

# Exploring the behavior of shales as seals and storage reservoirs for CO<sub>2</sub>

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Daniel J. Soeder  
USDOE/NETL/ORD

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Developing the Technologies and  
Infrastructure for CCS  
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# Project Overview:

## Goals and Objectives

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- Program Goals
  - Support industry's ability to predict CO<sub>2</sub> storage capacity in geologic formations to within  $\pm 30$  percent.
  - Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness
- Project Objectives
  - Assess how shales behave as caprocks in contact with CO<sub>2</sub> under a variety of conditions
  - Assess the viability of depleted gas shales to serve as storage reservoirs for sequestered CO<sub>2</sub>
  - Determine economic usefulness of CO<sub>2</sub> for enhanced oil or gas recovery in shales

# Benefits to the Program

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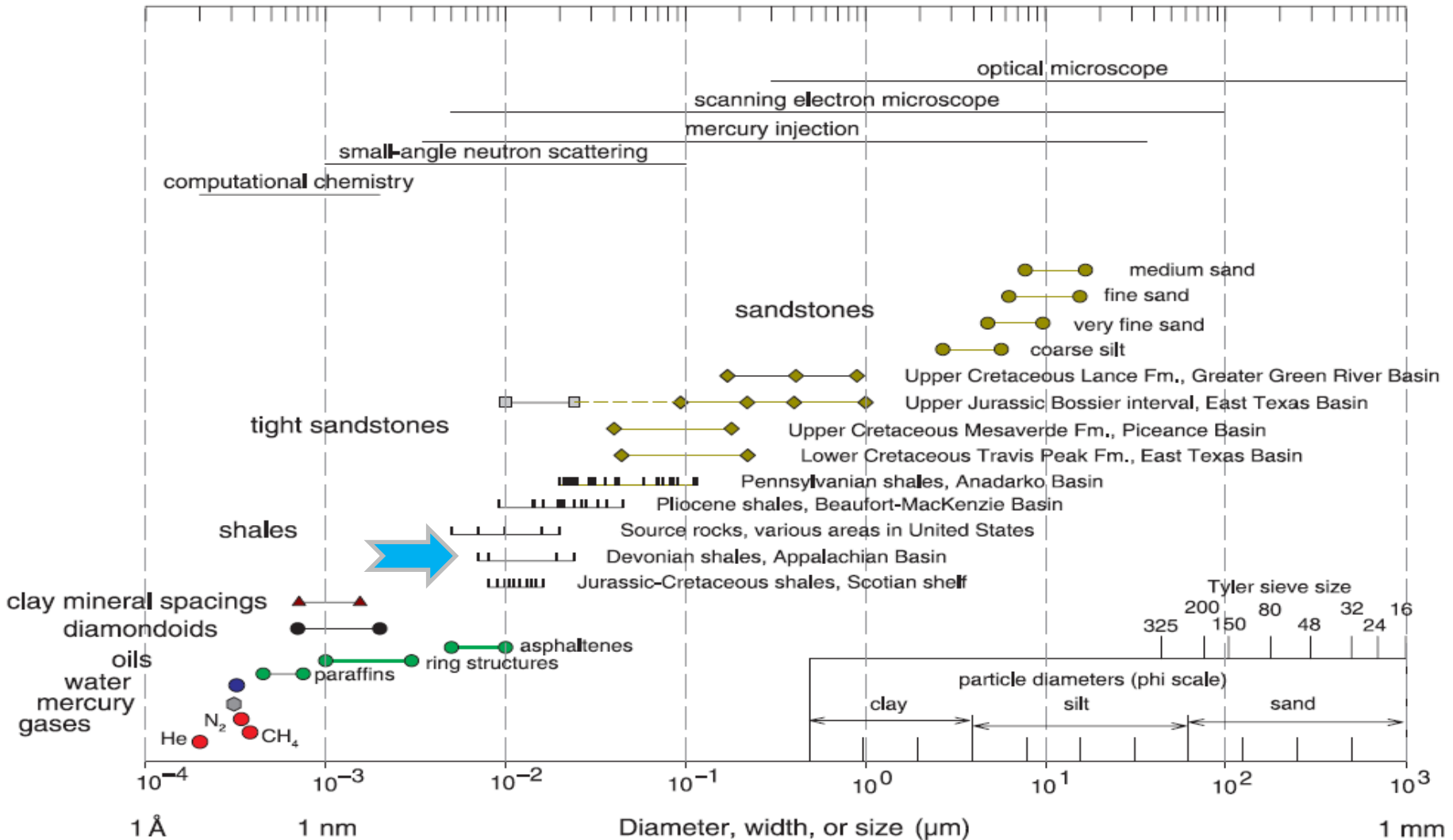
- **Greater confidence of seal integrity in the presence of CO<sub>2</sub>**
- **Reduced uncertainty about what type of shale seal should be sought for CO<sub>2</sub> geologic storage**
- **Develop a methodology to assess basin-scale storage resources in shales using publicly-available data under defined conditions.**

