

Supporting information

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

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A. Sample cell

A sketch of the sample cell used for the experiments is shown in Figure 1.

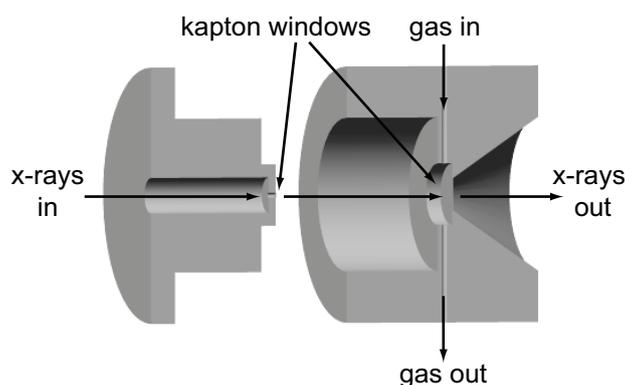


Figure 1. Cross sectional sketch of the sample cell, consisting of one bolt-shaped part (left) and one hollow part (right) screwed together during the measurements. On the hollow part there are gas-connections leading directly into the sample volume.

B. Background subtraction

The Fit2D software¹ was used for integrating the two-dimensional diffractograms into one-dimensional plots of intensity vs. scattering vector $q = 4\pi \sin(\theta) / \lambda$, where 2θ is the scattering angle, and $\lambda = 1.54 \text{ \AA}$ is the wavelength. An example of a diffractogram and the resulting line plot are shown in Figure 2. This particular curve shows partial intercalation, and the three visible peaks are from left to right: peak originating from the cell Kapton windows, peak from CO₂ intercalated clay and peak from dehydrated clay. Since the small-angle scattering from platelets are known to follow a decaying power law,² regions around the peak were fitted to a function of the form $aq^b + c$. The intervals used for the fit were a region at lower q than the kapton peak and a region at higher q than the dehydrated-peak. These regions are assumed to contain scattering contributions that are not related to the diffraction peaks of the present study. Figure 3 shows the fitting of the baseline to the plot, and the resulting diffraction pattern after baseline subtraction (for an arbitrary diffraction pattern).

We see from the position of the three peaks in Figure 2 that diffraction from a two-CO₂ layer structure would coincide with the peak from the Kapton window. However, we did not observe any signs of such a peak in these experiments. The intensity plot in Figure 4 confirms this, as the growth of a two-layer peak would entail decay of the one-layer peak.

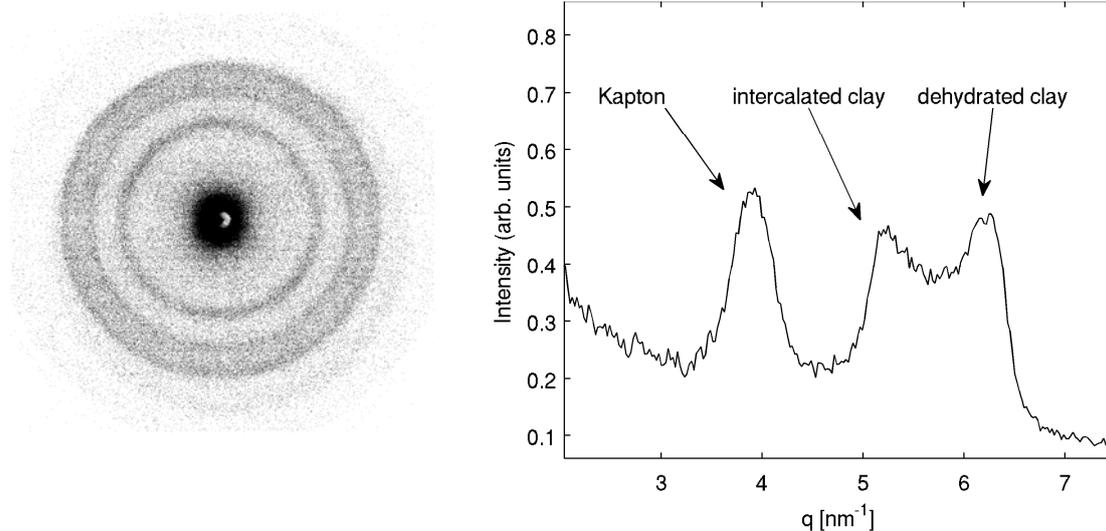


Figure 2. Diffractogram (left) and the corresponding one-dimensional line-plot (right).

