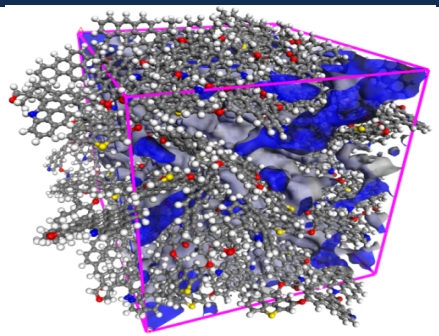
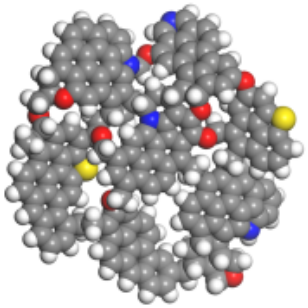
SAND2022-7067C





Molecular simulations of gas adsorption and transport in kerogen and the associated chemo-mechanical effects

Tuan A. Ho
Sandia National Laboratories, USA

Workshop: Modeling adsorption in microporous carbons
Jun 14-17, 2022, Bordeaux

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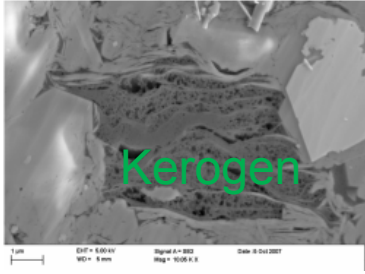
Introduction

Kerogen

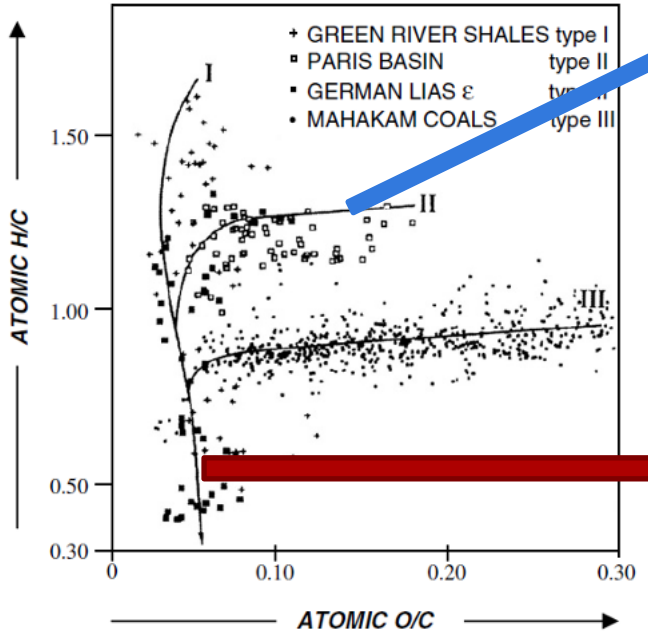


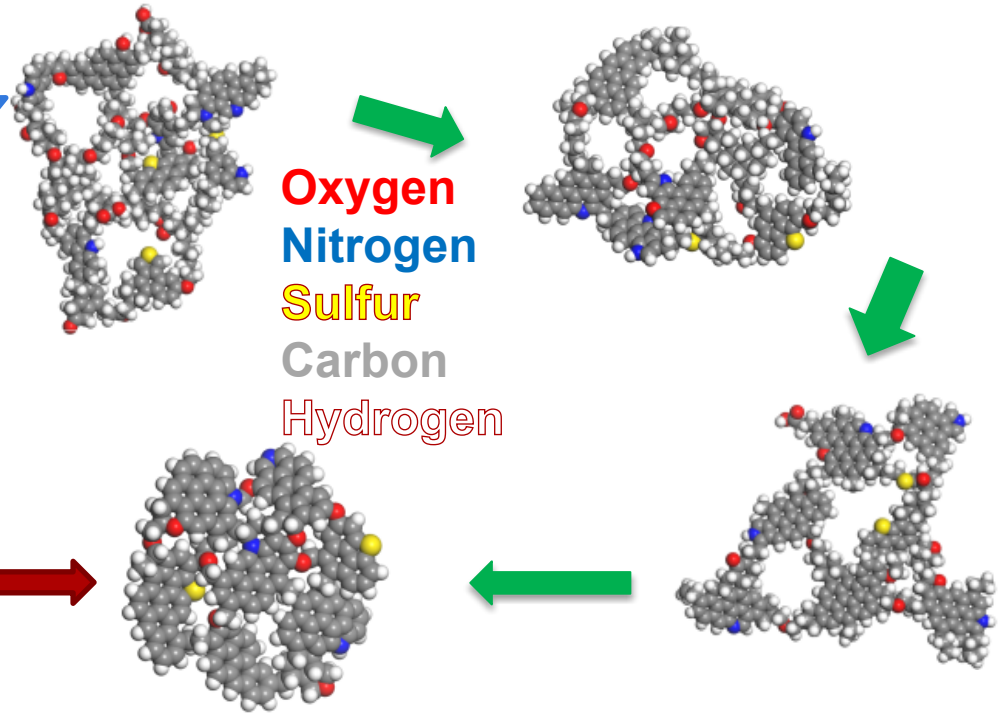
- Insoluble organic matter found in sedimentary rocks (geochemistry)

- Cracks into petroleum products (kerogen maturation, petroleum generation)

  Van Krevelen diagram

Organic Geochemistry 38, 719-833 (2007)





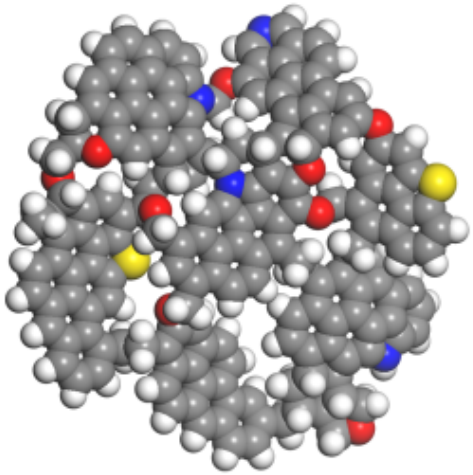
Ungerer et al., Energ Fuel 29, 91-105

- **Hosts pore space responsible for petroleum storage and transport**

Overmature Kerogen

- Use the available elemental analysis and functional data from XPS and ^{13}C NMR
  - *(Energy & Fuels, 2007, 21, 1548-1561)*

Oxygen
Nitrogen
Sulfur
Carbon
Hydrogen



	II-D	
	analytical data	model unit
H/C	0.56	0.58
O/C	0.047	0.051
N/C	0.021	0.023
S/C	0.01	0.011
% of aromatic carbon from XPS(a) or NMR(b)	72(a), 80(b)	79
avg. number of C atoms per aromatic cluster	20	19.9
fraction of aromatic carbons with attachments (sp^3 C, N, S, O)	0.24	0.28

Formation of condensed kerogen

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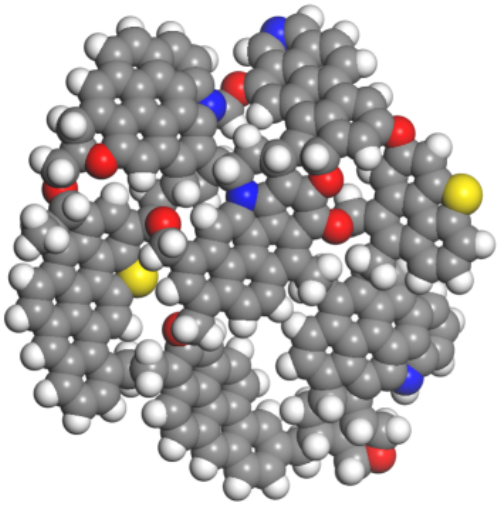


