Evaluating Petroleum Character and Charge from Different Source-Rock Lithologies in the Woodford Shale and Caney Shale with Hydrous Pyrolysis*

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Abstract

Representative lithologies from the Woodford Shale and Caney Shale exposed in Carter County, OK were sampled for hydrous pyrolysis experiments to determine their influence on petroleum character or charge. The lithologies include shale, siliceous shale, chert, and dolomitic marlstone. These source-rocks range in total organic carbon from 6.5 wt% in chert to 25 wt% in siliceous shale. Hydrous pyrolysis was used because it generates oil that is compositionally similar to natural crude oils and expels it by processes considered operative in sedimentary basins. Characteristics of the expelled oil include API gravity, alkane distribution, biomarker signatures, and C15+ fractions. Characteristics of the generated gas include molecular composition of hydrocarbons and non-hydrocarbons, and stable carbon isotopes of the hydrocarbon gases. Collectively, these analyses provide information on oil-expulsion efficiency, gas potential, transition metal catalysis, oil quality, and gas:oil ratios for each source-rock lithology. This information can be used to better understand variations in petroleum character and quantities generated from the Woodford Shale and Caney Shale. Two different scales of hydrous pyrolysis were used in this study. Small-scale runs were made in 50-mL stainless steel reactors to establish biomarker signatures, and large-scale runs used 1-liter reactors to evaluate character and charge of oil and gas at the end of the oil window for each lithology.

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EVALUATING PETROLEUM CHARACTER AND CHARGE FROM DIFFERENT SOURCE-ROCK LITHOLOGIES IN THE WOODFORD SHALE AND CANEY SHALE WITH HYDROUS PYROLYSIS

V.S. Nowaczewski, M. Lewan (Consultant), J. Barton, C. Palmer, A. Tang and S. Chipera

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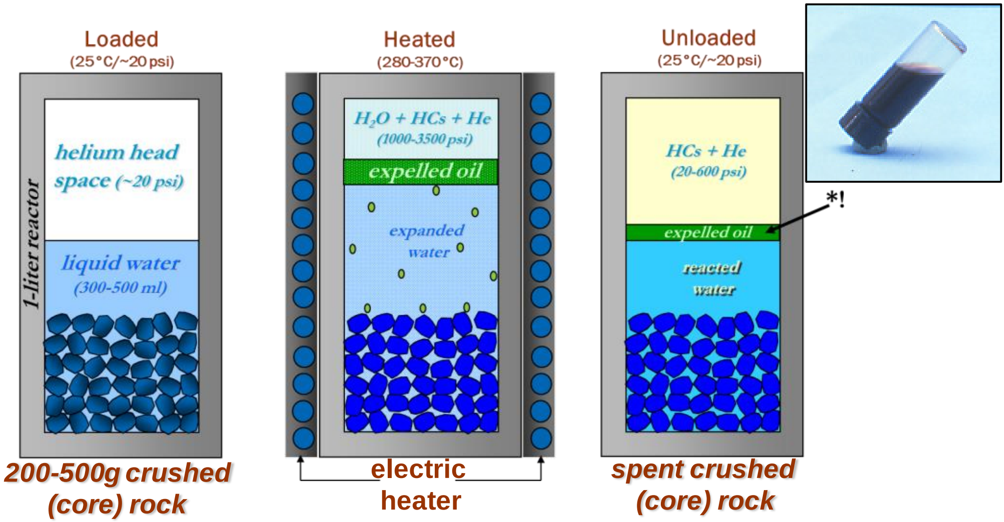
PILOT STUDY OBJECTIVES AND RELEVANCE

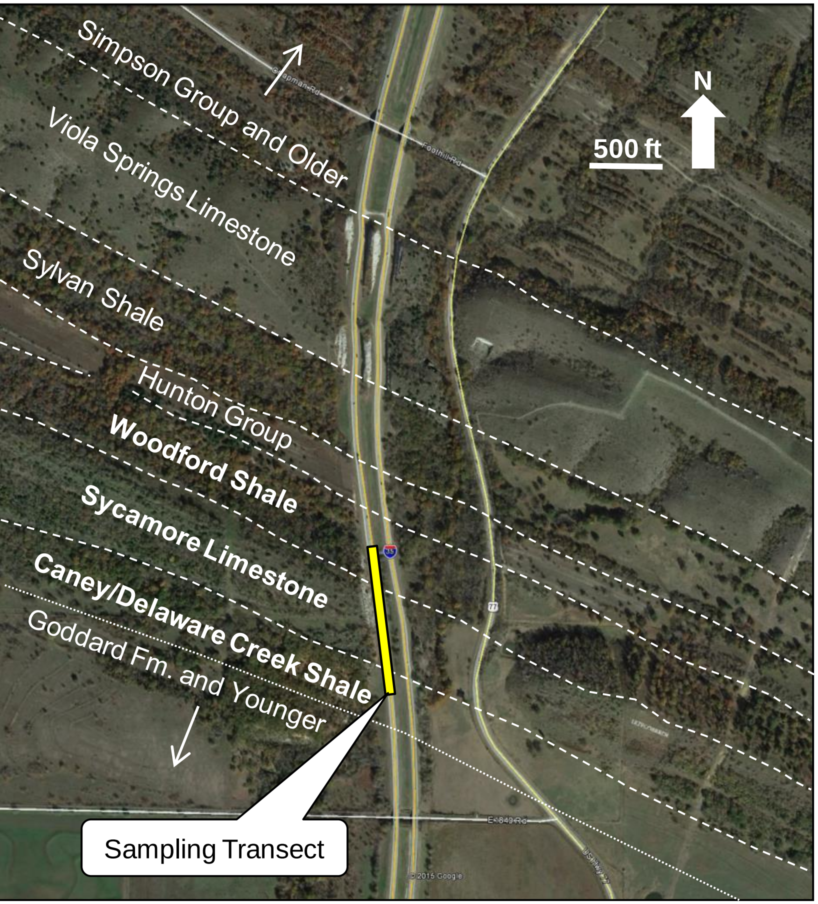
- Determine the relationships between lithology, molecular organic geochemistry characteristics and charge efficiencies simulated by hydrous pyrolysis.
  - > Relevance in regard to risking charge volumes in migrated oil prospects, and in risking storage in unconventional prospects.
- Evaluate the character of oils generated by hydrous pyrolysis relative to nearby produced Woodford Shale wells.
  - > Relevant to allocating production to different stratigraphic units and lithofacies.

Schematic of Hydrous Pyrolysis

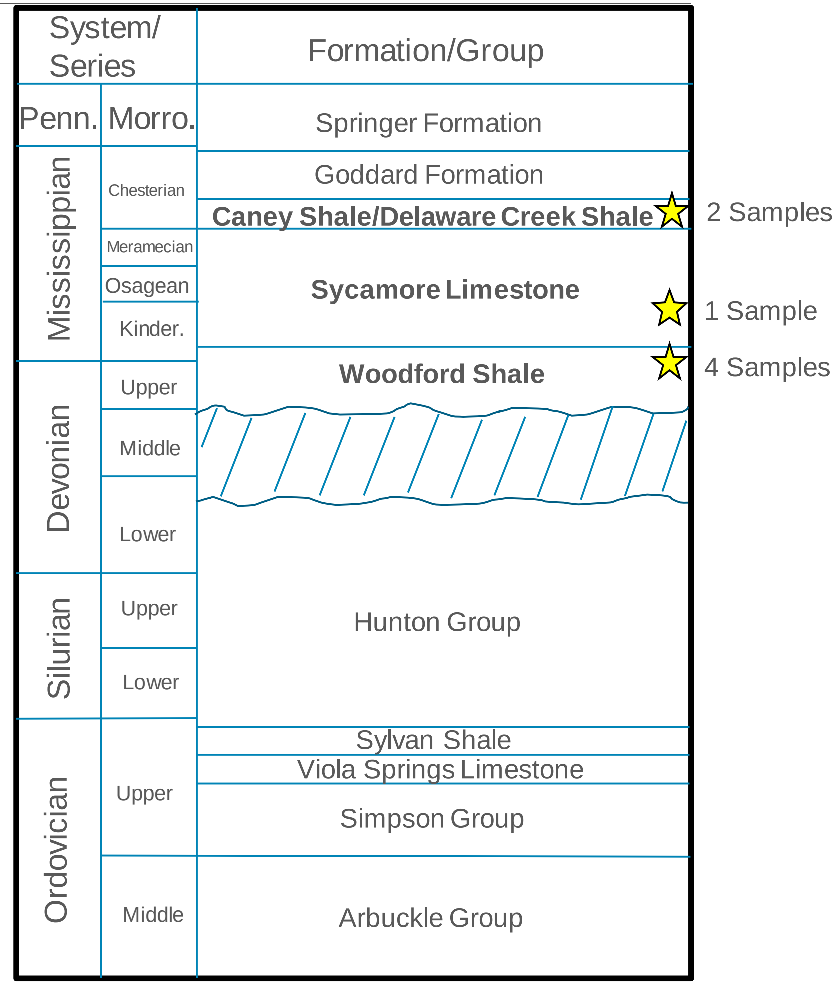


OUTCROP SAMPLES

N end of transect: 34º 21’ 7.95”N, 97º 8’ 55.40”W
S end of transect: 34º 20’ 58.95”N, 97º 8’ 53.64”W



- The outcrop samples were taken from the upper Woodford Shale, lower Sycamore Limestone and middle Caney/Delaware Creek Shale.
- Seven large samples were taken in total.



