PS A Multiple Isotope (C, H, S & O) Approach to Characterizing Crude Oil Families Within Oil Basins*

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Abstract

Stable isotope analyses of crude oil samples have been part of the petroleum geochemists tool kit since at least the 1950's. Although a range of isotopic systems; carbon ($\delta^{13}C$), sulfur ($\delta^{34}S$) and hydrogen ($\delta^{2}H$), have been utilized previously to help understand the origin of and relationships between petroleum samples, this has largely given way to studies focusing upon bulk (or compound-specific) $\delta^{13}C$ signatures. That is not to say that there is not a body of work on these additional bulk isotopic signatures in petroleum studies, there is, but the majority of it is dated. Although carbon is the dominant constituent of crude oils (>80%) the other constituent hydrocarbon and non-hydrocarbon elements (Hydrogen, Nitrogen, Sulfur, and Oxygen) offer potential insight into understanding the origins and history of complex petroleum systems. This study looks at the potential range of C, H, N, and S isotopes in petroleum samples, from a global context before focusing on $\delta^{13}C/\delta^{34}S$ and $\delta^{13}C/\delta^{34}S/\delta^{2}H$ correlation case studies from a number of complex oil basins. The oil basins discussed (Williston Basin and Western Canada Sedimentary Basin) have previously been analyzed and the petroleum systems within the basins defined via principal component analysis (PCA) of genetic-biomarkers and stable carbon isotopes. All of the results suggest that a multi-isotope approach (CHNOS) can separate petroleum samples into distinct oil families which closely mimic those generated by multivariate statistics of genetic biomarkers in the same oils. Not all of the oils analyzed match their biomarker defined oil families, but this can be explained by a combination of subtle mixing between petroleum systems, enhanced maturity separation - from concentrating on the isotopes exclusively - and the limitations of using just 3 parameters to define as many as 8 individual petroleum systems. The results of this study emphasize the important role that combining $\delta^{13}C$, $\delta^{2}H$, $\delta^{34}S$ and potentially $\delta^{18}O$ composition and isotopic signatures can play in helping to define individual petroleum systems within complex oil basins and the potential in correlating oil-oil and oil-source rock relationships.

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1. Introduction

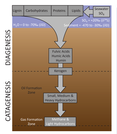
GeoMark Research Ltd. has an active research program which covers a range of geochemical techniques, proxies and study areas. The research outlined in this poster focuses upon utilizing a range of light stable isotope systems (C, H, N, O, S) to enhance our understanding of crude oil samples. To better understand the viability of these isotope systems for separating out distinct oil families, within complex basins, all of the basins discussed have previously been characterized by GeoMark Research using our standard geochemical/biomarker protocols.

The utilization of bulk $\delta^{13}C$ signatures of crude oil samples, and their fractions (saturate & aromatic), is a standard geochemical tool utilized in crude oil characterization and fingerprinting. However, $\delta^{13}C$ has a relatively restricted isotopic range in crude oils (-22 to -38 permil) and other systems, including $\delta^{34}S$, $\delta^{2}H$, $\delta^{15}N$ & $\delta^{18}O$ offer, in some cases, larger isotopic ranges and potentially enhanced oil family characterization and definition.

This poster presents correlated $\delta^{13}C$, $\delta^{34}S$ & δD isotope results for the 'Williston Basin' (Canada & USA) and the 'Western Canada Sedimentary Basin' (Canada) and discusses the utility of these systems for fingerprinting crude oils, relative to standard biomarker assessment, and their potential use in 'Time Lapse Geochemistry'(TLG) studies. A number of crude oil samples from the Williston Basin were also analyzed for $\delta^{18}O$ isotope signatures and the utility of and problems associated with this system, in crude oil samples, is discussed briefly.

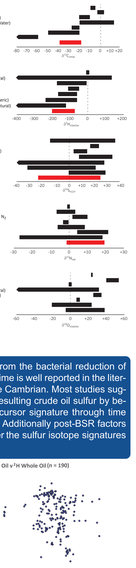
2. Isotope Systems & Crude Oils

Presently, the most common isotope system analyzed in crude oil samples is carbon (^{13}C) with a range from around -38‰ to -22‰. Older studies also reported results for hydrogen (^{2}H) & sulfur (^{34}S) isotopes but these are not commonly reported in current studies. Nitrogen (^{15}N) isotopes are reported from some recent studies but data collection is the most difficult of the 4 reported systems.

