PS Nano-scale Pore Structure of Middle Devonian Organic-Rich Black Shale and its Evolution through Thermal Maturation*

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Abstract

The pore structures and the evolution of porosity were analyzed in samples from three wells that penetrated the Marcellus Shale in Appalachian basin. The thermal maturity ranges from Ro (vitrinite reflectance) 1.36% to Ro 2.89%. Total organic carbon (TOC) of Mahantango Formation to Marcellus Shale samples from West Virginia and Pennsylvania used in this study varies from 0.25 to 9.12 wt.%. Subcritical N2 adsorption and Scanning Electron Microscope (SEM) techniques were utilized to test nano-scale pore structures (pore sizes, pore volumes, and pore-size distributions) qualitatively and quantitatively. Also, X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis were conducted to study the heterogeneity of mineral composition and its influence on the pore structures. Before running N2 adsorption, shale samples were crushed, then degassed under high vacuum with heating. In order to find an appropriate procedure for sample preparation, one set of rock sample was crushed and hand-grounded, then degassed under five different temperatures (25°C, 80°C, 120°C, 200°C, 300°C). Based on the results, size and more critically temperature for degassing are important factors. A size of <250 microns (60 mesh) degassed under 120°C for 24 hours is the recommended procedure. After the measurements, BET, t-Plot, H-K, and BJH models were used to interpret the results. The results, combined with SEM image analysis indicate that, as thermal maturity increases, specific surface areas (SSA), pore volumes, and pore-size distributions varies significantly. Among all the factors we tested, thermal maturity appears to be the major control on evolution of pore structures of organic-rich mudrocks.

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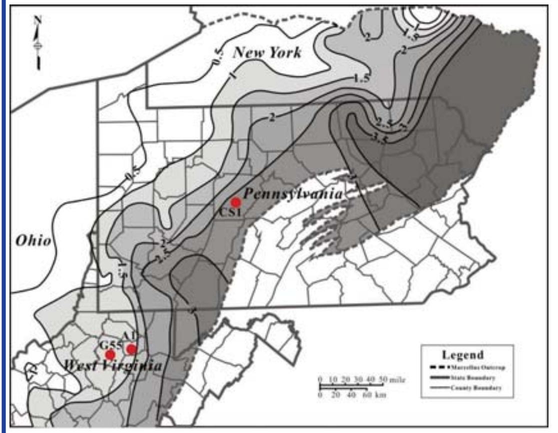
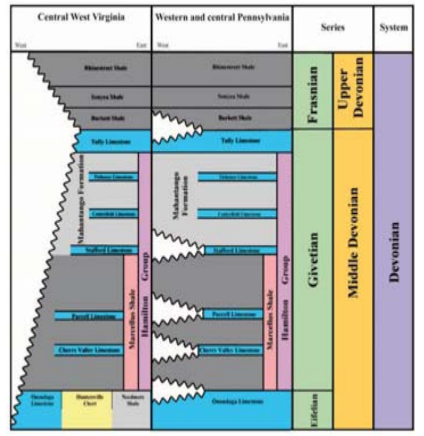
Geological Background and Introduction



Location of the three sampling wells. Contours show thermal maturity by vitrinite reflectance of the Marcellus Shale. (Modified from Zagorski et al., 2012)

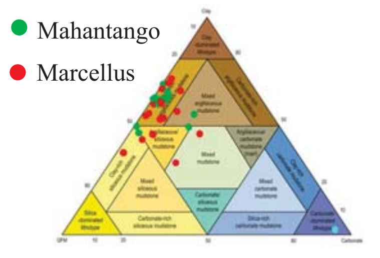


Hamilton Group Stratigraphy in West Virginia and Pennsylvania (modified from Zagorski et al., 2012)

Motivation of research:

- Determining porosity in mudrock reservoir remains challenging because of the extremely small pore sizes and complex pore structures.
- Free gas only makes a part of the whole reserve of mudrock reservoir, the enormous surface area that could adsorb hydrocarbon molecules makes a contribution to the storage capacity as well. A detailed study of pore structure in mudrock reservoir is necessary.

