[PS]Direct Kerogen Characterization of Marcellus Shale Collected from Marcellus Shale Energy and Environment Laboratory*

Vikas Agrawal[1] and Shikha Sharma[2]

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Abstract

Kerogen is an insoluble macromolecule, formed by degradation and condensation of different biomolecules. It is the source of all hydrocarbon generated from the organic rich shales. Despite its importance, it still remains to be one of the least studied components of shales. Previous work has indicated that shale with similar kerogen type and reservoir parameters such as thermal maturity, produces different amounts and type of hydrocarbons (HCs). This indicates that chemical structure and composition of kerogen play a major role in HC generation and production. To determine the sweet spots of HC extraction and increase the efficiency of HC production there is a need to better characterize chemical properties of kerogen at the molecular level.

We extracted kerogen from core samples collected from Mahantango and different zones of Marcellus Shale at the Marcellus Shale Energy and Environment Laboratory (MSEEL) site in Morgantown, West Virginia. Direct kerogen analytical techniques such as XPS (X-ray photoelectron spectroscopy), ATR-FTIR (Attenuated total reflection-Fourier transform infrared spectroscopy), 13C solid state NMR (Nuclear magnetic resonance) and Raman spectroscopy were used to determine the molecular structure of kerogen. Our results indicate that kerogen from all samples are mainly composed of highly aromatized carbon with minor amount of aliphatic carbon chains. The aromatic carbon fraction was dominated by aromatic bridgeheads carbon atoms and protonated aromatic carbon atoms indicating these carbon chains are refractory in nature and does not contribute significantly in hydrocarbon generation potential. Additionally, only minor amount of carbon chains such as such as mobile and immobile alkyl, methoxyl and alkyl-substituted aromatic carbons were observed, indicating that these functional groups are more prone to thermal degradation and have higher hydrocarbons generating potential.

Direct Kerogen characterization of Marcellus shale collected from Marcellus Shale Energy and Environment Laboratory

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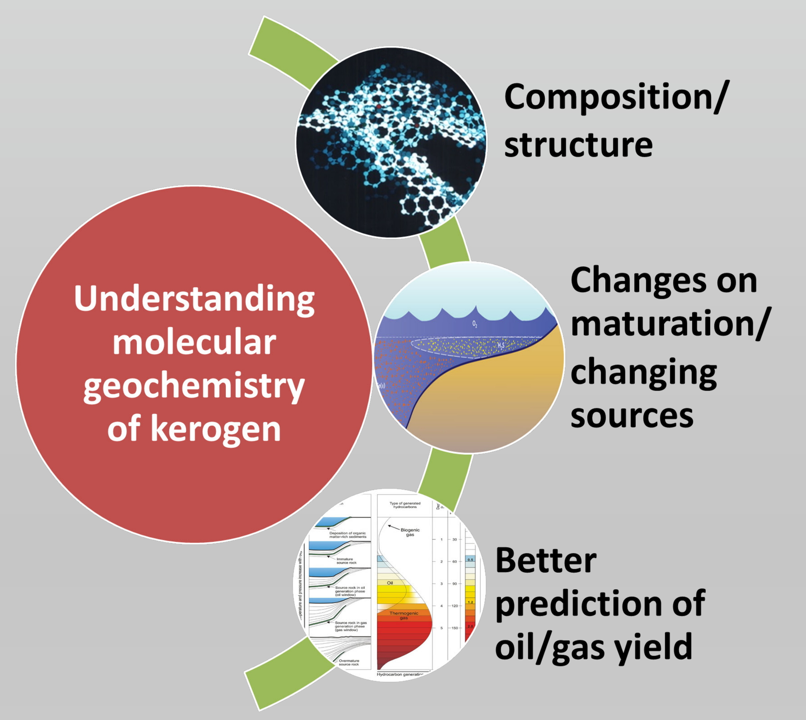
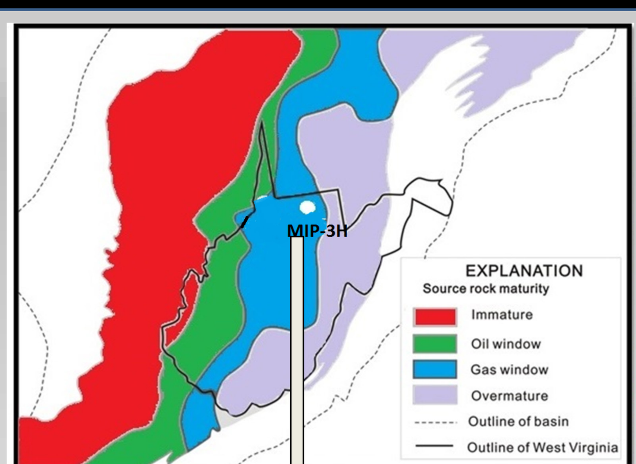
Objectives

