STANFORD UNIVERSITY

The Role of Kerogen versus Clay in the Adsorption Mechanisms of CO_2 in Gas Shales

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Advantages and Goals - Storage in Shale

Advantages:

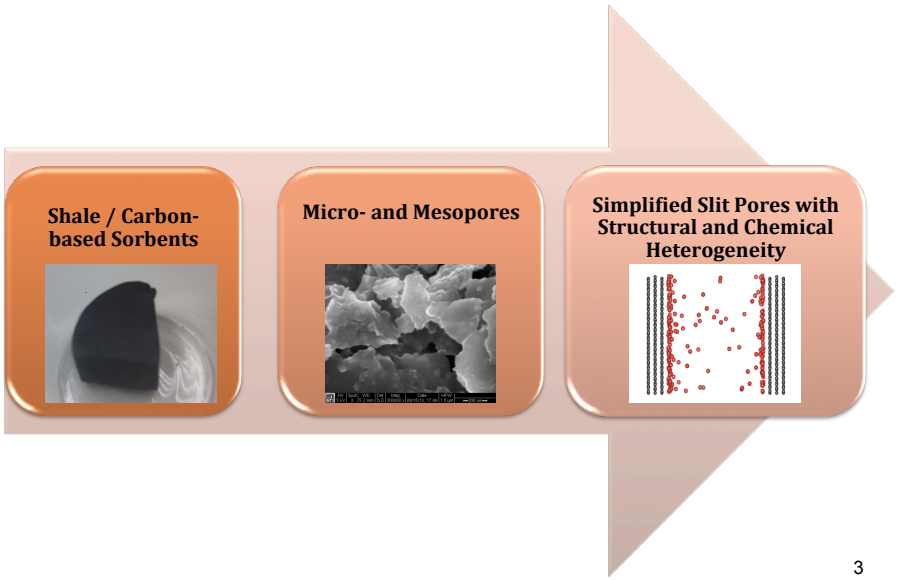
- CO_2 injection into depleted shale gas reservoir may enhances shale gas recovery, similar to Enhanced Coal Bed Methane recovery

Goals:

- To investigate adsorption mechanism of CO_2/CH_4 on gas shale
- To study gas adsorption behavior on various components of shale, including kerogen and clay, by characterizing their structure, pore size and gas capacity

Ref: White C M, Smith D H, Jones K L, et al. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery a review[J]. Energy & Fuels, 2005, 19(3): 659-724.

Methodology



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Outline

- Shale Characterization
- Adsorption Isotherm Measurements
- Adsorption Simulations – Grand Canonical Monte Carlo

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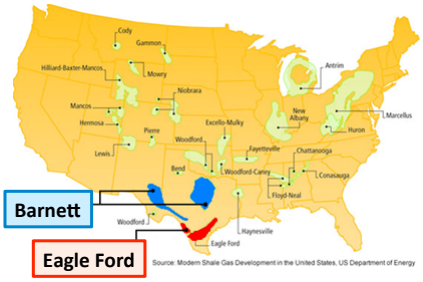
Shale Deposits in US

Shale deposit in US and corresponding temperature and pressure conditions



Source: Energy Information Administration: International Energy Agency

Shale	Barnett	Haynesville	Fayetteville	Marcellus	Eagle Ford
Depth [m]	1950-2550	3150-4050	300-2100	1200-2550	1200-3650
T [˚C]	68.5-86.5	104.5-131.5	19-73	46-86.5	46- 125
P [MPa]	20-25	30-40	3-20	12-25	12-36

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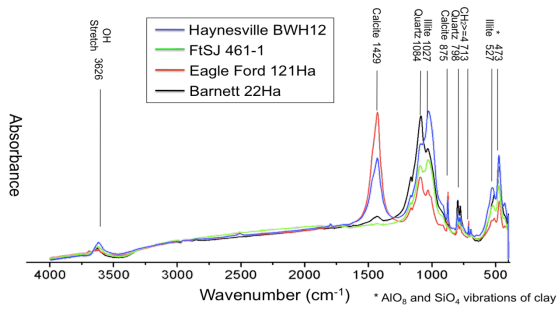
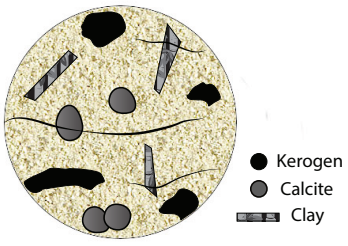
Shale Mineralogy





