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Depositional Environment and Impact on Pore Structure and Gas Storage Potential of Middle Devonian Organic Rich Shale, Northeastern West Virginia, Appalachian Basin

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Abstract

Characterizing the pore structure of a shale-gas reservoir is significant for calculating the original gas in place and fluid-flow characteristics. To better understand the impact of organic matter accumulation, redox condition, and depositional environment on pore structure and storage capacity, integrated geological and petrophysical characterization of the Devonian organic-rich shale was conducted. Core samples from a newly drilled science well from the Marcellus Shale Energy and Environment Laboratory (MSEEL) project and other wells in the Appalachian basin were selected to undertake this research. X-ray fluorescence (XRF), X-ray diffraction (XRD), and pyrolysis were performed to understand variations in composition, mineralogy and total organic carbon (TOC). Samples were examined from an interval including the overlying Tully Limestone, organic-lean Mahantango Shale, organic-rich Marcellus Shale and top of the underlying Onondaga Limestone.

We introduce the application of subcritical N_2 adsorption to measure pore volume, pore-size distribution, and pore-surface area, which are critical properties in characterization of the nano-scale pore regime of mudstone reservoirs. Results of the test are used to build models of the mudstone pore systems. With variations of TOC and mineralogy, changes in the characteristics of pore structure are observed. Middle Devonian shales have complex, heterogeneous pore size distributions as identified by subcritical N_2 adsorption. XRD results suggest a high content of clay minerals (mainly illite) through both Mahantango and Marcellus shales. Hysteresis of N_2 adsorption isotherm indicates slit-shape pores between 2nm and 50nm, possibly formed by clay particles. Organic matter shows strong influence on pore volume and pore surface area (BET specific surface area), which strongly influences storage mechanisms of shale-gas reservoirs. Carbonate-rich intervals show very low pore volume especially micropore (pore width smaller than 2nm) volume, and surface area. The results of N_2 adsorption are compared with NMR log to upgrade the evaluation.

Introduction

Micro- to mesoporous structures of unconventional reservoirs are challenging to characterize because of the extremely small pore sizes. Investigation of the micro- or mesoporous structures and their impact on flow properties requires experimental approaches, and sample preparation that will not affect the physical structure of samples while removing water, hydrocarbon, and other contaminants. To study shale pores more accurately, techniques such as gas adsorption and nuclear magnetic resonance (NMR), have been applied. The low-temperature nitrogen N_2 adsorption method can offer micro-pore volume, meso-pore size distribution, and pore surface area. Understanding the limitations of the analyses is also important, since at the scale of micro- to meso-pores, the measurement techniques influence the result. In this paper, we review some of the sample preparation procedures to find an appropriate and repeatable measurement. The NMR T2 spectra of core samples can be used to calculate porosity and permeability, and characterize pore-throat structures of rock. Significant variations in pore structures can be expected within a formation due to lithologic variations resulting from depositional environment, sediment influx, and preservation.

