Tipping Point for Expansion of Layered Aluminosilicates in Weakly Polar Solvents: Supercritical CO\textsubscript{2}

Herbert T. Schaef\textsuperscript{1,*}, Narasimhan Loganathan\textsuperscript{2}, Geoffrey M. Bowers\textsuperscript{3}, R. James Kirkpatrick\textsuperscript{2}, A. Ozgur Yazaydin\textsuperscript{2,4}, Sarah D. Burton\textsuperscript{5}, David W. Hoyt\textsuperscript{5}, K. Sahan Thanthiriwatte\textsuperscript{6}, David A. Dixon\textsuperscript{6}, B. Peter McGraw\textsuperscript{1}, Kevin M. Rosso\textsuperscript{7}, Eugene S. Ilton\textsuperscript{8,*}, John S. Loring\textsuperscript{1,*}

\textsuperscript{1}Pacific Northwest National Laboratory, Richland WA 99356
\textsuperscript{2}College of Natural Science, Michigan State University, East Lansing, MI, 48824
\textsuperscript{3}Department of Chemistry and Biochemistry, St. Mary’s College of Maryland, St. Mary’s City, MD 20686
\textsuperscript{4}Department of Chemical Engineering, University College London, London, WC1E 7JE, United Kingdom
\textsuperscript{5}William R. Wiley Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99356
\textsuperscript{6}Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487

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\textbf{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 H\textsubscript{2}O 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. CO\textsubscript{2}), uptake into the interlayer is not well-understood. Using novel high pressure capabilities, we investigated the interaction of dry supercritical CO\textsubscript{2} with Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, and Cs\textsuperscript{+}-saturated montmorillonite, comparing results with predictions from molecular dynamics simulations. Despite the known trend in H\textsubscript{2}O, and that cation solvation energies in CO\textsubscript{2} suggest a stronger interaction with Na\textsuperscript{+}, both the NH\textsubscript{4}\textsuperscript{+}- and Cs\textsuperscript{+}-clays readily absorbed CO\textsubscript{2} and expanded while the Na\textsuperscript{+}-clay did not. The apparent inertness of the Na\textsuperscript{+}-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 CO\textsubscript{2} intercalation in the Na\textsuperscript{+}-clay, but little or no energy barrier for the NH\textsubscript{4}\textsuperscript{+} - and Cs\textsuperscript{+}-clays. Indeed, the combination of experiment and theory clearly demonstrate that CO\textsubscript{2} intercalation of Na-montmorillonite clays is prohibited in the absence of H\textsubscript{2}O. 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.

\textbf{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,\textsuperscript{1,2} gas absorptivity\textsuperscript{3,4}, and ductility\textsuperscript{5} in sedimentary rocks, their specific behavior, even in small concentrations, can control the geomechanical response of caprocks that seal reservoir formations\textsuperscript{6} or the extraction of natural gas from organic rich shales that are the source rocks driving the present fracking boom.\textsuperscript{7} They are also used widely in industrial applications that range from catalytic substrates\textsuperscript{8} to metal and gas sorbents\textsuperscript{9,10} to reactive barrier materials.\textsuperscript{11} A key characteristic is their ability to expand or contract by absorbing or ejecting solvent and ions in response to changing fluid chemistry.\textsuperscript{12} Layered aluminosilicates known as smectites are of particular interest, because they can swell substantially in the presence of certain volatiles\textsuperscript{13,14} 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 CO\textsubscript{2} (scCO\textsubscript{2}) during and after injection of CO\textsubscript{2} into geologic reservoirs is often a crucial unknown.\textsuperscript{15} Unlike swelling performance requirements for clay based barriers in nuclear repositories\textsuperscript{16}, geologic exploration operations using non-aqueous based technologies (i.e. scCO\textsubscript{2}) 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+montmorillonites15, 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 (CO2(g)) or scCO2. 17, 23-30 For example, a number of studies17, 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 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.35-45 Calculations by Makarem et al.36, 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) = 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 energy decreases 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.41 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 (GCMD) 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., 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 (~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 for Na-SWy-2 is slightly larger than the reported value (9.66 Å) for a completely dehydrated Na-SWy-1;\(^{46}\) 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.\(^{46,52-53}\) 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 \( d(001) = 10.4 \) 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>
<thead>
<tr>
<th>Clay</th>
<th>Cation</th>
<th>atmosphere</th>
<th>Vacuum (10(^{-3}) Torr)</th>
<th>CO(_2) (90 bar, 50°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWy-2</td>
<td>Cs</td>
<td>12.30</td>
<td>11.13</td>
<td>12.03</td>
</tr>
<tr>
<td></td>
<td>NH(_4)</td>
<td>12.10</td>
<td>10.39</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>12.10</td>
<td>9.75</td>
<td>9.75</td>
</tr>
</tbody>
</table>

**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).

**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 (FWHHs: ~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.,\(^{52}\) 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\(^3\) Hz) reorientation about an axis normal to the clay basal surface.\(^{55}\)

\(^{13}\)Cs

The \(^{13}\)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 \(^{13}\)Cs\(^+\), 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.\(^{49,52}\)
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 FWHM 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-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 to a combination of interlayer expansion and Cs$^+$ solvation by CO$_2$.

