Multiple Approaches to Characterizing Pore Structure in Barnett Shale

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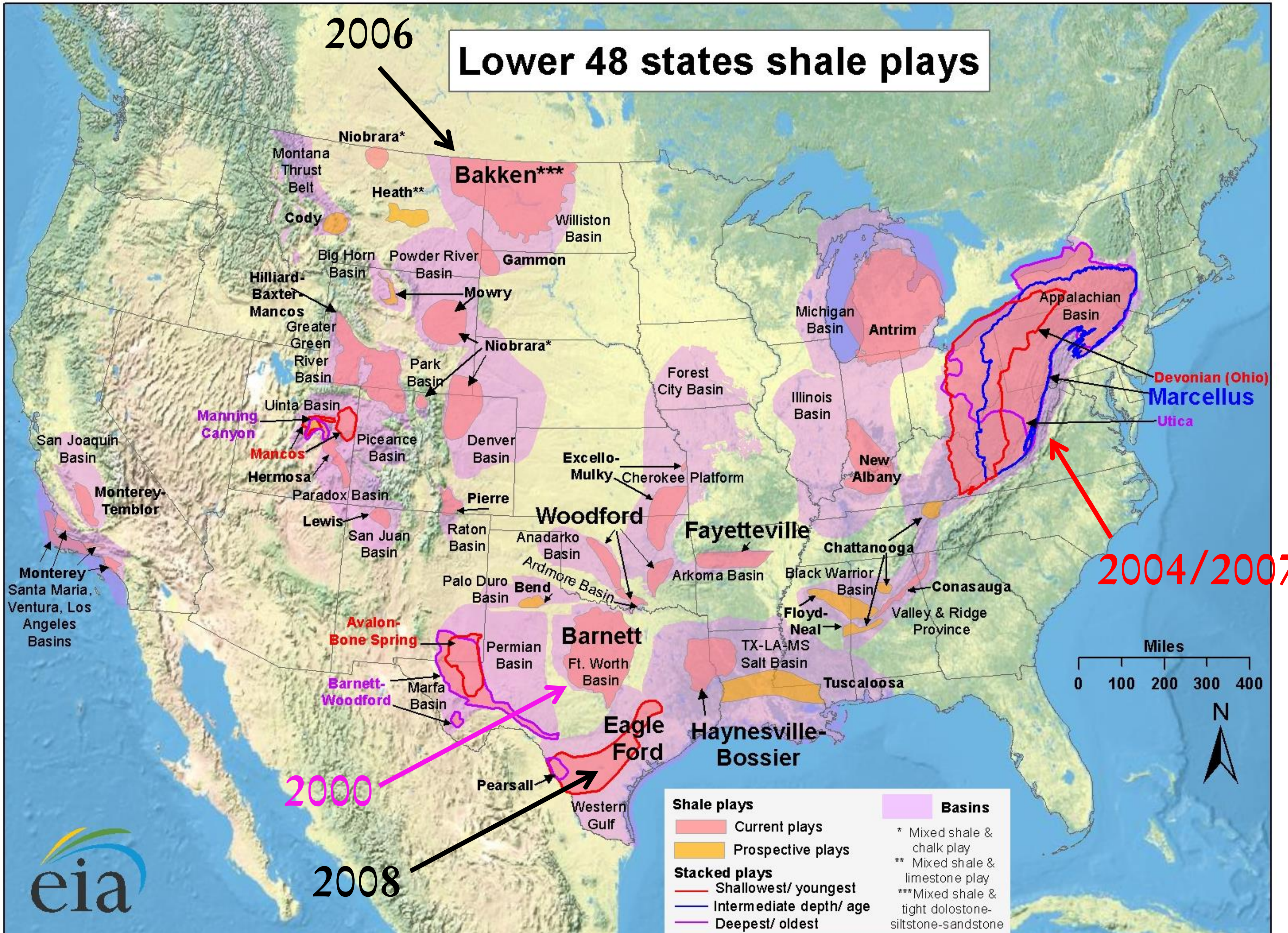
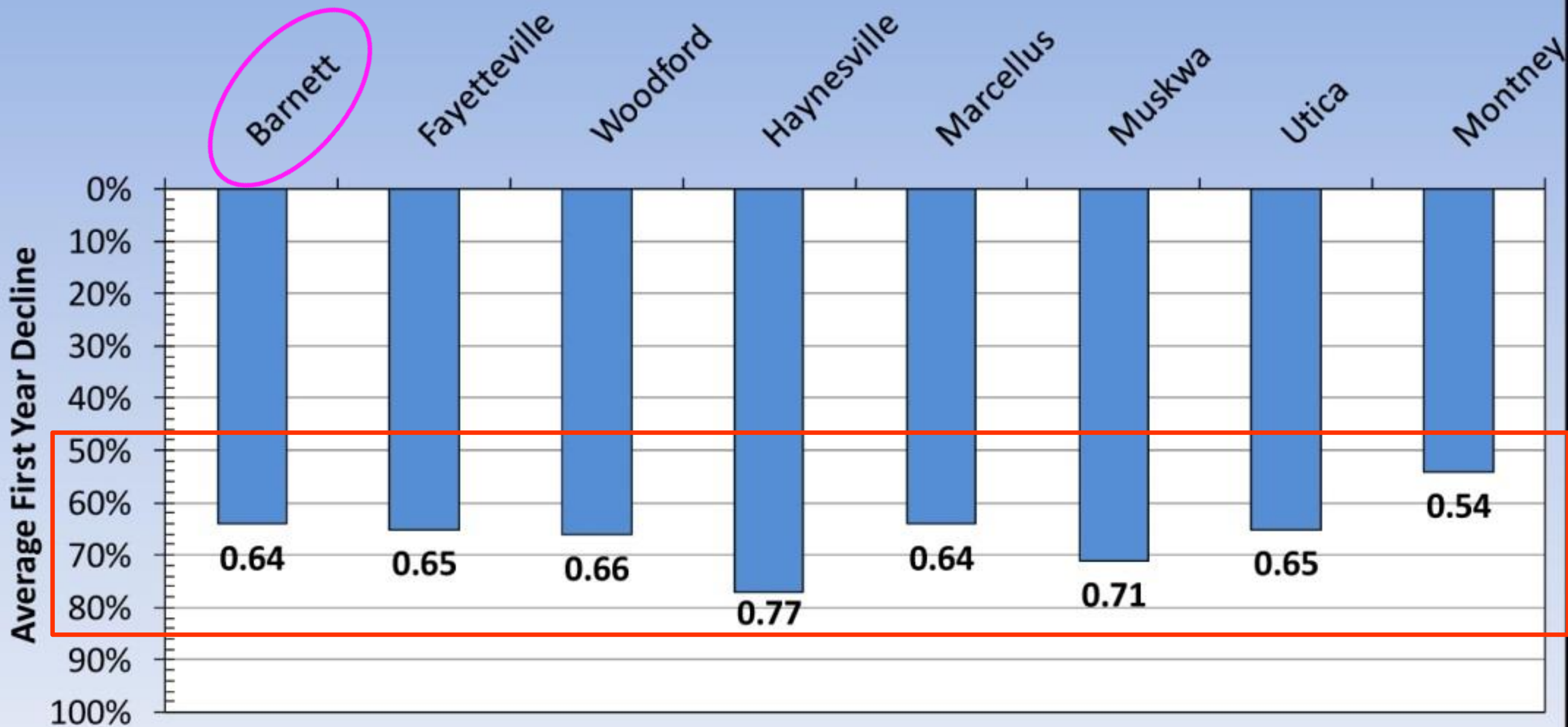


Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

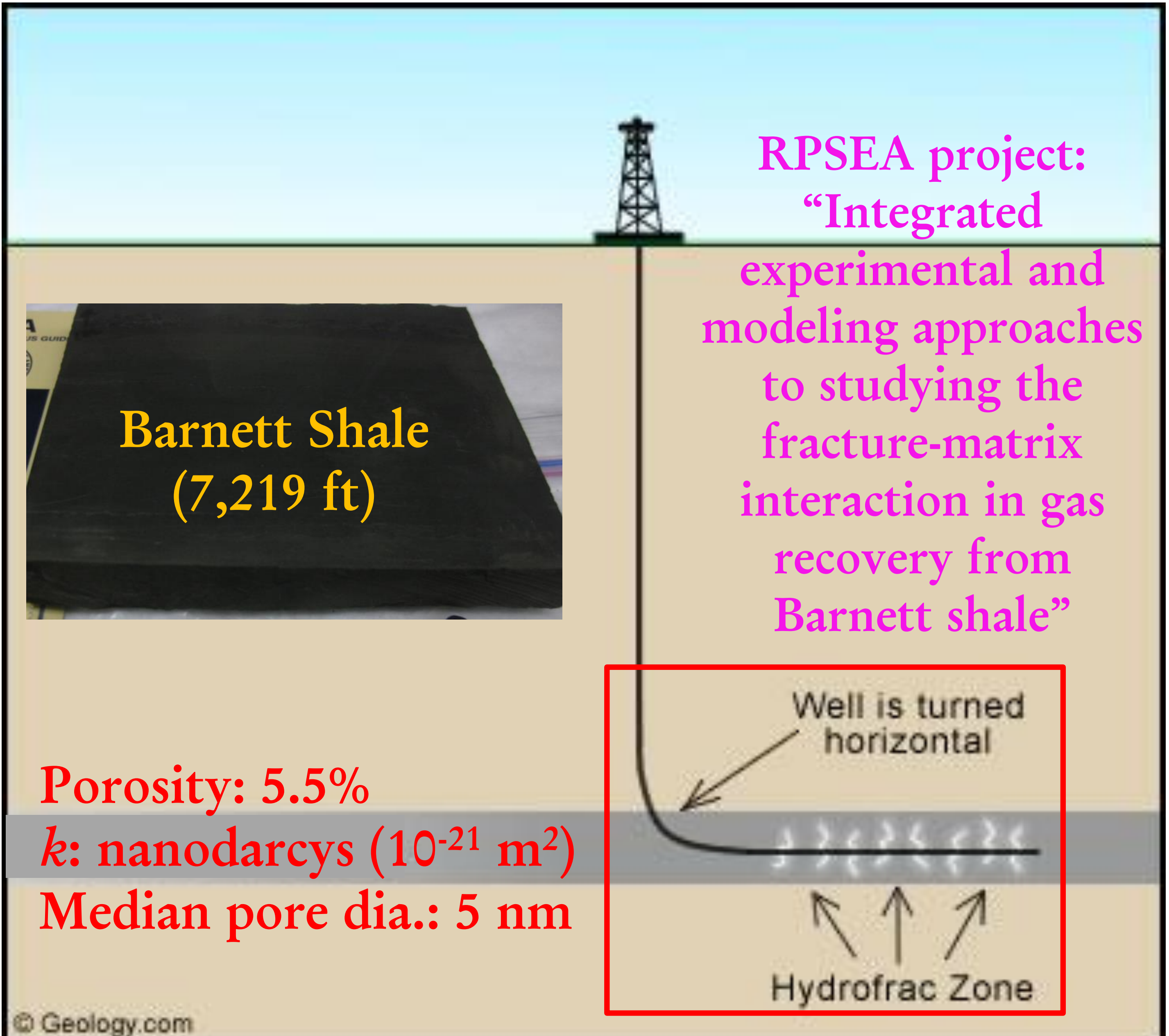
http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/maps/maps.htm

Average First Year Decline



Low gas recovery factor 15–30% for Barnett Shale (King, 2012)

Pore Structure and Low Hydrocarbon Production



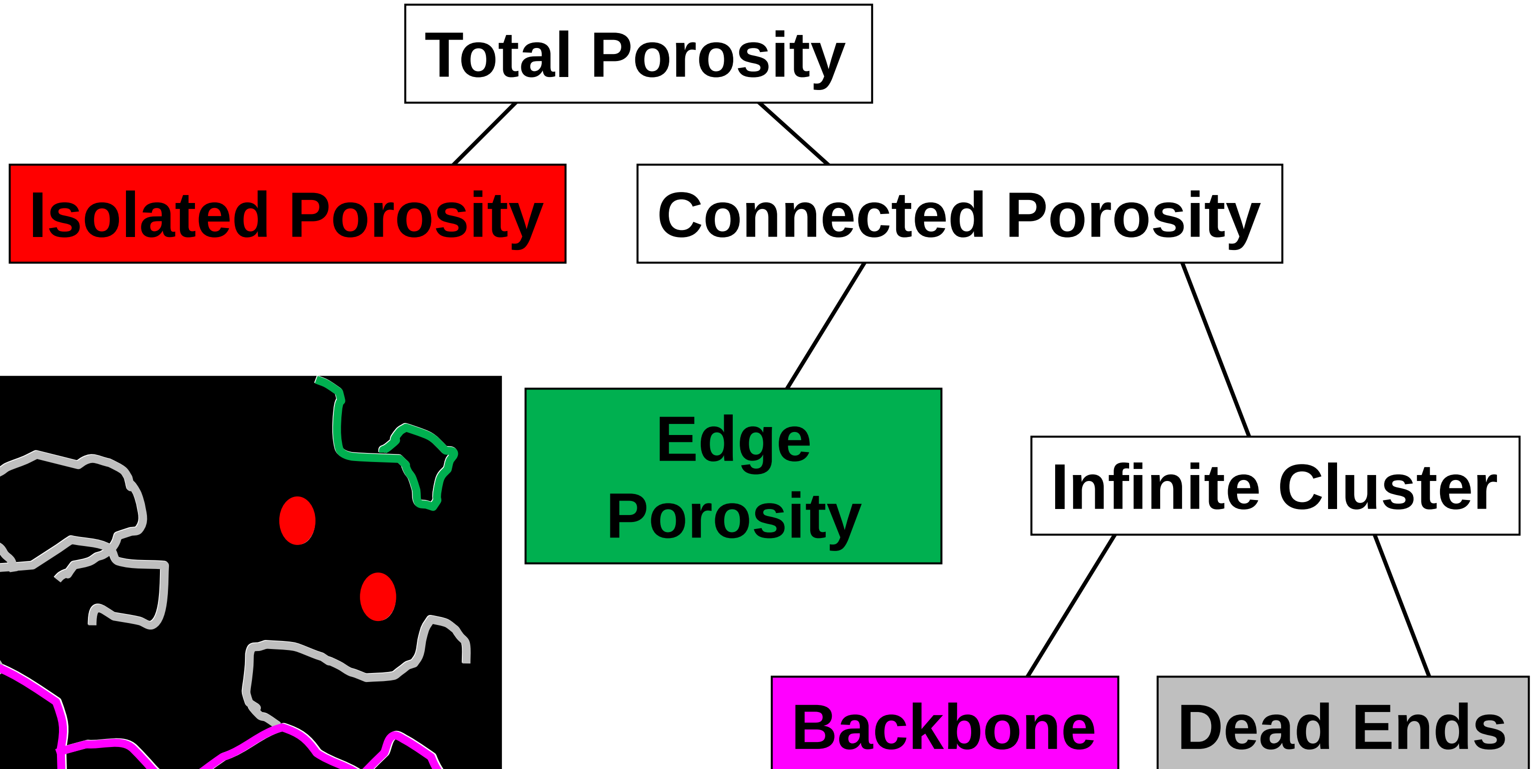
RPSEA project: "Integrated experimental and modeling approaches to studying the fracture-matrix interaction in gas recovery from Barnett shale"

