Geochemical Characterization of Post-Mature Gases from Middle Devonian Marcellus Formation, Northern Appalachian Basin, USA – Insights into Deep Basin Hydrocarbon Generation, Alteration, and Productivity*

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Abstract

The Middle Devonian Marcellus Formation in northeast Pennsylvania produces natural gas from post mature marine mudrocks. The reservoirs consist of laminated to thinly bedded or bioturbated, organicrich, fossiliferous, calcareous, quartzose mudstone and mud shale. The original organic matter in in these rocks consisted of ±95 to 100 percent unstructured kerogen and spores (Type II). It is now dominated by inert amorphous material, solid hydrocarbons, semi-fusinite, and inertinite due to thermal maturation. The Marcellus Formation occurs within two third-order transgressive-regressive sequences deposited in an elongate foreland basin that formed in response to the Acadian orogeny (Lash and Engelder, 2011). The average depth of the reservoirs in the study area is 2.6 km and their average temperature is 90°C. However, maximum burial depths and temperatures of the Marcellus Formation in northeast Pennsylvania were on the order of 10 to 12 km and ~250° to 300°C, respectively (Beaumont et al., 1987). Approximately 9 km of overburden was eroded since the Alleghanian orogeny.

Organic matter in the Marcellus Formation in northeast Pennsylvania reached the metagenetic stage of thermal evolution (VR VR_o > 2%, Huc, 2013). Mean vitrinite reflectance increases from 2.5 percent in Bradford County to ~4.5 percent in Sullivan and Wyoming counties, before decreasing to 3.2 percent adjacent to the Jack's Mountain Anticlinorium in Luzerne County. In the Marcellus samples discussed in this report, vitrinite reflectance ranges from 3.2 to 4.6%, measured kerogen H/C and O/C ratios are 0.4 and 0.06, respectively, mean illite crystallite thickness is 211 Å, and the Kübler Index is 0.428 (Figures 1, 2, and 3).

Published conodont alteration indices range from 4.0 to 5.0 (Repetski et al., 2008). These observations suggest that deep burial diagenetic to incipient metamorphic (anchizone) processes operated in the Marcellus Formation at PT conditions characteristic of the prehnite-pumpellyte facies during maximum burial approximately 250 Ma (Abad, 2008).

The stable isotope composition of production and mud gases collected from 24 wells in the study area also indicates high thermal stress. Production $\delta^{13}C_1$ ranges from -28.69 to -24‰ (Figure 4). Mud gas $\delta^{13}C_1$ ranges from -27.3 to -21.5‰. All gases exhibit carbon isotope reversals with respect to carbon number (Figures 5, 6, and 7). $\delta^{13}C_1$ approaches, or is heavier than, $\delta^{13}C_{KEROGEN}$. Production gases exhibit hydrogen isotope reversals (methane δ^2H > ethane δ^2H) (Figure 6).

The $\delta^{13}C$ and δ^2H isotope reversals may be interpreted in one of four ways: (1) mixing of gases from different sources (Jenden et al., 1996; Xia et al., 2012), (2) a combination of mixing, Rayleigh fractionation of C_2 and C_3, and exchange of methane hydrogen with formation water (Burruss and Laughrey, 2010), (3) water-reforming followed by Fischer-Tropsch synthesis (Tang and Xia, 2011), and (4) destruction of C_{2+} alkanes followed by reforming via gas-phase radical recombination reactions (Telling et al., 2013). Strong correlation between $\delta^{13}C_1$ and $\delta^{13}C_2$ (R^2 = 0.986) and $\delta^{13}C_1$ and $\delta^{13}C_3$ (R^2 = 0.923) in most samples, along with light $\delta^{13}CO_2$ (-19.7 to -10.2‰), appears to support certain aspects of the Rayleigh fractionation, water-reforming, and radical recombination hypotheses.

