Title: Comparison of isotopic and geochemical characteristics of sediments from a gas- and liquids-prone wells in Marcellus Shale from Appalachian Basin, West Virginia

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ABSTRACT

The Middle Devonian age Marcellus Shale contains one of the largest shale gas plays in North America. Hydrocarbon production in the eastern part of the play is mostly “dry gas,” consisting of essentially pure methane. Production of natural gas liquids (condensate) increases toward the west, which is the area currently, being targeted by developers. Two Marcellus Shale cores from West Virginia were analyzed to compare the isotopic and geochemical characteristics of a liquids-prone well (WV-7) in Wetzel County with a gas-prone well (WV-6) in Monongalia County. The contrasts between the cores indicate that the conditions of the Marcellus Shale deposition were different between the two sites. The dominant organic matter preserved in each core is isotopically different; $\delta^{13}\text{C}_{\text{org}}$ values are lighter on average in WV-6 compared with WV-7. A possible explanation is that a larger fraction of terrestrial organic matter was preserved in the WV-6 core, whereas WV-7 may contain a greater percentage of marine organic matter. Clastic-influx proxies (e.g. Ti/Al, Ca/Al and Mg/Al) also suggest that the WV-6 core site received a higher siliciclastic input compared to WV-7, consistent with a more proximal location to dry land and the delivery of greater amounts of terrestrial organic matter. Depleted $\delta^{13}\text{C}_{\text{carb}}$ values, low concentrations of redox sensitive elements (e.g. V, Cr, Ni and U), and high

variability $\delta^{15}\text{N}$ values in the WV-6 core all suggest the presence of higher dissolved oxygen concentration and short term shifts in an oxic/anoxic boundary near the sediment-water interface during deposition. These lines of evidence indicate that the depositional conditions were favorable for the accumulation of predominantly gas-prone Type III kerogen in the Marcellus Shale at the WV-6 site. In contrast, the Marcellus Shale at the WV-7 site was deposited in a more distal area that received a low terrestrial sediment supply, organic matter primarily derived from marine algae, and bottom water conditions that were dominantly anoxic. Such conditions were favorable for the accumulation of Type II kerogen that has a greater capacity to generate liquid hydrocarbons. Differences between the liquids-prone and gas-prone parts of the Marcellus Shale may have been largely ascribed to depth-of-burial and thermal maturation history; this study indicates that depositional environment and sedimentary facies may have played significant roles as well.

1. Introduction

Middle and Upper Devonian-age shales in the Appalachian Basin have a long history of marginal gas production (Piotrowski and Haper, 1979; Milici et al, 2002; Milici and Swezey, 2006; Haper, 2008; King, 2008), and are considered to be the primary source rocks for Upper Devonian sandstone and younger conventional reservoirs in the basin (Boyce and Carr, 2010). The Marcellus Shale is the basal shale unit of a thick clastic sequence of shales and siltstones that dominated the Appalachian Basin deposition during the late Middle Devonian and Upper Devonian – Lower Mississippian time (Potter et al., 1980). Shales with organic carbon contents greater than 2 percent are generally black in color (Hosterman and Whitlow, 1980), and have been sought after for many years as potential sources of natural gas.

The Marcellus Shale is one of these black shale units and is composed of two members, the lower Marcellus/Union Springs Shale and the upper Marcellus/Oatka Creek Shale, which are separated by Purcell/Cherry Valley Limestone (Werne et al., 2002; Segaman et al, 2003). The Union Springs consists of an organic-rich silty shale, siltstone, and limestone (Cooper, 1930). This member is the most organic-rich and gas productive part of the Marcellus Shale. The upper unit of the Marcellus Shale is called the Oatka Creek Member (Cooper, 1930). This is less organic and more clay-rich than the Union Springs, and often contains abundant siderite concretions. There is disagreement about whether the Purcell Limestone is a southern equivalent of the Cherry Valley Limestone, or a totally separate unit (Repetski et al., 2012). In this study, the Purcell and Cherry Valley are treated as separate members. The Cherry Valley Limestone separates the Union Springs and Oatka Creek shales. The Purcell Limestone is present within the Oatka Creek Shale and for this study we named the shale unit above the Purcell Limestone upper Oatka Creek Shale and the one below it is called lower Oatka Creek Shale (Fig. 1). From the gamma ray log, the thickness of the Union Springs Shale decreases from east to west and is only 1.2 m in WV-7 core. Examination of closed-spaced wireline logs from this basin reveals the occasional presence of the Union Springs Member as a thin, radioactive, low-density interval immediately above the Onondaga Formation and below the Cherry Valley Limestone (e.g. Rickard, 1984; Lash and Engelder, 2011). Griffing and Ver Stratten (1991) suggest the faunas and sedimentary fabrics of the limestone beds in the Marcellus Shale are comparable to the Devonian limestones in Europe and North Africa, which can be interpreted as very slow pelagic and hemipelagic sedimentation on sediment-starved marine platforms and adjacent slopes (Tucker, 1974; Wendt et al., 1984).

Figure 1: Study site location and a generalized stratigraphic chart of the Marcellus Shale in West Virginia, correlating to WV-6 and WV-7 wells. Modified from Lash and Engelder (2008), East et al., (2012) and Zagorski et al.(2012).

Ettensohn and coworkers have proposed that much of the black shale was accumulated under persistent and widespread anoxia (Ettensohn et al., 1979; Ettensohn and Barron, 1981; Ettensohn, 1985a, b). Based on Ettensohn's model, accumulation of black shale with high organic carbon content (>10%) was associated with deepening of the Acadian foreland basin and widespread water column anoxia. The interbedded limestone units represent shallowing-upward periods during deposition (Ettensohn and Barron, 1981; Boyce and Carr, 2010).

