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## **Using XRF, SEM, and Pyrolysis for an Economic Appraisal of the Marcellus Formation of Western Virginia for Hydraulic Fracturing Purposes\***

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### **Abstract**

Analysis of a core from the Marcellus Formation of western Pennsylvania was undertaken using three laboratory tools: X-ray fluorescence (XRF), scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDX or EDS) capability, and a pyrolysis instrument. These instruments are designed and calibrated for a quick and cost-effective turn-around. Further, the instruments are portable and sufficiently robust to be used in a field laboratory. A fourth parameter used was porosity measurements from a PHIE and PHIT neutron emitting tool. The analyzed samples originated from a vertical well in western Virginia that penetrated the Devonian Burkett, Tully Limestone, Hamilton, and Marcellus formations, as well as the topmost parts of the Onondaga Formation. Good agreement between the results from the different technologies was observed, but unexpected relationships emerged when comparing the various downhole curves.

### **Introduction**

It is paramount to understand the geological, geochemical, and petrophysical properties of an organic-rich reservoir rock to perform an appraisal of its economic potential and identify the best locations along the wellbore for development. Nevertheless, often only a very limited suite of measurement while drilling (MWD) and logging while drilling (LWD) tools is employed while drilling wells into this type of reservoir, keeping costs low. The same is true for wireline logging after the well has been drilled. However, analysis of cuttings samples is a cost-effective alternative to generate such essential data. An advanced sample analysis (ASA) is proposed including XRF, SEM with automated mineral identification through EDX or EDS, and pyrolysis for characterization of organic components, such as kerogen and total organic carbon (TOC). Such data can be complimented by MWD/LWD and/or wireline tool responses.

For the present study, a single vertical well penetrating through the Devonian Burkett, Tully Limestone, Hamilton, and Marcellus formations, as well as the top parts of the Onondaga Formation, underwent the proposed ASA. Additional data were available from wireline tools. The main objective was to demonstrate the feasibility of an economic appraisal of the Marcellus Formation. The Marcellus is the target reservoir section for which core material is available and thus provides an opportunity to validate this approach. Although only some information from this particular well is presented here, the well data (not presented here) were successfully used to correlate with other wells in the vicinity, as well as to its lateral daughter wells.

## **XRF**

Analytical results from XRF provided chemical fingerprints (35 elements) of the analyzed rock samples (i.e., core and cuttings samples). These included the major elements Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe, which were reported as oxides in weight percent (wt%), and minor and trace elements including Cl, V, Ni, Cu, Zn, As, Br, Rb, Mo, Th, and U, reported in ppm, to name a few. Combinations of these elements in the form of ratios and indices, as well as the relative abundance/absence of them, can be interpreted in terms of their underlying mineralogy by recalculation of the metal oxides as minerals using a normative mineralogy algorithm, called “mingen,” relative organic content, as well as petrophysical properties. For example, the concentrations of potassium (K), thorium (Th), and uranium (U) have been computed into a theoretical gamma ray response, Chemogamma<sup>®</sup>, which is expressed in American Petroleum Institute (API) equivalent units. This enables a direct comparison with gamma ray responses recorded from downhole tools. Consequently, a quantification is possible of the sample quality and position in the borehole, particularly when working with cuttings. Where required, a correction of the reported depth/position of cuttings samples resulting from lag time/hole cleaning issues can be undertaken. In this study, the entire Marcellus Formation was cored and only cuttings samples from the Burkett, Tully Limestone, and Hamilton formations had to be used. The computed geochemical gamma ray motif showed good agreement with the tool-derived gamma ray log after application of the core shifts.

Additionally, element distributions and ratios enable differentiation of long known and already named stratigraphic intervals, as well as enabling subdivision of those into more detailed geochemical units (chemostratigraphy). This process can be used not only for correlation purposes between wells but also for geosteering purposes (depending on the rate of penetration [ROP]).

The major elements were used to model the mineralogy of the samples. However, some trace elements, such as Ba and Zr, can also be used to model minor minerals, such as barite and zircon, respectively. The modeled mineralogy showed good agreement to the SEM-EDX determined mineralogy. The modeled mineralogy was then used 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.

Certain trace elements can be used as proxies for estimating the organic content through calculations of enrichment factors (EF) (Tribovillard et al., 2006) and regressions with actual measured organic components. In this study, the EF of vanadium (EFV) was determined to be the best proxy for organic matter.

