[PS]Understanding Kerogen Composition and Structure in Pristine Shale Cores Collected from Marcellus Shale Energy and Environment Laboratory*

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Search and Discovery Article #42049 (2017)**
Posted April 3, 2017

*Adapted from oral presentation given at AAPG Eastern Section Meeting, Lexington, Kentucky, September 25-27, 2016

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Abstract

Organic-rich black shales have become a vital component of the U.S. energy portfolio. Kerogen is the high molecular weight organic matter (OM) that serves as starting material for the oil and gas in these shales. Despite its importance, kerogen still remains one of the least studied components because traditional methods used to study it have limited applicability, especially in mature shale reservoirs. It has been noted that shales with a similar amount and type of kerogen and similar reservoir parameters, such as maturation, have different biomarker distribution, carbon (organic) isotopic signature, and produce different amount of hydrocarbons. These heterogeneities highlight the need to better understand the variability in composition and structure of kerogen to identify sweet spots for hydrocarbon production.

This study utilizes sidewall cores collected from the experimental well at Marcellus Shale Energy and Environment Laboratory (MSEEL) in Morgantown, West Virginia. Samples were collected from different organic-rich zones in Marcellus Shale, and from its contact with the underlying Onondaga and overlying Mahantango formations. Samples were grounded to a particle size less than 500 μm and homogenized. Kerogen was extracted from grounded samples by removing soluble OM and mineral matrix using chemical and physical separation. Soluble OM, carbonate minerals, and silicate minerals were dissolved using di chloromethane (DCM), hydrochloric acid (HCl), and hydrofluoric acid (HF) respectively. Heavy minerals and pyrite were separated using zinc bromide ($ZnBr_2$) solution. Different functional groups such as C=O, CH_2, CH_3, C=C, C-O, OH, C-OH were identified using FTIR (Fourier Transformed Infrared) analysis and the molar percentage of different carbon bonds were quantified using XPS (X-ray Photoelectron Spectroscopic) analysis. The data on functional groups and carbon bonds will be used in conjunction with isotopic, geochemical, and mineralogical data to understand the effect depositional environment and redox conditions have on structure and composition of kerogen.

Understanding kerogen composition and structure in pristine shale cores collected from Marcellus Shale Energy and Environment Laboratory

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Abstract

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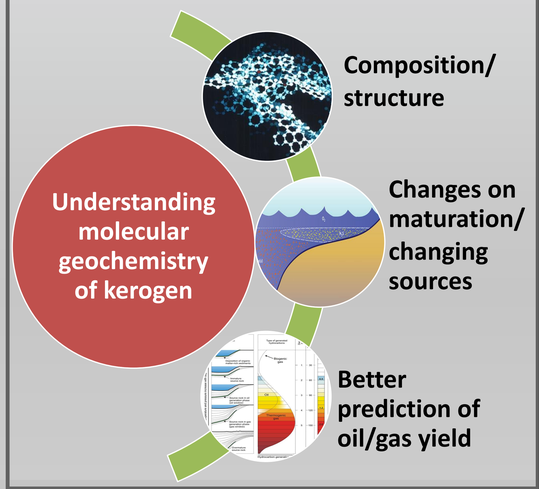
Objectives



Methods

~50 grams of sample from the inner section of the cores is crushed to 200 mesh powder

Powdered samples is sonicated in 100 ml of DCM for 30 minutes and filtered. This step is repeated multiple times until the color of the solution is transparent

Residue is sonicated again with 100 ml MeOH–acetone–CHCl3 (15:15:70 v/v) mixture to dissolve the remaining soluble OM and filtered

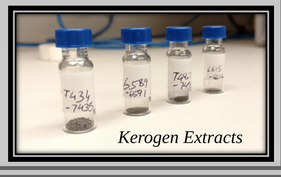
~100ml of 12N HCl is added to the residue at 60-70ºC and kept for 12 hours. This step will be done multiple times until no effervescence are observed

Residue is rinsed with DI until neutrality

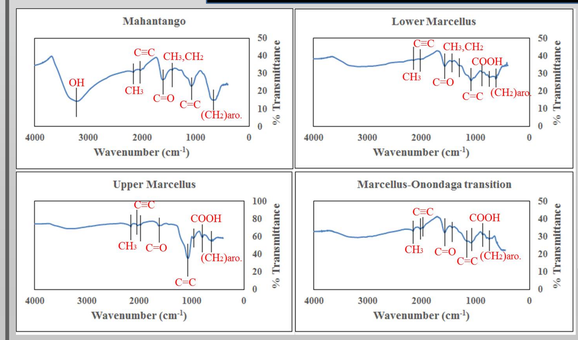
Conc. HF is added. Solution is kept for 24 hours in a sand bath at ~60ºC. Solution is then rinsed until neutrality.