79 Recently, micro-anoxic environment ideas have been proposed, which dispute
80 widespread bottom water anoxia, and focus on enhanced organic matter preservation due to
81 localized anoxia resulting from high primary productivity with possible seasonal fluctuations
82 (Macquaker et al., 2009; Boyce and Carr, 2010). Other investigators have proposed that black
83 shales were deposited on the shallower, distant edge of the Appalachian Basin, far from land
84 (Schieber, 1994; Smith and Leone, 2010). In this model, the distal side of the basin away from
85 the sediment source areas received relatively little inorganic mineral sedimentation, and was thus
86 “starved” of sediment. The resulting clear, shallow water allowed algae to bloom and contribute
87 significant amounts of organic matter to the fine grained sediment that did accumulate, creating
88 black shale sequences that onlap shallow-water limestone. These ideas suggest that the entire
89 basin was not synchronously anoxic. Therefore, other factors besides anoxia would have
90 influenced the preservation of organic matter and the subsequent quality of the source rock,
91 contributing to the preferential production of natural gas liquids or dry gas.

92 The distribution of liquids- and gas-prone areas within a shale play is important for
93 evaluating the economics of an exploration venture and assessing source rock resources. Liquids-
94 prone plays are of greater interest to industry because of the current low prices of dry natural gas.
95 Study of the key factors controlling hydrocarbon production from shale plays suggested many
96 currently producing shale-gas reservoirs have over-mature source rocks (Passey et al., 2010).
97 However, whether shale reservoirs generate liquids or gas is dependent on not only their thermal
98 maturities but also the types of organic matter within the source rock. Organic matter derived
99 from marine algae (Type II kerogen) contained lipids that typically generated liquids during
100 thermal maturation, whereas terrestrial-sourced organic matter (Type III kerogen) was typically
101 composed of woody or cellulose-dominated plant matter that primarily generated gas during the

thermal maturation process (Leckie et al., 1988). Spatial variation of the types of organic matter within the Marcellus Shale may play an important role in controlling the types of hydrocarbon (gas or liquids) generation. Although the thermal maturity of the Marcellus Shale is considered to be quite high throughout most of the basin (Rowan, 2006), a relatively narrow band along the western margin appears to contain both the right kind of kerogen and the proper levels of thermal maturity to produce significant quantities of natural gas liquids.

In order to test this hypothesis, we examined two Marcellus Shale drill cores from West Virginia. These cores were collected in the late 1970s as part of the Eastern Gas Shales Project (EGSP), a resource assessment and engineering research study funded by the U.S. Department of Energy between 1977 and 1992 to investigate the natural gas resource potential of domestic black shale formations (Soeder, 2012). One core was obtained from EGSP WV-7, a liquids-prone well in Wetzel County, WV near the Ohio River. The other core was obtained from EGSP WV-6, a gas-prone well located on the grounds of the National Energy Technology Laboratory in Monongalia County, WV.

Vitrinite reflectance (R_o) studies of the Marcellus Shale in the Appalachian Basin (Zagorski et al., 2012) indicate that the deeper, eastern WV-6 core has a higher thermal maturity ($R_o=1.5$ to 2.0) compared to the shallower, western WV-7 core ($R_o=1.0$ to 1.5). Thermal maturity is ranked as the number one factor controlling natural gas production from black shales, with total organic carbon content ranked second (Zagorski et al., 2012). It is unclear, however, whether differences in the type of organic matter contained within the source rock may also be responsible for the observed variation in liquids- or gas-prone hydrocarbon production in the Marcellus Shale. To investigate the types of organic matter and their preservation conditions within these two cores, we employed an integrated, multi-proxy approach that characterizes the

relative influences of different processes (biological, physical and chemical) and conditions related to the organic matter accumulations during the shale deposition.

Stable carbon isotope composition of organic matter has been widely used to determine the types of organic matter (terrestrial vs. marine) present in source rocks, and its links to the environment of deposition and/or sediment supply (Maynard, 1980; Meyers, 1994; Calvert et al., 1996). Here we address this issue further by examining the geochemistry of the WV-6 and WV-7 cores in order to determine ways in which the two cores may be chemically similar or different. Thus, we have chosen a multi-proxy approach to evaluate the differences in redox conditions of the bottom water (e.g. V/Cr, U/Th), as well as the detrital clastic influx (e.g. Ti/Al, Mg/Al) during shale deposition.

2. Methods

Representative samples were collected from approximately one meter (3 ft.) intervals from each core for isotopic and geochemical analysis. The samples were ground to very fine powder in a SPEX mixer mill and then oven-dried for 24 hours at a temperature of 50°C. Carbon and nitrogen isotope analysis were performed by the Stable Isotope Laboratory at West Virginia University. Carbon isotopic composition of inorganic carbon was measured using a GasBench device coupled to a Delta Advantage isotope ratio mass spectrometer (IRMS). To determine the isotopic compositions of organic carbon and organic nitrogen, all carbonate was removed from the samples using 1 mol/L hydrochloric acid (HCl) followed by centrifugation and 4-5 rinses with ultrapure DI water until the decanted liquid tested with pH paper was neutral. After decanting the final wash water, the samples in the centrifuge tubes were placed in a drying oven at a temperature of 50°C. Once dried, the samples were transferred to plastic tubes for storage for organic carbon and nitrogen isotopic analysis. A Costech ECS 4010 combustion

elemental analyzer (EA) coupled to isotope ratio mass spectrometer via Conlo 1V interface was used for the determination of the organic nitrogen and carbon isotopic compositions. The measurement precision was assessed by replicate analysis of samples and internal lab standards and was better than $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of internal laboratory normalization and check standards were calibrated against their respective IAEA standards (i.e. NBS 18, NBS19 and LSVEC for $\delta^{13}\text{C}$ of carbonates; USGS 40 and USGS 41 for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of organics) and values are reported in per mil (‰) relative to V-PDB and AIR, respectively.