Post-mature Marcellus prospects are limited by thermal maturity, geologic structure, and loss of organic porosity. Gas isotope data help to predict well performance (Figure 7). Productive wells have $\delta^{13}C_1$ </= $\delta^{13}C_{KEROGEN}$, $\delta^{13}C_{2-3}$ < $\delta^{13}C_{KEROGEN}$, and high δ^{13}C1-3 correlation. Marginal wells have $\delta^{13}C_1$ >/= $\delta^{13}C_{KEROGEN}$, $\delta^{13}C_{2-3}$ < $\delta^{13}C_{KEROGEN}$, and variable $\delta^{13}C_{1-3}$ correlation. Unproductive wells have $\delta^{13}C_1$ > $\delta^{13}C_{KEROGEN}$, $\delta^{13}C_2$ >/= $\delta^{13}C_{KEROGEN}$, trace C_{3+}, and poor $\delta^{13}C_{1-3}$ correlation.

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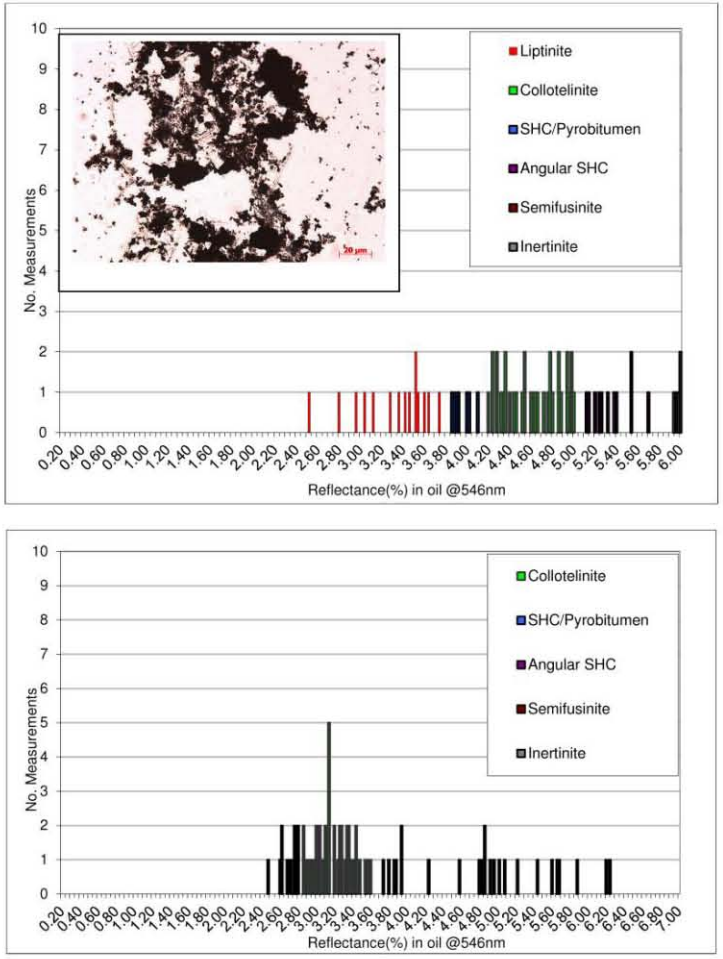

Figure 1. Kerogen type distribution and reflectance in oil at 546 nm of Marcellus Formation samples from 8250 ft. (mean VR_o = 4.61%) in the Chief Severcool Unit #1 well, Wyoming County, PA (top) and from 7931 ft. (mean VR_o = 3.20%) in the Encana Buda 1H well, Luzerne County, PA (bottom). Dark grey to black amorphous organic matter and solid hydrocarbons dominate the kerogen in the samples (inset photomicrograph).

