Shale Nano-Pore Structures and Confined Fluid Behavior

Project Number: FWP FE 406/408/409 2

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National Energy Technology Laboratory

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Presentation Outline

- Technical Status
  - Experimental Studies (SANS)
  - Computer Simulations (LBM)
- Accomplishments to Date
- Synergy Opportunities
- Project Summary

Why Shale Matrix?

Problem

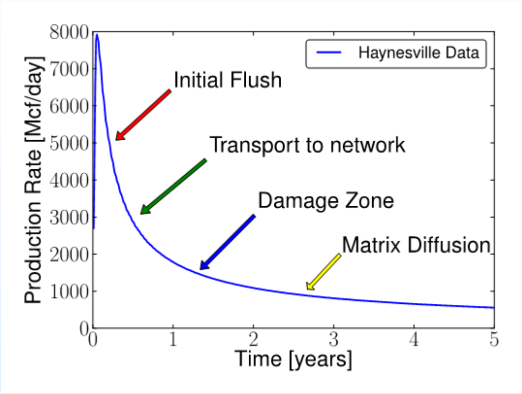
- Although shale oil/gas production in the U.S. has increased exponentially, the current energy recovery rates are extremely low: <10% for oil and <35-40% for gas.
- The production rate for a given well typically declines rapidly within one year or so.

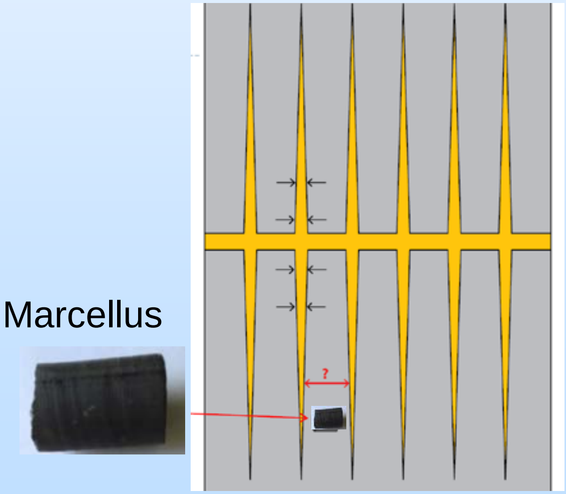
Cause

- Small pore sizes (a few to a few hundred nm) and low permeability (10^{-16}-10^{-20} m^2) of shale matrices.

Technical Challenge

- Characterize shale nanopore structures and understand the confined fluid behavior.

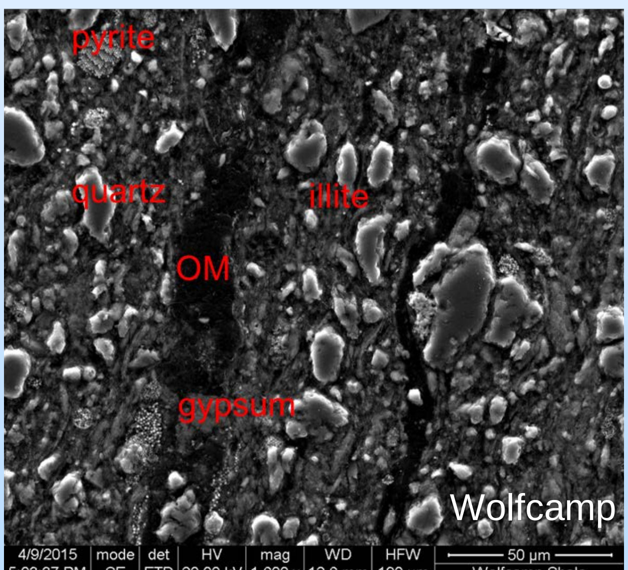


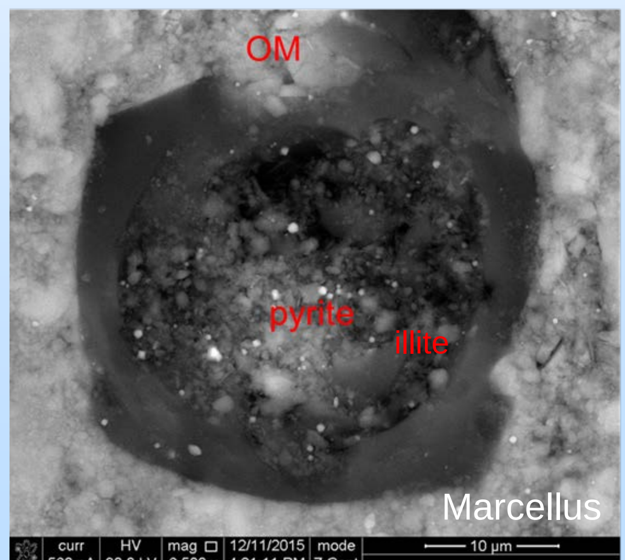


Matrix-fracture fluid transfer

Shale Nano-Pore Structure (Open vs. Closed)

- Open vs. closed nanopores - the proportion and distribution of which are tied to the permeability of a shale matrix.
- Estimate original oil/gas in place (OOIP/OGIP) more reliably.
- Intrinsically heterogeneous; in organic (kerogen) and inorganic (clay) components.
- Unconventional formations - a mix of different lithologies and their hydrocarbon productions vary (i.e., one shale can produce much better than the other).