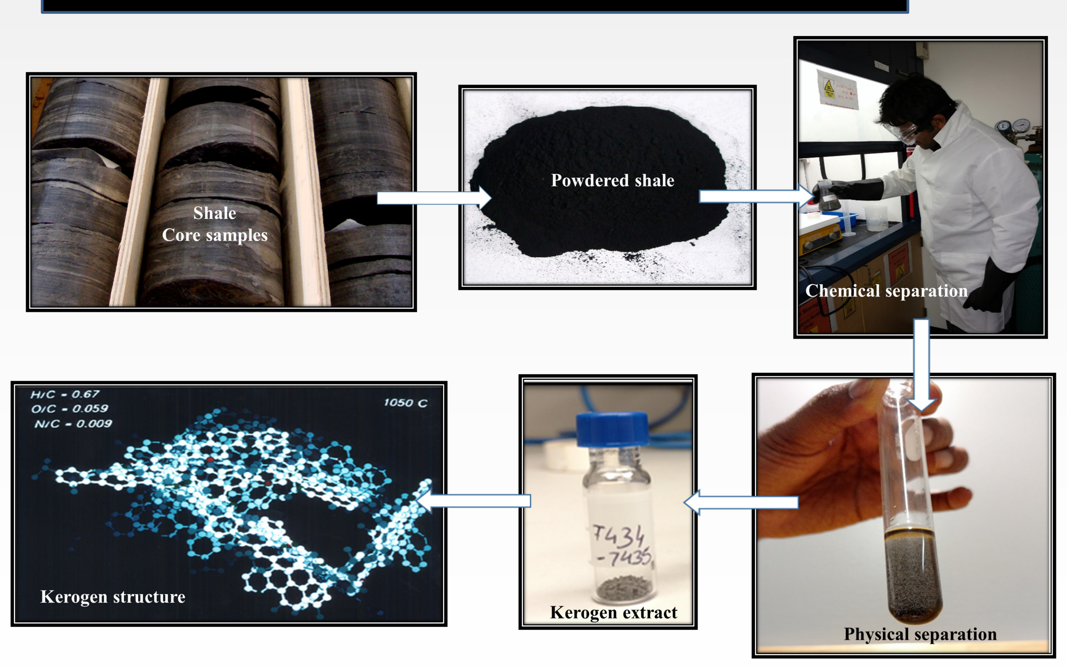


Sampling Area

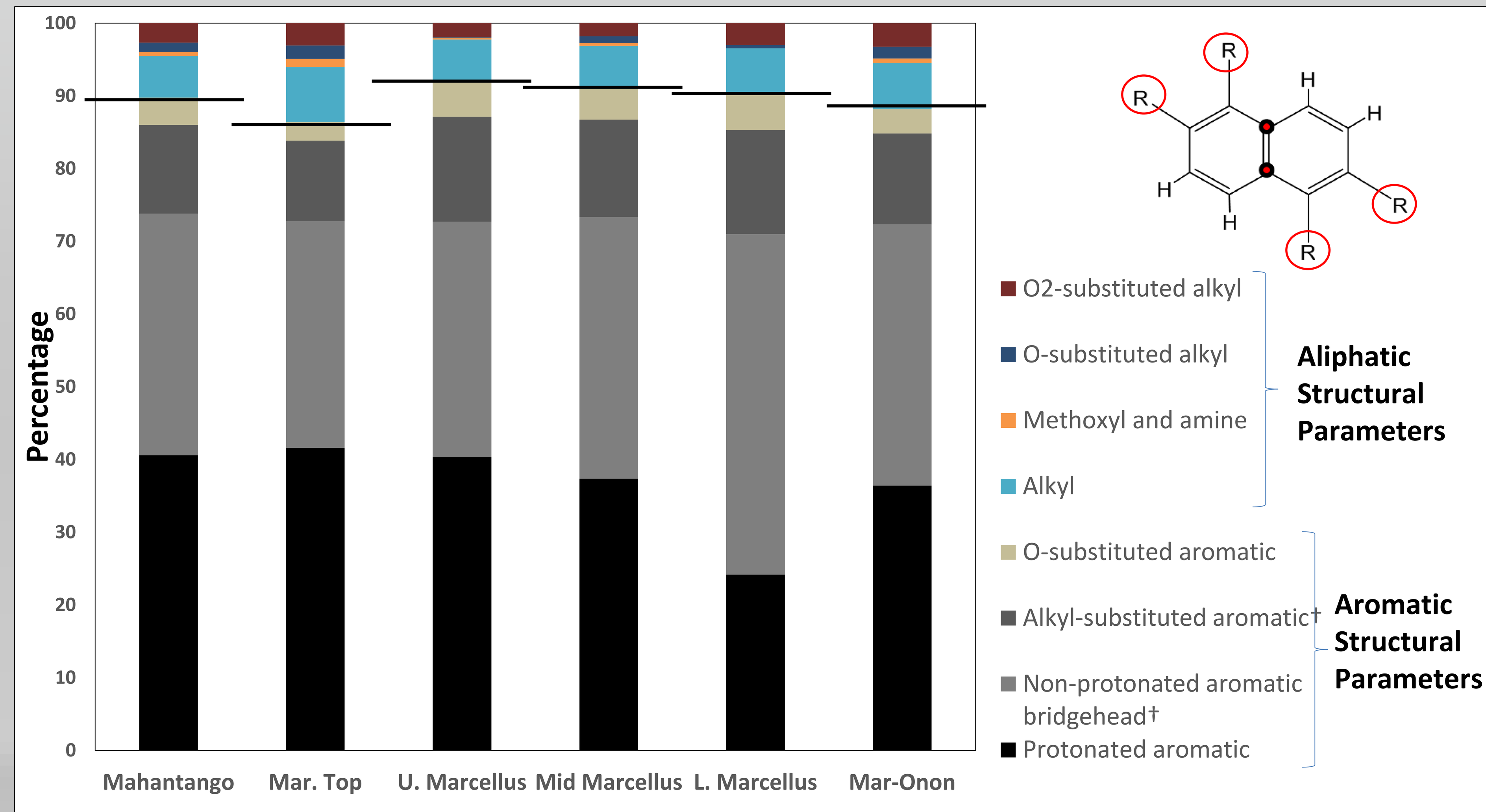


The Marcellus shale underlies 90,000 square miles of NY, PA, and WV with 65 trillion cubic feet of proven natural gas reserves (USEIA)

