Biomarkers in the Upper Devonian Lower Huron Shale as Indicators of Biological Source of Organic Matter, Depositional Environment, and Thermal Maturity*

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Abstract

The Lower Huron Shale (Upper Devonian) is considered the largest shale gas reservoir in the Big Sandy Field in Kentucky and West Virginia. The potential for gas shales, such as the Lower Huron, to produce natural gas is a function of type, amount, and thermal maturation of their organic matter. Twenty-one Lower Huron Shale samples from eight wells located in eastern Kentucky and southern West Virginia were analyzed for biomarker content to interpret biological source of organic matter, depositional environment conditions, and thermal maturity. The following biomarkers were identified: n-alkanes (C15 to C35), pristane (Pr), phytane (Ph), steranes (αααR, αααS, ααβR, ααβS isomers of C27 to C30 steranes), and hopanes (C27, C29, C30 and C31 hopanes).

The TAR (terrigenous versus aquatic n-alkanes ratio), n-C17/n-C31, Pr/n-C17, Ph/n-C18, and sterane distribution indicate the source of organic matter in the samples analyzed is predominately marine algae and bacteria. The most source-specific biomarkers identified in the samples were the C30 steranes indicative of marine brown algae. The Pr/Ph, Pr/n-C17, Ph/n- C18, Ts/Tm ratios and sterane distribution indicate the samples were deposited in a deep water (>100 m) environment with alternating oxic and anoxic conditions. These results and paleogeographic information support depositional models involving a seasonally stratified water column.

The C27-20S/(20S+20R), C28-20S/(20S+20R), C29-20S/(20S+20R), C29-αββ/(αββ+ααα), C29- αββ/(αββ+ααα), Ts/(Ts+Tm), and 22S/(22S+22R) ratio values indicate thermal maturities within the early to peak oil generation stages. Contour maps of the biomarker ratio values indicate increasing thermal maturities toward the southeast within the study area, which corresponds to the direction of increasing maximum burial depth. Biomarker data suggest that gas produced from the Lower Huron Shale in the Big Sandy Field is biogenic or that thermogenic gas has migrated to the Big Sandy Field from more thermally mature areas to the east.
Biomarkers in the Upper Devonian Lower Huron Shale as Indicators of Biological Source of Organic Matter, Depositional Environment, and Thermal Maturity

John Kroon and Dr. James W. Castle
September 27th, 2011
Objectives

- Identify biomarkers in samples of the Upper Devonian Lower Huron Shale from the Appalachian Basin
- Interpret biological origin of the biomarkers identified
- Use the biomarkers to interpret environmental conditions represented by the samples analyzed
- Use the biomarkers to interpret thermal maturity of the samples
Biomarkers

- Preserved remnants of molecules originally synthesized by organisms
  - Distinctive chemical structures closely related to the biological precursor molecule
  - Biological precursors molecules are common in certain organisms that may have been abundant and widespread
  - Are chemically stable during sedimentation and early burial
Devonian Black Shales

- **Big Sandy Field**
  - 2.5 Tcf of gas has been produced from gas shales
  - 6 Tcf undiscovered recoverable reserves

- **Lower Huron Shale** is the primary reservoir
## Lower Huron Shale

<table>
<thead>
<tr>
<th>Period</th>
<th>Stage</th>
<th>Age Ma</th>
<th>E. Kentucky</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippian</td>
<td></td>
<td>363</td>
<td>Sunbury Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Berea Sandstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cleveland Shale</td>
</tr>
<tr>
<td>Upper Devonian</td>
<td>Famennian</td>
<td>367</td>
<td>Three Lick Bed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Upper Huron Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Middle Huron Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lower Huron Shale</td>
</tr>
<tr>
<td>Frasnian</td>
<td></td>
<td>385</td>
<td>Olentangy Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rhinestreet Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Corniferous Formation</td>
</tr>
</tbody>
</table>

- **Age Ma**: 363-385 Ma
- **E. Kentucky**: Sunbury Shale, Berea Sandstone, Cleveland Shale, Three Lick Bed, Upper Huron Shale, Middle Huron Shale, Lower Huron Shale, Olentangy Shale, Rhinestreet Shale, Corniferous Formation

