Petrophysics of Shale Reservoirs: Understanding the Rocks, Pores, Fluids and Their Interactions

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What is a Shale Reservoir? Definitions from the Technical Literature

“........organic-rich formations previously regarded only as source rocks and seals for oil and gas accumulating in the stratigraphically-associated sandstone and carbonate reservoirs of traditional onshore environments........”

“Shale reservoirs are further defined as:

- sedimentary rock composed mostly of consolidated clay-sized particles;
- deposited as mud in low-energy depositional environments such as deep water basins where fine-grained clay particles fall out of suspension;
- there can also be deposition of organic matter in the form of algae-, plant-, and animal-derived organic debris;
- tabular clay grains compacted due to additional sediment deposition resulting in mud with thin laminar bedding.”

What is a Shale Reservoir? Definitions from the Technical Literature

“A shale reservoir is described as:

• a sedimentary rock that was once deposited as mud (clay and silt) and is generally a combination of clay, silica (e.g. quartz), carbonate (calcite or dolomite), and organic material;

• thin beds or laminae of sandstone, limestone, or dolostone mixed with organic matter;

• mud deposited in deep, quiet waters such as large lakes, deep seas and oceans;

• organic matter in the mud was algae, plant matter, or plankton that died and sank to the sea floor or lake bed before being buried.”

What is a Shale Reservoir?
Definitions from the Technical Literature

• “Shale, an abundant sedimentary rock of extremely low permeability, is often considered a natural barrier to the migration of oil and gas.”

• “In gas shales, the gas is generated in place; the shale acts as both source rock and the reservoir.”

• “The gas can be stored interstitially within the pore spaces between rock grains or fractures in the shale, or it can be adsorbed to the surface of the organic components contained in the shale.”

What is a Shale Reservoir?  
Definitions from the Technical Literature

Characteristics of a shale gas reservoir include:

• “shales contain less than 50 wt% organic matter. Methane is generated from the transformation of this organic matter by bacterial (biogenic gas) and geochemical (thermogenic gas) processes during burial.

• shale-gas reservoirs have low sorbed-gas content and contain a much larger volume of free gas in the pore space.

• shale reservoirs also have low permeabilities with values in the nano- to microdarcy range.

• production is through more-permeable sand or silt layers interbedded with the shale, through natural fractures, or from the shale matrix itself.”

What is a Shale Reservoir?
Dan Jarvie’s Definition

• A shale reservoir is:
  – A continuous organic-rich source rock that is also a reservoir rock, or
  – A combination of juxtaposed and continuous organic-rich source rock with organic-lean lithofacies.

• Thus, a shale reservoir may consist of:
  – Only of primary migration (within the source rock itself), or
  – Secondary migration into juxtaposed (overlying, interbedded, or underlying) non-source rocks.

What is a Shale Reservoir?
The Total Petroleum System Approach

Conventional Petroleum System

- Source rock within which hydrocarbons are generated and from which hydrocarbons migrate long distances
- Reservoir acts as hydrocarbon “container” by receiving and accumulating hydrocarbons migrating from source rock
- Seal encloses reservoir and prevents hydrocarbon migration out of the “container”

Unconventional Petroleum System

- Total reservoir includes organic matter (source rock) and sandstone / carbonate (reservoir)
- Hydrocarbons are generated in-situ but may migrate short distances to adjacent reservoirs
- Hydrocarbons remain within total reservoir (self-sourced system)
- Seal encloses total reservoir and prevents hydrocarbon migration out of total “container”
Key Learnings
General Characteristics of Shale Reservoirs

- Sedimentary rocks deposited in environments associated with deep, quiet waters such as large lakes, deep seas and oceans.

- Composition is fine-grained materials including clays, silica, carbonates, and organic material, which may be in the form of algae-, plant-, and animal-derived organic debris.

- Hydrocarbons are generated in-situ from degradation of organic materials during burial; shales act as both source rock and reservoir (self-sourced systems).

- Characterized by low porosity where hydrocarbons may be stored in conventional pore space, adsorbed onto the rock surfaces, and/or in natural fractures.

- Characterized by nano- to micro-darcy permeability with production from either organic or non-organic rock matrix and from natural fracture systems.
Presentation Outline

1) Depositional Environment: Sedimentary Provenance, Processes & Products


3) Geochemical Rock Properties: Composition & Hydrocarbon Generation from Organic Rocks

4) Pores and Pore Networks: Distribution, Morphology & Connectivity of Total Reservoir System

5) Rock-Fluid Interactions in Total Reservoir System
   a) Fluid Storage & Transport Mechanisms
   b) Fluid Phase Behavior
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Sedimentary Shale Geology
General Considerations

• Shales are classified as **Detrital Sedimentary Rocks**
  – Deposits are composed of pre-existing rock “clasts” or “detritus”
  – Clasts are fragments and pieces of smaller rocks broken off other pre-existing rocks
  – Initially deposited in one location (the provenance), but clasts subsequently “re-deposited” in present-day location

• Provenance (from French word “provenir” meaning “to come from”)
  – Provenance for sedimentary rocks can be from any location and any depositional environment
  – Composition, mineralogy, and texture are often mixed but provenance can be identified from mineral composition
Sedimentary Shale Geology
General Considerations (continued)

• Processes
  – Weathering (physical disintegration and/or chemical decomposition)
  – Erosion (physical removal of weathered products from weathered location)
  – Transport (movement of weathered products to current depositional site)
  – Diagenesis (post-depositional physical and chemical alteration of rock)

• Products
  – Non-organic rocks or minerals: clays, silica (quartz), carbonate (calcite or dolomite)
  – Organic rocks: algae-, plant-, and animal-derived organic debris
The Sediment Depositional Cycle

Provenance
Source rock providing detritus to shale reservoir

Process
Weathering / Erosion

Product
• Mechanically disintegrated rock
• Chemically unstable rock

Process
Transport

Product
• Mixing of detritus
• Loss of mechanically unstable rock
• Mechanical alteration of rock

Process
Deposition

Product
• Stratification
• Sorting by clast size, density
• Addition of chemical species

