PS Decoding Molecular Geochemistry of Kerogen from Marcellus Shale*

Vikas Agrawal[1], Shikha Sharma[2], and Ajay Warrier[2]

Search and Discovery Article #42153 (2017)**
Posted November 20, 2017

*Adapted from poster presentation given at AAPG 2017 Annual Convention and Exhibition, Houston, Texas, April 2-5, 2017

[1]Department of Geology and Geography, West Virginia University, Morgantown, West Virginia, United States (vikasagrawal175@gmail.com)
[2]Department of Geology and Geography, West Virginia University, Morgantown, West Virginia, United States

Abstract

Organic-rich black shales have become one of the most important components of the US energy sector. The majority of the organic matter (OM) in black shales is in the form of kerogen. Kerogen is an insoluble high molecular weight macromolecule which on maturation cracks to form oil and gas. Kerogen, although being the largest reservoir of organic carbon on earth still remains one of the least studied components of OM, especially in mature source rocks. This is mainly because of tedious kerogen isolation procedure and lack of efficient analytical instruments to directly analyze kerogen. Recent advancement in mass spectrometry, spectroscopic and imaging techniques and instrumentation can provide key information on the structure of kerogen. Understanding the structure of kerogen, its evolution on maturation, kinetics of kerogen cracking, and effect of kerogen structure on gas retention and sorption is extremely vital to unraveling the hydrocarbon (HC) generation and retention potential of source rocks. This study utilizes isolated kerogen from Marcellus Shale cores of different maturity. An array of analytical techniques including Py-GC (Pyrolysis-Gas Chromatography), MSSV (Microscale sealed vessel) pyrolysis, FT-ICR MS (Fourier transform ion cyclotron resonance-Mass spectrometry), 13C solid state NMR(Nuclear magnetic resonance), XPS (X-ray photoelectron spectroscopy), and ATR-FTIR (Attenuated total reflection-Fourier transform infrared spectroscopy) will be used to determine 1) structure of kerogen by evaluating types of carbon chains and functional groups present in kerogen and their association with aliphatic and aromatic components, 2) changes in aliphatic vs aromatic fraction with maturation, 3) evolution of carbon isotopes of kerogen and HC produced by cracking of kerogen, and 4) kinetics of kerogen cracking. These results will be further utilized to understand the HC generation potential at different maturity levels, chemical kinetics of HC generation, the effect of the mineral matrix and molecular geochemistry on HC retention and sorption, and the artifacts created by different pyrolysis techniques.

Decoding Molecular Geochemistry of Kerogen from Marcellus Shale

Vikas Agrawal[1], Shikha Sharma[1] , Ajaya Warrier[1]

[1]Dept. of Geology and Geography, West Virginia University, Morgantown, WV-26505, U.S.

