

Aromatic Compounds as Maturity Indicators – Comparison with Pyrolysis Maturity Proxies and R_o (Measured and Calculated) Using the New Albany Shale as an Example*

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Abstract

Aromatic compounds such as alkylbenzenes, naphthalenes, phenanthrenes, and dibenzothiophenes are useful as maturity indicators in basin analysis. They are resistant to biodegradation, can span a wide range of thermal maturities, and under elevated temperatures, can still be identified and analyzed. These indicators respond to an increase in thermal stress with a predictable alkylation progression of a given parent compound or a shift in the isomer distribution of alkyl-aromatic homologues towards thermally more stable isomers. Numerous studies on the maturity trends of the New Albany Shale within the Illinois Basin have utilized vitrinite reflectance (R_o) measurements, T_{max} (temperature at which the maximum rate of hydrocarbon generation occurs during pyrolysis of a kerogen sample) data, and conodont analysis. Interpretation of maturity trends determined from this data can be problematic due to vitrinite suppression, measurements derived from bitumen reflectance (vs R_o), paleogeotherm control on vitrinite reflectance, and differing laboratory protocols in geochemical analyses. Sweeney and Burnham (1990) developed a model for vitrinite maturation that integrates chemical kinetic equations over time and temperature to account for the elimination of water, carbon dioxide, methane, and bitumen from vitrinite. Using the EASY % R_o method, calculated R_o can be determined for specific time/temperature conditions and constrained using aromatic compounds such as methylphenanthrenes and triaromatic steroids. These correlations provide an alternative method for mapping thermal maturity across basins with complex burial histories. Source rock extracts from the New Albany Shale were analyzed from various depths across the Illinois basin using gas chromatography-mass spectrometry (GCMS) to calculate specific aromatic compound concentrations. These data were plotted against calculated and measured R_o values. Problematic zones of suppressed vitrinite were identified along with indications of higher maturity (than previously interpreted) trends within the New Albany Shale.

Maturity indices calculated within the New Albany Shale in central and eastern Illinois are elevated relative to R_o determination from reflectance measurements. Utilization of aromatic maturity markers (when calibrated appropriately) provide an invaluable measure of thermal maturity in basins with complex burial histories that may cause other methods to be problematic.

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Aromatic compounds as maturity indicators – Comparison with pyrolysis maturity proxies and R_o (measured and calculated) using the New Albany Shale as an example

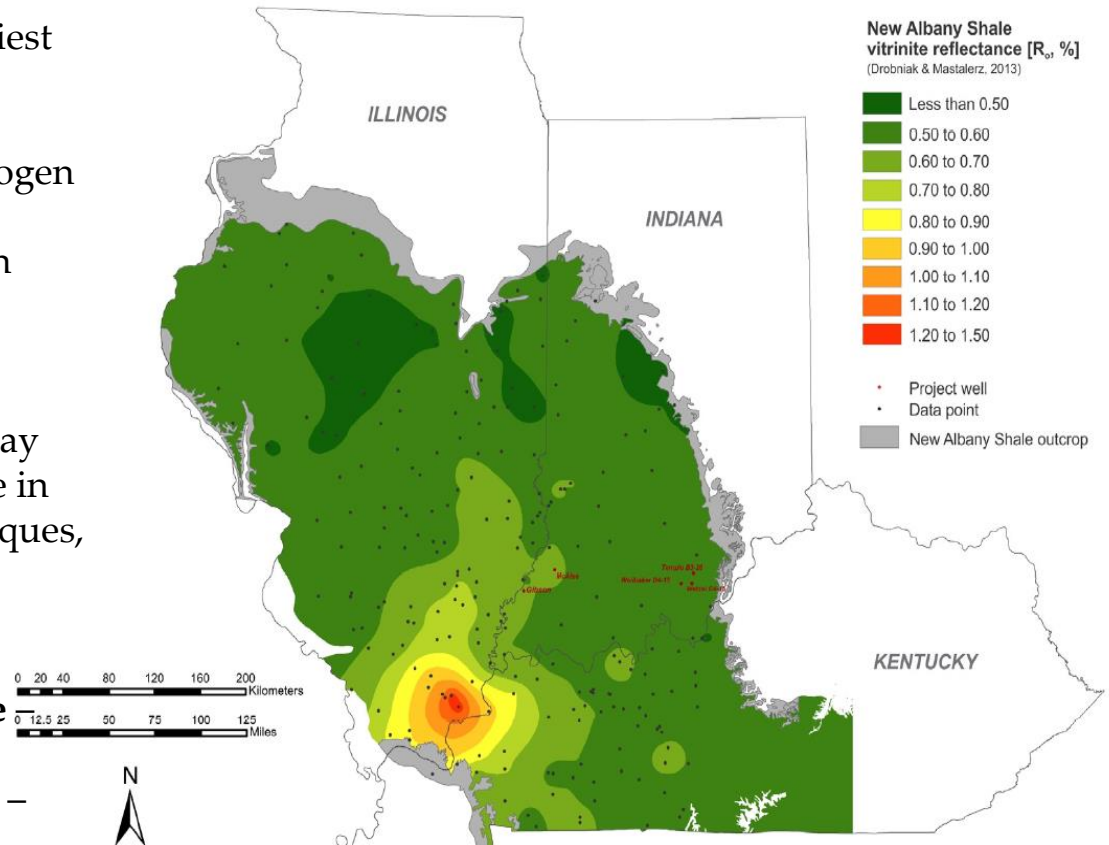
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Background

- **Vitrinite reflectance ($VR_o\%$)** – earliest measure of source maturity
- **Pyrolysis maturity proxies** – Hydrogen Index(HI), TMAX (temperature at maximum S2 peak height), bitumen reflectance ($B_o\%$), etc.
- **Problems using reflectance measurements** – Paleozoic rocks may contain little/no vitrinite, difference in lab/researcher measurement techniques, bitumen reflectance, and vitrinite suppression.
- **Suppression in New Albany Shale**
0.20 – 0.21% V_{ro} (2014, Akar), 0.17 – 0.25% V_{ro} (Mastalerz, et al., 2014), 0 – 0.30% V_{ro} (Nuccio and Hatch, 1996)



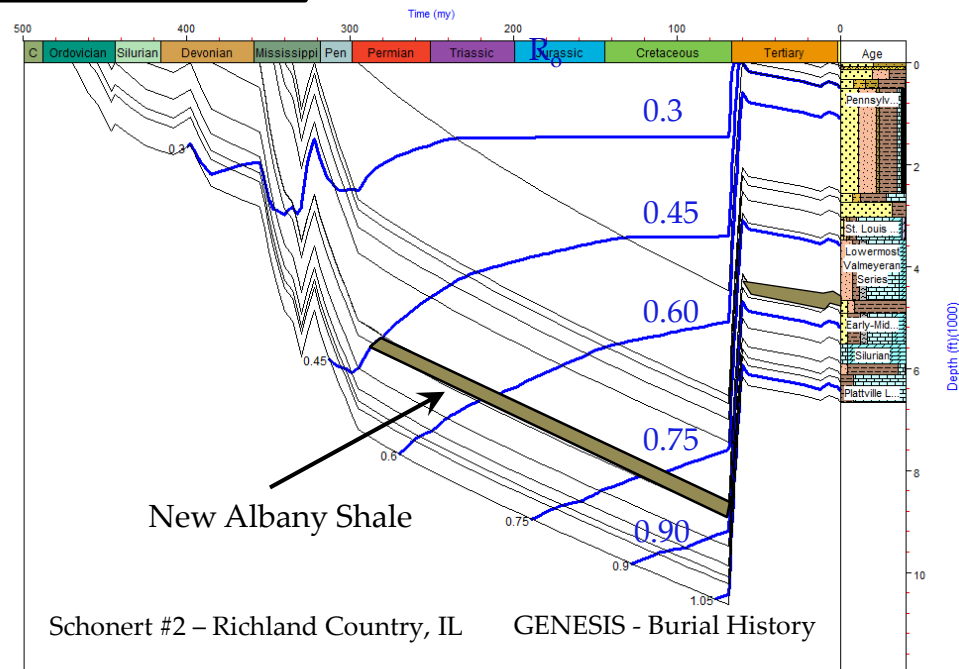
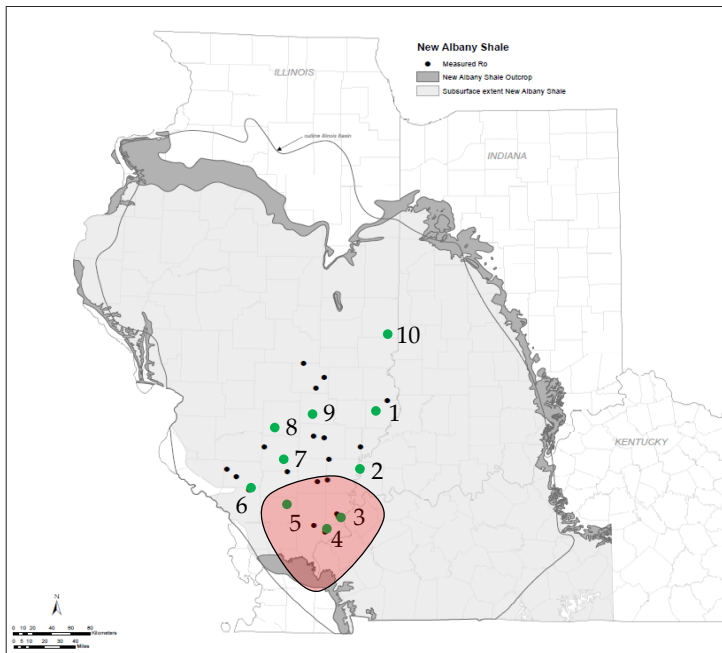
Compiled by Drobniak, Mastalerz, and Crockett, 2013

Why is this Important – Recent kinetic modeling and experimental work indicate that with initial (and slight increases in maturation), asphaltenes and resins produce significant non-HC and HC gas. May significantly increase internal pressures and deliverability to well-bore.

