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MOLECULAR EVOLUTION OF SEDIMENTARY ORGANIC MATTER IN MARCELLUS SHALE

Vikas Agrawal

**Dissertation submitted
to the Eberly College of Arts and Sciences at West
Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in
Geology**

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Department of Geology and Geography

**Morgantown, West Virginia
2018**

**Keywords: Marcellus Shale; Organic Matter; Biomarkers; Kerogen; structural models;
Hydrocarbon Potential, Thermal Maturity.**

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ABSTRACT

Molecular Evolution of Sedimentary Organic Matter in Marcellus Shale

Vikas Agrawal

Several biological and physico-chemical processes lead to the transformation of organic matter (OM) from simple organic compounds to a complex macromolecule and a mixture of hydrocarbons during the geological evolution of sedimentary rocks. These changes are controlled by biological activity in the early stages of burial, and by temperature and pressure in the later stages. The increasing temperature and pressure conditions with burial is termed as maturation, in which biomolecules are converted into petroleum. Three consecutive stages of maturation namely: diagenesis, catagenesis and metagenesis produce irreversible changes in the composition of sedimentary OM. The bulk characteristics (such as elemental composition) of OM starting from its deposition to the formation of oil and gas are well understood in the past using traditional methods such as source rock analyzer (SRA). However, a large knowledge gap still exists in understanding the processes involved in the transformation and evolution of OM during maturation at the molecular level. Understanding the molecular level properties of shale OM is important for precise estimation of hydrocarbons, increasing efficiency of HC recovery and production, designing effective CO₂ sequestration and waste disposal strategies, and understanding mechanisms of contaminant release and sorption.

The primary objective of my PhD dissertation is to understand evolution of sedimentary OM at molecular scale in Marcellus Shale. The Marcellus Shale is the largest natural gas producing reservoir in the United States and has been extensively drilled in the past decade. The amount of natural gas extracted from the reservoir has almost tripled due to advancements in horizontal

drilling technologies. As a result, thousands of wells have been drilled in areas of Pennsylvania, Ohio and West Virginia covering a wide range of maturation (from early oil window to over-mature window) and paleo-depositional environments. Drilling of these wells provides access to several thousand feet deep core samples for biogeochemical analysis. In my study, I utilized core samples of Marcellus shale with variable maturity (ranging from 0.8 VRo to 3 VRo) and depositional environment.

The variability in sources of OM, paleo-redox conditions and thermal maturation was determined using pyrolysis and biomarker proxies especially in samples from mature part of the basin. Once the information about source of OM and maturation was established, kerogen was extracted from the Marcellus Shale maturity series. Chemical composition and structural properties of the extracted kerogen was determined using advanced spectroscopic techniques. Using the distribution and changes in structural parameters of kerogen, an understanding was developed about kerogen cracking mechanism, its primary molecular components, and sources of hydrocarbon potential. Our findings indicated that previously published kerogen models significantly overestimated or underestimated HC potential, thermal maturity and other physicochemical properties of kerogen from Marcellus Shale. Reasons for such discrepancies are because the old models were derived from very limited number of shale samples and they do not account for heterogeneity in kerogen structure. This heterogeneity arises primarily due to variations in sources of OM (within a particular depositional environment), paleo-environmental conditions, and effect of differential kerogen cracking on thermal maturation. In our study, we developed new structural models and regression models of kerogen to determine thermal maturity and hydrocarbon potential of shales for almost the entire maturity window of HC generation (from peak oil window to dry gas window). Further, we compared the molecular structure of kerogen obtained from Marcellus Shale

with kerogen structures of other Shale Formations with similar kerogen type and thermal maturity. This comparison was done to examine the applicability and limitations of modelling physico-chemical properties of shales based on kerogen “type”.

STRUCTURE OF THE DISSERTATION

I have divided my dissertations in four research papers focusing on research topics as follows:

Chapter 1 is a research paper entitled ‘**Testing Utility of Organogeochemical Proxies to Assess Sources of Organic Matter, Paleoredox Conditions and Thermal Maturity in Mature Marcellus Shale**’. This research paper focuses on the efficacy of pyrolysis and biomarker proxies to determine source of OM, thermal maturation and paleo redox environment especially in mature shales. The highlight of this paper is that by using an improved methods of biomarker extractions and analysis, accurate information about the thermal and depositional history of mature shales like the Marcellus Shale can be determined. This paper is publised in the journal *Frontiers in Energy Research*.

Chapter 2 is a research paper entitled ‘**Molecular Characterization of Kerogen and its Implications for Determining Hydrocarbon Potential, Organic matter sources and Thermal Maturity in Marcellus Shale**’. This paper focuses on using direct kerogen analysis to understand changes in structural properties of kerogen extracted from samples from three wells covering a thermal maturity range of 0.8 to 2.5 VR₀. In this paper, molecular structural parameters of kerogen from upper and lower Marcellus Shale Formation of all the three wells were determined. Using these structural parameters, schematic models of unit kerogen were developed using theoritical calculations. This paper is publised in the journal *Fuel*.

Chapter 3 is a research paper entitled ‘**Improved Kerogen Models for Determining Thermal Maturity and Hydrocarbon Potential of Shales**’. In this research paper, we showed that the previous models based on structural parameters of kerogen overestimate the HC generation potential and underestimate the thermal maturity of Marcellus Shale samples. Further, by utilizing the kerogen molecular parameters determined in the Marcellus maturity series (covering thermal maturity from 0.8 to 3 VRo using core samples from 6 different wells), we proposed improved models for accurate estimation of thermal maturity and HC potential of shales like Marcellus Shale. This paper is in review in journal *Nature Scientific Reports*.

Chapter 4 is a research paper entitled ‘**Pitfalls in Modelling Physico-Chemical Properties of Shales Using Kerogen Type**’. In this research paper, we showed that the previous molecular models based on kerogen “type” does not incorporate heterogeneities that exists within a particular kerogen “type”. This could lead to underestimation/overestimation of several physico-chemical properties of kerogen and shale which can have several implications. This paper is in review in journal *Nature Scientific Reports*.

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Chapter I:

Testing Utility of Organogeochemical Proxies to Assess Sources of Organic Matter, Paleoredox Conditions and Thermal Maturity in Mature Marcellus Shale

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1. Testing Utility of Organ geochemical Proxies to Assess Sources of Organic Matter, Paleoredox Conditions and Thermal Maturity in Mature Marcellus Shale

Key words: Marcellus Shale, biomarkers, pyrolysis, organic matter, paleo-redox, thermal maturity

1.1 ABSTRACT

It is generally accepted that in mature shales, biomarkers and pyrolysis proxies are not very helpful in understanding the source/type of organic matter (OM), paleo-redox conditions during deposition and thermal maturity. The purpose of the study was conducted to test the efficacy of these proxies in mature Marcellus shale ($VR_o > 1$). Samples were collected from oil-prone (WV-7) and gas-prone (WV-6) wells in Wetzel and Monongalia Counties, West Virginia, respectively. These wells were chosen for this test study because high-resolution geochemical and isotopic studies have previously been conducted on these cores and depositional model had been proposed. The model suggests that sediments in WV-6 well are more mature, received higher terrestrial OM influx and were deposited in less anoxic environment as compared to WV-7 well. We used an improved method to extract the small amount of biomarkers preserved in the samples. Further, the extracts were analyzed by a high-resolution GC×GC FID method to quantify the distribution of aliphatic biomarkers. The hydrogen and oxygen indices (HI vs. OI plot) determined by Source Rock Analysis could not be used to determine the kerogen type due to their very low values. However, interpretations were derived from S1 vs. S2 and S2/S3 vs. TOC cross plots, thermal maturity parameter (T_{max}), fraction conversion of OM to hydrocarbon (HC), and residual carbon/pyrolysable carbon (RC/PC) ratio. The conclusions drawn from the biomarkers and SRA data are in agreement with the HC production data from these wells as well as interpretations derived from geochemical and isotopic studies conducted on these cores. Therefore, we propose

that despite some limitations biomarker and pyrolysis proxies can be used to determine the thermal and depositional history of mature shales like the Marcellus Shale.

1.2 INTRODUCTION

The Middle Devonian Marcellus Shale is rapidly evolving as a major shale gas play in Northern America with an approximate aerial extent of 34,000,000 acres (Engelder and Lash, 2008), with recent estimates that approximately 15,000 MCF/day of gas is produced each day (EIA, 2016). Oil shales have been estimated to contribute 32% of the world's recoverable natural gas and 10% of the world's crude oil (EIA, 2013). As a result, their exploration has increasingly become economical and profitable. However, there is a lot of spatial and temporal heterogeneity in these shale reservoirs due to variations in the source(s) of OM, thermal maturity, and the depositional environment. To precisely evaluate hydrocarbon potential and to delineate or target sweet spots for production there is a need to better understand these spatiotemporal variations (Boyer *et al.*, 2006). These shales could form in a wide range of sedimentary environments including lacustrine fresh/saline water, terrestrial swamps, marine evaporitic or deltaic environments (Tourtelot 1979, Littke 2006). The organic geochemical analysis can help infer the quantities of expected oil and gas production in a basin and its relation to OM source/type, and thermal maturity (Hunt 1979, Hunt 1996, Jarvie et al., 2007; Horsfield and Schulz, 2012; Romero and Philp, 2012). Also, compositional characteristics of the OM can provide valuable information about the changes in depositional environments during sedimentation (Romero and Philp, 2012). The organic geochemical analysis also helps in distinguishing oil and gas derived from different OM sources and depositional environments (Meyers 1997). However, the role of organic geochemistry in the petroleum industry remains underestimated for mature shales.

Open system pyrolysis of shales using Source Rock Analyzer (SRA) is one of the primary methods used to distinguish sources of OM and the depositional environmental of petroleum systems (Lafargue et al., 1998). In the pyrolysis technique, total evolved HC can be monitored as a function of temperature by steady heating of rock samples (Behar et al., 2001; Lafargue et al., 1998). However, this method has limited applicability in high maturity rocks, primarily because the traditional HI vs OI plots used to identify sources of OM and kerogen (such as van Krevelen diagram) cannot be used due to very low HI and OI values.

The preserved remnants of biomolecules also known as “Biomarkers” have characteristic chemical structures that closely resemble the biological precursor molecules at the time of deposition and have been proven to be valuable in petroleum geology (Peter and Moldowan., 1993; Peters et al., 2005a). Biomarkers can also provide valuable clues about paleoenvironmental conditions, effects of maturity, and biodegradation of rock sediments (e.g., Philp, 1985; Peter and Moldowan, 1993; Peters et al., 2005; Olcott, 2007). Biomarker analysis has been used to decipher depositional conditions of the sources of oil and gas reserves (e.g. Peters et al., 2005; Forster et al., 2004, Kroon et al., 2011). However, majority of the studies on black shales have been conducted on lower maturity shale samples primarily because of low abundance and extraction efficiency of biomarkers in mature shales.

The primary goal of this study was to test the power and limitations of SRA analysis, and biomarkers to understand the source of OM, environmental conditions of deposition, and thermal history of mature shale samples. The samples were collected from two mature Marcellus Shale well cores, an oil-prone WV-7 well with R_o between 1- 1.5 in Wetzel County and a gas-prone WV-6 well in Monongalia County with R_o greater than 2.5 (Zagorski et al., 2012).

The geochemical and isotopic characteristics of these two cores were extensively studied by

Chen et al., 2015, and authors proposed that the sediments in the gas-prone well WV-6 were deposited under alternating redox conditions close to ocean margin and received a greater influx of terrestrial OM. On the other hand, WV-7 sediments were deposited in a more distal anoxic environment dominated by marine OM influx (Chen et al., 2015). For this study, SRA, and biomarker analysis was conducted on samples collected from the same two well cores, i.e., WV-6 and WV-7. Our aim was to test if the SRA and biomarker data supports the inferences drawn by Chen et al., 2015 and to verify if these proxies provide meaningful interpretations for mature shales with $VR_o > 1$. To our knowledge, this would be the first attempt to use biomarkers in conjunction SRA analysis to assess maturity, depositional environment, and source of organic matter in the mature shales like Marcellus.

1.3 MATERIALS AND METHODS

1.3.1 Sampling and sample preparation

Marcellus shale contains two shale members: lower Marcellus (Union Spring Shale) and upper Marcellus (Oatka Creek shale). These two members are divided by Purcell/Cherry Valley limestone (Werne et al., 2002; Sageman et al., 2003). However, other workers consider Purcell and Cherry Valley limestone to be the same unit (Lash and Engelder 2008, 2011). For this study, samples were collected from cores obtained from two wells namely WV-6 core from a gas-prone well in Monongalia County and WV-7 core from an oil-prone well in Wetzel County (location of wells shown in Fig. 1). Both cores were stored under room temperature conditions at the West Virginia Geological and Economic Survey, Morgantown, West Virginia. The majority of samples from lowermost shale interval for both WV-6 and WV-7 wells have high TOC values ($>5\%$) whereas many of the samples in the overlying shale interval have relatively lower TOC values

(<5%) (Chen et al., 2015). Simplified nomenclature of Chen et al., 2015 was followed in this study where the lowermost Marcellus formation is defined as organic-rich zone (OR) zone and the overlying zone with lower TOC as organic intermediate zone (OI) zone (Fig. 1). For the SRA analysis, samples were collected at ~ 1-meter intervals from both OI zones and OR zones in WV-6 and WV-7 cores. For biomarker analysis, one sample was selected from OR zone and one from OI zone from both the WV-6 and WV-7 wells (4 samples in total) (as shown in Fig. 1). To avoid possible effects of contamination related to contact with drilling fluids and oxidation of OM (Martinez and Escobar 1995, Elie et al., 2000) at least 5mm of the outer layer of samples was pared. It is highly unlikely for fluids or air to penetrate >5mm of shale layer and contaminate/oxidize the inner part of the core. After paring, the inner portion was crushed to 200 mesh and homogenized using a sterile SPEX mixer mill and oven dried for 24 hours at 50° C.

1.3.2 Source Rock Analysis (SRA)

80 mg of pulverized shale sample was weighed into a SRA crucible and placed in the autosampler and held isothermally at 300 °C for 3 minutes. To minimize the effect of grain size, care was taken to keep the grain size of all the samples to be consistent (200 mesh). During this isothermal heating, the free hydrocarbons are volatilized and detected by the FID detector where they are quantitatively detected and reported as milligrams (mg) of S1 per gram of rock. The free CO₂ is simultaneously liberated and detected by the IR cell and reported as milligrams (mg) of S3 per gram of rock up to 400 °C. After the isothermal period, the temperature is increased at the rate of 25°C/minute until the temperature reaches to 600 °C. Between 300°C and 600°C HCs are generated from the pyrolytic degradation of the kerogen in the shale. The hydrocarbons are detected by the FID are labeled as S2 and reported as milligrams (mg) of S2 per gram of rock. The temperature at the maximum generation of S2 is known as Tmax. Tmax is generally used to

estimate thermal maturity of shales. However, for lower values of S2, Tmax is not reliable (Peters et al., 1986). Therefore, Tmax for samples with S2 values less than 0.5 mg HC/g rock is not reported. Residual carbon is also measured by SRA and is reported as S4. To measure the reliability of data especially for over-mature shale sample, sample with low S1, S2, S3 values (values less than 0.5 HC/g rock) was measured in quadruplicates. The standard deviation of the SRA parameters S1, S2 and S3 determined was measured to be less than 0.05 mg/g rock, indicating that these parameters are reliable for samples having a low quantity of HCs. WFT Source Rock Standard 533 (P/N 810-141) was used as a standard and was run after every five sample. SRA analysis was performed at the National Energy Technology Laboratory in Morgantown.

1.3.3 Calculations

From the SRA analysis, S1, S2 S3, S4 and thermal maturity parameter (Tmax temperature at which maximum amount release of hydrocarbon takes place) were obtained. (Table 1). Using these basic measurements, several other parameters were calculated for the samples as follows (Table 1):

TOC = $0.1 \times [0.082 \times (S1 + S2) + S4]$, in wt. %

Hydrogen Index (HI) = $[(S2/TOC) \times 100]$. The ratio of S2 hydrogen (in mg HC/g rock) to total organic carbon (TOC).

Oxygen Index (OI) = $[(S3/TOC)] \times 100$. The ratio of S3 (mg CO₂/g rock) to TOC

Production Index (PI) = $[S1 / (S1 + S2)]$. The production index is the ratio of already generated hydrocarbon to potential HC from kerogen cracking.

Pyrolysable Carbon (PC) = $[0.083 \times (S1 + S2)]$. It corresponds to the carbon content of HC volatilized and pyrolyzed during the SRA analysis.