XRD Compositional Data(wt%)			
Component	Formula	Barnett	Eagle Ford
Quartz	SiO_2	38%	21.2%
Feldspar	$KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8$	3.8%	0%
Calcite	$CaCO_3$	0.9%	54.2%
Pyrite	FeS_2	1.8%	3.6%
Clay	Illite	39%	15.8%
TOC		16%	4.97%

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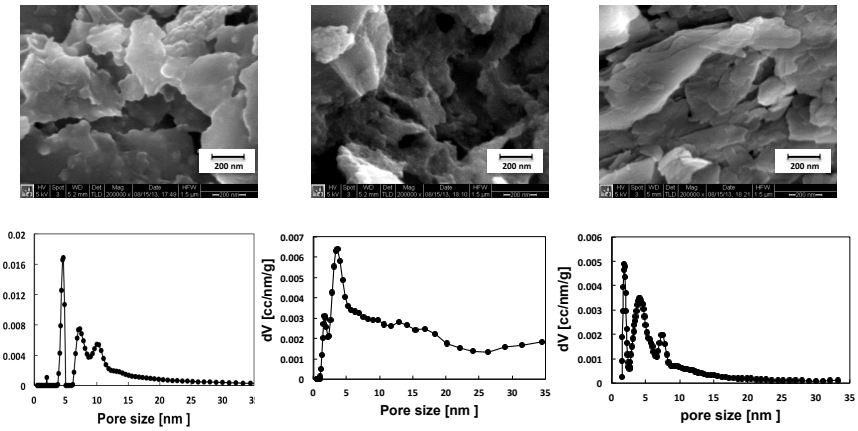
SEM Analysis and Pore Size Distribution

Shale(Barnett) Kerogen Clay



0.058 cc/g 0.068 cc/g 0.020 cc/g

Probe gas: N_2 Method: Non-Localized Density Functional Theory

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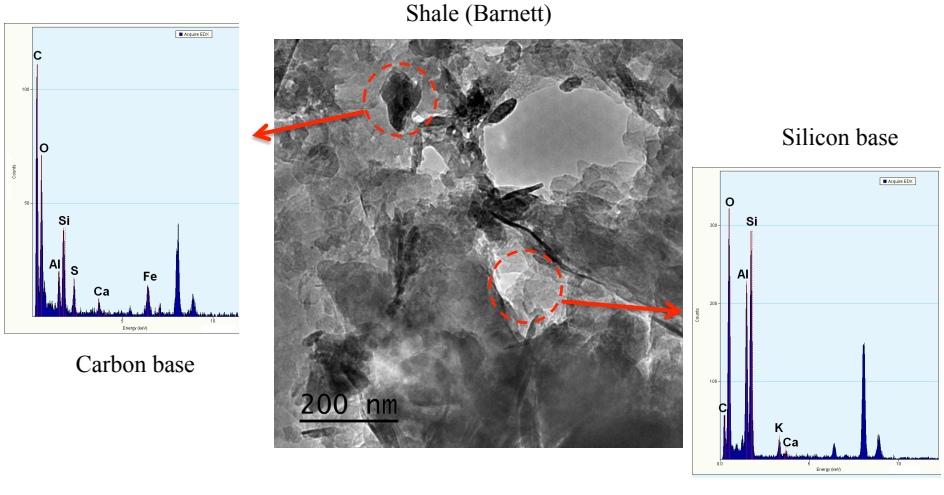
TEM Image with C-based and Si-based Composition

Shale (Barnett)



