Interdisciplinary Investigation of the CO_2 Sequestration in Depleted Shale Gas Formations

Project Number DE-FE-0004731

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage
August 21-23, 2012

Outline

- **Project Benefits**
- Technical Status
    - Imaging at mm- to micron-scales using CT
    - Permeability measurements and application of the Klinkenberg effect
    - Molecular Dynamics simulations for permeability and viscosity estimates
- Accomplishments to Date
- Summary

Benefit to the Program

- Carbon Storage Program major goals
  - Imaging of gas shale from nano to mmCT scanning provides knowledge of the pore connectivity at micro (less than 2nm), meso (2 – 50nm), and macro (> 50 nm) scales
  - Gas permeability measurements taking into account the Klinkenberg effect can lead to pore-size estimates and contributions of different length scales to transport mechanisms
  - Molecular simulation using Monte Carlo and Molecular Dynamics approaches can lead to prediction of density and viscosity estimates at nano and mesoscales

Benefit to the Program

- Project benefits statement
  - The research project is to conduct a multscale, multiphysics, laboratory study coupled with molecular simulations to assess the feasibility of depleted organic-rich gas shale reservoirs for large-scale CO_2 sequestration. This project supports the Carbon Storage Program's efforts to identify and utilize geological formations capable of storing appreciable volumes of CO_2 with 99% storage permeance in addition to laying the groundwork for realistic estimates of storage capacity of gas shales.

Project Overview: Goals and Objectives

- Determine how physical and chemical processes of CO_2 storage in organic-rich gas shales affect injectivity and storage capacity
- Determine the ability of gas shale to sequester CO_2 (as free vs adsorbed gas) over long periods of time
- Dilineate the physical and chemical aspects of CO_2-shale interaction
- Characterize transport processes and mobility of CO_2 in fractures, shale matrix, and pores
- Probe potential interactions of CO_2 with ground water
- Develop a trap and seal framework for CO_2 storage in gas shale reservoirs

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Technical Status

- **Imaging at mm- to micron-scales using CT**
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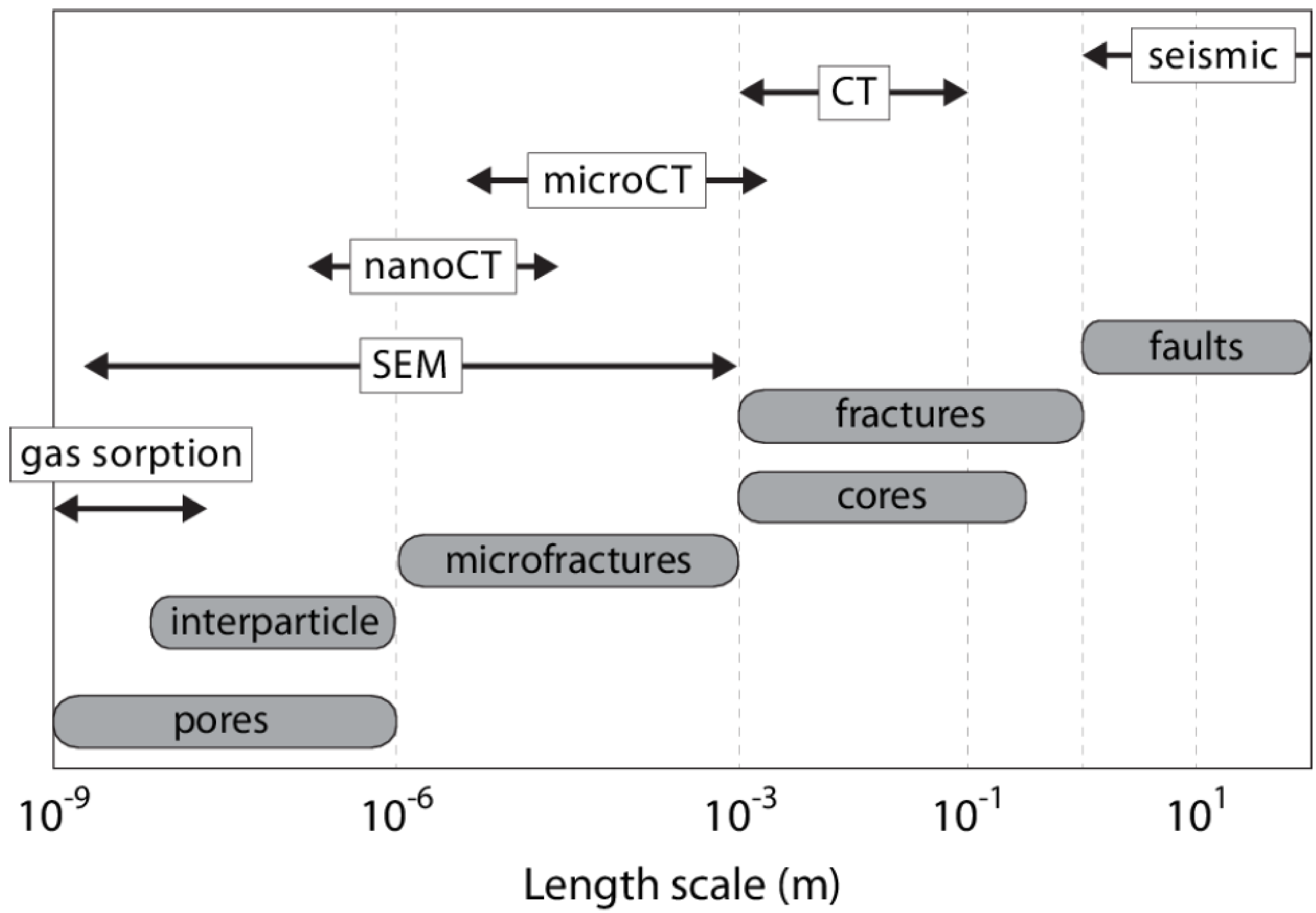
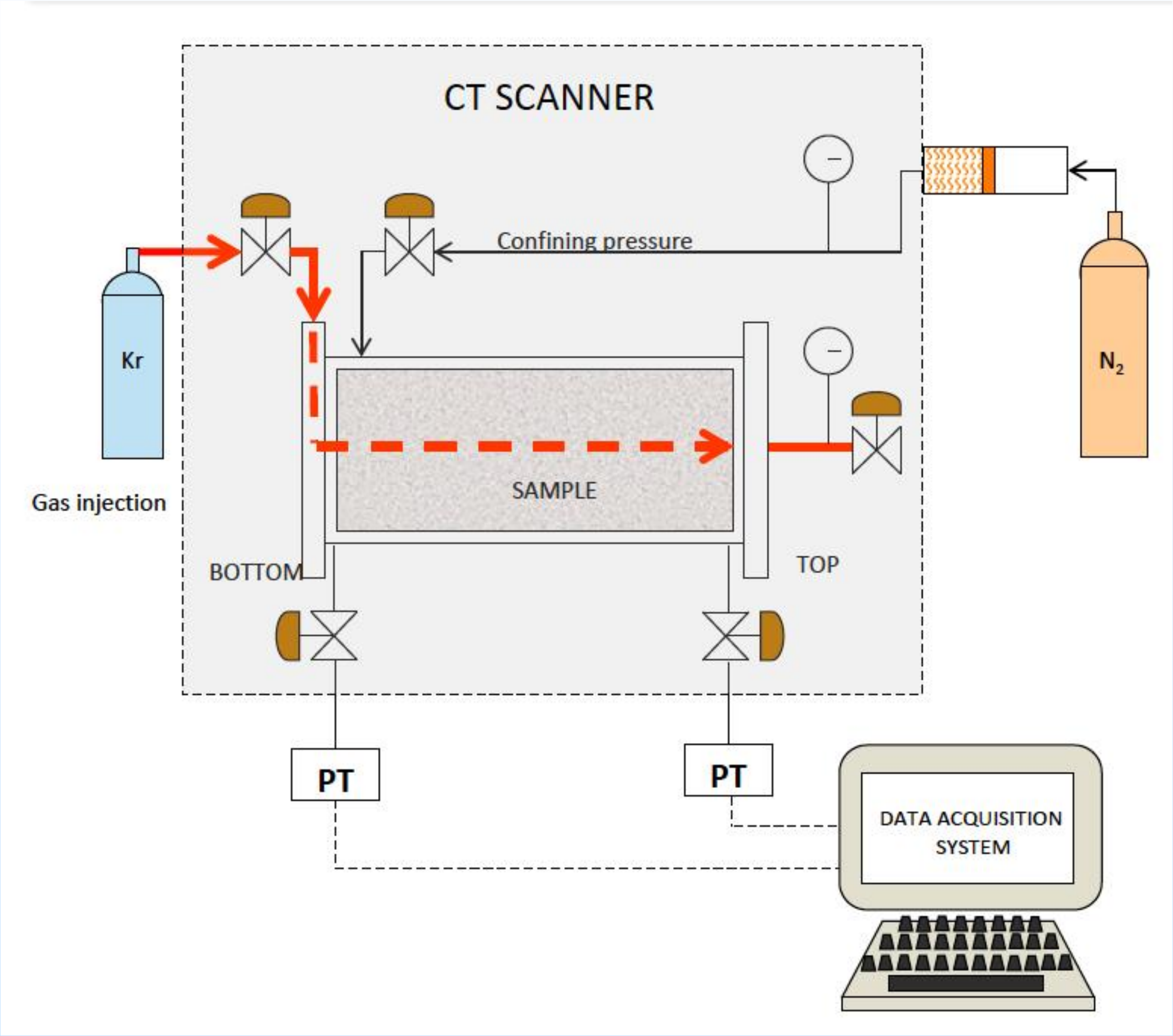
Shale Imaging Tools