Methods



13C solid state NMR analysis



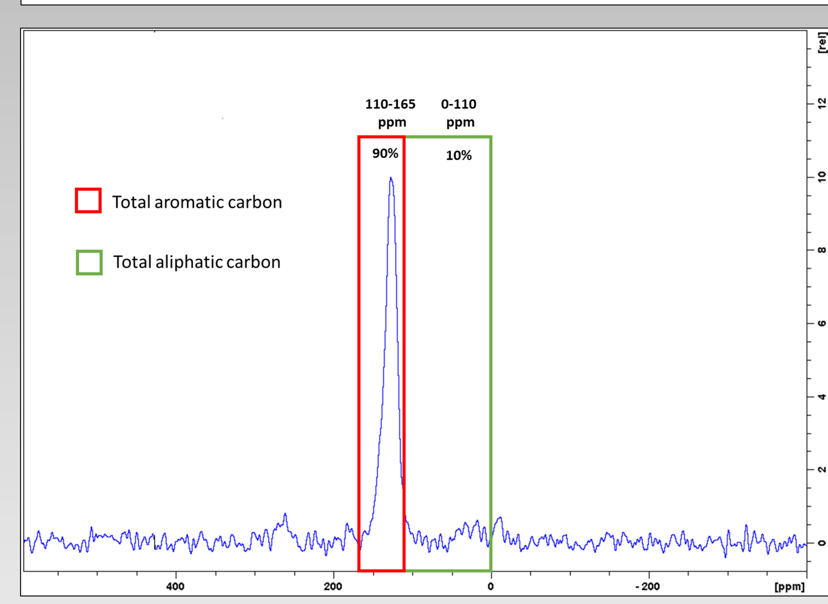


Figure 1. Multiple CP (cross polarization) ^{13}C NMR spectra of kerogen sample from lower Marcellus formation. Peak area distribution shows kerogen contains 10% aliphatic carbon chains and 90% aromatic carbon chains.

