Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation*

Lucy (Ting-Wei) Ko¹,², Tongwei Zhang¹, Robert G. Loucks¹, Stephen C. Ruppel¹, Deyong Shao³

Search and Discovery Article #51228 (2016)**
Posted February 29, 2016

*Adapted from poster presentation given at AAPG 2015 Annual Convention and Exhibition, Denver, Colorado, May 31 – June 3, 2015
**Datapages © 2016 Serial rights given by author. For all other rights contact author directly.

¹Bureau of Economic Geology, University of Texas at Austin, Austin, Texas, USA (cole7259@gmail.com)
²Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA
³The School of Geosciences, Lanzhou University, P. R. China

Abstract

It is now well known that pore development in organic-rich mudrocks is associated with organic matter (OM) thermal maturation. Organic-rich mudrocks usually contain mixed types of kerogen. Therefore, routinely used vitrinite reflectance measurements cannot define exact OM transformation stages. Understanding the evolution of OM-hosted pores and mineral pores to well-defined oil and gas generation stage is essential to characterize mudrock reservoirs. Immature Barnett (quartz and clay mineral-rich), Woodford chert and mudstone (quartz and clay mineral-rich), and low-maturity Boquillas (carbonate-rich) core and outcrop samples were heated anhydrously in gold tubes to study the evolution of OM and OM pores during maturation. Geochemical characterization such as oil and gas yields, Rock-Eval, and Leco TOC analyses were used to characterize kerogen type and OM transformation stages. Samples were also prepared using Ar-ion milling to investigate pore development with field-emission scanning electron microscopy (FE-SEM). The OM in these immature and low-maturity mudrocks can be dominantly kerogen (Barnett) or bitumen (Boquillas) or a mixture. The difference between kerogen (insoluble, in-situ OM) and bitumen (soluble migrated OM) did not affect much of the pore evolution, even though theoretically kerogen contains more inert (dead) carbon than bitumen. In all samples, modified mineral pores are dominant during bitumen and oil generation, while during gas generation, nm-sized equant OM-hosted pores are dominant. The nanometer-sized equant OM-hosted pores observed during wet gas and dry gas window are interpreted to be related to gas generation. In the Barnett and Woodford mudstone, as maturation begins, OM first shrinks, forming artificial shrinkage pores. Later, the volume of OM significantly decreases. These pores continue to develop into the gas generation stage.
Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation

Lucy (Ting-Wei) Ko¹,², Tongwei Zhang¹, Robert G. Lourie¹, Stephen C. Ruppel¹, Deyong Shao³

¹. Bureau of Economic Geology, University of Texas at Austin, Austin, Texas, USA
². Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA
³. The School of Geosciences, Lanzhou University, P. R. China

Problem Statement and Objectives

It is well accepted that organic matter (OM) pores in mudrocks are predominantly formed by thermal maturation. We have demonstrated that the change of size and shape of OM pore is related to stepwise transformation of organic matter and can be associated with generated pre-oil bitumen, oil, gas, post-oil bitumen (pyrobitumen), char, and irreducible formation water by combined geochemical characterization, laboratory pyrolysis, and SEM petrography methods (Ko et al., 2014).

In this study, we investigate and compare the effects of bulk mineralogy, total organic content (TOC), and initial organic matter type (kerogen vs. bitumen) on the evolution of OM pores and mineral pores in mudrocks.

Immature Barnett siliceous mudrock (clay mineral-rich), Woodford chert and siliceous mudrock, and low-maturity Boquillas calcareous mudrock samples were artificially matured. OM pore evolution in each was investigated and compared.

Specific research questions include:
1. Do differences in kerogen type affect OM pore development and evolution?
2. Does bulk mineralogy affect timing of OM transformation and thus pore evolution?
3. Does Woodford chert or mudstone develop better porosity?
4. Does pore evolution differ in kerogen and bitumen?

Flow Chart of Research Objectives

gaseous, liquid, and solid geochemical characterization
N: adsorption, SEM pore imaging for pore characterization
oil and gas generation stages
pore type, structure, distribution and PSD
pore evolution in OM thermal maturation

Methods

1. Immature or low-maturity Barnett, Eagle Ford-equivalent Boquillas, and Woodford mudrocks were collected from cores and outcrops. For each sample, 8 small-diameter rock cylinders (6 mm diameter and 2-3 cm length) were drilled perpendicular to bedding planes.

2. The cylinders were pyrolyzed in sealed gold tubes that were placed in stainless steel autoclaves.

3. The pyrolysis experiments were conducted under isothermal conditions at temperatures of 130, 300, 310, 333, 367, 425°C for 72 hrs reaction time. A constant confining pressure was maintained at approximately 68.85 MPa (10,000 psi) during experiments.

4. All generated petroleum (gas, liquid, and solid) were collected for compositional analyses. HC yield was determined by gas chromatography (GC). Saturate, aromatic, resins, and asphaltene (SARA) separation and quantification were done on each sample.