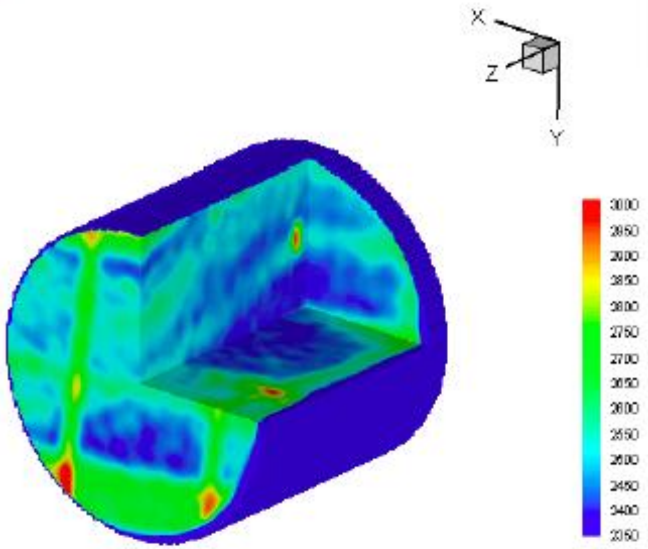


Experimental CT Set up for Kr Flow
mm-scale

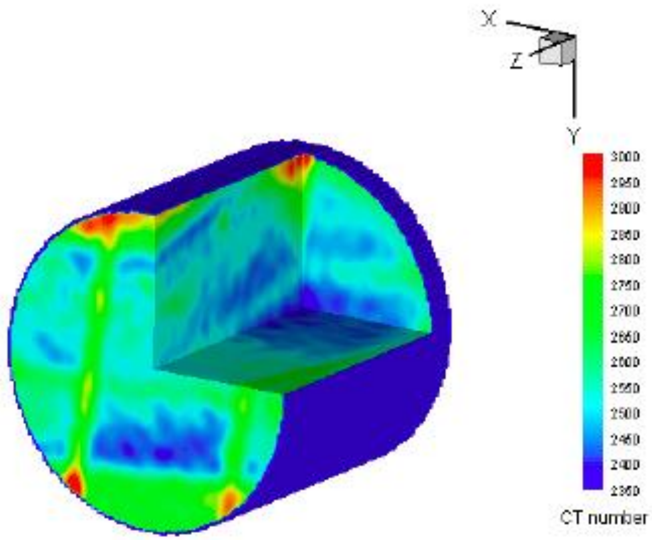


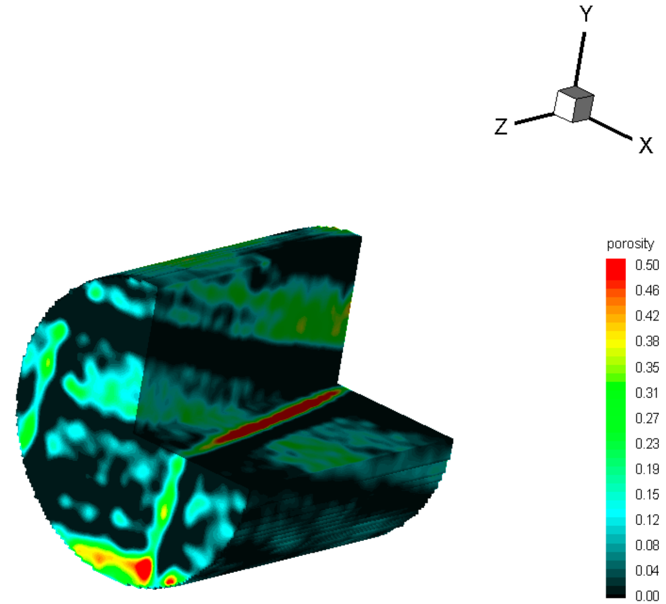
Porosity 3D Image Reconstruction

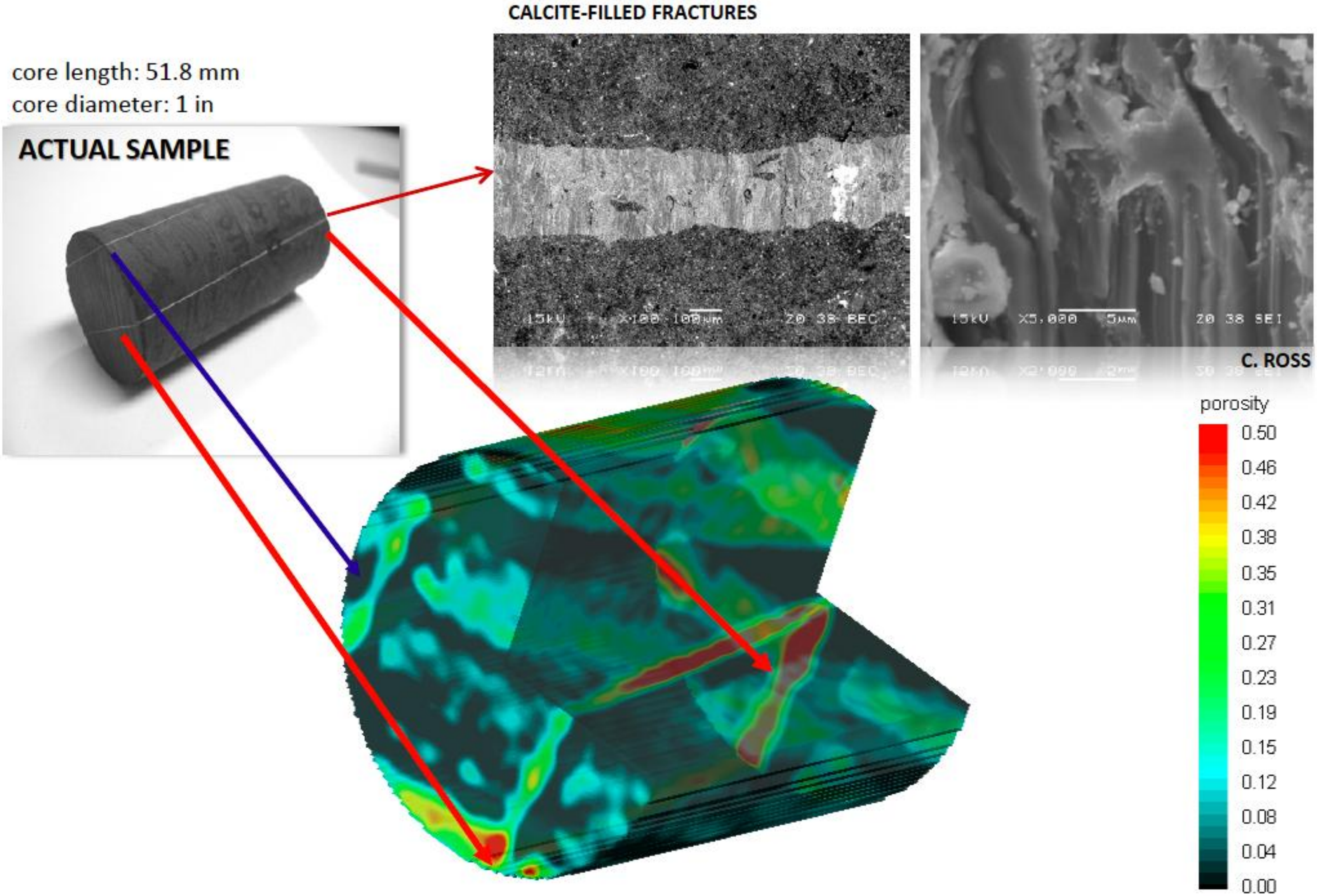
DRY SAMPLE



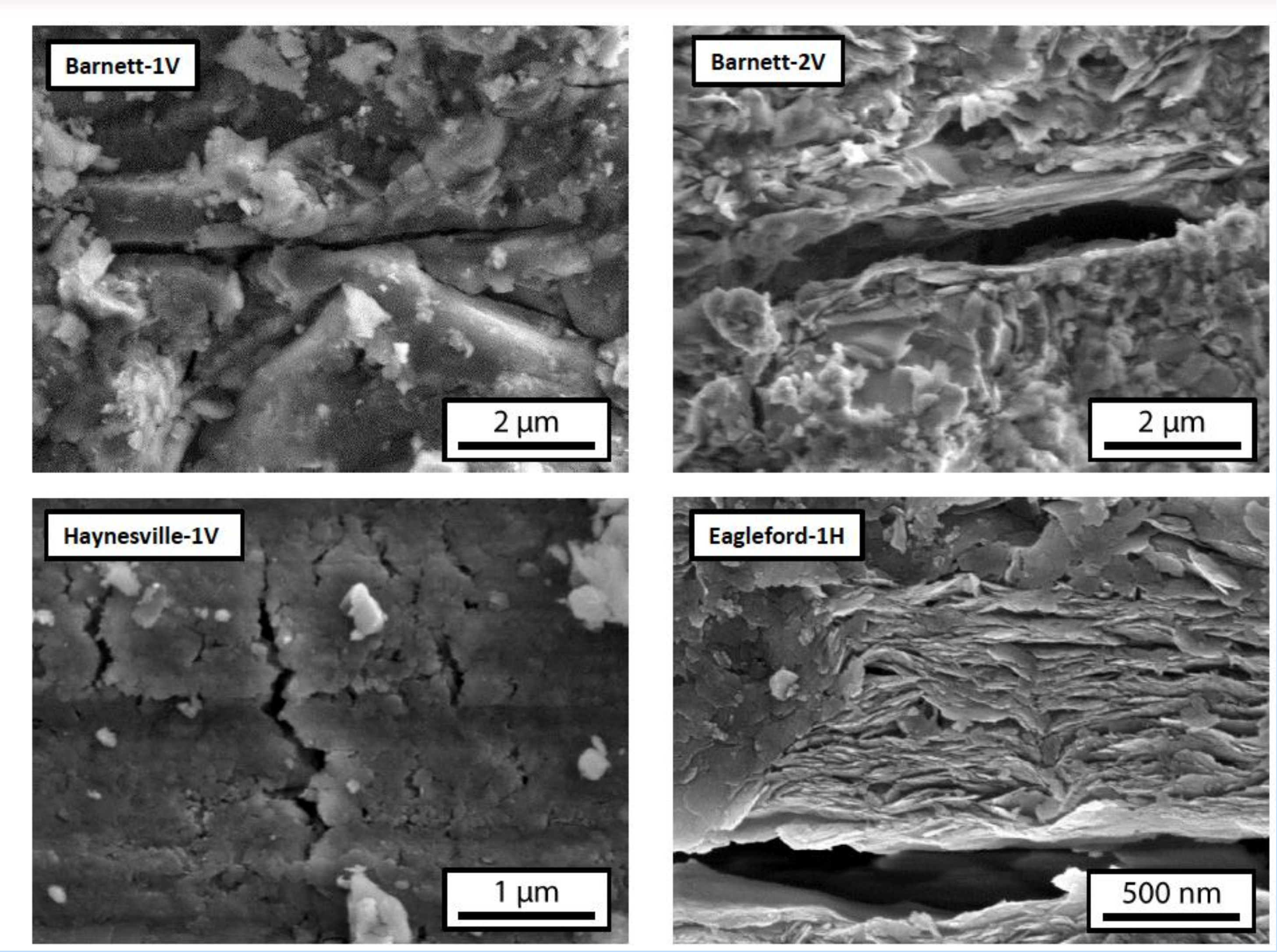
SAMPLE + KR



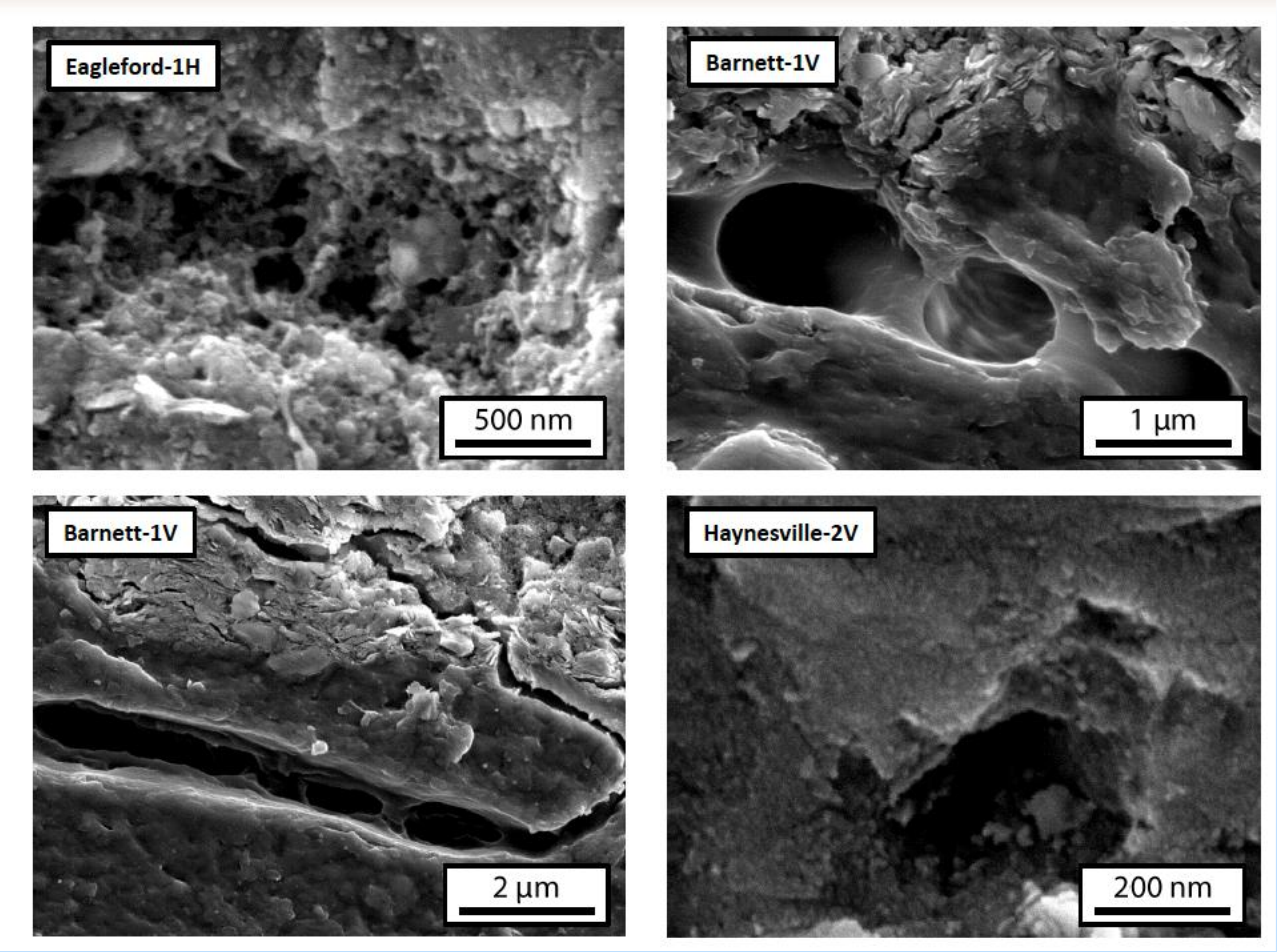



CALCITE-FILLED FRACTURES
core length: 51.8 mm
core diameter: 1 in
ACTUAL SAMPLE
C. ROSS
porosity
0.50
0.46
0.42
0.38
0.35
0.31
0.27
0.23
0.19
0.15
0.12
0.08
0.04
0.00

Shale Porosity - Microfractures *using microCT*



