C, ²³Na, ¹⁵N, and ¹³³Cs MAS NMR spectra were collected under pressurized conditions at 90 bar CO₂ and 50°C after first exposing each sample to dry nitrogen at 50°C and 1 bar. The NMR spectra were acquired at an H₀ magnetic field of 7.0 T with a Varian VNMRs console. The solid-state probe was a 7.5 mm HXMAS Chemagnetics style probe with a ceramic housing. The zirconia rotors were altered and fitted with gas tight valves for pressurization. The ¹³C MAS NMR data were acquired using a standard Bloch-decay pulse sequence with a π/2 pulse width of 7.75 microseconds to obtain 700 transients. These data involved a spectral width of 50 kHz, a number of points per transient of 30k, and a spin rate of approximately 3 kHz. The ¹³³Cs data were referenced to a 0.1 M solution of CsCl using a secondary standard of CsCl (s). Spectra represent Bloch-decay data acquired using a spectral width of ~200 kHz, 18k-28k transients, a spin rate of 3.5 kHz, π/2 pulse width of 8 μs, and a pulse delay of 0.5 s. The ¹⁵N data were also acquired with a Bloch-decay pulse sequence with a π/2 pulse width of 7 μs, a spectral width of 100 kHz, pulse delay of 1 s, and a spin rate of 3 kHz to obtain 5000 transients. The ²³Na data were acquired using a standard quadrupolar echo sequence to improve flatness of the baseline. These data sets involved acquiring ~5k transients for the low pressure sample and 10k transients for the sample exposed to scCO₂. Both used a MAS frequency of 4 kHz, spectral width of 100 kHz, pulse delay of 0.5 s, and a π/2 pulse width of 4.5 μs. All NMR data were processed using iNMR, a commercial program by MestReC (<http://www.inmr.net>), and all NMR results were iteratively fit using Abscissa, a freeware app written by Rudiger Bruhl (<http://rbruehl.macbay.de>). For the ¹³C MAS NMR, the time domain spectra were zero filled to a Fourier number (FN) of 32k points and given 5 Hz of exponential apodization prior to the Fourier transform (FT). For the ¹³³Cs MAS NMR spectra, the data were zero filled to a FN of 64k points, the first three points were removed, and 200 Hz of exponential apodization applied before the FT. For the ²³Na MAS NMR spectra data were left shifted by one data point, zero filled to a FN of 32k points, and received 200 Hz of exponential apodization prior to the FT. The ¹⁵N NMR spectra used a zero fill to an FN of 16k points, a left shift of four data points, and 50 Hz of exponential apodization before the FT. In almost all cases a standard baseline correction was performed to flatten the baseline. All peak fits were performed by iteratively fitting the data set to Lorentzian lineshapes.

Molecular Dynamics Simulations

Molecular dynamics simulations were conducted in the grand canonical ensemble (GCMD)⁶¹ for Na⁺, Cs⁺, NH₄⁺-montmorillonite. The SWy-2 model was obtained from Ngouana and Kalinichev⁴⁸ and has a structural formula of M⁺_{0.75}(Si_{7.75}Al_{0.25})(Al_{3.5}Mg_{0.5})O₂₀(OH)₄. The distributions of the octahedral and tetrahedral isomorphic substitutions follow a disordered pattern in accordance with Loewenstein's rule.⁶³

The simulation supercells for all the systems consist of 32 crystallographic unit cells of montmorillonite (4 x 4 x 2) and encompass two interlayers with surface areas of 740.2Å². The large surface

areas are necessary to overcome finite size effects in the simulated models. The basal spacings were varied from 9.5Å to 14.0Å at steps of 0.2Å. Both interlayer galleries were constrained to have same dimensions, which were held constant throughout the simulation runs. All of the cations were initially placed at the mid-plane of the interlayers. The T-O-T layers were allowed to move only laterally, parallel to the basal surface, without disrupting the structure. Such translational movement is essential, because the x-y displacement of the minimum energy interlayer structure depends on the cation and the number of intercalated fluid molecules, here CO₂, as has been reported in previous studies.³⁷