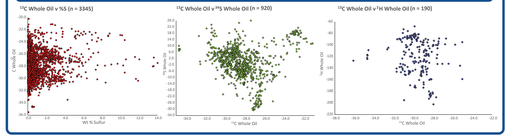


The isotopic signature of crude oils is affected by four parameters:

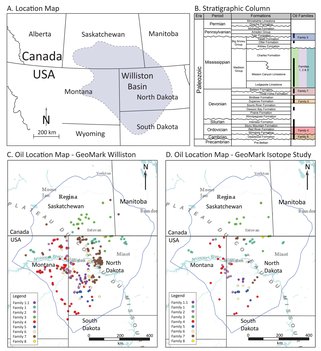
1. The precursor organic material (C, H & N).
2. The fractionation processes during the transformation from organic matter to crude oil (all systems).
3. Input from inorganic material (S & H)
4. Post-depositional alteration processes (All systems).

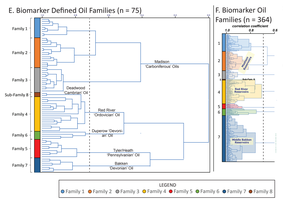


Sulfur (^{34}S) isotope signatures of crude oils are generally considered to result from the bacterial reduction of seawater sulfate. The seawater sulfate sulfur isotope signature through geologic time is well reported in the literature and varies from a low value of around +11‰ in the Permian to +36‰ in the Cambrian. Most studies suggest that bacterial sulfate reduction (BSR) fractionates the isotopic value in the resulting crude oil sulfur by between 5-20‰. This range of fractionation combined with the change in the precursor signature through time means that different oil families can have very different sulfur isotope signatures. Additionally post-BSR factors such as migration, thermal maturity, biodegradation & water washing can also alter the sulfur isotope signatures both between and within oil families.



3. Case Study 1: The Williston Basin

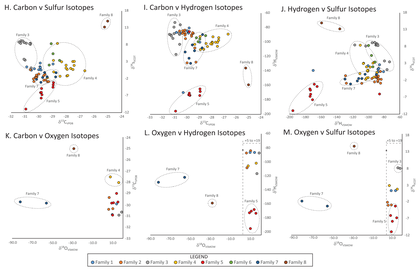


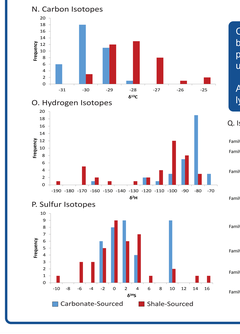


The Williston Basin is located across the USA (North Dakota, South Dakota & Montana) and Canada (Saskatchewan & Manitoba) (A) and the primary hydrocarbon resources are all sourced from and reservoired in a range of Paleozoic Formations (B). GeoMark Research's 'Williston Basin study' includes crude oil samples from 364 individual Wells across the Williston Basin (C). For the multi-isotope study of this basin, 75 crude oil samples were selected from across the 7 oil families, previous defined from biomarker results (D, E, F). The individual oil families from the Williston Basin have been defined through principal component (PCA) and cluster analyses (E, F & G). Both the full suite of 354 oils (F) and the 75 sub-sampled set of oils (E) define the same distinct oil families when statistically compared via biomarker results.

The 75 crude oil samples in this study were all analyzed for carbon ($\delta^{13}C$), hydrogen ($\delta^{2}H$) & sulfur ($\delta^{34}S$) isotope signatures. Additionally 17 crude oil samples were analyzed for oxygen ($\delta^{18}O$) isotope signature. The cross-plots of C, H & S show distinct clustering of the samples with oil families 3, 4, 5, 7 and 8 generally standing out from the data (H, I & J). Drilling down into the sulfur data (I), the isotopic trends in oil families 3 and 5 appear to be related to geographical distribution/waterwashing and thermal maturity respectively.

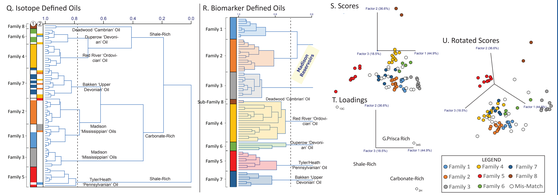
Carbon & sulfur isotope signatures preserve the most distinct seperations across the sample set while hydrogen signatures generally range between -130‰ and -70‰, but with considerable overlap across families. The only oil families which appear distinct when analyzed via H isotopes are families 5, and to a lesser extent, 8 (I, J). The oxygen isotope results (K, L, M) are interesting with all of the oil families, except 7 and 8, preserving signatures >10‰. The two family 7 oils preserve signatures between -90‰ & -50‰ with the one family 8 oil preserving a signature of -30‰. Cross-plots with C, S and H allow separation of additional oil families but the exact relationship of this system and what it represents is poorly understood in crude oils.