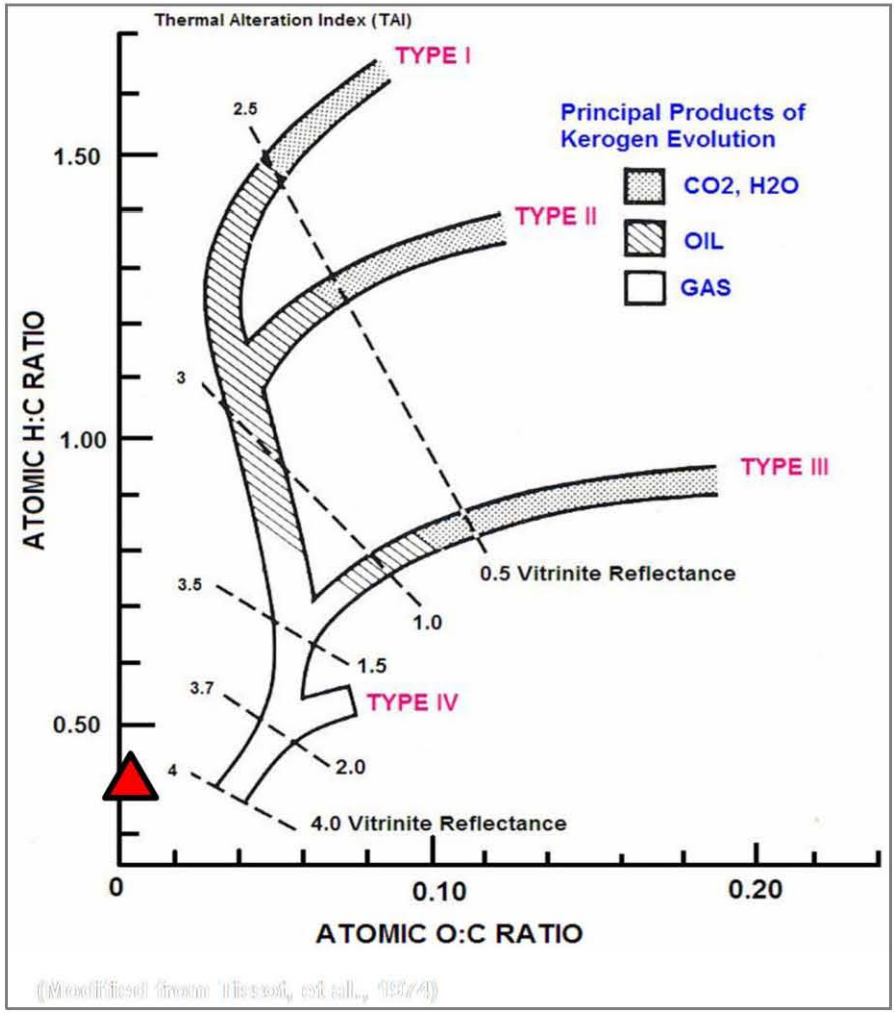

Figure 2. Van Krevelen diagram of H/C versus O/C of Marcellus kerogen from 7931 ft. in the Encana Oil and Gas Buda #1 well, Luzerne County PA. H/C = 0.4, O/C = 0.06, and kerogen $\delta^{13}C$ = -28.8‰. VR_o is 3.2% (see Figure 1). All measurements made at Weatherford Laboratories.

