Using XRF, SEM and Pyrolysis for an Economic Appraisal of the Marcellus Formation of Western Pennsylvania for Fracking Purposes

Presented at: AAPG 2015 Annual Convention & Exhibition, Denver, Colorado, May 31st – June 3rd by Paul Comet[1]; Chuck Stringer[1]; Christian Scheibe[1]; Albert Maende[2]; Erik Boice[3]
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Abstract

An analysis of a core from the Marcellus Formation of Western Pennsylvania was undertaken using three laboratory instruments; Spectro XEPOS® XRF, FEI Wellsite® SEM with EDX capability and HAWK pyrolyzer. A fourth parameter that was taken into consideration was porosity measurements from a PHIE and PHIT neutron emitting tool. Unexpected relationships emerged from a comparison between the various downhole curves.

Hydrocarbons that were generated from kerogen pyrolysis (S2) varied greatly in value with the neutron probe's total porosity. Macroporosity as detected by the SEM (analyzed greater than 5 microns) showed more agreement when compared to the Total Organic Carbon (TOC). Macroporosity data varied with the siliceous microfossil content, particularly radiolaria within the Marcellus Formation, and non-specific shell hash in the overlying Burkett Formation. According to the analyses there is evidence of redeposited or transported silica paralleling these zones.

The free oil (S1) showed a similar distribution to the S2 and indicated locations of three prospective "sweet spots"; Burkett Formation, Upper Marcellus Formation, and Lower Marcellus Formation. Carbonate horizons indicate low porosity due to the presence of clay. The SEM images also show the presence in the limestone with extensive bioturbation, shell fragments, and phosphatic enrichment. Pyrolysis analysis reveals low TOC values within these horizons as well. The carbonate-rich, relatively oxidizing paleoenvironment allowed various species of burrowing organisms to thrive. The remainder of the Marcellus Formation appears to have been deposited under substantially anoxic conditions and is largely composed of silty clay; the siltiest region is situated near the base of the formation. The zones of lowest clay content located in the middle of the Lower Marcellus Transgressive System Tract (TST) also contain the greatest macroporosity and highest oil content (S1, S2). This TST sequence likely corresponds to the best of the three prospective sweet spots.

Organic richness is optimal within the Marcellus Formation, ranging between 2 and 12 percent (%) TOC. Based on the analyses, this zone is evidently a source rock; S2 values reported averaged greater than 5 milligrams hydrocarbons per gram of rock. The Burkett and Tully Limestone often contains more than 2% TOC. Tmax maturity data shows the Marcellus Formation is situated in the Condensate/Wet Gas window (Tmax of 455 – 475 °C). The Lower Marcellus sweet spot shows a relatively low clay and high silt content making it the best candidate for frac stage placement. This zone shows high brittleness and elevated hydrocarbons content (S1 and S2). At the base of the Marcellus and immediately above the Onondaga Limestone there is a very thin zone of extreme ductility that appears to correspond to a bentonitic ash layer. The combination of detailed lithological analyses with an appraisal of the hydrocarbons within the Marcellus and adjacent formations allows zonation in terms of potential economic productivity and engineering suitability for fracking purposes.

Introduction

An economic appraisal of the Marcellus Formation of Western Pennsylvania and West Virginia (Figure 1) was done for purposes of determining its best producible hydrocarbons-bearing facies and suitable frac stage placement. The appraisal is comprised of reservoir characterization and a geochemical study of core and drill cuttings retrieved from a single vertical well. The analyzed well penetrated the Devonian-age Burkett, Tully Limestone, Hamilton and Marcellus Formations as well as the top portion of the Onondaga Formation (Figure 2).

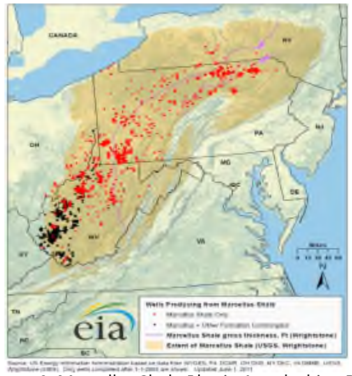

Figure 1. Marcellus Shale Play in Appalachian Basin (EIA, 2011)

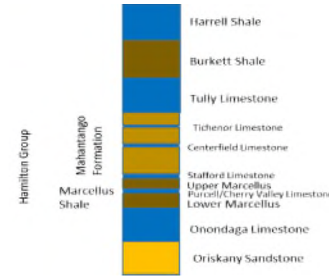

Figure 2. Stratigraphy of Lower and Middle Devonian in Appalachian Basin (After, Wrightstone, 2009)

This economic appraisal seeks to demonstrate that analyses of drilled rock cuttings by using the Advanced Sample Analysis (ASA) methodology is a cost-effective alternative to generate the essential data required for identifying the best producible hydrocarbons-bearing facies and suitable frac stage placement. ASA methodology comprises of the use of XRF, SEM-EDX (or EDS) and Pyrolyzer. ASA data can also be correlated with MWD/LWD and wire-line tool responses.

