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Published in:
Scientific Reports

DOI:
[10.1038/srep08775](https://doi.org/10.1038/srep08775)

2015

[Link to publication](#)

Citation for published version (APA):

Michels, L., Fossum, J. O., Rozynek, Z., Hemmen, H., Rustenberg, K., Sobas, P., Kalantzopoulos, G., Knudsen, K., Janek, M., Plivelic, T., & da Silva, G. (2015). Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cations. *Scientific Reports*, 5, Article 8775. <https://doi.org/10.1038/srep08775>

Total number of authors:
11

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Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cations

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Received
12 November 2014Accepted
29 January 2015Published
5 March 2015Correspondence and
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A good material for CO₂ capture should possess some specific properties: (i) a large effective surface area with good adsorption capacity, (ii) selectivity for CO₂, (iii) regeneration capacity with minimum energy input, allowing reutilization of the material for CO₂ adsorption, and (iv) low cost and high environmental friendliness. Smectite clays are layered nanoporous materials that may be good candidates in this context. Here we report experiments which show that gaseous CO₂ intercalates into the interlayer nano-space of smectite clay (synthetic fluorohectorite) at conditions close to ambient. The rate of intercalation, as well as the retention ability of CO₂ was found to be strongly dependent on the type of the interlayer cation, which in the present case is Li⁺, Na⁺ or Ni²⁺. Interestingly, we observe that the smectite Li-fluorohectorite is able to retain CO₂ up to a temperature of 35 °C at ambient pressure, and that the captured CO₂ can be released by heating above this temperature. Our estimates indicate that smectite clays, even with the standard cations analyzed here, can capture an amount of CO₂ comparable to other materials studied in this context.

Interactions between CO₂ and clay minerals have attracted interest in the scientific community in recent years, partly because geological structures are being investigated as storage sites for anthropogenic CO₂. The cap-rock formations which act as flow barriers and seals in this context are known to contain high proportions of clay minerals¹, and the long-term integrity of these formations is a prerequisite for avoiding CO₂ losses to the atmosphere^{2,3}. However, the physical parameters affecting the interactions between CO₂ and clay minerals under reservoir conditions are still not well understood⁴.

Clay minerals are materials based on two-dimensional stacks of inorganic layers⁵. In some clay minerals (smectites), non-equivalent substitutions of atoms generate a negative charge on each layer surface which is balanced by exchangeable interlayer cations. These cations are responsible for the differences in the physico-chemical behavior of smectites such as water adsorption and retention, plasticity, swelling etc^{6,7}. Smectite clay mineral particles typically consist of approximately hundred layers. Smectites have the ability to intercalate additional molecules into the interlayer space, thereby changing the repetition distance along the layer normal (z-direction), a process which is known as swelling^{8,9}. Intercalation of water can also occur, since H₂O is a polar molecule, and this has been extensively studied with a wide range of techniques, such as neutron^{8,10,11} and X-ray scattering^{9,12,13}, NMR spectroscopy^{14–16} tracer experiments¹⁷ or numerical modeling^{14,18}.

Experiments^{19–28} and simulations^{18,29–32} have also shown that CO₂ intercalates in some smectite clays, both in supercritical and in gaseous/liquid form. We have recently demonstrated that CO₂ is able to intercalate in Na-fluorohectorite (NaFh) smectite clay mineral at conditions close to ambient (−20 °C, 5 bar)²². In that work we also showed that under the same conditions neither H₂O vapor nor N₂ gas intercalates. These are not the typical conditions found in geological storage sites, but the conditions are relevant if clays are considered as a potential material for the capture or sequestration of CO₂, and it is also of interest to study CO₂ capture and retention under these conditions for the purpose of understanding the underlying molecular mechanisms. Several porous materials are currently being assessed for the purpose of CO₂ capture and retention^{33–35}. In this context, clay-containing materials could have a distinct advantage in that they are both cheap and ubiquitous³¹, and also



because they generally provide a very large accessible effective surface area that arises from nanolayered stacked structures embedded in a mesoporous powder matrix.

Fluorohectorites (Fh) are synthetic smectites which have been used as a representative and clean model system of natural smectite clays³⁶. Synthetic clays have the advantage that they possess a more homogeneous charge distribution, and also contain significantly fewer impurities (e.g. carbonates, (hydr)oxides, silica, and organic matter) than their natural counterparts⁷.

In the present work we studied the intercalation of CO₂ in Li-fluorohectorite (LiFh), Na-fluorohectorite (NaFh) and Ni-fluorohectorite (NiFh). The only differences between these samples are the interlayer charge compensating cations used. Intercalation experiments under different temperature and pressure conditions were conducted. In order to investigate the potential of fluorohectorite clays for CO₂ storage and capture, we also quantified the CO₂ adsorption (wt%).

Results

CO₂ Intercalation. The layered nature of smectite clays gives rise to well-defined (001) diffraction peaks, and the angular position of these peaks is a direct measure of the interlayer repetition distance (the *d-spacing*). Figure 1 displays how the intensity of the (001) diffraction peak grows with time as the samples are exposed to CO₂ at -20°C and 20 bar. All the samples were pre-dried before the measurements (see Methods section below). Intercalation of CO₂ in the interlayer space manifests itself as the growth of an intercalation peak at a lower scattering angle (higher *d-spacing*) than the peak of dry, non-intercalated clay. As the intercalation progresses, the intensity of the CO₂-intercalation peaks increase whereas the scattering from non-intercalated part of the sample decreases and eventually vanishes. LiFh and NaFh show similar intercalation behaviors in the X-ray diffractogram (XRD). The (001) peaks develop to *d-spacings* of 1.196 nm and 1.240 nm, for LiFh and NaFh respectively. This could correspond to a monolayer of intercalated CO₂, in analogy to what occurs for H₂O. For the NiFh sample we observe a similar intercalation state with *d-spacing* of 1.219 nm, and in addition the development of another state with a larger *d-spacing* of 1.311 nm. To our knowledge, this is the first time such a complex CO₂ intercalation state has been observed in a clay mineral, although other authors have found evidence of multiple intercalated layer type^{9,37}. One may note that the secondary low-angle peak is at a *d-spacing* of ca. 1.3 nm, which is distinct from the ≈1.25 and ≈1.55 nm spacings of the one (1WL) and two water layer (2WL) smectite states as reported by Ferrage et al.^{38,39}. Other XRD studies have generally observed only blurred peaks in this region and have interpreted them as mixtures of peaks with the 1WL and 2WL spacings.

Figure 2 shows the comparison of (001) peak intensity vs. time for LiFh, NaFh and NiFh. In this Figure we plot the NiFh (001) peak intensities of *d-spacing* ≈ 1.21 nm, *d-spacing* ≈ 1.31 nm and the sum of them. We observe that the intercalation rate is significantly higher for NiFh and LiFh than for NaFh. This is similar to the case of water intercalation, where cations have been found to determine the stable states at varying relative humidity^{18,40–43} as well as the way that clay minerals exfoliate in aqueous dispersion^{6,44}. Fripiat et al.²⁷ suggested that the access of CO₂ molecules to the interlayer space of montmorillonite clay is dependent on the size of the interlayer cation. Giesting et al.²³ studied CO₂-intercalation behavior of K- and Ca-montmorillonite, performing repeated measurements under the same conditions, and also reported a significant dependence of dynamics on the cations. The dynamics of the CO₂ intercalation can also be followed by observing the disappearance of the scattering intensity of the dehydrated peak, shown in Figure S1 in supporting information, which represents the *d-spacing* in the portion of the sample with no water or CO₂ intercalated.