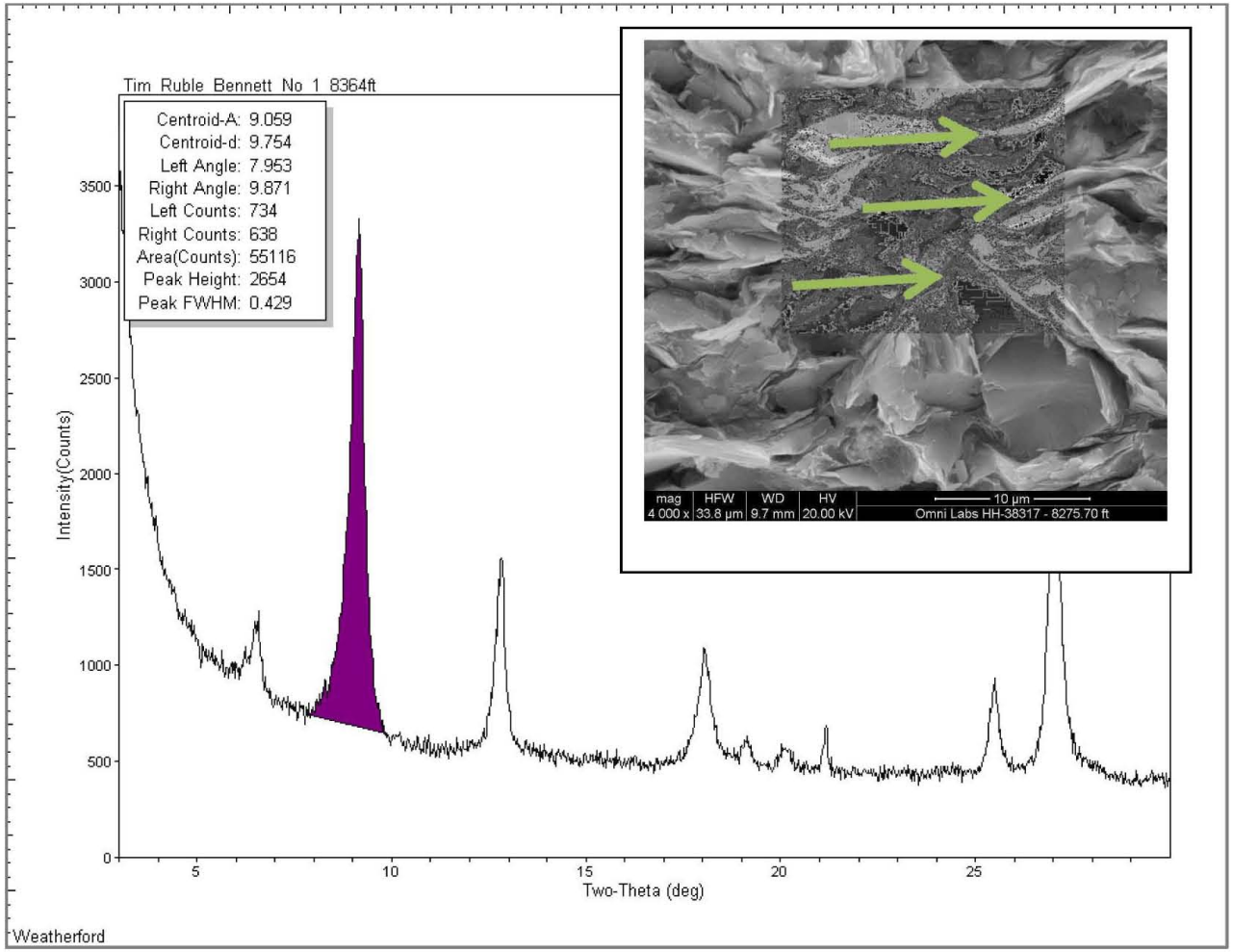

Figure 3. X-ray diffraction and SEM results for a sample of the Marcellus Formation from 8364 ft. in the Bennett #1 well, Sullivan County, PA. The Kübler Index of this sample is 0.428 and the mean illite crystallite index is 211 Å, values that indicate the Marcellus Formation is at the boundary between deep burial diagenesis and incipient anchizone metamorphism (Abad, 2008). Arrows point to the crenulated microfabric of illite in a Marcellus mudrock sample from the same core.

