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Identifying Links Between Hydrocarbon Stable Isotopes, Noble Gases, and Tectonic Processes in Marcellus Formation (Devonian) Natural Gases, Appalachian Basin USA

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The stable isotopes of natural gas components provide information regarding the origin, thermal history, migration, and mixing of fluids in sedimentary basins. Isotopes also reflect fluid responses to tectonics, particularly with regard to dynamic changes in fluid temperatures, pressure, and chemistry during burial, uplift, folding, and faulting. Changing fluid conditions, manifested in isotope data, are particularly evident in Middle Devonian shales at the Allegheny structural front in the central Appalachian basin. Fluctuations in hydrocarbon and noble gas geochemistry indicate alterations in fracture connectivity and fluid communication associated with tectonic processes.

Marcellus Formation gases produced at the Allegheny front in Pennsylvania are overmature. Hydrocarbons exhibit carbon isotope reversals ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$). These reversals result from secondary alteration effects during deep burial. Hydrogen isotope reversals ($\delta^2H_{C1} > \delta^2H_{C2}$), ostensibly due to high-temperature hydrogen isotope exchange between CH_4 and water, characterize these gases. However, some gases produced at the structural front initially exhibit normal hydrogen isotope distributions ($\delta^2H_{C1} < \delta^2H_{C2}$) which shift to reversed distributions over production time. One plausible explanation for these δ^2H variations is retrograde isotope exchange during cooling of subsurface temperatures accompanying episodes of uplift. Published experimental evidence shows that the rate and direction of hydrogen isotope exchange between methane and water is sensitive to the rate of exhumation during uplift, particularly as the rocks pass upward from maximum burial through temperatures between 130 and 160°C. Hydrogen isotope trends in some gases may reflect uplift and cooling variations related to individual structures and to the kinematics of discrete faults and folds. Noble gas systematics support this interpretation.

Noble gases also facilitate the assessment of open system/closed system conditions across fault-controlled reservoir compartments. Congruent $^{20}Ne/^{36}Ar$ and $^{4}He/^{40}Ar^*$ trends define mixing between ASW and diffusional, light isotope-enriched patterns which identify fractionations associated with fluid migration. $^{4}He/CH_4$ - $^{20}Ne/^{36}Ar$ trends disclose advective fluid migration patterns similar to those observed in conventional reservoirs sourced by the Devonian shales in the region. The distributions of ASW noble gases discriminate the extent of closed versus open system conditions in specific structural compartments.