Creation of Porosity in Tight Shales during Organic Matter Maturation*

Jeremy Dahl¹, J.M. Moldowan², Joel Walls³, Amos Nur³, and Juliana DeVito³

Search and Discovery Article #40979 (2012)**
Posted July 23, 2012

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Long Beach, California, USA, April 22-25, 2012
**AAPG©2012 Serial rights given by author. For all other rights contact author directly.

¹Advanced Materials, Stanford University, Palo Alto, CA (dahl@stanford.edu)
²Geological and Environmental Science, Stanford University, Stanford, CA
³Ingrain, Houston, TX

Abstract

It has been suggested that porosity and permeability are created in tight shales during the organic matter maturation process; i.e., kerogen conversion to oil and gas followed by oil cracking to gas. We have tested this hypothesis by examining changes in porosity, using FIB-SEM and following our experimental protocol, as given here:

• Started with oil-window maturity samples of Woodford and Bone Spring shales
• Heated them into wet and dry gas window
• Observed changes in porosity microscopically

Artificial maturation (laboratory pyrolysis) was carried out on these samples by heating them in pressure vessels under argon for a sequence of times and temperatures to induce oil generation and oil cracking. Porosity was recorded at various stages of maturation. These experiments were compared with results from a variety of naturally-matured shales of varying maturities. Kerogen maturity and hydrocarbon generation were determined by Rock-Eval pyrolysis. The extent of oil cracking to gas was measured by diamondoid analysis; i.e., quantitative measurements of nanometer-sized hydrogen-terminated diamonds dissolved in the generated liquids. Our results show that the process of organic matter maturation can produce porosity in tight shales, with the amount of porosity creation varying from sample to sample. Further, pressure due to oil cracking may cause natural fracturing and/or aid in hydrofracing.

Reference

Creation of Porosity in Tight Shales during Organic Matter Maturation

By
Jeremy Dahl, J.M. Moldowan, Joel Walls, Amos Nur, Juliana DeVito

Stanford University, Ingrain Technologies
Porosity creation and destruction during maturation of organic matter

1. Kerogen conversion to gas and liquids and migration of those hydrocarbons out of pore space
Porosity creation and destruction during maturation or organic matter

2. Oil conversion (cracking) to gas causing fracturing.
Porosity creation and destruction during maturation or organic matter

3. Formation of pyrobitumen (porosity destruction)
Conclusion: Porosity is created and destroyed during maturation but process shows wide variation from sample to sample.
Considerations: Natural Samples

• With natural samples you don’t know if porosity creation is related to heating or facies (could be comparing apples and oranges).
• Therefore we did heating experiments to see if we see same trends and features that you do in natural situations.
Experimental Protocol

• Started with oil-window maturity samples
• Heated them into wet and dry gas window
• Measured the extent of oil cracking
• Observed changes in porosity microscopically
Samples

Woodford Shale
$Ro = 0.9$

Bone Spring
$Ro = 1.06$
Heated samples in sealed pressure vessels (no confining pressure)

**Woodford**
- Unheated
- Heated Wet Gas Window

**Bone Spring**
- Unheated
- Heated Dry Gas Window
Measure Maturity (Oil Cracking) Using Diamondoids
What are diamondoids?

They are nanometer-size, hydrogen-terminated diamonds.
What happens to diamondoids when we crack an oil?
50% Oil Cracking Doubles the Diamondoid Concentration

1 ml
5 ppm

0.5 ml
10 ppm
Crack Another 50% of the Oil and the Diamondoid Concentration Doubles Again

0.5 ml 10ppm

Methane

0.25 ml 20ppm
And So On According to the equation:

\[ \text{% Cracking} = \left[ 1 - \frac{\text{Co}}{\text{Cc}} \right] \times 100 \]
# Results of Heating Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ro</th>
<th>Diam Conc. ppm</th>
<th>% Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woodford Unheated</td>
<td>0.9</td>
<td>2.6</td>
<td>0</td>
</tr>
<tr>
<td>Woodford Heated</td>
<td></td>
<td>3.8</td>
<td>32%</td>
</tr>
<tr>
<td>Bone Spring Unheated</td>
<td>1.06</td>
<td>3.9</td>
<td>0</td>
</tr>
<tr>
<td>Bone Spring Wet Gas Window</td>
<td></td>
<td>11.6</td>
<td>66%</td>
</tr>
<tr>
<td>Bone Spring Dry Gas Window</td>
<td></td>
<td>69.5</td>
<td>95%</td>
</tr>
</tbody>
</table>
Tight Shale Porosity

