Stanford Center for Carbon Storage
2015 Annual Meeting

Atomistic Modeling of Fluid Wetting and Transport Processes in Confined Space

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Molecular Simulation Studies of Fluid-Clay Systems

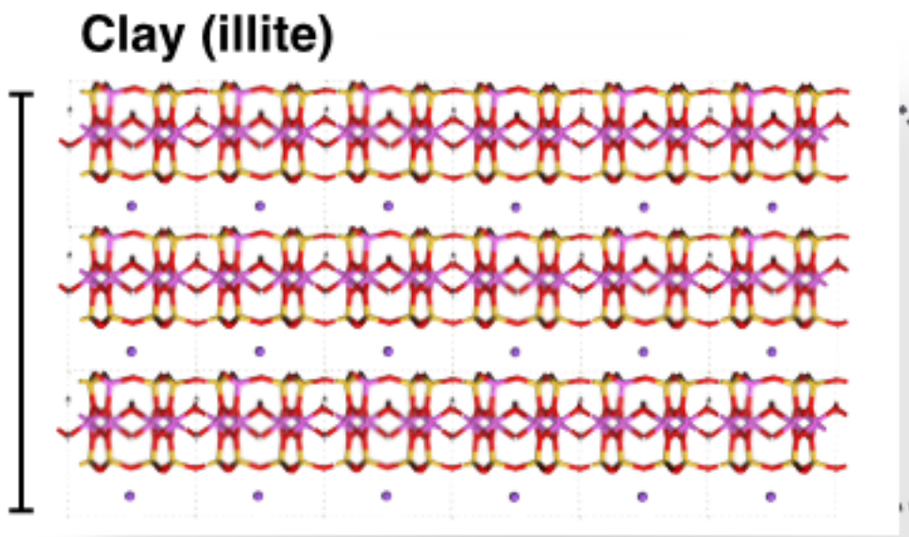
- **Static**

  Structure
  Density
  Thermodynamics
  Phase diagram

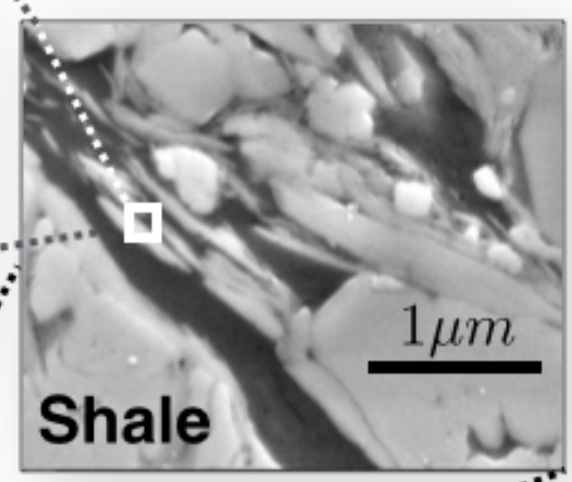
- **Dynamic**

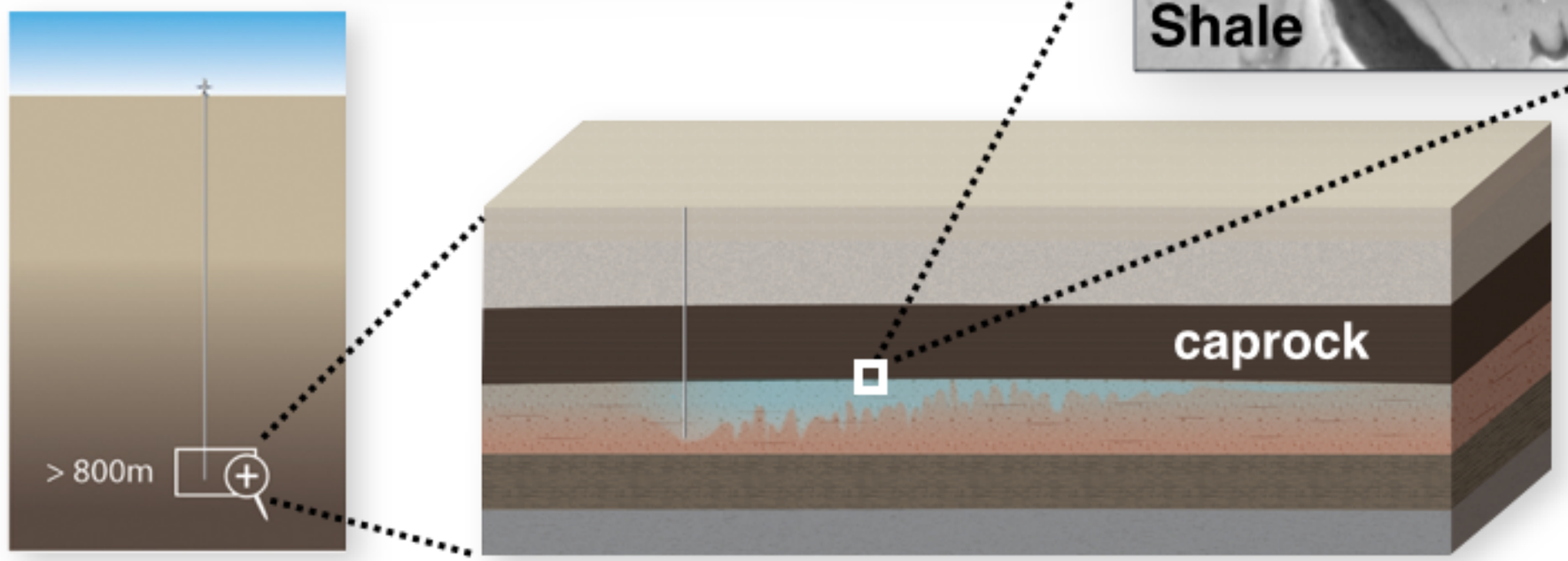
  Transport
  Rate

Nano scale



Pore scale





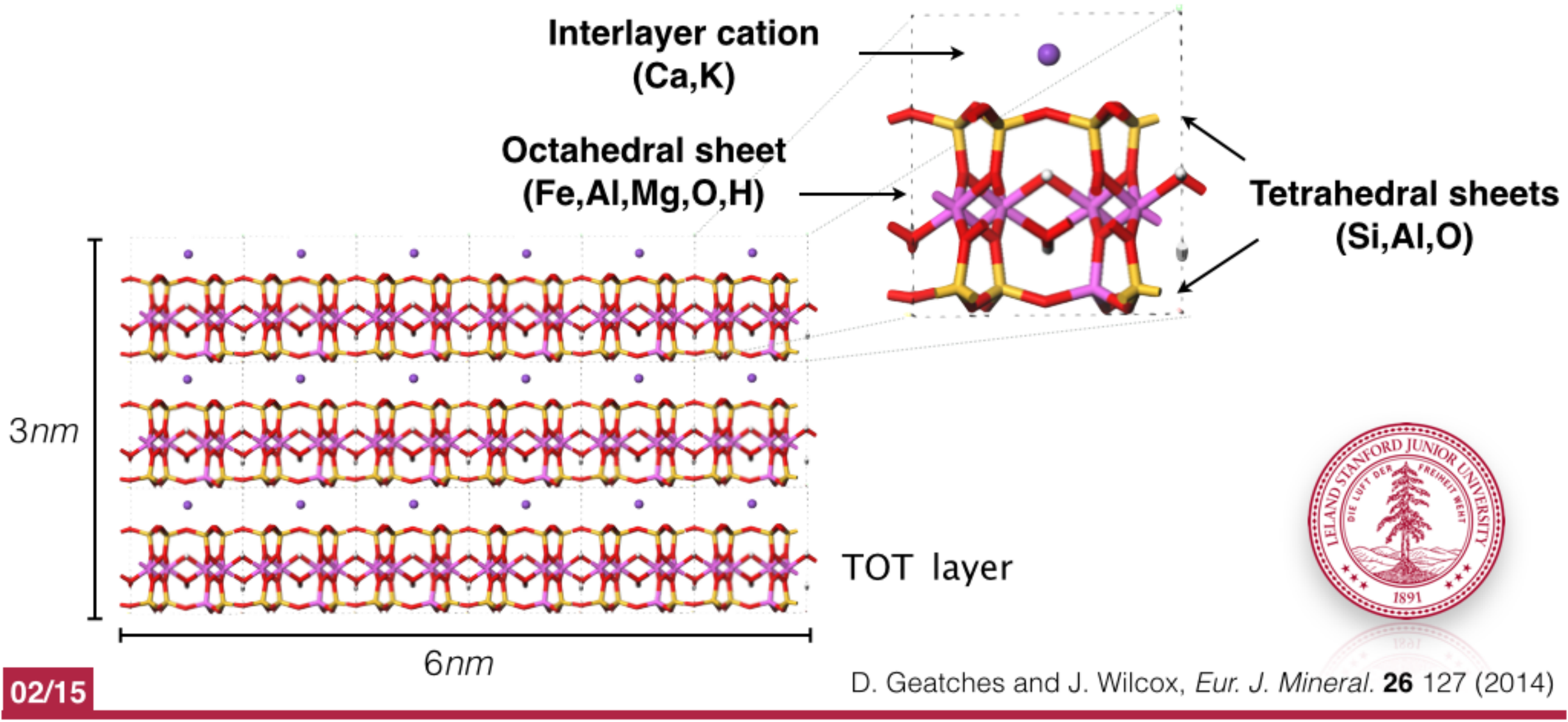
IEAGHG report June (2011)

Atomistic Model of Illite (Quantum DFT)

Expensive (<200 atoms) !!

General formula

$$Ca_{0.059}K_{0.655}(Si_{3.597}Al_{0.403})(Fe_{0.628}Al_{0.969}Mg_{0.428})O_{10}(OH)_2$$



D. Geatches and J. Wilcox, *Eur. J. Mineral.* **26** 127 (2014)

Atomistic Model of Illite (ClayFF Empirical Potential)

> 1M atoms

Empirical potential for Hydroxide, Oxyhydroxide, and Clay

by Randall T. Cygan et.al. (2004)

$$U_{tot} = U_{coul} + U_{vdw} + U_{bond} + U_{angle}$$

LJ-pairs Stretching Bending

Molecular Dynamics (MD)

$$F = -\nabla U = ma$$

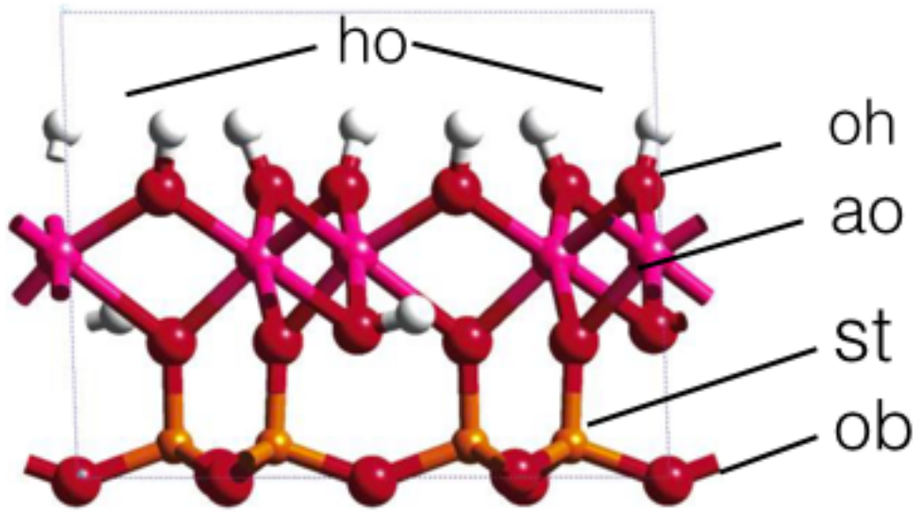
$$\frac{dp}{dt} = -\frac{\partial H}{\partial q} \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}$$

$$U_{coul} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$

$$U_{vdw} = \sum_{i \neq j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

$$U_{bond} = k_{sp}(r_{ij} - r_0)^2$$

$$U_{angle} = k_\theta(\theta_{ijk} - \theta_0)^2$$

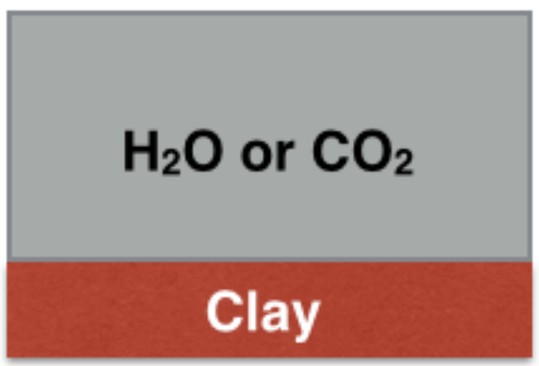


kaolinite

Randall T. Cygan *et.al. J. Phys. Chem. B*, **108**, 1255 (2004)

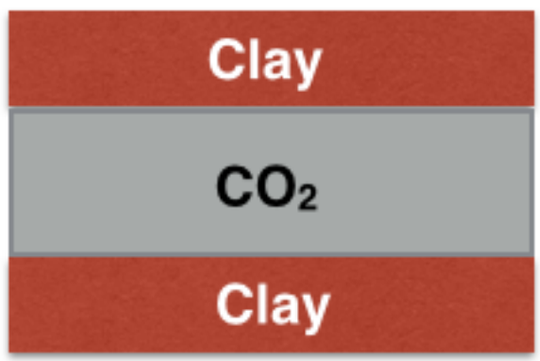
Outline of the Systems

1.



