Organic Matter and Thermomaturation Trends in the Ohio and Sunbury Shales, Eastern Kentucky, Central Appalachian Basin*

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Abstract

One hundred fifty-eight samples of Ohio and Sunbury shale core and well cuttings, from 14 bore holes, were sampled along a north/northwest (NNW) to south/southeast (SSE) transect in eastern Kentucky. The transect essentially parallels regional dip, with the NNW end representing an area where the shale is relatively thin (<200 m) with minimal burial depth (0 to 600 m), and the SSE end representing an area where the shale is thicker (>200 m) and more deeply buried (600 to 1,400 m). Sample points from individual cores were selected to best represent the black shale interval at each core location. An additional 21 samples were collected from locations along the Ohio/Sunbury shale outcrop belt in northeastern Kentucky. All the samples were analyzed for total organic carbon content (TOC) and vitrinite reflectance (VRo). Selected samples were analyzed for solid bitumen reflectance (BRo), Rock Eval pyrolysis, and major, minor and trace element composition as determined from x-ray fluorescence (XRF). TOC values ranged from 0.23 % to 21.64 %, with core average TOC values being higher towards the NNW. Vitrinite reflectance values range from 0.5 - 0.6 % VRo random on the NNW end of the transect to 1.2 to 1.3 % on the SSE end. Solid bitumen reflectance measurements were collected on 21 samples and show a similar pattern, being lowest (0.3 to 0.4 %, BRo random) on the NNW end of the transect, and highest (1.4 to 1.5 %, BRo random) on the SSE end. Rock Eval analyses performed on 64 samples, show a pattern of increasing Tmax from NNW (420 to 4300 C) to SSE (440 to 4600 C), and decreasing Hydrogen Indices (HI) from >500 at locations to the NNW, to <100 at the SSE end. Collectively, the petrographic and Rock Eval thermomaturation data all show an increase from the NNW end of the transect to the SSE end, which is the
direction of increasing shale thickness and present depth of burial. Major, minor and trace element concentrations, determined for 21 samples from the outcrop belt on the NNW end of the transect, indicate the Ohio/Sunbury shale to be dominated by SiO$_2$ (avg. 57.9 %) and Al$_2$O$_3$ (15.8 %). The shale samples are also enriched in several trace elements including Cr (avg. 179 ppm), Mo (avg. 241 ppm), Ni (avg. 197 ppm), V (avg. 1194 ppm), Zn (avg. 259 ppm), and Zr (avg. 263 ppm). Element ratios (e.g., Ni/Co, V/Cr and V/V+Ni), used to assess paleoredox conditions, indicate mainly dysoxic to anoxic conditions during sediment and organic matter accumulation.

**Selected References**


Organic Matter and Thermomaturation Trends in the Ohio and Sunbury Shales, Eastern Kentucky, Central Appalachian Basin

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\textsuperscript{1}Kentucky Geological Survey
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Reston, Virginia
The Berea SS is an upper Devonian "tight sand" (siltstone across much of KY)

- Interfingers with the Bedford Shale
- Overlain by the Sunbury Shale and underlain by the Ohio Shale (potential source rocks)
Late Devonian Ohio Shale / Early Mississippian Sunbury Shale

<table>
<thead>
<tr>
<th>Interval ID</th>
<th>TC</th>
<th>TIC</th>
<th>TOC</th>
<th>TS</th>
<th>VR₀</th>
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<tbody>
<tr>
<td>Sunbury (top)</td>
<td>15.01</td>
<td>0.00</td>
<td>15.01</td>
<td>1.61</td>
<td>0.53</td>
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<tr>
<td>Sunbury (middle)</td>
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<td>14.01</td>
<td>1.52</td>
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<td>Sunbury (base)</td>
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<td>0.51</td>
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<tr>
<td>Cleveland (top)</td>
<td>13.14</td>
<td>0.00</td>
<td>13.14</td>
<td>1.73</td>
<td>0.54</td>
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<tr>
<td>Cleveland (middle)</td>
<td>15.72</td>
<td>0.03</td>
<td>15.69</td>
<td>0.96</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Farmers Member of Borden Formation

