Producing mobile hydrocarbons from shale depends in part on the chemistry of the immobile hydrocarbons in shale. In addition to mobile oil and gas, shales typically contain two phases of immobile hydrocarbons: bitumen, a viscous material defined as soluble in organic solvent; and kerogen, a solid material defined as insoluble (pyrobitumen is included in this definition). These phases control many of the key processes involved in economic recovery from shales, and their detailed chemistry is relevant to understanding fundamental mechanisms involved in shale production. For example, oil and gas are formed by the decomposition of kerogen and bitumen, such that the chemistry of the initial kerogen dictates when producible fluids are generated and what their properties are. Oil and gas generation leaves nanoscopic pores in kerogen, and kerogen's surface chemistry and structure dictate how different components in the mobile phase are stored and transported through kerogen, similar to the role of the stationary phase in chromatography. Additionally, kerogen is typically the most ductile component of shale and can be bonded to minerals in complex manners; so the chemistry of kerogen may impact fracture propagation.

Despite their importance, kerogen and bitumen are complex mixtures that are not amenable to chemical characterization by common experimental techniques. As a result, relatively little is known about their detailed chemistry, hindering the development of first-principles understanding of these fundamental mechanisms. However, several advanced spectroscopic methods able to characterize kerogen and bitumen at the molecular level have been implemented recently. These methods include X-ray absorption near-edge structure (XANES) spectroscopy, which can measure the distribution of sulfur-containing functional groups; high-resolution 13C NMR spectroscopy, which can measure the relative abundance of aromatic carbon
(similar to benzene) and aliphatic carbon (similar to wax); X-ray Raman scattering (XRS) spectroscopy, which can measure the geometry of fused aromatic ring systems; and infrared (IR) spectroscopy, which can measure the configuration of aliphatic carbon and some oxygen-containing functional groups. Taken together, these analyses are beginning to paint a picture of the molecular composition of kerogen and bitumen, including their evolution with thermal maturity. We find that immature kerogen contains mostly aliphatic carbon and sulfur, as well as several oxygen-containing functionalities. During maturation, carbon and sulfur in kerogen become more aromatic, the size of fused rings grow, and all oxygen-containing functionalities are diminished. Like kerogen, bitumen converts from mostly aliphatic carbon at low maturities to mostly aromatic carbon at high maturities. However, several chemical differences between kerogen and bitumen are observed: kerogen is dominated by reduced sulfur (which is non-polar), while bitumen is dominated by oxidized sulfur (which is polar); aliphatic chains monotonically shorten with maturity in kerogen, while they reach a maximum length at intermediate maturities in bitumen; and aromatic ring systems grow with maturity in kerogen, while their size remains unchanged in bitumen. These measurements provide some insights into the mechanisms involved in petroleum generation, hydrocarbon storage, and oil/water transport in shale.

References Cited


Modern Spectroscopies for Characterizing the Chemical Composition of Kerogen and Bitumen

Drew Pomerantz
Schlumberger-Doll Research
Cambridge, MA
Acknowledgements
Definition of kerogen & bitumen

Minerals:
inorganic

Bitumen:
soluble organic

Kerogen:
insoluble organic
Traditional Geochemistry:
Chemical fingerprints indicate history
- Maturity
- Biodegradation
- Allocation

Analytical Chemistry:
Chemical composition predicts future
- Materials
- Medicine
- Oil

Dong et al., Fuel, 2014

Chemical composition enables prediction
## Chemical Controls on Shale Production

<table>
<thead>
<tr>
<th>Process</th>
<th>Molecular Mechanism</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maturation</td>
<td>Breaking chemical bonds</td>
<td>Reserves</td>
</tr>
<tr>
<td>Porosity development</td>
<td>Removing light molecules</td>
<td>Permeability</td>
</tr>
<tr>
<td>Storage</td>
<td>Gas adsorption</td>
<td>Recovery Factor</td>
</tr>
<tr>
<td>Mechanical Properties</td>
<td>Breaking bonds in the rock</td>
<td>Hydraulic fracturing</td>
</tr>
</tbody>
</table>

