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, 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

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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), MSVV (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 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.

Methods

13C solid state NMR analysis

Aromatic Structural parameters

Aliphatic Structural parameters

Lattice parameters

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

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Sampling Area

Understanding molecular geochemistry of kerogen

Better prediction of oil/gas yield

Objectives

Changes on maturation/changing sources

Composition/structure

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.

XPS analysis

Three major peaks of C-C bond, C-O bond and hydrocarbons are observed at 286.2 cm-1 and 285.6 cm-1 respectively in all kerogen samples.

In both WV-6 kerogen samples, C-C=C-C carbon percent is higher than that of WV-7 sample.

Upper Marcellus kerogen samples have a higher distribution of aromatic carbons as compared to lower Marcellus kerogen samples in both WV-6 and WV-7 samples.

Distribution of all the aliphatic and aromatic functional groups in kerogen were very similar in upper and lower Marcellus formation in both wells.

In WV-6 kerogen samples, C-C+C-H is 30.4% and C-C/C-H is 38.2%.

In WV-7 kerogen samples, C-C+C-H is 30.4% and C-C/C-H is 38.2%.

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