Low Pore Connectivity in Barnett Shale

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Pore Geometry and Topology

Total Porosity

- Isolated Porosity
- Connected Porosity

- Edge Porosity
- Infinite Cluster

- Backbone
- Dead Ends

Pore structure: shape, volume, size, size-distribution, connectivity, and surface area
Multiple Approaches to Studying Pore Structure

- Imbibition with samples of different shapes
- Edge-accessible porosity
- Liquid and gas diffusion
- Mercury injection porosimetry
- $\text{N}_2$ adsorption/desorption isotherms
- Vapor absorption
- SEM imaging after Wood’s metal impregnation
- Focused Ion Beam/SEM imaging
- Pore-scale network modeling
(Spontaneous) Imbibition Test

- Rock sample epoxy-coated along length → 1D flow
- Imbibition rate monitored continuously over time
- Sample size (cm range) and shape
- Different initial water contents
- Tracer solution
Imbibition: Low Pore-Connectivity

Cumulative imbibition (mm) in log scale vs. Time (min) in log scale

Imbibition slope = 0.262

Barnett Shale
2,166.8 m (7,109 ft)
Rectangular prism (1.33 cm long × 1.76 cm wide × 1.43 cm tall)
• $p$ is pore connectivity probability;

• $p_c$ is the percolation threshold

• Slope = 0.5 at high $p$

• Slope = 0.26 at $p=p_c$

• At intermediate $p$ values, at some time or distance to the wetting front, the slope transitions from 0.26 to 0.50
LA-ICP-MS instrumentation
3D Elemental Mapping: Edge-Accessible Porosity

ReO$_4^-$ (non-sorbing)

Rb (intrinsic)

Co$^{2+}$ (sorbing)
Averaged Concentration (N=121) vs. Depth

\[ \phi_a(h) = \phi_p \begin{cases} (h/\chi)^{\beta/\nu} & h < \chi \\ 1 & h > \chi \end{cases} \]

slope = \(-\beta/\nu \approx 0.47\)
Saturated diffusion tests of Barnett Shale samples \( \sim 1 \) L tracer reservoir
Saturated Diffusion

\[ \frac{C}{C_0} = \frac{1}{2} \text{erfc} \frac{x}{2\sqrt{D_e t}} \]

\[ \tau = \frac{D_0}{D_e} \]

- **Re exterior data**
- **Re interior line 1**
- **Re interior line 2**
- **Re background (avg +/- stnd dev)**

Fitted De: 1.46E-11 m²/s
Fitted De: 1.46E-13 m²/s

Barnett shale: 7,136 ft (2,175 m)
saturated diffusion time: 24 hr

Fitted tortuosity: **100** (exterior) and **10,000** (interior)
Gas diffusion of unsaturated Barnett Shale powder (<75 \( \mu m \))
### Tortuosity vs. Water Saturation: Powdered Barnett Shale

<table>
<thead>
<tr>
<th>Water saturation</th>
<th>Air porosity (%)</th>
<th>$D_e$ (m$^2$/s)</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-dry</td>
<td>39.2</td>
<td>$2.13 \times 10^{-6}$</td>
<td>9.59</td>
</tr>
<tr>
<td>10%</td>
<td>33.9</td>
<td>$1.56 \times 10^{-6}$</td>
<td>13.1</td>
</tr>
<tr>
<td>20%</td>
<td>20.0</td>
<td>$5.11 \times 10^{-7}$</td>
<td>39.8</td>
</tr>
</tbody>
</table>

Powdered shales (with pore networks effects minimized) still exhibit tortuous pathways
Mercury Injection Porosimetry (MIP); or Mercury Injection Capillary Pressure (MICP)

Measurable pore diameter range: 3 nm to 360 μm
MIP Intrusion Results: Pore-Throat Size Distribution

Barnett Shale

- 7,109 ft
- 7,136 ft
- 7,169 ft
- 7,199 ft
- 7,219 ft

Porosity: 1.05%

Porosities: ~3.5%
<table>
<thead>
<tr>
<th>Depth</th>
<th>Porosity (%)</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Apparent density (g/cm$^3$)</th>
<th>Median pore-throat diameter (nm)</th>
<th>Permeability (nanodarcy)</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,109 ft (2,167 m)</td>
<td>4.32</td>
<td>2.47</td>
<td>2.58</td>
<td>6.2</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>7,136 ft (2,175 m)</td>
<td>1.05</td>
<td>2.63</td>
<td>2.66</td>
<td></td>
<td>1.14</td>
<td>40,603</td>
</tr>
<tr>
<td>7,169 ft (2,185 m)</td>
<td>2.88</td>
<td>2.56</td>
<td>2.64</td>
<td>8.9</td>
<td>2.21</td>
<td>27,795</td>
</tr>
<tr>
<td>7,199 ft (2,194 m)</td>
<td>5.96</td>
<td>2.37</td>
<td>2.52</td>
<td>6.5</td>
<td>4.96</td>
<td>10,352</td>
</tr>
<tr>
<td>7,219 ft (2,200 m)</td>
<td>2.61</td>
<td>2.51</td>
<td>2.57</td>
<td>7.5</td>
<td>1.78</td>
<td>23,591</td>
</tr>
</tbody>
</table>