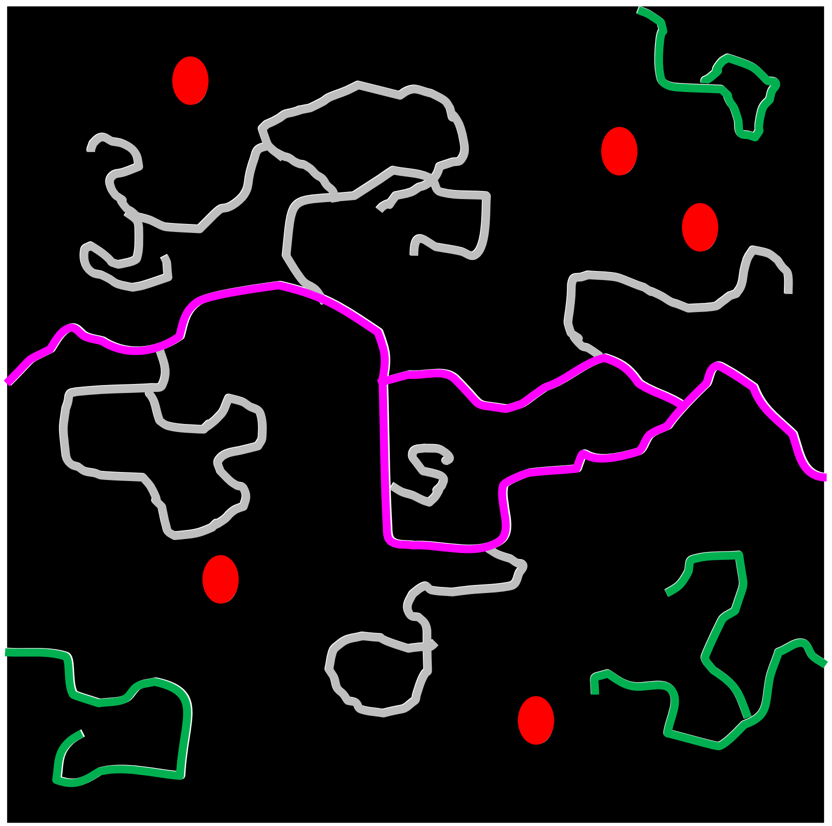
Porosity: 5.5%
k: nanodarcys (10^{-21} m^2)
Median pore dia.: 5 nm

Pore structure

- Amount of gas in place
- Free vs. adsorbed gas
- Tortuous transport pathways
- Gas deliverability from nanopores to well bore

Pore Geometry and Topology





Pore structure: shape, volume, size, size–distribution, connectivity, and surface area

Intraparticle organic nanopores

Where is the porosity?

Ar ion–beam milling and field emission gun SEM: resolve pores as small as 5 nm

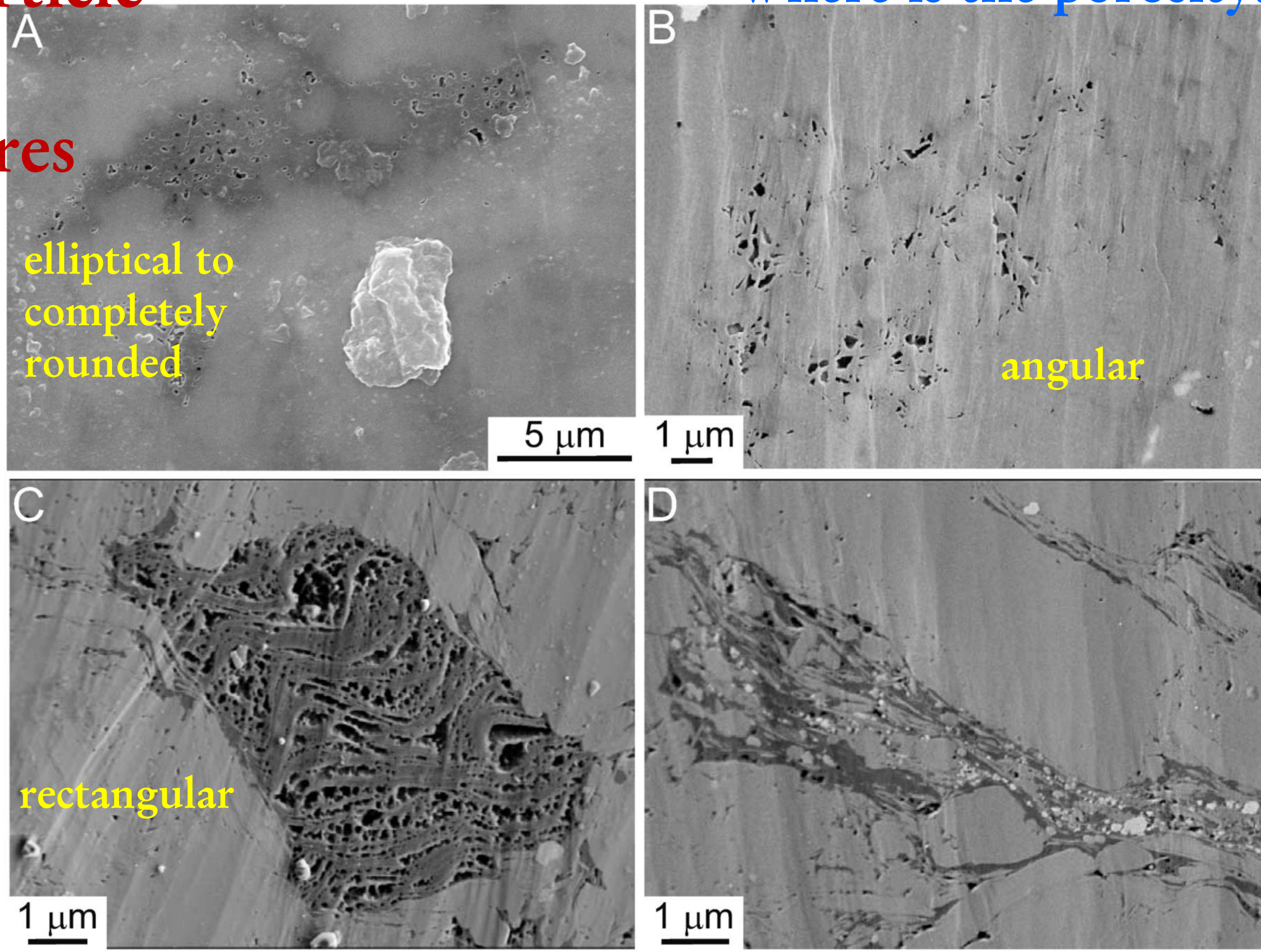
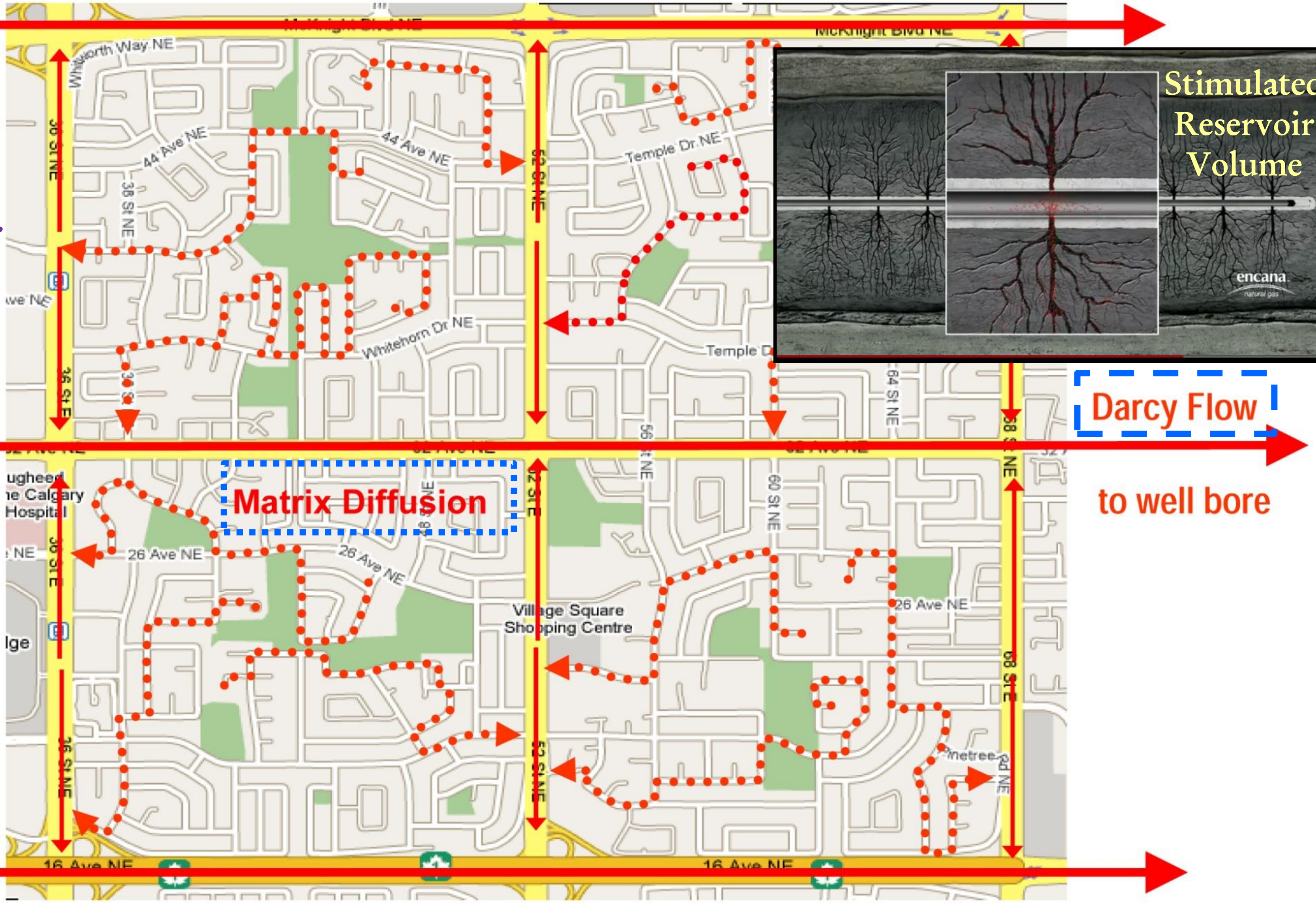


FIG. 5.—Nanopores associated with organic matter in the Barnett Shale. **A)** Elliptical to complexly rounded nanopores in an organic grain. Darker materials are organics. BSE image. Blakely #1, 2,167.4 m. **B)** Angular nanopores in a grain of organic matter. SE image. Blakely #1, 2,167.4 m. Accelerating voltage = 10 kV; working distance = 6 mm. **C)** Rectangular nanopores occurring in aligned convoluted structures. SE image. T.P. Sims #2, ~ 2,324 m. Accelerating voltage = 2 kV; working distance = 3 mm. **D)** Nanopores associated with disseminated organic matter. Carbon-rich grains are dark gray; nanopores are black. SE image. T.P. Sims #2, ~ 2,324 m. Accelerating voltage = 2 kV; working distance = 2 mm.

Loucks et al. (2009)

Shale Gas Flow: Matrix "diffusion" vs. "Darcy" flow

drive your car out of neighbor hood blind-folded



http://www.transcanada.com/customerexpress/docs/presentations_general/2009_North_American_Shale_Gas_Overview_NECA.pdf