## SEM-EDX (-EDS)

Although mineralogy can be modeled from chemical elements determined by XRF analysis, SEM-EDX or -EDS also provides an accurate mineralogical composition of a rock sample. Mineralogy is reported in tabulated form and in false color images of the analyzed core area or cuttings. The images also provide insight into textural and micro-features.

Further, SEM-EDX analysis can provide porosity determination but is limited to the X-ray beam spot size (i.e., the SEM-EDX can only determine porosity equal to or larger than its spot size); in this study, 5  $\mu\text{m}$  was used. The 5  $\mu\text{m}$  resolution applied in this study enabled the identification of pore sizes in the range of micro-pores (1 to 62.5  $\mu\text{m}$  (Loucks et al., 2012)) but not smaller (e.g., nano- and/or pico-pores).

Because of its calibration, the SEM-EDX could not identify organic components, such as kerogen. This incapacity to accurately measure organic components was remediated by using a pyrolysis instrument.

## Pyrolysis

Pyrolysis is a programmed, controlled heating of a rock sample and measurement of its volatile components at different temperature intervals, which determines the TOC and several properties of the organic matter. The S1 value (or oil yield) provides the amount of free hydrocarbons (oil yield) in the sample in milligrams of hydrocarbon per gram of rock (mg HC/g rock).

S2 (or kerogen yield) is the amount of hydrocarbon freed through the pyrolytic breakdown of kerogen and thus is an indicator of kerogen itself (in mg HC/g rock). During generation of the S2 peak, the temperature at which the maximum amount of hydrocarbon is produced provides the Tmax value ( $^{\circ}\text{C}$ ). This value provides insight into the maturity of the kerogen.

In addition to these three key parameters, S3 and S4 values are determined, which are, respectively, the amount of  $\text{CO}_2$  produced during kerogen breakdown (mg  $\text{CO}_2$ /g rock) and the amount of residual carbon (i.e.,  $\text{CO}_2$  and CO (mg  $\text{CO}_2$ /g rock)) produced by the combustion of residual carbon (i.e., after the completion of pyrolysis (non-generative residual organic carbon content)). TOC (wt%) was calculated from the carbon of S1 and S2 plus the carbon of S4. Additionally, oil saturation indices (OSI) were calculated following Jarvie and Baker (1984) and Jarvie (2007). However, it should be noted that the interpretation of pyrolysis measurements must be performed with care, as outlined by Dembicki (2009).

Neutron porosities, PHIE and PHIT, were available for the studied well, which complemented the porosities determined from SEM-EDX. All three instruments in this study were designed to be sufficiently robust to use at the wellsite, enabling near real-time analysis of cuttings samples while drilling.

## Combining the Three Technologies and Neutron Porosity

Although the Burkett, Tully Limestone, and Hamilton formations were sampled and analyzed by means of cuttings samples, these formations are only briefly mentioned here, as the main focus lies on the Marcellus shale. The Burkett, Tully Limestone and Hamilton formations can be identified and characterized based on their geochemical composition. However, because of a lack of high-resolution data (as only cuttings samples were available), further subdivision into distinct geochemical units was hampered. As a result, the Tully Limestone was preliminarily subdivided into only two geochemical units. The Burkett Formation consists of high-TOC (6 to 7%) shaly siltstones with low carbonate content and is further characterized by high S and relatively high U concentrations, but it has only moderate EFV.

The Tully Limestone Formation was subdivided into two geochemical units based on its geochemical and hence mineralogical compositions. The upper Tully Unit 1 consists of limestone with shaly components, showing high Ca concentrations (calcite) and low Si and Al (quartz and aluminosilicates). The upper part is also characterized by lower Sr concentrations than the lower part. It is further characterized by high Mn and P concentrations, the latter probably associated with biogenic productivity. The TOC is high (6 to 7%). The lower Tully Unit 2 comprises marls also with high Mn and is similar to the underlying Hamilton Formation but has a much higher Ca content. The term “Hamilton Formation” is used in a stratigraphically narrow sense; here, it refers to rocks positioned directly above the Marcellus and below the Tully limestone.

