

A Tale of Two Shales: Time-Series Geochemistry of the Devonian Marcellus and New Albany Shale Formations

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Time-series carbon, nitrogen, and sulfur elemental and isotopic analyses of the Middle Devonian Marcellus Shale and Late Devonian New Albany Shale reveal strong stratigraphic variations related to changes in physical and chemical depositional environments. In the Marcellus Shale, collected from outcrop near Kistler, PA, peak abundances of carbon (up to 8 wt.%), nitrogen, and sulfur are recorded at the maximum flooding surface near the base of the ~120 meter thick unit, suggesting a target horizon for horizontal drilling. Carbon isotope compositions at the base of the Marcellus up to the MFS are low (ca. -36‰), and then step up 4‰ abruptly after the MFS followed by a gentle climb to more ¹³C enriched values through the rest of the succession. Sulfur isotope compositions vary widely, but define a broad positive excursion from near -30‰ at the base to near 0‰ in the middle and back again to -30‰ at the top. The wide variation in sulfur isotope compositions may reflect low sulfate concentrations in Devonian seawater, while the low $\delta^{13}\text{C}$ compositions leading up to the MFS suggests the possibility of a stratified water column and chemoautotrophic inputs of organic matter. Thereafter the more positive $\delta^{13}\text{C}$ signatures and variable sulfur isotope systematics in the Marcellus Shale are interpreted in terms of ventilation of the shallow marine environment. Core samples intersecting the New Albany Shale in Pike County, IN also reveal significant variations in the abundance and isotopic composition of carbon, nitrogen, and sulfur likely associated with strong environmental perturbations. While peaks in carbon, nitrogen, and sulfur occur near the base of the sampled interval, significant isotope shifts are not recognized until the top of the unit where there are coincident enrichments in ¹³C, ¹⁴N, and ³⁴S, with a remarkable positive excursion in sulfur isotope values of over 20‰. Previous studies have suggested that the carbon and nitrogen isotope shifts are a result of the transition from anoxic/stratified ocean water (where sulfate reducing bacteria could occupy the water column) to ventilated ocean water (where the bacteria would be forced to hide in anoxic sediment pore waters). In this case sulfate in pore water available to sulfate reducers would be diffusion limited, potentially leading to progressive ³⁴S enrichment.