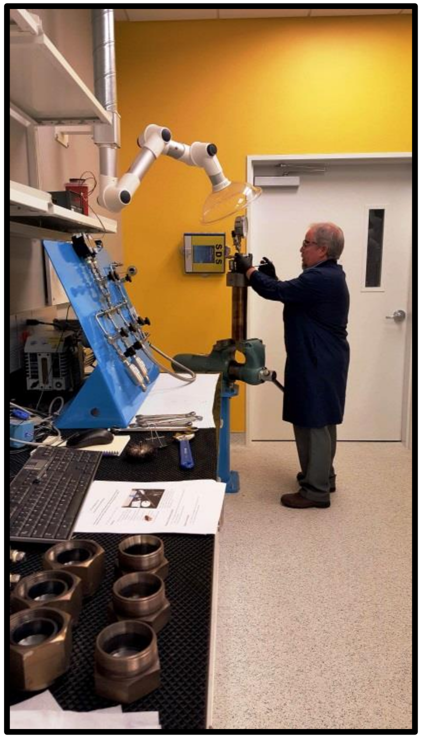
Abbreviated Stratigraphic Column for the Arbuckle Mountains adapted from Johnson and Cardott (1992).

LABORATORY TECHNIQUES USED

- Leco TOC
- Rock Eval 6 (RE6)
- X-Ray Diffraction (XRD)
- Gas Chromatography (GC)
- Coupled Gas Chromatography/Mass Spectrometry (GCMS)
- Swagelok and Parr vessel Hydrous Pyrolysis

- All analyses performed at the Chesapeake Reservoir Technology Center (CRTC)

Gas Chromatography



Hydrous Pyrolysis

Leco TOC

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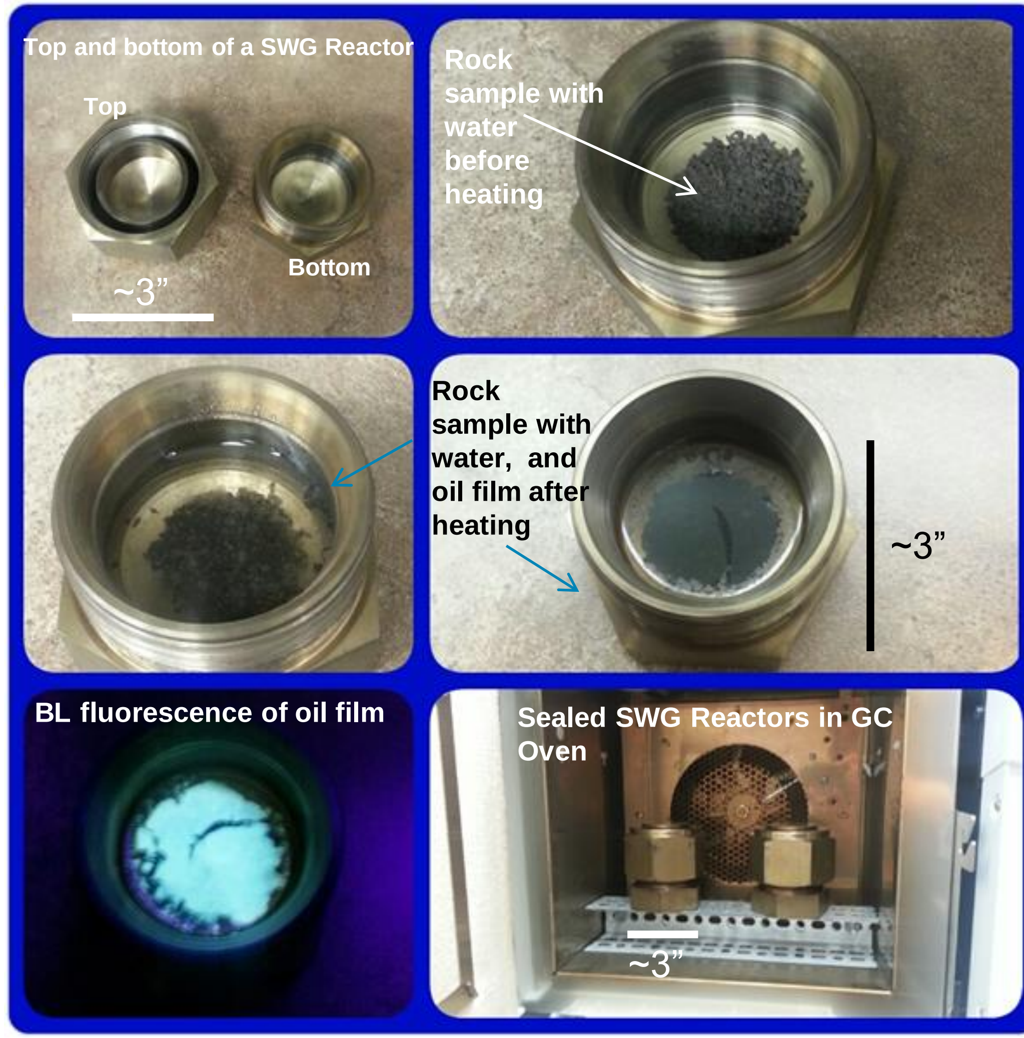
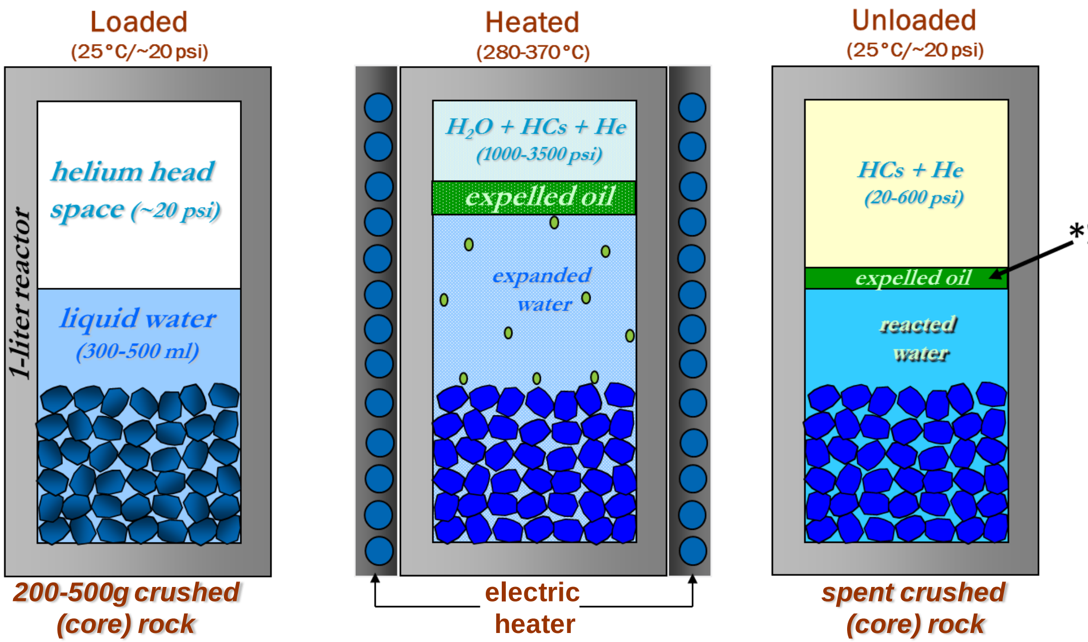
SWAGELOK REACTORS

- Swagelok (SWG) reactors are basically large sealed steel caps and plug nuts.
- We use these to conduct heating experiments on small aliquots of rock.
- These can be cuttings, core or outcrop mesh.
- We cover the samples with a calculated amount of water, seal the top and bottom of the reactor and heat isothermally at a desired temperature for a set time.
- In this pilot study we heated samples for 72 hours at 310 ^{o}C. This pushes our immature samples into the early oil window.
- Expelled/retained oil & bitumen and spent rock can be analyzed.

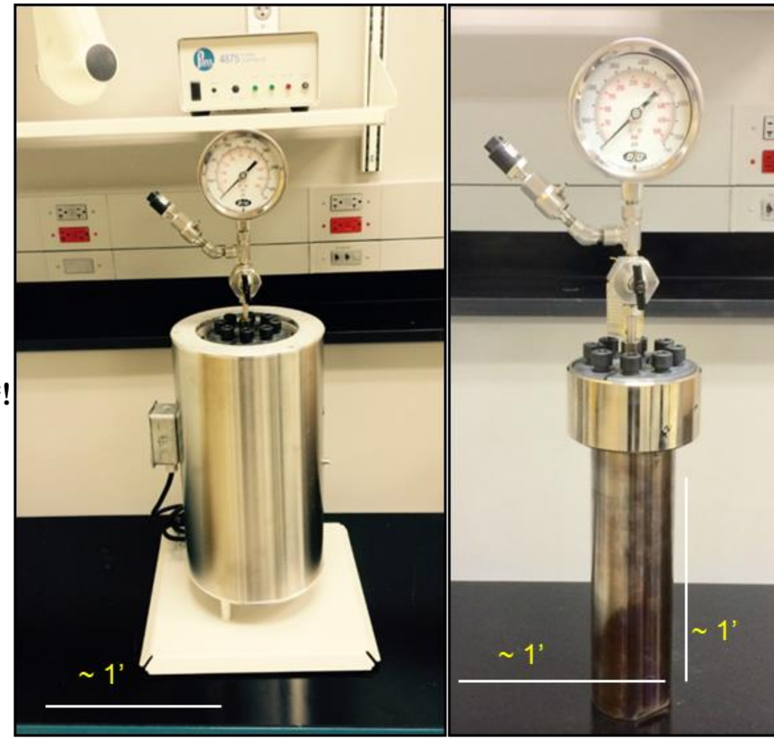


PARR VESSEL REACTORS

Schematic of Hydrous Pyrolysis



1L Parr Reactors



Heater+Reactor Reactor

- When, it becomes important to collect and characterize in detail the products of generation, much larger steel Parr reactors are used.
- With these vessels expelled/retained oil & gas, and spent rock can be characterized in detail.