# Technical Status

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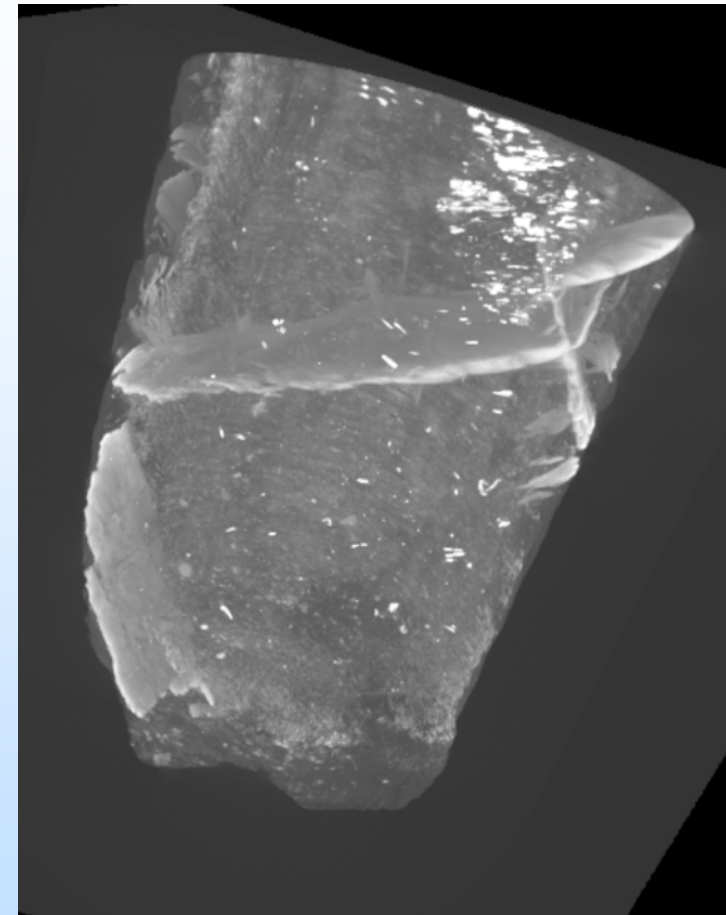
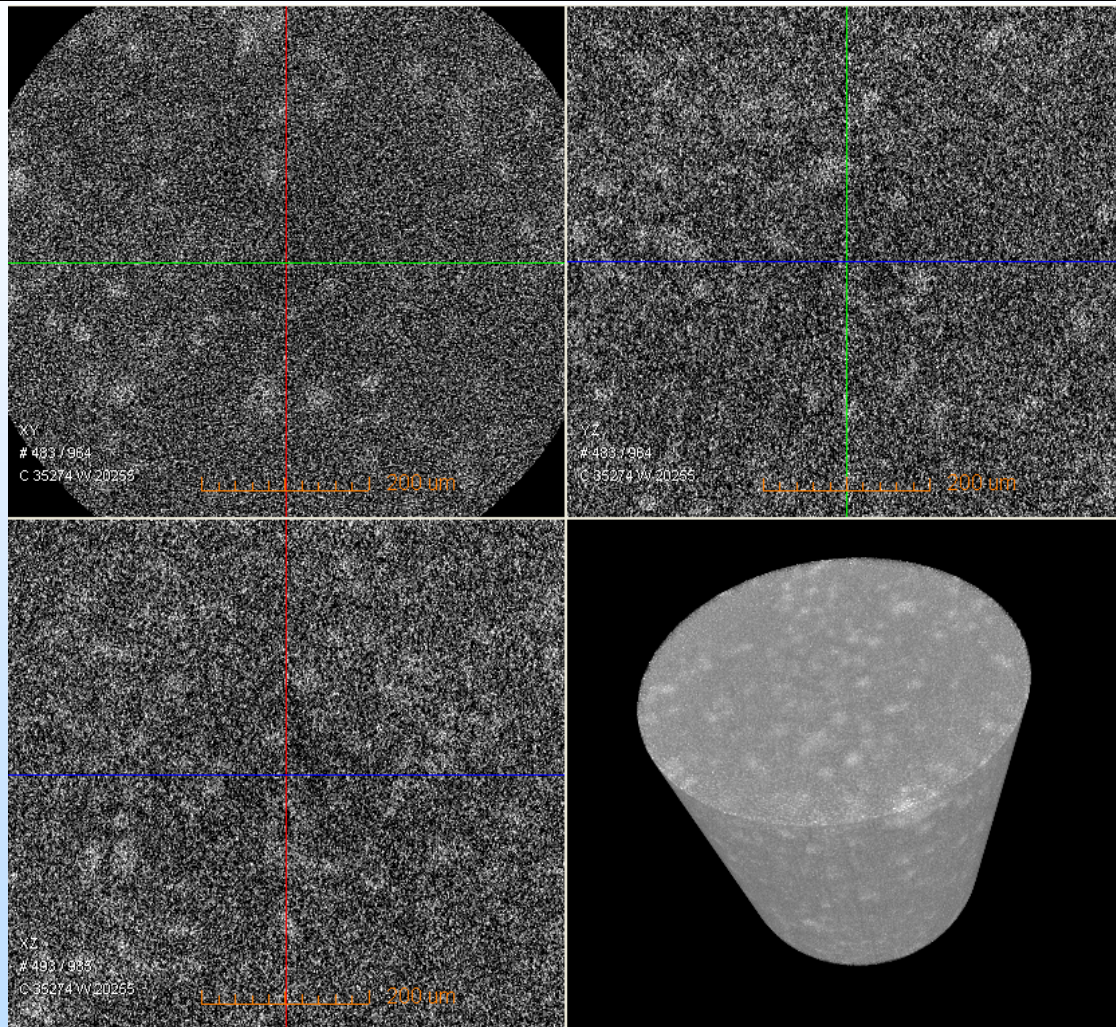
- Understanding shale pore structure
  - Shale pore types and how to visualize
  - Devonian shales have pores in the 5 to 15 nm range
  - How are these pores connected?
- Pores and fluids
  - Capillary pressure and relative permeability of gas versus liquid
  - Behavior of methane versus CO<sub>2</sub> – molecule size, chemical properties
  - Gas adsorbed on organics and clays or dissolved into organics
- Understanding petrophysical behavior of shale
  - Horizontal versus vertical anisotropy
  - Sensitivity to stress
  - Dealing with really low permeability