Measured R_o and R_{oEq}

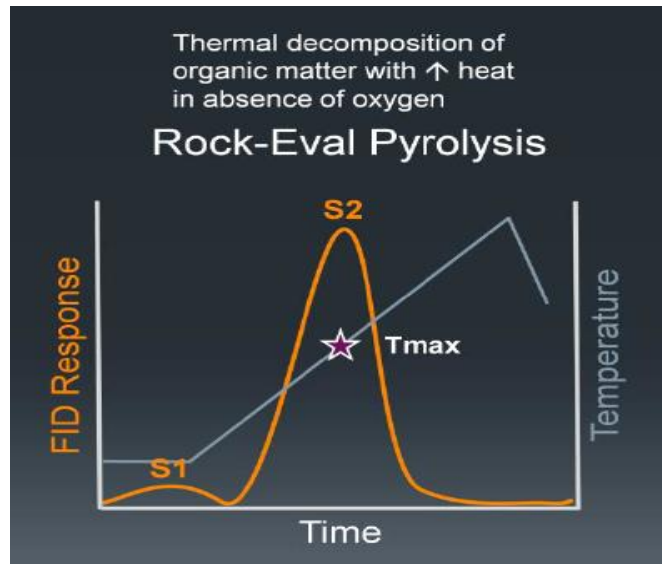
Wells	R_o measured	R_{oEq} Jarvie et al., 2001	R_{oEq} Hower et al., 1994	R_{oEq} GENESIS models
1	0.61	0.69	0.78	0.73
2	0.69	0.69	0.82	0.76
3	1.04	0.87	1.04	1.10
4	1.10	1.05	1.08	1.18
5	0.82	0.83	0.91	0.90
6	0.57	0.71	0.75	0.82
7	0.65	0.83	0.80	0.92
8	0.44	0.74	0.67	0.72
9	0.52	0.78	0.72	0.75
10	0.55	0.36	0.74	0.70

- At lower maturities ($< 0.7 R_o$) – significant disparities in measured R_o and R_{oEq}
- Convergence of measured and calculated at high maturities
- R_o calculated from basin models is uniformly higher than measured R_o

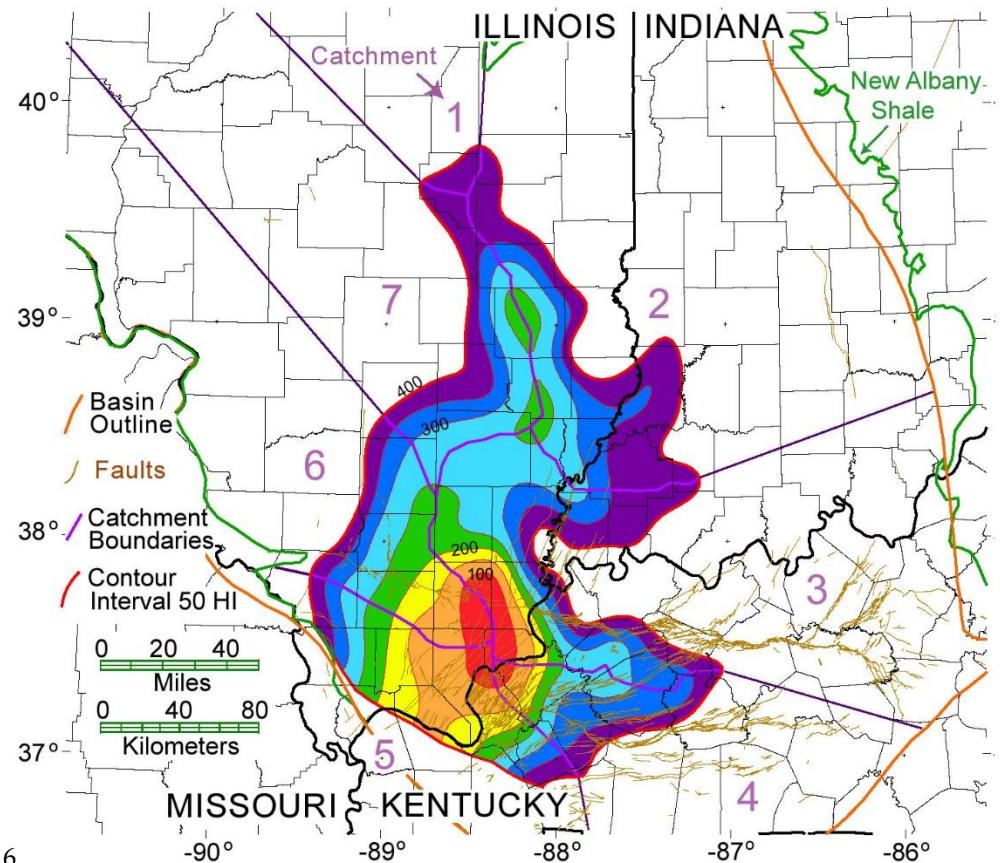


Geochemical Maturity Proxies

- **Commonly used proxies** – HI, TMAX, and transformation ratio (TR) determined from source rock pyrolysis
- $HI = (S2/TOC) \times 100 \text{ mgHC/gTOC}$
TMAX= temperature at maximum thermal decomposition of S2 peak
- TR = original convertible kerogen to present day $(S1/(S1+S2)) \text{ mgHC/grx}$
- **Application issues** – TMAX influenced by instrument and inclusion of mud additives, high MW hydrocarbons, TR is relative to original organic content and HC migration, and **HI is not uniform in nature, varies laterally and vertically**

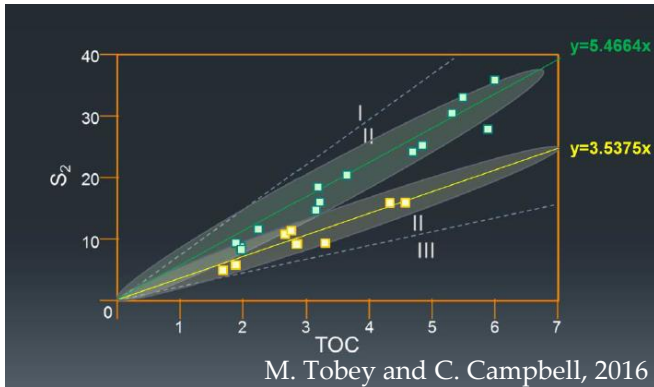


M. Tobey and C. Campbell, 2016



USGS Open-File Report 03-037, 2003

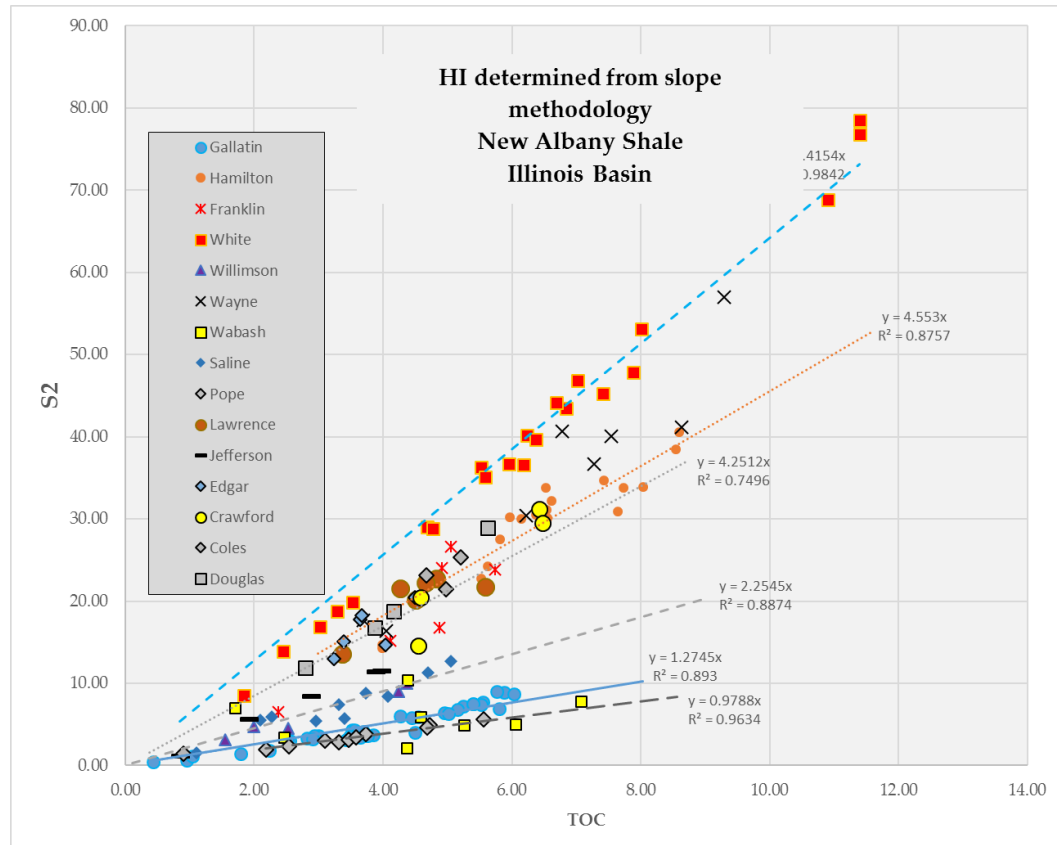
Hydrogen Index (HI) Slope Method



Problem: How do you pick an HI (single point) when it varies in the source rock column?