5. A flat surface was prepared by Ar-ion beam milling from post-pyrolysis rock cylinders (without solvent extraction) for SEM analysis. A FE-SEM was used to image pores and their association with OM and mineral grains.

6. The remaining sample was pulverized and analyzed for Rock-Eval and Leco TOC.

Geochemical Characterization of Generated Components

<table>
<thead>
<tr>
<th>Petroleum Stage of Formation</th>
<th>Immature</th>
<th>Early Oil Window</th>
<th>Oil Window</th>
<th>Oil Cracking to Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>130</td>
<td>300</td>
<td>310</td>
<td>333</td>
</tr>
<tr>
<td>Peak Oil</td>
<td>0.0</td>
<td>130</td>
<td>220</td>
<td>340</td>
</tr>
<tr>
<td>Hydrogen Index (HI)</td>
<td>0.0</td>
<td>110</td>
<td>170</td>
<td>220</td>
</tr>
<tr>
<td>Oxygen Index (OI)</td>
<td>0.0</td>
<td>2.0</td>
<td>4.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Rock-Eval Tmax (°C)</td>
<td>0.0</td>
<td>80</td>
<td>170</td>
<td>220</td>
</tr>
<tr>
<td>Rock-Eval Ss (mg/gTOC)</td>
<td>0.0</td>
<td>6.20</td>
<td>16.7</td>
<td>9.70</td>
</tr>
<tr>
<td>Rock-Eval Sr (mg/gTOC)</td>
<td>0.0</td>
<td>6.20</td>
<td>16.7</td>
<td>9.70</td>
</tr>
<tr>
<td>Rock-Eval S (mg/gTOC)</td>
<td>0.0</td>
<td>6.20</td>
<td>16.7</td>
<td>9.70</td>
</tr>
<tr>
<td>Rock-Eval Tm (°C)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Calculated Ro (%)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Leco TOC (wt %)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Rock-Eval S (mg/gTOC)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Rock-Eval Tm (°C)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Calculated Ro (%)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Leco TOC (wt %)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Rock-Eval S (mg/gTOC)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Rock-Eval Tm (°C)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Calculated Ro (%)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
<tr>
<td>Leco TOC (wt %)</td>
<td>0.0</td>
<td>425</td>
<td>437</td>
<td>432</td>
</tr>
</tbody>
</table>

Immature or Low-maturity Mudrock Properties

<table>
<thead>
<tr>
<th>Immature or low-maturity sample</th>
<th>Woodford chert</th>
<th>Woodford mudstone</th>
<th>Barnett mudstone</th>
<th>Boquillas mudstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Carbonate</td>
<td>3.33</td>
<td>4.25</td>
<td>11.43</td>
<td>89.61</td>
</tr>
<tr>
<td>Leco TOC (wt %)</td>
<td>6.20</td>
<td>16.7</td>
<td>9.70</td>
<td>1.48</td>
</tr>
<tr>
<td>Rock-Eval S (mg/gTOC)</td>
<td>0.88</td>
<td>1.91</td>
<td>1.14</td>
<td>0.77</td>
</tr>
<tr>
<td>Rock-Eval Sr (mg/gTOC)</td>
<td>37.69</td>
<td>90.56</td>
<td>53.72</td>
<td>9.53</td>
</tr>
<tr>
<td>Rock-Eval Tmax (°C)</td>
<td>432</td>
<td>425</td>
<td>420</td>
<td>437</td>
</tr>
<tr>
<td>Calculated Ro (%)</td>
<td>0.60</td>
<td>0.49</td>
<td>0.42</td>
<td>0.70</td>
</tr>
<tr>
<td>Hydrogen Index (HI)</td>
<td>610</td>
<td>542</td>
<td>554</td>
<td>644</td>
</tr>
<tr>
<td>Oxygen Index (OI)</td>
<td>6</td>
<td>4</td>
<td>15</td>
<td>30</td>
</tr>
</tbody>
</table>
Pore Evolution in the Barnett, Eagle Ford (Boquillas), and Woodford Mudrocks Based on Gold-Tube Pyrolysis Thermal Maturation

**Types and Evolution of OM Pores and Mineral Pores**

**Kerogen:** solid insoluble organic geopolymer. Kerogen can form pores by maturation and the pores are voids left behind by HCs that were generated and expelled or were original pores associated with plant material. Kerogen can contain (A) primary OM pores and (B) convoluted-OM pores. The primary OM pores are present before any diagenesis begins.

**Bitumen:** soluble, viscous, liquid OM, from thermal cracking of kerogen under immature or low-maturity conditions. It can have a wide range of viscosities. This term is equivalent to “pre-oil bitumen” used by Curiale (1986) and Mastalerz and Glikson (2000). Bitumen is liquid and cannot host pores over long periods of time.