Lithology



Courtesy from Schlumberger

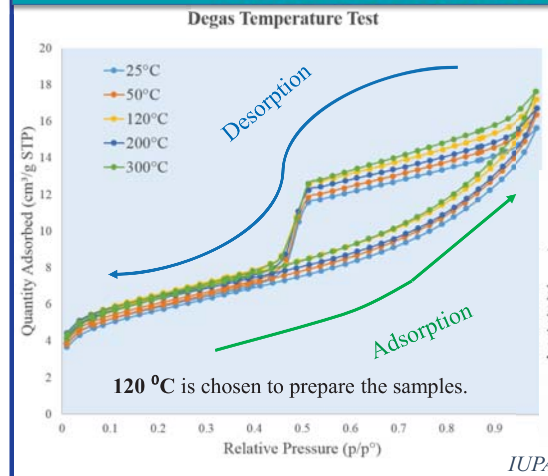
Silica-rich argillaceous mudstone
Argillaceous siliceous mudstone

Dark gray to black shale

Thermal Maturity

Well #	Depth/ft	TOC/wt. %	Ro/%
CS1	7019	1.80	***2.59***
CS1	7070	2.67	***2.67***
CS1	7099.5	7.28	***2.68***
CS1	7128	4.38	***2.79***
CS1	7155.5	8.25	***2.89***
A1	7555	2.10	***1.40***
A1	7605	2.24	***1.38***
A1	7655	1.94	***1.37***
A1	7714	4.34	***1.46***
A1	7752	4.62	***1.40***
A1	7765	5.12	***1.41***
G55	7099	0.65	***1.36***
G55	7149.5	4.28	***1.36***
G55	7200	2.21	***1.39***

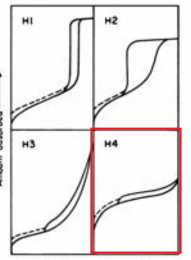
Low Pressure N_2 Adsorption

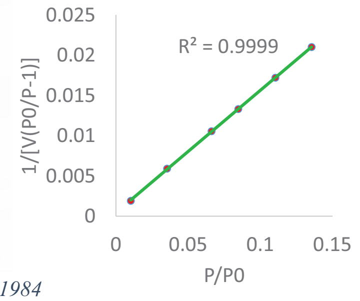


120 °C is chosen to prepare the samples.

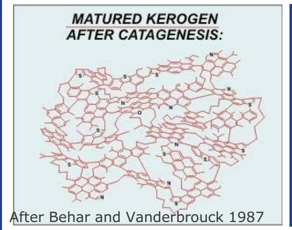
Brunauer–Emmett–Teller (BET) theory

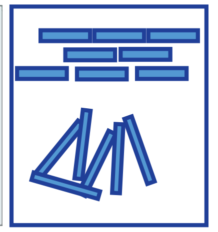
$$\frac{1}{v\left[(p_0/p)-1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c},$$





IUPAC Recommendation 1984

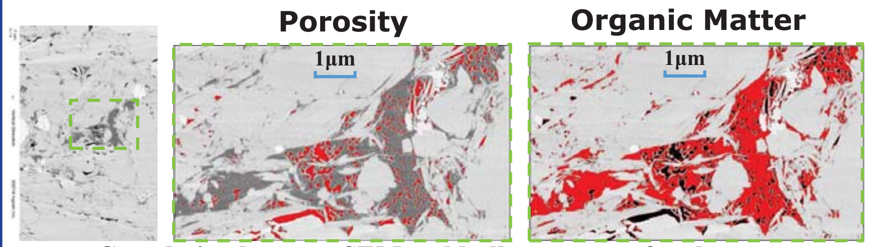




The Type H4 loop, which does not exhibit any limiting adsorption at high p/p0, is observed with aggregates of plate-like particles giving rise to slit-shaped pores, often associated with narrow slit-like pores with microporosity (*IUPAC Recommendation 1984*).

