

# Mechanistic Approach to Analyzing and Improving Unconventional Hydrocarbon Production

**U.S. Department of Energy  
National Energy Technology Laboratory  
Mastering the Subsurface Through Technology Innovation,  
Partnerships and Collaboration:  
Carbon Storage and Oil and Natural Gas Technologies Review Meeting  
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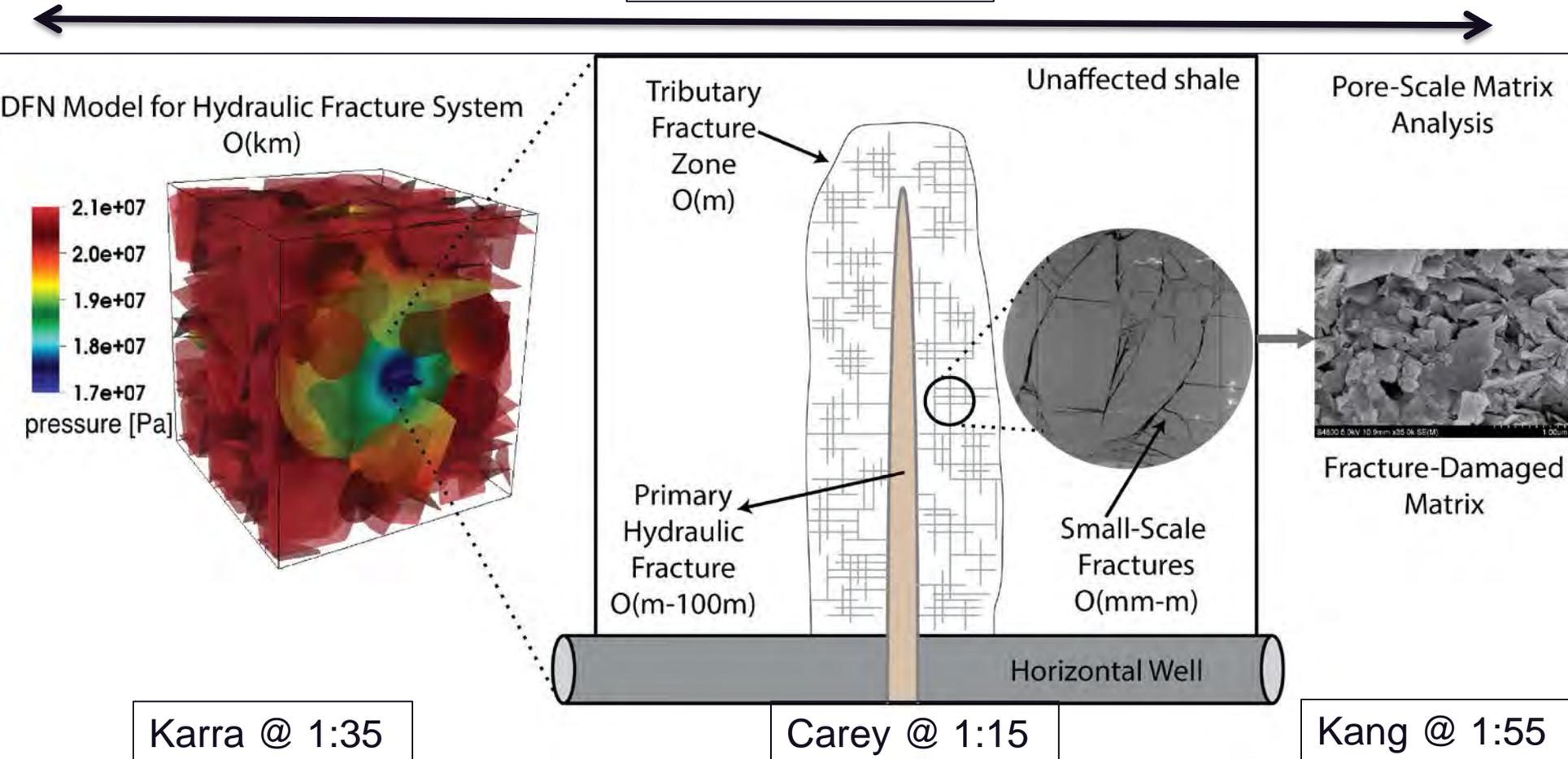
Part 3: Fundamental Matrix Properties in Relation to Predicting Hydrocarbon Migration into Fractured Marcellus Shale  
Presented by Qinjun Kang



# Overview of Project

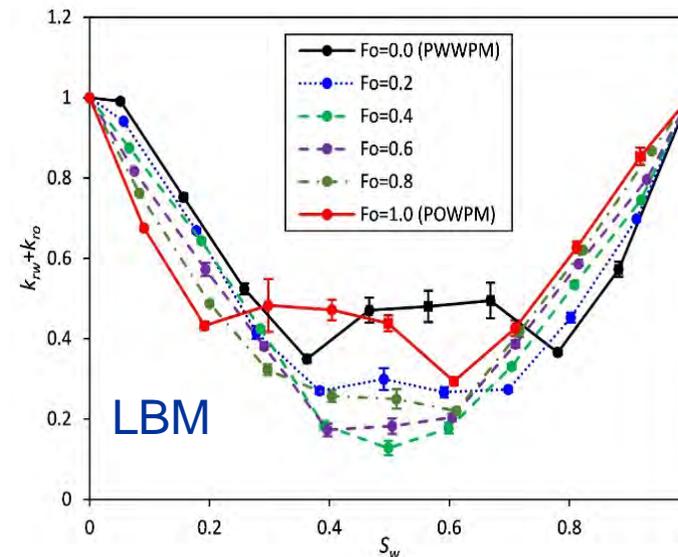
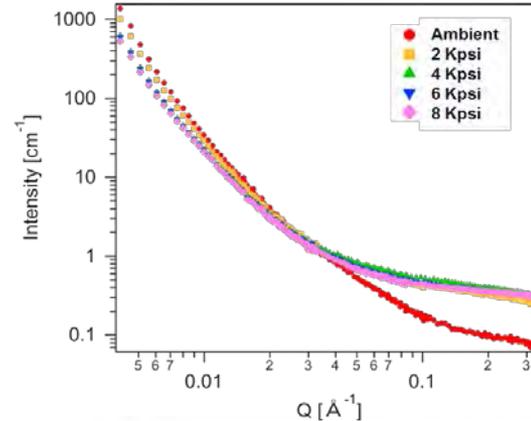
*Target: Enable technological solutions to improve recovery efficiency through an improved fundamental understanding*