The major, minor, and trace element compositions of the shale samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICPMS). Powdered and homogenized samples that had passed through a 100 mesh sieve were digested using lithium metaborate fusion. The method is effective at digesting silicate-rich rock samples without the use of dangerous HF or HClO₄ (Walsh, 1980). In this method, 0.4 g of LiBO₂ is mixed with 0.05 g of sample in a platinum crucible. The mixture is heated in a microwave oven (CEM) at 1100°C for 4 minutes. The melt is removed from the microwave and cooled to a glass, which is then dissolved in 5% HNO₃ and 2% HCl while stirring and heating on a hot plate. The dissolved sample is transferred from the platinum crucible and diluted in a beaker to a final volume of 100 ml. For quality control, blanks and reference standards including the Green River shale and the Brush Creek shale were also digested. Elemental concentrations were measured using the ELAN DRC II ICPMS in standard mode. Data were collected after final dilutions of 20 and 100. An online internal standard of 200 ug/l Rh was used for analyses. The instrument was calibrated between 1 and 1000 ppb. Quality checks were included every 10 samples and included sample duplicates, sample spikes, certified reference materials, and blanks. Sample recovery and

precision were calculated for each batch of samples. The analytical precision is better than better than 3% of the measured value for major elements and ~4%–10% of the measured value for trace elements.

3. Results

To better characterize and compare the isotopic and geochemical differences between WV-6 and WV-7 cores, both cores were subdivided into various zones based on gamma ray, total organic carbon (TOC) content and lithology (Table 2). In WV-6, Organic-rich (OR)-Shale Zone is the shale interval (Union Springs Shale) that has the highest average TOC in the Marcellus Shale. The gamma ray signal is also constantly high through this zone. Organic-intermediate (OI)-Shale Zone is an intermediate organic carbon content- shale interval, while Organic-poor (OP)-Shale Zone represents the shale interval with relatively poor TOC content and low gamma ray signal. Carbonate zone is composed of the Purcell and the Cherry Valley limestones (Fig. 2). In WV-7, OR-Shale Zone is a high TOC interval between the Purcell and Cherry Valley limestones, OI-Shale Zone is an intermediate organic carbon-interval above the Purcell Limestone, whereas Carbonate Zone represents the Purcell and Cherry Valley limestones (Fig. 3). The TOC values and isotopic compositions of WV-6 and WV-7 cores are listed in Table 1.

WV-6					WV-7				
Depth (m)	%TOC	$\delta^{13}\text{C}_{\text{carb}}\text{‰}$	$\delta^{13}\text{C}_{\text{org}}\text{‰}$	$\delta^{15}\text{N}\text{‰}$	Depth (m)	%TOC	$\delta^{13}\text{C}_{\text{carb}}\text{‰}$	$\delta^{13}\text{C}_{\text{org}}\text{‰}$	$\delta^{15}\text{N}\text{‰}$
2256.2	4.8	-4.5	-29.8	0.0	2005.4	9.9	-3.7	-29.6	-0.8
2256.8	4.7	-7.6	-29.8	-1.6	2005.7	10.1	-3.8	-29.6	-0.9
2257.4	4.6	-4.1	-30.0	-0.2	2006.3	8.8	-7.8	-29.5	-0.3
2258.0	5.4	-8.2	-30.0	-0.1	2007.3	7.8	-5.7	-29.5	0.0
2258.9	5.3		-30.0	-0.1	2008.5	9.8	-5.6	-29.6	0.6
2259.4	4.2	0.5	-29.8	-0.1	2009.1	9.7	-5.7	-29.5	0.8
2260.1	4.7		-29.7	-0.8	2010.0	8.1	-5.4	-29.6	-1.3
2260.1	3.6		-29.4	-0.7	2010.9	8.4	-4.4	-29.5	0.0
2260.7	3.7	-4.7	-29.5	-0.3	2011.4	7.9	-4.6	-29.4	0.0
2261.6	4.3	-3.8	-29.6	-0.2	2011.8	7.7	-2.7	-29.2	0.7
2262.6	3.2		-29.5	-0.2	2013.1	3.1	-9.0	-29.1	0.4
2263.5	3.3	-6.1	-29.8	-0.3	2013.7	6.5	-4.8	-29.4	-0.3
2264.1	3.4		-29.7	-1.6	2014.6	6.1	-4.7	-29.4	-1.2
2264.6	3.9	-5.6	-29.7	0.0	2015.5	11.6	-5.2	-29.4	0.3
2265.3	3.8	-5.2	-29.6	0.1	2016.4	12.5	-3.1	-29.0	0.6
2266.0	3.7	-15.2	-29.9	-0.2	2016.9	13.5	-10.1	-29.5	-0.3
2266.0	4.2	-14.3	-29.8	-0.2	2017.3	13.7	-2.0	-29.6	-0.9
2266.6	4.4	-6.3	-29.8	0.1	2018.2	2.5	-2.1	-29.6	0.1
2267.1	4.6	-7.5	-29.9	0.2	2019.0	13.3	-1.9	-30.1	-0.1
2267.0	6.1	-11.0	-29.8	0.2	2019.2	6.6	-4.5	-30.1	0.2
2268.0	6.9	-6.8	-29.9	-0.1	2019.9	0.4	-1.5	-28.9	0.0
2269.0	8.6	-4.3	-29.8	-1.4	2020.1	1.8	-1.0	-30.0	0.1
2269.9	8.5	-6.1	-29.7	-0.3					
2270.8	8.5	-3.9	-29.8	-1.3					
2271.7	9.7	-6.4	-29.9	-1.7					
2272.6	8.0	-3.8	-29.8	-0.6					
2273.4	6.4	-5.5	-29.7	-0.9					
2273.4	6.2	-9.8	-29.6	0.6					
2274.4	7.9	-8.7	-29.8	-0.5					
2275.4	7.3	-4.1	-29.9	-0.1					
2276.0	3.8	-4.9	-30.0	0.0					
2276.5	6.0	-2.9	-30.4	0.2					
2277.2	5.5	-7.0	-31.3	0.3					
2278.1	6.1	-10.1	-30.7	-1.6					
2278.8	6.6	-7.2	-30.6	-1.0					
2279.9	7.8	-2.4	-30.8	-1.3					
2280.8	9.1	-3.3	-30.8	-0.5					
2281.8	13.0	-2.4	-30.5	1.0					
2282.7	14.2	-2.7	-30.8	0.5					
2283.6	10.9	-3.5	-30.9	-2.0					
2284.5	4.4	-3.9	-30.9	1.0					
2285.4	8.8	-2.5	-30.9	-1.4					
2286.0	9.2	-2.8	-30.6	1.4					

Table 1: The total organic Carbon (TOC) and isotope values of all samples collected from the WV-6 and WV-7 cores. The carbon and nitrogen isotope values are reported in per mil (‰) relative to V-PDB and AIR, respectively.