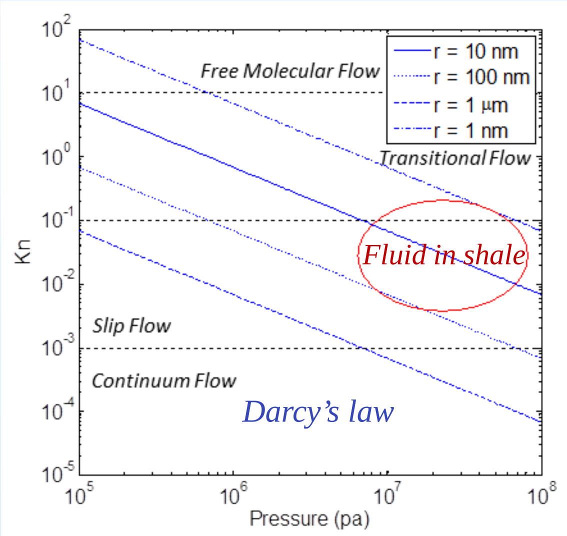


OM-rich; no carbonate

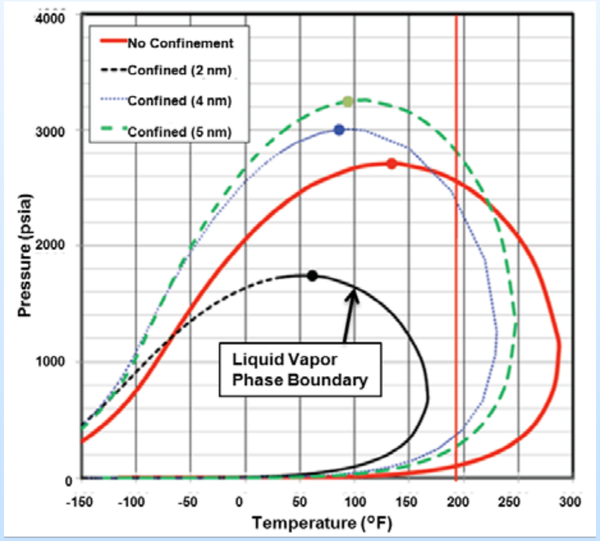
OM-poor, carbonate-rich

Nano-Pore Fluid Confinement (Pressure Mgmt.)

- Changes in fluid flow behavior: the traditional, Darcy's-law-based approaches are inadequate.
- Shifts in liquid/vapor phase boundaries/diagrams (bubble/dew points).



Knudsen number: $Kn = \lambda/r$, r - average pore size; λ - mean free path of gas molecules

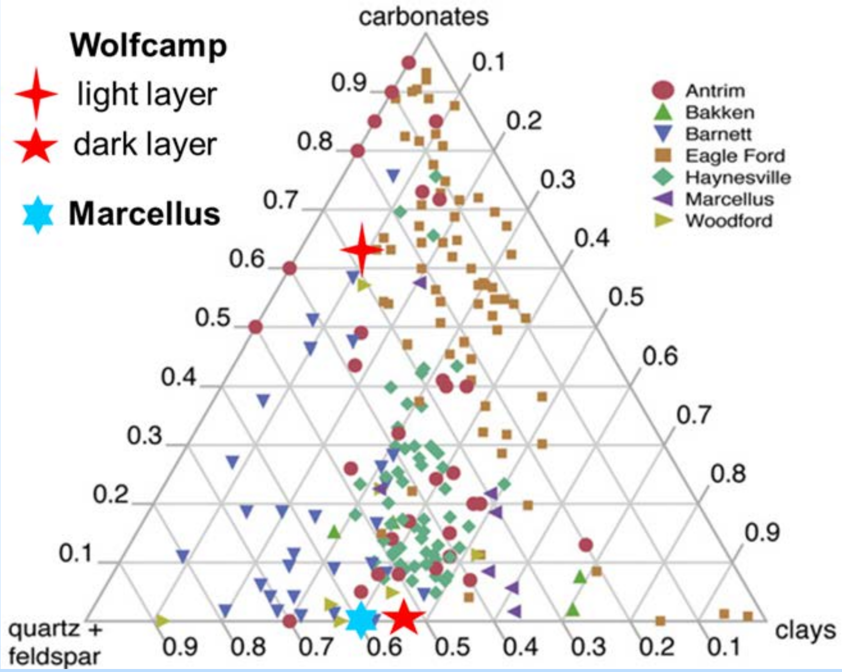


Failure to take into account the nano-confinement effects can underestimate the ultimate oil/gas recoveries by as high as 50% (Sapmanee 2011; Nojabaei et al. 2012).

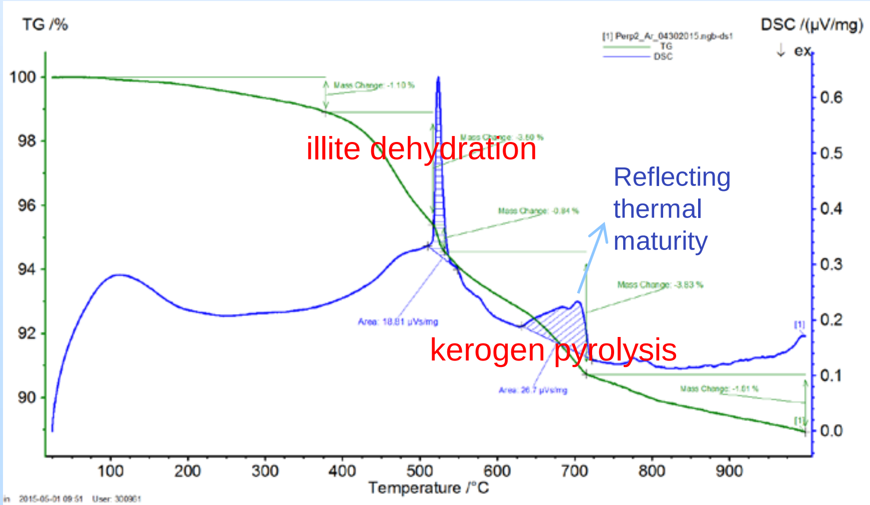
This understanding is critical for developing optimum field production strategies.

Basic Shale Matrix Characterization

- Compositions (mineralogy & chemistry)
  - X-ray diffraction (XRD) – Mineral compositions
  - X-ray fluorescence (XRF) – Chemical compositions
  - Differential scanning calorimetry (DSC) / Thermogravimetry (TG) – TOC/water contents; kerogen thermal maturity
- Microstructure
  - Scanning electron microscopy (SEM) / Focused ion beam (FIB); X-ray/neutron tomography



