

## **Origin and Distribution of Natural Gas in Devonian Black Shales, Northern Appalachian Basin**

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Geochemical and microbial studies of Devonian black shales in the Michigan and Illinois basins have shown that methane is generated dominantly by microbial processes at the shallow basin margins and by thermogenic processes at depth. Distinguishing the origin of natural gas is important for exploration, production, and resource assessments. The adjacent Appalachian Basin contains age-equivalent organic-rich shales with copious natural gas resources. This on-going study evaluates the origin and distribution of natural gas and formation water geochemistry in Devonian shales across the northern Appalachian Basin margin. Gas samples were collected from oil and gas wells producing from Devonian formations in NY, OH, PA, and Ontario (Spring 2007 and 2008), and analyzed for composition, and C and H isotopes of CH<sub>4</sub>, C<sub>2</sub>, and CO<sub>2</sub>. Co-produced formation waters were analyzed for cation, anion and isotope (O,H,C) chemistry. Chloride concentrations generally increase with depth towards the basin center from less than 1.3 mole/L to levels inhibitory for methanogenesis (>2 mole/L). Positive  $\delta_{13}C_{DIC}$  values (up to 27‰ VPDB), low alkalinities (<12 meq/kg), and low SO<sub>4</sub> concentrations (<5 mmole/L) may indicate early stages of methanogenesis and/or an open hydrologic flow system. Gas samples have low gas wetness values (4-25%), and enriched  $\delta_{13}C$  (>-50‰ VPDB) and  $\delta_D$  values of CH<sub>4</sub>, which increase with depth and thermal maturity. There is no correlation between  $\delta_D$  values of CH<sub>4</sub> and co-produced waters, as would be expected for microbial fractionation. The combined water and gas results suggest a dominantly thermogenic gas origin with some potential contribution from microbial methanogenesis.