Extracted residue is treated again with DCM to remove the soluble organic matter as done in Step: 2

ZnBr is added to the solution to separate 2 phases one containing floating kerogen and other with heavy minerals and pyrite. Floating kerogen is then filtered

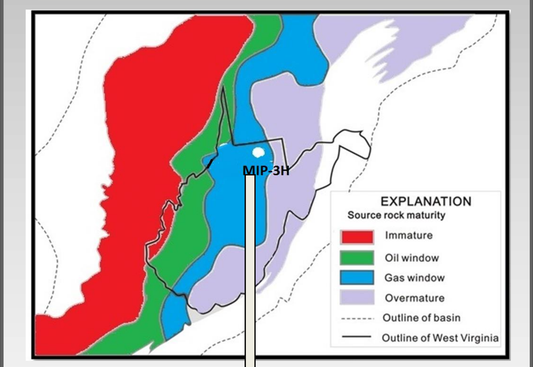


FTIR analysis



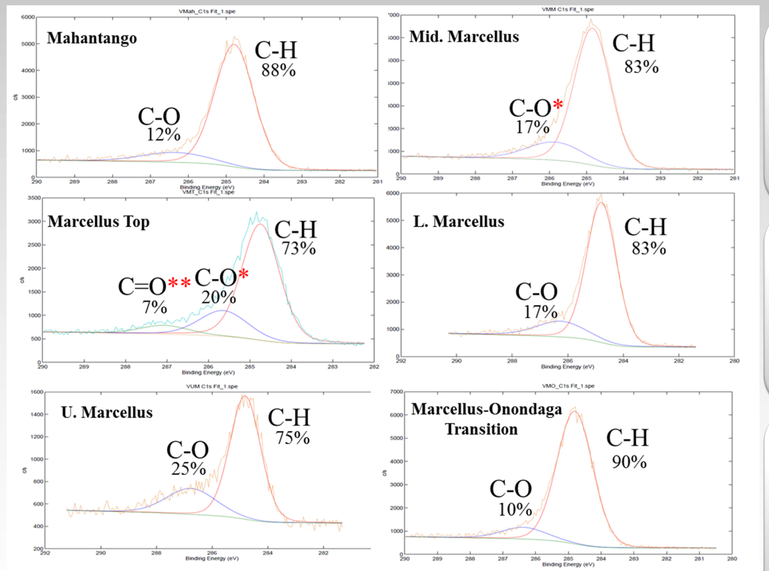
- Bonds identified are CH2(aromatic), C-OH, CHO, C=O, COOH, C=C, C≡C CH2 and CH3
- FTIR-ATR analysis will be used to quantify and compare different functional groups
- FTIR analysis provides a robust tool for correlation of samples from different wells

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)

XPS analysis



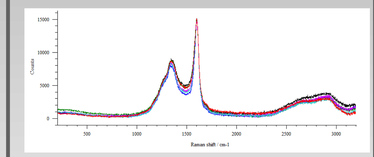
XPS Carbon (1s) Spectra of kerogen and curve resolution into different components

Majority of the bonds present in kerogen are C-H bond, followed by C-O, then by C=O

Percentage of C-H bond increases and C-O decreases with depth/maturation in Marcellus shale

This indicates that the aliphatic chains of kerogen consisting of hydroxyl, ether and carbonyl bonds breaks on maturation, increasing the percentage molar contribution of aromatic C-H bonds

Raman analysis



Structural arrangement (2d to 3d ratio) throughout the Marcellus shale is similar

Acknowledgements

DE# FE0024297

EAR # 1205596
DEB # 1342732

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

Future Work

Pyrolysis-GC

13C solid state NMR

FTIR-ATR

West Virginia University Static Reactor System