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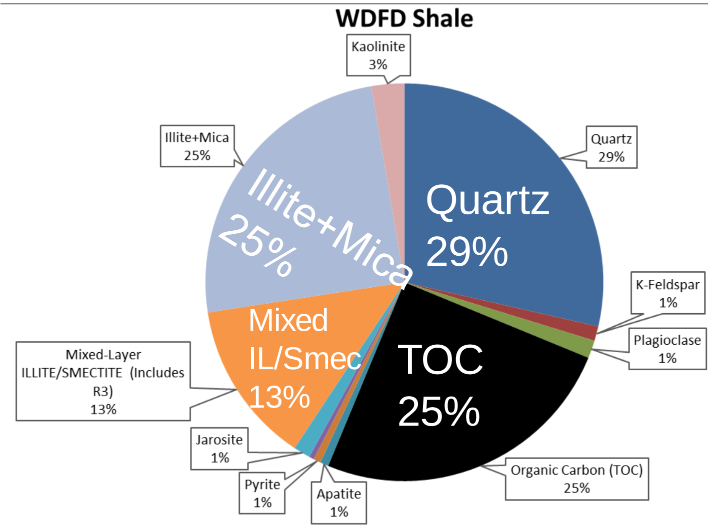
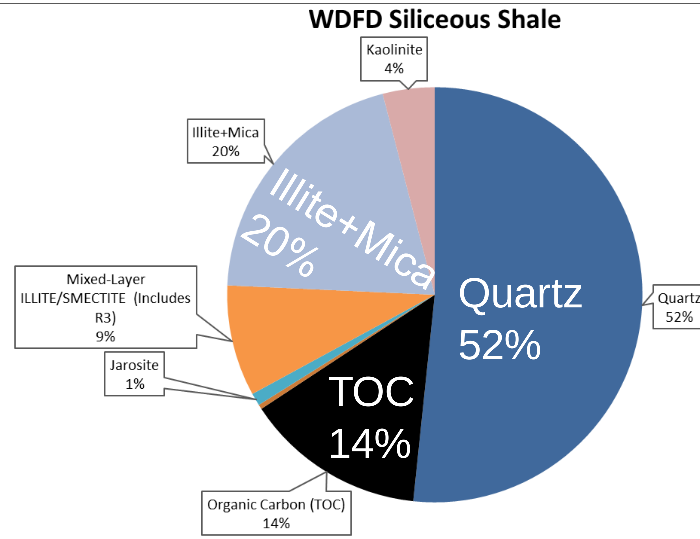
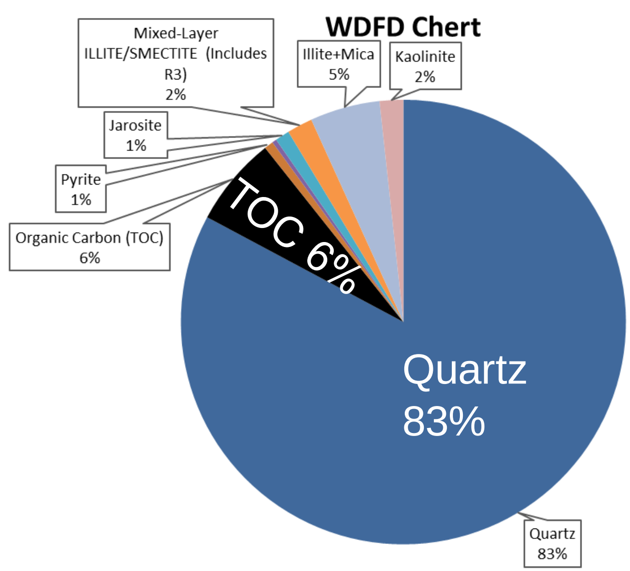
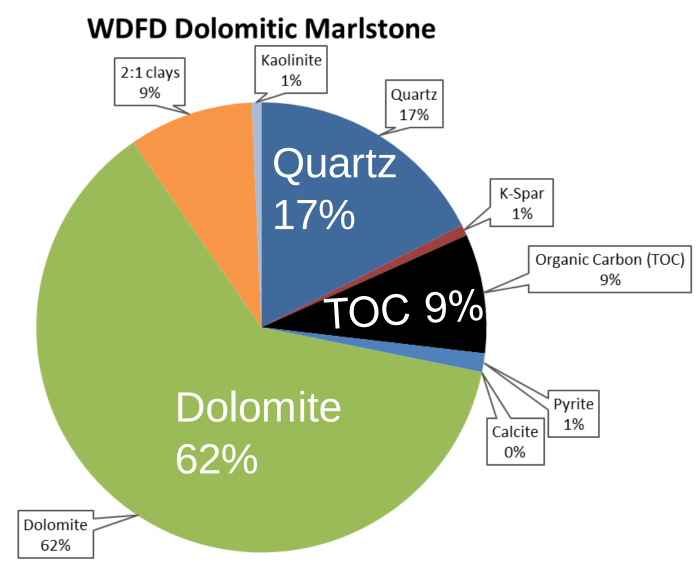
WOODFORD LITHOLOGIES AND THEIR BULK MINERALOGY (BY XRD)









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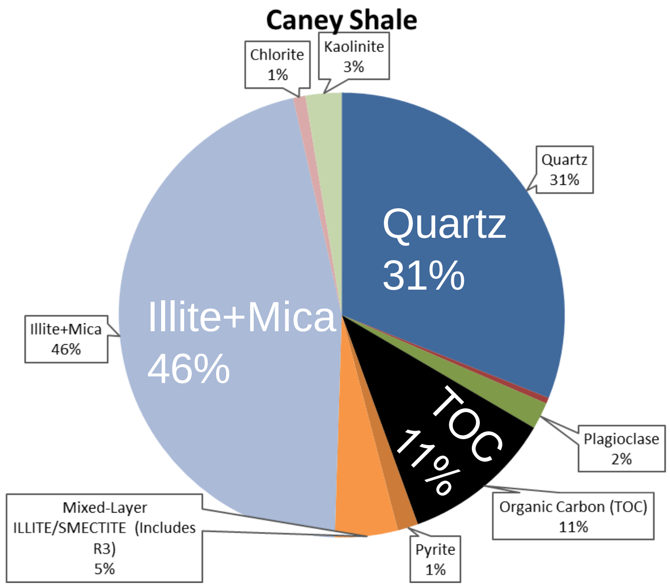
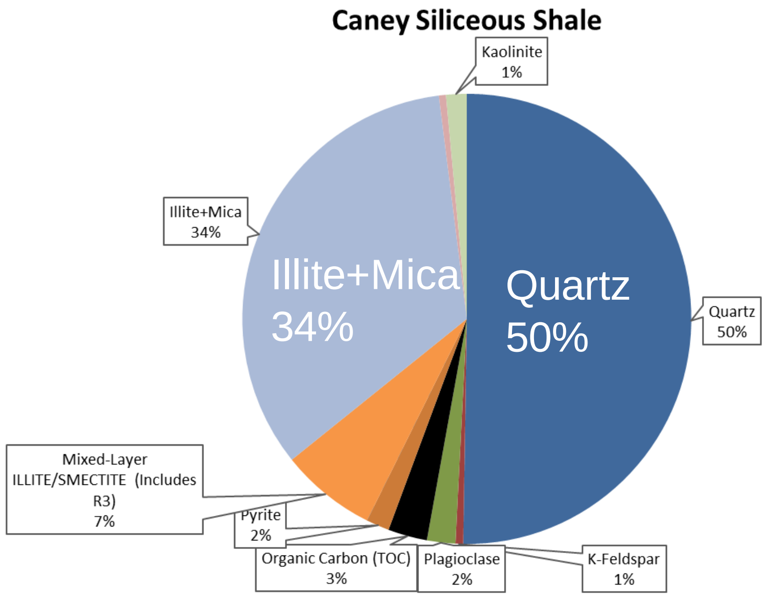
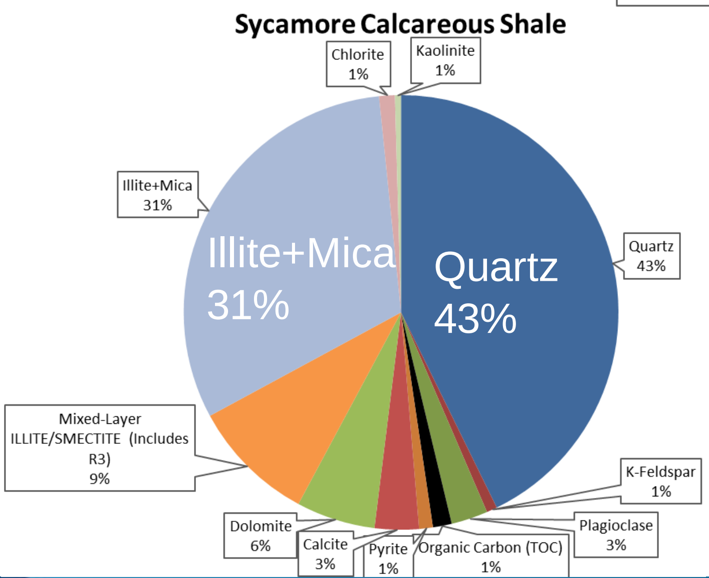
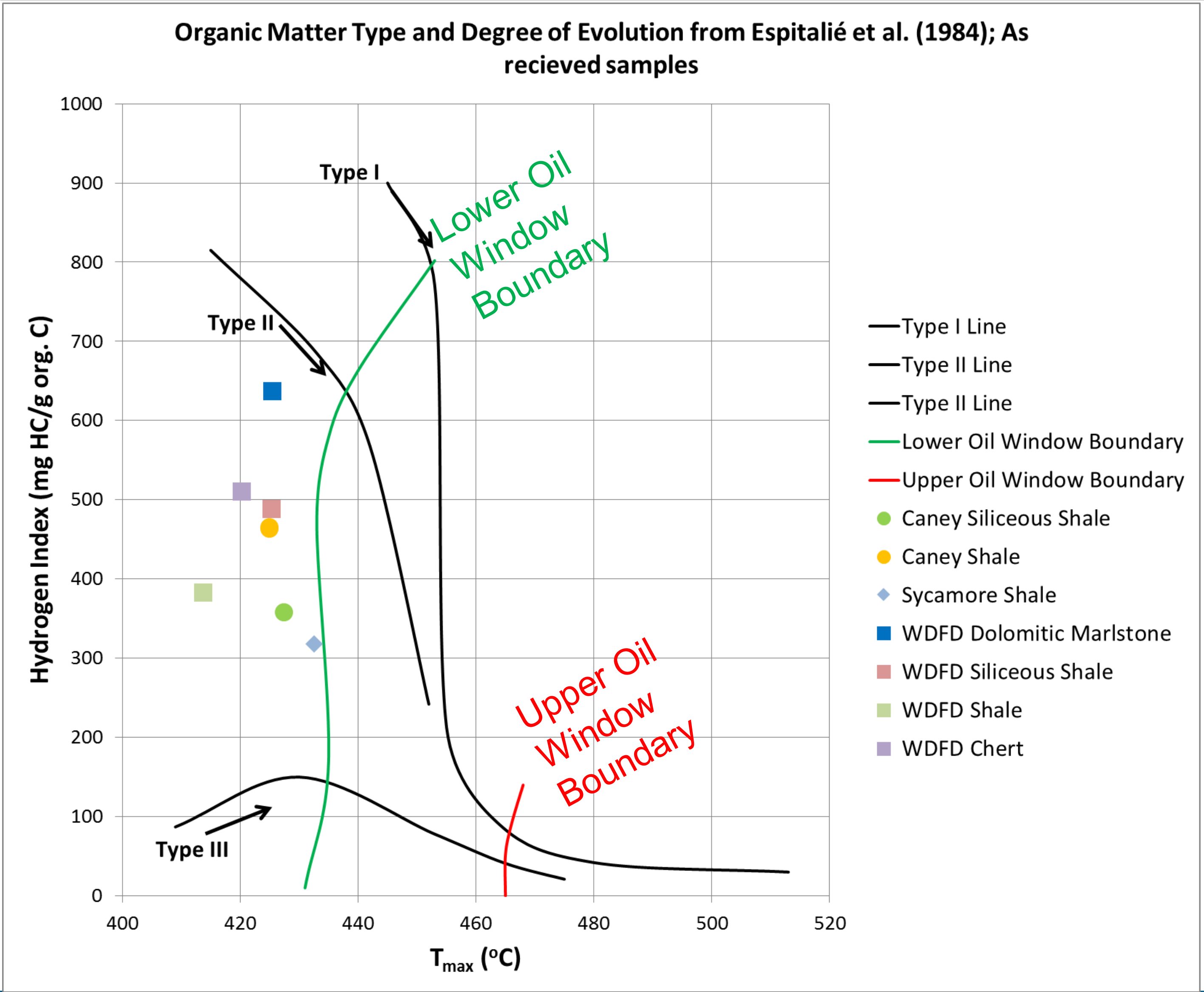
CANEY-SYCAMORE LITHOLOGIES AND THEIR BULK MINERALOGY (BY XRD)







