

X-ray studies of carbon dioxide intercalation in Na-fluorohectorite clay at near-ambient conditions

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We show experimentally that gaseous CO₂ intercalates into the interlayer space of the synthetic smectite clay Na-fluorohectorite at conditions not too far from ambient. The mean interlayer repetition distance of the clay when CO₂ is intercalated is found to be 12.5 Å for the conditions -20 °C and 15 bar. The magnitude of the expansion of the interlayer upon intercalation is indistinguishable from that observed in the dehydrated-monohydrated transition for H₂O, but the possibility of water intercalation is ruled out by a careful analysis of the experimental conditions and repeating the measurements exposing the clay to nitrogen gas. The dynamics of the process is observed to be dependent on the pressure, with a higher

intercalation rate at increased pressure. The rate of CO₂ intercalation at the studied conditions is found to be several orders of magnitude slower than the intercalation rate of water or humidity at ambient pressure and temperature.

I. Introduction

An aspect of clay physics that is well known, but still not completely understood, is the intercalation of molecules into the interlayer space of swelling smectite clays. Intercalation of water in particular has been extensively studied, but also more complex molecules may be intercalated to functionalize such clay particles, or to allow the particles to disperse in polymeric matrices.¹

Due to current awareness of global warming and the challenges related to carbon capture and sequestration, the interactions between clays and CO₂ are attracting attention in the scientific community. A recent molecular dynamics study by Cygan et al.² shows the possibility of intercalation and retention of CO₂ in smectites at 37 °C and 200 bar. This has led the authors to suggest that clay minerals may prove suitable for carbon capture and carbon dioxide sequestration. Botan et al.³ have simulated intercalation of CO₂ into clays at conditions relevant to geological storage (temperature: 75 °C; pressure: 25 and 125 bar). They have found that Na-montmorillonite clay is capable of adsorbing CO₂ into its hydrated interlayer gallery without inducing swelling or shrinkage.

There exist however only a handful of experimental reports on intercalation of CO₂ into clays. Thomas et al.⁴ found intercalation of CO₂ into montmorillonite while doing surface area determinations, with the degree and rate of intercalation dependent on the type of intercalated cation. In a follow-up experiment,⁵ this observation was confirmed by x-ray diffraction and infrared absorption. More recently, Wang et al. used infrared spectroscopy to show that CO₂ and CO can be incorporated into the structure of pyrophyllite during dehydroxylation.⁶

Surface areas of clays are typically measured by the BET method,⁷ in which the adsorption isotherms are found by exposing the clays to inert gases.⁸⁻¹⁰ In a study of the microporosity of montmorillonites, D.W. Rutherford et al.¹¹ concluded that the interlayer space of montmorillonites exchanged with small metal cations (such as Na⁺), is too narrow to be accessible even to small nonpolar gases (like N₂).

Using hyperpolarized xenon NMR, Sozzani et al.¹² have studied the nanoporosity of hectorites pillared with tetraethylammonium. In pillared clays, the interlayers are permanently expanded by spacers such as large organic cations. Sozzani et al. found that the nanoporous space generated by this expansion is accessible to CO₂, benzene and methane gases. For CO₂ adsorption at -78 °C and 100 torr, they found an uptake per weight of clay of 18%. The sorption of guest molecules into pillared clays however differs from intercalation of molecules into non-modified clays with small exchangeable cations. This is because intercalation in the latter case requires mechanical work to be done in expanding the clay galleries. Tsiao et al.¹³ studied the interlayer spacing of Ca²⁺-bentonite and -montmorillonite (both untreated and pillared), and found that ¹²⁹Xe gas was able to penetrate in both cases, although with no expansion of the interlayer space (the larger size of the Ca²⁺ molecule means that the unpillared bentonite already has an outgassed d-spacing of 15.2 Å).

