

**ASSESSMENT OF NATURAL GAS PRODUCTION POTENTIAL IN THE
DEVONIAN MARCELLUS SHALE OF PENNSYLVANIA**

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Abstract

A stratigraphic sampling and high resolution geochemical analysis of the Middle Devonian Marcellus Formation, an organic rich black shale of the Appalachian basin, reveals a changing environment of deposition and a horizon that may be the most productive of natural gas. Stratigraphic trends were determined after detailed analysis of hand samples collected in Kistler, PA from the most complete stratigraphic section exposed in the state. Elemental and isotope abundances of C, N, and S were used to evaluate changes in depositional environment, and at what depths those changes encouraged the formation of natural gas source rock. TOC data show the base of the formation is the most organic rich, and steadily decreases up-section. $\delta^{13}\text{C}$ values show changes in the type of deposited organic matter, alternating between possibly terrestrial input at the top of the formation and marine organic matter at the base. A C/S plot shows the bottom water during deposition was predominantly anoxic. $\delta^{34}\text{S}$ values are the most depleted at the base, indicating the lowest rate of clastic sediment supply. The horizon with the most conducive environment to source rock formation was found between 10 and 14 m above the base. This horizon likely represents the maximum flooding surface of the first transgression event of the Acadian orogeny.

Table of Contents

Title page	1
Abstract	2
Table of contents	3
List of tables and figures	4
Introduction	5
Analytical Methods	8
Presentation of Data	10
Discussion	12
Future Work	15
Conclusions	15
Acknowledgements	15
Bibliography	19

List of Figures and Tables

Figure 1	Paleogeography of North America during middle Devonian	6
Figure 2	Tectonic model of the creation of the Appalachian foreland basin during two separate mountain building events of the Acadian orogeny (Werne 2002).	7
Figure 3	The Devonian Marcellus Fm. The sample area in Kistler, PA is marked.	8
Figure 4	Stratigraphic section of Middle Devonian with age constraints (ver Straeten 2004).	8
Figure 5	Outcrop of the Marcellus showing a typical carbonate concretion (Engelder 2004)	9
Table 1	Elemental and isotopic abundances of standards used in geochemical analysis	9
Figure 6	Stratigraphic column of the Marcellus Fm. with plots of TOC, $\delta^{13}\text{C}$, %S, $\delta^{34}\text{S}$, %N, and $\delta^{15}\text{N}$. Red data points represent samples that were analyzed with carbonate present.	11
Figure 7	Stratigraphic column showing sedimentary response to mountain building and eustatic sea level rise in Appalachian basin (Werne 2002).	13
Figure 8	Van Krevelen diagram used to classify organic matter by kerogen type.	13
Figure 9	C/S plot showing Marcellus values in blue and a normal oxic environment in red.	14
Appendix 1	Spreadsheet of geochemical data	19

Introduction

Many studies have been conducted on the Marcellus Fm., most of which focused on interpretation of the depositional environment and the conditions which led to the formation of organic rich shale (Maynard 1980, Leventhal 1987, Dennison 1994, Werne et al. 2002, Rimmer 2003, Sageman et al. 2003, Rimmer et al. 2004). As a result of these and similar studies a consensus has emerged that the formation of organic carbon rich facies is controlled by three factors, primary photosynthetic production, bacterial decomposition, and bulk sedimentation rate (Sageman et al. 2003). The relative importance of each process however, is still under debate. This study utilized geochemical analysis to interpret depositional environment, and used that data to infer how changes in depositional environment affect the formation of natural gas source rock.

Analyses of C, N, and S elemental and isotopic abundances provide evidence about changes in the depositional environment of the Marcellus Fm. Specifically, the type and amount of organic matter deposited, the rate of clastic sediment input, and the oxygenation of bottom waters. TOC and $\delta^{13}\text{C}$ values represent the amount of organic material present in a rock and the whether it was derived from marine or terrestrial plant sources (Maynard 1980). TOC is generally above 0.5% to produce hydrocarbons and the organic matter is most productive of natural gas when derived from terrestrial plants (Maynard 1980). Marine organic matter can also produce natural gas but in lesser quantities. $\delta^{34}\text{S}$ is analyzed to determine the rate of clastic sediment supply. This can be used because of the effect sedimentation rate has on sulfate reducing bacteria (Hailer 1982). With an increased rate of clastic sedimentation bottom water is covered and bacteria cannot fractionate light sulfur from the water column (Maynard 1980, Hailer 1982). Low clastic sediment supply leaves sulfate reducing bacteria exposed to the water column and depleted sulfur is deposited in the sediment (Maynard 1980, Hailer 1982). Oxygenation of bottom water is estimated with a C-S plot. Weight percent S is plotted against TOC with a linear regression line (Leventhal 1987). A normal oxic environment will show a regression line through the origin while an anoxic environment produces a regression line that intersects with the S axis (Leventhal 1987).