### Diagram
- Various geological formations and time periods are depicted with timelines and corresponding thickness indicators.
Study Area and Samples

- 21 cutting samples were analyzed from 8 horizontal wells
Methods: Biomarker Identification

- Ultrasonication
- Sulfur Removal
- Asphaltene Removal
- Column Chromatography
  - GC-FID
  - GC-MS-MS
Identified Biomarkers: GC-FID
Identified Biomarkers: GC-MS-MS

Cholestanes (C\textsubscript{27})
m/z 372 $\rightarrow$ 217

24-Methylcholestane (C\textsubscript{28})
m/z 386 $\rightarrow$ 217

24-Ethylcholestane (C\textsubscript{29})
m/z 400 $\rightarrow$ 217

24-Propycholestane (C\textsubscript{30})
m/z 414 $\rightarrow$ 217

C\textsubscript{27} Hopanes
m/z 370 $\rightarrow$ 191

C\textsubscript{29} Hopanes
m/z 398 $\rightarrow$ 191

C\textsubscript{30} Hopanes
m/z 412 $\rightarrow$ 191

C\textsubscript{31} Hopanes
m/z 426 $\rightarrow$ 191
Methods: Biological Source of OM

- N-alkane parameters
  - TAR (Terrigenous vs. aquatic ratio)
  - \( \text{n-C}_{17}/\text{n-C}_{31} \)
- Pr/\text{n-C}_{17} vs. Ph/\text{n-C}_{18}
- Distribution of \( \text{C}_{27} \) to \( \text{C}_{30} \) steranes
N-alkane parameters

- TAR: 0.10 to 0.33 indicate marine algae source of OM
- n-C\textsubscript{17}/n-C\textsubscript{31}: 3.30 to 40.0 indicate marine algae source of OM

Type II Kerogen – originates from zooplankton, phytoplankton, and bacteria
Sterane Parameters

- $C_{29}/C_{27}$ steranes: 0.13 to 0.88 indicate marine algae source of OM

- $C_{30}$ steranes diagnostic of marine chrysophyte algae
Methods: Depositional Conditions

- Pr/Ph – Redox conditions
- Pr/n-C\textsubscript{17} vs. Ph/n-C\textsubscript{18} – Redox conditions
- Ts/Tm – Redox conditions
- Distribution of $C_{27}$ to $C_{30}$ steranes – Depositional environment
Pr/Ph

- Pr/Ph values range from 1.14 to 1.69 in samples analyzed indicating alternating oxic and anoxic conditions

Ts/Tm

- Ts/Tm values range from 1.20 to 3.7 except for a value of 7.40 in one sample
- Ts/Tm value is between 1.0 and 2.0 in 11 of the 18 samples indicating alternating oxic and anoxic conditions
Pr/n-C$_{17}$ vs. Ph/n-C$_{18}$
Sterane Distribution
## Depositional Model

<table>
<thead>
<tr>
<th>Warm Season - Stratified</th>
<th>Cool Season - Mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxic</strong></td>
<td>Elevated primary productivity</td>
</tr>
<tr>
<td>Thermocline at 30 m depth</td>
<td>Phosphorus and Nitrogen</td>
</tr>
<tr>
<td><strong>Anoxic</strong></td>
<td>Organic Matter</td>
</tr>
<tr>
<td>Accumulation of phosphorus and nitrogen due to anaerobic decomposition of organic matter</td>
<td>Oxygen</td>
</tr>
<tr>
<td><strong>Sediments</strong></td>
<td>Sediments</td>
</tr>
</tbody>
</table>
# Evidence Supporting Model

<table>
<thead>
<tr>
<th>Biomarker</th>
<th>Modern Environments</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Pr/Ph, Pr/n-C\textsubscript{17} vs. Ph/n-C\textsubscript{18}, and Ts/Tm support alternating oxic and anoxic conditions</td>
<td>• Modern subtropical oceans are characterized by a warm season with a thin mixed layer and shallow thermocline and during the cool season the thermocline is broken down (Red Sea)</td>
</tr>
<tr>
<td>• Sterane distribution supports a deep water environment</td>
<td>• South China Sea and Arabian Sea algal blooms have been observed in winter due to upwelling of nutrient rich water</td>
</tr>
<tr>
<td>• N-alkanes and steranes identified support an elevation in algal productivity</td>
<td></td>
</tr>
</tbody>
</table>
Methods: Thermal Maturity

