Interlayer Cation-Controlled Adsorption of Carbon Dioxide in Anhydrous Montmorillonite Clay

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ABSTRACT: Widely available natural layered expandable clay minerals (smectites) can sorb carbon dioxide in their interlayer space under specific conditions and hence may show potential for gas separation or carbon sequestration processes. This work presents experimental adsorption and desorption measurements of gaseous, sub-critical carbon dioxide (p = 0.1 bar up to 20 bar, T = −20 °C up to 300 °C) on well-characterized anhydrous smectite (Wyoming montmorillonite) and focuses on the effect of the interlayer cation (size). Using seven alkali and alkaline-earth metal cations and three quaternary ammonium cations, a wide range of ionic radii are studied. Physiosorption of CO2 in the interlayer space is confirmed via infrared spectroscopy measurements. The results show that optimally sized interlayer cations—comparable to the thickness of a carbon dioxide monolayer—open the interlayer space to make it easily accessible for CO2 up to 1.7 mmol g−1. In particular, Cs− exchanged and tetramethylammonium-exchanged montmorillonite facilitate the rapid sorption of carbon dioxide even at ambient pressure and temperature. These results provide valuable insights into the applicability of widely available natural adsorbent clays for carbon capture and sequestration for the mitigation of climate change.

INTRODUCTION

Global warming is arguably the biggest challenge faced by the society. The effects of rising global temperatures and atmospheric CO2 levels include ocean acidification, rising sea levels, increases in the frequency, duration, and intensity of weather extremes (e.g., heat waves, heavy precipitation events, droughts, and so forth), and threats of biodiversity losses and food scarcity.1 In addition to drastically reducing carbon emissions, the capture and subsequent storage of (anthropogenic) CO2 via negative emission technologies (NETs) on a global scale of 100−1000 GT over the 21st century is required to limit global warming to 1.5 °C.2 Obviously, methods and materials used for capturing and/or storing carbon dioxide thus need to be safe and scalable to the GT-scale.

Existing sequestration strategies include the sub-soil storage of supercritical CO2 captured from flue gas (“conventional” carbon capture and storage, CSS), or BECCS (bioenergy with CSS; if captured from biomass) in suitable geological formations, and the mineral carbonation via (enhanced) rock weathering. For the CO2 capture part in (BE)CCS, most often, aqueous amine solutions are used in a regenerative process but solid sorbents can also be used—often synthetic “designer” materials such as activated carbon, metal−organic frameworks, and zeolites. Some abundant natural clays (in particular, expandable clays such as smectites) are also known to sorb CO2 under specific conditions and may thus provide a low-cost alternative for the “designer” materials used in regenerative gas separation processes. Alternatively, given their low costs, clays can potentially be used as CO2 traps for carbon sequestration. This approach may circumvent the need for highly pressurized supercritical CO2 injection encountered in conventional CCS (which risks leaking and hence may face societal opposition)3 or inherent long sequestration time scales associated with, for example, olivine carbonation under ambient conditions.4

Montmorillonite (MMT), a member of the layered aluminosilicate smectite clay mineral group, has attracted substantial attention for sorption purposes due to its natural abundance, thermal and mechanical stability, and large (interlayer) specific surface areas of up to ~800 m2 g−1.5 In the absence of solvents sorbed in the interlayer space, its interlayer spacing is—to a large extent—set by exchangeable cations in the interlayer space compensating for negative charges in each MMT layer.6−8 Due to the large interlayer surface area of MMT and smectites in general, their interlayer adsorption capacity for solvents (in particular water,5,14 and also for CO2,5,14 and/or methane25−28) can be significantly larger than their sorption capacity on the external surfaces only, provided that the interlayer space is accessible for the species to be sorbed.

Beyond the use of MMT as a CO2 sorbent, understanding the interactions between MMT and CO2 is vital to the cap rock integrity assessment for the storage of supercritical CO2.
(scCO₂) in depleted geological reservoirs (CCS), as the swelling of the smectite-bearing cap rock upon the sorption of CO₂ may induce or prevent leaks. Understanding the dynamic exchange of CO₂ between smectite-bearing soil and the atmosphere is also important in the context of altered freeze–thaw exchange cycles upon global warming. Furthermore, CO₂ was suggested as an agent for enhanced gas recovery from (clay-bearing) shales, where adsorbed methane in the clay interlayer space is displaced by CO₂, hence requiring an understanding of the interaction of both gases with the shale material.

Experimental and molecular simulation studies reveal that anhydrous smectites with small interlayer cations (e.g., Na⁺) generally do not allow CO₂ to penetrate into their interlayers spontaneously (i.e., adsorption is limited to the external surfaces) but require a sub-monolayer of water to “prop open” the interlayer for CO₂ sorption. On the other hand, in the case of larger interlayer cations (e.g., Cs⁺), CO₂ is sorbed in the interlayer space even in the absence of water, as sketched in Figure 1. Sorbed CO₂ is then (on average) oriented with their main axis parallel to the MMT layer (Figure 1) and aggregated in a slipped parallel or T-shaped average) oriented with their main axis parallel to the MMT layer arrangement. Contrary to the studies discussed above, some authors report that long-term high-pressure exposure at low temperatures may still lead to the interlayer sorption of CO₂ even in anhydrous synthetic smectite exchanged with small cations (i.e., Li⁺, Na⁺) and that the smectite may then be able to retain sorbed CO₂ at temperatures up to 35 °C. Advanced experimental work featuring in situ diffraction measurements or in situ spectroscopic techniques (e.g., X-ray diffraction, Fourier transform infrared spectroscopy [(FT)IR], nuclear magnetic resonance [13,18 Raman scattering, or inelastic neutron scattering) provided conclusive evidence for the presence and orientation of CO₂ in the interlayer space. These studies, however, either only consider a limited number of (pressure and/or temperature) sorption conditions (often scCO₂ under reservoir conditions) or consider clays exchanged with only a limited number of different interlayer cations and thus only cover a rather small part of the relevant parameter space. Furthermore, the use of different base clay materials (e.g., Wyoming- or Texas-MMT, MMT from other sources (synthetic fluoro)hectorite) prevents the direct comparison of the effect of the interlayer cation (size) on the CO₂ sorption capacity between different data sets. A quantitative analysis of the (isolated) effect of the interlayer cation (size) on the CO₂ adsorption capacity of anhydrous MMT, in particular under gaseous CO₂ at variable exposure pressures and temperatures, complementary to the existing in situ experimental and molecular simulation works, is thus lacking.

