[PS]Pore Structure Inhibits Gas Diffusion in the Barnett Shale*

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Abstract

The Barnett Shale is a profitable gas field, but at current recovery rates, only 10-15% of the estimated gas-in-place will be extracted. Gas recovery in this tight formation is limited by diffusive transport from the matrix storage to the stimulated fracture network. However, despite the central role of diffusion, there are no systematic studies examining the measurements and effects of pore structure on diffusion of the Barnett Shale. We present results of a study of pore structure (pore connectivity, tortuosity, and pore-size distribution) in the Barnett Shale. Pore-size distribution was measured by both mercury intrusion porosimetry (MIP) and vapor absorption porosimetry. The pores are predominantly in the nm size range (with a measured medium pore diameter of 6.5 nm), but pore size is not the major contributor to low gas recovery. The low gas diffusion appears to be caused by low pore connectivity in the Barnett Shale. This was established by imbibition tests, a relatively easy screening technique for determining whether a rock sample has low connectivity. Where gravity effects are negligible, water imbibition into a hydrophilic porous medium with well-connected pore spaces leads to mass uptake proportional to time 0.5. With sparsely connected pores, an imbibition exponent of 0.26 is obtained, as we have consistently observed for the shale samples. We also directly measured chemical diffusion in the Barnett shale using a suite of tracers, followed by chemical mapping using laser ablation-ICP-MS. Tortuosity calculated from both mercury intrusion porosimetry and saturated diffusion tests is quite low, as expected from the low pore connectivity.

Pore structure inhibits gas diffusion in the Barnett Shale

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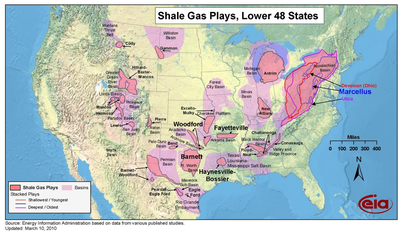
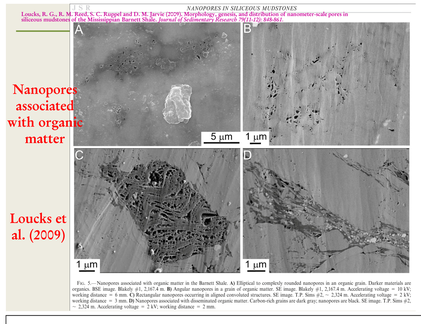
Introduction

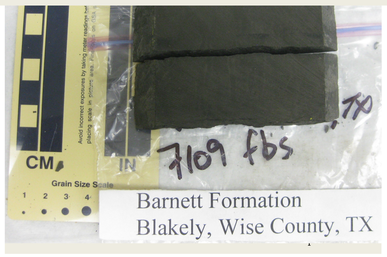
- Barnett shale: located in the Fort Worth Basin of north-central Texas
- A major gas-producing field after hydraulic fracturing
- Current gas recovery only 8-15% of the estimated gas in place (Curtis, 2002)
- Low gas diffusion & transport likely due to nano-sized pores and low pore connectivity
- Multiple approaches used to evaluate pore structure and connectivity in tight shale



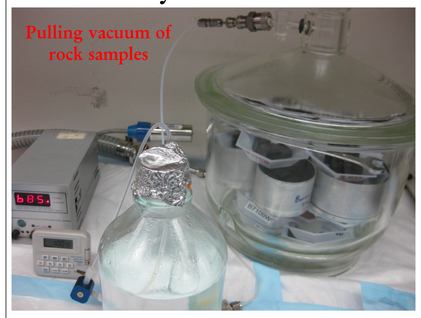
Hydrogeological Properties of the Barnett Shale

	Curtis (2002)	Bowker (2007)	Gale et al. (2007)	Grieser et al (2006)	Hill et al. (2007)	Sigal and Qin (2008)	Zhao et al. (2007)
Porosity (%)	4.4	6	5.52±0.28		6	4–8	3.8–6.0
Permeability (μd)				0.07–5	20	0.01–0.6	0.15–2.5
TOC by weight (%)	4.5			4.5			3.5–4.5
Free gas (%)					55		
Sorbed gas (%)					45		
Water saturation (%)	43	25	28.9±7.2				





Porosity Measurement and Saturated Sample Preparation



Measured Physical Properties of Barnett Shale

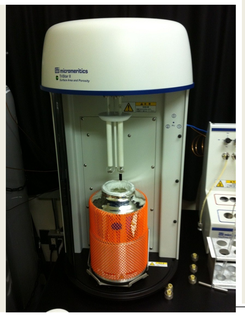
Depth (replicates)	Porosity (%)	Bulk density (g/cm³)	Particle density (g/cm³)
7,109 ft (2,167 m) (N=5)	2.77±0.98	2.31±0.04	2.38±0.04
7,136 ft (2,175 m) (N=6)	1.27±0.24	2.52±0.06	2.56±0.07
7,169 ft (2,185 m) (N=6)	3.11±0.88	2.40±0.06	2.47±0.07
7,199 ft (2,194 m) (N=6)	3.77±1.21	2.25±0.05	2.34±0.06
7,219 ft (2,200 m) (N=6)	2.67±1.15	2.40±0.07	2.47±0.08

