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_2O_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.

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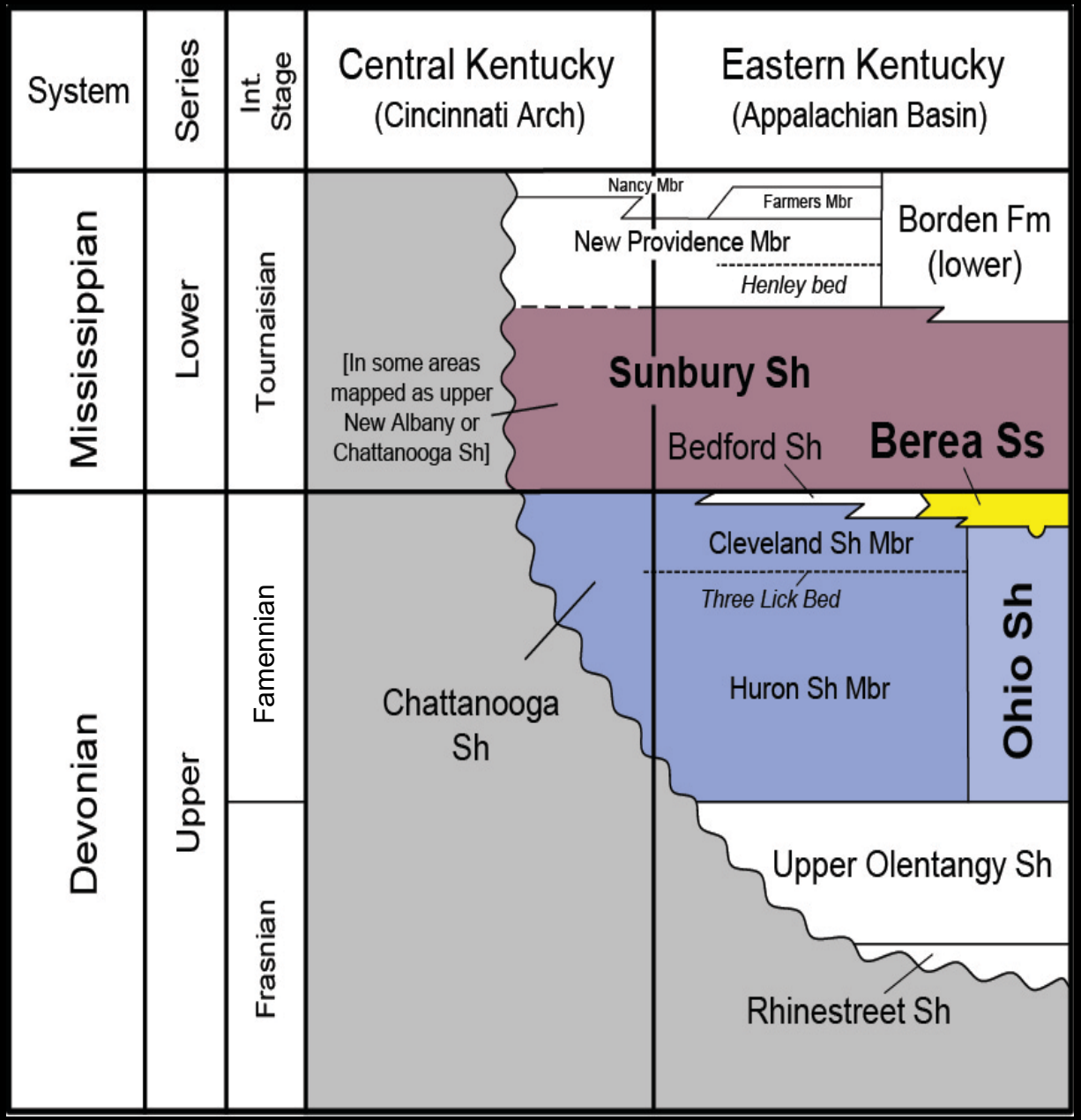
Stratigraphy



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)

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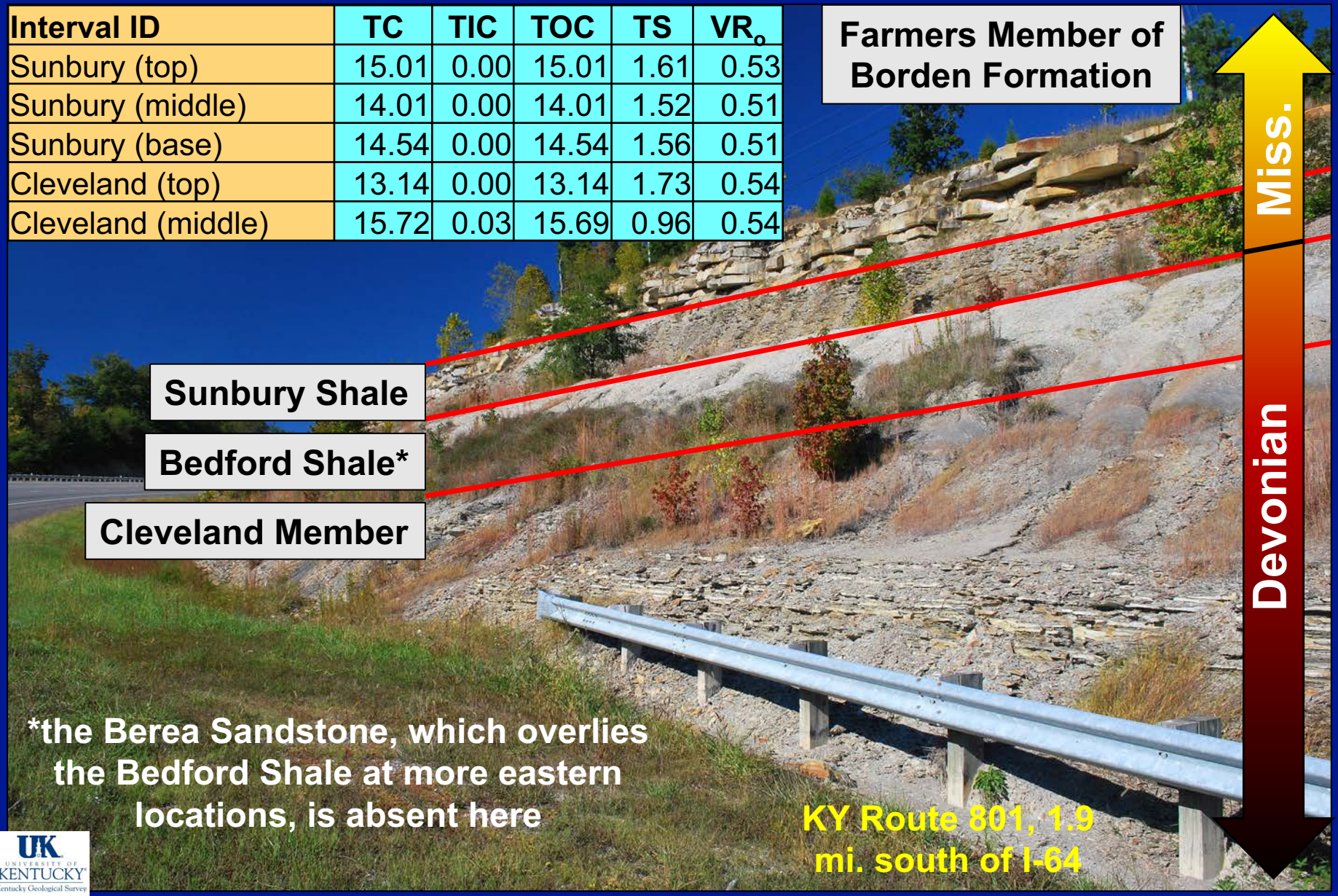
Late Devonian Ohio Shale / Early Mississippian Sunbury Shale

Interval ID	TC	TIC	TOC	TS	VR_o
Sunbury (top)	15.01	0.00	15.01	1.61	0.53
Sunbury (middle)	14.01	0.00	14.01	1.52	0.51
Sunbury (base)	14.54	0.00	14.54	1.56	0.51
Cleveland (top)	13.14	0.00	13.14	1.73	0.54
Cleveland (middle)	15.72	0.03	15.69	0.96	0.54



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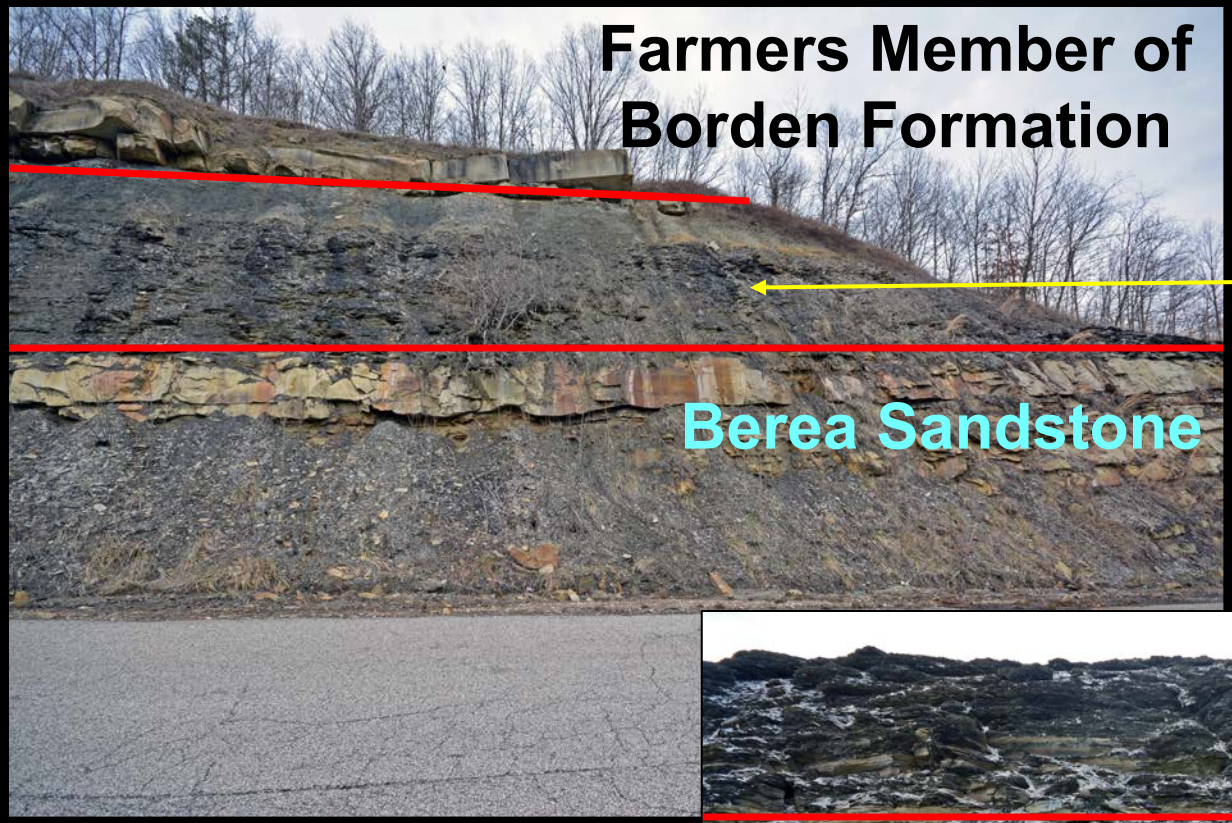
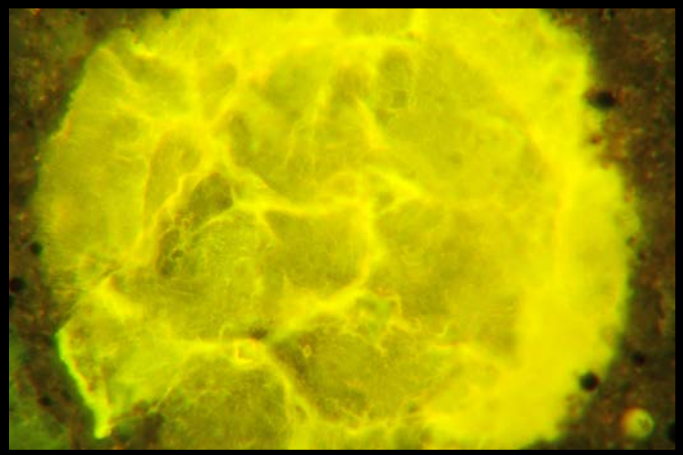


Kentucky Route 9 (AA Hwy)

Sunbury Shale

TOC = 21.4 %
TS = 1.7 %
VR_o = 0.53 %

Tasmanites



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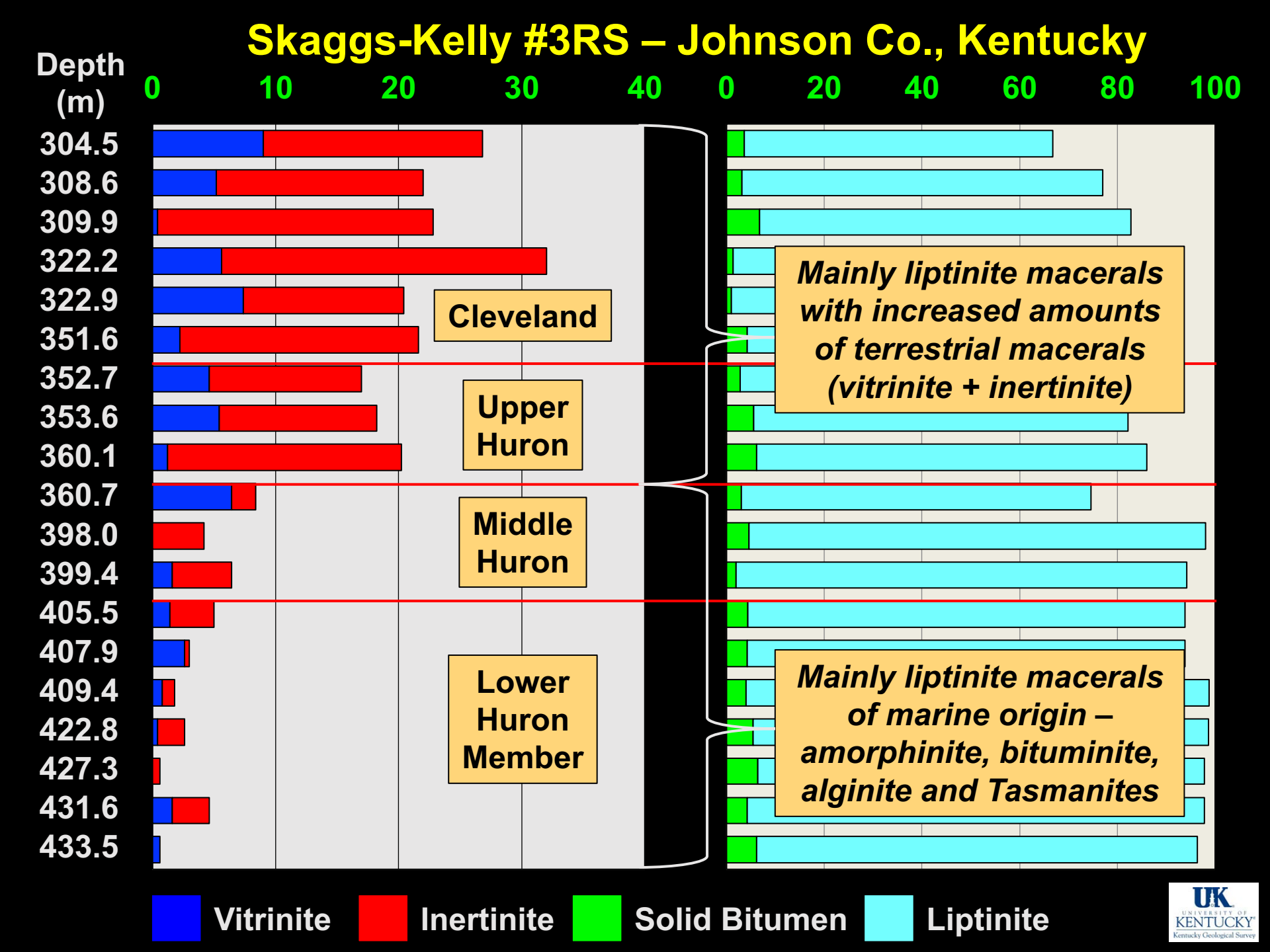
Skaggs-Kelly #3RS – Johnson Co., Kentucky
Depth (m)
0
10
20
30
40
0
20
40
60
80
100
304.5
308.6
309.9
322.2
322.9
351.6
352.7
353.6
360.1
360.7
398.0
399.4
405.5
407.9
409.4
422.8
427.3
431.6
433.5
Cleveland
Upper Huron
Middle Huron
Lower Huron Member
Mainly liptinite macerals with increased amounts of terrestrial macerals (vitrinite + inertinite)
Mainly liptinite macerals of marine origin – amorphinite, bituminite, alginite and Tasmanites
Vitrinite
Inertinite
Solid Bitumen
Liptinite
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Dispersed Organic Material