Before considering where in the Marcellus to look for natural gas the thermal maturity must be determined. If source rock is present but has not reached the required temperature and pressure no gas will be produced. Thermal maturity is calculated in a number of ways, but most commonly from vitrinite reflectance (Ro%), which represents the degree to which white light reflects off of polished vitrinite (Gurba 2000). Vitrinite is an organic compound that makes up a large percentage of kerogen, the organic matter from which oil and gas are produced (Rooney 1995). As temperature increases, the chemical composition of vitrinite changes and it becomes more reflective (Gurba 2000). Thus reflectivity of vitrinite can be used to determine the maximum temperature a rock experienced. Since oil and gas are produced at different temperatures Ro% is used to estimate what has been produced from a certain rock. Ro% values from 0 to 0.6 represent rocks that are thermally immature and have remained below 60° C (Gurba 2000). Ro% values from 0.6 to 1.4 represent the oil window and have reached temperatures between 60° and 120° C (Gurba 2000). At these temperatures kerogen produces crude oil in a process known as catagenesis. As the organic matter is further heated it reaches the gas window, where crude oil production stops and natural gas

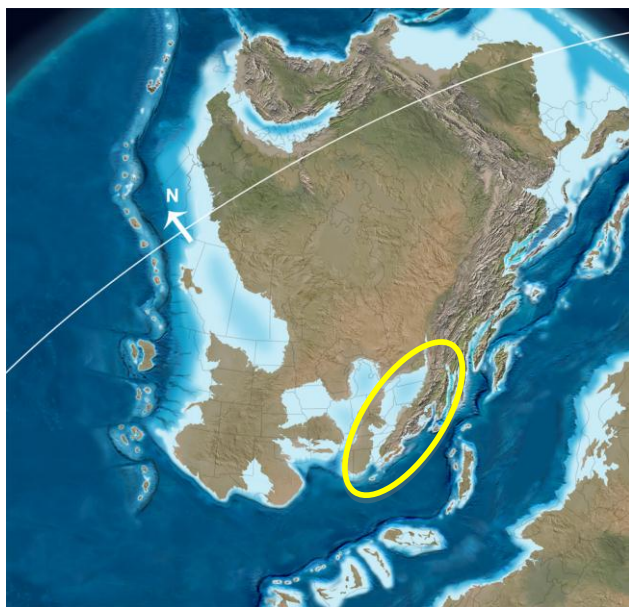
production begins. The gas window represents Ro% values from 1.4 to 3.0 and temperatures from 120° to 150° C. After 150 degrees C the organic matter no longer produces hydrocarbons (Gurba 2000). Several workers have studied the thermal history of the Marcellus Fm. and determined it is currently in the gas window. Vitrinite reflectance measurements throughout the formation range from 1.5 to 3.0% (Milici 2006, Rowan 2006). Therefore horizons that have source rock will produce natural gas.

I hypothesize that time series trends within the Marcellus will reveal peaks in TOC near the base of the formation that correspond with enrichment of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and depletion of $\delta^{34}\text{S}$.

Geologic Background

The Devonian Period

The Devonian period (~418 Ma to ~360 Ma) was characterized by major changes in Earth's biosphere, climate, and continental organization. Changes to the biosphere included the first appearance of insects, amphibians, and ammonoids, as well as the radiation of fish (Stanley 2009). Land plants flourished with adaptations such as vascular tissue and seeds for reproduction (Meyer-Berthaud 1999; Algeo 1995). These plants thrived around marshes and swamps, providing some of the first terrestrial organic matter for the production of hydrocarbons (Meyer-Berthaud 1999). However as land plants spread, they made a significant impact on Earth's climate (Stanley 2009). Plant life accelerated weathering of rocks and soil, which consumed atmospheric CO_2 . As plants spread across land they greatly reduced the concentration of atmospheric CO_2 , weakened the greenhouse effect, and lowered global temperatures (Algeo 1995). The end of the Devonian was marked by a significant extinction event, most likely due to the spread of land plants (Algeo 1995, Stanley 1999). Most of the continental land mass was located south of the Equator during the Devonian period (Stanley 1999). During the Acadian orogeny Baltica and the microcontinent Avalonia collided with Laurentia creating the supercontinent Euramerica (Stanley 1999). Eastern portions of North America including the Appalachian basin were located 15-30 degrees south latitude (Werne 2002).



The Appalachian Basin

The Appalachian Basin covers approximately 536,000 km^2 extending from southern Quebec to northern Alabama. Major development of the basin began in the Ordovician period approximately 472 Ma with the start of the Taconic orogeny (Faill 1997; Stanley 2009). Numerous islands located between Laurentia and Gondwana collided with the eastern coast of Laurentia, creating the foreland basin. Local deposition changed from coastal carbonates to deep water black shales and turbidites, reflecting the transgressive

Fig. 1. Paleogeography of North America during the middle Devonian, 380 Ma. The Appalachian basin is circled (Blakey, R. 2002).

sedimentary response to nearby mountain building (Ettensohn 1987). Near the end of the Ordovician sediment supply from the newly formed mountains filled in the basin faster than it subsided. Deep water shales gave way to coarse shallow marine clastics which appear today as the Juniata and Tuscarora formations of the central Appalachians (Faill 1997). At the conclusion of the Taconic orogeny the Appalachian basin had migrated westward, and coarse grained clastic sediments were deposited near present day Ohio (Faill 1997).