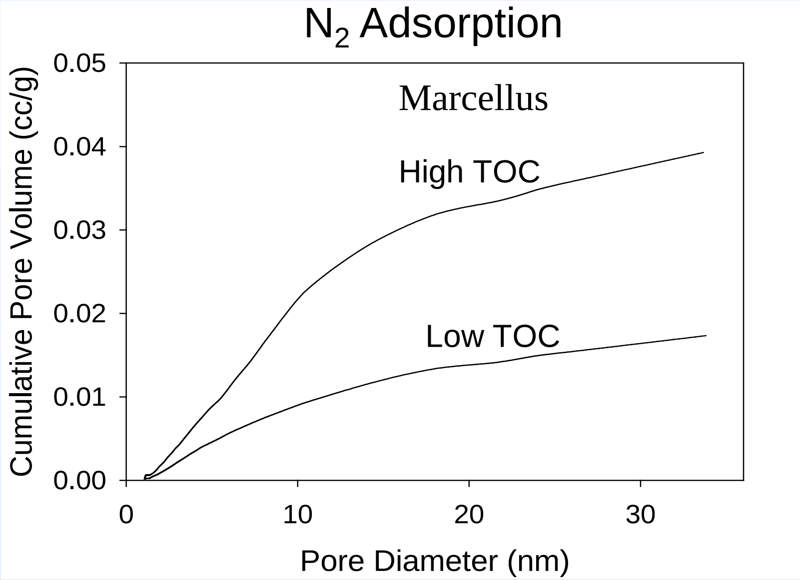
Wolfcamp Dark Layer

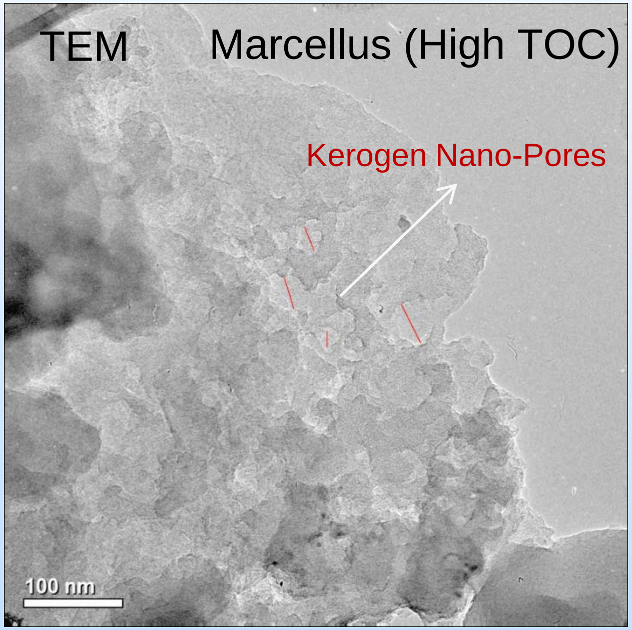


Shale Nano-Pore Characterization

<u>Conventional Techniques</u>

- Gas adsorption and mercury intrusion/immersion porosimetry
- Transmission electron microscopy (TEM)





- ➢ Larger pores dominate the overall pore volumes and pore surface areas.
- ➢ The high TOC shale is more porous than the low TOC shale: Kerogen is more porous.

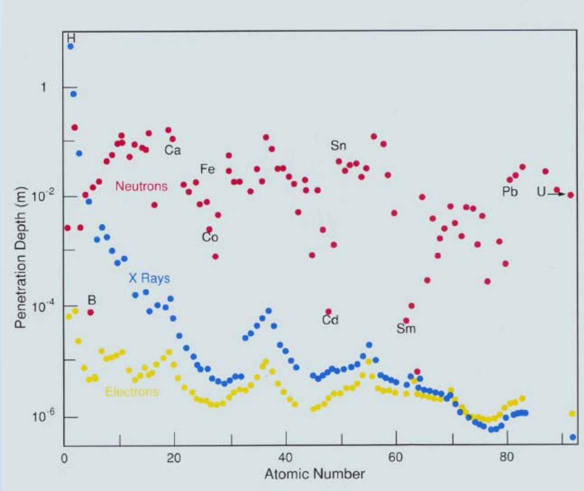
Shale Nano-Pore Characterization

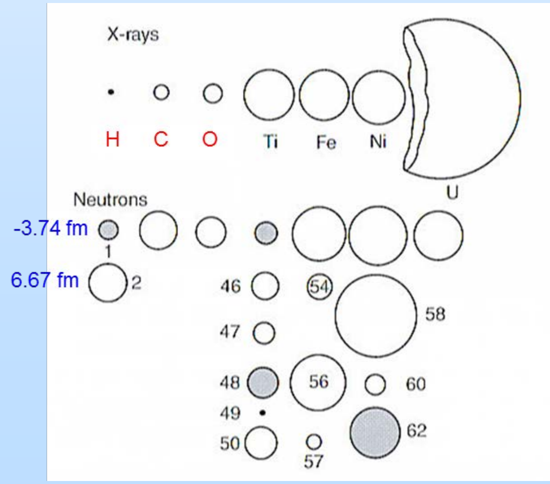
Conventional Techniques

- Gas adsorption / mercury porosimetry: limited to measuring open pores
- TEM: requires thin specimens and measures a small area.

Neutron Scattering

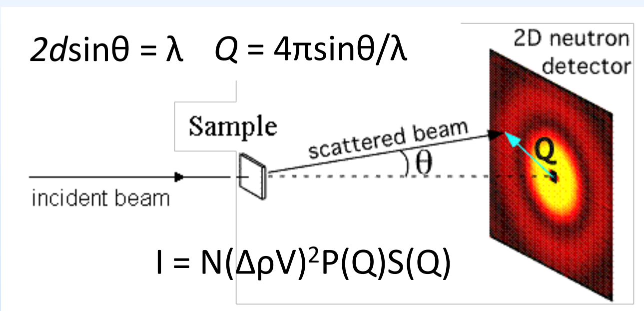
- Neutrons are highly penetrating (e.g. compared with X-rays)
  - ➢ Probing samples at depths
  - ➢ Ease of combination with sample environments (e.g. a pressure cell)
- Neutrons are sensitive to hydrogen (rich in hydrocarbons and water) & its isotopes

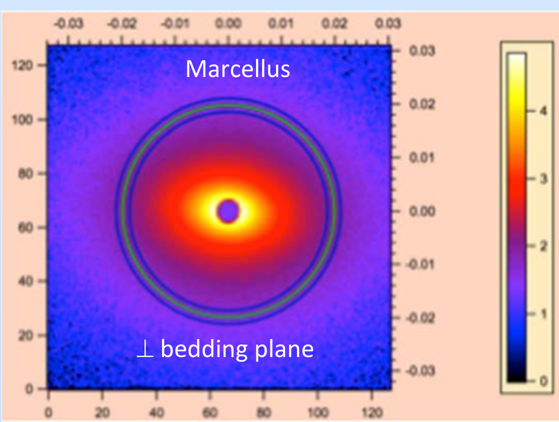




Small-Angle Neutron Scattering

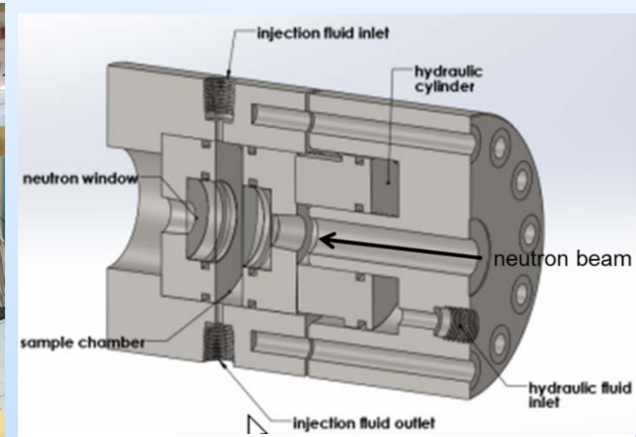
- Small- and ultra-small-angle neutron scattering (SANS/USANS) characterize pores ranging from 1 nm to 10 μm (SANS: 1-100 nm; USANS: 100 nm-10 μm).
- Combine with controlled environment cells to probe the properties of fluids (hydrocarbon/water) in nanopores.