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

Terrestrial Macerals	Origin
Vitrinite	Wood and wood-like tissues of land flora
Inertinite	Oxidized tissues of land flora
Sporinite	Spores and pollen of land flora

Open Water Macerals	Origin
Alginite	Algae
Lamalginite	Laminar shape
Telalginite	Polygonal (ovoid) shape
Bituminite	Degraded algae, laminar to ovoid shape
Amorphinite	Degraded algae, amorphous morphology
Solid Bitumen	Secondary maceral, mobilized and re-solidified kerogen
Tasmanites / Leiosphaeridia	Spores of prasinophyte algae

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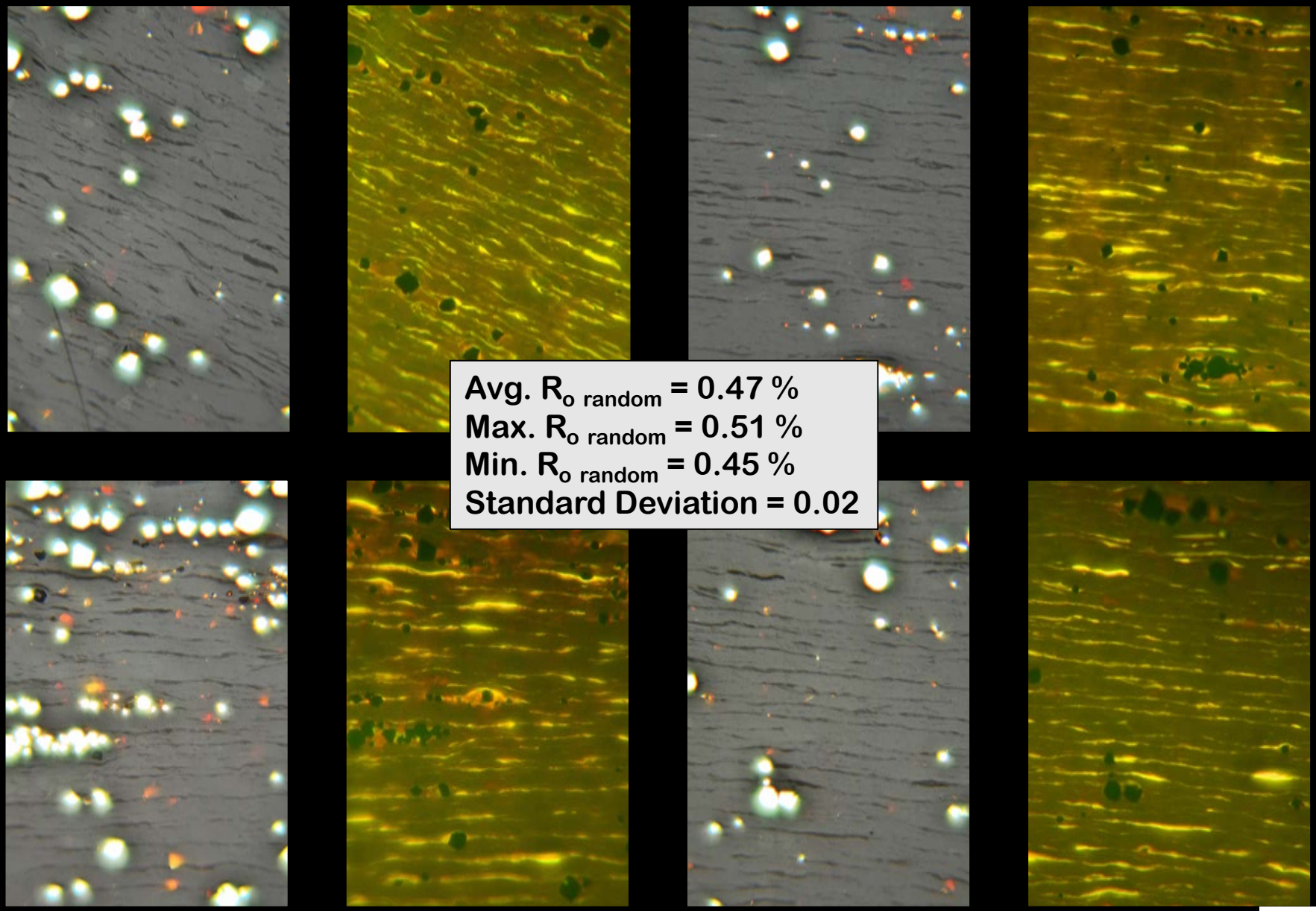
Vitrinite (from Devonian coal)

White Light

UV Light



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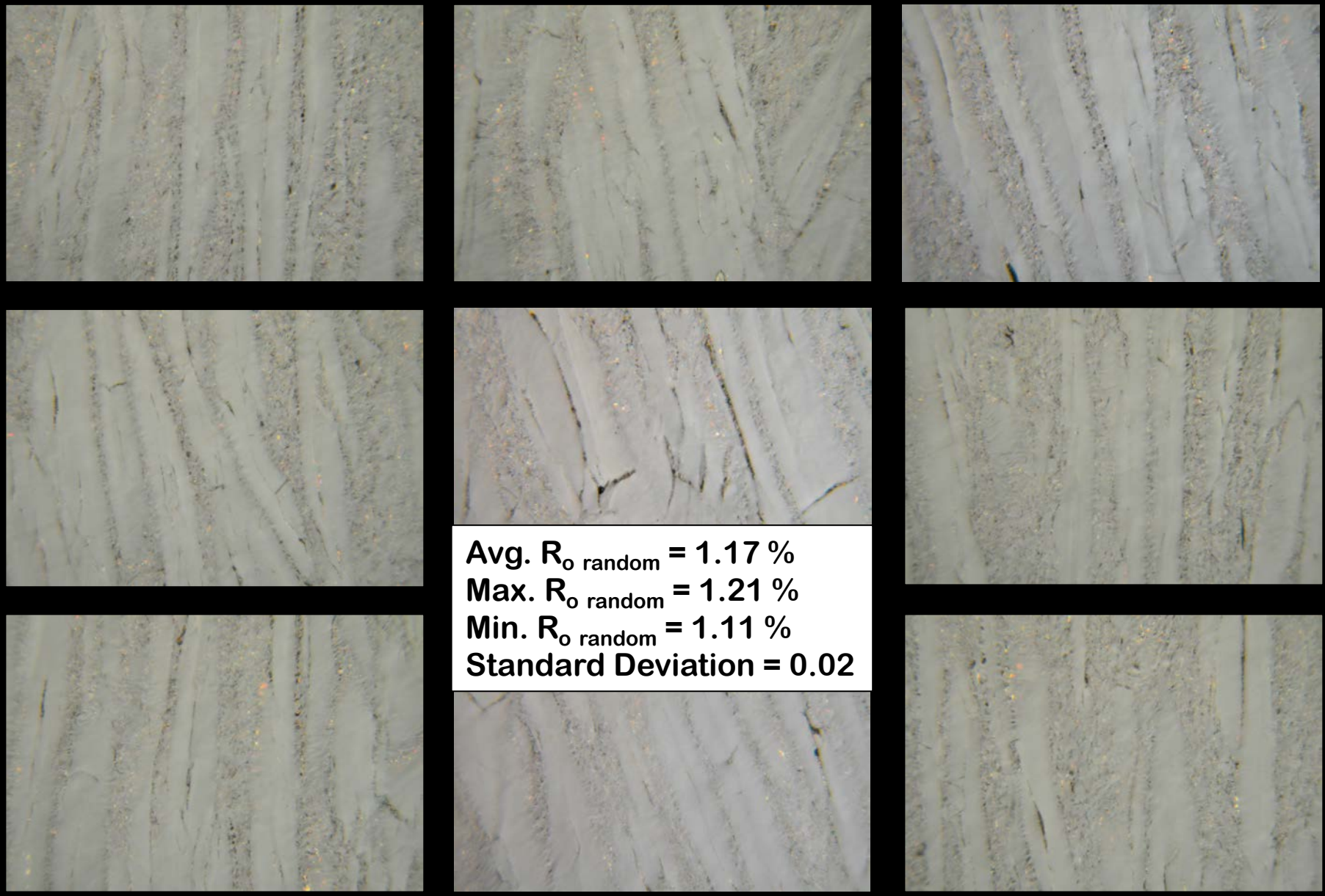
White Light

Semifusinite (from Devonian coal)

White Light



Avg. $R_{o\ random}$ = 1.17 %
Max. $R_{o\ random}$ = 1.21 %
Min. $R_{o\ random}$ = 1.11 %
Standard Deviation = 0.02

0 50 100µ

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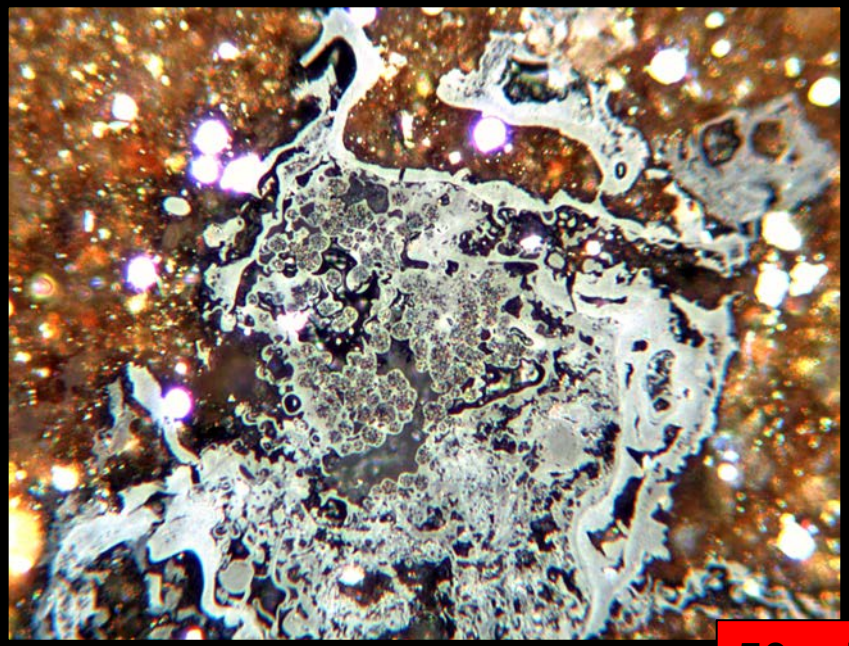
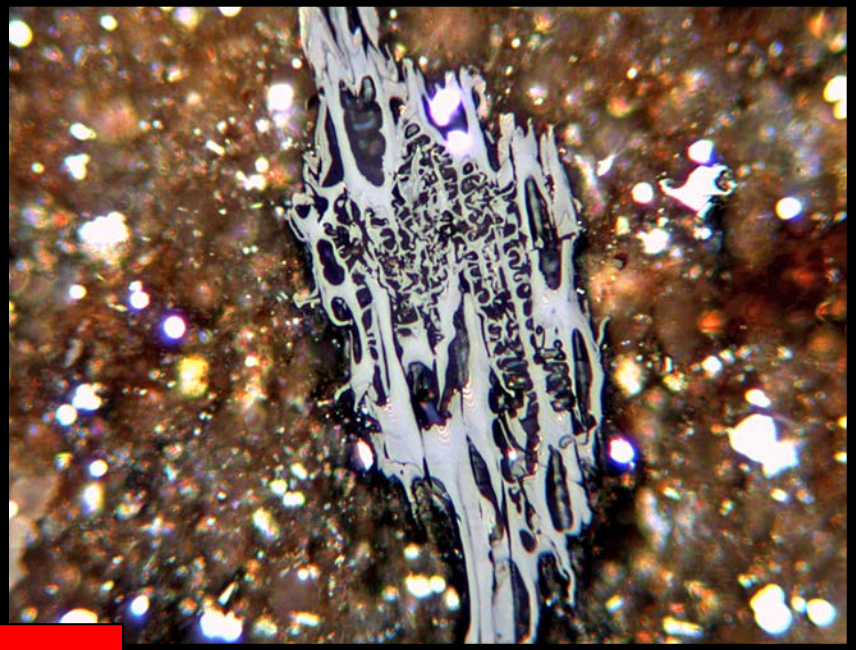
White Light

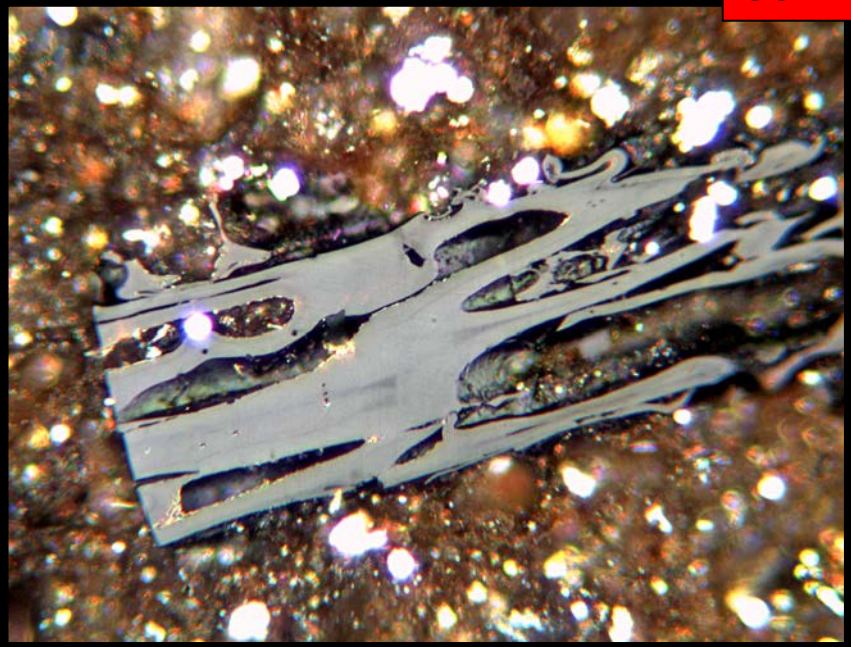
Fusinite (Inertinite)