Residual Carbon (RC) = $[TOC - PC] \times 10$. This is the portion of kerogen with no HC generation potential.

Calculated Vitrinite reflectance (VRo) = 0.018 * Tmax - 7.16 (Jarvie and Lundell, 1991)

Fraction conversion to HC (f) = $\frac{[(1 - HI^0) * \{1200 - [HI^0 / (1 - PI^0)]\}]}{HI^0 * \{1200 - [HI / (1 - PI)]\}}$

$$HI^0 * \{1200 - [HI / (1 - PI)]\}$$

where HI^0 and PI^0 are hydrogen Index and production index of immature samples. (Peters et al., 2005a). HI^0 obtained for immature Marcellus shale ranges from 250-400 mg HC/g rock. (Bruner and Smosna, 2011) So, the value of HI^0 should be at least 250mg HC/g rock. Hence this value is assumed for the calculations whereas as PI^0 can be assumed to be 0.02 for the most immature source rocks (Peters *et al.*, 2005a). Using the parameters obtained from SRA and the parameters calculated above, several plots were made to determine the source, type, HC generation potential, quality of kerogen for HC generation, redox conditions of formation, thermal maturity.

1.3.4 Biomarker extraction and analysis

The abundance of biomarkers in mature shales ($VRo > 1$) is very low and significant number of biomarkers are also bound to the mineral matrix of shales (Sherman et al., 2007). Therefore, for this study, we modified the common extraction methods (e.g., Brocks et al., 2003, Forster et al., 2004) to enhance the recovery of biomarkers bound in a mineral matrix. About 50 grams of crushed and homogenized shale samples were extracted by sonication using 100 ml of dichloromethane (DCM) for 30 minutes. This step was repeated twice to enhance recovery. Shale residue was then treated with HCl and HF respectively to dissolve carbonate and silicate minerals. Shale residue was treated again with 50ml of DCM and sonicated for 30 minutes to remove carbonate bound and silicate bound biomarkers. Both the DCM extracts were mixed and free sulfur present in the extracts was removed by adding 5 grams of activated copper pellets. The extracts were filtered and blow dried using N_2 blowdown method. Then 25 ml of pentane was added to

precipitate asphaltene present in the extracts. The extracts were then filtered and dried under N₂ blowdown. The dried extracts were redissolved in 2ml of DCM, and the aliphatic fraction was separated using silicic acid column chromatography. The aliphatic fraction was separated by passing the extract through 8cm silica gel column and eluting with hexane. The extraction procedure was adopted and modified from Sherman et al., 2007.

The aliphatic fraction of the biomarkers was analyzed using a 2-dimensional gas chromatography-gas chromatography-flame ionization detector (GC×GC-FID) at Woods Hole Oceanographic Institute (WHOI). Multi dimensional GC×GC analysis was used for this study because it provides higher resolution and sensitivity due to the re-concentration of the fraction through the modulation process. This allows the detection of biomarkers present in trace concentrations and separation of related compounds in other dimension (Adahchour et al., 2008). This type of high resolution analysis is not possible using conventional GC techniques.

Leco GC×GC-FID used for the biomarker analysis was equipped with an Agilent 6890 GC configured with a split/splitless auto-injector (7683 series) and a dual-stage cryogenic modulator (Leco, Saint Joseph, Michigan). Samples were injected in splitless mode (inlet temperature was 310 °C) and modulated with a cold and hot jet. The cold jet gas was dry N₂, chilled with liquid N₂. The hot jet gas was compressed air and the temperature offset between the main oven and the hot jet was 15 °C. Two capillary GC columns were installed in the GC×GC instrument. The first-dimension column was a non-polar Restek Rxi-1ms, (60 m length, 0.25 mm I.D., 0.25 µm film thickness) and the second-dimension separations were performed on a 50% phenyl polysilphenylene-siloxane column (SGE BPX50, 1.5 m length, 0.10 mm I.D., 0.1 µm film thickness).

The temperature program of the main oven remained isothermal at 40 °C (10 min) and was then ramped from 40 to 335 °C at 1.25 °C min⁻¹. The hot jet pulsed width was 0.75 seconds, and the modulation period was 6 seconds with a 2.25 second cooling period between stages. The second-dimension oven was programmed from 45 °C (10 min) to 340 °C at 1.25 °C min⁻¹. FID detector data was sampled at an acquisition rate of 100 Hz. A 750-second data acquisition delay (solvent delay) was programmed into the method of each GC×GC chromatogram. For quantification and comparison of the biomarkers, two external standards from National Institute of Standards & Technology Standard Reference Materials (SRM-2779 Gulf of Mexico Crude Oil and SRM-1582 Petroleum Crude Oil) were injected at a concentration of 10mg/ml. Each chromatogram was then normalized to the largest component in the mixture. The standard deviation of the analysis of the standards was 8.33%.

1.4 RESULTS

1.4.1 SRA data

Sediment core values for free or thermo-labile hydrocarbons (S1) for WV 6 ranged between 0.05-1.36 mg HC/g rock while the bound HC released (S2) ranged from 0.02 to 1.68 mg HC /g rock (Table 1). The range of S1 and S2 did not change significantly for the OR and OI zone. The minimum values of S1 and S2 were in OI zone, and the maximum values were in OR zone. For the WV-7 core, the values of S1 and S2 were comparatively higher ranging between 0.26-5.53 mg HC/g rock and 0.29- 10.67 mg HC/g rock (Table 1). The S1 and S2 values were also lower for the OI zone and higher for the OR zone. The average values of S1 and S2 for WV-7 samples was much higher compared to WV-6 samples (Fig. 2).

1.4.2 BIOMARKER Data

1.4.2.1 Inter-core comparison

Based on the TOC data, two samples were selected from the OI and OR zone from both WV-6 and WV-7 cores. Samples were analyzed to identify and quantify the composition of different aliphatic biomarkers present. The biomarkers identified in OI zone of WV-6 includes *n*-alkanes ranging from *n*-14 to *n*-33, pristane (Pr), phytane (Py), Diasteranes (DiaC27 $\beta\alpha$ -20S, DiaC27 $\beta\alpha$ -20R), steranes (C27 $\alpha\beta\beta$ -20S, C27 $\alpha\alpha\alpha$ -20R, C28 $\alpha\beta\beta$ -20R, C28 $\alpha\beta\beta$ -20R, C28 $\alpha\beta\beta$ -20S, C28 $\alpha\alpha\alpha$ -20R, C29 $\alpha\alpha\alpha$ -20S, C29 $\alpha\beta\beta$ -20R, C29 $\alpha\beta\beta$ -20S, C29 $\alpha\alpha\alpha$ -20R) and hopanes (Ts, Tm, NH, C29-Ts 17a(H), 21B(H)-hopane, HH(S), HH(R), 2HH(S), 2HH(R)). The OI zone of the WV-7 core was composed primarily of *n*-11 to *n*-30 *n*-alkanes, and biomarkers Pr, Py, diasteranes, steranes or hopanes, which were detectable but not quantifiable due to extremely low concentrations. The distribution of *n*-alkanes for OI zone for both cores is shown in Fig. 3a and b. The *n*-alkane distribution shows that OI zone of WV-7 core sediments had a higher concentration of shorter chain *n*-alkanes and lower concentration of higher chain *n*-alkanes as compared to OI zone of the WV-6 core (Fig. 3a). On the other hand, *n*-alkane distribution in OR zone ranged from *n*-14 to *n*-33 for both WV-6 and WV-7 core sediment samples. However, WV-6 core sediments (both OI and OR zone) had higher concentrations of higher chain *n*-alkanes compared to WV-7 sediment cores (Fig. 3b). Both also showed the presence of biomarkers Pr, Py, and hopanes (Ts, Tm, NH, C29-Ts, H, HH(S), HH(R), 2HH(S), 2HH(R)) and an unquantifiable amount of sterane and diasterane isomers.

1.4.2.2 Intra-core comparison

Biomarker distribution of WV-6 core sediments shows a depletion of shorter chain *n*-alkanes and an enrichment of higher chain *n*-alkanes from both OR zone and OI zone. The relative concentration of total *n*-alkane also decreases and is accompanied by an increase in the

concentration of pristane, phytane, steranes, and hopane biomarkers. For WV-7 core, a similar trend for n-alkane distribution is observed. Although, the relative concentration of total n-alkanes increases in OI of WV-7 core sediments, the pristane, phytane, steranes, diterpanes or hopane biomarkers were not detected. To determine the relative contribution of marine and terrestrial OM, terrigenous to aquatic ratio ($TAR = (nC_{27} + nC_{29} + nC_{31}) / (nC_{15} + nC_{17} + nC_{19})$) were calculated using the n-alkane distribution (Peters et. al., 2005 a).

1.5 DISCUSSION

1.5.1 SOURCE AND TYPE OF OM

It is necessary to understand the impact of different OM sources, maturity, and biodegradation on both the elemental, bulk, as well as the principal biomarker properties before biomarkers can be used to assess depositional environmental conditions. When OM from different sources is exposed to increasing pressure and temperature, they expel hydrocarbons that are directly related to the chemistry of the original OM. Therefore, OM analysis can serve as a vital tool for understanding petroleum generation potential as well as the thermal maturity (Langford and Blanc-Valleron, 1990). In this study, molecular properties are dependent both on maturity and OM source. Pyrolysis method which involves the thermal degradation of OM with sequential heating is a standard method for characterizing and evaluating source rocks (Hunt *et al.*, 2002). The quantitative peaks generated from pyrolysis by hydrocarbon per gram of rock depends on the chemical components of the rocks like carbohydrates, proteins, and lignins. Marine sources such as phytoplanktons, zooplanktons, bacteria, and algae have a higher amount of proteins and lipid biomolecules whereas terrestrial sources are rich in carbohydrates and lignin. Proteins and lignin biomolecules contain higher aliphatic carbon chains and lower concentrations of carbon-oxygen bonds in their structure as compared to carbohydrates and lignin. Therefore, H/C ratio of marine

OM (Type I kerogen) is higher than terrestrial OM (Type III kerogen), whereas O/C ratio is higher for terrestrial OM and lower for marine OM. The H/C and O/C ratios for different types of kerogen are: H/C ~1.5 and O/C <0.1 (Type I), H/C ~ 1.2 – 1.5 and O/C ratio between 0.1 and 0.3 (Type II), and Type III kerogen has H/C less than 1.0 and O/C ~0.3. (Van Krevelen, 1961, Peter and Moldowan, 1993). For each type of kerogen, atomic ratios H/C and O/C decreases on increasing maturity due to the removal of aliphatic chains (composed of CH₂ bonds) and oxygen-rich compounds such as asphaltene and resins on increasing maturation (Hunt, 1996). The H/C and O/C ratios and their ‘evolution path’ with increasing maturation are used to classify different types of kerogen in the van Krevelen diagram. The HI and OI indices calculated from S₂ and S₃ peaks of SRA are analogous to H/C, and O/C atomic ratios of source rocks (Tissot and Welte, 1978,) and can be used to determine the kerogen type. However, in our samples due to high maturity, the HI and OI values for both WV-6 and WV-7 cores are very low and fall in the common range of all types of kerogen (Fig. 4) in the van Krevelen diagram (van Krevelen, 1961), limiting the applicability of this plot to determine kerogen type.

However, individual parameters determined from SRA analysis can still provide some useful insight on sources of organic matter. The amount of free HC (S1) and kerogen bound HC (S2) depends on the type of source of OM and thermal maturity. If the source of OM is constant the relative fraction of free (S1) and bound (S2), HC remains similar unless the thermal stress regime changes. Therefore, the constant source will give a positive correlation between S1 and S2 values (Dayal *et al.*, 2014).

From the SRA data, a significant linear correlation ($R^2 = 0.94$) is obtained between the S1 and S2 values for the WV-7 cores (Fig. 5a). Using this observation, it can be inferred that the same source of OM was dominant during the deposition of the WV-7 sediments. A relatively poor

correlation between the S1 and S2 values for WV-6 core sediments ($R^2 = 0.44$) (Fig. 5b) indicates that probably more than one dominant source of OM was prevalent during the deposition of WV-6 sediments. The poor correlation can also be indicative of surficial contamination of shale samples or due to sample degradation associated with long-term storage of the core. But since the samples were taken from the inner portion of both cores and cores were stored under similar conditions, it is less likely that the difference observed is related to contamination and/or storage related issues. It can be inferred that probably WV-6 was deposited more towards basin margin and therefore received a higher influx of mixed OM, from both marine and the terrestrial origin and hence is more gas prone. The isotopic and geochemical proxies also support this conclusion (Chen *et al.*, 2015). Additionally, terrestrially derived OM contains more amount of oxygen as compared marine-derived OM. So, OM which has more terrestrial input will give a larger S3 peak and a lower S2/S3 ratio. In the S2/S3 vs. TOC plots, it can be noted that for the same amount of TOC WV-6 samples consistently have much lower S2/S3 ratios as compared to WV-7. This further supports the conclusion that WV-7 had less influx of terrestrial OM as compared to WV-6. (Fig. 6),

For any particular OM, at any particular maturity, the ratio between kerogen bound HC (S2) and TOC should remain constant. Hence, to determine the type of HC produced S2 vs. TOC plots (Fig. 7) can also be used (Dahl *et al.*, 2004). In this plot, WV-7 lies in the wet gas prone region and WV-6 lies in the dry gas prone region (Fig. 7). These plots also support the argument that WV-7 had a lower influx of gas prone terrestrial OM as compared to WV-6. Additionally, the lower R^2 (0.54) values for WV-6 samples as compared to WV-7 samples ($R^2=0.92$) also provides evidence that WV-6 samples received mixed sources of OM during deposition.

Different types of OM contain different amount/type of biomolecules and have a different distribution of *n*-alkanes. Thus, the relative distribution of *n*-alkanes has also been used to determine the sources of OM in shales (Cranwell, 1982; Meyers, 1997; Peters et al. 2005 a,b). The majority of *n*-alkanes contributed by marine OM sources such as bacterial and algal OM possesses shorter chains mainly at C-15, C-17, and C-19 while terrestrial OM possesses odd-numbered long-chain *n*-alkanes predominantly at C-23, C-25, C-27, C-31 and C-33 (Clark and Blumer 1967; Cranwell, 1973; Ahad *et al.* 2011). The longer chains of *n*-alkanes are primarily associated with the waxy protective coatings of the leaf cuticles that protect them from infection, damage, and desiccation (Eglinton and Hamilton, 1967). Marine organisms such as bacteria and algae do not have this protective coating and hence do not contain long-chain *n*-alkanes.

The presence of higher shorter chain *n*-alkanes in WV-7 compared to WV-6 in both the OI zone and OR zone further indicates that WV-7 shales were deposited in a more marine geological setting and the major influx of OM was from marine organisms such as algae or cyanobacteria (Fig. 3a, b). Concentrations and ratios of pristanes (Pr) and phytanes (Py) were also used as additional proxies to determine the source of OM and redox conditions. Phytanic acid, which is the precursor of pristane is formed by aerobic degradation of chlorophyll. Since aerobic degradation is favorable in regions closer to land, greater production of pristane takes, and a higher Pr/Py ratio is generally observed in terrestrial settings (Powell and Mckirdy, 1973; Peters et al. 2005b) which is determined by the ratios of Pr/Py in marine and terrestrial sources of OM. Pr/Py ratios less than 1 indicates a marine sourced organic matter deposited in an anoxic environment and Pr/Py ratios greater than 3 indicates terrigenous organic matter input deposited in an alternating anoxic-oxic environments (Didyk et al., 1978, Peters et al. 2005). Due to the absence of Pr, Py, and *n*-31 in the OI zone of WV-7 these comparisons are based on the data obtained from

the OR zone only. The Pr/Py ratio in the OR zone of WV-6 and WV-7 are 1.65 and 1.33 respectively. This indicates that both sites were primarily dominated by a contribution from marine OM sources deposited in an anoxic-suboxic environment in the OR zone. However, the higher Pr/Py ratio in WV-6 compared to WV-7 indicate it was probably deposited in relatively more oxic or shallower part of the marine basin as compared to WV 7. The *n*-alkane distribution also suggests that WV-6 had a higher influx of terrestrial OM.