TransCanada

Multiple Approaches to Studying Pore Structure

- Pore-scale network modeling (ISU)
- Imbibition with samples of different shapes (UTA-Gao)
- Edge-accessible porosity
- Liquid and gas diffusion
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- N_2 adsorption isotherm (Saitama Univ.; Quantachrome)
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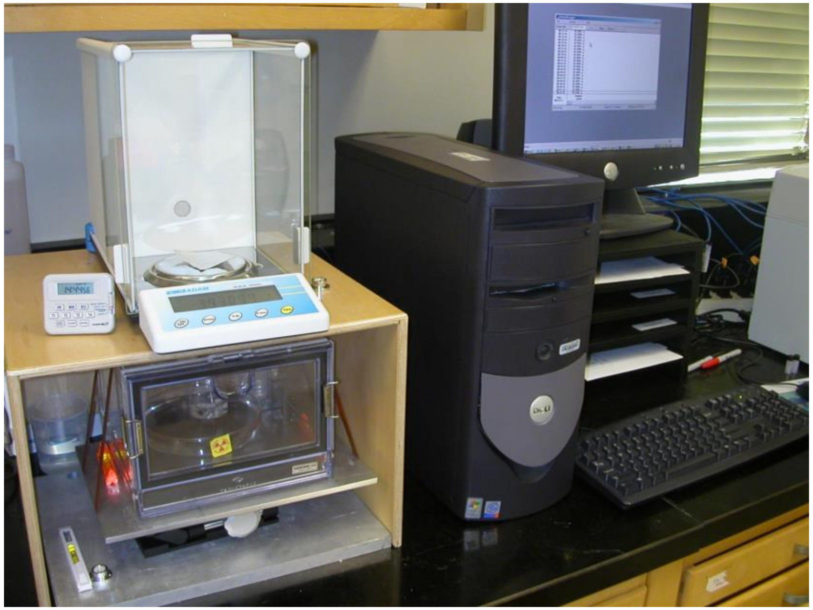
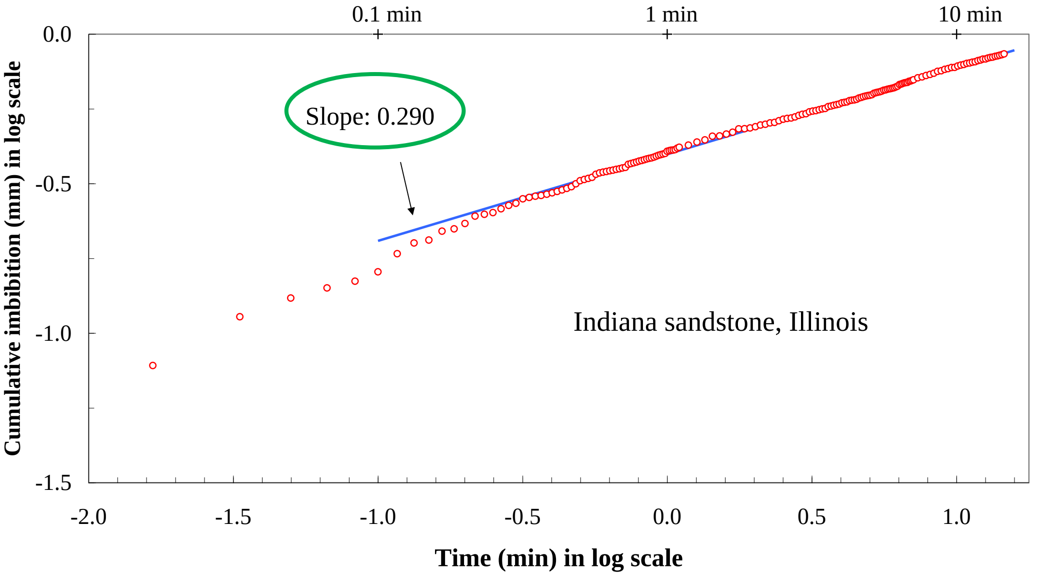
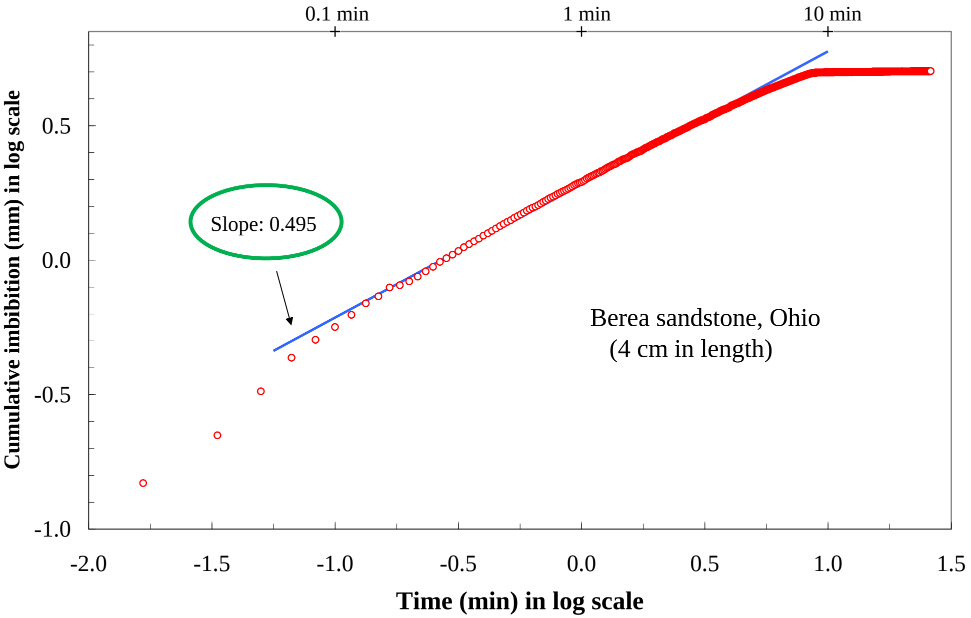
(Spontaneous) Imbibition Test







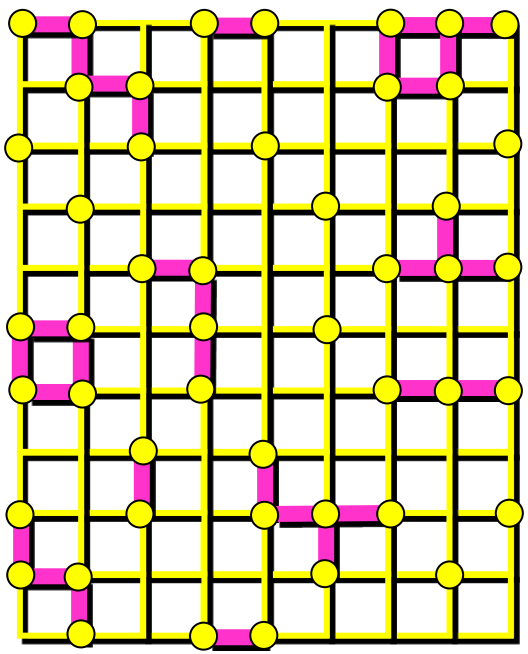
- Rock sample epoxy-coated along length → 1D flow
- Imbibition rate monitored continuously over time

Imbibition Results for Barnett Shale Samples

Depth	Sample dimension	Height/width	Imbibition slope
7,109 ft (2,167 m)	1.33 cm L × 1.76 cm W × 1.43 cm H (Vertical)	0.93	0.214 ±0.059 (N=3)
	1.76 cm L × 1.72 cm W × 1.32 cm H (Horizontal)	0.76	0.291 ±0.027 (N=3)
7,136 ft (2,175 m)	1.38 cm L × 1.71 cm W × 1.72 cm H (Vertical)	1.12	0.269 ±0.0045 (N=3)
	1.73 cm L × 1.73 cm W × 1.21 cm H (Horizontal)	0.70	0.216 ±0.040 (N=3)
7,169 ft (2,185 m)	1.35 cm L × 1.79 cm W × 1.81 cm H (Vertical)	1.16	0.273 ±0.050 (N=3)
	1.24 cm L × 1.78 cm W × 1.32 cm H (Horizontal)	0.87	0.357 ±0.006 (N=3)
7,199 ft (2,194 m)	1.24 cm L × 1.74 cm W × 1.67 cm H (Vertical)	1.12	0.284 ±0.062 (N=3)
	1.74 cm L × 1.72 cm W × 1.26 cm H (Horizontal)	0.67	0.282 ±0.047 (N=3)
7,219 ft (2,200 m)	1.37 cm L × 1.74 cm W × 1.95 cm H (Vertical)	1.25	0.306 ±0.019 (N=3)
	1.69 cm L × 1.71 cm W × 1.36 cm H (Horizontal)	0.80	0.264 ±0.046 (N=3)

Percolation Theory

The mathematics of how macroscopic properties result from local (microscopic) connections



$p = 0.5$

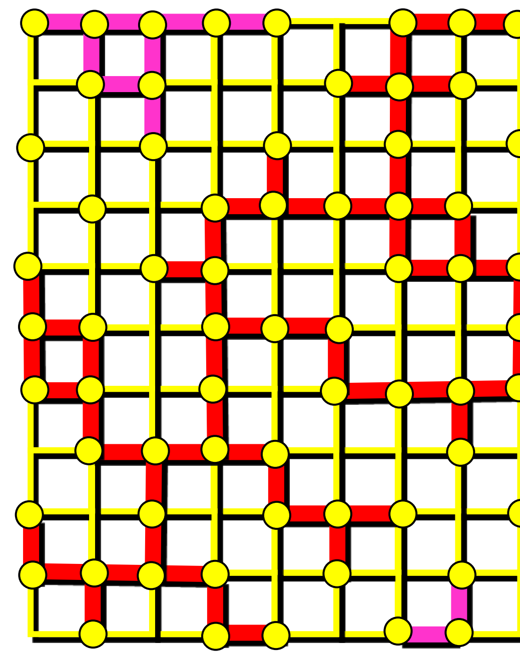
***p* is the local connection probability**

percolation threshold
$0.5 < p_c < 0.66$
(for 2D square lattice)

"Ant in a labyrinth"