The next stage in the development of the Appalachian basin began in the mid Silurian period (~430 Ma) with the onset of the Acadian orogeny (Faill 1997; Stanley 2009). Two landmasses collided with the Eastern margin of Laurentia, Baltica in the north and Avalonia in the south (Faill 1997). By now the mountains that formed during the Taconic orogeny had been completely eroded and a passive margin with a large carbonate shelf formed Laurentia's east coast. As with the Taconic orogeny, the Acadian orogeny brought with it a drastic change in deposition within the Appalachian basin (Ettensohn 1987). Mountains rose once again, and the calm carbonate shelf subsided to form a large foreland basin. The first deep water shale deposit of the Acadian orogeny was the Marcellus shale (Fig. 2) (Werne 2002). This was followed by the Catskill clastic wedge, a massive body of molasse deposits that recorded the western migration of sedimentary deposits (Faill 1997).

The construction of the Appalachian basin concluded with the Alleghanian orogeny during the Carboniferous period (~330 Ma). This collision between Euramerica (Laurentia, Baltica, and Avalonia) and Gondwanaland created the modern Appalachian fold and thrust belt known as the Valley and Ridge Province. It caused an influx of clastic sediments into the Appalachian basin which hosts coal deposits such as the Pottsville Formation (Faill 1997).

The Marcellus Formation

The Marcellus Formation is a sedimentary rock unit located in the Appalachian Basin of the eastern United States. It covers an area stretching southwest from New York to West Virginia, and from eastern Ohio to eastern Pennsylvania (Fig. 3). It is composed predominantly of black shale, a rock that forms by the deposition of fine grained silts, clay sized particles, and marine organisms in calm deep oceanic environments. The shale's black color is a result of the high concentration of preserved organic matter. The

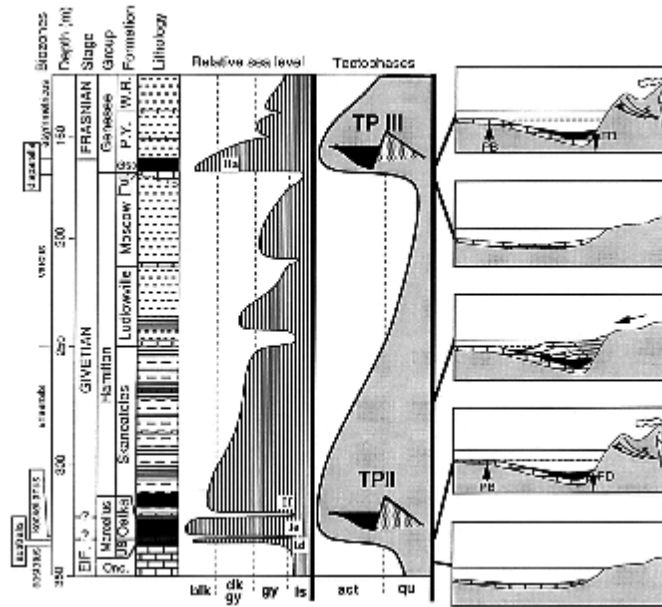


Fig. 2. Tectonic model of the creation of the Appalachian foreland basin during two separate mountain building events of the Acadian orogeny (Werne 2002).

Marcellus Fm. was deposited over 380 Ma ago in the Devonian Period when eastern North America was located south of the equator (Fig. 1) (Werne et al. 2002). Sediments



Fig. 3. The Devonian Marcellus Fm. The sample area in Kistler, PA is marked.

accumulated in a continental deep-water basin forming the western border of the Acadian Mountains, a mountain chain that would later become part of the modern Appalachians. Thickness of the Marcellus Formation varies depending on where the sediments were deposited within the marine basin. The greatest thickness occurs in eastern Pennsylvania where it reaches 240 m. The formation thins westward toward Ohio where it is only 1-2 m thick (Denison 1994). As sea levels fluctuated throughout the Devonian several lithologic units were deposited including siltstone, mudstone, and limestone. These facies changes represent periods of increasing siliciclastic content of sediments

characteristic of regressive depositional packages (Sageman 2003). In the area of this study the Marcellus overlies the Onondaga limestone, and is overlain by the Mahantango Fm., a siltstone.

Analytical Methods

To analyze the Marcellus Fm. for natural gas production potential I first collected hand samples from an outcrop located in Kistler, PA (Fig. 3, Fig. 4). This location was chosen because it is the most complete stratigraphic section exposed in the region. The outcrop covers a lateral distance of 635 m, so I measured the dip angle of bedding three times every 210 m. Dip values were 8° SW at the base, 10° SW near the middle, and 12° SW at the top. I assumed a constant dip of 10° to calculate a vertical thickness of 112 ± 22.5 m. I chose a vertical sample interval of 2 m, which meant one sample at the same height every 11.5 m laterally. I also sampled the overlying Mahantango Fm, a coarse grained sandstone, the underlying Onondaga limestone, and three intervals with carbonate concretion layers within the Marcellus at depths of $29 \text{ m} \pm 5.8$, $53.0 \text{ m} \pm 10.6$, and 56.3 ± 11.3 below the top (Fig 5).