$C_{175}H_{102}O_9N_4S_2$

Energy Fuels 2015, 29, 91-105

24 Kerogens in 10x10x10nm^3 box, 1000K

NVT

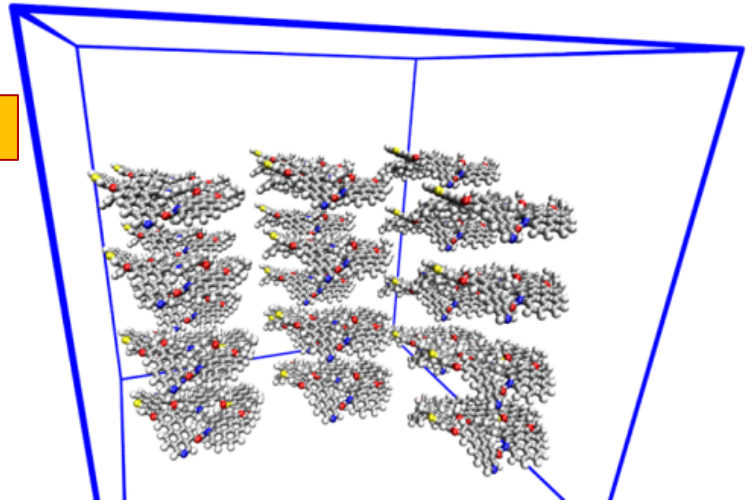
9 snapshots

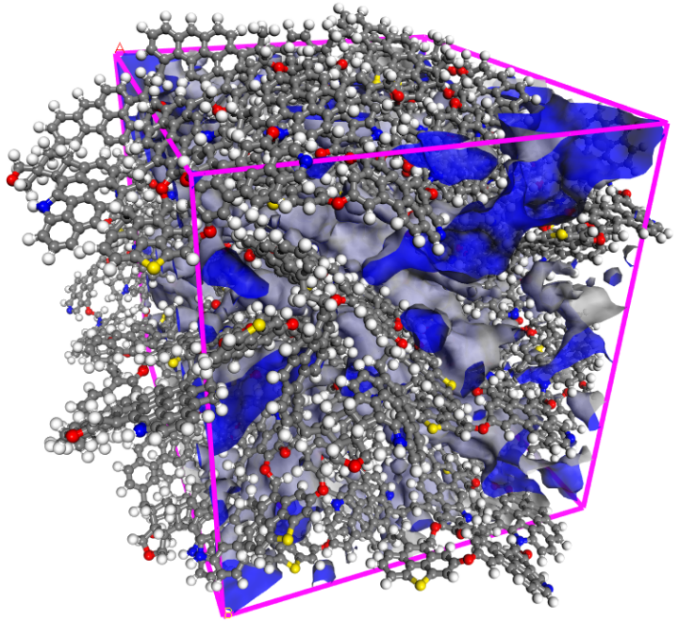
NPT, 100at, 900K to 300K

300K and 100atm

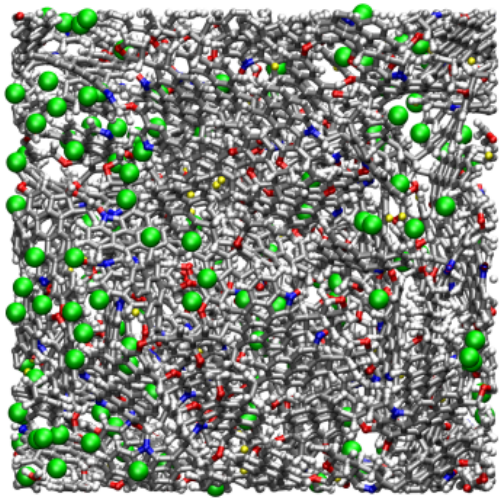
NPT, 1atm, 300K

9 samples at 300K and 1atm





Characterization



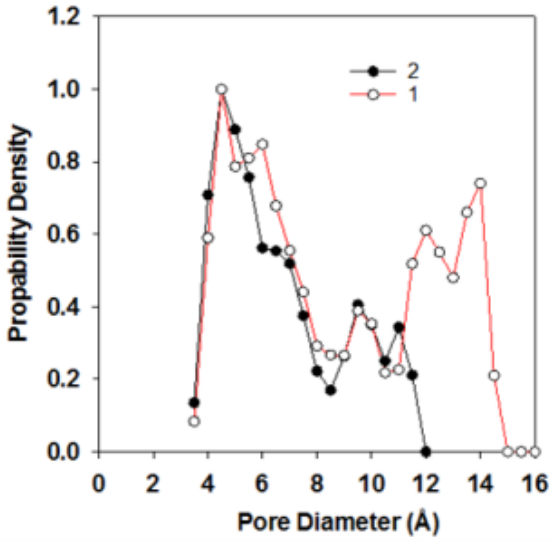
Density

Average :1.22±0.04 g/cm^3

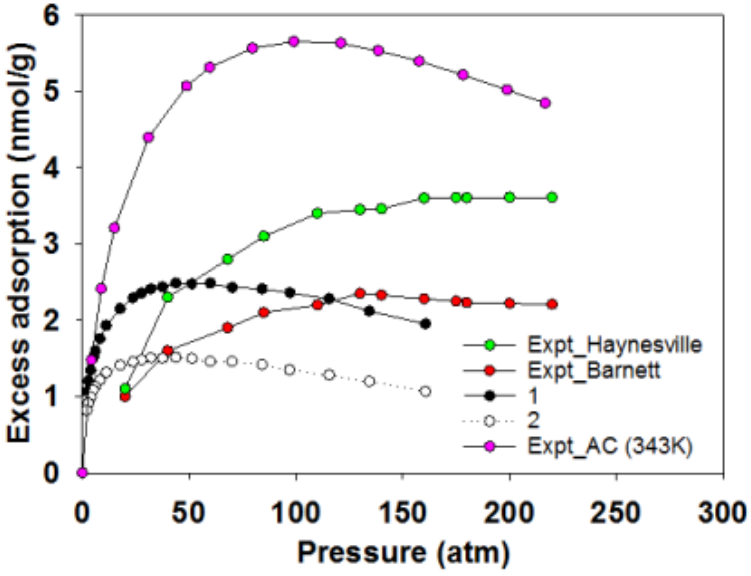
Experiment: 1.28±0.3g/cm^3

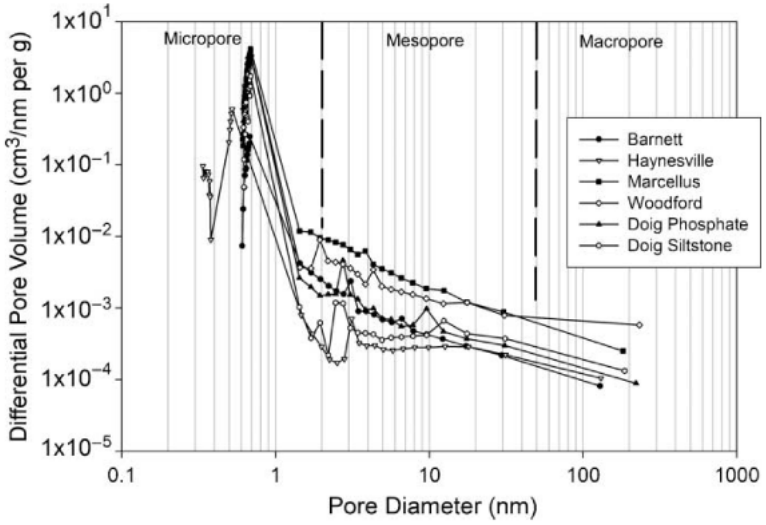
Stankiewicz A, *et al.* (2015) Kerogen density revisited – lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

Pore size distribution



CH_4 Adsorption (Ho, et al., Sci. Rep. 6, 28053)





AAPG 96 (2012), 1099-1119

Methane diffusion in kerogen

(Ho, et. al., Scientific Reports 6, 28053)

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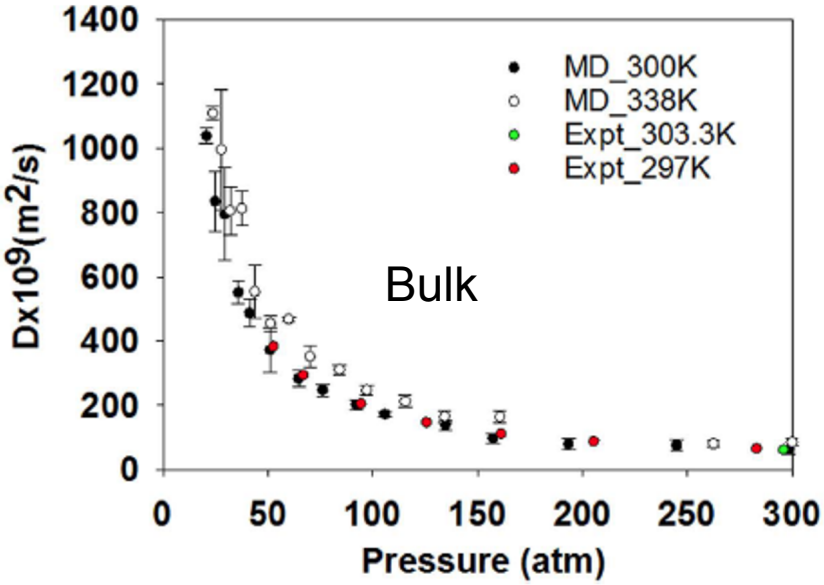

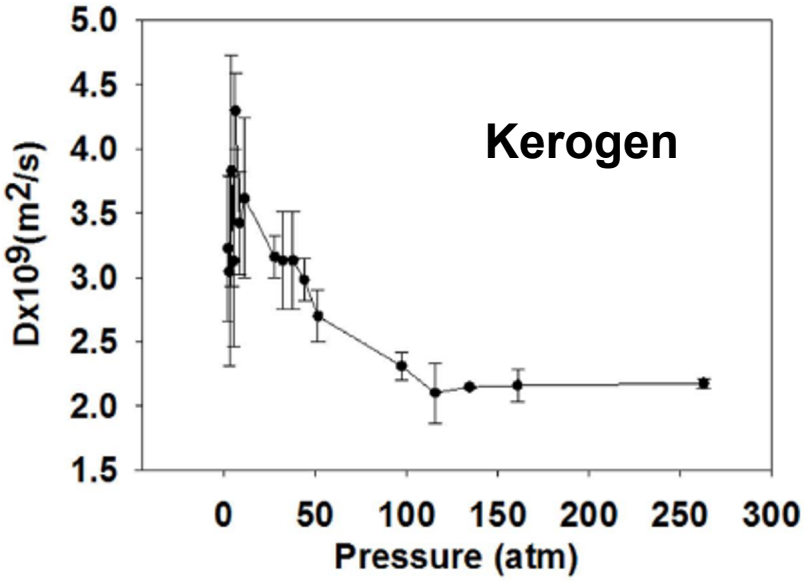

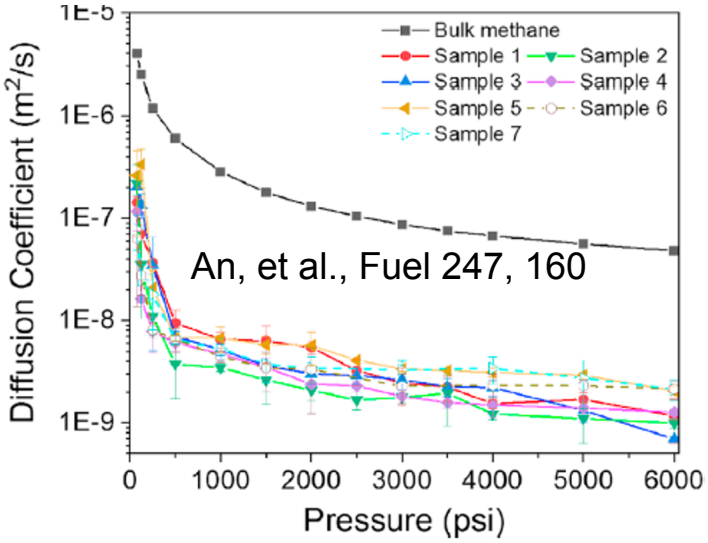

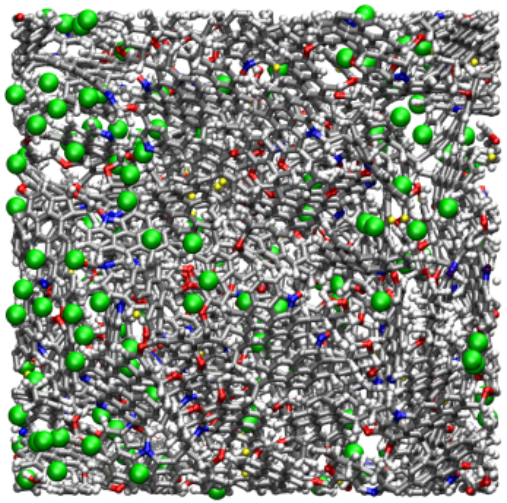

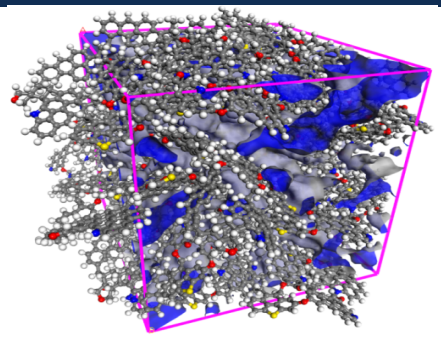

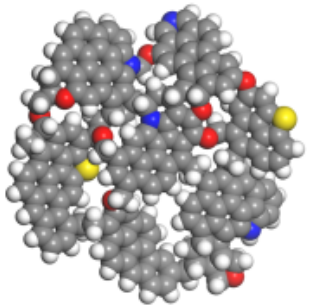

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Outline:

1. **CH_4/CO_2 adsorption onto kerogen**
2. **Kerogen swelling**
3. **Wettability and wettability alteration**
4. **Fluid transport**

Differential retention and release of CO_2 and CH_4 in kerogen nanopores (Ho, et al., Fuel 220, 1-7, 2018)