In Figure S2 of the supporting information we show the *d-spacing* dynamics of the CO₂ intercalated peak for each sample. Although the procedure used involves pre-drying of the samples it is possible that there is a minor amount of remaining H₂O within the sample. This amount must in any case be very small since there is no detectable 1WL peak in the XRD patterns. Any residual H₂O could affect the kinetics of the CO₂ intercalation.

A general equation for describing sorption kinetics is⁴⁵:

$$\frac{dn}{dt} = n_0 \frac{1}{\tau} f\left(\frac{n}{n_0}\right) \quad (1)$$

where *n* is the amount of adsorbed molecules on a surface and $\frac{1}{\tau}$ is a rate constant that depends on temperature and pressure. The equation for the function $f\left(\frac{n}{n_0}\right)$ depends on the type of adsorption mechanism. For a first order adsorption process, i.e. a process where the adsorbed molecules statistically occupy a single adsorption site⁴⁶, $f\left(\frac{n}{n_0}\right) = 1 - \frac{n}{n_0}$. In the present case, $\frac{n}{n_0}$ is proportional to the normalized X-ray intensity (*NI*), where normalization is performed with respect to the intensity observed at the longest times, where the adsorption capacity of the material is reached. By integrating equation (1), we obtain

$$NI = 1 - \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

which is an exponential growth function towards saturation at 1. Applying the natural logarithm, we have a linear equation with the slope proportional to the rate constant $\frac{1}{\tau}$:

$$-\ln(1 - NI) = \frac{t}{\tau} \quad (3)$$

The results of plotting the observed normalized intensity in this manner are shown in Figure 3. It is evident that equation (3) describes the data for NiFh and LiFh reasonably well, before the full adsorption capacity is reached, i.e. before all the sites have been occupied. However, for NaFh we observe deviation for $-\ln(1 - NI) < 1.6$, which we relate to the Na⁺ ion providing a stronger layer adherence than the other two ions investigated here, and thus the swelling is more difficult to achieve for the case of Na⁺, since the clay layers are closer together in the dehydrated state of NaFh, as shown in Figure 1 (*d-spacing* ≈ 0.97 nm). The difference in *d-spacing* between the dehydrated and the CO₂ intercalated peaks is almost two times higher for NaFh compared to LiFh and NiFh (Figure 1). The horizontal line in Figure 3 represents the threshold between two regimes for the case of NaFh: Clay expansion accompanied by partial adsorption of CO₂ (below the line), and adsorption of CO₂ into the expanded interlayer of the clay mineral (above the line). This is in agreement with Figure 1, where it is noticeable that for the case of NaFh there is small shift with time of the monolayer CO₂ Bragg peak even after expansion, indicating that more CO₂ is adsorbed into the interlayer.

After the swelling process is finished, which means that the clay does not expand significantly anymore, the intercalation process is cation independent since the slopes of the curves shown in Figure 3 are the same for all samples, i.e. $\frac{1}{\tau} = 0.05 \pm 0.005 \text{ hours}^{-1}$. This corresponds to a time constant τ of approx. 20 hours. A single exponential growth function $NI = A \left[\exp\left(\frac{t}{\tau_1}\right) - 1 \right]$ (shown in Figure 2), with $\tau_1 \approx 51$ hours, related to the clay swelling, describes well the data in the initial phase for NaFh, i.e. for $-\ln(1 - NI) < 1.6$ in Figure 3.

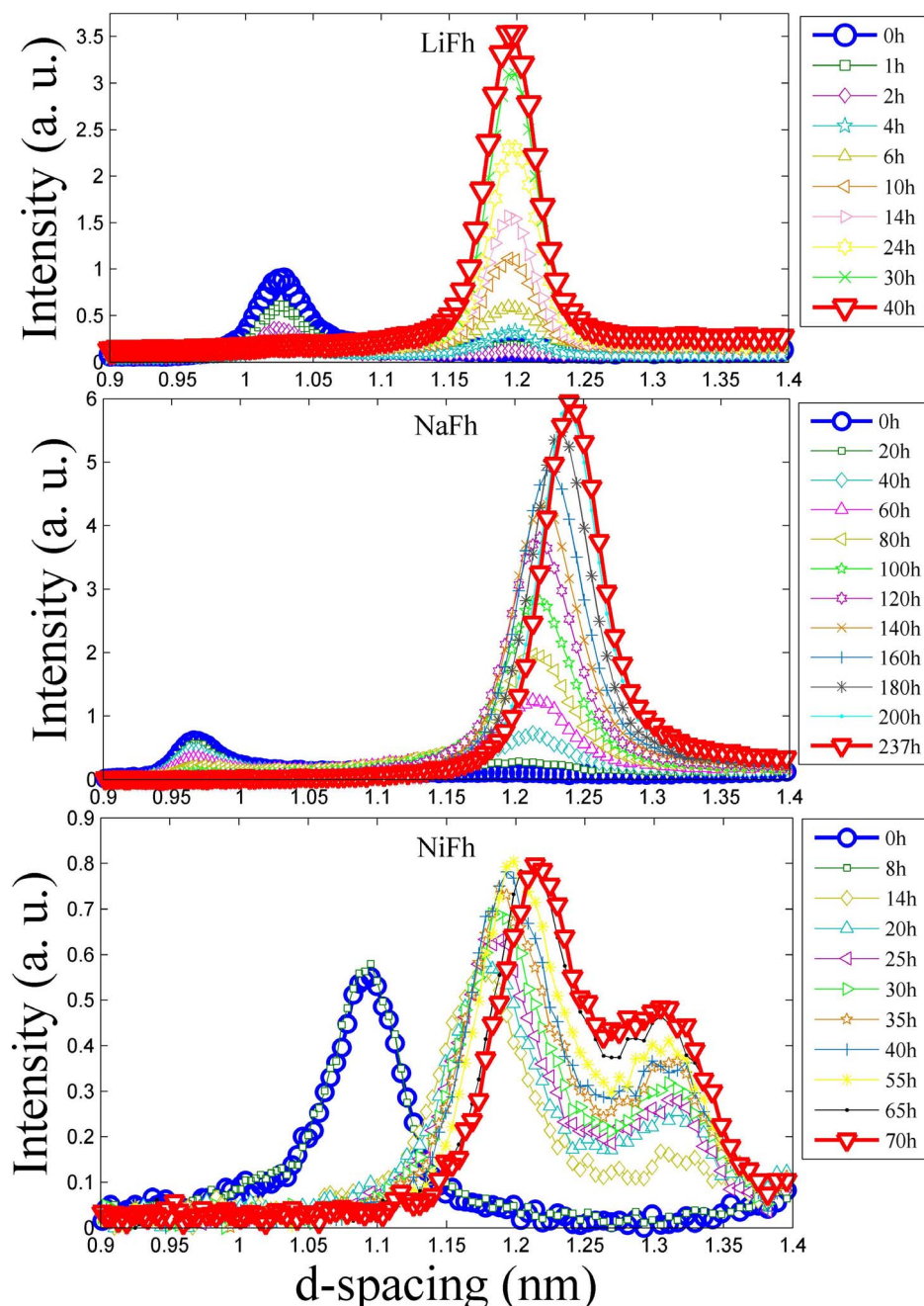


Figure 1 | The scattering intensity (arb. units) over a range of d -spacing values at different times (hours), for LiFh, NaFh and NiFh, respectively. In all cases the CO₂ adsorption conditions were -20°C and 20 bar. The red line (∇) shows the time at saturation. Experiment performed at NTNU.