Shale Porosity – Organic Matter *using microCT*



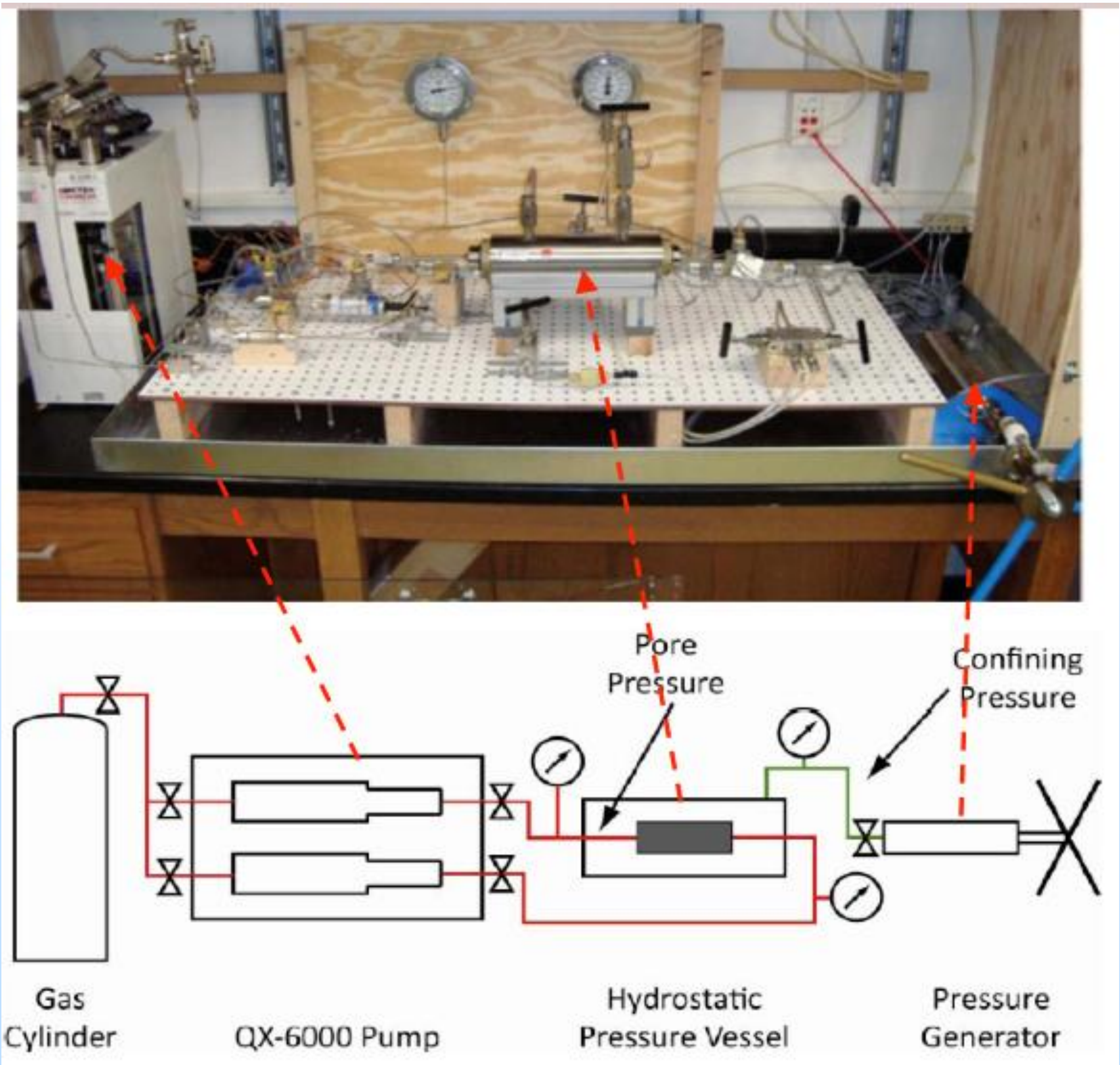
Technical Status

- Imaging at micron to mm-scales using CT
- **Permeability measurements and application of the Klinkenberg effect**
- Molecular Dynamics simulations for permeability and viscosity estimates

Permeability, Effective Stress and Slip Flow

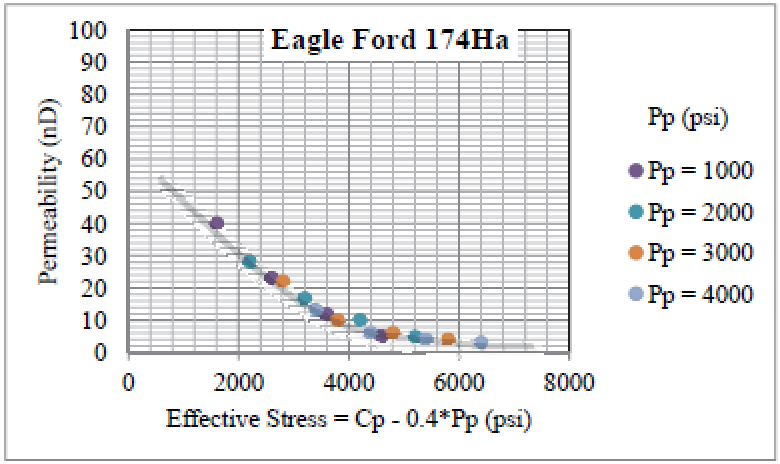
- Permeability varies with Pp and Cp due to:
  - Effective stress effects
  - Slippage effects
- Laboratory studies to date have neglected to account for both of these effects

