

## **Black Shale Diagenesis: Preliminary 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 northeastern Pennsylvania is post-mature. The reservoirs reached maximum burial temperatures characteristic of prehnite facies low-grade metamorphism. Although methane can be generated and remain stable under these conditions, this degree of burial diagenesis raises critical questions regarding metagenesis and reservoir quality. Late diagenesis implicates compaction, cementation, redox reactions involving formation fluids and transition metals, water loss, and dissolution/re-precipitation processes that may enhance or diminish reservoir potential.

Using a suite of high-resolution analytical techniques, we examined selected core samples from Sullivan County, Pennsylvania to characterize the reservoir and develop a diagenetic history of the Marcellus Formation in the region. The organic-rich intervals in these samples comprise mostly quartz, illite, and calcite. Quartz occurs as detrital silt, authigenic overgrowths, cryptocrystalline replacement of allochems, pore-filling microquartz and megaquartz, and patchy sheets of silica platelets. Illite occurs as crenulated detrital platelets and authigenic clay. The mean illite crystallite thickness is 211 Å and the average Kübler index is 0.428 confirming the shales reached the low anchizone prehnite-pumpellyite metamorphic facies. Calcite occurs as crystalline spar replacing allochems and filling fossil molds, as crystals dispersed in clay and organic matrix, and as discontinuous parallel laminations of microspar. Anhydrite occurs along with calcite in these laminations. Additional minerals include plagioclase, illite-smectite, chlorite, pyrite, and, remarkably, graphite. Whole pattern fitting and Reitveld refinement quantify the abundance of graphite.

TOC ranges from 0.6 to 11 wt. percent. The original kerogen was mostly Type II. Microscopy and 3D modeling show that pyrobitumen comprises a significant volume of the rocks. 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. We suspect that the pyrobitumen was undetectable by the FID due to its highly aromatized graphitic nature. Most porosity in the Marcellus is associated with this graphitic pyrobitumen.

Early diagenesis of Marcellus sediments involved mechanical compaction and dewatering of muds during burial to approximately 500 m. Chemical compaction at greater burial depths was dominated by quartz cementation and clay mineral transformations. 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 graphitic pyrobitumen matrix. These observations extend the potential for thermogenic shale-gas production into the metamorphic realm.