LITHOLOGIES AND BULK ORGANIC GEOCHEMISTRY PROPERTIES (LECO TOC & ROCK EVAL 6)



- Woodford, Caney and (bonus) Sycamore organic-rich mudstone samples from the outcrop are in a pre-oil window state.
- T_{max} values are all below 435°C with the majority less than 430°C.
- Samples are oil-prone with kerogen types ranging from Type II to Type II-III.

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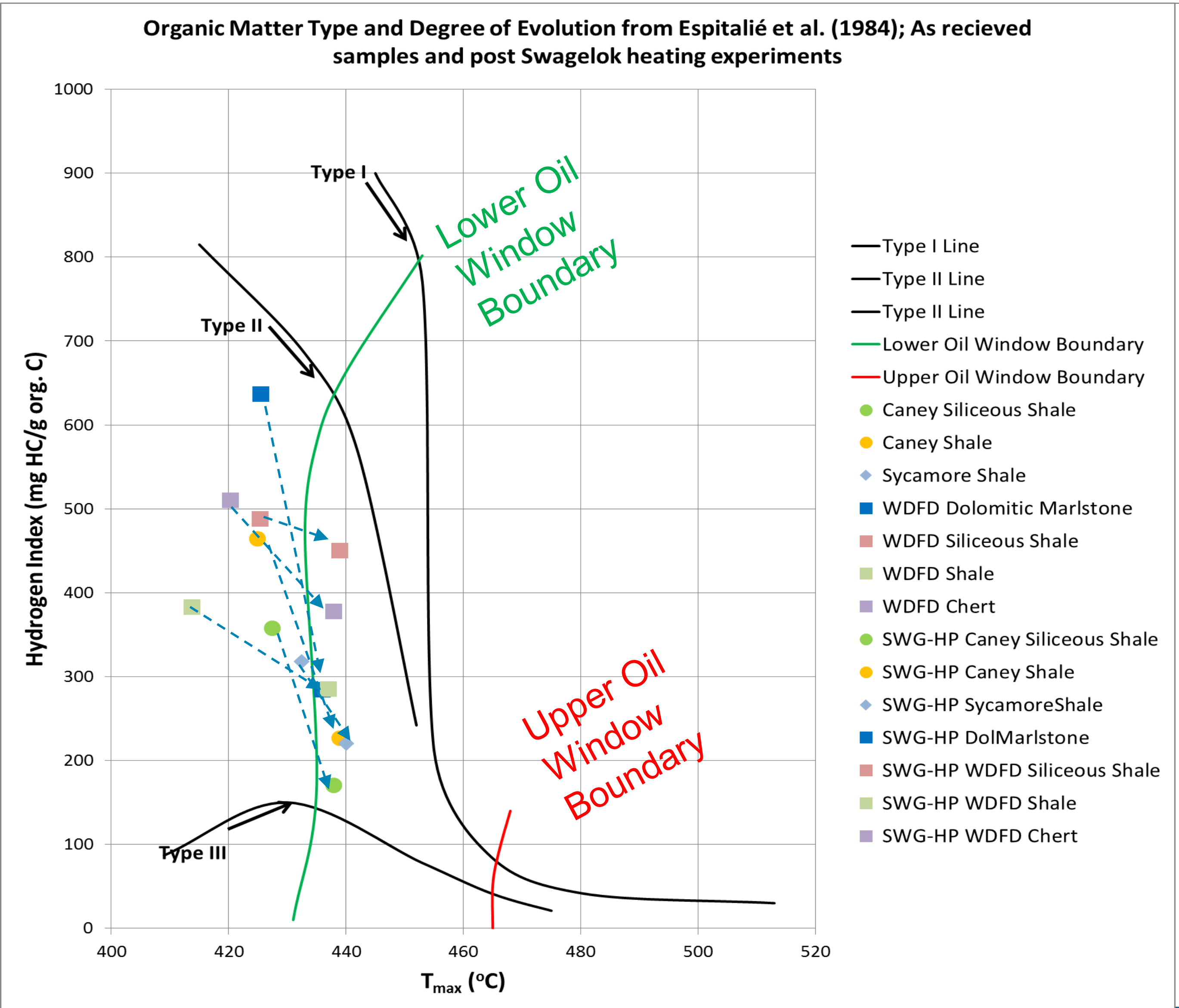
SWAGELOK REACTOR EXPERIMENTS FOR BIOMARKER TRACES (72 HOURS @ 310^{O}C)



- Swagelok reactor experiments are designed to push immature samples into the early oil window.
- After Swagelok heating experiments, sample Tmax values fall between 435ºC and 440ºC.
- This allows us to liberate more bitumen to oil and inspect oil window biomarker signatures.

