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Appalachian Basin Devonian Shales—Regional Organic Geochemistry and Hydrocarbon Genesis

Small amounts of methane were formed in the Devonian black shales of the Appalachian basin during early, low-temperature stages of diagenesis, but most of the natural gas was generated by thermochemical conversion of solid and liquid organic matter during later, higher temperature stages. At any given locality, the amount of methane generated in the Devonian shales was determined by the amount of organic matter originally present and the extent of the transformation process; transformation was determined by the maximum depth of burial and subsurface temperature to which the rock was subjected. The transformation process was halted in its early stages in rocks of the western part of the basin, but approached completion in the east. The degree of transformation is indicated by systematic, west-to-east changes in the geochemistry of gas ( $\delta^{13}\text{C}$  of methane changes from  $-55$  to  $-25\%$ ), in the extractable organic matter (saturated hydrocarbons evolve from an immature to an incipiently metamorphosed assemblage), and in the solid organic matter (atomic H/C changes from 1.1 to 0.4).

The hydrocarbon geochemistry of oils derived from Devonian shales also changes systematically. On the basis of correlations with Devonian source rocks, oils on the western margin of the basin in the Mississippian Berea Sandstone must have been generated in and migrated from shales located about 100 km to the east. In contrast, the easternmost oil occurrences in lenticular sandstones were products of very local migration from adjacent shales. In the eastern part of the basin, the advanced stage of thermal maturity of both oils and extractable hydrocarbons in adjacent source rocks suggests that hydrocarbons, both in the reservoir and source rock, underwent parallel thermal maturation after migration and emplacement of the oil.

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Geochemical Effects of Early Diagenesis of Organic Matter, Sulfur, and Trace Elements in Devonian Black Shales, Appalachian Basin

The relation between organic carbon and sulfides in Devonian black shales can be used to identify these units as having been deposited in ancient marine euxinic environments. Based on the modern Black Sea analogy, the euxinic environment is indicated by a positive intercept for sulfur at zero organic carbon on a carbon-sulfur plot. Furthermore, the slope of the plot can be related to position in the basin and to deposition rate. Sulfur-isotope ratios of fine-grained, early diagenetic iron sulfides are typically light, indicating that a majority of the sulfide formed in the water column and near the sediment-water interface. Isolated heavier values are observed, however, which demonstrate that sulfide formation persisted into later diagenesis at least locally. Carbon and oxygen isotopes of carbonate minerals

show the effects of both early diagenesis of organic matter by micro-biological processes and later redistribution of carbonate into veins and nodules. A range of  $\delta$ -values suggests that anaerobic oxidation of organic matter is more important than methane generation for carbonate diagenesis. Trace-element abundances (U, Mo, V, Ni, Hg) are related to organic-carbon and sulfide content. These relations can be explained by invoking an organic-concentration mechanism and aqueous-sulfide protection and redistribution processes. Trace-element/organic and trace-element/sulfide ratios do not change greatly in the basin, although deposition rates vary by more than one order of magnitude.

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Stratification Types in Intertidal Sediment, Willapa Bay, Washington

Intertidal areas contain a number of subenvironments, many of which generate distinctive types of internal structures. Experimental studies conducted over a 5-year period in intertidal areas in Willapa Bay, Washington, indicate the origin of different types of structures. The experiments consisted of establishing a datum by scattering fine particles of lead over the surface in six subenvironments and repetitively coring the experimental plots at daily, seasonal, or yearly intervals. The subenvironments studied include the upper and middle accretionary bank of a tidal runoff channel, the uppermost bank of a tidal river, muddy tidal flats covered by (1) *Zostera* and (2) low mounds of blue-green algae, and sandy tidal flat.

The internal structure in each subenvironment depends on the dominant processes and on the rate of sedimentation. The middle accretionary bank of the runoff channel accreted at a rate of more than 5 cm per month during the summer of 1976; the stratification reflects the semidiurnal ebb and flood of the tides. On the upper accretionary banks of the runoff channel and on the tidal river, the sediment responds more to seasonal variations, accreting during the summer and eroding during the winter. On the uppermost bank of the tidal river, these processes were recorded over a 5-year period in 8 cm of alternating mud (summer) and fine sand (winter) laminae.

Very little net accumulation of sediment occurred on the tidal flats. The *Zostera*-covered muddy flat and the sandy flat are dominated by bioturbational processes and no lamination is preserved. On the algal mounds, the binding of the sediment by algal filaments and the inhibition of faunal activity by oxygen depletion combine to produce well-defined thin laminations. Repeated sedimentation and algal growth produce stratification similar to the upper accretionary bank of the tidal river.

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Relation of Depositional Facies and History to Hydrocarbon Generation in New Albany Shale Group (Devonian-Mississippian) of Illinois