Effect of texture of nanopores


Hydrostatic cell (3 kbar)

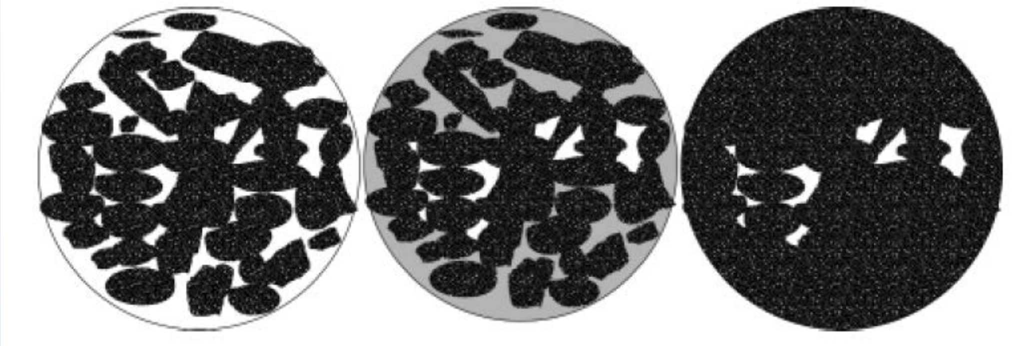


Oedeometer for simulating pore pressure (500 bar) + overburden stress (100 bar).

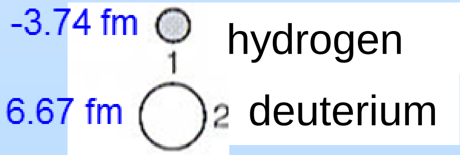
LANL-Developed Pressure Systems

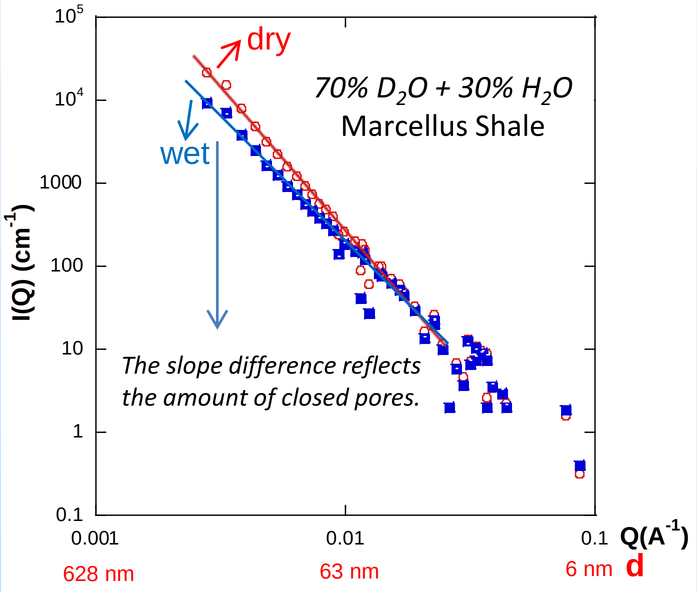
Develop an Approach to Distinguish Open vs. Closed Shale Nano-Pores

- SANS/USANS signals reflect the difference in scattering length density between the rock matrix and the pore space of a rock.
- Sensitive to isotopes, especially H & D (opposite signs of neutron scattering).
- Use a H/D mixture (e.g. H_2O/D_2O & CH_4/CD_4) to match the scattering of the rock matrix to reveal ***closed versus open pores*** — *Contrast Matching*.