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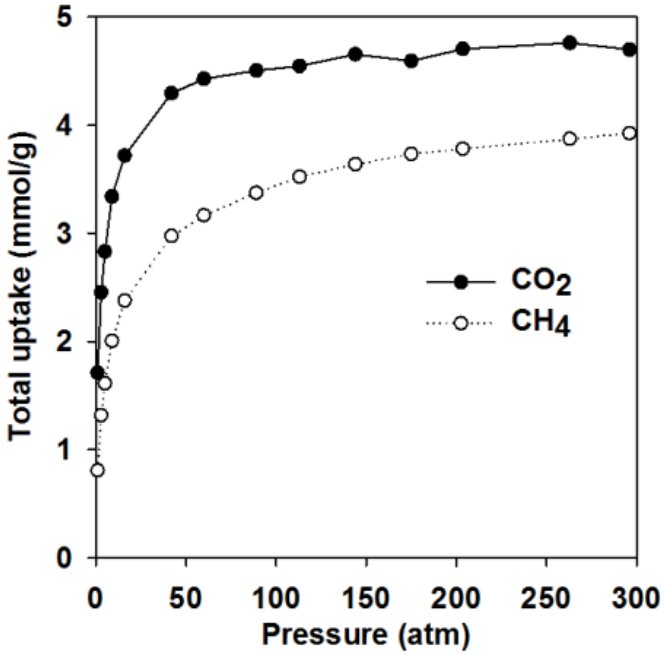
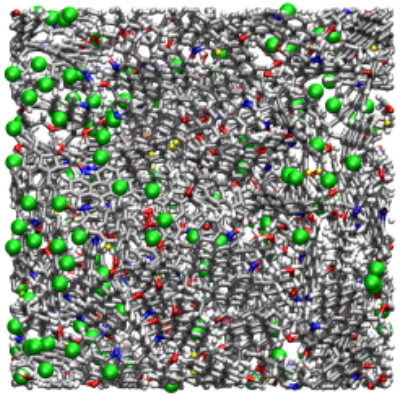
Implications for gas enhanced recovery and carbon sequestration

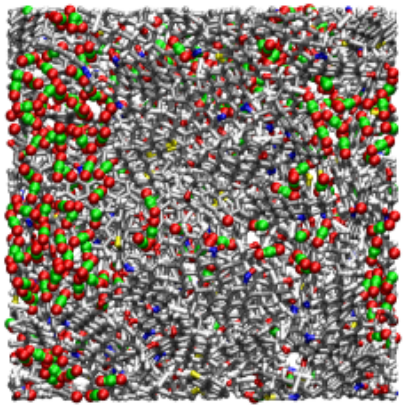
Pure gas adsorption



CH_4



CO_2



Differential retention and release of CO_2 and CH_4 in kerogen nanopores (Ho, et al., Fuel 220, 1-7, 2018)

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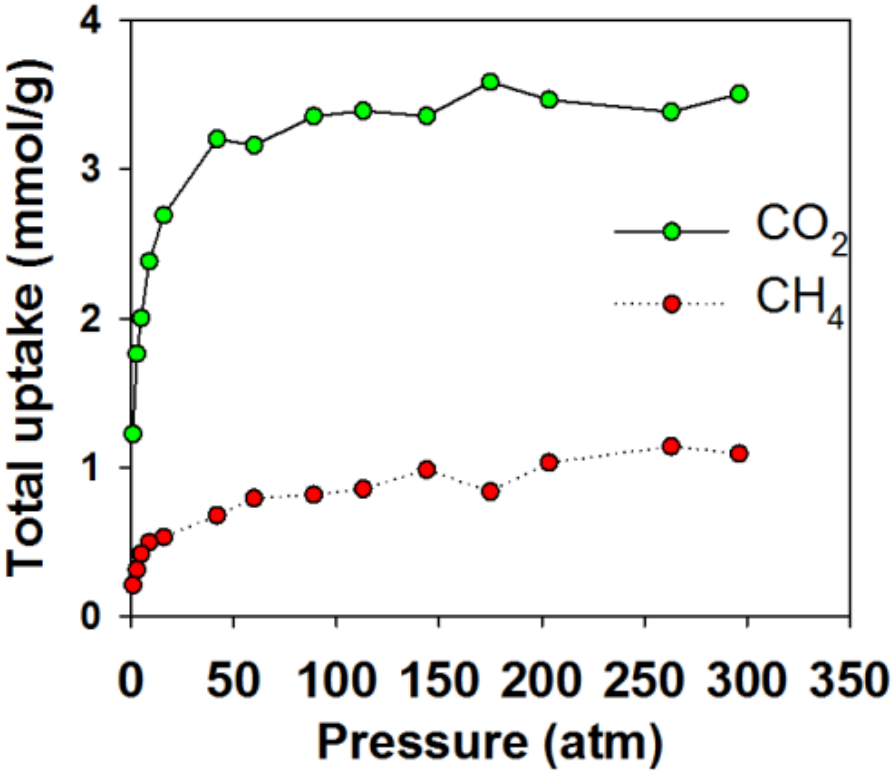
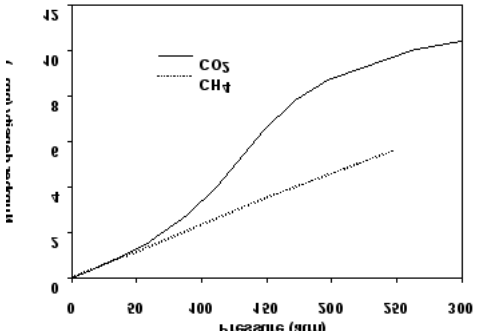
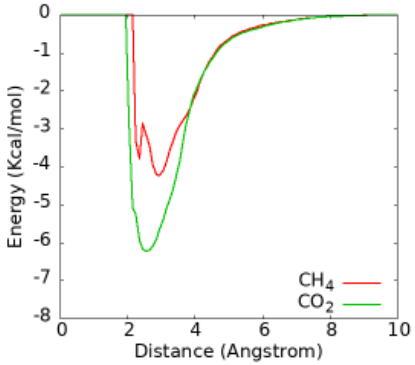
Implications for gas enhanced recovery and carbon sequestration

1:1 binary gas adsorption

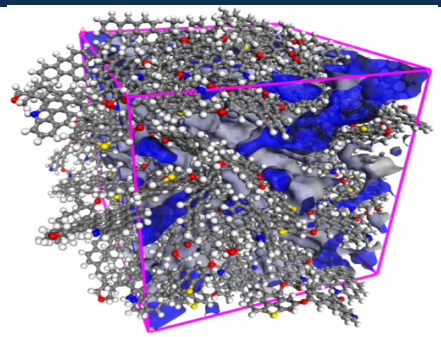


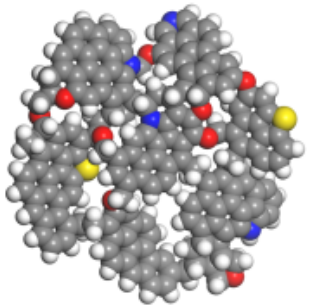
Kerogen preferentially retains CO_2 over CH_4





Ho, et al., ACS Applied Materials & Interfaces 13 (34), 41330–41338





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Kerogen swelling

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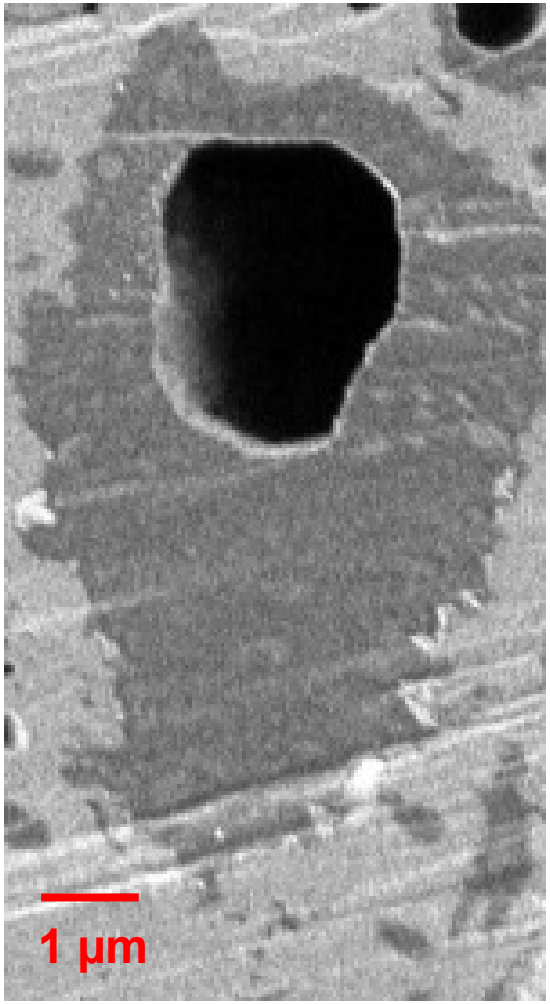
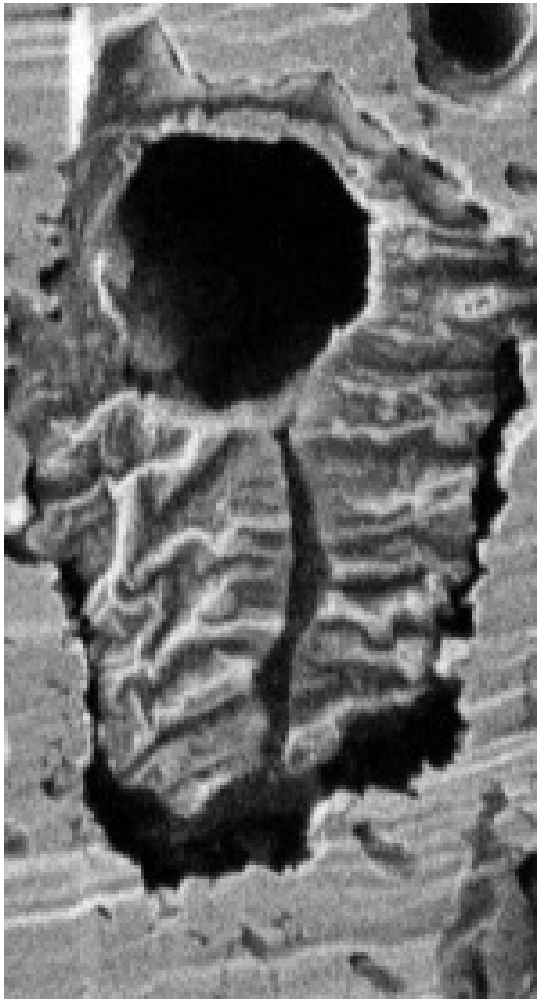
Rubber swelling in oil

From: **Drew Pomerantz**, Schlumberger

Will kerogen swell upon gas adsorption?