Structure of the fluid/clay interface

2.

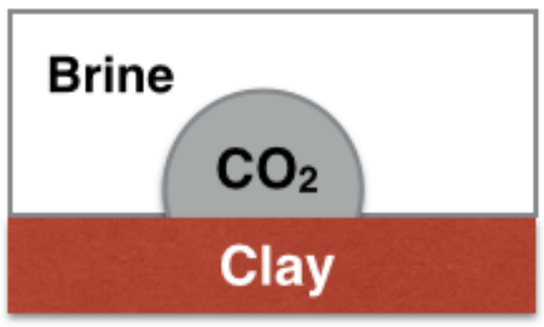


Fluid diffusion in clay slit pore

3.

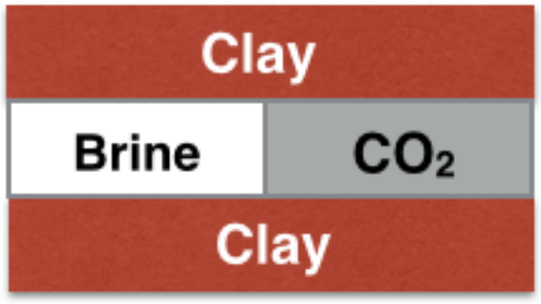
Static contact angle of brine on clay

4.



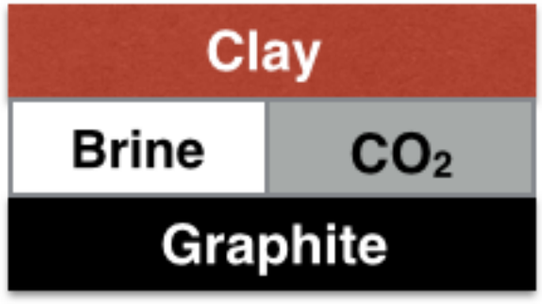
Static contact angle of CO_2/brine on clay

5.



Structure of the CO_2/brine interface in clay slit pore

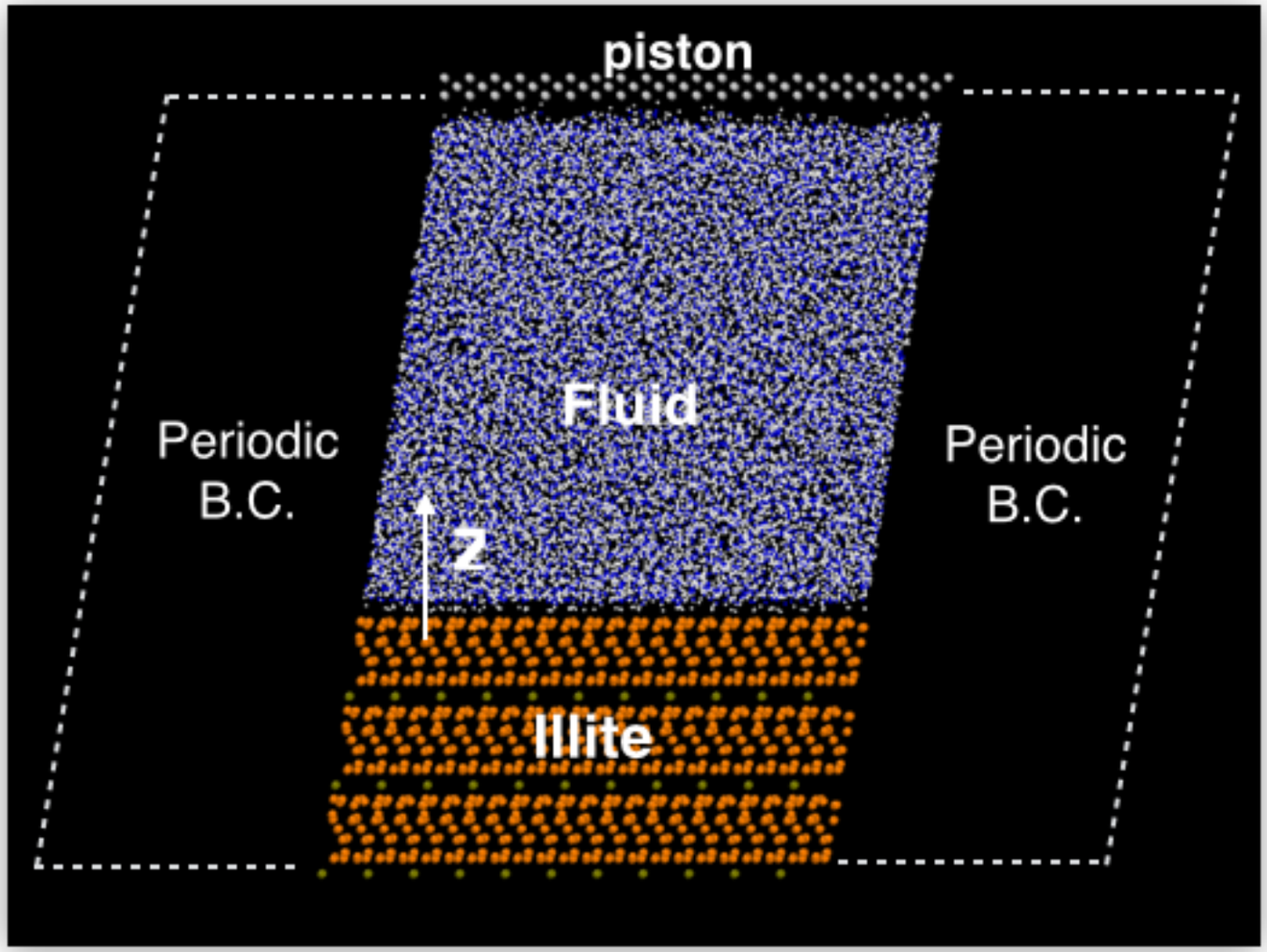
6.



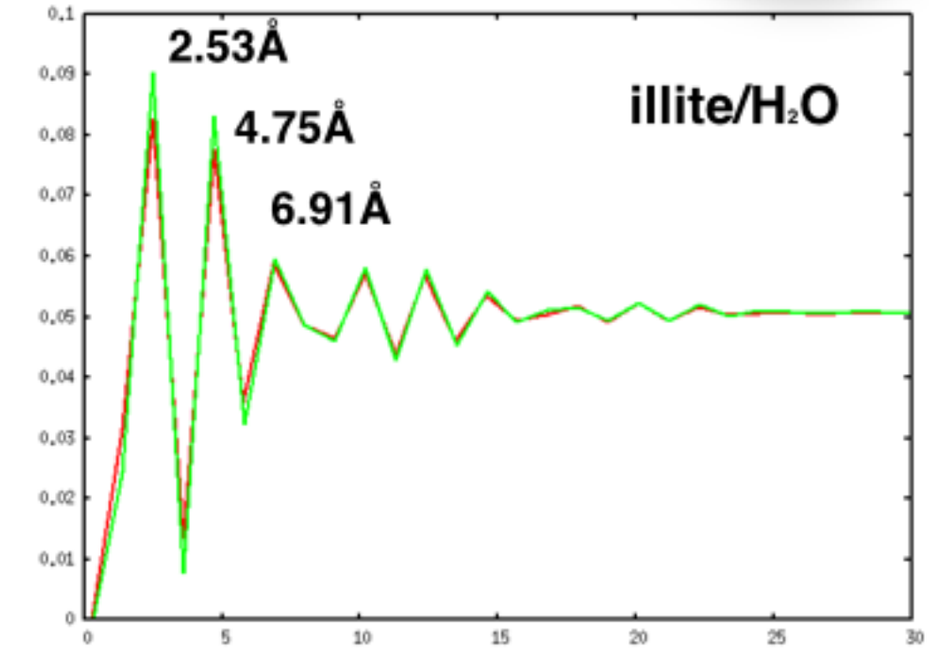
Structure of the CO_2/brine interface in clay-graphite slit pore

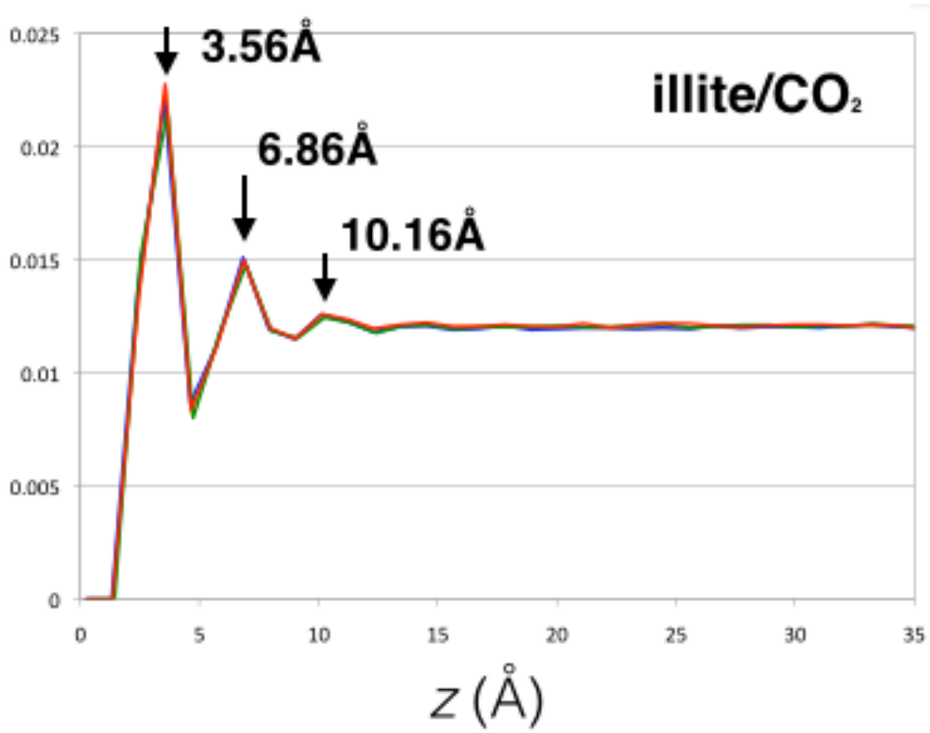
1. Fluid Density Profile

Liquid density profile (z direction)