## Across Scales

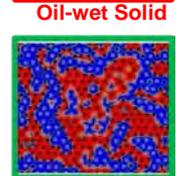
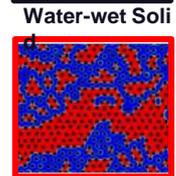
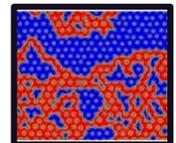


# Technical Status: Fundamental Matrix Properties Studies

- Completed development of experimental apparatus and protocols to probe pores and fluids using neutrons
- Simulated pore-scale transport using Lattice Boltzmann method to elucidate transport phenomena in shale-matrix



Oil/Water ~ 1/1



Oil-wet:Water-wet = 2:3

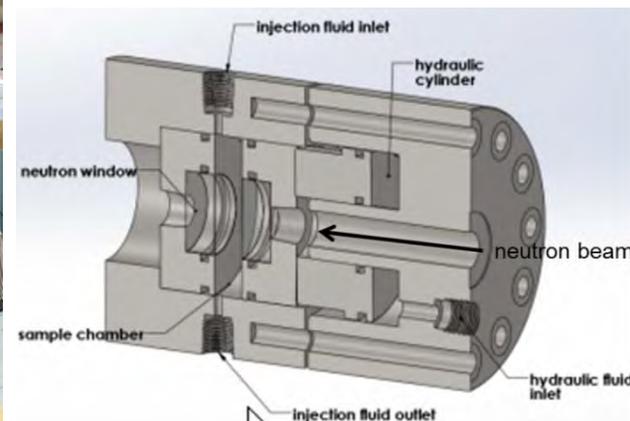
# Shale Nanopore Characterization using SANS

## Conventional Techniques

- Gas adsorption / mercury intrusion: limited to measuring open pores
- TEM: requires thin specimens that are transparent to electron beams and only measures a small area

## Small-Angle Neutron Scattering (SANS)

- Neutrons are highly penetrating and are sensitive to hydrogen
  - Probing samples at depths
  - Ease of combination with sample environments (e.g. pressure cells)
  - An ideal tool for studying hydrocarbons and water

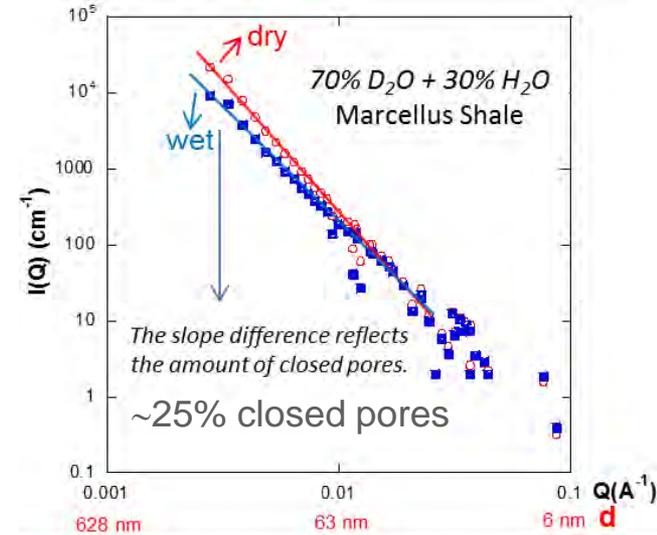
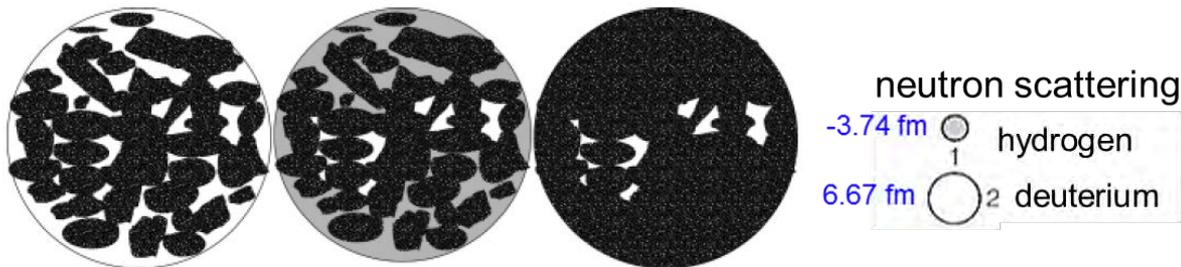


Flow-through compression cell for simulating pore pressure (500 bar) + overburden stress (100 bar).