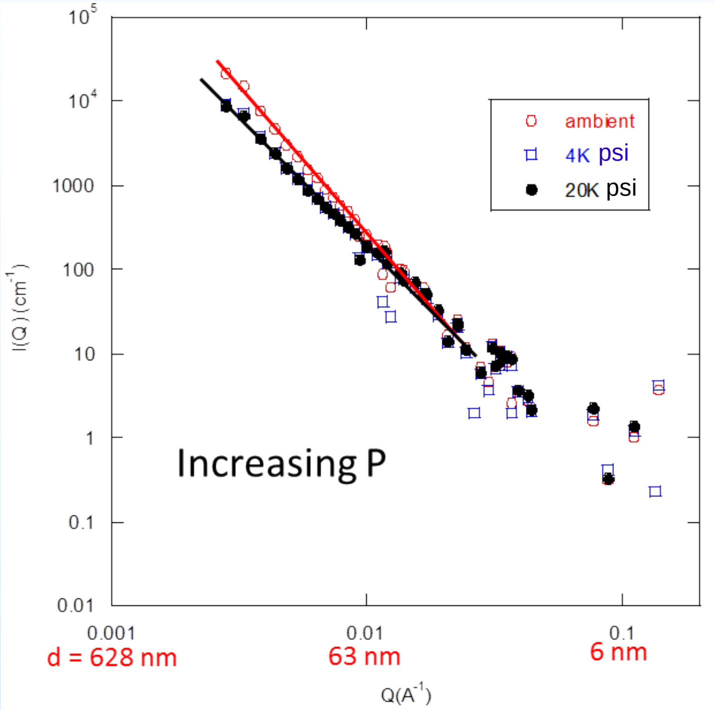


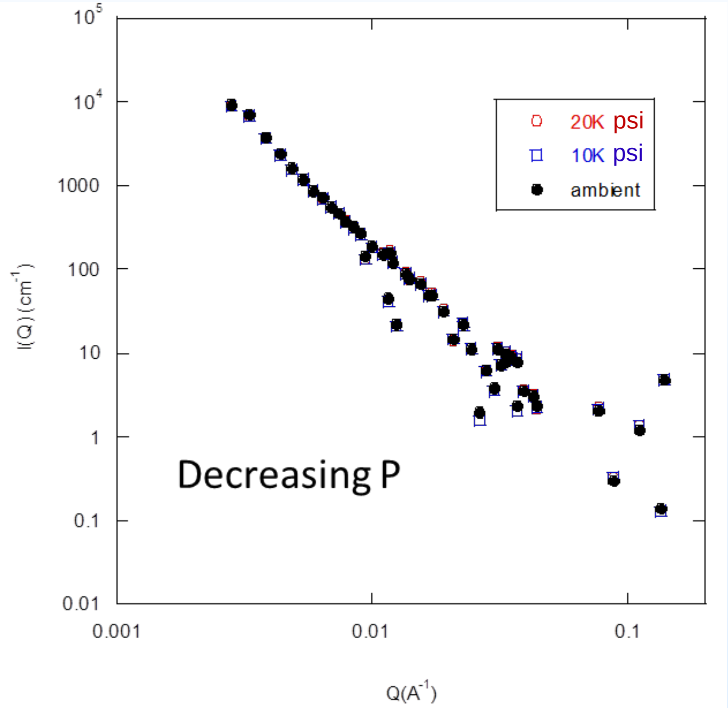
neutron scattering





Water Imbibition – Water Stays in the Matrix

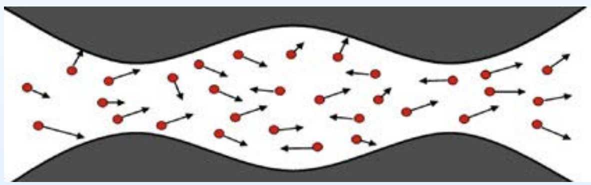




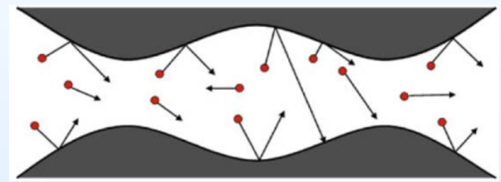
- Higher pressures (> 4K psi) had little effect.
- Water entered into larger pores (tens of nm).
- On decreasing P, water remained in the pores.

LBM Modeling of Gas Flow in Shale Matrix

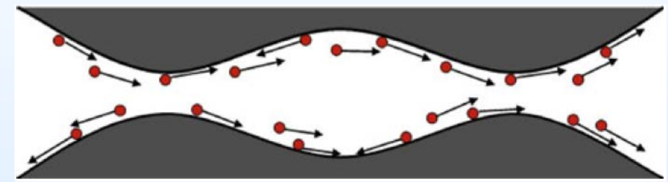
- **Dusty gas model (a superimposition model):** Gas flow through nanopores consists of contributions from viscous flow, Knudsen diffusion & surface diffusion.



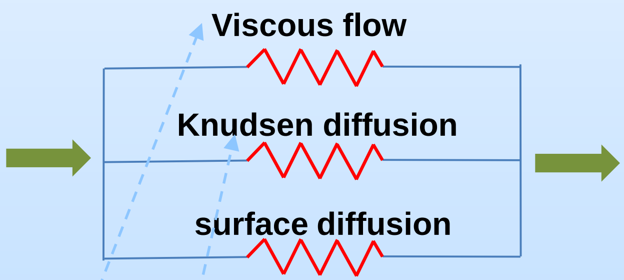
Viscous flow



Knudsen diffusion



Surface diffusion



f_c

$$J = J_d + J_k = -k_d \left(\boxed{1 + \frac{D_{k,eff}\,\mu}{p k_d}} \right) \frac{\rho}{\mu} \nabla p$$

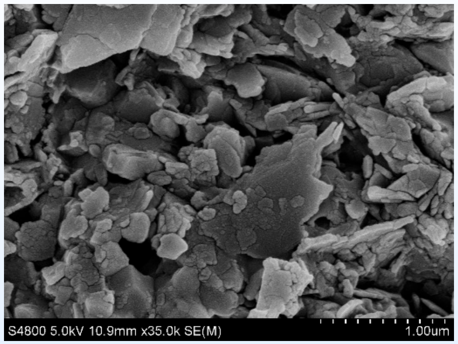
Cunningham & Williams (1980)

Correction Factor

$$f_c = k_a / k_d = 1 + \frac{D_{k,eff}\,\mu}{p k_d}$$

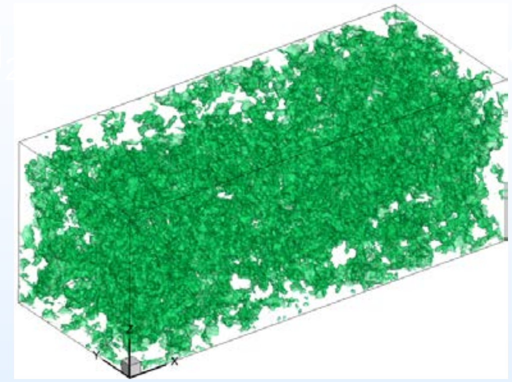
- For conventional porous media, apparent permeability k_a = intrinsic permeability k_d, correction factor = 1.
- For tight formations, $k_a > k_d$.
- The traditional, Darcy's law underestimates the gas transport rate in shale matrix.

Develop a Predictive Method for Modeling Gas Flow in Shale Matrix

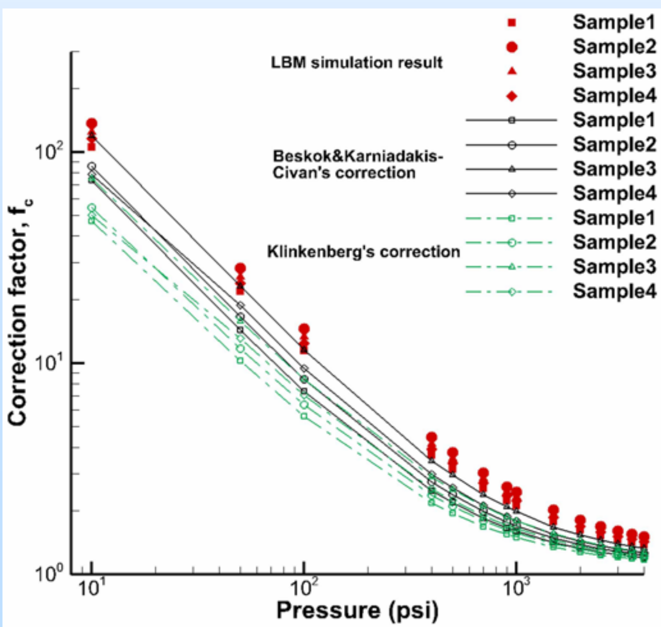


SEM image of a shale

Markov Chain Monte Carlo (MCMC) method (2.8 nm/pixel)