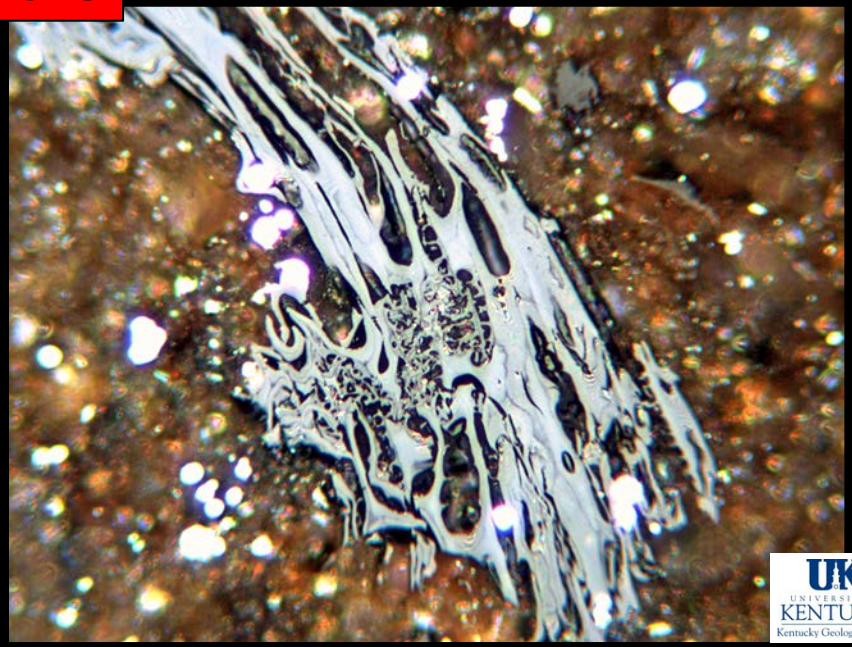
White Light





50 microns





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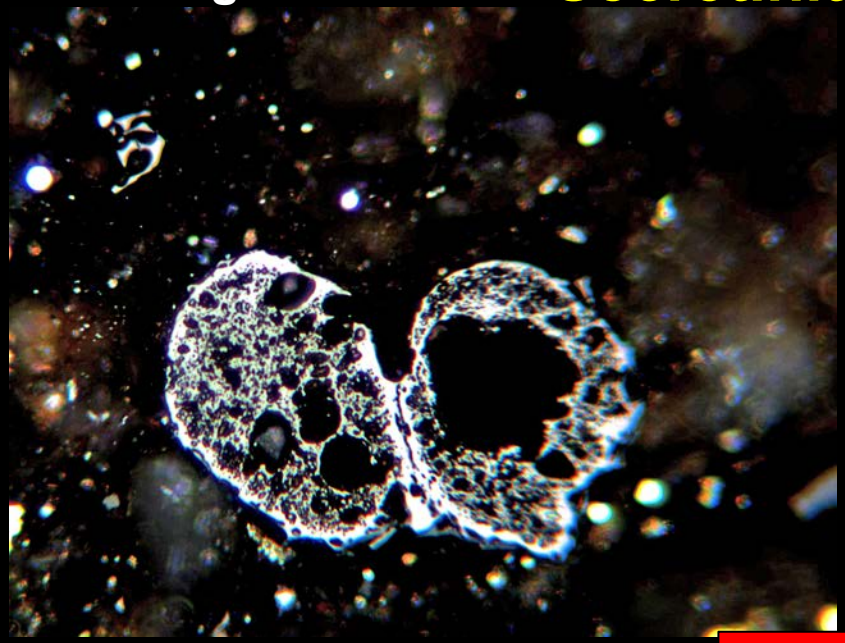
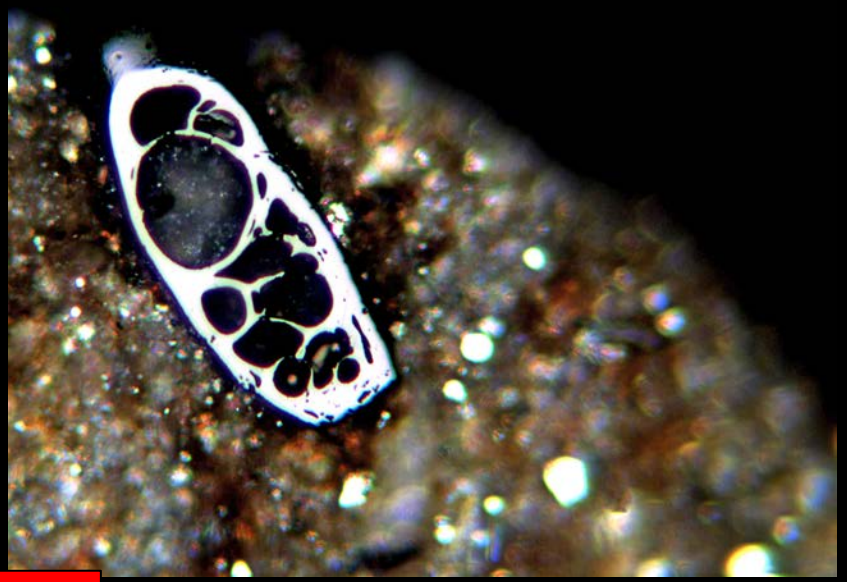
White Light

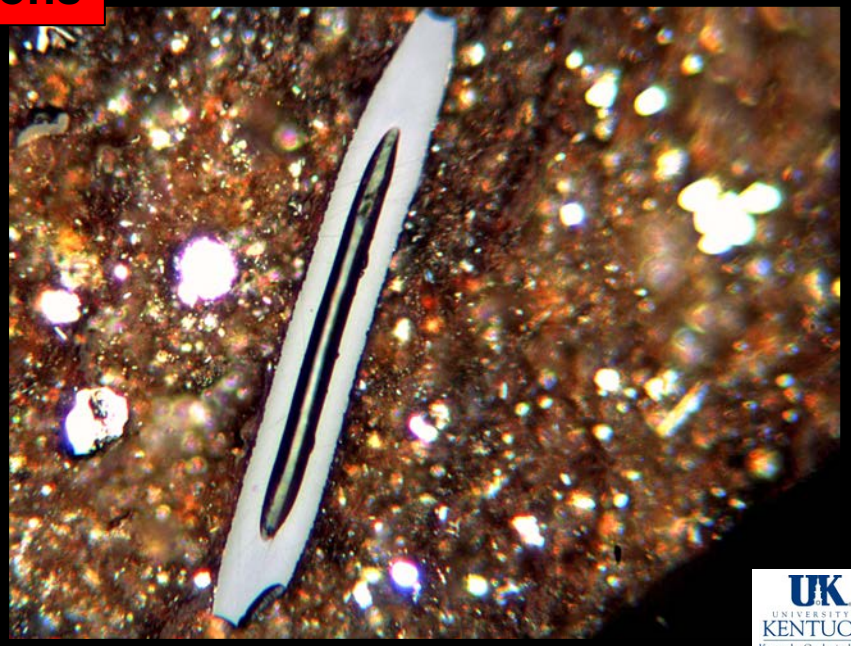
Secretinite (Inertinite)

White Light





50 microns



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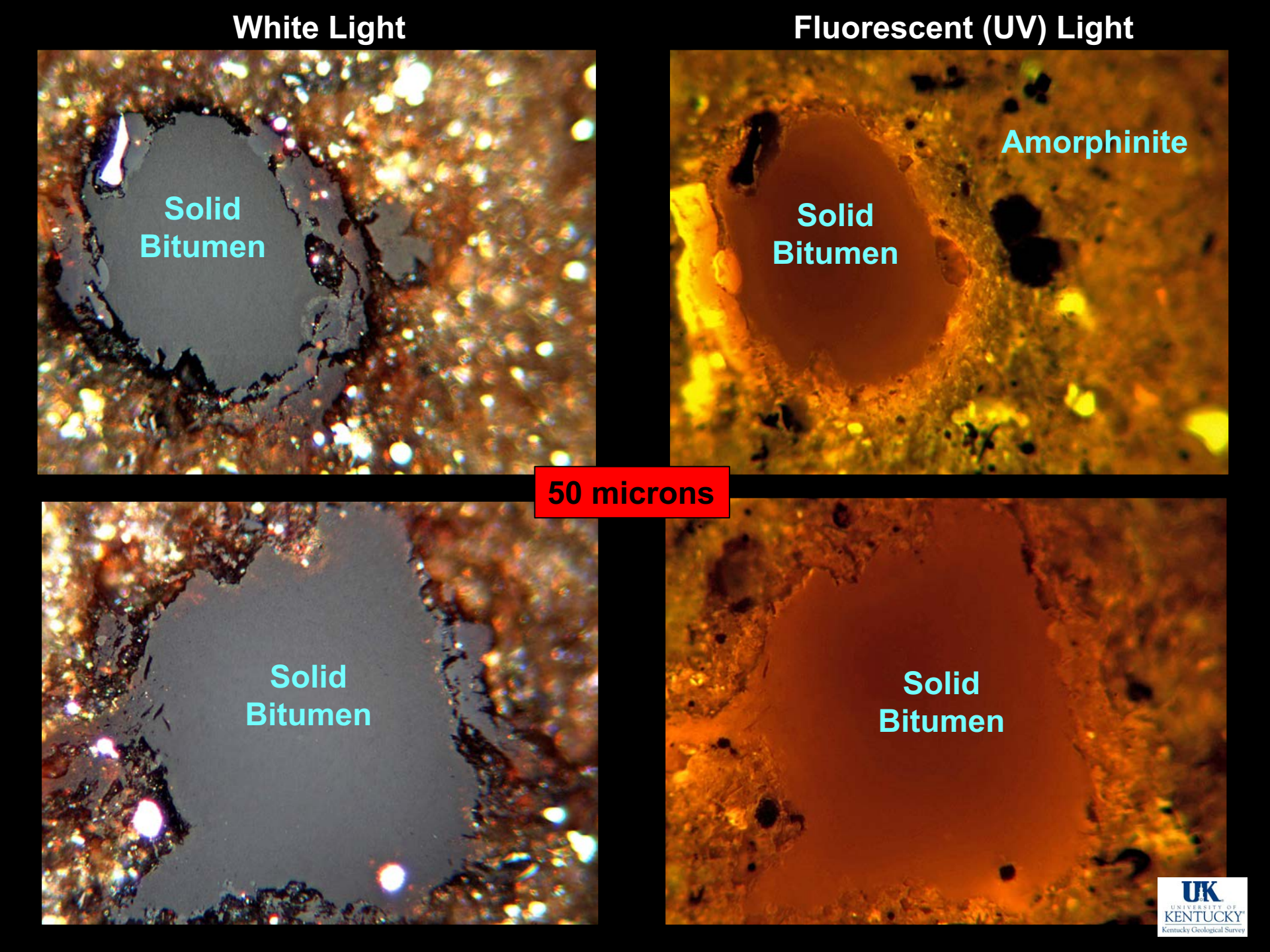
White Light
Fluorescent (UV) Light
Solid Bitumen
Amorphinite
Solid Bitumen
50 microns
Solid Bitumen
Solid Bitumen
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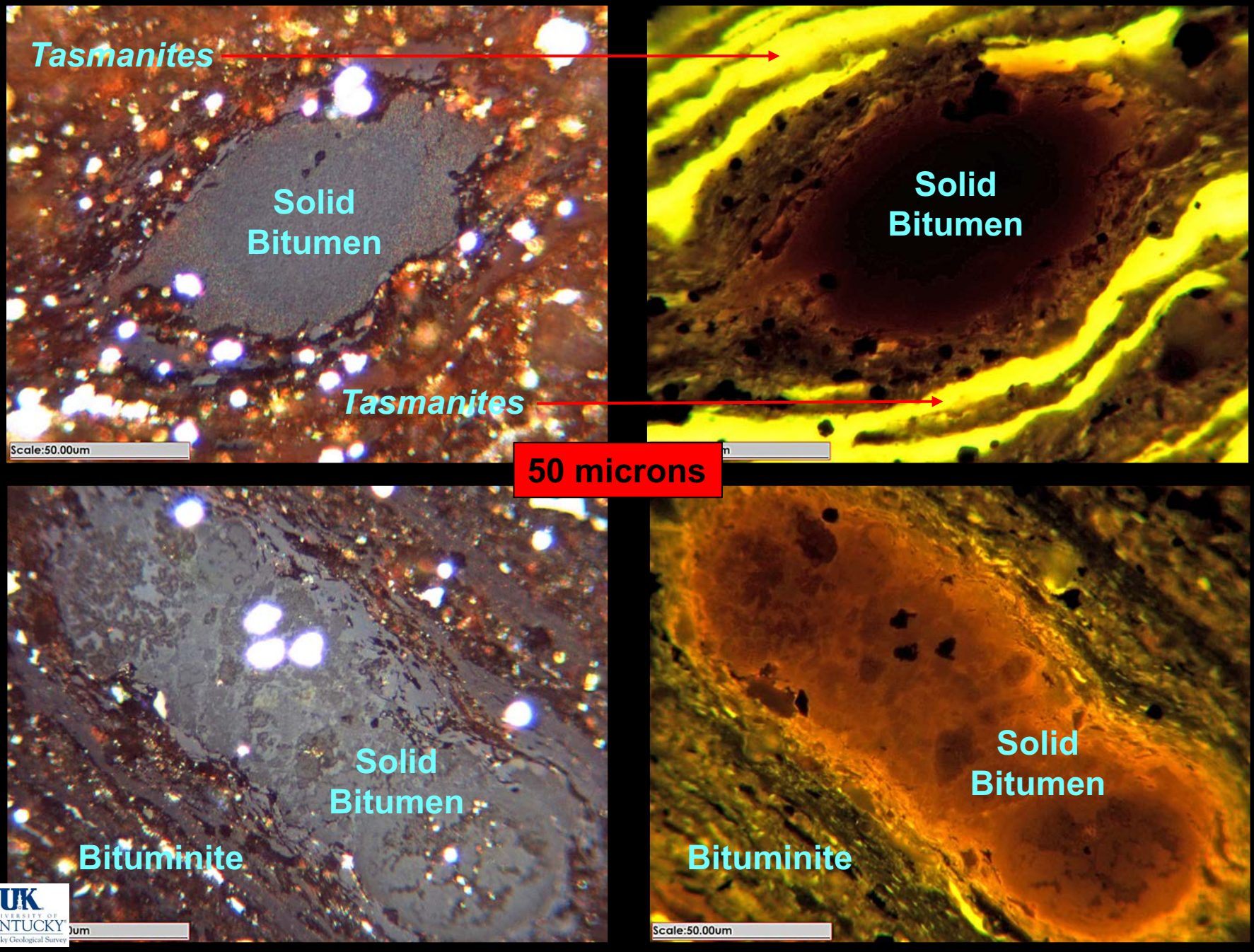
Solid Bitumen