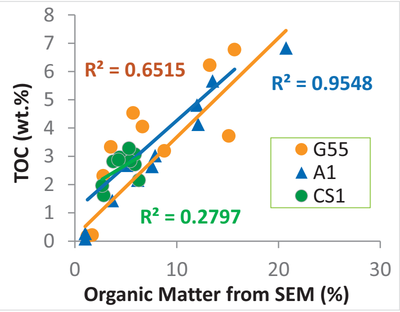
Pore Micro Texture

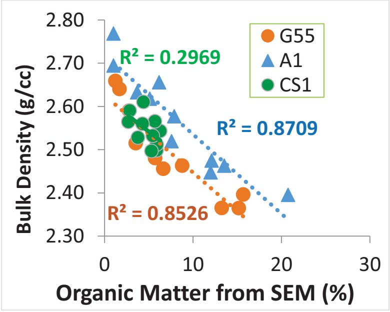
Digitized SEM Analysis



On Scanning Electron Microscope (SEM) images, The gray scale of each pixel depends on the atomic number of the specimen and its density, which hinges the different density of mineral grains (white to light gray) and organic matter (dark gray), and pore space (black).

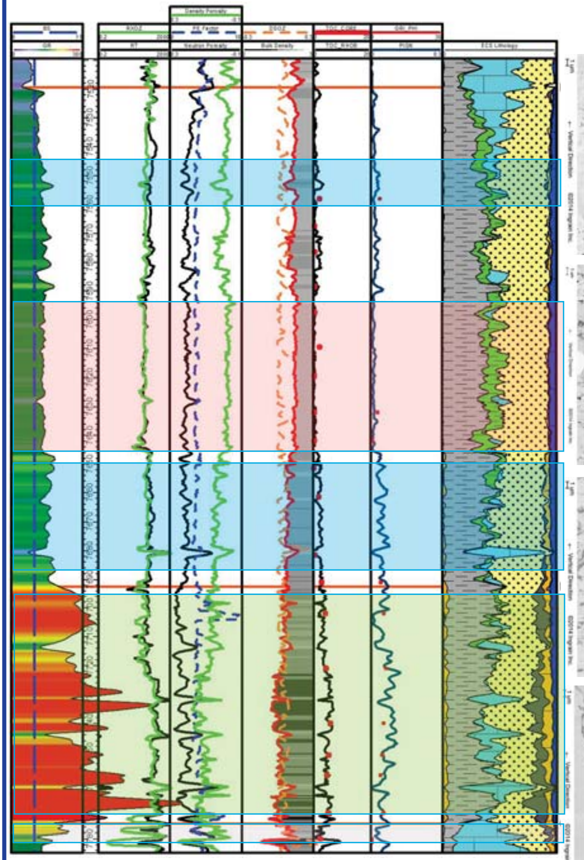
Correlation between SEM and bulk property of rocks





- SEM property can be correlated to bulk petrophysical properties
- Organic Matter derived from SEM has an overall positive correlation with TOC and a negative correlation with bulk density
- Better correlations from well G55 and A1 are noticed

Pore Micro Texture Facies



Clay-rich

	Ø (%)	OM (%)	$Ø_{OM}$(%)	TR	$Ø_{OM}/Ø$
Mean	0.57	1.52	0.06	0.03	0.1053
Max	0.7	2.68	0.23	0.08	0.3286
Min	0.27	1	0.02	0.02	0.0741

Triangular pore space between clay particles, low porosity, low OM

Organic-lean

	Ø (%)	OM (%)	$Ø_{OM}$(%)	TR	$Ø_{OM}/Ø$
Mean	1.1207	5.3394	0.3198	0.06	0.2854
Max	2.7583	8.7827	0.9344	0.1373	0.3388
Min	0.2737	2.7886	0.0853	0.0117	0.3117