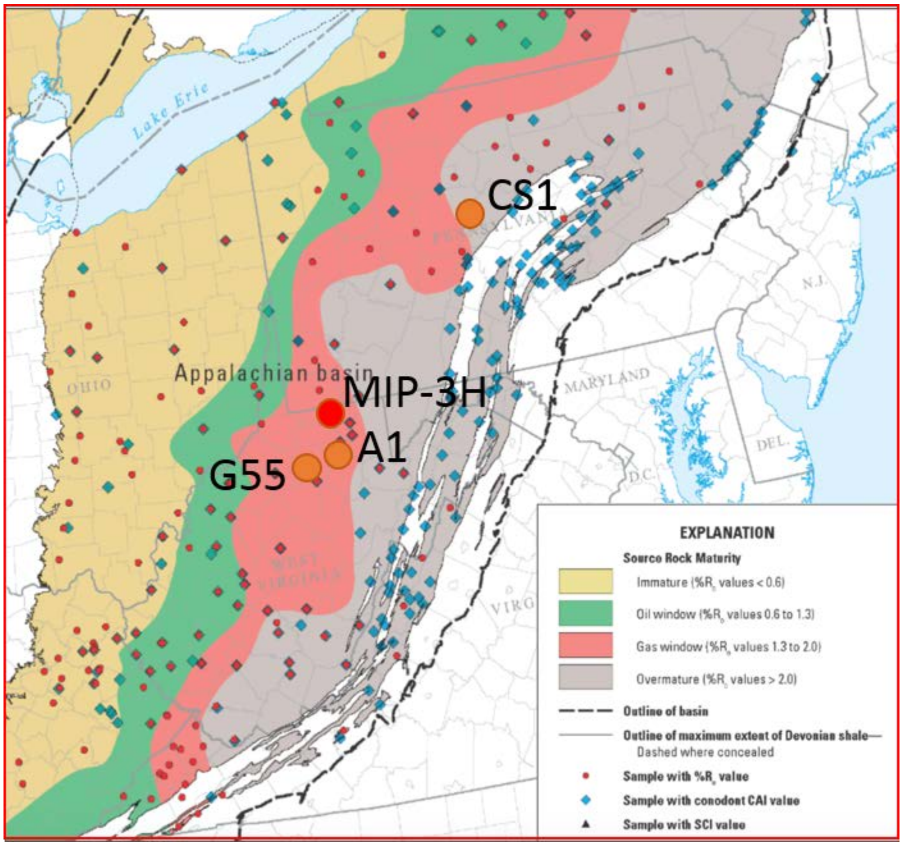

Figure 1: The Map shows the location of wells in West Virginia and Pennsylvania used in this paper, and the thermal maturity trend of the Marcellus Shale (modified after East et al., 2012).

In this research, shale samples were obtained from four wells penetrating Mahantango and Marcellus shale formations in West Virginia and Pennsylvania, covering a wide spectrum of thermal maturity (Figure 1). Total organic carbon content and mineralogy also vary significantly. Core samples from Marcellus Shale Energy and Environment Laboratory (MSEEL) project (MIP-3H well) were selected to run XRD, XRF, TOC and BET analyses and to compare to other wells. These techniques were used to characterize the pore-system characteristics of the Middle Devonian organic-rich shale in Appalachian basin, including the pore type, pore size, surface area, and pore volume. This research will help improves our understanding of the characteristics of the Marcellus and other organic-rich shale reservoirs and could further benefit evaluation of the storage capacity of shale-reservoirs.

Method

Source Rock Analysis (SRA)

Approximately 60 - 100 mg of pulverized rock was accurately weighed into an SRA crucible and placed in the SRA-Agilent autosampler, and held isothermally at 300°C for 3 minutes. 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 ramped at 25°C/minute to 600°C. Between 300°C and 600°C organic hydrocarbons are generated from the pyrolytic degradation of the kerogen in the rock. The hydrocarbons are detected by the FID, labeled as S2, and reported as milligrams (mg) of S2 per gram of rock. Residual carbon is also measured and is recorded as S4 peak. TOC is calculated by using the equation: $\%TOC = 0.1\times[0.082\times(S1 + S2) + S4]$ (Espitalie et al., 1985). WFT Source Rock

Standard 533 (P/N 810-141) was run after every five samples. The standard deviation of the analysis was 0.07%. SRA analysis was performed at the National Energy Technology Laboratory in Morgantown.

X-ray Diffraction Geochemical Analysis

Sixty-two samples collected as side-wall plugs from the MSEEL project were analyzed for x-ray diffraction (XRD) geochemical analysis to determine bulk mineralogy. These samples were ground in a steel grinding container for 5-10 minutes until powdered. Powder samples were pressed into chemplex pellets for loading of samples into the diffractometer. XRD analysis was performed using the PANalytical X'Pert Pro X-ray Diffractometer at West Virginia University Shared Research Facilities. Samples for this project were analyzed at 2θ angles between 5° and 75°, with a step time of ~75 seconds, leading to each sample being ran for approximately 13.5 minutes. X-rays were concentrated through a 20mm brass opening. The raw spectra were interpreted using the X'pert HighScore Plus Program to establish percentage of various mineral phases present. Bulk mineralogical interpretations were semi-quantitatively determined using reference intensity ratios (RIR).

Portable X-ray Fluorescence Geochemical Analysis

X-ray fluorescence (XRF) was performed on the same 62 samples that were prepared for x-ray diffraction analysis. The chemplex pellets were analyzed using a Bruker portable x-ray fluorescence spectrometer Tracer III-SD provided by the Division of Plant and Soil Sciences at West Virginia University. Each sample was analyzed for 120 seconds. Runs were completed to acquire major and trace elemental concentrations reported as weight percent. All runs were calibrated using the Bruker Mudrock calibration.