The dependence of the intercalation intensity at various pressures is shown in Figure 4 for LiFh. The results show that the intercalation rate increases with pressure and this observation is in agreement with a previous study of NaFh²². We also measured intercalation at various temperatures (at a constant pressure of 20 bar) in the limited temperature range -5 , -10 and -20°C and the data suggests (inset of Figure 4) faster adsorption at lower temperature. We have not measured the T-dependence of τ here, but for simplicity, we may assume this to follow an inverse Arrhenius behavior⁴⁷.

The intensity of the CO₂ intercalation peak follows a linear behavior for small times, in agreement with equation (2), which for short times $t \ll \tau$ becomes $NI \approx t/\tau$. In Figure 4 we have not normalized the measured intensities to their saturation at long times, because we did not follow the experiments until saturation, thus the slopes (S) of the

straight lines at short times in Figure 4 (left panel) can be expressed as $S \approx \frac{C_0}{\tau}$ where C_0 is a constant. As suggested above, one can assume that the adsorption dynamics after swelling is governed by an average inverse Arrhenius like trapping time:

$$\tau = \tau_0 e^{-\frac{E}{k_B T}} \quad (4)$$

where, $\frac{1}{\tau_0}$ is an average attempt frequency, E is an average energy barrier, k_B is Boltzmann constant and T is the absolute temperature.

Further we can assume that the attempt frequency $\frac{1}{\tau_0}$ increases with pressure, P , i.e. the higher the pressure, the more attempts are made by the CO₂ molecules to cross the adsorption trapping energy barrier E . In the right panel of Figure 4, we have tested this assumption and

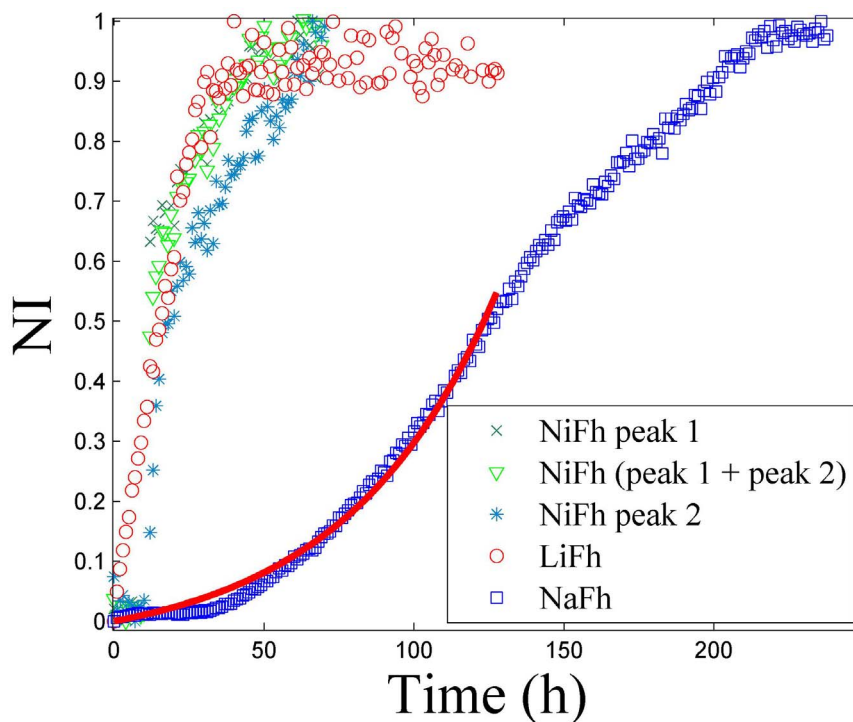


Figure 2 | Intensity of the intercalation peak, normalized to the maximum intensity (NI), as a function of time for different cations at 20 bar and -20°C . The NiFh diffractogram has two contributions: Peak 1 is the peak with the maximum intensity with $d\text{-spacing} \approx 1.21$ nm while peak 2 is the peak with $d\text{-spacing} \approx 1.31$ nm.

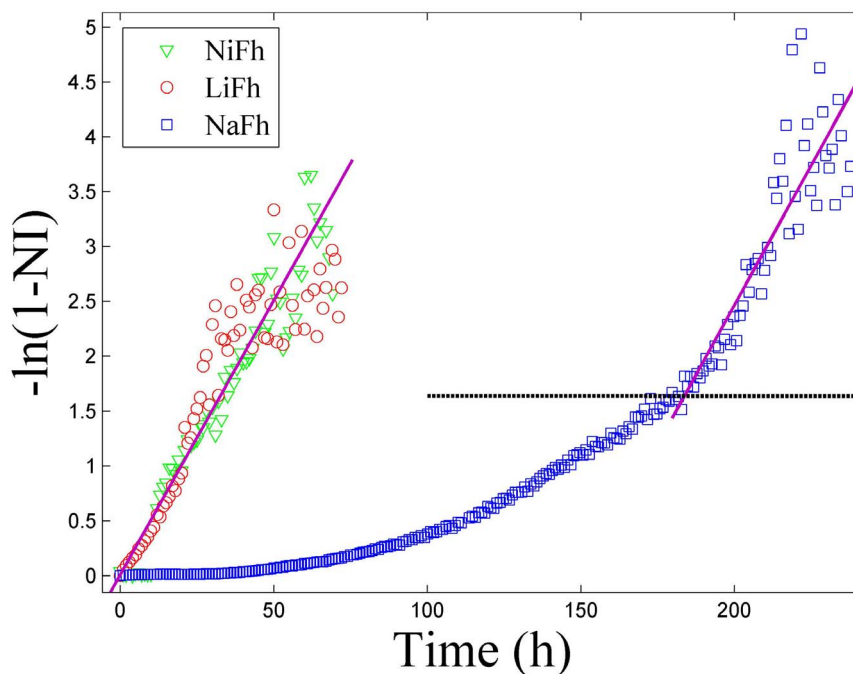


Figure 3 | The linearized intensity as function of time. The horizontal line represents the threshold between two regimes for NaFh: Clay swelling accompanied by some intercalation of CO_2 (below the horizontal line), which is described by the exponential function $NI = A \left[\exp\left(\frac{t}{\tau_1}\right) - 1 \right]$, and intercalation of CO_2 into the swollen interlayer of the clay mineral (above the horizontal line) described by equations (2) and (3). The initial swelling part of the dynamics is much faster for NiFh and LiFh as compared to NaFh, which is also confirmed in Figure S1 in the supporting information.