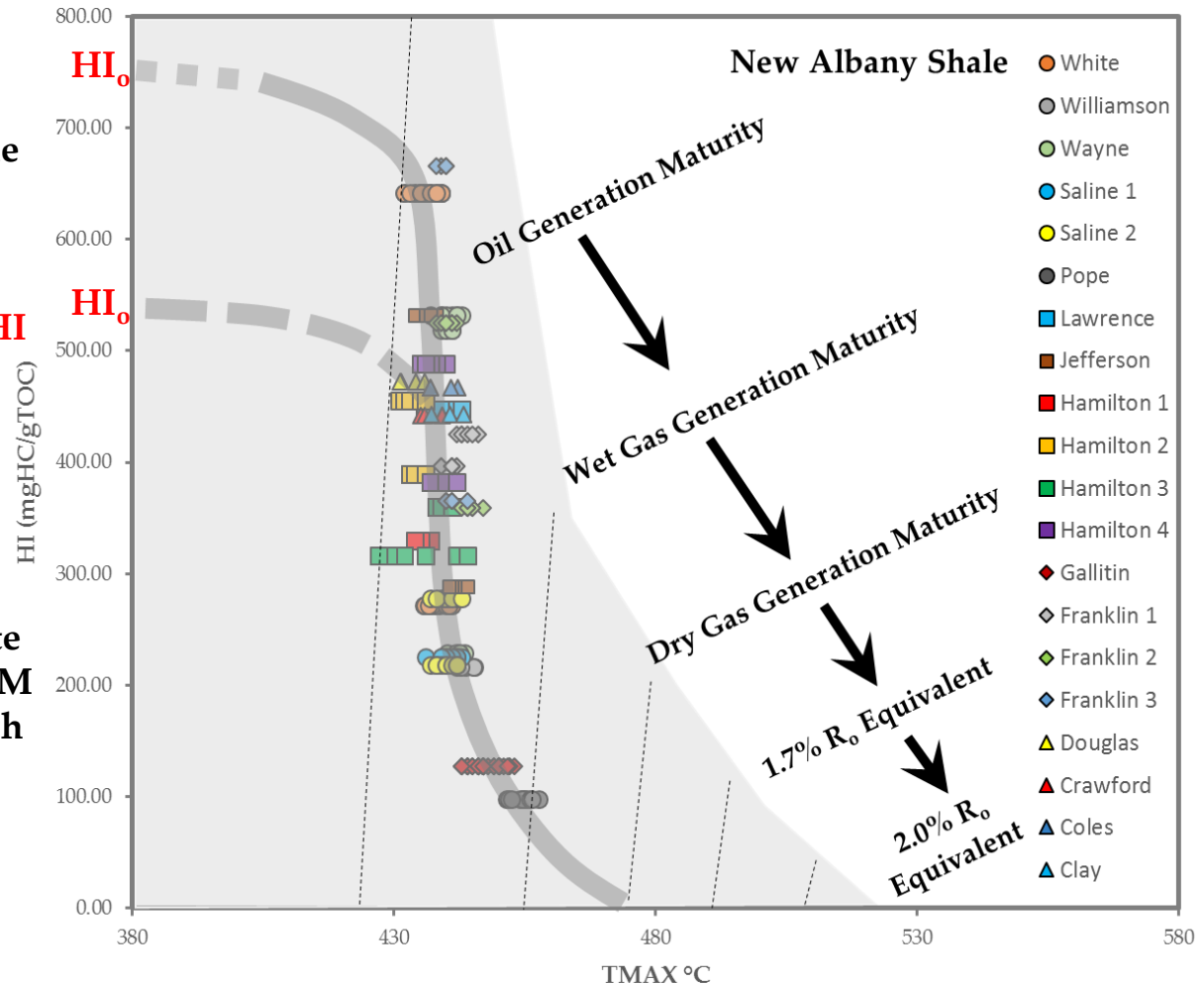
HI is ratio of S₂ and TOC. The slope of a cross-plot can be used as a mean HI for the well. Multiply the slope by 100 to determine HI. The slope needs to intersect the origin because as TOC approaches zero, so should S₂.

County	HI (slope)	HI (USGS, 2003)
White	641.5	380
Wayne	230.2	250
Saline	278.3	150
Pope	97.9	90
Jefferson	532.0	430
Hamilton	330.1	250
Hamilton	530.3	285
Franklin	524.8	330
Effingham	360.2	350
Douglas	472.7	320



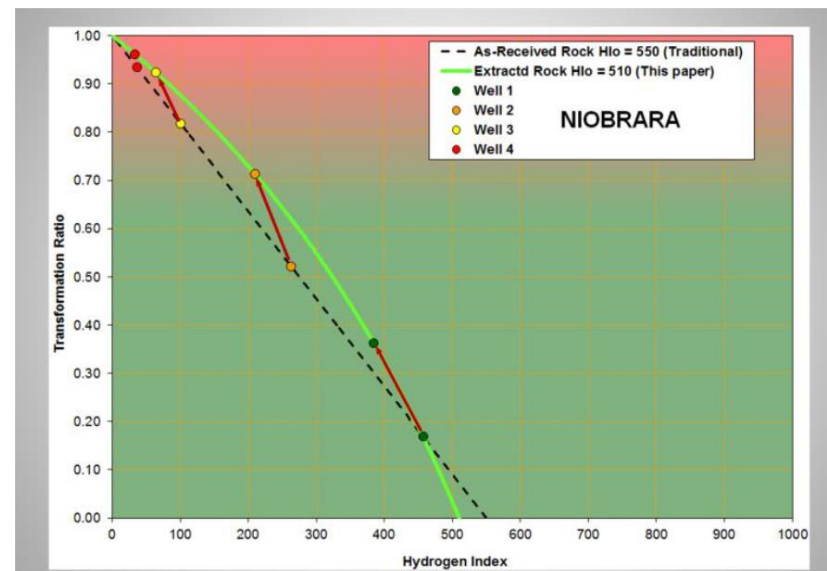
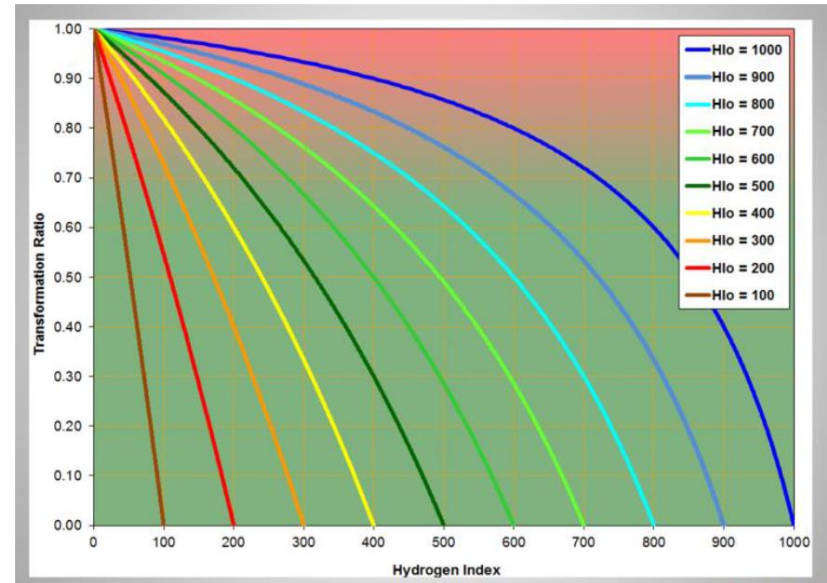
Determine Original HI

- NAS organofacies are fairly consistent
- Based upon the transformation of convertible organic matter to thermal stress – at least 2 kerogen types may be present in the NAS. $HI_o = 760 \text{ HI and } 530 \text{ HI}$
- DO NOT USE Type I, II, III geochemical descriptors
- NAS contains very high concentrations of alginate (*tasmanites*) and amorphinite which means the kerogen/OM is anomalously hydrogen rich



Why reliable HI and original HI are important in determining transformation ratio

- Transformation ratio (TR) – a parameter that quantifies the relative progress of hydrocarbon generation (0.0-1.0)
- Ideally, work with extracted rock in source rock analysis (eliminates heavy bitumen)
- Curved relationship between TR and HI – error greatest at moderate maturities
- TR =
$$\frac{(HI_o/100) - [(HI_m \times (60 - (5 \times HI_o)))] / 6000 - (5 \times HI_m)]}{(HI_o/100)}$$
- Assumptions were made: S2 peak represented by $C_{10}H_{22}$ and TOC_o equal to one to simplify derivation

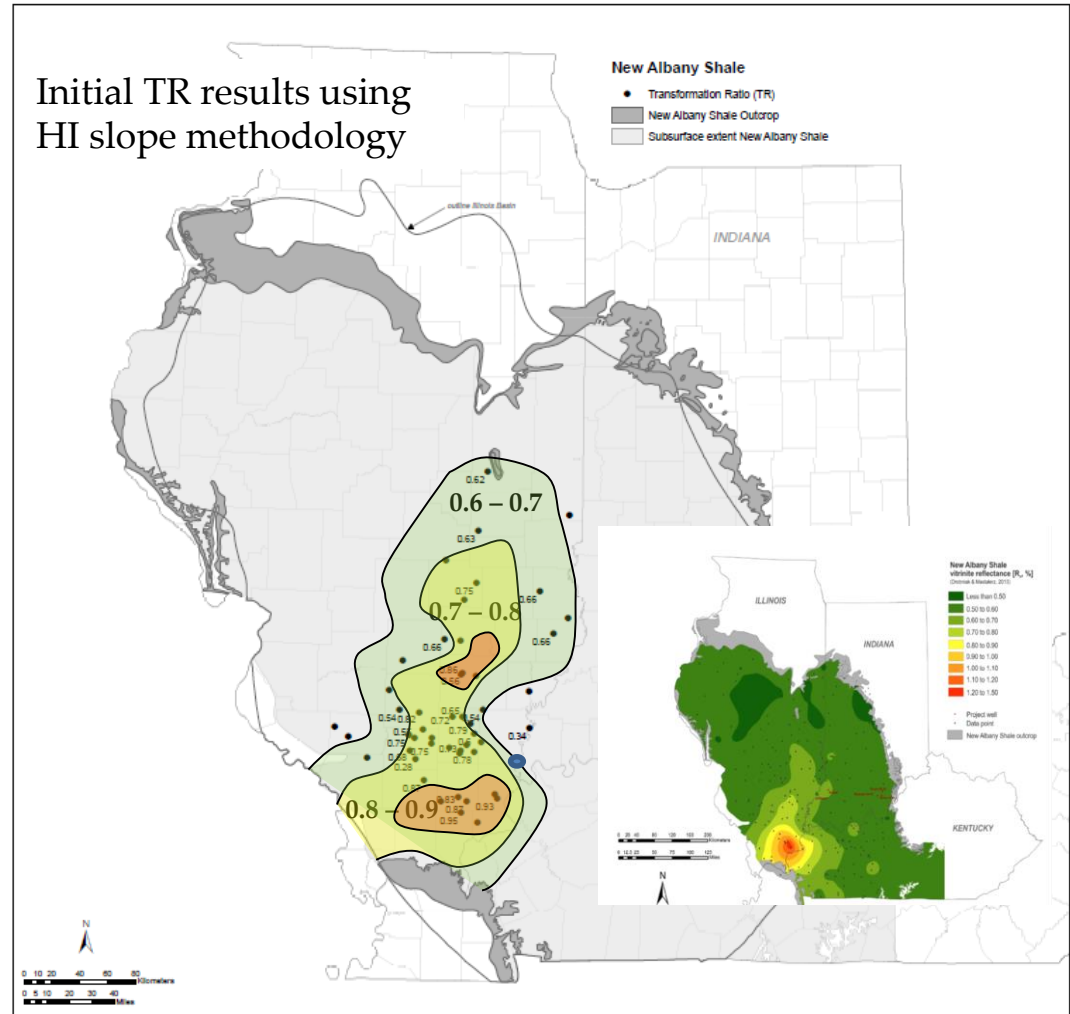
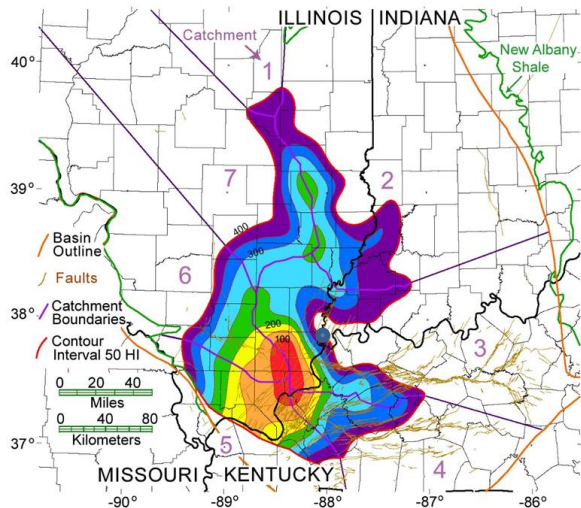


