PS Characterization of the Pore System and its Storage Capacity in Devonian Black Shale of Appalachian Basin*

Liaosha Song[1] and Tim Carr[1]

Search and Discovery Article #42085 (2017)**
Posted May 29, 2017

*Adapted from poster presentation given at 2017 AAPG Annual Convention & Exhibition, Houston, Texas, April 2-5, 2017

[1]Department of Geology and Geography, West Virginia University, Morgantown, West Virginia (liaoshasong@gmail.com)

Abstract

Unlike porosity within the conventional rock matrix, the generation and primary migration of hydrocarbons in organic-rich shale leaves void space in organic matter, which is the porosity associated with organic matter commonly observed under scanning electron microscopy (SEM). In this study, Devonian black shale core samples were collected from four wells penetrating Mahantango and Marcellus shale units in Pennsylvania and West Virginia. Pyrolysis, organic petrology, XRD and low pressure N2 adsorption analysis were conducted to investigate the organic richness, thermal maturity, minerology and the properties of the pore system (including porosity, pore volume, specific surface area, and pore size distribution).

The black shale samples have total organic carbon (TOC) values from 0.65% to 8.90% and vitrinite reflectance (Ro) values are in the range of 1.36% to 2.89%. SEM analysis indicates that the pore systems are made of both organic-matter pores and inorganic-matrix pores. Organic-matter pores are well developed and comprise the majority of the Marcellus Shale with pore sizes ranging from less than ten to hundreds of nanometers. Also, the pore micro-texture shows a stratigraphic distribution vertically controlled by the lithology and rock texture of individual thin beds. The total porosity estimated from BET test for the samples ranges from 2.44% to 10.94%. The BET specific surface area ranges from 4.10 m^2 /g to 47.58 m^2 /g and the micropore (pore width < 2 nm) surface area estimated by the t-plot method ranges from 0 to 25.422 m^2 /g. TOC values show positive correlations with the porosity, specific surface area, and micropore volume and surface area. Increasing thermal maturity correlates with a significant decrease of pore volume and surface area, primarily through diminishing or vanishing of micropores. The richness, depositional environment, and thermal maturity of organic matter in organic-rich Devonian shale can be effective parameters for evaluation of reservoir quality and upscaling the appraisal.

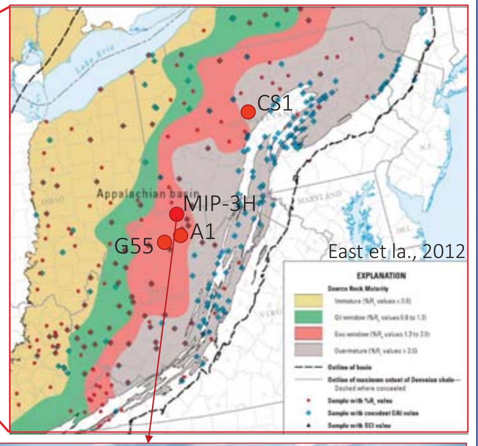
Characterization of the Pore System and its Storage Capacity in Devonian Black Shale of Appalachian Basin

Liaosha Song and Timothy Carr, Department of Geology and Geography, West Virginia University, Morgantown, WV