Intact shale with swollen kerogen



Bitumen-extracted shale with collapsed kerogen

Chemo-mechanical coupling in kerogen gas adsorption (PCCP 20, 11390, 2018)

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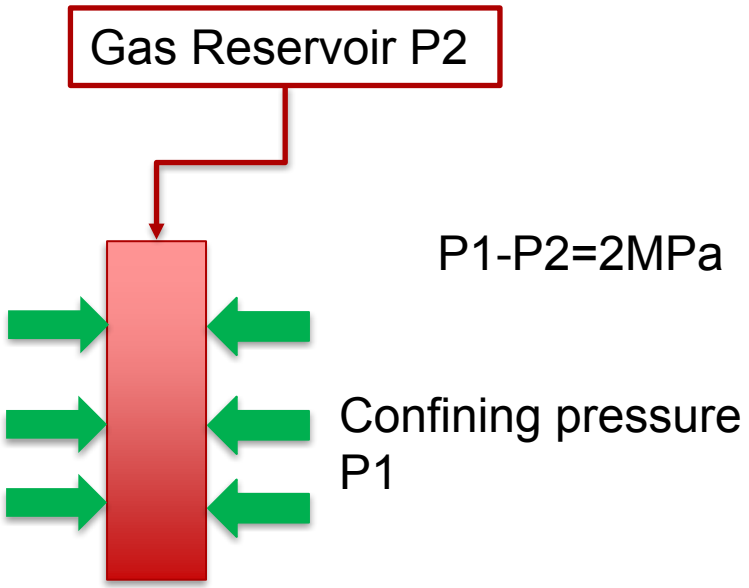
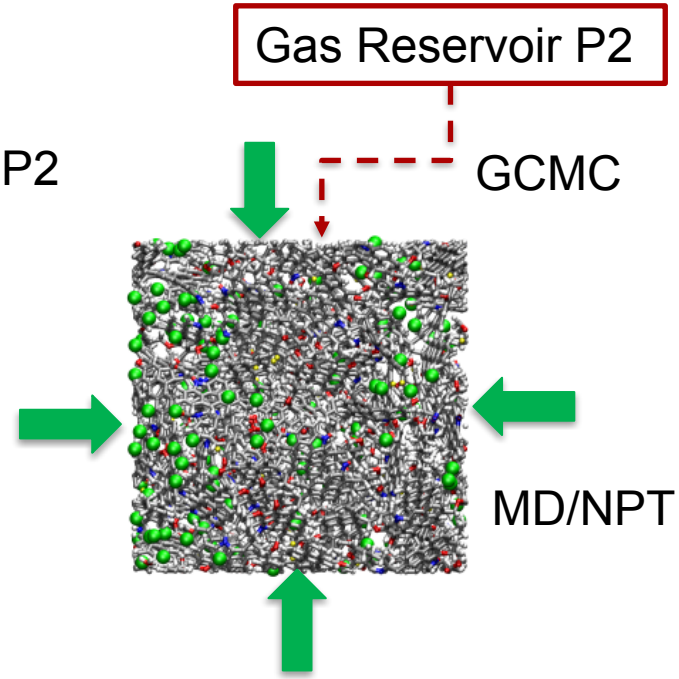
Experimental setup

(J. Unconv. Oil Gas Resour., 2014)



Simulation: Hybrid MD/MC

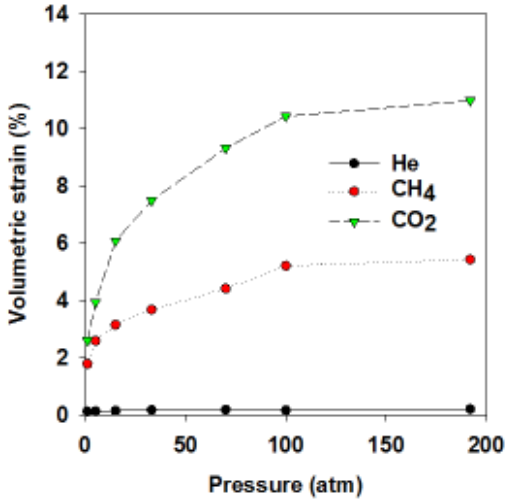


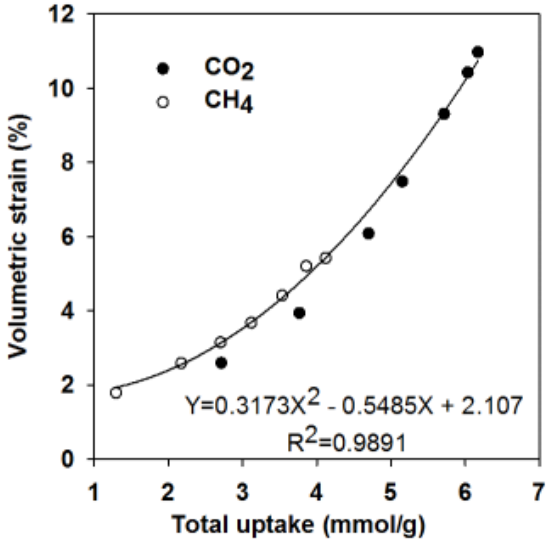
$$Volumetric\ strain = \frac{V - V_o}{V_o}$$

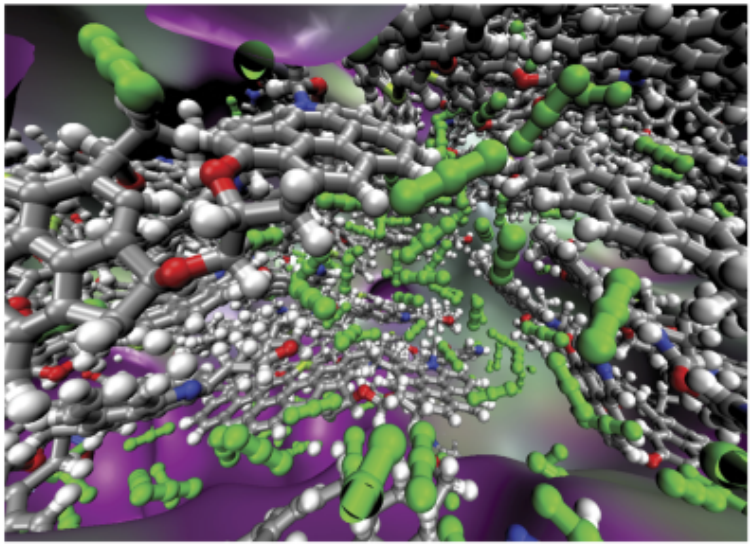
V: kerogen volume after gas adsorption

V_o: kerogen volume before gas adsorption

Chemo-mechanical coupling in kerogen gas adsorption (PCCP 20, 11390, 2018)







Highlighting shale gas research from the Geoscience Group, Sandia National Laboratories, NM, USA. This work was conducted by Dr Tuan Ho, thanks to funding granted to Dr Yifeng Wang by the DOE National Energy Technology Laboratory.

Chemo-mechanical coupling in kerogen gas adsorption/desorption

We use an integrated experimental and modeling approach to fundamentally understand the interaction of gas and fluid with kerogen and clay under reservoir conditions. Specifically, nanostructural properties of subsurface porous media, gas adsorption and release from the kerogen network, deformation of shale associated with adsorption and lithostatic stress, and wettability of inorganic and organic matter.

As featured in:

See Tuan Anh Ho et al., *Phys. Chem. Chem. Phys.*, 2018, 20, 12390.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/pccp

Upon shale gas extraction kerogen shrinks

Kerogen swelling with gas (PCCP 20, 11390, 2018)

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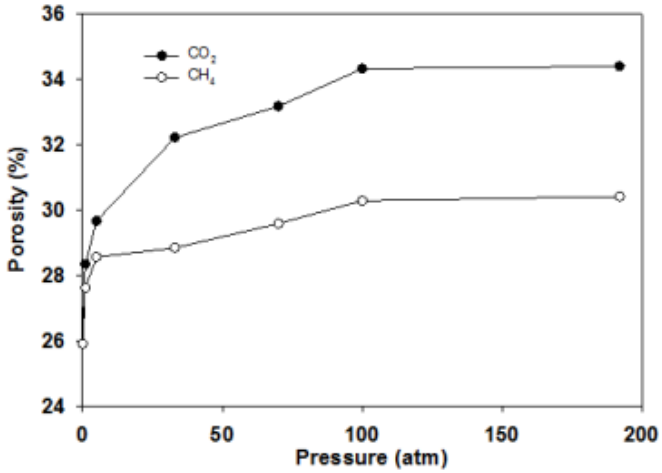
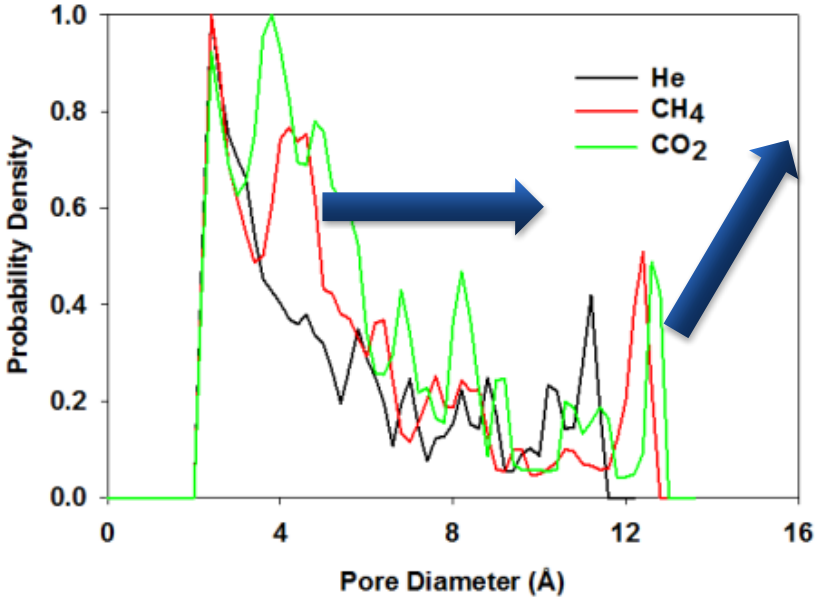
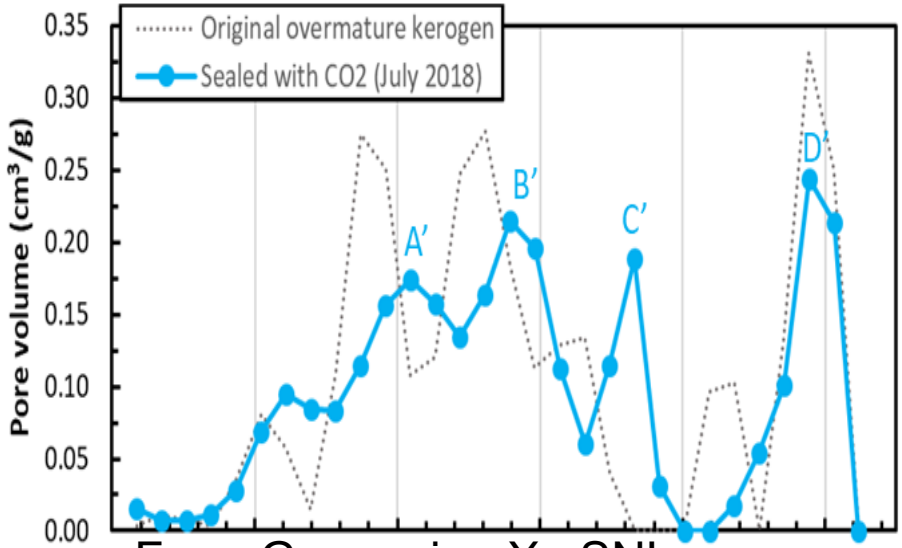
Effects of kerogen swelling on porosity

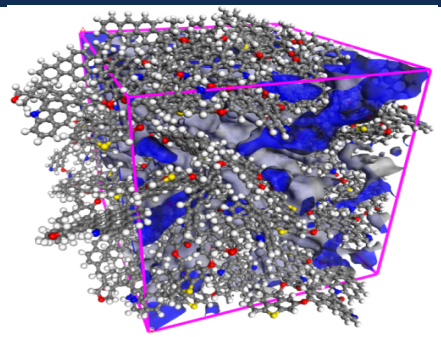


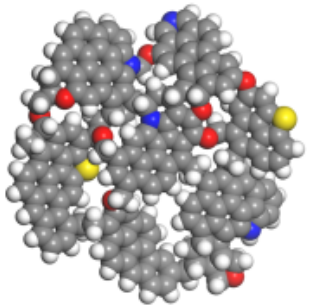
Effects of kerogen swelling on pore size distribution