Low-pressure N_2 adsorption (BET test)

Low-pressure N_2 adsorption were conducted on a Micromeritics ASAP-2020 instrument at -196^{0}C (77K). About 1 gram of shale sample was crushed with mortar and pestle until the whole mass passes through a 60-mesh sieve to prevent potential sample biasing due to sieving. One sample from well CS1 is chosen to run the temperature test. About 5 gram of core sample was crushed and separated to 5 portions. Then samples were outgassed under high-vacuum apparatus at 120^{0}C for 24 hours to remove adsorbed water and volatile matter before analyses with N_2. The relative pressure (P/P0) ranged from 0.009 to 0.990. Both adsorption and desorption data points were acquired. Adsorption branch of the isotherms were used to obtain information about micropores (<2 nm in diameter) and mesopores (2~50 nm in diameter). The classification of pore sizes used in this article follows the classification system of the International Union of Pure and Applied Chemistry. This classification of pore sizes has proven to be very convenient in coal and shale studies (Bustin et al., 2008; Clarkson et al., 2012; Mastalerz et al., 2013).

Specific surface area (SSA) was calculated based on Brunauer-Emmet-Teller (BET) theory Pore volumes, and pore distributions based on Barrett-Joyner-Halenda (BJH) model, t-Plot, H-K model (Brunauer et al., 1938; Barrett et al., 1951; Sing, 2001).

Results and Discussion

1. Selection of degassing conditions

Prior to the BET test, samples need to be degassed. The impact of degassing procedure on the results must be considered before the test, because the interpretation models are based on clean surfaces for the adsorbent. The ultimate goal of degassing is to remove all the water and volatiles (such as remaining hydrocarbons), and other impurities, so that N_2 can reach out to most of pore space of the sample, while avoiding irreversible damage to organic matter, minerals, and sample texture. For this purpose, the nano Darcy range permeability of shale makes it impractical to run this test on intact or large pieces of core sample. Most reservoir properties measurements of mudrocks are performed on crushed core samples, because with crushed powder, the total path length for the gas to access the entire pore structure is significantly shorter than intact core samples, thereby, the test can be finished within reasonable time (Luffel and Guidry, 1992; Kuila and Prasad, 2013).

Adesida et al., 2011 studied the effect of crushing on pore-structure parameters measured by N_2 gas adsorption. The results show that the specific surface area and total specific pore volume measured increases with decreasing sample particle size, which make sense since by crushing the sample to a finer size, extra surface area is created (Adesida et al., 2011). The increased pore volume is related to better pore accessibility at smaller grain sizes. When crushing the core sample, the different mechanical properties of the constituents (organic matter and minerals) of mudrocks are noticed. This difference results in variance tendency to grind. By sieving the crushed sample into different sizes, it may result in a bias in the composition and mineralogy of each separated fraction (Kuila and Prasad, 2013). Therefore, the crushed samples are used for BET test. The crushing procedure will follow Kuila and Prasad (2013) with a different grain size. Samples are crushed until the entire mass passes through a 60-mesh sieve (40 mesh in their research) to prevent potential sample biasing due to sieving. The samples preparation procedure should also be repeatable. After literature review, most research on N_2 adsorption on mudrocks has been conducted on 60 mesh samples (Table 1). Thus the result can be compared with former research, and benefit future study.

Table 1 Sample preparation procedures of former researches

Authors	Year	Gas	T (^{0}C)	Mesh Size	Time (hour)	Sample Location	BET SSA (m^2/g)
Lu et al.	1995	He, CH_4	50~60	18~25	24	Antrim Shale from WV and KY	
Chalmers and Bustin	2006, 2007	N_2, CO_2	105	60	>12	North America coal and shale	0.01~7.9
Chalmers and Bustin	2008	N_2, CO_2	150	60	12	Lower Cretaceous NE British columbia	N_2: 2.5~19.5; CO_2: 16.1~62.9
Ross and Bustin	2009	N_2, CO_2	110	60	24	Jurassic, D-M, North British Columbia	3.4~44.5
Adesida	2011	N_2	100	20~40	3	Barnett	0.06~11.16
Strapoc et al.	2010	N_2, CO_2		60		New Albany Shale (D-M)	4~20
Mastalerz et al.	2012	N_2, CO_2	110	60	14	New Albany Shale (D-M)	N_2: 0.2~2.4; CO_2: 10.9~12.8
Zhang et al.	2012	CH_4	200	100	over night	Green River, Barnett	
Clarkson et al.	2012	N_2, CO_2		4	over night	Triassic Montney, Western Canada	0.62~3.05
Clarkson et al.	2013	N_2, CO_2	60	60	> 4 days	North America	2.3~17.1
Kuila	2013	N_2	200	40	24	Haynesville	22.85~23.11
Heller and Zoback	2014	CO_2	40	100~270		Eagle Ford, Barnett, Marcellus, Montney	
Maria-Fernanda Romero-Sarmiento	2014	N_2	80		6	Mississippian Barnett Shale	14~39

