New Directions in Geosciences for Unconventional Resources

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Application of CSIA of Light Oils and Utility of Carotenoid Biomarkers in Resource Plays of North America

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Abstract

Here we examine the value in crude oil correlations and source rock depositional environment predictions based on non-standard compound-specific isotope analysis and carotenoid biomarker data. Results from various unconventional plays (e.g., Late Devonian Bakken and Woodford Fms from the Williston and Anadarko Basins; Cretaceous Second White Specks, Niobrara, Mowry and Eagle Ford Fms in the Western Interior Seaway) are discussed and compared. These data provide new insights into resource plays using novel and relatively rapid analytical methods. Molecular isotopic data and carotenoid biomarker distributions of petroleum systems tend to be distinct so that, in combination with commonly used sterane and hopane biomarkers, oil-oil and oil-source correlations can be made with much greater fidelity.

Statement of the background

This paper addresses novel application of compound-specific isotope analysis and carotenoid hydrocarbon characterization to better understand, and perhaps predict the productivity of hydrocarbons from source-rock reservoirs. This work provides new and detailed insight into resource play petroleum systems.

Aims and Objectives

Stable isotope analysis is a powerful tool in understanding the generation, history and correlation of hydrocarbons. Compound-specific $\delta^{13}C$ measurements of oils allow detailed comparison of individual compound groupings; however, most studies separate and isolate individual fractions based on the chemistries of particular compound groups, potentially losing or corrupting valuable data. Even where a number of sub-fractions are created for samples, many of these processes result in the loss of sample integrity, particularly in the gasoline range compounds. GC/IRMS of untreated, whole crude oils allows immediate collection of larger more accurate suites of isotopic data for these studies.

This stable isotope work is complemented by the study of C40 carotenoids, diagnostic biomarker hydrocarbons derived from the pigments of algae and photosynthetic bacteria. Recent studies show that they have application as correlation tools in basins with complex oil-source rock relationships and for paleoenvironmental reconstruction. These carotenoid hydrocarbons convey information about the redox structure of sedimentary environments and, thus, provide information that complements that of the more commonly used sterane, hopane and tricyclic terpane biomarkers.

Materials and methods

Compound-Specific Isotope Analysis (CSIA)

The analysis of $\delta^{13}C$ compound specific isotopes (CSIA) in hydrocarbon samples has generally involved separation of whole oil samples into isolated fractions and the analysis of specific compound classes only. This methodology is time-consuming and has drawbacks which include the loss of light-end gasoline compounds and isotopic fractionation during processing (Grice et al., 2008; Xu and Sun, 2005). By injecting 'neat' whole crude oil samples we remove the need for any pre-analysis preparation, retain full chromatographic integrity and can collect more reliable isotopic information on the n-alkane envelope (potentially from nC-4 to nC35+) and a whole range of additional compounds (i.e. toluene, benzene, pristane, phytane, etc).

The compound-specific isotope measurements in this study were carried out using a Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC/IRMS). The lab was specifically equipped with a visION IRMS, GC5 combustion furnace interface and a modificed Agilent 7890B GC (elementar, UK) (Figure 1). Whole oil samples are injected into the GC in split mode and a ramped heating method is employed ranging from 39°C to 325°C with a run time of just over 2 hours per sample. The isotopic ($\delta^{13}C$) precision of the n-alkane, cycloalkane, isoprenoid and aromatic peaks is generally <0.4 ‰, with certain peaks (particularly n-C8) in some samples showing poorer precision – up to c. 0.8 - 1.0 ‰ – due to co-elution effects. This isotopic precision is equivalent to that reported for studies of isolated n-alkane fractions, which generally report $\delta^{13}C$ precisions in the range of c. 0.3 - 0.5 ‰ for compounds which present as clean, baseline separated peaks. $\delta^{13}C$ measurements for analytes which produce more problematic peaks (e.g. co-elution, low concentration) is reported to vary by as much as 1.5 ‰ across replicate measurements (Cortes et al., 2010; George et al., 2002). Since the majority of GC/IRMS studies for petroleum research focus upon correlation and contrast between oil samples (and therefore target and compare multiple compounds within each oil sample), this reproducibility is generally considered acceptable (Mansu and Philp, 1997).