Pr/n-C17 vs. Py/n-C18 plot has been used extensively by researchers (For, e.g., Peters et al., 2005, Song et al., 2014, Adegoke et al., 2014) to determine types of kerogen and redox conditions of deposition. Pr/n-c17 and Py/ n-c18 ratios in the plot lies inside or on the boundary of Type II-III kerogen field (Fig. 8) indicating that both sites received mixed sources of OM. It also indicates that OI zone of WV-6 shale cores might have received higher terrestrial influx and was deposited in a more oxidizing environment as compared to OR zone. Using both SRA and biomarker proxies, it can be interpreted that both cores had mixed sources of OM with WV-6 having higher terrestrial matter influx, making it more gas prone. This, in conjunction with all other parameters discussed above clearly support that WV-6 was probably deposited near the basin margin and received relatively more input of terrigenous organic matter as compared to WV-7 which agrees with interpretations made by Chen et al. 2015.

These observations suggest that S1 vs S2 plots, S2/S3 vs TOC plots, S2 vs TOC plots derived from SRA parameters as well as *n*-alkane distribution, Pr/Py ratio and Pr/n-C17 vs. Py/n-C18 plots derived from biomarker analysis can be used to determine changes in sources of OM and kerogen type for mature shales ($VR_o > 1$). It is important to note that all samples used in this study had TOC values > 1.13 wt. % and thermal maturity between $VR_o = 1$ to 2. Therefore, we

propose that these SRA and biomarker proxies can be used for determining OM sources in mature shales with similar TOC and maturity values in other basins of the world.

1.5.2 PALEOREDOX CONDITIONS

For WV-7 shale cores, a positive correlation is observed between HI vs. TOC plot and a negative correlation in OI vs. TOC plot (Fig. 9 a, b). This correlation trend indicates that OM was deposited in dominantly anoxic and reducing depositional conditions in low oxygen, low Eh and low pH conditions which are more prone for the generation of HC (Tissot and Welte, 1984). On the other hand, the samples from the WV-6 core show a poor correlation between HI, OI, and TOC (Fig. 10a, b). This might indicate fluctuating paleoredox and relatively poor OM preservation during the deposition of the WV-6 core.

In addition to OM source and type, biomarker ratios are also used to determine the paleoredox conditions at the time of deposition. The Ts/Tm hopane ratio can be used to interpret paleoredox because the oxidizing conditions favor preservation of Tm and reducing conditions favor preservation of Ts (Moldowan *et al.*, 1985). The Ts/Tm values greater than 2.0 indicate predominately anoxic conditions, values less than 1.0 indicate predominately oxidizing conditions, and the values between 1.0 and 2.0 indicate alternating oxic and anoxic conditions (Solevic *et al.*, 2008). The Ts/Tm ratios for both WV-6 and WV-7 were very similar ranging from 0.94 to 1. This indicates hopane ratios cannot be used to determine the paleo-redox environment in samples at maturity levels of VRo > 1.

The Pr/n-C17 and Py/ n-C18 cross plots (Fig. 8) suggest that OI zone of WV-6 shale cores were deposited in more oxidizing environment as compared to OR zone. This plot cannot be used to decipher any significant difference between the OR zone of WV-6 and WV-7. However, as discussed earlier, the higher Pr/Py ratio for OR zone of WV-6 as compared to the OR zone of WV-

7 (Table. 3) suggest that sediments in OR zone of WV-6 cores were deposited in comparatively more oxic conditions as compared to OR zone of WV-7. These observations complement the interpretations derived from the calculated SRA parameters (this study) and the established geochemical proxies in the previous study by Chen et al., 2015. This suggests that HI vs. TOC plot and OI vs. TOC plot derived from SRA parameters and Pr/n-C17 and Py/n-C18 derived from biomarker analysis might serve as an important tool for determining paleo-redox conditions during deposition of mature black shale in other basins of the world.

1.5.3 THERMAL MATURITY

Every oil or natural gas shale play is unique, and this distinction is not only dependent on the source rock but also on the thermal maturity of the basin. The traditional way to determine the thermal maturity of shales is by determining Tmax from SRA or vitrinite reflectance (VRo). Tmax values and calculated vitrinite reflectance of WV-7 shale cores, (Table 1) suggests WV-7 belongs to the wet-gas window (average Tmax =464 °C, average calculated VRo =1.19). However, Tmax determined for WV-6 shales show anomalous values possibly due to very low values of S2, and it cannot be used to determine thermal maturity. However, the presence of a higher ratio of RC/PC (Average RC/PC of WV-7 is 167.42 and of WV-6 is 1104.12) and the conversion of a greater fraction of OM to hydrocarbon (f) for WV-6. (average f for WV-7 is 84 %, average f for WV-6 is 97%) (Table 1) indicates that WV-6 is more mature than WV-7 shales. This also suggests that WV-6 shale should probably belong to dry gas maturity stage. Fraction conversion to HC from organics depends on the hydrogen index of immature shale samples (HI⁰) which is assumed to be 250 mg/g rock as observed for immature Marcellus shales in New York (Bruner and Smosna, 2011). PI⁰ is assumed to be 0.02 (Peters et al. 2005 a).

Several biomarker proxies have been used to determine the thermal maturity of source rocks including Pr/n-17, Py/n-18 and Ts/Ts+Tm (Peter and Moldowan, 1993, Peters et al., 2005 b). On maturation, Pr/n-17, Py/n-18 ratios increase while Ts/Ts+Tm decrease (Peter and Moldowan, 1993, Peters et al., 2005 b). For the OR zone of WV-6 and WV-7 shales, Pr/n17 and Py/n-18 are higher for WV-6 shales (Table. 2) which is consistent with the inferences drawn from the SRA data. However, Ts/Ts+Tm ratio is very similar in both WV-6 and WV-7 shale samples probably due to selective thermal degradation/alteration of hopane biomarkers (Farrimond et al., 1998). This indicates that hopane biomarker ratios cannot be used to determine thermal maturity for mature source rocks. ($V_{Ro} > 1$). However, parameters such as fraction of OM to hydrocarbon (f), RC/PC ratio as well as Pr/n17 and Py/n-18 ratios can be utilized to evaluate thermal maturity in mature shales.

1.6 CONCLUSIONS

Source rock analysis (SRA) and aliphatic biomarker analysis was conducted on mature Marcellus Shale samples. Due to low concentrations of biomarkers in our samples we used an improved biomarker extraction procedures and analyzed them using high resolution GCxGC technique. Source rock analysis (SRA) indicate that sediments in WV-7 core had comparatively higher amounts of free HC (S1), and HC released from cracking of kerogen (S2) than the samples from the WV-6 core. The traditional hydrogen and oxygen indices (HI vs. OI plot) could not be used to determine the kerogen type due to very low values of HI and OI. However, S1 vs. S2 and S2/S3 vs. TOC cross plots indicate that both cores received mixed sources of OM indicative of Type II-III kerogen. These plots also indicate WV-6 core received a higher influx of terrestrial OM and therefore the kerogen is more gas prone as compared to that in the WV-7 core. The fraction conversion of OM to HC, the ratio of residual carbon/pyrolysable carbon (RC/PC), thermal

maturity parameter ($T_{\max}$), and calculated vitrinite reflectance (VR_o), together suggest that samples from WV-7 and WV-6 belong in the wet and dry gas window respectively which is in agreement with hydrocarbon production data of these wells. The higher maturity of WV-6 samples is also supported by higher values of Pr/n17 and Py/n-18 ratios as compared to WV-7 in OR zone. The Pr/n-17 vs. Py/n-18 cross plots as well as n-alkane biomarker distribution indicate both cores have mixed Type II-III kerogen complementing the interpretations from SRA analysis. The higher Pr/Py ratio in OR zone of WV-6 samples indicate that sediments were deposited in more oxic conditions compared to OR zone of WV-7. Our data indicate that hopane biomarkers are not useful for interpreting paleoredox or thermal maturity in shale samples with $VR_o > 1$.

The interpretations based on the SRA and biomarker data match well with the conclusions drawn from a previously published study on these two cores and the hydrocarbon production data of the wells. We propose that the methods used in this study could be used to determine OM sources, paleoredox conditions, and thermal maturation in mature shales with similar TOC values, and maturity ranges in other basin of the world.

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TABLES

Table 1: Sample depths and parameters calculated from Source rock analyzer (SRA)

Sample ID	Depth Range (m)		Tmax °C	%TOC	Mean S1 mg HC/g	Mean S2 mg HC/g	S3 mg CO2/g	HI mg HC/g TOC	OI mg CO2/g TOC	PI ratio	Pyrolysable Carbon(PC) (mg HC/g of rock)	Residual carbon(RC) (mg HC/g of rock)	RC/PC	Calculated VRo
WV6-81a	2240	2240.8896	-	2.75	0.52	0.58	0.40	21	14	0.48	0.09	26.59	291.20	-
WV6-1a	2241.8	2242.7184	-	2.92	0.18	0.23	0.17	8	6	0.42	0.03	28.86	850.59	-
WV6-2a	2242.7	2243.6328	-	2.80	0.17	0.14	0.17	5	6	0.54	0.03	27.74	1085.29	-
WV6-3a	2243.6	2244.5472	-	3.23	0.16	0.19	0.19	6	6	0.46	0.03	32.01	1085.29	-
WV6-4a	2244.5	2245.4616	-	2.68	0.16	0.16	0.14	6	5	0.50	0.03	26.53	994.02	-
WV6-5a	2245.5	2246.376	-	3.14	0.19	0.25	0.23	8	7	0.43	0.04	31.04	850.59	-
WV6-6B-a	2246.4	2246.6808	-	3.40	0.17	0.17	0.20	5	6	0.47	0.03	33.72	1194.82	-
WV6-6C-a	2246.9	2247.2904	-	3.18	0.13	0.10	0.18	3	6	0.53	0.02	31.62	1711.17	-
WV6-7a	2247.3	2247.65616	-	2.93	0.26	0.12	0.21	4	7	0.69	0.03	28.98	916.78	-
WV6-8a	2247.9	2248.2048	-	2.90	0.12	0.12	0.21	4	7	0.49	0.02	28.81	1496.02	-
WV6-9B-avg	2248.2	2249.1192	-	3.08	0.15	0.11	0.17	4	6	0.56	0.02	30.62	1424.19	-
WV6-10a	2249.1	2250.0336	-	2.84	0.20	0.11	0.22	4	8	0.66	0.03	28.14	1085.29	-
WV6-11a	2250	2250.948	-	3.25	0.55	0.52	0.29	16	9	0.52	0.09	31.61	355.10	-
WV6-12	2250.9	2251.5576	-	3.08	0.48	0.35	0.28	11	9	0.57	0.07	30.15	435.49	-
WV6-15a	2252.8	2253.29496	-	3.91	0.23	0.27	0.65	7	17	0.49	0.04	38.68	916.78	-
WV6-17a	2253.7	2254.6056	-	3.69	0.37	0.22	0.33	6	9	0.60	0.05	36.41	743.01	-
WV6-18avg	2254.6	2255.52	-	2.97	0.14	0.17	0.15	6	5	0.46	0.03	29.43	1113.36	-
WV6-19a	2255.5	2256.4344	-	3.83	0.23	0.23	0.24	6	6	0.50	0.04	37.92	994.02	-
WV6-20a	2256.4	2256.86112	-	3.88	0.27	0.39	0.42	10	11	0.40	0.05	38.25	698.72	-
WV6-22a	2257.3	2258.2632	-	4.37	0.22	0.31	0.91	7	21	0.40	0.04	43.26	994.02	-
WV6-24a	2259.2	2259.36048	-	3.44	0.28	0.17	0.34	5	10	0.61	0.04	34.03	916.78	-
WV6-84a	2259.5	2259.6348	-	1.13	0.23	0.27	0.14	24	12	0.46	0.04	10.89	263.82	-
WV6-25a	2259.7	2260.092	-	3.28	0.20	0.13	0.29	4	9	0.60	0.03	32.53	1194.82	-
WV6-29a	2262.8	2263.7496	-	3.25	0.16	0.16	0.45	5	14	0.52	0.03	32.23	1194.82	-
WV6-32a	2264.7	2265.5784	-	3.50	0.32	0.25	0.20	7	6	0.57	0.05	34.54	743.01	-
WV6-85a	2266	2266.188	-	3.52	0.05	0.02	0.27	1	8	0.71	0.01	35.19	6057.52	-
WV6-36a	2266.5	2267.4072	-	3.95	0.28	0.36	0.54	9	14	0.43	0.05	38.98	743.01	-
WV6-37a	2266.5	2267.1024	-	4.11	0.16	0.16	0.47	4	12	0.50	0.03	40.83	1496.02	-
WV6-39a	2267.4	2268.3216	-	4.66	0.19	0.33	0.37	7	8	0.39	0.04	46.17	1085.29	-
WV6-40a	2268.3	2269.236	-	5.60	0.39	0.50	0.44	9	8	0.43	0.07	55.26	743.01	-
WV6-41a	2269.2	2270.1504	-	7.05	0.42	0.71	0.40	10	6	0.36	0.09	69.56	743.01	-
WV6-43a	2271.1	2271.9792	-	7.61	0.38	0.76	0.50	10	7	0.34	0.09	75.15	793.21	-
WV6-45a	2272.9	2273.5032	-	5.76	0.23	0.40	0.42	7	7	0.37	0.05	57.07	1085.29	-
WV6-86a	2273.5	2273.808	-	5.48	0.27	0.33	0.70	6	13	0.46	0.05	54.30	1085.29	-
WV6-47a	2274.7	2275.6368	-	5.83	0.23	0.41	0.52	7	9	0.36	0.05	57.77	1085.29	-
WV6-47a	2274.7	2275.6368	-	6.10	0.24	0.43	0.42	7	7	0.35	0.06	60.44	1085.29	-
WV6-49a	2276.6	2277.4656	-	4.88	0.34	0.44	0.43	9	9	0.41	0.06	48.15	743.01	-
WV6-52a	2278.4	2278.8372	-	5.47	0.27	0.49	0.55	9	10	0.36	0.06	54.06	850.59	-
WV6-53a	2279.3	2280.2088	-	6.56	0.39	0.72	0.37	11	6	0.38	0.09	64.67	698.72	-
WV6-54a	2280.2	2281.1232	-	7.59	0.23	0.46	0.58	6	8	0.33	0.06	75.33	1328.69	-
WV6-54a	2280.2	2281.1232	-	7.65	0.23	0.46	0.44	6	6	0.35	0.06	75.93	1328.69	-
WV6-55a	2281.1	2282.0376	-	9.64	0.29	0.58	0.60	6	6	0.29	0.07	95.68	1328.69	-
WV6-55a_R	2281.1	2282.0376	-	9.74	0.29	0.68	0.60	7	6	0.30	0.08	96.59	1194.82	-
WV6-56a	2282	2282.952	-	9.10	0.17	0.47	0.56	5	6	0.27	0.05	90.95	1712.10	-
WV6-57a	2283	2283.8664	-	7.99	1.36	1.68	0.56	21	7	0.45	0.25	77.38	307.06	-
WV6-59a	2284.8	2285.6952	-	7.03	0.21	0.42	0.78	6	11	0.32	0.05	69.77	1328.69	-
WV6-60a	2285.7	2286	-	6.67	0.13	0.33	0.57	5	9	0.28	0.04	66.31	1711.17	-
WV6-60a	2285.7	2286	-	6.83	0.14	0.34	0.59	5	9	0.31	0.04	67.90	1711.17	-
WV6-61a	2286	2286.6096	-	2.42	0.44	0.48	0.31	20	13	0.48	0.08	23.44	307.06	-
			-											
WV7-52a	1998	1998.8784	-	1.78	0.41	0.46	0.33	26	18	0.47	0.07	17.08	235.88	-
WV7-2a	1999.8	2000.7072	-	1.41	0.27	0.39	0.40	28	29	0.40	0.06	13.55	246.34	-
WV7-3a	2000.7	2001.6216	462	2.06	0.49	0.72	0.23	35	11	0.40	0.10	19.59	194.21	1.2
WV7-5a	2001.9	2002.536	457	1.88	0.39	0.60	0.33	32	18	0.39	0.08	17.97	217.32	1.1
WV7-5a	2001.9	2002.536	459	1.85	0.41	0.54	0.26	29	14	0.43	0.08	17.72	226.24	1.1
WV7-6a	2002.5	2003.4504	455	1.91	0.34	0.46	0.35	24	18	0.42	0.07	18.43	276.86	1.0
WV7-9a	2005.3	2005.584	445	7.02	2.18	2.39	0.44	34	6	0.47	0.38	66.41	175.36	0.9
WV7-10a	2005.6	2006.1936	467	7.85	2.83	5.50	0.60	70	8	0.34	0.69	71.59	103.66	1.2
WV7-12a	2007.1	2008.0224	472	5.69	1.82	3.53	0.30	62	5	0.34	0.44	52.46	118.17	1.3
WV7-13a	2008.3	2008.9368	475	3.13	0.91	1.41	0.22	45	7	0.39	0.19	31.11	161.55	1.4
WV7-14a	2008.9	2009.8512	462	7.58	2.43	5.69	0.45	75	6	0.30	0.67	69.07	102.60	1.2
WV7-16a	2010.8	2011.2228	469	6.62	2.25	4.17	0.17	63	3	0.35	0.53	60.87	114.21	1.3
WV7-18a	2011.7	2012.442	471	6.27	2.13	4.26	0.38	68	6	0.34	0.53	57.39	108.12	1.3
WV7-53a	2012.4	2012.8992	475	1.26	0.26	0.29	0.20	23	16	0.48	0.05	12.14	263.82	1.4
WV7-19a	2012.9	2013.5088	446	5.20	1.51	1.61	0.35	31	7	0.49	0.26	49.41	190.80	0.9
WV7-21a	2014.4	2015.0328	461	8.47	2.54	5.17	0.52	61	6	0.33	0.64	78.30	122.40	1.1
WV7-22a	2015.3	2016.252	475	8.75	2.89	6.04	0.52	69	6	0.32	0.74	80.09	108.12	1.4
WV7-23a	2016.3	2016.7092	475	12.91	5.53	10.67	0.27	83	2	0.34	1.34	127.76	95.01	1.4
WV7-24a	2016.7	2017.1664	470	9.89	3.36	6.03	0.27	61	3	0.36	0.78	91.10	116.82	1.3
WV7-25a	2017.2	2018.0808	462	2.33	0.51	0.77	0.25	33	11	0.40	0.11	22.24	209.06	1.2
WV7-26a	2018.1	2018.9952	466	9.29	2.79	6.13	0.60	66	6	0.31	0.74	85.50	115.50	1.2
WV7-27a	2019	2019.3	460	3.02	0.85	1.06	0.28	35	9	0.45	0.16	28.62	181.24	1.1
					1.69	3.09								
Samples marked in red were selected for biomarker analysis														

Table 2: The biomarker ratios calculated from samples collected from OR and OI zone in WV-6 and WV-7.