Another import factor for degassing is the temperature. Olson, 2012 summarized degassing temperature for 6 categories of materials (Table 2). Unfortunately, there isn't a category for mudrock. While it still shed some light on the selection of temperature. Amorphous oxides (e.g. silica, alumina) are similar to numerous minerals in mudrock, and a temperature from 100°C to 200°C did not change the pore structure (Olson, 2012). To find the best temperature for this research, one sample was split into 5 portions and degassed under 5 different temperatures. Figure 2 shows the pore size distributions of this sample at these temperatures. The overall trends are the same over all the five tests. However, as temperature increases, we noticed an increase in pore volume. Samples degassing under 80^{0}C and 120^{0}C show almost the same pore size distribution (PSD), which agrees with another research on Barnett Shale (Adesida et al., 2011) and other research studies (Table 1). In the rest of this study, 120^{0}C is used as the degas temperature.

2. Pore size distributions

Isotherms are the direct result from low pressure N_2 adsorption tests. Figure 3 shows the isotherms of the six samples from MIP-3H, all of which are type IV isotherm with H3 or H4 hysteresis loop. This shape of isotherm indicates that the shale samples are micro- to meso-porous materials, and this type of hysteresis loop often is observed with aggregates of plate-like particles forming slit-shaped pores. At high P/P0 section (P/P0 > 0.9), the isotherm shows a steep increase and no limit when P/P0 close to 1. This is attribute to the sample also has macro pores, and the steep increase is representative of macro pore filling (Sing et al., 1982).

Table 2 Summary of outgassing conditions by material type (Olson, 2012)

Material Type	Flow or Vacuum	Temp. (°C)	Duration (hr)
Active pharmaceutical ingredients	Either	40 or ½ melting point	≥ 2
Activated carbon, zeolites, catalysts	Vacuum	90 then 300	1 then ≥ 3
Magnesium Stearate	Vacuum	40	2
Excipients, e.g. starches, celluloses, sugars, polymers	Either	20o < Tg or ½ melting point	≥ 2
Amorphous oxides, e.g. silica, alumina	Either	100 to 200	≥ ½
Metal oxide, e.g. titanium dioxide, zinc oxide, iron oxide, nickel oxide	Flow	300	≥ 2
Ionic salts & crystalline nonmetals	Either	300 or ½ melting point	≥ 2

The pore size distribution of the six samples from MIP-3H are calculated with BJH model (Figure 4). The variation in pore structure are mainly controlled by TOC and mineralogy (Figure 7). Tully Limestone and Onondaga Limestone show significantly less pores compared with the Marcellus Shale within the meso-pore zone (2~50nm), and very few pores below 20 nm. In the Marcellus Shale, the pore structure also varies. The Marcellus top sample has a spike at 7 nm and a bigger pore volume than upper Marcellus sample. The Marcellus top sample also has the highest clay content (Figure 7). Upper and middle Marcellus samples have similar PSD in 20nm to 50nm interval. The lower Marcellus sample, which has the highest TOC content, has the highest pore volume.

3. TOC, pore surface area, and pore volume

The specific surface area (SSA) of the six samples ranges from 1.09 m^2/g to 52.9 m^2/g (Table 3). The BJH pore volume of samples range from 0.003052 cm^3/g to 0.051914 cm^3/g (Table 3). The micro pore volume and surface area are calculated by T-plot. The BET specific surface area and BJH pore volume indicate an overall positive correlation with TOC (Figure 5, 6). MIP-3H, G55 and A1 (listed as $1.36<Ro<1.41$) shows a better correlation compare to CS1 (listed as $2.67<Ro<2.89$). There is a significant decrease in micro- to meso-pores with increasing carbonate content.

