ANAEROBIC BIODEGRADATION OF ORGANIC MATTER IN THE DEVONIAN ANTRIM SHALE

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The Antrim Shale, one of the largest unconventional natural gas reserves in North America, is a finely laminated, pyritic, organic-matter rich, thermally immature Devonian black shale located in the Michigan Basin. Previous studies have demonstrated an anaerobic microbial origin for this gas by measuring $\delta^{13}C$ fractionation between produced methane and DIC, as well as ΔD fractionation between co-produced methane and water. This geologic setting may resemble documented syntrophic communities in which high molecular weight organic molecules are biodegraded into acetate, CO_2 and H_2 with subsequent and rapid product removal by acetoclastic methanogenesis and CO_2 reduction with H_2. Unknown, however, are which suite of organic materials within the shale is most readily degraded by these communities, and how they provide the necessary substrates to support methanogenesis.

Investigations on anaerobic biodegradation of organic matter have focused on migrated petroleum, petroleum-contaminated aquifers, or deep marine sediments, and have established a quasi-stepwise elimination of increasingly complex and refractory classes of molecules. In this study, we investigate the geochemical imprint left by *in-situ* anaerobic decomposition of organic matter on a pair of archived Antrim Shale cores. Four samples were obtained: two from methane-producing and two from non-producing sections of the Michigan Basin. Variability in bulk geochemical parameters is greater within each core than between cores, suggesting that OM biodegradation and methanogenesis have not substantially impacted rock TOC content or kerogen elemental composition. However, analysis of *n*-alkanes and isoprenoids isolated from the cores reveals substantial degradation of saturated straight-chain and branched hydrocarbons within the methane-producing core. This is the first documented occurrence of *in-situ* anaerobic hydrocarbon degradation in an organic matter-rich sedimentary rock. These results suggest that these two classes of molecules may be especially available and susceptible to degradation by the microbial communities within the producing core. The anaerobic degradation of organic matter in sedimentary rocks holds implications for the viability of associated metabolic pathways in the absence of electron acceptors (O_2, SO_4^{2-}, or NO_3^-), as well as the subsequent distortion or removal of biomarker signatures important in petroleum exploration.