# Pore Sizes



**Figure 2.** Sizes of molecules and pore throats in siliciclastic rocks on a logarithmic scale covering seven orders of magnitude. Measurement methods are shown at the top of the graph, and scales used for solid particles are shown at the lower right. The symbols show pore-throat sizes for four sandstones, four tight sandstones, and five shales. Ranges of clay mineral spacings, diamondoids, and three oils, and molecular diameters of water, mercury, and three gases are also shown. The sources of data and measurement methods for each sample set are discussed in the text.

# Micro CT Results



Larger flowpaths can be recognized and analyzed.

CT scanning allows for 3D reconstruction of density contrasts.



10  $\mu\text{m}$

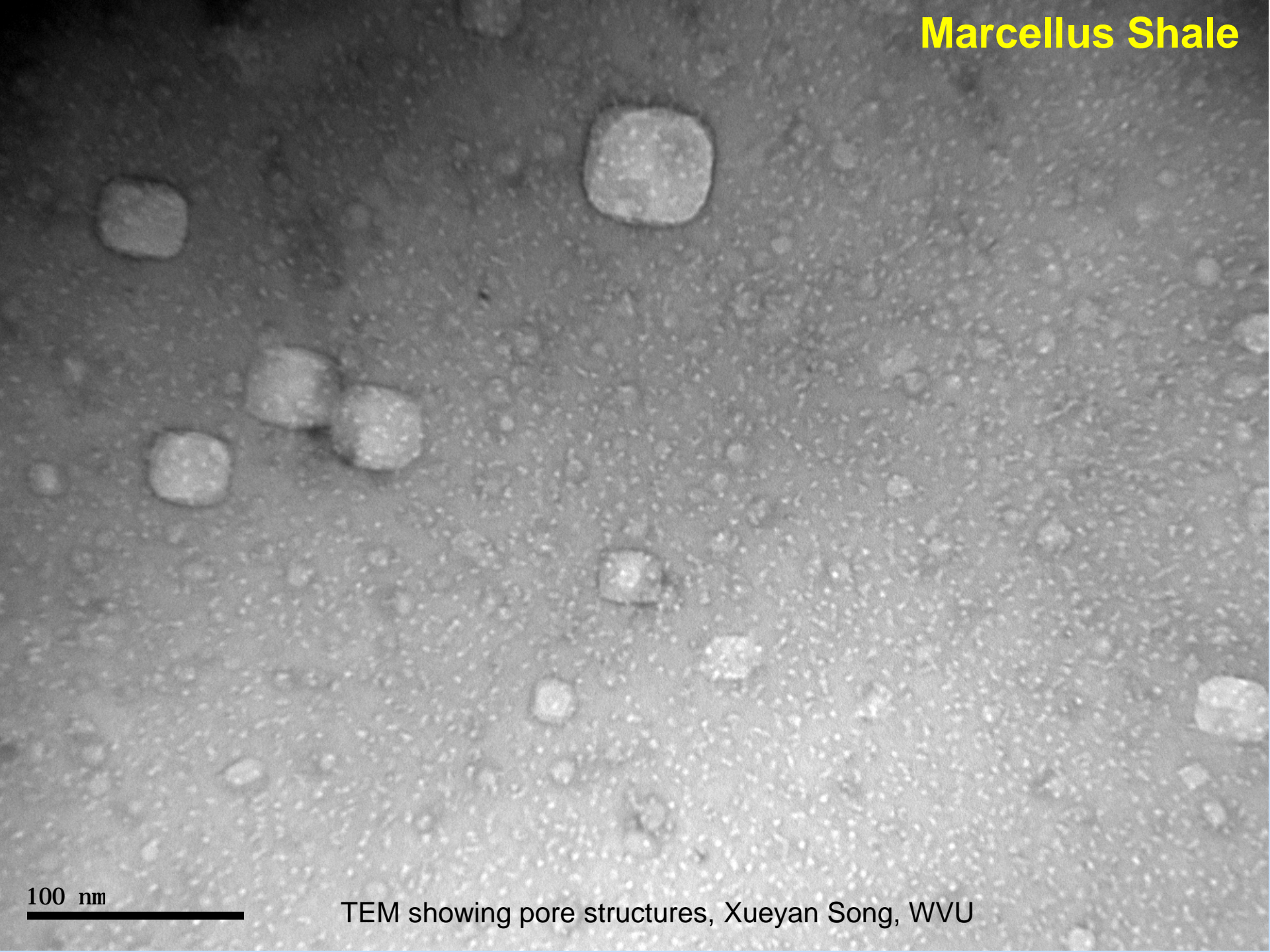
Parallel clay flakes

Microfracture

Woody  
organic

Pyrite >

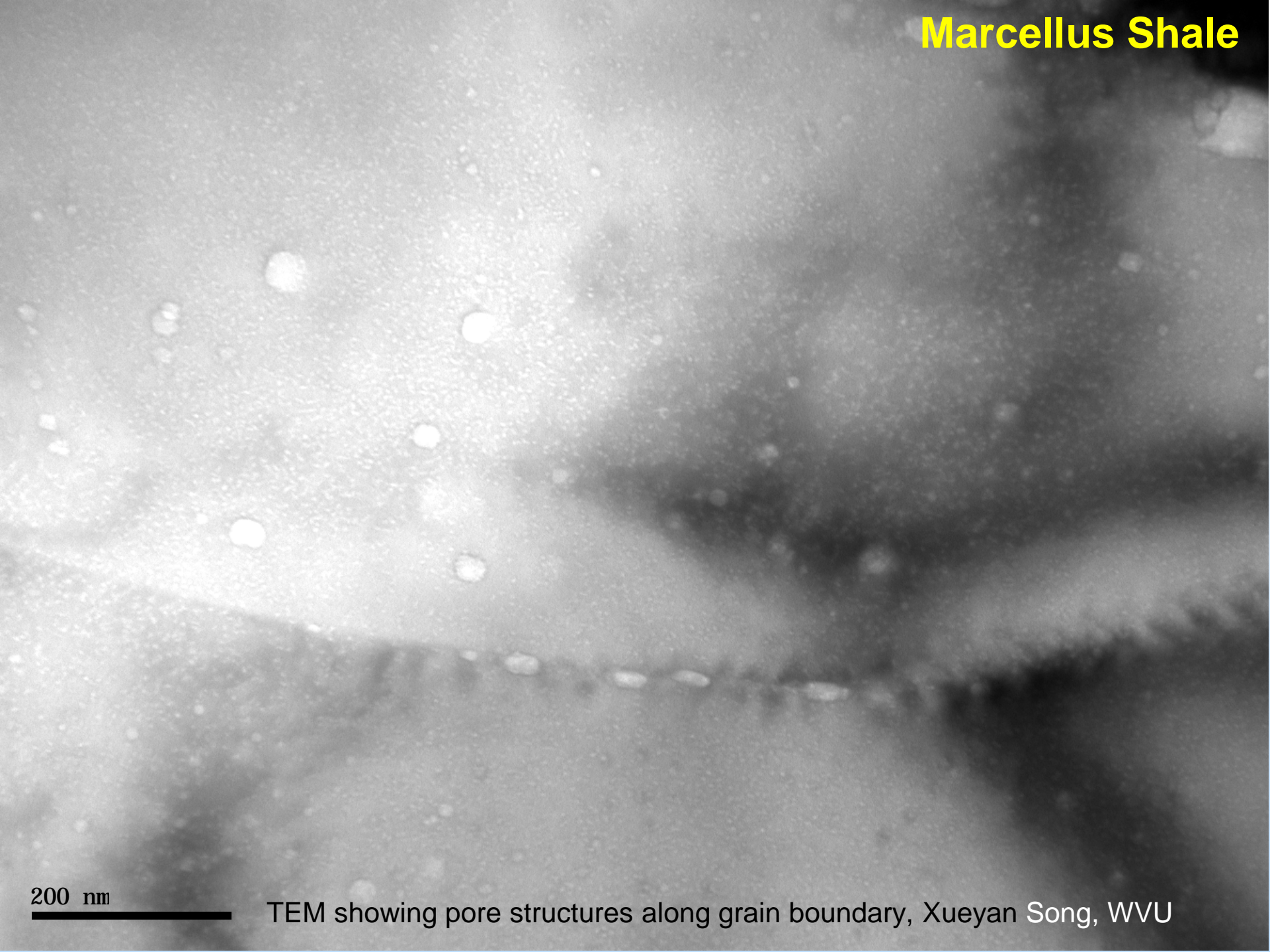