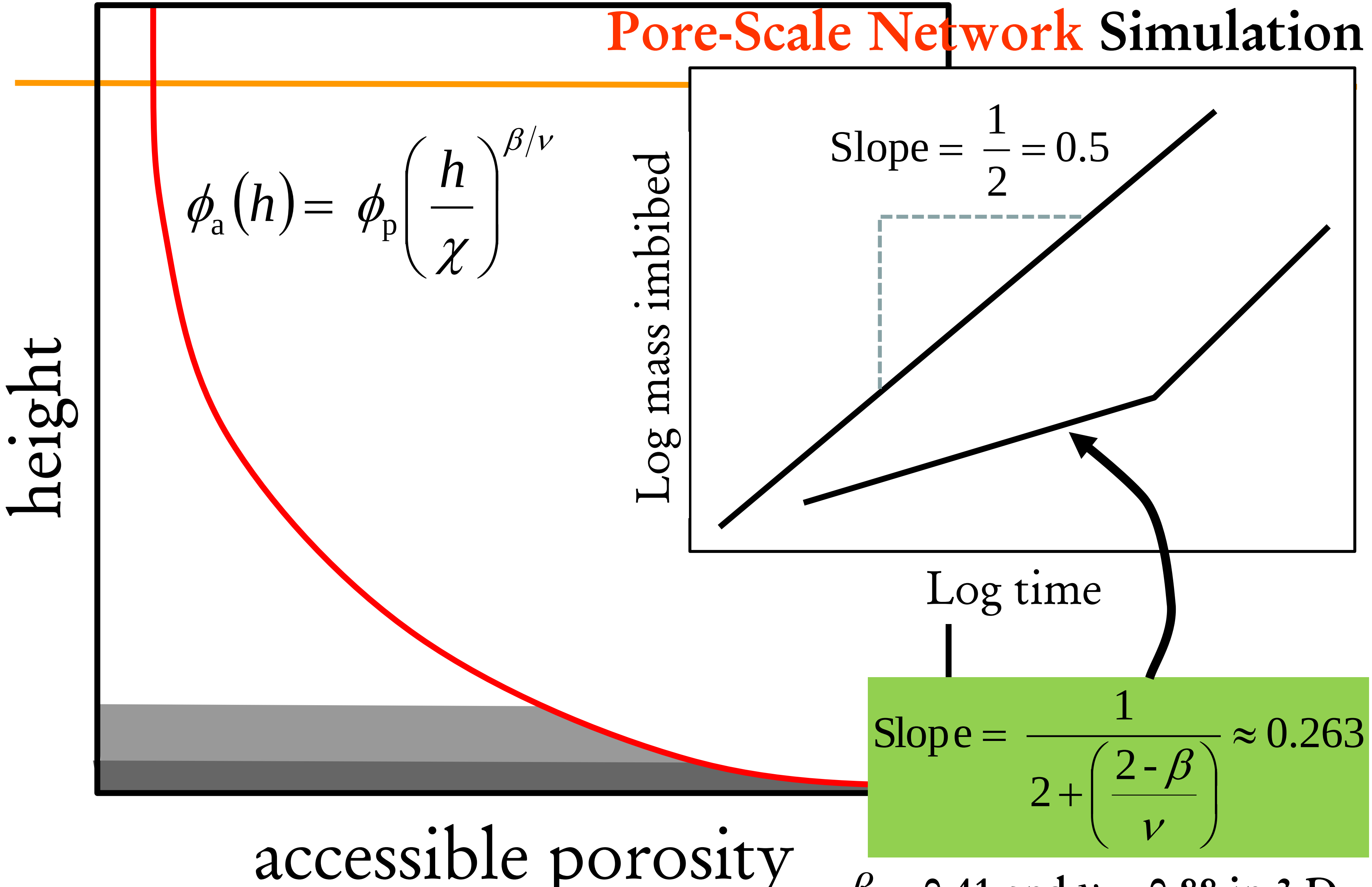
↕

Solute in a pore system



$p = 0.66$

Pore-Scale Network Simulation

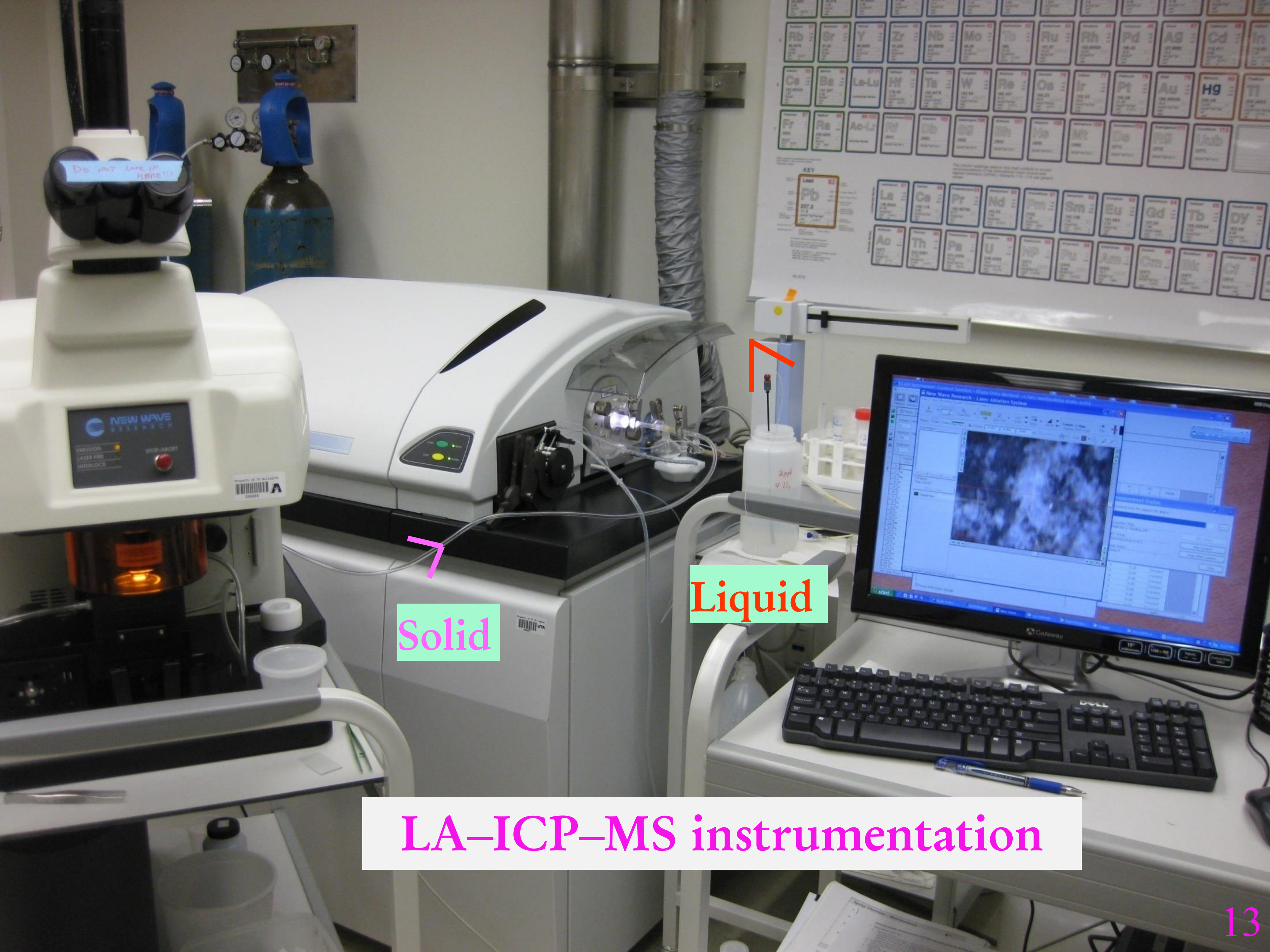


$$\phi_a(h) = \phi_p \left(\frac{h}{\chi}\right)^{\beta/\nu}$$

$$\text{Slope} = \frac{1}{2+\left(\frac{2-\beta}{\nu}\right)} \approx 0.263$$

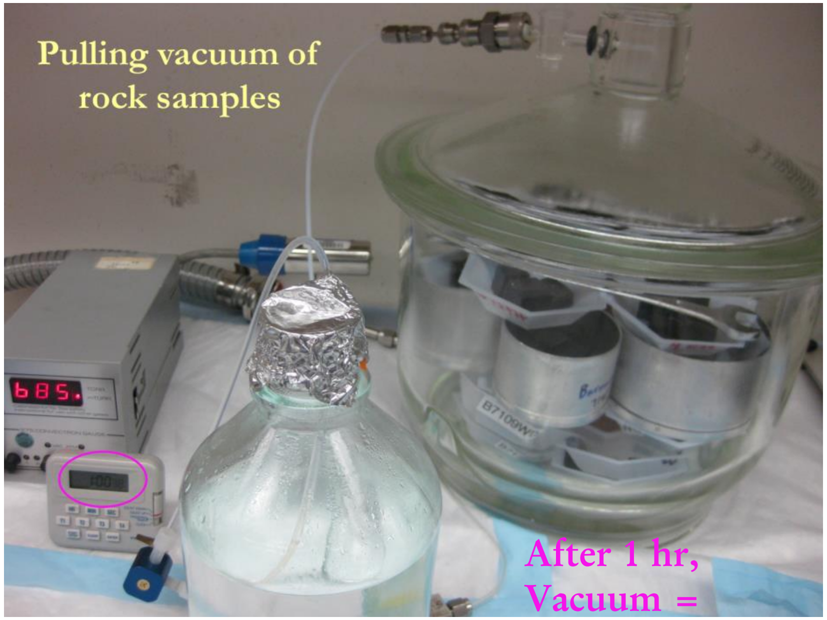
$\beta \approx 0.41$ and $\nu \approx 0.88$ in 3-D

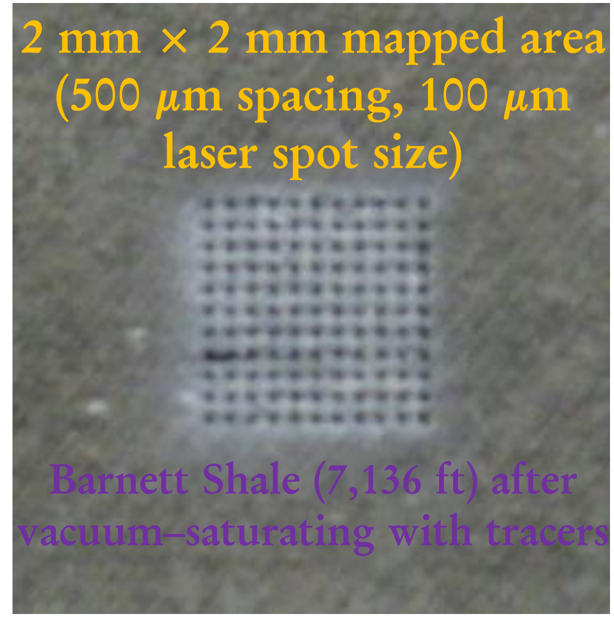
Stauffer, D., Aharony, A., 1994. *Introduction to Percolation Theory* (2nd Ed.). Taylor and Francis, London.

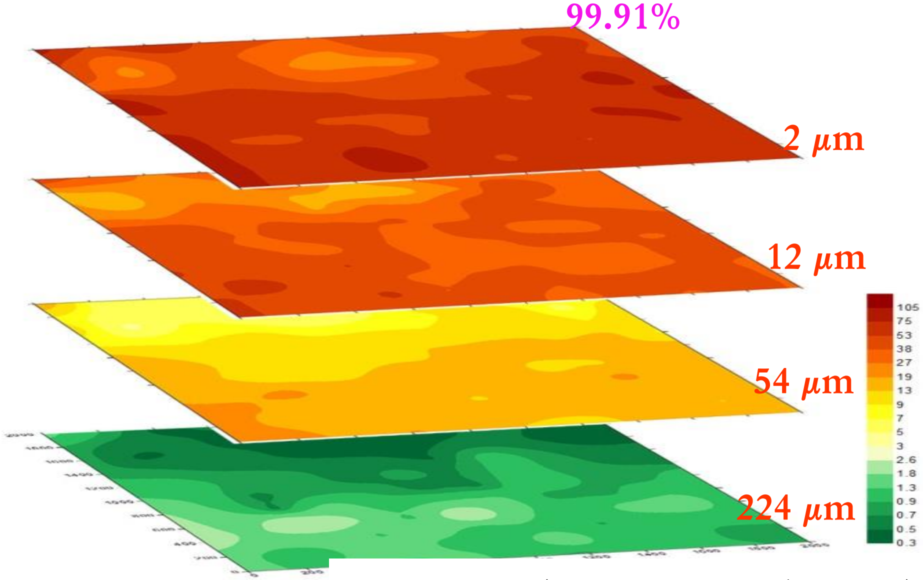


LA–ICP–MS instrumentation

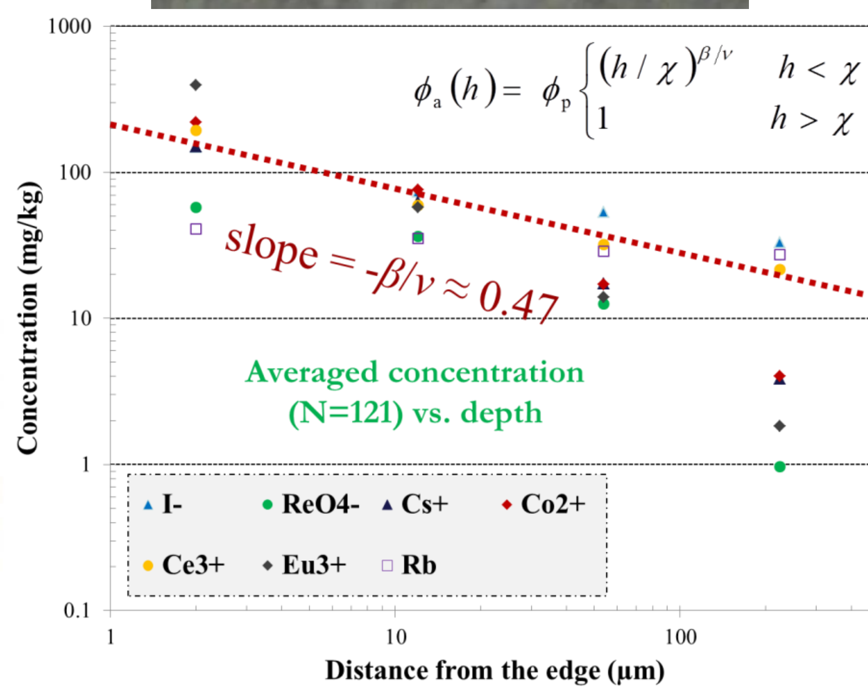
3D Elemental Mapping: Edge–Accessible Porosity







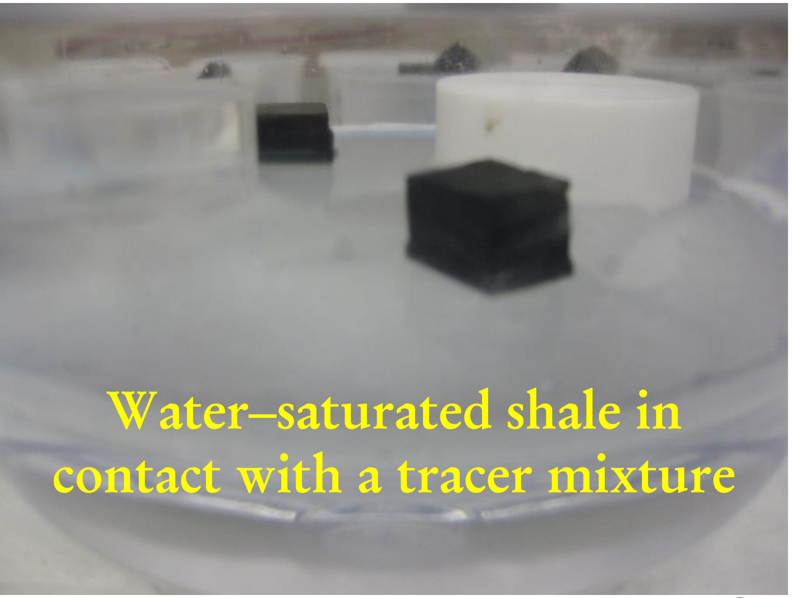
ReO$_4^-$ (non–sorbing)



Liquid Tracer Diffusion in Saturated Intact Shale

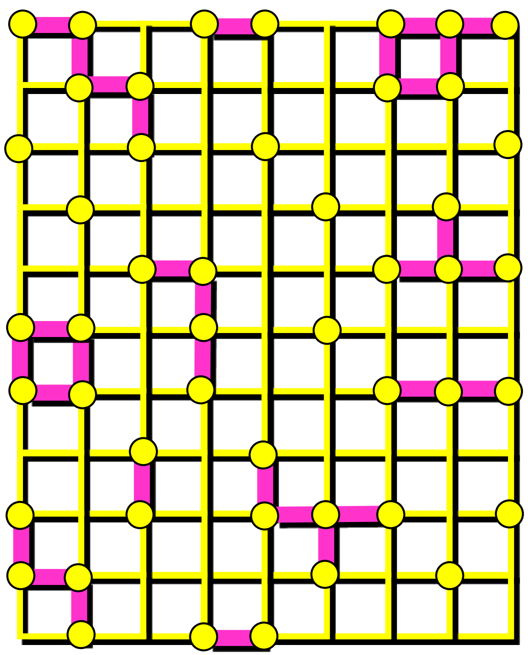
$$\frac{C}{C_0} = \frac{1}{2} erfc \frac{x}{2\sqrt{D_e t}}$$

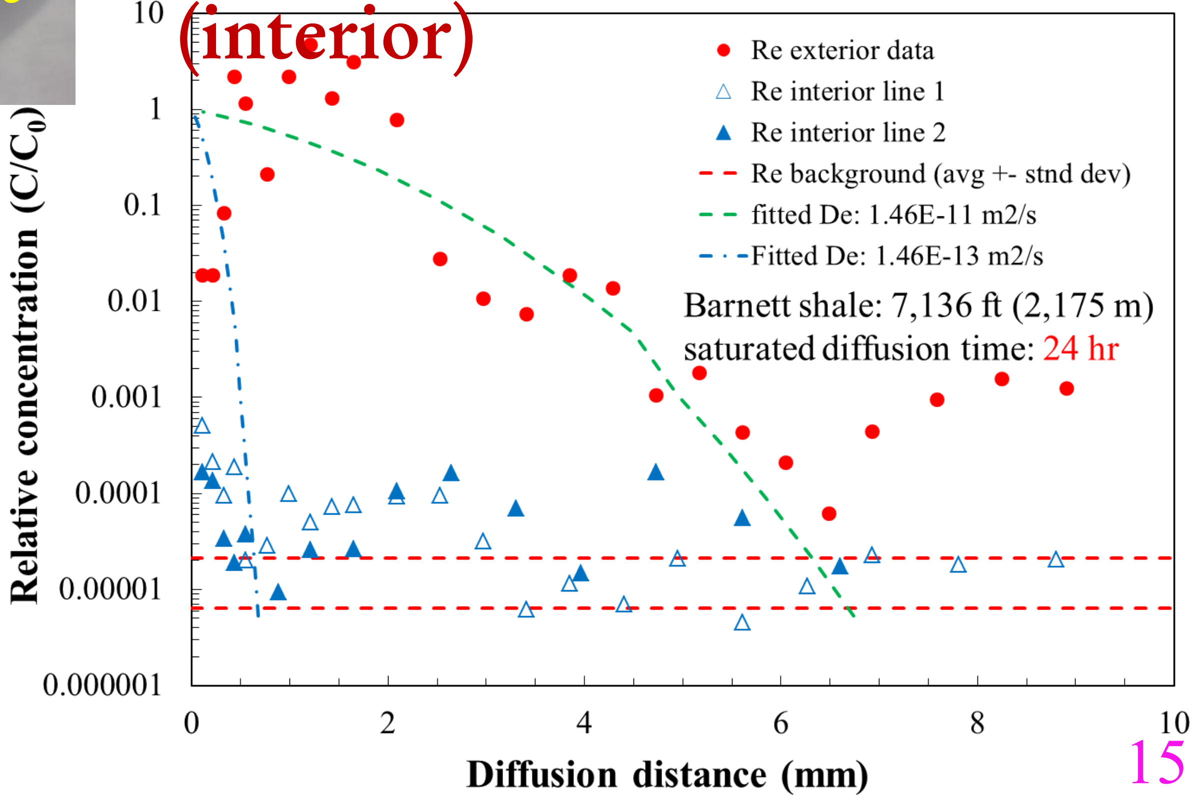
$$\tau = \frac{D_0}{De}$$



Fitted tortuosity

100 (exterior); <10,000 (interior)





Three Data Points ← anecdotal

- Gas molecule movement in shale on the order of 10 feet in the lifetime of a well - Dr. Mohan Kelcar, University of Tulsa.