4. Mineralogy, lithology, and depositional environment

The MIP-3H well utilizes both common and advanced logging tools to provide insight into TOC and mineralogy at the log-scale (Figure 8). The Marcellus Shale at the MSEEL location is defined by three high gamma ray peaks (greater than 300 API) separated by thin carbonate intervals (lower than 110 API). Linear relations between SRA derived TOC measurements and uranium and gamma ray help to predict the organic content throughout the Marcellus Shale interval. Generally, there is an increase in organic content with depth from about 5 wt.% in the upper Marcellus to 15 wt.% in the most organic portion of the lower Marcellus. This trend is reiterated by an increase in resistivity (figure 8, tract 2 orange), which denotes organic matter and carbonate through this interval.

Mineralogy is determined using the XRD (Figure 7). The abundance of organic matter in volume percentage is calculated from TOC wt.% following Crain's workflow(Crain and Holgate, 2014). Then the XRD results are converted into volume fraction of minerals and organic matter with average mineral density. The average density of organic matter is set to be 1.26 g/cc (Crain and Holgate, 2014). Overall, there is a decrease in the clay content with depth in the Marcellus Shale with an increase in the organic matter. In lower Marcellus, the volume fraction of organic matter is 33% (Figure 7).

The NMR log shows relatively consistent porosity ranging from about 2 to 4% through the Marcellus Shale interval (Figure 8, tract 7). There is, however overall decrease in the T2 distributions, with slower T2 arrivals in the upper Marcellus (3ms and greater) and faster in most organic portion of the Lower Marcellus (<3ms). This trend could be related to a change in pore fluid type or an overall decrease in the pore size distribution.

The XRF data (Figure 8) provide general trends that relate the Marcellus unit to redox environment and the amount of detrital influence using relative quantities of major and trace elements, as well as, how they relate to one another. Descending through the stratigraphy, there is a decrease in detrital delivery which is represented by a decrease in Aluminum. In middle and lower Marcellus, the reduction of Al corresponds with GR log and TOC peaks. The interpreted redox conditions range from dysoxic in the upper Marcellus to anoxic to slightly euxinic in the middle and lower Marcellus. The covariance of Uranium (represent by TOC_URAN) and GR log readings indicate a reducing environment. The decrease of Th/U hinges with the TOC peaks, and the Th/U values remain less than 1 indicating a suboxic to anoxic environment. These are expressed by an overall increase in the concentration of trace elements, specifically in V+Cr trends, which show denitrification (Sageman et al., 2003; Lash and Blood, 2014; Chen et al., 2015; Chen and Sharma, 2017).

Table 3. Low-pressure N_2 adsorption test and TOC results

Depth(ft.)	Formation	BET SSA (m²/g)	Micropore Area (m²/g)	Micropore Volume (cm³/g)	BJH Pore Volume (cm³/g)	TOC wt.%
7201	Tully	1.09	0.1823	0.000078	0.004566	0.36
7452	Marcellus Top	19.43	4.3996	0.001861	0.027743	3.14
7466	Upper Marcellus	20.8849	5.6005	0.002382	0.024733	4.14
7508	Mid Marcellus	42.93	14.7628	0.006300	0.039927	6.48
7544	Lower Marcellus	52.90	10.5677	0.004379	0.051914	8.9
7555	Onondaga	1.74	0.5313	0.00022	0.003052	0.85