## LANL-Developed Pressure Systems

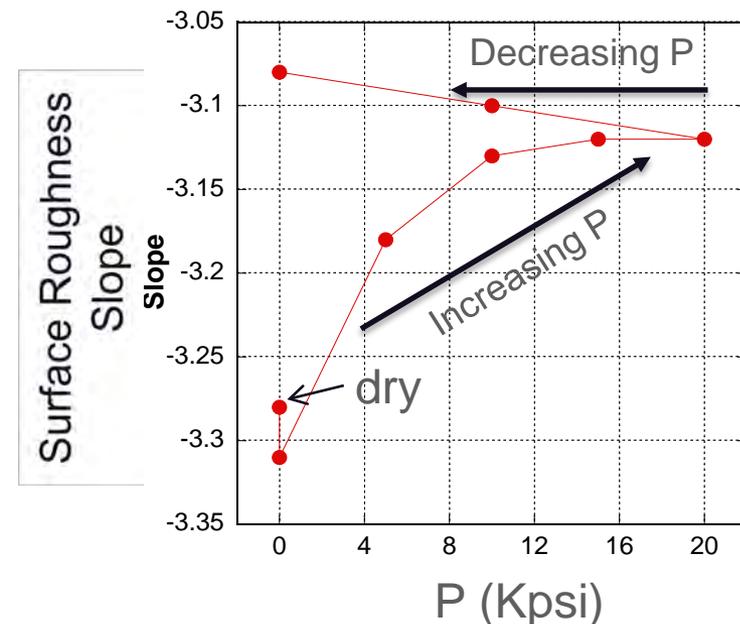
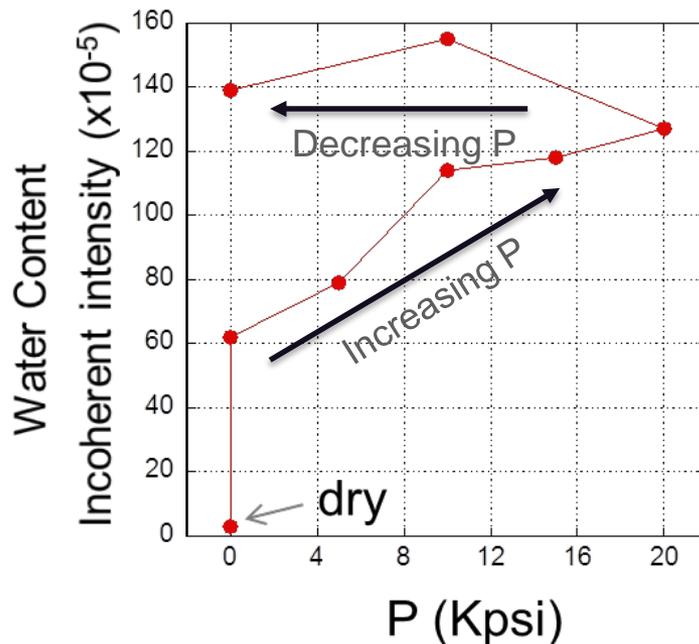
# Distinguish Open vs. Closed Shale Nanopores

- Developed a neutron-based approach to distinguish and quantify open vs. closed nano-pores at reservoir conditions – important for better estimating original gas/oil in place and predicting well production performance.
  - Used a H/D mixture (e.g.  $H_2O/D_2O$ ) to match the SANS/USANS intensities of the rock matrix to reveal closed versus open pores - *Contrast Matching*.



# Water Imbibition – Water Stays in the Matrix

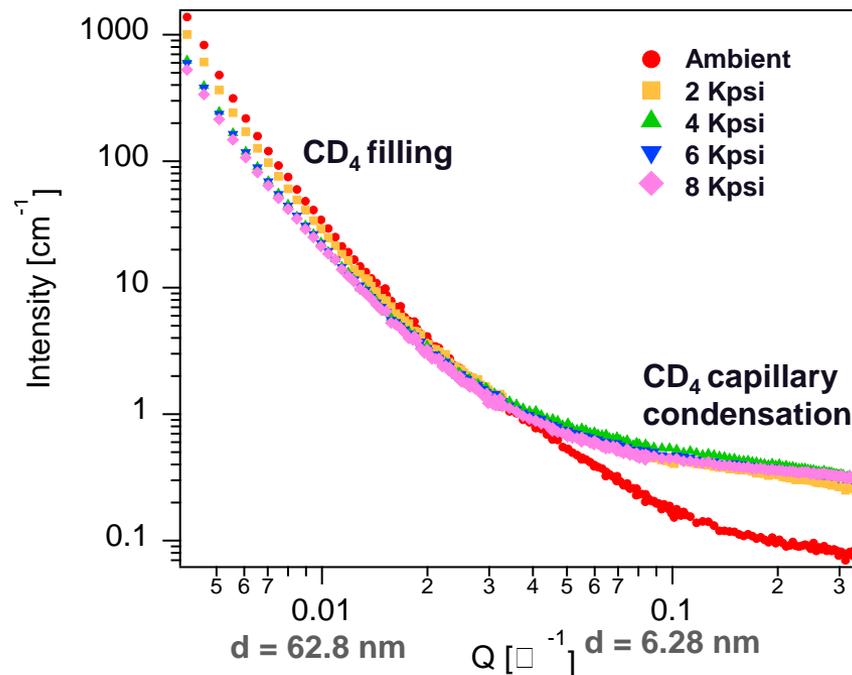
- Examined the “water imbibition” phenomenon in shale matrix – important for addressing the question of ‘where does the water go during fracking?’
  - SANS: Upon pressure cycling, water stays in the matrix (left), and the pore surfaces become rougher (right).
  - Implication: Does “water imbibition” potentially lead to fracture narrowing/closing and thus impede hydrocarbon flow? Is a non-aqueous fracking fluid better?