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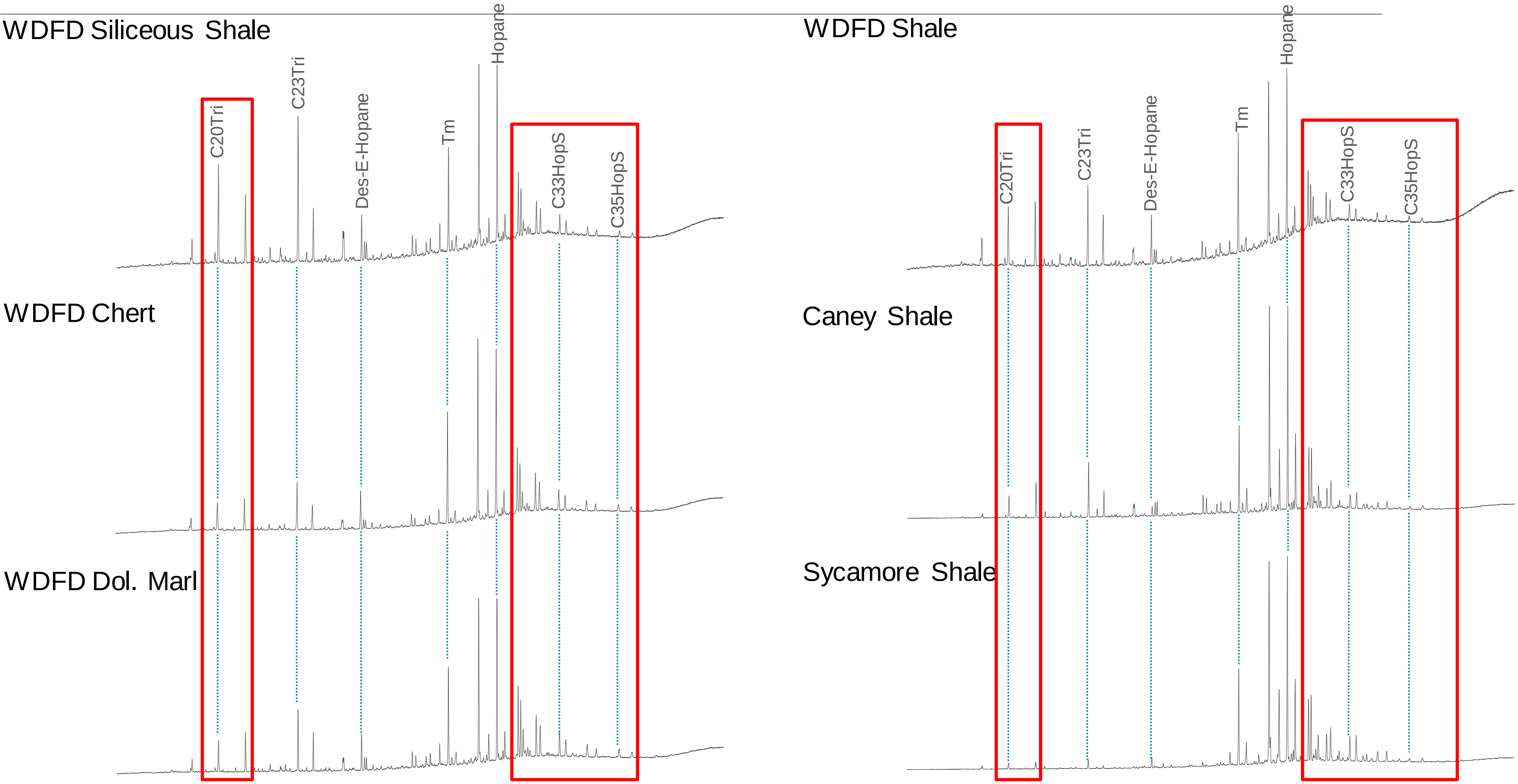
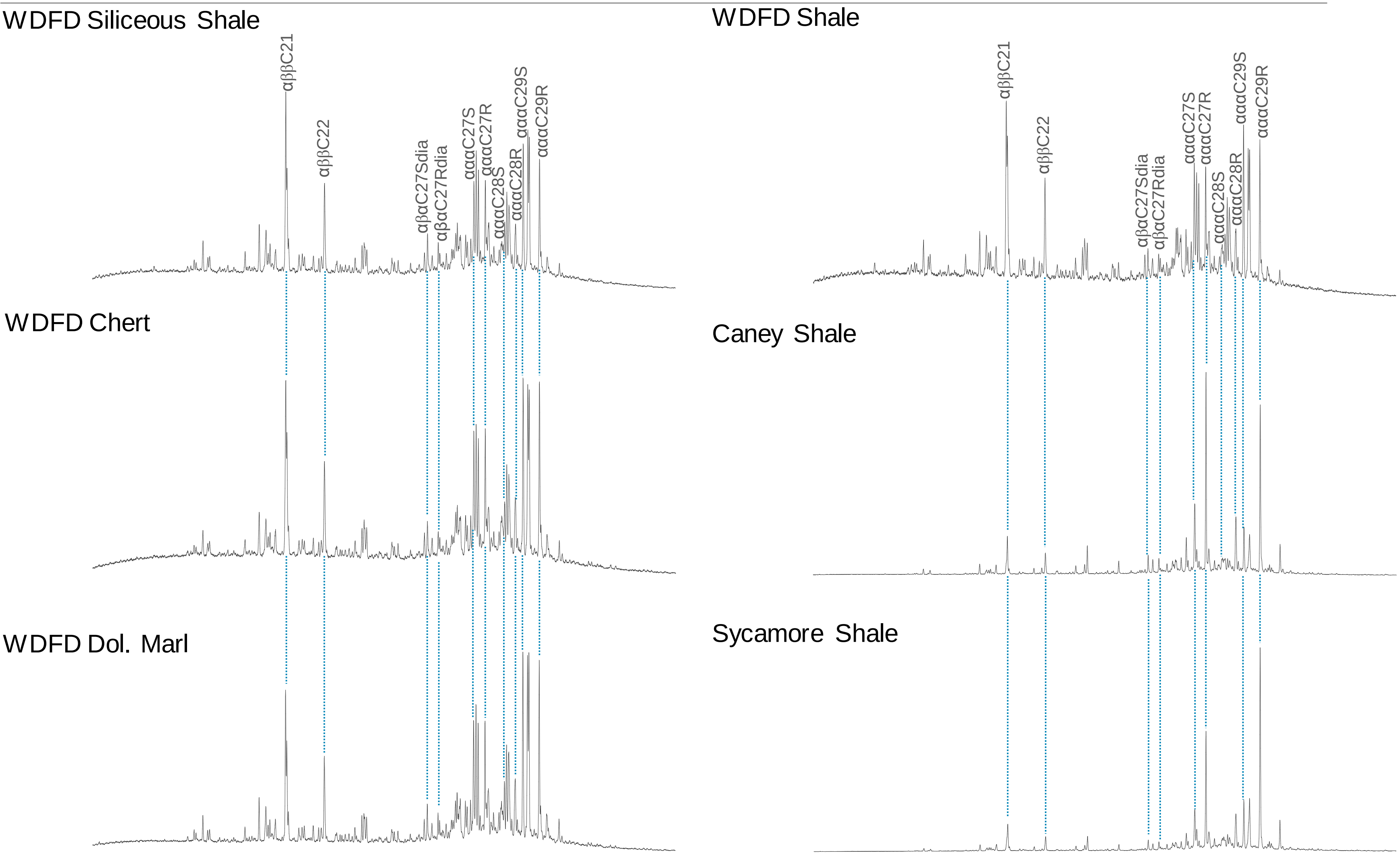
LOW MATURITY M/Z 191 BIOMARKER TRACES (SWAGELOK REACTORS; 72 HOURS @ 310^{O}C)



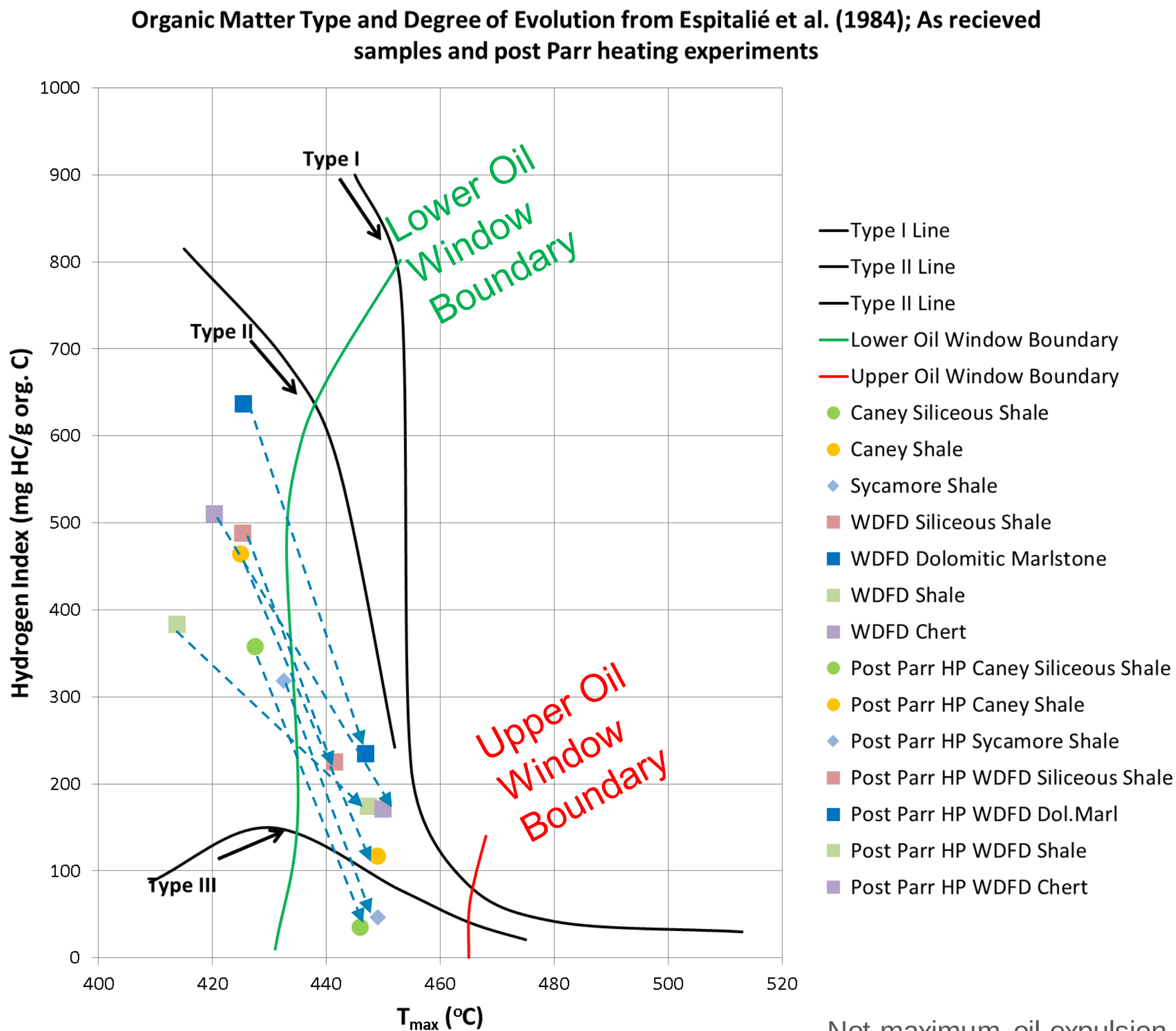
- Certain aspects of the m/z 191 are exaggerated due to relatively quick heating (e.g., norhopane/hopane, Ts/(Ts+Tm) and Des-E-Hopane/C_{26} Tricyclic Terpane).
- However, these can provide a preview for how biomarkers could look from the oil-phase of these rocks.
- Observing these it is clear that lithofacies and formations can be distinguished based upon tricyclic terpane and homohopane distributions.

