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Isotope reversals and rollovers: The last gasp of shale gas?

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Several studies of the stable isotopic composition of gases as a function of depth, thermal maturity, and gas wetness in unconventional shale gas accumulations have identified features described as isotope reversals and rollovers. In some cases, claims have been made that these features identify the most productive intervals within shale gas systems. However, isotopic rollovers and reversals are poorly defined and no published geochemical studies of shale gas accumulations clearly describe these phenomena.

During studies of unconventional gas accumulations in strata of Silurian and Ordovician age in the northern Appalachian basin we have observed several types of reversals of stable isotopic compositions and rollover of the isotopic composition of ethane with decreasing wetness and with increasing depth. The gases were generated from organic carbon-rich mudrocks in the Ordovician Utica Formation, a potential shale gas reservoir. We developed a model to explain the isotopic characteristics of the gases, including rollover, based on mixing of normal, oil-associated gas (OAG) with a non-associated gas (NAG) containing a relatively low concentration of isotopically light ethane. In the most deeply buried parts of the gas productive system, high thermal maturity (CAI > 5, T > 250°C) drove cracking of higher hydrocarbons to the extent that the isotopically light ethane ("rollover ethane") was progressively destroyed, causing the composition to become isotopically heavier as the fraction of ethane decreased (Rayleigh-type fractionation). Furthermore, the hydrogen isotopic composition (δ^2H) of methane in OAG and NAG reservoirs at depths < 2600 m show a normal trend that increases with depth, but then reverses and δ^2H decreases with increasing depth for samples in reservoirs at depths > 2600 m. The hydrogen isotopic reversal appears to be be caused by exchange of hydrogen between methane and formation water during organic-mineral oxidation-reduction reactions involving iron. Similar reactions may cause the Rayleigh-type fractionation of ethane. Simultaneously with these phenomena, we observe complete reversal of the carbon isotopic compositions of the gases, such that $\delta^{13}C$ methane > $\delta^{13}C$ ethane > $\delta^{13}C$ propane. We interpret these observations to indicate that at the highest levels of thermal maturity in the Appalachian basin, the carbon and hydrogen isotopic reversals show that the system has gone beyond "ethane rollover" to a stage of hydrocarbon destruction. If this is correct, then shale gas explorationists must exercise care in interpretation of gas isotope reversals and rollovers because they may indicate the end ("the last gasp") rather than the beginning of high productivity shale gas plays.