

Controls on the D/H composition of individual petroleum hydrocarbons

ALEX L. SESSIONS

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Compound-specific D/H measurements are increasingly used to study petroleum systems. Thus far, it has been unclear how such measurements should be used to maximum advantage. A review of existing data suggests that potential uses likely extend beyond simple oil-oil and oil-rock correlation and apportionment studies to include catagenetic reactions, mineral catalysis, and thermal maturation.

Four categories of fractionations will determine the ultimate D/H ratio of a particular hydrocarbon molecule: (i) kinetic fractionations during the biosynthesis of precursor biomolecules, (ii) kinetic fractionations associated with diagenetic and catagenetic reactions, (iii) equilibrium and/or kinetic fractionations accompanying processes such as migration, water-washing, biodegradation, evaporation, etc., and (iv) equilibrium fractionations resulting from isotope exchange of carbon-bound H. Reactions in categories *i* and *iv* are currently thought to be the largest effects. Reactions in category *ii* have received relatively little attention with respect to isotopic fractionations of individual molecules.

Fractionations between environmental water and fixed organic H are approximately constant for all plants. Terrestrial source rocks thus possess much greater isotopic variability than do marine source rocks, and D/H ratios will be more useful for source correlation in terrestrial-sourced oils. Several recent studies have documented a rapid increase in D/H ratios of sedimentary hydrocarbons at depths near the beginning of oil generation. Such shifts have been variously attributed to isotope exchange or to catagenetic fractionations, but the true origins remain uncertain. A strong correlation between *n*-alkane D/H ratio and chain length represents a second, persistent but unexplained pattern, and is possibly related to hydrocarbon cracking reactions.

Similarities in D/H ratios of *n*-alkanes and pristane/phytane seem to indicate that isotopic exchange is nearly complete in many oils, yet large down-core variations in D/H can be preserved. The resolution of this apparent enigma may teach us about the sources and mobility of both organic and inorganic hydrogen during petroleum generation.

Indicators of anaerobic hydrocarbon degradation in petroleum reservoirs

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Introduction

Biodegradation of crude oil in subsurface petroleum reservoirs is an important alteration process. It has long been thought that the mechanism is dominated by aerobic processes; however, recent geochemical and geological work shows that anaerobic processes are more likely. We have analysed several crude oils and rock extracts during our search for metabolites or products peculiar to anaerobic hydrocarbon degradation and describe the results here.

Results and Discussion

2-Naphthoic acids and reduced 2-naphthoic acids have been reported as metabolites during anaerobic degradation of naphthalene (Zhang et al., 2000). Trace amounts of reduced 2-naphthoic acids have been identified only in biodegraded oils and are thus assigned exclusively to anaerobic hydrocarbon degradation. 25-Norhopanes have always been regarded as indicative of heavy biodegradation of oil here we review their potential as indicators of anaerobic hydrocarbon degradation.

Conclusion

Reduced 2-naphthoic acids, specific to anaerobic hydrocarbon degradation, have been detected in several biodegraded oil reservoirs and this together with geological evidence suggests the oils are produced by anaerobic biodegradation in most cases. 25-Norhopane production by microbial demethylation of hopane also seems to be indicative of anaerobic degradation processes.

Reference

Zhang, X., Sullivan, E.R. and Young, L.Y. (2000) *Biodegradation* **11**, 117-124.