In the present manuscript we have studied with x-ray diffraction the intercalation of CO₂ into the synthetic smectite Na-fluorohectorite (NaFh), which is a representative clean model system of natural smectite clays. The choice of this particular clay as a starting point for our investigation is both due to its chemical and structural similarities with natural Na-montmorillonite and other clays of the same family, and also because its swelling behaviors at different H₂O humidities have previously been extensively characterized by our group with the use of Wide Angle X-ray Scattering (WAXS),¹⁴⁻¹⁶ and MR spectroscopy.¹⁷ Compared with its natural counterparts, this synthetic clay system contains significantly fewer impurities

that could mask the behavior of the clay. Furthermore, the more homogenous charge distribution in synthetic clays reduces coexistence of different hydration states and leads to well-defined swelling characteristics that allows for pure monohydrated and bihydrated states.¹⁸

In the synthetic fluorohectorite used here, all the hydroxyl groups normally present in natural hectorite have been exchanged for fluorine. We do not believe this has a huge impact on the reported observations since the main parameters determining the intercalation properties are the layer charge and the type of intercalated cation.¹⁹ In addition, Thomas et al.²⁰ showed that even natural hectorite have as much as 50% of its hydroxyl groups substituted with fluorine. Hence, even if fluorine played a major role in the intercalation process of CO₂, one could still expect the observed behaviour to be also valid for natural hectorites.

The purpose of the present experiment is to submit Na-fluorohectorite to gaseous CO₂ and look for intercalation processes similar to what has been observed in the case of H₂O. We expect pressure and temperature to be parameters governing this process, in the same way that temperature and relative humidity (i.e. the partial pressure of water) determine the H₂O intercalation states.

II. Experimental methods

X-ray measurements were performed using a Bruker NanoSTAR x-ray scattering instrument, attached to a Xenocs electron impact source with a copper anode producing K_α - radiation. The scattered intensity was recorded on a 2D multiwire grid Xe gas- detector. The beam diameter in this setup is 400 μm, and the available range of momentum transfer q on the detector was $(0.4 < q < 7) \text{ nm}^{-1}$. Prior to these experiments, preliminary synchrotron x-ray scattering experiments were performed at the I711 beamline of MAX-lab, Sweden.²¹

A custom made sample holder was used for all experiments (Figure in Supporting Information). The temperature of the sample holder was controlled by means of Peltier elements and measured with a thermocouple connected to the sample block. Gas pressure was controlled by standard reduction valves. The sample holder was made of copper for good thermal conduction, and 0.15 mm thick Kapton windows were used to allow passage of X-rays through the cell. The sample was located in the 1 mm gap between the windows, which together with the beam size gave a scattering volume of about 0.12 mm³.

The NaFh clay used in the experiment was purchased from Corning Inc. as Li-fluorohectorite and then subjected to a standard ion-exchange process in order to produce a pure Na-fluorohectorite sample (a description of the process can be found in Lovoll et al.¹⁶). The nominal chemical formula after the ion-exchange is $\text{Na}_{0.6}\text{Mg}_{2.4}\text{Li}_{0.6}\text{Si}_4\text{O}_{10}\text{F}_2$ per half unit cell.¹⁹

At ambient conditions the clay is in a monohydrated state.¹⁵ To get the clay into the dehydrated state it was placed in a furnace at a temperature of 150 °C for more than three hours. Ideally, to produce pure dehydrated clay, the clay should also be outgassed in a vacuum. However, the above method was chosen for its simplicity, and proved to be sufficient. In order to remove residual humidity from the cell, the volume inside was flushed with CO₂ for several minutes after loading the sample, and an x-ray measurement at ambient temperature was used to confirm that the clay was still dehydrated. Subsequently, the cell was cooled to the desired temperature, the gas outlet of the cell plugged, and the pressure increased.

The CO₂ used in this experiment had a purity of 99.999% (Yara Praxair, grade 5). The measurements with N₂ were done with a gas purity of 99.6% (Yara Praxair, industry grade). In order to get a sufficient signal to noise ratio, the acquisition time was set to one hour. For the same reason it was also decided not to do experiments with liquid CO₂, as the increased

density in the liquid phase significantly reduces the transmission of x-rays through the sample.

III. Results

A. CO₂ intercalation

Our preliminary experiments at MAX-lab were used to test various conditions for pressure and temperature (PT) to determine whether CO₂ intercalation was taking place. In particular we wanted to reduce the temperature from room-temperature and test if intercalation occurred before reaching -70 °C (the temperature used by Fripiat et al.⁵). The number of conditions we could test was limited by the timeframe of the synchrotron experiment, but we found indications of an intercalation process already at -10 °C, with slightly higher pressure than 1 bar. At ambient conditions, no significant changes in the diffraction patterns with CO₂ exposure were visible on a time scale of hours.

