Black Shale Diagenesis: Insights from Integrated High-Definition Analyses of Post-Mature Marcellus Formation Rocks, Northeastern Pennsylvania

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Thermogenic shale-gas produced from the Marcellus Formation in the northeastern most region of the play in Pennsylvania is post-mature. Petrologic and geochemical parameters suggest that Marcellus shale-gas reservoirs reached maximum burial depths and temperatures characteristic of zeolite and prehnite facies low-grade metamorphism. Although methane can continue to be generated and remain stable under these conditions in organic-rich sediments, this degree of burial diagenesis raises several critical questions regarding metagenetic gas generation and the reservoir quality of the rocks. Deep burial diagenesis implicates compaction, cementation, redox reactions involving hydrocarbons, transition metals, and water, water loss, and dissolution/re-precipitation processes. All of these processes may enhance or diminish reservoir potential by retaining or releasing gas from the system at high thermal maturities and by diagenetically altering shale rock properties.

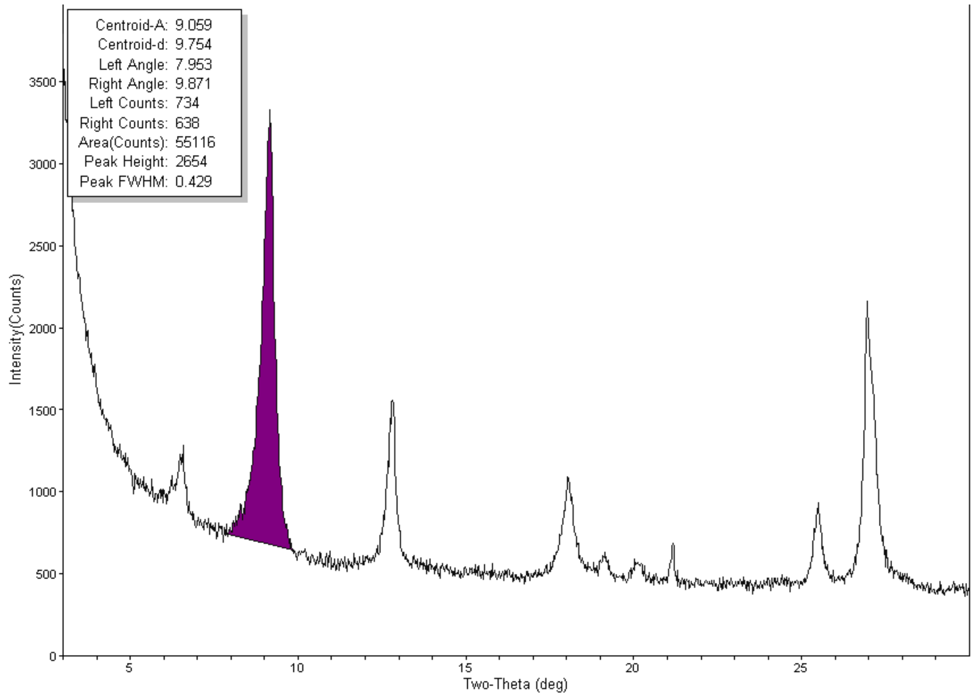
To help understand such post-mature thermogenic shale-gas reservoirs, we studied selected core samples of Marcellus Formation organic-rich mudstones from the Bennett #1 well in Sullivan County, Pennsylvania. We employed an integrated suite of high-resolution analytical techniques to determine quantitative mineralogy, measure quantity, quality and thermal maturity of organic matter, describe and classify porosity, and develop a diagenetic history of the Marcellus Formation in the region.