The GCMD simulations were performed with the RASPA⁶² simulation package. GCMD is a hybrid method which involves coupling of Monte Carlo and MD methods. In the grand canonical ensemble system temperature, system volume, and the chemical potential of the fluid molecules are fixed, but the number of adsorbed molecules fluctuates. This is achieved by sampling insertion and deletion of fluid molecules with equal probability at every MD step. The interatomic interactions for the smectite T-O-T layers and cations were obtained using the *CLAYFF* force field, which is used widely in clay simulations.^{48, 53, 64} The CO₂ molecules were represented with the rigid EPM2 model.³⁵ The parameters for the rigidly held NH₄⁺ ions were obtained from the literature.⁶⁵ All the GCMD simulations were performed at T=323 K and P=90 bars for 12 ns to reach equilibration followed by another 8 ns for the production run. The MD time step was 1 fs. Periodic boundary conditions in three dimensions were employed with a cutoff of 9.0 Å for short range non-electrostatic interactions. Ewald summation was used for computing long-range electrostatic interactions with an accuracy of 10⁻⁶. A Nosé-Hoover thermostat were used to control the temperature.⁶⁶ Fugacities required to run the simulation were obtained using the Peng-Robinson equation of state.⁶⁷ The critical temperature, critical pressure and acentric factor used to automatically compute the fugacity in RASPA using the equation of state.⁶⁷ The computed fugacity coefficient of CO₂ molecules at 323K and 90 bar corresponds to 0.654. The adsorption isotherms and related immersion energies were calculated using the data from the last 2 ns of the equilibrium trajectory. The reported mean values are obtained using statistical averages over 5 equal time blocks of 400 ps each. The use of immersion energies to investigate the equilibrium states of smectite systems has been discussed previously for water adsorption⁵²⁻⁵³ and is extended here to CO₂.

ASSOCIATED CONTENT

Supporting Information. Methods section detailing the infrared and quartz crystal microbalance techniques; X-ray diffraction tracings of clays exposed to vacuum and pressurized CO₂; electronic structure calculations of the solvation energy of the cations shown in Figure 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

HT Schaeff, todd.schaeff@pnnl.gov
ES Ilton, eugene.ilton@pnnl.gov
JS Loring, john.loring@pnnl.gov

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This material is based upon work supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Chemical Sciences, Geosciences, and Biosciences Division through its Geosciences program at Pacific Northwest National Laboratory (PNNL) (JSL, ESI, KST, DAD, KMR), and through its university grants DE-FG02-10ER16128 and DE-FG02-08ER15929 (GMB, NL, AOY, RJK). DAD also thanks the Robert Ramsay Fund at the University of Alabama for support. It is also based upon work supported by the DOE Office of Fossil Energy at PNNL through the National Energy Technology Laboratory, Morgantown, West Virginia (HTS, BPM). SDB and DWH collected the NMR data at the Environmental Molecular Science Laboratory (EMSL), a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at PNNL. The authors would like to thank Dr. Sebastian Kerisit for insightful comments.

