MECHANISMS OF CO_2 INTERACTION WITH EXPANSIVE CLAY

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Concept

- Clays represent abundant geomaterials with well-developed microporous structure.
- Expansive clays have the CO_2 sorption capacity comparable to or even greater than the sorption capacity of coal.
- CO_2 may intercalate into interlayer region via coordination to interlayer cations.
- The interlayer surface area of clays is larger than the values for the external surface area reported in the literature. However, penetration of CO_2 molecules into the interlayer region has not been sufficiently investigated.

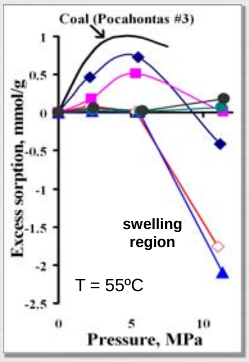
Scope

The objective of this project is to evaluate the GHG sequestration potential of clay and investigate what factors affect sorption capacity, rates, and permanence of CO_2 storage. We used source clay samples from CMS and analyzed XRD, DRIFTS, and TGA-MS data to compare the effects of various factors on CO_2 trapping and performed simulations of CO_2 interaction with free cations and with clay structures containing interlayer cations.

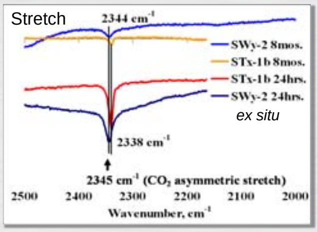
Future Work

- High-pressure experiments with in-situ measurements of the extent of sample swelling
- Study of the permanence of trapping mechanisms

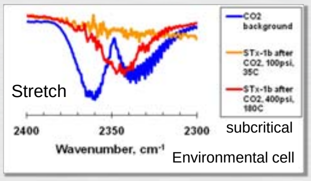
Storage in clay/shale

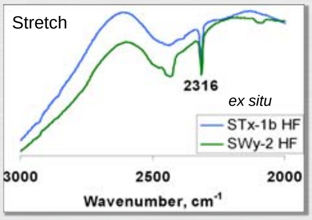


Low-pressure adsorption was observed for montmorillonite (STx-1b, SWy-2). Kaolinite (KGa-1b, KGa-2) and illite (Ward green shale, Pittsburgh shale) samples show negligible low-pressure adsorption, but kaolinite like montmorillonite swelled in sc-CO_2 and appeared to imbibe CO_2 at higher pressure.



Adsorption capacity of certain clays is comparable to coal. In addition, CO_2 molecules may intercalate between the lamellae and remain trapped there after release of the pressure, which is observed in IR (diffuse reflectance) spectra.

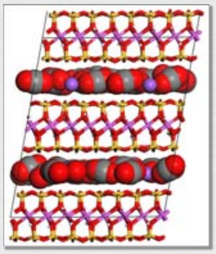




Models of trapping mechanisms

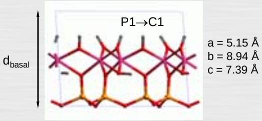
Molecular model of Wyoming montmorillonite used in the swelling simulations.

Basal *d*-spacing with H_2O = 12.35 Å
with CO_2 = 12.23 Å



Energy minimized

Kaolinite $Al_2Si_2O_5(OH)_4$

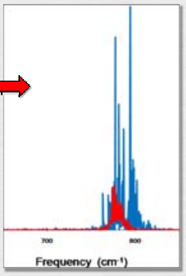


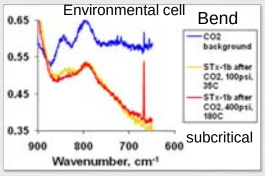
Geometry optimized structure of the unit cell of kaolinite based on CLAYFF; structure agrees with Bish (1993).

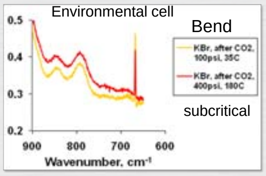
Snapshot from equilibrated molecular dynamics simulation of carbon dioxide intercalated in the interlayer of Na-montmorillonite; *NPT* ensemble equilibrated for 100 ps with single layer of CO_2 with approximately four CO_2 molecules coordinated to each Na^+.

Experimental verification of the models

Comparison of the bending mode for CO_2 in power spectra derived from molecular dynamics simulations of liquid CO_2 (red) and montmorillonite-intercalated CO_2 (blue). The intercalated montmorillonite exhibits a slight blue shift in frequency and a splitting of the bending mode peak.

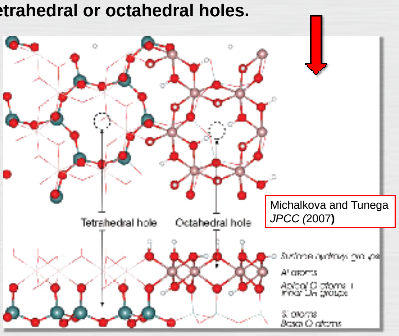




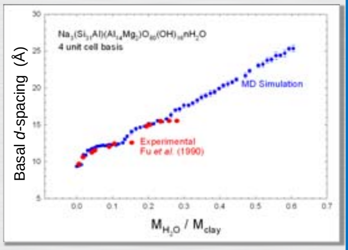


Experimentally, no IR (diffuse reflectance) bending mode of CO_2 was detected in excess of background (degassing) after exposure of clay samples to various temperature and pressure cycles.

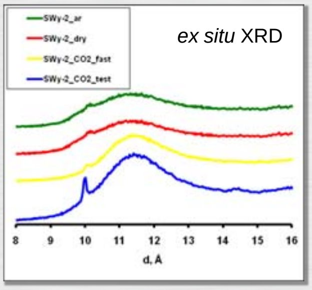
This may require significant improvement in quality of IR or Raman spectra and possibly a revision of the intercalation model. An alternative model is an orthogonal stacking of CO_2 molecules (perpendicular to the silicate sheets) against tetrahedral or octahedral holes.



Michalkova and Tunega *JPCC* (2007)



Swelling curve for the hydration of Na-montmorillonite derived from equilibrated molecular dynamics simulations (red) with experimental data (blue).



Experimental XRD spectra are convoluted by exposure to ambient, which is why the spectra for dry and as received clay samples are similar. The spectra for samples exposed to increased CO_2 pressure and temperature vary, depending on the ramping rates.

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