The organic-rich intervals of the Marcellus Formation in this core consist of laminated to thinly bedded or bioturbated, fossiliferous, calcareous, quartzose, mudstone and mudshale. The rocks are dominated by quartz, illite, and calcite. Quartz occurs as detrital silt and associated authigenic silica overgrowths, as a cryptocrystalline replacement of fossil materials, as pore-filling microquartz and megaquartz cements, and as patchy sheets of quartz cement platelets. Illite occurs as crenulated, flake-like detrital platelets and as thin flakes and filaments of pore-filling authigenic clay. The mean illite crystallite thickness is 211Å and the average Kübler index is 0.428 (Δº2θ); these parameters indicate that the shales reached the top of the low anchizone prehnite-pumpellyte metamorphic facies at maximum burial (Figure 1A). Calcite occurs as finely crystalline equant spar replacing allochems and filling fossil molds, as micron- and decimicron-sized crystals dispersed in clay and organic matrix, and as discontinuous parallel laminations of microspar and pseudospar. Minor amounts of anhydrite present in the rocks occur within these latter discontinuous laminations, often along with calcite. Additional minerals include feldspar, mixed-layer illite-smectite, chlorite, kaolinite, dolomite, apatite, pyrite, and graphite (Figure 1B). Whole pattern fitting and the Reitveld refinement method of a sample from 2550 m in the core quantify the abundance of graphite at 3 wt. percent, a value consistent with the measured total organic carbon (TOC) at that depth. The graphite was derived from carbonaceous organic matter during early metamorphism.

All of the organic-rich intervals meet the requirements for commercial thermogenic shale-gas reservoirs. Total organic carbon ranges from 0.58 to 11 wt. percent, with most of the cored interval having TOC between 2 and 4 wt. percent. The original kerogen was dominated by Type II organic matter. All thermal maturation parameters indicate the rocks reached the metagenetic zone of thermal maturity. Pyrobitumen appears to be abundant within the Marcellus rocks in the Bennett core. Microscopic and SEM examination along with 3D models derived from FIB-SEM analysis shows that pyrobitumen comprises a significant volume of the rocks (Figure 2). High-temperature pyrolysis of whole-rock samples, however, showed no response in the 600˚ to 800˚C region of the pyrogram where pyrobitumen is typically detected. Based on this lack of response, we suspected that the pyrobitumen was undetectable by the flame-ionization detector (FID) due to its highly aromatized graphitic nature. Most of the porosity in the Marcellus is associated with this graphitic pyrobitumen.

Early diagenesis of the Marcellus sediments mostly involved mechanical compaction and dewatering of the muds during burial to approximately 500 meters. Chemical compaction at greater burial depths was dominated by quartz cementation and clay mineral transformations which effectively destroyed most original porosity in the rocks. Organic porosity developed during late catagenesis and continued on into metagenesis at depths greater than 8 km where storage capacity continued to evolve within a pyrobitumen-graphite matrix. These observations, in conjunction with recent work on deep natural gas stable isotopes in the Appalachian basin, extend the potential for thermogenic shale-gas production into the early metamorphic realm.

Figure 1. X-ray diffraction results indicating (A) illite crystallinity indicative of the prehnite-pumpellyte metamorphic facies (Kübler index = 0.428) and (B) the presence of 3 wt. percent graphite in the Marcellus Formation, Bennett # 1 well core, 2550 m.



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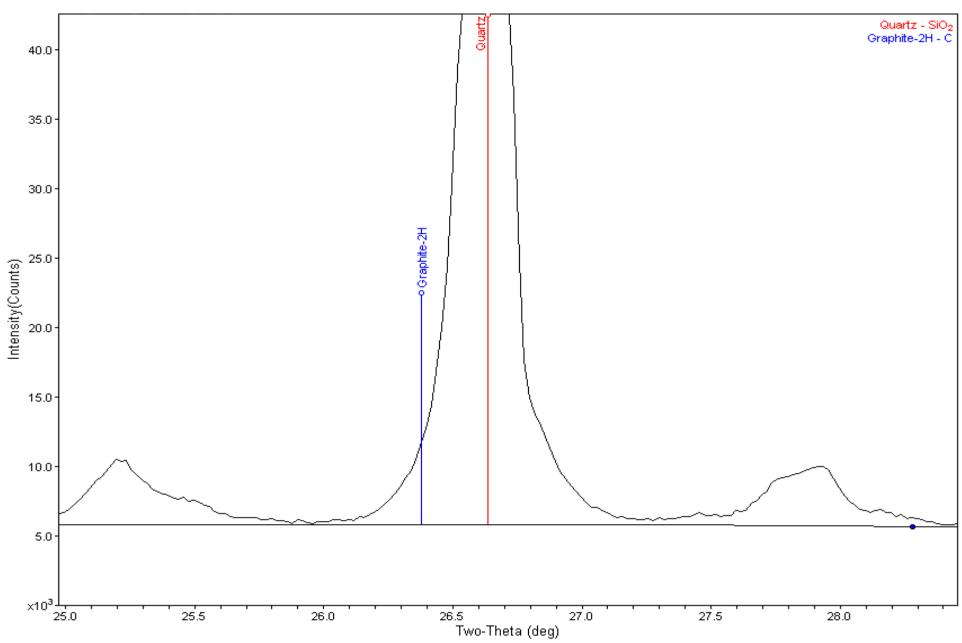

