Idealized shale:
Pore volume measurements for standard references in theoretical modeling

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05/27/15

Road map

Introduction

Background

Methodology

- Standardizing shale sample preparation for low pressure sorption
- Idealized shale samples explained
- Isotherm measurements
- Pore volume analysis: Model selection and DFT parameters

Results

- Idealized shale trends
- Validation shale trends

Next steps

- Idealized kerogen
- Resolving pore shape

Questions
On the Nanoscale

- **DNA**: 2 nm, 2 × 10^{-7} cm
- **Soccer Ball**: 2 × 10^8 nm, 20 cm
- **Earth**: 12.7 × 10^{16} nm, 12.7 × 10^9 cm
Shale on the Nanoscale

Pores of interest are micropores and fine mesopores < 15 nm

Mesopores

Micropores

2 nm

50 nm

Macropores

Clay (Green River Illite)                        Kerogen

Images courtesy of Stanford Nanocharacterization Lab via Beibei Wang.

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Adsorption/Desorption process

Lowell et al. (2006).

Pore Size Distributions

Idealized Shales

Validation Shales

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Truncated Data

Cutoff for shales ~ 15 nm diameter corresponds to ~0.87 and ~0.88 relative pressure when using argon and nitrogen, respectively.

\[
\gamma = \gamma_0 \left( 1 - \frac{T}{T_c} \right)^p = 12.6335
\]

\[
p = 1.281
\]

\[
T_c = 150.7 \text{ K}
\]

\[
\psi_0 = 38.07 \text{ dyn/cm}
\]

\[
\frac{T}{T_c} = 87.45/150.7 = 0.58 \text{ (same value from Quantachrome)}
\]

Cutoff for shales ~ 15 nm diameter corresponds to ~0.87 relative pressure

\[
r = \frac{2 \cdot \gamma \cdot V_m}{R \cdot T \cdot \ln \left( \frac{P}{P_0} \right)} = \frac{2 \cdot 12.6335 \left( \frac{\text{erg}}{\text{cm}^2} \right) + 28.7 \left( \frac{\text{cm}^3}{\text{mol}} \right)}{8.314E7 \left( \frac{\text{erg}}{\text{mol} \cdot \text{K}} \right) \cdot 87 \text{ K} \cdot \ln(0.873)} = 7.5448E - 7 \text{ cm} = 7.5 \text{ nm}
\]

\[
r_{max} = \frac{2 \cdot \gamma \cdot V_m}{R \cdot T \cdot \ln \left( \frac{P}{P_0} \right)} = \frac{2 \cdot 12.6335 \left( \frac{\text{erg}}{\text{cm}^2} \right) + 28.7 \left( \frac{\text{cm}^3}{\text{mol}} \right)}{8.314E7 \left( \frac{\text{erg}}{\text{mol} \cdot \text{K}} \right) \cdot 87 \text{ K} \cdot \ln(0.99)} = 9.975E - 6 \text{ cm} = 99.75 \text{ nm}
\]

Lambda equation values from Stansfield, 1958

\[V_m\] value obtained from Terry et al. 1969
Shale attributes and reservoir characterization properties not considered:

- Percent this pore volume represents relative to total porosity
- Permeability
- Wettability
- Multiphase flow
- Rock strength
- Reservoir stresses
- Faulting and orientation
- Etc…

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Adsorption/Desorption process

Lowell et al. (2006).
Adsorption/Desorption process

Lowell et al. (2006).

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Outgassing Effects

Argon isotherms on Barnett shale

Changes in Volume from Changes in Outgassing Temperature
Experimental - TGA

- Netzsch STA 449 F3 Jupiter Simultaneous Thermal Analyzer and Differential Scanning Calorimeter

- Performed in N₂ atmosphere
  - Constant flow rate of 80 mL/min
  - Sample temperature ramped at 10 °C/min up to 400 °C
  - Temperature lowered at 10 °C/min to 30 °C
  - Each sample 15-30 mg
    - Except for isolated kerogen (~3 mg)
TGA Results Graphical