T=300 K, P=200 bar





System dimension

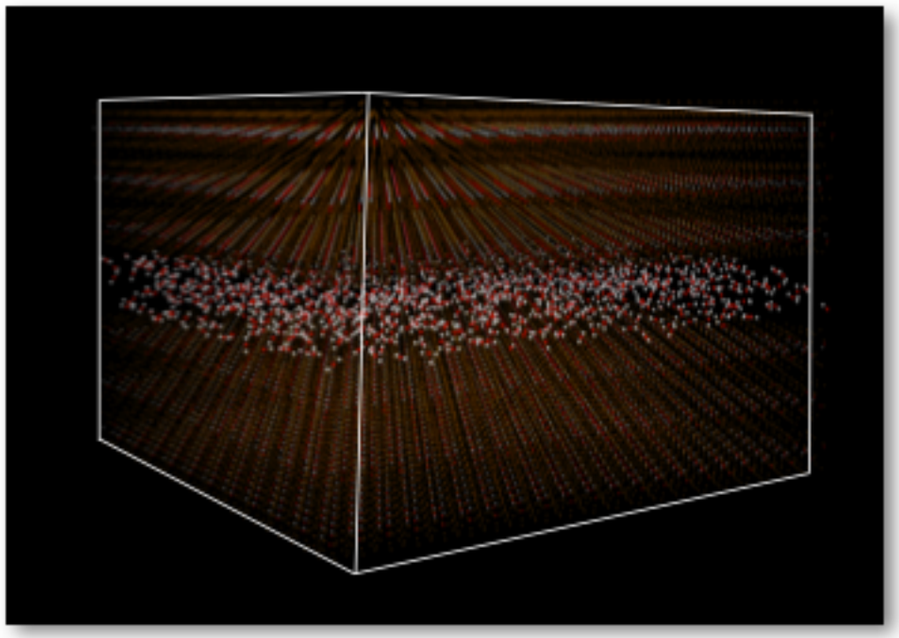
- 11x6x3 unit cell
- Fluid thickness~60Å
- ~15000 atoms
- ~2000 fluid molecules

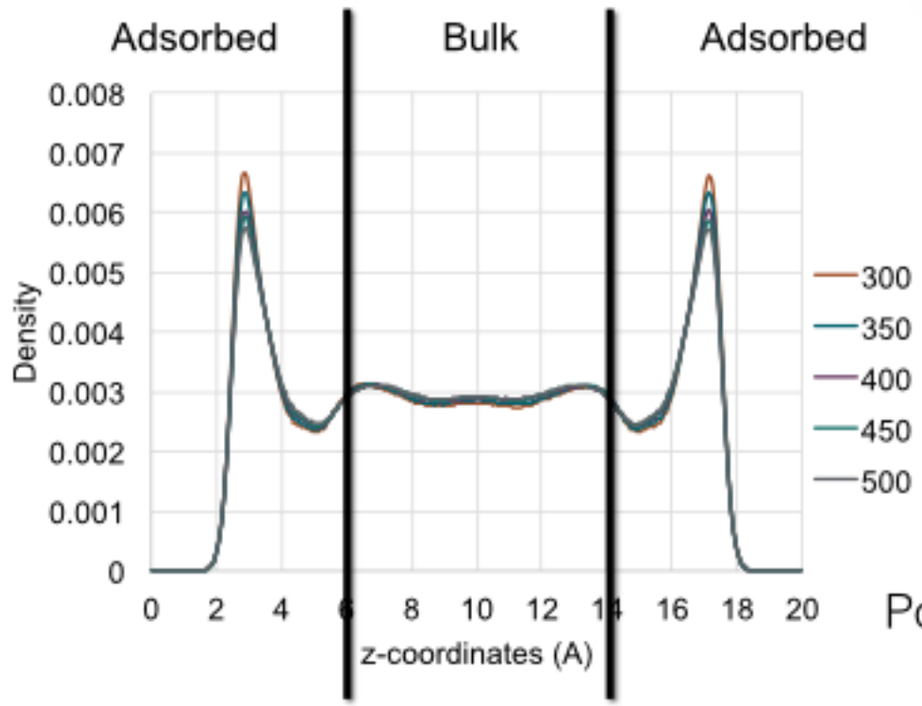
MD parameters

- 300 K 200 bar
- 500 *ps* with *dt*=1*fs*
- PBC in *x* and *y*
- *kspace: MSM 10*$^{-4}$

2. Fluid Structure and Diffusion in Clay Slit Pore

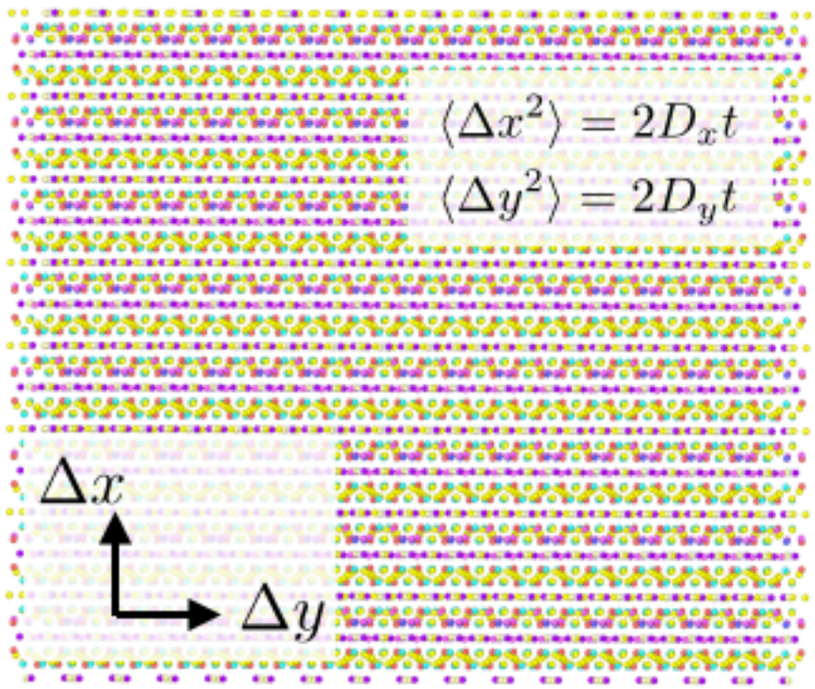
Data: Hassan Aljama

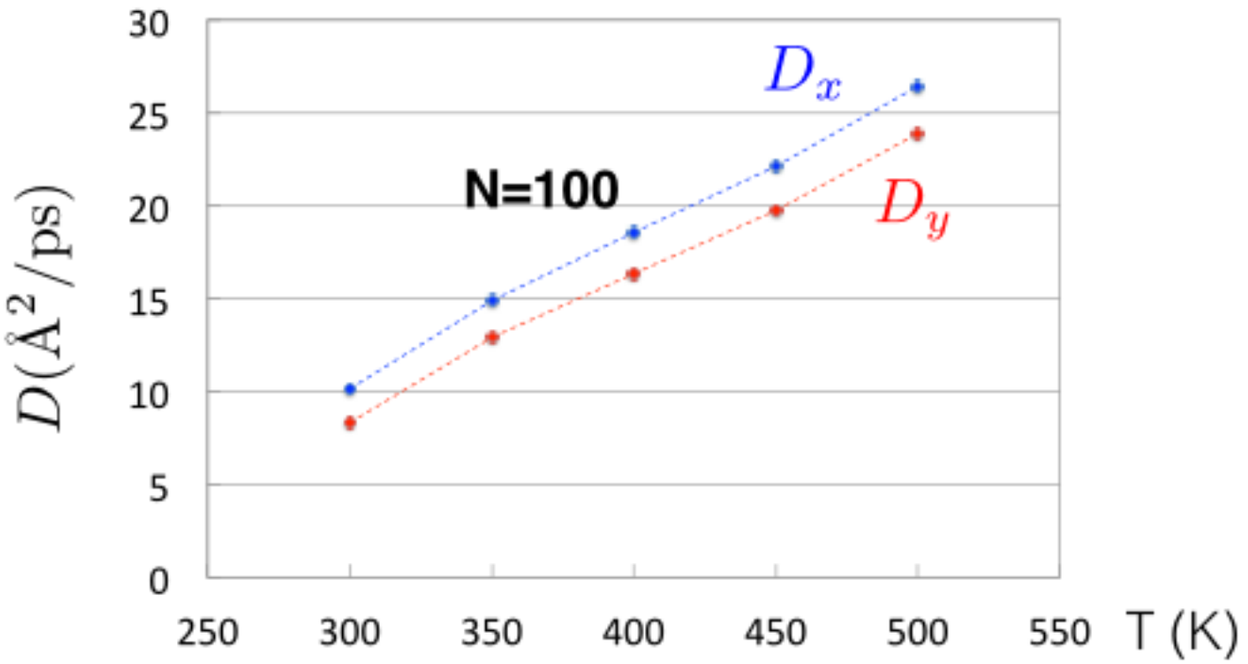




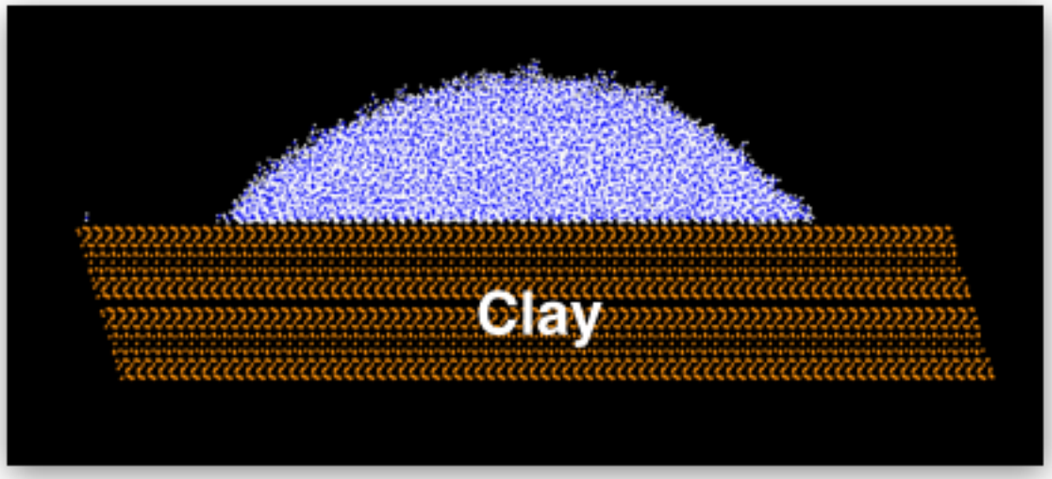
Pore size 20 Å
1200 CO_2

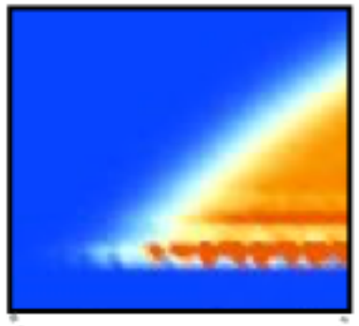
1-D self diffusivity

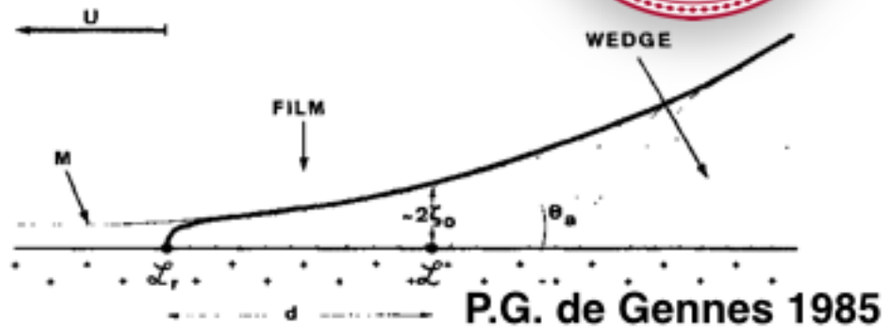




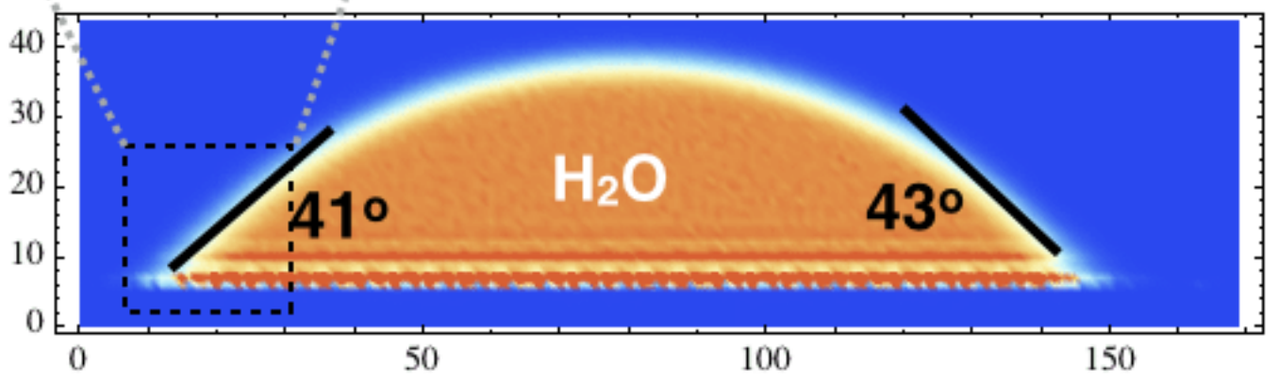
3. Static Contact Angle (Brine/clay)