Estimate of convertible organic matter transformation

Which maturity proxy/indicator is picked to model and quantify hydrocarbon generation?

- Similar overall trends
- R_o of approximately 0.6 – corresponds to 0.6-0.7 TR, i.e. significant HC generation
- HI maturity proxy map also indicates two areas of increased maturity in NAS compared to TR

TR areal extent of significant HC generation larger than other maturity indicators

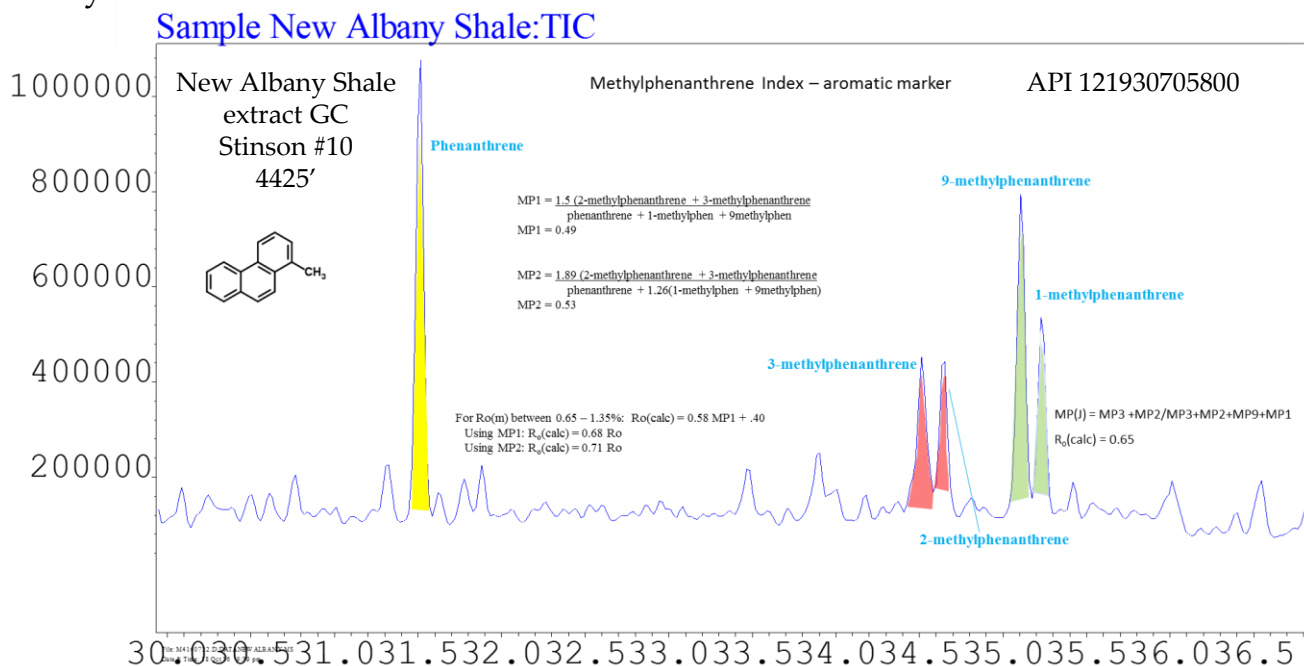
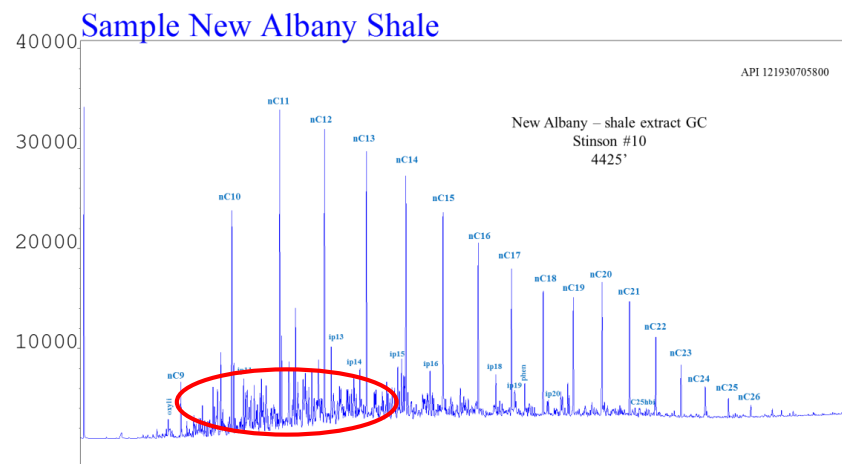


Aromatic markers from generated hydrocarbons are a direct measure of maturity

- **Biomarkers** – steranes, isoprenoids, hopanes are influenced by organic input, preservation potential (salinity and oxygen content of water column), and typically have limited utility at elevated maturities ($> 0.9 R_o$)
- **Aromatic markers** – naphthalenes, phenanthrenes, dibenzothiophenes rely either on degree of alkylation of a given parent compound with increasing thermal stress or a shift in the distribution of alkyl-aromatic homologues towards more thermally stable isomers

Aromatic markers

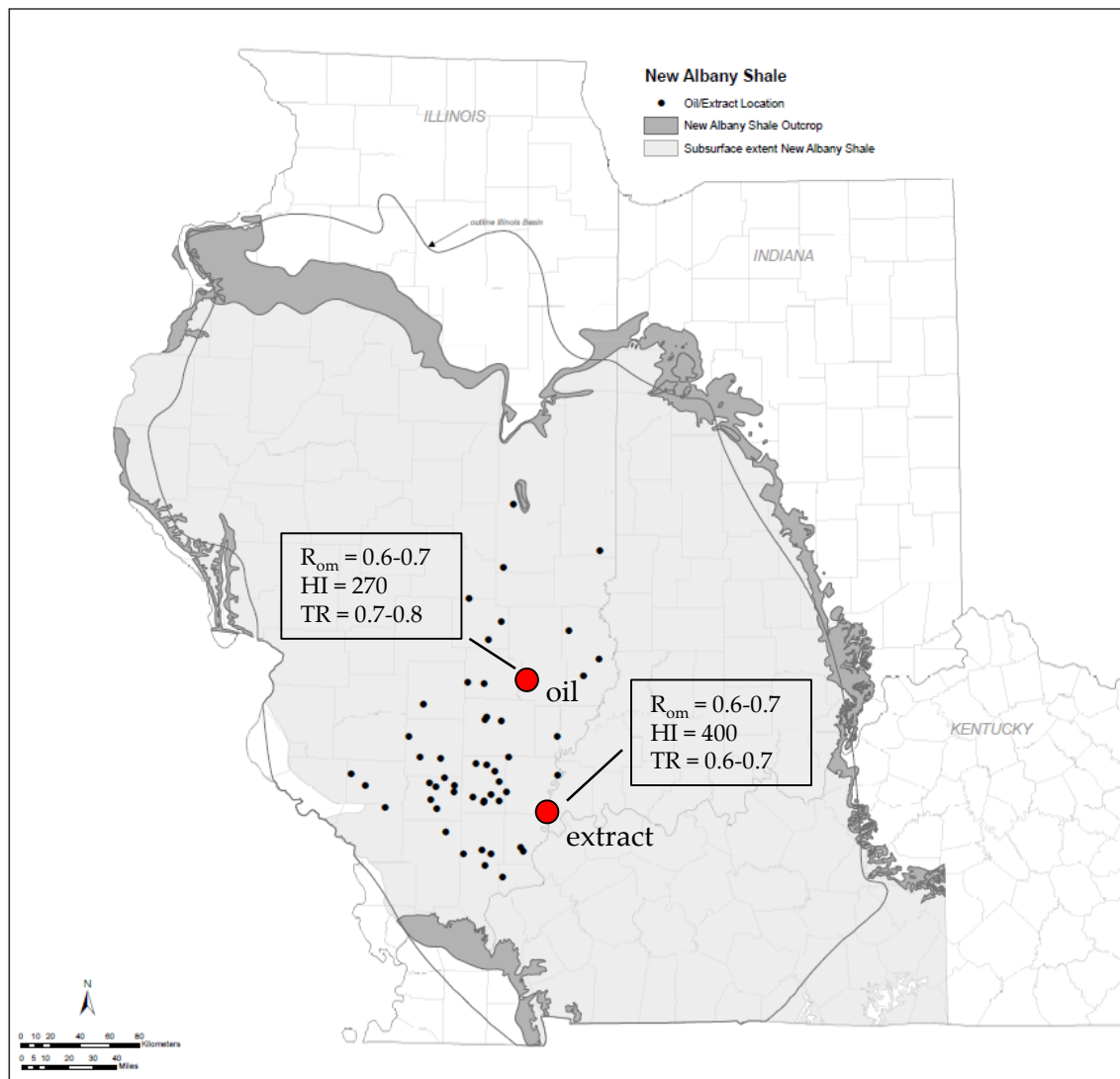
- Effects in changes of organic input are reduced
- Much higher concentrations at elevated maturities
- Trace maturity evolution over an expanded range