From Guangping Xu SNL





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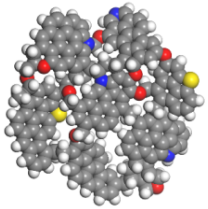
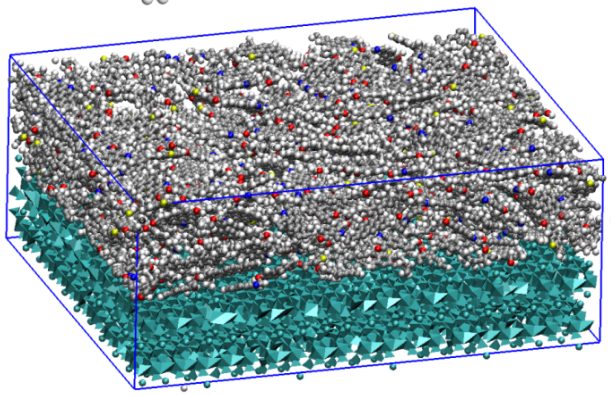
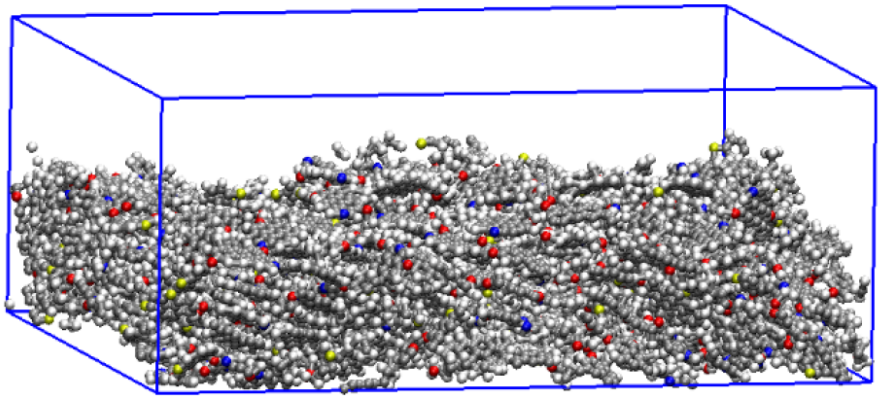
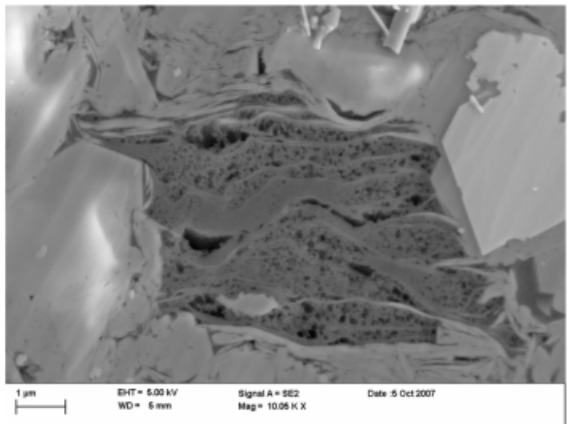
Kerogen wettability (Ho, et al., Nanoscale 10, 19957)

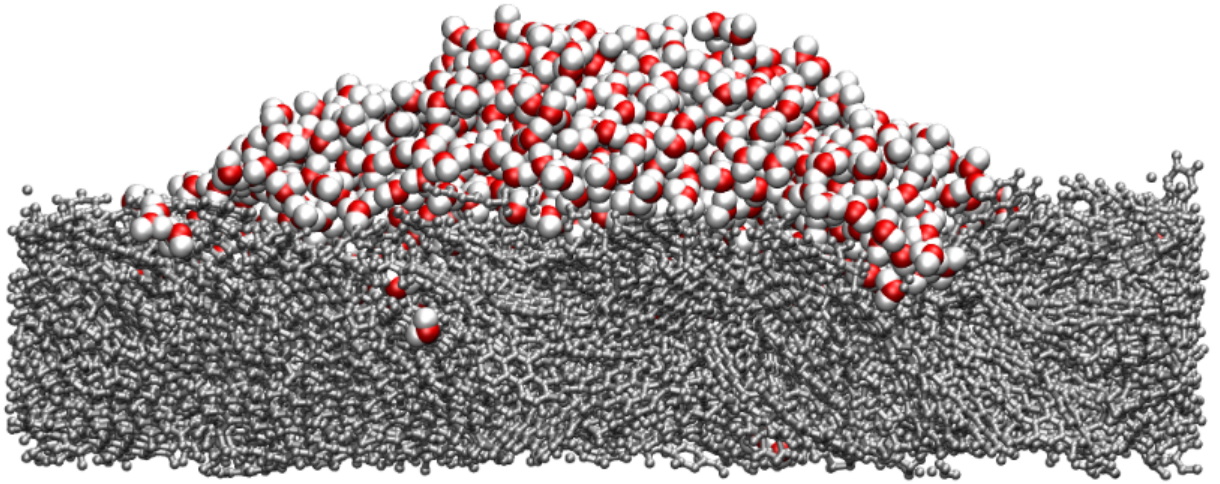






42.8°±6.5°





Wettability alteration

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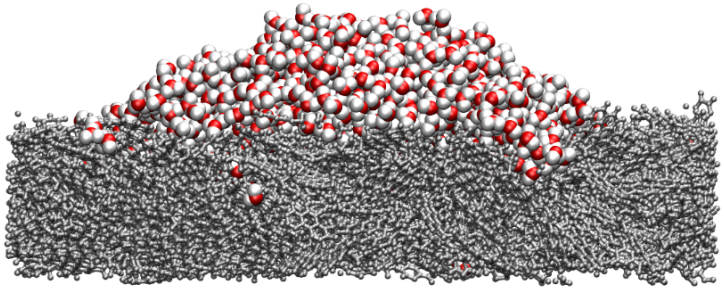
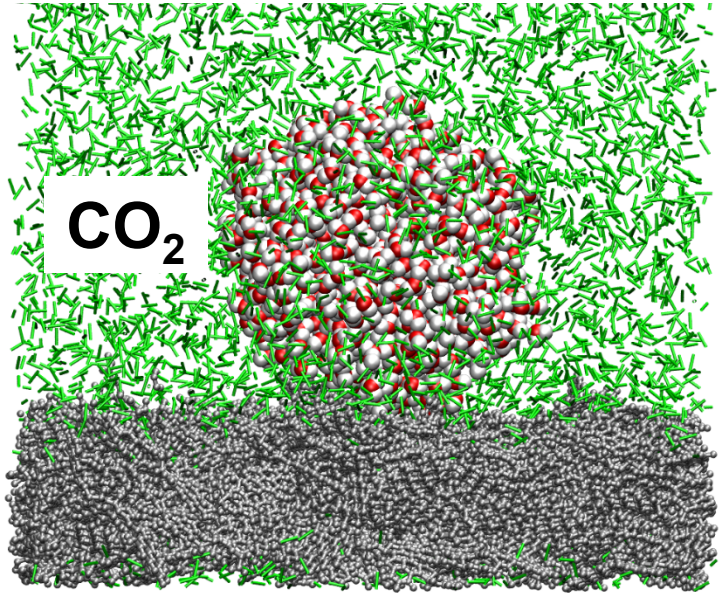
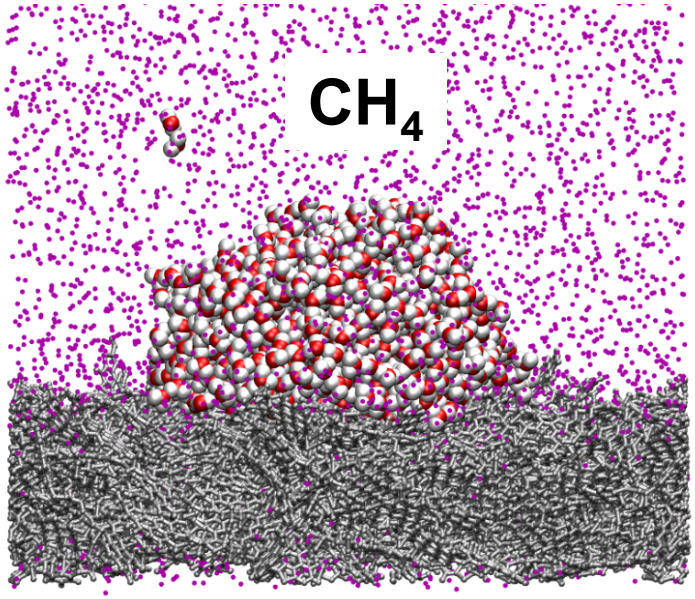
42.8°±6.5°