Abstract

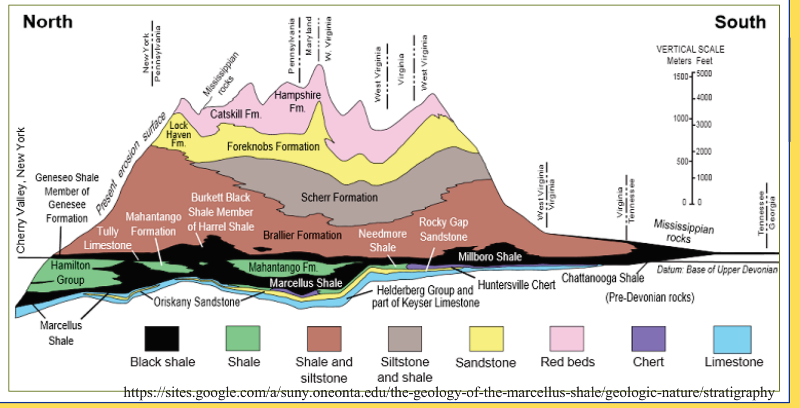
Unlike porosity within the conventional rock matrix, the generation and primary migration of hydrocarbons in organic-rich shale leaves void space in organic matter, which is the porosity associated with organic matter commonly observed under scanning electron microscopy (SEM). In this study, Devonian black shale core samples were collected from four wells penetrating Mahantango and Marcellus shale units in Pennsylvania and West Virginia. Pyrolysis, organic petrology, XRD and low pressure N_2 adsorption analysis were conducted to investigate the organic richness, thermal maturity, minerology and the properties of the pore system (including porosity, pore volume, specific surface area, and pore size distribution). The black shale samples have total organic carbon (TOC) values from 0.65% to 8.90% and vitrinite reflectance (Ro) values are in the range of 1.36% to 2.89%. SEM analysis indicates that the pore systems are made of both organic-matter pores and inorganic-matrix pores. Organic-matter pores are well developed and comprise the majority of the Marcellus Shale with pore sizes ranging from less than ten to hundreds of nanometers. Also, the pore micro-texture shows a stratigraphic distribution vertically controlled by the lithology and rock texture of individual thin beds. The total porosity estimated from BET test for the samples ranges from 2.44% to 10.94%. The BET specific surface area ranges from 4.10 m^2 /g to 47.58 m^2 /g and the micropore (pore width < 2nm) surface area estimated by the t-plot method ranges from 0 to 25.422 m^2 /g. TOC values show positive correlations with the porosity, specific surface area, and micropore volume and surface area. Increasing thermal maturity correlates with a significant decrease of pore volume and surface area, primarily through diminishing or vanishing of micropores. The richness, depositional environment, and thermal maturity of organic matter in organic-rich Devonian shale can be effective parameters for evaluation of reservoir quality and upscaling the appraisal.