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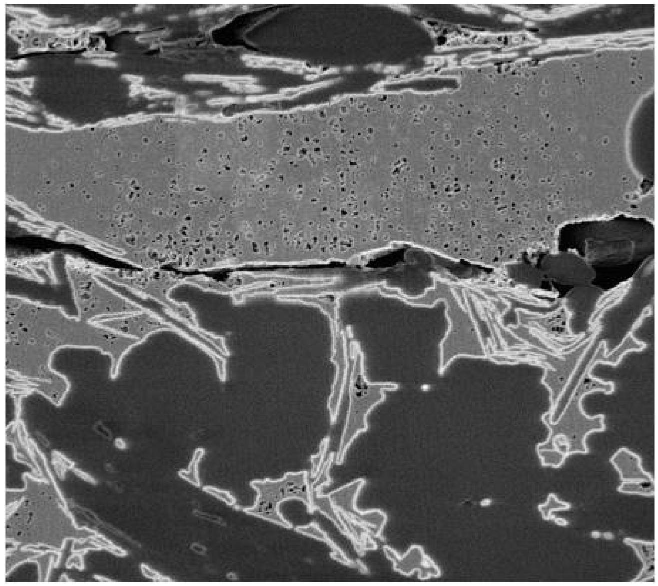
Figure 2. Electron microscopy of the same sample shown in Figure 1 showing (A) organic porosity formed within graphitic pyrobitumen matrix. TOC is 4.39 wt. percent. (B) 3D model of graphitic pyrobitumen (orange) and interconnected organic porosity (yellow) in the Marcellus. Horizontal field width is 8 μm.



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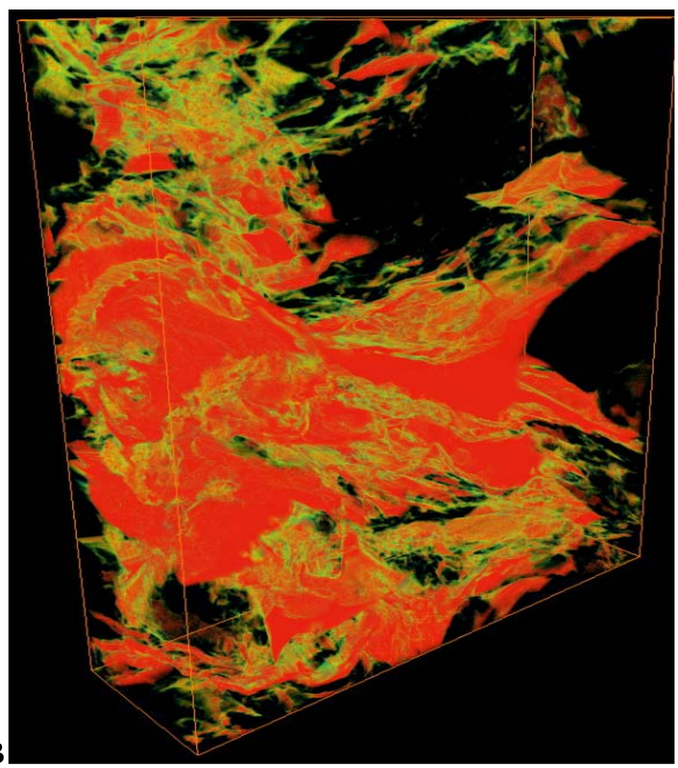

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