The aim of this study is to experimentally quantify the effect of the interlayer cation (size) on the sorption characteristics of MMT for gaseous, sub-critical CO₂. We present sorption measurements of CO₂ on 10 (Table S1) cation-exchanged forms of anhydrous MMT (Wyoming SWy-2). By using the same base clay material, we highlight unambiguously the effect of the (size of the) interlayer cation on the CO₂ sorption capacity for a wide range of exposure pressures (0.1−20 bar), temperatures (−20−300 °C), and both shorter and longer exposure times. Structural properties of each MMT were well characterized using energy-dispersive X-ray spectroscopy (EDX), CHN elemental analysis, thermogravimetric analysis coupled with FTIR spectrometry (TGA−FTIR), and nitrogen sorption measurements. Ex situ IR spectroscopy confirms the location of the physisorbed CO₂ in the interlayer space on MMTs that readily sorb CO₂ and demonstrates the reversibility of CO₂ loading on the time scale of several minutes.

### EXPERIMENTAL DETAILS

**Clay Preparation.** Wyoming MMT (SWy-2) with structural formula (Ca0.12Na0.31K0.05)[Al3.01Fe(III)0.41Mn0.01Mg0.54Ti0.02]−[Si7.98Al0.02]O20(OH)4,34 Brunauer−Emmett−Teller (BET) surface area S₃₈ ᵃᵥ 30 m² g⁻¹ and layer charge of −0.55e per unit cell (UC) mostly in the octahedral aluminum

### Table 1. Energy-Dispersive X-ray Data of As-Received and Cation-Exchanged MMTs, Normalized on the Basis of 7.98 Si per Unit Cell

| MMT          | structural | both | interlayer |
|--------------|------------|------|------------|
|              | Si         | Al   | Fe         | Mg         | Ca | Ba | Na | K | Cs |
| nonexchanged | 7.98       | 3.19 | 0.69      | 0.52       | 0.04 | 0.42 |
| Mg-MMT       | 7.98       | 3.18 | 0.37      | 0.85       | 0.24 | 0.43 |
| Ca-MMT       | 7.98       | 3.36 | 0.15      | 0.54       | 0.08 | 0.04 | 0.04 |
| Ba-MMT       | 7.98       | 3.02 | 0.43      | 0.46       | 0.08 | 0.055 |
| Li-MMT       | 7.98       | 3.08 | 0.39      | 0.47       | 0.08 | 0.03 | 0.61 |
| Na-MMT       | 7.98       | 3.11 | 0.66      | 0.45       | 0.08 | 0.03 | 0.80 |
| K-MMT        | 7.98       | 3.20 | 0.51      | 0.45       | 0.03 | 0.03 |
| Cs-MMT       | 7.98       | 3.06 | 0.49      | 0.44       | 0.03 | 0.03 |
| NH₄-MMT      | 7.98       | 3.02 | 0.23      | 0.41       | 0.03 | 0.03 |
| TMA-MMT      | 7.98       | 2.99 | 0.69      | 0.41       | 0.03 | 0.03 |
| TEA-MMT      | 7.98       | 3.24 | 0.20      | 0.51       | 0.03 | 0.03 |
oxide sheet,\textsuperscript{35} was purchased from the Clay Mineral Society Source Clays Repository.\textsuperscript{35} To exchange its charge-compensation interlayer cation, approximately 15 g of the as-received MMT in a dialysis tube (SnakeSkin, 3.5 kDa MOW) was suspended in 200 mL of a 1 M solution (g 2 fold excess of the cation exchange capacity) of the chloride (nitrite in the case of Li\textsuperscript{+}) salt (Sigma Aldrich, $\geq$98\%) of the respective cation at room temperature for 2 weeks. Excess salt was washed off the cation-exchanged MMT in multiple cycles by suspending the dialysis tube containing the MMT in 200 mL of Milli-Q water until the supernatant conductivity was below $\leq$50 $\mu$S cm\textsuperscript{-1} (typically 6–8 cycles over $\sim$1 week). Subsequently, the clays were dried in an oven at 60 °C. The dried MMT was ground manually using a mortar and used for analysis without size fractioning and further purification.

