

Hydrogen isotopes in organic matter maturation: A synthesis

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The D/H ratio of live biomass correlates well with D/H of ambient water used by organisms for primary production and metabolism of biochemicals. As ocean water and meteoric waters occupy a very wide range of D/H ratios, the D/H ratios of immature sedimentary organic matter (SOM) provide valuable paleoenvironmental and paleoclimatic information, especially on the molecular, compound-specific level. The biogeochemistry and isotopic composition of SOM change, however, during long-term maturation from early diagenesis into metamorphism.

Much has been learned from laboratory experiments and naturally matured samples about isotopic exchange between organic hydrogen and inorganic hydrogen at higher temperatures since Tom Hoering's (1984) pioneering hydrous pyrolysis experiments. On the compound-specific level, significant isotopic exchange of C-bound organic hydrogen with other ambient hydrogen is apparent at higher temperature, but seems to have affected many hydrocarbons only during their chemical genesis from precursor molecules. Some organic hydrogen moieties are prone to continually exchange (e.g., some aromatic hydrogen), whereas others seem to retain their D/H ratios over geologic time (e.g., *n*-alkanes; Sessions et al., 2004).

Published data from field studies document that increasing thermal maturity tends to transfer deuterium from inorganic sources into coal, kerogen, NSO-compounds and hydrocarbons, in qualitative agreement with hydrous pyrolysis results. However, D/H ratios of moderately mature fossil organic matter can still (i) distinguish kerogens from marine and freshwater paleoenvironments, (ii) identify oil families, (iii) correlate petroleum to their source rocks, and (iv) retain sufficient hydrogen isotopic information from the original biomass to assist in paleoenvironmental reconstruction (e.g., Schimmelmann et al., 2004).

References

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Carbon and hydrogen isotope measurements in abiogenic hydrocarbon synthesis

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Controversy surrounds the issue of possible contributions of abiogenic hydrocarbons to economic hydrocarbon systems, in large part because the characteristics of proposed abiogenic hydrocarbons have not been well defined. In particular, one of the key tools used for differentiating hydrocarbons of diverse origin – stable isotope signatures – are still largely unconstrained for abiogenic end-members. Based on field observations, an abiogenic isotopic signature of carbon isotope depletion in ¹³C and hydrogen isotope enrichment in ²H from methane to ethane has been proposed. This is based on the hypothesis that during polymerization of methane to produce higher hydrocarbons there will be a preferential rate of reaction for the light isotopes resulting in preferential incorporation of ¹²C into the products of the reaction but preferential loss of ¹H. To date however there has been very little laboratory verification of fractionation in abiogenic processes in general, particularly for hydrogen isotope effects.

This presentation describes the analytical developments involved in measuring both carbon and hydrogen isotopes on small sample volumes produced by experimental apparatus used for a variety of processes of abiogenic hydrocarbon synthesis. Synthesis of higher alkanes from methane in a spark discharge apparatus was a key experiment in developing the earliest models of carbon isotopic fractionation during polymerization. In this study we have revisited those experiments to verify the carbon isotope fractionation patterns and to incorporate measurement of hydrogen isotope effects for the first time as well.