*the Berea Sandstone, which overlies the Bedford Shale at more eastern locations, is absent here

KY Route 801, 1.9 mi. south of I-64
Farmers Member of Borden Formation

Kentucky Route 9 (AA Hwy)

Sunbury Shale

TOC = 21.4 %
TS = 1.7 %
VR₀ = 0.53 %

Berea Sandstone

Tasmanites
Skaggs-Kelly #3RS – Johnson Co., Kentucky

- **Mainly liptinite macerals with increased amounts of terrestrial macerals (vitrinite + inertinite)**
- **Mainly liptinite macerals of marine origin – amorphinite, bituminite, alginite and Tasmanites**

**Vitrinite**

**Inertinite**

**Solid Bitumen**

**Liptinite**
**Dispersed Organic Material**

Organic components in petroleum shales are called “macerals”. Macerals are the organic equivalents of minerals in rocks.

<table>
<thead>
<tr>
<th>Terrestrial Macerals</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>Wood and wood-like tissues of land flora</td>
</tr>
<tr>
<td>Inertinite</td>
<td>Oxidized tissues of land flora</td>
</tr>
<tr>
<td>Sporinite</td>
<td>Spores and pollen of land flora</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Open Water Macerals</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginite</td>
<td>Algae</td>
</tr>
<tr>
<td>Lamalginite</td>
<td>Laminar shape</td>
</tr>
<tr>
<td>Telalginate</td>
<td>Polygonal (ovoid) shape</td>
</tr>
<tr>
<td>Bituminitite</td>
<td>Degraded algae, laminar to ovoid shape</td>
</tr>
<tr>
<td>Amorphinitite</td>
<td>Degraded algae, amorphous morphology</td>
</tr>
<tr>
<td>Solid Bitumen</td>
<td>Secondary maceral, mobilized and re-solidified kerogen</td>
</tr>
</tbody>
</table>

*Tasmanites / Leiosphaeridia*  Spores of prasinophyte algae
Vitrinite (from Devonian coal)

- Avg. $R_o$ random = 0.47%
- Max. $R_o$ random = 0.51%
- Min. $R_o$ random = 0.45%
- Standard Deviation = 0.02
Semifusinite (from Devonian coal)

Avg. $R_o_{\text{random}} = 1.17\%$
Max. $R_o_{\text{random}} = 1.21\%$
Min. $R_o_{\text{random}} = 1.11\%$
Standard Deviation = 0.02
Fusinite (Inertinite)
50 microns

White Light

50 microns

White Light
Fluorescent (UV) Light

White Light

Solid Bitumen

Tasmanites

Solid Bitumen

50 microns

Solid Bitumen

Bituminite

Solid Bitumen

Bituminite

Solid Bitumen

Solid Bitumen

Solid Bitumen

50 microns

Solid Bitumen

Bituminite

UK

Kentucky Geological Survey
"Godzillinite" (unusually large pieces of solid bitumen)
**Total Organic Carbon (TOC)**

1. Aristech #4 8.0 %
2. Newman #1 7.8 %
3. Hanson #1 8.1 %
4. EKY Lumber #1 7.5 %
5. B. Cassady #50 6.1 %
6. S. Young #1 2.8 %*
7. G. Roberts #1420 7.1 %
8. M. Moore #1122 9.7 %
9. R. Moore #1087 10.4 %
10. Skaggs-Kelly #3RS 7.1 %
11. Columbia #20336 5.0 %
12. Interstate #10 4.4 %
13. J.B. Goff Land #1 6.3 %
14. EQT 504353 3.6 %

*One value is marked with an asterisk (*) indicating a notable difference from the others.