**Clay Characterization.** Completeness of the cation exchange was verified with EDX spectroscopy (Zeiss MERLIN SEM with an Oxford Instruments EDX analyzer under N\textsubscript{2}) on all MMTs. CHN-elemental analysis (Flash 2000 Elemental Analyzer, Thermo Scientific) and the TGA-FTIR combination (Bruker IR Tensor 27 FTIR apparatus connected to the output of a Netsch STA 449 F3 Jupiter thermal gravimetric analyzer; Figures S1–S4) were used for characterizing the MMTs exchanged with quaternary ammonium cations [ammonium (NH\textsubscript{4}+), tetramethylammonium (TMA\textsuperscript{+}), and triethylammonium (TEA\textsuperscript{+})]. An overview of the abundance of each measured element is given in Table 1 for EDX data, and in Table 2 for CHN-elemental analysis and TGA–FTIR data, respectively. [Li, C, H, and N cannot be detected (accurately) by EDX, such that the completeness of the cation exchange for the Li- and quaternary ammonium MMT can only be deduced from the absence of the original cations (mostly Na\textsuperscript{+} and Ca\textsuperscript{2+}) in Table 1.]

From Table 1, it is evident that the desired interlayer cations have replaced most (approximately 0.5–0.8 e/UC) of the initial interlayer cations in Ca\textsubscript{2+}, Ba\textsubscript{2+}, Na\textsubscript{+}, K\textsuperscript{+}, and Cs-MMT. For Mg-MMT, the increase in the Mg content from $\sim$0.5 to 0.84 per UC points toward a similar progression of the exchange. The absence of (most of) the initial cations in MMT exchanged with quaternary ammonium cations and Li\textsuperscript{+} also suggests that most of the initial cations have been exchanged on these MMTs. The CHN-elemental analysis data in Table 2 shows ratios of C/N of 3.6:1 and 6.7:1 for TMA-MMT and TEA-MMT, respectively; slightly smaller than the expected 4:1 and 8:1. The total C and N mass corresponds to 0.54, 0.54, and 0.53 cations per unit cell for NH\textsubscript{4}+, TMA\textsuperscript{+}, and TEA-MMT, respectively. The cation mass derived from TGA-FTIR measurements of the cation thermal decomposition is slightly higher and corresponds to $\sim$0.8, 0.69, and 0.57 cations per unit cell, respectively (see Figure S1 for TGA curves and Figure S2–S4 for FTIR spectra of evolved gases). Altogether, the results in Tables 1 and 2 prove that the major fraction of interlayer cations consists of the desired cation after exchange. Additionally, FTIR spectral features of nonexchanged and cation-exchanged MMT, including the stretching and bending frequencies, satisfactorily agree with the Wyoming MMT structure (see Figure S5).\textsuperscript{36–39}

The surface area and porosity of each MMT (outgassed at 150 °C for $\geq$16 h under N\textsubscript{2}) were determined from N\textsubscript{2} sorption isotherms at $-196$ °C measured using a Gemini VII 2390t surface area analyzer. The adsorption–desorption isotherms (Figure S6) show characteristics of macroporosity (no saturation in the limit p/p\textsubscript{0} $\rightarrow$ 1), mesoporosity (type H\textsubscript{4} adsorption–desorption hysteresis), and (interlayer) microporosity (steep uptake in the low p/p\textsubscript{0} limit in particular for Cs-MMT and TMA-MMT), following the definitions in Thommes et al.\textsuperscript{40} N\textsubscript{2} adsorption isotherms of MMT exchanged with cations smaller than the Cs\textsuperscript{+} overlap with the desorption branch of nonexchanged MMT in the low p/p\textsubscript{0} limit with altered hysteresis loops in the high p/p\textsubscript{0} limit, indicating only changes in their meso- and/or macroporous structure after cation exchange. In contrast, MMT exchanged with Cs\textsuperscript{+}, TMA\textsuperscript{+}, or TEA\textsuperscript{+} demonstrates an upward shift of the isotherm compared to nonexchanged MMT, indicating increased interlayer micropore accessibility for these MMTs.

From the isotherms, the BET surface area ($0.05 \leq p/p_0 \leq 0.30$) and the external surface area and accessible interlayer surface area using the t-plot method are calculated, as listed in Table 3 (details in the Supporting Information). Clearly, the external surface area is almost independent of the interlayer cation ($\sim$20–30 m\textsuperscript{2} g\textsuperscript{-1}, in reasonable agreement with earlier reports\textsuperscript{39,32,34,41}). The accessible interlayer surface area increases with increasing cation size until TMA-MMT (in line with earlier reports\textsuperscript{41}) and decreases again for TEA-MMT, likely due to the large fraction of the interlayer space that is occupied by the large TEA\textsuperscript{+} cations,\textsuperscript{36} thereby limiting the number of available sorption sites. Given the cation-independent external surface area, it follows that the increased accessible interlayer surface area and thus the enhanced adsorption capacity for, in particular, Cs- and TMA-MMT must be attributed to the opening of the interlayer space by the relatively large cations.

![Table 2. CHN Elemental Analysis and TGA–FTIR Data of As-Received and Quaternary Ammonium-Exchanged MMTs\textsuperscript{46}](https://journals.acs.org/doi/10.1021/acs.jpcc.0c06746)

| MMT         | CHN elemental analysis | TGA–FTIR |
|-------------|------------------------|----------|
|             | C (m\% ) | N (m\% ) | H (m\% ) | $\Delta m$ | $T_d$ (°C) |
| nonexchanged MMT | 0.20    | 0.00    | 1.45     | -         | -          |
| NH\textsubscript{4}MMT | 0.20    | 0.83    | 1.03     | $\sim$2 | 300–400 |
| TMA-MMT      | 3.70    | 0.88    | 1.86     | 7.02      | 460        |
| TEA-MMT      | 7.04    | 0.90    | 2.01     | 10.15     | 440        |

“TGA–FTIR data refer to the temperature of the cation decomposition (i.e., they do not include dehydration and dehydroxylation of the MMT).”