The fully cored Marcellus Formation was initially divided into five lithostratigraphic units with sequence stratigraphic interpretation. The top Marcellus was further subdivided into two geochemical units (UM-U3 and -U2), underlain by the Upper Marcellus transgressive system track (TST), geochemical Unit UM-U1. The Upper Marcellus is separated from the Lower Marcellus by the Cherry Valley Limestone. The Lower Marcellus is divided into an upper high-stand system track (HST) and a lower TST. Geochemical Unit LM-5 refers to the Lower Marcellus HST, which was not further subdivided because of its geochemical signatures or mineralogy.

The Lower Marcellus TST was further subdivided into four geochemical units based on combining geochemical ratios and element abundances with mineralogy (Units LM-4 to LM-1). Out of a range of ratios, two key ratios are shown in [Figure 1](#): potassium/rubidium (K/Rb) and iron/titanium (Fe/Ti) ratios, respectively (Tracks 5 and 6). The significance of the K/Rb ratio is not fully understood at this point of the study but is believed to originate from the underlying clay mineralogy.

The mineralogy as determined from SEM-EDX analyses is displayed in Track 7. It becomes apparent that the “hot shale” of the Lower Marcellus TST (Units LM-4 to LM-2) also comprises the highest concentrations of silica/quartz. Note that the SEM-EDX does not distinguish between detrital, diagenetic, and biogenic silica. However, SEM-EDX photos (not shown) clearly indicate that many of the silica grains of the Marcellus are angular and might have a pyroclastic origin (Droste and Vitaliano, 1973). The increase in silica content causes increased brittleness in the rocks, as expressed in the RBI (Track 8). The RBI display follows a color scheme, where green colors indicate more ductile and red more brittle properties. Rock brittleness is an important factor in hydraulic fracturing planning processes.

Units LM-4 to LM-2 also contain the highest concentrations of TOC and have high S1 (oil yield) values (Tracks 8 and 9). However, an “oil crossover” plot (also in Tracks 8 and 9) (after Jarvie and Baker, 1984; and Jarvie, 2010) indicates the largest separation from the middle of LM-4 up into LM-5. Interestingly, this coincides with a reduced brittleness of the rocks (Track 8). The TOC log displays a range of distinct very

high peaks in the Lower Marcellus TST. These highest TOC sediments (ranging up to 39%) can be termed “pseudocoals” (Track 9) but have, on the other hand, the lowest hydrocarbon index (HI) values (Track 12), as determined by pyrolysis, and thus the lowest hydrocarbon-generating potential, which probably indicates their Type 3 (woody) or Type 4 (charcoal) origin. The high TMax from kerogen in the limestone immediately below the lowest “pseudocoal” could indicate a “fusinite” or charcoal origin for the TOC, perhaps linked to the felling and partial combustion of primitive trees by a pyroclastic event. Vanadium and EFV show good correspondence in their log characteristics to TOC (Track 11), except for the previously mentioned high-TOC peaks. Buller et al. (2014) used regressions between V and TOC to calculate a pseudo-TOC log from the V concentration, which is not displayed here.

TMax values (Track 10), as maturity indicators, vary only slightly, mainly between approximately 460 and 470°C, which is indicative of maturity that is within the condensate/wet gas window. The presented data for characterizing rocks can also be input into advanced petrophysical software for further data analysis and modeling of petrophysical properties, as demonstrated by Buller et al. (2014).

The porosity, as determined from SEM-EDX analyses, shows good correlation with the kerogen yield (S2) from pyrolysis (Track 13). The relation is not linear; rather, it follows an exponential regression line with correlation coefficient R2 of 0.89. The discrepancy between the SEM-derived porosity and PHIT and respectively PHIE from neutron porosity tools was expected, as the neutron tool measures conditions in the formation, including all fluids present, such as formation water, which are not present in dried cuttings and core samples.

## **Conclusions**

The combination of using XRF, SEM-EDX, and pyrolysis analytical techniques on cuttings and core samples (in combination with downhole tool readings, such as gamma ray and neutron porosity, if available) can be used to cost-effectively characterize organic-rich (shale) reservoir rocks. XRF elemental data enable a depth correction of cuttings and/or core through a computed theoretical gamma ray log. Certain element ratios and index values aid in a subdivision of the formation(s) into geochemical units, which can be used for characterization, correlation, and geosteering purposes.

Mineralogy observed from SEM-EDX further assists the rock characterization, providing an accurate mineralogy. In addition to mineralogy, porosity can also be determined, depending on the resolution of the EDX beam spot size. The mineralogy then can be used to estimate the rock brittleness, which is paramount for hydraulic fracture design.