Geologic Setting

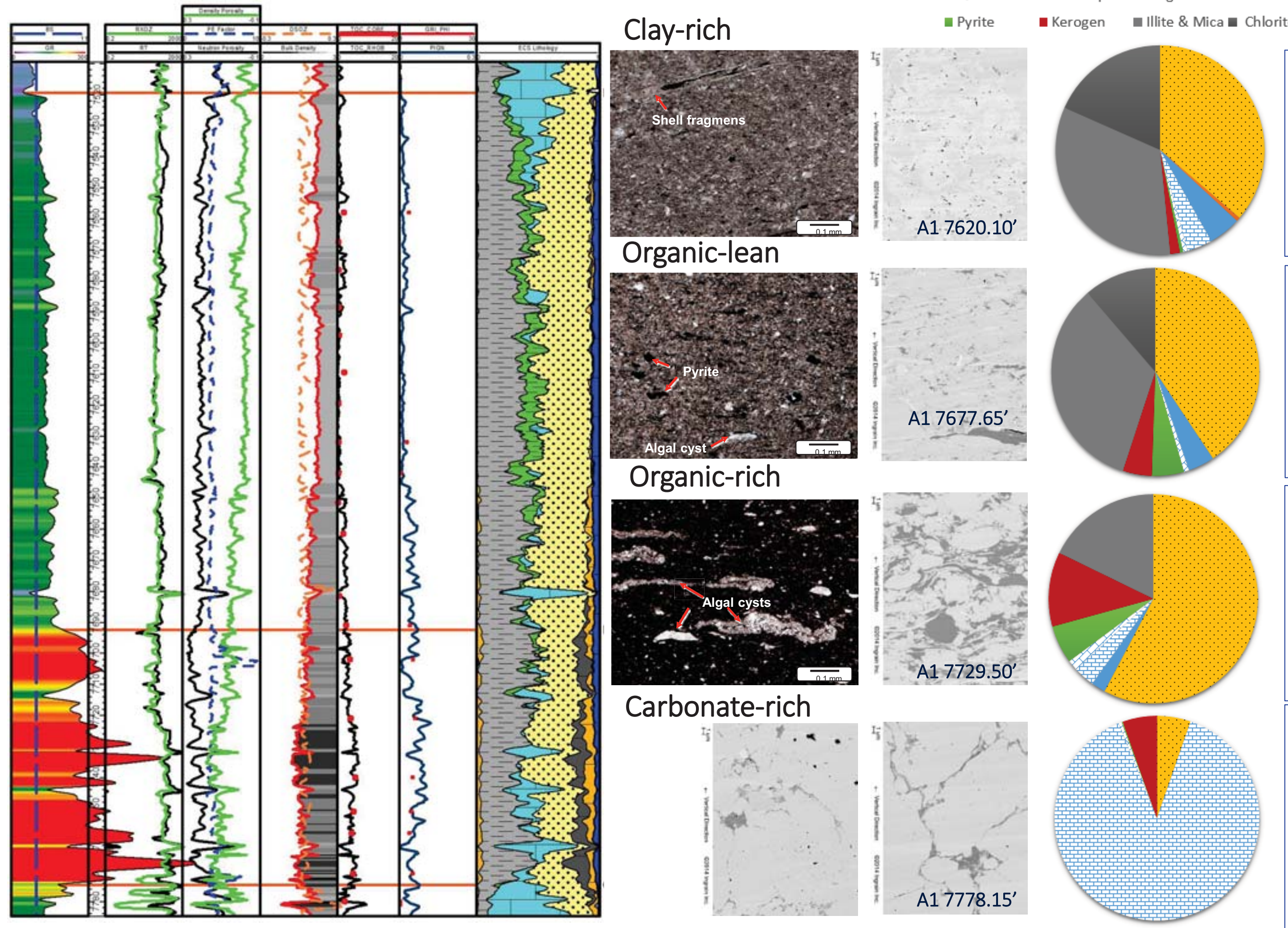


The objective of the Marcellus Shale Energy and Environment Laboratory (**MSEEL**) is to provide a long-term field site to develop and validate new knowledge and technology to improve recovery efficiency and minimize environmental implications of unconventional resource development. The MSEEL project will provide a long-term field site at NNE's Morgantown Industrial Park (MIP) just outside of Morgantown, West Virginia.

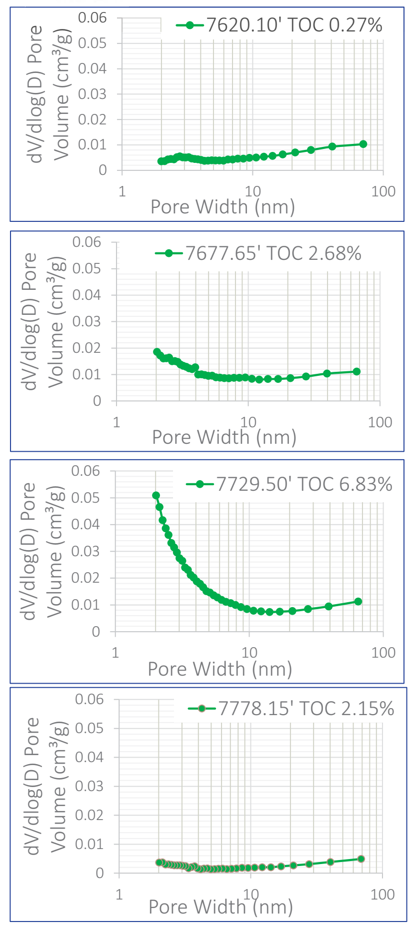
Geologic cross section of upper to middle Devonian strata from Cherry Valley, New York southwest across the Allegheny Plateau and then along the Ridge-and-Valley Appalachians to Tennessee. The Marcellus Shale is an organic-rich black shale, and it is the bottom section of Hamilton Group.



Pore Micro Texture



Pore Size Distribution



In clay-rich beds, most of the pores are inter clay particles (phyllosilicate pores). It features high clay content, low TOC, and it has small SSA.