WV-6								
	OR-Shale Zone		OI-Shale Zone		OP-Shale Zone		Carbonate Zone	
	Average	SD	Average	SD	Average	SD	Average	SD
TOC %	9.7	3.1	7.7	1.2	4.3	0.6	5.2	1.3
$\delta^{13}\text{C}_{\text{carb}} \text{‰}$	-2.9	0.6	-6.4	2.5	-6.6	4.1	-6.4	2.7
$\delta^{13}\text{C}_{\text{org}} \text{‰}$	-30.8	0.2	-29.8	0.1	-29.8	0.2	-30.4	0.6
$\delta^{15}\text{N} \text{‰}$	-0.1	1.3	-0.6	0.7	-0.3	0.5	-0.4	0.8
WV-7								
	OR-Shale Zone		OI-Shale Zone		Carbonate Zone			
	Average	SD	Average	SD	Average	SD		
TOC %	10.5	4.3	8.8	1.0	3.6	2.6		
$\delta^{13}\text{C}_{\text{carb}} \text{‰}$	-4.1	2.9	-4.9	1.4	-4.2	3.2		
$\delta^{13}\text{C}_{\text{org}} \text{‰}$	-29.6	0.4	-29.5	0.1	-29.4	0.4		
$\delta^{15}\text{N} \text{‰}$	0.0	0.5	-0.1	0.7	-0.2	0.6		

Table 2: Average values and standard deviations of total organic carbon content (TOC) and isotopic compositions in different zones in WV-6 and WV-7 cores.

3.1 Isotopic composition

In WV-6, $\delta^{13}\text{C}_{\text{org}}$ shows the most depleted value (average = $-30.8 \pm 0.2 \text{‰}$) in OR-Shale Zone followed by a slightly positive change at the Cherry Valley Limestone member. This trend is interrupted by a sharp positive shift to $\sim -30.0 \pm 0.1 \text{‰}$ at the base of OI-Shale Zone. OP-Shale Zone keeps generally constant values of $-30.8 \pm 0.2 \text{‰}$ (Fig. 2). In WV-7, $\delta^{13}\text{C}_{\text{org}}$ displays a

different pattern (Fig. 3). The $\delta^{13}\text{C}_{\text{org}}$ values are relatively negative (average $-29.6 \pm 0.4\text{‰}$) at OR-Shale Zone and reach a minimum of -30.1‰ at 2016.5 m, and then followed by a slight positive shift in the Purcell Limestone member with an average value from -29.7‰ to -29.5‰ . After that, the $\delta^{13}\text{C}_{\text{org}}$ values fluctuate around -29.6‰ at the OI-Shale Zone.

Figure 2: Total organic carbon content and carbon isotopic profiles of organic and carbonate carbon in the WV-6 core.

Figure 3: Total organic carbon content and carbon isotopic profiles of organic and carbonate carbon in the WV-7 core.

In WV-6 (Fig. 2), the $\delta^{13}\text{C}_{\text{carb}}$ values are around $-2.9 \pm 0.6\text{‰}$ in OR-Shale Zone, followed by a sharp negative shift to $-6.4 \pm 2.7\text{‰}$ in the Cherry Valley Limestone, and then maintain a consistent average value $\sim -6.4 \pm 2.5\text{‰}$ in OI-Shale Zone. In OP-Shale Zone, the values trend in a slight negative shift at around $-6.6 \pm 4.1\text{‰}$. In WV-7 (Fig. 3), the $\delta^{13}\text{C}_{\text{carb}}$ values are $\sim -1.2\text{‰}$ in Cherry Valley Limestone, which is close to marine carbonate $\delta^{13}\text{C}_{\text{carb}}$ values ($\sim 0\text{‰}$). This is followed by a negative shift in OR-Shale Zone with the average value around $-4.1 \pm 2.9\text{‰}$. Finally, the average value is more negative in OI-Shale Zone (average = $-4.9 \pm 1.4\text{‰}$) compared to OR-Shale Zone and Carbonate Zone.

The nitrogen isotope results show that there is a slight difference in the isotopic composition of organic nitrogen between the two cores (Fig. 4). In WV-6, the $\delta^{15}\text{N}$ values range from -2‰ to $+1.4\text{‰}$ in OR-Shale Zone, and from -1.8‰ to $+0.6\text{‰}$ in OI-Shale Zone. In WV-7, the $\delta^{15}\text{N}$ values are relatively consistent in OR- and OI-Shale zones throughout the core and ranging from -1.3‰ to $+0.8\text{‰}$ in both.

Figure 4: Nitrogen isotopic compositions of two cores WV-6 (right) and WV-7 (left).

3.2. Geochemical Data

Profiles for geochemical data are shown in Fig 5 and 6 with values listed in Tables 1S. The Ti, Ca, Mg and Mn concentrations indicate clastic influx and were divided by Al concentration to eliminate the effect of varying input sources (Fig. 5). The profiles for Ti/Al indicate a

231 significant increase in Ti concentration in WV-6. Ca, Mg and Mn exhibit a distinct increase in
232 concentration at the bottom of the Marcellus Formation in WV-7, but the values are relatively
233 consistent through WV-7 core. Redox-sensitive metals (e.g. Ni, V, U) are represented as trace
234 element ratios, such as $V/(V+Ni)$, to reconstruct the paleoredox conditions (Fig. 6). The profile
235 for $V/(V+Ni)$ indicates a decrease in OR-Shale Zone in WV-6 compared to that zone in WV-7.
236 The V/Cr profiles do not indicate any significant enrichment in any one zone in WV-6, but the
237 values are higher on average in WV-7, in particular in OR-Shale Zone. The profile for U/Th in
238 WV-7 appears scattered and values are slightly higher on average than WV-6. Mo/Al profile
239 shows no distinct changes through the WV-7 core while the values decrease upward through
240 WV-6.