Aromatic markers – Location of oil and extract data

Aromatic Markers Calculated

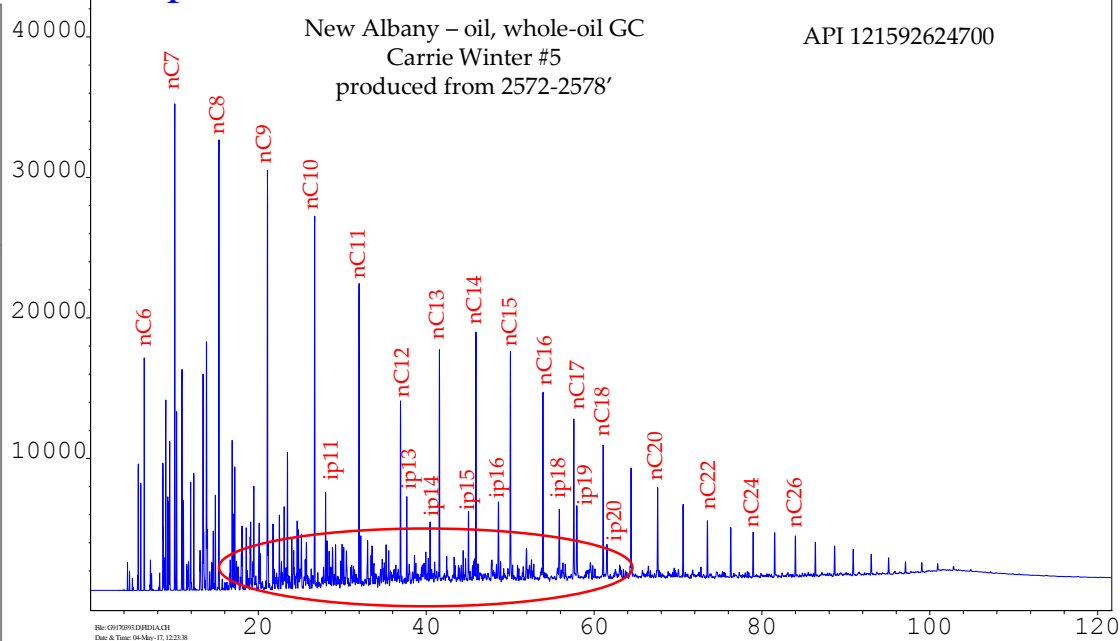
- **Methylphenanthrene Index**
$$MP1 = \frac{2-MP + 3-MP}{PH + 1-MP + 9MP}$$
$$MP2 = \frac{1.89(2-MP + 3-MP)}{PH + 1.26(1-MP + 9-MP)}$$
- **Dibenzothiophenes ratio**
$$MDR = 4 \text{ MDBT} / 1 \text{ MDBT}$$
- **Tetramethylnaphthalenes**
$$TeMN = \frac{1,3,5,7 \text{ TeMN}}{(1,3,5,7 \text{ TeMN} + 1,2,5,6 \text{ TeMN})}$$
- **Triaromatic Steroids (TAS)**
$$TAS \text{ (C21 + C22)} / \sum TAS$$
$$TA I / (TA I + MA I)$$



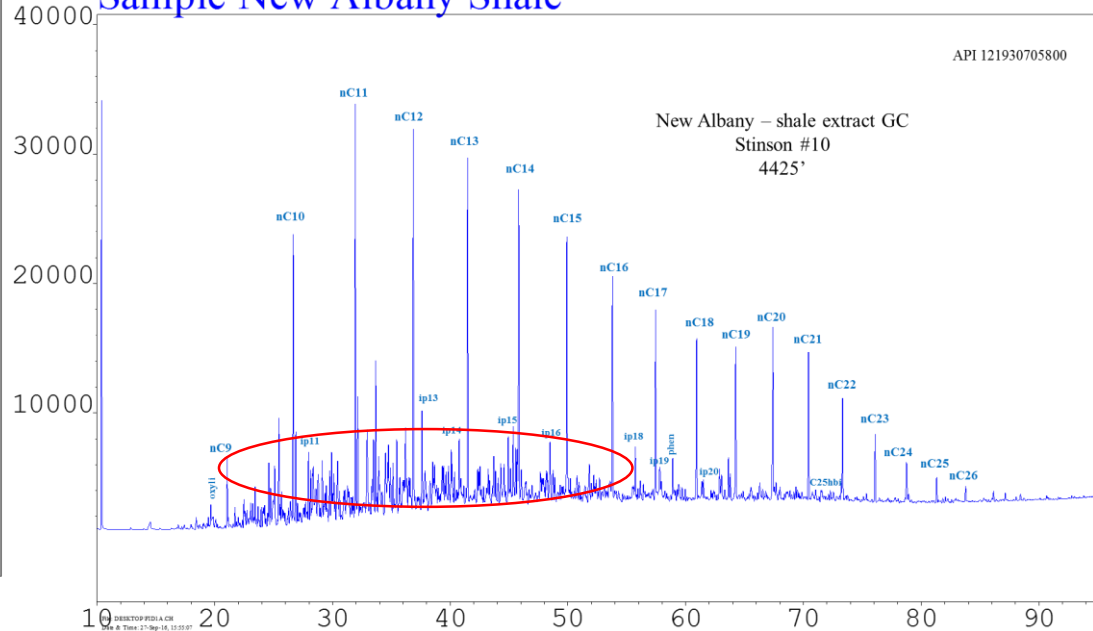
Whole-oil high resolution GC of natural oil and rock extract

- No evidence of biodegradation
- Extract GC does not include light fraction of oil – evaporated
- Both chromatograms indicate a mature-early mature liquid hydrocarbon
- Pristane/Phytane ratios between 1.62-1.79 – not indicative of paleoenvironment
- Profiles consistent with *n*-alkane patterns, isoprenoid distributions, and isoprenoid ratios with previous research

Sample Carrie Winter No 5



Sample New Albany Shale

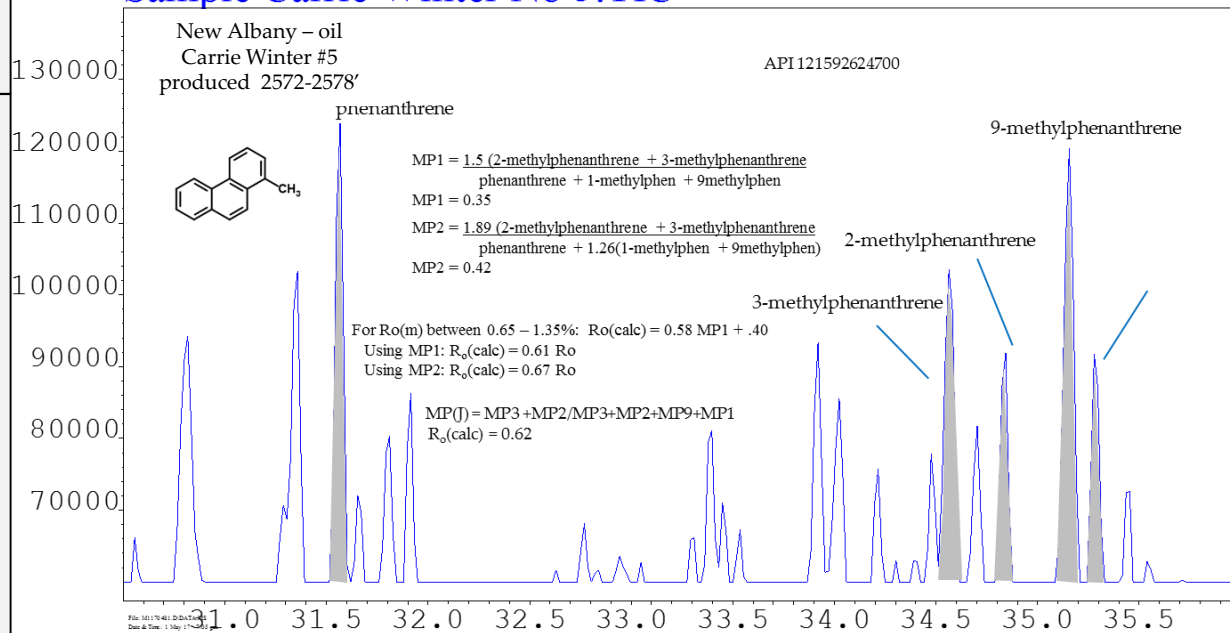


Aromatic Markers

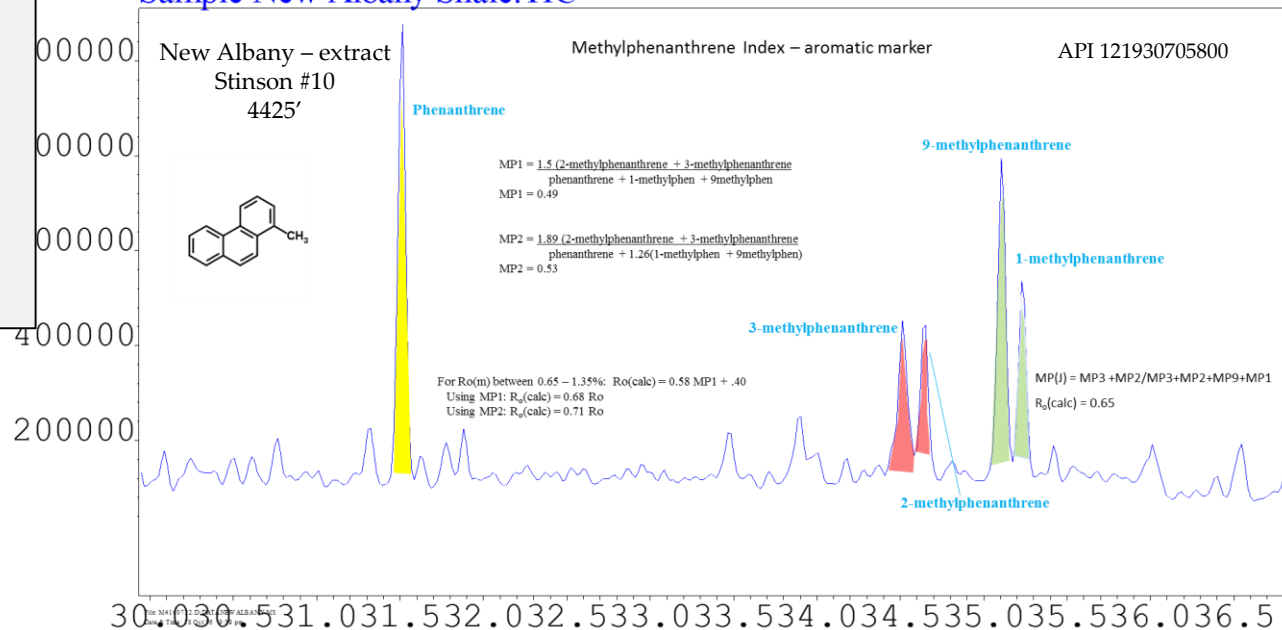
- Standard indices developed by Radke et al., 1988
- Useful for rock samples that do not contain vitrinite or where R_o measurements are suspect
- Estimate R_o of the source rock at time of expulsion for oils