BET N_2 Adsorption/Desorption

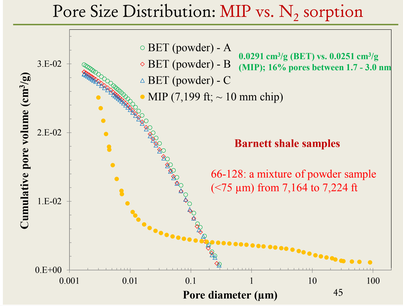
Nitrogen adsorption/ desorption measurements

TriStar II (Micrometrics)

Shoichiro Hamamoto (Saitama University, Japan)

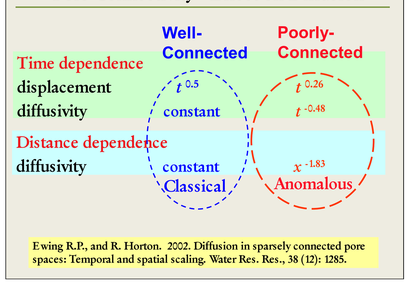


Pore Size Distribution: MIP vs. N_2 sorption



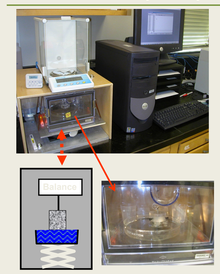
Imbibition (analog to diffusion) to Probe Pore Connectivity

Pore Connectivity - Effect on Diffusion



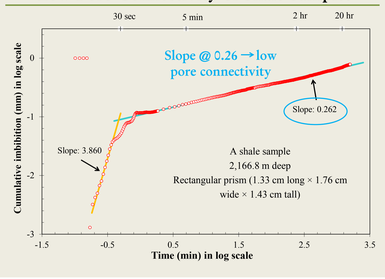
Ewing R.P., and R. Horton. 2002. Diffusion in sparsely connected pore spaces: Temporal and spatial scaling. Water Res. Res., 38 (12): 1285.

Unsaturated Transport-Sorption (Imbibition) Approach



- Cylindrical rock cores epoxy-coated along length
- Imbibition rate monitored continuously over time
- Sample size (cm range) and shape
- Different initial water contents
- Tracer solution

Low Pore-Connectivity of Shale Samples

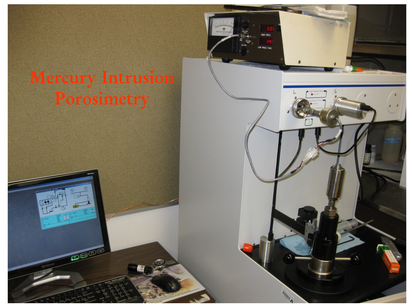


Imbibition Results for Five Barnett Shale Samples

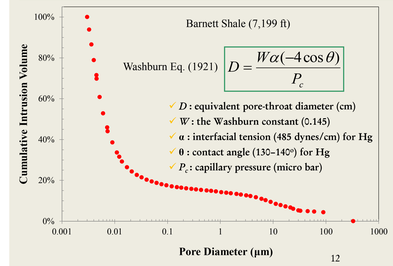
Sample	Sample dimension	Height/width	Imbibition slope
7,109 ft	1.33 cm L × 1.76 cm W × 1.43 cm H (Vertical)	0.93	0.214±0.059 (N=3)
	1.76 cm L × 1.72 cm W × 1.32 cm H (Horizontal)	0.76	0.291±0.027 (N=3)
7,136 ft	1.38 cm L × 1.71 cm W × 1.72 cm H (Vertical)	1.12	0.269±0.0045 (N=3)
	1.73 cm L × 1.73 cm W × 1.21 cm H (Horizontal)	0.70	0.216±0.040 (N=3)
7,169 ft	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	0.353±0.001 (N=2)
7,199 ft	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	0.283 (N=1)
7,219 ft	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)

Vertical: transverse to the horizontal bedding; Horizontal: parallel to the bedding.