Product
• Physical & chemical processes altering non-organic deposits
• Biological & chemical processes altering organic deposits

Sedimentary Rock Depositional Environments

- Glacier
- Alluvial fan
- Lake
- Stream
- Tidal flat
- Beach/barrier island
- Delta
- Swamp
- Beach
- Arid, restricted circulation
- Dunes
- Shelf/platform
- Slope/rise
- Deep-marine

Shale Petrophysics: Understanding Rocks, Pores, and Fluids
Shale Depositional Environments

• Major Categories of Shale Depositional Environments
  – Intrabasinal: sediments deposited in the same basin as the source rock from which they are weathered
  – Extrabasinal: sediments deposited outside of the basin in which the source rock is deposited

• Extrabasinal or Detrital Depositional Environments
  – Non-Marine
    • River Floodplains
    • Lacustrine
  – Marine
    • Muddy Coastlines
    • Nearshore and Mid-Shelf Mud Belts
    • Open-Shelf Mud Blankets
    • Basinal Slopes
    • Basin Floors

### Relationship Between Shale Facies, Organic Matter Content, and Marine Fauna

#### Normal Marine
- **Shale Facies**: Anoxic
- **Water Circulation**: Good
- **Fossils**: Rich epifauna, infauna
- **OM Preservation**: Poor
- **Sediment Color**: Light gray

#### Restricted
- **Shale Facies**: Oxic
- **Water Circulation**: Reduced
- **Fossils**: Improvised benthos
- **OM Preservation**: Good
- **Sediment Color**: Dark gray

#### Euxinic
- **Shale Facies**: Anoxic
- **Water Circulation**: Poor
- **Fossils**: No benthos, only pelagic fauna
- **OM Preservation**: Excellent
- **Sediment Color**: Black
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Physical Properties Used to Describe Non-Organic Rocks

• Color: reflects major constituent materials (framework, matrix, and cements); may also provide insight into depositional environment

• Texture
  - Grain types (clastic or crystalline)
  - Grain size distribution, and sorting
  - Grain shape (sphericity, angularity, etc.)
  - Fabric (spatial and geometric configuration of major constituents)

• Composition: mineralogy of constituent materials (framework, matrix, and cements)
Physical Properties Used to Describe Non-Organic Rocks (continued)

• Sedimentary Structures
  – Structures formed during original deposition of sediments
  – Type and scale of structures reflect depositional environment

• Fossil Content
  – Organic remains (e.g., shells, bones, etc.) or traces of organisms (e.g., tracks, trails, burrows, etc.)
  – Type and quantity of fossils reflect original depositional environment

• Diagenesis: physical, chemical, & biological processes
  – Early diagenesis (weathering, erosion, and early deposition)
  – Late diagenesis (late deposition, burial, and/or uplift)
Physical Rock Properties
Color (Marcellus Shale Core)

Limestone
Argillaceous Limestone
Mudstone
Calcareous Mudstone
Organic Mudstone

Reference: “Shale Reservoir Evaluation: Critical Elements of Reservoir Characterization”
Short Course by Integrated Reservoir Solutions, Core Laboratories, Houston, TX (Aug. 2011).
Texture of Detrital Sedimentary Rocks

Grain Size

**Detrital Rocks**

- Principal Clast Size

- Particle diameters, $d > 1/16$ in or 0.0625 mm
  - Conglomerate / Breccia
  - Sandstones

- Particle diameters, $d < 1/16$ in or 0.0625 mm
  - Mudrocks
    - Siltstone
    - Claystone
    - Mudstone
    - Shale

Mudrock Texture
Classification Based on Grain Size

Mudrocks

- Size Range of Principle Particles
- Percent of Silt-or Clay-Sized Particles

Siltstone
- Silt-sized particles: $0.0039 \text{ mm} < d < 0.0625 \text{ mm}$
- 50% or more silt-sized particles

Claystone
- Clay-sized particles: $d < 0.0039 \text{ mm}$
- 50% or more clay-sized particles

Mudstone
- Indurated mud
- Mixture of silt & clay with 1/3 to 2/3 clay

Shale
- Any mudrock exhibiting lamination, fissility, or both

Mudrock Texture
Grain Shape and Size Distribution

Silaceous Mudrock

Detrital quartz grains embedded in organic-rich mudrocks. Note angular shape and size variation of quartz grains.
Mudrock Texture
Grain Shape and Size Distribution (continued)

Silaceous Mudrock

Detrital quartz grains embedded in organic-rich mudrocks. Note angular shape and size variation of quartz grains.
Mudrock Texture
Rock Fabric (Spatial & Geometric Structure of Constituents)

Clay-rich mudrock with parallel alignment of flat, flake-shaped clays particles (fissility). (Haynesville Shale)

Clay-rich mudrock with parallel alignment of flat, flake-shaped clays particles (fissility). (Marcellus Shale)
Composition of Mudrocks
General Observations

• Mudrock composition can be described as a “dogs breakfast”
  – British slang for “a confused mess or mixture” (Reference: Urban Dictionary)
  – Mudrock composition is often derived from multiple provenances with quite different initial depositional settings
  – Composition often seems to be a “confused mess” but can be understood with detailed geological and petrophysical studies

• Significant variability in mudrock composition
  – Composition varies not only regionally (from basin to basin) but also locally within a mudrock field or reservoir
  – Compositional variability governs resource-in-place, productivity, and ultimate reserves
Composition of Mudrocks
General Observations (continued)

- Mudrock composition consists of three basic mineral “building blocks”
  - Quartz and feldspars
  - Calcites and dolomites
  - Clays

- Percent of basic minerals is quite variable among mudrock plays

- Mudrock compositional variability best illustrated with ternary diagram

Composition of Mudrocks
Common Clay Materials

Kaolinite
$\text{Al}_4\text{Si}_4\text{O}_{10}\text{(OH)}_8$

Chlorite
$(\text{Al},\text{Mg},\text{Fe})_{12}\text{[(Si,Al)}_{2}\text{O}_{20}\text{]}\text{(OH)}_{16}$