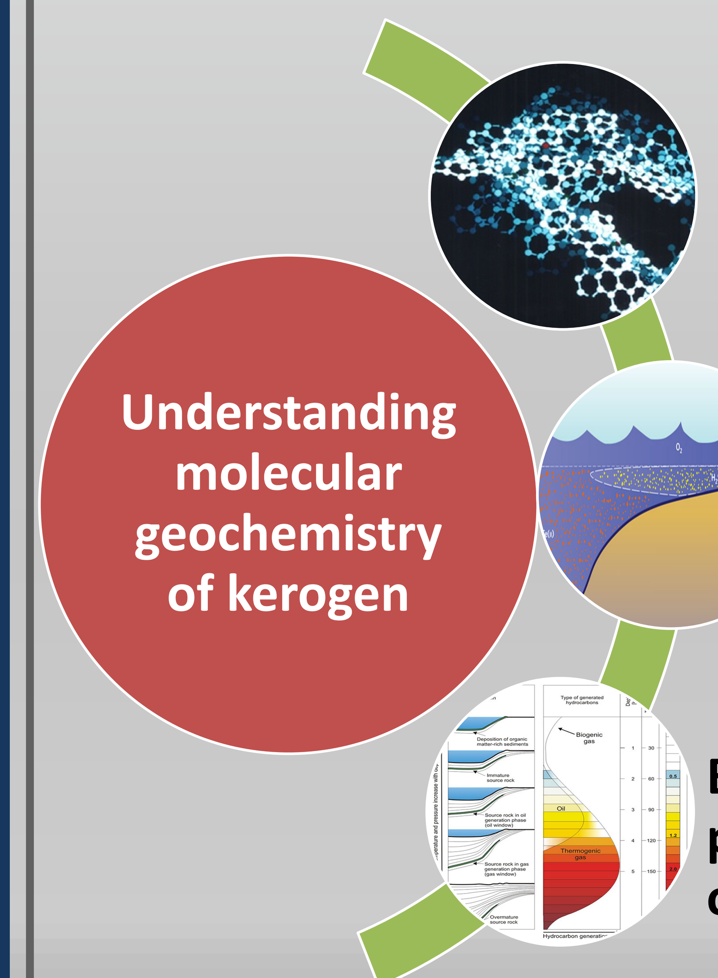
SHARMA IδoTOPE LAB

U.S. DEPARTMENT OF ENERGY

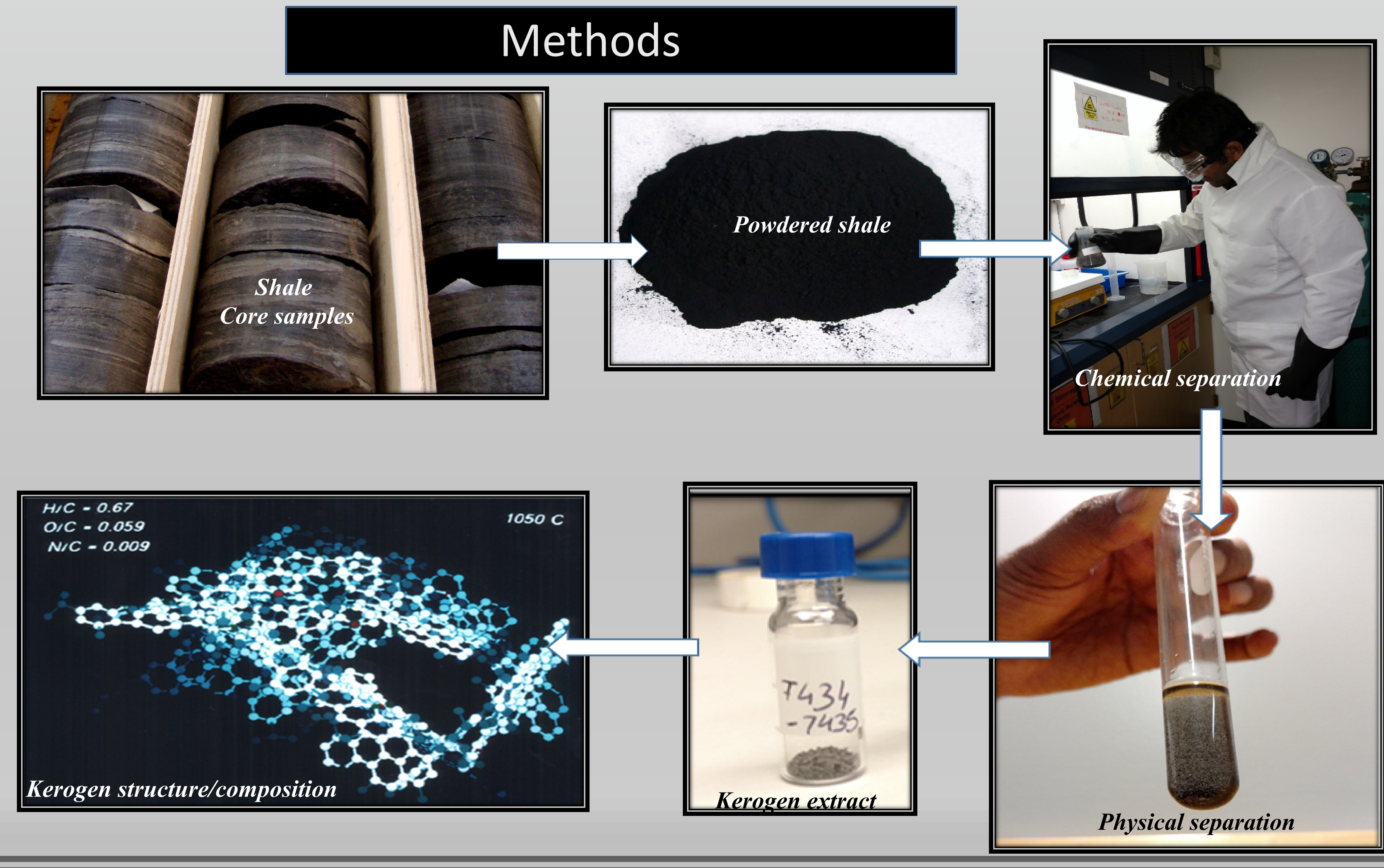
Abstract

Organic-rich black shales have become one of the most important components of the US energy sector. The majority of the organic matter (OM) in black shales is in the form of kerogen. Kerogen is an insoluble high molecular weight macromolecule which on maturation cracks to form oil and gas. Kerogen, although being the largest reservoir of organic carbon on earth still remains one of the least studied components of OM, especially in mature source rocks. This is mainly because of tedious kerogen isolation procedure and lack of efficient analytical instruments to directly analyze kerogen. Recent advancement in mass spectrometry, spectroscopic and imaging techniques and instrumentation can provide key information on the structure of kerogen. Understanding the structure of kerogen, its evolution on maturation, kinetics of kerogen cracking, and effect of kerogen structure on gas retention and sorption is extremely vital to unraveling the hydrocarbon (HC) generation and retention potential of source rocks. This study utilizes isolated kerogen from Marcellus shale cores of different maturity. An array of analytical techniques including Py-GC (Pyrolysis-Gas Chromatography) , MSSV (Microscale sealed vessel) pyrolysis, FT-ICR MS (Fourier transform ion cyclotron resonance-Mass spectrometry, ^{13}C solid state NMR (Nuclear magnetic resonance), XPS (X-ray photoelectron spectroscopy), and ATR-FTIR (Attenuated total reflection-Fourier transform infrared spectroscopy) will be used to determine 1) structure of kerogen by evaluating types of carbon chains and functional groups present in kerogen and their association with aliphatic and aromatic components 2) changes in aliphatic vs aromatic fraction with maturation 3) evolution of carbon isotopes of kerogen and HC produced by cracking of kerogen 4) kinetics of kerogen cracking. These results will be further utilized to understand the HC generation potential at different maturity levels, chemical kinetics of HC generation, the effect of the mineral matrix and molecular geochemistry on HC retention and sorption, and the artifacts created by different pyrolysis techniques.

