Science of kerogen: Engineering applications for shale E&P

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Schlumberger-Doll Research, Cambridge, MA
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Kerogen: reservoir science to application

**INTRODUCTION**

What is kerogen?
Why is it important?

**SCIENCE**

Chemical insights → Petrophysical properties
Microstructural insights → Kerogen-pore interactions

**APPLICATION**

Reservoir characterization
Reservoir storage, transport, production
Kerogen: what is it?

Solid, black powder in sedimentary rocks (coal-like)
From degradation & burial of fossil plants/algae
Organic matter source of oil & gas
Kerogen: “type”

Freshwater Algae  “type I”
Marine plankton  “type II”
Coastal land plants “type III”
Kerogen: "thermal maturity"

Windows of petroleum generation/destruction

- Immature kerogen
- Oil window
- Wet-gas window
- Dry-gas window

Deep burial & thermal maturation

Less "cooking" → More "cooking"


Freshwater Algae “type I”
Marine plankton “type II”
Coastal land plants “type III”
Kerogen: “thermal maturity”

Windows of petroleum generation/destruction
- Immature kerogen
- Oil window
- Wet-gas window
- Dry-gas window

Maturity window

\[ R_o, \% \]

- 0.2
- 0.3
- 0.4
- 0.5
- 0.6
- 0.8
- 1
- 1.2
- 1.5
- 2
- 2.5
- 3
- 4
- 5

Kerogen: why is it important?

Oil & gas generation controlled by kerogen
Kerogen: why is it important?

Oil & gas storage & transport controlled by minerals

Oil & gas storage & transport controlled by kerogen?
Kerogen: how to study it?

→ Diversity → location, age, thermal maturity

![Map of Kerogen Locations]

### PERIOD
- Cambrian
- Ordovician
- Silurian
- Devonian
- Miss.
- Pennsylv.
- Permian
- Triassic
- Jurassic
- Cretaceous
- Paleogene

### AGE (Ma)
- 500
- 400
- 300
- 200
- 100
- 0
Kerogen: how to study it?

Shale core or cuttings

Crush to powder
Solvents to remove soluble organics
Non-oxidizing acids to remove inorganic minerals

Kerogen isolate

Analyze using novel and diverse techniques
Kerogen: reservoir science to application

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Reservoir storage, transport, production
Kerogen: chemical abundances

→ Large spread → As big as between oil and gas → Controlled by thermal maturation

![Graphs showing molar carbon fraction and hydrogen/carbon ratio vs. thermal maturity for different rock types.](image)

- $R^2 = 0.93$
- $R^2 = 0.90$

e.g., Buchardt & Lewan, 1990, AAPG; Lis et al., 2005, Org. Geochem; Kelemen et al., 2007, Energy Fuels; Cheshire et al., 2017, Int. J. Coal Geol; Craddock et al., 2019 Org. Geochem, French et al., 2020, MPG
Kerogen: chemical structures

→ Solid state spectroscopies → e.g., infrared, nuclear magnetic resonance, Raman, X-ray

IR excitation causes bond vibrations

IR in

IR out

IR absorption intensity

Wavenumber, cm⁻¹ (Energy)

Thermal maturity

→

\[ R^2 = 0.89 \]

Thermal maturity →, \( R_o \) %

\[ \text{‘graphite’/‘wax’ ratio} \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \]

oil
wet-gas
dry-gas

**App 1: Diffuse reflectance IR spectroscopy**

**Measurement of rock characteristics:**
- Mineral type & concentrations
- Kerogen concentration
- Kerogen chemistry/properties
- Kerogen thermal maturity

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e.g., Christy et al., 1991, Org. Geochem; Charsky & Herron, 2012; Herron et al., 2014, SPWLA; Craddock et al., 2017, Org. Geochem.; Craddock et al., 2018, Petrophysics
App 1: Diffuse reflectance IR spectroscopy

**Measurement of rock characteristics:**
- Mineral type & concentrations
- Kerogen concentration
- Kerogen chemistry/properties
- Kerogen thermal maturity