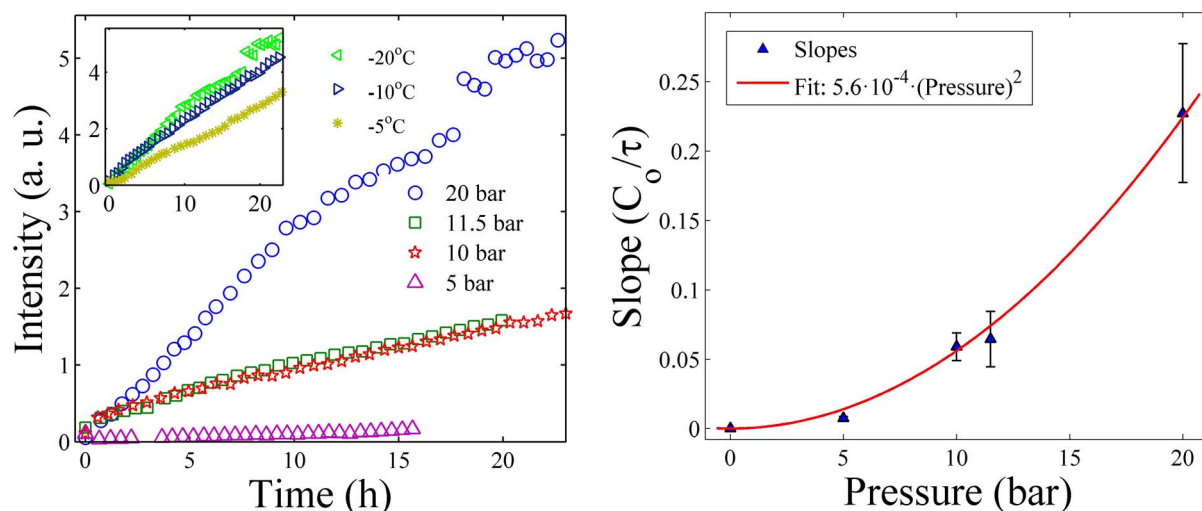


Figure 4 | Left panel: The intensity of the (001) CO₂ intercalation peak in LiFh as a function of time for different pressures (at constant temperature of -20°C). The intercalation rate increases with the pressure. Right panel: The quadratic dependence of the linear fit slopes C_0/τ on CO₂ pressure. Experiment performed at Maxlab.

fitted an empiric parabolic function to the pressure dependence of $\frac{1}{\tau_0}$. Our temperature measurements are in such a limited range in absolute temperature that they do not allow us to test inverse Arrhenius trapping time assumption or any other temperature model for τ , but the desorption data for LiFh (shown below) indicates that the sorption trapping barrier is of the order of magnitude of $\frac{E}{k_B} \approx 300\text{K}$. This gives $\tau \approx \tau_0 \frac{6 \times 10^{-4}}{P^2} e^{-\frac{300}{T}}$ where P is in units of bar and T in units of absolute temperature (K). From Figure 3 we estimated $\tau \approx 20$ hours for P and T equal to 20 bar and 253 K, respectively. This enables us to estimate $\tau_0 \approx 5 \cdot 10^7$ hours, and thus the adsorption time would be $\tau \approx 14$ min for P and T equal to 200 bar and 250 K respectively, if we assume that trapping mechanism for liquid and gas CO₂ are the same.

CO₂ retention under ambient conditions. After exposing the three types of clay mineral samples to CO₂ pressure for a sufficiently long time, the CO₂ pressure was released and the cell was continuously flushed with N₂, at atmospheric pressure, while increasing the temperature in steps of 5°C. It is known that the dry N₂ does not intercalate into Na-fluorohectorite²². A plot of peak intensity versus time at different increasing temperatures is shown in Figure 5.

It has previously been concluded that the interlayer CO₂ may cause an irreversible adsorption in clay, i.e. even if a clay sample is not exposed to the CO₂ gas, CO₂ molecules remain in the interlayer space^{48,49}. This means that once intercalated with CO₂ the clay mineral will retain these molecules. However, a temperature change can affect the CO₂ retention^{50,51} and this makes the process of intercalation and release truly reversible. We found that at a certain threshold temperature, the intensity decreases until the contribution to the scattered intensity from the clay mineral with intercalated CO₂ is negligible. Simultaneously, the peak corresponding to the dehydrated LiFh and NaFh reappears (data not shown). The threshold temperature, at which the CO₂ is desorbed from the interlayer space of the clays, is highly dependent on the type of interlayer cation used. For LiFh, this temperature is about 35°C, whereas for NaFh it is about -15°C (Figure 5). This is consistent with the difference in size between the smaller Li⁺ cation versus the larger Na⁺ cation. Li⁺ has a more concentrated charge distribution than Na⁺ and can thus polarize the CO₂ molecule more, forming a stronger bond to it. Loring et al also give a description of the CO₂ intercalation

mechanism²⁰. In the case of NiFh the release, like the intercalation, has more complex features, as shown in Figure 6.

Comparing the NiFh spectrum in Figure 1 with Figure 6 one can see that upon heating, the second CO₂ peak merges with the first CO₂ peak for NiFh. With increasing temperature, the intensity of the peak at the highest *d-spacing* value (about 1.31 nm) decreases, and at 45°C it completely disappears while the lowest *d-spacing* value peak shifts to lower values and eventually contains all the (001) scattering. It appears that the final intercalation state is different from the original dehydrated state. This could suggest the formation of a complex CO₂-Ni²⁺ structure within the interlayer space of the NiFh clay mineral, not present in the case of LiFh and NaFh. It is known that water intercalation experiments with NiFh can form a structure called Brucite (Ni(OH)₂). Such a structure is formed in the cation exchange process from LiFh to NiFh⁶⁰. It is possible that a Brucite-CO₂ interaction could have an effect on the behavior. In addition this could occur due to the partially occupied d-orbitals of the Ni²⁺ ions, which allow multiple coordination geometries with CO₂. These geometries can be possibly achieved by interactions of Ni d-orbitals with free oxygen orbitals present in polarized CO₂ molecules.

Pressure composition Temperature Experiments. Figure 7 shows the excess CO₂ adsorption isotherm of LiFh, obtained with the pCT-setup described in the Methods section. The excess adsorption is the amount of fluid taken up by the sample. The adsorption measurements were performed at room temperature and a pressure range from 1 bar up to 45 bar. The initial part of the isotherm (0 to ca. 9 bar) represents diffusion of CO₂ into the mesoporous and interlayer network⁵² of the clay powder. Above approximately 9 bar it is likely that the swelling process of the clay has nearly finished, and this will result in increased intercalation kinetics. With further increase in CO₂ pressure, the excess of CO₂ is seen to rise up to around 11 wt. % at a pressure of about 38 bar. At higher pressures, the apparent amount of adsorbed CO₂ starts to decrease, likely due to the formation of an adsorbed layer with higher density and comparable to the volume of the clay mineral, associated with approaching the critical pressure for CO₂^{53,54}.