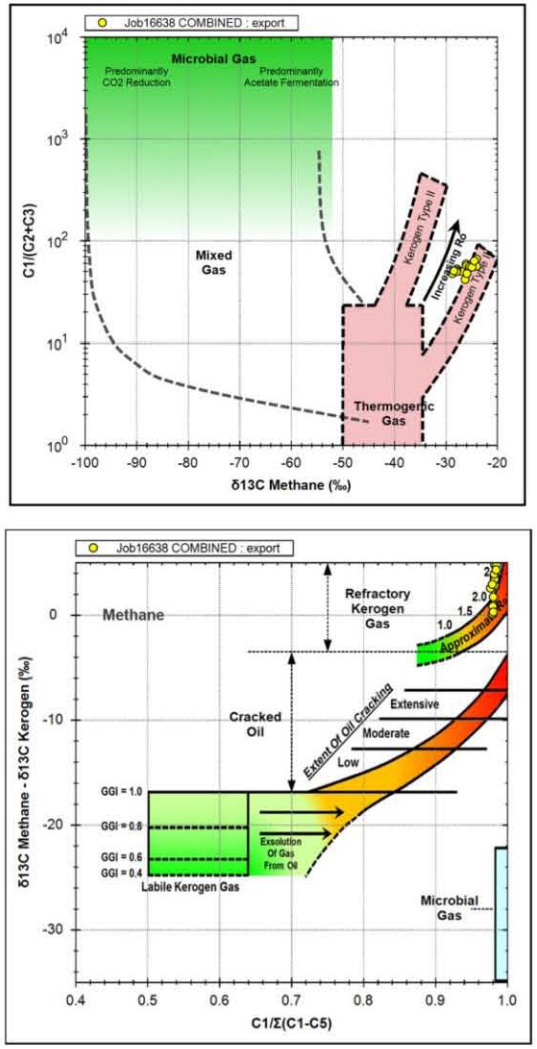

Figure 4. Bernard et al. (1978; top) and Clayton (1991; bottom) plots of methane $\delta^{13}C$ versus the relative amounts of higher hydrocarbons in Marcellus production gases in northeast Pennsylvania.

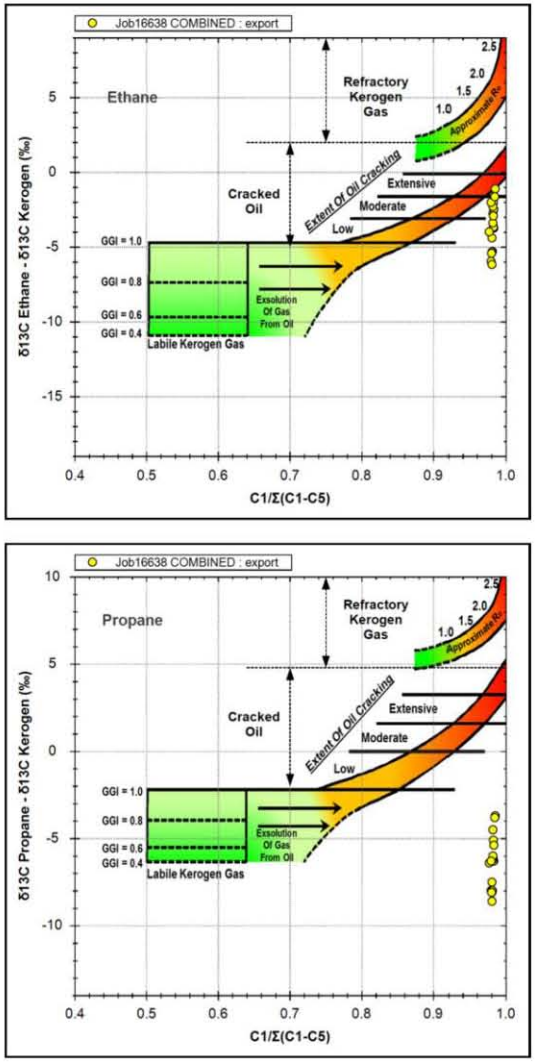

Figure 5. Clayton (1991) plots of ethane (top) and propane (bottom) $\delta^{13}C$ versus the relative amounts of higher hydrocarbons in Marcellus production gases in northeast Pennsylvania.