REFERENCES

- (1) Kuila, U.; McCarty, D. K.; Derkowski, A.; Fischer, T. B.; Topor, T.; Prasad, M. Nano-Scale Texture and Porosity of Organic Matter and Clay Minerals in Organic-Rich Mudrocks. *Fuel* **2014**, *135*, 359-373.
- (2) Kuila, U.; Prasad, M. Specific Surface Area and Pore-Size Distribution in Clays and Shales. *Geophys. Prospect.* **2013**, *61* (2), 341-362.
- (3) Ross, D. J. K.; Bustin, R. M. The Importance of Shale Composition and Pore Structure Upon Gas Storage Potential of Shale Gas Reservoirs. *Mar. Pet. Geol.* **2009**, *26* (6), 916-927.
- (4) Busch, A.; Bertier, P.; Gensterblum, Y.; Rother, G.; Spiers, C. J.; Zhang, M.; Wentinck, H. M. On Sorption and Swelling of CO₂ in Clays. *Geomechanics and Geophysics for Geo-Energy and Geo-Resources* **2016**, *2* (2), 111-130.
- (5) Josh, M.; Esteban, L.; Delle Piane, C.; Sarout, J.; Dewhurst, D. N.; Clennell, M. B. Laboratory Characterisation of Shale Properties. *J. Pet. Sci. Eng.* **2012**, *88-89*, 107-124.
- (6) Gaus, I. Role and Impact of CO₂-rock Interactions During CO₂ Storage in Sedimentary Rocks. *Int. J. Greenhouse Gas Control* **2010**, *4* (1), 73-89.
- (7) Middleton, R. S.; Gupta, R.; Hyman, J. D.; Viswanathan, H. S. The Shale Gas Revolution: Barriers, Sustainability, and emerging Opportunities. *Appl. Energy* **2017**, *199*, 88-95.
- (8) Liu, S. Y.; Yan, Z. L.; Fu, L. J.; Yang, H. M. Hierarchical Nano-Activated Silica Nanosheets for Thermal Energy Storage. *Sol. Energy Mater. Sol. Cells* **2017**, *167*, 140-149.
- (9) Guo, Z. Q.; Li, Y.; Zhang, S. W.; Niu, H. H.; Chen, Z. S.; Xu, J. Z. Enhanced Sorption of Radiocobalt from Water by Bi(III) Modified Montmorillonite: A Novel Adsorbent. *J. Hazard. Mater.* **2011**, *192* (1), 168-175.
- (10) Yang, R. T.; Baksh, M. S. A. Pillared Clays as a New Class of Sorbents for Gas Separation *AIChE Journal* **1991**, *37* (5), 679-686.
- (11) De Pourcq, K.; Ayora, C.; Garcia-Gutierrez, M.; Missana, T.; Carrera, J. A Clay Permeable Reactive Barrier to Remove Cs-137 from Groundwater: Column Experiments. *J. Environ. Radioact.* **2015**, *149*, 36-42.
- (12) Segad, M.; Jonsson, B.; Akesson, T.; Cabane, B. Ca/Na Montmorillonite: Structure, Forces and Swelling Properties. *Langmuir* **2010**, *26* (8), 5782-5790.
- (13) Schaef, H. T.; Ilton, E. S.; Qafoku, O.; Martin, P. F.; Felmy, A. R.; Rosso, K. M. In situ XRD Study of Ca²⁺ Saturated Montmorillonite (STX-1) Exposed to Anhydrous and Wet Supercritical Carbon Dioxide. *Int. J. Greenhouse Gas Control* **2012**, *220-229*.
- (14) Ferrage, E.; Lanson, B.; Sakharov, B. A.; Drits, V. A. Investigation of Smectite Hydration Properties by Modeling Experimental X-ray Diffraction Patterns: Part I. Montmorillonite Hydration Properties. *Am. Mineral.* **2005**, *90* (8-9), 1358-1374.
- (15) Busch, A.; Alles, S.; Gensterblum, Y.; Prinz, D.; Dewhurst, D. N.; Raven, M. D.; Stanjek, H.; Krooss, B. M. Carbon Dioxide Storage Potential of Shales. *Int. J. Greenhouse Gas Control* **2008**, *2* (3), 297-308.
- (16) Sun, L. L.; Hirvi, J. T.; Schatz, T.; Kasa, S.; Pakkanen, T. A. Estimation of Montmorillonite Swelling Pressure: A Molecular Dynamics Approach. *J. Phys. Chem. C* **2015**, *119* (34), 19863-19868.
- (17) Pei, P.; Ling, K. G.; He, J.; Liu, Z. Z. Shale Gas Reservoir Treatment by a CO₂-Based Technology. *J. Nat. Gas Sci. Eng.* **2015**, *26*, 1595-1606.
- (18) Berend, I.; Cases, J. M.; Francois, M.; Uriot, J. P.; Michot, L.; Masion, A.; Thomas, F. Mechanism of Adsorption and Desorption of Water-Vapor by Homoionic Montmorillonites 2. The Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺-Exchanged Forms. *Clays Clay Miner.* **1995**, *43* (3), 324-336.
- (19) Cases, J. M.; Berend, I.; Besson, G.; Francois, M.; Uriot, J. P.; Thomas, F.; Poirier, J. E. Mechanism of Adsorption and Desorption of Water-Vapor by Homoionic Montmorillonite. 1. The Sodium-Exchanged Form *Langmuir* **1992**, *8* (11), 2730-2739.
- (20) Cases, J. M.; Berend, I.; Francois, M.; Uriot, J. P.; Michot, L. J.; Thomas, F. Mechanism of Adsorption and Desorption of Water vapor by Homoionic Montmorillonite .3. The Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ Exchanged Forms. *Clays Clay Miner.* **1997**, *45* (1), 8-22.
- (21) Whitley, H. D.; Smith, D. E. Free Energy, Energy, and Entropy of Swelling in Cs-, Na-, and Sr-Montmorillonite Clays. *J. Chem. Phys.* **2004**, *120* (11), 5387-5395.
- (22) Teich-McGoldrick, S. L.; Greathouse, J. A.; Jove-Colon, C. F.; Cygan, R. T. Swelling Properties of Montmorillonite and Beidellite Clay Minerals from Molecular Simulation: Comparison of Temperature, Interlayer Cation, and Charge Location Effects. *J. Phys. Chem. C* **2015**, *119* (36), 20880-20891.
- (23) Loring, J. S.; Schaef, H. T.; Turcu, R. V. F.; Thompson, C. J.; Miller, Q. R. S.; Martin, P. F.; Hu, J. Z.; Hoyt, D. W.; Qafoku, O.; Ilton, E. S.; Felmy, A. R.; Rosso, K. M. In Situ Molecular Spectroscopic Evidence for CO₂ Intercalation into Montmorillonite in Supercritical Carbon Dioxide. *Langmuir* **2012**, *28* (18), 7125-7128.
- (24) Loring, J. S.; Schaef, H. T.; Thompson, C. J.; Turcu, R. V.; Miller, Q. R.; Chen, J.; Hu, J.; Hoyt, D. W.; Martin, P. F.; Ilton, E. S.; Felmy, A. R.; Rosso, K. M. Clay Hydration/dehydration in Dry to Water-saturated Supercritical CO₂: Implications for Caprock Integrity. *Energy Procedia* **2013**, *37* (0), 5443-5448.
- (25) Ilton, E. S.; Schaef, H. T.; Qafoku, O.; Rosso, K. M.; Felmy, A. R. In Situ X-ray Diffraction Study of Na⁺ Saturated Montmorillonite Exposed to Variably Wet Super Critical CO₂. *Environ. Sci. Technol.* **2012**, *46* (7), 4241-4248.