**Real-time rock characterization:**
- Horizontal well cuttings, any mud type
- Integrated with logging measurements

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e.g., Christy et al., 1991, Org. Geochem; Charsky & Herron, 2012; Herron et al., 2014, SPWLA; Craddock et al., 2017, Org. Geochem.; Craddock et al., 2018, Petrophysics
Kerogen: petrophysical properties

→ Porosity → key reservoir property → density & neutron (hydrogen index) logs
→ Use large difference between rock and pore properties

Density $\text{g/cm}^3$

<table>
<thead>
<tr>
<th>minerals (rock)</th>
<th>pore fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Hydrogen Index

<table>
<thead>
<tr>
<th>minerals (rock)</th>
<th>pore fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Kerogen: petrophysical properties

→ Porosity → key reservoir property → density & neutron (hydrogen index) logs
→ Use large difference between rock and pore properties

Density

- Minerals (rock)
- Kerogen (rock)
- Pore fluids

Hydrogen Index

- Minerals (rock)
- Pore fluids

Thermal maturity $\rightarrow$, $R_o$ %

$R^2 = 0.90$

Kerogen: petrophysical properties

→ Porosity → key reservoir property → density & neutron (hydrogen index) logs
→ Use large difference between rock and pore properties

Kerogen: petrophysical properties

→ Kerogen (matrix) properties determine shale evaluations
→ Kerogen properties are variable and rarely known

e.g., Craddock et al., 2020 Petrophysics
App 2: TMALI THERMAL MATURITY-ADJUSTED LOG INTERPRETATION

Input: Thermal maturity

TMALI property correlations (type II kerogen)

Output: Type II kerogen endpoints

- Grain Density
- Electron Density
- Log Density
- Photoelectric Factor
- Formation Volumetric Factor
- Carbon Mole Fraction
- Hydrogen Mole Fraction
- H/C Mole Fraction Ratio
- Carbon Weight Fraction
- Hydrogen Weight Fraction
- Conversion Factor (TOC-to-TOM)
- Hydrogen Index
- Thermal Neutron Porosity
- Epithermal Neutron Porosity
- Sigma
- Fast Neutron Cross Section

Craddock et al., 2020 Petrophysics
Gas-in-place: 152 bcf/section
<table>
<thead>
<tr>
<th>Gamma Ray</th>
<th>Resistivity</th>
<th>Neutron Density</th>
<th>Late-oil Kerogen volume</th>
<th>Gas volume</th>
<th>Dry-gas Kerogen volume</th>
<th>Gas volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>K + Th + U</td>
<td>0 gAPI</td>
<td>0.2 ohm.m</td>
<td>2000</td>
<td>0 %</td>
<td>100</td>
<td>0 %</td>
</tr>
<tr>
<td>K + Th + U</td>
<td>0 gAPI</td>
<td>0.2 ohm.m</td>
<td>2000</td>
<td>0 %</td>
<td>100</td>
<td>0 %</td>
</tr>
</tbody>
</table>

**Kerogen properties for late oil**
- Kerogen volume: 217 bcf/section

**Kerogen properties for dry gas**
- Kerogen volume: decreases
- Gas volume: increases

**Gas-in-place:** 217 bcf/section

**ΔGIP:** 40%

**Δ$:** 100M
Kerogen: reservoir science to application

**SCIENCE**

Chemical insights

**APPLICATION**

Petrophysical log responses

Reservoir characterization
Kerogen: reservoir science to application

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Kerogen: high-resolution imaging

Conventional sandstone
(Photomicrography)

Unconventional shale
(Scanning Electron Microscopy)

→ Porosity can be all in organics!
→ Physical differences at grain scale!
→ Other differences at grain scale?

Kerogen: ‘nano-IR’

→ Atomic force microscopy (AFM) + IR spectroscopy → ‘nano-IR’

Size of AFM tip much smaller than individual grains! Smallest size of IR ‘spot’ bigger than individual grains!

IR absorption → Thermal expansion

Measure AFM deflection

IR absorption intensity

Wavenumber, cm\(^{-1}\) (Energy)

Yang et al., 2017, Nature Commun.
Kerogen: ‘nano-IR’ chemical mapping

SEM image

Grain X

Grain Y

Grain Z

Nano-IR ‘chemistry’

Absorption intensity, a.u.