![Table 3. BET Surface Area, t-Plot External Surface Area, and Interlayer Surface Area From Nitrogen Sorption Measurements (Figure S6) Listed according to the Ionic Radius of the Interlayer Cations](https://journals.acs.org/doi/10.1021/acs.jpcc.0c06746)

| MMT      | S\textsubscript{BET} (m\textsuperscript{2} g\textsuperscript{-1}) | S\textsubscript{e} (m\textsuperscript{2} g\textsuperscript{-1}) | S\textsubscript{a} (m\textsuperscript{2} g\textsuperscript{-1}) |
|-----------|------------------|-----------------|-----------------|
| nonexchanged MMT | 30.4             | 21.0            | 9.4             |
| Mg-MMT    | 30.5             | 21.9            | 8.6             |
| Li-MMT    | 39.3             | 22.5            | 16.8            |
| Ca-MMT    | 31.3             | 22.2            | 9.0             |
| Na-MMT    | 34.5             | 19.8            | 14.7            |
| Ba-MMT    | 31.2             | 20.5            | 10.7            |
| K-MMT     | 43.6             | 22.3            | 21.3            |
| NH\textsubscript{4}-MNT | 51.2             | 28.5            | 22.7            |
| Cs-MMT    | 110.7            | 28.7            | 82.0            |
| TMA-MMT   | 168.2            | 22.9            | 145.3           |
| TEA-MMT   | 63.6             | 20.5            | 43.1            |

![Figure S6](https://journals.acs.org/doi/10.1021/acs.jpcc.0c06746)

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CO₂ Adsorption–Desorption. A calibrated home-built Sieverts apparatus was used, equipped with two Gems 3100 digital pressure transducers (0–25 bar, accuracy: 0.25% of full-scale) that allows for manometric excess adsorption and volumetric desorption measurements in the temperature range −20–300 °C (schematic in Figure S7). Approximately ∼5 g of the sample was dried either at (i) 150 °C for approximately 20 h in an (nonvacuum) oven, at (ii) 300 °C for approximately 2 h in vacuum, or at (iii) 450 °C for approximately 2 h in vacuum.

For manometric measurements of the CO₂ adsorption isotherms, the sample CO₂ exposure pressure was increased stepwise (equilibration time >10 min) from 0 to 10 or 20 bar, while continuously monitoring the pressure and temperature in each compartment of the Sieverts apparatus. The adsorbed quantity of CO₂ was then calculated using the Van der Waals equation to account for nonideality of the gas. For volumetric desorption measurements, the apparatus was connected to a gas expansion vessel in which water is displaced (monitored using a digital pressure transducers (0−25 bar, accuracy: 0.25% of full-scale)). The water has pH ≈ 1 and is saturated with NaCl to minimize the loss of CO₂ via dissolution. From a separate set of experiments, errors are estimated to be ∼0.05 mmol g⁻¹ at the end of each experiment. In these volumetric measurements, the sample is first exposed to 15–17 bar CO₂ at −20 °C for 16–20 h (unless stated otherwise). After releasing the pressure to 1 bar and an equilibration time of 5 min, the sample is heated to 70 °C or 300 °C (typically around 3 °C min⁻¹), while continuously monitoring the water level in the expansion vessel.

For a subset of the MMTs [predried at 150 °C for 1 h under a N₂ atmosphere (flow rate: 100 mL min⁻¹)], sorption isotherms were measured gravimetrically under a controlled mixed flow of N₂ and CO₂ (stepwise increase/decrease from 0 to 80% CO₂) in a Netzsch STA449 F3 thermogravimetric analyzer. The gained weight was regarded as CO₂ adsorption capacity, and the final mass loss as the CO₂ desorption capacity. Saturated samples were also regenerated under the pretreatment conditions.

IR Spectroscopy. IR measurements were made using a Bruker Tensor 27 IR spectrometer coupled with a DLA TGS detector and a PIKE MIRacle ATR accessory. FTIR spectra were also regenerated under the pretreatment conditions. In these volumetric measurements, the sample is heated to 70 °C or 300 °C under N₂ purge (flow rate: 100 mL min⁻¹). IR spectra of the evolved gas were recorded with a resolution of 4 cm⁻¹ with an average of 32 scans per sample in the range 4000−650 cm⁻¹ throughout the heating process.

RESULTS

CO₂ Adsorption Capacity. First, we analyze the sorption capacity as determined using the volumetric method. The MMTs, predried under three different conditions, are loaded by exposing them at −20 °C to 15–17 bar CO₂ for >16 hours, similar to refs 22 and 24. Subsequently, the CO₂ pressure is released to 1 bar and after 5 min, the temperature is gradually increased, and the quantity Qₐ(T) of released CO₂ is monitored as a function of temperature (reported results are already corrected for the thermal expansion of the nonadsorbed gas in an autoclave). Nonechanged MMT, which is dominated by Na⁺ cations, hardly displays any CO₂ release over the entire T-range up to 500 K (Figure 2). In contrast, most cation-exchanged MMTs display a finite release that initially increases linearly with...
T and subsequently saturates at some characteristic temperature in a plateau value. Because the plateau indicates the completion of CO₂ desorption, we interpret the corresponding maximum value of \( Q_b(T_{\infty}) \) as the sorption capacity of the material. The initial slope, the saturation temperature, and sorption capacity all depend on the type of cations and the predrying conditions of the clay prior to CO₂ loading (Figure 2). Notwithstanding a few notable exceptions (i.e., Mg-MMT predried at 150 °C, and TEA-MMT) to be discussed below, the results show in general that ions with a size of Na⁺ (\( r_{Na} = 102 \text{ pm} \)) and smaller display a small sorption capacity \( Q_b < 0.3 \text{ mmol g}^{-1} \), whereas ions with a size of Ba²⁺ (\( r_{Ba} = 135 \text{ pm} \)) and larger can sorb substantially more CO₂ with a maximum of \( \approx 1.4 \text{ mmol g}^{-1} \) for Cs⁺ at low predrying temperatures. In general, higher predrying temperatures reduce the sorption capacity for all materials, albeit to a cation-specific extent (difference between blue, yellow, and red lines in Figure 2; see Discussion).