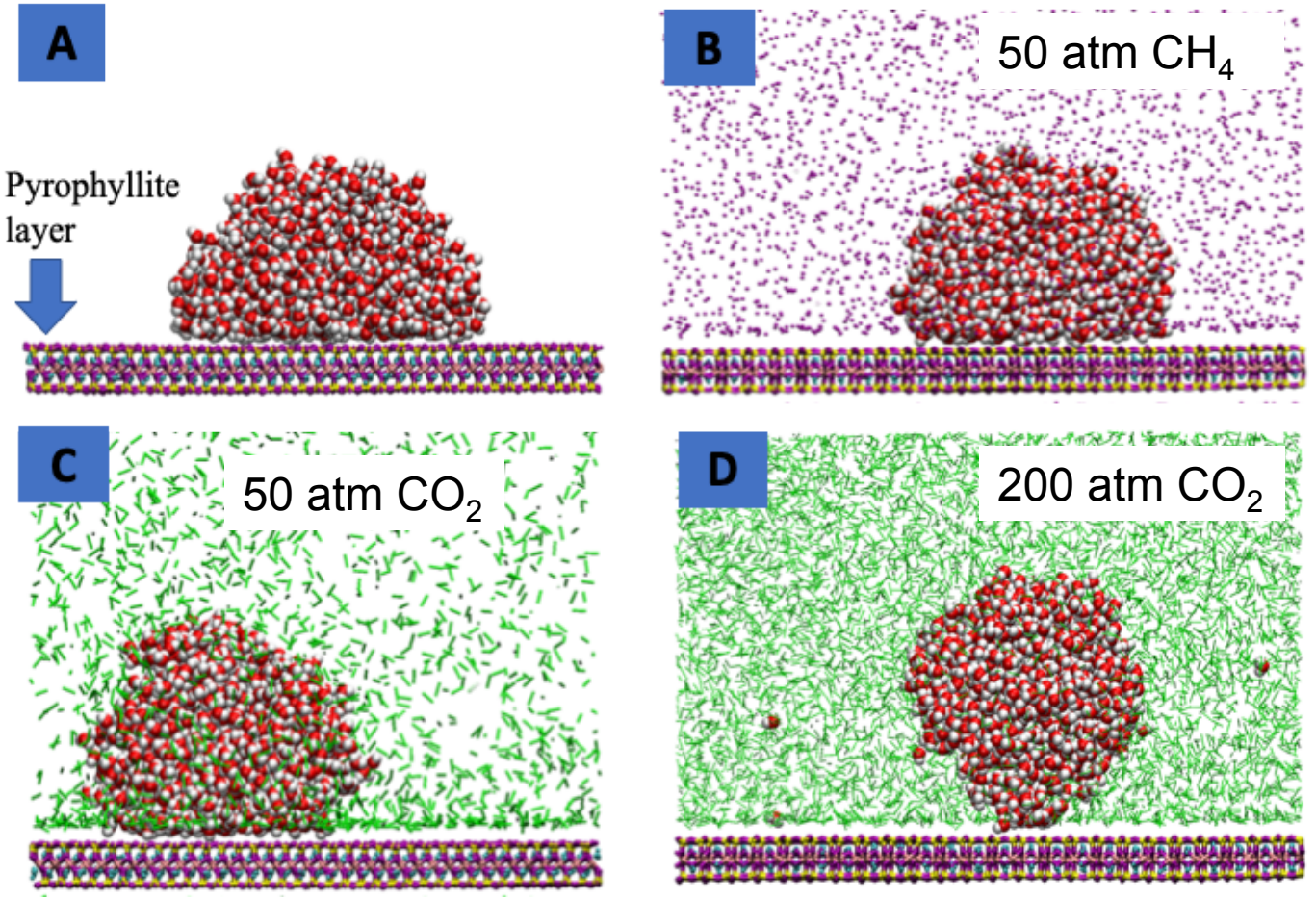


79.18°±1.97°



Hydrophilic to hydrophobic transition

Wettability alteration

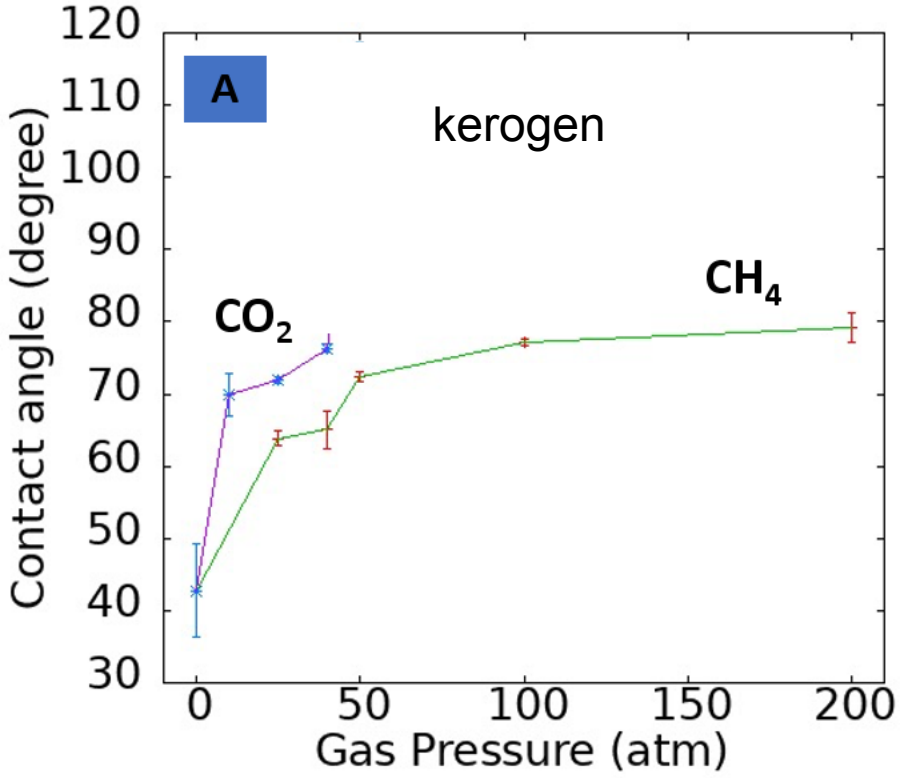


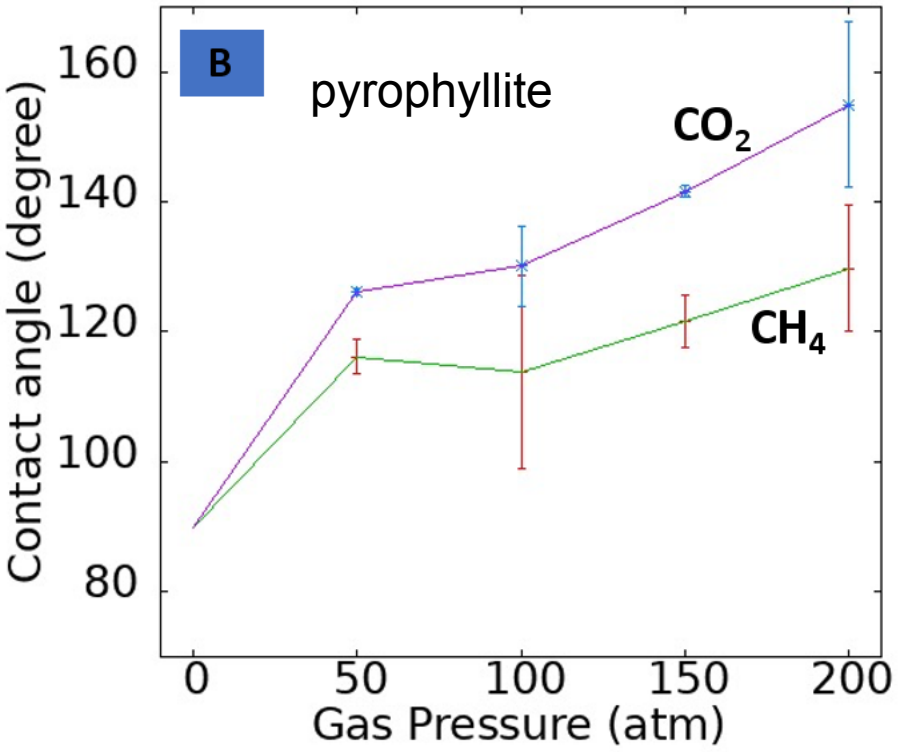
Ho, et. al. ACS Applied Materials & Interfaces (2021)

Wettability alteration

Sandia National Laboratories

1. Contact angle increases with increasing gas pressure on kerogen and pyrophyllite surfaces





Ho, et. al. ACS Applied Materials & Interfaces (2021)

Wettability alteration

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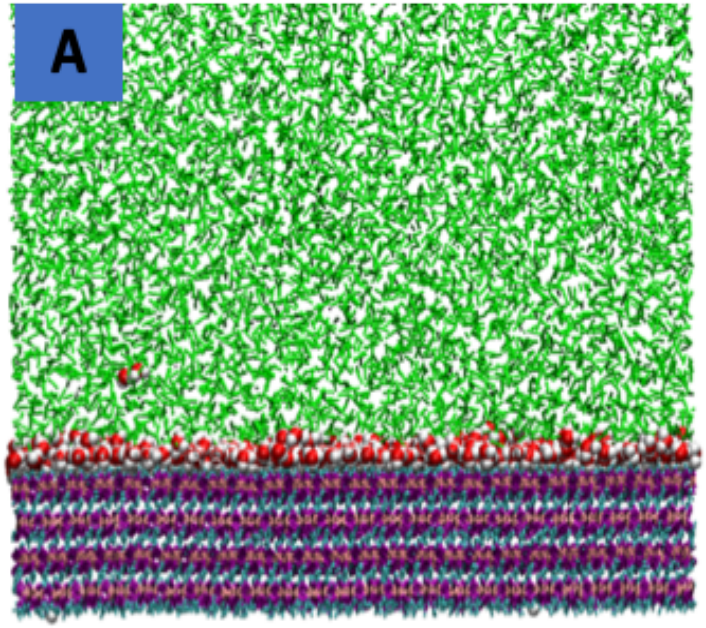
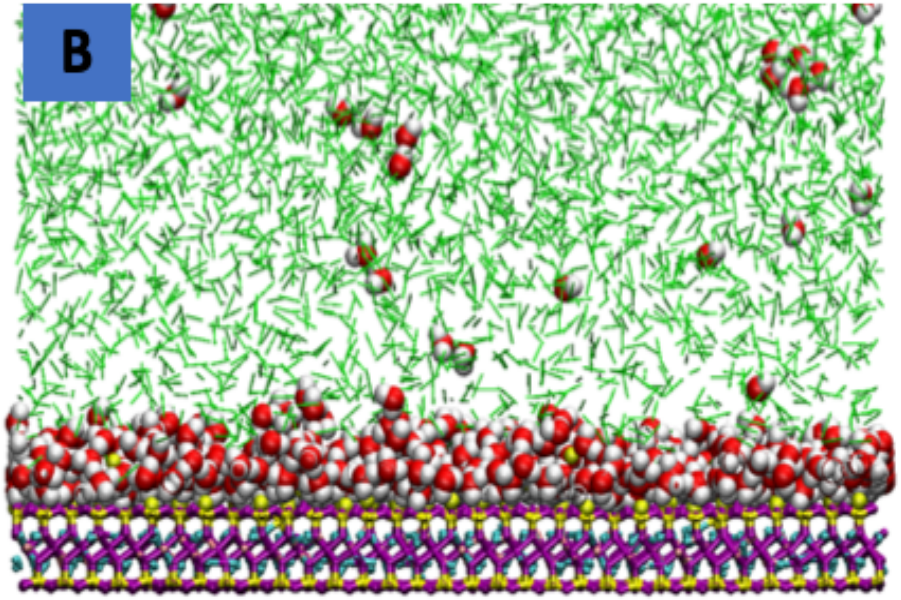
2. Contact angle remains constant with increasing gas pressure on gibbsite and montmorillonite