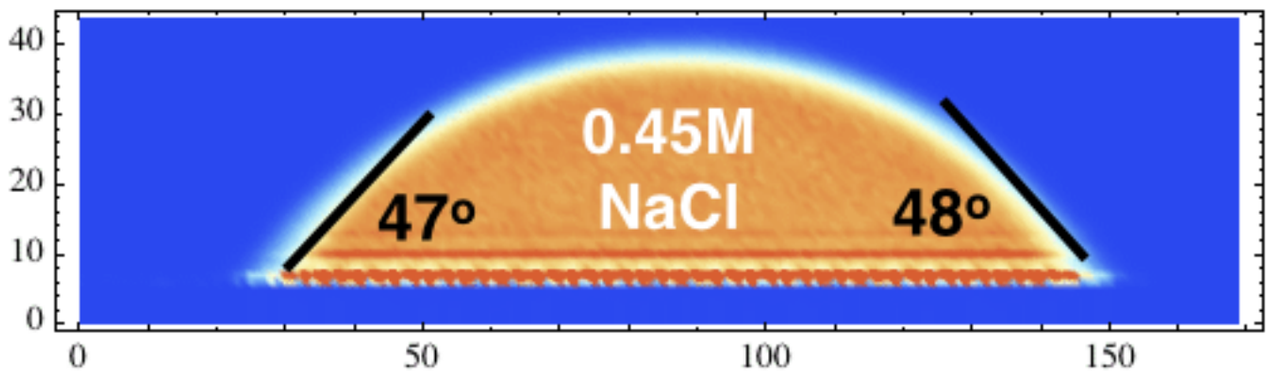


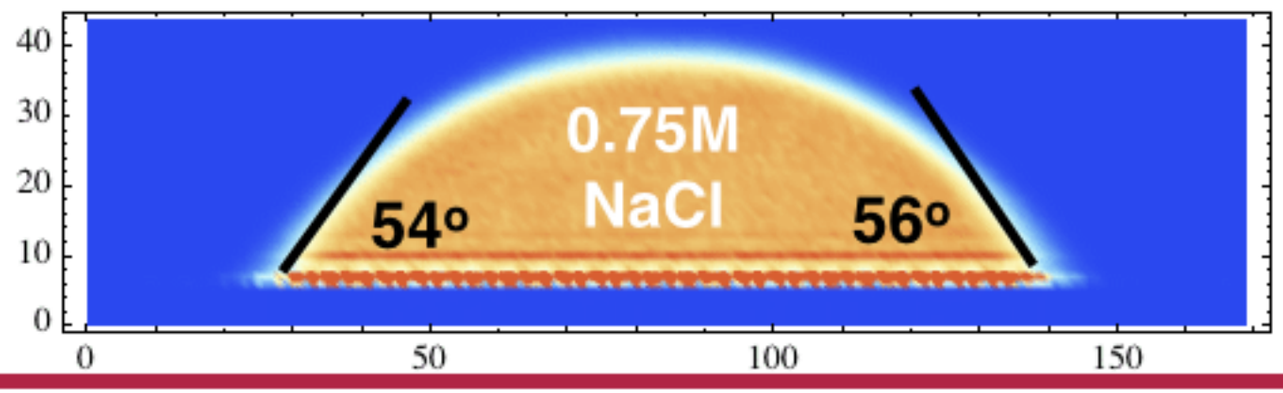


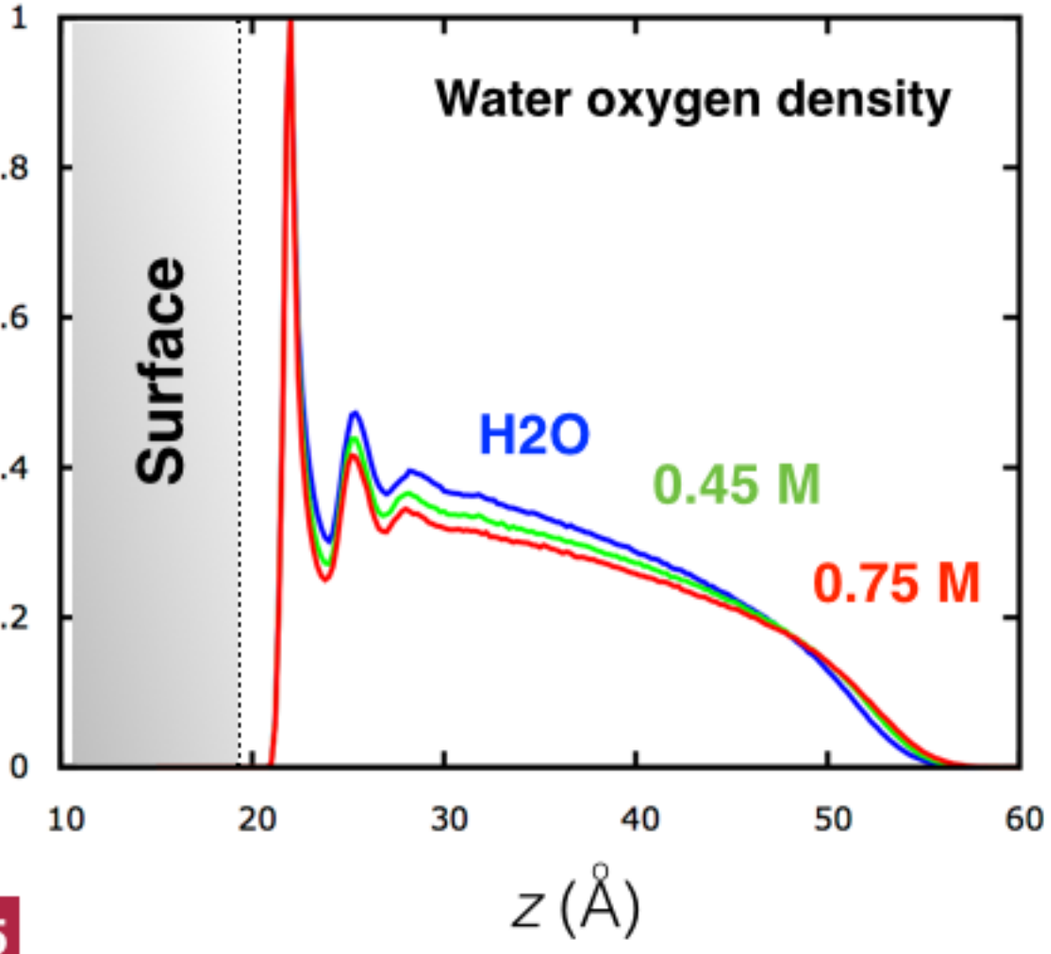


P.G. de Gennes 1985

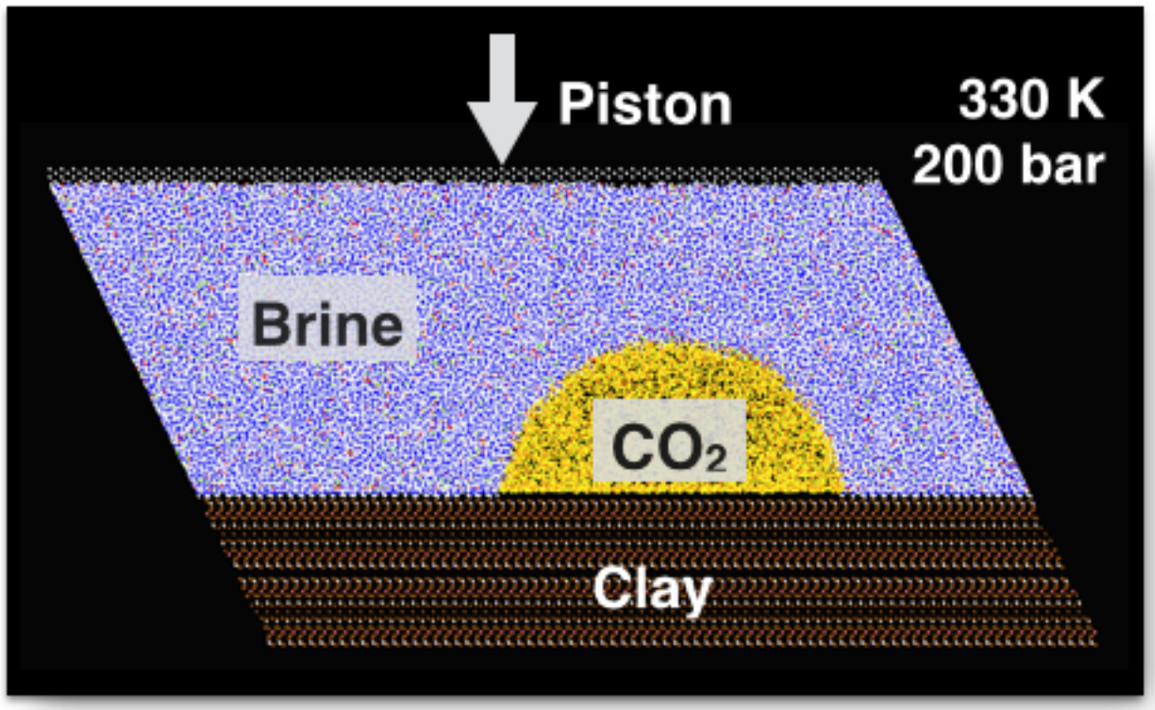


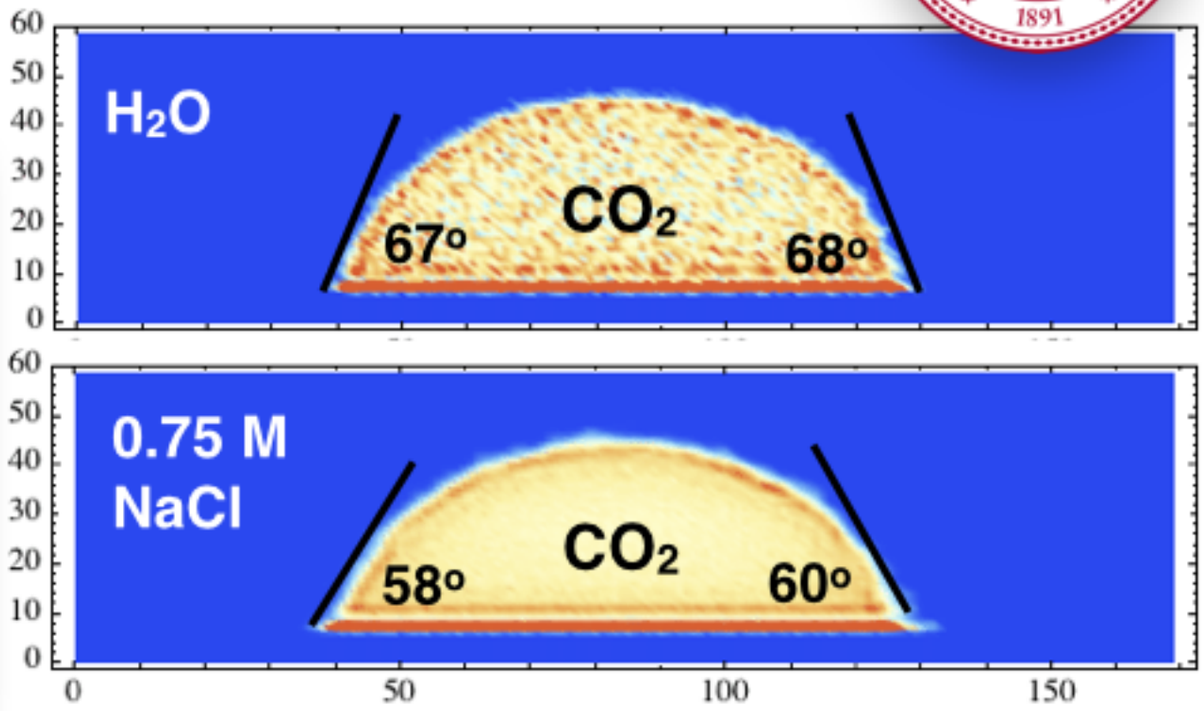


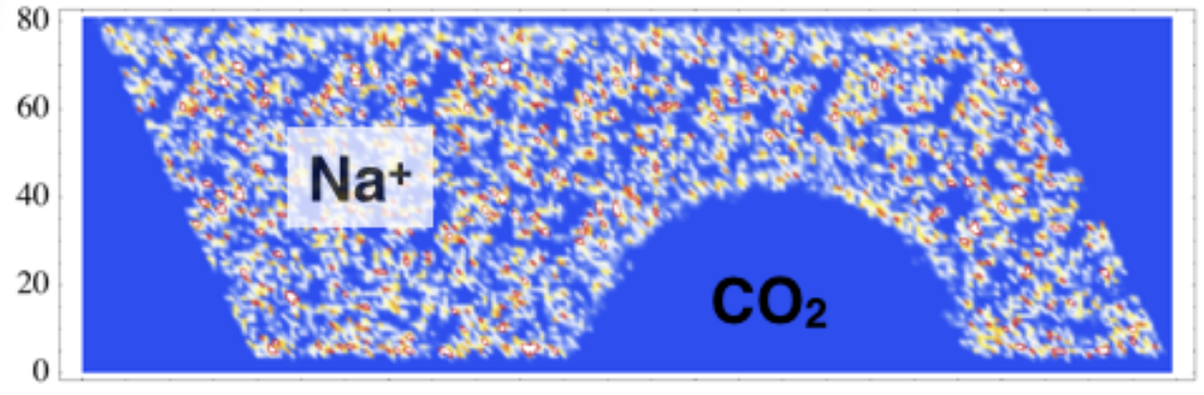


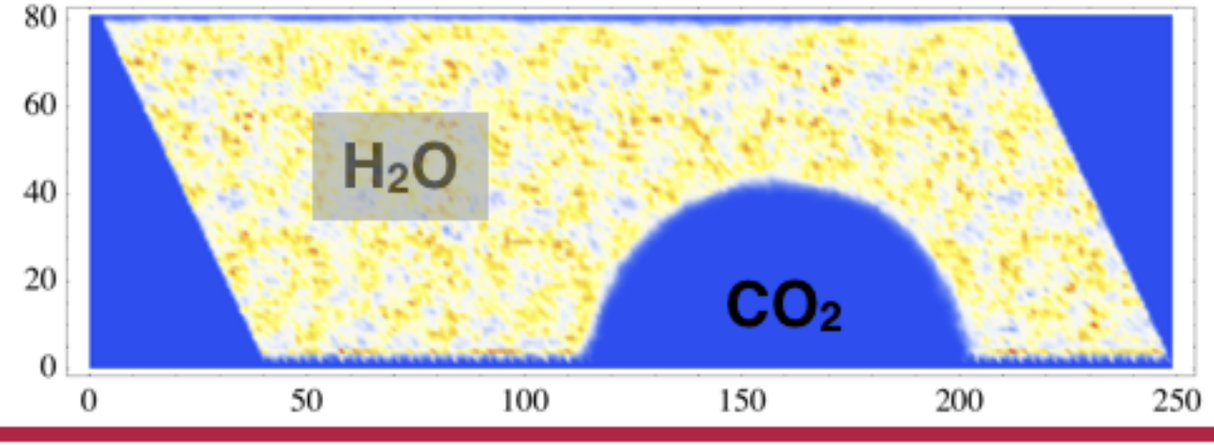


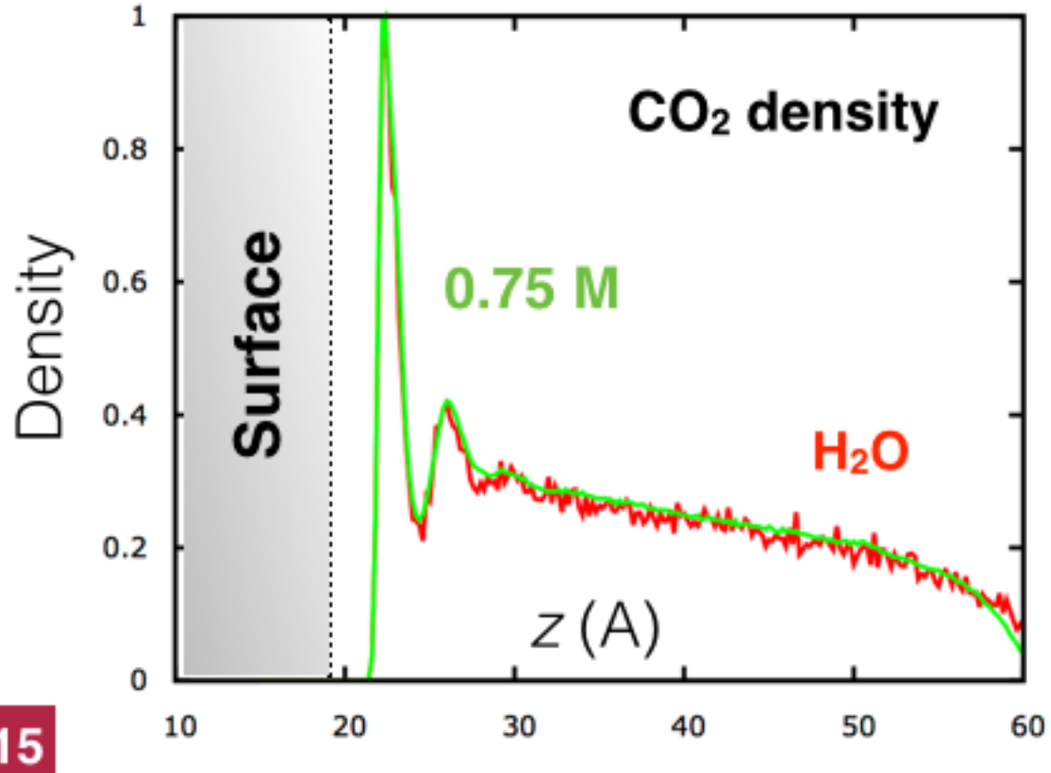
4. Static Contact Angle (Brine/CO_2/clay)