Sample preparation and analysis took place at the University of Maryland in the Isotope Geochemistry Laboratory. Each sample was first washed to remove surface

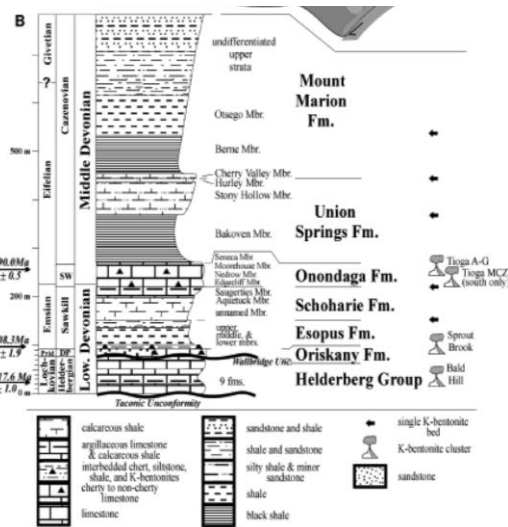


Fig. 4. Stratigraphic section of Middle Devonian with age constraints (ver Straeten 2004).



Fig. 5. Outcrop of the Marcellus showing a typical carbonate concretion (Engelder 2004)

contamination then crushed into a fine powder using an alumina mortar and pestle. 25% HCl was dropped on a number of samples that did not react, and it was assumed that all samples contained no carbonate. Samples for TOC and $\delta^{13}\text{C}$ analysis were measured by adding 0.25-1.0 mg aliquots into tin cups. Total sulfur and $\delta^{34}\text{S}$ were measured in 0.5-2.0 mg aliquots combined with 1.0-2.0 mg of vanadium pentoxide (V_2O_5). Total nitrogen and $\delta^{15}\text{N}$ were measured in 8.0 mg aliquots. C and N analyses were compared with 0.08-0.1 mg aliquots of NIST standard Urea. S analyses were compared with 0.1 mg aliquots of NIST standard NBS-127 (BaSO_4). The samples

were analyzed in duplicate using a Eurovector elemental analyzer (EA) and GV Instruments gas source mass spectrometer.

Before running an analytical session both machines have to be tuned and calibrated. First, the optimal position of the ion beam in the mass spectrometer must be determined. This is done by introducing a beam of reference gas, followed by increasing the voltage across the source to get an optimum signal. This optimum signal will show where the beam needs to be placed for the most accurate results. A pressure test must then be run to make sure there are no leaks in the system. Pressure on the EA must be adjusted every day to account for small changes in tank pressure, room temperature, and humidity. The most important test to run is the stability test. This test determines how consistent the flow rate of gas is, if the reference gas box is working correctly, and if the Faraday collectors are working correctly. If this stability test is passed the machine is

Standard	Weight %	Isotopic Abundance (‰)
NBS-127 (Barium Sulfate)	S – 13.47	$\delta^{34}\text{S} +21.1$
Urea	C – 20	$\delta^{13}\text{C} -29.39$
	N – 47	$\delta^{15}\text{N} +1.18$
NBS-19 (Limestone)	C – 12	$\delta^{13}\text{C} +1.95$
	O – 48	$\delta^{18}\text{O} -2.2$

Table 1. Elemental and isotopic abundances of standards used in geochemical analysis

ready to go. For each analytical session five to six standards were placed in the loading carousel first, followed by ten samples and two standards. For the rest of the session ten samples were loaded followed by two standards. Once the analysis was completed the data was reviewed and corrected. The process of correcting the data is described in the

uncertainty discussion. Invalid analyses were discarded and re-run. This happened for several reasons including machine malfunction and too much or too little element to be analyzed in the sample.

Presentation of Data

TOC content of the Marcellus Fm. ranges from $1.0\% \pm 1.3$ to $8.9\% \pm 0.64$ (Fig. 6, Appendix 1). Values in the upper 50 m of the formation are scattered and range from $1.3\% \pm 2.0$ to $3.42\% \pm 1.33$. TOC follows an increasing trend from $1.55\% \pm 1.33$ at 50 m below the top of the formation to $8.9\% \pm 1.2$ at 4 m above the base of the formation. $\delta^{13}\text{C}$ values for the Marcellus Fm. show an 11 per mil variation from $-20.0\text{‰} \pm 0.14$ near the top to $-32.0\text{‰} \pm 0.14$ near the base. Values are generally scattered throughout the upper 40 m of the formation with no general trend, but then show a steadily depleting through the base.