Figure 5: Profiles of Al%, Ti/Al, Ca/Al, Mg/Al and Mn/Al ratios of two cores WV-7 (upper) and WV-6 (lower).

Figure 6: Profiles of V/(V+Ni), V/Cr, U/Th and Mo/Al ratios of two cores WV-7 (upper) and WV-6 (lower).

4. Discussions

4.1 Carbon and nitrogen isotopes

Organic carbon isotope ratios ($\delta^{13}\text{C}_{\text{org}}$)

The organic carbon isotope results in this study show that the $\delta^{13}\text{C}_{\text{org}}$ values in WV-6 are on average 0.5‰ lighter than WV-7 throughout the Marcellus Formation (Fig. 7a). In OR-Shale

Zone of WV-6, the $\delta^{13}\text{C}_{\text{org}}$ values are significantly lighter ($\sim 1.2\text{‰}$) than OR-Shale Zone in WV-7 (Fig. 7b). The $\delta^{13}\text{C}_{\text{org}}$ values in OI-Shale Zone in WV-6 are also on average 0.3‰ lighter than OI-Shale Zone in WV-7 (Fig. 7c). The differences in organic carbon isotope ratios in both zones can be due to differences in the source of organic matter or microbial diagenesis (Beier and Hayes, 1989).

Figure 7: Histograms of $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{15}\text{N}$ values in overall Marcellus Formation, Organic-rich (OR)-Shale Zone and Organic-intermediate (OI)-Shale Zone in two cores WV-6 and WV-7.

Carbon isotopic ratios are useful to distinguish marine and terrestrial plant sources in organic matter (e.g. Faganeli et al., 1988; Meyers and Ishiwatari, 1993; Meyers, 1994). Most photosynthetic plants incorporate carbon into organic matter using the C3 Calvin pathway, which discriminates against ^{13}C . Therefore, organic matter produced from atmospheric CO_2 ($\delta^{13}\text{C} = \sim -7\text{‰}$) by land plants using the C3 pathway consequently has an average $\delta^{13}\text{C}$ (PDB) value of about -27‰ . However, for marine algae and phytoplankton, the source of inorganic carbon is dissolved bicarbonate, which has a $\delta^{13}\text{C}$ value of about 0‰ . Hence, marine organic matter typically has $\delta^{13}\text{C}$ values between -20‰ and -22‰ (Meyers, 1994), which is heavier than the $\delta^{13}\text{C}$ values in terrestrial organic matter. Several studies have suggested that diagenesis does not significantly affect the $\delta^{13}\text{C}$ of organic matter in sedimentary rocks, particularly in black shales (e.g. Ader et al., 2009; Bekker et al., 2008; Young et al., 2008). It has been suggested that in black shales, removing or altering a portion of the primary organic carbon may not change organic carbon isotopic compositions (Jiang et al., 2012). Therefore, lower $\delta^{13}\text{C}_{\text{org}}$ values in WV-6 core could possibly suggest that the organic matter in the shale contained a higher percentage of terrestrial organic matter composed of gas-prone Type III kerogen. In contrast, the shale in WV-7 probably had a larger contribution of lipid-rich, marine organic matter (i.e. Type II kerogen), which significantly helped its potential to generate wet gas and liquids during the thermal maturation process.

Meyers (1994) also concluded that two of the bulk identifiers of organic matter sources - the C/N ratio and the $\delta^{13}\text{C}_{\text{org}}$ appear to undergo little change under diagenetic processes. In particular, the organic matter in marine sediments typically accumulates at slower rates and over longer periods of time. Thus, the C/N ratio and the $\delta^{13}\text{C}_{\text{org}}$ values consequently have the potential to record longer paleoceanographic histories and reveal the effects of slow-acting diagenetic

alterations. Hence, for marine sedimentary deposits, the $\delta^{13}\text{C}_{\text{org}}$ values do not change drastically after a significant amount of time after burial.

The $\delta^{13}\text{C}_{\text{org}}$ values in organic matter could be affected by other microbial processes. For example, the microbial cycling of methane, via bacterial methane oxidation could potentially contribute isotopically depleted organic carbon to sediments (Jahnke et al., 1996; Freeman, 2001). Therefore, the lighter $\delta^{13}\text{C}_{\text{org}}$ value in WV-6 could also be associated with bacterial methane oxidation, which provides isotopically depleted carbon to the inorganic carbon reservoir. Oxidation of methane would suggest the presence of a relatively high oxygen concentration in the bottom waters or the presence of other oxidants like SO_4 , NO_3 . These conditions are also more likely to exist in the shallower/ marginal part of the basin during the deposition of Marcellus Shale. Hence, based on carbon isotope signatures of organic and inorganic carbon we infer that sediments of well WV-6 were deposited near the basin margin.

Carbonate carbon isotope ratios ($\delta^{13}\text{C}_{\text{carb}}$)

In general, $\delta^{13}\text{C}_{\text{carb}}$ values are slightly positive in OR-Shale zones compared to other shale zones within the Marcellus Formation in both cores (Fig. 2 and 3). The relatively high $\delta^{13}\text{C}_{\text{carb}}$ values may be due to the rapid burial of large amounts of organic carbon which is rich in ^{12}C (Louis-Schmid et al., 2007; van Hengstum and Grocke, 2008; Spofforth et al., 2010). The high photosynthetic demand is likely to preferentially remove lighter ^{12}C leaving the dissolved inorganic carbon pool enriched in ^{13}C , resulting in an increase in $\delta^{13}\text{C}$ of the precipitating carbonate.

