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Integrating CO_2, H_2S, N_2, and Noble Gas Data with Post Mature Hydrocarbon Geochemistry in Deep Ordovician and Silurian Reservoirs, Appalachian Basin, Eastern USA

Christopher D. Laughrey
Weatherford Laboratories, Golden Colorado, USA

Deep (>2 km) fractured dolostone and tight sandstone reservoirs of Ordovician and Silurian age, and their Ordovician source rocks (Utica Formation and equivalents) are important hydrocarbon resources in eastern North America. These reservoirs produce thermally post mature non-associated natural gas from strata that was buried to depths of 8 - 13 km in late Permian time. Recently published data and models suggest that these hydrocarbon gases have undergone some degree of subsurface alteration and destruction, and their unique stable isotope geochemistry may signal limits to the stability of hydrocarbon gases in deep basins (Burruss and Laughrey, 2010). These same reservoirs produce variable amounts of CO_2, H_2S, and N_2 gases which are sometimes present in concentrations high enough to be problematic (Laughrey and others, 2004; Laughrey and Kostelnik, 2007). Combined stable isotope geochemistry of the non-hydrocarbon and hydrocarbon gases, along with specific noble gas data, constrains the genetic origins of CO_2, H_2S, and N_2 in these rocks. An understanding of the origins of these non-hydrocarbon gases supports published interpretations that these reservoirs are approaching the maximum limit of stability of hydrocarbons in the deepest areas of the plays and helps to predict economic and safety risks associated with high H_2S and N_2.

The reservoirs of interest in this discussion are Middle Ordovician Black River Formation dolostones, Lower Silurian Tuscarora Formation sandstones, and organic-rich clastic mudrock/carbonate mudstones and wackestones of the Middle Ordovician Utica and Point Pleasant Formation source rocks. The Black River Formation produces natural gas from fractured hydrothermal dolomite across much of the Appalachian basin. In the deepest parts of the play (2.2 – 4.2 km) the hydrocarbon gases are dry and isotopically heavy. Wetness ranges from 0.38 to 1.08 percent and $\delta^{13}CH_4$ ranges from -34.85 permil to -26.02 permil. All methane through propane samples exhibit carbon isotopic reversals with $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$, and many show reversals in hydrogen isotope trends as well with $\delta^2H_{CH4} > \delta^2H_{C2H6}$. These gases exhibit a negative correlation between δ^2H and $\delta^{13}C$ of methane, with hydrogen becoming isotopically lighter as the $\delta^{13}CH_4$ becomes heavier. Burruss and Laughrey (2010) interpreted these trend to be a combined result of thermogenic gas mixing and Rayleigh fractionation of ethane and propane, the latter process being driven by redox reactions between hydrocarbons, transition metals, and formation water at temperatures on the order of 250° - 300°C.

Although thermogenic methane is the principal component of the deep Black River Formation gases, CO_2, H_2S, and N_2 warrant consideration. Carbon dioxide ranges from 0 to only 0.46 mole percent in the gases. The $\delta^{13}CO_2$ compositions of these gases ranges from -3 to -6.7 permil, relatively heavy values characteristic of CO_2 generated by the thermal destruction of carbonate rocks (Hunt, 1996). These data negate the potential role of water reforming followed by Fischer-Tropsh synthesis of hydrocarbon gases as a possible cause of the carbon isotope reversals observed in these reservoirs (see Tang and Xia, 2010).

Hydrogen sulfide occurs in only one sample, but its concentration (0.51 mole percent), presence in the most basinward portion of the play, and association with high N_2 (14.14 mole percent) was enough to hinder deeper exploration to the southeast. The $\delta^{34}S$ of the H_2S is +14.7 permil, which suggests thermochemical reduction of sulfate (TSR) occurred in the reservoir. Additional evidence for a TSR interpretation of the H_2S includes the presence of late-formed pyrobitumen with sulfur inclusions, replacement of $CaSO_4$ by calcite, reprecipitation of calcite and dolomite with Ca from dissolved sulfate minerals, abundant authigenic metal sulfides, and anhydrite and sulfur concentrated on stylolite surfaces. The well with this high H_2S gas also has the highest N_2 concentration measured in the Black River hydrothermal dolomite play, 14.14 mole percent. Hydrocarbon oxidation during TSR likely concentrated the relative fraction of N_2 in the reservoir.