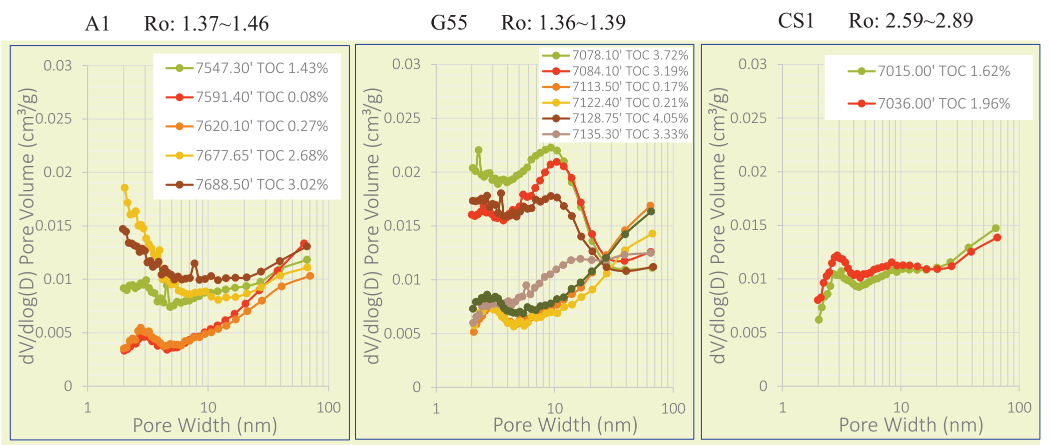
Organic-lean beds have medium clay content and TOC. Pore space are found between mineral grains and with organic matter. Medium SSA.

Organic-rich beds have low clay content and high TOC. Amorphous organic matter migrated and infilled pore space between mineral grains. BET test indicates significant portion of pore system is below 8nm.

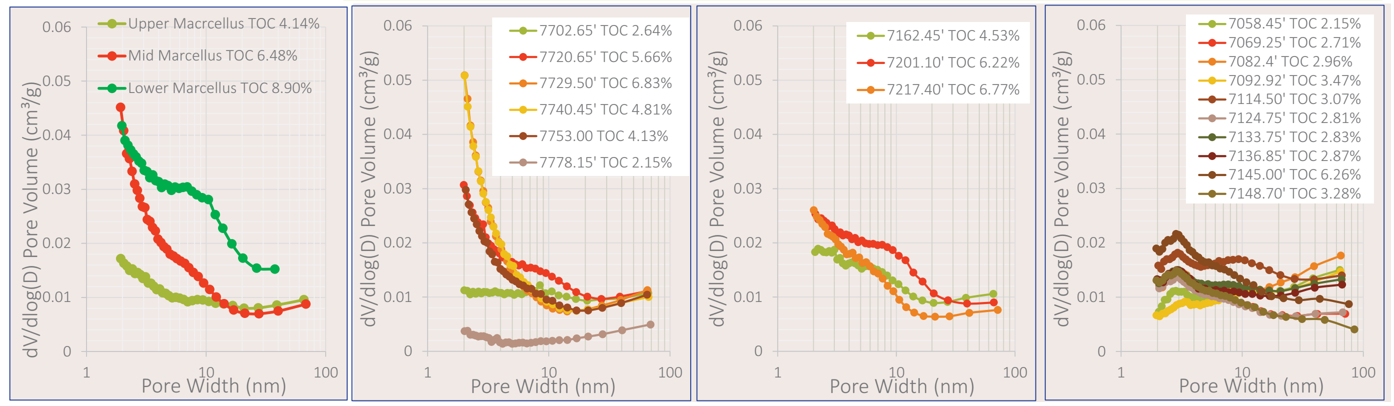
Carbonate-rich beds have high carbonate content. Amorphous organic matter migrated and infilled pore space between mineral grains. Small SSA.

Pore Size Distribution

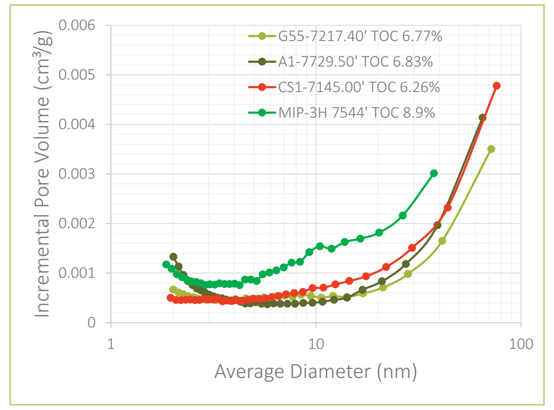
- Marcellus Shale has greater pore space than Mahantango Shale;
- As Ro increasing from 1.36 to 2.89, significant amount of pores disappeared;
- Well CS1 has highest clay content, especially chlorite, which also contributes to the porosity change.