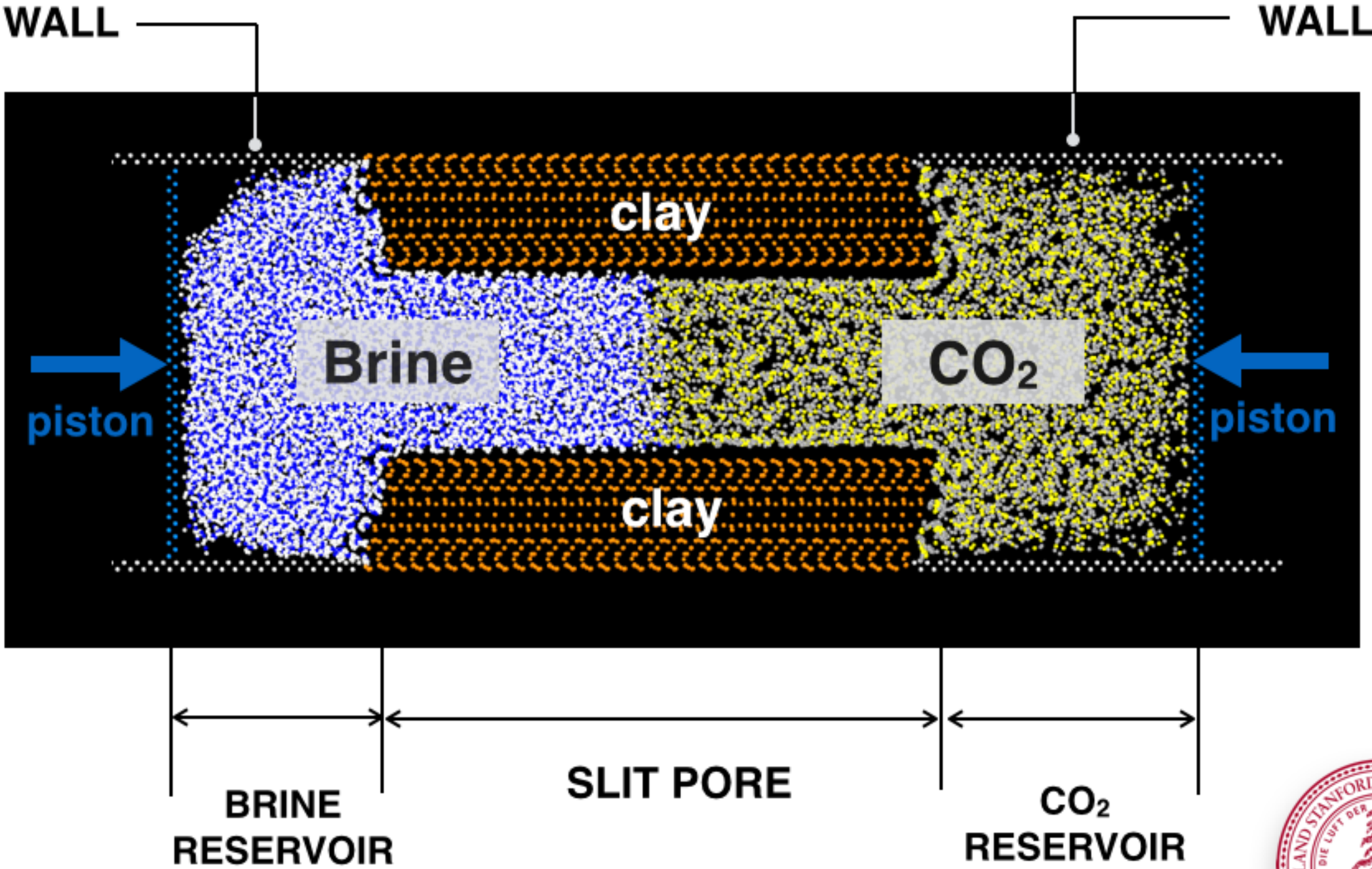




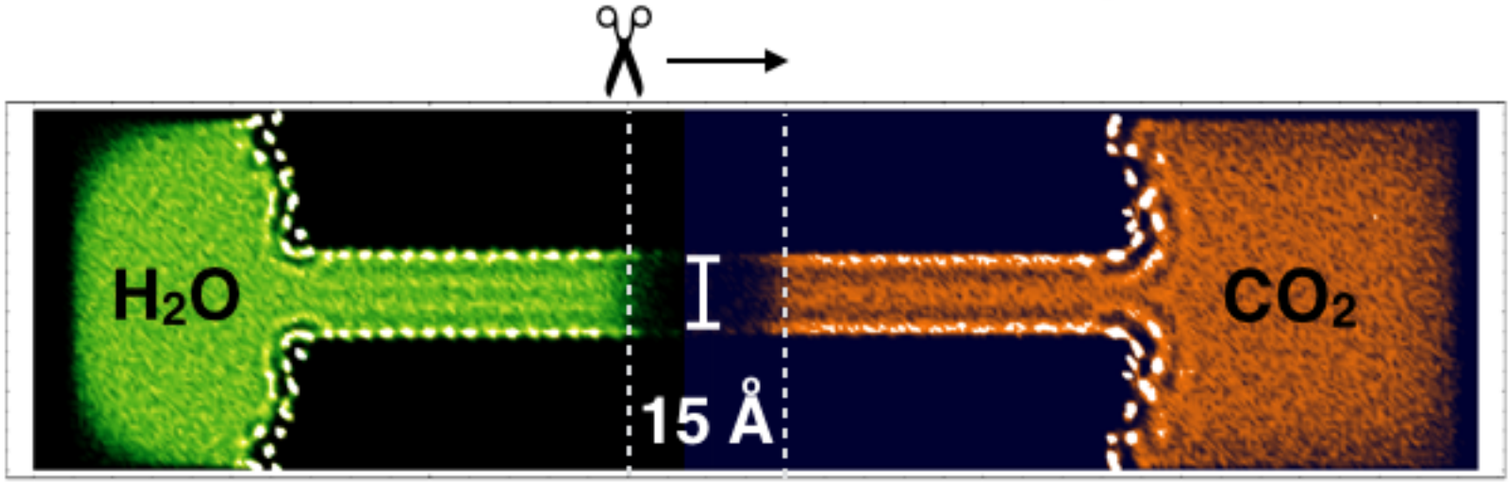




5. Brine/CO_2 in Clay Slit Pore

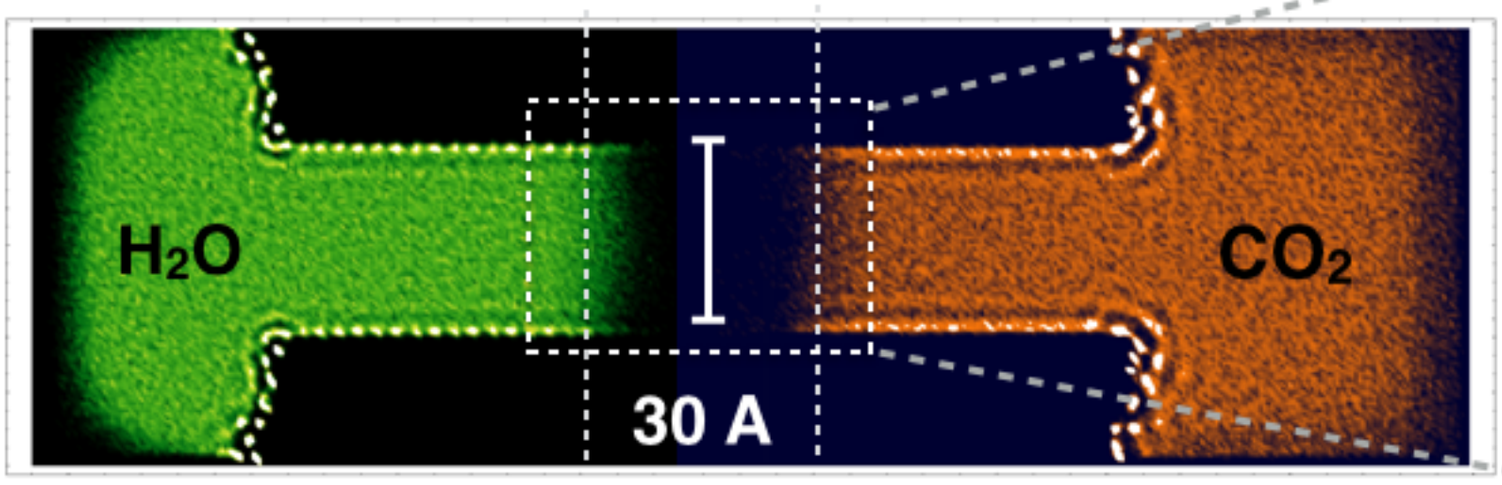


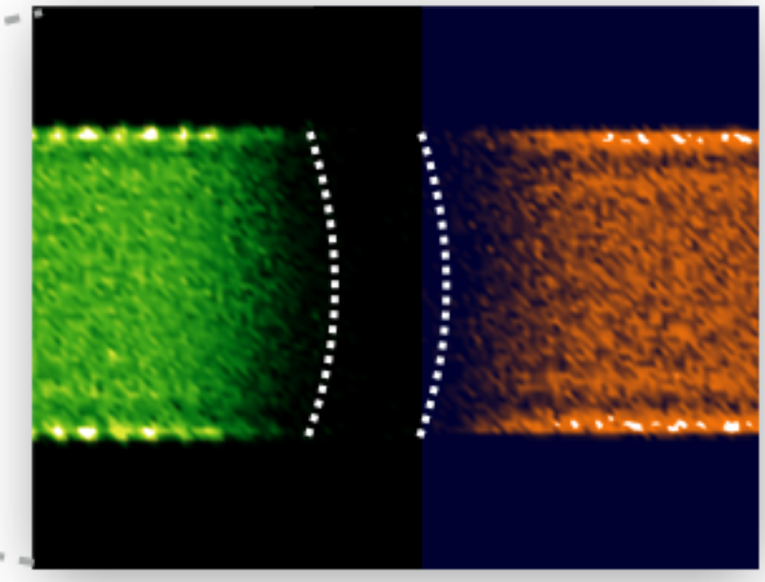
5. Brine/CO_2 in Clay Slit Pore

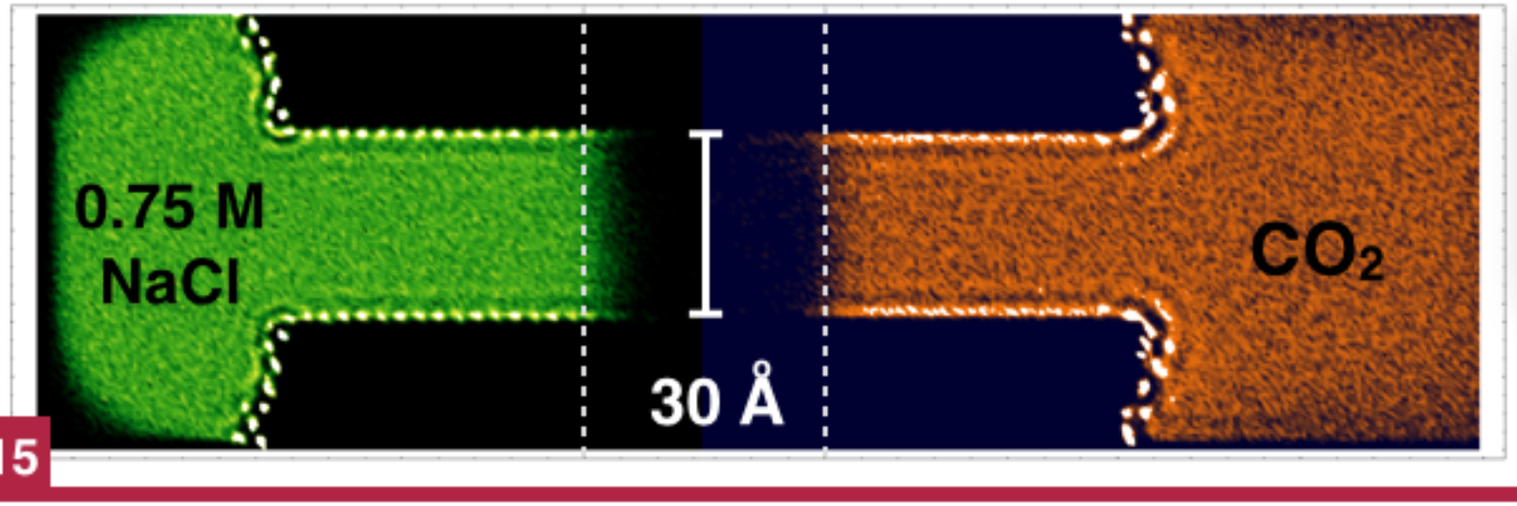