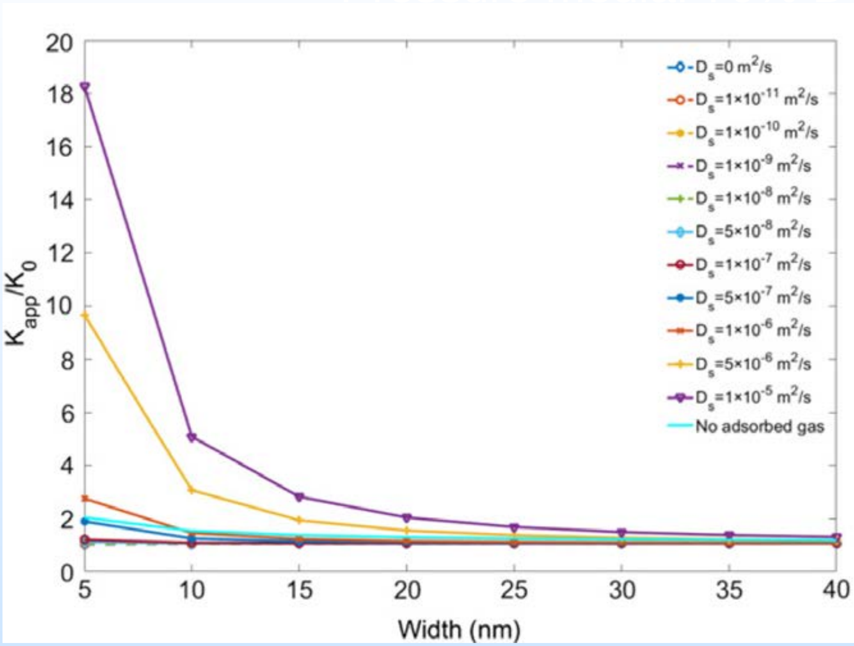


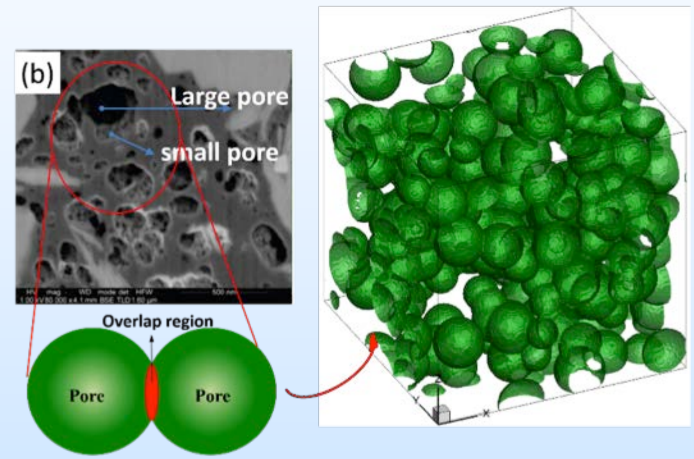
Reconstructed 3D pore structure



- The correction factors can be up to 100, depending on the pressure.
- Decreasing pressure can increase the matrix flow ability by 100 times — Wellbore pressure cycling to increase the production?
- First numerical study – providing a predictive capability.

Effect of Surface Diffusion on Gas Flow

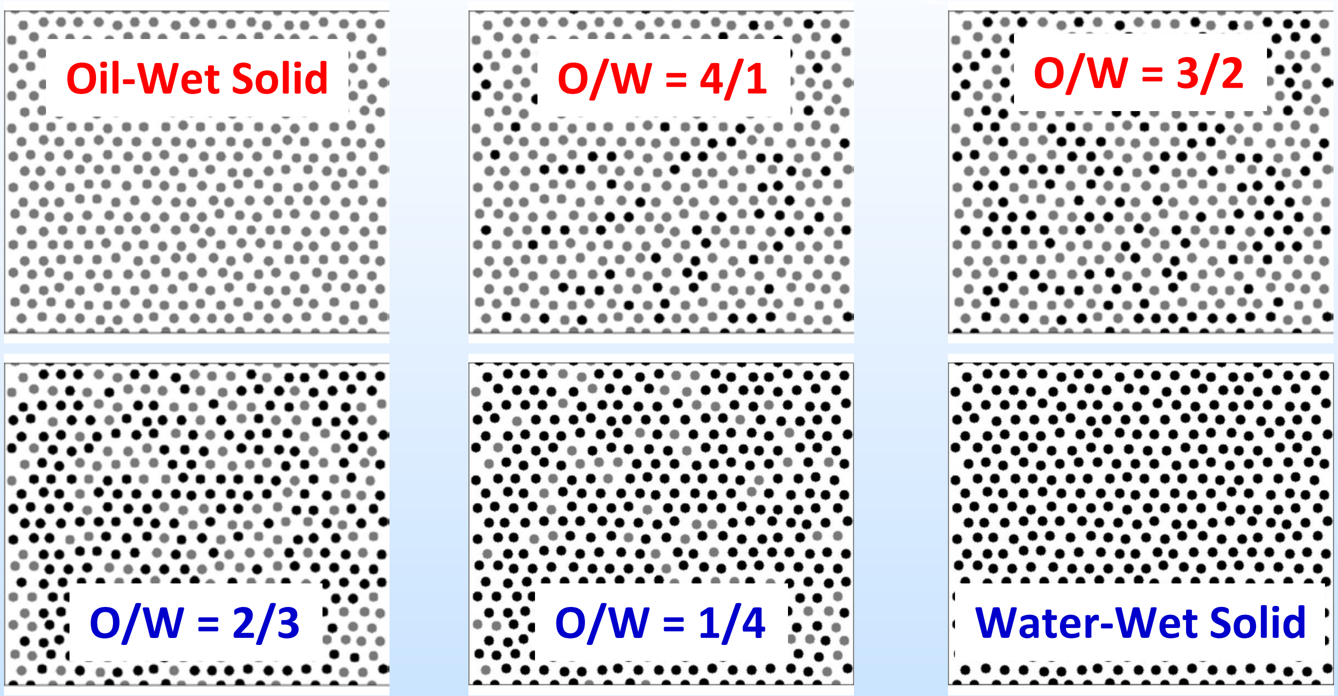




- Surface diffusion of the adsorbed gas in kerogen nanopores can enhance or reduce the apparent permeability. Most obviously, it enhances the permeability for smaller pores and higher diffusivities.