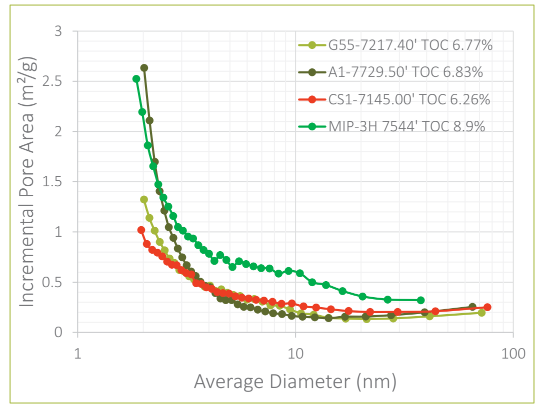


MIP 3H Marcellus Data

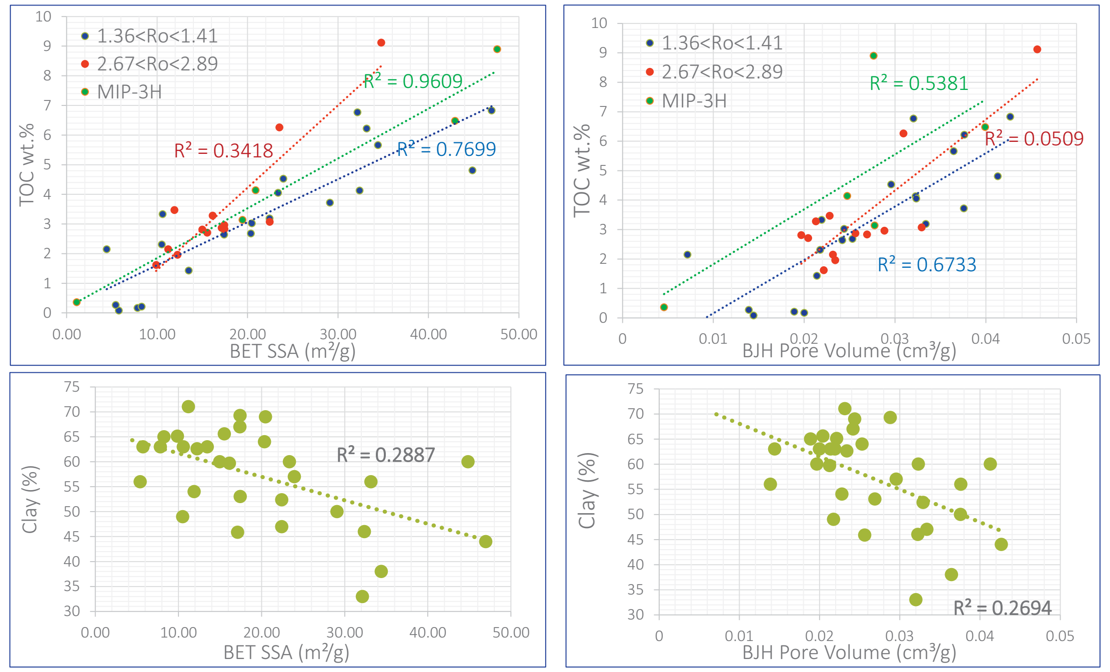


Pore Structure and Storage Capacity

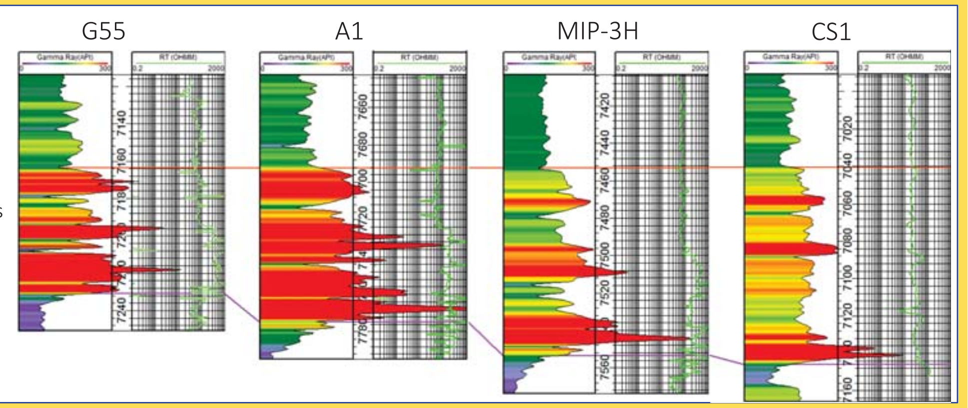




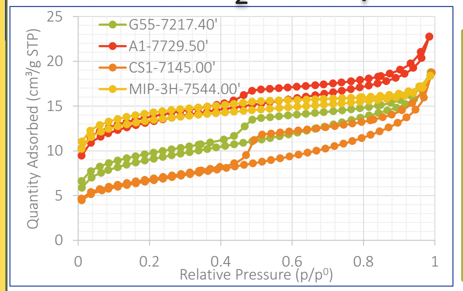
- Specific surface area and pore volume of higher thermal maturity samples are less than that of lower thermal maturity samples;
- Pores of diameters less than 5 nm make the greatest contribution to SSA, whereas pore volumes are affected by larger pores;
- Pore volume represents free-gas storage capacity, while surface area offers adsorption spots for methane molecules;
- At a similar TOC level, sample with higher thermal maturity (from well CS1) has less smaller pores (2~3nm).



Well CS1 is close to Catskill Delta front, while other three wells are in the middle of the basin. From G55 to CS1, Marcellus Shale gets thicker, and thermal maturity gets higher. However TOC of CS1 is lower than other wells. We suspect it is caused by higher amount of sediment supple from the delta front serve as a dilution.



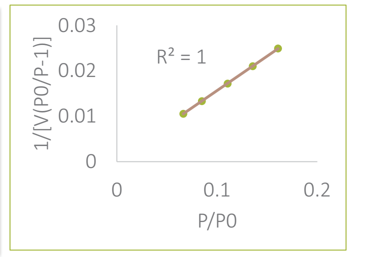
Subcritical N_2 Adsorption

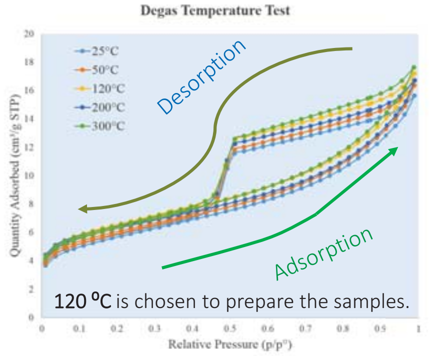


Brunauer–Emmett–Teller (BET) theory

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

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*).





120 °C is chosen to prepare the samples.

Conclusion

1) Four pore micro texture facies are found in Mahantango and Marcellus Shales, which are Organic-rich, Organic-lean, Clay-rich, Carbonate-rich, they show a stratigraphic distribution