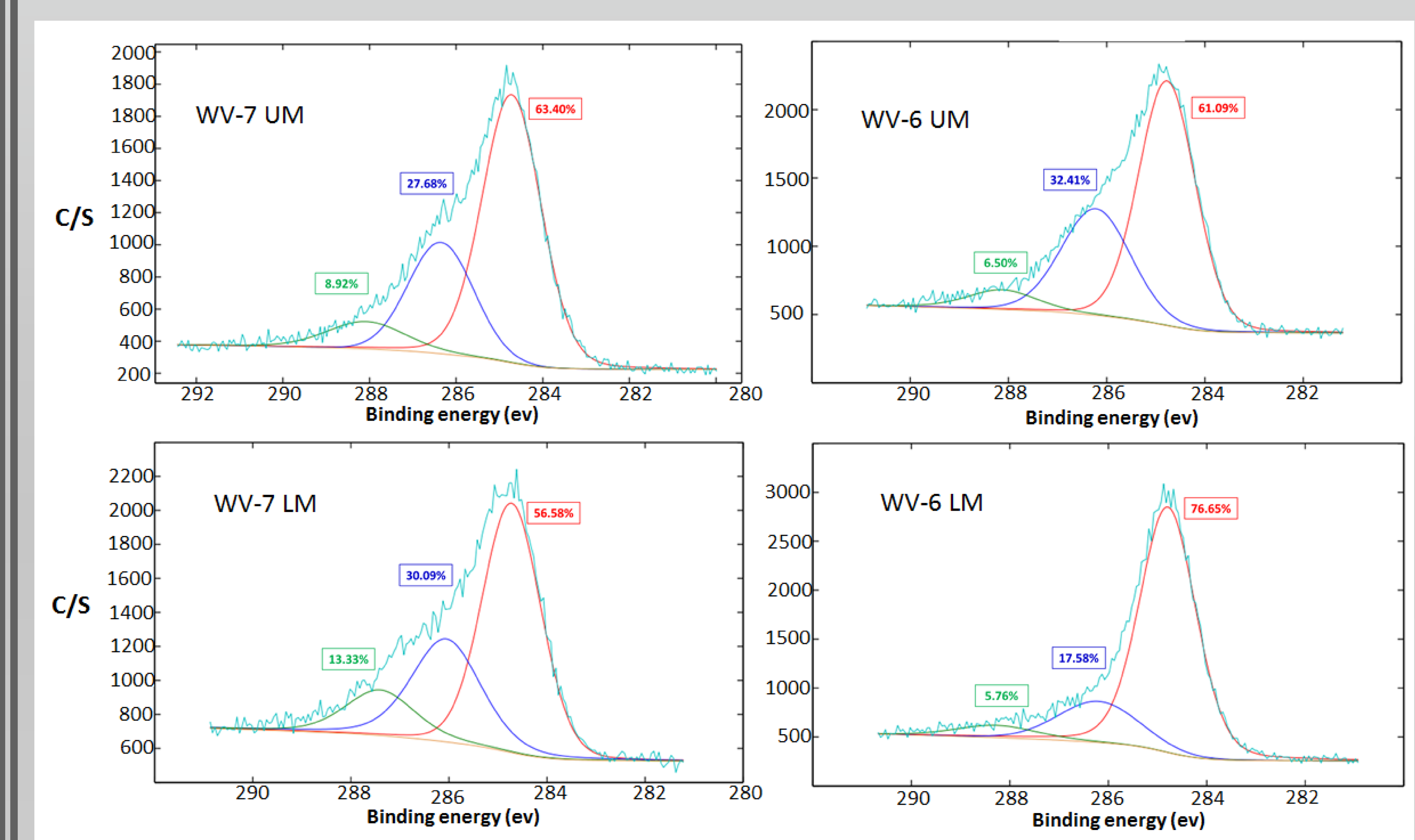
Objectives



Methods



XPS analysis



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

- Three major peaks of C-C bond, C-H bond and C-O bond were observed at 285 ev, 286.3 ev and 289.5 ev respectively in all kerogen samples
- Kerogen from both upper and lower Marcellus shale of WV-6 and WV-7 wells have C-C/C-H bond, followed by C-O, then by C=O bonds
- In both WV-6 kerogen samples, C-C+C-H molar percentage is higher than that of WV-7 sample
- Upper Marcellus kerogen samples have a higher distribution of C-H/C-C bonds as compared to lower Marcellus in both WV-6 and WV-7 samples