- Gas molecule movement of about a meter/year modeled by Nexen's Unconventional Team, presented at Global Gas Shales Summit, Warsaw, Poland.

→ ~1 m/yr movement (advection vs. diffusion ?)

- Gas molecule movement of a few feet/year modeled by Dr. Chunlou Li, Shale Gas Technology Group.

$$\boxed{\frac{C(x,t)}{C_0} = erfc\left(\frac{x}{2(D_e t)^{0.5}}\right)}$$

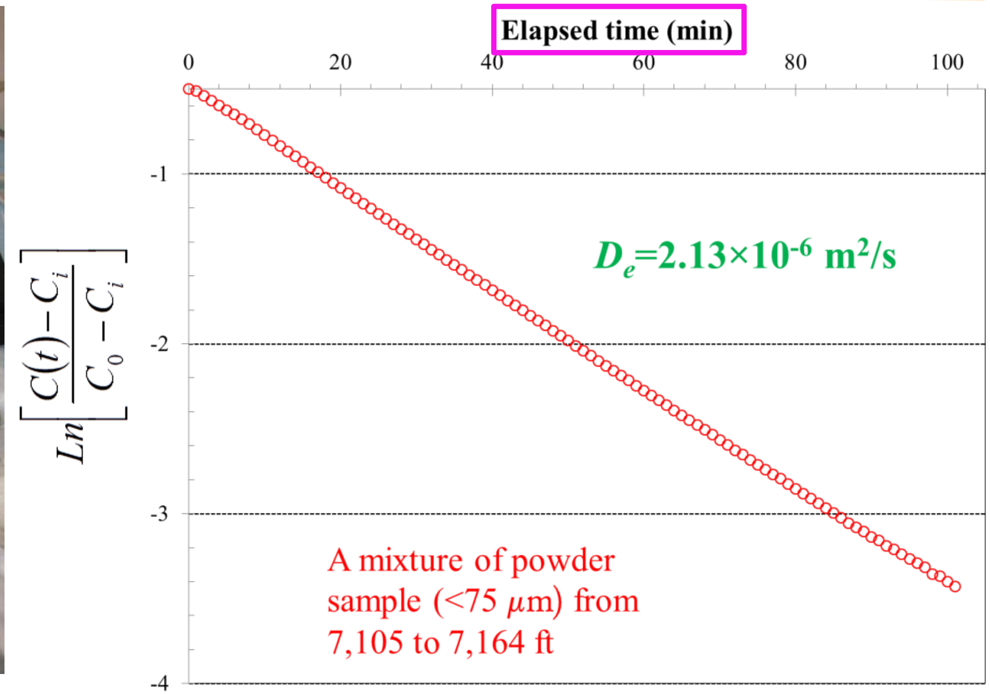
$$\boxed{D_e = \frac{\delta D_0}{\tau}}$$

For $C/C_0 = 0.5$ @ 1 m/y, $\tau = 613$

For $C/C_0 = 0.01$ @ 1 m/y, $\tau = 9{,}800$

LaFollette, R. 2010. Key Considerations for Hydraulic Fracturing of Gas Shales. Manager, Shale Gas Technology, BJ Services Company, September 9, 2010. www.pttc.org/aapg/lafollette.pdf

Gas Diffusion in Partially–Saturated Shale Powder



Water saturation	Air porosity (%)	D_e (m²/s)	Tortuosity
Air-dry	39.2	2.13×10^{-6}	9.59
10%	33.9	1.56×10^{-6}	13.1
20%	20.0	5.11×10^{-7}	39.8

- Powdered shales (with pore networks effects minimized) still exhibit tortuous pathways
- Tortuosity related to water saturation

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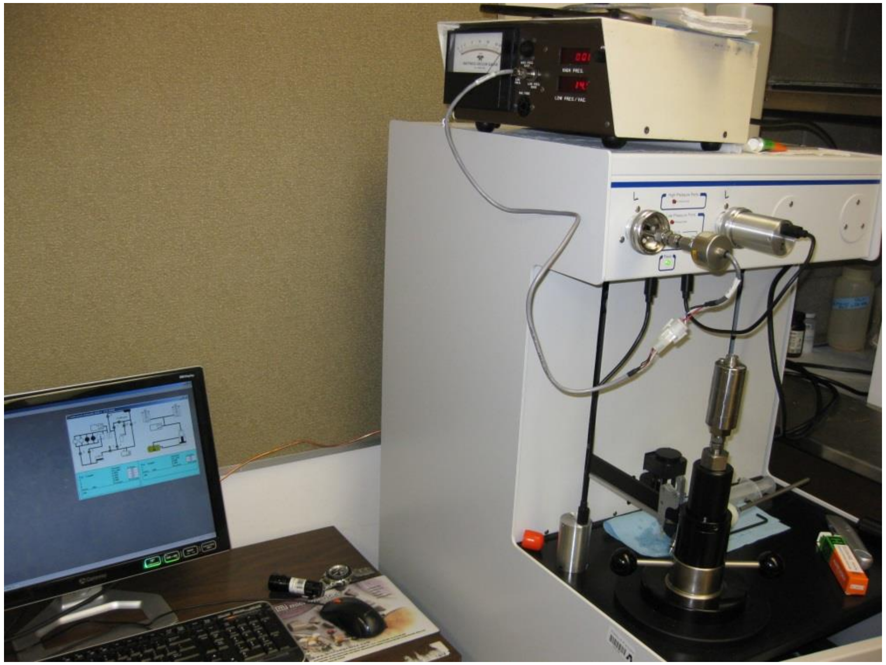
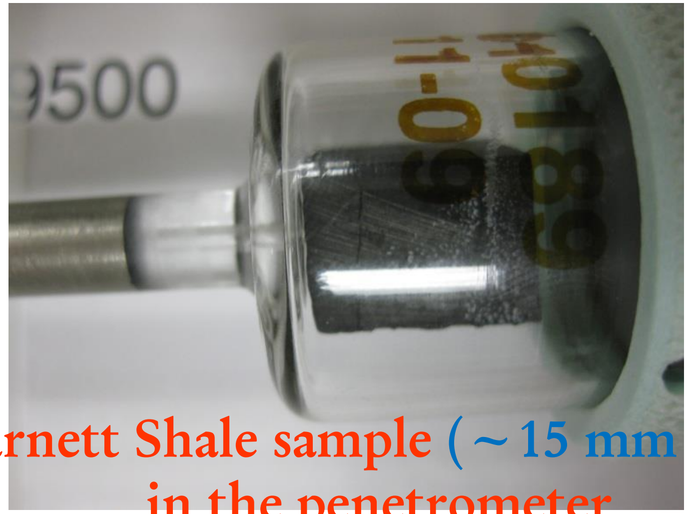
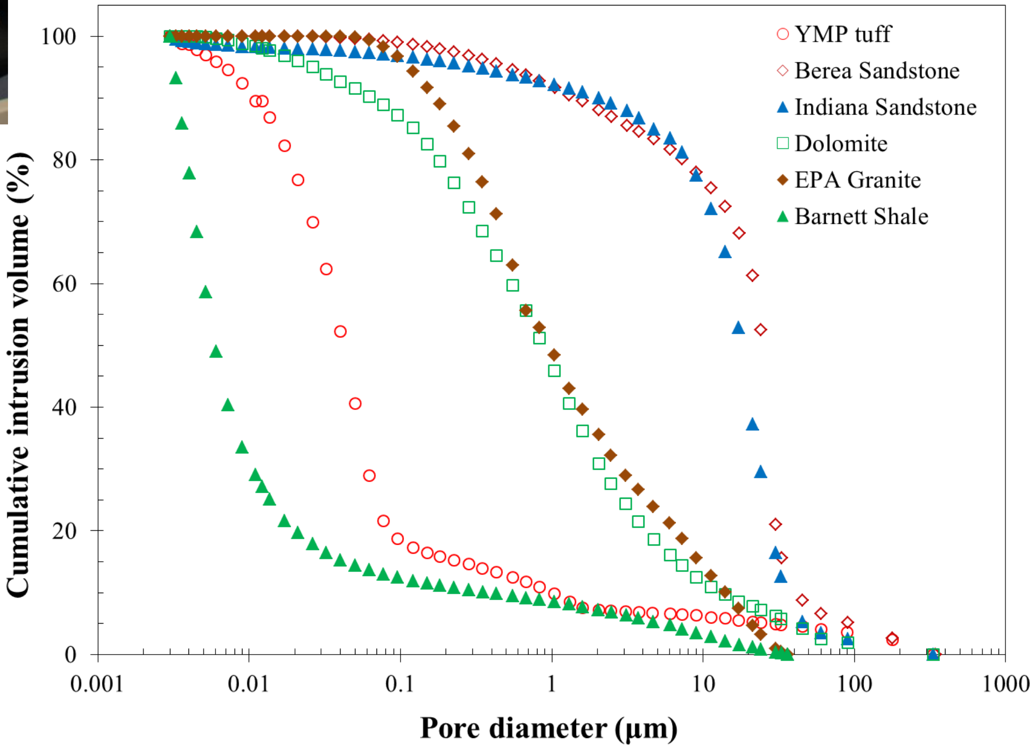
MIP: Pore–Throat Size Distribution





Barnett Shale sample (~15 mm cube) in the penetrometer

- Mercury Injection Porosimetry (MIP)
- Non–wetting Hg progressively intrude smaller pores with increasing pressures
- Measurable pore diameter range: 3 nm to 360 μm



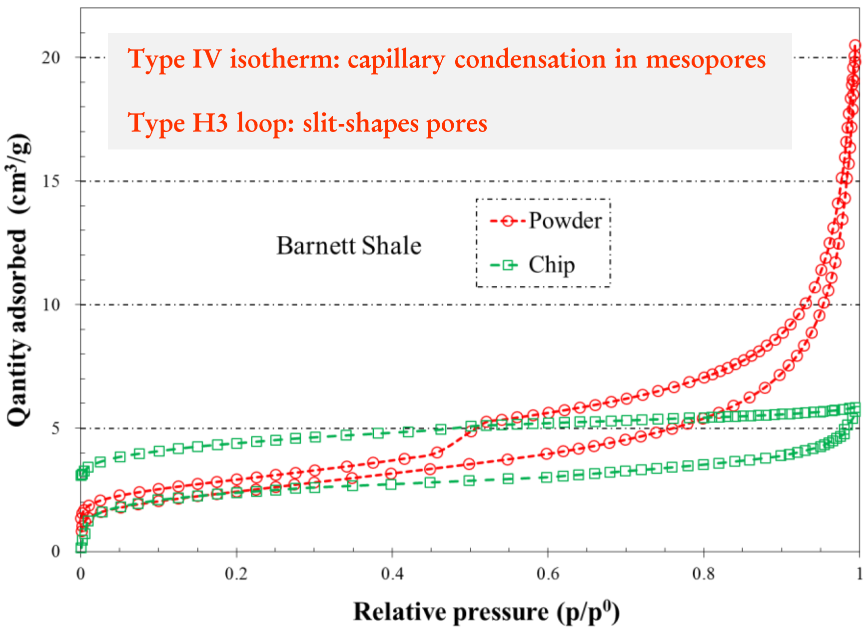
MIP Intrusion Results: 6 Representative Rocks

Depth	Porosity (%)	Median pore-throat diameter (nm)	Permeability (μdarcy)	Tortuosity
Berea Sandstone	22.9 ± 1.72	$23{,}776 \pm 876$	$(595 \pm 21.2) \times 10^3$	3.31 ± 0.33
Indiana Sandstone	16.4 ± 0.4	$19{,}963 \pm 2{,}932$	$(221 \pm 40.8) \times 10^3$	4.68 ± 1.68
Welded Tuff	10.0 ± 0.5	47 ± 7.1	0.83 ± 0.14	$1{,}745 \pm 66$
Dolomite	9.15	873	409	38.3
Barnett Shale (7,199')	5.97 ± 1.43	6.1 ± 0.3	$(4.96 \pm 1.42) \times 10^{-3}$	$12{,}867 \pm 16{,}224$
NC Granite	1.05	970	12.4	38.2

Permeability: Katz and Thompson (1986; 1987)

Tortuosity: Hager (1998)

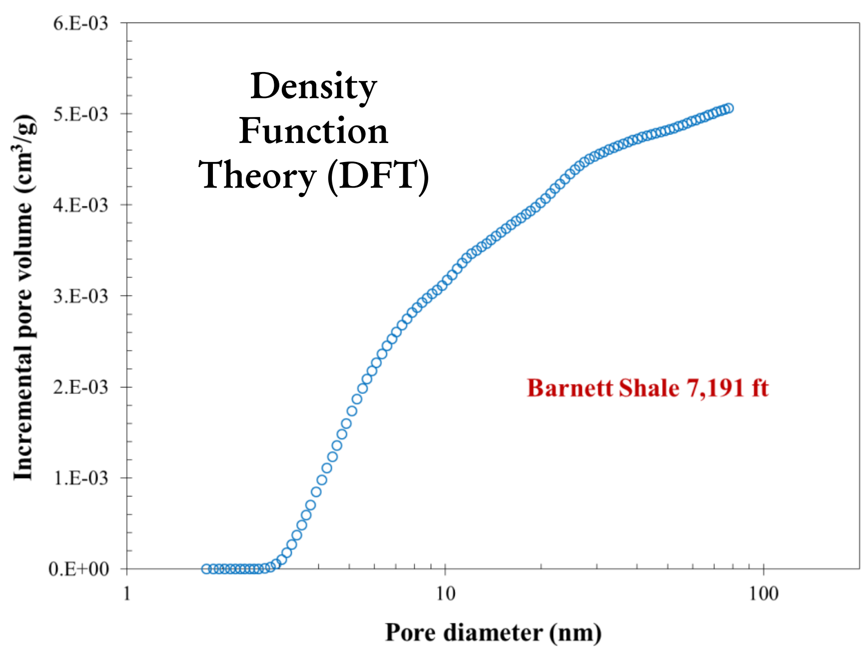
N_2 Sorption Isotherm



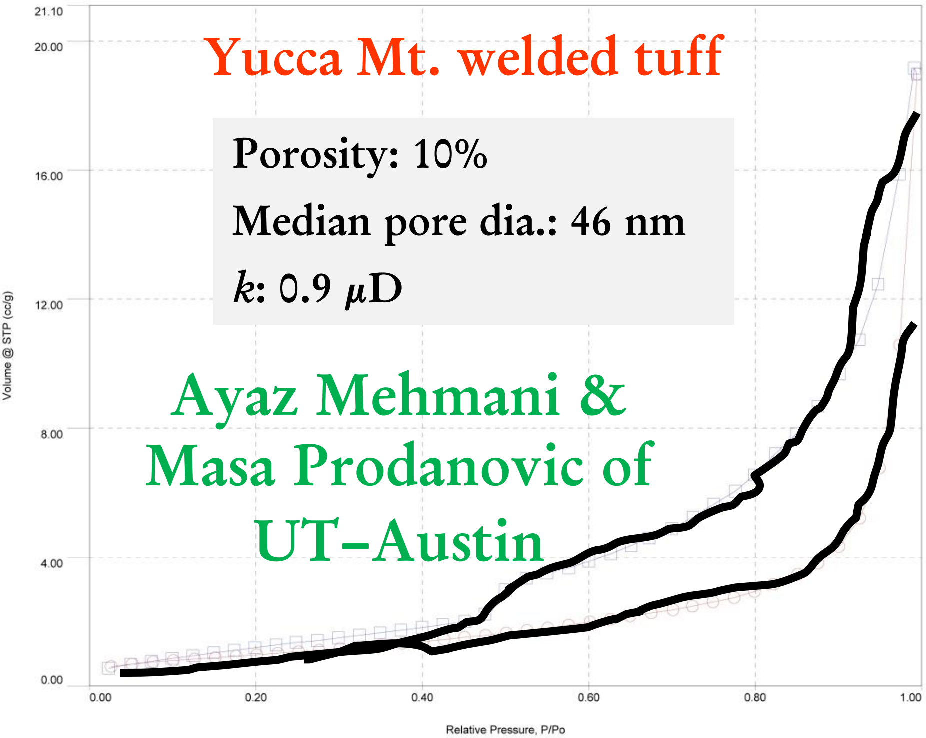
- Autosorb-IQ-MP by Quantachrome
- Pore size range: 0.35–500 nm