Permeability: Katz and Thompson (1986; 1987)
• Measure all connected pore types
• Turbomolecular vacuum pump and 1 torr pressure transducer
• Pore size range: 0.35 – 500 nm
• Surface area range: 0.01 m²/g (N₂) – no upper limit
• Samples: powders, pellets, and cores (4, 7, and 10 mm ID stem)
• Several models (density function theory, DFT) to interpret the data
• $65K

http://www.quantachrome.com/instruments.html
**N₂ Isotherm Hysteresis Loop**

**Yucca Mt. welded tuff**

- Porosity: 10%
- Median pore dia.: 46 nm
- \( k: 0.9 \mu D \)

**Barnett Shale (7,136 ft)**

- Porosity: 1.05%
- Median pore dia.: 7 nm
- \( k: 1.1 \text{ nD} \)

- **Isotherm will not close** for the Barnett shale from extremely complex pore network effects
- **CO₂ adsorption** indicates the presence of some volume of pores at \(~0.35–0.7 \text{ nm}\)

**Seaton (1991)**

- \( \text{N}_2 \) vaporization delay in pore C gives rise to hysteresis

**Quantachrome Instruments**
Sample Preparation – RH Technique

Partial saturation under different relative humidities to

• achieve desired initial rock saturation
• measure water retention curve (pore size distribution)

Chambers with different RHs

Saturated CaSO$_4$: 98% RH
### Drying and Wetting Curves with RH Chamber Methods

<table>
<thead>
<tr>
<th>Drying</th>
<th>NaOH</th>
<th>CH₃COOK</th>
<th>K₂CO₃</th>
<th>NaNO₂</th>
<th>NaCl</th>
<th>KCl</th>
<th>Na₂SO₄</th>
<th>CaSO₄</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH (%)</td>
<td>6.96</td>
<td>22.9</td>
<td>43.2</td>
<td>66</td>
<td>75.4</td>
<td>84.8</td>
<td>93</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>P_c (MPa)</td>
<td>363</td>
<td>202</td>
<td>114</td>
<td>56.5</td>
<td>38.5</td>
<td>22.6</td>
<td>9.88</td>
<td>3.52</td>
<td>1.37</td>
</tr>
<tr>
<td>Diameter of meniscus curvature (nm)</td>
<td>0.80</td>
<td>1.45</td>
<td>2.54</td>
<td>5.13</td>
<td>7.55</td>
<td>12.9</td>
<td>29.4</td>
<td>106</td>
<td>212</td>
</tr>
</tbody>
</table>
Capillary Pressure Curve: Hysteresis Loop

Barnett Shale (7,109 ft; 2,167 m)

Hysteresis effect on frac water imbibition & return percentage (4 – 30% for the Barnett Shale) of flow-back water?
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)
- Inject molten metal into the connected pore spaces using MIP instrument
- Image the metal distribution in polished sections 150 μm thick

Berea sandstone (porosity 21.3%)

Stefan Dultz (University of Hannover)

600 bars used (invade 20 nm)
Wood’s metal occupied crack and matrix pores connected to the sample surface.

Wood’s metal accumulation at the surface.

Barnett Shale 7,169 ft

SEM-BSE by Stefan Dultz (University of Hannover)

1,542 bars used (invade 9 nm in pore dia.) by Josef Kaufmann of EPMA
Bruce Arey at EMSL-PNNL

Electron column (imaging)

Ion column (milling)

FIB/SEM imaging
Slice No. 1

20 $\mu$m $\times$ 15 $\mu$m

Slice pitch (Z): 10 nm
Summary

• Pore structure information is essential in understanding hydrocarbon storage and transport

• Shales show low pore connectivity, which reduces gas diffusion from matrix to stimulated fractured network

• Several complementary approaches are needed to investigate pore structure in natural rock
  ✓ Imbibition and diffusion: macroscopic method
  ✓ Porosimetry and vapor condensation: indirect method
  ✓ Imaging (Wood’s metal, FIB/SEM): nano-scale tool