- (26) Loring, J. S.; Ilton, E. S.; Chen, J.; Thompson, C. J.; Martin, P. F.; Bénézeth, P.; Rosso, K. M.; Felmy, A. R.; Schaefer, H. T. In Situ Study of CO₂ and H₂O Partitioning Between Na–Montmorillonite and Variably Wet Supercritical Carbon Dioxide. *Langmuir* **2014**, *30* (21), 6120-6128.
- (27) Giesting, P.; Guggenheim, S.; van Groos, A. F. K.; Busch, A. X-ray Diffraction Study of K- and Ca-Exchanged Montmorillonites in CO₂ Atmospheres. *Environ. Sci. Technol.* **2012**, *46* (10), 5623-5630.
- (28) Giesting, P.; Guggenheim, S.; van Groos, A. F. K.; Busch, A. Interaction of Carbon Dioxide with Na-Exchanged Montmorillonite at Pressures to 640 Bars: Implications for CO₂ Sequestration. *Int. J. Greenhouse Gas Control* **2012**, *8*, 73-81.
- (29) Rother, G.; Ilton, E. S.; Wallacher, D.; Hauss, T.; Schaefer, H. T.; Qafoku, O.; Rosso, K. M.; Felmy, A. R.; Krukowski, E. G.; Stack, A. G.; Grimm, N.; Bodnar, R. J. CO₂ Sorption to Subsingle Hydration Layer Montmorillonite Clay Studied by Excess Sorption and Neutron Diffraction Measurements. *Environ. Sci. Technol.* **2013**, *47* (1), 205-211.
- (30) Schaefer, H. T.; Loring, J. S.; Glezakou, V.-A.; Miller, Q. R. S.; Chen, J.; Owen, A. T.; Lee, M.-S.; Ilton, E. S.; Felmy, A. R.; McGrail, B. P.; Thompson, C. J. Competitive Sorption of CO₂ and H₂O in 2:1 Layer Phyllosilicates. *Geochim. Cosmochim. Acta* **2015**, *161*, 248-257.
- (31) Kadoura, A.; Narayanan Nair, A. K.; Sun, S. Molecular Simulation Study of Montmorillonite in Contact with Variably Wet Supercritical Carbon Dioxide. *J. Phys. Chem. C* **2017**, *121* (11), 6199-6208.
- (32) Rao, Q.; Leng, Y. Molecular Understanding of CO₂ and H₂O in a Montmorillonite Clay Interlayer under CO₂ Geological Sequestration Conditions. *J. Phys. Chem. C* **2016**, *120* (5), 2642-2654.
- (33) Sena, M. M.; Morrow, C. P.; Kirkpatrick, R. J.; Krishnan, M. Supercritical Carbon Dioxide at Smectite Mineral–Water Interfaces: Molecular Dynamics and Adaptive Biasing Force Investigation of CO₂/H₂O Mixtures Nanoconfined in Na-Montmorillonite. *Chem. Mater.* **2015**, *27* (20), 6946-6959.
- (34) Criscenti, L. J.; Cygan, R. T. Molecular Simulations of Carbon Dioxide and Water: Cation Solvation. *Environ. Sci. Technol.* **2013**, *47* (1), 87-94.
- (35) Cygan, R. T.; Romanov, V. N.; Myshakin, E. M. Molecular Simulation of Carbon Dioxide Capture by Montmorillonite Using an Accurate and Flexible Force Field. *J. Phys. Chem. C* **2012**, *116* (24), 13079-13091.
- (36) Myshakin, E. M.; Saidi, W. A.; Romanov, V. N.; Cygan, R. T.; Jordan, K. D. Molecular Dynamics Simulations of Carbon Dioxide Intercalation in Hydrated Na-Montmorillonite. *J. Phys. Chem. C* **2013**, *117* (21), 11028-11039.
- (37) Botan, A.; Rotenberg, B.; Marry, V.; Turq, P.; Noetinger, B. Carbon Dioxide in Montmorillonite Clay Hydrates: Thermodynamics, Structure, and Transport from Molecular Simulation. *J. Phys. Chem. C* **2010**, *114* (35), 14962-14969.