Mercury (Wood's Metal) Intrusion Porosimetry



Mercury Intrusion Porosimetry Results



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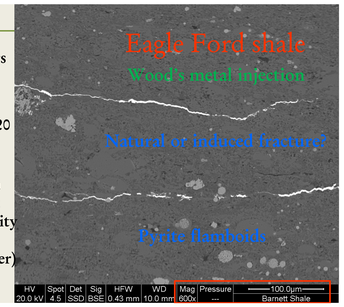
MIP Results of Five Barnett Shales

Sample depth	Total pore area (cm²/g)	Porosity (%)	Bulk density (g/cm³)	Particle (skeletal) density (g/cm3)	Median pore diameter (μm)	Permeability (mdarcy)	Tortuosity
7,109'	10.5	4.32	2.47	2.58	0.0062	4.24E-06	--
7,136'		1.05	2.63	2.66		1.22E-06	41,877
7,169'	5.31	2.88	2.56	2.64	0.0089	2.61E-06	27,325
7,199'	14.8	5.96	2.38	2.53	0.0065	6.93E-06	8,749
7,219'	5.58	2.61	2.51	2.57	0.0075	2.57E-06	21,389

Tortuosity: estimated from limited data points due to many pores in shales are smaller than 3 nm (MIP limit)

600 bars used (only invade 20 nm)

Stefan Dultz (University of Hannover)

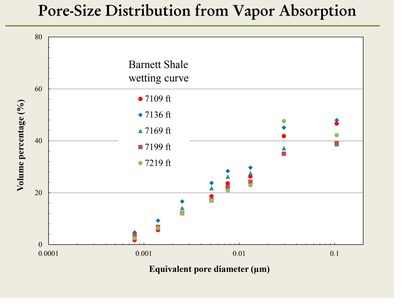


Vapor Absorption Porosimetry

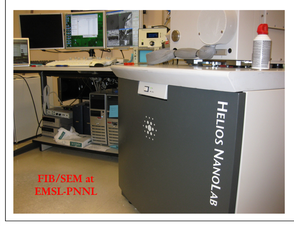
Drying and Wetting Curves with RH Chamber Methods

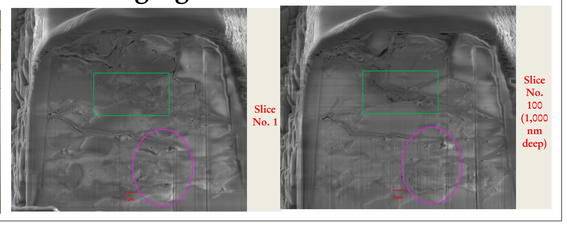
	NaOH	CH_3COOK	K_2CO_3	$NaNO_2$	NaCl	KCl	Na_2SO_4	$CaSO_4$	H_2O
Drying →									
Wetting →									
RH (%)	6.96	22.9	43.2	66	75.4	84.8	93	98	99
P_c (MPa)	363	202	114	56.5	38.5	22.6	9.88	3.52	1.37
Diameter of meniscus curvature (nm)	0.80	1.45	2.54	5.13	7.55	12.9	29.4	106	212

Pore-Size Distribution from Vapor Absorption



Focused Ion Beam/SEM Imaging of nm-Sized Shale Pores

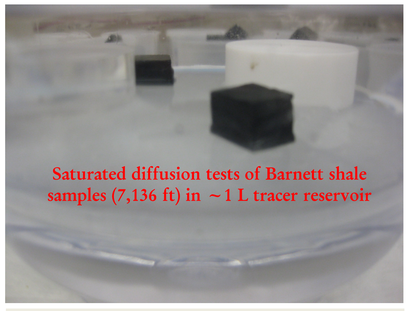




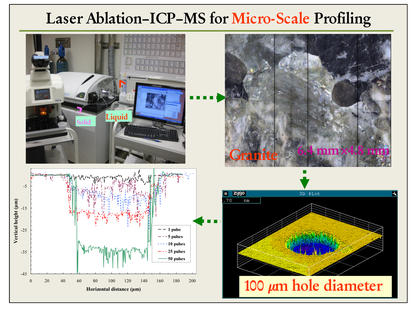
Summary

- Permeability in sub nano-darcy (10^{-21} m²) (MIP results)
- Medium pore throat in sub-nm ranges (MIP, N_2 sorption & vapor absorption)
- Nanometer-sized pores are poorly connected (imbibition)

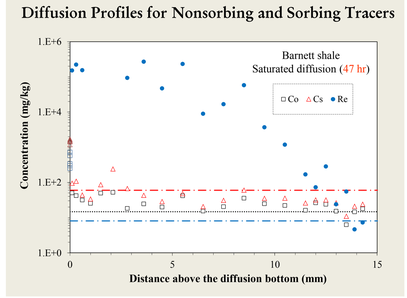
Tracer Diffusion in Saturated Barnett Shale



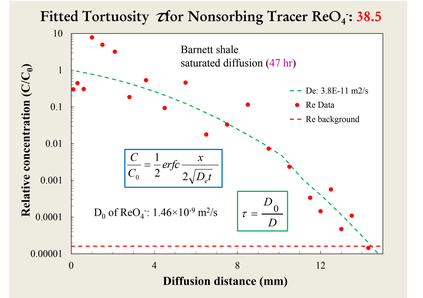
Laser Ablation–ICP–MS for Micro-Scale Profiling



Diffusion Profiles for Nonsorbing and Sorbing Tracers



Fitted Tortuosity τ for Nonsorbing Tracer ReO_4^-: 38.5



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