Sampling Area

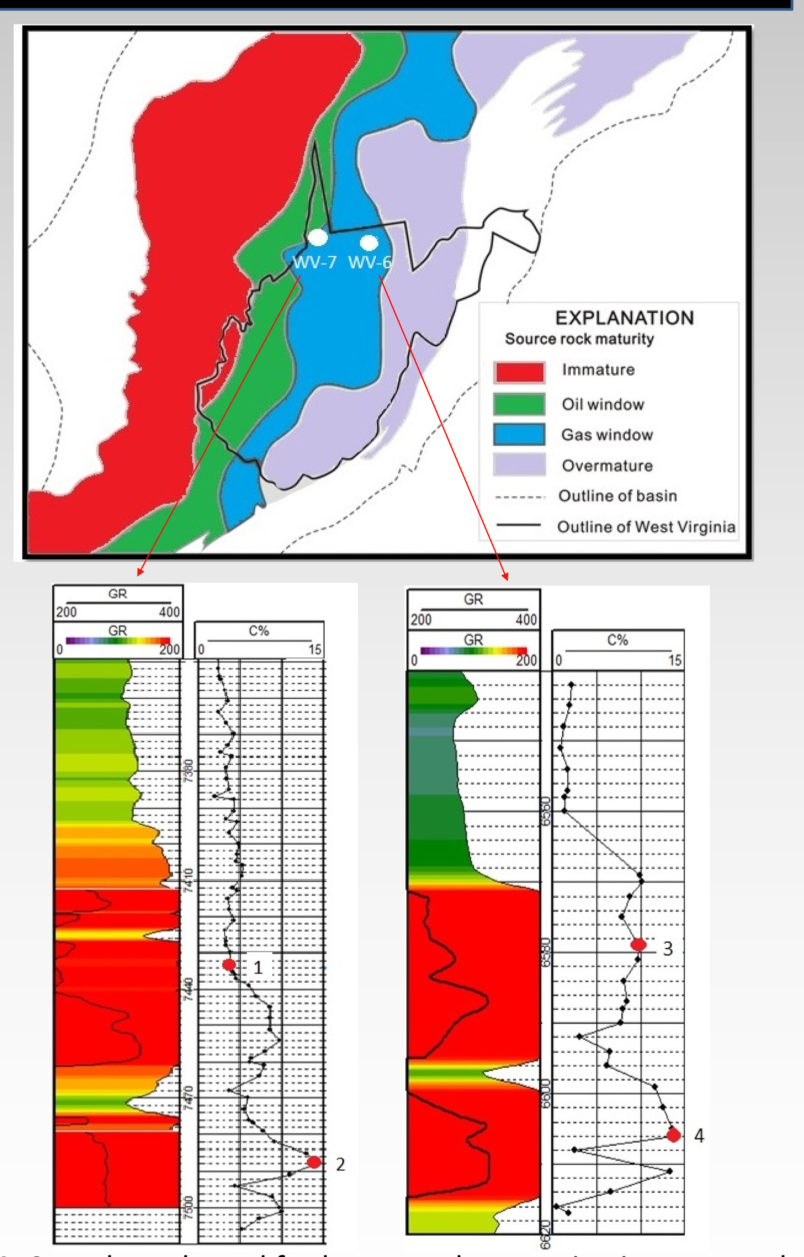