- (38) Zhang, W.; Hu, H.; Li, X.; Fang, Z. Interplay of Montmorillonite–H₂O–scCO₂ System Between Mechanical Behavior and Adsorption: Molecular Dynamics. *J. Phys. Chem. C* **2015**, *119* (38), 21959-21968.
- (39) Krishnan, M.; Saharay, M.; Kirkpatrick, R. J. Molecular Dynamics Modeling of CO₂ and Poly(ethylene glycol) in Montmorillonite: The Structure of Clay-Polymer Composites and the Incorporation of CO₂. *J. Phys. Chem. C* **2013**, *117* (40), 20592-20609.
- (40) Makaremi, M.; Jordan, K. D.; Guthrie, G. D.; Myshakin, E. M. Multiphase Monte Carlo and Molecular Dynamics Simulations of Water and CO₂ Intercalation in Montmorillonite and Beidellite. *J. Phys. Chem. C* **2015**, *119* (27), 15112-15124.
- (41) Myshakin, E. M.; Makaremi, M.; Romanov, V. N.; Jordan, K. D.; Guthrie, G. D. Molecular Dynamics Simulations of Turbostratic Dry and Hydrated Montmorillonite with Intercalated Carbon Dioxide. *J. Phys. Chem. A* **2014**, *118* (35), 7454-7468.
- (42) Lee, M.-S.; McGrail, B. P.; Glezakou, V.-A. Microstructural Response of Variably Hydrated Ca-rich Montmorillonite to Supercritical CO₂. *Environ. Sci. Technol.* **2014**, *48* (15), 8612-8619.
- (43) Sidey, V. On the Effective Ionic Radii for Ammonium. *Acta Crystallogr., Sect. B: Struct. Sci.* **2016**, *72*, 626-633.
- (44) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1991
- (45) Cruz-Guzmán, M.; Celis, R.; Hermosin, M. C.; Cornejo, J. Adsorption of the Herbicide Simazine by Montmorillonite Modified with Natural Organic Cations. *Environ. Sci. Technol.* **2004**, *38* (1), 180-186.
- (46) Morrow, C. P.; Yazaydin, A. O.; Krishnan, M.; Bowers, G. M.; Kalinichev, A. G.; Kirkpatrick, R. J. Structure, Energetics, and Dynamics of Smectite Clay Interlayer Hydration: Molecular Dynamics and Metadynamics Investigation of Na-Hectorite. *J. Phys. Chem. C* **2013**, *117* (10), 5172-5187.
- (47) Gautier, M.; Muller, F.; Le Forestier, L.; Beny, J. M.; Guegan, R. NH₄-Smectite: Characterization, Hydration Properties and Hydro Mechanical Behaviour. *Appl. Clay Sci.* **2010**, *49* (3), 247-254.
- (48) Ngouana, B. F.; Kalinichev, A. G. Structural Arrangements of Isomorphic Substitutions in Smectites: Molecular Simulation of the Swelling Properties, Inter layer Structure, and Dynamics of Hydrated Cs-Montmorillonite Revisited with New Clay Models. *J. Phys. Chem. C* **2014**, *118* (24), 12758-12773.
- (49) Kosakowski, G.; Churakov, S. V.; Thoenen, T. Diffusion of Na and Cs in Montmorillonite. *Clays Clay Miner.* **2008**, *56* (2), 190-206.
- (50) Shannon, R. D. Revised Effective Ionic-Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32* (SEP1), 751-767.
- (51) Masterton, W. L.; Bolocofsky, D.; Lee, T. P. Ionic Radii from Scaled Particle Theory of Salt Effect. *J. Phys. Chem.* **1971**, *75* (18), 2809-2815.