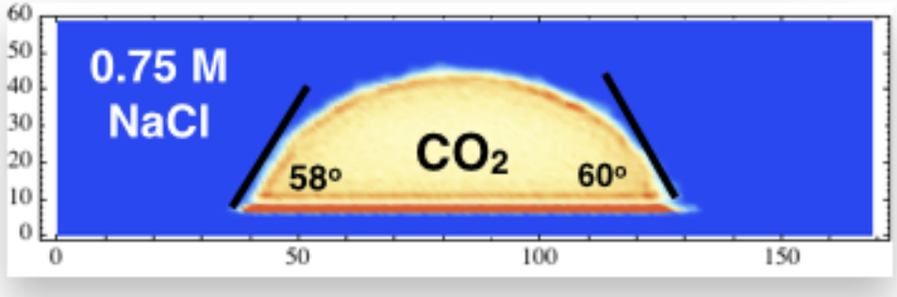
T=330 K

P=200 bar

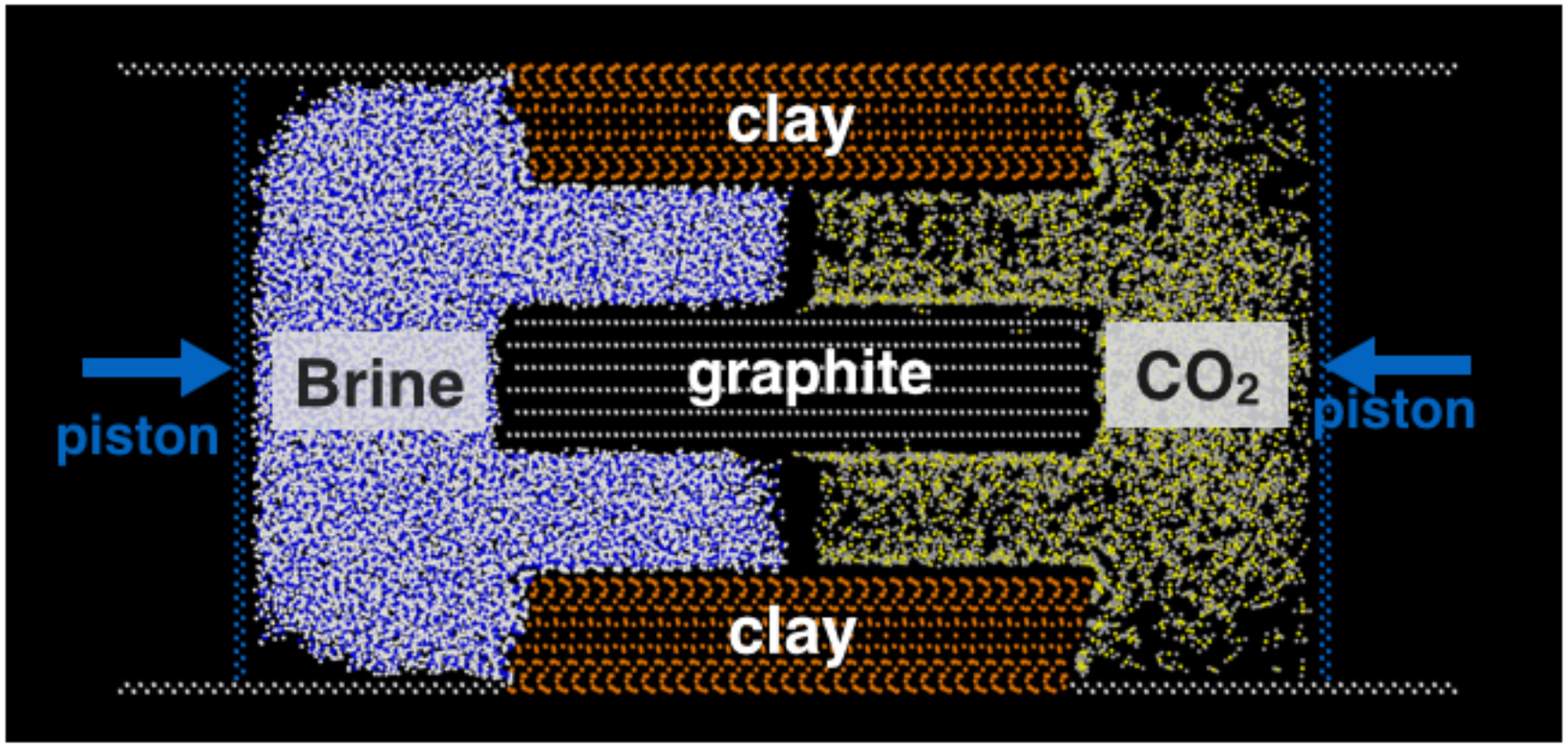




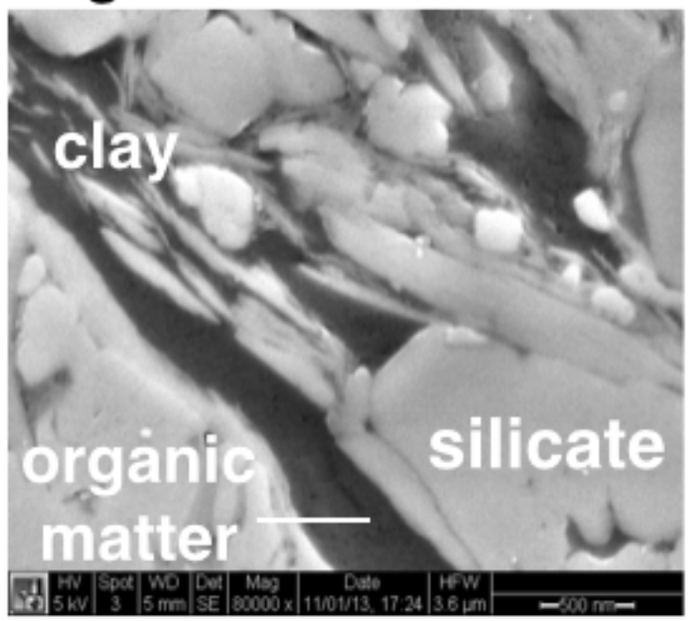




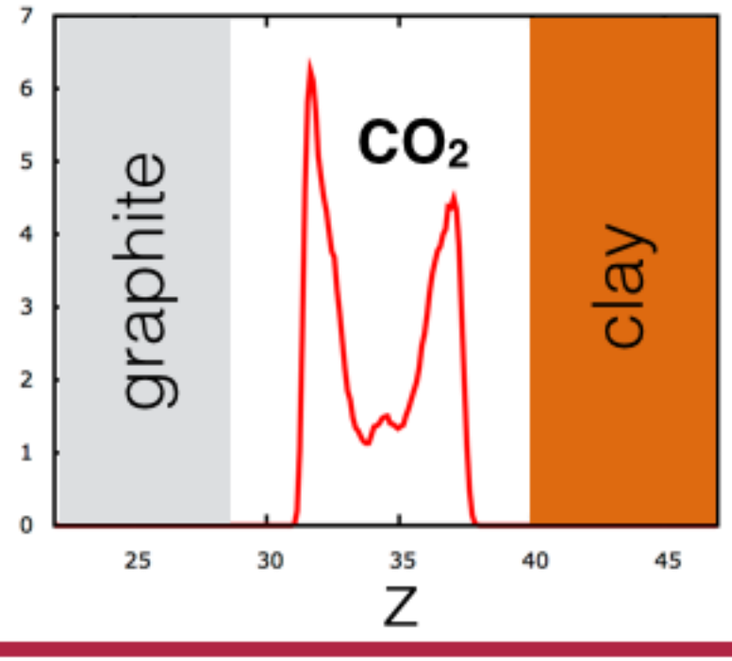
6. Clay-Graphite Slit Pore

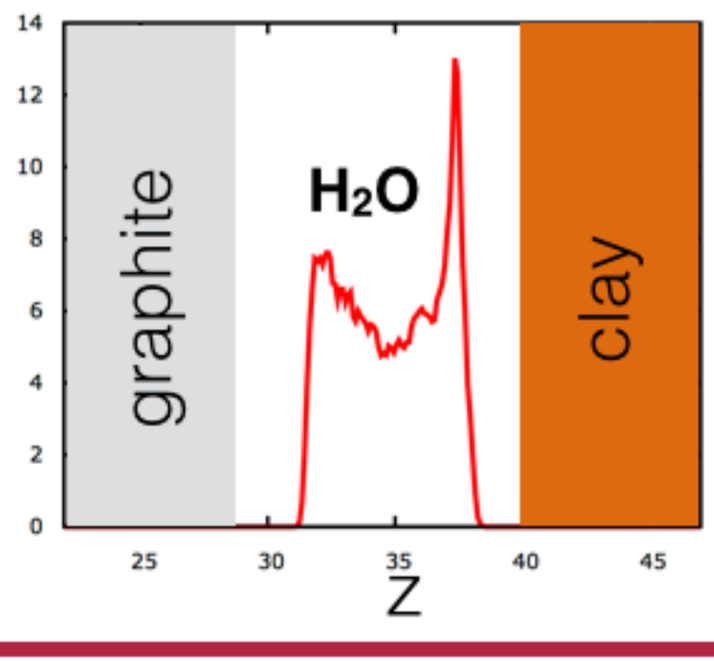