Carbon base

Silicon base

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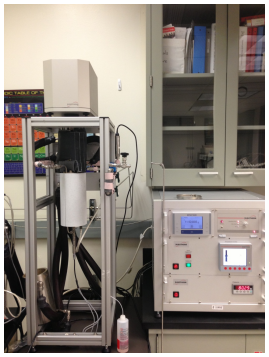
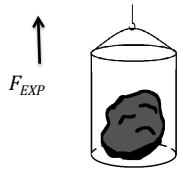
Rubotherm MSB





$$F_B = (V^{sc} + V^s + V^A) \cdot \rho(p,T,y) \cdot g$$

$$F_A = (m^{sc} + m^s + m^A) \cdot g$$

$$F_{EXP} = F_A - F_B = \left(m^{sc} + m^s + m^A - (V^{sc} + V^s + V^A) \cdot \rho(p,T,y)\right) \cdot g$$

$$\Delta m = \frac{F_{EXP}}{g} = m^{sc} + m^s + m^A - (V^{sc} + V^s + V^A) \cdot \rho(p,T,y)$$

What we want to know

$$m^A = \Delta m - m^{sc} - m^s + (V^{sc} + V^s + V^A) \cdot \rho(p,T,y)$$

Hard to measure

$$m^{excess} = m^A - V^A \cdot \rho(p,T,y)$$

Advantage:

High T/P

0.005 mg Accuracy

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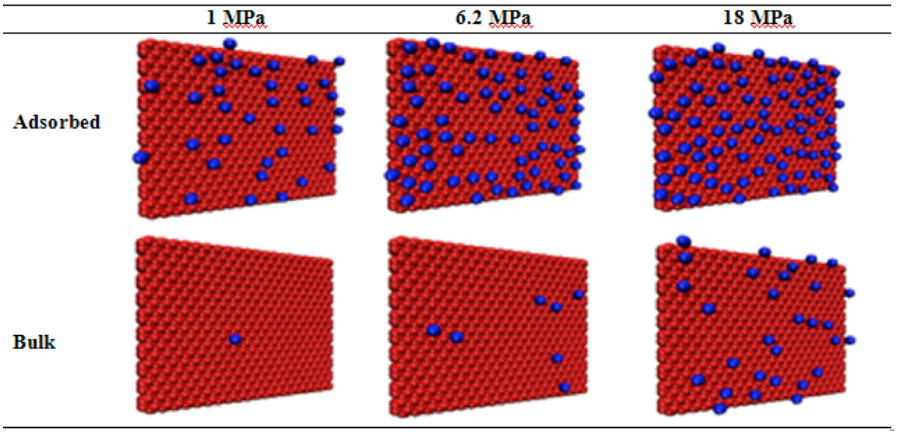
Absolute Adsorption vs Excess Adsorption

3D snapshots of slices through adsorbed and bulk phases at 298K in a 2-nm pore; red = surface carbon atoms and blue = methane molecules



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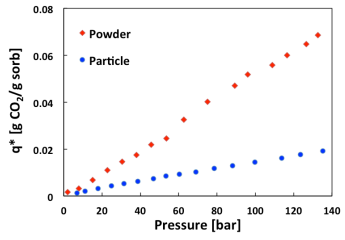
Ref: K. Mosher, J. He, Y. Liu, E. Rupp, J. Wilcox, Int. J. Coal. Geol. 109-110, 36-44 (2013)

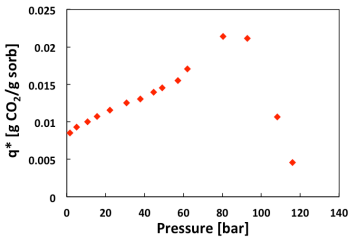
CO_2 Adsorption on Gas Shale from Eagle Ford

Isotherms of Particle vs. Powder at **125** °C



- Sample: Eagle Ford formation
- Chip and powdered forms studied.
- **Powder form gives higher gas capacity than chip form** probably due to reduced macro-pore mass transfer resistance and more pore space introduced to powder sample.

Isotherms on Powder at **50** °C



- The decreasing of excess adsorption under high pressure indicate that bulk density is approaching the pore density.
- At 125 ˚C, the inflection point is not reached, as the density of CO_2 at a specific pressure is greater at the lower temperature.