- (52) Smith, D. E. Molecular Computer Simulations of the Swelling properties and Interlayer Structure of Cesium Montmorillonite. *Langmuir* **1998**, *14* (20), 5959-5967.
- (53) Loganathan, N.; Yazaydin, A. O.; Bowers, G. M.; Kalinichev, A. G.; Kirkpatrick, R. J. Structure, Energetics, and Dynamics of Cs⁺ and H₂O in Hectorite: Molecular Dynamics Simulations with an Unconstrained Substrate Surface. *J. Phys. Chem. C* **2016**, *120* (19), 10298-10310.
- (54) Vivaldi, J. L. M.; Vilchez, F. G.; Hernaiz, M.; Castro, B. d.; Gallego, M. R. The Thermal Decomposition of NH₄ Montmorillonites. Part 1. *Mineralogical Society of Great Britain and Ireland* **1959**, 81-87.
- (55) Bowers, G. M.; Schaefer, H. T.; Loring, J. S.; Hoyt, D. W.; Burton, S. D.; Walter, E. D.; Kirkpatrick, R. J. Role of Cations in CO₂ Adsorption, Dynamics, and Hydration in Smectite Clays under in Situ Supercritical CO₂ Conditions. *J. Phys. Chem. C* **2017**, *121* (1), 577-592.
- (56) Bank, S.; Bank, J. F.; Ellis, P. D. Solid-State ¹¹³Cd Nuclear Magnetic-Resonance Study of Exchanged Montmorillonites. *J. Phys. Chem.* **1989**, *93* (12), 4847-4855.
- (57) Weiss, C. A.; Kirkpatrick, R. J.; Altaner, S. P. The Structural Environments of Cations Adsorbed Onto Clays ¹³³Cs Variable Temperature MAS NMR Spectroscopic Study of Hectorite *Geochim. Cosmochim. Acta* **1990**, *54* (6), 1655-1669.
- (58) Reinholdt, M. X.; Kirkpatrick, R. J.; Pinnavaia, T. J. Montmorillonite-poly(ethylene oxide) Nanocomposites: Interlayer Alkali Metal Behavior. *J. Phys. Chem. B* **2005**, *109* (34), 16296-16303.
- (59) Bowers, G. M.; Singer, J. W.; Bish, D. L.; Kirkpatrick, R. J. Alkali Metal and H₂O Dynamics at the Smectite/Water Interface. *J. Phys. Chem. C* **2011**, *115* (47), 23395-23407.
- (60) Aranda, P.; Ruizhitzky, E. Poly(Ethylene Oxide)-Silicate Intercalation materials *Chem. Mater.* **1992**, *4* (6), 1395-1403.
- (61) Boinepalli, S.; Attard, P. Grand Canonical Molecular Dynamics. *J. Chem. Phys.* **2003**, *119* (24), 12769-12775.
- (62) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: Molecular Simulation Software for Adsorption and Diffusion in Flexible Nanoporous Materials. *Mol. Simul.* **2016**, *42* (2), 81-101.
- (63) Loewenstein, W. The Distribution of Aluminum in the Tetrahedra of Silicates and Aluminates. *Am. Mineral.* **1954**, *39* (1-2), 92-96.
- (64) Cygan, R. T.; Liang, J. J.; Kalinichev, A. G. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J. Phys. Chem. B* **2004**, *108* (4), 1255-1266.
- (65) Loganathan, N.; Kalinichev, A. G. On the Hydrogen Bonding Structure at the Aqueous Interface of Ammonium-Substituted Mica: A Molecular Dynamics Simulation. *Zeitschrift Fur Naturforschung Section a-a Journal of Physical Sciences* **2013**, *68* (1-2), 91-100.
- (66) Shinoda, W.; Shiga, M.; Mikami, M. Rapid Estimation of Elastic Constants by Molecular Dynamics Simulation Under Constant Stress. *Phys. Rev. B* **2004**, *69* (13).
- (67) Peng, D.; Robinson, D. B. New 2-constant Equation of State *Ind. Eng. Chem. Fundam.* **1976**, *15* (1), 59-64.

TOC