Molecular Dynamics Simulations

Molecular dynamics simulations were conducted in the grand canonical ensemble for model Na$^{+}$-, Cs$^{+}$-, NH$_4^+$-montmorillonite (SWy-2) with imposed basal spacings using the RASPA software package. 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(001) basal spacing is substantially increased from the collapsed state at 9.5 ± 0.1 Å (vertical black line in Figure 6) to >10.7 Å. Consequently, the immersion energy increases from $d$(001) = 9.5 Å to 10.7 Å, predicting that the
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 NH\(_4\)-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 NH\(_4\)-systems the immersion energies of 1WL states (~12.5 Å) are significantly less than collapsed states, and there is no energy barrier to CO\(_2\) intercalation (Figure 6a). For instance, the immersion energy decreases from ~1700 kJ/mol (10.7 Å) to ~500 kJ/mol (12.5 Å) for Cs-SWy-2, while, the energy decreases from ~1400 kJ/mol (10.6 Å) to ~800 kJ/mol (12.5 Å) with NH\(_4\)-SWy-2. Consequently, and in contrast to Na-SWy-2, the simulations indicate that CO\(_2\) should readily enter the interlayer galleries of NH\(_4\)- 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 NH\(_4\)- and Cs-SWy-2 at \(d(001)\) = ~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 NH\(_4\)- and Cs-SWy-2 around the stable collapsed spacings (10.6 Å – NH\(_4\) and 10.7 Å – 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 CO\(_2\) intercalation begins with Cs- and NH\(_4\)- 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 CO\(_2\) content for NH\(_4\)-SWy-2 (2.61 mol CO\(_2\)/mol NH\(_4\)\(^+\)) that is slightly greater than for Cs-SWy-2 (2.40 mol CO\(_2\)/mol Cs\(^+\)) (Figure 6a) and that both are less than the value for the metastable 1WL state of the Na\(^+\) clay (2.99 mol CO\(_2\)/mol Na\(^+\)). Recall, however, that CO\(_2\) is not thermodynamically favored to intercalate the dry Na\(^+\) clay; in this case, small concentrations of interlayer H\(_2\)O are required for CO\(_2\) intercalation.\(^{26, 30}\)

The energetic contribution from different interacting pairs involved during CO\(_2\) 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 CO\(_2\) 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 NH\(_4\) and Cs-models. In particular, the difference in the Na/clay interaction energies between the collapsed state (9.5 Å) and at the transition state for CO\(_2\) intercalation (~10.8 Å) is ~125 kJ/mol (Figure 7a). In contrast, the difference in interaction energies for NH\(_4\)/clay and Cs/Clay between their collapsed states (10.6 Å – NH\(_4\), 10.7 Å – Cs) and their transition states for CO\(_2\) intercalation (~10.9 Å) is negli-

**Figure 6.** CO\(_2\) content (a) and immersion energy of the system (b) as a function of basal spacing for SWy-2. The solid line at 9.5 Å, 10.6 Å, and 10.7 Å indicate the collapsed basal spacing of Na\(^+\) (black), NH\(_4\)\(^+\) (green), and Cs\(^+\) (red) clays, respectively. The error bars show the 95% confidence level. The reference state for the immersion energies is the 14.0 Å basal spacing.

**Figure 7.** Variation in interaction energies between 3 different pairs. a) (SWy-2-Cation); b) Cation - CO\(_2\); c) SWy-2-CO\(_2\) as functions of interlayer spacing for Na-, Cs- and NH\(_4\)-SWy-2 at 323 K and 90 bar. Dotted vertical lines indicate respective collapsed interlayer distances for cations.
At \( d(001) \) values > 10.7 Å the interaction energies for Na/CO\(_2\) are significantly larger than for Cs/CO\(_2\) and NH\(_4\)/CO\(_2\), consistent with the solvation energy trends reported in Figure 1. Further, CO\(_2\)/clay interaction energies are relatively similar for all the cations (Figure 7c). The small, but significantly more favorable CO\(_2\)/clay interaction for Na-SWy-2 (Figure 7c) might reflect the stronger CO\(_2\)/Na interaction energy (Figure 7b). Lastly, the sum of CO\(_2\)/Na and CO\(_2\)/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 CO\(_2\) intercalation and the relatively weak interaction of Cs and NH\(_4\) with the clay that facilitates CO\(_2\) 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 CO\(_2\) under the experimental conditions to compare to the calculated concentrations. While these experimental techniques cannot distinguish external from intercalated CO\(_2\), the measurements help to validate the simulation results. Indeed, the IR intensity associated with the asymmetrical CO\(_2\) band (Figure 8) trends with the simulations if we use the experimental \( d(001) \) values in Table 1 to calculate the sorbed CO\(_2\) concentrations from the simulation results plotted in Figure 6a. Similarly, these computed concentrations of CO\(_2\) (0.0 mol CO\(_2\)/mol Na\(^+\), 1.55 mol CO\(_2\)/mol NH\(_4\)^+\), and 1.99 mol CO\(_2\)/mol Cs\(^+\)) trend well with our QCM measurements (0.5 mol CO\(_2\)/mol Na\(^+\), 1.74 mol CO\(_2\)/mol NH\(_4\)^+\), and 3.66 mol CO\(_2\)/mol Cs\(^+\)). We suggest that the higher values for the QCM measured concentrations from the simulation results plotted in Figure 6a. Similarly, these computed concentrations of CO\(_2\) (0.0 mol CO\(_2\)/mol Na\(^+\), 1.55 mol CO\(_2\)/mol NH\(_4\)^+\), and 1.99 mol CO\(_2\)/mol Cs\(^+\)) trend well with our QCM measurements (0.5 mol CO\(_2\)/mol Na\(^+\), 1.74 mol CO\(_2\)/mol NH\(_4\)^+\), and 3.66 mol CO\(_2\)/mol Cs\(^+\)).