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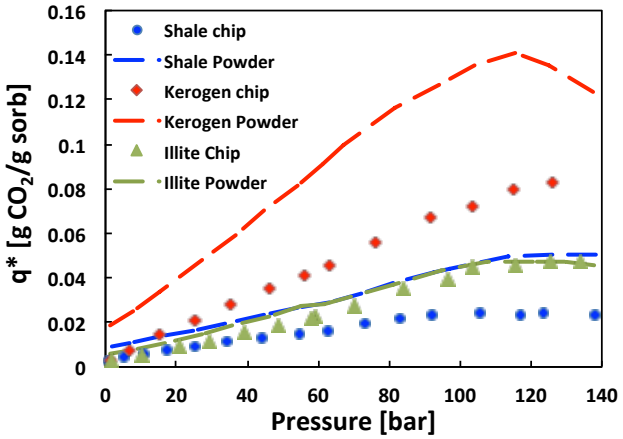
CO_2 Isotherm Compare on Chip and Powder

Isotherms of shale/kerogen/clay at **80** °C



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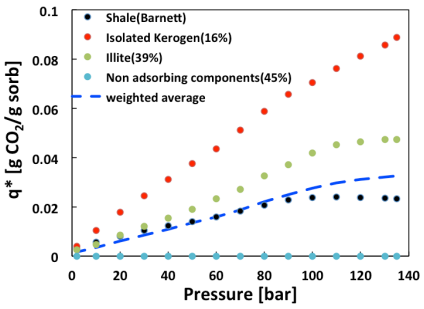
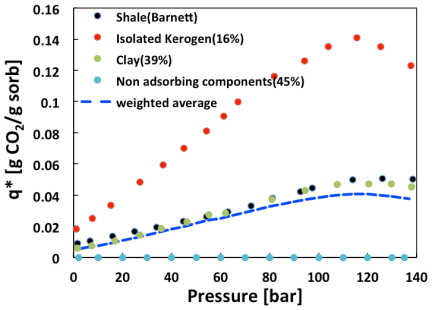
CO_2 Isotherm Compare on Chip and Powder

Chip form



Powder form



Weighted average is similar compared to the experimental measured CO_2 isotherm on shale

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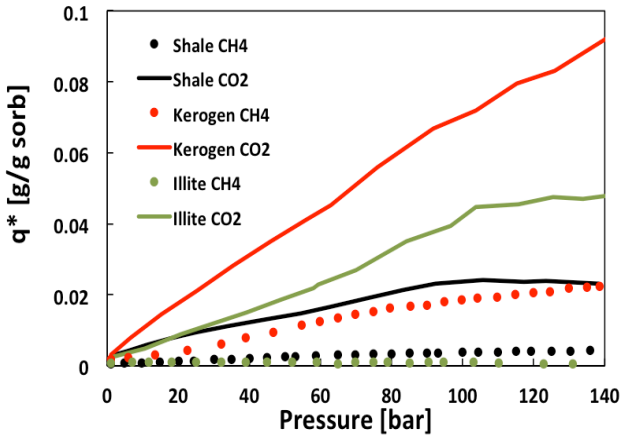
CO_2 and CH_4 Isotherm Compare

Isotherms of shale/kerogen/clay at **80** °C



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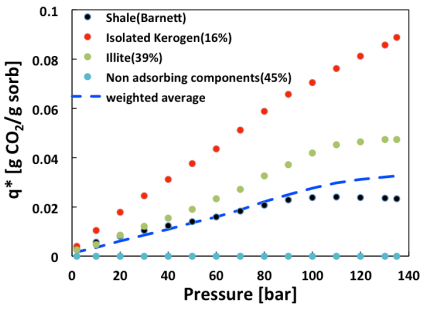
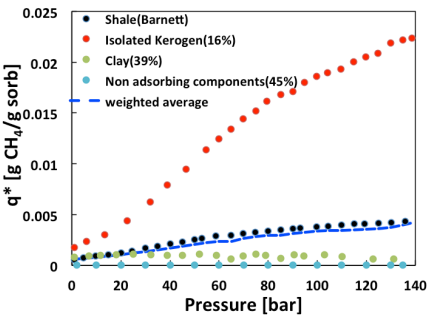
CH_4 Isotherm

CO_2 isotherm



CH_4 isotherm



For CH_4 isotherm, weighted average also shows similar adsorption compared to experiment measurement.