- Based on the ratio of a complex biologically produced compound to a thermodynamically stable compound produced from alteration of the less stable complex biological compound
  - Pr/n-C_17
  - Ph/n-C_18
  - C_{27}-20S/(20S+20R)
  - C_{28}-20S/(20S+20R)
  - C_{29}-20S/(20S+20R)
  - C_{28}-\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)
  - C_{29}-\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)
  - Ts/(Ts+Tm)
  - 22S/(22S+22R)
## Thermal Maturity Values

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Values</th>
<th>Thermal Maturity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr/n-C_{17}</td>
<td>0.40 – 0.70</td>
<td></td>
</tr>
<tr>
<td>Ph/n-C_{18}</td>
<td>0.32 – 0.52</td>
<td></td>
</tr>
<tr>
<td>C_{27}-20S/(20S+20R)</td>
<td>0.14 – 0.91</td>
<td>At or above peak oil generation</td>
</tr>
<tr>
<td>C_{28}-20S/(20S+20R)</td>
<td>0.50 – 0.90</td>
<td>Early to peak oil generation</td>
</tr>
<tr>
<td>C_{29}-20S/(20S+20R)</td>
<td>0.55 – 0.77</td>
<td>At or above peak oil generation</td>
</tr>
<tr>
<td>C_{28}-\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)</td>
<td>0.19 – 0.79</td>
<td>Early to peak oil generation</td>
</tr>
<tr>
<td>C_{29}- \alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)</td>
<td>0.46 – 0.71</td>
<td>Early to peak oil generation</td>
</tr>
<tr>
<td>Ts/(Ts+Tm)</td>
<td>0.55 – 0.88</td>
<td>Early to late oil generation</td>
</tr>
<tr>
<td>22S/(22S+22R)</td>
<td>0.55 – 0.84</td>
<td>At or above early oil generation</td>
</tr>
</tbody>
</table>
Ratio Values Vs. Depth

A. B.

Pr/n-C17
Ph/n-C18
C27-20S(20S+20R)
C28-20S(20S+20R)
C29-20S(20S+20R)

Peak Oil Generation
Early Oil Generation
Ratio Values Vs. Depth

C

D

C28-αββ/(αββ+ααα)  C29-αββ/(αββ+ααα)

Peak Oil Generation

Ts/(Ts+Tm)  22S/(22S+22R)

Early Oil Generation for 22S/(22S+22R)
Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area.

Pr/n-C$_{17}$

Contour interval = 0.05

0 15 30 60 Kilometers
Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area.

\[
\frac{C_{29}-20S}{(20S+20R)}
\]

Peak Oil = 0.55

Contour interval = 0.05
Contour maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area.

\[
C_{28-\alpha\beta\beta}/(\alpha\beta\beta+\alpha\alpha\alpha)
\]

Peak Oil = 0.70
Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area.

\[ \frac{Ts}{(Ts + Tm)} \]

Peak Oil = 0.70

Contour interval = 0.05
Thermal Maturity Contours

- Contours of $R_o$ values indicate increased thermal maturity toward the southeast.
- An increase towards the southeast is expected, which corresponds to the direction of increasing maximum burial depth.

Peak Oil = 0.9%

Contour interval = 0.2%

Contour interval = 500 ft (152 m)
Conclusions

- Biomarkers indicate the biological source of organic matter in the Lower Huron Shale is marine algae and bacteria.
- Biomarker ratios in the samples analyzed indicate the Lower Huron Shale was deposited in alternating oxic and anoxic conditions.
- Sterane distributions in the samples analyzed indicate the Lower Huron Shale was deposited in deep waters (> 150 m).
Conclusions

- Biomarker ratios indicate that the samples analyzed have reached the early to late oil generation stages.
- Contour maps of the biomarker maturity ratio values indicate increasing thermal maturity toward the southeast within the study area.
- Biomarker data suggest that gas produced from the Lower Huron Shale in the south-eastern area of the Big Sandy Field is thermogenic.
Acknowledgments

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- Dr. Melissa Riley – Committee Member
- Dr. Cindy Lee – Committee Member