Analyses

LaserStrat® Spectro® XEPOS III EDX

Analytical results from X-ray Fluorescence (XRF) provide chemical signatures of over 35 elements of the analyzed rock core or cuttings. These include the major elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, potassium, calcium, titanium, manganese, and iron, reported as oxides in weight percent (wt %). The minor and trace elements including chloride, vanadium, nickel, copper, zinc, arsenic, bromine, rubidium, molybdenum, thorium, and uranium are reported in parts per million. The concentrations of potassium, thorium and uranium are computed into a theoretical gamma ray response (ChemoGR®) expressed in American Petroleum Institute (API) equivalent units. This enables a direct comparison with gamma ray responses recorded from down-hole tools. The major elements are utilized to model the mineralogy of the samples. In addition, some trace elements such as Ba and Zr are also utilized to model minor minerals such as barite and zircon respectively. The modelled mineralogy is then utilized to calculate a Relative Brittleness Index (RBI) (Buller *et al.*, 2010), where the RBI represents an enhancement of Jarvie's (2007) mineralogy based definition of rock brittleness for the Barnett Shale.

LithoSCAN® FEI Wellsite® SEM-EDX (EDS)

The SEM-EDX with QEMSCAN® analysis provides accurate mineralogical composition of a rock sample through the use of the SEM with Energy Dispersive X-ray and associated analysis program. Further, SEM-EDX analysis provides accurate porosity determination. In this analysis a 5µm Back Scatter Electron (BSE) resolution image was used for porosity calculations. The 5µm resolution enables identification of pore sizes in the micro-pore range of 1 to 62.5µm (Loucks *et al*. 2012).

HAWK® Pyrolysis and TOC

Pyrolysis instruments analyze suitably ground rock samples by using an initial isotherm to release the free oil of the rock (S1), detectable by a Flame Ionization Detector (FID), followed by temperature ramping in an inert environment to a suitable maximum temperature that allows for FID recognition of any bitumen and asphaltene that may be present, as well as measurement of hydrocarbons that are yielded from the break-down of the rock's kerogen component (S2), whose peak generation temperature is recorded as the Tmax maturity parameter (Dow, 2011). On completion of the pyrolysis cycle, air is passed through the pyrolysis instrument, while ramping the temperature to a suitable maximum that allows for the rock sample's oxidation products which consist of carbon monoxide and carbon dioxide to be measured by Infra-Red detectors.

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Results

The XRF, SEM, Pyrolysis and TOC analytical results for the Burkett, Tully, Hamilton, Marcellus, Upper Marcellus (U.M.) Transition Stand Track (TST), Lower Marcellus (L.M.) High Stand Track (HST) and Lower Marcellus Transition Stand Track (TST) are summarized in Table 1 whereby the mean value for S1, S2, Tmax, TOC, OSI (Jarvie and Baker, 1984), HI, Porosity, Siliceous Mudstone, Argillaceous Mudstone and Carbonate contents are displayed. Maturity wise, a Tmax of less than 430° C is deemed to indicate immaturity (Peters, 1986) while the Oil window is delineated by a 430 to 455° C range with the Condensate/Wet Gas zone falling within the 455 to 475° C range (Jarvie, 2012). The Dry Gas to Post Mature zone is at temperatures greater than 475° C.