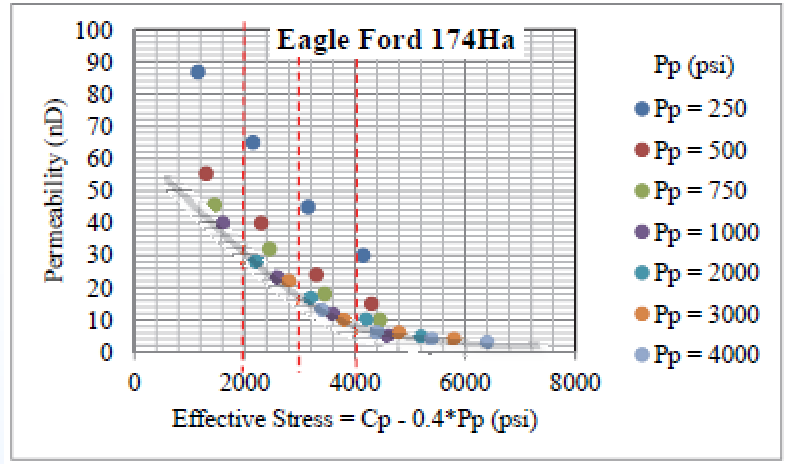
Permeability System Setup

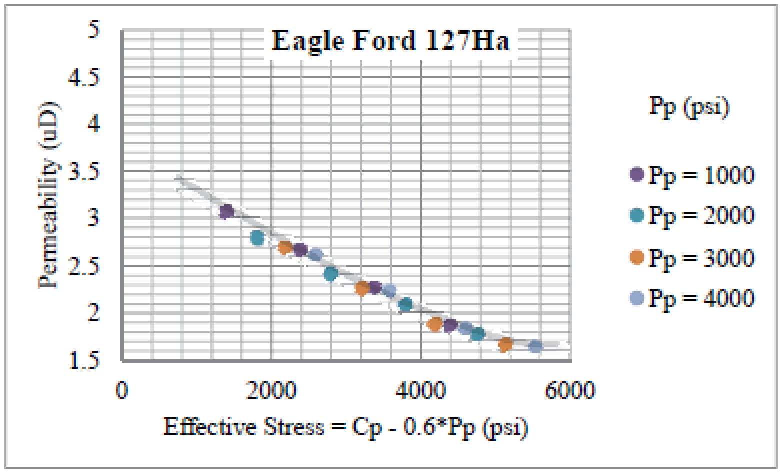


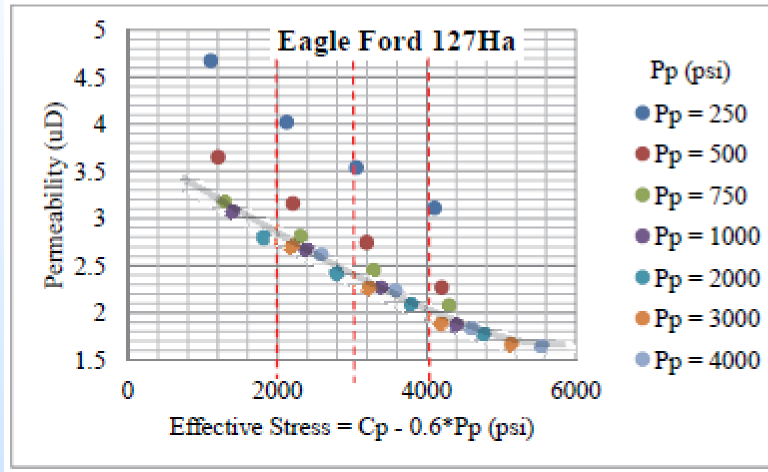
Summary of all Samples Measured

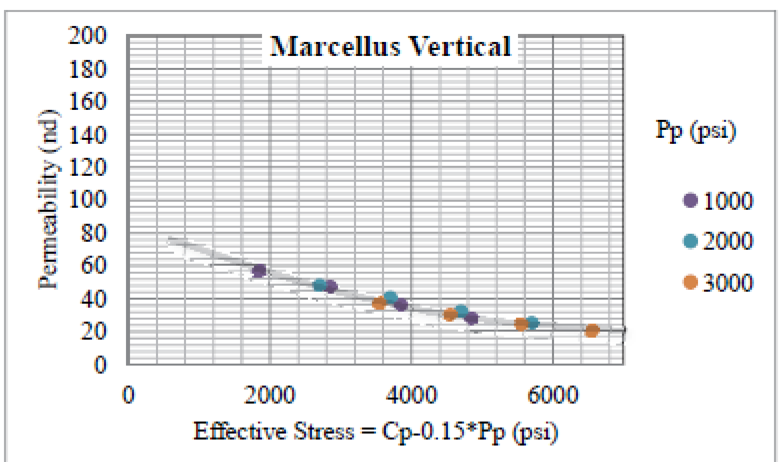
Barnett 31 H -	60 – 160 nd
Barnett 27 H -	800 – 1800 nd
Haynesville G31 -	50 – 150 nd
Montney H1 -	1 – 5 ud
Eagle Ford 127Ha -	1.5 – 3.5 ud
Marcellus Vertical -	20 – 180 nd
Eagle Ford 174Ha -	5 – 90 nd

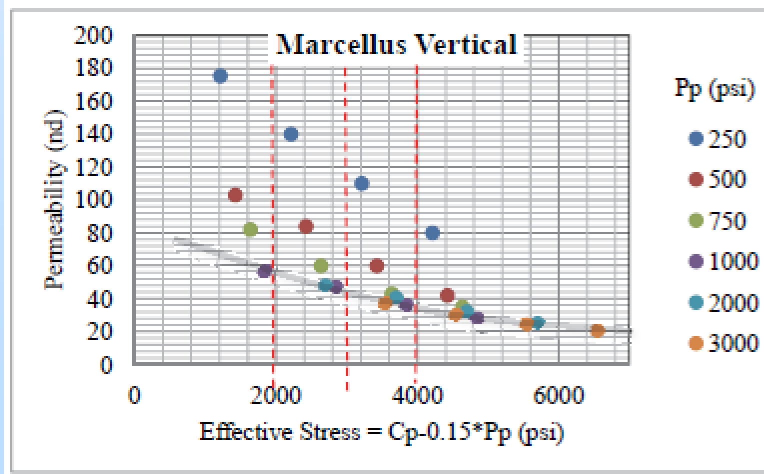

Eagle Ford 174Ha
Permeability (nD)
Effective Stress = Cp - 0.4*Pp (psi)
Pp (psi)
Pp = 1000
Pp = 2000
Pp = 3000
Pp = 4000

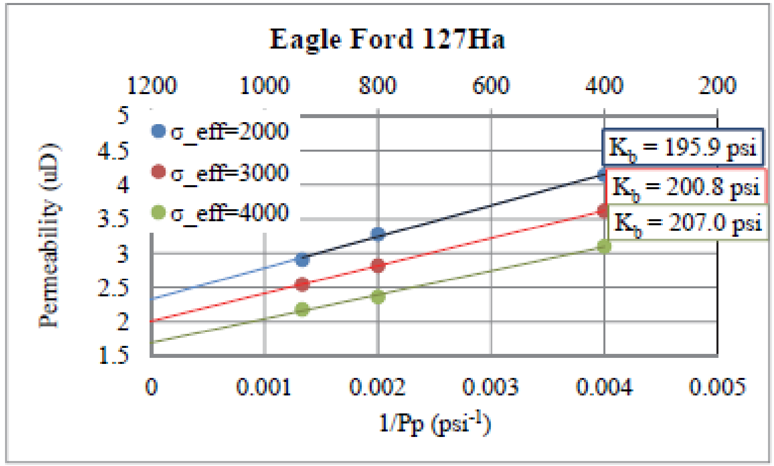

Eagle Ford 174Ha
Permeability (nD)
Effective Stress = Cp - 0.4*Pp (psi)
Pp (psi)
Pp = 250
Pp = 500
Pp = 750
Pp = 1000
Pp = 2000
Pp = 3000
Pp = 4000

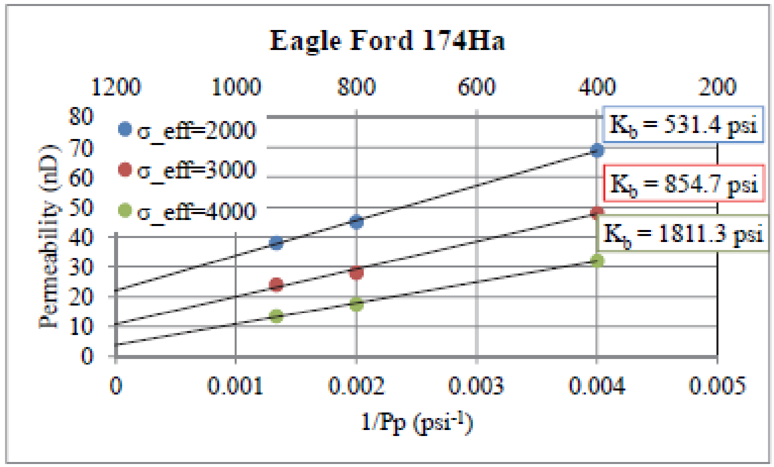

Eagle Ford 127Ha
Permeability (uD)
Effective Stress = Cp - 0.6*Pp (psi)
Pp (psi)
Pp = 1000
Pp = 2000
Pp = 3000
Pp = 4000

