

Geochemical Interpretation on Clumped and Position-Specific Isotopes in Natural Gas

Daniel Xia¹, Yongli Gao²

¹Apache Corporation; ²UTSA

9.29.2020 - 10.1.2020 – AAPG Annual Convention and Exhibition 2020, Online/Virtual

Abstract

In the past decade some special isotopic compositions of hydrocarbon gas have been measurable and frequently reported, including the clumped isotopic compositions of methane ($\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$), clumped isotopic composition of ethane ($\Delta^{13}\text{C}_2\text{H}_6$), and position-specific (“intra-molecular”) carbon or hydrogen isotopic compositions in propane or normal butane. As for the interpretation on the data measured from natural gas, most previous works assumed isotopic equilibria, so that these special isotopic compositions can be applied as “geothermometers” of oil and gas accumulations. This assumption contradicts the well-established understanding on petroleum systems, that is, the generation and cracking of hydrocarbons are kinetically controlled (both time and temperature are governing factors), non-equilibrated and continuous processes. There is no single temperature point of hydrocarbon generation, migration or accumulation. The concepts of “geothermometers” and “equilibrium temperature” are inapplicable to an oil or gas reservoir. To understand the dependence of clumped and position-specific isotopic compositions on geological and geochemical factors, this work conducts chemical and numerical analyses on isotope distributions during the formation and alteration of oil and gas reservoirs, including biogenic and thermal generation, thermal cracking, and thermochemical sulfate reduction. Because hydrogen atoms in a hydrocarbon molecule come from two precursors during its generation reaction, isotopic compositions involving hydrogen/deuterium (bulk hydrogen isotopic composition δD , clumped isotopic compositions $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$, and position specific δD) demand more kinetic analysis on reaction steps and have more complicated fractionation patterns than the carbon isotopic composition

$\delta^{13}\text{C}$. Results show that major factors controlling special isotopic compositions are still the same as those controlling conventional ones ($\delta^{13}\text{C}$ and δD) of hydrocarbon gases: precursor, thermal history, and accumulating efficiency (continuous vs. instantaneous accumulation). Temperature is not the only factor determining specific isotopic compositions. Clumped and position-specific isotopic compositions may reverse at high thermal maturity, the same as $\delta^{13}\text{C}$ of ethane and propane, and are even less possible to be applied as “geothermometers”. Overall, chemical kinetic analyses and numerical simulations are more demanding to interpret clumped or position-specific isotopic compositions than to interpret $\delta^{13}\text{C}$ of natural gas. While these special isotopic compositions may provide more reaction details during hydrocarbon generation, preservation and alteration, oversimplified assumptions and correlations should be avoided during the interpretation.