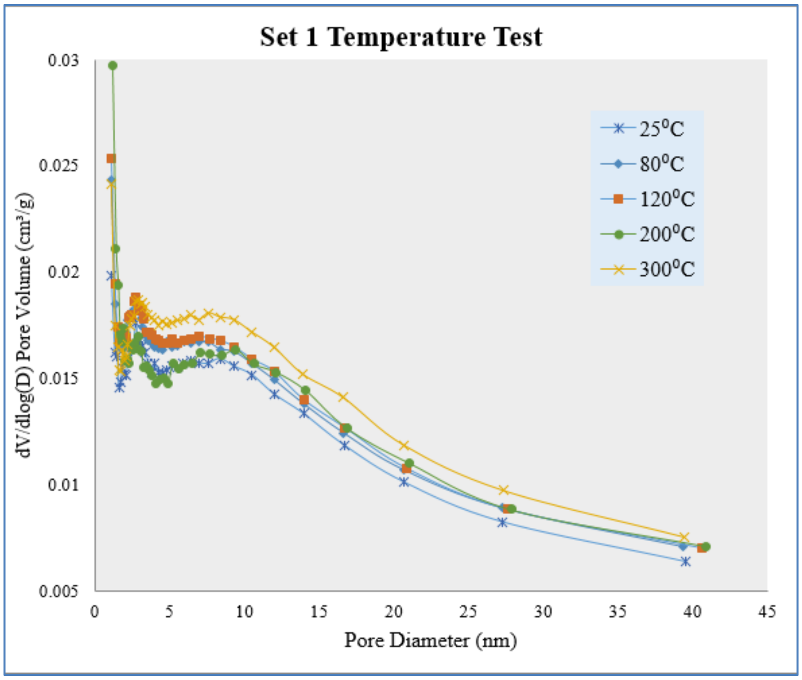

Figure 2. BJH pore-size-distributions of 5 samples degassed using 5 different temperatures.

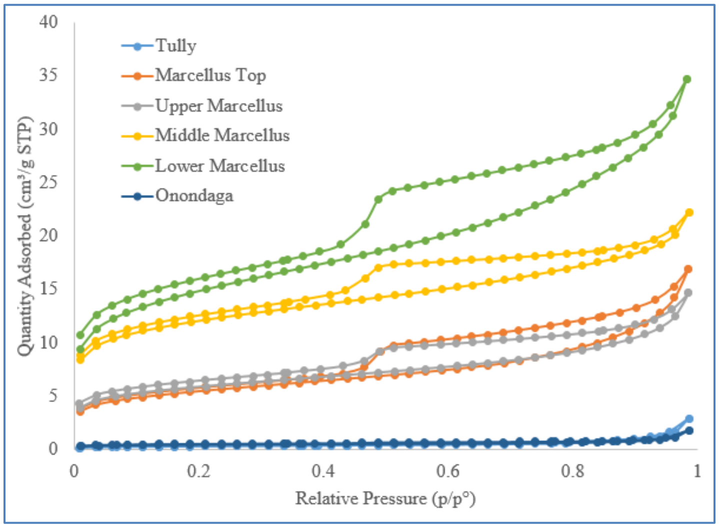

Figure 3. Isotherms of samples from MIP-3H.

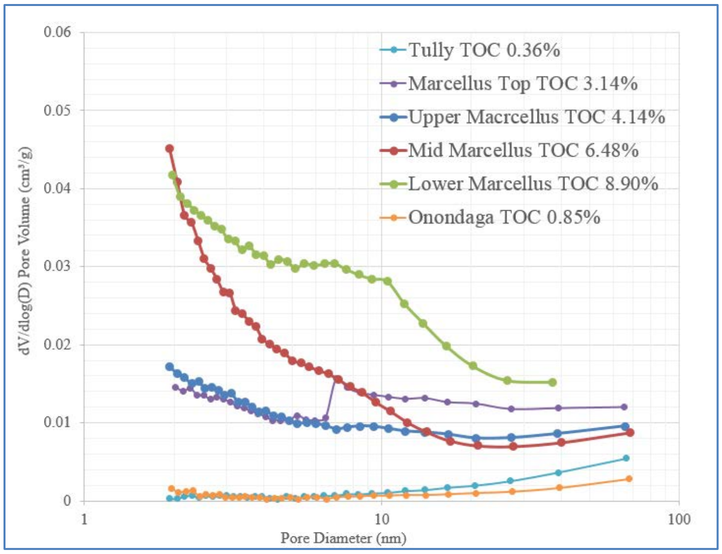

Figure 4: Pore size distribution of the samples across Tully Limestone, Marcellus Shale, and Onondaga Limestone with regard to the TOC weight perentage.

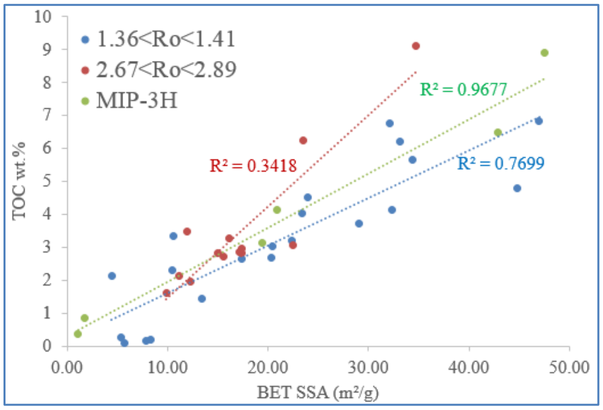

Figure 5: The relationship between BET specific surface area and TOC.