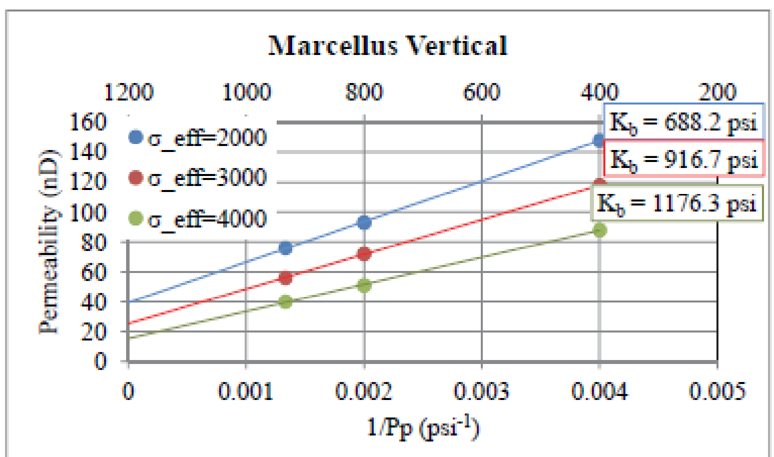

Eagle Ford 127Ha
Permeability (uD)
Effective Stress = Cp - 0.6*Pp (psi)
Pp (psi)
Pp = 250
Pp = 500
Pp = 750
Pp = 1000
Pp = 2000
Pp = 3000
Pp = 4000


Marcellus Vertical
Permeability (nd)
Effective Stress = Cp-0.15*Pp (psi)
Pp (psi)
1000
2000
3000

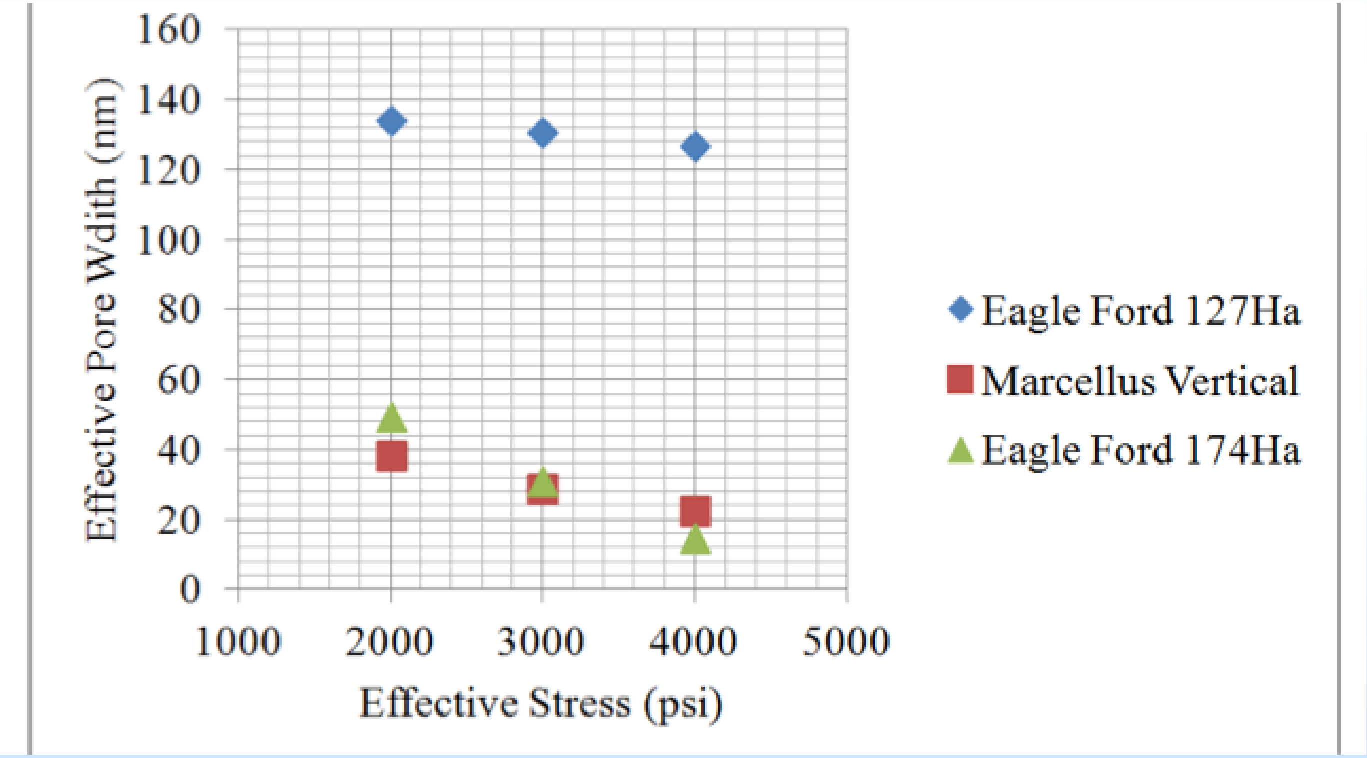

Marcellus Vertical
Permeability (nd)
Effective Stress = Cp-0.15*Pp (psi)
Pp (psi)
250
500
750
1000
2000
3000


Eagle Ford 127Ha
1200 1000 800 600 400 200
Permeability (uD)
5 4.5 4 3.5 3 2.5 2 1.5
σ_eff=2000
σ_eff=3000
σ_eff=4000
K_b = 195.9 psi
K_b = 200.8 psi
K_b = 207.0 psi
0 0.001 0.002 0.003 0.004 0.005
1/Pp (psi^{-1})


Eagle Ford 174Ha
1200 1000 800 600 400 200
Permeability (nD)
80 70 60 50 40 30 20 10 0
σ_eff=2000
σ_eff=3000
σ_eff=4000
K_b = 531.4 psi
K_b = 854.7 psi
K_b = 1811.3 psi
0 0.001 0.002 0.003 0.004 0.005
1/Pp (psi^{-1})

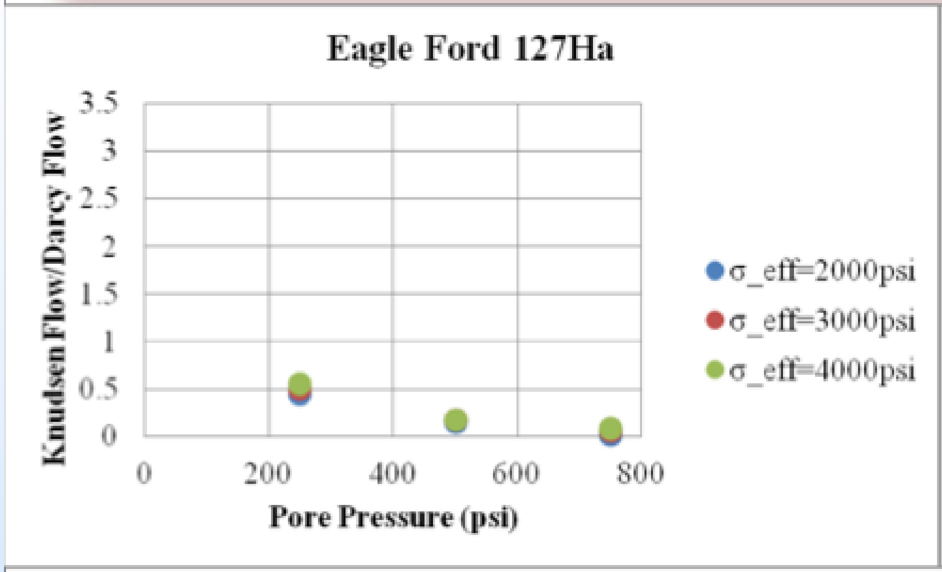

Marcellus Vertical
1200 1000 800 600 400 200
Permeability (nD)
160 140 120 100 80 60 40 20 0
σ_eff=2000
σ_eff=3000
σ_eff=4000
K_b = 688.2 psi
K_b = 916.7 psi
K_b = 1176.3 psi
0 0.001 0.002 0.003 0.004 0.005
1/Pp (psi^{-1})

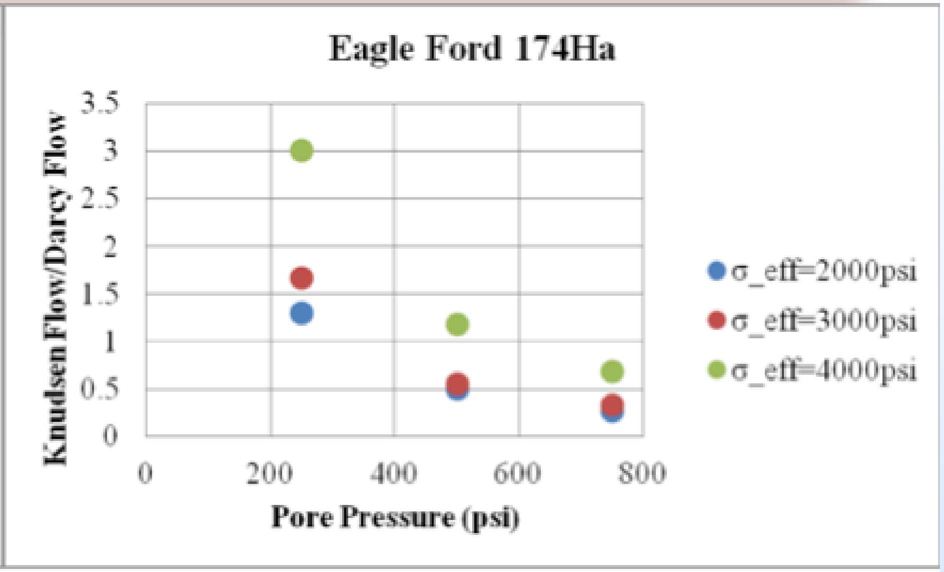
Effective Pore Size vs Effective Stress

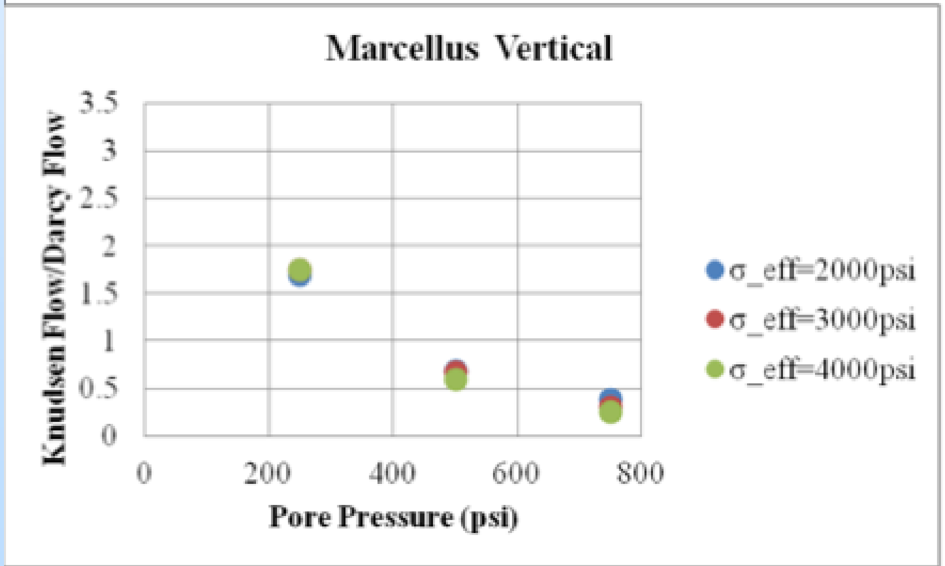


- Pore width decreases with increasing effective stress
- Pore widths range from 20 – 40 nm in Marcellus and Barnett samples, ~ 130 nm in Eagle Ford
- Klinkenberg pore sizes consistent with SEM images

To What Extent Does Knudsen Diffusion Contribute to Flow?