Appreciating that the sorbed quantity of CO₂ (which may include CO₂ retained from the high-pressure/low-temperature exposure and hence can be larger than measured in manometric adsorption measurements) at temperature \( T \) and \( p = 1 \text{ bar} \) is now given by \( Q_b(T_{\infty}) = Q_b(T_{\infty}) - Q_b(T) \), we calculate \( Q_b \) as a function of the ionic radius of the interlayer cation at various temperatures, as demonstrated in Figure 3 for MMTs predried at 150 °C. (We omit here Mg-MMT, see Discussion.) Reflecting the results in Figure 2, the sorption capacity of CO₂ of MMT exchanged with cations smaller than Ba²⁺ is relatively small (<0.3 mmol g⁻¹) at all temperatures studied. The trend of increasing sorption capacity with an increasing ionic radius for Ba²⁺, K⁺, NH₄⁺, and Cs⁺-MMT clearly occurs over a rather small range of ionic radii (tens of pm) compared to the range of ionic radii studied. Notably, most CO₂ is sorbed by TMA-MMT at \( T \geq 30 \text{ °C} \), whereas Cs-MMT sorbs most CO₂ at lower temperatures.

To quantify the sorption in more detail and to illustrate the effect of long-term (high-pressure/low-temperature) exposure on the sorption capacity, using the manometric and gravimetric methods we measured the adsorption isotherms for the MMTs dried at 150 °C with rather high sorption capacities (K⁺, NH₄⁺, Cs⁺, TMA⁺, and TEA-MMT) and nonexchanged MMT (Figure 4). Results obtained using the manometric method and—independently—the gravimetric method are in excellent agreement. The steepness of all adsorption isotherms decreases with increasing temperature. In line with the results obtained using the volumetric method, the adsorption capacity of nonexchanged MMT and TEA-MMT is small. Likewise, we only find significant sorption on K-MMT and NH₄-MMT at low temperatures and/or high CO₂ pressures. For K-MMT, saturation is not even achieved when the vapor pressure of CO₂ is approached at \(-20 \text{ °C} \). Finally, both Cs-MMT and TMA-MMT show relatively steep adsorption isotherms at the complete range of temperatures studied.

Additionally, the results using the volumetric method (Figures 2 and 3) are included in Figure 4 (circles). For Cs-MMT and TMA-MMT, these datapoints coincide with the adsorption isotherms measured using the manometric method and the gravimetric method, indicating no effect of the long-term exposure and fast desorption kinetics (in fact, within minutes—see also Figure S8) such that the desorption process occurs quasi-statically. For K-MMT and NH₄-MMT, on the other hand, these volumetric results show significantly larger sorption than measured using the manometric and gravimetric methods at \( p = 1 \text{ bar} \) (yet approximately equal to manometric measurements at \(-20 \text{ °C} \) and 15–17 bar, i.e., exposure conditions in the volumetric measurements). K-MMT and NH₄-MMT thus appear to be able to retain (rapidly) sorbed CO₂ for somewhat longer time scales at low temperatures due to rather slow desorption kinetics. Nevertheless, longer-term exposure does not appear to increase the sorption capacity for these MMTs. Admittedly, we do find a rather small increase of the adsorption capacity (from 0.2 to 0.4 mmol g⁻¹) with increasing exposure time (from 17 to 120 h) on Li-MMT (see Figure S9).

The manometrically and gravimetrically measured adsorption isotherms are well described with the Langmuir isotherm,

\[
Q_b = \frac{q_b P}{1 + b P}
\]

in which \( q_b \) is the (in theory temperature independent) saturation adsorption capacity (i.e., a proxy for the number of available adsorption sites) and \( b = b_0 \exp(-\Delta H/RT) \) is the temperature-dependent equilibrium constant that includes the adsorption enthalpy \( \Delta H \) and pre-exponential factor \( b_0 \) that is the ratio between the adsorption and desorption attempt frequencies with units of inverse pressure.

The fits to the Langmuir model in Figure 4 allow us to determine \( q_b \) and \( b \) as functions of temperature for the different clays, as shown in Figure S4a,b, respectively. \( q_b \) decreases with increasing ionic radius and decreases slightly with increasing temperature (except NH₄-MMT, where \( q_b \) is difficult to determine accurately as \( Q_b \) does not saturate). This temperature effect appears to be independent of the interlayer cation for Cs⁺, TMA⁺, and TEA-MMT and thus likely originates from adsorption on the external surface and/or a densification of the adsorbed layer with decreasing temperature that are not included in the Langmuir model.

As expected, \( b \) decreases exponentially with increasing temperature and clearly varies per interlayer cation (Figure Sb). Interestingly, \( b \) is larger for Cs-MMT than for TMA-MMT at \( T \leq 20 \text{ °C} \) (i.e., the adsorption isotherm of Cs-MMT is sharper than TMA-MMT under these conditions) and smaller at \( T \geq 20 \text{ °C} \). This fully reflects the measurements using the volumetric method, where indeed a crossover point between the adsorption capacity at 1 bar of Cs-MMT and TMA-MMT is observed around \( T = 20–30 \text{ °C} \). From the slope and intercept of the fit in Figure Sb, \( b_0 \) and \( \Delta H \) can be determined, as illustrated...
in Figure 5c. In Figure 5, nonexchanged MMT, K-MMT, and the higher temperature measurements of NH4-MMT are not shown because of large uncertainties in their fit. Likewise, for TEA-MMT, the small "qs imposes large uncertainties on parameter b.

