

## **The role of geocatalysis in abiogenic methanogenesis: evidence from biomarker transformations in a maturity transect of the Devonian New Albany Shale**

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The conventional paradigm for petroleum generation involves thermal cleavage of C-C bonds. However, there is convincing evidence that abiogenic methane production can occur in shale sequences whose thermal immaturity precludes catagenetic processes. These findings prompt evaluation of the role of catalytic methanogenesis in source rocks and assessment of its importance in the formation of unconventional gas reservoirs. Our studies focus on characterization of the molecular and isotopic composition of organic matter (OM) in the Devonian New Albany Shale (NAS) to examine evidence for the role of geocatalysis in the diagenetic transformation of OM. Several of the reactions involved in structural rearrangement and isomerization of key biomarkers are known to be catalyzed by clay minerals (e.g., montmorillonite, illite), prompting investigation of these target compounds in a suite of nine NAS samples covering a broad maturity spectrum with vitrinite reflectance values ranging from 0.39 to 1.42 %. For the two least mature samples, various biomarker indices based on diasterenes, diasteranes, steranes and hopanes confirm the occurrence of diagenetic reactions involving clay-catalyzed molecular transformations. The NAS sample suite also shows a progressive decrease with maturity in the chain-length distribution of isorenieratane homologs, a trend consistent with expected products of heterogeneous catalysis reactions. Determination of such compositional differences in biomarkers along the maturity transect serve as a baseline for evaluating results from low-temperature laboratory simulation experiments (60-100 °C) emulating those that generated abiogenic methane. Thus, utilization of evidence from diagenetic molecular transformations, especially when coupled with information on their isotopic compositions, can provide data that aid understanding of the mechanisms of geocatalytic shale gas generation from OM.