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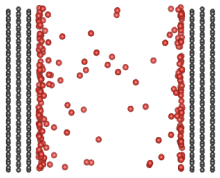
Pore Size Distribution for Modeling

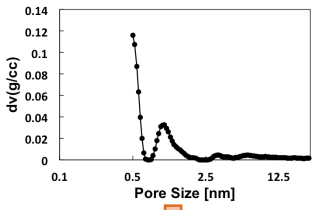
➢Three layered slit pores



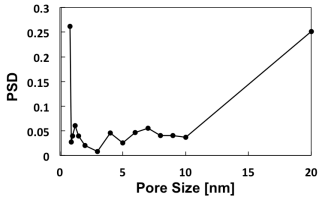
- Assumption: the real porous system is a linear combination of slit pores with varying widths
- Assume the total isotherm consists of a number of individual "single pore" isotherms multiplied by their relative distribution over a range of pore sizes.

$$\rho_{simulated}(j) = \sum_{i=1}^{m} a_i \rho_i(j)$$

Original PSD of AC sample



PSD truncated at 20 nm



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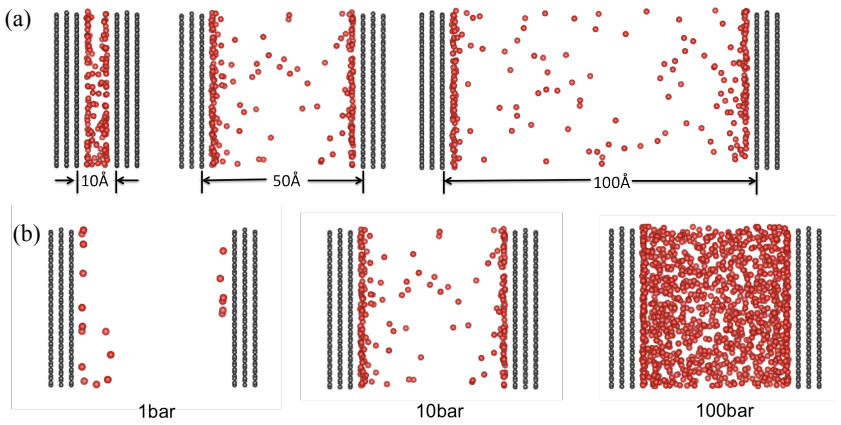
Interaction Between CO_2 and Graphite



(a) Comparative side views of adsorbed CO_2 in graphite slit pores with varying pore width at 333K and 10 bar; (b) Comparative side views of adsorbed CO_2 in graphite slit pores with pore width of 50Å at 333K and varying pressure.

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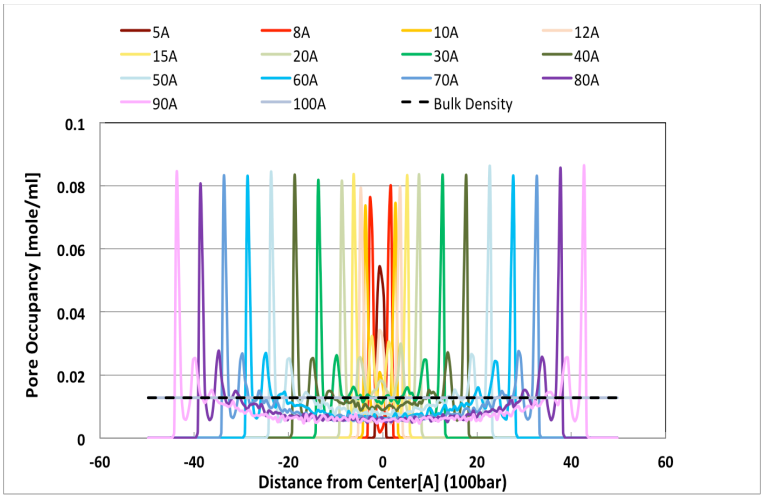
GCMC Density Plot for CO_2



Density plot of CO_2 adsorption in pores with different width. Compared with bulk density at same condition.