Pyrolysis analysis provides insight into the nature of present organic components. TOC, S1 and S2 values, and the calculated indices from those, such as OSI and HI, indicate the location of the sweet spot(s). Thus, a combination of these techniques provides stratigraphic control and identification of sweet spots and rock properties, enabling economic appraisal.

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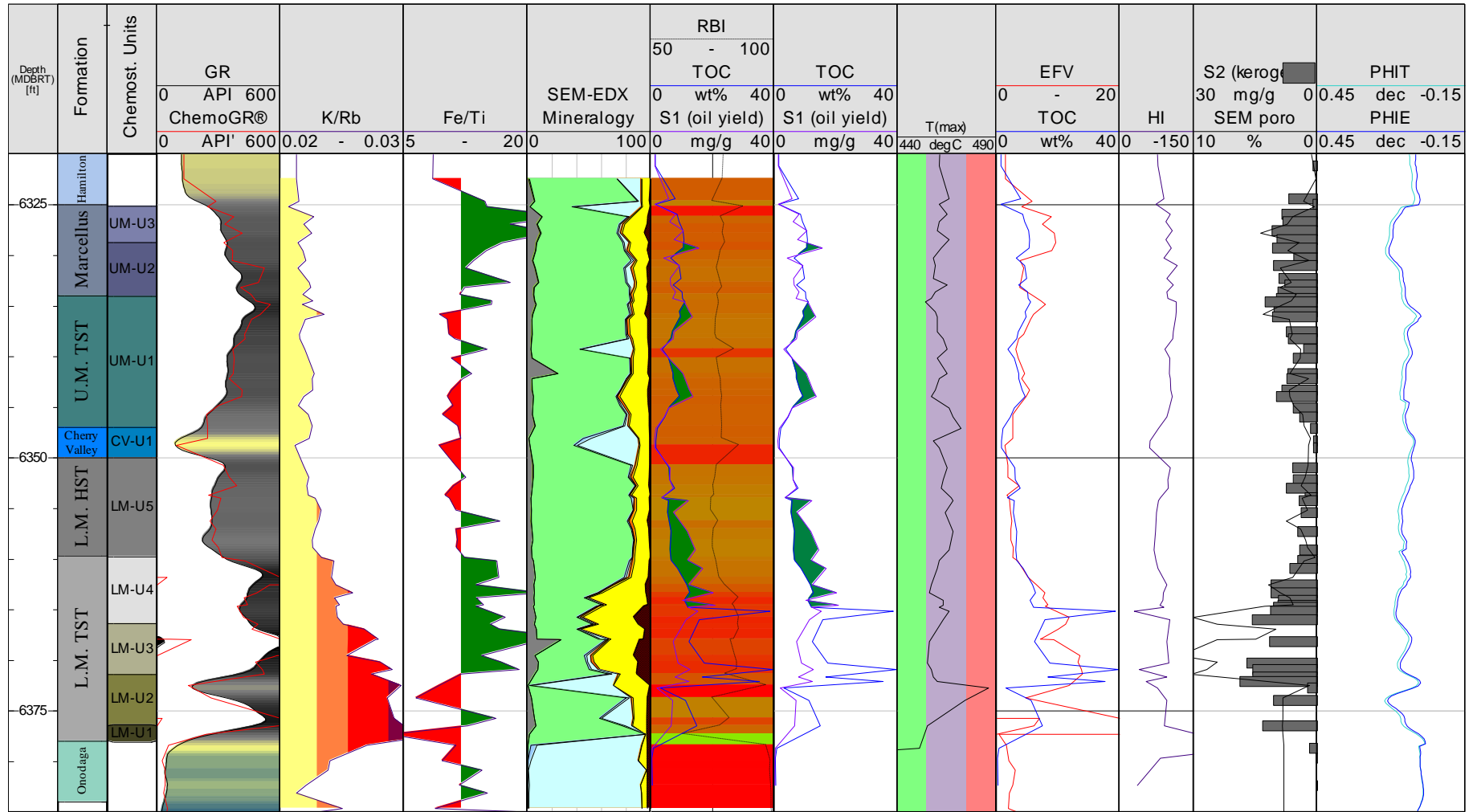


Figure 1. Geochemical and mineralogical characterization of an organic-rich reservoir based on XRF, SEM-EDX, and pyrolysis.