Illite
$\text{KAl}_4\text{Si}_7\text{AlO}_{20}\text{(OH)}_4$

Smectite
$(\text{Ca},\text{Na})(\text{Al},\text{Mg},\text{Fe})_4\text{[(Si,Al)}_{2}\text{O}_{20}\text{]}\text{(OH)}_4\text{nH}_2\text{O}$

Compositional Classification of Mudrocks

Compositional Classification of Mudrocks Based on Bulk Mineralogy

sCore: Classification for Organic Mudstones

Classification of organic mudstones:

“Dominated”: a mudstone containing more than 80% of a particular component

50% and 80% are described as:
- Siliceous (50%<WQFM<80%),
- Argillaceous (50%<WCLA<80%), and
- Carbonate (50%<WCAR<80%)

“Rich”: between 20 and 50%

Compositional Classification of Mudstones Based on Primary Lithology

Ref: Production of Mudrocks, Houston, TX (Bereskin & Milner, 2011)
Composition of Active Shale Plays

Calcereous Dolomitic Mudstone
- Niobrara “B” Chalk
- Bakken Silt
- Upper Eagleford

Mudstone
- Three Forks (Bakken Shale)

Argillaceous Mudstone
- Marcellus
- Pronghorn Shale

Siliceous Marlstone
- Niobrara Marl
- Pearsall
- Lower Eagleford

Siliceous Mudstone
- Fayetteville
- Bakken Shale
- Barnett Shale
- Woodford

Ref: AAPG Search & Discovery Paper #80354 (Anderson, 2014)
Sedimentary Structures
General Observations

• Primary Sedimentary Structures
  – Formed during initial depositional processes
  – Features formed primarily by physical processes
  – Their presence, scale, and orientation reflect depositional processes, e.g., the conditions of transport and deposition

• Secondary Sedimentary Structures
  – Formed after initial depositional processes
  – Features formed by physical, chemical and biological processes
  – Characteristics reflect post-depositional pressure and temperature conditions during burial

• Represent larger scale features than grain and pores……best observed and studied in whole core

Sedimentary Structures

Ripple laminae in silica-rich mudstones deposited in parallel bedding planes (Mowry Shale, Wyoming)

Bioturbated deposits re-worked by storm event (Mancos Shale, Colorado)

“Production from Mudrocks,” J. Macquacker (2011)
Fossil Content
General Considerations

- Fossils in Sedimentary Deposits
  - Indicators of the depositional environment
  - Also good markers for placing sediments in the proper space and time (e.g., stratigraphy)

- Form of Fossils found in Sediments
  - Organic remains, such as hard components (shells, bones or their replacements)
  - Organism traces, such as tracks, trails and burrows

Laminated, bioturbated organic-rich foraminifer marl with concentrations of skeletal particles and phosphatic grains (Ph). Large organic kerogen (OM) as discontinuous flakes aligned parallel to bedding. (Eagleford Shale, TX)

Clusters of calcite-cemented planktonic foraminifera (Fm), some of which are replaced by pyrite (Py). Laminar burrows are also present. (Eagleford Shale, TX)
Diagenesis
General Considerations

Sandstone
- Lithification or compaction
- Pressure dissolution
- Dissolution of unstable grains
- Grain replacement
- Cementation

Carbonates
- Lithification or compaction
- Pressure dissolution
- Dolomitization
- Biological replacement
- Cementation

Clays
- Lithification or compaction
- Clay alteration due to chemical change and water loss

Organic Matter
- Diagenesis
- Catagenesis
- Metagenesis

Examples of Sandstone Diagenesis

Grain coats are authigenic clays “coating” quartz grains forming subsequent to deposition and burial.

Grain rims are detrital clays “coating” quartz grains during burial.
Examples of Sandstone Diagenesis

Grain “sutures” caused by compaction

Bivalve (fossil) filled with quartz; quartz grains cemented with ankerite
Geological / Petrophysical Description from Whole Core

Eagleford Shale Core
Courtesy of Murphy Exploration & Production Co., Houston TX
Geological / Petrophysical Description from Whole Core

Eagleford Shale Core
Courtesy of Murphy Exploration & Production Co., Houston TX
**Geological Properties Interpreted from Physical Rock Properties**

<table>
<thead>
<tr>
<th>Interpretive Property</th>
<th>Best Indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Stratigraphy</td>
<td>1) Fossil Content</td>
</tr>
<tr>
<td>2) Provenance</td>
<td></td>
</tr>
<tr>
<td>a) Source area composition</td>
<td>a) Rock composition</td>
</tr>
<tr>
<td>b) Source area location</td>
<td>b) Primary directional structures; regional variations in texture &amp; thickness</td>
</tr>
<tr>
<td>3) Dispersal</td>
<td></td>
</tr>
<tr>
<td>a) Primary directional structures</td>
<td>a) Primary directional structures</td>
</tr>
<tr>
<td>b) Texture</td>
<td>b) Texture</td>
</tr>
<tr>
<td>c) Geometry</td>
<td>c) Geometry</td>
</tr>
</tbody>
</table>
Geological Properties Interpreted from Physical Rock Properties (continued)

<table>
<thead>
<tr>
<th>Interpretive Property</th>
<th>Best Indicators</th>
</tr>
</thead>
</table>
| 4) Transporting agent & depositional setting | a) Texture  
b) Sedimentary structures  
c) Geometry  
d) Fossil Content |
| 5) Diagenesis          | a) Composition  
b) Texture  
c) Sedimentary structures |
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Geochemistry of Organic Matter
General Concepts and Definitions

• Hydrocarbons generated as original organic matter exposed to pressure and temperature during burial history

• Type and quantity of hydrocarbons generated are function of:
  – Type and quantity of original organic matter in shale
  – Pressure and temperature to which organic matter is exposed

• Total organic carbon (TOC) is a measure of the current quantity of organic matter or organic “richness”

• Organic maturity quantified in terms of vitrinite reflectance
Mass Balance Model for TOC

Total Organic Carbon = Extractable Carbon + Convertible or Reactive Carbon + Residual Carbon

Extractable Carbon = Generated Oil & Gas Migrated Out of Shale + Generated In-Place Oil & Gas + In-Place Bitumen