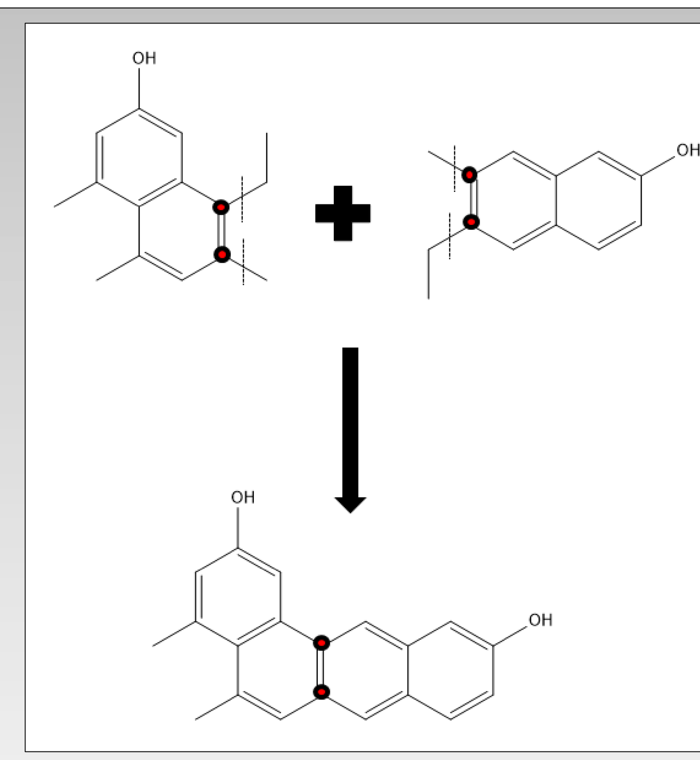


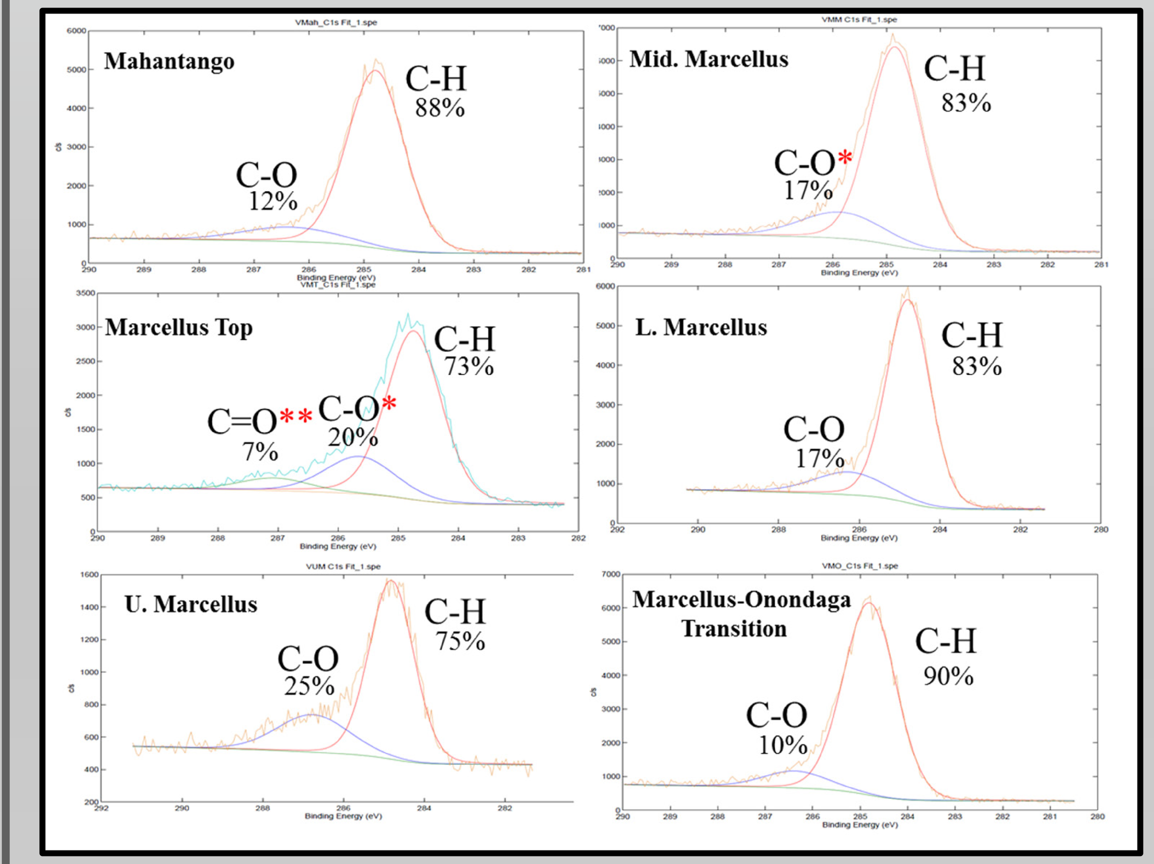
Figure 2. Reaction mechanism of kerogen cracking in Lower Marcellus. Aliphatic chains breakdown to form free radical aromatic carbon. The aromatic chains recondense to increase the amount of bridgehead carbon atoms .

The kerogen from Mahantango and different zones of Marcellus is dominated by aromatic carbon ranging from 86% to 92% and there appears to be no significant variation in the total percentage of aromatic vs aliphatic carbon in different units.

Analysis of fractions of different functional groups within the aliphatic and aromatic fractions show some differences.

Lower Marcellus has higher fraction of non-protonated aromatic bridgehead and lower fraction of protonated aromatic carbons as compared to other units. This is probably because lower Marcellus received higher influx of marine organic matter during deposition. Marine organic matter are rich in aliphatic carbon chains. These aliphatic chains on maturation breaks down to form free radicals that recondense to form bridgehead carbon atoms (Fig. 2)