- Diffusive flow contributes appreciably to total flow at pore pressure <800 psi
- Diffusive flow is sometimes more important than Darcy flow at pore pressure <500 psi
- As we increase effective stress for a given pore pressure, we narrow the pore aperture and the relative contribution of diffusion increases

Technical Status

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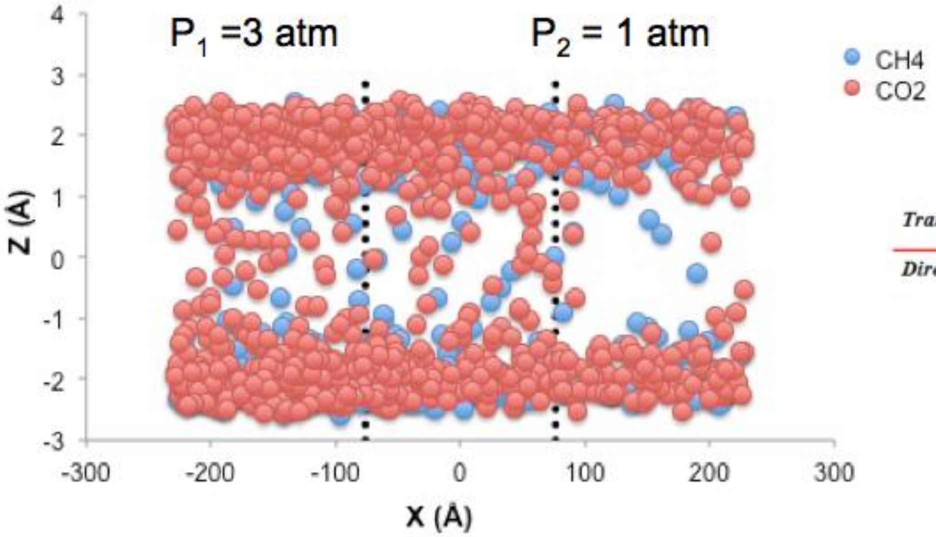
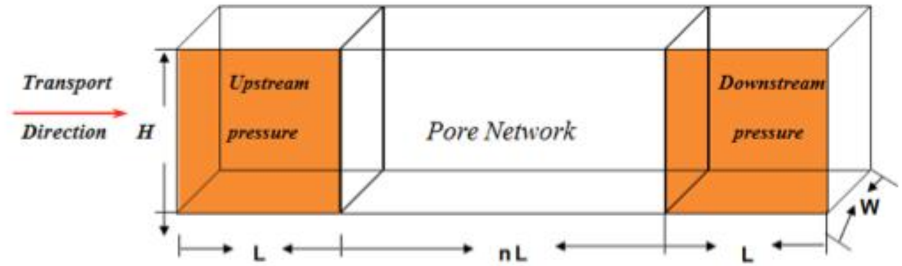
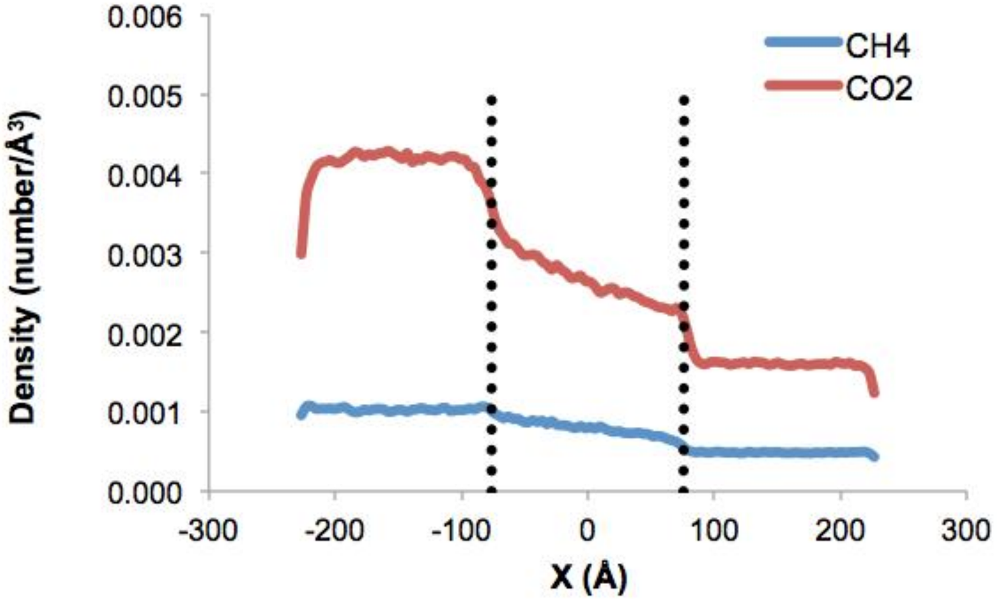
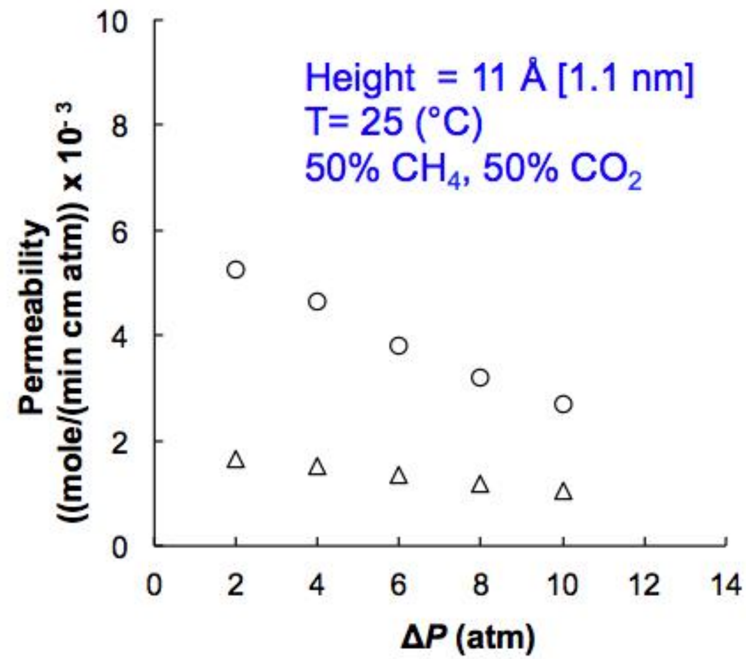
Transport in a Slit Pore Model