Convertible Carbon = Remaining In-Place Organics with Hydrocarbon Generation Potential

Residual Carbon = Portion of In-Place Organic Matter That Will Not Yield Hydrocarbons

Kerogen = In-Place Convertible Carbon + In-Place Residual Carbon

## Kerogen Types, Depositional Environments, and Hydrocarbon Generation

<table>
<thead>
<tr>
<th>Kerogen Type</th>
<th>Original Organic Matter</th>
<th>Maceral</th>
<th>Depositional Environment</th>
<th>Potential Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Fresh Water Algae</td>
<td>Alginite</td>
<td>Lacustrine</td>
<td>Black Oil</td>
</tr>
<tr>
<td>II</td>
<td>Marine Algae, Pollen, Spores, Leaf Waxes, and/or Fossil Resins</td>
<td>Exinite</td>
<td>Marine, Reducing Conditions</td>
<td>Volatile Oil; Gas Condensate</td>
</tr>
<tr>
<td>III</td>
<td>Terrestrial-Derived Woody Materials</td>
<td>Vitrinite</td>
<td>Marine, Oxidizing Conditions</td>
<td>Dry to Wet Gas</td>
</tr>
<tr>
<td>IV</td>
<td>Reworked Organic Debris of Any Origin, Highly Oxidized Material</td>
<td>Inertinite</td>
<td>Marine, Oxidizing Conditions</td>
<td>None</td>
</tr>
</tbody>
</table>

Impact of Depositional Environment on Kerogen Type

Type I: lacustrine: algae
Type II: predominantly marine: phytoplankton terrestrial input: pollen & spore
Type III: terrestrial: higher plant debris
## Kerogen Types, Convertible TOC, and Generated Hydrocarbons

<table>
<thead>
<tr>
<th>Kerogen Type</th>
<th>Original Organic Matter</th>
<th>Convertible TOC (%)</th>
<th>Potential Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Fresh Water Algae</td>
<td>&gt; 70%</td>
<td>Black Oil</td>
</tr>
<tr>
<td>II</td>
<td>Marine Algae, Pollen, Spores, Leaf Waxes, and/or Fossil Resins</td>
<td>30% ≤ TOC ≤ 70%</td>
<td>Volatile Oil; Gas Condensate</td>
</tr>
<tr>
<td>III</td>
<td>Terrestrial-Derived Woody Materials</td>
<td>&lt; 30%</td>
<td>Dry to Wet Gas</td>
</tr>
<tr>
<td>IV</td>
<td>Reworked Organic Debris of Any Origin, Highly Oxidized Material</td>
<td>0%</td>
<td>None</td>
</tr>
</tbody>
</table>

Kerogen Type Related to Efficiency of Hydrocarbon Generation

Examples

Type $I_o$
TOC = 7%
HI = 900

- Generative Organic Carbon (wt.%)
- Non-Generative

Type $II_o$
TOC = 7%
HI = 500

- Generative Organic Carbon (wt.%)
- Non-Generative Organic Carbon (wt.%)

Type $III_o$
TOC = 7%
HI = 200

- Generative Organic Carbon (wt.%)
- Non-Generative Organic Carbon (wt.%)

## Elemental Composition of Kerogen

<table>
<thead>
<tr>
<th>Kerogen Type</th>
<th>Atomic Hydrogen to Carbon Ratio</th>
<th>Atomic Oxygen to Carbon Ratio</th>
<th>Potential Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>High</td>
<td>Low</td>
<td>Black Oil</td>
</tr>
<tr>
<td>II</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>Gas Condensate; Volatile Oil</td>
</tr>
<tr>
<td>III</td>
<td>Low</td>
<td>High</td>
<td>Dry to Wet Gas</td>
</tr>
<tr>
<td>IV</td>
<td>Low</td>
<td>High</td>
<td>None</td>
</tr>
</tbody>
</table>

Measuring TOC of Organic Materials

Programmed Pyrolysis Method

- Laboratory method to measure properties of organic matter (OM) including:
  - Type and quantity of total organic carbon (TOC)
  - Hydrocarbon generative potential
  - Thermal maturity of rock

- Methodology
  - Gradually heat samples to 600°C in inert atmosphere (typically helium or nitrogen)
  - Organic compounds generated during heating are measured using a flame ionization detector (FID)

- Measurements
  - First peak ($S_1$) is quantity of free or thermally distilled OM
  - Second peak ($S_2$) is OM generated during pyrolytic degradation and high-molecular weight HC not vaporized at lower temperatures
  - Third peak ($S_3$) is CO2 generated during thermal breakdown of kerogen
  - Fourth peak ($S_4$) is residual OM released during final high-temperature stage

- Maximize temperature (Tmax) at which $S_2$ occurs is related to thermal maturity of OM

- TOC computed as follows:

$$\text{TOC} = \frac{0.83(S_1 + S_2)}{10} S_4$$

Organic Characteristics from Programmed Pyrolysis

- **Hydrogen Index, HI**
  - $S_2 / \text{TOC} \ (\text{mg HC} / \text{g TOC})$
  - Measures relative hydrogen index

- **Oxygen Index, OI**
  - $S_3 / \text{TOC} \ (\text{mg HC} / \text{g TOC})$
  - Measures relative oxygen index

- **Production Index, PI**
  - $S_1 / (S_2 + S_3) \ (\text{dimensionless})$
  - Measures ratio of “free” oil to total oil and kerogen in OM
  - Analogous to fluid saturation in conventional reservoir

Identifying Kerogen and Hydrocarbon Types from H/C vs. O/C Plots

Van Krevelen Diagram

Pseudo Van Krevelen Diagram
Thermal Maturity of Organic Matter (OM)

• Present-day thermal maturity is indicator of:
  – Type and quantity of hydrocarbons generated
  – Qualitative indicator of thermal history to which OM has been exposed

• Thermal maturity quantified using vitrinite reflectance technique:
  – Shiny surface (resembling glass surfaces) of vitrinite can be identified using fraction of incident light reflected from rock surface
  – Polished surface reflects more light as maturity increases (loss of molecular structure, often called “aromatization”)
  – Can also use other kerogen macerals such as:
    • Vitrinite subtypes
    • Inertinite
    • Grapolite
## Relationship Between Vitrinite Reflectance and Programmed Pyrolysis Tmax