Slope for a smooth surface: 4  
Slope for a fractal surface: 3

# Methane Condensation in Shale Nanopores

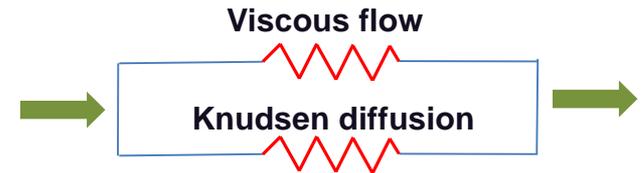
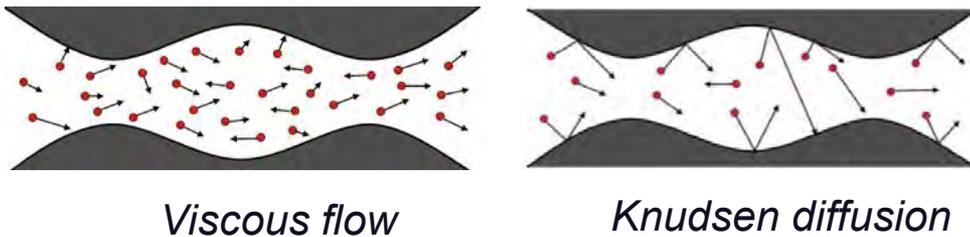
- Examined shale matrix – gas interactions at high pressures – important for improved estimation of original gas in place and development of better field production strategies to enhance hydrocarbon recovery
  - SANS: At low  $Q$ , the intensities decrease with increasing pressure ( $\text{CD}_4$  filling); At high  $Q$  (small  $d$ ), this trend is reversed, suggesting capillary condensation of  $\text{CD}_4$  in smaller pores.
  - Implication: More gas may exist in the reservoir than currently estimated



MSEEL Sample  
(Marcellus)

# Dusty Gas Model (DGM) for Gas Flow in Nanopores of Inorganic Minerals

- DGM is a superimposition model:** Gas flow through nanopores consists of contributions from viscous flow and Knudsen diffusion Cunningham & Williams (1980)



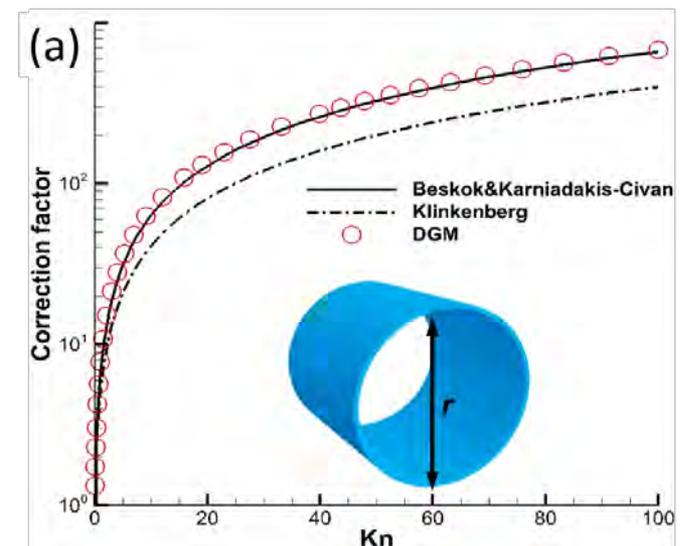
$$J_a = J_d + J_k = -k_d \left( 1 + \frac{D_{k,\text{eff}} \mu}{p k_d} \right) \frac{\rho}{\mu} \nabla p = -k_a \frac{\rho}{\mu} \nabla p$$

↓

**Correction Factor**  $k_a / k_d \equiv f_c$

➤ Gas flow in a tube

$$f_c = k_a / k_d = 1 + \frac{64}{3\pi} Kn$$



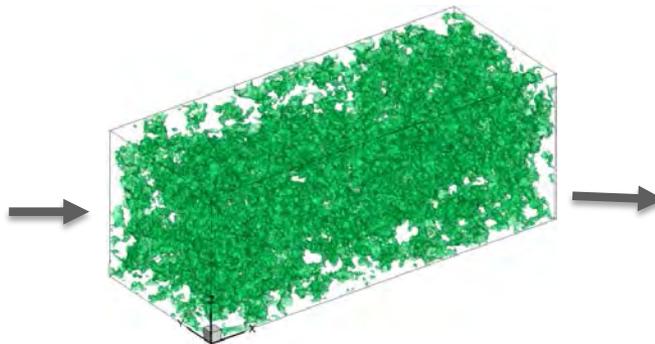
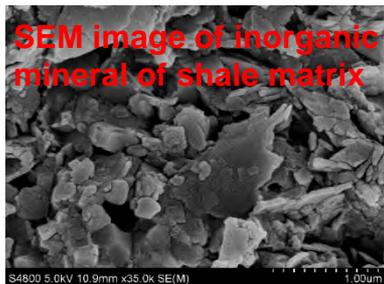
# First LB Model Based on the DGM

- Physics-based model for predicting apparent permeability at the pore scale
  - Consistent with existing empirical relations.
  - Can significantly reduce the number of experimental measurements
  - The gas flow ability in shale matrix can be enhanced by 100 times via decreasing pressure — wellbore pressure cycling to increase gas production.