The values for the Langmuir isotherm parameters, qs, b0, and ΔH, for the different MMTs are summarized in Table 4, from which we identify the following trends:

- qs, or the number of available adsorption sites (or the adsorption volume), decreases with increasing ionic radius,
- b0, a proxy for the accessibility of the interlayer, increases with increasing ionic radius,
- ΔH is approximately −30 kJ mol−1 for NH4- and Cs-MMT and approximately −21 kJ mol−1 for TMA-MMT.

| MMT     | qs (mmol g−1) at −20 °C | b (bar−1) at −20 °C | ΔH (kJ mol−1) | ln(b0) (bar−1) × 10−3 |
|---------|-------------------------|---------------------|---------------|----------------------|
| NH4-MMT | 2.20                    | 0.225               | −30.7         | 0.011                |
| Cs-MMT  | 1.61                    | 9.40                | −29.7         | 0.82                 |
| TMA-MMT | 1.50                    | 6.44                | −21.5         | 24.5                 |
| TEA-MMT | 0.46                    | 1.34                | −        | 24.5                 |

ΔH thus appears to decrease with increasing ionic radius beyond Cs+. Calculations of the isosteric heat of adsorption from the Clausius–Clapeyron relation yields similar values that are moreover (almost) independent of loading (Figure S10).
IR Spectroscopy. The dependence of the adsorption and desorption curves on the interlayer cations discussed so far provides strong yet indirect evidence that CO$_2$ is actually sorbed in the interlayer space. To confirm this conclusion more directly, we performed ex situ (i.e., in ambient air) FTIR measurements on Cs-MMT after it was exposed to CO$_2$, as indicated in Figure 6 and similarly for TMA-MMT in Figure S11. These measurements are not quantitative nor accurately time resolved, as they depend on the process of transferring the MMT from the autoclave (in which it was exposed to CO$_2$) to the ex situ ATR crystal. Nevertheless, the singlet band at 2345 cm$^{-1}$, corresponding to the asymmetric $\nu_4$ stretching vibration of a CO$_2$ molecule with its rotation inhibited by interaction with neighboring molecules, indicates remaining physically constrained adsorbed CO$_2$. Rotational sidebands typical for gaseous, nonadsorbed CO$_2$ are absent (Figure S12). The single peak is consistent with the work of Yeşilbaş et al., as well as to scCO$_2$ in clays and in other confined environments. This allows us to conclude that the CO$_2$ molecules are indeed adsorbed into the interlayer space of the MMT. As expected, given the absence of water in the interlayer, carbonate species were not detected in the FTIR spectra, indicating that the carbonation of adsorbed CO$_2$ did not occur in these MMTs.

**DISCUSSION**

Effect of Cation Size, Exposure Pressure, and Temperature on the Adsorption Capacity. Natural source clay SWy-2 (referred to as nonexchanged MMT in this work) is a well-studied MMT containing mostly Na$^+$ and Ca$^{2+}$ interlayer cations. At reservoir temperature ($45$–$50$ °C) under “dry” conditions, it nevertheless shows a rather wide range of sorption capacities spanning $0.08$–$0.4$ mmol g$^{-1}$ at $<20$ bar (e.g., due to different drying conditions and thus moisture contents). At $-10$ and $0$ °C, we indeed measured similar sorption capacities of no more than $0.3$ mmol g$^{-1}$ at $<20$ bar. (The higher sorption capacity at $-20$ and $-20$ bar—close to the CO$_2$ vapor pressure—is likely due to capillary condensation in the clay mesopores). Diffraction and spectroscopic techniques and simulations revealed that under anhydrous conditions nonexchanged MMT and Na-exchanged smectites do not readily sorb CO$_2$ in their interlayer space. Sorption on anhydrous nonexchanged MMT and Na-exchanged smectites, thus, is (mostly) limited to their external surface area. The CO$_2$ sorption capacity of cation-exchanged MMTs can clearly be significantly larger than the sorption capacity of nonexchanged MMT. The (almost) cation-independent external surface areas (see Table 3) suggest that cation-dependent sorption in the interlayer space must be responsible for these differences. We find that the interlayer sorption capacity is governed by three cation-dependent parameters: the number of available adsorption sites ($q_i$), the accessibility of the interlayer ($b_h$), and the sorption enthalpy ($\Delta H$), as discussed separately below.

The available number of adsorption sites, $q_i$, per smectite UC decreases with the increasing radius of the interlayer cation (in particular for monovalent cations), due to an increasingly large fraction of the interlayer space taken up by the cation (given that CO$_2$ is adsorbed in a monolayer and that the interlayer space is readily accessible) as suggested in earlier works by others on similar smectites. This effect is now confirmed in this work. Accounting for the unit cell mass, approximately $1.61, 1.31, 1.14,$ and $0.35$ molecules of CO$_2$ are sorbed per UC for NH$_4$-, Cs-, TMA-, and TEA-MMT at $-20$ °C, respectively. These trends are in qualitative accordance with the simulations by others, but approximately $20\%$ lower, likely due to (i) very different adsorption conditions used (scCO$_2$ 90 bar, 50 °C in their work), (ii) possible impurity of the MMT in our experimental work, and (iii) inherent differences between simulations and experimental works. The significantly stronger decrease of $q_i$ on TEA-MMT can be attributed to TEA$^+$ flattening out in the interlayer, thereby relatively taking in more space without significantly increasing the interlayer spacing and thus limiting the number of available gas adsorption sites (as confirmed in our N$_2$ sorption measurements in Figure S6). Furthermore, $q_i$ of NH$_4$-, Cs-, and TMA-MMT are in reasonable agreement with the measurements on slightly hydrated Mg-MMT (2.0 mmol g$^{-1}$) and slightly hydrated Ca-MMT (up to $\sim1.3$ mmol g$^{-1}$).