Discussion

The uptake of CO₂ per weight of clay mineral can be inferred if it is assumed that the number of CO₂ molecules coordinating exchangeable cations is similar to the number of H₂O molecules within the interlayer space for the corresponding H₂O-clay system (in the mono-

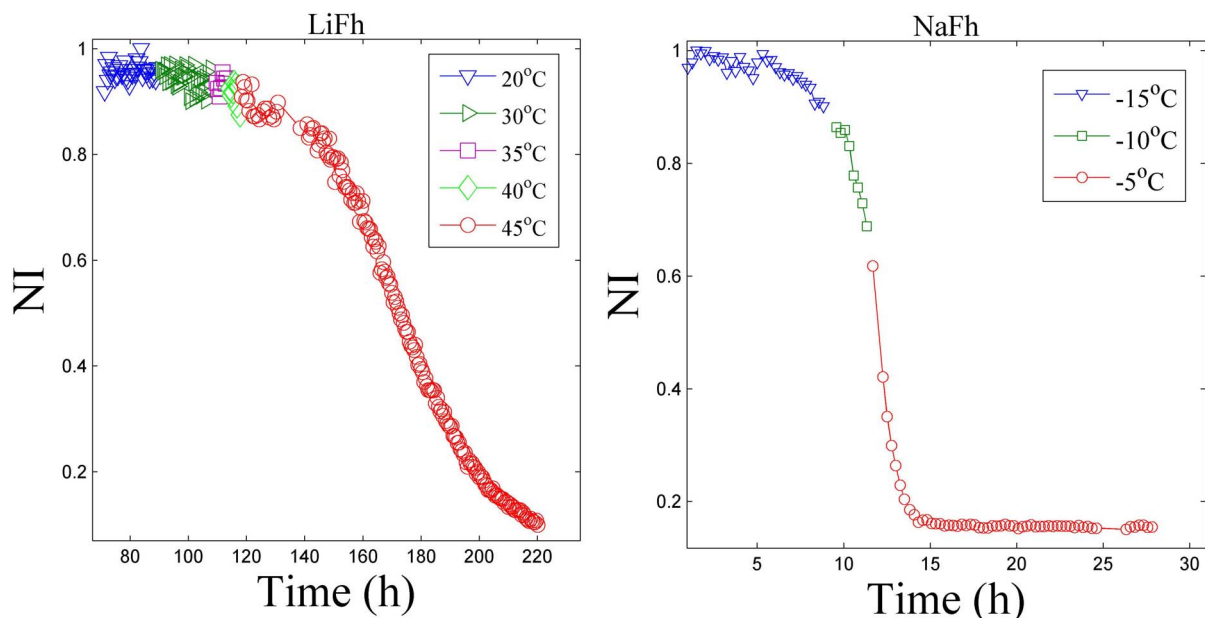


Figure 5 | Normalized Intensity (NI) of the (001) peak of LiFh (left) and NaFh (right) as a function of time for increasing temperatures. Experiments performed at NTNU.

hydrated state). This is approximately 2.4 molecules for each inter-layer cation^{16,15}. In case of LiFh and NaFh this would result in:

$$\frac{m_{\text{CO}_2}}{m_{\text{NaFh}}} \approx \frac{m_{\text{CO}_2}}{m_{\text{LiFh}}} \approx 14\% \quad (5)$$

which is the same order of magnitude as measured by pT (Figure 7), in this pressure range. This gives an amount of 3.2 mmol of CO₂/g of LiFh. For other relevant CO₂ capturing materials this number varies

from 6.00 mmol of CO₂/g, for e.g. metal organic frameworks (MOFs)⁵⁵, to 5.00 mmol of CO₂/g for Zeolites⁵⁶. Both numbers are higher than the one we find for the clay mineral fluorohectorite. However, if we compare the adsorbed amount of CO₂ per volume of the material, rather than per adsorbent mass, considering that the densities of zeolites (~2.2 g/cm³) and MOFs (~2.0 g/cm³) are lower than that of the clay minerals (~2.8 g/cm³). We find that a clay mineral, even with the cations considered here, is able to capture

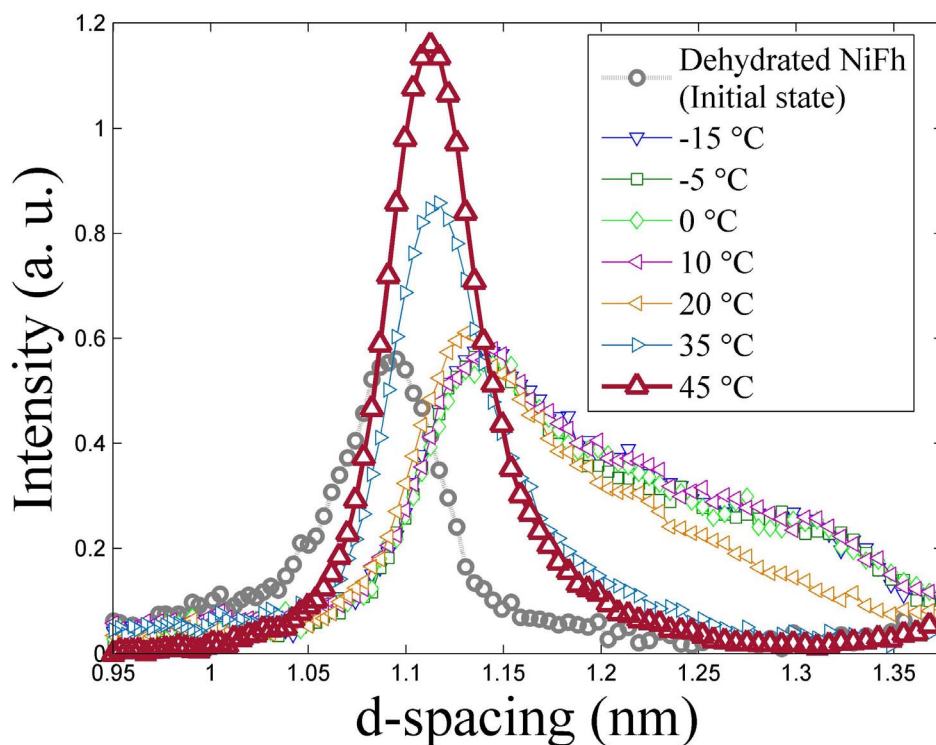


Figure 6 | (001) peak intensity of NiFh as a function of the *d*-spacing for different temperatures in N₂ at atmospheric pressure. As a reference the initial dehydrated peak of NiFh is included in the graph (circles, which is the same as the 0h curve in Figure 1). Experiments performed at NTNU.

