Position-Specific Isotope Compositions of Propane from Unconventional Natural Gases of Woodford Shale, OK

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The formation of natural gases and subsequent processes in the subsurface are of great interest for scientific and economic purposes. Conventional, bulk carbon and hydrogen isotopes of natural gases have been widely used to address these processes, but our understanding is still limited. Recently, new dimensions of information on the stable isotopes of natural gases have been explored, including clumped isotopes and position-specific isotope compositions.

We have developed a quantitative NMR method to determine both hydrogen and carbon position-specific isotope compositions of propane and other light hydrocarbons. This new technique is capable of analyzing intact molecules of light hydrocarbons with high-precision ($<\pm1$ and $<\pm10$ ‰ for position-specific carbon and hydrogen isotope compositions, respectively). The accuracy of the method has also been demonstrated by ^{13}C-labeled compounds and an inter-laboratory comparison of a light alkane.

A set of 15 natural gas samples have been collected from an unconventional natural gas reservoir from the late Devonian to early Mississippian Woodford shale in the Arkoma Basin in Oklahoma. The fraction of propane was separated and purified chemically and cryogenically. Our results show that the values of $\Delta_{center\text{-}terminal}$ ($=\delta_{center} - \delta_{terminal}$) vary relatively small for carbon isotope compositions (+1.7 to +4.8 ‰), but vary widely for hydrogen isotope compositions (-56 to +26 ‰). Combining these data with δ_{bulk} values from IRMS method, our data revealed that δ^2H_{center} values of the propane increased significantly (80 ‰) with the maturity of the Woodford shale (R_o=0.9 to 1.6), while $\delta^2H_{terminal}$ values remain nearly constant. The both values of $\delta^{13}C_{center}$ and $\delta^{13}C_{terminal}$ increased very slightly (1-2 ‰). The contrasting patterns of the carbon and hydrogen isotopic compositions of the terminal and central positions are likely caused by increasing hydrogen isotope exchange between the central H of propane and water during deep burial in the basin. These results clearly demonstrate the potential of position-specific isotope analysis of natural gases.