LOW MATURITY M/Z 217 BIOMARKER TRACES (SWAGELOK REACTORS; 72 HOURS @ 310^{O}C)



- Big differences between formations with respect to sterane isomer dominance.
- Differences between lithofacies with respect to pregnane and homopregnane abundance.

PARR REACTOR HYDROUS PYROLYSIS EXPERIMENTS (24 HOURS @ 360°C)



Not maximum oil expulsion.

- As mentioned previously, Parr vessel HP allows us to recover both oil and gas phases.
- Here we take the samples into the mid-oil-window (T_{max} ~450 °C) to estimate charge efficiencies and quality of expelled petroleum.
- Fluids are generated here for general fingerprinting purposes and expelled GOR determination.

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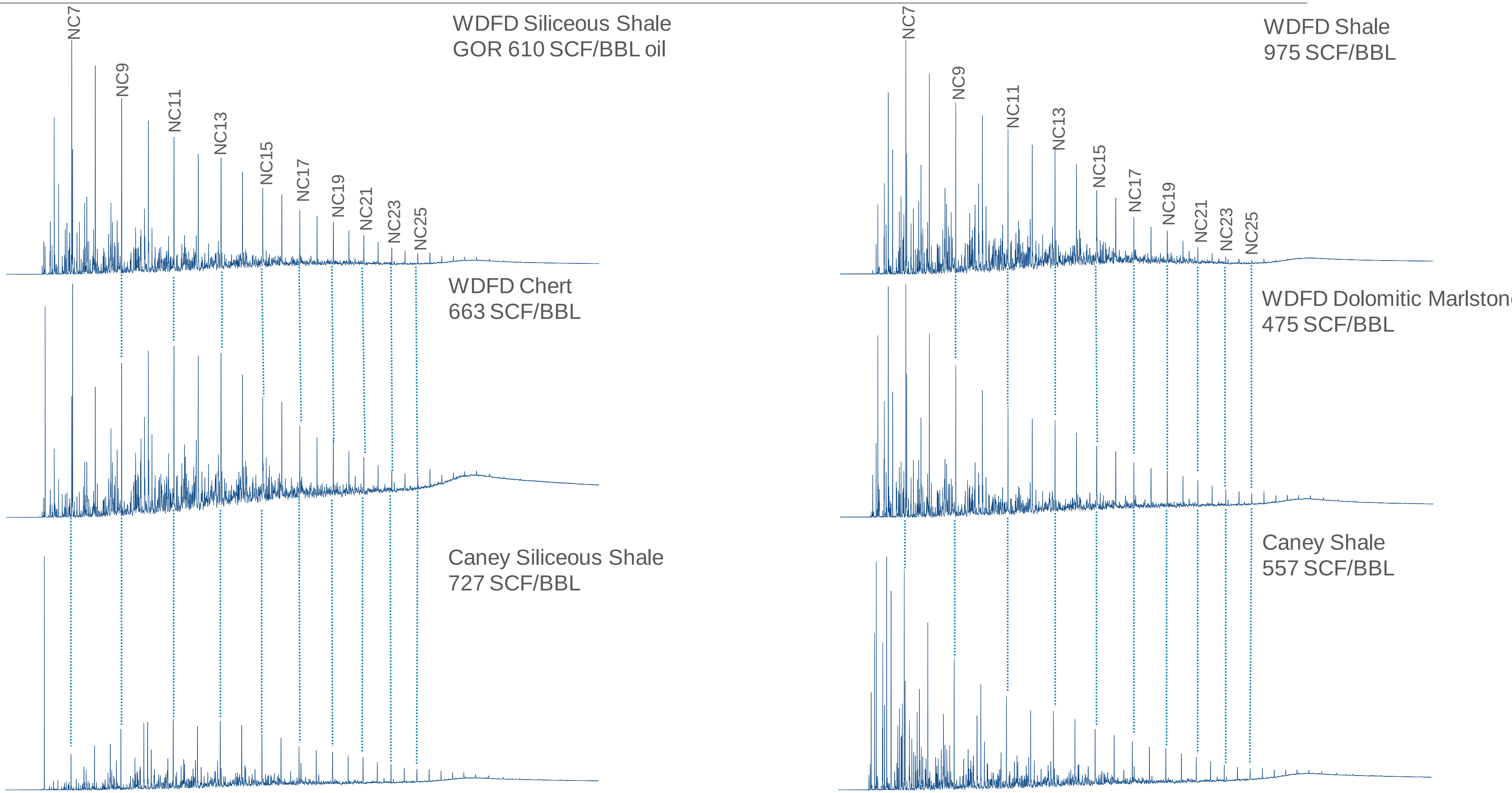
OIL TRACE AND GOR BY LITHOLOGY



Standard conditions 15ºC and 1 atm.
Average oil API gravity of 25º assumed.

No GC trace on CHP-24 (Sycamore Shale)

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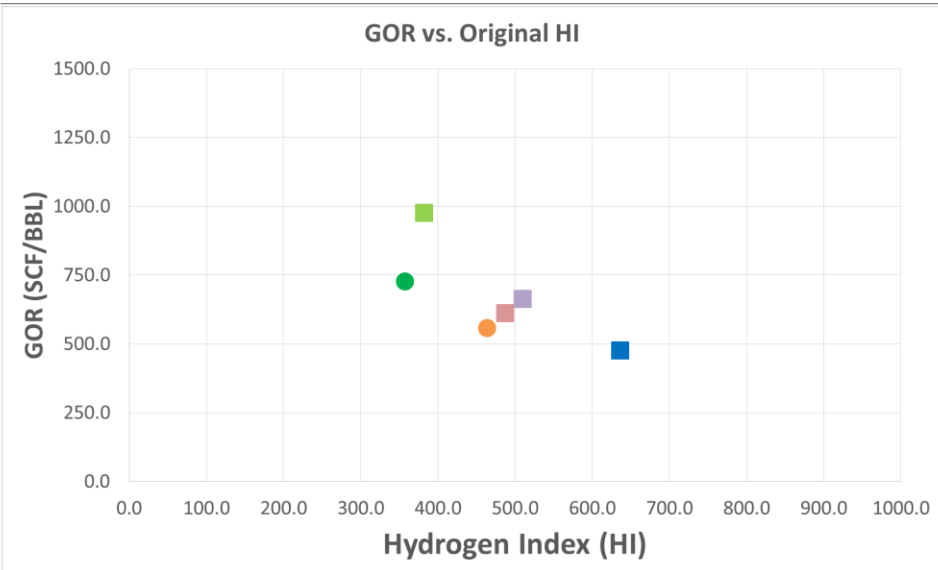
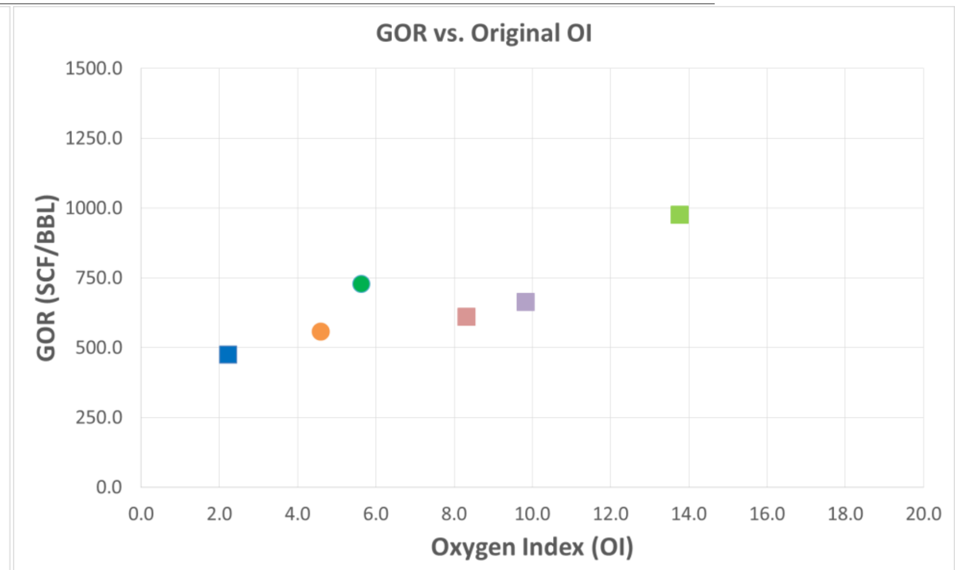
EXPELLED GOR VALUES COMPARED TO ORIGINAL RE6 PARAMETERS





- The measured GOR values for the expelled fluids of the different lithofacies do correlate significantly with original-organic-matter characteristics.
- Here, as we might expect, the GOR values correlate inversely and positively with the HI and OI respectively.
- Linear regressions through these points produce a 0.58 and 0.75 R^2 for GOR vs. HI and GOR vs. OI respectively.