Gibbsite



Montmorillonite

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Wettability alteration

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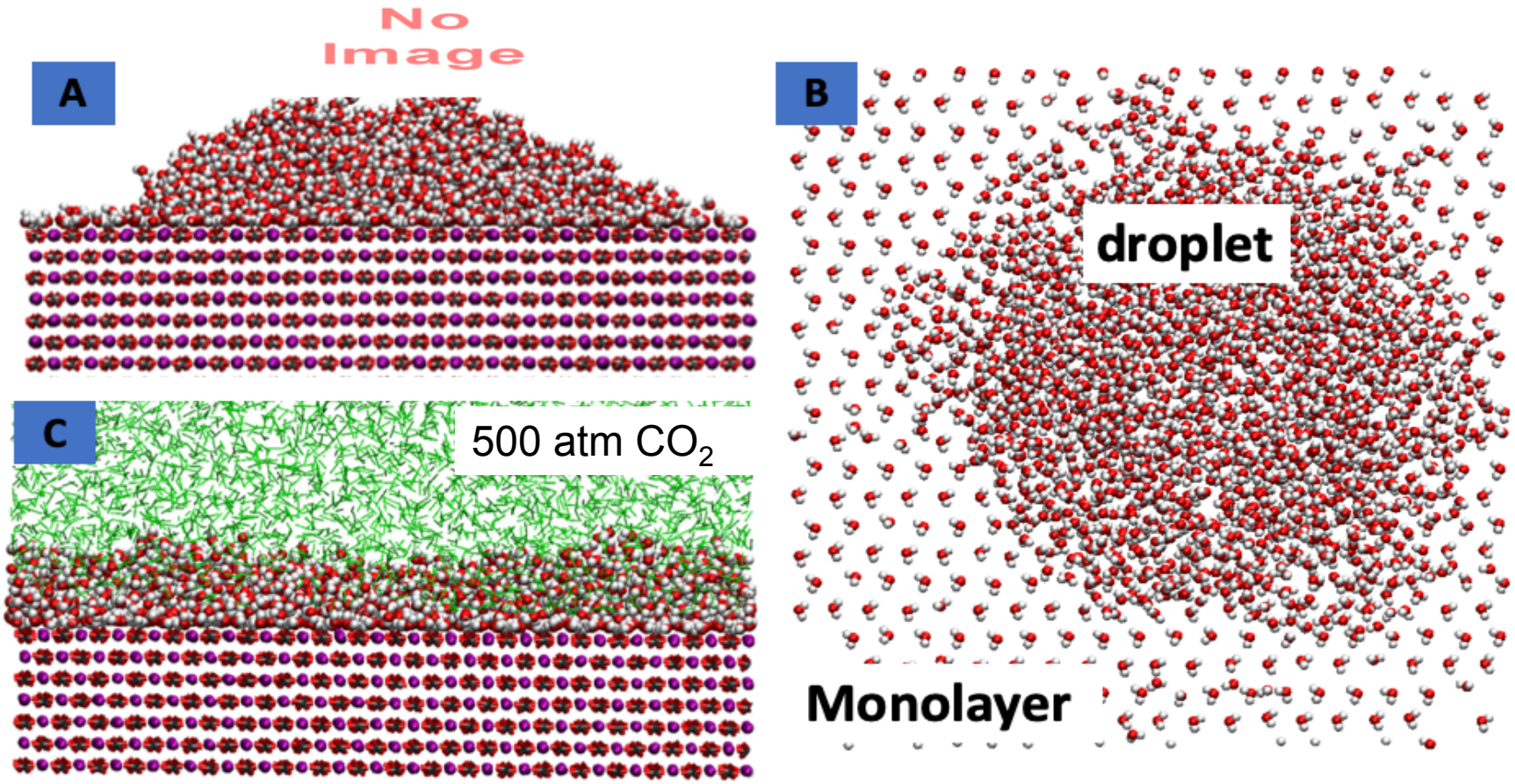
3. Contact angle decreases with increasing gas pressure on calcite

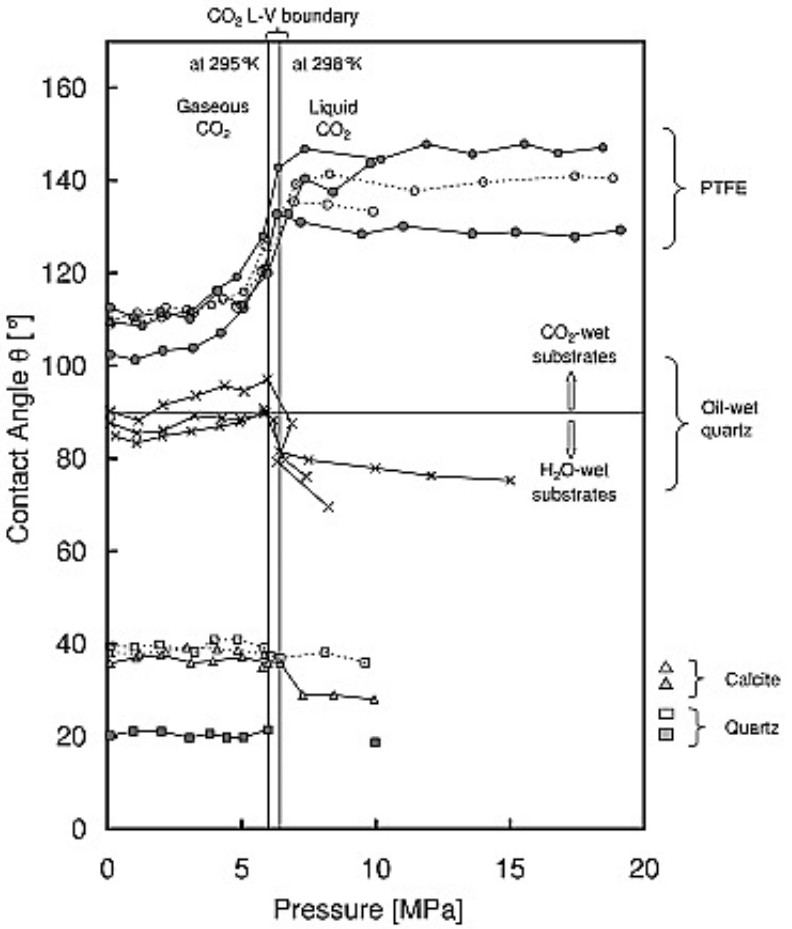


Ho, et. al. ACS Applied Materials & Interfaces (2021)

Wettability alteration

1. Contact angle increases with increasing gas pressure on kerogen and pyrophyllite surfaces
2. Contact angle remains constant with increasing gas pressure on gibbsite and MMT
3. Contact angle decreases with increasing gas pressure on calcite

- How good are the simulation data, compared with experimental data?



Water Resources Research **2010,** *46*, W07537

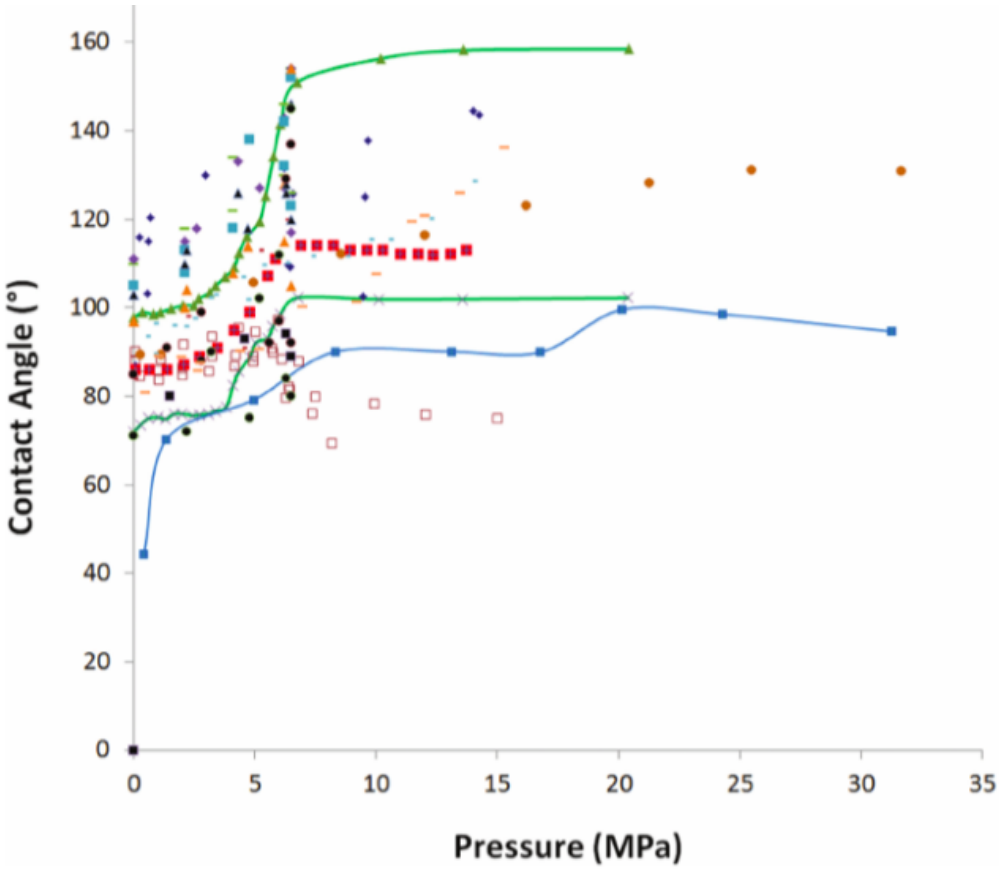
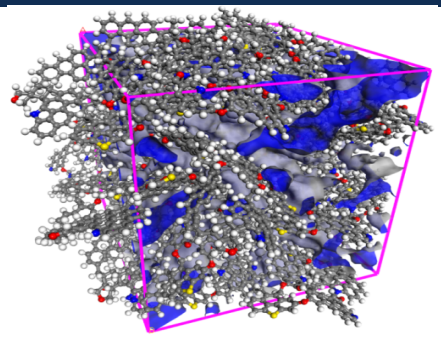
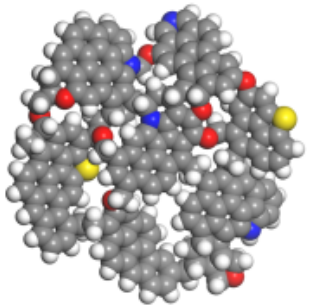


Figure 14. Water contact angles for CO_2-water systems on hydrophobic rock surfaces, including coal, oil-wet quartz/glass, and oil reservoir limestone rock.

Water Resources Research **2015,** *51* (1), 729-774





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Exceptional service in the national interest

Molecular simulations of gas adsorption and transport in kerogen and the associated chemo-mechanical effects

Outline:

1. **CH_4/CO_2 adsorption onto kerogen**
2. **Kerogen swelling**
3. **Wettability and wettability alteration**
4. **Fluid transport**

Kerogen wettability and fluid flow

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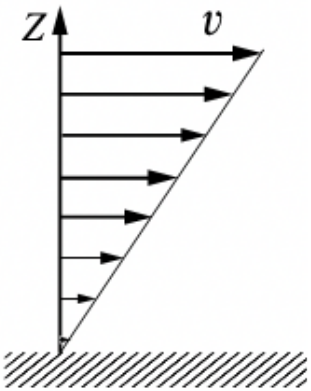
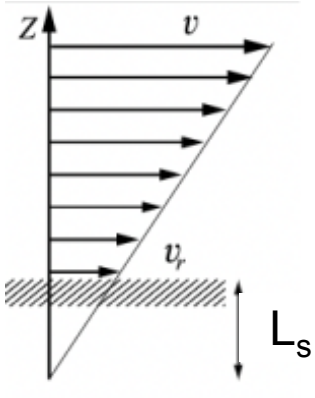
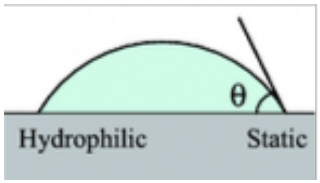
Hydrophilic to hydrophobic transition → Stick to slip flow transition