Nitrogen ranges from 0.10 to 14.14 mole percent in the Black River gases, with $\delta^{15}N$ values of +0.4 to -10.2 permil. The observed isotopic compositions are consistent with an origin from highly mature sedimentary organic matter with a possible deep crust or mantle component in some samples.

Noble gas data from the Black River reservoirs reveal variable flux of both mantle and radiogenic crustal gases. *R/Ra* in most of the gases ranges from 0.01 to 0.02 suggesting they contain helium of crustal origin. *R/Ra* in gases from the northernmost and shallowest field in the play, however, ranges from 0.109 to 0.196 indicating that a minor mantle gas component (1.2 to 2.3 percent) is mixed with the dominant crustal gases. The clear association of deep-seated basement faulting and this gas field's structure explains the minor flux of mantle helium into the reservoir. The generally low $^{3}He/^{4}He$ ratios of the Black River gases refute published claims of an abiogenic deep crustal/mantle origin for these hydrocarbons (Rasmussen and others, 2003). The Black River gases have low ^{20}Ne concentrations with notable amounts of ^{40}Ar***** and negligible atmospheric contamination. The $^{4}He/^{40}Ar$***** ratios approach radiogenic/nucleogenic production ratios and these trends, in conjunction with the observed low $^{20}Ne/^{36}Ar$ ratios, reflect high formation temperatures at maximum burial. The combination of isotopically heavy hydrocarbons and light noble gases indicates that diffusive leakage of isotopically light methane from the reservoirs was not important in these rocks and cannot be cited to explain the observed carbon isotope reversals as suggested by some workers (Prinzhofer and Huc, 1995).

Much like the Black River Formation, the Tuscarora Formation produces natural gas from fractured reservoirs in deep (> 2 km) parts of the Appalachian basin. The gases are dry, isotopically heavy ($\delta^{13}CH_4$ = -37.4 permil to -27.68 permil), and all methane through propane samples exhibit carbon and hydrogen isotopic reversals. Nitrogen ranges from 1.1 to 16.19 mole percent in our samples, but higher amounts up to 35 mole percent are reported in the basin (Avary, 1996). Measured $\delta^{15}N$ ranges from -10.9 to -11.4 permil. *R/Ra* is 0.015 to 0.021 at the Marshlands field in north central Pennsylvania indicating associated He is of crustal origin. The $^{4}He/^{40}Ar$***** ratios are near radiogenic/nucleogenic production ratios typical of post mature gases and $^{20}Ne/^{36}Ar$ ratios (0.975 to 1.194) support this interpretation, although some gas migration effects may be evident.

The Utica and Point Pleasant Formations are the established petroleum source rocks for the Black River and Tuscarora reservoirs, and are targets for thermogenic shale-gas exploration in the eastern USA. Deep (> 2 km) Utica and Point Pleasant gases are dry (> 96 mole percent CH_4), isotopically heavy ($\delta^{13}CH_4$ = -26.97 to -27.18 permil), and exhibit complete reversals in their carbon and hydrogen isotope composition. Carbon dioxide makes up only 0.87 to 1.08 mole percent of the gas and the $\delta^{13}CO_2$ of these gases is -0.39 to -0.9 permil, confirming that thermal destruction of carbonates during deep burial is the source. The N_2 content of the Utica and Point Pleasant gases is low (0.57 to 0.66 mole percent) and $\delta^{15}N$ is -9.2 permil, a value consistent with an origin from highly mature organic matter (Zhu and others, 2000). The low N_2 content of the gases in the source rocks, higher and variable N_2 content in associated carbonate and clastic reservoirs, comparable $\delta^{15}N$ contents, and an arguable connection to H_2S and TSR in the Black River Formation suggest that N_2 in the conventional traps may well be concentrated by processes that destroy hydrocarbons. Significant authigenic pyrite in these rocks likely sequesters most of the H_2S of deep TSR origin. *R/Ra* is 0.019 – 0.022 in the deep Utica and Point Pleasant reflecting the crustal He source, and combined use of $^4He/^{40}Ar$***** and $^{20}Ne/^{36}Ar$ ratios again shows high formation temperatures at maximum burial.

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