As the intercalation was slow (compared with H₂O intercalation), we have therefore used our in-house x-ray scattering setup to monitor the clay at a given PT condition for a long time. At sufficiently long waiting times, it should be expected that the intercalation process would reach a steady state, possibly a pure CO₂ intercalation state. Figure 1 shows the evolution of the 001 Bragg peak at the condition -20 °C and 15 bar during the transition from the dehydrated state to the intercalated state during a period of nine days. The 001 peak originates from the stacking of the crystalline clay layers, and its position is a direct measure of the repetition distance along the swelling direction. Intercalation will thus cause a discrete jump towards lower q due to increased distance between the layers. Note that the azimuthally integrated intensities shown in Figure 1-Figure 3, have been treated by subtracting a background and normalizing the intensities (see the Supporting Information for details).

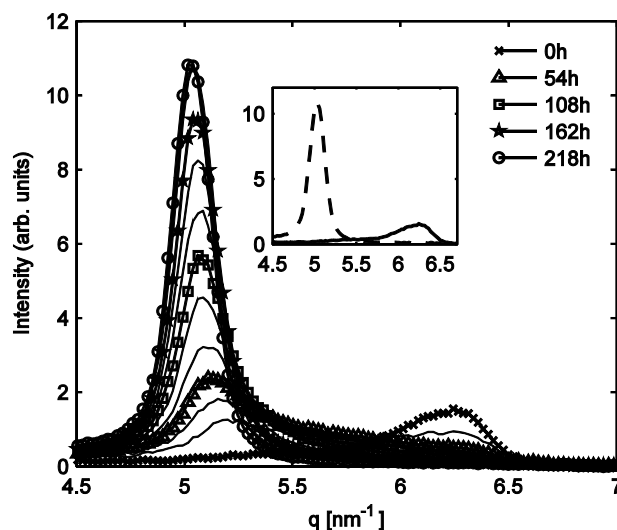


Figure 1. CO₂ intercalation at -20 °C and 15 bar. The time between each measurement shown is 18 hours, except the time between the last two, which is 20 hours. The inset shows only the first (solid line) and last (dashed line) measurements for comparison.

The intercalation progresses first by changes in the shape of the dehydrated Bragg peak (it becomes more asymmetric), before a new peak appears at $q \approx 5.22 \text{ nm}^{-1}$. At the final measurement in Figure 1, the dehydrated peak has disappeared, and only the peak due to intercalation is visible. This transition bears a resemblance to the H₂O transitions in NaFh between the dehydrated and monohydrated states, and between the monohydrated and bihydrated states.^{14,16} From about 50 to 200 hours after CO₂-exposure, the peak intensity increased approximately linearly with time, and the measurements were stopped after 218 hours, when the intensity had reached a plateau and stopped evolving (see the Supporting Information for a plot of peak intensity vs. time). At this point we do not know whether a transition to a higher intercalation state (two monolayers of intercalant) could take place with CO₂, as is commonly observed in this clay for the case of water.¹⁴⁻¹⁷

The differences in intensity profile between the initial dehydrated peak and the final intercalated peak have several possible explanations. Firstly we clearly observe a more symmetric shape and a smaller full width at half maximum for the intercalation peak

compared to the dehydrated peak. This observation points to a more regular structure in the intercalated system than in the dehydrated state. This is supported by the long tail of the initial dehydration peak, hinting at traces of intercalated water, possibly caused by the dehydration process chosen. Secondly, the contribution to the intensity from the layer structure factor and the Lorentz polarization factor is causing a more intense intercalation-peak,²² but accounting for those factors is out of the scope of the present work..

The intercalation state at the final measurement time was found centered at a scattering vector $q = 5.032 \text{ nm}^{-1}$, corresponding to an interlayer repetition distance $d_{001} = 12.49 \text{ \AA}$. This means that the NaFh unit cell has expanded approximately 2.5 \AA in the clay stacking direction compared with the initial dehydrated state. Cygan et al.² found in their molecular dynamics simulations on the similar clay Na-montmorillonite a mean basal d-spacing of 12.23 \AA with intercalated CO_2 . This is in fact 0.1 \AA smaller than the value they found for intercalated water. In the results presented here, we observe the opposite, i.e. a d-spacing for intercalated CO_2 which is about 0.1 \AA larger than the monohydrated case, for which we have measured a d-spacing of 12.4 \AA at $-20 \text{ }^\circ\text{C}$ (data not shown). However, previous work¹⁴ have shown that the d-spacing of NaFh during intercalation of water vapor displays shifts on the order of 0.3 \AA within a given hydration state when varying temperature or humidity. These shifts are larger than the estimated difference between the d-spacings of $\text{CO}_2/\text{H}_2\text{O}$ presented by Cygan et al.², and the differences in d-spacing that we observe. Hence it is clear that even with higher resolution measurements it would be impossible to distinguish H_2O or CO_2 intercalation based on observed d-spacing values alone.