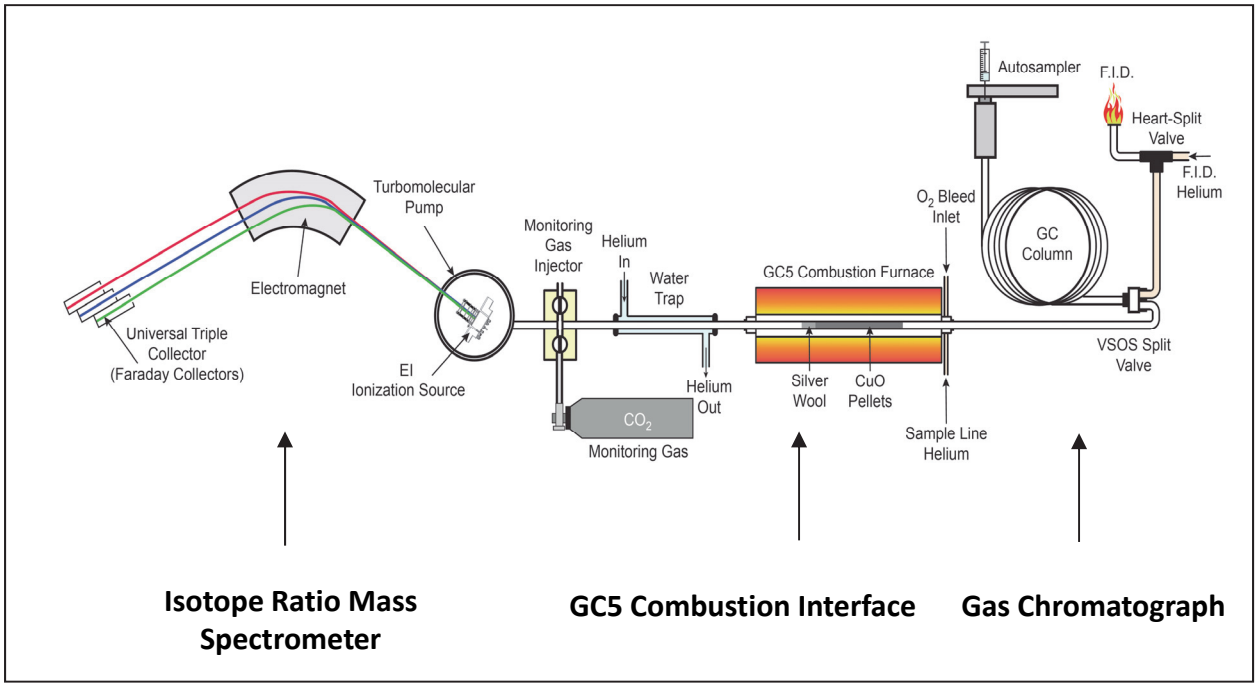

Figure 1. Schematic setup of a Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC-IRMS). A modified Agilent GC is connected to a combustion interface which converts the individual hydrocarbon compounds eluting from the GC to CO2 gas. The CO2 gas is then analyzed on an IRMS to calculate the $\delta^{13}C$ signature of the individual compounds. This setup allows the injection of whole crude oil, without any preparation, and can collect signatures from compounds between nC4 to nC35+ (Barrie et al., 2016).

GC/MSMS (QQQ) analysis of carotenoid hydrocarbons

A proprietary method using an Agilent triple quadrupole mass spectrometer (QQQ) interfaced with an Agilent 7890 GC (Figure 2) provides quantitative analyses of whole oils/extracts for a variety of terpane/sterane biomarkers as well as diamondoids, carotenoids, and a series of alkyl aromatics, all with a single run. The alkyl aromatics allows for a prediction of the level of thermal maturity (in units of vitrinite reflectance equivalent-VREQ), even for light oils (under discussion) and condensates that have lost the usual biomarkers. Internal standards are added to produce quantitative data.