Total sulfur within the Marcellus varies from $0.66\% \pm 2.9$ to $4.9\% \pm 0.73$, and follows a steadily increasing trend down-section. $\delta^{34}\text{S}$ remains scattered through most of the formation with values between $-9.6\text{‰} \pm 0.12$ and $-30.0\text{‰} \pm 0.18$. $\delta^{34}\text{S}$ values just above the base are generally more depleted than the rest of the formation.

Nitrogen composition is consistently low in the samples analyzed, but show a general increase with increasing depth. Values range from $0.16\% \pm 4.4$ to $0.43\% \pm 4.4$. $\delta^{15}\text{N}$ values show a general enrichment as depth increases from $-2.5\text{‰} \pm 0.14$ at 42 m below the top to $0.11\text{‰} \pm 0.14$ at 14 m above the base.

Uncertainty Analysis

In this study there were three sources of uncertainty, calculation of the stratigraphic height of the Marcellus Fm., measurements of geochemical data, and assumptions about the presence of carbonate in the samples. The first source of uncertainty was my assumption when I calculated the stratigraphic height of the Marcellus Fm. I measured the dip angle in three locations along the outcrop and got three different values, 8° at the base, 10° in the middle, and 12° at the top. With limited time in the field I assumed a constant dip of 10° to calculate a stratigraphic height of 112 m. Using the other measured dip values I calculated the maximum possible height at 135 m and the minimum possible height at 90 m. This gives an uncertainty of ± 22.5 m, or ± 0.2 per meter.

The second source of uncertainty was the measurement of geochemical data by the elemental analyzer and mass spectrometer. Uncertainty in each analytical session was calculated by running the samples against a suite of standards for which the weight percent and isotopic abundance values were known. Once the raw data was collected it was corrected based on the standard analyses. This process differs slightly depending on the element analyzed. Weight percent of C and N, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ were measured against NIST standard Urea (Table 1). First, the average and standard deviation of weight percent and isotope abundance were calculated using all of the standard analyses. The average isotopic abundance of the standard analyses was then subtracted from the known value of the standard, which gave the offset correction factor for the isotopic abundance. This number was added to each raw isotopic abundance to give the corrected value. Next the known weight percent of the standard was divided by the average weight percent

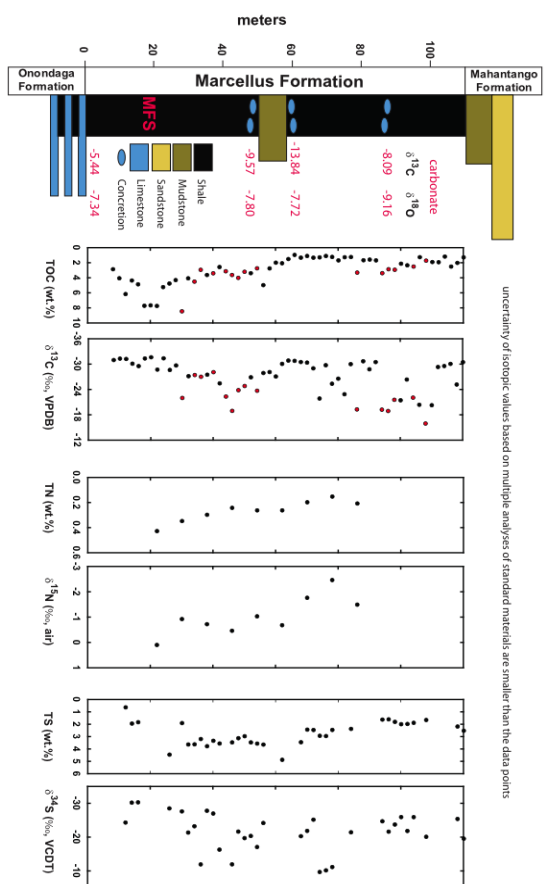


Fig. 6. Stratigraphic column of the Marcellus Fm. with plots of TOC, $\delta^{13}\text{C}$, %S, $\delta^{34}\text{S}$, %N, and $\delta^{15}\text{N}$. Red data points represent samples that were analyzed with carbonate present.

from the standard analyses. The raw weight percent from each sample was multiplied by this number to give the corrected weight percent. The 1- σ uncertainty of weight percent and isotopic abundance for each sample is the standard deviation of the weight percent and isotopic abundance of the standard analyses. The use of Urea for N elemental abundance caused a high uncertainty in the analyses. This is because Urea has a much higher N weight percent than the samples analyzed (Table 1). Weight percent S and $\delta^{34}\text{S}$ were measured against NIST standard NBS-127 (Table 1). Corrected values were calculated by first graphing the raw $\delta^{34}\text{S}$ of each standard versus the sample number. Each sample number was then multiplied by the slope of the linear regression line through the graph. This number was subtracted from the raw $\delta^{34}\text{S}$ of each standard to give the drift corrected $\delta^{34}\text{S}$. The remaining steps are identical to the C and N correction process. The 1- σ uncertainty of weight percent and isotopic abundance for each sample is the standard deviation of the weight percent and corrected $\delta^{34}\text{S}$ of the standard analyses.