# Marcellus Shale



100 nm

TEM showing pore structures, Xueyan Song, WVU





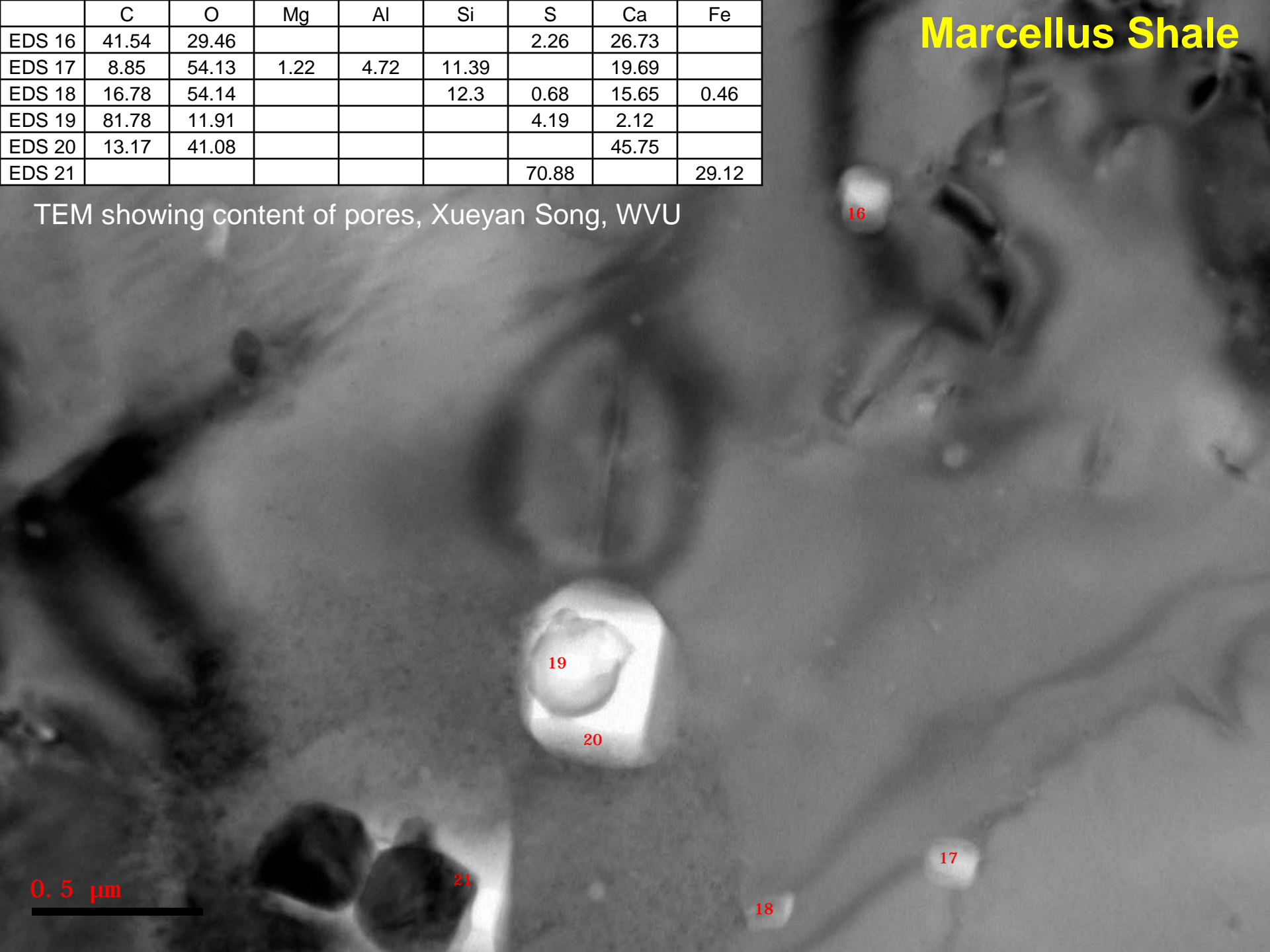
200 nm

TEM showing pore structures along grain boundary, Xueyan Song, WVU

# Marcellus Shale

	C	O	Mg	Al	Si	S	Ca	Fe
EDS 16	41.54	29.46				2.26	26.73	
EDS 17	8.85	54.13	1.22	4.72	11.39		19.69	
EDS 18	16.78	54.14			12.3	0.68	15.65	0.46
EDS 19	81.78	11.91				4.19	2.12	
EDS 20	13.17	41.08					45.75	
EDS 21						70.88		29.12