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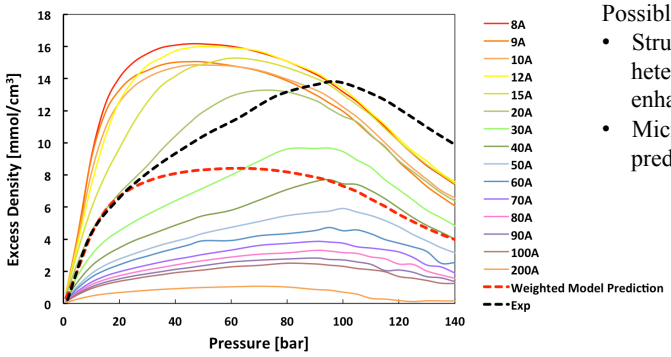
Adsorption Isotherm Prediction Based on PSD

Predicted excess adsorption isotherms of CO_2 using GCMC and with the experimental measurement at 333K



Consistent in the low-pressure region, under predict in high-pressure region.

Possible Explanation:

- Structural and heterogeneity that enhance CO_2 adsorption
- Micro-pore size under prediction

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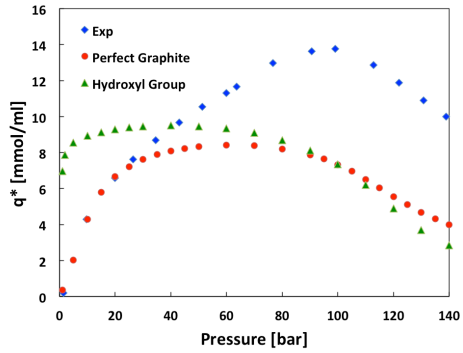
Adsorption Isotherm on Functionalized Model

CO_2 density in different functionalized slit pores at 313 K (supercritical).

		PG	OX	OH	C=O	C=O_COH	COH_C=O	COOH	Hydrated
9.2 Å	Avg. density [mmol/cm3]	18.53	20.15	26.22	23.86	23.86	17.01	19.40	17.90
	Increase [%]	0.00	8.78	39.77	27.21	27.21	−9.36	3.41	−4.61
20 Å	Avg. density [mmol/cm3]	19.41	21.34	23.17	22.56	22.57	21.82	21.05	19.83
	Increase [%]	0.00	9.93	19.36	16.21	16.26	12.42	8.42	2.14

Ref: Y. Liu, J. Wilcox / International Journal of Coal Geology 104 (2012) 83–95



- Comparison of experimental measurement with simulated isotherm on perfect and hydroxyl functionalized graphite.
- Functionalized model enhances adsorption in low pressure range, but still underestimate adsorption in high pressure range.

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Conclusion

- Investigated gas adsorption mechanism and storage capacity on gas shale/kerogen/illite by measuring CO_2 adsorption isotherms
- Characterized the structure, pore size and chemistry of shale/ kerogen/illite
- Simulated the gas adsorption behavior of carbon based material using GCMC

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Acknowledgements

- This work is supported under Stanford Graduate fellowship.
- SEM/TEM experiments performed in Nanocharacterization Laboratory at Stanford University
- The computations were carried out on the Center for Computational Earth & Environmental Science (CEES) cluster at Stanford University.

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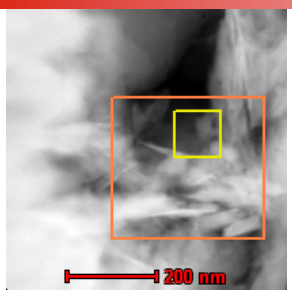
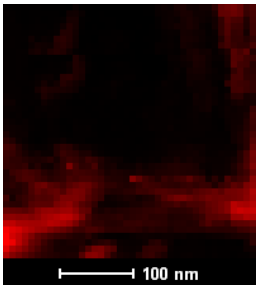
TEM and EDS Elemental Mapping

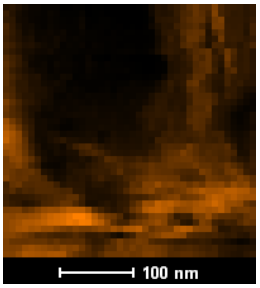


EDS elemental mapping in STEM mode. The signal intensity within the orange rectangular for each element is shown as follows. Si and O signals are in good consistent with each other, indicating clay content within shale, while carbon map shows some overlapping with Si/O.