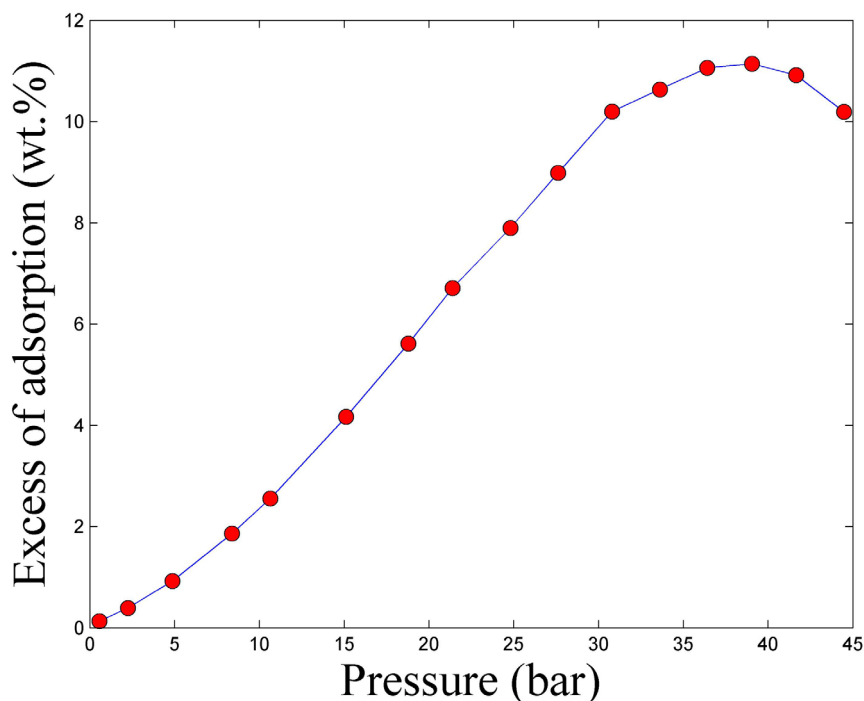


Figure 7 | Excess CO₂ adsorption isotherm of Li-fluorohectorite at room temperature and pressure range 0 to 45 bar. The initial part of the isotherm (0 to ca. 9 bar) represents diffusion of CO₂ into the mesoporous and interlayer network⁵² of the clay powder. Experiment performed at IFE.

nearly the same mass of CO₂ per volume (0.23 ton of CO₂ per m³ of sample) as compared to the “best” zeolites (0.29 ton of CO₂ per m³ of sample), or MOFs (0.32 ton of CO₂ per m³ of sample). These numbers were calculated assuming 60% of packing density for all the materials. The commonly used benchmark Zeolite 13X captures 0.14 ton of CO₂ per m³ of sample.

Methods

X-ray diffraction measurements were primarily performed on an in-house (NTNU, Trondheim) Bruker NanoSTAR X-ray scattering instrument, attached to a Xenox stationary electron impact source with a copper anode, producing K α -radiation. The scattered intensity was recorded by a two-dimensional multiwire grid Xe gas detector (HI-STAR, Bruker). The beam diameter of the setup is 400 μ m and the detectable range of momentum transfer q is ($2.5 < q < 7.5$) nm⁻¹ (q is defined here as $q = 4\pi \sin\theta/\lambda$, where θ is the scattering angle and λ the wavelength of the X-rays). The relation between q and d -spacing is d -spacing = $2\pi/q$ nm which means that the d -spacing interval is between 2.5 and 0.84 nm. Complementary X-ray scattering data were collected at the I911-4 beamline of MAX IV laboratory using a 2D CCD detector (165 mm diameter, from Marresearch, GmbH) and 0.91 Å wavelength.

The samples were mounted in a custom-made sample holder²² which allows temperature control in the range of -30°C to 45°C and pressures in the range from ambient to 20 bar. To allow X-rays to pass through the sample, the cell has Kapton windows on both sides of the sample volume. Internal channels connect gas from valves on the surface of the cell to the sample volume, and the gas pressure is controlled by standard reduction valves. The sample cell is depicted in Figure S3 in the supporting information.

In both X-ray setups, two-dimensional diffractograms were recorded and then azimuthally averaged to produce plots of intensity versus scattering vector, I vs q . Data reduction consisted in subtracting a background and normalizing the intensity profiles to the peak produced by the Kapton windows (see Hemmen et al.²² for details). The intensity, position and width of the intercalation peaks were found by fitting the peaks to Pseudo-Voigt profiles^{57,58}.

The LiFh clay mineral used in the experiments was purchased from Corning Inc., with nominal chemical formula: $M_x(Mg_{6-x}Li_x)Si_8O_{20}F_4$ per unit cell⁵⁹, where M is the interlayer cation (Li⁺, Na⁺ and Ni²⁺) and x the amount which balances the charge of clay mineral layers ($x = 1.2$ for monovalent ions, and $x = 0.6$ for divalent ions). Each sample consisted of 7 ± 1 mg of clay powder packed in the available space in the sample chamber. Typically such packed clay powder samples have a mesoporosity of about 40%⁵², which in the present case enables access of the employed gases to the layered nanoporous structures that make up the individual powder grains (here the terms mesopore and nanopore follow the IUPAC definition).

At ambient conditions (23° and 40% of relative humidity), these clay mineral samples are in the monohydrated state⁶⁰. Since the uptake of the CO₂ molecules may be affected by the initial H₂O concentration⁶¹, we investigated dehydrated native

samples. For dehydration, the samples were heated in an oven at near 150°C for more than 10 hours and in a N₂ flushed atmosphere. To remove residual humidity from the cell after loading the clay, and to ensure that the sample remained dry, the cell was flushed with N₂-gas. An X-ray scan was also recorded at ambient temperature and pressure while flushing with N₂ to confirm that the sample remained dehydrated before starting the CO₂ intercalation experiments. The sample was subsequently cooled to -20°C before the gas was changed to CO₂. The gas outlet of the cell was closed and the pressure increased.

The CO₂ used for experiments has a purity of 99.999% (Yara Praxair, grade 5). The N₂ gas has a purity of 99.9999% (Yara Praxair, grade 6). To obtain a satisfactory signal-to-noise ratio, we varied the acquisition times from 30 to 60 minutes, depending on CO₂ pressure, due to differences in X-ray absorption.

Pressure-composition-Temperature (pCT) isotherms were measured in a calibrated in-house built (IFE, Kjeller) volumetric Sieverts-type apparatus in order to obtain information on CO₂ adsorption. Approximately 300 mg of Li-fluorohectorite was inserted in a sample holder and was degassed at 115°C under dynamic vacuum (<10⁻⁶ mbar) overnight, to remove residual humidity. Adsorption isotherms were acquired in the 0–45 bar range, with 3 bar step between each aliquot measurement at room temperature. The CO₂ adsorption data were baseline corrected by the adsorption data collected from N₂.

1. Cole, D. R., Chialvo, A. A., Rother, G., Vlcek, L. & Cummings, P. T. Supercritical fluid behavior at nanoscale interfaces: Implications for CO₂ sequestration in geologic formations. *Phil. Mag.* **90**, 2339–2363, doi:10.1080/14786430903559458 (2010).
2. Hildenbrand, A., Schlomer, S. & Krooss, B. M. Gas breakthrough experiments on fine-grained sedimentary rocks. *Geofluids* **2**, 3–23, doi:10.1046/j.1468-8123.2002.00031.x (2002).
3. Wollenweber, J. et al. Experimental investigation of the CO₂ sealing efficiency of caprocks. *Int. J. Greenhouse Gas Control* **4**, 231–241, doi:10.1016/j.jggc.2010.01.003 (2010).
4. de Jong, S. M., Spiers, C. J. & Busch, A. Development of swelling strain in smectite clays through exposure to carbon dioxide. *Int. J. Greenhouse Gas Control* **24**, 149–161, doi:10.1016/j.jggc.2014.03.010 (2014).
5. Boulet, P., Greenwell, H. C., Stackhouse, S. & Coveney, P. V. Recent advances in understanding the structure and reactivity of clays using electronic structure calculations. *J. Molecular Structure-Theochem* **762**, 33–48, doi:10.1016/j.theochem.2005.10.028 (2006).
6. Hansen, E. L. et al. Swelling transition of a clay induced by heating. *Sci. Rep.* **2**, doi:10.1038/srep00618 (2012).
7. Bergaya, F. & Lagaly, G. in *Developments in Clay Science* Vol. Volume 5 (eds Bergaya Faiza & Lagaly Gerhard) 213–221 (Elsevier, 2013).
8. Bordallo, H. N. et al. Quasi-elastic neutron scattering studies on clay interlayer-space highlighting the effect of the cation in confined water dynamics. *J. Phys. Chem. C* **112**, 13982–13991, doi:10.1021/jp803274j (2008).