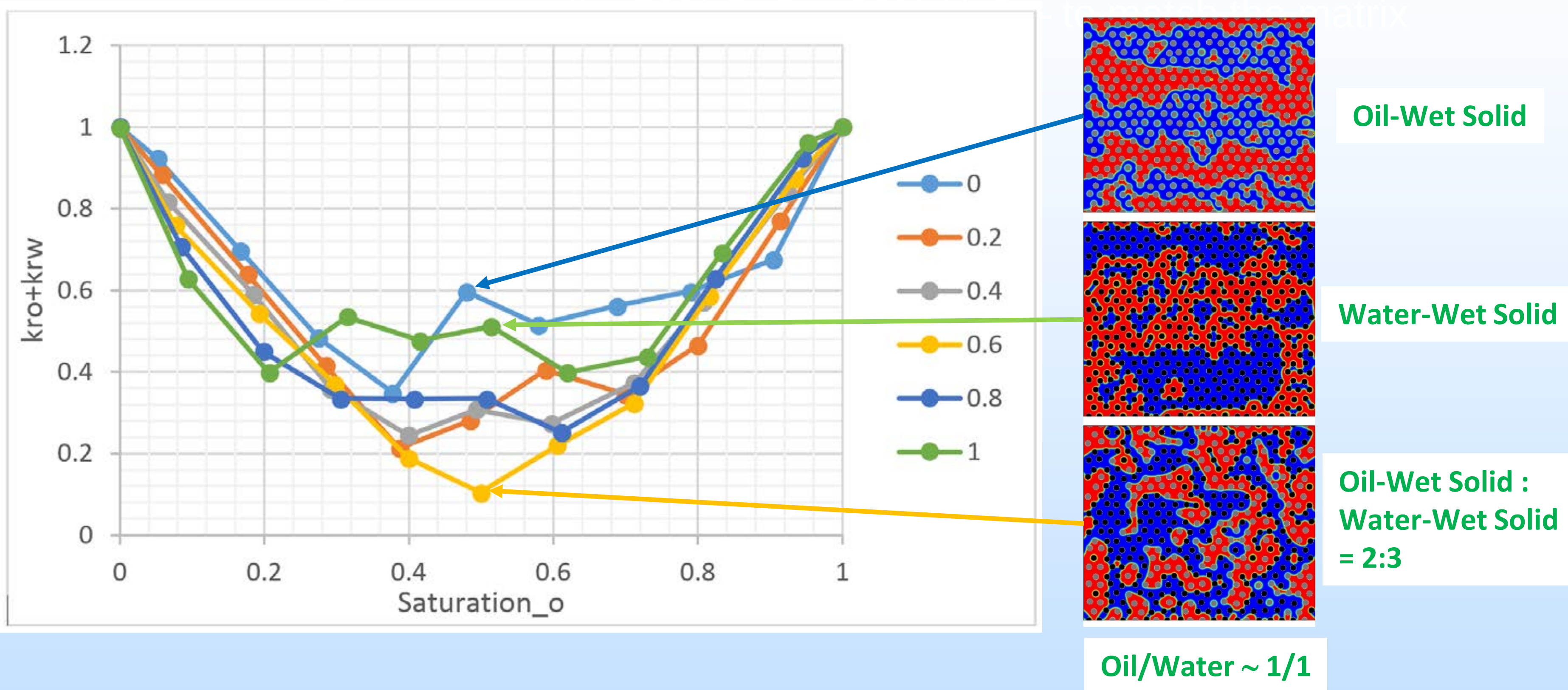
Effect of Mixed Wettability on the Relative Permeability of Oil-Water flow

Pressure media: 70% D_2O + 30% H_2O – to match the matrix



Porous media with different wettability properties. Grey color denotes oil wet and black color water wet. The fractions of water wet solids are 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively, from top left to bottom right.

Flow Blockage of Two-Phase Fluids (Oil/Gas – Water)



When the oil saturation is moderate (0.3-0.7), the total relative permeability of the mixed wet porous media is smaller than that of the purely oil-wet or water-wet porous media, indicating higher resistance to oil-water flow.

Accomplishments to Date

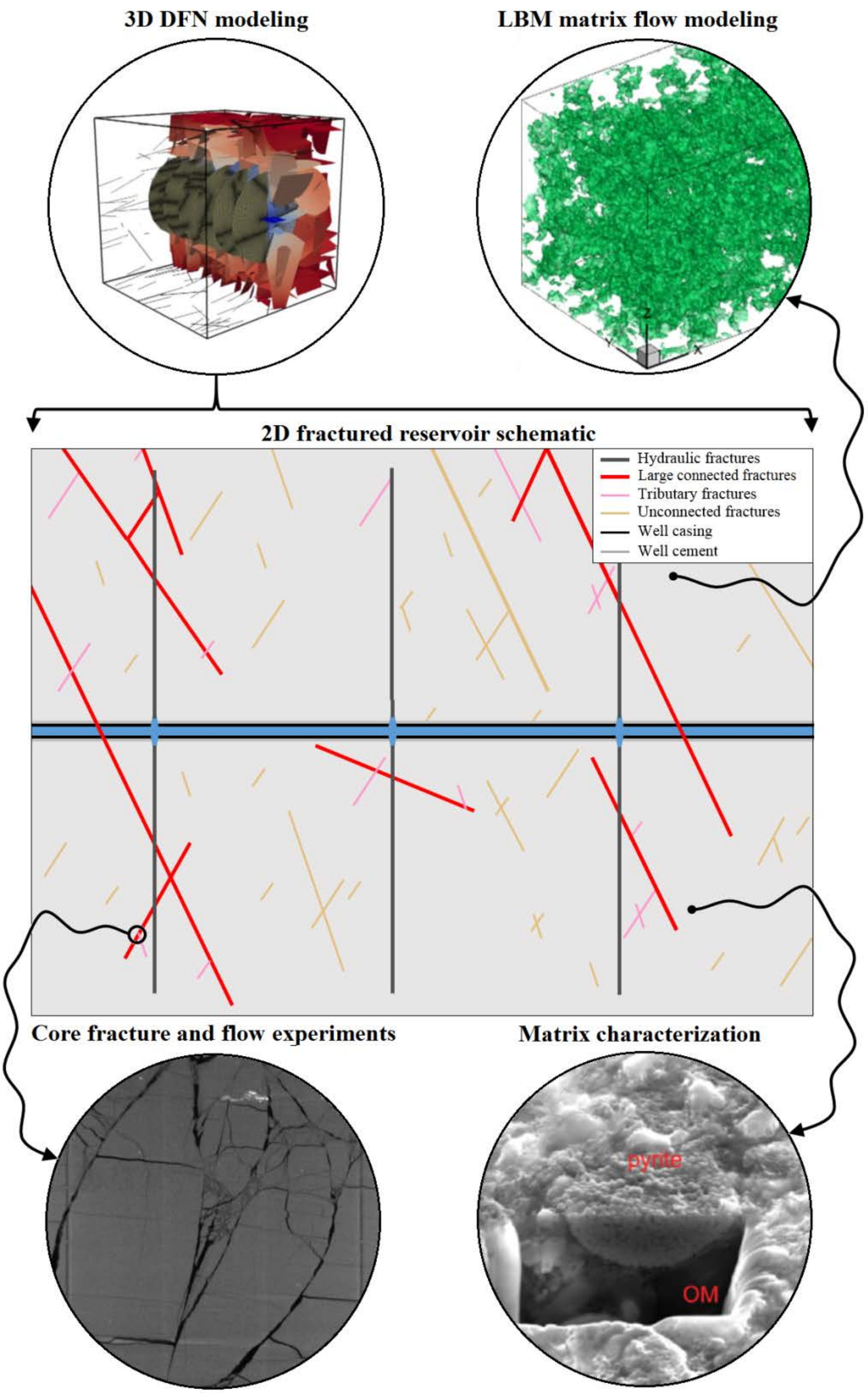
- Developed a capability/approach to measure open vs. closed shale nanopores at reservoir conditions — important for better estimating original gas/oil in place.
- Examined the water imbibition phenomenon in shale matrix — important for addressing the question of 'where does the water go during fracking?'.
- Discovered the enhanced gas flow ability in shale matrix by 100 times via decreasing pressure — wellbore pressure cycling to increase gas production?
- Predicted the reduced total relative permeability of mixed wet porous media compared to that of a purely oil-wet or water-wet medium — higher resistance to two-phase oil/gas-water flow.