**Kentucky**
VR$_o$ = measured vitrinite reflectance (oil immersion)
BR$_o$ = measured solid bitumen reflectance (oil immersion)
VR$_{equivalent}$ = (BR$_o$ measured * 0.618) + 0.4 (Jacob, 1989)
Well Name | Avg. VR<sub>o</sub>  
--- | ---  
1. Aristech #4 | 0.51 %  
2. Newman #1 | 0.58 %  
3. Hanson #1 | 0.58 %  
4. EKY Lumber #1 | 0.58 %  
5. B. Cassady #50* | 0.62 %  
6. S. Young #1* | 0.69 %  
7. G. Roberts #1420 | 0.58 %  
8. M. Moore #1122 | 0.61 %  
9. R. Moore #1087 | 0.59 %  
10. Skaggs-Kelly #3RS | 0.66 %  
11. Columbia #20336 | 0.72 %  
12. Interstate #10 | 0.74 %  
13. J.B. Goff Land #1 | 0.75 %  
14. EQT 504353 | 1.24 %  

*VR<sub>o</sub> calculated from T<sub>max</sub>
<table>
<thead>
<tr>
<th>Depth (ft)</th>
<th>Ro random</th>
<th>Cleveland</th>
<th>Upper Huron</th>
<th>Middle Huron</th>
<th>Lower Huron</th>
<th>avg. = 0.66</th>
<th>avg. = 6.71</th>
<th>avg. = 432 Ro calc. = 0.62</th>
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</table>
Thermomaturation – Rock Eval

\[ T_{\text{max}} \ (^{0}\text{C}) = S2 \text{ peak} \]
\[ VR_{\text{calculated}} = (T_{\text{max}} \times 0.018) - 7.16 \text{ [Jarvie et al., 2002]} \]
\[ HI = (S2 / TOC) \times 100 \]
\[ \text{Adjusted } T_{\text{max}} = T_{\text{max}} + ((HI - 150) / 50) \text{ [Snowdon, 1995]} \]
\[ \text{Production Index} = S1 / (S1 + S2) \]
Calc. Vitrinite Reflectance ($VR_{\text{calc.}}$)

Well Name | Avg. $T_{\text{max}}$
---|---
1. Aristech #4 | 421.6
2. Newman #1 | no data
3. Hanson #1 | 420.0
4. EKY Lumber #1 | no data
5. B. Cassady #50 | 432.5
6. S. Young #1 | 436.0
7. G. Roberts #1420 | 425.9
8. M. Moore #1122 | 425.8
9. R. Moore #1087 | 424.6
10. Skaggs-Kelly #3RS | 432.1
11. Columbia #20336 | 439.3
12. Interstate #10 | 436.0
13. J.B. Goff Land #1 | no data
14. EQT 504353 | 444.7

Kentucky
<table>
<thead>
<tr>
<th>Well Name</th>
<th>Avg. HI</th>
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<td>1. Aristech #4</td>
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<td>2. Newman #1</td>
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<td>3. Hanson #1</td>
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<td>4. EKY Lumber #1</td>
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<td>5. B. Cassady #50</td>
<td>443.9</td>
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<td>6. S. Young #1</td>
<td>365.8</td>
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<tr>
<td>7. G. Roberts #1420</td>
<td>394.8</td>
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<td>8. M. Moore #1122</td>
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<td>10. Skaggs-Kelly #3RS</td>
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<td>Well Name</td>
<td>Avg. VR (adjusted)</td>
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<td>------------------------</td>
<td>--------------------</td>
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<tr>
<td>1. Aristech #4</td>
<td>0.59</td>
</tr>
<tr>
<td>2. Newman #1</td>
<td>no data</td>
</tr>
<tr>
<td>3. Hanson #1</td>
<td>0.54</td>
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<tr>
<td>4. EKY Lumber #1</td>
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<tr>
<td>5. B. Cassady #50</td>
<td>0.73</td>
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<tr>
<td>6. S. Young #1</td>
<td>0.77</td>
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<td>7. G. Roberts #1420</td>
<td>0.58</td>
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<td>8. M. Moore #1122</td>
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<td>10. Skaggs-Kelly #3RS</td>
<td>0.77</td>
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<td>11. Columbia #20336</td>
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<td>12. Interstate #10</td>
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<td>13. J.B. Goff Land #1</td>
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<td>14. EQT 504353</td>
<td>(N/A)</td>
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Paleoenvironmental Considerations