Formation	Depth (ft) Corrected	S1-Free Oil (mgHC/g rock)	S2-Kerogen Yield (mgHC/g rock)	Tmax-Maturity (°C)	TOC (Total Organic Carbon) (wt. %)	OSI Oil Saturation Index (S1/TOC x 100)	HI Hydrogen Index (S2/TOC x 100) mg HC/g TOC	LiS_Porosity	LiS_Siliceous Mudstone*	LiS_ Argillaceous Mudstone *	LiS_Carbonate*
Burkett_mean	6246.75-6275.8	5.00	6.41	470	7.16	70	89		66.92	32.78	0.34
Tully	6260.45	2.5	2.89	471	3.37	74	86		19.7	77.9	2.3
Hamilton_mean	6284.25-6302.05	1.63	2.19	466	2.33	66	67		16.27	43	40.63
Marcellus_mean	6320.4-6327.7	4.42	5.51	463	6.12	78	85	1.08	20.4	62.86	15.52
U.M.TST_mean	6329.5-633.5	6.35	8.67	458	9.16	69	94	1.5	19.73	76.53	2.07
L.M HST_mean	6354.65-6356.5	9.6	4.36	466	5.97	159	73	1.1	19.05	79.15	0.65
L.M. TST_mean	6359.35-6373.2	8.72	10.93	464	11.75	81	90	4.57	42.61	41.07	11.69
Onondaga_mean	6375.7-6378.9	2.36	5.21	430	5.33	45	144				
Huntersville_mean	6381.6	0.13	0.17	331	0.49	27	35				

*Note: Lists of the mineralogical composition whose sum provided the LiS_Siliceous Mudstone, LiS_Argillaceous Mudstone and LiS_Carbonate analytical results

LiS_Siliceous Mudstone	LiS_Argillaceous Mudstone	LiS_Carbonate
Silica	Illite	Calcite
Silica Carbonate Clay	Muscovite	Dolomite
Silica Clay	Biotite	Ankerite
K-Feldspar	Kaolinite	
Plagioclase	Chlorite	
Rutile	Glauconite	
Apatite	Pyrite	
Gypsum/Anhydrite		

Table 1. Mean S1, S2, Tmax, TOC, OSI, HI, Porosity, Siliceous Mudstone, Argillaceous Mudstone and Carbonate contents for the Burkett, Tully, Hamilton, Marcellus, Upper Marcellus (U.M.) TST, Lower Marcellus (L.M.) HST and Lower Marcellus TST

From Table 1, it can be seen that all the represented formations, except for the Huntersville, have a TOC of at least 2%, which happens to be what is considered to be the minimum TOC required for a viable shale oil or shale gas resource system. The Lower Marcellus (L.M.) TST not only contains the highest TOC but also the highest porosity, S1 and S2 values. Therefore, it appears to have the greatest free oil content as well as the greatest kerogen generation potential while the second in rank for these TOC, S1 and S2 parameters is the Upper Marcellus (U.M.) TST. The data identifies the Lower Marcellus TST and the Burkett as containing a siliceous mudstone content exceeding 40% (by weight). All of the formations are within the Condensate/Wet Gas zone. The maturity data for the Onondaga and Huntersville samples are not indicative of these formation's actual maturity due to their very low yield of hydrocarbons from kerogen (S2 parameter) which makes their Tmax maturity measurement to be unreliable.

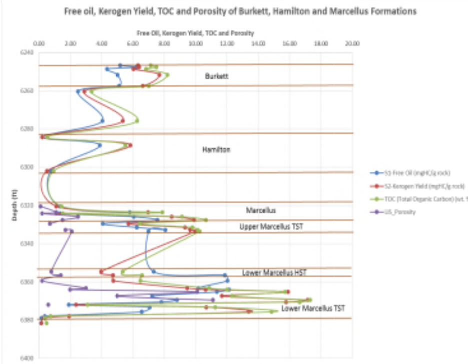

Figure 3. Free oil (S1), kerogen yield (S2), TOC and porosity of the Burkett, Hamilton and Marcellus Formations

The free oil (S1), kerogen yield (S2), TOC and porosity of the Burkett, Hamilton and Marcellus Formations are plotted in Figure 3 where it is evident that these three parameters parallel each other but are at their highest within the Lower Marcellus TST. Figure 3 also shows a gradual reduction trend in S1 values in conjunction with sudden increase in porosity as the Lower Marcellus TST is drilled deeper. Evidently this S1 trend shows free oil within macropores of the Lower Marcellus TST migrating downward to the Onondaga Formation. This migration is attributed to the down-hole increasing content of siliceous radiolaria that, in turn, created increased porosity through diagenesis.