Aliquots of whole oils or sedimentary bitumens are flooded with pentane to precipitate the asphaltenes. The resulting total hydrocarbon fractions are spiked with standards and injected directly onto the gas chromatograph. The GC provides the first phase of separation. As the carotenoids exit the column they are quantified by reaction monitoring mass spectrometry using QQQ technology. The first quadrupole (Q1) mass analyzer filters out the molecular ions (eg 546 in the case of isorenieratane). These are dissociated in a collision chamber (Q2) and the second mass filter (Q3) separates out the characteristic product ions. Picogram detection limits are routinely possible and the method works on all but the most mature oils and condensates. We call this simplified approach “Dilute and Shoot”.

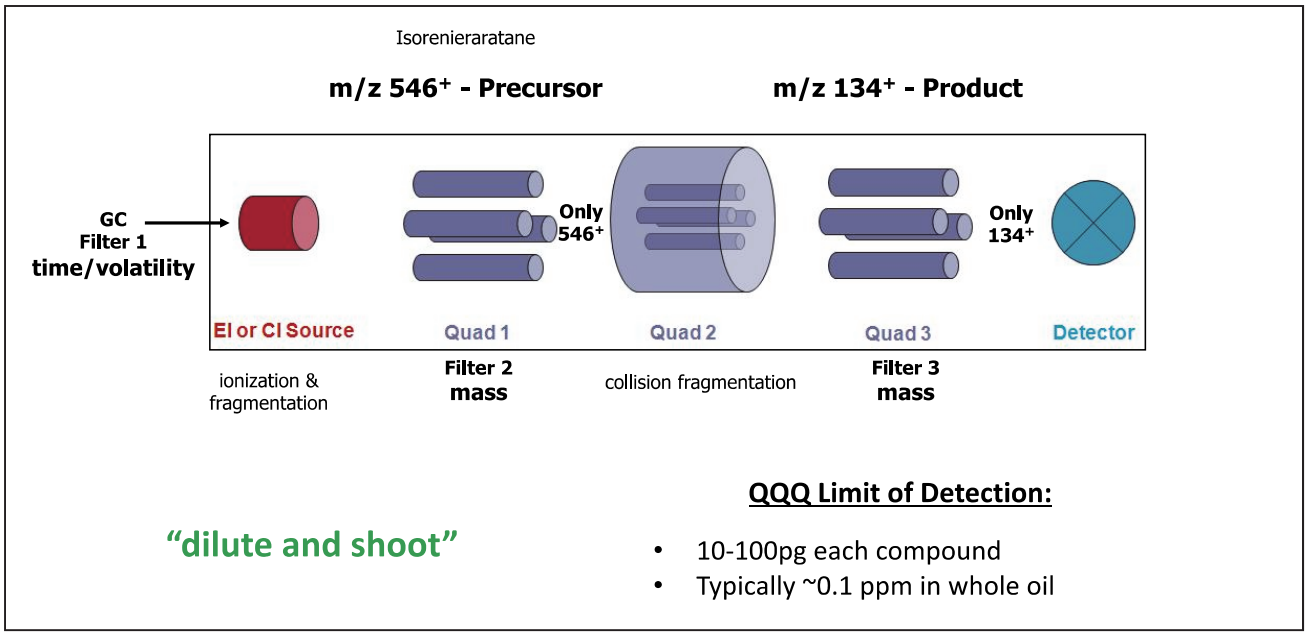

Figure 2. GC-QQQ setup configured for analyzing carotenoids on whole oil samples (French et al., 2015).

