

The isotopic structures of hydrocarbon compounds

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Stable isotope structures (i.e., proportions of various site-specific and 'clumped' isotope species) of hydrocarbons could potentially inform many problems in environmental geochemistry, petroleum geoscience, and perhaps other fields, such as chemistry and chemical engineering. For example, there is evidence to suggest that such data constrain forensic source identification (e.g., in air or waters); temperatures of formation (and/or storage); source substrates; formation mechanisms; and mixing and transport processes. The study of isotopic structures of hydrocarbon compounds is currently driven by rapidly advancing innovations in analytical technologies — the numbers, abundances and types of isotopologues, the types of compounds that can be measured, and the forms and sample sizes that can be analyzed are all changing at an unprecedented pace. Particularly important 'growth' technologies include natural-abundance NMR, chemical and pyrolytic degradations (followed by conventional IRMS), high-resolution gas source mass spectrometry (HR-IRMS), and, most recently, Fourier transform mass spectrometry. Methane clumped isotope geochemistry is by far the most mature of the tools to emerge in this field — approximately 500 samples have been measured covering diverse natural and experimental sources; three research groups work actively in this field at another 2-3 are likely to enter it within the year. Demonstrated uses include: measurement of gas formation temperatures; discrimination of biogenic from thermogenic gases; and quantification of end-member proportions in mixed gases. Key variables that must be considered in such applications include the kinetic isotope effects associated with some microbial metabolisms and some conditions of kerogen or coal pyrolysis, and unexplained, anomalously high apparent temperatures in some oil-associated unconventional gases. The carbon isotopic structures of *n*-alkanes have been shown to reflect: inheritance from biomolecule substrates; mechanisms of formation (i.e., primary vs. secondary cracking); and destruction, such as by 'cracking' of gas compounds. Arguably the greatest challenge to the interpretation of such data is the fact that the isotopic structures of kerogen precursors of petroleum compounds are currently unknown (and it is not obvious how they will be measured). Emerging tools that examine the hydrogen isotope structures of petroleum compounds hold the promise of leading to a very large family of thermometers and/or proxies for sources and formation mechanisms. In particular, site-specific variations in rates of hydrogen isotope exchange between these compounds and environmental water suggest it may be possible to identify isotopic proxies that record several stages in a molecule's temperature-time history — synthesis, migration, storage, and emission or extraction.