Synergy Opportunities

- Multi-Lab Synergies and Collaborations on Unconventional Gas/Oil Research
  - Common field site: Marcellus and MSEEL
  - Sample sharing: Avoid redundant sample characterization and provide/share complementary information obtained with different techniques
  - Geochemistry/mineralogy collaboration between LANL, SLAC, Sandia, LBL and NETL.
- Synergies with CO_2 Sequestration (caprock properties)

Project Summary

- **Key Findings**
  - Determination of open vs. closed shale nanopores is important for better estimating original gas/oil in place and for predicting well production performance.
  - While increasing pressure generally opens fractures to facilitate gas flow, decreasing pressure can also enhance gas flow in shale matrix. This finding suggests the production can potentially be increased via wellbore pressure cycling.
- **Next Steps**
  - Characterize open/closed nanopores for a set of representative shale lithologies and link the characteristics with the production data.
  - Predict the gas flow in shale matrix based on the determined nanopore structures and incorporate the results into DFN modeling to simulate the production curve.


3D DFN modeling
LBM matrix flow modeling
2D fractured reservoir schematic
Hydraulic fractures
Large connected fractures
Tributary fractures
Unconnected fractures
Well casing
Well cement
Core fracture and flow experiments
Matrix characterization
pyrite
OM

Questions?

Appendix: Benefit to the Program

- Program goals being addressed:

  The magnitude of the natural gas resource recoverable from domestic fractured shales has only been recognized within the past decade as a combination of drilling and well completion technology advancements, which have made it possible to produce gas from shales at economic rates. NETL research efforts focus on further refining these technologies, characterizing the geology of emerging shale plays, and accelerating the development of technologies that can reduce the environmental impacts of shale play development.

- Project benefits statement:

  This research project is developing an approach for characterizing shale nanopore structures and their confined fluid behavior with high fidelity. The obtained new knowledge will reveal the key factors controlling the production tail and thus will help develop optimum long-term field production strategies to enhance hydrocarbon recovery.

Appendix: Project Overview

Goals and Objectives

- Develop a fundamental understanding of what controls hydrocarbon transport at different scales, using an integration of experimental and modeling methods.
  - Experimental studies and pore-scale modeling of shale matrix nanopore structures and their fluid behavior
    - What are the characteristics of shale nanopores?
    - How to better estimate the original gas/oil in place?
    - How do fluids move within the matrix and to fractures?

Appendix: Organization Chart

- George Guthrie (Project Lead)
  - Task 1: Reservoir-scale Modeling (Satish Karra PI)
    - Jeffrey Hyman
    - Nataliia Makedonska
    - Hari Viswanathan
    - Richard Middleton
  - Task 2: Core-scale experiments (Bill Carey PI)
    - Mark Porter
    - Joaquín Jiménez-Martínez
    - Luke Frash
  - Task 3: Micro-scale (Hongwu Xu PI)
    - Li Chen
    - Mei Ding
    - Rex Hjelm
    - Qinjun Kang
    - Rajesh Pawar

Appendix: Gantt Chart

	FY16	FY17	FY18
Understanding Basic Mechanisms in Natural Gas Production using Reservoir-Scale Modeling	Concluded		
Experimental Study of In Situ Fracture Generation and Fluid Migration in Shale.	Concluded		
Probing Hydrocarbon Fluid Behavior in Nanoporous Formations to Maximize Unconventional Oil/Gas Recovery	Concluded		
Assessment of current approaches to understanding Hydrocarbon production		Concluded	
Large-scale fracture controls on hydrocarbon production in the Marcellus shale		On	track
Tributary zone fractures (small-scale) contributions to hydrocarbon production in the Marcellus shale		On	track
Fundamental Matrix Properties in Relation to Predicting Hydrocarbon Migration into Fractured Marcellus Shale		On	track
Integration of Large-Scale Fractures, Tributary Fractures and the Matrix			

Appendix: Bibliography

- Wang, J., Kang, Q., Chen, L., and Rahman, S. S., 2017, Pore-scale lattice Boltzmann simulation of micro-gaseous flow considering surface diffusion effect. International Journal of Coal Geology, v. 169, p. 62-73.
- Wang, J., Kang, Q., Wang, Y., Pawar, R., and Rahman, S. S., 2017, Simulation of gas flow in micro-porous media with the regularized lattice Boltzmann method. Fuel, in press.
- Li, Z., Min, T., Kang, Q., He, Y., and Tao, W., 2016, Investigation of methane adsorption and its effect on gas transport in shale matrix through microscale and mesoscale simulations. International Journal of Heat and Mass Transfer, v. 98, p. 675-686.
- Wang, J., Chen, L., Kang, Q., and Rahman, S. S., 2016, Apparent permeability prediction of organic shale with generalized lattice Boltzmann model considering surface diffusion effect. Fuel, v. 181, p. 478-290.
- Chen, L., Hyman, J.D., Zhou, L., Min, T., Kang, Q., Rougier, E., and Viswanathan, H., 2016, Effect of fracture density on effective permeability of matrix-fracture system in shale formations. AGU books, in press.
- Wang, J., Chen, L., Kang, Q., and Rahman, S. S., 2016, The lattice Boltzmann method for isothermal micro-gaseous flow and its application in shale gas flow: A review. International Journal of Heat and Mass Transfer, v. 95, p.94-108.