

Methane Clumped Isotope Constraints on the Equilibrium and Kinetics of Unconventional Gases

GUANNAN DONG^{1*}, HAO XIE¹, MICHAEL FORMOLO²,
MICHAEL LAWSON³, ALEX SESSIONS¹, JOHN EILER¹

¹Division of Geological and Planetary Sciences, California
Institute of Technology, Pasadena, CA 91125, USA
(*correspondence: gdong@caltech.edu)

²ExxonMobil Upstream Research Company, Spring, TX
77389, USA

³ExxonMobil Exploration Company, Spring, TX 77389, USA

Thermal cracking of kerogen and other organic matter is widely recognized as the primary source of non-biogenic natural gas. This chemistry is generally considered to be irreversible, involving isotopic fractionations controlled by kinetic isotope effects. However, the clumped isotopologues ($^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$) of most thermogenic methane are consistent with equilibrium at the temperatures of gas generation. Clumped isotope thermometry constrains the temperature of formation/equilibration when methane forms in thermodynamic equilibrium. However, two cases are known where nonequilibrium clumped isotope contents are observed in thermogenic methane: unconventional oil-associated gases and coal pyrolysis experiments. It is hypothesized that the non-equilibrated signature may be a result of a specific formation mechanism, with cracking of aliphatic hydrocarbons as the leading guess.

In order to test this hypothesis, we performed controlled pyrolysis experiments on an oil-analog aliphatic compound, n-octadecane ($\text{C}_{18}\text{H}_{38}$). We characterized the gas chemistry, carbon and hydrogen isotope, and $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ compositions of the products. We also examined the carbon and hydrogen isotope, and $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ compositions of several suites of unconventional gases from Marcellus, Haynesville, Eagle Ford and Bakken formations.

Results to-date show that pyrolysis products have $^{13}\text{CH}_3\text{D}$ composition relatively close to equilibrium at the experimental temperature whereas $^{12}\text{CH}_2\text{D}_2$ are highly depleted than expected for equilibrium. Similarly, unconventional oil-associated gases from Eagle Ford and Bakken formations show depleted $^{12}\text{CH}_2\text{D}_2$ abundance.

We fit an isotope-enabled reaction model to these results, demonstrating that the ‘combinatorial effect’ can explain the inconsistency between the behaviors of $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$. The close-to-equilibrium $^{13}\text{CH}_3\text{D}$ composition and highly-depleted $^{12}\text{CH}_2\text{D}_2$ composition can be a novel signature for secondary cracking of oil and wet gases in nature.