Compound-Specific Isotope Results & Discussion

Most studies of carbon isotope signatures ($\delta^{13}C$) in hydrocarbon samples focus upon the n-alkanes, which are generally the dominant compounds in non-degraded crude oil samples. Due to the samples not being pre-treated in this methodology, not only is there no time-consuming preparation stage, but the lack of solvent usage means there is no requirement for a solvent delay in the GC/IRMS run. The absence of pre-fractionation steps ensures that even the lowest molecular weight compounds in the samples (<nC-8) can potentially be analyzed and analyzed more reliably. Figure 3 is an example m/z 44 extracted ion current chromatogram of a whole crude oil, with peaks from n-C4 through n-C30 identified, all from a single ‘neat’ injection. In most methods, where n-alkanes are separated out and isolated prior to analysis, all peaks prior to at least the n-C8 alkane peak would be absent from this chromatogram; moreover, there would most likely be a varying degree of discriminative loss of n-alkanes > n-C20 (Grice et al., 2008). The baseline at the retention window for the gasoline range of n-alkane peaks (n-C4 to n-C8) shows virtually no column bleed and is completely flat with both excellent peak shape and compound separation (Figure 3). The n-alkanes from n-C9 to n-C20 lie within the most complex retention window of the whole oil chromatogram (Figure 3). However, with the exception of n-C14 (for which baseline definition is complicated by closely eluting peaks) all of the other n-alkane peaks are sufficiently separated from the

surrounding peaks (which include isoprenoid and branched compounds) to enable reliable peak integration.

Although considered a detriment to generating a clean GC/IRMS baseline, the injection of whole crude oils offers the benefit of being able to investigate potentially informative non *n*-alkane compounds present in crude oils. Considering the complexity of whole crude oil, not all of these compounds manifest as viable, reproducible peaks in GC/IRMS chromatograms (Figure 3). However, a series of low molecular weight cycloalkanes (2-methylpentane (2-MP), methylcyclopentane (MCP) cyclohexane (C-H) & methylcyclohexane (MCH)) and aromatics (benzene (Bz) & toluene (Tol)) do show potential (Figure 3). Moreover, other studies of these compounds have previously suggested they may offer insight into the history of related oils (Whiticar and Snowdon, 1999). The gasoline range hydrocarbons, particularly benzene and toluene, were described in this earlier study as robust indicators of changing maturity in crude oils but correlation can be limited due to benzene not being a constant compound in crude oils (particularly where biodegradation and/or water-washing is evident). Although isotopic trends in gasoline range hydrocarbons, as a proxy for maturity or oil source, would be useful in any case, there are few studies of the light-end hydrocarbons in crude oils in the literature, meaning this work has abundant and unrealized potential. In addition to the n-alkane envelope and the gasoline range compounds, whole oil GC/IRMS also open up the ability to collect heavier isoprenoid compound peaks, including the two most commonly reported, pristine (Pr) and phytane (Ph). Although other isoprenoid peaks are present in whole oil chromatograms, specifically *i*-C_{13} to *i*-C_{18} baseline separation of these peaks is problematic and integration issues compounded by low signal intensity relative to baseline. The ratio of Pr to Ph concentration (determined *via* traditional GC quantification techniques) has been used extensively to assess a number of factors in crude oils, including: origins (marine vs terrestrial), maturity, biodegradation, and levels of oxidation, to varying degrees of success (Powel and McKirdy, 1973; Ten Haven et al., 1987). The isotopic signature of these compounds varies both with organofacies and thermal maturity and comparison of sample material both across petroleum systems and within oil families can provide useful insight into their origins.