The $\delta^{13}\text{C}_{\text{carb}}$ values in the WV-6 core are on average 1.1‰ lighter than the WV-7 core (Fig. 7d). Such a difference may be ascribed to microbial oxidation of organic matter which can produce isotopically light dissolved inorganic carbon (DIC) in the pore waters of deep-sea

sediments (von Breymann et al., 1991). This process added ^{13}C -depleted carbon to the photic zone, thus the remineralized CO_2 can precipitate as carbonate with $\delta^{13}\text{C}_{\text{carb}}$ values as light as -19‰ (Meyers and Snowdon, 1993). Therefore, the lighter $\delta^{13}\text{C}_{\text{carb}}$ values in WV-6 indicate that there has been enrichment of ^{12}C during the post-depositional microbial reworking of organic matter under oxic conditions. The lighter $\delta^{13}\text{C}_{\text{carb}}$ values in WV-6 may also be due to methane oxidation processes, which delivered isotopically light carbon to the source of the DIC. Thus, the precipitating carbonate would be enriched in ^{12}C and display lighter $\delta^{13}\text{C}_{\text{carb}}$ values. The $\delta^{13}\text{C}_{\text{carb}}$ values suggest that the dissolved oxygen concentration was relatively high during the deposition of the sediments in WV-6 core.

Moreover, in OI-Shale Zone (Fig. 7f), more negative $\delta^{13}\text{C}_{\text{carb}}$ values ($\sim -6.4\text{‰}$) were observed in WV-6 compared to WV-7 ($\sim -4.9\text{‰}$) and could be due, once again, to the intermittent oxygenated conditions during the shale deposition, which promote the isotopically lighter CO_2 generated from the deposited organic matter, resulting in more negative isotopic compositions in the WV-6 carbonate. In contrast, OR-Shale Zone in WV-6 (Fig. 7e) displays average $\delta^{13}\text{C}_{\text{carb}}$ values that are significantly higher ($\sim -2.9\text{‰}$) due to strongly anoxic/euxinic environments, which generated less isotopically light CO_2 from altered organic matter. However, the average $\delta^{13}\text{C}_{\text{carb}}$ values in WV-7 are nearly consistent between OR- and OI-Shale Zones, suggesting that the sediments were deposited under persistently anoxic conditions.

Ocean margins and continental-type seaways can also influence $\delta^{13}\text{C}_{\text{carb}}$ in DIC (Holmden et al., 1998). The inorganic carbon near the basin margin can be easily influenced by input from groundwater and surface waters that are typically depleted in ^{13}C relative to open marine carbon (Freeman, 2001). Therefore, the lighter $\delta^{13}\text{C}_{\text{carb}}$ values in WV-6 core could also suggest the increasing influx of fresh water from the land area during the deposition. This further

supports our hypothesis that WV-6 site was closer to the basin margin compared to WV-7 at the time of deposition.

Nitrogen isotope ratios ($\delta^{15}\text{N}$)

The nitrogen isotope in marine sediments is a reliable proxy for reconstructing the redox states in the water column (e.g. Altabet and Francois, 1994; Ganeshram et al., 1995, 2000, 2002; Calvert et al., 2001; Jenkyns et al., 2001; Kienast et al., 2002; Altabet, 2006; Quan et al., 2008; Quan et al., 2013a, b). In the WV-6 core, the fluctuation in $\delta^{15}\text{N}$ values for the entire core is relatively large (ranging from -2‰ to $+1.4\text{‰}$) compared with the WV-7 core (ranging from -1.3‰ to $+0.8\text{‰}$) (Fig. 7g). In particular, the $\delta^{15}\text{N}$ values in OR-Shale Zone range from -2‰ to $+1.4\text{‰}$ in WV-6 while in WV-7 they only range from -0.9‰ to $+0.6\text{‰}$ (Fig. 7h). In OI-Shale Zone, the $\delta^{15}\text{N}$ values vary between -1.8‰ and 0.6‰ in WV-6 core while range from -1.3‰ to 0.8‰ in WV-7 core (Fig. 7i).

A well-preserved $\delta^{15}\text{N}$ signal reflects two dominating local processes superimposed on the average ocean $\delta^{15}\text{N}$ signal: 1) nitrogen fixation, which results in a small, depleted $\delta^{15}\text{N}$ value of nitrate; and 2) water column denitrification, which contributes to enriched $\delta^{15}\text{N}$ values of residual nitrate (Quan et al., 2008). Since nitrifying bacteria are aerobes, while denitrifiers are anaerobes, sedimentary organic nitrogen isotope signatures can indirectly reflect the redox conditions of the water column at the time of deposition (Quan et al., 2008). When there is little to no oxygen in the water column, nitrate can hardly be formed and, as a result, $\delta^{15}\text{N}$ value is close to 0‰ . As oxygen concentration increases, nitrate concentration rises, leading to an increase in the levels of denitrification. This process removes isotopically light nitrate, leaving the residual nitrate enriched in heavier ^{15}N , which contributes to positive $\delta^{15}\text{N}$ in the organic matter produced (Quan et al., 2008; Quan et al., 2013b). Therefore, the relatively large variation

of $\delta^{15}\text{N}$ values in WV-6 Marcellus core suggest stronger oscillating redox conditions during the shale deposition, which can be attributed to vertical movement of the anoxic/oxic interface as it impinged on the Appalachian Basin margin. In contrast, Marcellus deposition at the WV-7 core site is interpreted to have occurred in a deep basin environment that was density stratified with the bottom water remaining predominantly anoxic.

3.2 Geochemical analysis

For comparison of geochemical characteristics both cores are divided into two broad groups (i.e. Shale Zone including OR-, OI- and OP-Shale Zones and Carbonate Zone including Purcell and the Cherry Valley limestones). Ti/Al ratios have been widely used as an indicator of sedimentation rate (Murphy et al., 2000; Rimmer et al., 2004). Ti often occurs independently as silt- and sand-sized minerals such as ilmenite, rutile and augite (Shimmiel, 1992). Therefore, a higher Ti/Al may indicate the presence of Ti-bearing heavy minerals often associated with coarse-grained sediments (Schmitz, 1987), and can be used as a proxy for higher clastic influx. Ti/Al ratios in WV-6 and WV-7 cores are plotted in Fig. 8a. Relatively higher Ti/Al were observed in both shale and carbonate intervals in WV-6 compared to WV-7. This suggests more Ti-containing heavy minerals were buried with sediments during the deposition of sediments at the core location. This higher Ti/Al ratio would imply a greater supply of terrestrial clastic input, indicating that the core site of WV-6 was located near the shelf margin of the basin. Likewise, the relatively low Ti/Al ratios in the WV-7 Marcellus core suggest a lower rate of clastic input and a location close to the center of the basin.