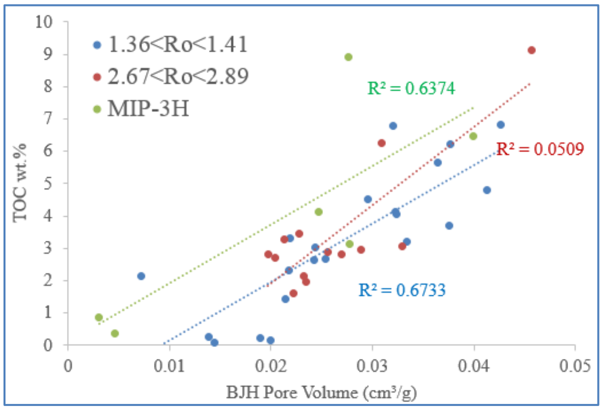

Figure 6: The relationship between BJH pore volume and TOC.

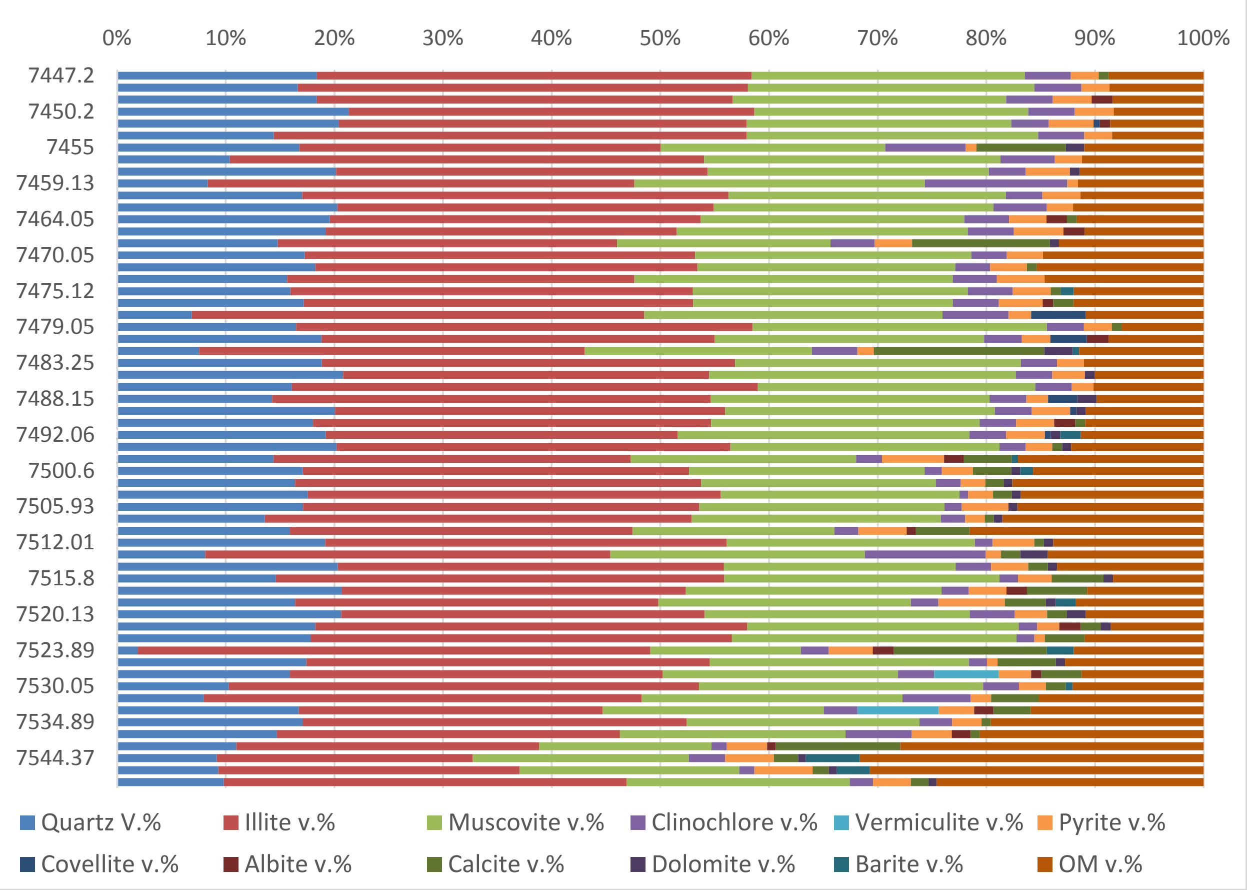

Figure 7: XRD data from well MIP-3H (in volume %) illustrating the mineralogical variations of the Marcellus Shale.