<table>
<thead>
<tr>
<th>Maturity / Hydrocarbon Generation</th>
<th>Vitrinite Reflectance (%)</th>
<th>Tmax (°C)</th>
<th>Type I Kerogen</th>
<th>Type II Kerogen</th>
<th>Type III Kerogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature</td>
<td>0.40 to 0.55</td>
<td>442 to 443</td>
<td>426 to 435</td>
<td>424 to 433</td>
<td></td>
</tr>
<tr>
<td>Early Oil Generation (Black Oil)</td>
<td>0.60 to 0.70</td>
<td>443 to 444</td>
<td>435 to 441</td>
<td>433 to 438</td>
<td></td>
</tr>
<tr>
<td>Peak Oil Generation (Black to Volatile Oil)</td>
<td>0.80 to 1.00</td>
<td>444 to 445</td>
<td>445 to 451</td>
<td>444 to 454</td>
<td></td>
</tr>
<tr>
<td>Retrograde Gas Condensate to Wet Gas</td>
<td>1.20 to 1.40</td>
<td>446 to 448</td>
<td>451 to 456</td>
<td>454 to 458</td>
<td></td>
</tr>
<tr>
<td>Dry Gas</td>
<td>1.60 to 1.80</td>
<td>446 to 449</td>
<td>456 to 458</td>
<td>458 to 497</td>
<td></td>
</tr>
</tbody>
</table>

Short Course presented at Apache Corp., Midland, TX (June 2012)
Thermal Transformation of Kerogen: Processes and Products

Kerogen Diagenesis and Hydrocarbon Generation

**Diagenesis**

- Initial transformation process characterized by low-temperature (T < 50°C) chemical alteration of OM
- Biological processes also break down OM and generate biogenic methane
- Increasing temperature and changes in pH convert OM to kerogen and bitumen

**Catagenesis**

- Further burial causes increasing temperature (50°C < T < 150°C) which breaks chemical bonds in kerogen and creates hydrocarbons
  - Type I kerogen: oil
  - Type II kerogen: waxy oils
  - Type III kerogen: gas
- Further increases in temperature causes secondary cracking of oil, which creates additional gas (both wet and dry)

**Metagenesis**

- Further burial and associated temperature increase (T > 150°C) which causes conversion of remaining kerogen into carbon
- Both dry gas and non-hydrocarbon gases (CO₂, N₂, H₂S) are generated
- No liquid hydrocarbons are generated during this phase

Presentation Outline

1) Depositional Environment: Sedimentary Provenance, Processes & Products


3) Geochemical Rock Properties: Composition & Hydrocarbon Generation from Organic Rocks

4) Pores and Pore Networks: Distribution, Morphology & Connectivity of Total Reservoir System

5) Rock-Fluid Interactions in Total Reservoir System
   a) Fluid Storage & Transport Mechanisms
   b) Fluid Phase Behavior
Range of Pore Sizes in Shale Reservoirs

Reference: AAPG Bull. vol. 93, no. 3 (Nelson, 2009)

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Pore Classification for Shale Reservoirs

- Several pore classifications proposed by industry in last 5 years

- The two most comprehensive classifications are:
  - Pore type, quantity, and connectivity depends on shale mineralogy, texture, fabric, and diagenesis

- Commonalities between classification methods
  - Both interparticle and intraparticle porosity in non-organic rocks
  - Complex pore structure associated with organic materials and clays
  - Micro-channels, micro-fractures, and fractures
Loucks’, et al. Pore Classification

Mineral Matrix Pores: Interparticle (Between Particles)

- Represents primary pore system that is interconnected
- Formed during original deposition processes
- Pores may be reduced and/or isolated by diagenetic processes post-deposition
- Type and severity of diagenesis depend on reservoir p, T conditions; rock lithology
- Primary diagenetic processes include:
  - Mechanical compaction
  - Cementation

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Interparticle Pores

Interparticle pores between grains (Haynesville/Bossier Shale, TX)

Smectite-Illite clays with quartz silt (Eagleford Shale, TX)

Interparticle pores between clay particles (New Albany Shale, IL)

Interparticle pores between grains with overgrowths (Pearsall Shale, TX)

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Interparticle Pores

Interparticle pores between rigid grain edges

Pores between clay platelets

Interparticle pores between grain edges

Pores between individual crystals

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Interparticle OM Pores

Interparticle pores between rigid grain edges (Marcellus Shale)

Loucks’, et al. Pore Classification
Mineral Matrix Pores: Intraparticle (Within Particles)

- Represents both primary and secondary pore system
- Formed during original deposition and altered during post-depositional diagenesis
- Degree of continuity is less than primary interparticle pores
- Continuity depends on mineral, texture, and fabric of system

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Intraparticle Pores

- Intraparticle pores in fossil cavity (Pearsall Shale, TX)
- Pores within pyrite framboids (Eagleford Shale)
- Cleavage pores in mica (Haynesville Shale)
- Sponge-like pores in phosphate grain (Pearsall Shale)

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Intraparticle Pores

Examples of Intraparticle Pores

Loucks’, et al. Pore Classification
Organic and Fracture Porosity

Organic-Matter Intraparticle Pores
(Pores within Organic Particle)

- Formed during thermal maturation and hydrocarbon generation
- May represent as significant pore volume as interparticle pores
- May also be as well connected as interparticle pores
- Type, quantity and connectivity depends on p, T conditions and type of organic matter

Fracture Pores
(Pores not Controlled by Individual Particles)

- Few open or closed natural fractures observed in shale samples
- Open fractures contribute little to overall pore volume but affect fluid flow
- Closed fractures help propagate induced fractures during stimulation
- Some natural fractures formed in organic matter during thermal maturation

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Intraparticle OM Pores

Haynesville Shale

Marcellus Shale

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)
Examples of Intraparticle OM Pores

Intraparticle pores in OM (Eagleford Shale)

Examples of Natural Fractures in Whole Core

Reference: “Shale Reservoir Evaluation: Critical Elements of Reservoir Characterization”
Short Course by Integrated Reservoir Solutions, Core Laboratories, Houston, TX (Aug. 2011).
Mineral-Filled Natural Fractures in Whole Core from Woodford Shale

Thin Sections Showing Natural Fractures in Haynesville Shale

Reference: “Shale Reservoir Evaluation: Critical Elements of Reservoir Characterization”
Short Course by Integrated Reservoir Solutions, Core Laboratories, Houston, TX (Aug. 2011).