XPS analysis



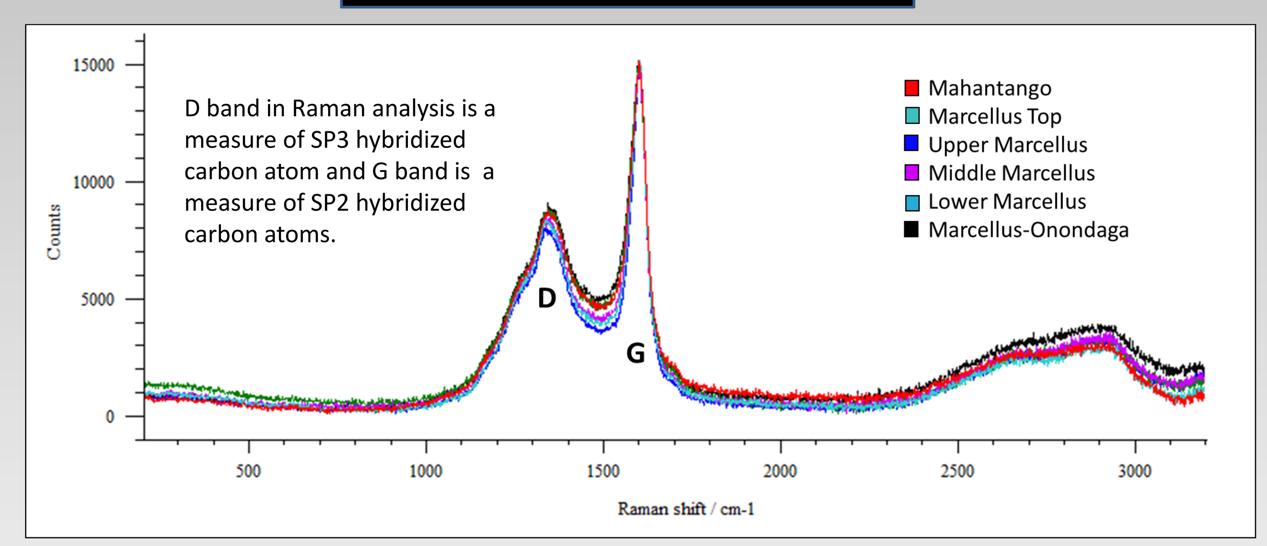
XPS Carbon (1s) Spectra of kerogen and curve resolution into different components

Majority of the bonds present in kerogen derived from all units are C-H type, followed by C-O, then by C=O

Presence of C-O in all kerogen samples indicates that this bond type is more refractory in nature compared to C=O or C bonds found in samples from less mature part of the basin

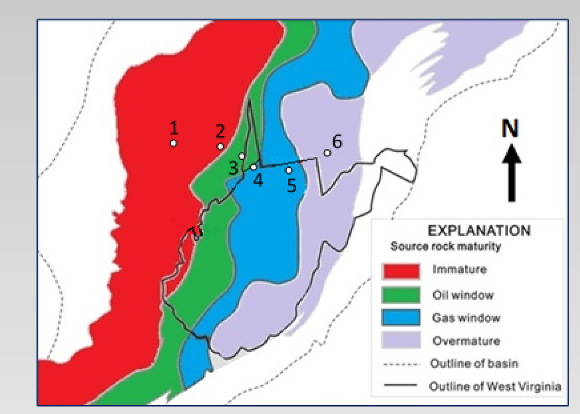
Higher percentage of C-H bond in kerogen from Mahantango and Marcellus-Onondaga transition are indicative of greater contribution from longer chain dominated terrestrial OM sources

Raman analysis



The ratio of the D band and G band was similar in kerogen samples of Mahantango and Marcellus shale units. It indicates structural rearrangement of the kerogen samples (SP2 vs SP3 ratio) is similar in all the samples.

Future Work



Open and closed system pyrolysis experiments in Marcellus maturity series to understand origin, type, amount and kinetics of hydrocarbons generated

Conclusions

- In mature shales it is difficult to delineate organic matter sources using bulk aliphatic/aromatic carbon ratios in kerogen as OM is highly aromatized in the dry gas window.
- Molecular level characterization of different functional groups in the aromatic fraction can help in determining changes in OM sources in these high mature shales.

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