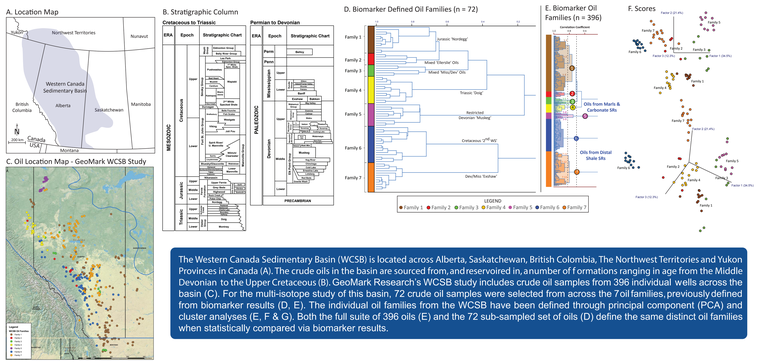


Comparing the isotope results for C, H & S relative to their proposed source (shale or carbonate) results in some clustering becoming apparent (N, O, P), although most notably in the C signature (N). Generally, the carbonate-sourced oils are isotopically depleted in C and enriched in H relative to the shale sourced oils (N,O). The S signatures are not as clear cut (P) but unlike the other factors, geologic age (and the seawater sulfate signature) is likely playing a greater role in the distribution.

Analyzing the isotope data via cluster and principal component analyses (Q, R, S) reveals that the majority of oils (79%) analyzed by this method coalesce into the same clusters as defined using 18 distinct biomarker parameters.



4. Case Study 2: The Western Canada Sedimentary Basin



The Western Canada Sedimentary Basin (WCSB) is located across Alberta, Saskatchewan, British Colombia, The Northwest Territories and Yukon Provinces in Canada (A). The crude oils in the basin are sourced from, and reservoired in, a number of formations ranging in age from the Middle Devonian to the Upper Cretaceous (B). GeoMark Research's WCSB study includes crude oil samples from 396 individual wells across the basin (C). For the multi-isotope study of this basin, 72 crude oil samples were selected from across the 7 oil families, previously defined from biomarker results (D, E). The individual oil families from the WCSB have been defined through principal component (PCA) and cluster analyses (E, F & G). Both the full suite of 396 oils (E) and the 72 sub-sampled set of oils (D) define the same distinct oil families when statistically compared via biomarker results.

The 72 crude oil samples in this study were all analyzed for carbon ($\delta^{13}C$), hydrogen ($\delta^{2}H$) & sulfur ($\delta^{34}S$) isotope signatures (G, H, I). The cross-plots of C, H & S show distinct clustering of the samples with oil families 1 & 4-7 all clustering as distinct groupings. In contrast the 2 mixed oil families (2 & 3) preserve much more variable signatures. The C & S isotope signatures in the WCSB samples (G) preserve the most distinct fingerprinting characteristics. In contrast H signatures used in cross-plots only seperate out oil families 5 and 6 from the other oil families.

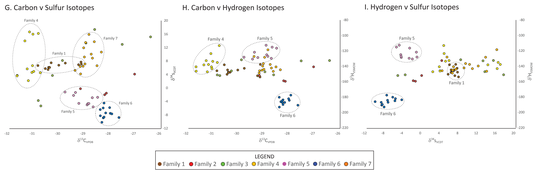
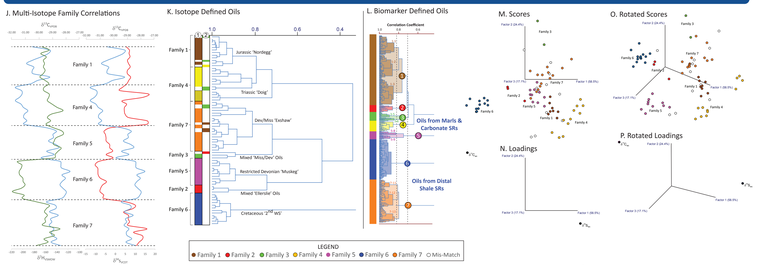


Figure J compares changes in isotope signature for C, H & S relative to their defined biomarker oil families. Although there is variation within oil families, the common trend is that where one isotope signature changes between families, the other isotope signatures also change. Isotopically, Family 4 is depleted in ^{13}C relative to Family 5 but is enriched in ^{34}S and shows minimal variation in ^{2}H. Similarly, Family 5 is is slightly depleted in ^{13}C relative to Family 6, but is enriched in ^{34}S and ^{2}H.