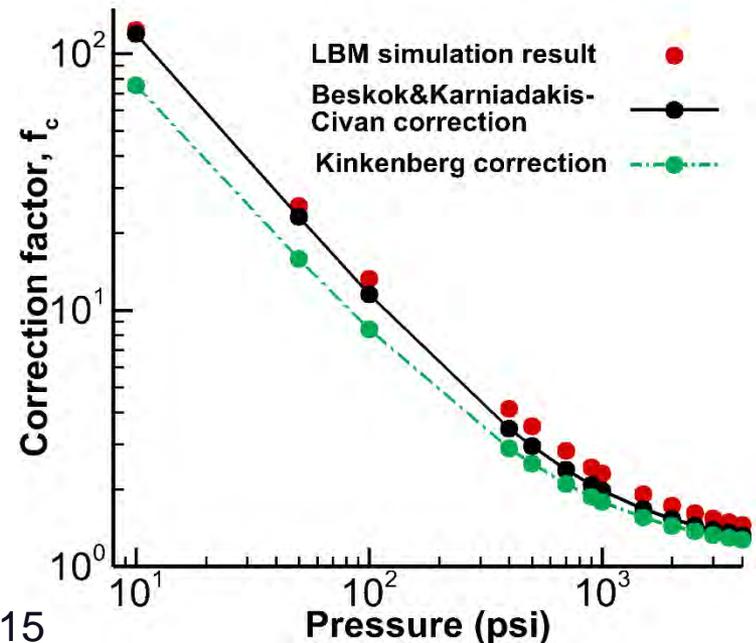
Solve pore-scale flow  $\longrightarrow k_d$

Solve pore-scale diffusion  $\longrightarrow D_{k,eff}$

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



Chen et al. Sci. Reports, 2015

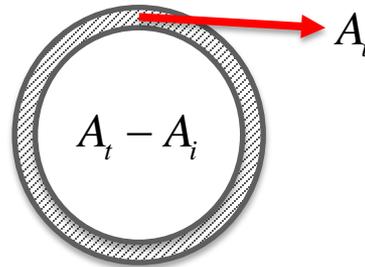


# LBM for Flow in Nanopores Based on Slip Length and Effective Viscosity

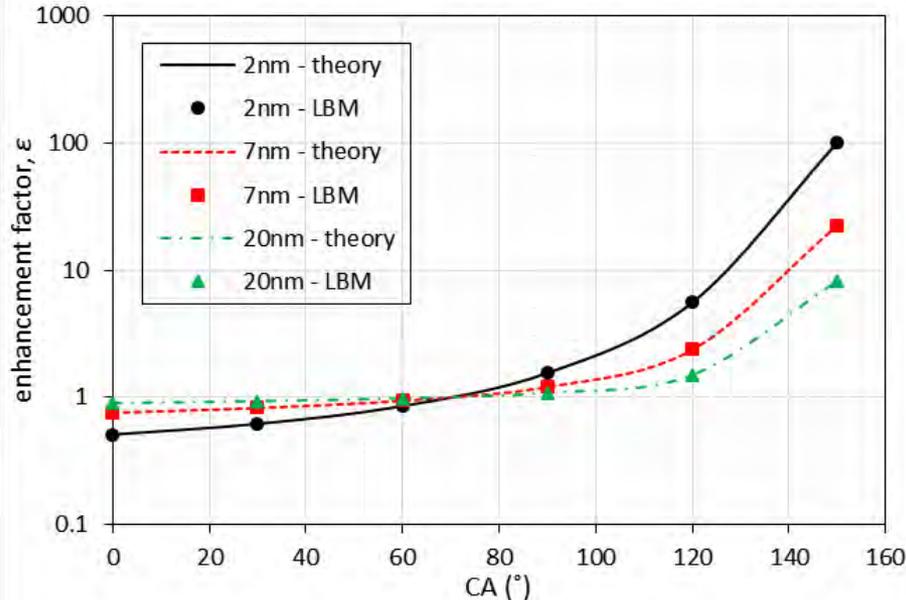
- Applicable to both gas and liquid

slip length and effective viscosity

$$\mu_{eff} = \mu_i \frac{A_i}{A_t} + \mu_\infty \left( 1 - \frac{A_i}{A_t} \right)$$



Wu et al. PNAS, 2017

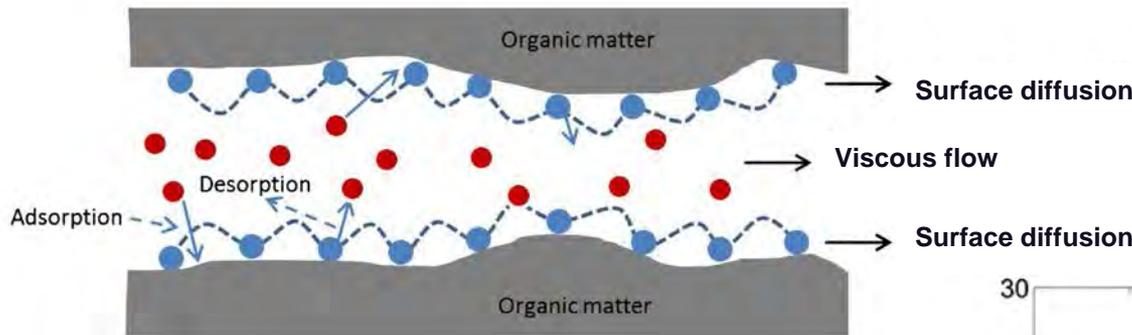


Enhancement factor  $\varepsilon$  ( $Q_{nano}/Q_{intrinsic}$ ) as a function of fluid-solid interaction force (contact angle). The nanoscale effect can either decrease or significantly increase water flux in the nanochannel, depending on the water-solid interaction force.