Shoichiro Hamamoto (Saitama University)

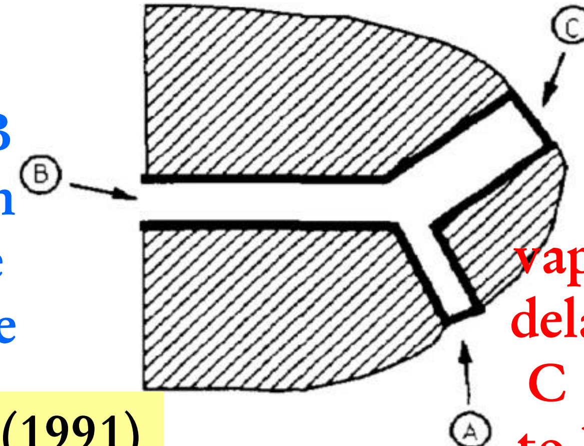
- Physical adsorption of N_2 at cryogenic temperatures (77K, -196°C)
- Molecular sorption by van der Waals forces; monolayer coverage; multilayer formation; capillary condensation; total pore volume filling
- Various theory to estimate pore-size distribution



N_2 Sorption Isotherm: Hysteresis Loop

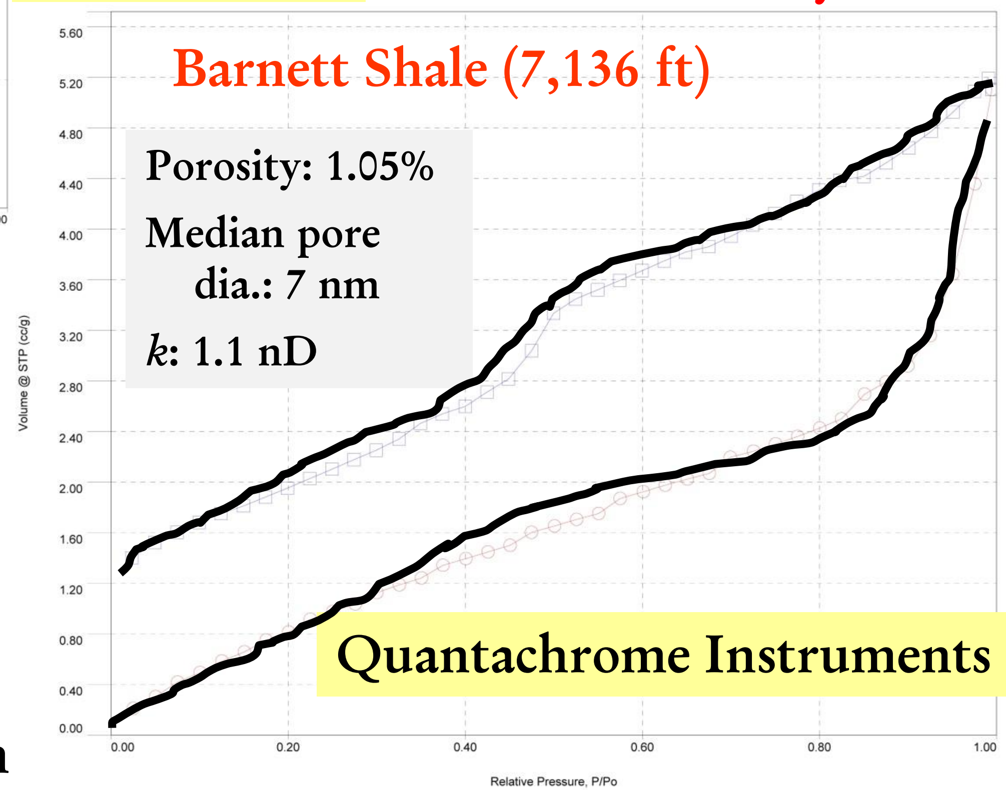


Only pore B is open to the surface



Seaton (1991)

N_2 vaporization delay in pore C gives rise to hysteresis

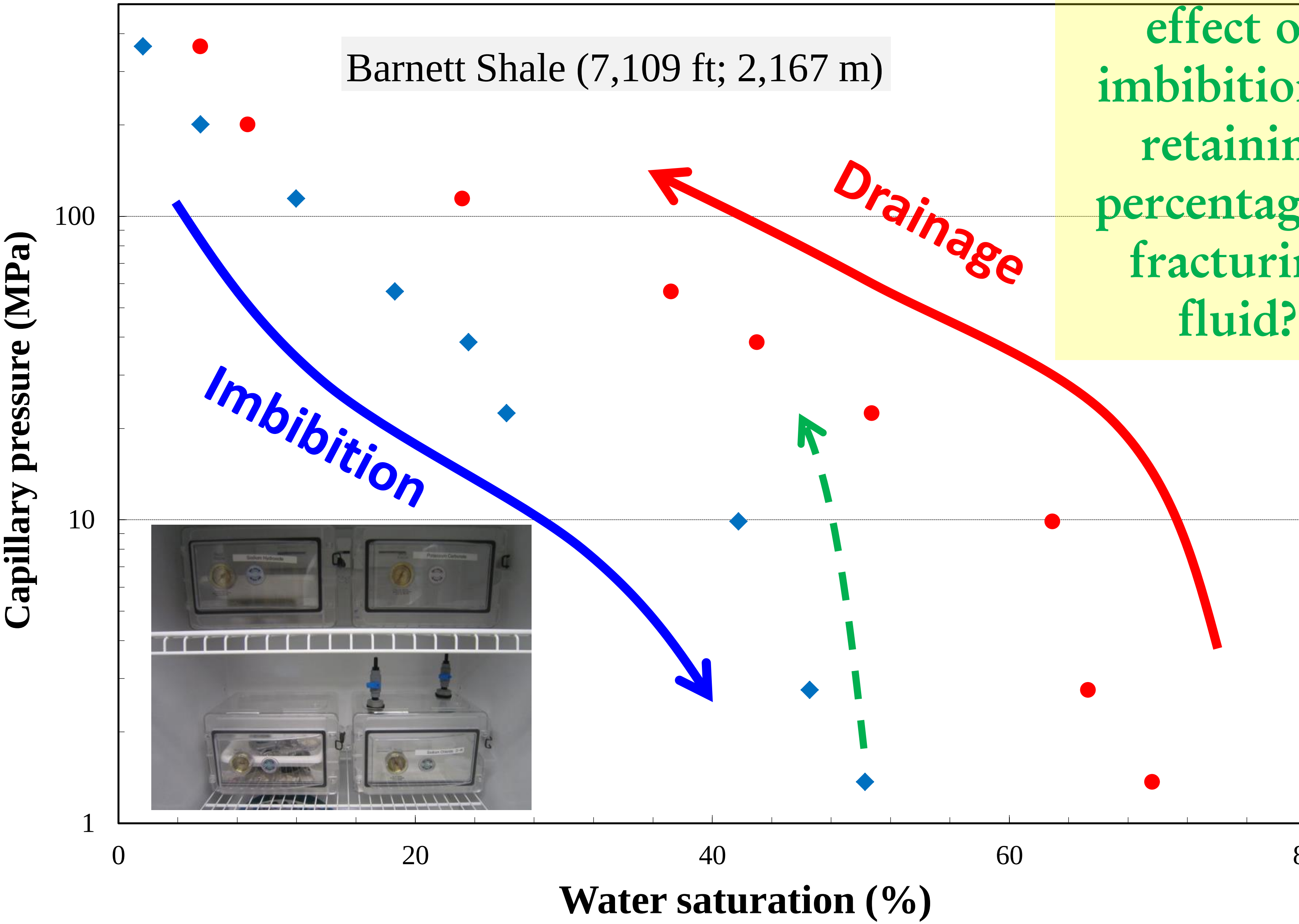


- Isotherm does not close for the Barnett Shale from extremely complex pore network effects
- CO_2 adsorption at 273.15K for micropore (0–2 nm) analysis indicates the presence of some volume of pores at ~0.35–0.7 nm

Water Vapor Sorption with RH Chambers

Drying ←									
	NaOH	CH_3COOK	K_2CO_3	$NaNO_2$	NaCl	KCl	Na_2SO_4	$CaSO_4$	H_2O
Wetting →									
RH (%)	6.96	22.9	43.2	66	75.4	84.8	93	98	99
P_c (MPa)	363	202	114	56.5	38.5	22.6	9.88	3.52	1.37
Dia. of meniscus curvature (nm)	0.80	1.45	2.54	5.13	7.55	12.9	29.4	106	212

Capillary Pressure Curve: Hysteresis Loop



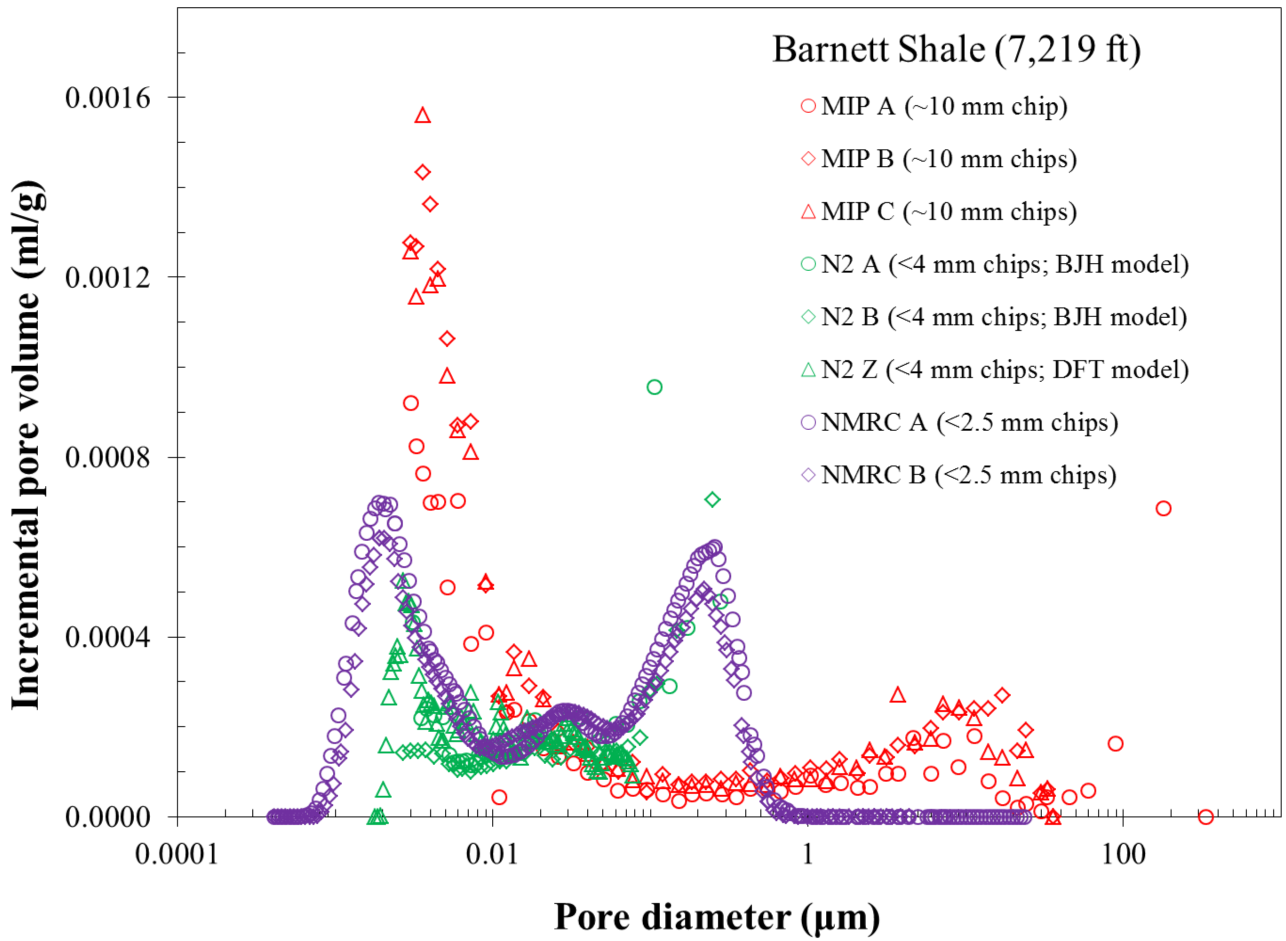
Hysteresis effect on imbibition & retaining percentage of fracturing fluid?