9. da Silva, G. J., Fossum, J. O., DiMasi, E., Maloy, K. J. & Lutnaes, S. B. Synchrotron x-ray scattering studies of water intercalation in a layered synthetic silicate. *Phys. Rev. E* **66**, doi:10.1103/PhysRevE.66.011303 (2002).
10. Malikova, N. *et al.* Water diffusion in a synthetic hectorite clay studied by quasi-elastic neutron scattering. *J. Phys. Chem. C* **111**, 17603–17611, doi:10.1021/jp0748009 (2007).
11. Jimenez-Ruiz, M., Ferrage, E., Delville, A. & Michot, L. J. Anisotropy on the Collective Dynamics of Water Confined in Swelling Clay Minerals. *J. Phys. Chem. A* **116**, 2379–2387, doi:10.1021/jp201543t (2012).
12. da Silva, G. J., Fossum, J. O., DiMasi, E. & Maloy, K. J. Hydration transitions in a nanolayered synthetic silicate: A synchrotron x-ray scattering study. *Phys. Rev. B* **67**, doi:10.1103/PhysRevB.67.094114 (2003).
13. Dazas, B. *et al.* Smectite fluorination and its impact on interlayer water content and structure: A way to fine tune the hydrophilicity of clay surfaces? *Microporous and Mesoporous Materials* **181**, 233–247, doi:10.1016/j.micromeso.2013.07.032 (2013).
14. Porion, P., Michot, L. J., Faugere, A. M. & Delville, A. Structural and dynamical properties of the water molecules confined in dense clay sediments: A study combining H-2 NMR spectroscopy and multiscale numerical modeling. *J. Phys. Chem. C* **111**, 5441–5453, doi:10.1021/jp067907p (2007).
15. Tenorio, R. P., Engelsberg, M., Fossum, J. O. & da Silva, G. J. Intercalated Water in Synthetic Fluorhectorite Clay. *Langmuir* **26**, 9703–9709, doi:10.1021/la100377s (2010).
16. Tenorio, R. P., Alme, L. R., Engelsberg, M., Fossum, J. O. & Hallwass, F. Geometry and dynamics of intercalated water in Na-fluorhectorite clay hydrates. *J. Phys. Chem. C* **112**, 575–580, doi:10.1021/jp0766407 (2008).
17. Jansson, M. & Eriksen, T. E. In situ anion diffusion experiments using radiotracers. *J. Contaminant Hydrology* **68**, 183–192, doi:10.1016/s0169-7722(03)00149-9 (2004).
18. Tambach, T. J., Hensen, E. J. M. & Smit, B. Molecular simulations of swelling clay minerals. *J. Phys. Chem. B* **108**, 7586–7596, doi:10.1021/jp049799h (2004).
19. Schaeff, H. T. *et al.* In situ XRD study of Ca²⁺ saturated montmorillonite (STX-1) exposed to anhydrous and wet supercritical carbon dioxide. *Int. J. Greenhouse Gas Control* **6**, 220–229, doi:10.1016/j.ijggc.2011.11.001 (2012).
20. Loring, J. S. *et al.* In Situ Molecular Spectroscopic Evidence for CO₂ Intercalation into Montmorillonite in Supercritical Carbon Dioxide. *Langmuir* **28**, 7125–7128, doi:10.1021/la301136w (2012).
21. Ilton, E. S., Schaeff, 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. & Tech.* **46**, 4241–4248, doi:10.1021/es300234v (2012).
22. Hemmen, H. *et al.* X-ray Studies of Carbon Dioxide Intercalation in Na-Fluorhectorite Clay at Near-Ambient Conditions. *Langmuir* **28**, 1678–1682, doi:10.1021/la204164q (2012).
23. 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. & Tech.* **46**, 5623–5630, doi:10.1021/es3005865 (2012).
24. 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* **8**, 73–81, doi:10.1016/j.ijggc.2012.01.011 (2012).
25. Busch, A. *et al.* Carbon dioxide storage potential of shales. *Int. J. Greenhouse Gas Control* **2**, 297–308, doi:10.1016/j.ijggc.2008.03.003 (2008).
26. Sozzani, P. *et al.* Nanoporosity of an organo-clay shown by hyperpolarized xenon and 2D NMR spectroscopy. *Chemical Commun.* 1921–1923, doi:10.1039/b620040b (2006).
27. Fripiat, J. J., Cruz, M. I., Bohor, B. F. & Thomas, J. Interlamellar Adsorption of Carbon-Dioxide by Smectites. *Clays and Clay Minerals* **22**, 23–30, doi:10.1346/ccmn.1974.0220105 (1974).
28. Thomas, J. & Bohor, B. F. Surface Area of Montmorillonite from Dynamic Sorption of Nitrogen and Carbon Dioxide. *Clays and Clay Minerals* **16**, 83–87, doi:10.1346/ccmn.1968.0160110 (1968).
29. 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* **117**, 20592–20609, doi:10.1021/jp405321t (2013).
30. Yang, N. & Yang, X. Molecular simulation of swelling and structure for Na-Wyoming montmorillonite in supercritical CO₂. *Molecular Simulation* **37**, 1063–1070, doi:10.1080/08927022.2010.547939 (2011).
31. Cygan, R. T., Romanov, V. N., Myshakin, E. M. *Natural Materials for Carbon Capture. Report No. SAND2010-7217*, (Sandia National Laboratories, Albuquerque, New Mexico, 2010).
32. 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* **114**, 14962–14969, doi:10.1021/jp1043305 (2010).
33. Yang, S. *et al.* A partially interpenetrated metal-organic framework for selective hysteretic sorption of carbon dioxide. *Nature Materials* **11**, 710–716, doi:10.1038/nmat3343 (2012).
34. Vaidhyanathan, R. *et al.* Direct Observation and Quantification of CO₂ Binding Within an Amine-Functionalized Nanoporous Solid. *Science* **330**, 650–653, doi:10.1126/science.1194237 (2010).
35. Banerjee, R. *et al.* High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture. *Science* **319**, 939–943, doi:10.1126/science.1152516 (2008).
36. Hemmen, H., Alme, L. R., Fossum, J. O. & Meheust, Y. X-ray studies of interlayer water absorption and mesoporous water transport in a weakly hydrated clay. *Phys. Rev. E* **82**, doi:10.1103/PhysRevE.82.036315 (2010).
37. Michels, L. E. *et al.* in *2nd International Workshop on Complex Physical Phenomena in Materials* (Hotel Armação, Porto de Galinhas - PE, Brazil, 2012).
38. 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. *American Mineralogist* **90**, 1358–1374, doi:10.2138/am.2005.1776 (2005).
39. Ferrage, E. *et al.* Hydration Properties and Interlayer Organization of Water and Ions in Synthetic Na-Smectite with Tetrahedral Layer Charge. Part 2. Toward a Precise Coupling between Molecular Simulations and Diffraction Data. *J. Phys. Chem. C* **115**, 1867–1881, doi:10.1021/jp105128r (2011).
40. Malikova, N., Dubois, E., Marry, V., Rotenberg, B. & Turq, P. Dynamics in Clays - Combining Neutron Scattering and Microscopic Simulation. *Zeitschrift Fur Physikalische Chemie-International J. Research in Phys. Chem. & Chem. Phys.* **224**, 153–181, doi:10.1524/zpch.2010.6097 (2010).
41. Gates, W. P. *et al.* Neutron Time-of-Flight Quantification of Water Desorption Isotherms of Montmorillonite. *J. Phys. Chem. C* **116**, 5558–5570, doi:10.1021/jp2072815 (2012).
42. Tamura, K., Yamada, H. & Nakazawa, H. Stepwise hydration of high-quality synthetic smectite with various cations. *Clays and Clay Minerals* **48**, 400–404, doi:10.1346/ccmn.2000.0480311 (2000).
43. Ferrage, E., Lanson, B., Michot, L. J. & Robert, J.-L. Hydration Properties and Interlayer Organization of Water and Ions in Synthetic Na-Smectite with Tetrahedral Layer Charge. Part 1. Results from X-ray Diffraction Profile Modeling. *J. Phys. Chem. C* **114**, 4515–4526, doi:10.1021/jp909860p (2010).
44. Skipper, N. T., Smalley, M. V., Williams, G. D., Soper, A. K. & Thompson, C. H. Direct Measurement of the Electric Double-Layer Structure in Hydrated Lithium Vermiculite Clays by Neutron-Diffraction. *J. Phys. Chem.* **99**, 14201–14204, doi:10.1021/j100039a003 (1995).
45. Gasparini, E. *et al.* Thermal dehydroxylation of kaolinite under isothermal conditions. *Appl. Clay Science* **80–81**, 417–425, doi:10.1016/j.clay.2013.07.017 (2013).
46. Liu, Y. & Shen, L. From Langmuir Kinetics to First- and Second-Order Rate Equations for Adsorption. *Langmuir* **24**, 11625–11630, doi:10.1021/la801839b (2008).
47. Beach, W. F. Model for Vapor-Deposition Polymerization of Para-Xylylene. *Macromol.* **11**, 72–76, doi:10.1021/ma60061a014 (1978).
48. Romanov, V. N. Evidence of irreversible CO₂ intercalation in montmorillonite. *International J. Greenhouse Gas Control* **14**, 220–226, doi:10.1016/j.ijggc.2013.01.022 (2013).
49. 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* **116**, 13079–13091, doi:10.1021/jp3007574 (2012).
50. Azzouz, A. *et al.* Truly reversible capture of CO₂ by montmorillonite intercalated with soya oil-derived polyglycerols. *Int. J. Greenhouse Gas Control* **17**, 140–147, doi:10.1016/j.ijggc.2013.04.013 (2013).
51. Azzouz, A. *et al.* Polyol-modified layered double hydroxides with attenuated basicity for a truly reversible capture of CO₂. *Adsorption-J. Int. Adsorption Soc.* **19**, 909–918, doi:10.1007/s10450-013-9498-3 (2013).
52. Knudsen, K. D., Fossum, J. O., Helgesen, G. & Bergaplass, V. Pore characteristics and water absorption in a synthetic smectite clay. *J. Appl. Cryst.* **36**, 587–591, doi:10.1107/s0021889803001778 (2003).
53. Schaeff, H. T. *et al.* Surface Condensation of CO₂ onto Kaolinite. *Environmental Sci. & Tech. Lett.* **1**, 142–145, doi:10.1021/ez400169b (2013).
54. Melnichenko, Y. B., Wignall, G. D., Cole, D. R. & Frielinghaus, H. Adsorption of supercritical CO₂ in aerogels as studied by small-angle neutron scattering and neutron transmission techniques. *J. Chem. Phys.* **124**, doi:10.1063/1.2202324 (2006).
55. An, J. & Rosi, N. L. Tuning MOF CO₂ Adsorption Properties via Cation Exchange. *J. American Chem. Soc.* **132**, 5578–+ doi:10.1021/ja1012992 (2010).
56. Walton, K. S., Abney, M. B. & LeVan, M. D. CO₂ adsorption in Y and X zeolites modified by alkali metal cation exchange. *Microporous and Mesoporous Materials* **91**, 78–84, doi:10.1016/j.micromeso.2005.11.023 (2006).
57. Wertheim, G. K., Butler, M. A., West, K. W. & Buchanan, D. N. Determination of Gaussian and Lorentzian Content of Experimental Line-Shapes. *Rev Sci Instr* **45**, 1369–1371, doi:10.1063/1.1686503 (1974).
58. Cox, D. E., Toby, B. H. & Eddy, M. M. Acquisition of Powder Diffraction Data with Synchrotron Radiation. *Australian J. Phys.* **41**, 117–131 (1988).
59. Kaviratna, P. D., Pinnavaia, T. J. & Schroeder, P. A. Dielectric properties of smectite clays. *J. Phys. Chem. Solids* **57**, 1897–1906, doi:10.1016/s0022-3697(96)00076-5 (1996).
60. Michels, L. *et al.* EXAFS and XRD studies in synthetic Ni-fluorhectorite. *Appl. Clay Science* **96**, 60–66, doi:10.1016/j.clay.2014.04.031 (2014).