TEM showing content of pores, Xueyan Song, WVU



16

19

20

17

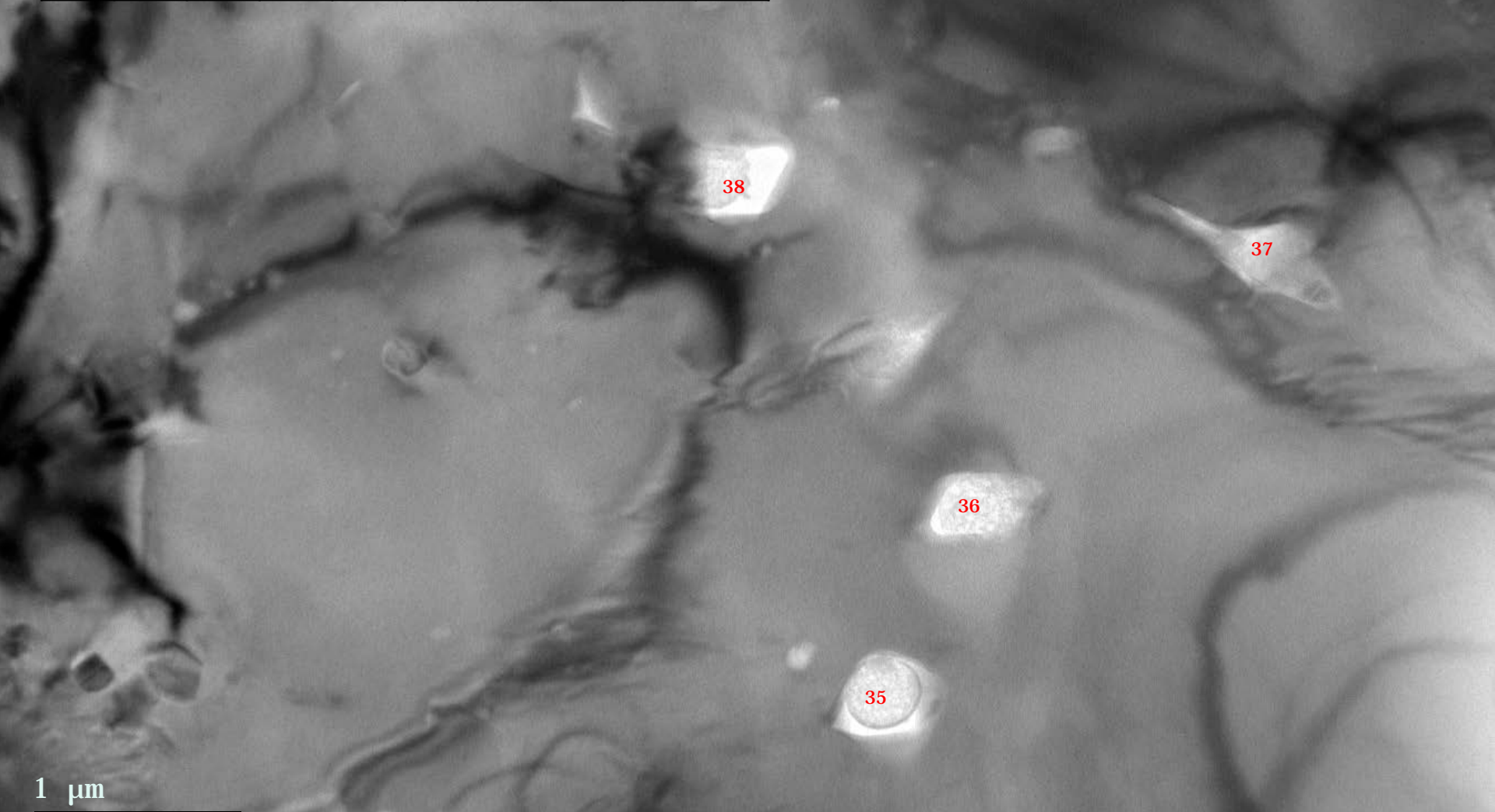
18

21

0.5  $\mu\text{m}$

# Marcellus Shale

	C	O	Mg	Al	Si	S	K	Ca	Fe
EDS 35	91.58	3.55				4.88			
EDS 36	89.92	4.41				5.67			
EDS 37	12.14	51.24	1.94	8.79	18.84		1.74	4.61	0.69
EDS 38	74.24	15.71				3.6		6.45	



1 μm

TEM showing content of pores, Xueyan Song, WVU

# Petrophysical Behavior

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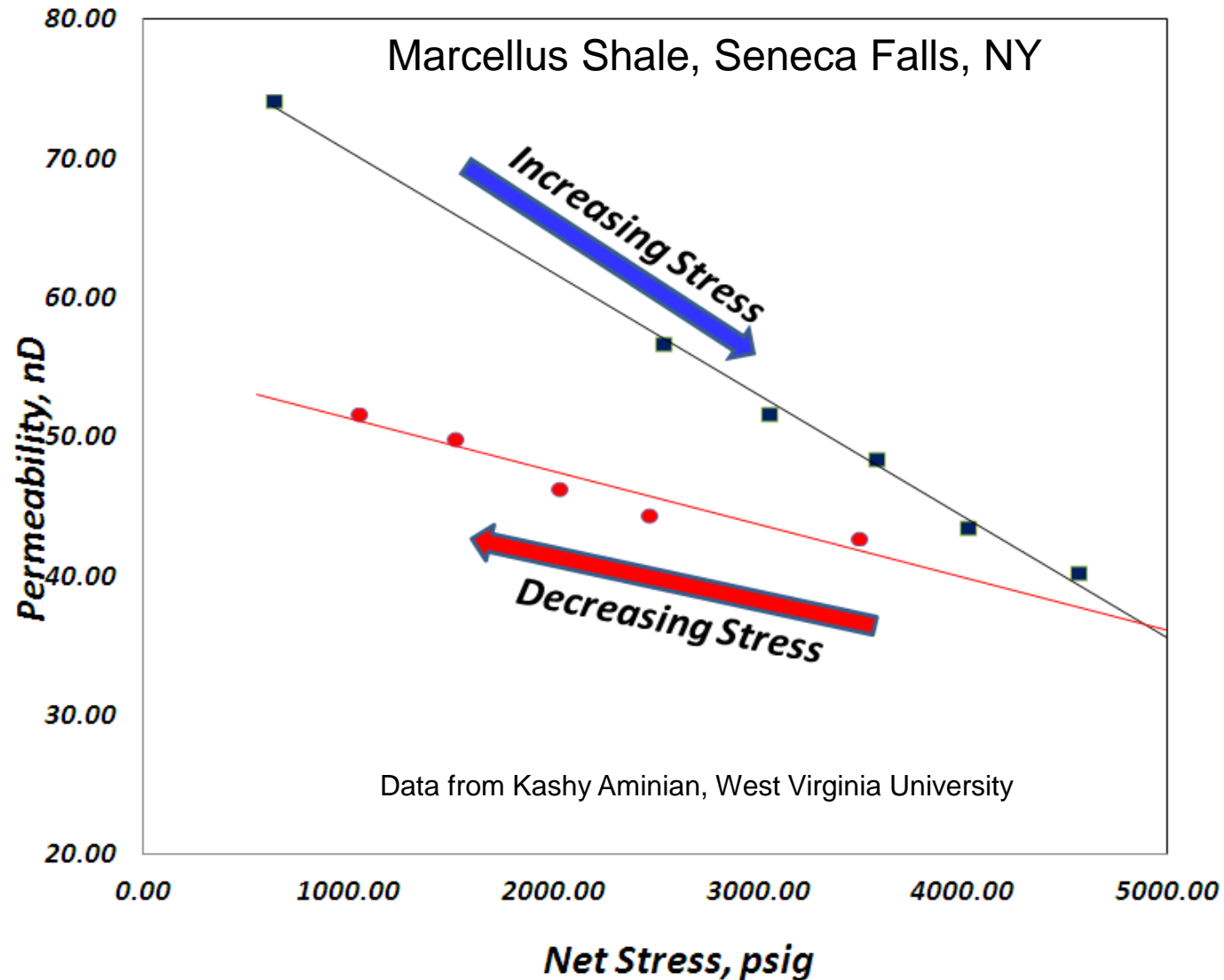
- Very low permeability to gas – nanodarcy range
- Mass flow versus diffusion; movement of gas through nanopores on a molecular scale
- Importance of the Klinkenberg effect and gas slippage
- Exactly how low is a permeability of one nanodarcy? Is molecule size important?
- Oil wet versus water wet (black shale vs. gray)
- High capillary pressures at gas-liquid interface (500 psi to 900 psi typical)