Calcium (Ca), magnesium (Mg) and manganese (Mn) are positively correlated with the carbonate carbon contents. These elements were normalized to Al and plotted in Fig. 8b, 8c and 8d. In the shale and carbonate intervals, higher average Ca/Al, Mg/Al and Mn/Al ratios were

376 observed in WV-7, which reflects the higher carbonate content in the Marcellus Shale at this
377 location. Carbonate precipitation usually occurs in open marine environments where there is low
378 clastic input into the water. Clastic input increases the turbidity of the water and prevents
379 sunlight from penetrating. Moreover, siliciclastic minerals have greater hardness than carbonate
380 minerals and tend to abrade the carbonates (Armenteros and Huerta, 2006). Thus, the higher
381 carbonate content in the WV-7 Marcellus core is another line of evidence supporting deposition
382 in an open marine setting where the organic matter accumulation was not greatly influenced by
383 clastic influx. On the other hand, Marcellus deposition at the WV-6 site occurred on the basin
384 margin more proximal to land, where it presumably experienced periodic episodes of clastic
385 sediment input from storms and runoff, leading to the lower average Ca/Al, Mg/Al and Mn/Al
386 ratios observed in the WV-6 core.

Figure 8: Average major and minor element ratios in shale and carbonate zones of two cores WV-6 and WV-7.

Although the nitrogen isotope measurement clearly records the differences in redox conditions between WV-6 and WV-7, it is critical to connect the nitrogen isotope results to the trace metal results. The behavior of trace metals has been extensively investigated in modern marine environments under a wide range of benthic oxygen levels. Several metallic elements like Mo, Cr, Fe, V, Ni, Th and U are known to be highly concentrated in black shales (e.g. Hatch and Leventhal, 1992; Calvert and Paderson, 1993; Jones and Manning, 1994; Crusius et al., 1996; Dean et al., 1997; Morford et al., 2001; Algeo and Maynard, 2004; Quan et al., 2008; Leventhal, 2009). Their accumulations are mostly related to the anoxic or euxinic conditions at the time of deposition, therefore, those elements are considered to be redox-sensitive elements. Previous studies have used Al-normalized elemental ratios such as Cu/Al (Calvert et al., 1996; Calvert and Pedersen, 1993; Rimmer et al., 2004) and trace element ratios such as V/(V+Ni), V/Cr, Ni/Co, U/Th (Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer et al., 2004) to evaluate redox conditions.

Ni and V are known to occur in tetrapyrrole structures that can be preserved well under anoxic conditions (Lewan and Maynard, 1982; Algeo and Maynard, 2004; Tribovillard et al., 2006). They suggest that the ratio of V to Ni in crude oil, which is unaltered by diagenesis, indicates the environmental conditions at the time of deposition. Hatch and Leventhal (1992) suggested that V/(Ni+V) greater than 0.84 represent euxinic conditions, while ratios between 0.54 and 0.82, and 0.46-0.60 represent anoxic and dysoxic conditions, respectively. In our study the samples from Shale Zone in WV-7 (Fig. 8e), display significantly higher V/(V+Ni) (average = 0.69) compared to the Shale Zone in WV-6 core (average = 0.57), which indicates that more anoxic conditions prevailed during Marcellus black shale deposition at the WV-7 location. However, the V/(V+Ni) is slightly higher (average = 0.6) in the WV-6 core than in the WV-7

core (average = 0.55) during the Marcellus carbonate deposition. In addition, Lewan and Maynard (1982) suggested that extremely high V and Ni concentrations (>100 ppm) only occur in bitumen that is associated with Type I and II kerogen, whereas relatively low V and Ni concentrations (<100 ppm) are derived from bitumen that is associated with Type III kerogen. The Marcellus Shale core samples from WV-7 have V and Ni concentrations greater than 100 ppm (Table. 3b), whereas the V and Ni concentrations in a number of Marcellus shale core samples from WV-6 are less than 100 ppm (Table 1S). This indicates that the Marcellus at the WV-7 location contains a greater proportion of marine organic matter associated with Type II kerogen which is also supported by our carbon and nitrogen isotope results.

V/Cr is another useful indicator of bottom water redox conditions. V, initially incorporated into tetrapyrrole structures, is more favorably accumulated under reducing conditions (Calvert and Piper, 1984; Tribovillard et al., 2006; Soua, 2010). V may also be adsorbed onto clay minerals during burial (Breit and Wanty, 1991) while Cr is thought to be associated with the detrital fraction and is not influenced by redox conditions (Dill, 1986). Therefore, high V/Cr ratios indicate anoxic conditions during deposition. In our study, V/Cr ratios are high in WV-7 core, particularly in the Shale Zone (Fig. 8f), implying anoxic conditions during deposition in basin-center; however, relatively low ratios in the WV-6 core may suggest dysoxic or alternating anoxic and dysoxic bottom water conditions nearer the basin margin during deposition of Marcellus.

U/Th have also been used as excellent redox indicators (Dill, 1986; Jones and Manning, 1994; Rimmer et al., 2004). The U concentration is dependent on redox conditions. In oxygen-deficient or reducing environments U(VI) is reduced to U(IV), which is insoluble and becomes fixed onto sediments (Algeo and Maynard, 2004; Tribovillard et al., 2006). In contrast, Th is

relatively immobile and is associated mostly with insoluble detrital clay minerals or heavy minerals (Anderson et al., 1983). Therefore, higher U/Th values (>1.25) indicate deposition in anoxic conditions and lower values (<0.75) result from oxic environments (Jones and Mannings, 1994). In our study (Fig. 8g), high U/Th ratios were observed in the Marcellus Shale in the WV-6 and WV-7 cores (above ~ 2), suggesting anoxic depositional conditions. But the WV-7 core displays a much higher U/Th ratio (3.97), suggesting more anoxic (euxinic) environments during the shale deposition.