61. Loring, J. S. *et al.* In Situ Study of CO₂ and H₂O Partitioning between Na-Montmorillonite and Variably Wet Supercritical Carbon Dioxide. *Langmuir* **30**, 6120–6128, doi:10.1021/la500682t (2014).

Acknowledgments

L.M., J.O.F., Z.R., P.S. and K.D.K. acknowledge the CLIMIT Program of the Research Council of Norway (Project number 200041). MAX IV laboratory is acknowledged for providing the beamtime at I911-4 under the proposal 20110154. The authors acknowledge Geir Helgesen for discussions and Ole Tore Buset for technical assistance.

Author contributions

J.O.F. and K.D.K. planned the experiments. H.H., K.R. and L.M. designed the sample cell used for the X-ray experiments. L.M., Z.R. and G.J. da S. performed the X-ray experiments at NTNU. H.H., K.R., J.O.F. and T.P. performed the synchrotron experiments at Maxlab. P.A.S., G.N.K. and K.D.K. performed the pcT experiments and the associated data analysis. L.M., M.J. and G.J. da S. did the main part of the X-ray data analysis. J.O.F., K.D.K. and L.M.

wrote the discussion of the results. L.M., H.H. and J.O.F. wrote the manuscript, and all authors revised the manuscript before submission.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Michels, L. *et al.* Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cations. *Sci. Rep.* **5**, 8775; DOI:10.1038/srep08775 (2015).



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