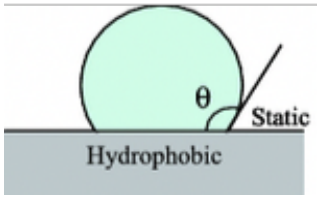


No slip

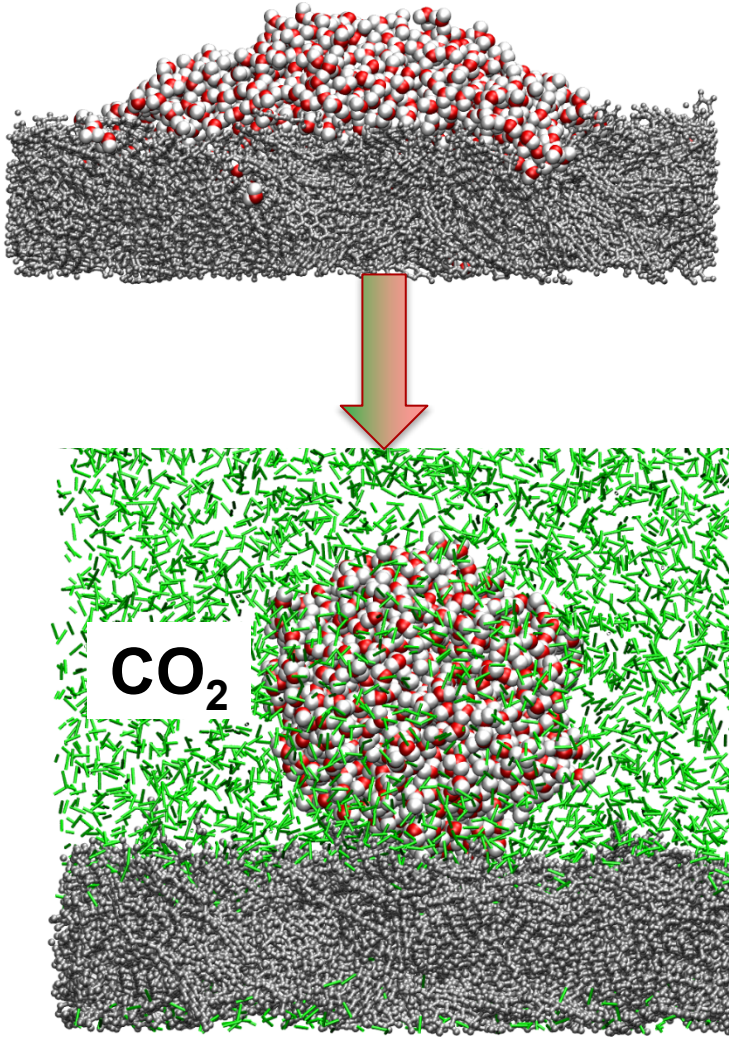


Slip

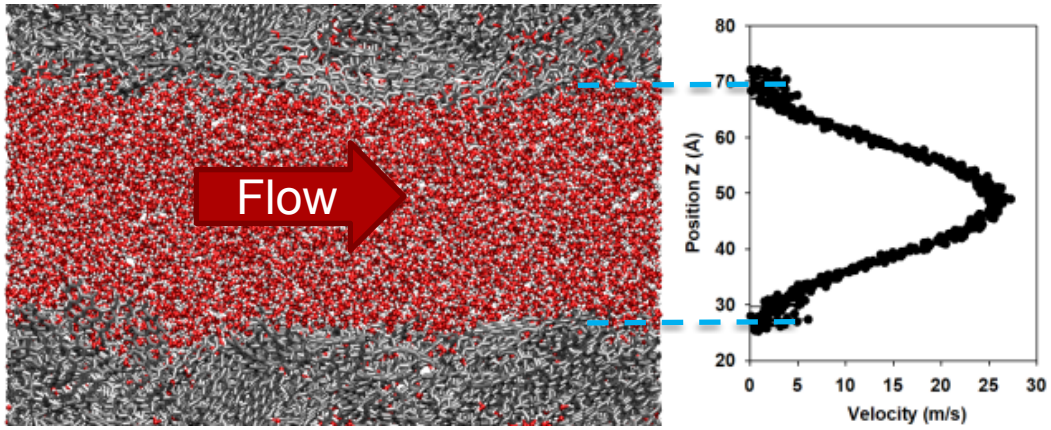




42.8°±6.5°

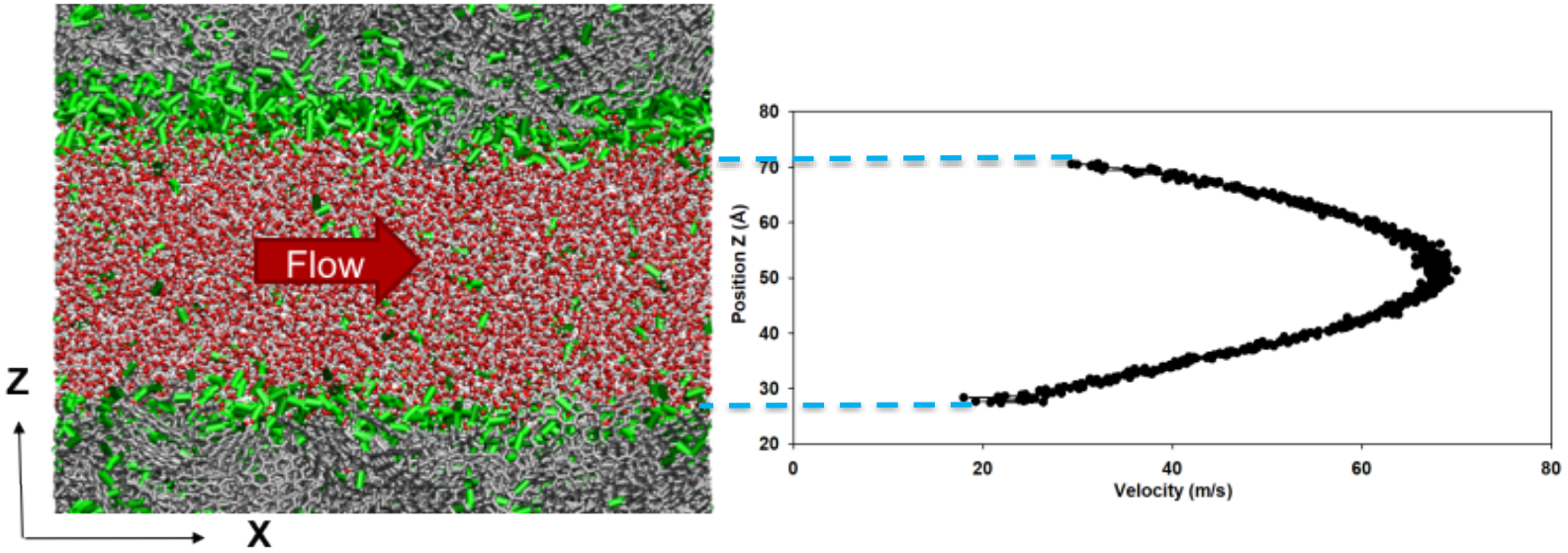


Kerogen wettability and fluid flow



$$\frac{\text{Flow Rate (w } CO_2\text{)}}{\text{Flow Rate (w/o } CO_2\text{)}} \sim 4$$

CO_2 thin layer → Lubricant



(Ho, et al., Nanoscale 10, 19957)

Summary

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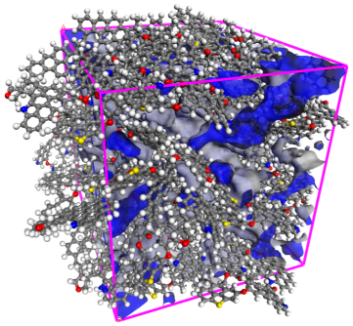
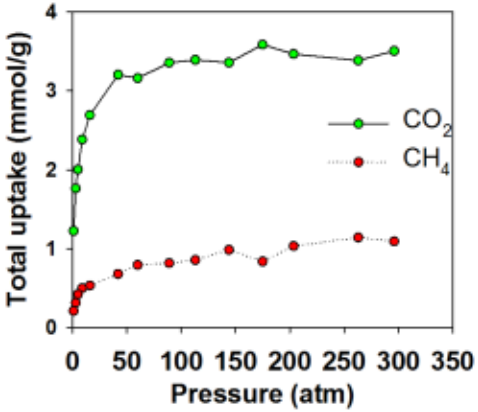
1. CH_4/CO_2 adsorption onto kerogen

(Fuel 2018 & Sci. Rep. 2016)





3. Wettability alteration

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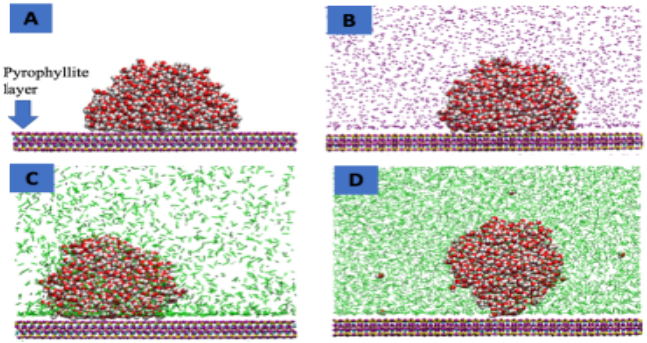
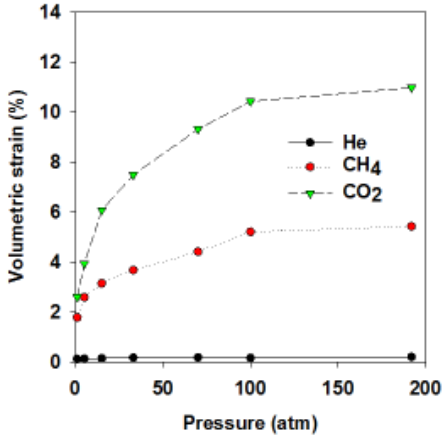


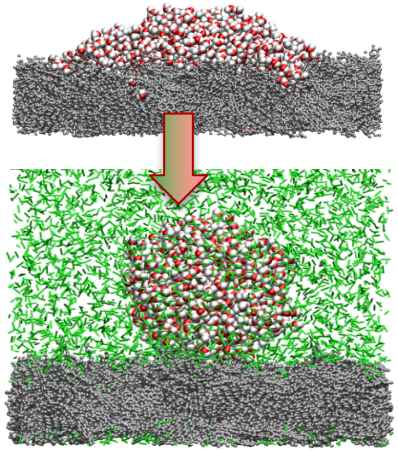
2. Kerogen swelling

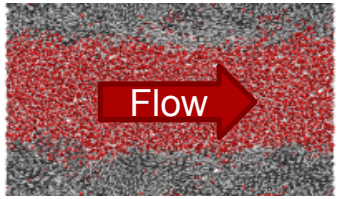
(PCCP 2018)

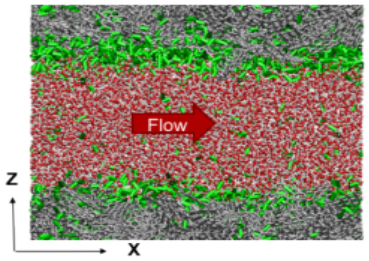


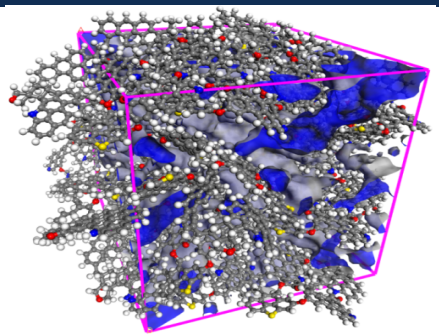
4. Fluid flow

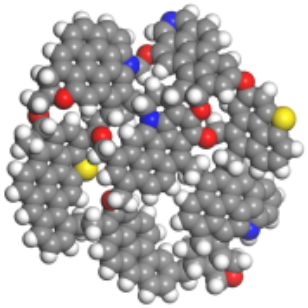
(Nanoscale 2018, J Nat Gas Sci Eng 2020, PCCP 2019)











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Centre Européen de Calcul Atomique et Moléculaire

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Louise Criscenti

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Thank you!

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