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Hydrogen isotope systematics of individual hydrocarbons in gasoline fraction of Western Canada Sedimentary Basin oils

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In a previous paper, Whiticar and Snowdon, reported the carbon isotope characterization of 42 oils/condensates in the Western Canada Sedimentary Basin [1]. We extend that Compound Specific Isotope Correlation (CSIC) study to include the stable hydrogen isotope ratios ($^2\text{H}/^1\text{H} = \text{D}/\text{H}$) of individual hydrocarbon species from pentane to nonane on the same sample suite. We have developed an on-line SPME-GC-Reduction-IRMS analytical platform to routinely make D/H measurements on $\text{C}_5\text{-C}_9$. These initial measurements have produced surprising and exciting results. The overall range in $\delta\text{D}_{\text{cpd}}$ values is between ca. -22‰ and -395‰ (vs. V-SMOW, Figure 1). Between compounds in any given oil the average $\delta\text{D}_{\text{cpd}}$ range is ca. 250‰ , and the largest range is 373‰ . Comparing the same compound in different oils shows a remarkable consistency, i.e., pattern of excursions in $\delta\text{D}_{\text{cpd}}$ for specific compounds is generally mirrored in most oils. However, for any specific compound a $\delta\text{D}_{\text{cpd}}$ range of 50‰ to 200‰ is observed. Compound classes (e.g., n-alkanes) show intriguing systematic shifts with carbon number. In particular isomers of can consistently have dramatically different D/H ratios. Of further interest is the possible connection between the carbon and hydrogen isotope ratio signatures. These various aspects, and their consequence on understanding the process of petroleum formation and oil fingerprinting are examined.

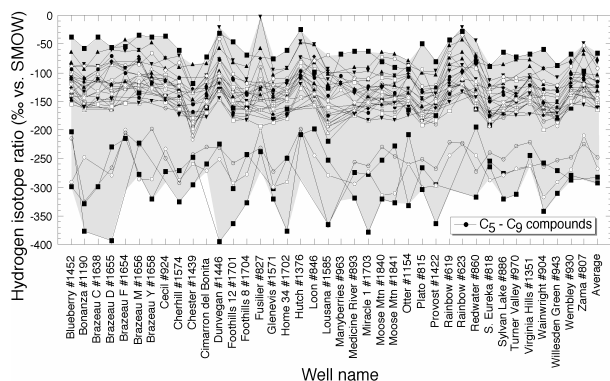


Figure 1. Hydrogen Isotopograms for WCSB oils.

Reference

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The influence of biodegradation on the isotopic signature of light hydrocarbons

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Biodegradation of light hydrocarbons is a well-known process. However, the effect of biodegradation on the carbon and hydrogen isotopic composition of light hydrocarbons was investigated only recently. Anaerobic biodegradation of alkylbenzenes (BTEX) is associated with an enrichment of the heavier isotopes (^{13}C , D) in the residual compound fraction [1,2]. Hydrogen isotope fractionation tends to be at least one order of magnitude higher than carbon isotope fractionation [2], indicating higher sensitivity in the assessment of microbial degradation processes. Currently, we are investigating isotope fractionation during anaerobic biodegradation of *n*-alkanes. Initial results for the first time show that the residual fraction of *n*-hexane utilized by a denitrifying bacterium is enriched in ^{13}C . The Rayleigh-equation, correlating the changes in concentration and isotopic signature, will be used to determine fractionation factors which then can be applied to the quantification of *in situ* biodegradation in field studies [3].

Biodegradation of light hydrocarbons in petroleum reservoirs leads to a significant change in crude oil composition and highly influences its economic value. To evaluate these microbial processes, stable isotopic signatures of light hydrocarbons may be applied. Several samples of crude oils, showing initial to moderate levels of biodegradation, were analysed concerning the stable isotopic composition of the light hydrocarbons. This presentation will relate the results from laboratory degradation experiments to isotopic analysis of crude oil samples. The applicability of this stable isotope approach to identify and quantify microbial degradation processes in petroleum reservoirs will be examined.

References

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[3] Richnow H.H., Vieth A., Kästner M., Gehre M., Meckenstock R.U. (2002) *The Scientific World Journal* **2**, 1227-1234.