Both organic and inorganic porosities, relatively high porosity, medium OM

Organic-rich

	Ø (%)	OM (%)	$Ø_{OM}$(%)	TR	$Ø_{OM}/Ø$
Mean	0.4175	14.637	0.1899	0.0135	0.4549
Max	0.6754	20.736	0.3569	0.0262	0.5284
Min	0.1205	11.981	0.0349	0.0017	0.2896

An average of 45% pore space is in OM, highest OM, lowest TR

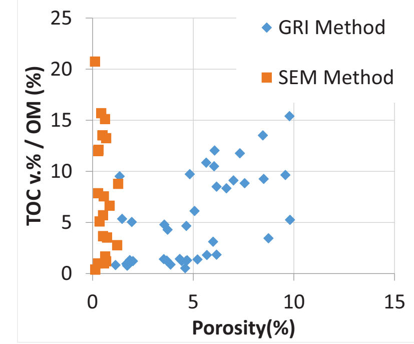
Carbonate-rich

	Ø (%)	OM (%)	$Ø_{OM}$(%)	TR	$Ø_{OM}/Ø$
Mean	0.43	6.16	0.11	0.02	0.2558

Inorganic pores inter-/intra-carbonate minerals

Organic Matter: OM
Transparent Ratio: TR
TR= OMØ/(OMØ+OM)

The pore micro texture facies have been found in all the three studied wells, the vertical distribution of which can be tied back to lithology of each layer.



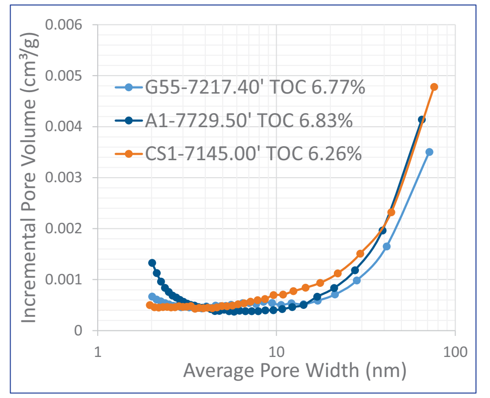
SEM underestimates the porosity

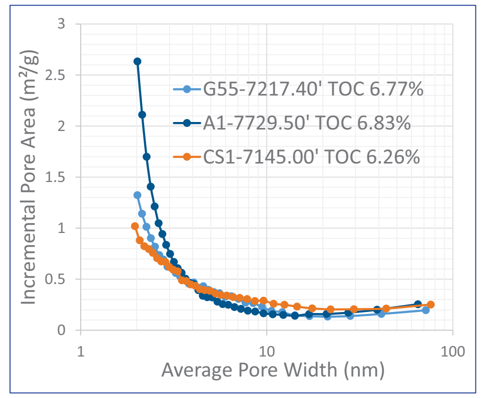
After being normalized to TOC volume percentage or OM, porosity yields from two methodologies show different trends. The porosity value was significantly underestimated by digitized SEM images. Moreover, the positive correlation between porosity and TOC by GRI method cannot be seen at SEM method.
Large amount of pore space within OM may be ignored due to the nanometer scale of OM pores.