<table>
<thead>
<tr>
<th>Pore Type</th>
<th>Image</th>
<th>Distinctive Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous Floccules</td>
<td><img src="image1.png" alt="Image" /></td>
<td>Clumps of electrostatically charged clay flakes arranged in edge-face or edge-edge cardhouse structure. Pores up to 10’s of microns in diameter. Pores may be connected.</td>
</tr>
<tr>
<td>Organo-porosity</td>
<td><img src="image2.png" alt="Image" /></td>
<td>Pores in smooth surfaces of organic flakes or kerogen. Pore diameters are at nanometer scale. Pores are generally isolated. Porous organic coatings can also be adsorbed on clays.</td>
</tr>
<tr>
<td>Fecal Pellets</td>
<td><img src="image3.png" alt="Image" /></td>
<td>Spheres/ellipsoids with randomly oriented internal particles, giving rise to intrapellet pores. Pellets are sand-size and may be aligned into laminae.</td>
</tr>
<tr>
<td>Fossil Fragments</td>
<td><img src="image4.png" alt="Image" /></td>
<td>Porous fossil particles, including sponge spicules, coccoliths, radiolaria, and cysts (Tasmanites?). Interior chamber may be open or filled with detrital or authigenic minerals.</td>
</tr>
<tr>
<td>Intraparticle Grains/Pores</td>
<td><img src="image5.png" alt="Image" /></td>
<td>Porous grains, such as pyrite frambooids which have internal pores between micro-crystals. Grains are of secondary origin, and are usually dispersed within the shale matrix.</td>
</tr>
<tr>
<td>Microchannels and Microfractures</td>
<td><img src="image6.png" alt="Image" /></td>
<td>Linear nano-micrometer-sized openings that often cross-cuts bedding planes. Occur at nano-meter and larger scales.</td>
</tr>
</tbody>
</table>
How are Pores & Networks Generated?

- **Initial Deposition**
  - Initial inter- and intraparticle pore volume created (primary & secondary)
  - Some alterations due primarily to mechanical compaction, cementation, quartz dissolution
  - Significant pyrite formation

- **Shallow to Intermediate Burial**
  - Significant mechanical compaction alters inter- & intraparticle pore volume
  - Begin clay diagenesis processes

- **Hydrocarbon Generation Window**
  - Initial organic-matter pores created during oil generation window
  - Intraparticle pores may be altered significantly by clay & grain diagenesis

- **Deep Burial**
  - Additional organic-matter pores created during gas generation window
  - Little to no more alteration to inter- or intraparticle pore structure

Reference: AAPG Bull. vol. 96, no. 6 (Loucks, et al., 2012)

Jay A. Rushing
TAMU PETE 631 Lecture
College Station, TX (USA) — 07 April 2014
Shale Petrophysics: Understanding Rocks, Pores, and Fluids
Kerogen Diagenesis and Hydrocarbon Generation

Assumptions:
- 7.00 wt.% TOC₀
- 2.50 wt.% GOC₀
- 14.00 vol.% TOC₀
- TOC₀ is 37% GOC
- GOC density 1.2g/cc

Presentation Outline

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   a) Fluid Storage & Transport Mechanisms
   b) Fluid Phase Behavior
Gas Storage Mechanisms

Mineral (Non-Organic) Interparticle Pores

Compressed gas in interparticle pores

Mineral (Non-Organic) Intraparticle Pores

Gas expelled and lost from reservoir

Organic-Matter (OM): Pores + Solid Particles

Organic & Non-Organic Fracture Pores

Compressed gas in fracture pores

Compressed gas in interparticle clay pores. Gas adsorbed on clay surfaces

Compressed gas in intraparticle pores

Compressed gas in intraparticle clay pores.

Gas adsorbed on OM surfaces

Gas expelled and lost from reservoir

Compressed gas in pores + gas adsorbed on OM surfaces

Migrated Gas

Migrated Gas

Migrated Gas

Migrated Gas

Solid Clay Particles

Compressed gas in pores + gas adsorbed on OM surfaces
Oil Storage Mechanisms

Mineral (Non-Organic) Interparticle Pores

Mineral (Non-Organic) Intraparticle Pores

Compressed liquid in interparticle pores

Compressed liquid in intraparticle pores

Organic-Matter (OM): Pores + Solid Particles

Liquid expelled and lost from reservoir

Solid Clay Particles

Oil stored in interparticle clay pores.

Compressed liquid in fracture pores

Compressed liquid in intraparticle pores

Compressed liquid in pores + liquid adsorbed (?) on OM surfaces

Oil stored in interparticle clay pores.

Mineral (Non-Organic) Interparticle Pores

Compressed liquid in interparticle pores

Mineral (Non-Organic) Intraparticle Pores

Compressed liquid in intraparticle pores

Solid Clay Particles

Oil stored in interparticle clay pores.
Fluid Adsorption Phenomena

General Considerations

• Adsorption of hydrocarbon molecules on organic rock surfaces is:
  – Surface phenomenon caused by inter-molecular attractive forces (van der Waals forces) between rock and fluid (gas or liquid)
  – Generally a physical process (physisorption) with weak rock-fluid bonds
  – Exothermic process (heat released during adsorption process)

• Strength of molecular attraction is proportional to molecular polarizability (reference) and molecular weight
  – Smaller molecules have lower molecular polarizability values, while larger, more complex molecules have larger values
  – Larger molecules (hydrocarbon and non-hydrocarbon) will preferentially adhere to rock surfaces and displace smaller molecules