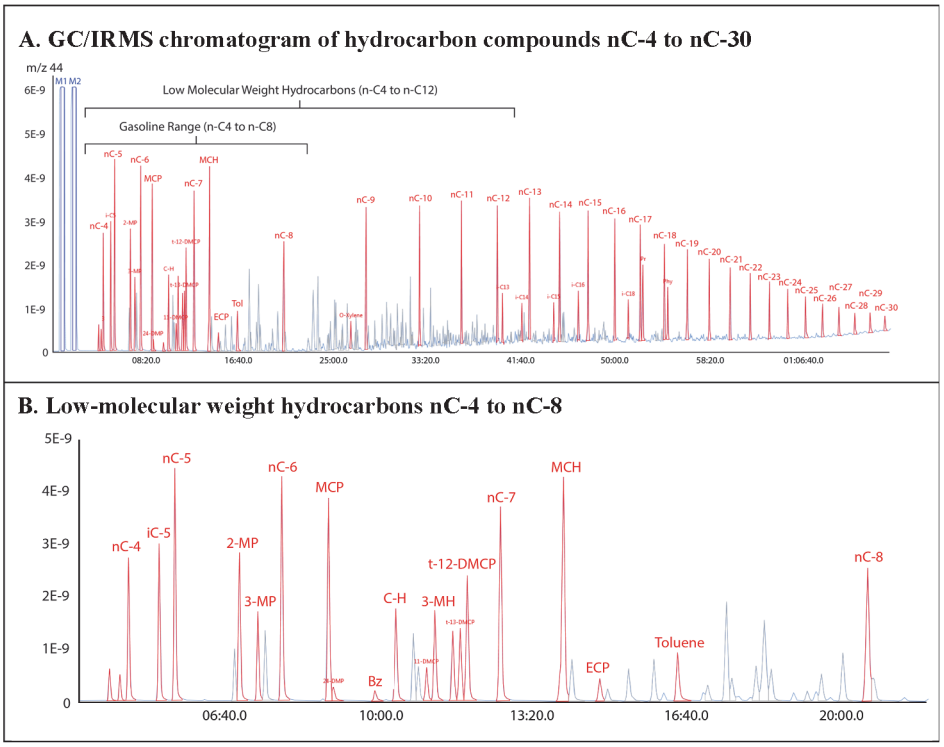

Figure 3. Example GC-IRMS chromatography highlighting the range of peak data which can be collected from this technique on whole crude oil (A). In addition to the usual n-alkane envelope from isolation techniques (nC-8 to nC30+) this methodology allows the gasoline range compounds (B) and a host of isoprenoids (including pristine & phytane) to be assessed (Barrie et al., 2016).