The last source of uncertainty was my original assumption about the presence of carbonate in the samples. I first dropped 25% HCl on a group of samples spread evenly through the formation and observed no reaction. Based on these results I assumed that all samples were free of carbonate and bulk powders would provide accurate results. Once all the TOC and $\delta^{13}\text{C}$ data were completed, the five samples directly above the base appeared to have unrealistic values despite no obvious problems with each analysis. TOC was high as expected, but the $\delta^{13}\text{C}$ values were extremely enriched compared with the rest of the formation reaching $-9.8\text{‰} \pm 0.28$. The presence of carbonate in the samples could produce this result, and because none of these samples were tested with acid that was likely the cause. Each powder was tested and reacted immediately, so they had to be acidified and re-analyzed to obtain valid data. Because of the presence of carbonate in these samples, the other enriched $\delta^{13}\text{C}$ values became uncertain. The other 52 samples were then tested for the presence of carbonate, 15 of which reacted. The carbonate present in these 15 sample made their TOC and $\delta^{13}\text{C}$ values unreliable.

Discussion

The first step in estimating the horizons within the Marcellus Fm. that contain the best natural gas source rock is to locate stratigraphically where these changes occurred. The next step is to determine what effect these changes had on the formation of natural gas source rock. Horizons with the greatest number of depositional characteristics conducive to the formation of natural gas source rock should be the most productive.

The amount of organic matter in a sample is given by its elemental abundance of organic carbon. TOC values are at their lowest in the upper half of the formation, but in the lower half follow a steady increase until just above the base. This shows that the percentage of organic matter was greatest in the early sedimentary response to mountain building during the Acadian orogeny (Fig. 2). A combination of eustatic sea level rise and basin subsidence due to the deformational loading on the eastern coast of Laurentia is likely responsible for the transgressive stratigraphic sequence visible in cross section (Ettensohn 1987, Werne 2002, Fig. 7). The horizon between the base and 14 m above it with the highest TOC is a likely candidate for the presence of natural gas source rocks.

TOC is one of the most important factors in determining a formation's natural gas production capability (Rooney 1995).

The isotopic abundance of carbon represents the source of the organic matter. $\delta^{13}\text{C}$ values are scattered in the upper 50 m of the Marcellus, fluctuating between $-20.0 \pm 0.14 \text{ ‰}$ and $-31 \pm 0.06 \text{ ‰}$. In the lower 60 m there is a gradual enrichment from $-31 \pm 0.06 \text{ ‰}$ to $-25 \pm 0.14 \text{ ‰}$ followed immediately by a gradual depletion back down to $-32 \pm 0.28 \text{ ‰}$. Terrestrial organic matter has a carbon isotopic signature around -20.0 ‰ compared with marine organic matter around -30.0 ‰ (Maynard 1980, Calvert et al 1996). During the Devonian, atmospheric pCO_2 was ten times higher than modern values which led to a higher surface water PCO_2 and a higher fractionation of carbon isotopes (Calvert et al. 1996).

The scattered values at the top of the formation may then represent variations between plant and marine organic matter as the dominant source. The trend toward heavier $\delta^{13}\text{C}$

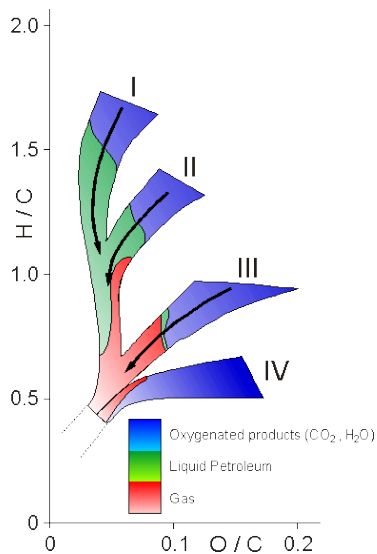


Fig. 8. Van Krevelen diagram used to classify organic matter by kerogen type (Van Gijssel 1982).

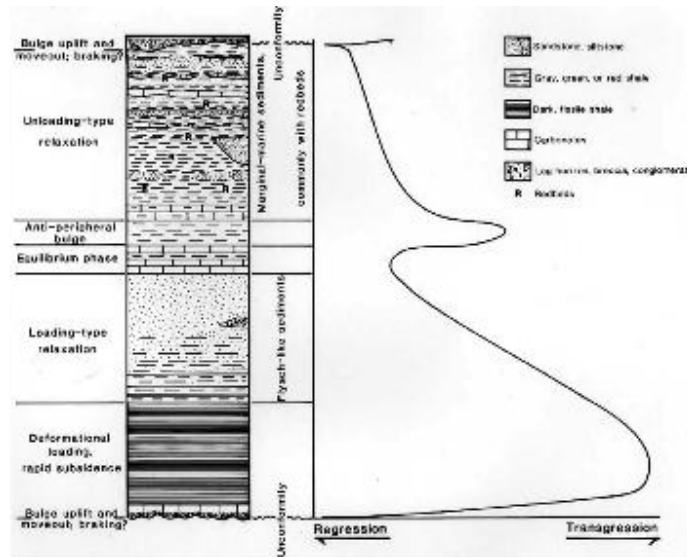


Fig. 7. Stratigraphic column showing sedimentary response to mountain building and eustatic sea level rise in Appalachian basin (Werne 2002).