White Light

Fluorescent (UV) Light



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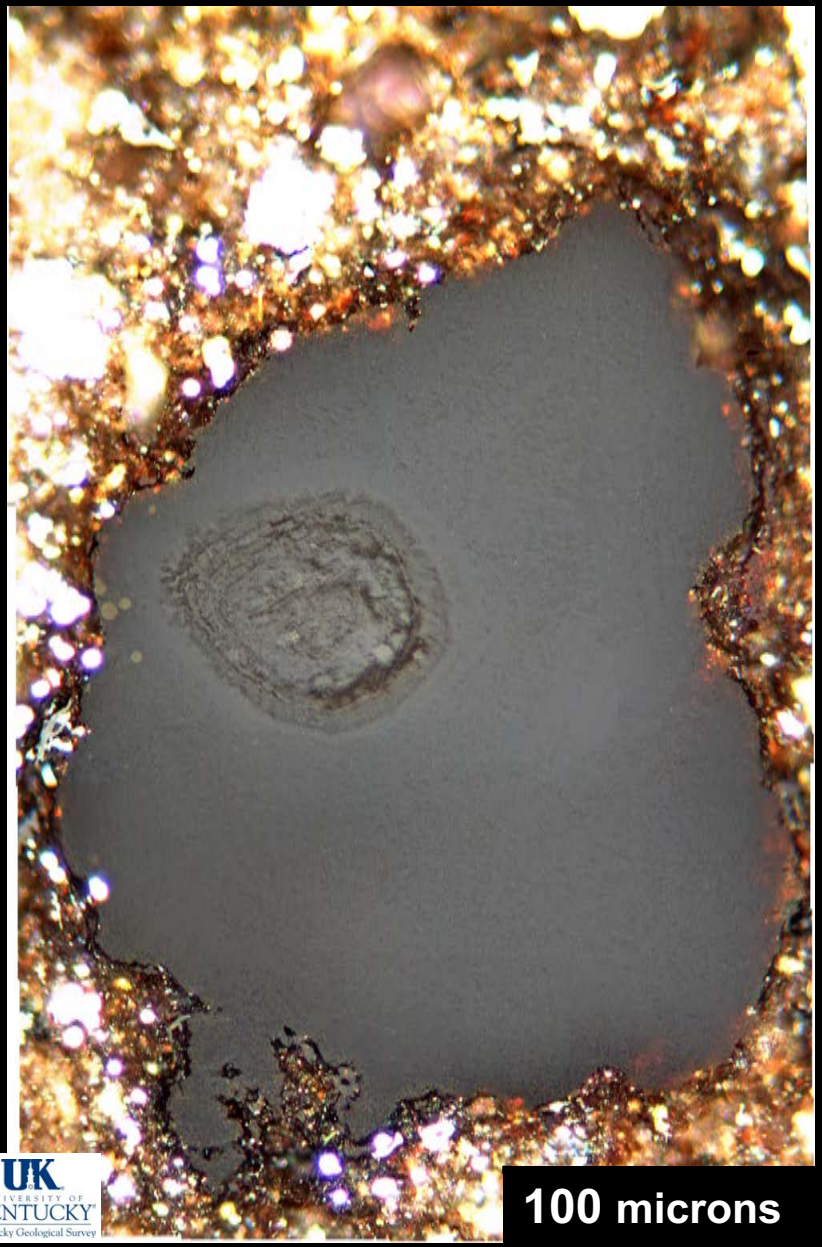
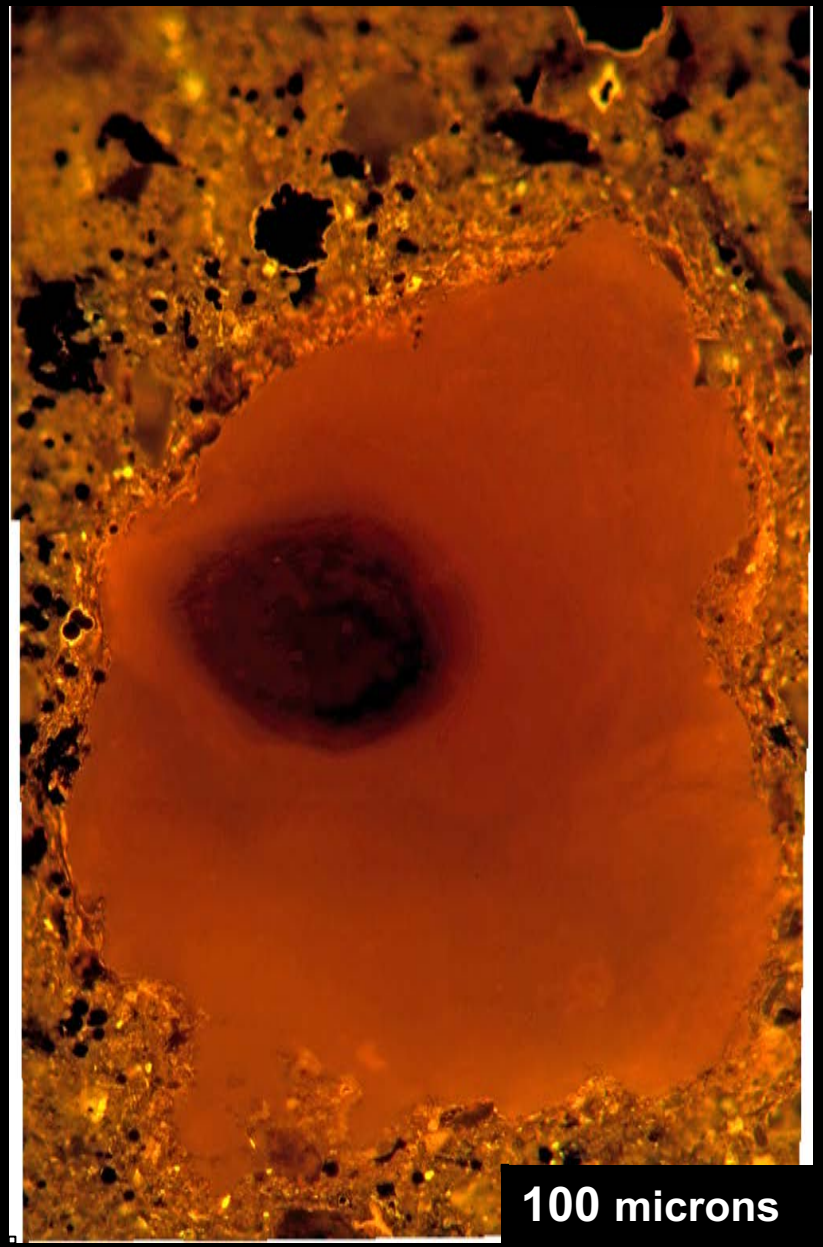
“Godzillinite” (unusually large pieces of solid bitumen)

White Light



100 microns

Fluorescent (UV) Light



100 microns

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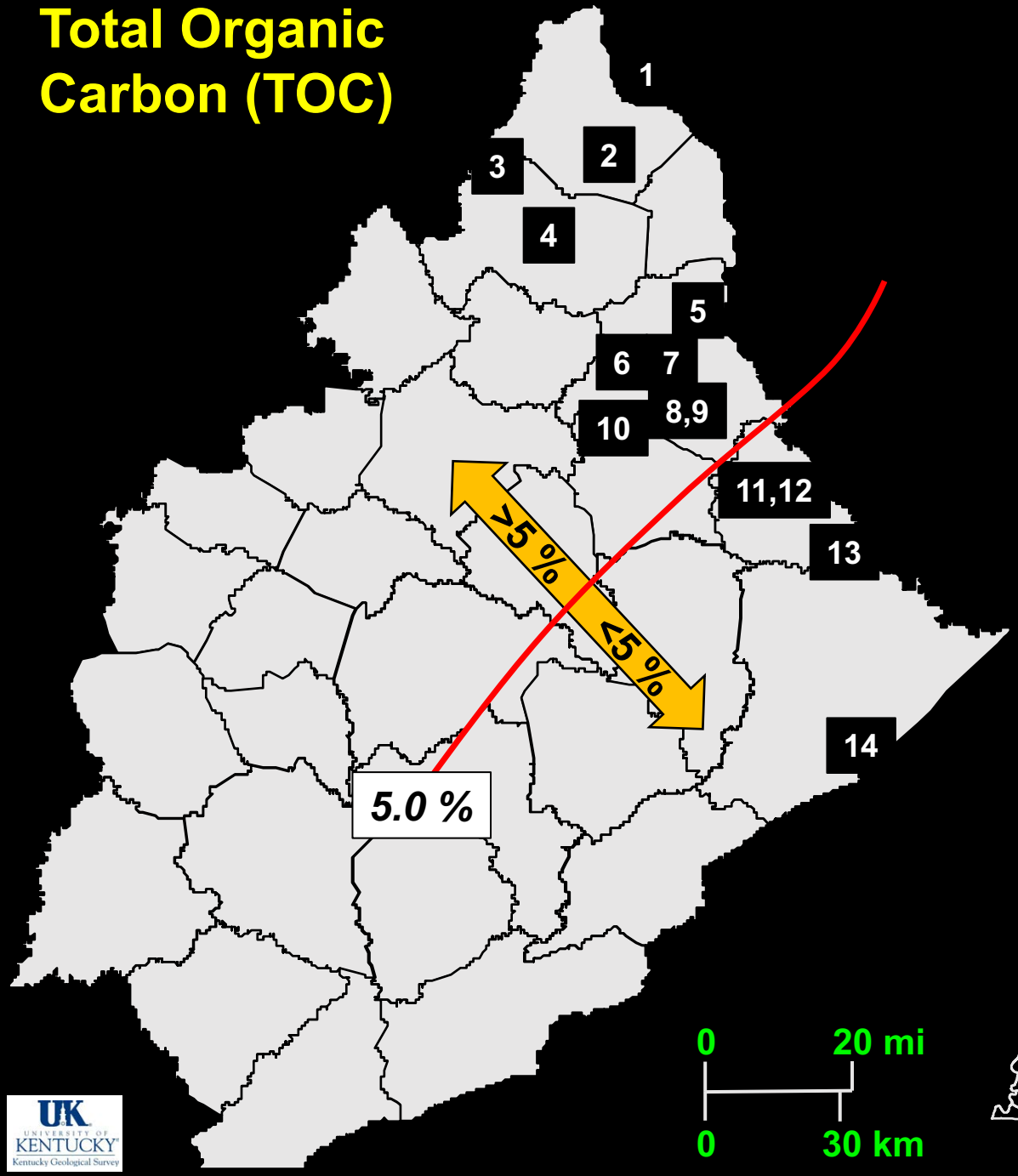
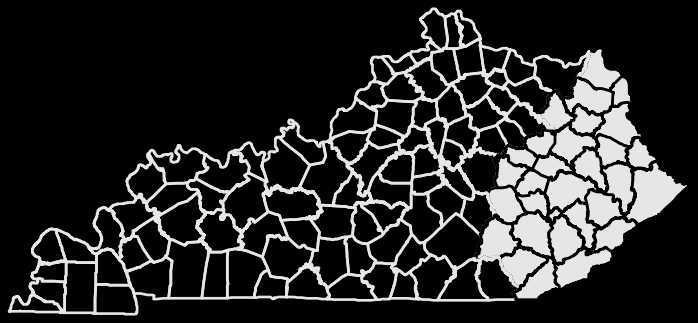
Total Organic Carbon (TOC)



	Well Name	Avg. 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 %



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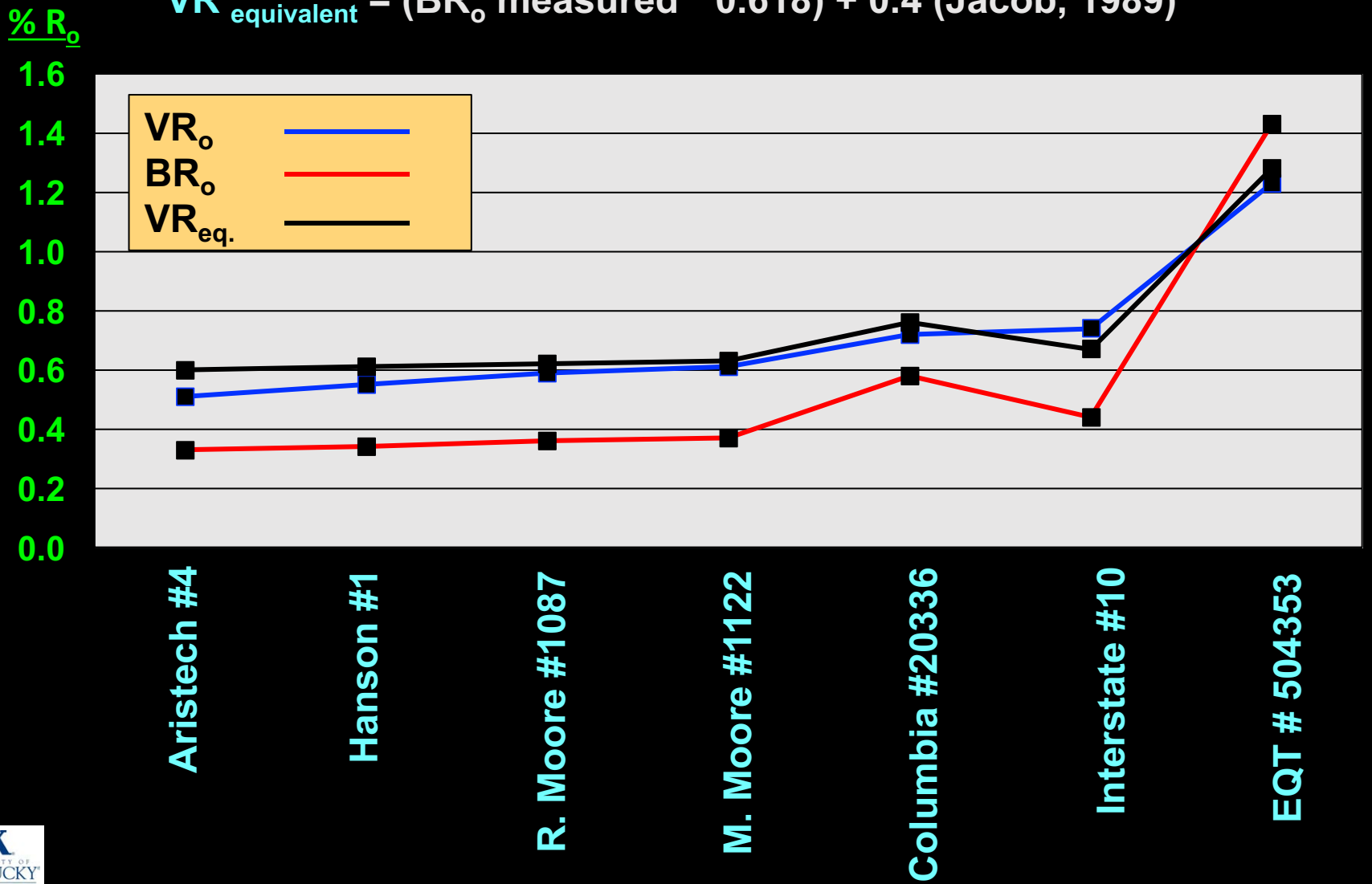
Thermomaturation – Organic Petrology