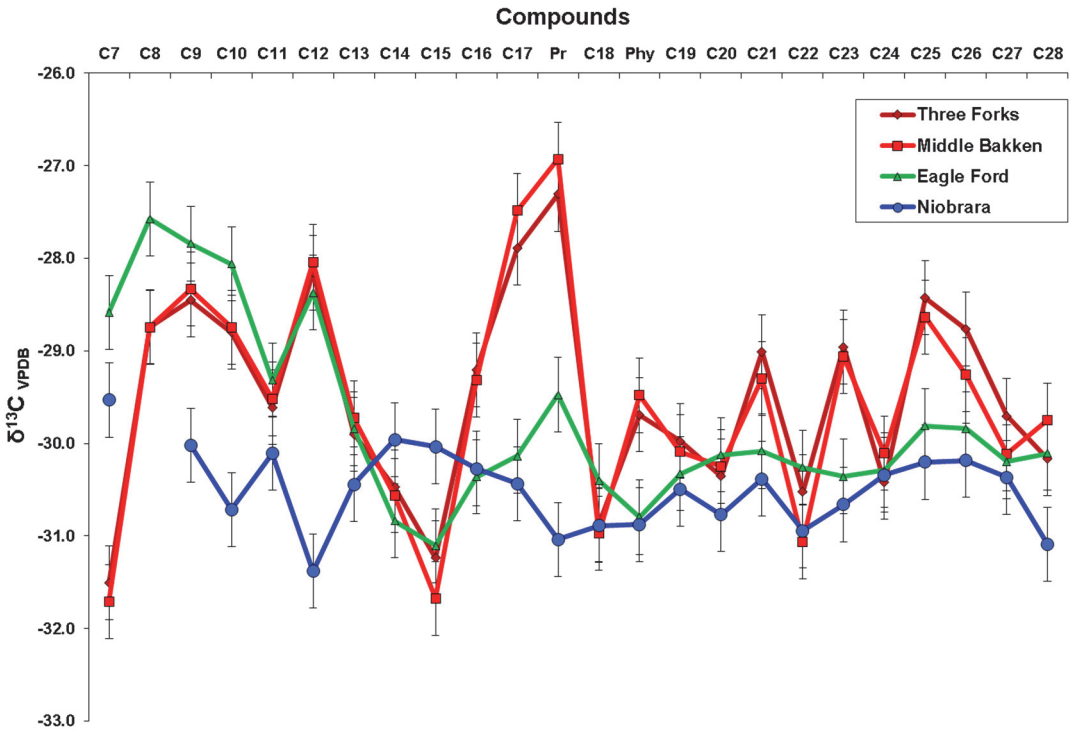

Figure 4. Graph of n-alkanes (C7 to C28), pristane & phytane compounds from oils sourced from 4 different oil samples (Three Forks, Middle Bakken, Eagle Ford & Niobrara). The Three Forks and Middle Bakken samples preserve identical signatures. These 2 samples also preserve a distinct isotopic shift >nC-18 with a saw tooth $\delta^{13}C$ pattern. The Eagle Ford and Niobrara samples are generally isotopically depleted relative to the Three Forks/Bakken samples and the saw tooth pattern is not evident. Although showing some overlap the $\delta^{13}C$ trend is very different between these three groups of oils.

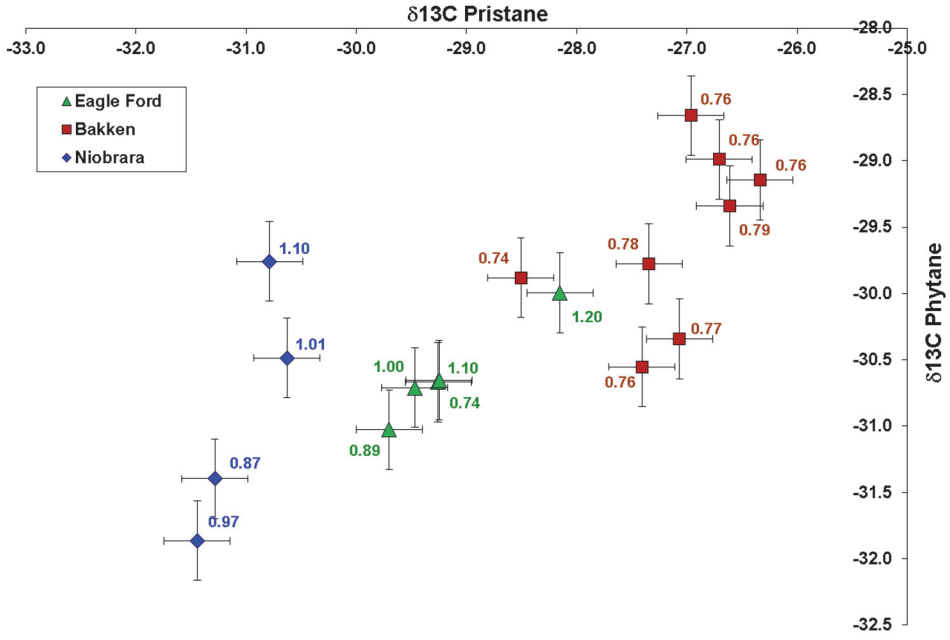

Figure 5. Cross-plot of the $\delta^{13}C$ signatures of pristane vs phytane from a series of oils from the Bakken, Eagle Ford and Niobrara Formations. The values shown next to the oil symbols are the VREQ (thermal maturity) numbers associated with the samples.