![Graph showing weight fraction of organic matter](image)

Passey et al., 2010, SPE 131350
Petroleum Chemistry

Light Hydrocarbon Ends

Asphaltenes

2008

Gas chromatography
Challenges in Mol. Weight Measurement

Mass Analysis Requires:

- Volatilization
- Ionization
- Break physical bonds
- Preserve chemical bonds
- Treat all components equally
Laser desorption laser ionization mass spectrometry (L²MS)

- Extract asphaltenes
- Place powder in a high vacuum chamber
- Desorb sample with pulse from ~ 0.1 eV laser (10⁸ K/sec)
- Ionize sample with pulse from ~ 10 eV laser
- Detect ions with a mass spectrometer
Camera and monitor

CO2 laser

UV laser

Sample transfer interlock

XYZ manipulator

Electronics
L²MS Results: Molecular Weight

Petroleum Asphaltene

GR Bitumen Asphaltene
Nuclear Magnetic Resonance (NMR)

Local magnetic field strength
$^{13}$C NMR Methodology

Chemical shift (ppm)

Carbon NMR Spectrum

- **aromatic**
- **CDCl$_3$ solvent**
- **aliphatic**
$^{13}$C NMR: Aromaticity

Kelemen et al., E&F 2007

Feng et al., E&F 2013
$^{13}$C NMR: Bitumen Aliphatic Structure

(a) Aliphatic carbon % vs EASY%$R_0$

(b) Aliphatic carbon % vs EASY%$R_0$
$^{13}$C NMR: Bitumen Aromatic Structure

(a) Aromatic ring structure vs EASY$\%R_0$

(b) Aromatic ring structure vs EASY$\%R_0$
Infrared Spectroscopy

- Molecules absorb IR photons and vibrate
- Vibrational frequency reflects chemical bonds
- Common measurement in lab and downhole
IR Signature of Maturity

CH$_2$:CH$_3$ index

Oil window

Gas window
Sulfur Bonds in Kerogen/Bitumen: X-ray Absorption Near Edge Structure (XANES)

Energy diagram showing transitions of sulfur states:
- $\sigma^*$
- $\pi^*$
- $\pi$
- $\sigma$
- $2s$
- $1s$

Photon energy:
- 5,000 eV
- 0.25 nm
- 40,000,000 cm$^{-1}$
- 1,000,000,000,000 MHz

Graph showing intensity ($I/I_0$) vs. photon energy (eV) for various sulfur compounds:
- Pyrite
- Elemental S
- Sulfide
- Thiophene
- Sulfoxide
- Sulfone
- Sulfate (x0.5)
XANES Results

Kerogen & Bitumen

Bitumen

Native State

log(TTI_{ARR})

Elemental

Sulfate

Sulfone

Sulfoxide

Thiophene

Sulfide

EASY%Ro

0.78

0.83

0.90

0.92

0.92

0.95

0.95

1.19

1.28

1.65

0.48

0.75

0.78

0.83

0.90

0.92

0.92

0.95

0.95

1.19

1.28

1.65

0.75

0.48
## Trends with Maturity

<table>
<thead>
<tr>
<th></th>
<th>Bitumen</th>
<th>Kerogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>Subtle increase</td>
<td>N/A</td>
</tr>
<tr>
<td>Carbon backbone</td>
<td>Mostly aliphatic $\rightarrow$</td>
<td>Mostly aliphatic $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td>Mostly aromatic</td>
<td>Mostly aromatic</td>
</tr>
<tr>
<td>$\text{CH}_2/\text{CH}_3$</td>
<td>Increase, then decrease</td>
<td>Decrease</td>
</tr>
<tr>
<td>Sulfur speciation</td>
<td>Sulfoxide $\rightarrow$ thiophene</td>
<td>Sulfide $\rightarrow$ thiophene</td>
</tr>
</tbody>
</table>
Conclusions

**L²MS**: Asphaltene Molecular Weight & Architecture

**XANES**: Sulfur speciation in kerogen, bitumen & oil

**NMR**: Aliphatic/aromatic carbon structures in kerogen, bitumen & oil