The sorption enthalpy, $\Delta H$, is approximately $-30$ kJ mol$^{-1}$ for NH$_4$- and Cs-MMT, and approximately $-21$ kJ mol$^{-1}$ for TMA-MMT, indicating physisorption. A rather large $\Delta H$ on materials with more narrow micropores is also observed in simulations and on activated carbon, and can be attributed to the increased interactions of the adsorbing molecules due to the close presence of two surfaces at the same time (instead of one). The value found for the sorption enthalpy $\Delta H$ for TMA-MMT, where the interlayer spacing is large and hence simultaneous interactions with two surfaces are suppressed, is also in good agreement with the sorption enthalpy on the external surface of similar MMTs ($20$–$21$ kJ mol$^{-1}$). The accessibility of the interlayer, $b_h$, increases with increasing radius of the interlayer cation and varies almost 2 orders of magnitude between NH$_4$- and Cs-MMT and between Cs- and TMA-MMT. Even small variations in the ionic radius (in particular NH$_4^+$ to Cs$^+$) thus strongly affect the sorption characteristics of the respective MMTs. Indeed, as found by Schaef et al., under equivalent conditions ($50$ °C, 90 bar), the sorbed quantity of CO$_2$ on NH$_4$-MMT is smaller than on Cs-MMT, whereas the number of available adsorption sites ($q_i$) on NH$_4$-MMT is larger than on Cs-MMT. We strictly did not find a minimal interlayer cation size required to open the interlayer space for CO$_2$, but in practice MMT with cations smaller than NH$_4^+$ show minimal sorption capacity within the range of ($p,T$) conditions studied in this work. Loganathan et al. reported a somewhat smaller (minimal) cation size to allow for interlayer CO$_2$ adsorption ($K^+$ or Sr$^{2+}$). This is likely related to a higher density supercritical adsorbate phase used in their work.
increases the frequency of adsorption events \( \rho_{\text{CO}_2}(50^\circ \text{C}, 90 \text{ bar}) \approx 300 \text{ kg m}^{-3} \), compared with in our work \( \rho_{\text{CO}_2}(20^\circ \text{C}, 19.9 \text{ bar}) \approx 51 \text{ kg m}^{-3} \). Likewise, (sub-monolayer) adsorption of CO2 into the interlayer space was even found on Na-MMT at very low temperatures \( (\sim −70 \text{ °C}) \) by Fripiat et al.\(^9\) (where parameter \( b \) is approximately 2 orders of magnitude larger than at room temperature, as extrapolated from Figure 5) but is not significant in the temperature range studied in this work. In other words, interlayer sorption on MMT with rather small interlayer cations requires low temperatures and/or high CO2 pressures (or densities). As an alternative to large cations, the interlayer space can be opened by water in the cation hydration shell, as demonstrated by Grekov et al.\(^{28}\) and also observed in our work for Mg-MMT (predried at 150 °C, Figure 2). Equilibrium constant \( b(20^\circ \text{C}) = 0.8 ± 0.1 \text{ bar}^{-1} \) in their work—approximately 2.5 times smaller than for Cs-MMT and TMA-MMT in our work at the same temperature (Figure 5). The ability of (a sub-monolayer of) water to open up the interlayer space of smectites with small interlayer cations (in particular Na\(^+\) and Ca\(^{2+}\)) was also demonstrated by others using various diffraction-12,20 and spectroscopic12,13 techniques and simulations.8–11 Other “props” as inorganic oxides also yield similar adsorption capacities up to 1.18 mmol g\(^{-1}\) at 273 K and 1 bar but no (Langmuir) fit parameters are reported.59

Furthermore, our results support that the interlayer sorption of CO\(_2\) is dominated by cation-alumino silicate sheet interactions.16,17 Electrostatic cation-alumino silicate sheet interactions strongly oppose expansion from the collapsed state to the state of an adsorbed CO\(_2\) monolayer in particular for smectites with small interlayer cations as Na\(^+\).16,17 Even though cation CO\(_2\) interactions become more favorable with increasing cation charge density (i.e., decreasing cation size for a given charge), the sorbed quantity in the low-pressure limit on Cs-MMT is higher than that on NH\(_4\)-MMT under the same conditions and significantly higher than on MMT exchanged with even smaller cations. This opposes the situation in the clay–water system, where the cation hydration free energy contributes significantly to sorption and swelling.5,7

Altogether, it is the interplay between \( q_{\text{m}}, b_0 \) and \( \Delta H \) that requires optimization under the desired \((p,T)\) conditions. Increasing the size of the interlayer cation favors the accessibility of the interlayer (i.e., the cations “prop open” the interlayer space) but in turn, decreases the available number of adsorption sites and eventually the sorption enthalpy. The optimum cation radius in the low-pressure limit lies between that of Na\(^+\) and Cs\(^+\). It is known that the interlayer space of smectites with small interlayer cations (in particular Na\(^+\) and Ca\(^{2+}\)) was also demonstrated by others using various diffraction-12,20 and spectroscopic12,13 techniques and simulations.8–11 Other “props” as inorganic oxides also yield similar adsorption capacities up to 1.18 mmol g\(^{-1}\) at 273 K and 1 bar but no (Langmuir) fit parameters are reported.59