- Carrie Winter #5 - oil
 $R_{o(calc)} = 0.61 - 0.67$
- Stinson #10 - extract
 $R_{o(calc)} = 0.65 - 0.71$

Sample Carrie Winter No 5:TIC



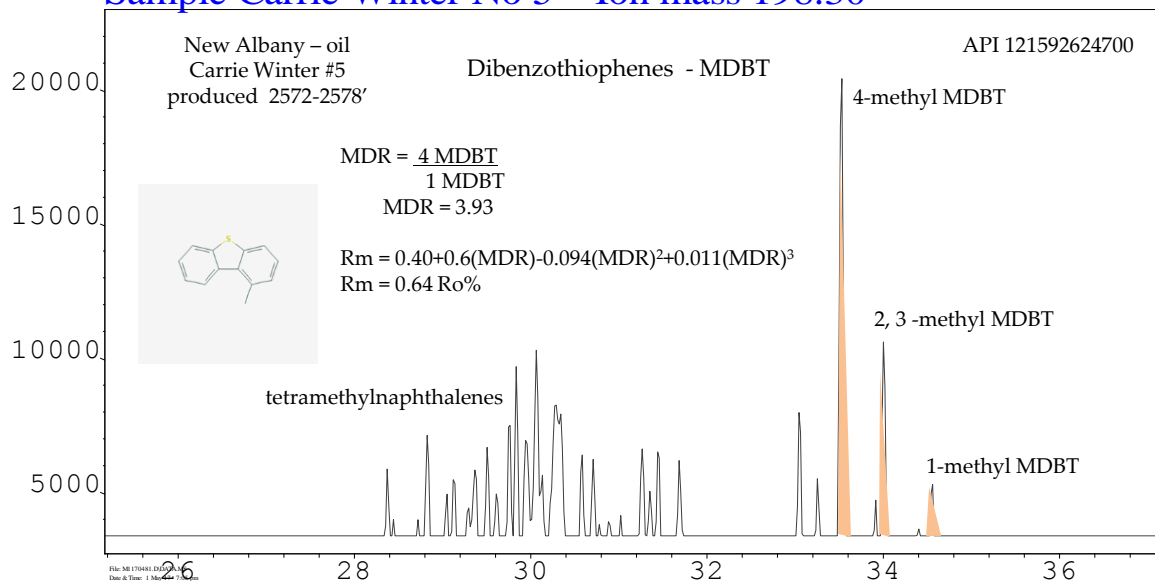
Sample New Albany Shale:TIC



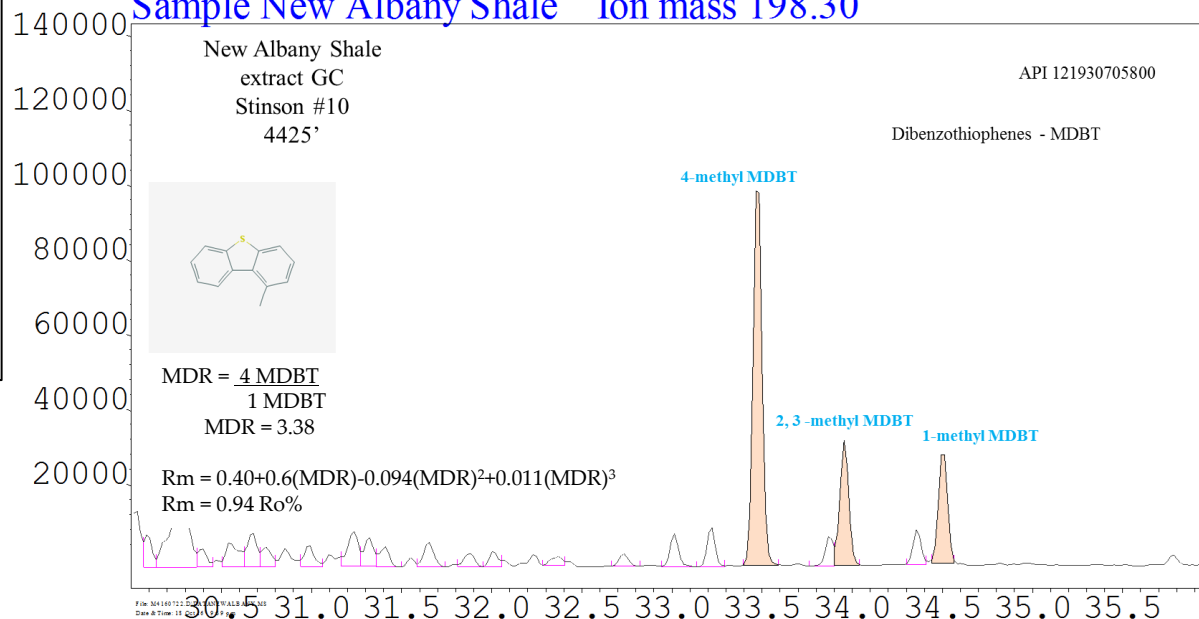
Aromatic Markers

- Standard indice developed by Radke et al., 1988. Somewhat resistant to biodegradation
- Can modify equation to predict TMAX trends
- **Carrie Winter #5 - oil**
 $R_{o(calc)} = 0.61$
- **Stinson #10 – extract**
 $R_{o(calc)} = 0.94$
- First indication that extract from source rock may be higher maturity than measured by R_o or HI

Sample Carrie Winter No 5 Ion mass 198.30



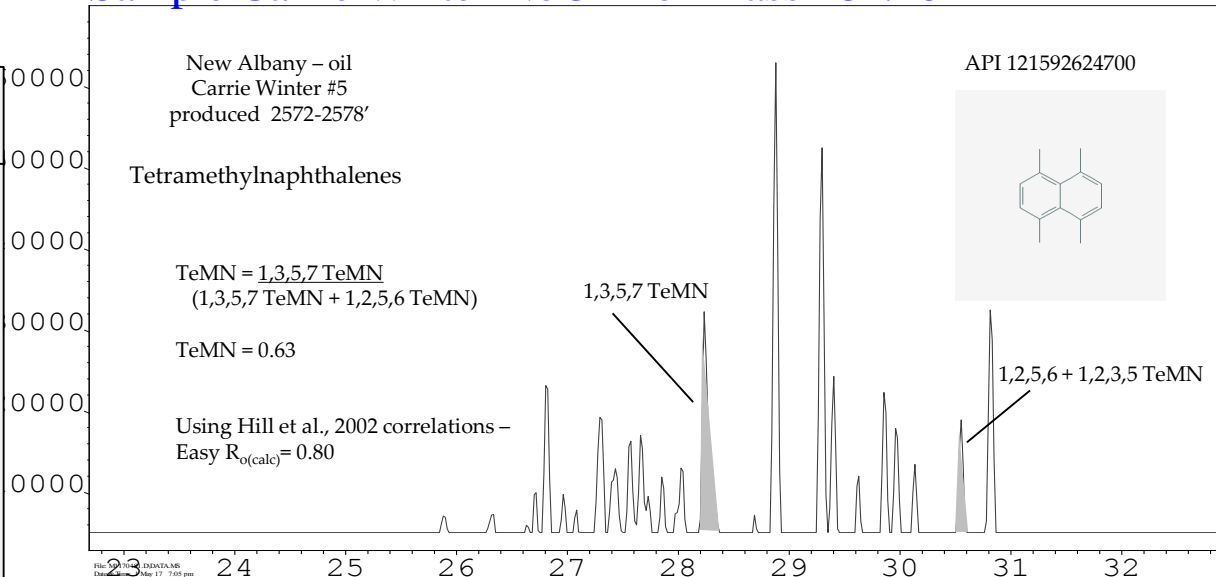
Sample New Albany Shale Ion mass 198.30



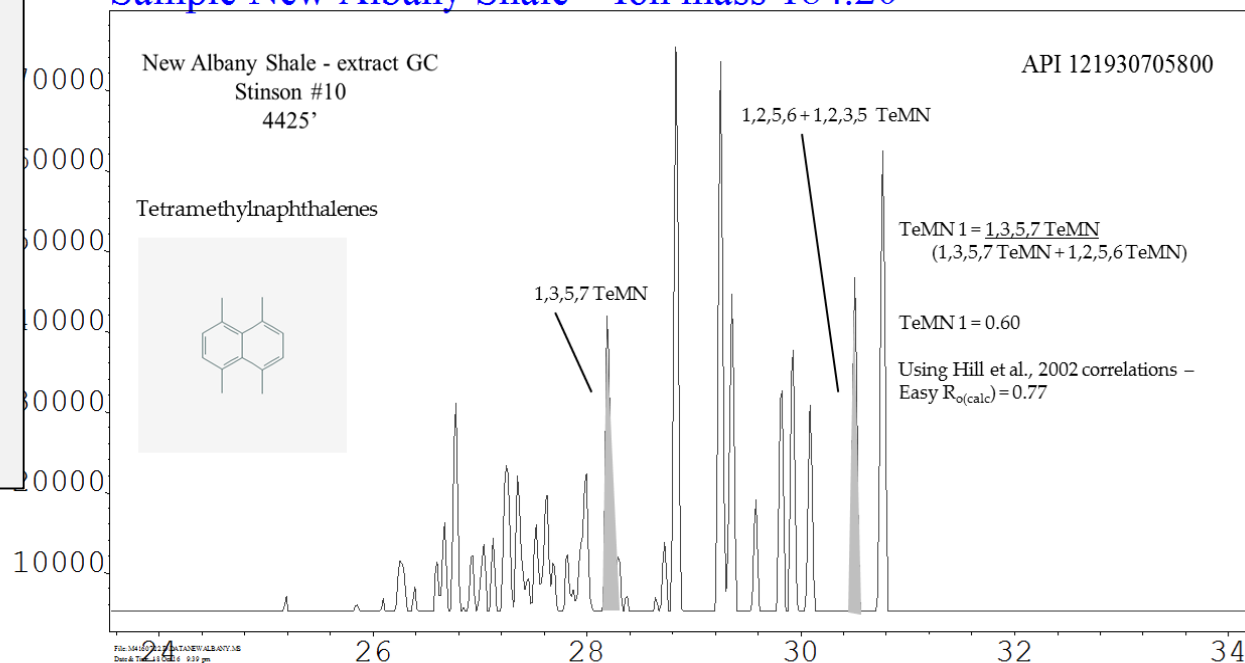
Aromatic Markers

- Utilizing closed-system pyrolysis of Devonian oil to correlate ratios with Easy R_o calculations (Hill et al, 2002)
- TeMN isomer ratios increase with increasing maturity
- Carrie Winter #5 - oil
Easy $R_{o(calc)} = 0.80$
- Stinson #10 – extract
Easy $R_{o(calc)} = 0.77$
- Higher estimated maturity than other geochemical indicators