Parameters	WV-7(OR zone)	WV-6(OR zone)	WV-7(OI zone)	WV-6(OI zone)
Pr/n-c17	0.5	0.93	-	0.57
Py/n-18	0.45	1	-	0.32
Pr/n-c18	0.6	1.65	-	0.67
n-c17/N-n31	9.6	11.27	-	5.87
Pr/Py	1.33	1.65	-	2.08
Tm/Ts	0.94	1	-	0.96
Ts/(Ts+Tm)	0.52	0.5	-	0.51
TAR	0.23	0.22	-	0.31

Pr, Py, n-c31 and hopanes (Ts and Tm) were present in unquantifiable amount in OI zone of WV-7.

FIGURES

Figure 1: Samples for biomarker analysis are marked in red. Samples marked as 1, 3 are from OI (organic intermediate) zone while 2 and 4 are from OR (organic rich) zone. Samples marked by black dots in both zones were collected at approximately at 1 meter intervals for SRA analysis. This figure is modified from Chen et al. (2015)

Figure 2: Average S1 and S2 values of WV-6 and WV-7 shale samples.

Figure. 3. Graphs depicting normalized *n*-alkane distribution in the shale samples collected from the organic intermediate (OI) (a) and organic rich (OR) (b) zones of wells WV-6 and WV-7. The normalized value of each normalized *n* alkane biomarker is calculated by dividing concentration of that particular *n*-alkane with the total concentration of *n*-alkane biomarkers.

Figure. 4: Van-krevelen diagram for WV-6 and WV-7 samples

Figure 5: The S1 vs. S2 plots for (a) WV-7 and (b) WV-6 samples.

Figure 6: The S2/S3 vs TOC plots for (a) WV-6 and (b) WV-7 samples.

Figure 7: The S2 vs TOC plots for (a) WV-6 and (b) WV-7 samples

Figure. 8 Pristane *n*-17 vs Phytane/*n*-18 plots for WV6 (grey circle) and WV 7(black circles) samples. OR represents organic rich sample, OI represents organic intermediate sample.

Figure. 9 (a) HI vs TOC and (b) OI vs TOC plots for WV-7 samples

Figure. 10 a) HI vs TOC and b) OI vs TOC plots for WV-6 samples.

Chapter II:

Molecular Characterization of Kerogen and its Implications for Determining Hydrocarbon Potential, Organic matter sources and Thermal Maturity in Marcellus Shale

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2. Molecular Characterization of Kerogen and its Implications for Determining

Hydrocarbon Potential, Organic matter sources and Thermal Maturity in Marcellus Shale

Keywords: Kerogen, organic matter, thermal maturity, Marcellus Shale, NMR

2.1 ABSTRACT

Organic-rich shales are a vital component of the US energy sector. Kerogen, a high molecular weight macromolecule is the largest reservoir of organic carbon on earth and serves as the starting material for the oil and gas generation in these shales. Despite its importance, kerogen structure and its evolution on maturation are still not well understood, especially for mature shales ($V_{Ro} > 1$). Moreover, most of the models built to determine hydrocarbon (HC) potential and thermal maturity of the source rocks have used the structural parameters of kerogen extracted from immature shales ($V_{Ro} < 1$). Therefore, these models might not yield accurate results for mature and over-mature shales like Marcellus. In this study, we determine the structural parameters of kerogen extracted from three Marcellus Shale cores using ^{13}C solid-state Nuclear magnetic resonance (NMR). Samples were acquired from the upper and lower Marcellus Shale Formation from a dry gas well WV-6 ($V_{Ro} > 2.5$), a wet gas well WV-7 ($V_{Ro} \sim 1.4$) and an oil window well BG-1 ($V_{Ro} \sim 0.81$) in Wetzel, Monongalia and Brooke County, West Virginia, respectively. Our results indicate that the percentage of carbon chains such as mobile (freely rotating) and immobile alkyl without heteroatoms (with restricted rotation), and alkyl-substituted aromatic carbons decrease with increasing maturity indicating that these chains are more prone to thermal degradation and might have higher HC generating potential. However, carbon chains such as O-substituted alkyl (ether), O_2 substituted alkyl (dioxy alkyl), amine, protonated aromatic carbons, O-substituted aromatic (phenol) and bridgehead aromatic carbons does not decrease directly with

thermal maturity suggesting that these groups are either more refractory in nature or their carbon fraction is influenced by changing sources of OM. Our results also indicate that the previous models based on the structural parameters of kerogen derived from immature shales overestimate the HC generation potential and underestimate the thermal maturity in mature shales. In addition, H, O, C ratios derived from structural parameters of kerogen can be utilized to determine the kerogen type in these mature shales where traditional pyrolysis analysis fails to characterize the kerogen.

2.2 INTRODUCTION

Kerogen, the insoluble fraction of organic matter (OM) in sediments— is the largest and economically most important reservoir of sedimentary organic carbon and source of all hydrocarbons in the subsurface. Therefore, it is essential to accurately characterize the structure of kerogen and its HC generation potential. However, there is a significant gap in understanding the mechanism of kerogen cracking and HC generation especially for mature shales ($VR_o > 1$) mostly due to the insolubility and chemical heterogeneity of kerogen. Additionally, limited analytical techniques are capable of providing quantitative molecular-level information on the chemical structure of kerogens (Boucher et al., 1990, Espitalie 1985, Vandenbroucke and Largeau, 2007).

Kerogen is formed by the degradation, condensation, and polymerization of biomolecules contributed by different sources of OM (e.g., Huc and Durand, 1974, Tissot and Welte, 1984, Hedges 1988, Vandenbroucke and Largeau, 2007). Kerogen formed in the diagenetic stage of burial later cracks to form oil and gas in catagenetic and metagenetic stages of burial. Most of the current studies on kerogen have been focused on methods such as visual kerogen analysis and pyrolysis using a Source Rock Analyzer (SRA). These methods are helpful in determining the type of kerogen, maturity, and oil vs. gas generating potential but do not provide any information on

the chemical structure or composition of kerogen (Vandenbrouke and Largeau, 2007). Moreover, for mature/over-mature source rocks SRA produces biased results about the OM sources and maturity due to low amounts of free/bound hydrocarbons, and incomplete combustion of refractory OM, and/or the hydrocarbons bound in a mineral matrix (Vandenbrouke and Largeau, 2007). Biomarker ratios have also been used to determine the thermal maturity of source rocks (Peters et al., 2005 b, Shen and Huang, 2007; Arfaoui et al., 2007, Kroon et al., 2011). However, due to thermal degradation and alteration of biomarkers on maturation and low extraction efficiency in high maturity samples, the results can be biased.

To understand kerogen cracking mechanism at the molecular level and to accurately predict HC potential from any source rock, it is vital to understand the molecular structure of kerogen (Behar and Vandenbroucke 1987, Vandenbroucke 2003, Vandenbrouke and Largeau, 2007). Several analytical techniques have been developed for characterization of the chemical structure of kerogen, which are commonly classified into two major groups: destructive (pyrolytic) and non-destructive (spectroscopic) methods (Tong et al., 2011; Cao et al., 2013a, 2013b). The pyrolytic techniques analyses can provide valuable information about the labile/pyrolyzable fraction of kerogen (Behar and Vandenbroucke 1987, Horsfield 1989, Siskin et al., 1995, Lille et al., 2003). However, the products generated from pyrolysis can interact among themselves and yield biased results about the components present in the labile fraction of kerogen (Horsfield 1989). Moreover, most of the kerogen models developed using the yield from pyrolysis experiments are conducted under elevated temperature (~250 to 650°C) and then extrapolated to ~100 to 170 °C (Freund et al., 2007, Walters et al. 2007). These results may not reliable as the time span differs by ~14 orders of magnitude (Freund et al., 2007, Walters et al. 2007). Additionally, the pyrolysis results depend on whether the reaction is conducted in an open vs. closed systems (Behar et al., 1997) or in

hydrous vs. anhydrous conditions (Lewan and Ruble, 2002). Due to this, the reactions taking place in laboratory conditions might not be representative of sedimentary basin conditions. Due to these limitations, non-destructive methods such as Fourier transform infrared (FT-IR), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and ^{13}C solid-state nuclear magnetic resonance (^{13}C NMR) have been employed for the qualitative, semi-quantitative, and quantitative measurements of kerogen (Dennis et al., 1982; Witte et al., 1988; Kelemen et al., 2007; Petersen et al., 2008; Tong et al., 2011).

The ^{13}C solid-state NMR techniques provide the maximum amount of structural information on kerogen due to its higher accuracy and quantification capacity compared to other direct analytical methods, (Mao et al., 2010). The most extensively used solid-state NMR technique for kerogen characterization is ^{13}C cross polarization/magic angle spinning (CP/MAS) (Dennis et al., 1982; Witte et al., 1988; Patience et al., 1992, Mann et al., 1991, Lille et al., 2003; Wei et al., 2005; Keleman et al., 2007, Werner-Zwanziger et al., 2005, Longbottom et al., 2016, Longbottom et al., 2017). However, by using ^{13}C CP/MAS alone, the fraction of non-protonated carbons and mobile groups (with non-restricted rotation) cannot be determined. Therefore, advanced solid-state NMR techniques such as multiple CP /MAS, multiple CP /MAS plus dipolar dephasing have been developed and applied in the recent years for systematically characterizing kerogen (Mao et al., 2010, Johnson and Schmidt-Rohr, 2014). These advanced ^{13}C NMR techniques can be used for determining specific functional groups, aromaticity, and aromatic cluster size and better understanding the chemical structure of kerogen. A few researchers have used advanced NMR techniques, to determine the molecular structure of kerogen (For, e.g. Kelemen et al., 2007, Tong 2011, Longbottom et al., 2016, Longbottom et al., 2017). However, most of these studies were conducted mainly on low maturity or immature samples. The models developed using these

immature shales (Kuangzong et al., 1991, Longbottom et al., 2016, Wei et al., 2005) can result in underestimation/overestimation of HC potential (especially gas) and thermal maturity especially in mature shales with $V_{Ro} > 1$. For accurate estimation of HC potential in newly emerging mature shale plays like Marcellus, there is a need to develop better understanding of the molecular structure of kerogen in mature shales with $V_{Ro} > 1$

The goal of the study is to determine changes in structural parameters of kerogen using ^{13}C solid-state NMR in Marcellus Shale maturity series with V_{Ro} ranging from 0.8 to 2.5. Kerogen was extracted from sediments from upper and lower Marcellus Shale Formation from three wells lying in the oil window (BG-1), wet gas window (WV-7) and in the dry gas window (WV-6). The location of the three wells is shown in Fig. 1. The easternmost WV-6 core has a thermal maturity of $V_{Ro} > 2.5$, WV-7 core has $V_{Ro} \sim 1.4$ (Agrawal and Sharma 2017a, Zagorski. et al., 2012), and the BG-1 core has $V_{Ro} \sim 0.81-1.05$. The depositional environment of the wells WV-6 and WV-7 has been established using geochemical, isotopic, pyrolysis and biomarker proxies (Chen et al., 2015, Agrawal and Sharma, 2017a). The depositional model proposed by these studies suggest that the terrestrial sediment influx was from east to west part of the basin, and the model suggests that sediments in dry gas WV-6 well were deposited in shallower part of the basin and received higher terrestrial OM influx as compared to WV-7 shale that was deposited in the deeper and anoxic part of the basin. Further, it was shown that upper Marcellus Formation received more terrestrial OM input as compared to lower Marcellus Shale Formation. Although, detailed isotopic and geochemical study is not available for the well BG-1, since this well is located in the western part of the basin (Fig. 1), the sediments must have been deposited further away from the terrestrial sediment source in the eastern part of the basin.

2.3 MATERIALS AND METHODS

2.3.1 Sampling

Core samples have been collected from three wells (WV-6, WV-7, and BG-1) in the upper and lower zones of the Marcellus Shale Formation. Location of WV-6 is in Monongalia County, WV-7 is from Wetzel County, and BG-1 is from Brooke County, West Virginia. (as shown in Fig.1). To avoid any effects of contamination due to contact with drilling fluids and oxidation of OM (Martinez and Escobar 1995, Elie et al., 2000) at least 5mm of the outer layer of samples was removed before kerogen extraction. It is highly unlikely for fluids or air to penetrate >5mm of shale layer and contaminate/ oxidize the inner part of the core. After paring, the inner portion was crushed to 200 mesh and homogenized using a sterile SPEX mixer mill and oven dried for 24 hours at 50° C. Kerogen was extracted from ~50 grams shale cores using following steps (modified from Durand 1980, Vandenbroke and Largeau, 2007, Ibrahimov et al., 2010) as discussed below.

2.3.2 Kerogen Extraction

Soluble OM was extracted by sonicating 50 grams of powdered samples in approximately 120 ml of dichloromethane DCM multiple times till the color of the solution was transparent. The residue was sonicated again with ~120 ml MeOH–acetone–CHCl₃ (15:15:70 v/v) mixture to dissolve the remaining polar soluble OM. The carbonates mineral was then dissolved from the residue of by adding 6N HCl for 48-72 hours. This step was done multiple times until no effervescence was observed. Silicate minerals and the carbonates bound in silicate minerals was dissolved using a 1:1 mixture of 6N HCl and 50% HF for 24 hours. The residue was thoroughly rinsed with distilled water to avoid the formation of fluoride minerals. Remaining silicate minerals was dissolved by using 50% HF multiple times until all the silicate minerals are dissolved. Every time the HF step was followed by multiple rinsing with distilled water to avoid neo-fluoride formation. Heavy

minerals such as pyrite were removed by separating the denser phase by using 2.4gm/cc zinc bromide. The lighter phase containing the kerogen was decanted. The extracted residue was sonicated again with DCM to remove the soluble OM which was bound in mineral matrix and kerogen. Kerogen extraction was done at Sharma Isotope Lab at Geology and Geography Department, West Virginia University, Morgantown.

Figure 1. Location of wells BG-1, WV-7 and WV-6.