TGA Tabular Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Weight (mg)</th>
<th>Δwt% → 400 °C</th>
<th>Δwt% → 250 °C</th>
<th>Δwt% → 110 °C</th>
<th>Δwt% on cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barnett 1</td>
<td>19.834</td>
<td>-0.24</td>
<td>-0.15</td>
<td>0</td>
<td>0.07</td>
</tr>
<tr>
<td>Barnett 2</td>
<td>15.327</td>
<td>-1.43</td>
<td>-0.94</td>
<td>-0.55</td>
<td>-0.1</td>
</tr>
<tr>
<td>Barnett 3</td>
<td>30.133</td>
<td>-1.29</td>
<td>-0.8</td>
<td>-0.47</td>
<td>-0.11</td>
</tr>
<tr>
<td>Barnett 3 (duplicate)</td>
<td>38.142</td>
<td>-1.34</td>
<td>-0.81</td>
<td>-0.45</td>
<td>-0.11</td>
</tr>
<tr>
<td>Eagle Ford 1</td>
<td>26.356</td>
<td>-0.5</td>
<td>-0.36</td>
<td>-0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>Eagle Ford 2</td>
<td>17.219</td>
<td>-1.13</td>
<td>-0.88</td>
<td>-0.63</td>
<td>0.05</td>
</tr>
<tr>
<td>Illite</td>
<td>17.061</td>
<td>-2.32</td>
<td>-1.83</td>
<td>-1.27</td>
<td>-0.02</td>
</tr>
<tr>
<td>Kerogen</td>
<td>3.618</td>
<td>-7.3</td>
<td>-4.26</td>
<td>-3.07</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

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Determination of activation energy and pre-exponential factor for individual compounds on release from kerogen by a laboratory heating experiment

MASAHIRO OBA, HAJIME MITA and AKIRA SHIMOYAMA*
Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan
(Received August 30, 2001; Accepted November 27, 2001)

Table 2. Activation energies, pre-exponential factors and rate constants at 120°C of benzene, hexane, toluene, phenol, heptane, and indene on release from kerogen samples in Shingo sediments

<table>
<thead>
<tr>
<th>Me</th>
<th>Compounds</th>
<th>Kerogen</th>
<th>Activation energies (kcal/mol)</th>
<th>Pre-exponential factors (e^A)</th>
<th>Rate constants at 120°C (e^C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>Benzene</td>
<td>93109</td>
<td>47.0</td>
<td>1.03 x 10^12</td>
<td>7.65 x 10^15</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heptane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Indene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Summary of Rate Constants at 250 °C Averaged Over Six Evolved Species (min/max for individual kerogens)

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Max</th>
<th>Ave</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.384E-10</td>
<td>3.76E-08</td>
<td>7.67E-09</td>
<td>4.75E-09</td>
<td></td>
</tr>
</tbody>
</table>

Average Rate Constants Calculated at 250 °C
(averaged over five kerogens per compound)

<table>
<thead>
<tr>
<th>Evolved Species</th>
<th>Activation energies from Oba et al. (kcal/mol)</th>
<th>Pre-exponential factors (1/s)</th>
<th>Rate Constant at 120 °C from Oba et al.</th>
<th>Rate Constant Calculated at 250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>49</td>
<td>2.46E+12</td>
<td>1.41 x 10–15</td>
<td>8.34E-09</td>
</tr>
<tr>
<td>Hexane</td>
<td>55.3</td>
<td>2.60E+14</td>
<td>4.69 x 10–17</td>
<td>2.06E-09</td>
</tr>
<tr>
<td>Toluene</td>
<td>50.5</td>
<td>6.83E+12</td>
<td>5.75 x 10–16</td>
<td>5.47E-09</td>
</tr>
<tr>
<td>Phenol</td>
<td>52.8</td>
<td>4.95E+13</td>
<td>2.19 x 10–16</td>
<td>4.34E-09</td>
</tr>
<tr>
<td>Heptane</td>
<td>54.6</td>
<td>2.21E+14</td>
<td>9.77 x 10–17</td>
<td>3.43E-09</td>
</tr>
<tr>
<td>Indene</td>
<td>46.7</td>
<td>4.90E+11</td>
<td>5.34 x 10–15</td>
<td>1.52E-08</td>
</tr>
</tbody>
</table>
Repeatable Isotherms Barnett Shale at 250 C

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Barnett Repeats PSD

Barnett Cumulative Pore Volume and PSDs
Effects of temperature on clays

Interlayer cation loss?

Interlayer collapse?

Dehydroxilation? Most likely, no. (>450 C)
Four Components Mechanically Mixed

Kerogen to represent total organic carbon (TOC)

Illite to represent clay

Silicon dioxide (SiO$_2$) for quartz

Calcium carbonate (CaCO$_3$) as itself

Images courtesy of Stanford Nanocharacterization Lab via Beibei Wang.