• Inter-molecular forces between rock and fluid also determine wettability of rock surfaces with reservoir fluids

Gas Adsorption Phenomena
General Considerations

Gas Adsorption on Organic Matter

- Relatively weak physical (not chemical) bonds
- Bonds can be broken by increasing T or reducing p
- Larger, more complex molecules will preferentially adsorb over smaller, less complex molecules
- Greater adsorption capacity in kerogen with more TOC
- Adsorption as function of pressure described by Langmuir isotherm

Gas Adsorption on Clays

- Hydrocarbon gases also adsorb onto clay surfaces because of large surface areas
- Adsorptive capacity is less than on organic matter
- Adsorption on clays may provide significant “secondary” source of GIP in shales
- Adsorption as function of pressure described by Langmuir isotherm

Gas Adsorption Phenomena

Langmuir Adsorption Model

- Langmuir model typically used for gas (adsorbate) adsorption on rock surfaces (adsorbent)

- **Model Assumptions**
  - Rock surfaces are flat, homogeneous, and isotropic
  - Adsorbing gas adsorbs into an immobile state
  - Each adsorbing site holds at most one molecule (mono-layer coverage only)
  - No interactions between adsorbate molecules at adjacent sites

**Langmuir Model**

- Models gas adsorption as function of partial pressure or species concentration at constant temperature

- **Langmuir Equation**

\[
G_c = \frac{V_L p}{p_L + p}
\]

where

- \( G_c \) = adsorbed gas concentration (scf/ton)
- \( V_L \) = Langmuir volume defined as maximum volume of gas adsorbed at infinite pressure (scf/ton)
- \( p_L \) = Langmuir pressure defined as pressure at which half of VL is achieved (psia)
- \( p \) = partial pressure of species (psia)
Langmuir Gas Adsorption Isotherms

- Adsorptive capacity of gases depends on molecular weight (both hydrocarbon and non-hydrocarbons)

- Gas adsorption also depends type of porous media
  - Adsorptive capacity increases as percent of TOC increases
  - Clays also adsorb gases because of large surface areas
  - Sandstone / carbonates have no gas adsorptive capacity

- Gas adsorptive capacity decreases as temperature increases (increasing temperature also breaks bonds)
**Liquid Wettability on Rock Surfaces**

**Conventional Reservoirs**

- **Definition of Wettability**
  - Measure of the ability of one fluid in multi-fluid system to preferentially adhere to or “wet” rock surface
  - Caused by intermolecular interactions between liquid and rock surface
  - Degree of wettability determined by force balance between adhesive and cohesive forces

- **Cohesion vs. Adhesion**
  - Cohesive forces are intermolecular forces between molecules of like or the same substance causing liquids to resist separation
  - Adhesive forces are attractive intermolecular forces between unlike or different substances
  - Stronger adhesive forces between fluid and rock surface will cause fluid to coat or “wet” rock
Liquid Wettability on Rock Surfaces
Unconventional Reservoirs

• van der Waals forces determined by distance between molecules, their relative orientation, and thermal motion

• Molecular orientation and distance between molecules (fluid-fluid and rock-fluid) change when fluids occupy smaller pores

• Question 1: do fluids in closer proximity to rock surfaces alter adhesive vs. cohesive force balance?

• Question 2: do fluids in closer proximity to rock surfaces impact wettability of fluids in nano-size pores?
Liquid Wettability on Rock Surfaces and Capillary Pressure

Young-Laplace Equation

- Fluid interface curvature caused by preferential wetting of capillary walls by one of the fluids

\[ P_c = \frac{2\sigma_{nw-w} \cos \theta_{nw-w}}{r} \]

- Density difference between non-wetting and wetting fluid phases

\[ P_c = (\rho_{nw} - \rho_w)gh \]
Oil & Gas Transport Mechanisms

Mineral (Non-Organic) Interparticle Pores

Gas Diffusion / Viscous Flow

Oil Diffusion / Viscous Flow

Mineral (Non-Organic) Intraparticle Pores

Gas Diffusion / Viscous Flow

Oil Diffusion / Viscous Flow

Organic-Matter (OM): Pores + Solid Particles

Gas Diffusion

Oil Diffusion

Gas Diffusion / Viscous Flow

Oil Diffusion / Viscous Flow

Hydraulic Fracture

Viscous Oil Flow

Viscous Gas Flow

Stimulated Reservoir Volume

Oil & Gas Transport Mechanisms include:

- Gas Diffusion
- Oil Diffusion
- Viscous Flow

Organic & Non-Organic Fracture Pores

Viscous Gas Flow

Viscous Oil Flow

Horizontal Well

Shale Petrophysics: Understanding Rocks, Pores, and Fluids
Physics of Various Flow Mechanisms

- **Viscous (Darcy) Flow**
  - Driving force is pressure gradient in each phase
  - Typically described by Darcy’s Law
  - Types of viscous flow
    - Within fractures (natural and induced)
    - Within connected interparticle / intraparticle pore networks

- **Viscous (non-Darcy) Flow**
  - Driving force is pressure gradient in each phase
  - Types of non-Darcy flow
    - Gas slippage effects
    - Inertial flow
Physics of Various Flow Mechanisms (continued)

• Diffuse Flow
  – Driving force is molecular concentration gradient
  – Types of diffusion in porous media
    • Knudsen
    • Continuum
    • Surface
    • Combined
  – Flow induced by molecule-to-molecule and / or molecule-rock surface interactions
Viscous (Poiseuille) Flow in Porous Media

- Occurs when mean free path of molecules is much less than pore throat diameter.

- Flow inside pore throat is assumed laminar so velocity profile is parabolic shape (zero velocity at wall surfaces).

- Driving force is total pressure gradient of a continuum fluid mixture.
  - Parameter characterizing transport is viscosity of fluid mixture.
  - Also characterized by a viscous flow parameter which is a function of the porous media (units of length squared......permeability).

- All molecular species in mixture move through pore throat without separation regardless of molecular weight.