Sample Carrie Winter No 5 Ion mass 184.20



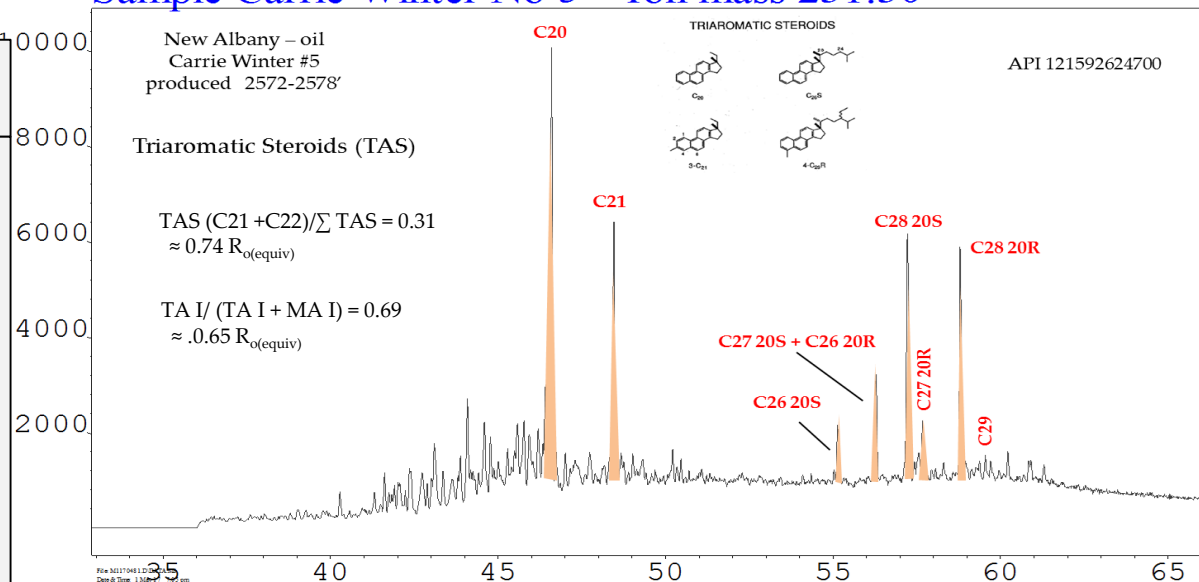
Sample New Albany Shale Ion mass 184.20



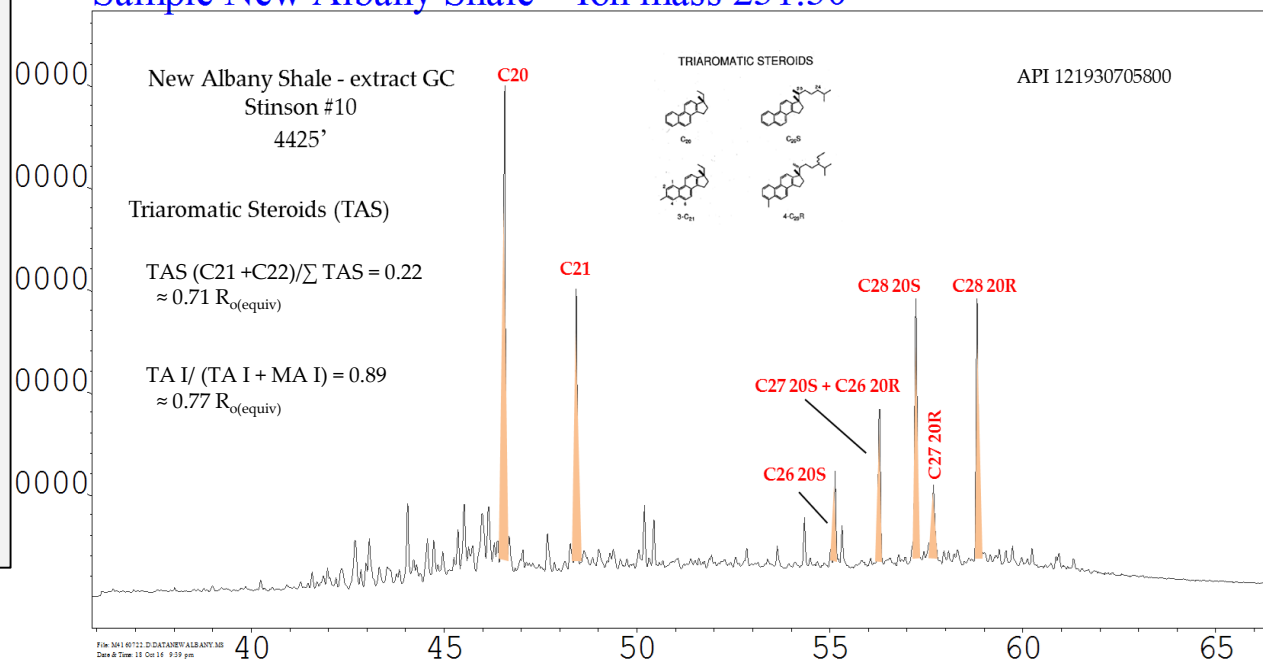
Aromatic Markers

- Aromatization of monoaromatic steroids yield triaromatic steroids – TAS best used for mature to peak mature – TA/MA – highly specific for immature-mature range
- Reliable maturity trend indicator – some interference from source input and TAS may be preferentially retained in bitumen compared to oil
- Carrie Winter #5 - oil
TAS ratio = $0.74 R_{o(equiv)}$
TA/MA ratio = $0.65 R_{o(equiv)}$
- Stinson #10 – extract
TAS ratio = $0.71 R_{o(equiv)}$
TA/MA ratio = $0.77 R_{o(equiv)}$