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 (9.5 Å) is the most stable state, with energy minimum of ~4500 kJ/mol when compared to ~700 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 CO\(_2\) intercalation (see SI),\(^{26}\) and then systematically dehydrated the clay. The hydrated clay was first exposed to scCO\(_2\) 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 CO\(_2\) injected on every upward-pressure leg. The results show that as the clay dehydrated, eventually to the collapsed state (9.67 Å), intercalated CO\(_2\) was systematically and nearly completely expelled from the interlayer region. We then performed a similar experiment except the clay was cycled between scCO\(_2\) at 90 bars and 50°C, and liquid CO\(_2\) at 90 bars and 25°C, with CO\(_2\)+H\(_2\)O leaked on the upward-temperature leg of the cycle and fresh ChyO\(_2\) injected on every down-pressure leg. The results were the same: As the clay dehydrated, CO\(_2\) was expelled from the interlayer region. Consequently, these experiments are in agreement with our GCMD 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 scCO\(_2\).

CONCLUSIONS AND IMPLICATIONS

Experiments and complementary GCMD simulations for Na-, NH\(_4\)-, and Cs-SWy-2 exposed to dry scCO\(_2\) at 50°C and 90 bars reveal that while 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 CO\(_2\). Further, the Na-clay exhibits a large energy barrier for CO\(_2\) intercalation. In contrast, the stable state of the NH\(_4\)- and Cs-clay is an expanded, 1WL-like state, containing substantial interlayer CO\(_2\), coupled with little to no energy barrier for CO\(_2\) 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-H\(_2\)O 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 H\(_2\)O-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.,\(^{26}\) saturated with Na\(^+\), NH\(_4\)^+\), 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 CO\(_2\) (3.45 or 90 bar) at 50°C using a high pressure and temperature X-ray diffraction technique described previously.\(^{19,55}\) 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
CO$_2$ 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.

$^{13}$C, $^{23}$Na, $^{15}$N, and $^{133}$Cs MAS NMR spectra were collected under pressurized conditions at 90 bar CO$_2$ and 50°C after first exposing each sample to dry nitrogen at 50°C and 1 bar. The NMR spectra were acquired at an H$_0$ magnetic field of 7.0 T with a Varian VNMR 10 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 $^{13}$C 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 $^{13}$C 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 $^{15}$N 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 11 s, and a spin rate of 3 kHz to obtain 5000 transients. The $^{23}$Na 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 scCO$_2$. 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.mnrr.com), and all NMR results were iteratively fit using Abscissa, a freeware app written by Rudiger Bruhl (http://rbruhe.macbay.de). For the $^{13}$C 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 $^{13}$Cs 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 $^{23}$Na 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 $^{15}$N 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 raw data set to Lorentzian lineshapes.

**Molecular Dynamics Simulations**

Molecular dynamics simulations were conducted in the grand canonical ensemble (GCMD)$^{61}$ for Na$^+$, Cs$^+$, NH$_4^+$-montmorillonite. The SWy-2 model was obtained from Ngouana and Kalinichev$^{68}$ and has a structural formula of M$^{y}_{0.75}$(Si/2.75Al)$_{2.25}$(Al$^{3+}$)$^{0.3}$Mg$_{0.3}$O$_{2}$OH$_{2}$. The distributions of the octahedral and tetrahedral isomorphous 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 740.2 Å$^2$. 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 CO$_2$, as has been reported in previous studies.$^{37}$

The GCMD simulations were performed with the RASPA$^{62}$ 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 CO$_2$ molecules were represented with the rigid EPM2 model.$^{55}$ The parameters for the rigidly held NH$_4^+$ 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 andacentric factor used to automatically compute the fugacity in RASPA using the equation of state.$^{67}$ The computed fugacity coefficient of CO$_2$ 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 adsorption$^{2,25}$ and is extended here to CO$_2$.

**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 CO$_2$; 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 Schaef, todd.schaef@pnnl.gov
ES Ilton, eugene.ilton@pnnl.gov
JS Loring, john.loring@pnnl.gov

**Author Contributions**

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