B. Nitrogen test

Because of the approximately equal d-spacing for the intercalated and monohydrated state, we repeated the intercalation experiments with gaseous N_2 , with the purpose of investigating if the intercalation peak could be due to water present in the system instead of CO_2 . In a

previous work in the literature, at different experimental conditions and for another clay, Aylmore²³ criticized Thomas and Bohor's conclusions⁴ for using a relatively mild outgassing procedure. It was claimed that the residual water molecules in the system could explain the intercalation observed in their experiments. The same criticism could be directed to the flushing procedure used in our present experiment. Residual water molecules could possibly originate from water vapor in cavities of the sample holder, residual water in the mesopores of the clay, or from a residual water film on the copper surfaces inside the closed sample cell. It could therefore be possible that the clay was packed in the sample holder in such a way that traces of water vapor surrounding the clay in the sample cell were transferred into the clay which was subjected to the incident X-ray beam. As humidity transport has been shown to be slow in this sample (days/cm),¹⁴ we expect that it would take some time before a water intercalation front reaches the scattering volume and a pure hydration state is detected on the diffraction patterns.

Furthermore, nitrogen penetration into the interlamellar space is reported for montmorillonite to depend on the packing and the influence of the interlayer cation, but the penetration does not progress to allow significant expansion of the host layer.²⁴ A dramatic change in d-spacing or transition caused by intercalation of nitrogen is therefore not to be expected.

Figure 2 shows the evolution in the scattering while exposing the NaFh to nitrogen gas at -20 °C and 13 bar. The sample cell and the experimental procedures were the same as those employed with CO₂, with the gas outlet plugged during the measurement. It is evident that even after two days, there are only minor changes to the scattered intensity, indicating that the main proportion of clay particles still remain in the dehydrated state. Comparing the diffraction patterns after two full days of nitrogen exposure, to the corresponding measurement with CO₂, the degree of intercalation is negligible. Thus we can with confidence

assume that the peak observed in the samples with CO₂ does not come from residual water inside the sample holder or clay, but instead arises from intercalation of CO₂.

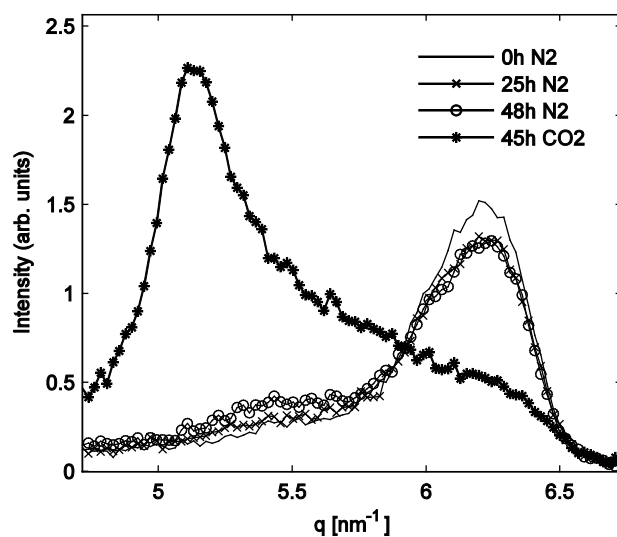


Figure 2. Scattered intensity from NaFh exposed to nitrogen gas at -20 °C and 13 bar. The plot legend shows the time after the first scan (ambient) in hours. For comparison, a measurement from the CO₂ experiment is also shown.

C. Effect of pressure

We also tested the intercalation of CO₂ at a reduced pressure. Figure 3 shows the results obtained at -20 °C and 5 bar CO₂. From the figure we can see that intercalation is still taking place, and also that the reduced pressure results in a reduced intercalation rate compared to the measurements at 15 bar. This also rules out the possibility that the lower pressure in the nitrogen-test (13 vs. 15 bar) was the reason for the lack of observed intercalation. These measurements were interrupted before a pure intercalation peak had been reached.