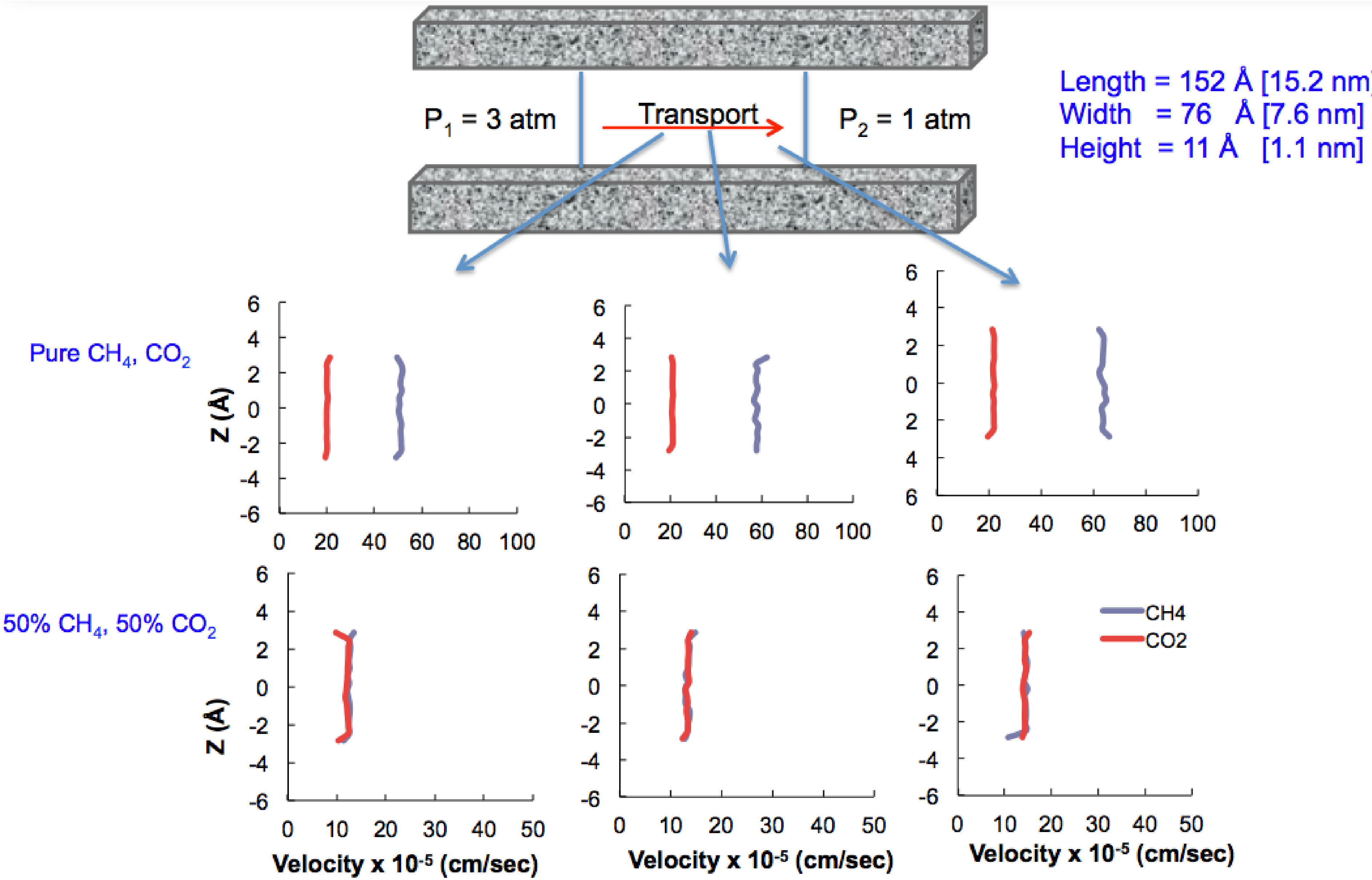






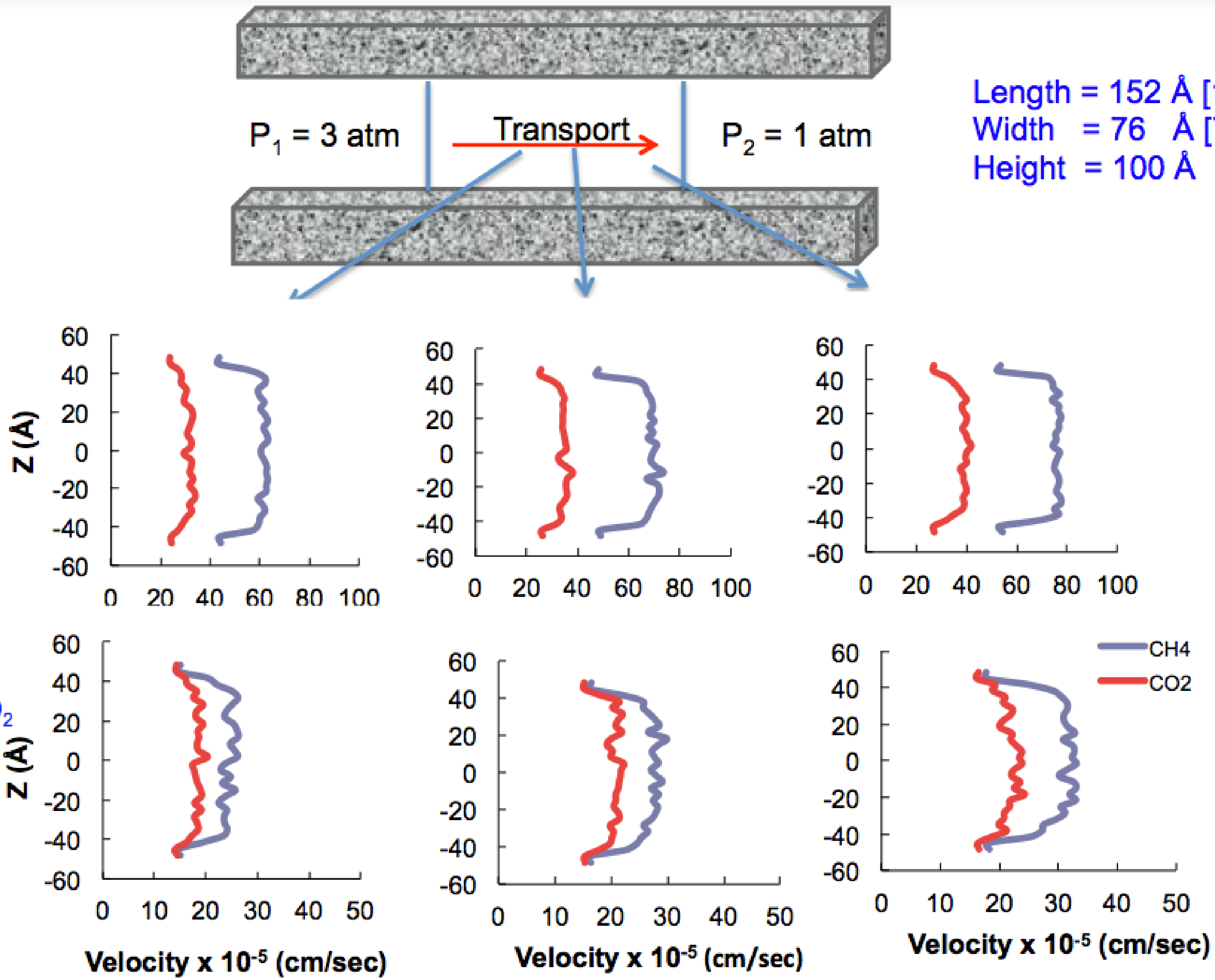


CH_4, CO_2 Velocity Profiles in Micropores (~ 1nm)



CH_4, CO_2 Velocity Profiles in Mesopores (10 nm)

Length = 152 Å [15.2 nm]
Width = 76 Å [7.6 nm]
Height = 100 Å [10 nm]



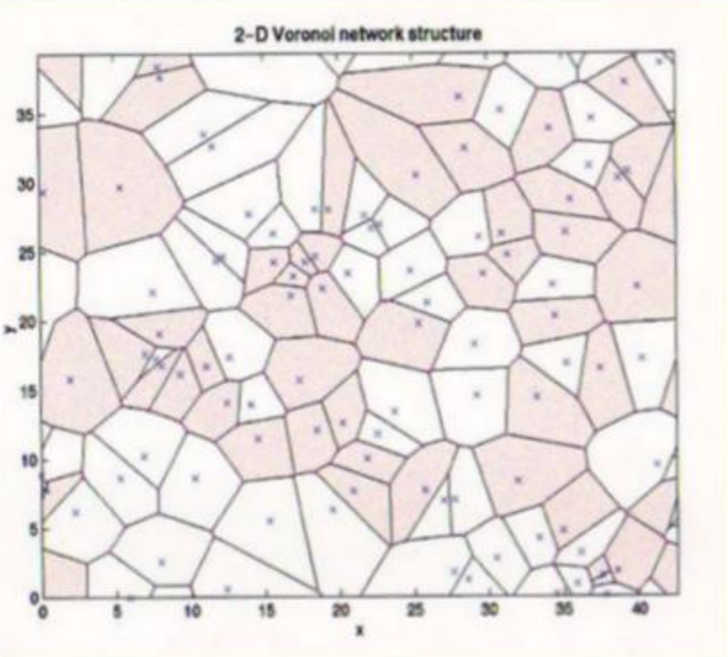
Pure CH_4, CO_2

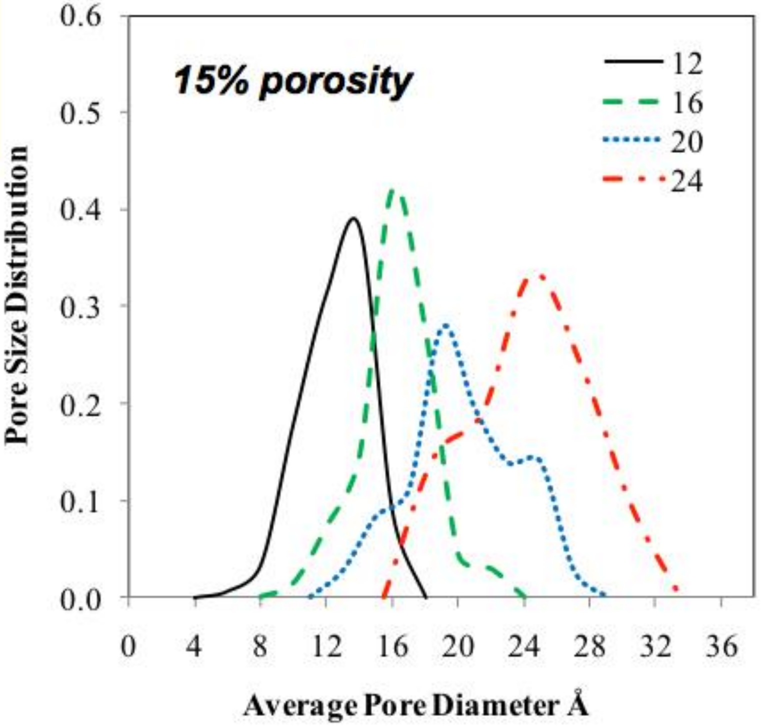
50% CH_4, 50% CO_2

3D Pore Network Model

- 3D molecular pore network model based on the *Voronoi* tessellation method

First, we create a 3D simulation box of structural atoms corresponding to porous structure and then we tessellate the atomic structural box