2.3.3 ^{13}C solid-state NMR analysis

Solid-state NMR experiments were performed at Environmental NMR Service at Old Dominion University in Norfolk, Virginia, USA on a Bruker Advance III 400 spectrometer operating at 400-MHz ^1H and 100-MHz ^{13}C frequencies. The ^{13}C chemical shifts were referenced to tetramethyl silane, using the COO resonance of glycine in the α -modification at 176.46 ppm as a secondary reference. The high-spinning speed multi-ramped amplitude cross polarization/magic angle spinning technique developed by Johnson and Schmidt-Rohr, 2014 was applied for acquiring

quantitative ^{13}C NMR spectra for all the kerogen samples. This multiple-cross polarization (multiCP) technique provides a simple, robust way to obtain quantitative solid-state ^{13}C NMR spectra of organic materials, with good signal-to-noise ratio. The spectra were measured at a spinning speed of 14 kHz, where spinning sidebands are fairly small (<3%) and have little overlap with center bands. To differentiate nonprotonated C from total C and to determine fractions of mobile groups (with no restricted rotation), ^{13}C multiCP/MAS with dipolar dephasing was performed under the same conditions as for ^{13}C multiCP/MAS but combined with a dipolar dephasing time of 68 μs (Mao and Schmidt-Rohr, 2004). The relative proportion of different carbon chains such as mobile and immobile alkyl without heteroatoms (written just as alkyl in this study), methoxy and amine, O-substituted and O_2 substituted alkyls (ethers and dioxy alkyl), protonated aromatic, bridgehead aromatic, alkyl substituted aromatic, O- substituted aromatic (phenol), carboxyl, carbonyl were obtained for ^{13}C NMR spectrum using an NMR peak fitting program *TopSpin* (as shown in Fig. 2, area of spectra from 0-240 ppm was considered to be 100%). Error associated with NMR analysis is reported as $\pm$ Standard deviation (Table 1). Standard deviation is calculated as: Integral of area of interest $\times$ 1/SINO, where SINO is signal to noise ratio. Noise to signal ratio for the total region (from 0-240ppm) was generally less than 2%.

2.4. RESULTS & DISCUSSION

2.4.1 Structural parameters of kerogen

Different aliphatic and aromatic carbon chains have characteristic chemical shifts in an NMR spectra as shown in Table. 1 (Solum et al., 1989, Kuangzong et al., 1991, Baldock et al., 2004, Smernik et al., 2001). Dipolar dephasing method with multiple CP method allows the quantification of mobile aliphatic and protonated (and non-protonated) aromatic carbon chains along with other aliphatic and aromatic chains as shown in Table. 1 (Mao et al., 2007, 2010, Mao and Schmidt-Rohr, 2003, 2004; Cao et al., 2013a). The aliphatic and the aromatic fraction in the NMR spectra lies in 0-90 ppm and 90-165 ppm chemical shift range respectively. The fractions of different aliphatic and aromatic chains of kerogen extracted from upper and lower Marcellus of BG-1, WV-6 and WV-7 shale cores were calculated using the peak area of the respective chemical shifts in a NMR spectra (Table. 1, Fig. 2). The fractions of aliphatic carbon, alkyl (without heteroatoms), methoxy and amine, O and O₂ substituted alkyl carbons (ether and dioxy alkyl), total aromatic carbon, alkyl substituted aromatic, O-substituted aromatic (phenol), carboxyl and amide, aldehyde and ketone were determined using the multiple CP method (without dipolar dephasing). However, the fractions of mobile (freely rotating) and immobile (restricted rotation) methyl, mobile and quaternary alkyl (without heteroatoms), methoxy, protonated aromatic, non-protonated aromatic bridgehead carbon (fa^B) were determined using dipolar dephasing method with multiple CP (Table. 1, fig.2). Using these aliphatic and aromatic structural parameters, several lattice structural parameters such as fraction of aromatic carbons with attachments or substituents (FAA), average aliphatic carbon chain length (Cn'), average carbons per aromatic cluster (C) and SP²/ SP³ hybridized carbon ratio was determined (Hockaday et al., 2009, Keleman et al., 2007) to construct kerogen models (Table 1 of supplementary information). FAA was determined by dividing the

sum of alkyl substituted aromatic carbon fraction and phenolic carbon fraction with the total aromatic fraction. C_n' was determined by dividing the fraction of aliphatic carbon with the alkyl substituted aromatic fraction. Average carbons per aromatic cluster (C) was determined by the equation proposed by Solum et al., 2001. SP^2/SP^3 hybridized carbon was determined by dividing the peak area 90-240 ppm to 0-90 ppm in multiple CP NMR spectra.

The peak area distribution using ^{13}C multiple CP NMR spectra shows that BG-1 kerogen samples have the highest average percentage of aliphatic carbon chains (28%) followed by WV-7 (26%) and WV-6 (~14%) (Fig. 3a). In all the six kerogen samples, the majority of aliphatic chains are alkyl chains with no heteroatoms (Fig. 3a). Alkyl carbon chains (without heteroatoms) followed a similar trend as total aliphatic carbon, and BG-1 kerogen samples had the highest average fraction of these carbon chains (23%) followed by WV-7 kerogen samples (~22%) then by WV-6 kerogen samples (9%). However, O and O_2 substituted alkyl carbon also does follow a single trend with increasing maturity as it decreases from BG-1 (~3.5%) to WV-7 (~2.2%) kerogen samples and then increases in WV-6 kerogen (~4.1 %). It was also observed that BG-1 upper Marcellus (~30% aliphatic and 26% alkyl) had relatively higher total aliphatic and alkyl fraction than lower Marcellus (25% aliphatic and 20% alkyl) kerogen sample but the total aliphatic and alkyl fraction in lower and upper Marcellus was similar for both WV-6 and WV-7 wells (Fig. 3a) within the same well. On the contrary, O and O_2 substitute alkyl groups were significantly different for upper and lower Marcellus kerogen for all the three wells (Fig. 3a).

Peak area distribution shows a lowest fraction of aromatic carbon in kerogen samples from BG-1 (67-70%) followed by WV-7 (73-75%) and WV-6 (85-89%) (Fig. 3b). A similar trend was observed for protonated aromatic carbon and bridgehead aromatic carbon, but an opposite trend was observed for alkyl substituted aromatic carbon (Table 1, Fig. 3b). The percentage fraction of

O-substituted aromatic carbons decreases from BG-1 to WV-7 kerogen, but increases on further from WV-7 to WV-6, similar to the trend observed for O and O₂ substituted aliphatic carbon chains. Comparison of the upper and lower Marcellus kerogen sample in individual wells shows that in BG-1 well, upper Marcellus Formation had relatively higher protonated aromatic carbon fraction and lower total aromatic and bridgehead fraction compared to lower Marcellus Formation (Fig. 3b). However, in wells WV-6 and WV-7 samples from both upper and lower Marcellus Formation had similar fractions of total aromatic, protonated, aromatic bridgehead and alkyl substituted aromatic carbon chains within the individual well (Fig 3b).

Lattice structural parameters FAA shows a general decrease in average no. of carbon per aromatic cluster (C) and a general increase in SP²/ SP³ hybridized carbon ratio from BG-1 to WV-7 to WV-6 (Fig. 3c, Table 1 in supplementary information). However, Cn' increases from BG-1 (1.82) to WV-7 kerogen (2.13) then decreases in WV-6 kerogen (1.49). The lattice structural parameters in lower and upper Marcellus Formation are similar in individual wells except for the least mature BG-1 well. In the BG-1 well, upper Marcellus has longer aliphatic chain length (Cn'), but lower C and SP²/SP³ hybridized carbon ratio.

2.4.2 Control of OM sources and maturity on kerogen structure

Major controls on kerogen structure are sources of OM and thermal maturity (Mann et al., 1991, Patience et al., 1992). If the contribution from marine OM sources is high, the kerogen will have higher alkyl fraction, a longer aliphatic chain length, less fraction of oxygen functional groups and less fraction of bridgehead aromatic carbons as compared to the kerogen composed of more terrestrial OM sources. (Mann et al., 1991). On the other hand, increasing maturity will result in a decrease of alkyl fraction, shortening of aliphatic chain length and an increase of total aromatic and bridgehead aromatic fraction (Patience et al., 1992). The kerogen samples used in this study

lie in the oil window (BG-1), wet gas window (WV-7), and dry gas window (WV-6) as supported by production data, geochemical, pyrolysis and biomarker analysis (Chen et al., 2015, Agrawal and Sharma, 2017a). The depositional model proposed by these studies and several other studies (Chen and Sharma, 2016, 2017) suggest that the terrestrial sediment influx was from east to west part of the basin. These studies also suggest that sediments in WV-7 well had a lesser influx of terrestrial OM as compared to WV-6 well. Further, it was proposed that upper Marcellus Formation in both WV-6 and WV-7 wells received higher input of terrestrial OM as compared to lower Marcellus Formation. Detailed isotopic and geochemical data is not available for BG-1 well. However, since this well lies in the western part of the basin (Fig. 1), it must have been deposited further away from the terrestrial sediment influx coming from the east.

The kerogen sample from upper Marcellus Formation from well BG-1 well (oil window; VRo ~0.8 to 1.05) shows higher percentage of total aliphatic fraction, alkyl carbon chains (without heteroatoms), protonated aromatic carbon, longer C_n' and lower percentage of aromatic bridgehead carbon, C, and SP² vs. SP³ hybridized carbon ratio compared to lower Marcellus Formation (Fig. 3a,b,c). This suggests that upper Marcellus Formation in the well BG-1 well received less terrestrial OM influx compared to the lower Marcellus Formation. This was probably because the sediments in the upper Marcellus Formation in well BG-1 were deposited in the up-dip section of the basin further away from the terrestrial sediment source (as shown by Parrish et al., 2013). This suggests that in the oil maturity window (VRo ~0.8 to 1.05) sources of OM can play a vital role in controlling the kerogen structure. Therefore, in this maturity range, the different structural parameters of kerogen can provide valuable information about changes in sources of OM. In wet gas (WV-7; VRo ~1.4) and dry gas (WV-6; VRo ~2.5) maturity windows, most of the structural parameters such as alkyl carbon percentage (without heteroatoms), total aromatic

carbon percent, protonated aromatic percentage, alkyl substituted aromatic, aromatic bridgehead, C, FAA, SP² to SP³ hybridized carbon ratio (Fig 3 a,b,c) were similar for upper and lower Marcellus Formations within the same well. However, isotopic and geochemical evidence from previous studies (Chen et al., 2015 and Agrawal and Sharma, 2017a) indicate that in both these wells lower Marcellus Formation received less influx of terrestrial OM than upper Marcellus. This observation suggests that at higher maturity window (VRo>1.4), thermal maturity dominantly controls the kerogen structure. A continuous decrease in total aliphatic, alkyl, alkyl substituted aromatic, FAA and a continuous increase in the total aromatic, protonated aromatic carbon, bridgehead carbon, C, SP² to SP³ hybridized carbon ratio from BG-1 to WV-7 to WV-6 kerogen (Fig. 3 a,b,c) also supports that thermal maturity played a major role in structural evolution of mature kerogen. Similar trends for these structural parameters are reported by previous studies (Patience et al., 1992, Keleman et al., 2007, Longbottom et al., 2016). However, variations in structural parameters such as O and O₂ substituted alkyl and O- substituted aromatic carbon are contrary to observations made by previous studies (Kuangzong et al., 1991, Patience et al., 1992, Keleman et al., 2007, Longbottom et al., 2016). A higher fraction of O and O₂ substituted alkyl groups and O- substituted aromatic carbon for WV-6 kerogen samples is probably because of the higher flux of terrestrial OM received by WV-6 shale cores as proposed by Chen et al., 2015, Agrawal and Sharma 2017a. These observations suggest that although thermal maturity plays a dominant role in the structural evolution of mature kerogen, the source of OM can still have some effect on a few key structural parameters of kerogen. This hypothesis is further supported by the fact that variations observed in mobile methyl carbon, amine, and Cn' between the upper and lower Marcellus kerogen from wells WV6 and WV-7 match with the inferences drawn from isotopic and geochemical proxies (Fig. 3 a,b,c). Therefore, we propose that although maturity primarily controls

the kerogen structure in mature shale ($VRo > 1.4$) some inferences can be drawn about sources of OM using selective structural parameters.

2.4.3 Modeling kerogen evolution, HC generation potential, and maturity

Using the aliphatic, aromatic and lattice structural parameters of kerogen, we propose schematic models for kerogen in oil, wet gas and dry gas windows of Marcellus Shale. (Fig. 4). The schematic representation shows a single cluster of kerogen molecule in upper and lower Marcellus from wells BG-1, WV-7 and WV-6 well (other isomers are also possible). Each cluster is composed of several aromatic rings (based on C and bridgehead carbon atoms) and aliphatic attachments. The models show that kerogen structure gets more aromatized with an increase in thermal maturity as seen by previous researchers (for eg. Patience et al., 1992, Keleman et al., 2007). The model also shows that mobile and immobile alkyl, alkyl-substituted aromatic carbons are more prone to thermal degradation compared to carbon chains such as O- substituted alkyl, O_2 substituted alkyl, amine, protonated aromatic carbons, O- substituted aromatic and bridgehead aromatic carbons as they do not show a decline with thermal maturity. It is also observed that lower Marcellus kerogen of BG-1 well is more aromatized and has more aromatic rings as compared to the upper Marcellus Formation indicating higher terrestrial OM input. Samples from the lower and upper Marcellus in WV-7 and WV-6 wells show similar the number of aromatic rings and aromatic fractions. However, previous studies from these wells have proposed that lower Marcellus had more marine OM input compared to upper Marcellus (Chen et al., 2015, Agrawal and Sharma, 2017a). This suggests that at maturity level $VRo > 1.4$ thermal maturity is the dominant control on kerogen structure as discussed in the previous section.

We also propose that due to lack of understanding of kerogen structure and its cracking mechanism in mature shales, the models proposed to determine their HC potential and thermal maturity might

not be accurate. To test this argument, we used regression equations proposed by Longbottom et al., 2016 and Wei et al., 2005 to determine the HC potential and thermal maturity of these samples respectively. We compared the hydrocarbon potential values, S2 (hydrocarbons bound to kerogen calculated using pyrolysis analysis) determined from the two equations proposed by Longbottom et al., 2016 with the actual values determined by source rock analyzer. We observed that both regression models highly overestimated the S2 values especially for mature and over mature WV-7 and WV-6 kerogen samples (Table 4, column 3 and column 4). The primary reason for this overestimation of S2 might be the less HC potential of O and O₂ substituted aliphatic chains in mature shales. We propose that since Longbottom et al., 2016 used parameters derived from less mature kerogen samples (VRo<0.8) compared to kerogen samples used in this study, their multiple regression models did not yield reliable results. In this study, the major changes in structural parameters from wet to dry gas window was observed in alkyl chains, mainly immobile alkyl chains (Table 1, Fig 3a). We postulate that from the oil window to dry gas window, the immobile alkyl chains are the main contributors of HC by kerogen cracking.

Wei et al., 2005 suggested an equation for determining thermal maturity using kerogen structural parameters. However, the equations proposed underestimates the VRo values for the kerogen samples of WV-7 and WV-6 wells (Table. 4, column 6). Similar observations of overestimation

of S2 parameter and underestimation of thermal maturity with previously built models can be observed for another over mature well MIP-3H with VRo~2.9 (Agrawal and Sharma, 2017b). Therefore we propose for precise estimation of HC potential and thermal maturity in mature shales we need to construct new kerogen models that are based on structural parameters derived from samples from mature shales.