2) Significant part of the pore system in mudrock is beyond SEM resolution;
3) There is a general positive correlation between richness of organic matter and specific surface area and pore volume;
4) Organic matter makes the majority of the micropore (<2nm) and mesopore (2~50nm) space, while inter-clay particles pores make little contribution to the micro- and meso-pore regime;
5) The depositional environment, abundance and thermal maturity of organic matter in organic-rich Devonian shale are all effective parameters when evaluating pore structures.

Acknowledgement

The research undertaken in this study was funded through the U. S. DoE National Energy Technology Lab as part of their Marcellus Shale Energy and Environmental Laboratory (MSEEL) (DOE Award No.: DE-FE0024297).

Reference

Sing, K. S. W., D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewsta, 1986, Reporting Physisorption Data For Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity, Pure & Appl. Chem., Vol. 57, no. 4, p. 603—619,

Carr, T. R., G. Wang, T, McClain, 2013, Petrophysical analysis and sequence stratigraphy of the Utica Shale and Marcellus Shale, Appalachian Basin, USA: International Petroleum Technology Conference, Beijing, China, 26-28 March 2013,12p.

Joseph A. East, Christopher S. Swezey, John E. Repetski, and Daniel O. Hayba, "Thermal maturity map of Devonian shale in the Illinois, Michigan, and Appalachian basins of North America", US Geological Survey, Scientific Investigations Map 3214, 2012.