NMR Cyroporometry (NMRC)

- Use melting curve to calculate the pore size distribution by Gibbs–Thomson equation
- Measureable pore diameter range: ~1 nm to 10 μm
- Sample size: NMR probe/tube 2.5 mm dia. × 12 mm (30 to 300 mg)
- Measurement time: a few hrs to >24 hrs

Pore Size Distribution: Method Comparison

(NMRC data from Beau Webber, University of Kent)



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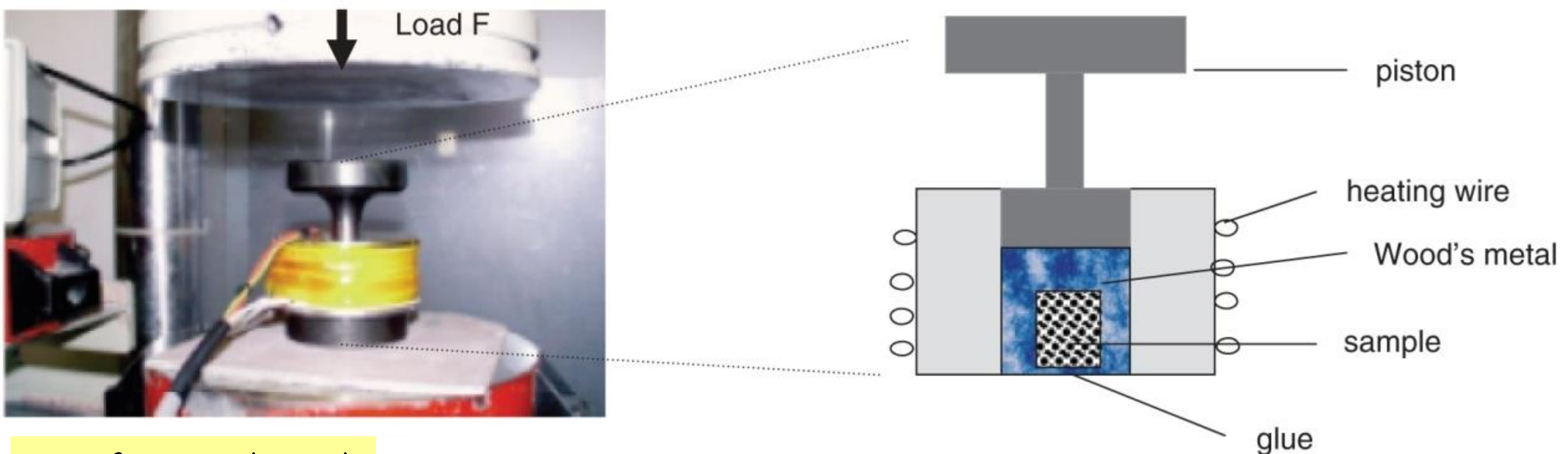
Wood's Metal Intrusion and Imaging

- Wood's metal (50% Bi, 25% Pb, 12.5% Zn, and 12.5% Cd) solidifies below 78°C without shrinking
- Heat the metal slowly (about 1 hr) above the melting point (120–150°C)

Dultz at al. (2006)

- Inject molten metal into the connected pore spaces under high pressure; sample size (up to 5 mm dia. and 15 mm long)
- Image metal distribution in polished sections 150 µm thick



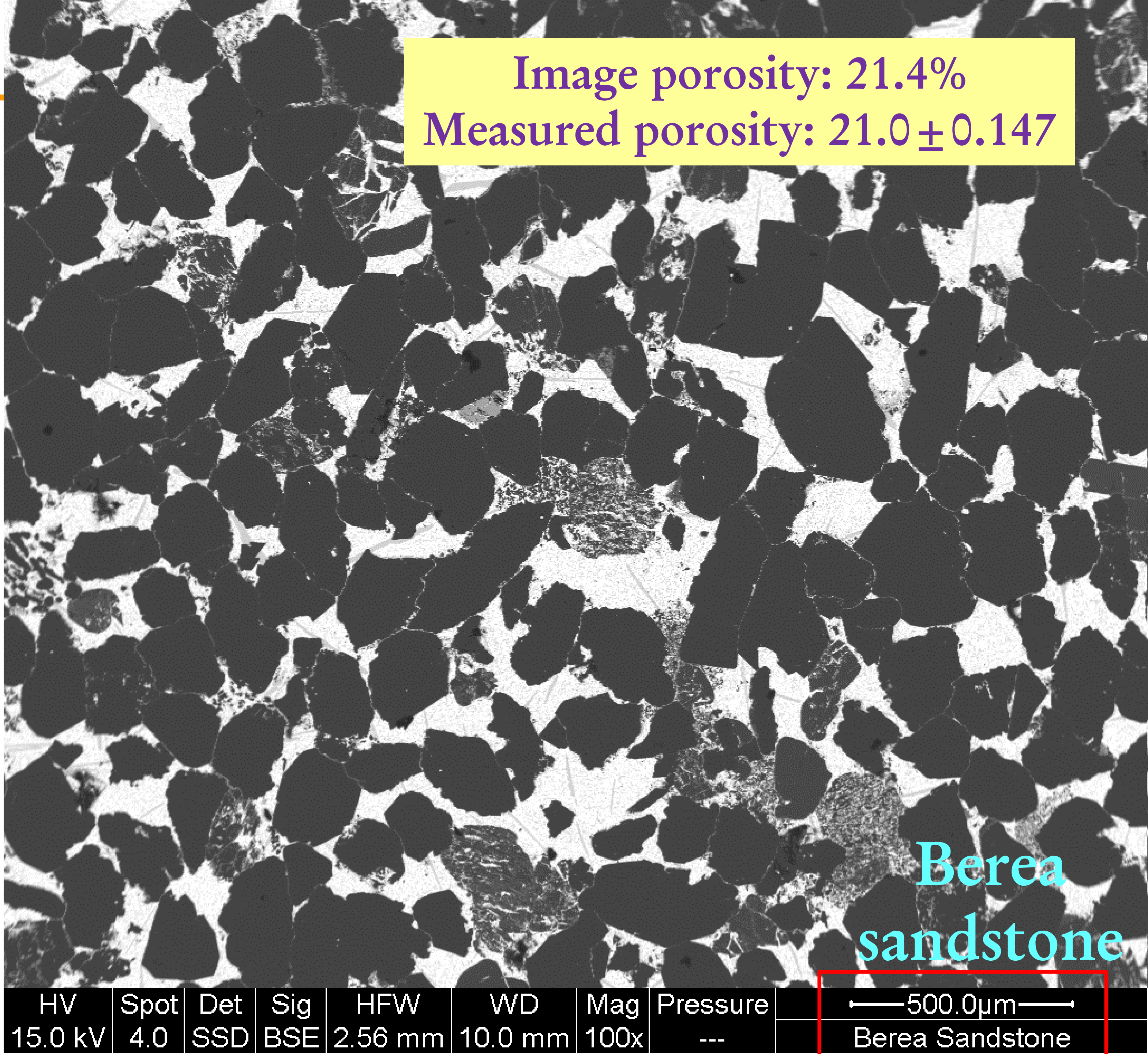
Kaufmann (2010)

Fig. 1. Apparatus Wood's metal intrusion.

600 bars used (invade 20 nm)

Wood's metal injection

Stefan Dultz (University of Hannover)



600 bars
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Wood's
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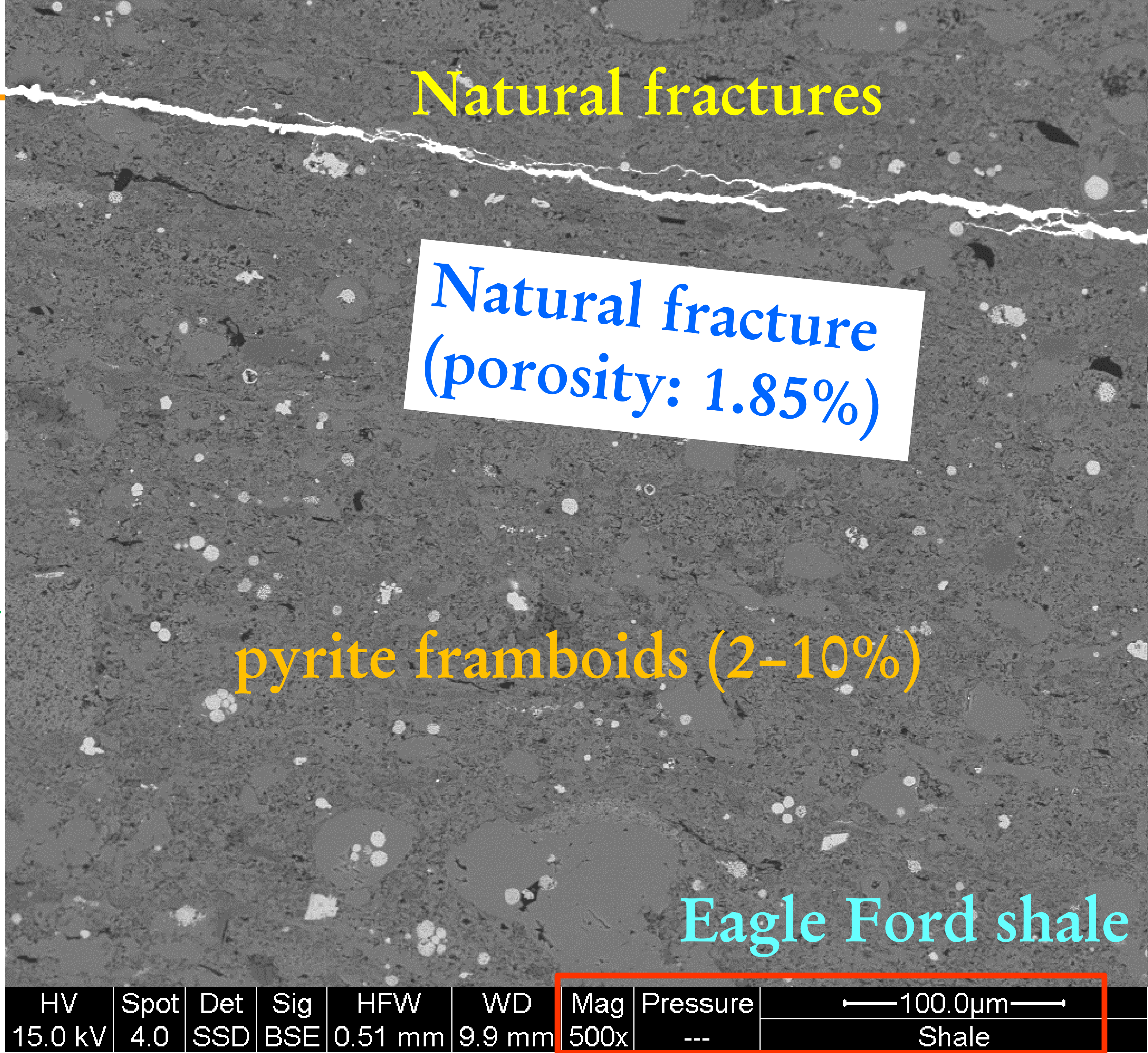
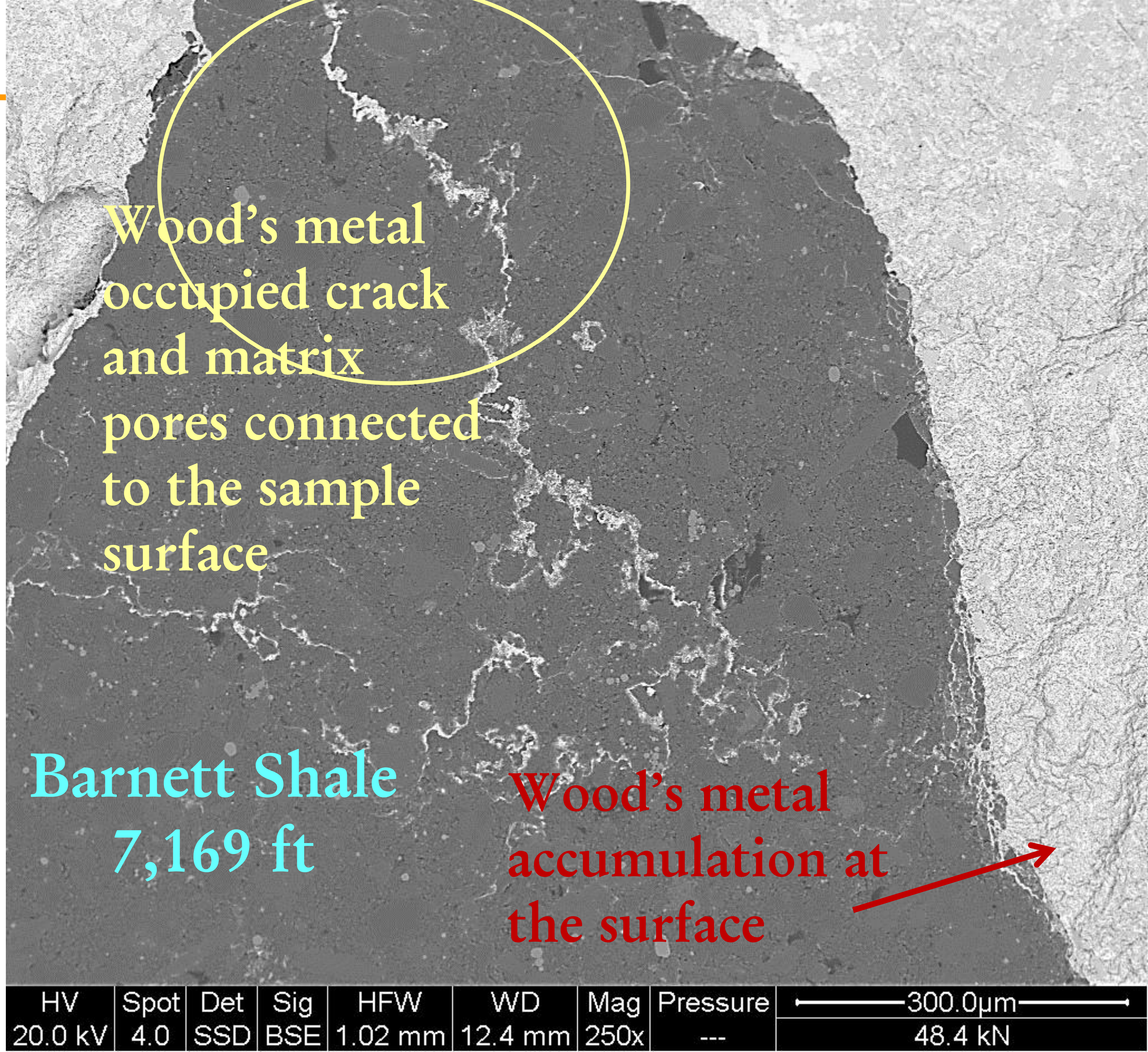