Eagle Ford shale



Density profile (pore size 11.7Å)





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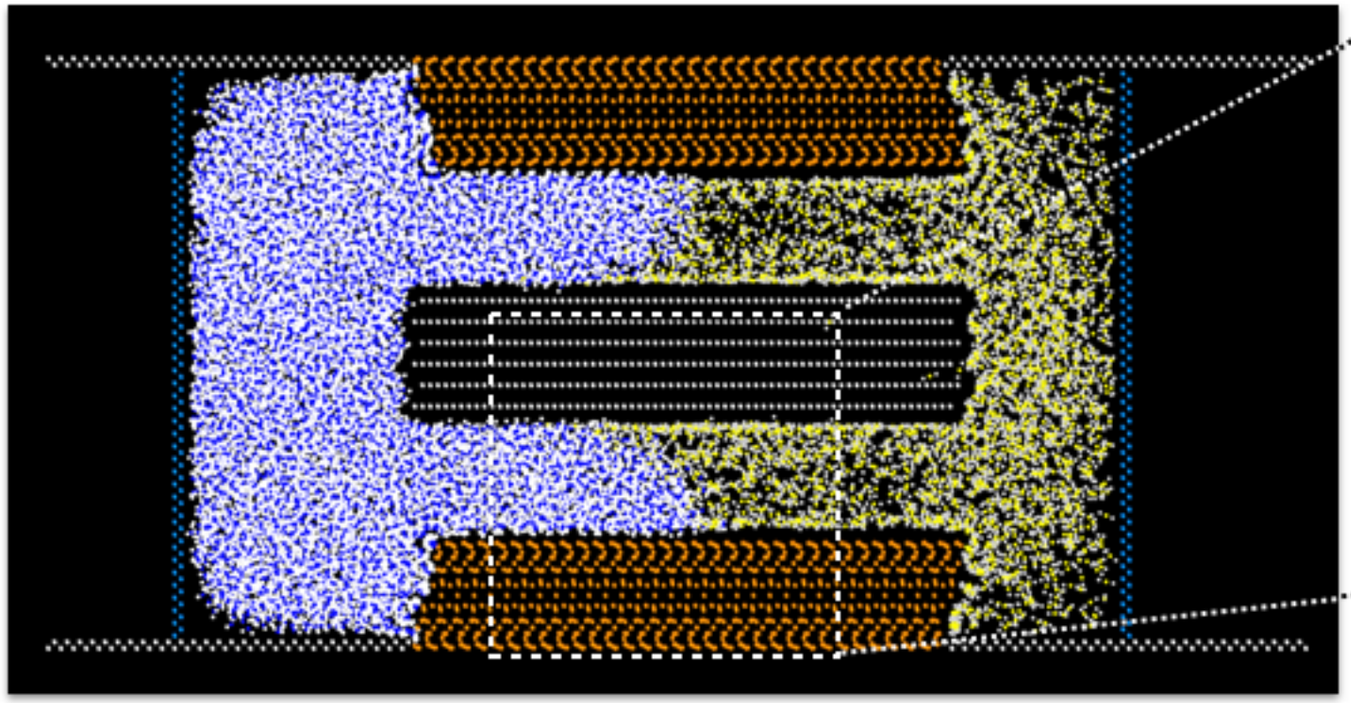
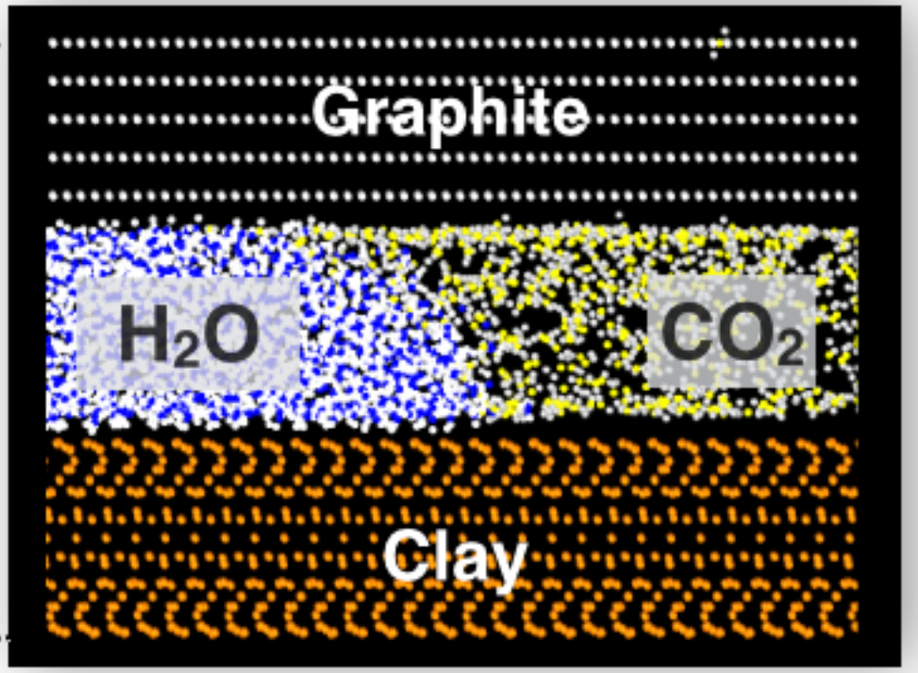
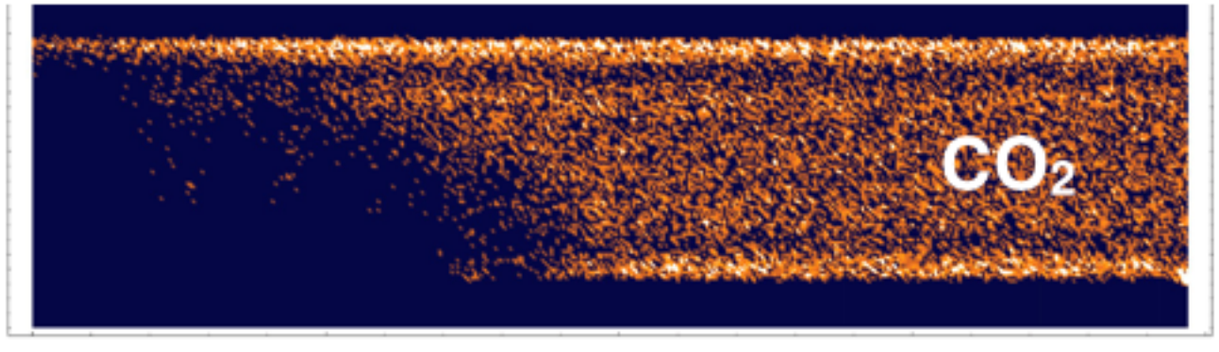
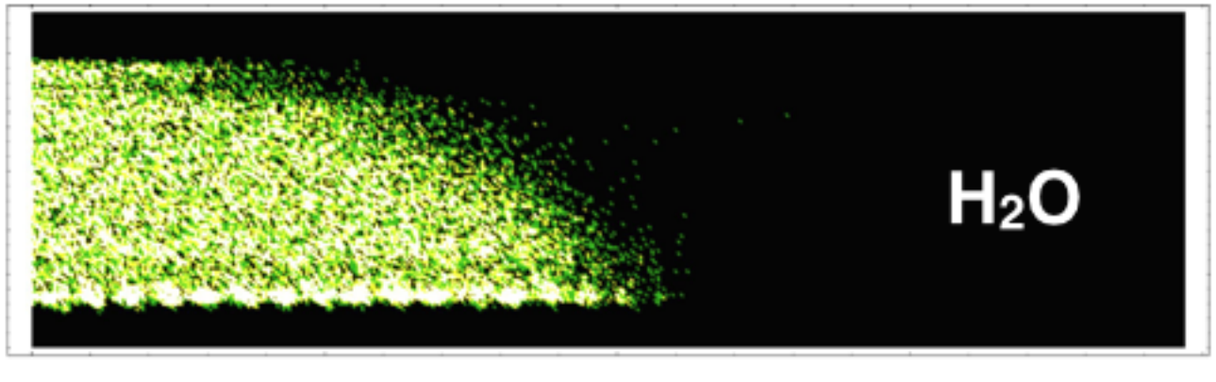