Table 1: Percentage of different structural parameters / functional groups

Structural parameters	Chemical Shift (ppm)	BG-1 UM	BG-1 LM	WV-7 UM	WV-7 LM	WV-6 UM	WV-6 LM
Total aliphatic ^a	(0-90)	30.43 ±1.62	25.49 ±1.36	25.94 ±1.38	26.94 ±1.44	14.82 ±0.79	13.60 ±0.73
Alkyl ^a	(0-45)	25.52 ±2.72	19.92 ±2.12	21.08 ±2.25	22.95 ±2.45	8.18 ±0.87	9.72 ±1.04
Mobile methyl ^b	(0-20)	3.46 ±0.83	3.34 ±0.80	3.27 ±0.78	3.23 ±0.78	0.29 ±0.07	1.14 ±0.27
Mobile and quaternary alkyl ^b	(20-45)	5.00 ±0.96	3.79 ±0.73	4.08 ±0.78	3.36 ±0.65	1.00 ±0.19	0.85 ±0.16
Methoxyl and amine ^a	(45-60)	0.92 ±0.29	2.25 ±0.72	2.18 ±0.70	2.14 ±0.68	1.59 ±0.51	0.65 ±0.21
Methoxyl ^b	(45-60)	0.36 ±0.12	0.30 ±0.10	0.45 ±0.14	0.14 ±0.04	0	0
O and O2 substituted alkyl ^a	(60-90)	3.99 ±0.64	3.31 ±0.53	2.68 ±0.43	1.85 ±0.30	5.05 ±0.81	3.23 ±0.52
Total aromatic ^a	(90-165)	66.61 ±4.26	70.45 ±4.51	75.50 ±4.83	74.60 ±4.77	84.90 ±5.43	89.00 ±5.70
Non-protonated aromatic bridgehead ^b	(90-135)	14.92 ±1.59	24.97 ±2.66	29.50 ±3.15	28.00 ±2.99	32.90 ±3.51	36.70 ±3.91
Protonated aromatic ^b	(90-135)	34.78 ±3.71	27.70 ±2.95	32.50 ±3.47	34.80 ±3.71	41.20 ±4.39	43.60 ±4.65
Alkyl-substituted aromatic ^c	(135-150)	14.86 ±4.76	16.07 ±5.14	12.98 ±4.15	11.86 ±3.80	10.10 ±3.23	9.04 ±2.89
O-substituted aromatic ^c	(150-165)	2.06 ±0.66	1.72 ±0.55	0.13 ±0.04	0.12 ±0.04	1.00 ±0.32	0
Carboxyl and amide ^a	(165-190)	4.68 ±0.90	2.69 ±0.52	0	0	0.77 ±0.15	0
Aldehyde and ketone	(190-240)	0*	1.38 ±0.13	0*	0*	0*	0

NMR method a = cross polarization, b = dipolar-dephasing

* Values reported as zero but negative values were observed for aldehyde and ketone functional group for some samples (within 2%)

Figure 3a. Percentage of i) Total aliphatic C, ii) alkyl C, iii) mobile methyl, iv) mobile and quaternary alkyl v) methoxy and amine vi) O and O2 substituted alkyl. **3b.** Percentage of i) Total aromatic C, ii) non-protonated aromatic C, iii) Protonated aromatic C, iv) Aromatic bridgehead carbon %, v) Alkyl substituted aromatic vi) O substituted. **3c. i)** Fraction of aromatic chains with attachments (FAA) ii) Average aliphatic chain length (Cn) iii) SP2 vs SP3 hybridized carbon ratio iv) No. of carbon atoms per aromatic cluster (C)

Figure 4. Schematic representation of transformation of a unit of kerogen cluster from low maturity BG-1 kerogen to higher maturity WV-7 kerogen to further higher maturity WV-6 kerogen. Each unit of kerogen cluster is formed using aliphatic, aromatic and lattice structural parameters a) upper Marcellus b) lower Marcellus. Values written in parentheses indicate the fraction of the particular functional group per unit of kerogen cluster. Other isomers of each kerogen unit are possible.

2.4.4 Evaluation of kerogen type

The traditional Van krevelen diagram generated from SRA analysis using the hydrogen index (HI) and oxygen index (OI) cannot be used to determine kerogen type in the mature shales used in this study. This is due to low HI and OI in all samples (as shown in Figure 5a, Agrawal and Sharma, 2017a). However, molecular level characterization of kerogen using solid-state methods gives us the opportunity to determine the accurate chemical composition of kerogen. Since each structural parameter has a particular composition (for example CH_3 for methyl group), an average chemical composition to each structural parameter of kerogen can be assigned (as shown in Table 3). Also, since the fraction of each structural parameter is known, the relative amount of H, C, and O of

each structural parameter of kerogen can be determined by multiplying the fraction of each structural parameter with the number of H/C/O present in the molecular formula of the functional group as shown in Table 2 (e.g., for methyl group CH_3 , 1 carbon atom a 3 hydrogen atoms will be considered). By dividing the relative total fraction of H, C, and O the H/C and O/C ratios can be determined as shown in Table 2. This method is known as direct assignment (DA) method as proposed by Hockaday et al. (2009). The values of H/C and O/C calculated from DA method suggests that shale samples both upper and lower Marcellus Formation of BG-1, WV-7, and WV-6 wells belong to type II to type III kerogen (Fig. 5b). Similar interpretations were made using the biomarker analysis for the same set of WV-6 and WV-7 samples by Agrawal and Sharma, 2017a. This observation suggests that H, C, and O amounts derived from structural parameters of kerogen can provide valuable information about OM sources/type in mature shale systems where traditional methods like SRA fail.

Figure 5. A) van krevelen diagram showing type of kerogen samples from upper and lower Marcellus Formation of WV-6 and WV-7 wells using pyrolysis (taken from Agrawal and Sharma,

2017a) b) van krevelen diagram showing mixed type II-type III kerogen for 6 kerogen samples from upper and lower Marcellus Formation of BG-1, WV-7 and WV-6 using DA method.

Table. 2 H/C and O/C values of upper and lower Marcellus Formation from WV-6 and WV-7 wells.

Sample	H/C	O/C
BG-1 UM	0.98	0.14
BG-1 LM	0.81	0.12
WV-7 UM	0.84	0.04
WV-7 LM	0.88	0.03
WV-6 UM	0.74	0.08
WV-6 LM	0.71	0.03

Table 3. Average chemical composition of different structural parameters

	Chemical shift (ppm)	Structural group formula	C	H	O
Mobile and immobile methyl ^a	(0-20)	CH ₃	1	3	0
Mobile, immobile and quaternary alkyl ^b	(20-45)	CH _{1.5}	1	1.5	0
Methoxy and amine ^a	(45-60)	C H _{1.5} O _{0.5} , CNH _{1.5}	1	1.5	0.5
O-substituted alkyl and O2 substituted alkyl ^a	(60-90)	CH _{2.5} O	1	2.5	1
Protonated aromatic ^b	Total aromatic (90-135)-non protonated (90-135)	CH	1	1	0
Bridgehead aromatic carbon ^b	(90-135)	C	1	0	0
Alkyl-substituted aromatic ^a	(135-145)	C	1	0	0
O-substituted aromatic ^a	(145-165)	COH _{0.5}	1	0.5	1
Carboxyl and amide ^a	(165-190)	CO _{1.75} H _{0.5} , CONH	1	0.5	1.75
Aldehyde and ketone ^a	(190-220)	COH _{0.5}	1	0.5	1

NMR method a = cross polarization or direct polarization, b = dipolar-dephasing

Table 4. True and calculated values of hydrocarbon potential (S2) and Vitrinite reflectance (VRo)

Sample	True S2 ^a	S2 ^b	S2 ^c	True VRo ^{a,d}	VRo ^e
BG-1 UM	5.11	12.51	10.56	1	1.06
BG-1 LM	15.84	12.32	27.69	0.81	0.71
WV 7 UM	1.41	10.77	26.35	1.4 ^a	0.56
WV-7 LM	10.67	12.12	40.35	1.4 ^a	0.47
WV-6 UM	0.02	7.60	14.61	>2.5 ^d	1.42
WV-6 LM	0.47	1.85	40.40	>2.5 ^d	1.80

a= taken from Agrawal and Sharma, 2017a

b=calculated using equation 1 of Longbottom et al., 2016

c=calculated using equation 2 of Longbottom et al., 2016

d= taken from Zagorski et al., 2012

e= calculated using equation 12 of Wei et al., 2005

2.5 CONCLUSIONS

Data generated from direct kerogen analysis suggests that samples from most mature Marcellus Shale well lying in a dry gas window (WV-6) had the highest fraction of aromatic carbon followed by samples from the wet gas window (WV-7) and oil window (BG-1). This is in agreement with the previously published studies on the structural evolution of kerogen. Our results also indicate that most of the aliphatic and aromatic structural parameters of kerogen in upper and lower Marcellus Formation are similar in wells WV6 and WV7 (VR0 > 1). However, previous studies

suggest sediments in these wells were deposited in different part of the basin and received different terrestrial and marine OM influx. This suggests that high maturity levels thermal maturity is the dominant control on kerogen structure. However, OM sources can still be discerned using certain kerogen lattice structural parameters such as O and O2 substituted alkyl, O- substituted aromatic carbon, mobile methyl carbon, and Cn'. In contrast, in lower maturity $V_{Ro} < 1$ OM sources play a key role in determining kerogen structure.

Our results indicate that carbon chains such as mobile and immobile alkyl, alkyl-substituted aromatic carbons are more prone to thermal degradation and therefore might have higher hydrocarbon generating potential as compared to functional groups such O- substituted alkyl, O2 substituted alkyl, amine, protonated aromatic carbons, O- substituted aromatic and bridgehead aromatic carbons. We also propose that previous models routinely used for determining hydrocarbon potential and thermal maturity of shales cannot be used for mature shale systems with $V_{Ro} > 1$ like Marcellus. We are currently in the process of acquiring shale samples ranging across the entire maturity series to conduct additional kerogen studies to develop precise HC generation and maturity models for mature shale systems.

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Chapter III:

Improved Kerogen Models for Determining Thermal Maturity and Hydrocarbon Potential of Shale

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3. IMPROVED KEROGEN MODELS FOR DETERMINING THERMAL MATURITY AND HYDROCARBON POTENTIAL OF SHALES

Keywords: Kerogen, Marcellus Shale, thermal maturity, hydrocarbon potential, regression models.

3.1 ABSTRACT

Kerogen is the insoluble component of organic-rich shales that controls the type and amount of hydrocarbon generated in conventional and unconventional reservoirs. Significant progress has recently been made in developing structural models of kerogen. However, there is still a large gap in understanding the evolution of molecular components of kerogen with thermal maturation and their hydrocarbon (HC) generative potential. Here, we determine the variations in different molecular fragments of kerogen in a Marcellus Shale maturity series (VRo ranging from 0.8 to 3). These molecular variations provide insight into the 1) evolution of the molecular structure of kerogen with increasing thermal maturity and, 2) the primary molecular contributors of HC generation. Our results also indicate that old model equations based on structural parameters of kerogen overestimate the HC generation potential and underestimate the thermal maturity of Marcellus Shale samples. This could primarily be because the kerogen samples used to reconstruct old models were mostly derived from immature shales (VRo <1) acquired from different basins with varying depositional environments. We utilized the kerogen molecular parameters determined in the Marcellus maturity series to propose improved models for accurate estimation of thermal maturity and HC potential of Marcellus Shale. The models generated in this study could also be applied to other shales with similar maturity ranges and deposited in similar paleo-environment.

3.2 INTRODUCTION

The advent of unconventional shale gas drilling has necessitated the need to develop a better understanding of the spatiotemporal variations in type and quality of organic matter in shale source rock units. Kerogen is a high molecular weight organic matter (OM) that serves as source and reservoir of all the hydrocarbons in these shales. Kerogen is formed by the degradation, condensation, and polymerization of biomolecules contributed by different sources of OM¹⁻³. Kerogen formed in the diagenetic stage of burial later cracks to form oil and gas in catagenetic and metagenetic stages of burial. The type and amount of HC generated, its sorption/retention and release on hydraulic fracturing operations is controlled by the molecular structure of kerogen³⁻⁶. Therefore, it is critical to understand the chemical structure of kerogen at the molecular level. In addition, molecular parameters of kerogen can serve as a more robust proxy for determining thermal maturity and hydrocarbon potential in mature shales (with $V_{Ro} > 1$) where traditional techniques such as vitrinite reflectance, SRA, and biomarker analysis fails.

Significant progress has been made in understanding the molecular structure of kerogen using destructive (pyrolytic) and non-destructive (spectroscopic) methods⁷⁻⁹. However, the results generated using pyrolytic experiments can be biased due to the interaction of products generated from the labile fraction of kerogen¹⁰ or because reactions taking place in laboratory conditions might not be representative of sedimentary basin conditions¹¹⁻¹⁴. Due to these limitations, non-destructive methods such as Fourier transform infrared (FT-IR), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), and ¹³C solid-state nuclear magnetic resonance (¹³C NMR) have been employed for the qualitative, semi-quantitative, and quantitative measurements of kerogen^{7,15-19}.

The most reliable and robust tool for determination of fractions of molecular components of kerogen is ^{13}C solid state NMR²⁰. Numerous studies have been conducted using ^{13}C solid-state NMR for kerogen characterization^{15–17,19,21–27}. A few recent attempts have been made to develop realistic structural models of kerogen^{28,29}. However, the evolution of different molecular components of kerogen on thermal maturation and the primary contributors to HC generation are still not well understood, especially for mature shales. A recent study by Agrawal and Sharma, 2018 indicated that kerogen structural parameters used in previous models for determining HC generative potential²⁶ and thermal maturity^{24,30} could highly over or under estimate these values.

In this study, we determine the stability/reactivity of different molecular fragments of kerogen with thermal maturation and predict the primary contributors of hydrocarbons in a Marcellus shale maturity series (VRo ranging from 0.8 to 3). The correlation of structural components of kerogen with maturation and HC potential parameter (S2), was used to develop regression models (linear and multiple) for accurate estimation of thermal maturity and hydrocarbon generated. The structural parameters of 15 kerogen samples were determined using ^{13}C multiple CP/MAS and multiple CP/MAS plus dipolar dephasing technique detailed in Agrawal and Sharma, 2018¹⁹. A total of 15 samples were obtained from six Marcellus shale wells BG-1, WV-7, WV-6, MIP-3H, MW-1 and BL-3H) across a thermal maturity gradient in Appalachian basin (Table 1). TOC, S2 and VRo values of six samples were obtained from Agrawal and Sharma, 2018^{19,42} as indicated in Table 1.

3.3 RESULTS AND DISCUSSION

Different aliphatic and aromatic carbon chains have characteristic chemical shifts in an NMR spectra^{31–34} as shown in Table. 1 of supplementary information. Dipolar dephasing method with multiple CP method allows the quantification of mobile aliphatic and protonated (and non-

protonated) aromatic carbon chains along with other aliphatic and aromatic chains^{8,20,35–37} as shown in Table. 1 of supplementary information. The aliphatic and the aromatic fraction in the NMR spectra lies in 0-90 ppm and 90-165 ppm chemical shift range respectively. The fractions of different aliphatic and aromatic chains of kerogen were calculated using the peak area of the respective chemical shifts in a NMR spectra. The fractions of aliphatic carbon, alkyl (without heteroatoms), methoxy and amine, O and O₂ substituted alkyl carbons (ether and dioxy alkyl), total aromatic carbon, alkyl substituted aromatic, O-substituted aromatic (phenol), carboxyl and amide, aldehyde and ketone were determined using the multiple CP method (without dipolar dephasing). However, the fractions of mobile (freely rotating) and immobile (restricted rotation) methyl, mobile and quaternary alkyl (without heteroatoms), methoxy, protonated aromatic, non-protonated aromatic bridgehead carbon (fa^B) were determined using dipolar dephasing method with multiple CP (Table. 1 in the supplementary information.). Using these aliphatic and aromatic structural parameters, several lattice structural parameters such as average aliphatic carbon chain length (Cn'), mole fraction of bridgehead aromatic carbon(Xb), and SP²/ SP³ hybridized carbon ratio were determined^{17,31,38}. The fractions of different structural parameters of 15 kerogen sample used in this study are shown in Table 1 of the supplementary information. Data of structural parameters of six samples are taken from Agrawal and Sharma, 2018¹⁹ (as indicated in Table 1 of the supplementary information). Multiple linear regression plots were made to determine the correlation of different structural parameters with VRo and S2. (refer Fig. 1, Fig. 2. Fig. 3, Fig. 4 in supplementary information).

Table 1. The TOC, S2 and VRo values of samples selected for from 6 different Marcellus Shale wells in the Appalachian basin

Sample ID	TOC	S2	VRo	Sample ID	TOC	S2	VRo
BG-1 UM ⁱ	4.68	5.11	1	WV-6 LM ⁱⁱ	9.10	0.47	2.5
BG-1 LM ⁱ	15.40	15.84	0.81	BL-3H UM	5.31	0.06	2.93
WV-7 UM ⁱⁱ	3.13	1.41	1.4	BL-3H LM	9.24	0.15	2.96
WV-7 LM ⁱⁱ	12.91	10.67	1.4	MIP-3H UM	4.14	0.12	2.94
MW-1 UM	8.63	1.84	1.49	MIP-3H LM	8.86	0.42	2.98
MW-1 LM	7.45	1.38	1.61	MIP 3H MT	3.14	0.08	2.92
WV-6 UM ⁱⁱ	3.52	0.02	2.5	MIP 3H MM	6.64	0.30	2.96
i: values from <i>Agrawal and Sharma, 2018</i> ¹⁹				MIP 3H MO	5.35	0.26	2.97
ii: values from <i>Agrawal and Sharma, 2018</i> ⁴²							

3.3.1 Kerogen models for thermal maturity

Thermal maturity is one of the most important parameter required for accurate determination of the hydrocarbon generated in source rocks. The traditional methods used for determining thermal maturity are the Tmax measurement using Source Rock Analyzer (SRA) and vitrinite reflectance measurement. However, Tmax may not be reliable in mature and over-mature samples (Peters et al., 2005), and vitrinite is present as a major maceral only in Type III kerogen. Errors are involved in measuring reflectance on macerals other than vitrinite³⁹ or measuring reflectance of vitrinite whose thermal maturation is different from that of the bulk OM³. Biomarker ratios have also been used to determine the thermal maturity of source rocks⁴⁰. However, due to thermal degradation and alteration of biomarkers on maturation^{41,42} and low extraction efficiency in high maturity

samples, the results can be biased. Recent advancement in ^{13}C solid-state NMR spectroscopic analysis, has led to an accurate quantification of different aliphatic, aromatic and lattice parameters of kerogen, even in over-mature shales^{19,42}. Understanding the variability in these parameters on maturation can provide an important tool for determining thermal maturity in a broader maturity range.