Non-Darcy Flow in Porous Media

**Gas Slippage Effects**

- Non-Darcy effect caused by non-laminar flow in pores
- Surface effect when mean free path of molecules approaches pore throat size
- Flow velocities tend to increase or “slip” as molecules accelerate off rock surfaces
- Klinkenberg showed the true permeability is a function of mean pore pressure \( p_m \) and gas slippage factor \( b \)

\[
k = k_\infty \left( 1 + \frac{b}{p_m} \right)
\]

**Inertial Flow Effects**

- Caused by fluid particles moving through tortuous rock pore throats of varying sizes
- Effects manifested by increase in pressure change without proportionate increase in fluid velocity
- Additional pressure change is associated with dissipation of inertial energy as fluid particles accelerate through smaller pore throats and decelerate through larger areas
- Acceleration creates secondary flow patterns and irreversible conversion of kinetic energy to heat through viscous shear

\[
\frac{dp}{dx} = -\frac{\mu}{k} v_x + \beta \rho v_x^2
\]
Diffusion Transport Modes in Porous Media
Knudsen (Free Molecular) Diffusion

- Occurs when mean free path of molecules is greater than pore throat diameter
- Flow induced as species molecules collide with and “bounce” off pore throat walls
- Momentum transfer due to molecule-molecule collisions are negligible so viscosity effect is inconsequential
- Driving force is concentration gradient defined by Knudsen diffusion coefficient
- Knudsen flux depends on molecular weight of diffusing species
  - Smaller molecular weight species travel faster than larger species
  - Transport of molecules of different type are independent of other molecules
  - Separation of mixtures (molecular sieving) is possible

Diffusion Transport Modes in Porous Media

Continuum Diffusion

- Occurs when mean free path of molecules is much less than pore throat diameter

- Flow induced from collisions among molecules of different types, not of the same type

- Driving force, which is momentum change from molecule-molecule collision, is characterized by binary diffusion coefficient

- Continuum flux depends on molecule-molecule collisions
  - These collisions dominate over collisions between molecules and pore throat wall
  - No net momentum change due to collisions among molecules of the same type
  - Molecules of different species move relative to each other

Diffusion Transport Modes in Porous Media

Surface Diffusion

- Occurs in materials with large internal surface areas and with large adsorptive capacities for hydrocarbons (e.g., organic matter).

- Flow induced when molecular activation energy exceeds surface energy, causing molecules to move or “hop” to next vacant site on rock surfaces.

- Mobility of adsorbed molecules varies with molecular weight of species and with surface loading, usually increasing sharply with loading.

- Surface diffusion flux depends on molecular density and level of surface energy between molecules and pore wall surface:
  - Different molecular species have different mobilities on surface due to different energies associated with van der Waals forces.
  - Surface diffusion increases with larger, heavier molecules because they are more easily adsorbed and condensed on surfaces.

Diffusion Transport Modes in Porous Media
Transition Between Viscous and Knudsen Flow

- Parameter defining flow mechanism is Knudsen number ($K_n$) which is defined as ratio of molecule free path to pore throat diameter

- Knudsen Flow: $K_n \gg 1$
  - Molecular flow induced by molecules “bouncing” to and from pore throat walls
  - Occurs at low mean pressures and when pore throat diameter on order of 10 nm to 100 nm

- Poiseuille Flow: $K_n \ll 1$
  - Molecular velocity at pore throat wall is zero
  - Occurs at high mean pressures and when pore throat diameters $\gg 100$ nm

- Transitional Flow: $1 < K_n < 1$
  - Molecular velocity at pore throat wall is not negligible
  - Occurs at intermediate mean pressures

Fluid Phase Behavior in Petroleum Reservoirs
Conventional vs. Unconventional Reservoirs

**Conventional Reservoirs**
- Rock pore sizes on order of 5 to 50 μm
- Fluid phase behavior depends on
  - Reservoir pressure, temperature
  - Fluid composition
  - Fluid-fluid molecular forces
- Pore surface-fluid forces have little to no impact on fluid phase behavior
- Conventional PVT measurements assume no effect from walls of laboratory cells (i.e., no interactions between fluids and rock surfaces)

**Unconventional Reservoirs**
- Rock pore sizes
  - Tight gas sands: 0.01 to 1.0 μm (10 to 1000 nm)
  - Shales: 0.01 to 0.10 μm (10 to 100 nm)
- Fluid phase behavior depends on
  - Reservoir pressure, temperature
  - Fluid composition
  - Fluid-fluid molecular forces
- Pore surface-fluid forces have significant impact on fluid phase behavior because of close proximity
- Should account for fluid-surface forces in phase behavior calculations
Impact of Pore Surface-Fluid Forces on Phase Behavior in Shale Reservoirs

- Physical Mechanisms Causing Changes in Phase Behavior
  - Small pores limit number of fluid molecules stored in rock
  - Small pore diameter and close proximity of fluids with rock surfaces increase importance of surface (van der Waals) forces
  - Variation of interactive forces with molecular weight affects larger molecules disproportionately more than smaller molecules
  - Higher capillary pressures affect fluid densities & saturation pressures

- Changes in Fundamental Fluid Properties in Smaller Rock Pores
  - Critical temperature and pressures generally decrease (SPE 160099)
  - Real gas deviation factors increase (SPE 160099)
  - Initial dew points in wet gas/gas condensates may either increase or decrease depending on location of reservoir pressure relative critical point (SPE 159258)
  - Initial bubble points in black oil/volatile oil systems decrease (SPE 158042 & 159258)
Impact of Pore Surface-Fluid Forces on Phase Behavior in Shale Reservoirs

Effects of Capillary Pressure on Phase Behavior for Pore Radius of 10 nm (SPE 159258)

Effects of Capillary Pressure on Phase Behavior for Pore Radius of 10 nm (SPE 159258)
Impact of Pore Surface-Fluid Forces on Phase Behavior in Shale Reservoirs

Effects of Pore Diameter on Gas and Liquid Densities for Binary Mixture (SPE 159258)
Impact of Pore Surface-Fluid Forces on Phase Behavior in Shale Reservoirs

Effects of Pore Radius and Pressure on Fluid Density (SPE 159258)

Effects of Pore Radius and Temperature on Bubblepoint Pressure (SPE 159258)