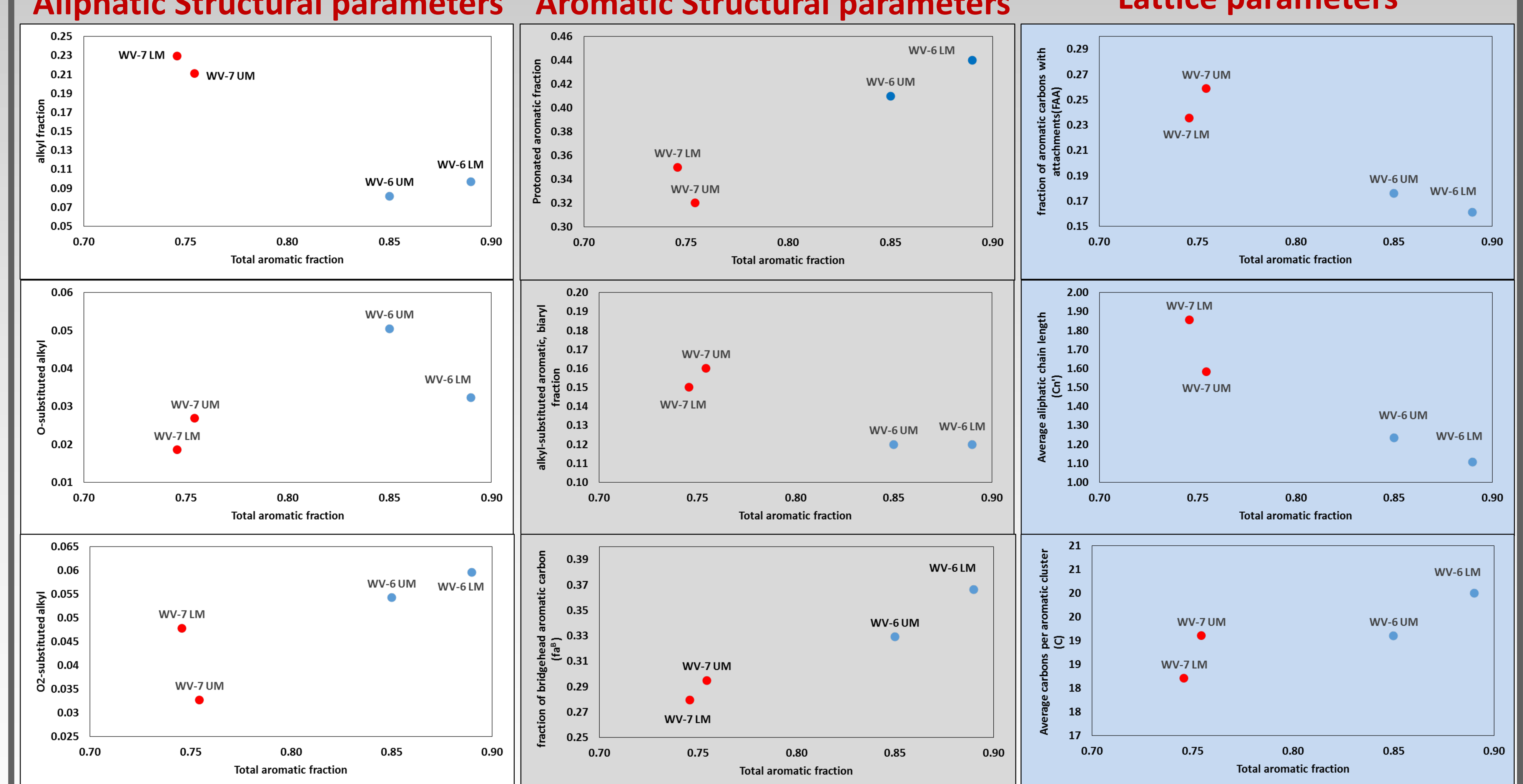