Zhao et al., IJHMT, 2018

# Effect of Surface Diffusion on Gas Flow in Kerogen Pores

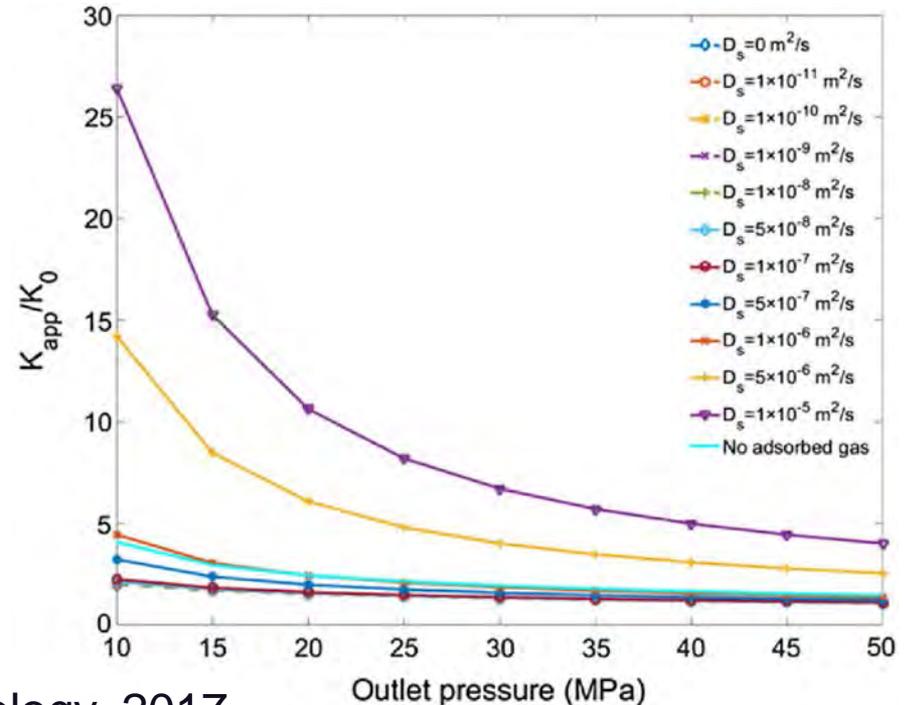
- Built on the LBM based on slip length and effective viscosity



Combined Maxwell-Stefan approach and Langmuir adsorption theory

$$u_{surface} = \frac{N_{surface}M}{\rho_{ads}} = \frac{q_{sat}M}{\rho_{ads}} \frac{bD_s}{1 + bP} \nabla P$$

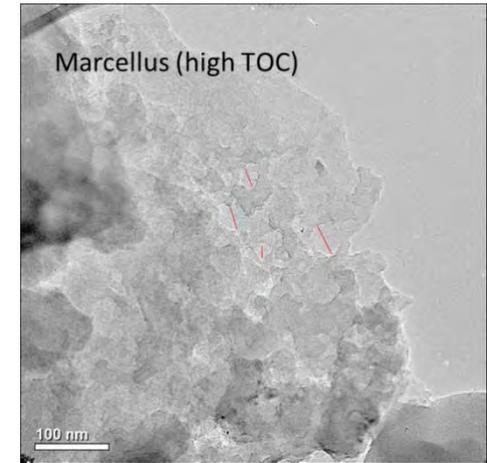
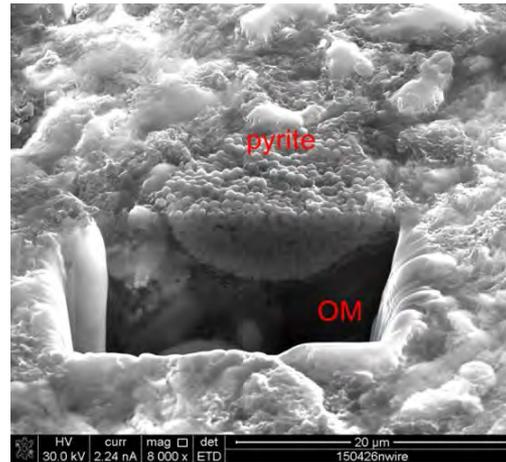
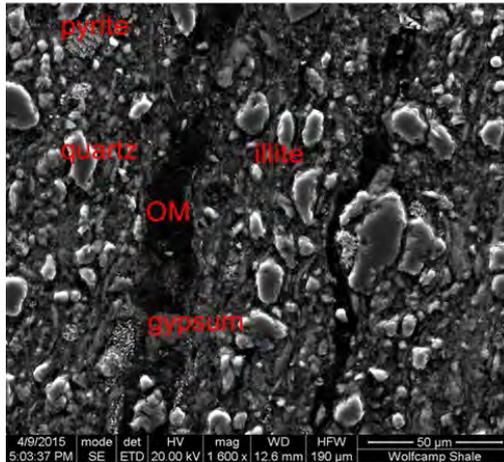
Surface diffusion of adsorbed gas can enhance the apparent permeability even at high pressure



Wang et al. Int. J. Coal Geology, 2017

# Two phase flow: Effect of Wettability Heterogeneity

In many situations, the shale matrix is non-uniformly (fractionally) wet. They can be generated due to the mineralogy heterogeneity or the organic species adsorption over the rock surfaces.