Dehydration. Especially for Mg-MMT, apparent complete dehydration of the interlayer was demonstrated to fully occur at a temperature between 150 and 300 °C.\(^{28,59}\) Therefore, Mg-MMT that is predried at 150 °C is likely still opened by water in the interlayer cation hydration shell. At higher predrying temperatures, this water is also removed. Even though the temperature at which the major fraction of water is removed is significantly lower for cations other than Mg\(^{2+}\) (60–130 °C, increasing with the increasing ratio charge over cation radius; see e.g., ref 59), it is possible that the remaining traces of the tightly bound water (partially) open up the interlayer space after predrying at 150 °C.60

Cation migration. It is said that alkali or alkaline-earth metal cations smaller than Rb\(^+\) (\( r_{\text{Rb}} = 152 \text{ pm} \)) are able to migrate (in)to the hexagonal silicon oxide ring (Kagomé-like pocket) or octahedral sheet of the smectite layers at \( T \leq 300 \text{ °C} \). The extent of this migration and its reversibility depend on the cation size and charge, the geometry and charge (location) of the smectite layer, and the heating temperature and duration.61–64 Also, one of the H atoms of NH\(_4\)-MMT may (re)position in the silicon oxide ring.65,66 Both effects may (locally) decrease the interlayer spacing and thus compromise the accessibility of the interlayer.

Cation decomposition. As shown in Figure S1, it was found that the quaternary ammonium cations used in this study decompose at a temperature around 300 °C (NH\(_4\)-MMT) or 450 °C (TMA-MMT and TEA-MMT). Cation decomposition, most likely, leads to the collapse of the interlayer space, again compromising the interlayer accessibility and hence CO\(_2\) sorption capacity.

The sole interlayer cation not sensitive to either of these three mechanisms is Cs\(^+\). Indeed, only Cs-MMT retains most of its adsorption capacity when predried at 450 °C (Figure 2).

**Adsorption and Desorption Kinetics.** Adsorption and desorption kinetics at 30 °C on MMT exchanged with large interlayer cations (i.e., Cs\(^+\) and TMA\(^+\)) are fast with typical time scales not longer than 2–3 min. On the other hand, MMT exchanged with somewhat smaller interlayer cations (i.e., K\(^+\) and NH\(_4\)-MMT) shows the ability to retain CO\(_2\) for longer timescales at low temperatures as evidenced by the differences between the manometric adsorption measurements and volumetric desorption measurements (Figure 4).
Yeşilbaş et al. reported that retention times of CO₂ adsorbed in a MMT interlayer are increased by a strong nanoconfinement (i.e., small interlayer spacings) and decreased by the coadsorption of water, which increases the interlayer spacing. In the driest (Na⁺)-MMT achieved in their work (containing ~1.4 mmol H₂O per gram MMT) with an average basal spacing of 9.9–10.2 Å close to that of anhydrous K-MMT (10.1 Å), (interpolated) retention times are of order 250 min at −20 °C, of around 20 min at 0 °C, and some 6 min at 60 °C. Considering our heating rate of approximately 3 °C min⁻¹, retention times are smaller or comparable to the heating times may be used in cyclic adsorption applications.

**CONCLUSIONS**

Anhydrous MMT exchanged with interlayer cations comparable in size to a CO₂ monolayer (in particular, Cs⁺ and TMA⁺) facilitate the interlayer sorption of CO₂. This sorption occurs even at rather low (partial) pressures (e.g., flue gas composition, ~15% CO₂) or room-temperature conditions. The easily accessible "popped open" interlayer facilitates the rapid sorption of CO₂ and a high CO₂ capacity, provided the interlayer cation size, and thus the interlayer spacing, is sufficiently large. Outside of this optimum cation size range, a further increase of the interlayer cation size decreases the available number of sorption sites due to space filling by the cations themselves. Even small decreases of the interlayer cation sizes below the optimum size already strongly compromise the accessibility of the interlayer requiring rather low temperatures and/or high pressures for significant CO₂ sorption. Exposure of the MMT to elevated pressures for prolonged times does not significantly improve sorption capacities on practical time scales, but MMTs with rather small interlayer cations are able to retain sorbed CO₂ for a short while after the elevated pressure is released. Due to their natural abundance and easy preprocessing, (cation-exchanged) MMT and other natural swelling clays in general provide an alternative approach to "designer" materials such as zeolites, in particular in terms of their scalability.

Qualitative trends associated with the effect of layer spacing on the CO₂ adsorption capacity of MMT identified in this work may also apply to other layered materials, such as other base clay minerals, layered double hydroxides, or graphene oxide. We thus believe that this work provides valuable insights into the applicability of widely available natural layered adsorbent materials in general for carbon capture and/or sequestration for the mitigation of climate change and beyond.

**ASSOCIATED CONTENT**

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.jpcc.1c06746.

Ionic radii; thermal decomposition of quaternary ammonium cation-exchanged MMT (including evolved gas FTIR); ATR-FTIR spectra of MMTs; nitrogen adsorption measurements; sketch of the setup; gravimetric adsorption and desorption measurements (Cs-MMT and TMA-MMT); volumetric long-term exposure (Li-MMT); isosteric heat of adsorption (Cs-MMT and TMA-MMT); FTIR spectra of CO₂-loaded TMA-MMT, atmospheric water, and CO₂; and comparison of MMT and Zeolite 13X equilibrium constants (PDF)

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**Notes**

The authors declare no competing financial interest.

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