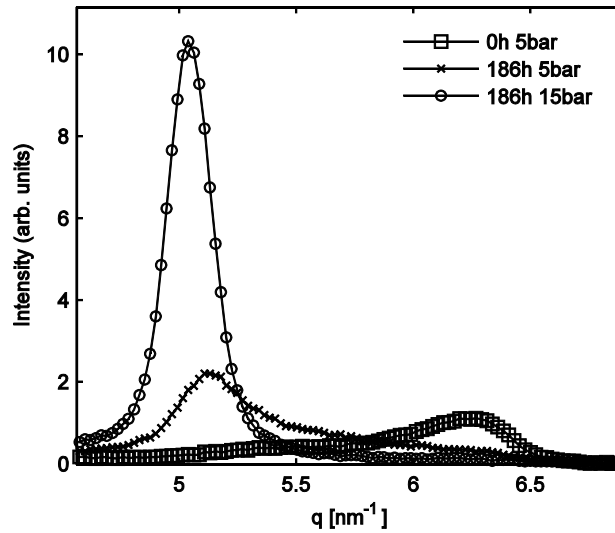


Figure 3. Diffraction patterns of NaFh exposed to 5 bar of CO₂ at -20 °C. The plot legend shows the time after the first scan in hours. The corresponding measurement at 15 bar pressure is included for comparison. It is evident that reducing the pressure reduces the rate of intercalation.

D. Quantitative estimation of the CO₂ adsorbed in the interlayers

The uptake of CO₂ per weight of clay cannot be inferred from one Bragg peak alone, but we can roughly estimate it by assuming the same number of CO₂ molecules per NaFh unit cell as was found for H₂O in the monohydrated state, namely 2.4 per unit cell.²⁵ Multiplying this number by the weight ratio between a CO₂ molecule and the NaFh unit cell (Na_{1.2}Mg_{2.4}Li_{1.2}Si₈O₂₀F₄), we obtain:

$$\frac{m_{\text{CO}_2}}{m_{\text{NaFh}}} \times 2.4 \approx 14\% .$$

This estimate is of the same order of magnitude as the value of 18% found for pillared hectorites by P. Sozzani et al.¹² using a gas adsorption technique. That it is lower is also reasonable, since in our case the basal distance after intercalation is only 12.5 Å, while in the pillared clay it is fixed at 14.7 Å.

IV. Conclusion

We have shown that CO₂ is able to intercalate into NaFh galleries at conditions close to ambient (-20 °C, 15 and 5 bar). The pressures and temperatures studied are different from most of the simulations in the literature related to geological storage, but demonstrating intercalation at less extreme conditions could prove useful in understanding the processes involved. By avoiding extreme conditions, experimental verification of theory and simulations should become much easier. The low pressures involved here enable the use of Kapton windows on the sample cell, thus allowing investigations with laboratory x-ray equipment instead of synchrotron sources.

We observed that the time scale of intercalation at -20 °C is slower at 5 relative to 15 bar, and that in both cases the intercalation of CO₂ is orders of magnitude slower than the intercalation of water at ambient conditions (days, compared to minutes¹⁴). The intercalation kinetics is likely dependent on the (partial) pressure of the intercalant and on the temperature, as well as on the affinity of the interlayer ions or surfaces for the intercalating molecules. The observation of the slow dynamics of intercalation should be considered when doing surface area measurements on clays, as the vapor uptake into the interlayers could continue for days if the conditions favour intercalation. We plan to continue these investigations in the future at different pressures and temperatures, as well as mapping out the phase diagram for intercalation of CO₂ in NaFh and in other types of clays.

So far, the in-situ structural observation of intercalation presented in the manuscript adds substantial information to the scarce experimental data in this field and to our knowledge this is the first time that intercalation of CO₂ has been reported in hectorites with monovalent cations. We believe that our finding could have relevance for CO₂ storage, and also for CO₂ capture and transport, where in both cases clay and clay-nanocomposites may play key roles in future applications.

Supporting Information Available: Sample cell, data reduction and normalization, quantitative estimate of the adsorbed CO₂. This material is free of charge via the internet at <http://pubs.acs.org>.

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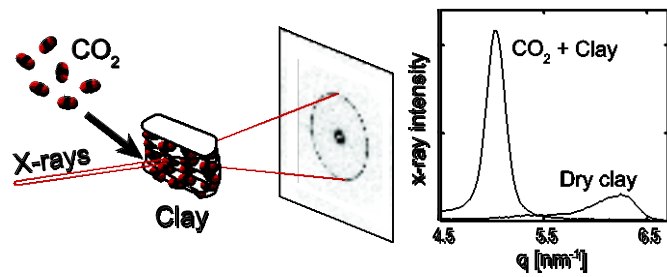


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