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)



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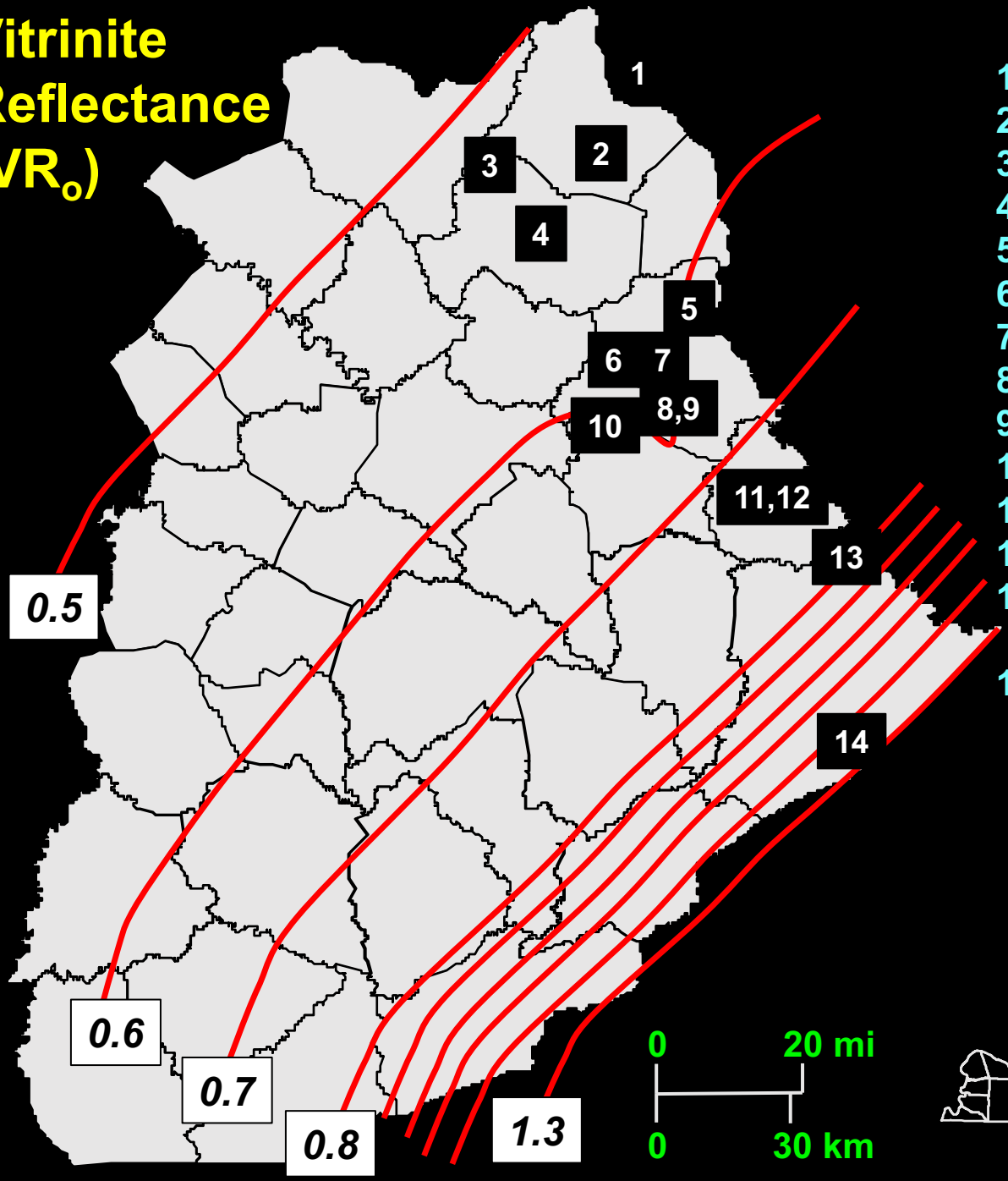
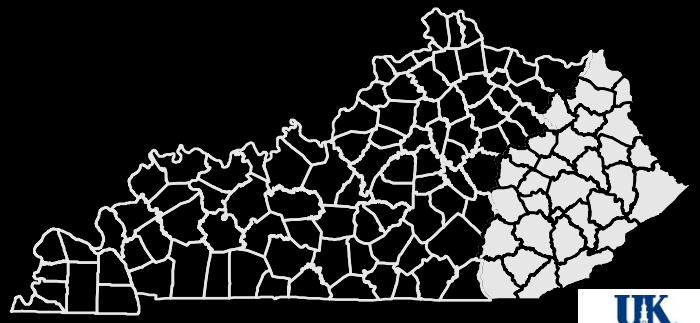
Vitrinite Reflectance (VR_o)



	Well Name	Avg. VR_o
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 %

*$VR_{calculated}$ from T_{max}



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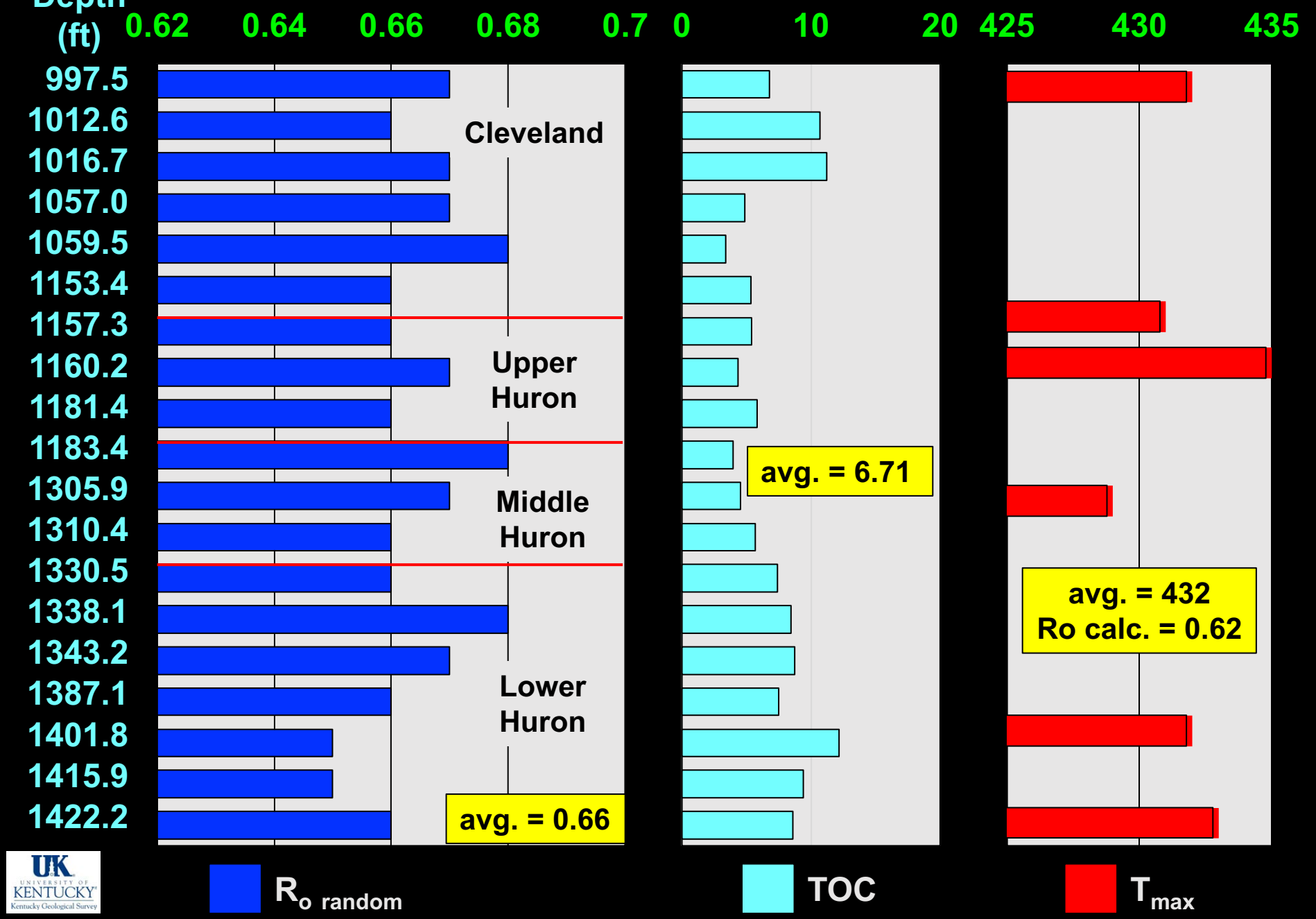
Skaggs-Kelly #3RS – Johnson Co., Kentucky



Thermomaturation – Rock Eval

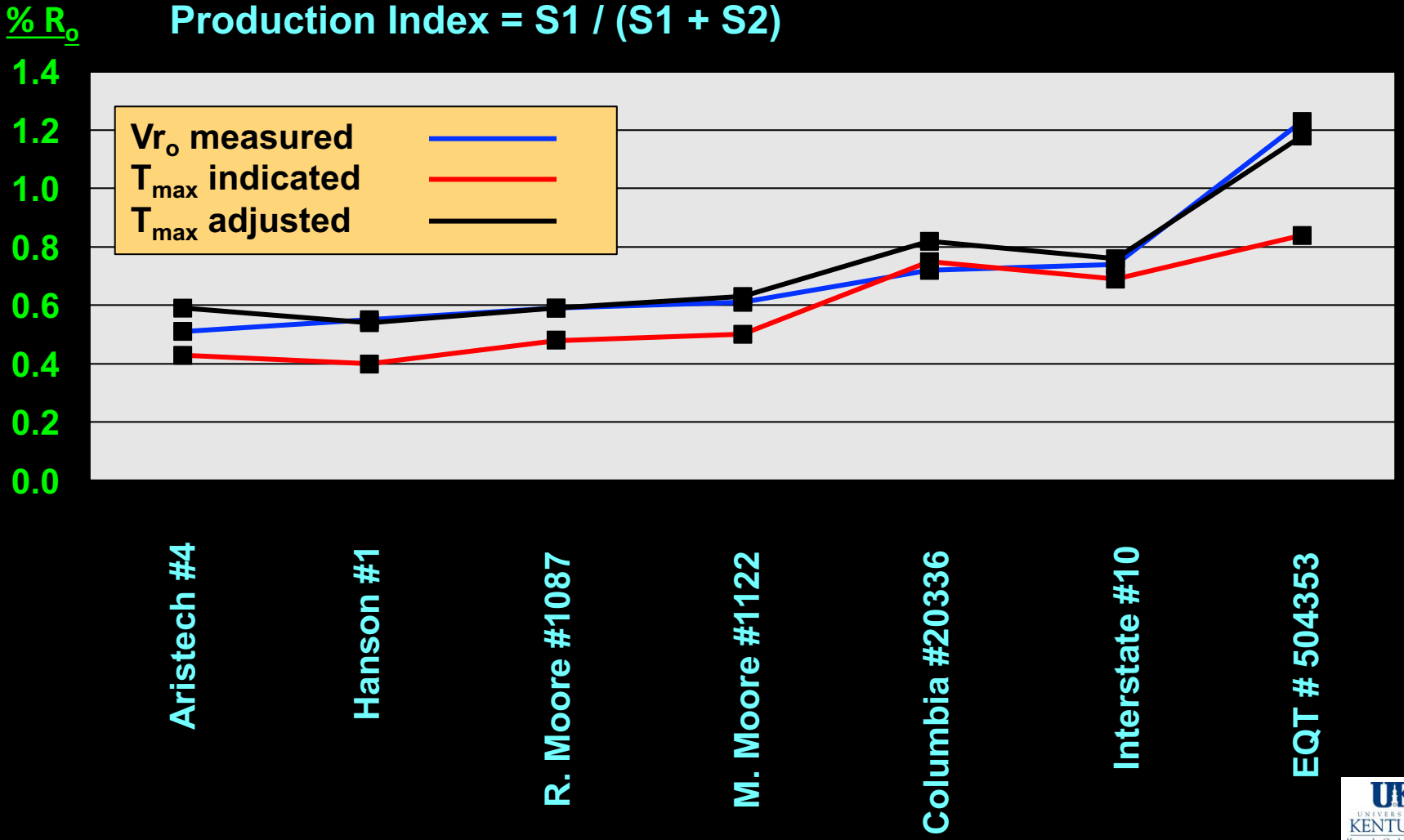
T_{max} (^{0}C) = S2 peak

$VR_{calculated}$ = (T_{max} * 0.018) – 7.16 [Jarvie et al., 2002]

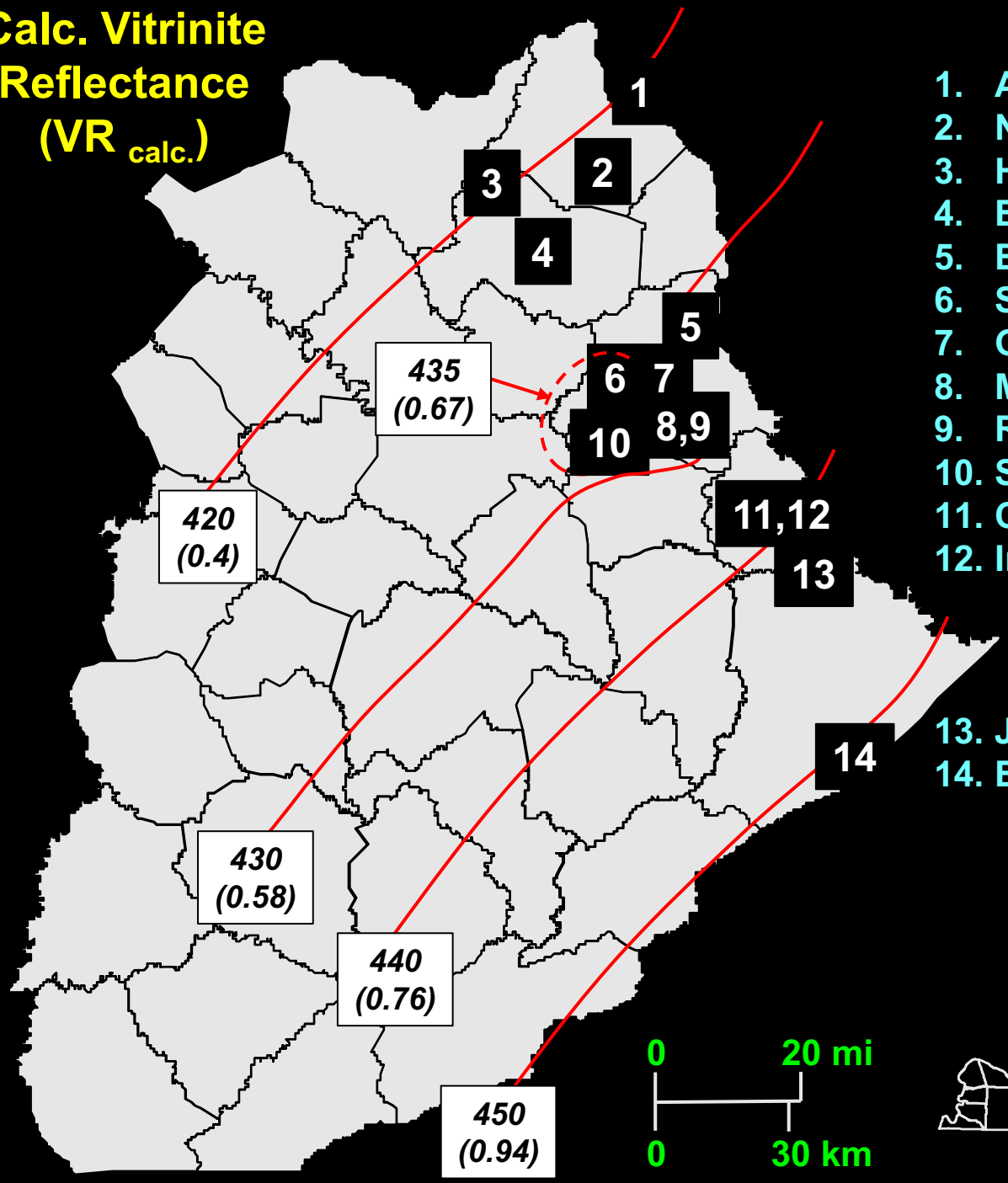
HI = (S2 / TOC) * 100

Adjusted T_{max} = T_{max} + ((HI – 150) / 50) [Snowdon, 1995]