at the base of the formation may represent more terrestrial organic matter, while the opposite trend immediately following may represent more marine organic matter. The dominant type of organic matter within a shale unit determines what type of hydrocarbons can be produced. A van Krevelen diagram (Fig. 8) is used to classify organic matter as one of four types of kerogen. Of the four different types of kerogen only Type II and Type III produce natural gas, and Type III kerogen produces a greater quantity of gas than Type II (Rooney et al. 1995, Calvert et al. 1996). Type II kerogen is produced from plankton and marine bacteria, and Type III kerogen is produced from terrestrial plants (Rooney et al. 1995, Calvert et al. 1996). Therefore a horizon within the Marcellus dominated by terrestrial organic matter should yield source rocks with the most natural gas. At 10 m, 14 m, and 20 m below the top of the Marcellus $\delta^{13}\text{C}$ values are near -20 ‰ and may represent predominantly terrestrial organic matter. However this does not mean that only horizons

dominated by terrestrial organic matter should be pursued for natural gas. Type II kerogen also produces gas, and although the quantity is less than Type III kerogen, it can still produce a viable reserve (Milici 2006). $\delta^{13}\text{C}$ values near the base are the most depleted in the formation, and likely represent the greatest concentration of marine organic matter.

Bottom water oxygenation and clastic sediment supply are two factors that affect the preservation of deposited organic matter. Oxygenation of the overlying bottom water is determined from a plot of weight percent S against TOC (Fig. 9). A linear regression line in the C/S plot intercepts the origin for normal oxic environments, and intercepts the sulfur axis in anoxic environments (Leventhal 1987). The reason for this relationship is sulfate reduction and organic matter catabolism by sulfate reducing bacteria in the sediment (Leventhal 1987). An intercept at the origin shows that if there is no organic

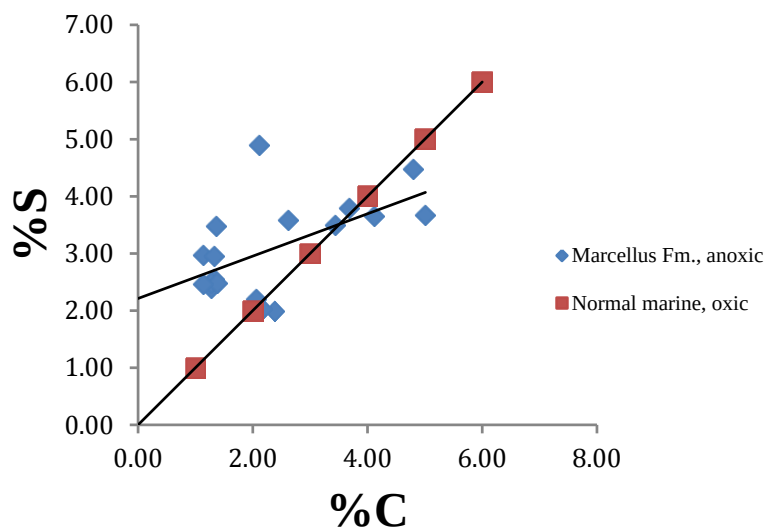


Fig. 9. C/S plot showing Marcellus values in blue and a normal oxic environment in red.

represent sulfate reduction without organic matter, but the extension of higher S/C values that were enhanced in sulfide due to sulfate reduction in the water column and at the sediment water interface (Leventhal 1987). Since the C/S regression line intersects with the S axis the water column was likely anoxic during deposition. This helps to preserve organic matter and increases the probability of source rock formation (Leventhal 1987).

The rate of terrestrial sediment supply affects the concentration of organic matter deposited (Maynard 1980). It has been shown that optimal organic matter preservation takes place in areas with low to moderate terrestrial sediment input (Sageman et al. 2003). $\delta^{34}\text{S}$ values were used to estimate the rate of terrestrial sediment supply. This is because sulfate-reducing bacteria require unlimited access to the marine sulfate pool in order to highly fractionate sulfur. When terrestrial sediment supply is high, access to the sulfate pool is diminished and the heavier ^{34}S is used by bacteria and incorporated into sulfides, enriching $\delta^{34}\text{S}$ (Maynard 1980, Hailer 1982). If the terrestrial sediment supply is high, organic matter concentration will be low, and natural gas production unlikely (Calvert 1996). $\delta^{34}\text{S}$ values in the Marcellus are consistently depleted, but the most

matter the depositional environment is not anoxic, and no sulfate reduction is possible. With increasing amounts of organic matter a constant fraction is metabolizable by microorganisms and H_2S is produced, some of which reacts with iron to form FeS and ultimately pyrite. When the regression line intersects the sulfur axis it does not

depleted values are located about 20 m above the base of the formation. Therefore this horizon may have had the lowest rate of terrestrial sediment input that helped preserve the greatest concentration of organic matter.