Average Trace Element Abundances in the Sunbury and Cleveland Shales

- TOC
  - Avg. 13.5 %
  - Max. 21.8 %
  - Min. 6.9 %
  - N = 20

- Elements: Co, Cr, Cu, Mo, Ni, Pb, Th, U, Zn, Zr, V
- Concentrations: ppm
- TOC Average Trace Element Abundances in the Sunbury and Cleveland Shales
- Beres ss
- Storm-dominated shelf
- Basin floor Turbidite fans/ aprons Feeder channel
- Paleoenvironmental Considerations

Diagram showing geological layers and environments such as sea level, fair-weather wave base, storm waves, and basement-related growth fault.
Cleveland

Ni/Co

Avg. 11.5
Max. 22.1
Min. 5.4

O = oxic
D = dysoxic
S/A = suboxic/anoxic

V/Cr

Avg. 6.2
Max. 11.0
Min. 1.6

V/V+Ni

Avg. 0.83
Max. 0.93
Min. 0.65

Sunbury
Summary - 1

Total Organic Carbon (TOC) – samples varied between 0.3 and 21.6 %. Well average TOC values are higher to the NW, and lower to the SE. In general:

Sunbury > L. Huron > Cleveland > U. Huron > M. Huron > 3 Lick

Total Sulfur Content (TS) – samples varied between 0.6 and 6.6 %. Pyrite is ubiquitous, and usually occurs as small framboids and isolated euhedral crystals. In general:

L. Huron > M. Huron > U. Huron > Sunbury > Cleveland > 3 Lick
Organic Petrology – all of the samples are dominated by liptinite macerals of marine origin (primarily amorphinite, bituminite, alginite). Vitrinite and inertinite (terrestrial macerals) become more common in the Upper Huron through Sunbury.

Vitrinite Reflectance – Well average VR₀ values ranged from 0.51 %, in the NW part of the study area, to 1.24 % in the SE part.

Solid Bitumen Reflectance – BR₀ ranged from 0.33 %, in the NW part of the study area, to 1.43 % in the SE part.

Rock Eval Pyrolysis – Thermomaturity parameters increase NW – SE.
Summary - 3

HI – 585 to 42 mg / g TOC
\( T_{\text{max}} \) - 420 to 445 C
VR calculated – 0.40 to 0.84 %
Production index (PI) - 0.03 to 0.44
Adjusted \( T_{\text{max}} \) – 428 to 463 C
Adjusted VR calculated – 0.54 to 0.82 %

VR\(_{o}\) and VR\(_{\text{equivalent}}\) (calculated from BR\(_{o}\) measurements) show close agreement

Thermomaturation indices from Rock Eval and petrographic methods are in general agreement after HI adjustments are made.

Although the NW portion of EKY appears to be immature to early mature based on VR\(_{o}\) (measured and calculated) and \( T_{\text{max}} \), adjusted \( T_{\text{max}} \) values place most of the area within the oil window.
Several trace elements show significant correlation with TOC. Regression analysis indicates the following r-values.

- Cr/Al = 0.88
- Cu/Al = 0.87
- Co/Al = 0.84
- Ni/Al = 0.82
- Zr/Al = 0.75
- Pb/Al = 0.74
- V/Al = 0.71
- Th/Al = 0.68
- U/Al = 0.62
- Zn/Al = 0.55
- Y/Al = 0.46
- Mo/Al = 0.44

Element ratios indicative of paleoredox conditions are suggestive of deposition in mainly dysoxic to suboxic/anoxic conditions.

<table>
<thead>
<tr>
<th>Element Ratio</th>
<th>Avg.</th>
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<tbody>
<tr>
<td>Ni/Co</td>
<td>11.5</td>
</tr>
<tr>
<td>V/Cr</td>
<td>6.2</td>
</tr>
<tr>
<td>V/(V + Ni)</td>
<td>0.83</td>
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</table>
Thank You

References