In the Marcellus Shale the evolution of most of the structural parameters of kerogen such mobile (freely rotating) and immobile alkyl without heteroatoms (with restricted rotation), and alkyl-substituted aromatic carbons¹⁹ are primarily controlled by thermal maturity. Similar observations have also been made for shales from other basins basin^{17,21,26}. However, the cracking mechanism of different structural parameters of kerogen can vary because of the difference in their thermal stability. To determine the sensitivity of different kerogen structural parameters with thermal maturation, linear correlation plots were made using the structural parameters of kerogen and calculated vitrinite reflectance (Fig. 1 and Fig. 2 of supplementary information). It has been previously shown that maturation leads to a decrease in all aliphatic carbon chains and an increase in aromatic carbon chains^{17,21,24,26}. However, the sensitivity and reactivity of carbon chains within the different aliphatic and aromatic carbon fraction are still not understood. Our results show that among different aliphatic chains, immobile alkyl chains are most prone to thermal degradation ($R^2 = 0.94$), followed by mobile and quaternary alkyl carbon chains ($R^2 = 0.61$) and mobile methyl carbon chains ($R^2 = 0.54$, Fig. 1 of supplementary information). In the alkyl carbon chains (without heteroatoms) the immobile methyl group is most resistant to breakdown during maturation ($R^2 = 0.20$). Immobile alkyl chains are mostly attached to the aromatic rings, restricting their rotation. The resistant nature of the immobile methyl group is possibly due to the instability of free radicals formed on thermal degradation (breaking of bond “a” in Fig.1). The instability of the free radical

is because of the disruption of resonance present the aromatic chains. However, for immobile alkyl groups, free radicals formed by thermal degradation (breaking of bond “c” in Fig.1) is stabilized by the resonance of conjugated double bonds of the aromatic ring, making it the most stable amongst all the other aliphatic carbon chains.

Figure. 1. Stability of free radicals formed on thermal degradation. Structure of unit kerogen taken from Agrawal and Sharma, 2018¹⁹.

In contrast, to the aliphatic structural parameters, the aromatic structural parameters showed relatively poor correlation to thermal maturation. Amongst the aromatic structural parameters, the highest correlation is observed between bridgehead aromatic carbons ($R^2 = 0.48$) followed by protonated aromatic carbon ($R^2 = 0.06$), O- substituted aromatic carbon ($R^2 = 0.06$), and alkyl substituted aromatic carbon chains ($R^2 = 0.02$). However, it is important to note that although individual aromatic parameters showed poor correlation with the vitrinite reflectance (Fig. 2 of supplementary information) the correlation of total aromatic with VRo is still significant ($R^2 = 0.90$). This indicates that good correlation of total aromatic carbon with increasing maturity as determined by several previous studies is due to increase in the relative percentage of aromatic

carbon due to the higher breakdown of aliphatic carbon chains rather than formation of new aromatic carbons. The similar mole fraction of bridgehead aromatic carbon (Xb) in all mature kerogen samples ($V_{Ro} > 1$, Fig. 2 in supplementary information) also supports that the total amount aromatic clusters does not increase significantly in mature shales. This observation is on the contrary to previous studies done at lower maturity^{24,30}.

Regression models have been developed to determine thermal maturity using kerogen structural models such as aromatic carbon percentage, the mole fraction of bridgehead carbon (Xb), SP^2 to SP^3 carbon ratio^{24,30,43}. In this study, we observed that immobile alkyl chains (C_nH_{2n} groups, with $n > 1$), alkyl chains (immobile and mobile C_nH_{2n} groups, with $n > 1$), total aromatic carbon and total alkyl (without heteroatoms) had highest correlation coefficient with thermal maturity ($R^2 > 0.85$) (Fig. 2) Based on these observations, we propose four new regression models for estimation of thermal maturity for shales with V_{Ro} between 0.8 to 3.0. The equations are as follows:

Equation 1: **$V_{Ro} = (0.17 - IA)/0.05$** where IA is fraction of immobile alkyl chains (C_nH_{2n} groups) with $n > 1$

Equation 2: **$V_{Ro} = (0.22 - TA_2)/0.06$** where TA_2 is fraction of total alkyl chains (C_nH_{2n} groups) with $n > 1$

Equation 3: **$V_{Ro} = (F_{ar} - 0.63)/0.08$** where F_{ar} is fraction of total aromatic chains.

Equation 4: **$V_{Ro} = (0.30 - TA)/0.08$** where TA are total alkyl chains (C_nH_{2n} groups) with $n > 0$

Figure 2. Correlation of different kerogen structural parameters with calculated vitrinite reflectance

3.3.2 Kerogen models for hydrocarbon potential

A recent study done on kerogen from Marcellus Shale by Agrawal and Sharma, 2018¹⁹ indicates that previously build kerogen models used for determining HC generative potential overestimate the S2 values at least by a factor of two¹⁹. This can lead to underestimation of the total amount of HC generated in the reservoir. We determined the structural components of kerogen that are primary contributors to HC generation by evaluating the correlation of different structural parameters of kerogen with S2. We observed that aliphatic chains mobile and quaternary alkyl group, mobile methyl group and immobile alkyl chains had the highest correlation with S2 (Fig. 3). Additionally, the relatively smaller correlation coefficient of immobile methyl, aromatic bridgehead carbon, aldehyde and ketone groups, and O and O₂ substituted alkyl chains (Fig. 3), shows there was little or no contribution from these structural components to the total hydrocarbon generative potential, contradicting the observations of Longbottom et al., 2016²⁶.

Therefore, we propose a new equation for determining the hydrocarbon potential that is based on a multiple regression model using the fractions of structural parameters: mobile and quaternary alkyl group, mobile methyl group and immobile alkyl chains:

$$\text{Equation 5: } S_2 = 0.60 \times MM + 2.02 \times MA + 0.12 \times IA - 1.85$$

where MM is mobile methyl chains ($-\text{CH}_3$ groups)

MA is mobile alkyl chains (C_nH_{2n} groups, $n > 1$)

IA is immobile alkyl chains (C_nH_{2n} groups, $n > 1$)

The coefficient of determination (R^2) between the true S_2 and modeled S_2 was 0.98, and the RMS error of prediction was ± 0.70 mg hydrocarbon per gram of rock. It was also, observed that the by adding additional structural parameters in the multiple regression model, the coefficient of determination (R^2) between true vs. modeled S_2 did not improve. This observation further suggests that the structural parameters used in the model are the primary contributors of hydrocarbon potential.

3.3.3 Model validation

To validate the model proposed for determining thermal maturity, we determined the V_{Ro} values from the four equations proposed in this study and compared it with the true V_{Ro} values and values determined using previous regression model proposed by Wei et al., 2005²⁴ (shown in Table 2 of the supplementary information). The V_{Ro} values predicted using the newly build regression model were comparable to the true values with RMS error in V_{Ro} for all the samples were 0.21, 0.26, 0.26, 0.31 using equation 1, equation 2, equation 3, equation 4 respectively. However, the V_{Ro} value predicted using equations proposed by Wei et al., 2005²⁴ underestimated the true values with a total RMS error 0.91 in V_{Ro} values (Fig 4a, Table.2 of the

supplementary information). The RMS error for predicting VRo in different maturity ranges using the proposed equations were also significantly less than the previously proposed model (Fig. 4a, Table.2 of the supplementary information).

To validate the model proposed for determination of hydrocarbon potential, we determined the total amount of HC generated using the modeled values of S2 and compared it with the true amount of HC generated. The true amount of total HC generated (in mg) per gram of rock is determined by equation $S2_{net} = S2_{org} - S2_{pd}$ (org stands for original and pd for the present day). $S2_{org}$ is calculated by the dividing the TOC_{org} by HI_{org} . TOC_{org} is calculated using equation given by Peters et al., 2005⁴⁰:

$$TOC_{org} = 83.33 (HI_{pd}) (TOC_{pd}) / HI_{org} (1 - f) (83.33 - TOC_{pd}) + (HI_{pd}) (TOC_{pd}),$$

$$\text{where } f = 1 - [HI_{pd} (1200 - (HI_{org} / 1 - PI_{org}) / HI_{org} (1200 - (HI_{pd} / 1 - PI_{pd})].$$

HI_{org} obtained for immature Marcellus shale is approximately 250mg HC/g rock⁴⁴. Similar HI_{org} were obtained from HI vs. VRo plot (Y-intercept of the curve Fig. 5 in supplementary information). PI_{org} is assumed to be 0.02 for the most immature source rocks⁴⁰. The S2 values modeled in this study are the $S2_{present\ day}$. The total amount of HC generated calculated using the true S2 values and modeled values are shown in Table 3 in supplementary information. We compared these values with true amount of HC generated and HC generated using previous regression models (Table 3 in supplementary information). The amount of HC generated predicted using the newly build regression model were comparable to the true values with RMS error for all the samples 0.70 mg HC/g rock. However, the amount of HC generated predicted using the two equations proposed by Longbottom et al., 2016²⁶ underestimated the true values with RMS error 3.93 mg HC/g rock and 27.05 mg HC/g rock (Fig 4b, Table.3 in supplementary

information). The RMS error for predicting HC generated in different maturity ranges using the proposed model was also significantly less than the previously proposed model (Fig. 4b, Table.3 in supplementary information). The higher RMS error of older models could be attributed to the fact that they 1) utilized kerogen derived from shales that were all below $V_{Ro} < 1$ and, 2) used shale samples acquired from different basins where the structure of kerogen might vary significantly due to variations in sources of OM and depositional conditions.

Figure 3. Correlation of different structural parameters of kerogen with true HC potential (S2)

The major strength of new models proposed in this study are that they were generated using

kerogen derived from the entire maturity range of hydrocarbon generation, hence might better represent the source rock in mature shale plays like Marcellus as compared to older models.

Future work will focus on acquiring samples from other shales to test the efficacy of our models.

It is also plausible that for more accurate estimation of HC generative potential and maturity, similar kind of models need to be developed for individual plays instead of utilizing generalized models.

Figure 4. Comparison of RMS error of a) thermal maturity and b) HC generation, determined using models proposed in this study with previous kerogen models.

3.4 METHODS

3.4.1 ¹³ C solid-state NMR analysis

Solid-state NMR experiments were performed at Environmental NMR Service at Old Dominion University in Norfolk, Virginia, USA on a Bruker Advance III 400 spectrometer operating at

400-MHz ^1H and 100-MHz ^{13}C frequencies. The ^{13}C chemical shifts were referenced to tetramethyl silane, using the COO resonance of glycine in the α -modification at 176.46 ppm as a secondary reference. The high-spinning speed multi-ramped amplitude cross polarization/magic angle spinning technique developed by Johnson and Schmidt-Rohr, 2014⁴⁵ was applied for acquiring quantitative ^{13}C NMR spectra for all the kerogen samples. This multiple-cross polarization (multiCP) technique provides a simple, robust way to obtain quantitative solid-state ^{13}C NMR spectra of organic materials, with good signal-to-noise ratio. The spectra were measured at a spinning speed of 14 kHz, where spinning sidebands are fairly small (<3%) and have little overlap with center bands. To differentiate nonprotonated C from total C and to determine fractions of mobile groups (with no restricted rotation), ^{13}C multiCP/MAS with dipolar dephasing was performed under the same conditions as for ^{13}C multiCP/MAS but combined with a dipolar dephasing time of $68\ \mu\text{s}$ ³⁷. The relative proportion of different carbon chains such as mobile and immobile alkyl without heteroatoms (written just as alkyl in this study), methoxy and amine, O-substituted and O_2 substituted alkyls (ethers and dioxy alkyl), protonated aromatic, bridgehead aromatic, alkyl substituted aromatic, O- substituted aromatic (phenol), carboxyl, carbonyl were obtained for ^{13}C NMR spectrum using an NMR peak fitting program *TopSpin* (area of spectra from 0-240 ppm was considered to be 100%).

3.4.2 SRA analysis

80 mg of pulverized shale sample was weighed into a SRA crucible and placed in the autosampler and held isothermally at $300\ ^\circ\text{C}$ for 3 minutes. To minimize the effect of grain size, care was taken to keep the grain size of all the samples to be consistent (200 mesh). During this isothermal heating, the free hydrocarbons are volatilized and detected by the FID detector where they are quantitatively detected and reported as milligrams (mg) of S1 per gram of rock. The free CO_2 is simultaneously

liberated and detected by the IR cell and reported as milligrams (mg) of S3 per gram of rock up to 400 °C. After the isothermal period, the temperature is increased at the rate of 25°C/minute until the temperature reaches to 600 °C. Between 300°C and 600°C HCs are generated from the pyrolytic degradation of the kerogen in the shale. The hydrocarbons are detected by the FID are labeled as S2, and reported as milligrams (mg) of S2 per gram of rock. The temperature at the maximum generation of S2 is known as Tmax. Tmax is generally used to estimate thermal maturity of shales. Residual carbon is also measured by SRA and is reported as S4. TOC of the sample is given by $0.1 \times [0.082 \times (S1 + S2) + S4]$, in wt %. Vitrinite reflectance is calculated using equation $(VRo) = 0.018 \times Tmax - 7.16^{46}$. WFT Source Rock Standard 533 (P/N 810-141) was used as a standard and was run after every five sample. SRA analysis was performed at the National Energy Technology Laboratory in Morgantown.

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AUTHOR CONTRIBUTION STATEMENT

VA and SS were involved in initial conception of idea of the research. VA conducted the analytical work needed for study and drafted the manuscript. VA and SS were both involved in data interpretation, revising and editing of the manuscript.

COMPETING INTERESTS

The authors declare no competing financial or non-financial interests.