Figure 1. Samples selected for kerogen characterization are marked in red. Sample marked as 1, 3 are from organic lean shale from upper Marcellus formation while 3 and 4 are from organic rich shale from lower Marcellus formation.

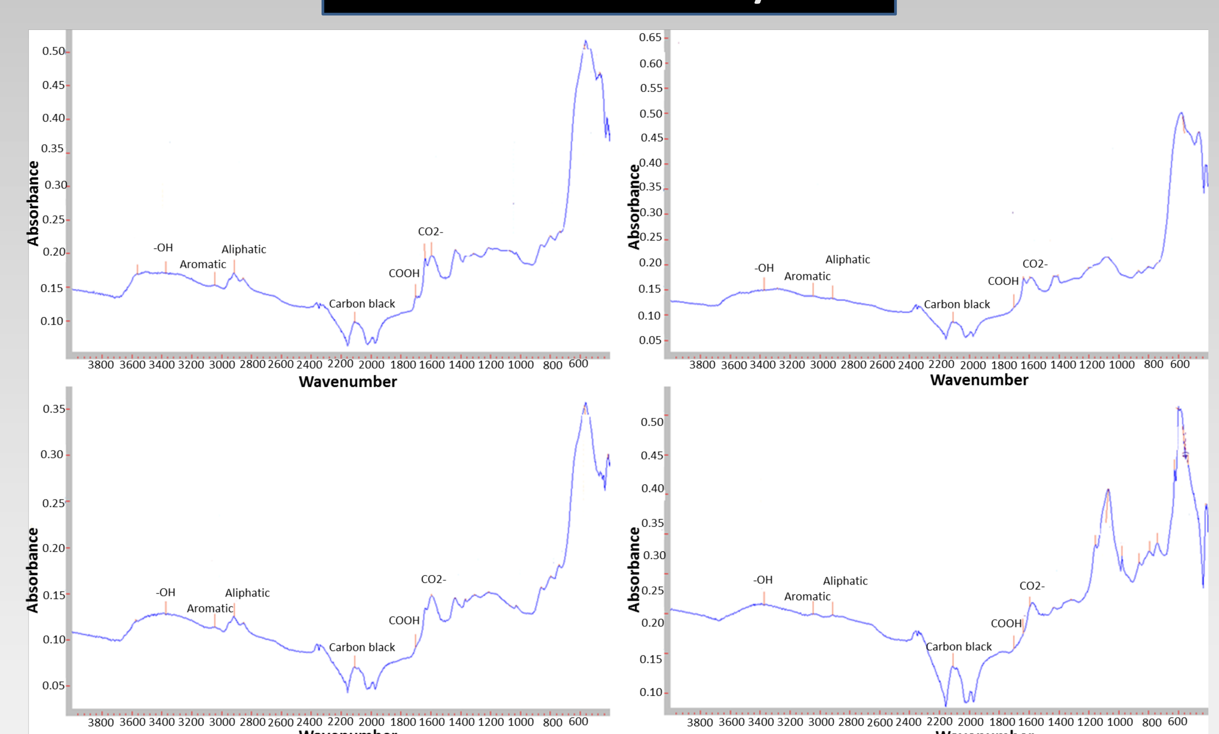
13C solid state NMR analysis

Aliphatic Structural parameters | Aromatic Structural parameters | Lattice parameters



- Distribution of all the aliphatic and aromatic functional groups in kerogen were very similar in upper and lower Marcellus formation in both wells
- WV-7 kerogen samples (less mature) had higher fraction of mobile and immobile alkyl groups, methoxyl and amine groups but a lower fraction of O-substituted alkyl and O_2 substituted alkyl group
- Higher fraction of protonated aromatic carbons and bridgehead aromatic carbons but a lower fraction of alkyl-substituted aromatic carbons were present in WV-6 (mature) kerogen samples
- Kerogen samples from WV-7 (less mature) well has higher fraction of aromatic carbons with attachments, average aliphatic carbon chain length but a lower fraction/amount of average carbon per atomic cluster (C) and SP^2/ SP^3 carbon ratio

ATR- FTIR analysis



- ATR- FTIR results shows presence of carboxylates (1596cm-1), amino or nitro-R functional group (1639 cm^{-1}), carboxylic acid (1703 cm^{-1}), aromatic (3046cm-1) ,aliphatic hydrocarbons (2919 cm^{-1}, 2851 cm^{-1}) and high levels of carbon black or "graphite" type material (2110 cm^{-1})
- WV-7 kerogen extracts from both upper and lower Marcellus formation has a higher concentration of aliphatic carbon, amino, carboxylic, carboxylate and hydroxyl functional groups as compared to WV-6 samples
- lower Marcellus formation from WV-6 core has the higher amount of dead aromatic carbon (carbon black) which represents higher aromatic cluster size as compared to WV-7

Future Work

- Open and closed system pyrolysis experiments to artificially mature kerogen and to understand composition of and origin of hydrocarbons
- FT-ICR MS technique to determine the compositional changes of polar compounds of kerogen with maturation and their contribution to hydrocarbon generation

Conclusions

- **Thermal maturity is the dominant control on the structure of kerogen from wet gas window to dry gas window**
- **Carbon chains from marine organic matter are preferentially degraded before entering into wet gas window**
- **Original signatures of sources of organic matter cannot be determined using kerogen structure/structural parameters if source rocks has entered wet gas window**

Acknowledgements

U.S. DEPARTMENT OF ENERGY NETL

DE# FE0024297

EAR # 1205596
DEB # 1342732

Dr. Wei Ding and Dr. Qiang Wang from WVU shared facilities is thanked for XPS, FTIR analysis