■ WDFD Dolomitic Marl
■ WDFD Siliceous Shale
■ WDFD Shale
■ WDFD Chert
● Caney Siliceous Shale
● Caney Shale

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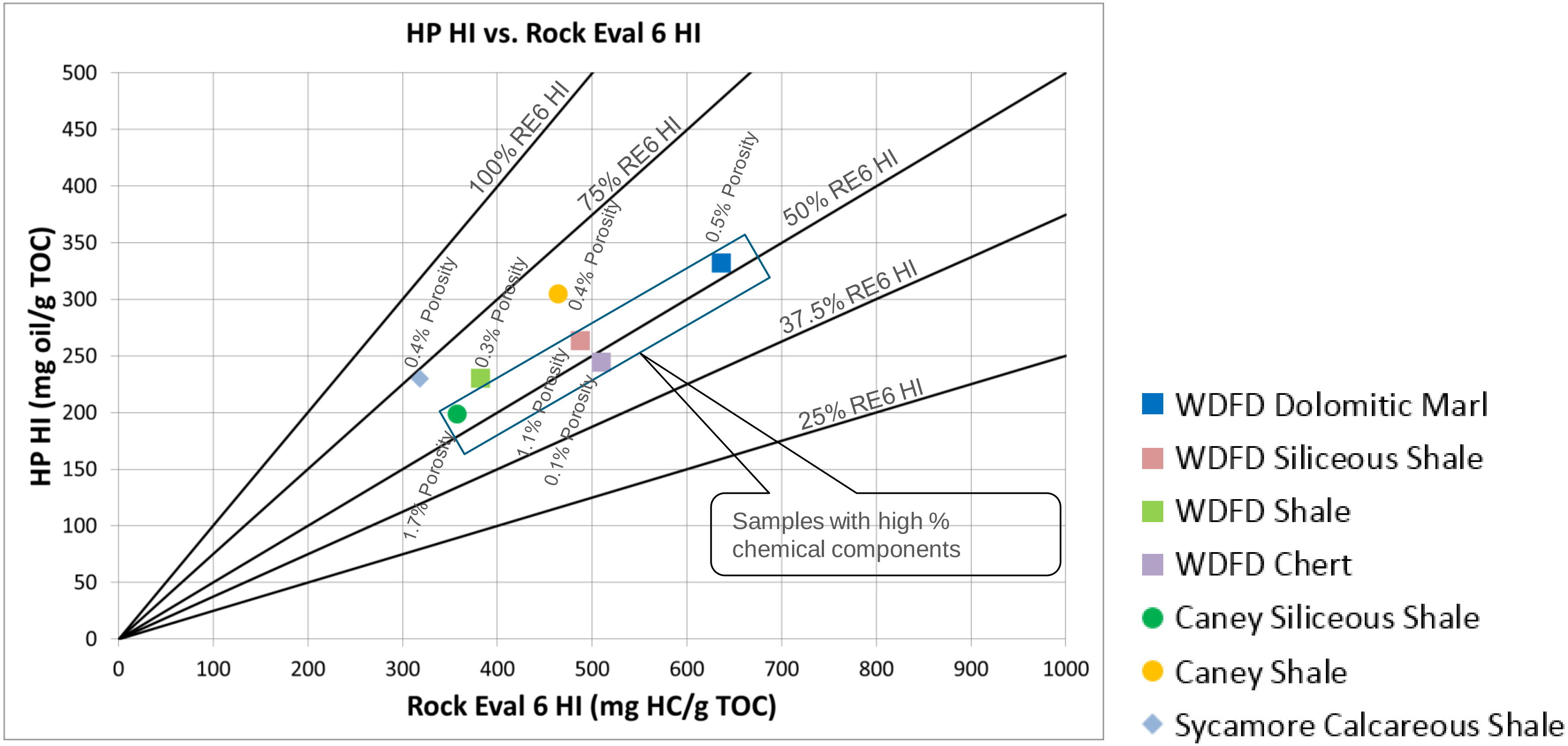
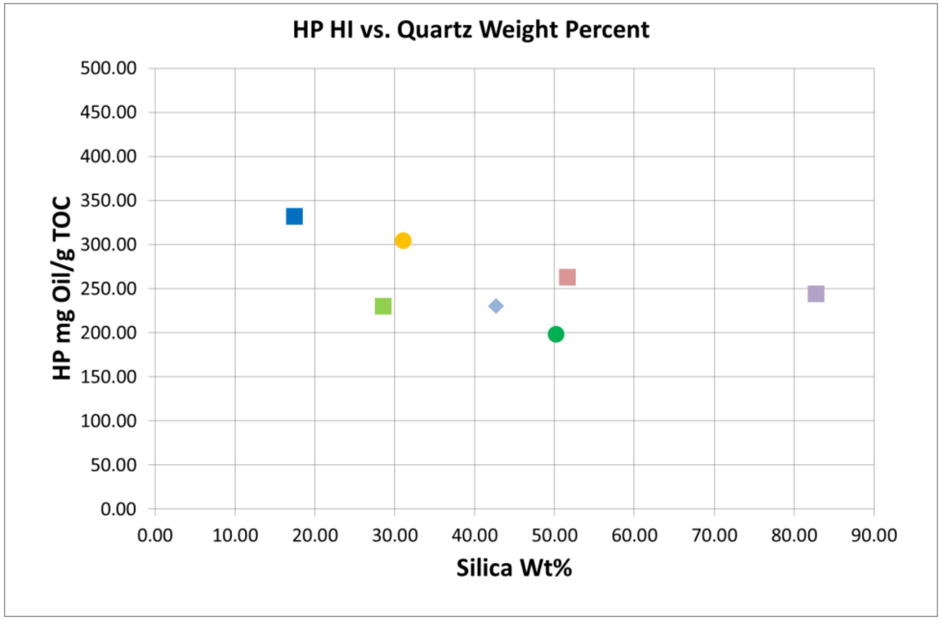
EXPULSION EFFICIENCY RELATIONSHIP TO ORIGINAL HI

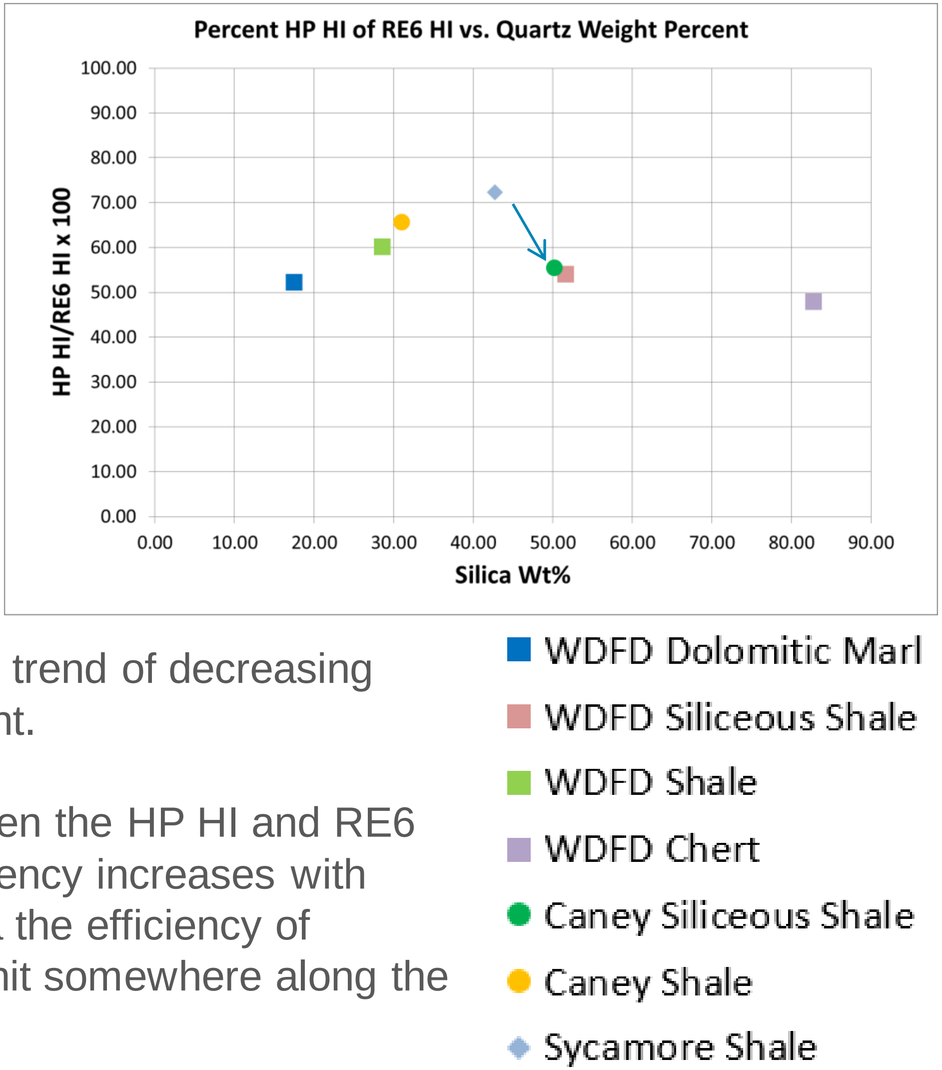


Lewan (1993)

- The lithologies with high proportions of chemical sedimentary components (silica and dolomite) have the expulsion efficiencies of approximately half the original Rock Eval 6 HI.
- Lithologies with a lower proportion of chemical sediments tend to have better expulsion efficiencies, approaching but not quite attaining 75% of the Rock Eval 6 HI.
- Pre-heating porosity does not control expulsion efficiency in this case.