The siliceous and argillaceous mudstone contents of these three formations are plotted in Figure 4. It is very significant that, as from the Hamilton Formation down-hole all the way to the Lower Marcellus HST, the argillaceous mudstone content is far higher than that of the siliceous mudstone content. When the Lower Marcellus TST is penetrated, there is a crossover and the siliceous mudstone content is greater than the argillaceous mudstone content. It is also significant that it is the Lower Marcellus TST that has the highest free oil, kerogen yield and TOC values. The only other unit that shows higher siliceous mudstone content when compared to the argillaceous mudstone content is the Burkett Formation. It's free oil, kerogen yield, and TOC values however, are lower than those of the Marcellus Formation. Table 2 shows the summary of pyrolysis, porosity and mineralogy values for the studied formations

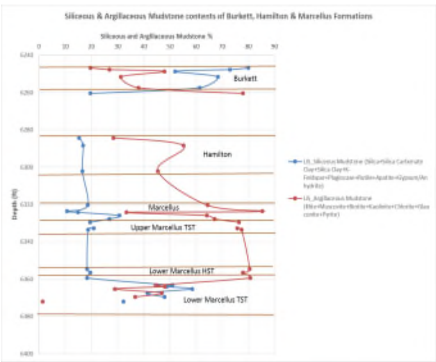

Figure 4 Siliceous and Argillaceous Mudstone contents of the Burkett, Hamilton and Marcellus Formations

Table 2. Summary of pyrolysis, porosity and mineralogy values for the Burkett, Tully, Hamilton, Marcellus, Upper Marcellus (U.M.) TST, Lower Marcellus (L.M.) HST and Lower Marcellus TST.

Formation	Depth (ft) Corrected	S1-Free Oil (mgHC/g rock)	S2-Kerogen Yield (mgHC/g rock)	S3 (mgCO2/g rock)	Tmax-Maturity (°C)	TOC (Total Organic Carbon) (wt. %)	PI Production Index (S1/S1+S2)	OSI Oil Saturation Index (S1/TOC x 100)	HI Hydrogen Index (S2/TOC x 100) mg HC/g TOC	OI Oxygen Index (S3/TOC x 100) mg CO2/g TOC	LiS_Porosity	LiS_Siliceous Mudstone*	LiS_Argillaceous Mudstone *	LiS_Carbonate*
Burkett_mean	6246.75-6275.8	5.00	6.41	0.18	470	7.16	0.44	70	89	2		66.92	32.78	0.34
Range for 6 samples		4.05-6.24	5.37-7.69	0.13-0.22	468-473	6.28-8.20	0.39-0.49	61-83	85-94	2-3		52-80	19-38	0.1-0.5
Tully	6260.45	2.5	2.89	0.15	471	3.37	0.46	74	86	4		19.7	77.9	2.3
Hamilton_mean	6284.25-6302.05	1.63	2.19	0.23	466	2.33	0.51	66	67	26		16.27	43	40.63
Range for 3 samples		0.25-3.89	0.21-5.86	0.22-0.26	464-467	0.53-5.54	0.40-0.60	47-82	40-106	4-49		15.3-16.9	28.4-55.2	27.9-56.1
Marcellus_mean	6320.4-6327.7	4.42	5.51	0.208	463	6.12	0.48	78	85	7	1.08	20.4	62.86	15.52
Range for 5 samples		1.33-7.56	1.11-9.89	0.16-0.25	461-466	1.44-10.65	0.42-0.55	66-92	73-89	2-16	0.1-2.5	10.8-30.7	33.4-85.3	2.5-51.3
U.M.TST_mean	6329.5-633.5	6.35	8.665	0.2075	458	9.16	0.42	69	94	2	1.5	19.73	76.53	2.07
Range for 4 samples		4.08-8.06	5.73-9.97	0.16-0.27	457-459	6.44-10.26	0.40-0.46	63-79	89-97	2-3	0.7-2.1	18.8-20.9	75.8-77.4	1.2-2.1
L.M HST_mean	6354.65-6356.5	9.6	4.355	0.13	466	5.97	0.68	159	73	2	1.1	19.05	79.15	0.65
Range for 2 samples		7.33-11.87	3.97-4.74	0.12-0.14	464-468	5.36-6.58	0.65-0.71	137-180	72-74	2-3	0.8-1.4	18.4-19.7	77.9-80.4	0.4-0.9
L.M. TST_mean	6359.35-6373.2	8.72	10.93	0.16	464	11.75	0.45	81	90	2	4.57	42.61	41.07	11.69
Range for 9 samples		1.9-12.04	2.37-17.16	0.11-0.21	456-486	3.11-17.32	0.33-0.72	31-101	73-101	1-7	0.2-11.1	13.4-58.6	1.4-80.7	0.6-65.6
Onondaga_mean	6375.7-6378.9	2.36	5.21	0.24	430	5.33	0.28	45	144	34				
Range for 3 samples		0.17-6.56	0.32-13.37	0.17-0.34	385-455	0.39-14.85	0.16-0.35	44-49	82-261	1-54				
Huntersville_mean	6381.6	0.13	0.17	0.27	331	0.49	0.43	27	35	55				