**Modified Primary Mineral Pores (with Relic OM):**

- Combination mineral/OM pore
- Retention pore

**Solid/solidified bitumen:** very viscous, difficult to dissolve in organic solvent, also equivalent to “pre-oil bitumen” but solidified in the subsurface, able to form combination OM/mineral pores.

**Residual/retained oil:** the “liquid oil in subsurface but is solid or highly viscous at surface conditions resulted from expulsion of volatiles on the way up the wellbore and/or during handling and storage” (Bohacs et al., 2013), able to form retention pores.

**Pyrobitumen:** secondary product from bitumen. Pyrobitumen consists of insoluble, nomsoluble, solid HC residues that “still retain some hydrocarbon generation capacity upon further heating” and can host pores (Bohacs et al., 2013), able to form retention pores.

**Char:** the “ultimate residue of HC generation with minimal H content and essentially no remaining potential for generating HCs, derived from further heating of pyrobitumen and bitumen.” Char can also host (C) nanometer-sized spongy OM pores.

**Summary of pore evolution associated with generated petroleum Organic-Matter HC Chemical composition Pore type and pore evolution**

**Boquillas Mudstone: Pore Types and Evolution**

**Woodford Mudstone: Pore Types and Evolution**

**Barnett Mudstone: Pore Types and Pore Evolution**

**Overview of a typical surface**

**Early Bitumen**

- Oil window
- Peak oil
- Oil cracking

**Bitumen Peak**

- Oil window
- Peak oil
- Oil cracking

**Oil Window**

- Oil window
- Peak oil
- Oil cracking

**Peak Oil**

- Oil window
- Peak oil
- Oil cracking

**Oil Cracking**

- Oil window
- Peak oil
- Oil cracking

**Types of OM in the Barnett Mudstone (photos below):**

1. OM mineral admixture: most commonly observed
2. Stringy/flaky OM
3. Brittle, structural, particulate OM (terrestrial kerogen)

**Types of OM in the Barnett Mudstone (photos below):**

1. OM mineral admixture: most commonly observed
2. Stringy/flaky OM
3. Brittle, structural, particulate OM (terrestrial kerogen)
### Woodford Chert: Pore Types and Pore Evolution

<table>
<thead>
<tr>
<th>Stage</th>
<th>Dominant OM Pores</th>
<th>Sputum Pores</th>
<th>Bitumen Pores</th>
<th>IntraP Pores (dissolution or boring?)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Oil</td>
<td>Bitumen genotypes (crinoidal pores)</td>
<td>Bubble pores</td>
<td>Retention pores</td>
<td>Retention pores, slit pores, some spongy OM pores</td>
</tr>
<tr>
<td>Oil Cracking</td>
<td>Bitumen genotypes (crinoidal pores)</td>
<td>Bubble pores</td>
<td>Retention pores</td>
<td>Retention pores, slit pores, some spongy OM pores</td>
</tr>
</tbody>
</table>

### Woodford Mudstone: Pore Types and Pore Evolution

<table>
<thead>
<tr>
<th>Stage</th>
<th>Dominant OM Pores</th>
<th>Sputum Pores</th>
<th>Bitumen Pores</th>
<th>IntraP Pores (dissolution or boring?)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Oil</td>
<td>Bitumen genotypes (crinoidal pores)</td>
<td>Bubble pores</td>
<td>Retention pores</td>
<td>Retention pores, slit pores, some spongy OM pores</td>
</tr>
<tr>
<td>Oil Cracking</td>
<td>Bitumen genotypes (crinoidal pores)</td>
<td>Bubble pores</td>
<td>Retention pores</td>
<td>Retention pores, slit pores, some spongy OM pores</td>
</tr>
</tbody>
</table>

### Conclusions

1. The Barnett mudstone pore evolution summary:

- **Early Oil**: Dominant OM pores, bubble pores, retention pores, some spongy OM pores.
- **Oil Cracking**: Dominant OM pores, bubble pores, retention pores, some spongy OM pores.

2. The Woodford mudstone pore evolution summary:

- **Early Oil**: Dominant OM pores, bubble pores, retention pores, some spongy OM pores.
- **Oil Cracking**: Dominant OM pores, bubble pores, retention pores, some spongy OM pores.

### Selected References

- Bohacs, K. M., Q. M. Passey, M. Rudnicki, W. L. Esch, and O. R. Lazar, 2013, The spectrum of fine-grained reservoirs from "shale-gas" to "shale oil"//g415ght liquids: essen/g415al a/g425ributes, key controls, prac/g415cal characteriza/g415on: ... coal: Examples from the Bowen Basin and the Illinois Basin: Interna/g415onal Journal of Coal Geology, v. 42, p. 201–220.
- Zhang, T., S. Xun, L. T. Ko, S. C. Ruppel, D. Shao, 2014, Oil and gas genera/g415on and pore evolu/g415on of ar/g415ficially-matured Eagle Ford Shale by Non-hydrous Pyrolysis, MSRL annual consor/g415um, Aus/g415n, Texas.