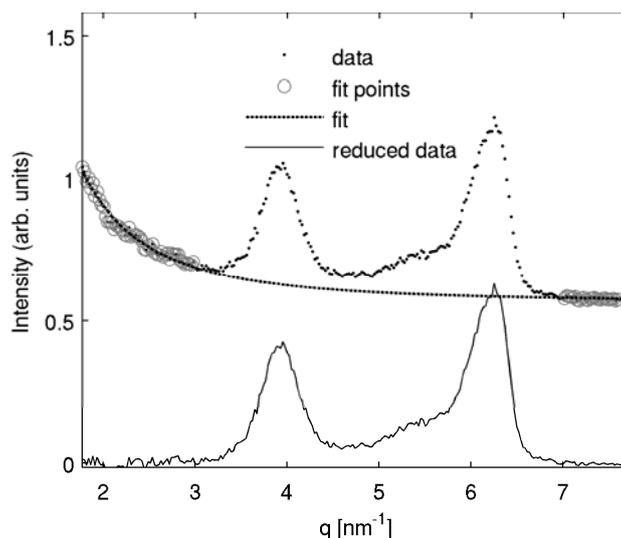


Figure 3. Top: The baseline is fitted to a power law evaluated on intervals not involving the diffraction peaks from the clay sample or Kapton window. Bottom: Data after subtracting the fit.

C. Normalization

Density differences arising from the intercalation lead to changes in absorption (powder packing) and small angle scattering (particle form factor) between the measurements. In order to correct for these differences, the plots were normalized on a point in the curve that is less affected by changes in temperature and pressure. The peak due to the scattering from the Kapton windows is not expected to vary significantly and was therefore chosen for this purpose. The normalization was done by fitting the Kapton peak to a pseudo-Voigt profile, and dividing each plot by its peak area.

D. Time evolution of the intercalation peak

In Figure 4 we have plotted the maximum intensity of the intercalation peak as a function of time for the measurements done at -20 °C and 15 bar. The plot shows that the intensity reaches a plateau after approximately 200 hours. The peak intensity was obtained by fitting pseudo-Voigt profiles to the peaks; hence only data where the peak was intense enough for a reasonable fit are shown.

The straight line fit to the data shows a linear growth in peak intensity for a large part of the intercalation process, giving an approximate time dependence of $I = -1.73 + 0.07t$, where I is intensity and t is time (in hours). However, note that the x-ray peak intensities can be affected by the clay layer structure factor if the interlayer organization of CO₂ molecules

changes during the intercalation process. Therefore, inferring the precise mechanisms and kinetic aspects of the intercalation from these XRD data is not straightforward.

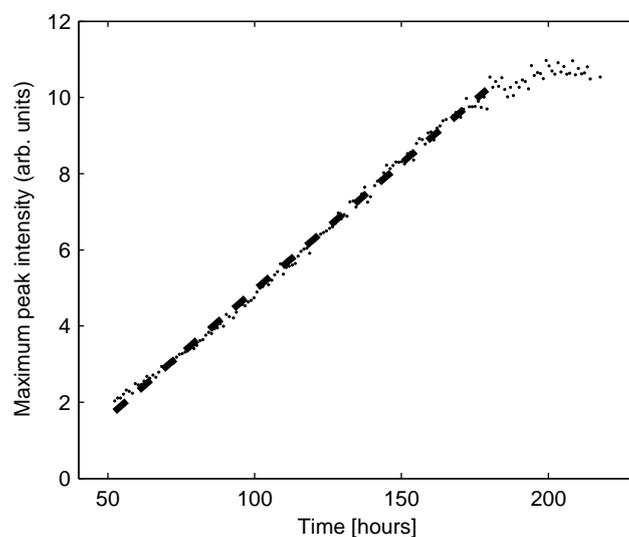


Figure 4. Maximum intensity of the intercalation peak as function of time after the start of the experiment.

References

- (1) Hammersley, A. P. *FIT2D: An Introduction and Overview*; ESRF Internal report ESRF97HA02T; European Synchrotron Radiation Facility: Grenoble, 1997.
- (2) Fonseca, D. M.; Meheust, Y.; Fossum, J. O.; Knudsen, K. D.; Parmar, K. P. S. *Phys. Rev. E* **2009**, *79*, 021402.