Sample Carrie Winter No 5 Ion mass 231.30

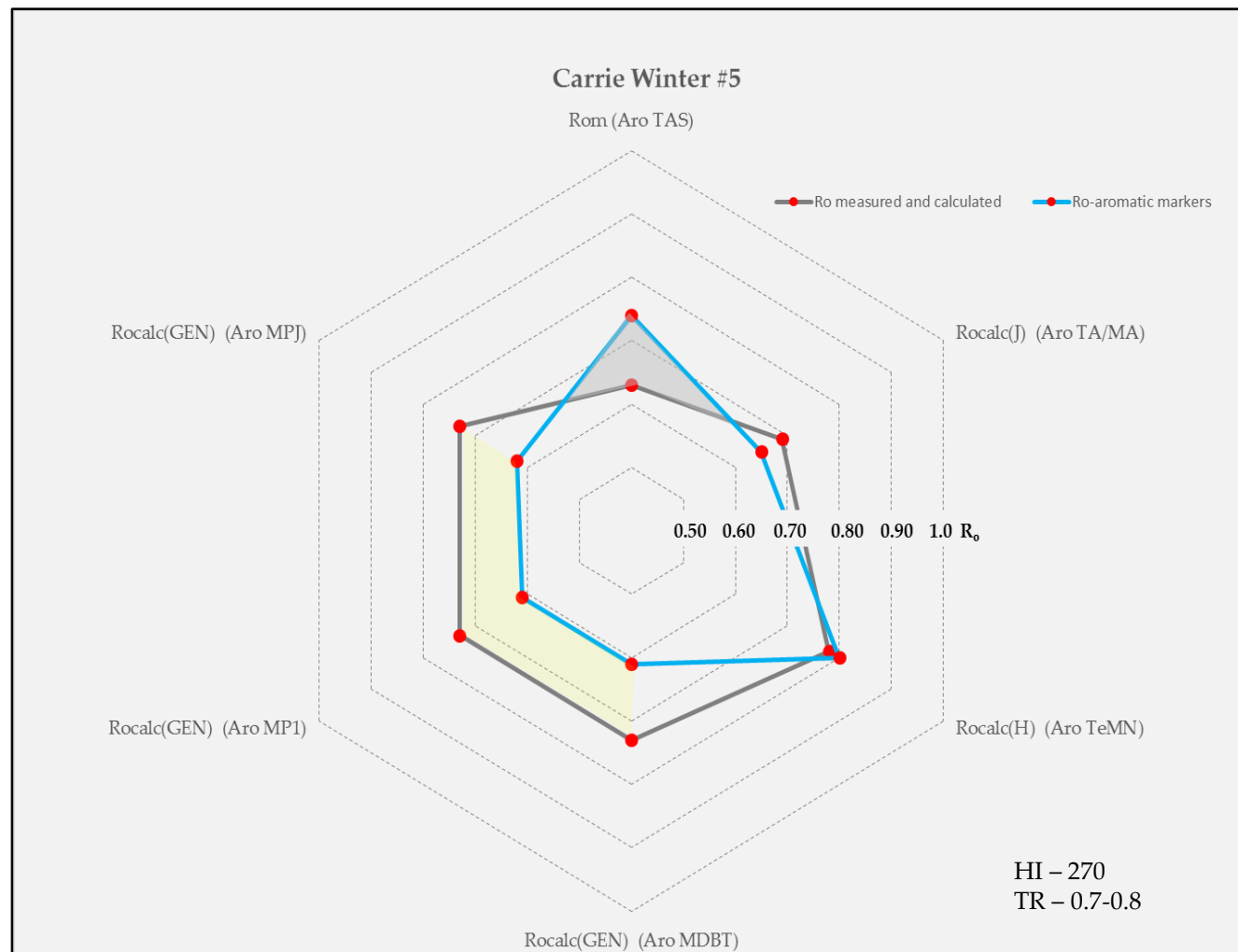


Sample New Albany Shale Ion mass 231.30



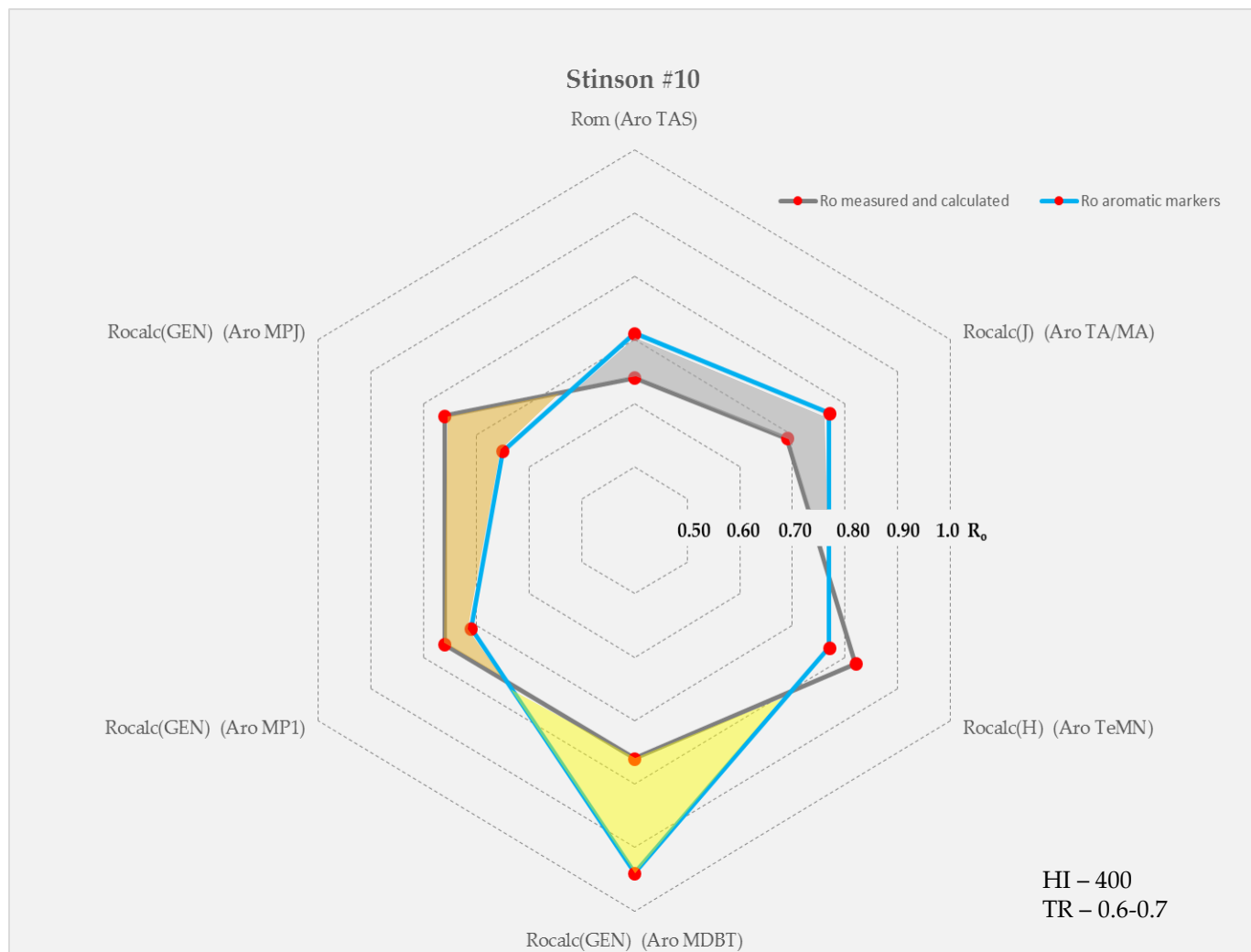
Comparison of aromatic markers with other geochemical indices

- Significant variation between **TAS** and R_o measured
- Significant variation between **Genesis Easy** R_o calculations and **MP** and **MDBT** aromatic markers
- Convergence of R_o calculated using **Hower** equation and **TeMN** aromatic marker
- R_o calculated from aromatic markers range from 0.65 – 0.80 R_o



Comparison of aromatic markers with other geochemical indices

- Elevated R_o between **TAS-TA/MA** and R_o measured and calculated
- Genesis Easy R_o** calculation is significantly lower **MDBT** aromatic marker
- Methyphenanthrene ratios are also lower than **Genesis Easy R_o calculations**
- Convergence of R_o calculated using **Howe** equation and **TeMN** aromatic marker
- R_o calculated from aromatic markers range from 0.65 – 0.96 R_o



Discussion of aromatic marker comparison with other geochemical indicators

- Aromatic markers support the interpretation that R_o measured is *too low*
- The R_o calculated by **Genesis** (burial history) Easy R_o is *too high*
- The methyphenanthrene ratios are *suspect* possible due to variations in OM and lithology of source rock, different rates of generation of phenanthrenes and the methyl isomers, or due to lack of calibration specific to the Illinois Basin
- Convergence of R_o (calculated) using the **Hower et al., 1994** equation (which is based off of random R_o measurements) and **TeMN ratios**. Research as demonstrated that the orientation of R_o measurement and maturity of the measured sample influence the average R_o value - *samples measured perpendicular to bedding plane exhibit higher reflectance*
- **TAS and TA/MA** (triaromatic steroid) ratios are generally considered fairly reliable (will have an overprint of source facies)

Conclusions and Future Work

- Using most reliable aromatic markers:

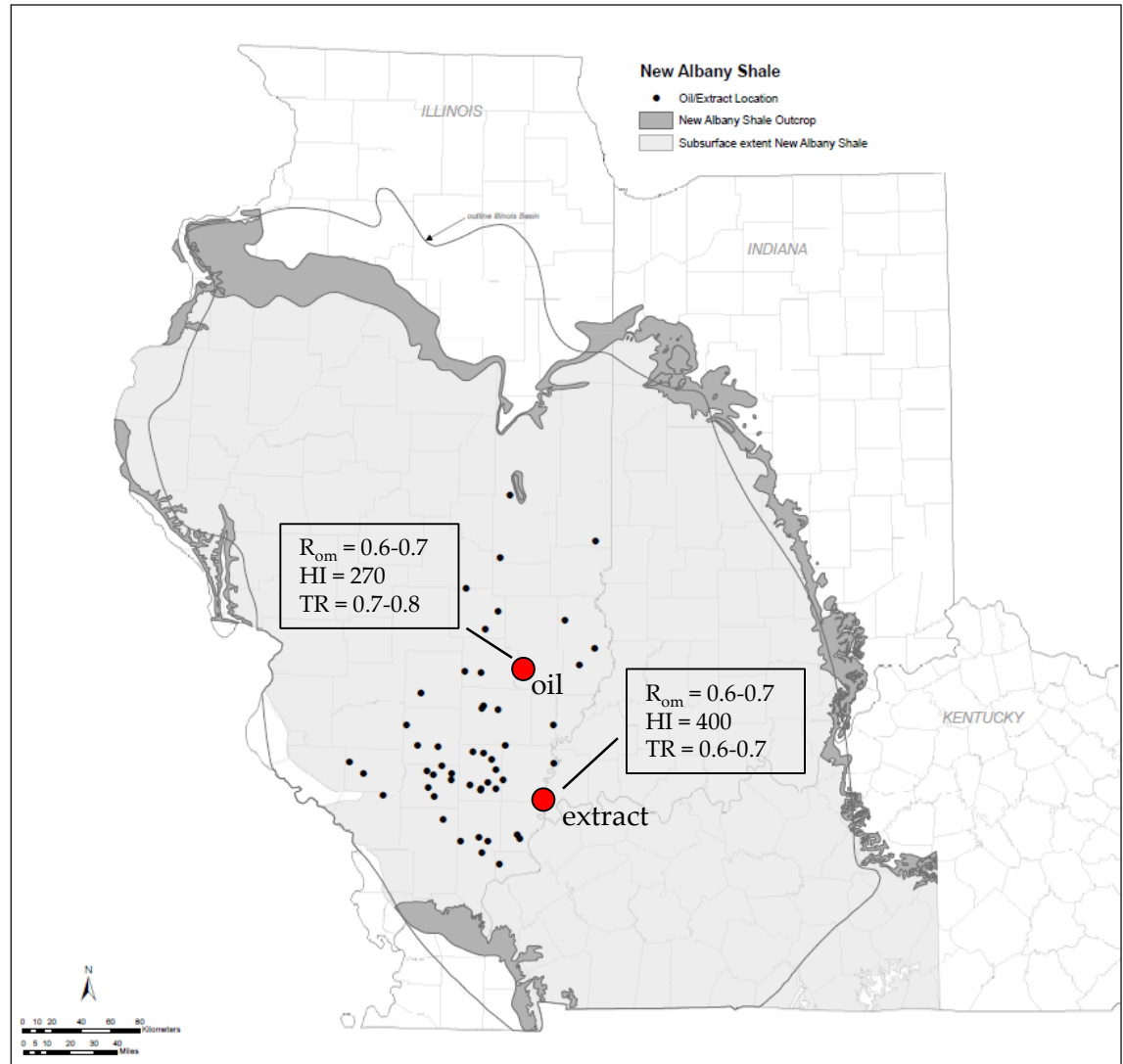
Carrie Winter #5

$R_o (am) = 0.73$

Stinson #10

$R_o (am) = 0.76$

- Expands maturity range in those areas. **Calculated TR makes more sense.** For Stinson #10, indicates HI derived just by averaging is in error
- More oils and extracts needed for calibration
- A more precise measure of maturity will provide a method to map volatile oil potential in NAS**



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