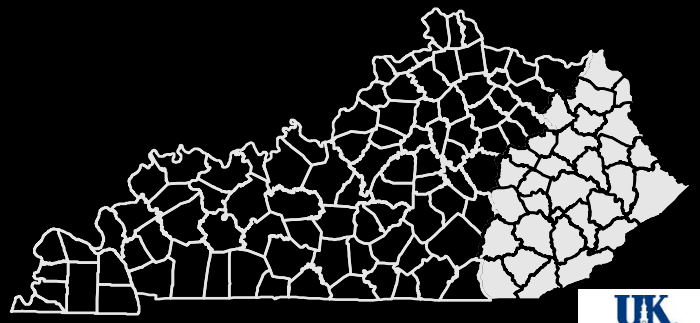
Production Index = S1 / (S1 + S2)



Calc. Vitrinite Reflectance ($VR_{calc.}$)



	Well Name	Avg. T_{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



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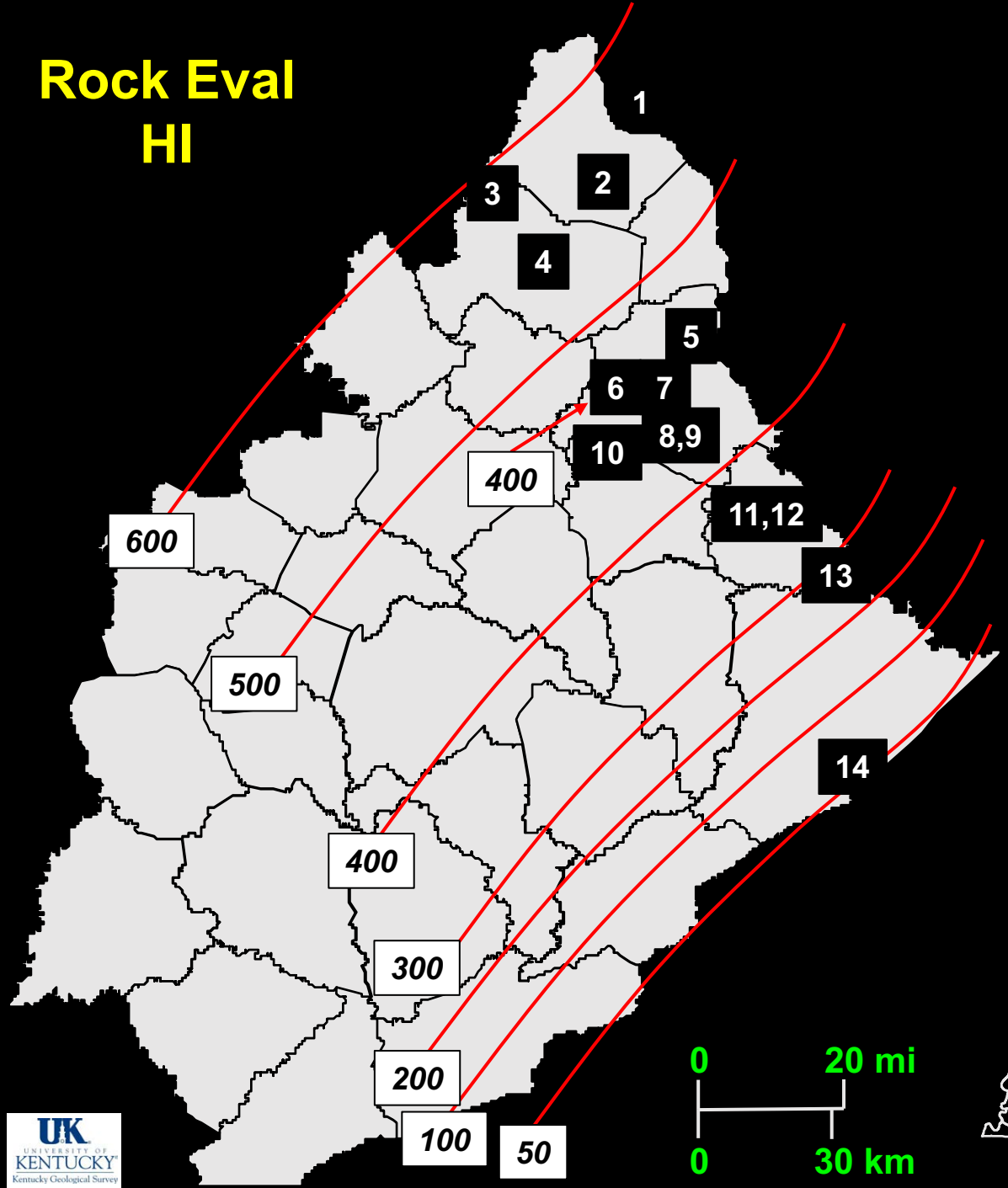
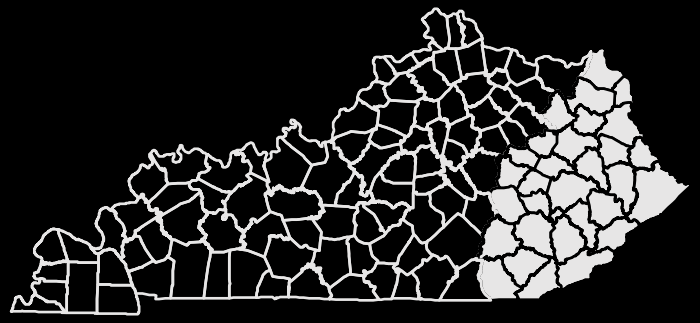
Rock Eval HI



Well Name	Avg. HI
1. Aristech #4	585.1
2. Newman #1	no data
3. Hanson #1	531.0
4. EKY Lumber #1	no data
5. B. Cassady #50	443.9
6. S. Young #1	365.8
7. G. Roberts #1420	394.8
8. M. Moore #1122	475.3
9. R. Moore #1087	504.4
10. Skaggs-Kelly #3RS	558.8
11. Columbia #20336	358.1
12. Interstate #10	340.6
13. J.B. Goff Land #1	no data
14. EQT 504353	41.8



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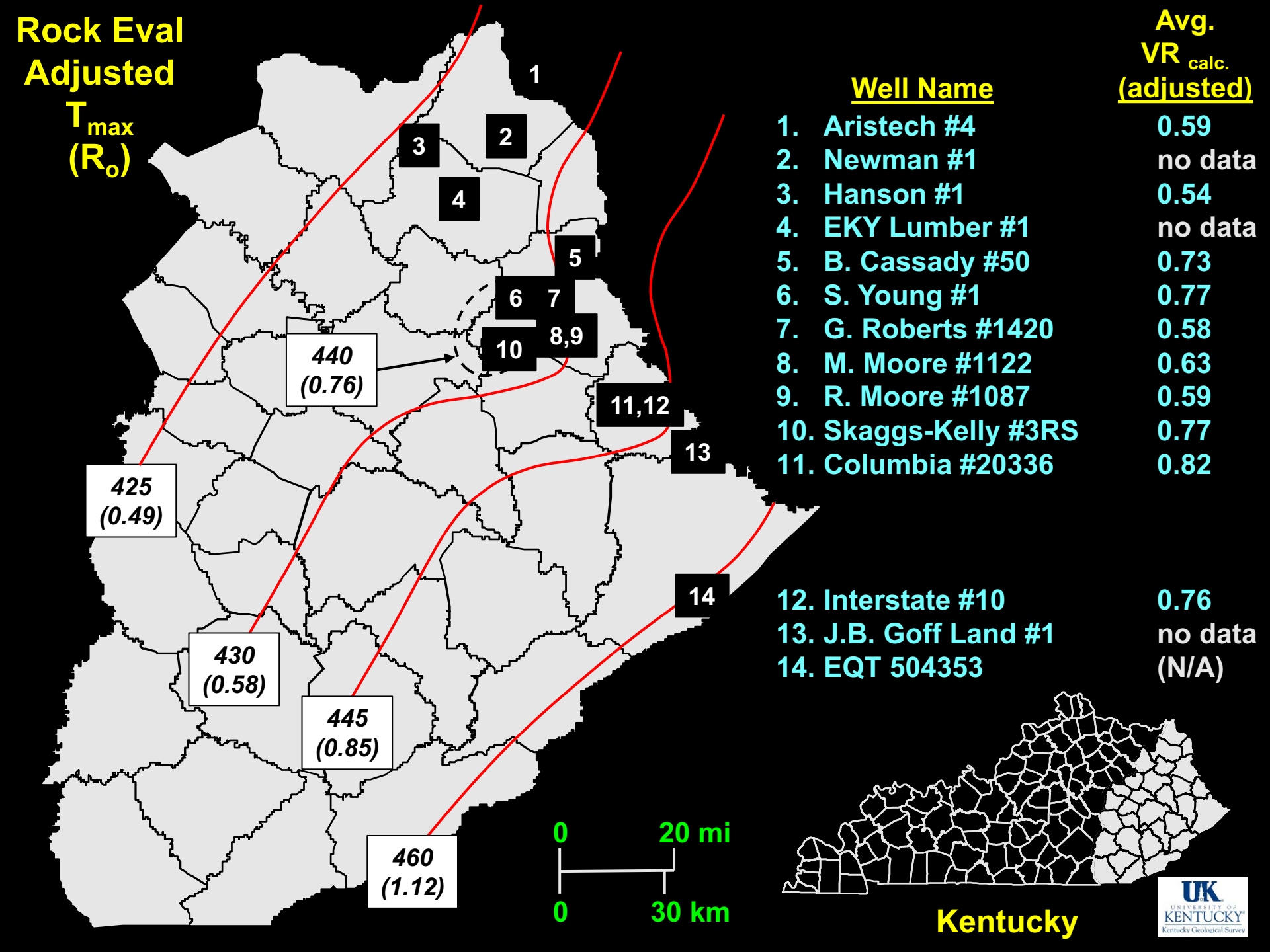
Rock Eval
Adjusted
T_{max}
(R_o)
1
2
3
4
5
6
7
8,9
10
11,12
13
14
440
(0.76)
425
(0.49)
430
(0.58)
445
(0.85)
460
(1.12)
0
20 mi
0
30 km
Well Name
Avg.
VR calc.
(adjusted)
1. Aristech #4 0.59
2. Newman #1 no data
3. Hanson #1 0.54
4. EKY Lumber #1 no data
5. B. Cassady #50 0.73
6. S. Young #1 0.77
7. G. Roberts #1420 0.58
8. M. Moore #1122 0.63
9. R. Moore #1087 0.59
10. Skaggs-Kelly #3RS 0.77
11. Columbia #20336 0.82
12. Interstate #10 0.76
13. J.B. Goff Land #1 no data
14. EQT 504353 (N/A)
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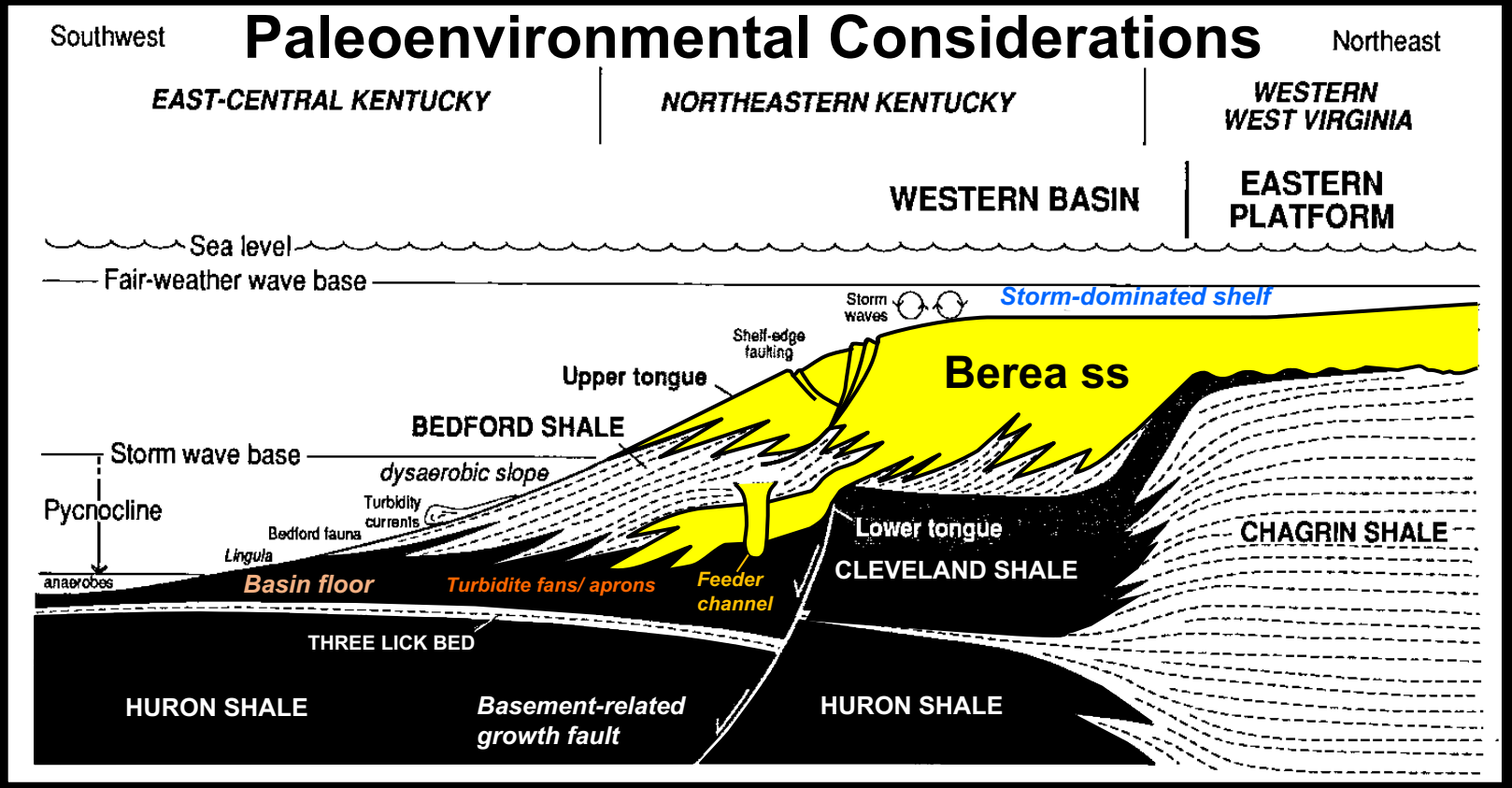
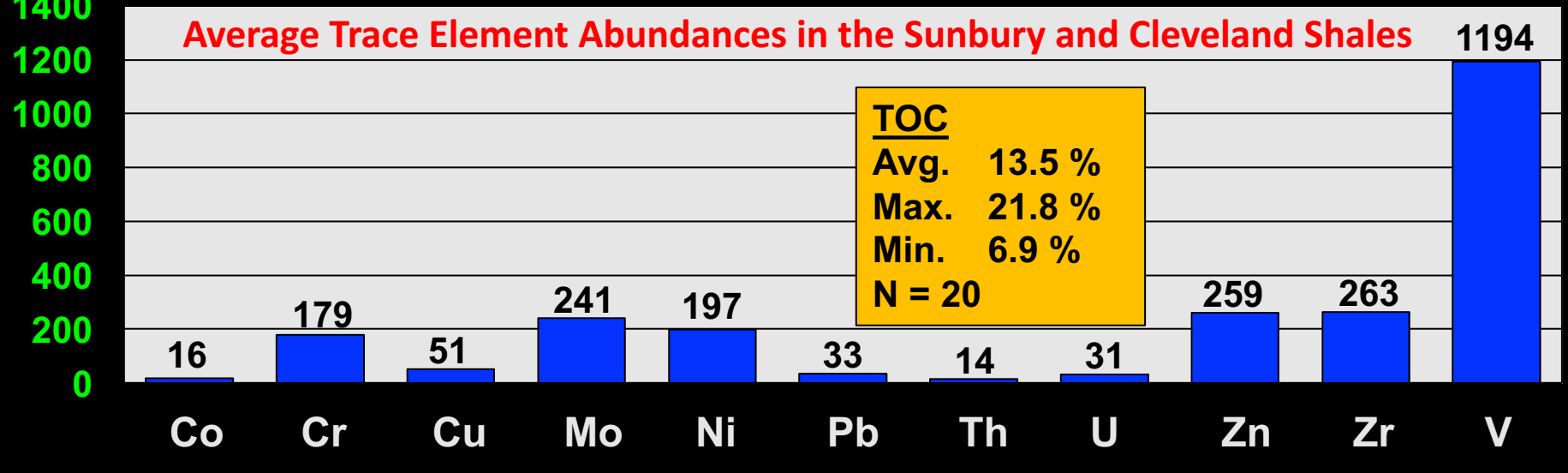
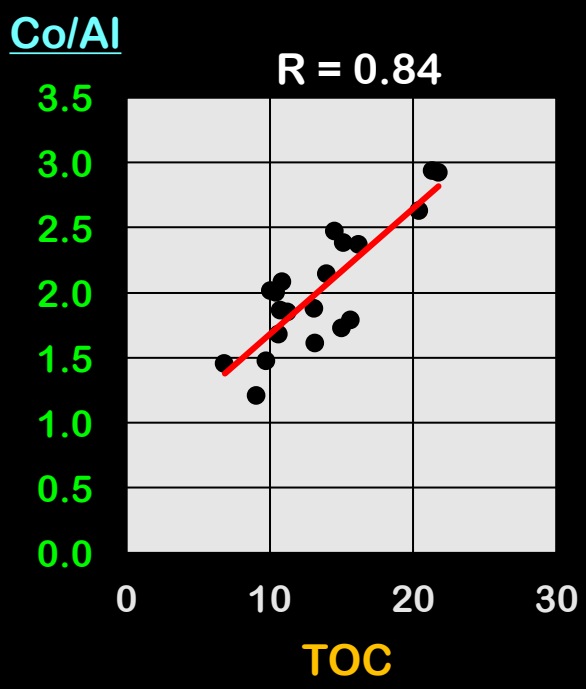
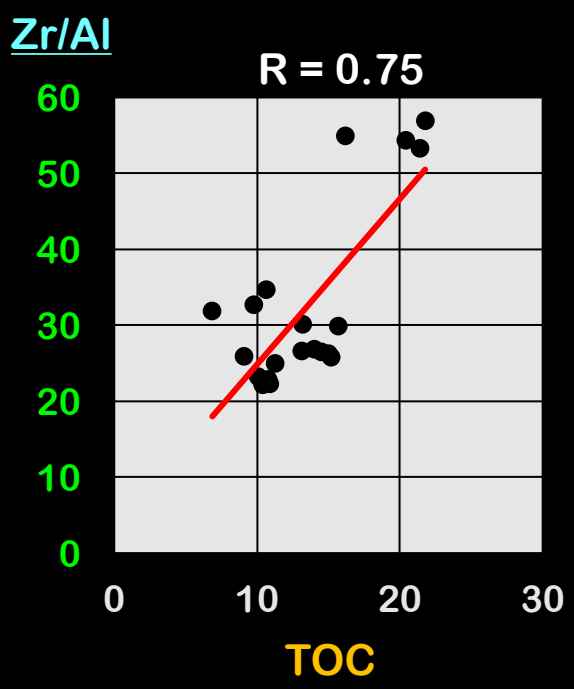
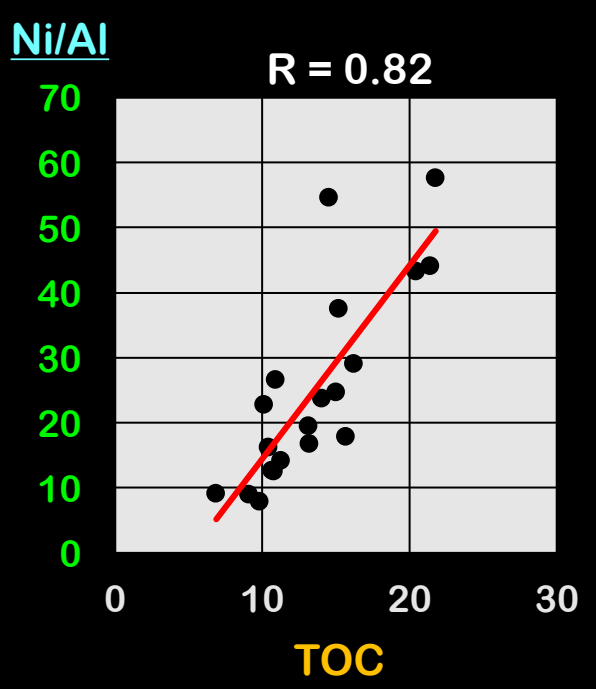
Paleoenvironmental Considerations

