Multiple Approaches to Characterizing Pore Structure in Natural Rock

(Max) Qinhong Hu\textsuperscript{a}, Stefan Dultz\textsuperscript{b}, Shoichiro Hamamoto\textsuperscript{c}, and Robert P. Ewing\textsuperscript{d}

\textcolor{green}{(maxhu@uta.edu)}

\textsuperscript{a} University of Texas at Arlington, Arlington, TX, USA
\textsuperscript{b} Leibniz University of Hannover, Hannover, Germany
\textsuperscript{c} Saitama University, Saitama, Japan
\textsuperscript{d} Iowa State University, Ames, IA, USA
Why Study (Fractured) Natural Rock?

- Fluid flow and mass transport
- Oil, gas, and geothermal production (*since 1858 the Drake well*)
- Sustainable and safe groundwater sources (*since 1880 the Dakota sandstone*)
- Geological repository for high-level nuclear wastes (*since 1970*)
- Remediation of contaminated sites (*since 1980*)
- Carbon sequestration (*since 1997*)
- ......
Pore Geometry and Topology

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
- Nuclear Magnetic Resonance Cryoporometry
- SEM imaging after Wood’s metal impregnation
- Microtomography (high-resolution, synchrotron)
- Focused Ion Beam/SEM imaging
- Pore-scale network modeling
(Spontaneous) Imbibition Test

- Rock sample epoxy-coated along length $\rightarrow$ 1D flow
- Imbibition rate monitored continuously over time
### Imbibition Results: Shape Effect

<table>
<thead>
<tr>
<th>Rock</th>
<th>Core height/width</th>
<th>Imbibition slope</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Berea Sandstone</strong></td>
<td>1.18</td>
<td>0.649 ± 0.022</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>0.488 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>4.71</td>
<td>0.494 ± 0.008</td>
</tr>
<tr>
<td><strong>Welded tuff</strong></td>
<td>0.40</td>
<td>0.513 ± 0.014</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.371 ± 0.024</td>
</tr>
<tr>
<td><strong>Dolomite</strong></td>
<td>0.40</td>
<td>0.487 ± 0.035</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.344 ± 0.004 → 0.556 ± 0.048</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>0.300 ± 0.036</td>
</tr>
<tr>
<td><strong>Indiana Sandstone</strong></td>
<td>0.40</td>
<td>0.272 ± 0.047</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>0.253 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>2.33</td>
<td>0.291 ± 0.008</td>
</tr>
</tbody>
</table>
Pore-Scale Network: Imbibition Simulation

- $p$ 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

Oral at Session H51N-04: 8:50 am (Fri.), Rm. 3016 (Moscone West)
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 = \(-\beta/\nu \approx 0.47\)
Liquid Tracer Diffusion in Saturated Samples

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

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

Saturated shale in contact with a tracer mixture

Fitted tortuosity

✓ 100 (exterior)
✓ 10,000 (interior)

Barnett shale: 7,136 ft (2,175 m)
saturated diffusion time: 24 hr
Gas Diffusion in Consolidated Samples

\[ \tau = \phi^{(m-1)} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea Sandstone</td>
<td>4.63</td>
</tr>
<tr>
<td>Indiana Sandstone</td>
<td>6.67</td>
</tr>
<tr>
<td>Dolomite</td>
<td>6.33</td>
</tr>
</tbody>
</table>
MIP Intrusion Results: Pore-Throat Size Distribution

- Mercury Injection Porosimetry (MIP)
- Measurable pore diameter range: 3 nm to 360 µm
# MIP Results: 6 Representative Rocks