Pores are selected randomly

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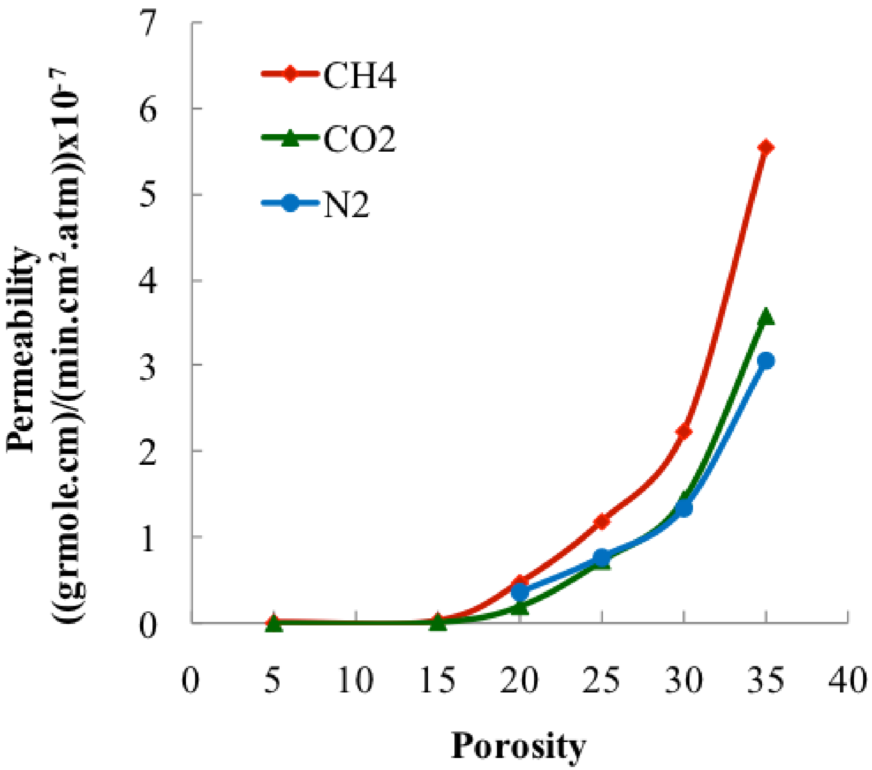
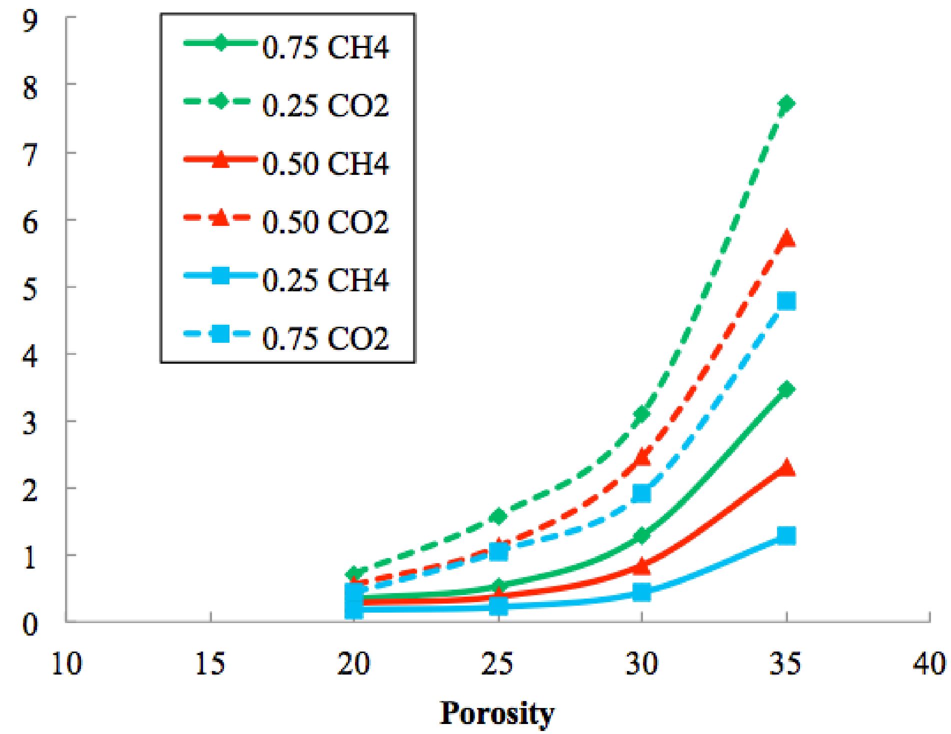
Permeability vs Porosity





The average pore size in the 3-D pore network is 12 Å [1.2 nm]
The upstream and downstream pressures are 50 and 20 atm, T = 25 (°C)

LJ sizes of CH_4, CO_2 and N_2 are 3.81, 3.794, and 3.694 Å respectively

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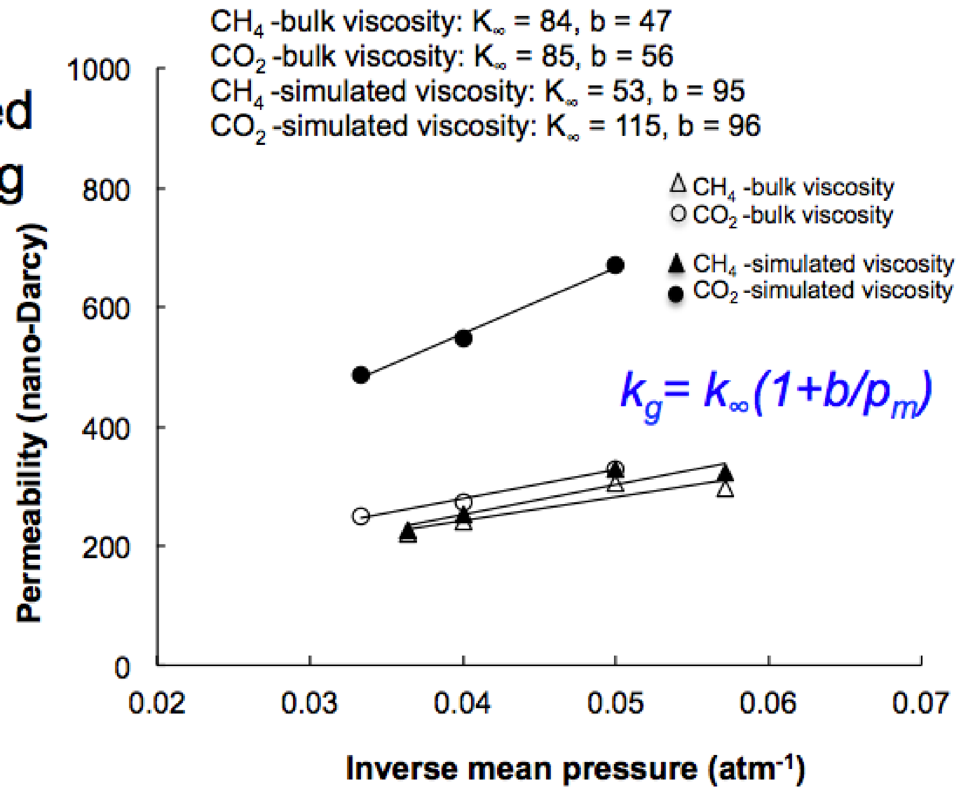
Viscosity Effect on Permeability

- The viscosity effect on the CO_2 permeabilities is more noticeable than CH_4, which results in increased permeability for CO_2 when reporting permeability in Darcy units using modeled viscosity
- The use of the bulk-phase CH_4 viscosity is a reasonable assumption as CH_4 is less influenced by the pore walls compared with CO_2



Green-Kubo and Einstein relations:

$$D = \frac{1}{3N} \sum_{i=1}^{N} \int_0^\infty < v_i(t).v_i(0) > \ dt \qquad \mu = \frac{k_B T}{3\pi d D}$$

The average pore size in the 3-D pore network is 20 Å and the porosity is 20%

The downstream pressure is fixed at 10 atm

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- **Summary**

Accomplishments to Date

- Furthered attempts to image in real time movement in situ of gas through shale cores in lab
- Imaged gas porosity of shale cores using X-ray CT scanning at mm and micron scales
- Investigated sorption, swelling and viscous creep in clays
- Designed and investigated model systems for simulating sorption and transport at micro and mesoscales
- Determined the extent of Knudsen diffusion on the transport mechanism at the nanoscale through application of the Klinkenberg effect
- Determined the difference in gas viscosity and density parameters from nano to micron scales

Summary

- Shale imaging across scales is required to understand the pore structure of the shale and the role the various pores play in gas transport and/or storage
- Gas slippage (Klinkenberg) can be used to determine the dominant transport mechanism at the nanoscale
- Future Plans
  - Continue with nano-scale imaging at SLAC
  - Continue with Klinkenberg investigations for adsorbing gas, CO_2
  - Compare scales and estimates of gas permeabilties of experiments vs theoretical predictions
  - Gas sorption will be used (Quantachrome Autosorb) to determine PSD of various shale samples

Appendix

- Organization
- Gantt Chart
- Bibliography

Organization

- Stanford University, School of Earth Sciences
  - PI: Professor Mark Zoback, Department of Geophysics
    - Dr. Sander Hol (Post-doc) and Rob Heller (PhD student)
  - Co-PI: Professor Tony Kovscek, Energy Resources Engineering Department
    - Bolivia Vega (Research Assistant), Dr. Cindy Ross (Research Associate) and Khalid Alnoaimi (PhD student)
  - Co-PI: Assistant Professor Jennifer Wilcox, Energy Resources Engineering Department
    - Dr. Mahnaz Firouzi (Post-doc), Dr. Dawn Geatches (Post-doc), and Dr. Yangyang Liu (graduated w/ PhD in June 2012)

Gantt Chart

Task	Description Quarters	1	2	3	4	5	6	7	8	9	10	11	12
1	**Project Management and Planning**	■	■	■	■	■	■	■	■	■	■	■	■
1.1	Project management plan	■											
1.2	Planning and reporting		■	■	■	■	■	■	■	■	■	■	■
2	**Physical and Chemical Aspects of CO_2/Shale Interactions**	■	■	■	■	■	■	■	■	■	■	■	■
2.1	Obtain gas shale samples	■	■	■	■	■	■						
2.2	Gas shale surface characterization experiments	■	■	■	■	■	■	■					
2.3	Gas shale bulk characterization experiments	■	■	■	■	■	■	■					
2.4	Development of model systems for adsorption/transport	■	■	■	■	■	■	■	■	■	■	■	
2.5	Adsorption simulations using Monte Carlo	■	■	■	■	■	■	■	■	■	■	■	
2.6	Physical property measurements					■	■	■	■	■	■	■	■
2.7	Shale swelling due to adsorption	■	■	■	■	■	■	■	■				
3	**Transport and Mobility of CO_2 in Fractures and Pores**	■	■	■	■	■	■	■	■	■	■	■	■
3.1	Transport simulations and permeability predictions				■	■	■	■	■	■	■	■	
3.2	In-situ imaging of gas transport pathways	■	■	■	■	■	■	■	■	■	■		
3.3	Shale permeability to CO_2	■	■	■	■	■	■	■	■	■	■	■	
3.4	Gas diffusivity within shale					■	■	■	■	■	■	■	■
4	**Groundwater and Stored CO_2 Interactions**									■	■	■	■
4.1	Model gas-water-CO_2 interactions with clay									■	■	■	■
5	**Trap and Seal Analysis of CO_2 in Shale Gas Reservoirs**						■	■	■	■	■	■	■
5.1	Examine evolution of fractures and seal properties						■	■	■	■	■	■	■

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