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### Three Test Groups of Idealized Shales

<table>
<thead>
<tr>
<th>Illite (%)</th>
<th>Kerogen (%)</th>
<th>TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>0-12%</td>
<td>0-8%</td>
</tr>
<tr>
<td>30%</td>
<td>0-12%</td>
<td>0-8%</td>
</tr>
<tr>
<td>55%</td>
<td>0-12%</td>
<td>0-8%</td>
</tr>
<tr>
<td>Remaining</td>
<td>Remaining</td>
<td>Remaining</td>
</tr>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Even Split</td>
<td>Even Split</td>
<td>Even Split</td>
</tr>
<tr>
<td>Quartz/Carbonate</td>
<td>Quartz/Carbonate</td>
<td>Quartz/Carbonate</td>
</tr>
</tbody>
</table>

### Three Validation Groups

- **Barnett**
  - 6-39% Clay
  - 1-6% TOC
  - Depth: ~2600 m

- **Eagle Ford**
  - 6-22% Clay
  - 2-5% TOC
  - Depth: 3900 m

**Baltic Sequence**
- 39-72% Clay
- 0-5% TOC
- Depth: 1416-4409 m

Selected those Baltic samples with ~55% clay for comparison to idealized 55% group.
Methodology III

ISO THERM MEASUREMENTS

Quantachrome Autosorb iQ2
Sorption Isotherm Begets PSDs

Quenched Solid Density Functional Theory (QSDFT)

Kerogen N₂ Isotherm

Quenched Solid Density Functional Theory (QSDFT)

Silurian Kerogen

Validation Sample

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Methodology IV

PORE VOLUME ANALYSIS:
MODEL SELECTION AND
DFT PARAMETERS
DFT parameters

Pore shape: Slit? Cylinder? Combination?
Basis for surface potential: Carbon? Silica?

Difficulties in Pore Analysis

- Exposure to high temperatures during outgas
  - Literature recommendation is 100 ° C
  - May not desorb species from micropore region

- Choice of adsorbate
  - \( \text{N}_2 \) @ 77K, \( \text{CO}_2 \) @ 273K, Ar @ 87 K

- How do you model the pore size distribution?
  - Traditional methods (BJH, DR/DA) rely on basic assumptions that may not be valid
  - Advanced DFT based methods also have basic assumptions that may not be valid
Pore Size Distribution Methods

- CO₂ – NLDFT, carbon equilibrium transition kernel at 273 K based on a slit-pore model
- N₂/Ar – QSDFT, carbon equilibrium transition kernel at 77/87 K based on a slit-pore model
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Conclusion

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Questions

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Results I

IDEALIZED SHALE TRENDS

Pore Volumes

Pore Volume vs TOC for pore diameters < 15nm

- $y = 0.003x + 0.0065$  $R^2 = 0.8438$
- $y = 0.0023x + 0.0048$  $R^2 = 0.8315$
- $y = 0.0015x + 0.0125$  $R^2 = 0.9836$

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Results II

Validation Shale Trends

Pore Volumes

Pore Volume vs TOC for pore diameters < 15nm

y = 0.0014x + 0.0158
R² = 0.2328

y = 0.0015x + 0.0125
R² = 0.9836

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Pore Volume vs % Clay

\[ y = 0.0002x + 0.0064 \]
\[ R^2 = 0.021 \]

Baltic ~55% Clay Group: Depth vs Pore Volume

\[ y = -166613x + 5785.5 \]
\[ R^2 = 0.8133 \]
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Pore Volumes

Pore Volume vs TOC for pore diameters < 15nm

\[ y = 0.0014x + 0.0158 \]
\[ R^2 = 0.2328 \]

\[ y = 0.0015x + 0.0125 \]
\[ R^2 = 0.9836 \]

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Next Steps

Better compositional proxies: This summer, we intend to use activated carbons and zeolites with known pore geometries and PSDs to simulate shales to provide the best possible benchmarkers

Finish 55% sequence

Create model to predict shale pore volume as function of %clay, %TOC and depth, and apply predictions to reservoir models

Run repeats

Monte Carlo simulations to substantiate pore geometry

Interlayer cation simulations

Questions?

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Stanford University
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- Quantachrome Instruments - Matthias Thommes, Katie Cychosz
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Additional References


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