

The clumped and position-specific isotope geochemistry of higher order (C2+) hydrocarbons

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The stable isotopes of H and C constraint the origins of hydrocarbons, but are often insufficient to uniquely constrain source substrates, conditions and mechanisms of generation, extents and conditions of secondary destruction, and proportions of endmembers in mixed gases and oils. And, some variables of interest are not recorded in any recognized way by stable isotopes (e.g., storage temperatures and times). Intramolecular isotopic properties— ‘clumped’ and position specific isotope compositions — offer additional constraints that may advance our understanding of these issues.

Recent innovations in high-resolution mass spectrometry and NMR spectroscopy have enabled site-specific C isotope analyses of propane and higher order hydrocarbons, site-specific H isotope analysis of propane, and ¹³C-D, ¹³C-¹³C and D-D ‘clumping’ in methane, ethane and propane. The clumped isotope geochemistry of methane is relatively well established in the recent literature and will be reviewed in another talk in this session. We focus instead on recent and ongoing advances in understanding of the C2+ n-alkanes.

¹³C-¹³C clumping in ethane exhibits ranges many times greater than predicted equilibrium effects. Suites of related gases exhibit correlations between ¹³C-¹³C clumping and gas wetness that suggest much of this range is created by an unrecognized form of secondary ethane cracking.

Site specific ¹³C in propane (i.e., the difference in $\delta^{13}\text{C}$ between terminal and central sites) in natural gases and experimental products indicate ranges in composition correlated with gas maturity, but following unexpected patterns of terminal vs. central position $\delta^{13}\text{C}$. These signals may be explained by partial cracking of propane at higher maturities, or by variable sampling of substrates that differ in site-specific C isotope structures.

Site-specific D/H ratios and ¹³C-D clumping in C2+ alkanes potentially provide geothermometers that likely differ in their blocking temperatures; if so, they will permit reconstruction of temperature-time histories spanning cracking, transport and storage conditions. We will provide an overview of this concept and report initial results of experiments constraining the blocking temperatures of these possible thermometers, through measurements of T-dependent rate constants for D/H exchange of various sites in several n-alkanes.