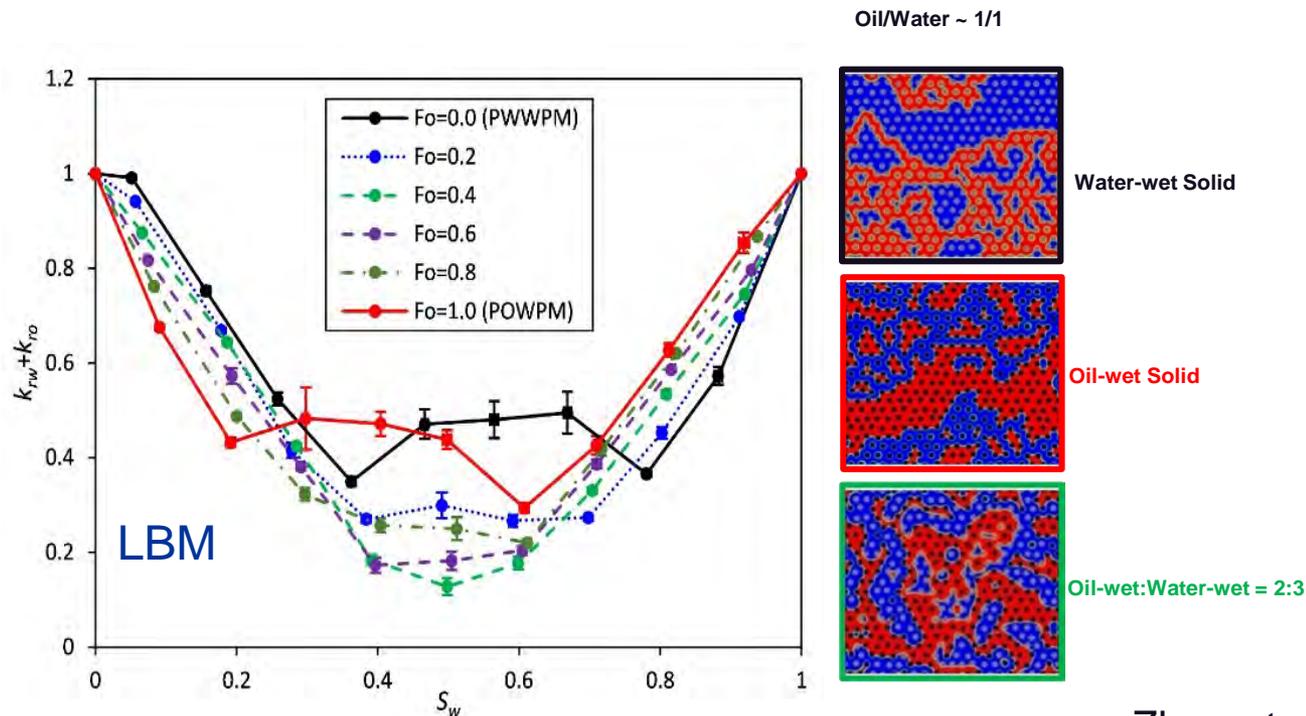
Xu et al. unpublished

Mineralogy heterogeneity induced fractional wettability

Organic species adsorption induced fractional wettability

# LBM Simulation of Effect of Wettability Heterogeneity

- Predicted the reduced total relative permeability of mixed (fractionally) wet porous media (Shale) compared to that of a purely oil-wet or water-wet medium.
  - LBM: Shale matrix exhibits high resistance to oil-water flow by a factor of  $\sim 3$ .
  - Implications: Non aqueous fracturing technologies (e.g.,  $\text{CO}_2$ ) may be more effective for shale hydrocarbon recovery.



Zhao et al., WRR, 2018

# Accomplishments to Date

- Developed a capability to study shale nanopores and the fluids using SANS at reservoir conditions.
- Examined the “water imbibition” phenomena.
- Examined shale matrix – methane interactions at high pressures.
- Developed the LB model based on the DGM for predicting apparent permeability of complex nanoporous media.
- Developed a LB model for flow in nanochannels applicable for both liquid and gas and accounting for surface diffusion.
- Predicted the reduced total relative permeability of mixed wet porous media (shale) compared to pure oil or water wet media.

# 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<sub>2</sub> 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.
- Examination of shale matrix – methane interactions at high pressures revealed gas capillary condensation in smaller pores.
- While increasing pressure generally opens fractures to facilitate gas flow, decreasing pressure can also enhance gas flow in shale matrix, suggesting the production can potentially be increased via wellbore pressure cycling.
- Surface diffusion of adsorbed gas can enhance the apparent permeability even at high pressure.
- As mixed (fractionally) wet porous media, shale exhibits reduced total relative permeability compared to that of a purely oil-wet or water-wet medium, suggesting non aqueous fracturing technologies (e.g., CO<sub>2</sub>) may be more effective for shale hydrocarbon recovery.

# Project Summary

- **Next Steps**

- Characterize open/closed nanopores for a set of representative shale lithologies using hydrocarbon/water as the pressure media and link the results with the production data.
- Apply the LBM to quantify the contributions from nano/meso processes using experimentally determined matrix pore structures.
- Apply the LBM to quantify the effects of pore-scale mineralogy and heterogeneity on apparent permeability.
- Initiate studies of pore-scale chemical reactions using SANS and LBM simulations.