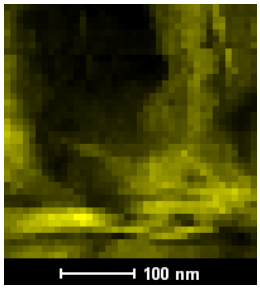
C



O

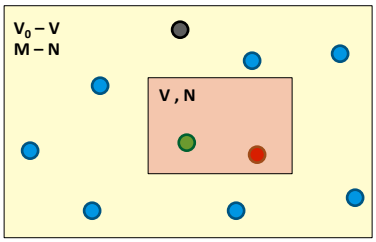


Si



Methodology - GCMC

- **Grand Canonical Monte Carlo** (GCMC) - the bridge to connect micro- and macroscopic properties
  - Fixed:
    - Chemical potential (pressure)
    - Pore volume
    - Temperature
  - To obtain Equilibrium properties to estimate maximum capacity of CO_2 adsorption



System volume: V_0

Total particle number: M

Movement for Gas

- **Displace** V → V
- **Remove** V → V'
- **Insert** V' → V

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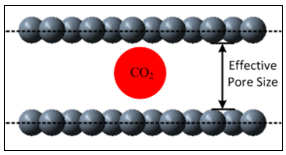
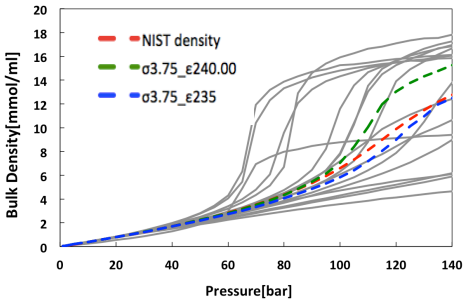
Model and Parameter Tuning

The 1C-LJ intermolecular model was proposed by Ravikovitch et al.. The collision diameter and the reduced well-depth of the interaction energy are tuned to be 3.750Å and 235.00 K, respectively, by comparing with NIST density data (experimental data).





	σ [Å]	ε [K]
$CO_2 - CO_2$	3.75	235.0
Carbon_pore – Carbon_pore	3.4	28.0
CO_2 – Carbon_pore	3.575	81.1172

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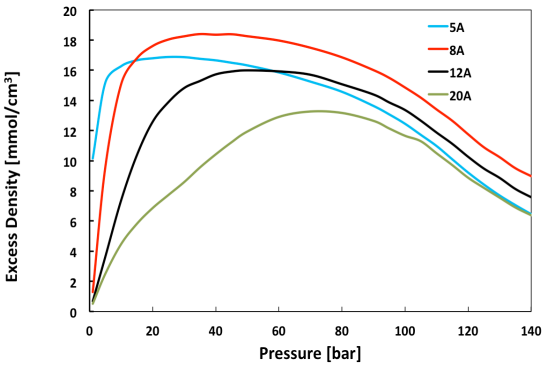
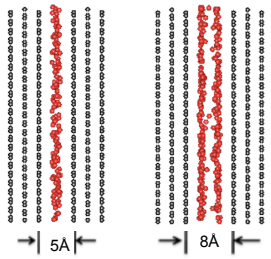
GCMC in Smaller Pores





5A- Pore is so narrow and can only fit one layer of gas in the space

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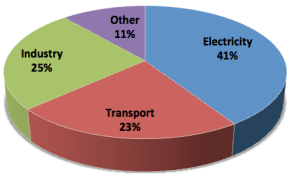
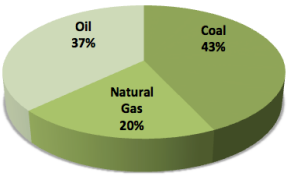
Motivation- CO_2 Emissions (US) and CCS

CO_2 emissions must be reduced by 30–85% by 2050 to be on track for stabilizing atmospheric CO_2 between 350 and 440 parts per million by volume



by sector



by energy resource

CO_2 capture and sequestration (CCS)

Ref: IEA Highlights, 2011

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