Molybdenum (Mo) is another widely-used indicator for identifying anoxic/euxinic conditions. Mo has a very low concentration in seawater (~ 10 ppm), but has been shown to be highly concentrated in marine sediments deposited under anoxic/sulfidic environments (Emerson and Huested, 1991; Werne et al., 2002; Lyons et al., 2003; Algeo and Maynard). The enrichment of Mo is usually associated with sulfate reduction under anoxic conditions because Mo content is directly controlled by availability of dissolved sulfide (Helz et al., 1996). The most probable means by which this element is transferred from the water column to the sediment is by rapid uptake as authigenic sulfides (Bodin et al., 2007). However, in our study, Mo was not effective for determining the bottom water conditions. Mo/Al ratios are very similar in the shale intervals of both Marcellus cores in WV-6 and WV-7 (Fig. 8h), which is inconsistent with other redox proxies. One possible explanation could be a greater influx of Mo during Marcellus time to the WV-6 site compared to WV-7. Harris (2013) suggested that the Mo recharge from the global ocean varies with the degree of restriction across barriers. Mo can be highly concentrated under weakly anoxic environments from a combination of greater Mo availability from the global oceans, and enhanced Mo transport to the sediment-water interface via Fe-Mn redox cycling (Algeo and Lyons, 2006). The high Mo/Al ratio in WV-6 may be possibly attributed to the

greater Mo availability due to nearshore currents bringing in a constant supply from the larger ocean during the weakly anoxic conditions, whereas the WV-7 core site was in a more distal, strongly anoxic, stagnant part of the basin without an adequate resupply of Mo. Another possible explanation could be the redox condition was too sulfidic during the deposition of black shale in the WV-7 core site, leading to depletion of the aqueous Mo reservoir, and therefore less Mo burial in this core (Algeo and Lyons, 2006; Quan et al., 2013).

5. Conclusions

The isotopic and geochemical data suggest that during deposition of the Marcellus Shale, the WV-6 core was located near the basin margin and relatively close to clastic sediment supply sources. This led to an increased input of land-derived sediment, along with a greater percentage of woody, terrestrial Type III kerogen, which tends to generate gas primarily when thermally cracked during deep burial. The oscillating redox conditions were also favorable for the accumulation of Type III kerogen. Along with a higher level of thermal maturity, terrestrial organic matter is responsible for the predominantly dry gas content of the Marcellus Shale at the WV-6 location.

Deposition of the Marcellus Shale at the site of the WV-7 core was relatively far from the sediment source areas, probably in an open marine environment with stagnant bottom waters and persistent anoxia. Such conditions were favorable for the accumulation of Type II kerogen, primarily derived from marine algae and phytoplankton within the water column. This marine organic material contains lipids, which tend to generate both liquids and gas during the thermal cracking processes. Lower thermal maturity and the predominance of Type II kerogen in the Marcellus Shale at the WV-7 site are responsible for the natural gas liquids production associated with shale gas wells in this location.

These interpretations are supported by multiple lines of evidence including the higher Ti/Al in the Marcellus interval from WV-6 core, suggestive of a higher content of land-derived sediment. The relatively lower Ca/Al, Mg/Al and Mn/Al ratios present in this core are also indicative of a higher clastic influx during the deposition of sediments. The WV-7 core site received less terrestrial sedimentary input as is supported by the observed changes in detrital or detrital-influenced elements. For instance, average Ti/Al decreased from WV-6 to WV-7, whereas average Ca/Al, Mg/Al and Mn/Al ratios increased significantly due to high carbonate precipitation at the open water WV-7 site.

The predominantly terrestrial source of organic carbon in the WV-6 Marcellus core is indicated by the lighter $\delta^{13}\text{C}$ values in the organic matter compared to the WV-7 core. Less clastic input contributed to lower terrestrial organic matter influx, resulting in a large proportion of marine organic matter within the Marcellus in the WV-7 core.

Preservation of the organic matter in shale requires dysoxic or anoxic conditions at the sediment-water interface. The high concentration of redox-sensitive elements such as $\text{V}/(\text{V}+\text{Ni})$, V/Cr and U/Th in the WV-7 core indicates persistent anoxic conditions in bottom waters during Marcellus deposition at the WV-7 site. The Marcellus sediments at the WV-6 location appear to have experienced short-term oxic/anoxic fluctuations in view of the relatively low concentrations of redox-sensitive elements. High variability of $\delta^{15}\text{N}$ values in the WV-6 Marcellus core is interpreted to indicate a range of conditions from suboxic to anoxic, with infrequent sulfidic conditions in the water column. These oscillating redox conditions were still effective at preserving organic matter, as evidenced by the presence of black shale in this core, but they also show that depositional environments were quite different between the WV-6 and WV-7 sites.

The distinct isotopic and geochemical signatures can be used to identify the environment of deposition for the Marcellus Shale in cores WV-6 and WV-7 which, in turn, controls the types of hydrocarbon (liquids or gas) produced from the Marcellus Shale. This study confirms that isotopic and geochemical assessments can be used to correlate and regionally map liquids and gas rich reservoirs in this basin. Besides the carbon isotopic signature in bulk organic matter, isotopic composition of biomarkers are more precise tools in determine the sources of organic matter in black shales. Certain organic compounds are excellent indicators of sources of organic matter as they retain their biological heritage (Meyers, 1993). For example, terrestrial organic matter can be distinguished from marine organic matter by higher abundance long chain, C₂₇, C₂₉, C₃₁n-alkanes and lower sterane/hopane ratios (Maynard, 1980; Calvert et al., 1996). Thus, the future work will focus on isolation of biomarkers and their isotopic analysis in order to better understand the different sources of organic matter preserved in the Marcellus Shale.

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