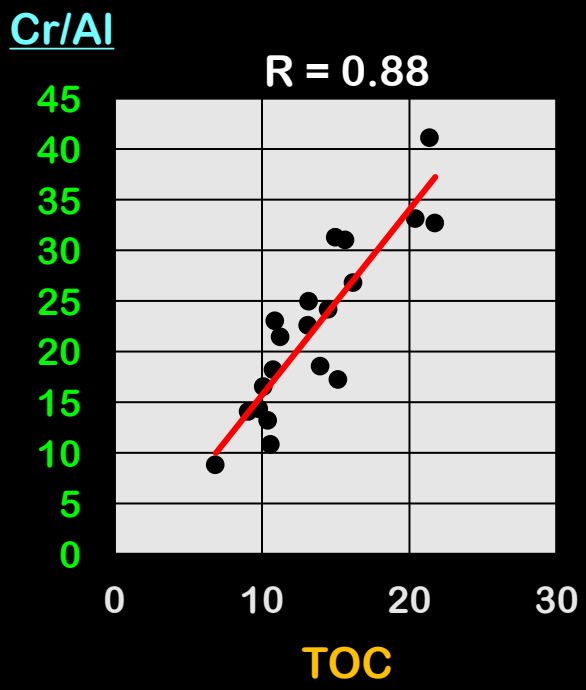


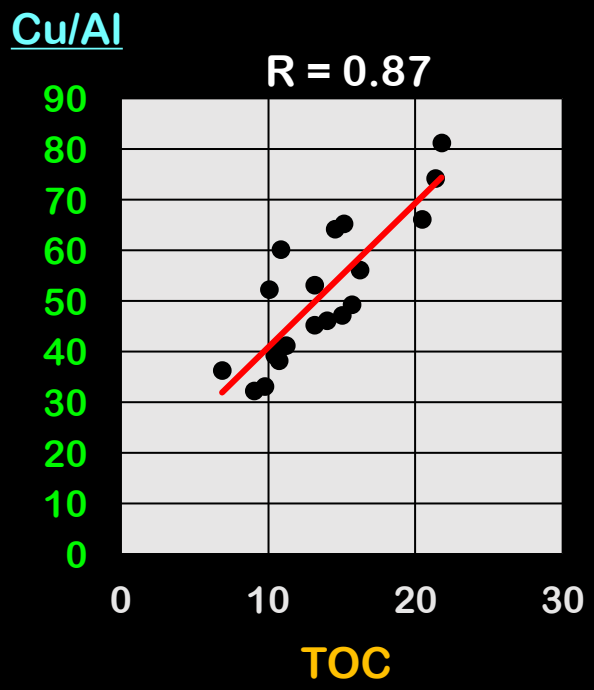


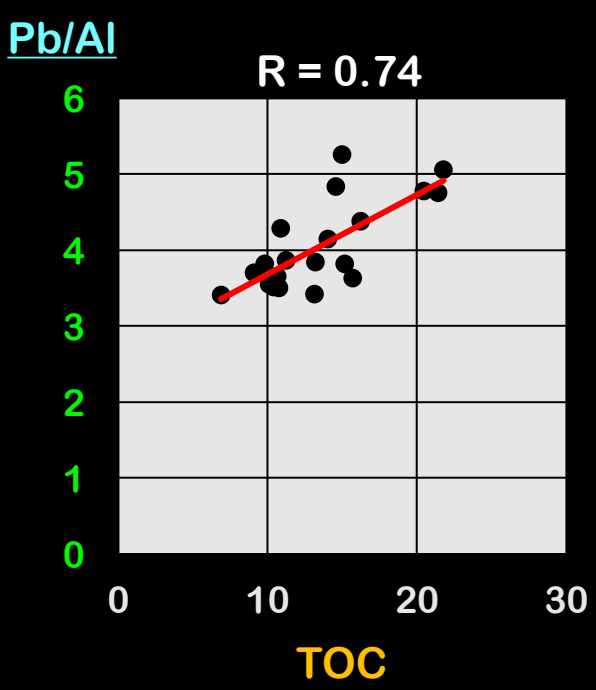

Co/Al
R = 0.84
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
TOC

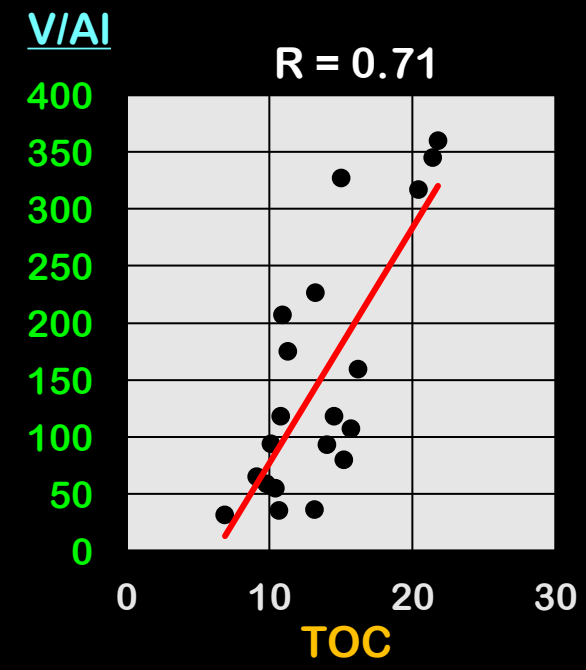

Zr/Al
R = 0.75
60
50
40
30
20
10
0
0
10
20
30
TOC

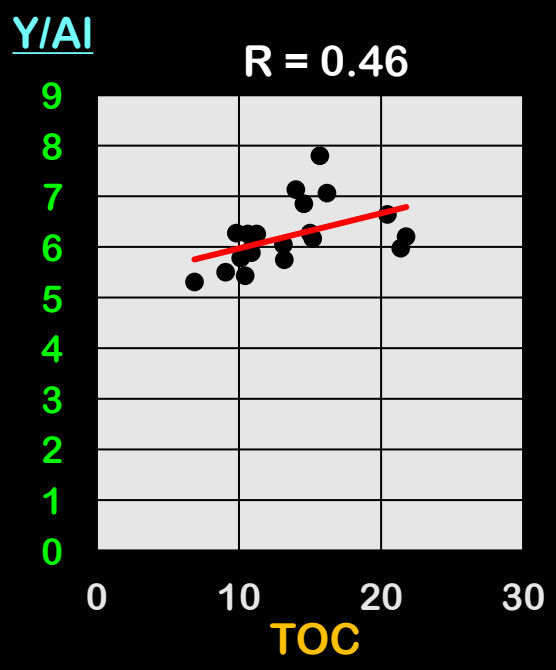

Ni/Al
R = 0.82
70
60
50
40
30
20
10
0
0
10
20
30
TOC

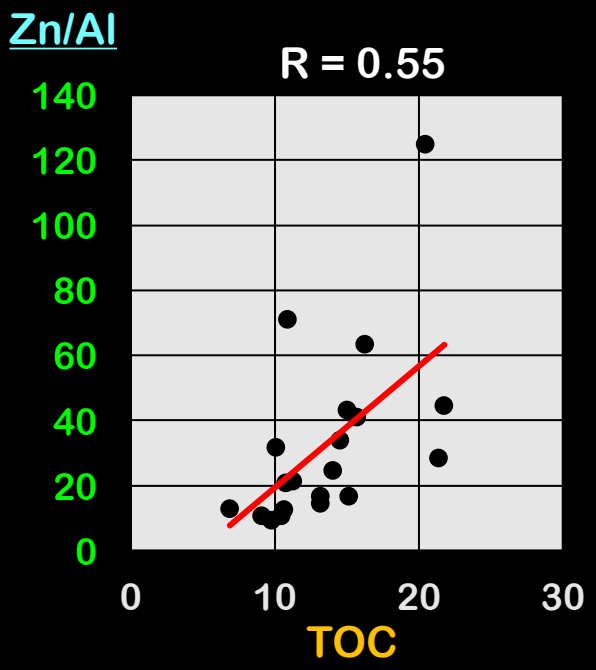

Cr/Al
R = 0.88
45
40
35
30
25
20
15
10
5
0
0
10
20
30
TOC

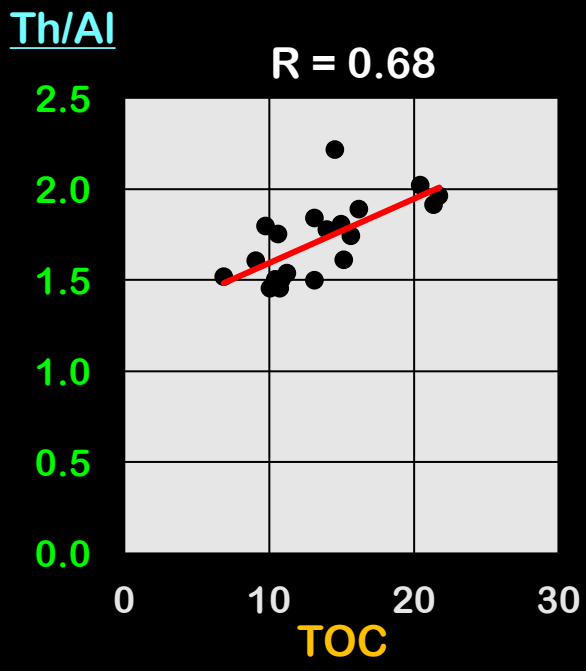

Cu/Al
R = 0.87
90
80
70
60
50
40
30
20
10
0
0
10
20
30
TOC

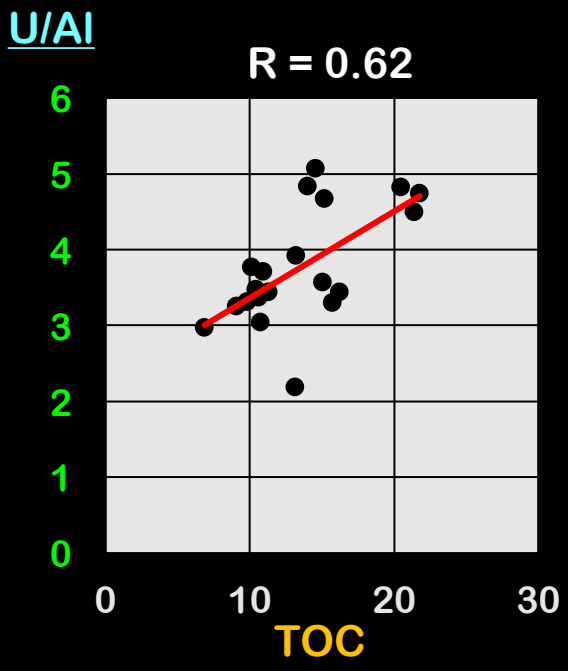

Pb/Al
R = 0.74
6
5
4
3
2
1
0
0
10
20
30
TOC

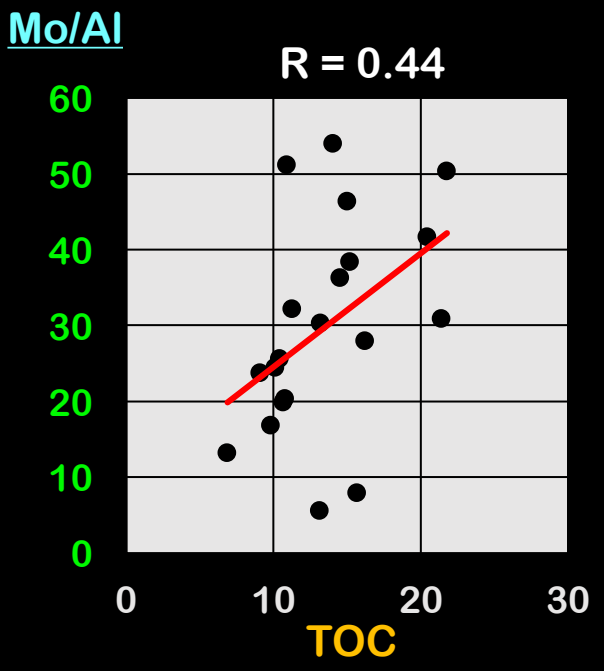

V/Al
R = 0.71
400
350
300
250
200
150
100
50
0
0
10
20
30
TOC

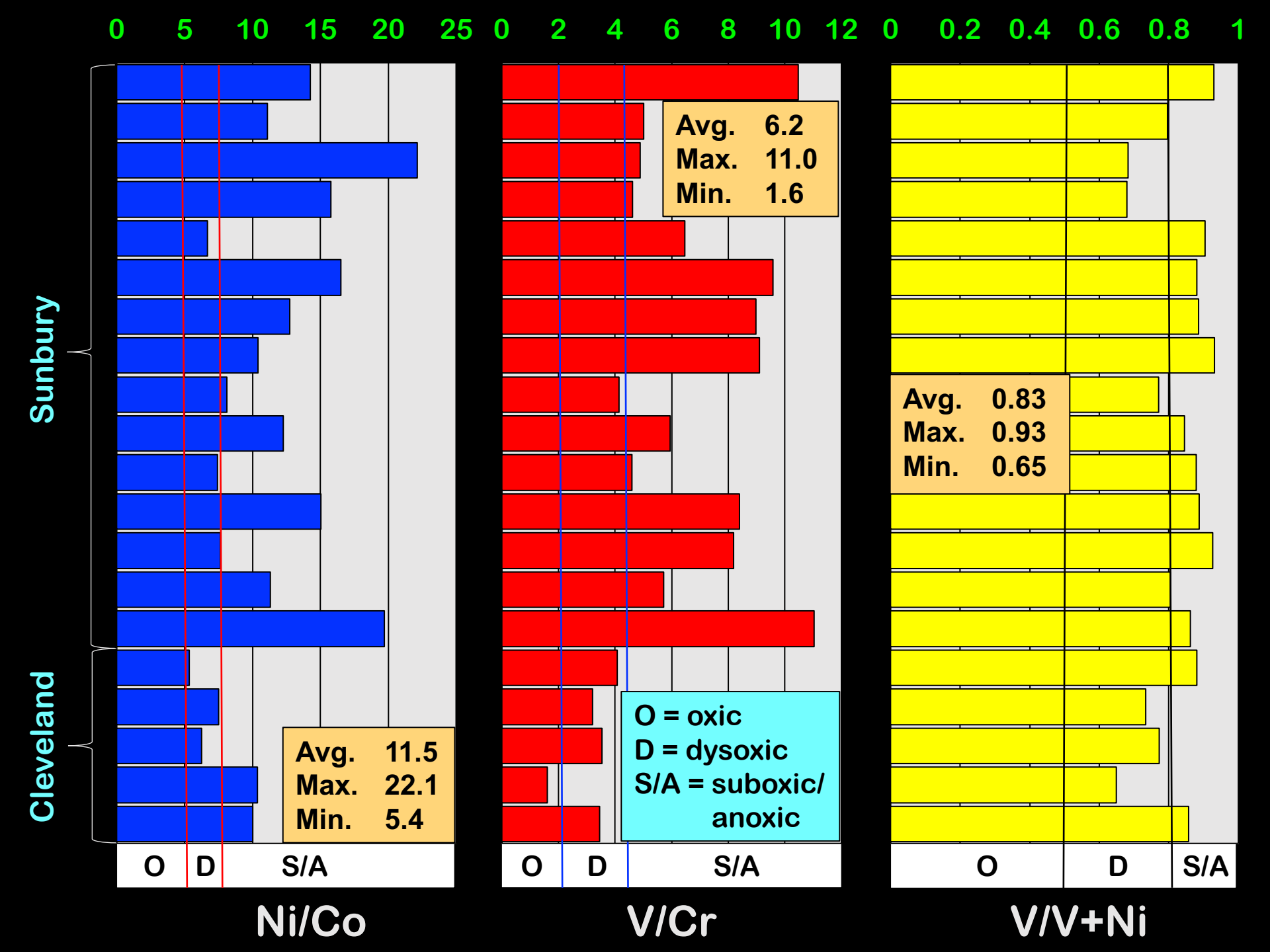

Y/Al
R = 0.46
9
8
7
6
5
4
3
2
1
0
0
10
20
30
TOC


Zn/Al
R = 0.55
140
120
100
80
60
40
20
0
0
10
20
30
TOC


Th/Al
R = 0.68
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
TOC


U/Al
R = 0.62
6
5
4
3
2
1
0
0
10
20
30
TOC


Mo/Al
R = 0.44
60
50
40
30
20
10
0
0
10
20
30
TOC


0 5 10 15 20 25
0 2 4 6 8 10 12
0 0.2 0.4 0.6 0.8 1
Sunbury
Cleveland
Avg. 11.5
Max. 22.1
Min. 5.4
Avg. 6.2
Max. 11.0
Min. 1.6
Avg. 0.83
Max. 0.93
Min. 0.65