<table>
<thead>
<tr>
<th>Depth</th>
<th>Porosity (%)</th>
<th>Median pore-throat diameter (nm)</th>
<th>Permeability (µdarcy)</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea Sandstone</td>
<td>22.9 ± 1.72</td>
<td>23,776 ± 876</td>
<td>(595 ± 21.2) × 10³</td>
<td>3.31 ± 0.33</td>
</tr>
<tr>
<td>Indiana Sandstone</td>
<td>16.4 ± 0.4</td>
<td>19,963 ± 2,932</td>
<td>(221 ± 40.8) × 10³</td>
<td>4.68 ± 1.68</td>
</tr>
<tr>
<td>Welded Tuff</td>
<td>10.0 ± 0.5</td>
<td>47 ± 7.1</td>
<td>0.83 ± 0.14</td>
<td>1,745 ± 66</td>
</tr>
<tr>
<td>Dolomite</td>
<td>9.15</td>
<td>873</td>
<td>409</td>
<td>38.3</td>
</tr>
<tr>
<td>Barnett Shale</td>
<td>5.97 ± 1.43</td>
<td>6.1 ± 0.3</td>
<td>(4.96 ± 1.42) × 10⁻³</td>
<td>12,867 ± 16,224</td>
</tr>
<tr>
<td>(7,199’)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC Granite</td>
<td>1.05</td>
<td>970</td>
<td>12.4</td>
<td>38.2</td>
</tr>
</tbody>
</table>

**Permeability:** Katz and Thompson (1986; 1987)

**Tortuosity:** Hager (1998)
• **N$_2$ Isotherm Hysteresis Loop**

Yucca Mt. welded tuff

Porosity: 10%
Median pore dia.: 46 nm
$k$: 0.9 $\mu$D

• Autosorb-IQ-MP by Quantachrom

• Pore size range: 0.35 – 500 nm

Barnett Shale (7,136 ft)

Porosity: 1.05%
Median pore dia.: 7 nm
$k$: 1.1 nD

• Isotherm will not close for the Barnett shale from extremely complex pore network effects

• CO$_2$ adsorption indicates the presence of some volume of pores at $\sim$ 0.35–0.7 nm

Shoichiro Hamamoto (Saitama University)
### Vapor Absorption with RH Chambers

<table>
<thead>
<tr>
<th>Drying</th>
<th>NaOH</th>
<th>CH$_3$COOK</th>
<th>K$_2$CO$_3$</th>
<th>NaNO$_2$</th>
<th>NaCl</th>
<th>KCl</th>
<th>Na$_2$SO$_4$</th>
<th>CaSO$_4$</th>
<th>H$_2$O</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>Dia. 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)
**Pore Size Distribution: Method Comparison**

(NMRC data from Beau Webber, University of Kent)

- **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

**Barnett Shale (7,219 ft)**
- MIP A (~10 mm chip)
- MIP B (~10 mm chips)
- MIP C (~10 mm chips)
- N2 A (<4 mm chips; BJH model)
- N2 B (<4 mm chips; BJH model)
- N2 Z (<4 mm chips; DFT model)
- NMRC A (2.5 mm dia. 12 mm high cylinder)
- NMRC B (2.5 mm dia. 12 mm height cylinder)
Berea sandstone (porosity 21.3%)
1,542 bars used (invade 9 nm in pore dia.) by Josef Kaufmann of EPMA

SEM-BSE by Stefan Dultz (University of Hannover)

Barnett Shale
7,169 ft

Wood’s metal occupied crack and matrix pores connected to the sample surface

Wood’s metal accumulation at the surface
CT Scanner Results: Indiana Sandstone

- Avg. pore diameter: 50 µm (20 µm pore-throat by MIP)
- Tortuosity: X-X 3.24; Y-Y 3.42; Z-Z 3.17 (3.22 from MIP)
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 (geometry and topology) controls flow and mass transport
- Natural rock exhibits a wide range of pore structure
- Imbibition and diffusion processes confounded by pore connectivity
- 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
Funding for this project is provided by RPSEA through the “Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources” program authorized by the U.S. Energy Policy Act of 2005. RPSEA (www.rpsea.org) is a nonprofit corporation whose mission is to provide a stewardship role in ensuring the focused research, development and deployment of safe and environmentally responsible technology that can effectively deliver hydrocarbons from domestic resources to the citizens of the United States. RPSEA, operating as a consortium of premier U.S. energy research universities, industry, and independent research organizations, manages the program under a contract with the U.S. Department of Energy’s National Energy Technology Laboratory.