Analyzing the isotope data via cluster and principal component analyses (K-P) reveals that the majority of oils (85%) analyzed by a multi-isotope approach coalesce into the same clusters as defined using 18 distinct biomarker parameters. Additionally, this sample set, unlike that from the Williston Basin, contains samples which are characterized as being a mix of more than one end member oil family. It is not unexpected that these mixed oil samples would be difficult, if not impossible, to type when using only 3 isotope parameters. If the mixed oils are removed from the assessment then 94% of the oil samples cluster into the same oil families when analyzed by either isotopes only or biomarkers.



5. Summary

The standard protocols for characterizing oil samples into distinct oil families utilizes biomarker ratios collected via GC-MS and saturate/aromatic isotope parameters. However, not all oil samples contain viable biomarkers, particularly light oils/condensates, where considerable interest is focused at the present day. Therefore, understanding whether multi-isotope parameters can be used to characterize these samples into the same groupings as other methods is crucial.

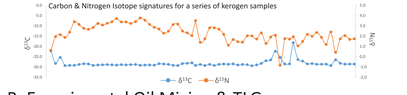
This study presents a number of findings:
1. Multi-isotope analysis ($\delta^{13}C$, $\delta^{34}S$ & $\delta^{2}H$) of oil samples within complex basins show similar oil family clustering as analysis using multiple biomarker ratios via Cluster and Principal Component Analyses.
2. Oxygen isotope ($\delta^{18}O$) signatures show some variation related to distinct oil groupings but the nature of these results is not well understood, data collection is difficult and more work is needed.
3. Where biomarkers are lacking within oil samples, multi-isotope data collection presents a relatively quick and effective approach to defining distinct oil families.
4. Combining the multi-isotope and biomarker approach opens up avenues for further identifying and understanding subtle variations and sub-families within oil basins/families.

6. Future Research

A. Inclusion of Nitrogen ($\delta^{15}N$) Isotope Data

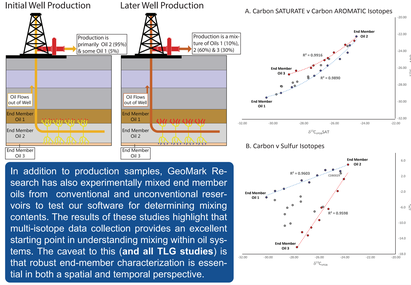
With the exception of oxygen isotopes, nitrogen isotope data is the most difficult to collect on crude oil samples, primarily due to its generally low to very low content (<0.2%) in samples. This low content, coupled with potential interference from atmospheric nitrogen and the high content of carbon in crude oil makes analysis difficult, a well reported problem with any low nitrogen content sample analysis.

Most studies try to maximize the signal by analyzing the NSO or Asphaltene fractions of oils , maximizing the sample size and using technology which can better seperate the C and N peaks to remove any tailing effects. However, there are still minimal studies of this isotope system in petroleum samples. In the future we intend to incorporate this data into our earlier studies to determine if it helps to further enhance oil family separation (>80%) and also matches similar subtle variations noted from sulfur and carbon isotope characterization.



B. Experimental Oil Mixing & TLG

Time Lapse Geochemistry (TLG) has become a prominent & developing tool in helping companies understand both production allocation and formation fluid mixing via unconventional extraction. These studies require end-member characterization of oils to be able to determine both initial mixing relationships and ultimately changes through time. Many of the oil families of interest in these studies lack sufficient biomarkers and so a multi-isotope approach (C, H & S) again offers another viable tool in both characterizing end member oil samples and mixing relationships.



In addition to production samples, GeoMark Research has also experimentally mixed end member oils from conventional and unconventional reservoirs to test our software for determining mixing contents. The results of these studies highlight that multi-isotope data collection provides an excellent starting point in understanding mixing within oil systems. The caveat to this (**and all TLG studies**) is that robust end-member characterization is essential in both a spatial and temporal perspective.

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