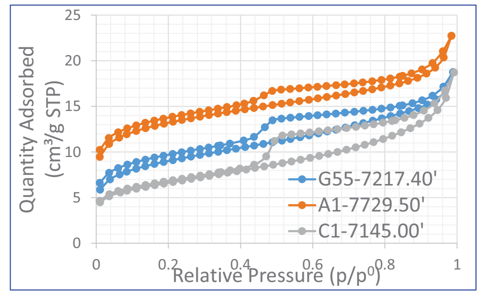
Specific Surface Area and Pore Volume

Pore size distribution, and its contribution to pore volume and surface area

Three samples from the most organic-rich intervals of each well





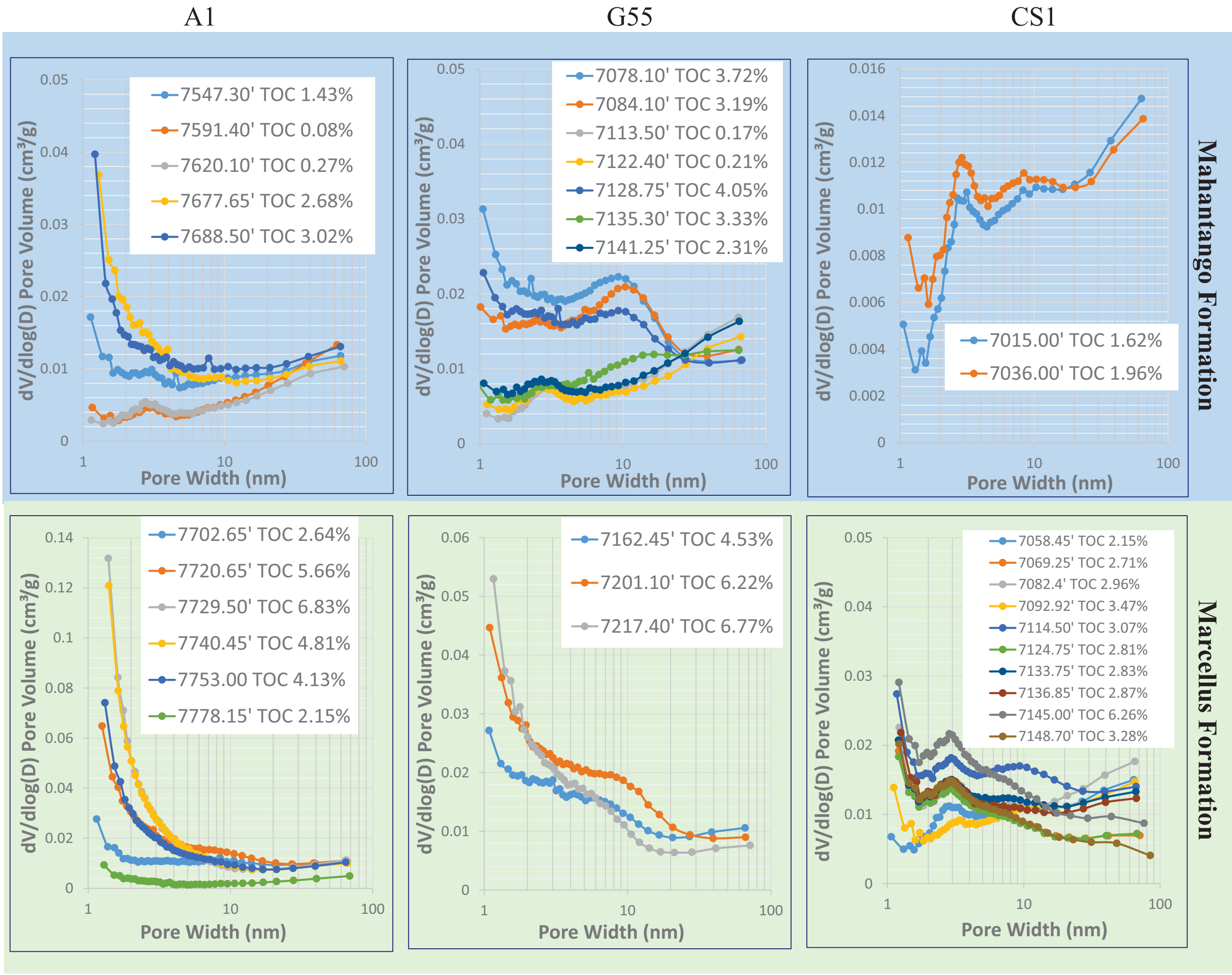


Observations:

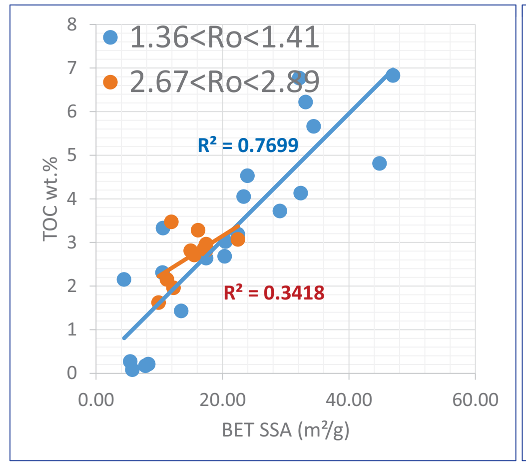
- Specific surface area and pore volume of higher thermal maturity samples are less than that of lower thermal maturity samples;
- Pores of diameters less than 5 nm make the greatest contribution to SSA, whereas pore volumes are affected by larger pores. Sample with higher thermal maturity has less smaller pores (pore diameter less than 5 nm).

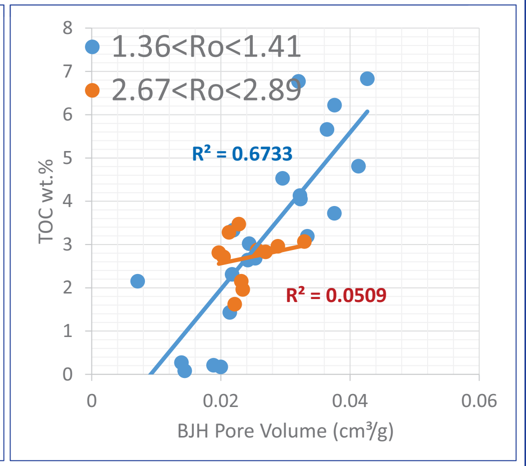
Pore Size Distribution

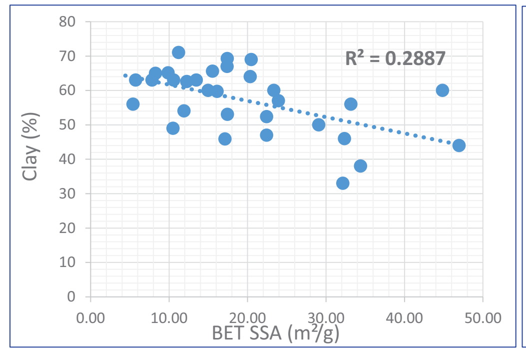
Samples with higher thermal maturity (well CS1) have less smaller pores
Notice the differences of vertical-axe scales

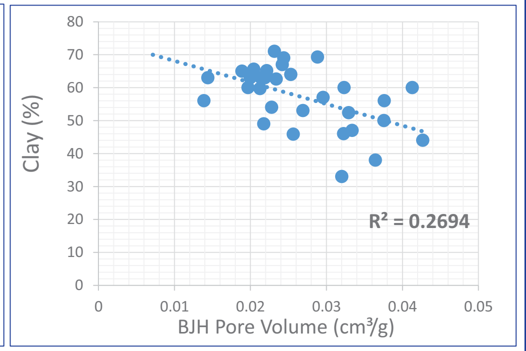


Pore Structure and Storage Capacity









Observations:

- There is a general positive correlation between richness of organic matter and specific surface area and pore volume;
- Samples with a lower thermal maturity showed a better correlation
- Organic matter makes the majority of the micropore (<2nm) and mesopore (2~50nm);
- Clay particles make little contribution to the micro and meso-pore regime.
- As thermal maturity increasing (from Ro 1.36 to 2.89), the volume and SSA of OM pores decrease significantly.

Conclusions

1) Four pore micro texture facies are picked, Organic-rich, Organic-lean, Clay-rich, Carbonate-rich;
2) SEM analysis can be correlated to bulk petrophysical properties of cores;
3) Significant part of the pore system in mudrock is beyond SEM resolution, which is 10 nm in this research;
4) There is a general positive correlation between richness of organic matter and specific surface area and pore volume
5) Organic matter makes the majority of the micropore and mesopore space;
6) As thermal maturity increasing from dry-gas zone to post-mature zone, pore volume and surface area decreases.

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