# Net Confining Stress

- Drawdown of a deep gas shale can easily double the net overburden stress.
- Measurements have shown that doubling the net stress decreases permeability by  $2/3^*$
- Changes in flowpath aperture and tortuosity occur due to increased net confining stress
  - Average aperture increases (smaller flowpaths close down)
  - Tortuosity increases significantly
- Hysteresis: once permeability is decreased by excursion to high stress, it does not recover

\* Soeder, D. J., 1988, Porosity and permeability of eastern Devonian gas shale: SPE Formation Evaluation, Vol. 3, No. 2, p. 116-124, DOI 10.2118/15213-PA.

# Hysteresis in shale



# Technical Challenges

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- Obtaining shale core samples
- Core sample bias? Clay vs. silica vs. carbonate
- Measuring flow through shale within a human lifetime
- Separating out actual petrophysical effects from low permeability
  - Capillary pressure: is it really that high, or does it just take a long time to equilibrate because of the low permeability?
  - Swelling of shale with CO<sub>2</sub> in the pores – how much is real, how much caused by CO<sub>2</sub> escaping very slowly?
- Methane and carbon dioxide behave differently in shale – why and how?
- CO<sub>2</sub> physical and chemical reactions with the shale
  - Reaction to oil-wet versus water-wet shales
  - Reaction to mineralogy (clays, carbonate, sulfides, etc.)

# Accomplishments to Date

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- Samples have been obtained
  - Ohio Shale, EGSP cores: Huron and Chagrin; Ohio Geological Survey
  - Mowry Shale, SCC core, Colorado, Univ. of Utah
  - Niobrara Shale, USGS core, SD, NE, WY, tribal college project
- Capillary pressure measurements underway
- Pore visualization assessments nearly complete, report in progress.
- New ultra-low permeability, steady-state flow lab under design for B-17 at NETL in Morgantown.



# Summary

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- Performance of shale as a seal (caprock) is influenced by
  - Mineralogy and CO<sub>2</sub> reactivity
  - Pore geometry and related permeability
  - Fluids in pores and capillary entry pressure
- Performance of shale for geologic storage of CO<sub>2</sub> is influenced by:
  - Bulk volume of rock
  - Percentage of porosity in that bulk volume
  - Percentage of accessible porosity from total
  - Factors that alter accessibility (liquids, hysteresis, etc)

# Organization Chart

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- Dan Soeder (DOE), Rebecca Rodriguez (ORISE), Dustin Crandall (URS), Roger Lapeer (URS), Dustin McIntire (DOE), Kashy Aminian (WVU), Xueyan Song (WVU), Henk Verweij (Ohio State)
- Key Pieces of Equipment: Precision Petrophysical Analysis Lab (PPAL), Micro CT Scanner, SEM, TEM, Threshold Pressure Tester, optical microscopes