Wavenumber, cm\(^{-1}\)

IR-proxy for ‘waxy’/‘graphitic’ carbon

Thermal maturity \(\rightarrow, R_o\) %
Kerogen: ‘nano-IR’ chemical mapping

SEM image

Grain X

Grain Y

Grain Z

Nano-IR ‘chemistry’

Absorption intensity, a.u.

Wavenumber, cm\(^{-1}\)

IR-proxy for ‘waxy’/‘graphitic’ carbon

Thermal maturation

Thermal maturity →, R_0 %

Yang et al., 2017, Nature Commun.
Kerogen: ‘nano-IR’ mechanical mapping

→ Chemical & Mechanical properties → correlated at molecular scale

SEM image

Nano-IR ‘chemistry’

AFM ‘stiffness’

Grain X

Grain Y

Grain Z

Absorption intensity, a.u.

Increasing aromatic (graphitic) carbon

Wavenumber, cm\(^{-1}\)

Probablity

Oscillation frequency, kHz

more stiff

less stiff

Increasing mechanical stiffness

Yang et al., 2017, Nature Commun.
Kerogen: pore-structure quantification

→ Kerogen surface area → generated by thermal maturity → high → surface interactions

Valenza et al., 2013, Geology; Suleimenova et al., 2014, Fuel; Cheshire et al., 2017, Int. J. Coal Geol; Craddock et al., 2018, Energy Fuels
Kerogen: pore ‘swelling’

Kerogen, *before* liquids extraction

Kerogen, *after* liquids extraction

→ Kerogen acts like a ‘sponge’
→ Adsorbs hydrocarbon gases
→ Swells with hydrocarbon liquids
→ Swelling blocks pores
→ Inhibits production

Reeder et al., 2016, Petrophysics
App 3: RPI  RESERVOIR PRODUCIBILITY INDEX

Conventional reservoirs

<table>
<thead>
<tr>
<th>Total Organic Carbon</th>
<th>Oil + Gas</th>
</tr>
</thead>
</table>

TOC ↑ ✔️

Unconventional tight-oil

<table>
<thead>
<tr>
<th>Total Organic Carbon</th>
<th>Oil + Bitumen + Kerogen</th>
</tr>
</thead>
</table>

TOC ↑ ?????

Oil (producible liquid)

Kerogen (swells)

Bitumen (non-producible liquid)

→ RPI ∝ Oil/TOC

→ RPI ↑ Production ↑

→ ‘Sweet spots’ in Tight Oil

Reeder et al., 2016, Petrophysics; Kausik et al., 2015, URTeC
App 3: RPI  RESERVOIR PRODUCIBILITY INDEX

**Eagle Ford, early-oil window**

<table>
<thead>
<tr>
<th>TOC</th>
<th>Bound water</th>
<th>Free water</th>
<th>RPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>12</td>
<td>0 %</td>
<td></td>
</tr>
<tr>
<td>Bitumen</td>
<td></td>
<td>Free oil</td>
<td>RPI &gt; 0.1</td>
</tr>
</tbody>
</table>

Similar TOC
Bitumen $\uparrow$
RPI $\downarrow$
Production $\downarrow$

3,000 bbl/month

**Eagle Ford, peak/late-oil window**

<table>
<thead>
<tr>
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<th>RPI</th>
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<td></td>
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<td>RPI &gt; 0.1</td>
</tr>
</tbody>
</table>

Similar TOC
Bitumen $\downarrow$
RPI $\uparrow$
Production $\uparrow$

18,000 bbl/month

Reeder et al., 2016, Petrophysics; Kausik et al., 2015, URTeC
Source-rock bitumen is common in oil window

(Important to know $R_o$)

Dissolve bitumen w/ solvent

Increase pore connectivity

Pump ‘green’ solvent downhole for initial stimulation or workover?

Valenza et al, 2013, Geology
Summary: SPE DL Tour of kerogen

Science to build knowledge of kerogen…

- Chemical/molecular properties
- Petrophysical properties
- Microstructure
- Diversity and heterogeneity
- Evolution during thermal maturation

Develop applications to improve…

- Surface reservoir evaluation
- Downhole reservoir evaluation
- ‘Sweet spot’ (target) identification
- Production strategies in shale
Selected readings


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