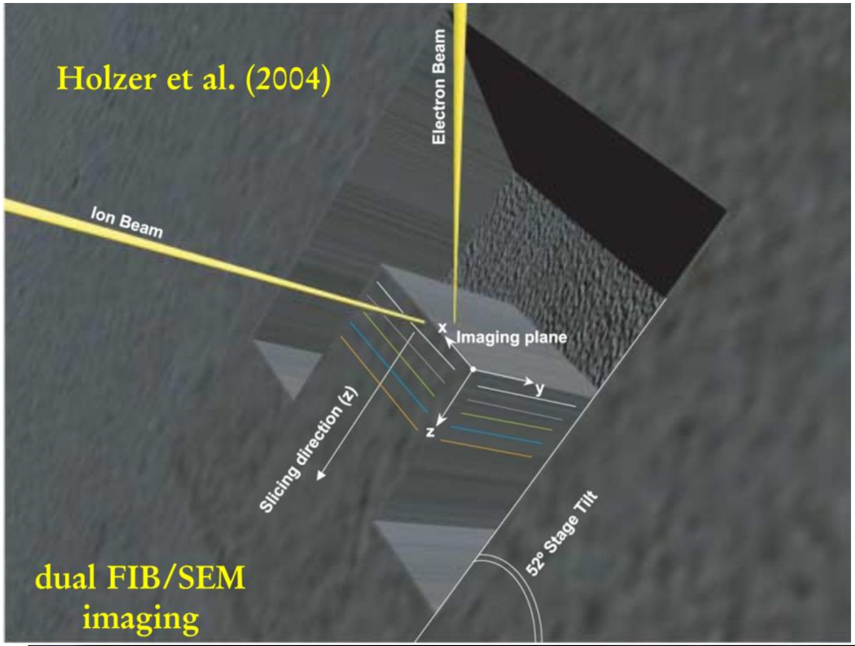
1,542 bars used (invade 9 nm in pore dia.) by Josef Kaufmann of EPMA

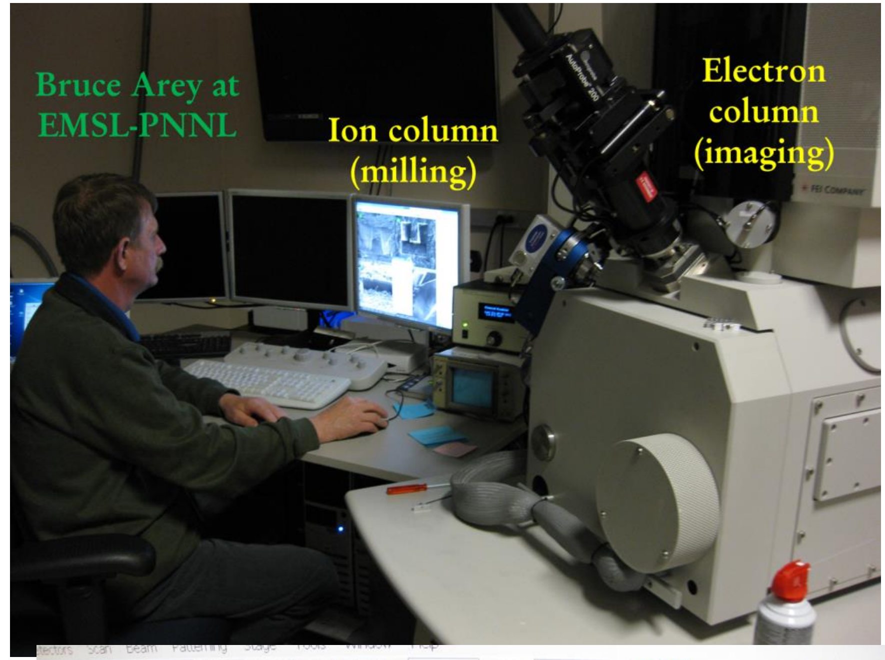
Wood's metal injection

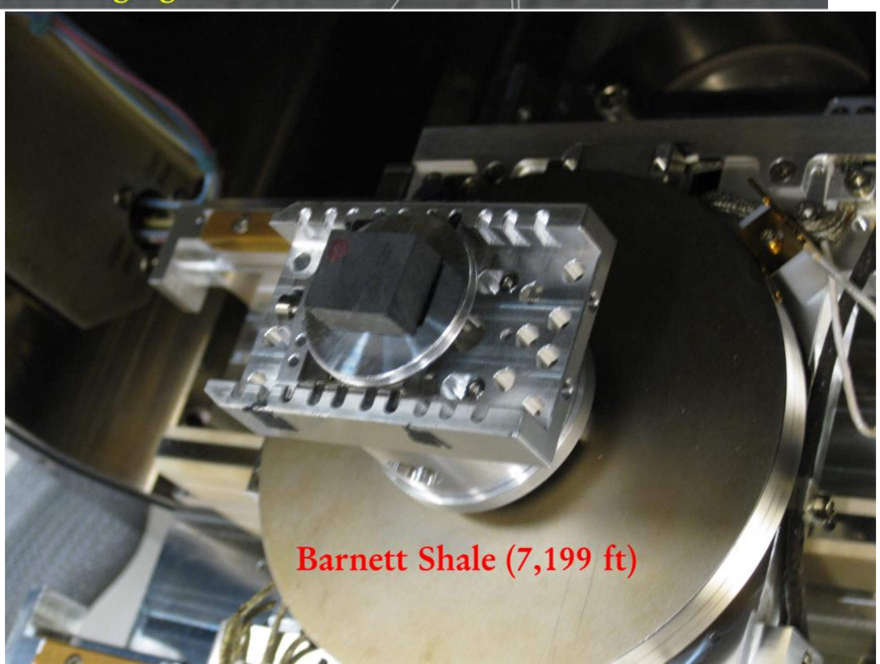
SEM-BSE by Stefan Dultz (University of Hannover)



Nano-Scale FIB-SEM Imaging







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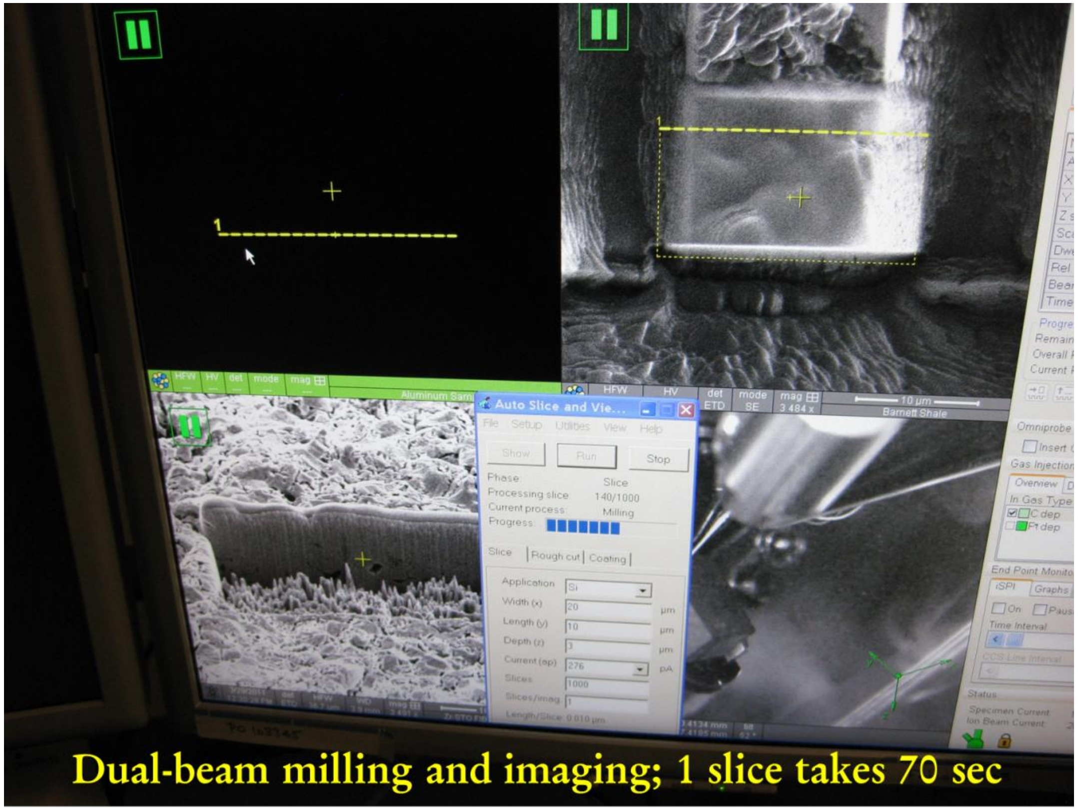
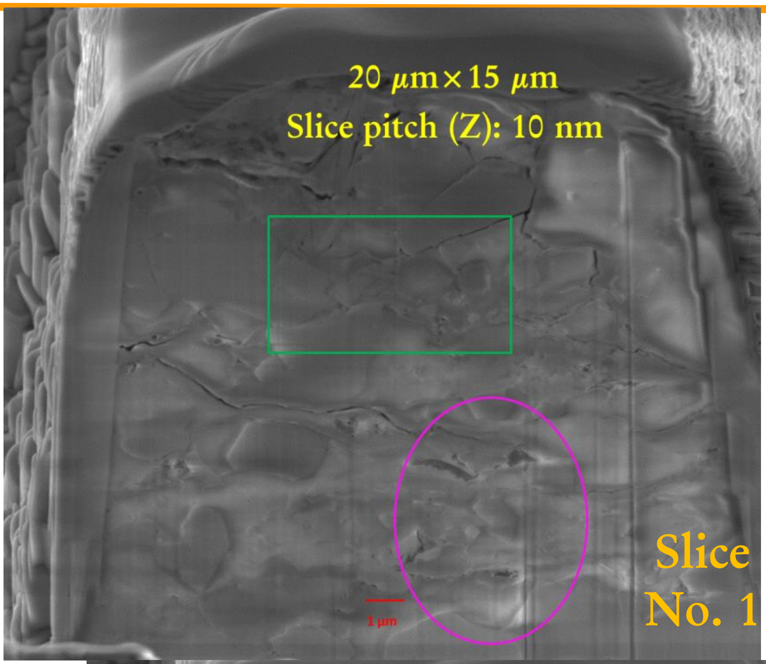
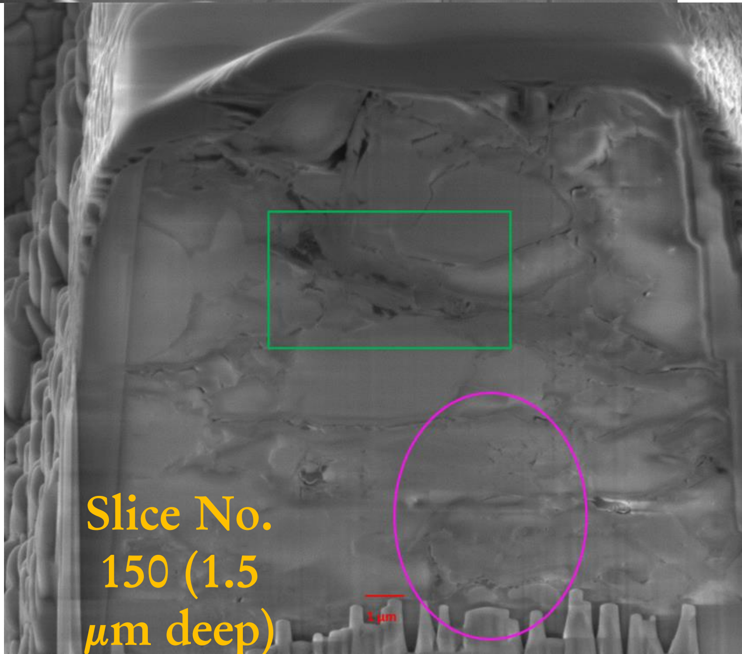


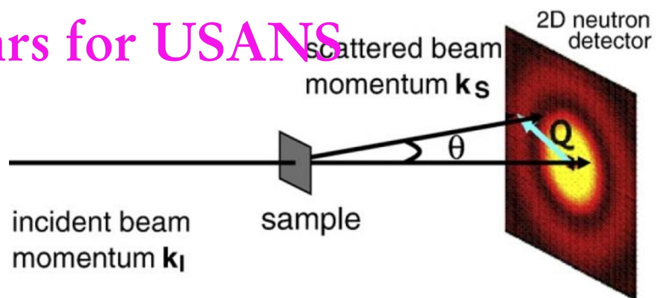




- μm scale observation scales
- Need 3-D reconstruction imaging software (e.g., Avizo Fire)
- Working with Hongkyo Yoon of Sandia Lab about pore structure processing

Small-Angle Neutron Scattering (SANS)

- Developed and refined over the past 2 decades for structural characterization of various natural and engineered porous materials
- Non-destructive nature
- Record the scattering from all pores (connected and closed); closed pores are inaccessible to fluids and, therefore, immeasurable by other techniques
- Have the ability to investigate *pore structure at realistic (reservoir) P-T conditions* and changes in pore structure at variable P-T conditions
- BT-5 perfect crystal USANS at NIST Center for Neutron Research (NCNR); General-Purpose SANS instrument at Oak Ridge National Lab (ORNL); The Lujan Neutron Scattering Center at Los Alamos National Lab (LANL)
- Measurable pore diameter range: 0.5 to 200 nm (for SANS) and ~10 μm (for ultra SANS or USANS)
- Measurement time: ~ 60 min for SANS and 7 hrs for USANS



Melnichenko, Y. B. and G. D. Wignall. 2007. Small-angle neutron scattering in materials science: Recent practical applications. *J. Appl. Phy.* 102(2), 021101.

Low gas recovery in Barnett Shale

Question

Hypothesis

Pore geometry and topology

Complementary measurements

Theory

Modeling

Analysis and evaluation

Ongoing work: CH_4 retention and transport in crushed and intact Barnett Shale

Summary

- Steep 1st year decline and low overall hydrocarbon production observed in stimulated shales
- Shales show low pore connectivity, which reduces gas diffusion from matrix to stimulated fractured network
- Several complementary approaches are used to investigate pore structure in tight shales
  - ✓ Imbibition and diffusion: macroscopic method
  - ✓ Porosimetry and vapor condensation: indirect method
  - ✓ Imaging (Wood's metal, FIB/SEM, SANS): nano–scale tool

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