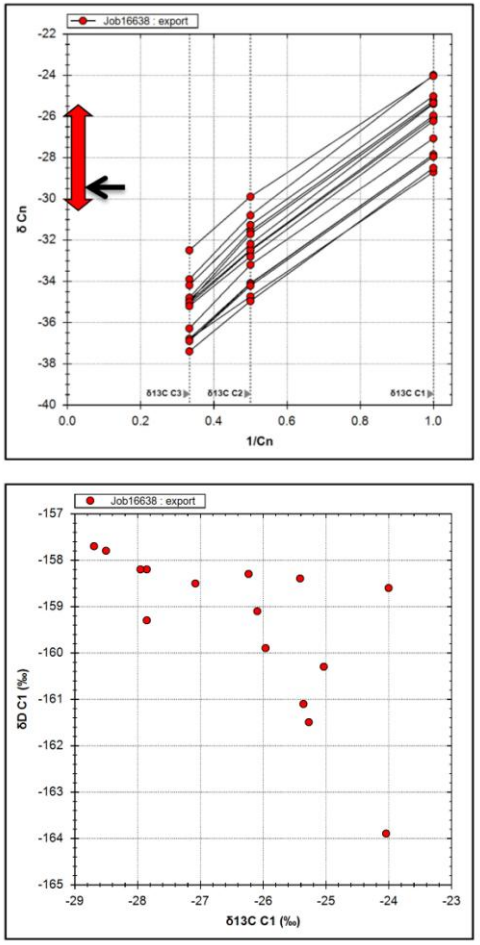

Figure 6. Top: Natural gas plot of Marcellus production gases from northeast Pennsylvania showing $\delta^{13}C$ isotope reversals with respect to carbon number. Red arrow indicates the reported range of Devonian black shale kerogen $\delta^{13}C$ in the Appalachian basin. Black arrow denotes Marcellus kerogen $\delta^{13}C$ measured in the Buda 1H well.
Bottom: $\delta^{13}C$ versus $\delta^{2}H$ of methane and ethane of the same Marcellus production gases showing hydrogen isotope reversals.

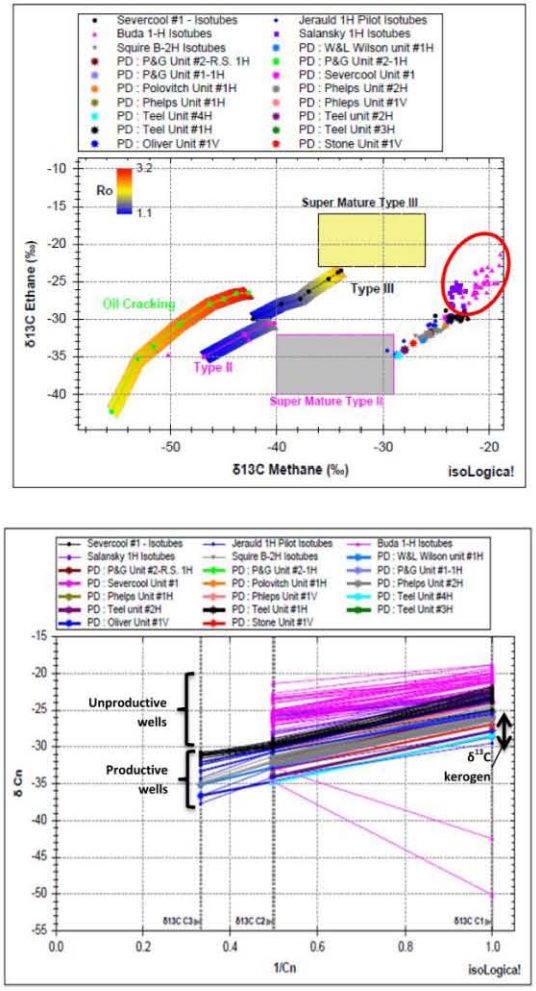

Figure 7. Top: $\delta^{13}C$ of methane versus ethane from production and mud gas samples of Marcellus hydrocarbons in northeastern Pennsylvania. Red circle encloses unproductive well samples.
Bottom: Chung plot of Marcellus production and mud gases from northeast Pennsylvania showing $\delta^{13}C$ isotope reversals with respect to carbon number.