Table 2 True vs Modeled amount of VRo

Sample	True VRo	Modeled VRo using eq 1	Modeled VRo using eq 2	Modeled VRo using eq 3	Modeled VRo using eq 4	Modeled VRo using Wei et al., 2005
VRo= 0.8-1.4						
BG-1 UM	1	0.74	0.56	0.44	0.51	1.06
BG-1 LM	0.81	1.16	1.09	0.85	1.22	0.71
WV-7 UM	1.4	1.27	1.13	1.39	1.07	0.56
WV-7 LM	1.4	0.95	1	1.3	0.84	0.47
RMS error		0.32	0.35	0.29	0.46	0.63
VRo= 1.4-2.5						
MW-1 UM	1.49	1.76	1.98	1.74	1.98	0.88
MW-1 LM	1.61	1.76	1.93	2.14	2.09	1.16
WV-6 UM	2.5	2.71	2.76	2.4	2.71	1.42
WV-6 LM	2.5	2.4	2.54	2.84	2.51	1.8
RMS error		0.19	0.32	0.34	0.36	0.75
VRo>2.5						
BL-3H UM	2.93	2.86	3	2.99	2.92	1.94
BL-3H LM	2.96	2.76	2.81	2.52	2.75	1.53
MIP-3H UM	2.94	2.96	2.92	2.88	3.06	1.84
MIP-3H LM	2.98	3	2.88	3.11	2.95	2.04
MIP 3H MT	2.92	3.07	2.96	2.8	2.8	1.76
MIP 3H MM	2.96	3.07	2.99	3	3.01	1.92
MIP 3H MO	2.97	2.9	2.82	2.94	2.95	1.94
RMS error		0.11	0.1	0.18	0.11	1.11
Net RMS error		0.21	0.26	0.26	0.31	0.91

Table 3 True vs Modeled amount of HC generated

Sample	True HC	Modeled HC generated	Modeled HC generated	Modeled HC generated
		This study	Longbottom eq 1	Longbottom eq 2
VRo= 0.8-1.4				
BG-1 UM	6.86	7.37	-0.54	-5.09
BG-1 LM	25.1	25.91	28.62	-4.85
WV-7 UM	7.85	7.53	-1.51	-22.51
WV-7 LM	25.27	24.69	23.82	-20.51
RMS error		0.58	6.26	31.85
VRo= 1.4-2.5				
MW-1 UM	24.2	24.47	20.67	4.11
MW-1 LM	21.18	20.2	18.1	4.86
WV-6 UM	11.01	11.96	3.43	-9.7
WV-6 LM	27.45	27.04	26.07	-25.37
RMS error		0.73	4.51	31.18
VRo>2.5				
BL-3H UM	16.49	17.4	12.78	-0.6
BL-3H LM	28.27	27.95	26.75	4.05
MIP-3H UM	12.78	13.53	8.7	-2.65
MIP-3H LM	26.8	25.47	29.72	0.3
MIP 3H MT	9.71	10.18	3.06	-4.38
MIP 3H MM	20.21	19.9	19.3	-3.78
MIP 3H MO	16.28	15.82	13.2	-4.51
RMS error		0.74	3.7	20.79
Net RMS error		0.7	3.93	27.05

Figure.1 Correlation of fraction of different aliphatic structural parameters of kerogen (Y axis) vs Vitrinite reflectance, VRo (X axis)

Figure.2 Correlation of fraction of different aromatic and lattice structural parameters of kerogen (Y axis) vs Vitrinite reflectance, VRo (X axis)

Figure.3 Correlation of fraction of different aliphatic structural parameters of kerogen, in mg/g rock (Y axis) vs HC generative potential, S2, in mg HC/g rock (X axis)

Figure.4 Correlation of fraction of different aromatic parameters of kerogen, in mg/g rock (Y axis) vs HC generative potential, S2, in mg HC/g rock (X axis)

Figure.5 HI vs VRo cross plot. The Y intercept of the curve represents HI_{org}

Chapter IV:

Pitfalls in Modelling Physico-Chemical Properties of Shale Using Kerogen Type

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4. PITFALLS IN MODELLING PHYSICO-CHEMICAL PROPERTIES OF SHALE USING KEROGEN TYPE

Keywords: Kerogen Type, Structural models, Marcellus Shale

4.1 ABSTRACT

Shale reservoirs are a rapidly progressing area of energy that has become a vital component in US economy. Much advancement has been made for extraction and production of hydrocarbons from shale reservoirs. However, fundamental physico-chemical properties of shales, especially that of kerogen are still not well understood. Different physico-chemical properties of kerogen are primarily controlled by its molecular structure. Although, recent progress has been made to model various kerogen structures and their properties, these studies are generally based in kerogen “type” do not account for heterogeneities that exists within a particular kerogen “type”. This could have implications on estimating the type and amount of extractable HCs, evaluating potential of shales for CO₂ sequestration and waste removal, understanding interaction of hydraulic fracturing fluid in subsurface environment. In this study, we discuss the limitations of previously built kerogen models by testing their applicability in Marcellus Shale.

4.2 MAIN

Advancements in horizontal drilling and hydraulic fracturing technologies for shale gas production have led to a transformation in the US economy. Although technological advancements have led to impressive growth in hydrocarbon (HC) production¹, some major limiting factors in shale gas development are i) low recovery of gas in place (<20%)² and (ii) a rapid decline in well productivity³, despite the use of advanced hydraulic fracturing fluids⁴ and multiple fracturing stages⁵. Improving the efficiency of production will improve the shale gas economics, provide more energy, and reduce the impact on the environment by allowing fewer wells to recover greater

amounts of gas or oil. One of the major hurdles in improving the efficiency of production is the lack of understanding of nanoscale physico-chemical properties of shales, especially that of kerogen⁶. Kerogen is a geo-macromolecular component of shales that contains the largest amount of hydrocarbon and exhibits pores spanning several orders of magnitude starting from the subnanometer scale⁷⁻⁹. The structure and morphology of pores present in kerogen are primarily controlled by its molecular structure¹⁰⁻¹². Several properties of kerogen such as its porosity, sorption capacity, swelling behavior, fluid flow and transport, density and resistivity, elastic and fracture properties are not well understood due to its complex nanoscale structure. Understanding these properties is crucial as they have a significant impact on the precise estimation of HCs, efficiency of HC recovery and production, designing effective CO₂ sequestration strategies, its interactions with the hydraulic fracturing fluid, and understanding mechanisms of contaminant release and sorption. Over last three years, more than 140 peer-reviewed publications including several publications in *Nature Scientific report*¹³⁻¹⁷ *Nature Materials*¹⁸, and *Nature Communications*^{9,13,19} have been published on understanding kerogen properties. However, the major limitations of these studies are that the models generated are based on kerogen “type” and the information is derived from a very limited number of shale samples. Kerogen ‘type’ classification was introduced by van Krevelan in the 1960s based on the bulk properties (H/C, O/C ratio) of kerogen and has been the standardized method for characterizing kerogen. Primarily there are three types of kerogen: type I, type II, type III (as shown in Table 1). The models based on kerogen “types” do not account for heterogeneity in kerogen that arises due to variations in sources of organic matter (within a particular depositional environment), paleoenvironmental conditions, and effect of differential kerogen cracking on thermal maturation²⁰. This can lead to overestimation or underestimation of the different physicochemical properties of kerogen and shale. In this article,

we discuss the limitations of models by testing the applicability of these models in Marcellus Shales of the Appalachian basin.

Table. 1: Types of kerogen

Kerogen type	Predominant hydrocarbon potential	Amount of hydrogen	Typical depositional environment
I	Oil prone	Abundant	Lacustrine
II	Oil and gas prone	Moderate	Marine
III	Gas prone	Small	Terrestrial

4.2.1 VARIATIONS IN “REALISTIC” STRUCTURAL MODELS AND VOLUMETRIC PROPERTIES OF KEROGEN

The most widely used “realistic” molecular model of kerogen was developed by *Bousigue et al., 2016*¹⁸ using a molecular dynamics-hybrid reverse Monte-Carlo (MD-HRMC) method. This method minimizes the configurational energy of the possible molecular configurations constrained by the pair distribution function, which is obtained from experimental diffraction data. Kerogen models generated in this study were validated by comparing the modeled structural parameters with experimental structural parameters derived mainly from ¹³C solid-state NMR experiments (with and without dipolar dephasing). The advantages of these models are that they provide a detailed 3D representation of the nanostructure of different kerogen “types” required for determining different physicochemical properties (such as density, porosity, adsorption, transport, mechanical properties) of such a heterogeneous and disordered media. However, the nonstructural models of kerogen proposed in this study have some limitations. This is because these models are based on kerogen “type”, and the structural rearrangement within the same kerogen type can be very different for samples with similar maturity even within the same basin. This is clearly evident when we compare the structural parameters of over-mature Marcellus shale samples studied by

Agrawal and Sharma, 2018²¹ and Bousigue et al., 2016¹⁸. Both the samples are taken from Marcellus shale and are primarily type II kerogen^{18,20,22}, with similar aromatic carbon percentage (89% for sample MIP-3H MT from Agrawal and Sharma, 2018²¹, 90% for sample MarK from Bousigue et al., 2016¹⁸). Although, both Marcellus Shale samples have similar kerogen type and similar maturity, a large difference can be observed in their structural parameters such as bridgehead aromatic C %, protonated C %, alkyl substituted aromatic C %, C (carbon/cluster), alcohol and ether C % as shown in Table. 2. This is significant because variations in these parameters indicate that the molecular models of both the kerogen samples will be very different. The difference in molecular structural parameters of kerogen can also be visualized by comparing the unit kerogen structure from both the studies (Fig. 1). The unit kerogen model for sample MIP-3H MT and sample MarK was constructed using the structural parameters of the samples reported by Agrawal and Sharma, 2018²¹ and Bousigue et al., 2016¹⁸ respectively. The observed variation in molecular structure between the two kerogen samples suggests that a large amount of molecular heterogeneity can exist between shales of similar kerogen type and maturity in different parts of a single basin. This difference could be possibly due to shrinkage/collapse of aromatic interlayers¹⁰ in sample Mark resulting in a decrease in average aliphatic chain length (Cn'), protonated aromatic C % and an increase in bridgehead aromatic C % (Table. 2). This heterogeneity could lead to underestimation or overestimation of several kerogen volumetric and thermodynamic properties. For example, using the structural model of sample Mark to model the kerogen properties of samples MIP-3H MT, could result in overestimation of kerogen density, underestimation of kerogen porosity, its sorption properties, swelling behavior and its brittleness. This as a result would provide misleading information about the shale frackability, amount of recoverable gas, sorption/release of different contaminants on shale-fracturing fluid interaction, potential for CO₂

sequestration. Hence, we advocate that a unique structural model for a particular kerogen “type” cannot be used to evaluate shale/kerogen properties in different basins across the world.

Fig.1: Differences in unit kerogen structure of two kerogen samples from Marcellus shale with similar thermal maturity and kerogen type (primarily type II) constructed using structural parameters obtained from a) Agrawal and Sharma, 2018²¹ and b) Bousige et al., 2016¹⁸. Values written in parentheses indicate the fraction of the functional group per unit of kerogen cluster. Other isomers of each kerogen unit are possible.

Table 2. Structural parameters of two kerogen samples obtained by using ^{13}C solid-state NMR (with and without dipolar dephasing). Data were taken from Agrawal and Sharma, 2018²¹ (sample MIP-3H MT) and Bousige et al., 2016¹⁸ (sample MarK).

Structural parameters	Agrawal and Sharma, 2018 ²¹	Bousige et al., 2016 ¹⁸
Aromatic C %	89	90
Carbons/cluster	20	54
Alkyl substituted aromatic C %	12	23
Bridgehead C %	33	60
Protonated C %	43	7
Alcohol/ether C %	2	1 ⁱ , ~50°
Cn'	0.85	0.25
i represents parameters derived from ^{13}C solid-state NMR		
o represents output parameters derived from molecular simulations		

Realistic structural models of kerogen have been constructed and used to estimate volumetric and thermodynamic properties of kerogen, based on its type and maturity by Ungerer et al. 2015²³. The models in this highly cited publication (70+ citation) were built using MD (molecular dynamics) molecular simulation technique. The input parameters of these models were obtained from kerogen structural parameters derived from a study by Keleman et al., 2007²⁴. However, the structural models for shales were generated from Green River shales, Duvernay shale maturity series (from 0.5 VRo to 1.3 VRo) and immature Proprietary Formation which falls in type I, type II and type III kerogen type respectively. This study applied a molecular modeling approach to construct realistic structural models and make quantitative predictions of thermodynamic properties based on quantum mechanics and volumetric properties of kerogen. This work is the foundation of multiple studies conducted to understand the effect of increasing maturity and OM sources on kerogen properties. This foundational study provides molecular structures of different kerogen types with empirical formulae having 175-260 carbon atoms which are easier to input into the molecular simulations as compared to the kerogen models provided by Bousige et al., 2016¹⁸. Therefore, models developed in this study have been used by several researchers to determine different kerogen properties^{14,15,25,26}. However, the major limitation of the models generated by this study are that there was no sample from type I and type III kerogen with VRo>0.9 or for type II kerogen with (VRo>1.4) and have limited applicability for mature shale systems such as Marcellus and Utica. This inference was tested by comparing the kerogen parameters from Marcellus shale (obtained from Agrawal and Sharma, 2018²⁰) to the kerogen structural parameters of Duvernay (type II) and the Proprietary Formation (type III) maturity series, obtained from Keleman et al., 2007²⁴ (the comparison is made within samples of similar thermal maturity). The structural parameters of kerogen from Marcellus shale

(type II) from early oil window was compared with the early oil window sample from Duvernay (type II) and Proprietary (type III) Formations (Fig. 2, Table 2). It was observed that kerogen structural parameters from type II Marcellus shale Formation were more similar to type III kerogen Proprietary Formation (RMSD= 5.35) as compared to the type II Duvernay shale Formation (RMSD= 27.60), as shown in Fig. 2 and Table 3. The comparative analysis clearly demonstrates the limitation of applicability of models of a particular “type” of kerogen to other shale basins. Therefore, we recommend that kerogen properties in different shale Formations should be based on the molecular parameters of the specific kerogen, rather than using a general kerogen “type”.

Table 3. Comparison of structural parameters of type II kerogen from Marcellus Shale Formation (obtained from Agrawal and Sharma, 2018²⁰) with the type II Duvernay Formation and type III kerogen Proprietary Formation (obtained from Keleman et al., 2007²⁴). All samples are from early oil window.

Structural parameters	Agrawal and Sharma, Type II Marcellus	Keleman, Type II Duvernay	Keleman, Type III Proprietary
Aromatic C %	70.5	54	73
Protonated C %	27.7	17	26
Bridgehead C %	25	21	28
Pehnoxy C %	1.7	3	4
Alkyl substituted aromatic C %	16	13	17
Aliphatic C %	25.5	44	27
alcohol/ether C %	3.31	5	3
C (Carbons/cluster)	17.8	19	19
FAA (Fraction of aromatics with attachments)	0.25	0.3	0.26
Cn' (average aliphatic chain length)	1.59	3.4	1.6
RMSD		5.35	27.6

Figure. 2 Cumulative distribution of structural parameters of kerogen determined using Kolmogorov-Smirnov test, a) between type II kerogen from Marcellus Shale Formation with the type II Duvernay Formation, b) between type II kerogen from Marcellus Shale Formation and type III kerogen Proprietary Formation. All samples belong to the early oil window. The structural parameters of kerogen from type II Marcellus shale matches better with Type III Proprietary Formation as compared to type II Duvernay Formation.

4.3 FUTURE DIRECTIONS

Determination of molecular properties of kerogen reveals that kerogen of same “type” in the same basin can have similar H/C and O/C ratio (therefore same kerogen type) but can have a very different molecular arrangement. This variation could be due to variations in sources of OM (variable amount of biomolecules), paleo-redox conditions, microbial diagenesis, kerogen cracking mechanism, etc. in different parts of the basin.

There are a number of studies (few published in Nature scientific reports) which have used the structural models of kerogen provided by Bousigue et al., 2016¹⁸ and Ungerer et al., 2015²³ to model different kerogen properties such as its swelling and confinement¹⁵, its sorption capacity for different gases and potential for CO₂ sequestration^{27–30}, its transport properties^{14,25,26}, its density²⁵, and porosity^{26,31,32}. We propose that since these studies rely on kerogen structures based on

kerogen type they can overestimate or underestimate different kerogen properties. Similar observations were made by Weck et al., 2017¹⁷ which showed that simulated FTIR generated using the previously established models fail to match experimental FTIR data of similar kerogen types. Therefore, we strongly advocate that models of physicochemical properties of shales should be based on molecular parameters of kerogen extracted from specific part of the basin rather than using a general model based on kerogen “type.”

4.4 METHODS

4.4.1 ¹³C solid-state NMR analysis

Solid-state NMR experiments were performed at Environmental NMR Service at Old Dominion University in Norfolk, Virginia, USA on a Bruker Advance III 400 spectrometer operating at 400-MHz ¹H and 100-MHz ¹³C frequencies. The ¹³C chemical shifts were referenced to tetramethyl silane, using the COO resonance of glycine in the α -modification at 176.46 ppm as a secondary reference. The high-spinning speed multi-ramped amplitude cross polarization/magic angle spinning technique developed by Johnson and Schmidt-Rohr, 2014³³ was applied for acquiring quantitative ¹³C NMR spectra for all the kerogen samples. This multiple-cross polarization (multiCP) technique provides a simple, robust way to obtain quantitative solid-state ¹³C NMR spectra of organic materials, with good signal-to-noise ratio. The spectra were measured at a spinning speed of 14 kHz, where spinning sidebands are fairly small (<3%) and have little overlap with center bands. To differentiate nonprotonated C from total C and to determine fractions of mobile groups (with no restricted rotation), ¹³C multiCP/MAS with dipolar dephasing was performed under the same conditions as for ¹³C multiCP/MAS but combined with a dipolar dephasing time of 68 μ s³⁴. The relative proportion of different carbon chains such as mobile and immobile alkyl without heteroatoms (written just as alkyl in this

study), methoxy and amine, O-substituted and O₂ substituted alkyls (ethers and dioxy alkyl), protonated aromatic, bridgehead aromatic, alkyl substituted aromatic, O- substituted aromatic (phenol), carboxyl, carbonyl were obtained for ¹³C NMR spectrum using an NMR peak fitting program *TopSpin* (area of spectra from 0-240 ppm was considered to be 100%).

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AUTHOR CONTRIBUTION STATEMENT

VA and SS were involved in initial conception of idea of the research. VA conducted the analytical work needed for study and drafted the manuscript. VA and SS were both involved in data interpretation, revising and editing of the manuscript.

COMPETING INTERESTS

The authors declare no competing financial or non-financial interests.