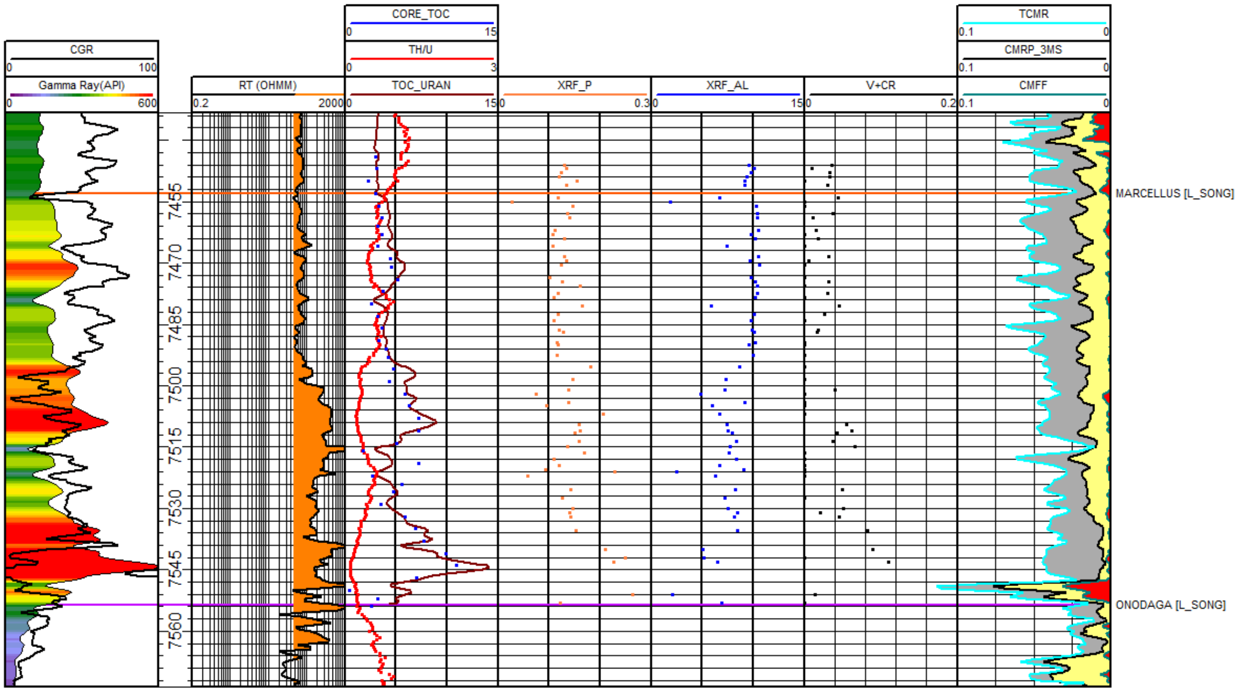

Figure 8. Geochemical and well-log profiles of the MIP-3H core showing abundances of P and Al from XRF test, Th/U from spectral GR, and NMR log.

Conclusions

Characterizing the pore structure of unconventional reservoirs is important for understanding the storage capacity and flow regime. Low pressure N_2 adsorption is a good method to study nano-scale pore structures especially micro- and meso-pores. It can provide pore surface area and pore volume information, which represents adsorbed gas and free gas storage capacity respectively. For accurate analysis, sample preparation is very important. We recommend crushing the sample until the entire mass passes through a 60-mesh sieve to prevent potential sample biasing due to sieving, then degas the sample at 120°C for 24 hours. The results indicate that micro- to meso-pores are concentrated in the organic content. Pore volume and pore surface area both show good positive correlations with TOC. Calibrated XRD results indicate that in lower Marcellus, the volume fraction of organic matter is approximately 30%, which offers great storage capacity especially for adsorbed gas.

Acknowledgement

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