Suggestions For Future Work

The high resolution data presented in this study provide a preliminary assessment of where the most productive natural gas horizons are likely to be found. However to better constrain these results additional work is required. First, to determine the exact source of organic matter in a horizon biomarkers must be analyzed. Biomarkers are organic molecules produced by organisms that retain a chemical signature indicative of the parent organism. A biomarker study can distinguish organic matter between different types of plant and marine sources.

Conclusions

A sedimentary response to tectonic activity and eustatic sea level rise is responsible for the deposition of the Marcellus Fm. Geochemical trends down-section indicate a maximum flooding surface 10 m to 14 m above the base. This flooding surface is representative of the highest concentration of organic matter, the lowest rate of clastic sediment delivery, and anoxic bottom water conditions. This interval contains the environment of deposition most conducive to the formation of natural gas source rock. These results are somewhat consistent with my hypothesis. Instead of multiple peaks there was one good peak at the base of the formation. I hypothesized that peaks would correspond with enrichment in $\delta^{13}\text{C}$, however these data were inconsistent with my hypothesis as the peak at the base correspond to the most depleted $\delta^{13}\text{C}$ values. N data that showed enrichment in $\delta^{15}\text{N}$ that corresponded to peak TOC is consistent with my hypothesis. Also $\delta^{34}\text{S}$ values were the most depleted at the peak TOC value are consistent with my hypothesis.

Acknowledgements

I would first like to thank Dr. Jay Kaufman for his support and motivation throughout the duration of this project. I would also like to thank Craig Hebert for his help with the mass spectrometer. Thanks to Natalie Sievers for her help teaching me the unimaginably tedious task of sample preparation.

Appendix 1

sample	depth (m)	%C (TOC)	$\delta^{13}\text{C}$	%S	$\delta^{34}\text{S}$	%N	$\delta^{15}\text{N}$
1	0	1.32	-30.4	2.55	-19.5		
2	2	2.06	-25.1	2.21	-25.3		
3	4	2.55	-30.0				
4	6	1.22	-29.5				
5	8	1.97	-29.3				
6	10	1.95	-20.2				
7	12	1.76	-15.9	1.68	-20.0		
8	14	1.30	-20.3				
9	16	2.55	-22.0	1.91	-25.8		
10	18	2.38	-26.3	2.00	-21.7		
11	20	2.17	-21.4	2.02	-25.9		
12	22	2.97	-21.5	1.83	-23.7		
13	24	2.90	-18.8	1.63	-21.5		
14	26	3.42	-19.2	1.65	-24.6		
15	28	1.72	-30.4				
16	30	1.62	-28.7				
17	32	1.71	-30.6				
18	34	3.35	-19.2			0.21	-1.5
19	36	1.28	-29.9	2.40	-21.4		
20	38	1.31	-22.8				
21	40	1.73	-26.5				
22	42	1.27	-25.3	2.48	-11.1	0.16	-2.5
23	44	1.14	-29.7	2.98	-10.1		
24	46	1.32	-21.8	2.96	-9.59		
25	48	1.37	-28.9	2.49	-25.1		
26	50	1.14	-30.3	2.46	-21.8	0.20	-1.8
27	52	1.36	-30.4	3.48	-20.2		
28	54	1.00	-30.7				
29	56	1.55	-30.8				
30	58	2.11	-30.0	4.90	-1.46	0.27	-0.7
31	60	2.03	-27.0				
32	62	2.79	-28.1				
33	64	5.01	-27.8	3.67	-24.1		
34	66	2.78	-23.6	3.59	-17.0	0.27	-1.0
35	68	3.43	-26.8	3.49	-20.3		
36	70	3.24	-24.8	2.99	-19.6		
37	72	4.05	-23.8	3.15	-21.6		
38	74	3.67	-18.9	3.49	-11.9	0.25	-0.5
39	76	3.17	-22.3				
40	78	2.61	-25.4	3.58	-16.2		
41	80	3.44	-28.0	3.36	-26.9		
42	82	3.67	-27.4	3.80	-27.7	0.30	-0.7
43	84	2.98	-27.0	3.22	-11.9		
44	86	4.55	-27.4	3.65	-23.1		
45	88	4.11	-27.1	3.66	-21.3		
46	90	8.49	-21.9	1.93	-27.5	0.35	-0.9

47	92	4.35	-29.6				
48	94	4.80	-28.6	4.48	-28.4		
49	96	5.27	-31.3				
50	98	7.78	-28.6			0.43	0.1
51	100	7.70	-31.6				
52	102	7.75	-31.3				
53	104	7.09	-29.5	1.86	-30.2		
54	106	6.28	-30.0	1.97	-30.1		
55	108	8.89	-31.2	0.66	-24.2		
56	110	5.88	-31.2				
57	112	4.19	-30.9				

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