# 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:**

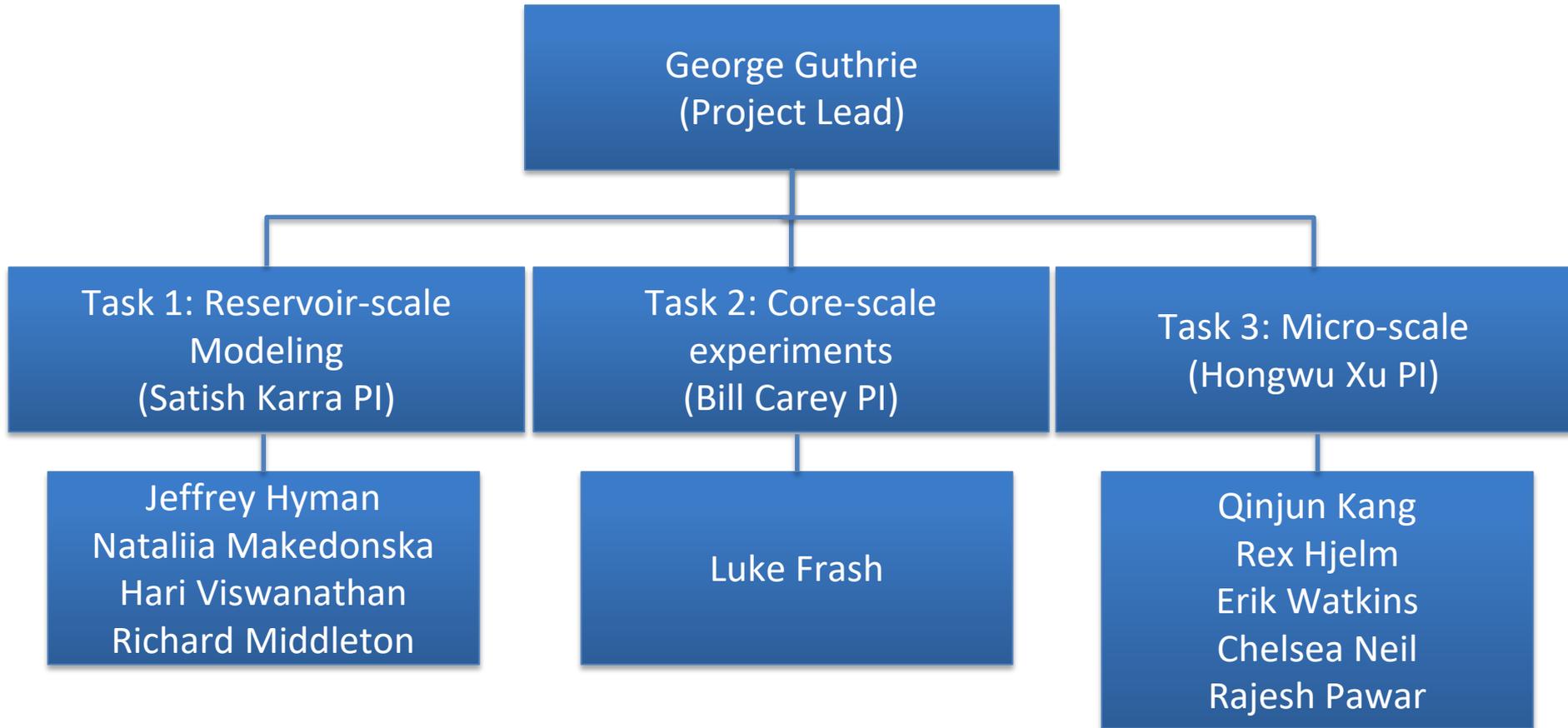
This research project is developing an approach for characterizing shale nanopore structures and their confined fluid behavior with high fidelity. The obtained new knowledge will reveal the key factors controlling the production tail and thus will help develop optimum long-term field production strategies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

# Appendix: Project Overview

## Goals and Objectives

- Characterization of nano-pore structure and nano-porosity of shale matrix
  - employ focused ion beam-scanning electron microscopy (FIB-SEM) to image shale matrix nano-pores and use the obtained images to reconstruct 3D nano-pore structures.
- Quantification of gas–water distribution in shale-matrix pores.
  - employ small-angle neutron scattering (SANS) coupled with high-pressure cells and LBM to quantify gas-water distribution
- Quantification of the effects of nano/meso-scale processes in shale-matrix pores.
  - use LBM simulations to quantify the effects of nano/meso-scale processes, including Knudsen diffusion, adsorption/desorption, and surface diffusion on transport rates of gas molecules in shale-matrix pores.

# Appendix: Organization Chart



# Appendix: Gantt Chart

Gantt Chart		FY16		FY17				FY18					
Task#	Task	Q3	Q4	Q1	Q1	Q2	Q4	Q1	Q2	Q3	Q4	Product	Dependencies
5.0	Fundamental Matrix Properties in Relation to Predicting Hydrocarbon Migration into Fractured Marcellus Shale												Start requires results from 2.3
5.1	Characterization of nano-pore structure and nano-porosity in Marcellus shale matrix					complete						Report detailing the nano-pore structure and porosities in shales.  Refer to the earlier quarterly reports for description of the results.	
5.2	Quantification of gas-water distribution in Marcellus shale-matrix pores											Report detailing the distribution of water and gas in shales as a function of pressure, pore characteristics, pore size, and time	Requires results from 5.1
5.3	Quantification of the effects of nano/meso-scale processes in Marcellus shale-matrix pores											Report detailing the Knudsen effects and other nano/meso processes in shales	Requires results from 5.1
5.4	Integration of matrix contributions to hydrocarbon flow with DFN simulations											Report detailing the potential effects of gas-migration from the matrix on reservoir behavior	Requires results from Tasks 3.1, 3.2, 5.1, 5.2

# Appendix: Bibliography

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