O = oxic
D = dysoxic
S/A = suboxic/
anoxic
O D S/A
O D S/A
O D S/A
Ni/Co
V/Cr
V/V+Ni

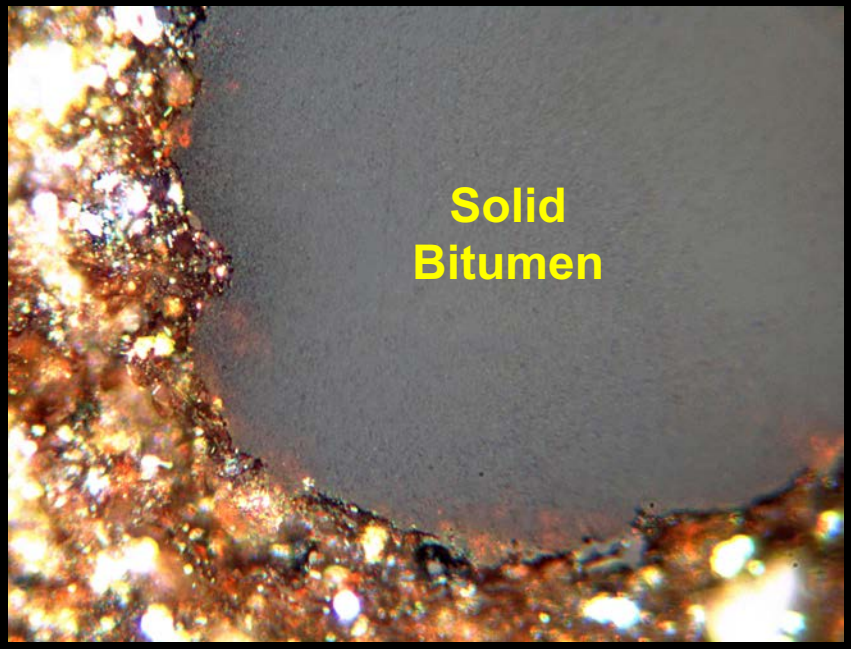
Summary - 1

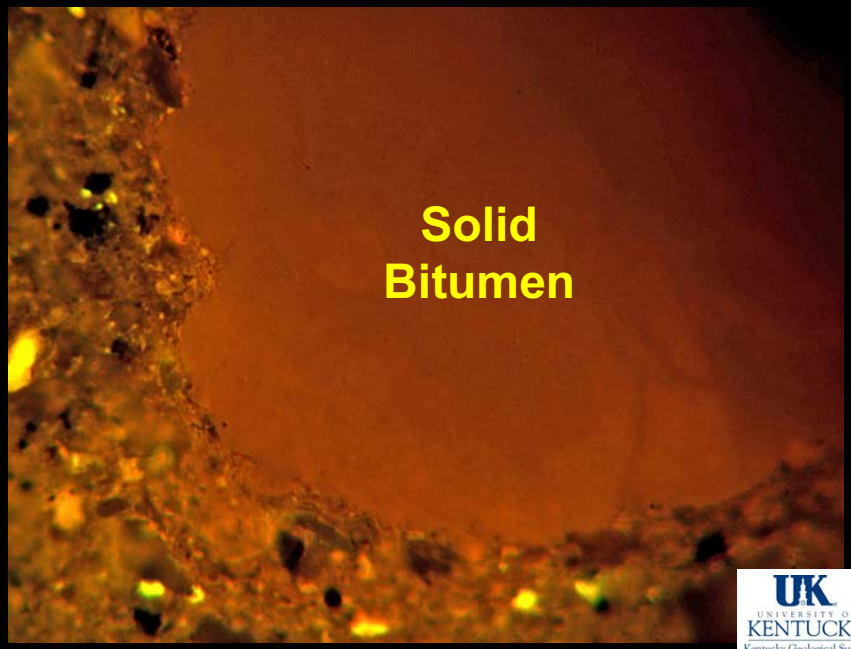
Total Organic Carbon (TOC) – samples varied between 0.3 and 21.6 %. Well average TOC values are higher to the NW, and lower to the SE. In general:

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





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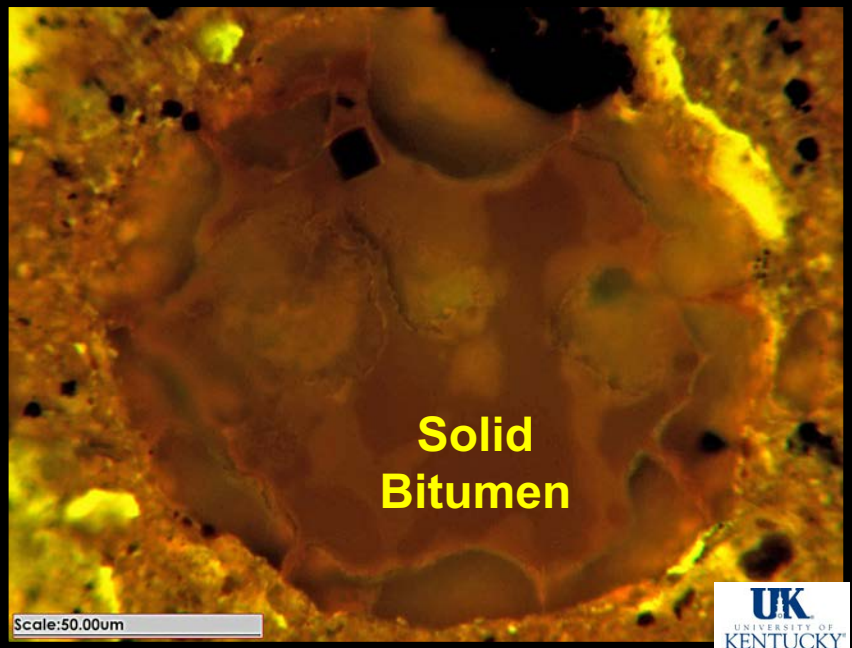
Summary - 2

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 VR_o values ranged from 0.51 %, in the NW part of the study area, to 1.24 % in the SE part.

Solid Bitumen Reflectance – BR_o 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.



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Summary - 3

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

VR_o and $VR_{equivalent}$ (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_{max}, adjusted T_{max} values place most of the area within the oil window.

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Summary - 4

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.

Element Ratio	Avg.
Ni/Co	11.5
V/Cr	6.2
V/(V + Ni)	0.83

Thank You

References

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