From Loucks, et al, GCAGS, April 2010
Three Classes of Organic Matter Texture

- Solid
- Pendular (bubble)
- Spongy
- Fracture
Porosity and Organic Matter

Interpretation of SEM image:

- **White**: High density material (e.g., iron rich)
- **Shades of Gray**: Minerals with densities of 2-3 g/cc
- **Dark Gray**: Organic Matter
- **Black**: Pore space

•**Phi_OM**: The percentage of space within the organic matter bodies that is classified as porosity
Bone Spring- Heated, Dry Gas
Heated Wet Gas Window

Phi_OM - Bone Spring

- Unheated
- Heated Wet Gas
- Heated Dry Gas

Total Porosity (%) vs. Phi_OM (%)

- Moderate Oil Cracking
- Severe Oil Cracking
- Pyrobitumen Formation
Woodford displays different behavior

Phi_OM - Woodford Shale

- Unheated
- Heated Wet Gas

Total Porosity (%) vs. Phi_OM (%)
What if kerogen converts to liquids and liquids to gas and there is no escape route?
Fracturing?

Gasoline Explosions
We can Estimate Maximum Pore Pressure Generated by Oil Cracking

1. Estimate the volume of pore space occupied by organic matter (TOC, microscopically, etc.)
2. Determine kerogen type to estimate H/C ratio
3. Determine the amount of cracking using diamondoid methodology
4. Calculate pressure using ideal gas law (correct for non-ideality of methane):
   \[ P = \frac{nRT}{V} \]
Calculating Pressures due to Oil Cracking

Example

Let’s say that the pore space is 75% full of organic matter.

We have Type II organic matter (e.g., Barnett); so the specific gravity should be about 1.5 g/ml.

So there is .75 ml X 1.5 g/ml or **1.12 grams** of organic matter in the pore.

We also need to estimate original Organic matter H/C ratio.

For Type I kerogen H/C >1.25
For Type II kerogen H/C <1.25 Let’s use 1.20
Oil Cracking

Methane

CH₄

Graphite

C

Hydrogen goes to methane production. The amount of Hydrogen plus the extent of cracking is used to calculate total amount of methane produced.

Then we can calculate the wt% H of organic matter with formula C₁H₁.₂₀ (the C/H ratio is 1.20)
Carbon 12 (mol wt) X 1 is 12
Hydrogen 1 (mol wt) X 1.2 is 1.2
Total weight = 13.2
So weight percent hydrogen = 1.2/13.2 = 0.091 X 100 = 9.1% H

In our example we have 1.12 g of organic matter of which 9.1 wt% is Hydrogen
So we have 1.12 X .091 = 10 grams of hydrogen

To calculate pressure produced by cracking oil to methane we will use the ideal gas equation

We have 0.1 g of hydrogen which is equal to 0.1 mols of Hydrogen.
To make 1 mol of CH₄ we need 4 mols of hydrogen. So in our example we can make 0.1/4 or 0.025 mols of methane.

PV = nRT or P = nRT/V
\[ P = \frac{nRT}{V} \]

\[ n = 0.025 \text{ mols of methane} \]
\[ R = 0.082 \text{ liter atmospheres/mol degree K} \]
\[ T = 200 + 273 = 473 \]
\[ V = 0.001 \text{ liter} \]

\[ P = \frac{(0.025) (0.082) (473)}{(0.001)} = 970 \text{ atm} \]

\[ 14.7 \text{ psi/atm} \times 970 \text{ atm} = 14,260 \text{ psi} \]

This is for 100% cracking. We can adjust calculation to measured amount; e.g., 50% cracking generates about 7000 psi for this example with 75% pore space organic matter. Typical hydrofracing pressures are 8000 psi at 10,000 ft. Pressure due to oil cracking may cause natural fracturing and/or aid in hydrofracing.
Heated Woodford

Fracture?
Heated-Dry Gas, Bone Spring

Fracture?
Conclusion: Porosity is created and destroyed during maturation but process shows wide variation from sample to sample.
Future Work

• More samples, different shales, different mineral facies, different organic facies, different TOC’s.
• Study process through entire oil window
• Compare lab results with natural samples
• Pyrolysis under pressure
• Continue to look for fracturing. Document extent, direction, size, etc.
• dahl@Stanford.edu