Z



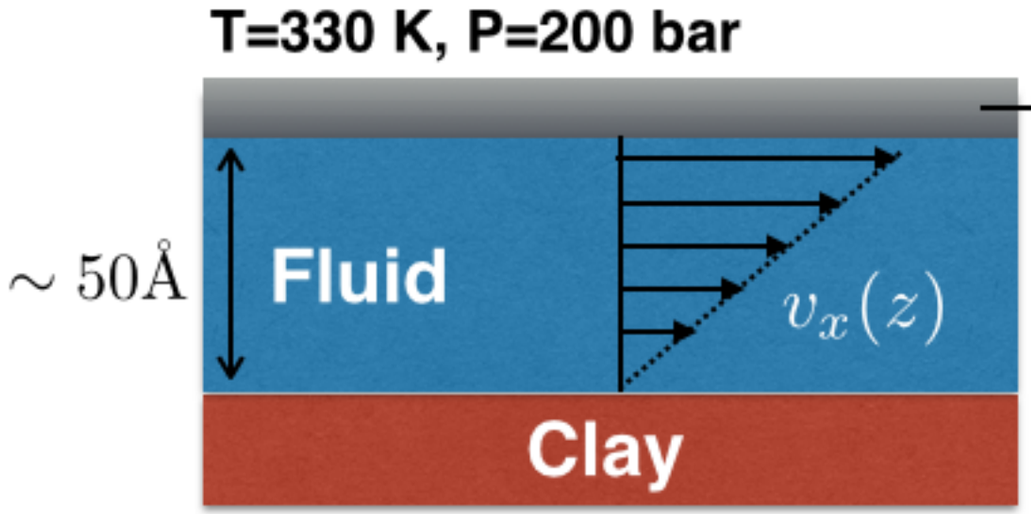


Fluid density plot

(Pore size = 21.7Å)

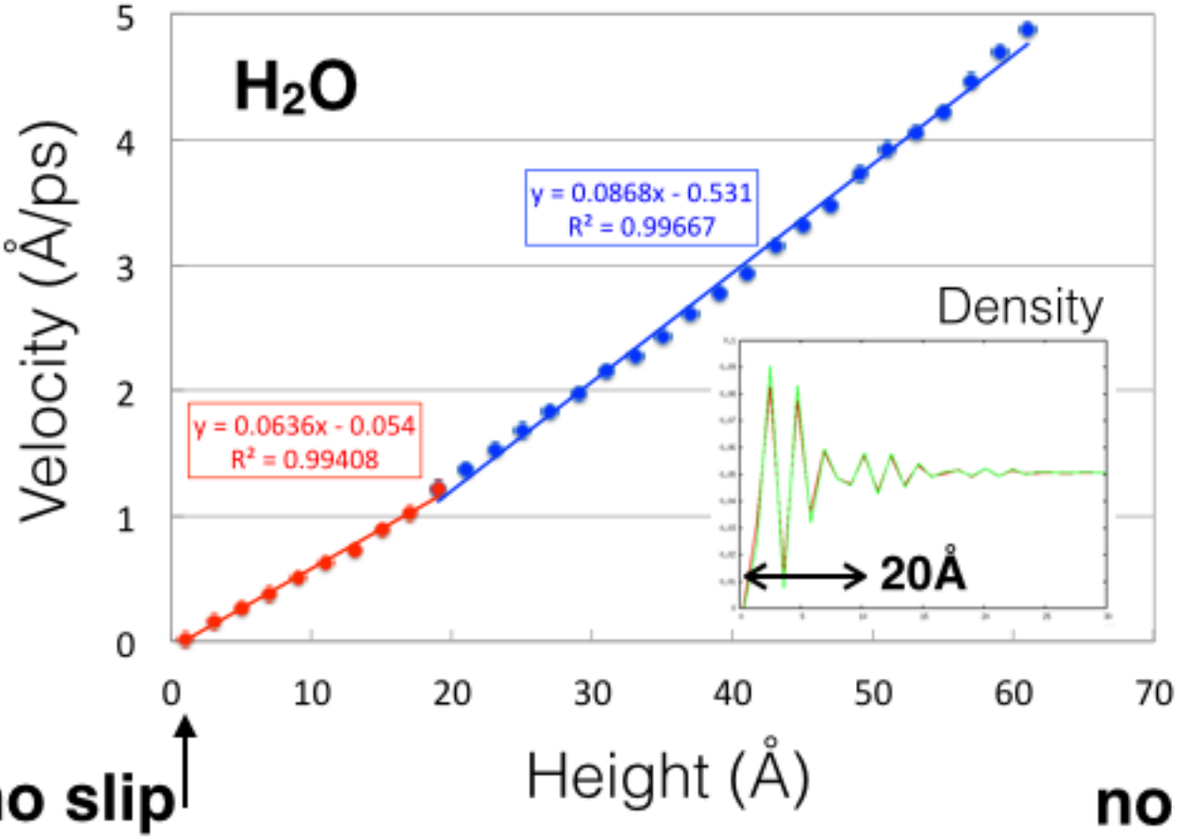
X

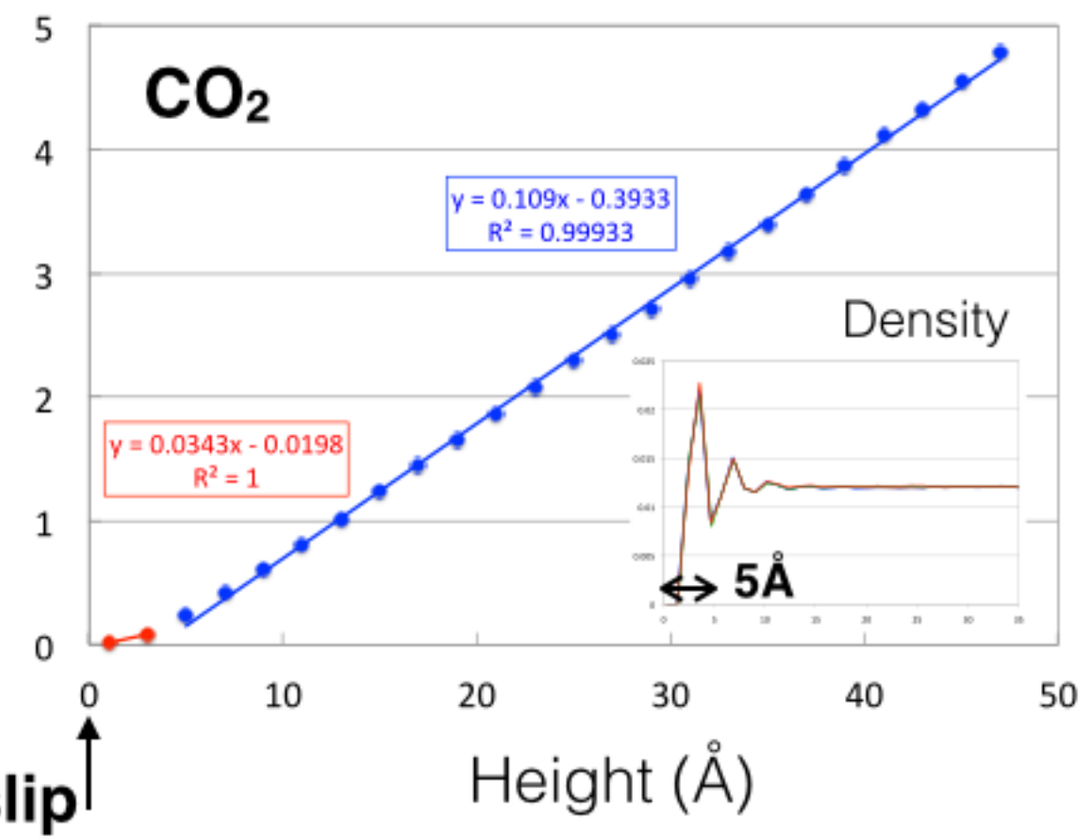
Local Shear Velocity and Viscosity



$$\frac{F_x}{A} = \mu \frac{\partial v_x}{\partial z}$$

force → F_x / area → A = μ (viscosity) $\frac{\partial v_x}{\partial z}$ ← shear velocity

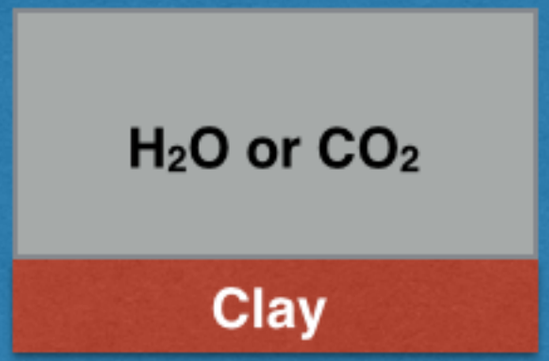




Summary

MOLECULAR DYNAMICS

1.



Structure of the fluid/clay interface

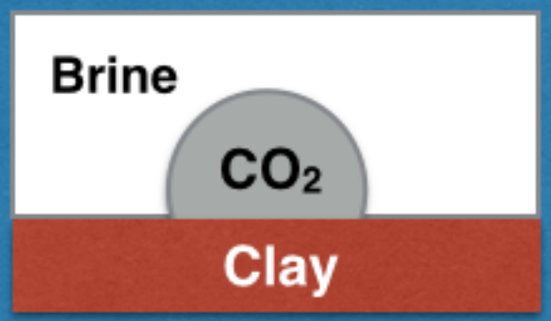
2.

Fluid diffusion in clay slit pore

3.

Static contact angle of brine on clay

4.

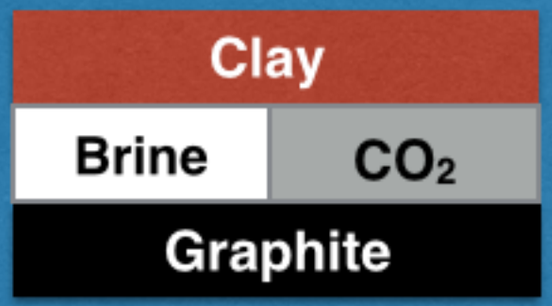


Static contact angle of CO_2/brine on clay

5.

Structure of the CO_2/brine interface in clay slit pore

6.



Structure of the CO_2/brine interface in clay-graphite slit pore

The Team

PI

Jennifer Wilcox

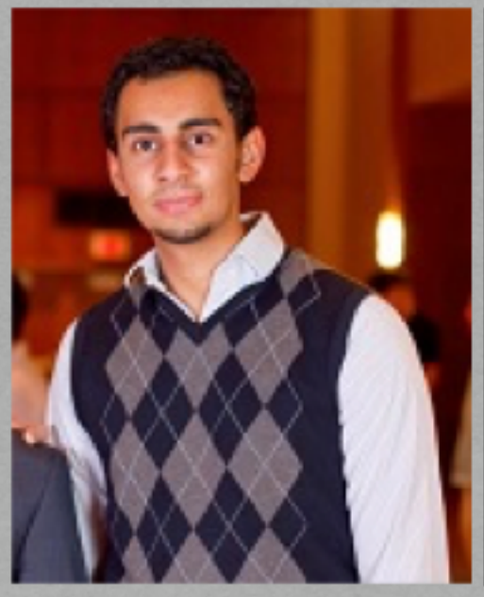
MD

Mahnaz firouzi

MD

C-Y Albert Lu

MD



Hassan Aljama

DFT

Dawn Geatches

Computational Resources

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Center for Computational Earth & Environmental Science

XSEDE

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1891