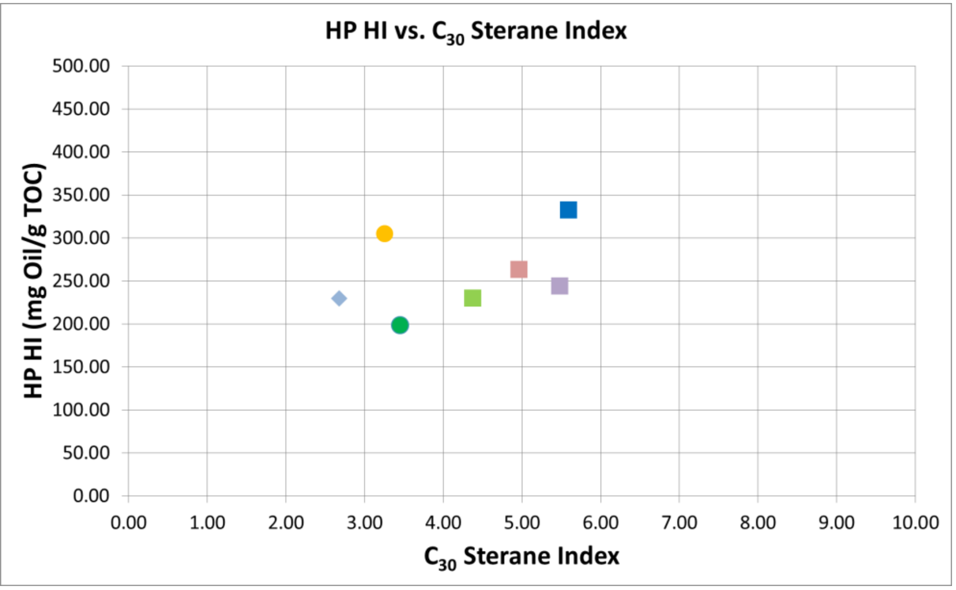
EXPULSION EFFICIENCY RELATIONSHIP TO MINERALOGY

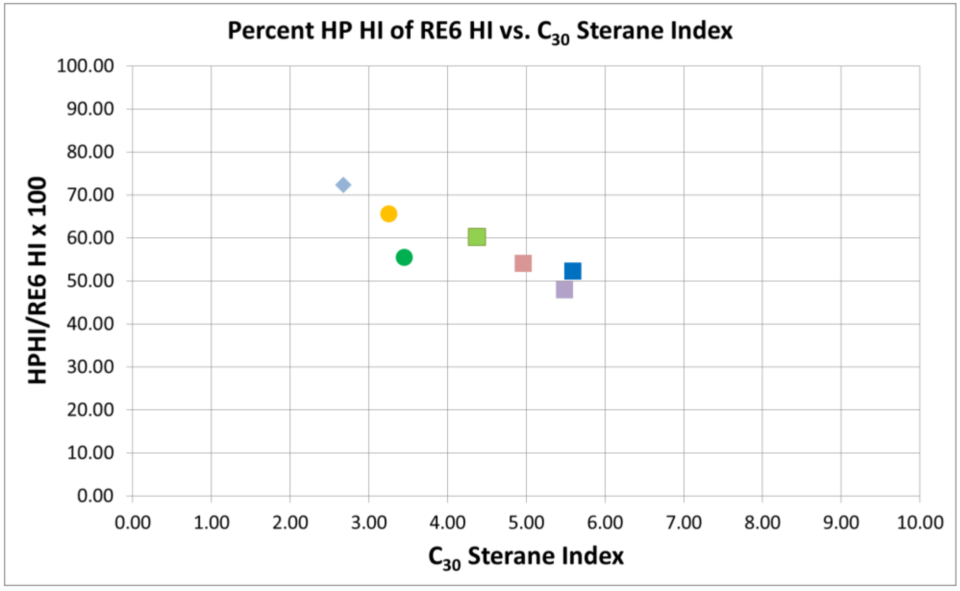




- In terms of the straight HP HI there is a general trend of decreasing expulsion efficiency with increasing silica content.
- When efficiency is quantified as the ratio between the HP HI and RE6 HI a more striking pattern emerges. While efficiency increases with increasing silica at values lower than 45% silica the efficiency of expulsion with respect original RE6 HI takes a hit somewhere along the continuum of 45-50 wt% silica.

EXPULSION EFFICIENCY RELATIONSHIP TO BIOMARKER PARAMETERS

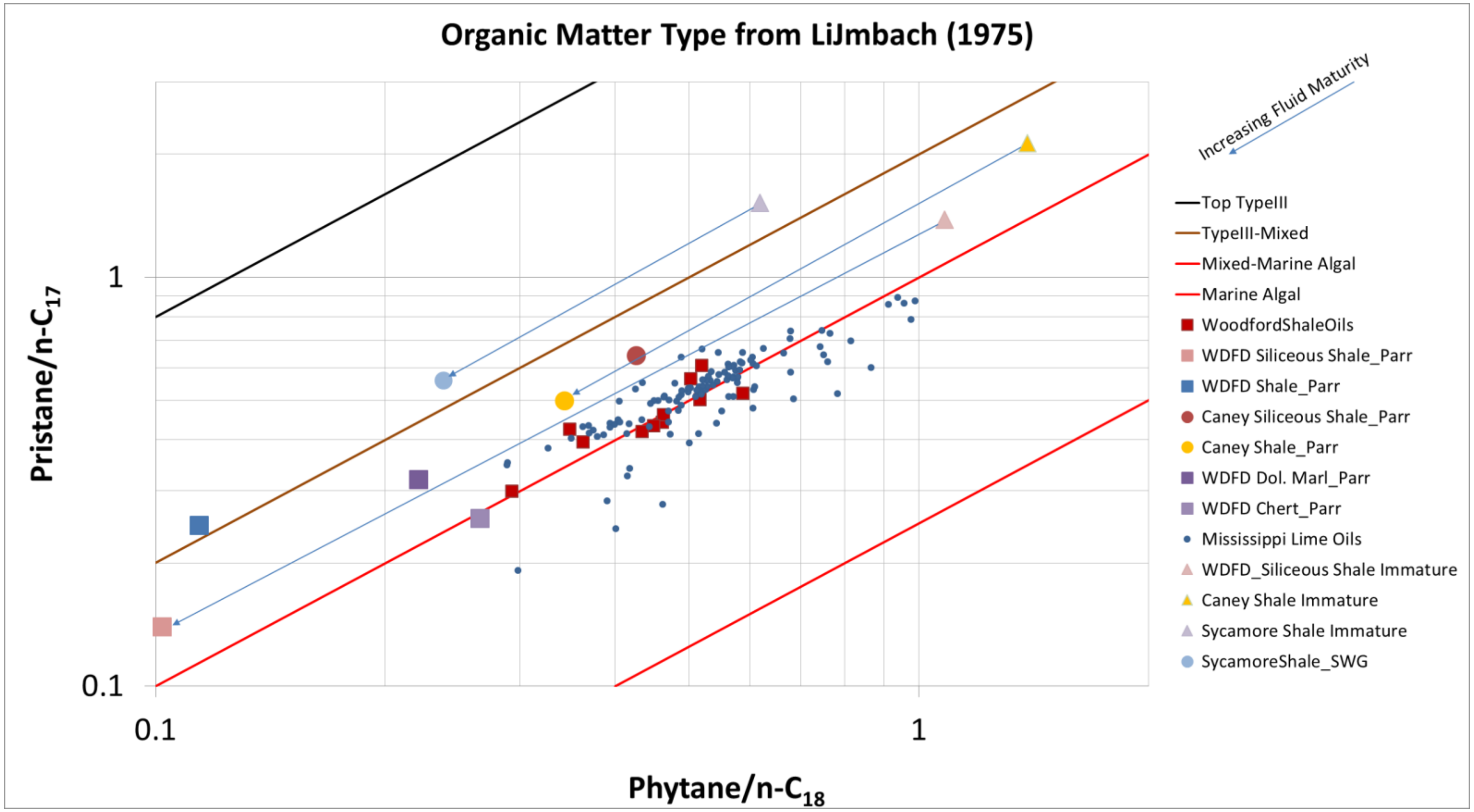




- Interestingly there is a generally positive correlation between the HP HI of samples and the C_{30} index.
- However, the ratio of the HP HI to the RE6 HI vs. the index has a strong negative correlation.
- Relationships such as these, once established may allow improved volumetric risking of hydrocarbon charge where only biomarker data are available.

WDFD Dolomitic Marl
WDFD Siliceous Shale
WDFD Shale
WDFD Chert
Caney Siliceous Shale
Caney Shale
Sycamore Shale

RELATIONSHIP OF HP PRODUCTS TO MIDCONTINENT OILS



- The GC data from the Parr experiments can also be used to attempt linkage between particular source facies and oils procured in the field.
- Here we use a conventional Pristane/n-C_{17} vs. Phytane/n-C_{18} to attempt linkage.
- Most Woodford produced oils and Woodford sourced Mississippi Lime oils fall along a trend which implies that siliceous shale and chert beds source the bulk of the fluids produced or expelled from the Woodford Shale.

KEY TAKE AWAY POINTS FROM PILOT STUDY

- Hydrous pyrolysis is a technique for simulating oil and gas generation/expulsion from source rock samples.

- The simulated efficiency of generation for source-rocks can have meaningful correlations with biomarker and mineralogy data. If these trends can be established for a given system they offer the potential to improve volumetric forecasting where physical rock samples are limited.

- Original porosities in immature samples do not always have a clear impact on expulsion efficiencies in source rocks.

- GOR is demonstrated to be significantly linked to original hydrogen index and oxygen index in these samples.

- Generated HP oils and gases can be used to link source rocks to oils and gases encountered in the field and may be able to determine the parentage of fluids at a lithofacies level. This could be a very useful technology for fluid allocation problems.

ACKNOWLEDGEMENTS

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- We thank Chesapeake Energy for allowing us to pursue this research and present these data and findings.

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