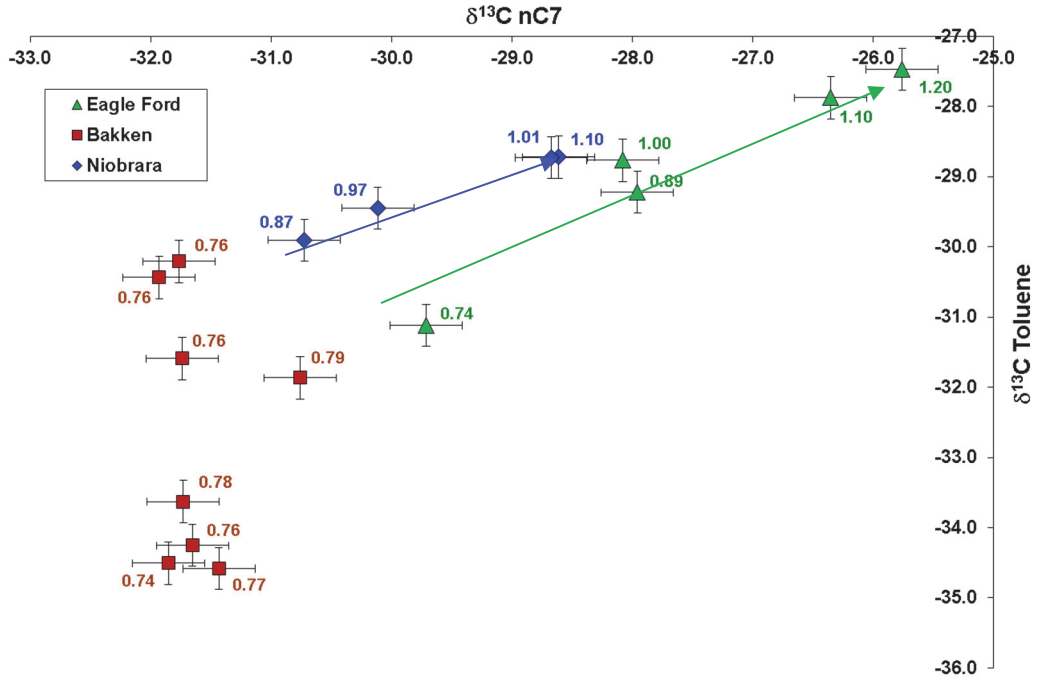

Figure 6. Cross-plot of the $\delta^{13}C$ signatures of Toluene vs nC7 from a series of oils from the Bakken, Eagle Ford and Niobrara Formations. The values shown next to the oil symbols are the VREQ (thermal maturity) numbers associated with the samples. The arrows indicate the direction of increasing thermal maturity in the samples. The Bakken oils are at equivalent maturities but have different migration distances, perhaps resulting in the isotopic fractionating of the more water-soluble toluene relative to nC7.

Carotenoid Results & Discussion

Carotenoids are yellow, orange or red colored pigments, whose prime function is for light harvesting & photoprotection in photosynthetic organisms. Carotenoid-derived hydrocarbons tend to be well preserved, even in mature samples, and are prevalent in oils sourced from both marine carbonates, deep-water shales and lacustrine sediments. All photosynthetic organisms utilize a combination of chlorophylls and carotenoids in their light-harvesting antennae. Each particular type of organism has its pigment complement optimized for the specific environment in which it inhabits. During diagenesis, these pigments are selectively degraded. Chlorophylls break down into a porphyrin core and a relatively more stable phytol moiety, which is ultimately converted to the redox-diagnostic hydrocarbons pristane and phytane. The porphyrin cores, although capable of providing valuable insights, are very difficult to analyze and not widely used in the petroleum industry. In this paper we focus on the carotenoid pigments which are relatively more stable than the chlorophylls and survive well into the oil window.

Eukaryotic algae and cyanobacteria use carotenes (β- mainly) and lycopene as their primary carotenoid pigments that are preserved as the saturated hydrocarbons γ-carotane, β-carotane and lycopane. Because algae and cyanobacteria produce and consume oxygen, and live in relatively shallow water; these hydrocarbons must reflect photosynthesis in oxygenated marine and lacustrine water bodies.

The green and purple sulfur bacteria (GSB and PSB, respectively), in contrast, are anaerobes and are typically found in the water columns of stratified and euxinic marine basins and in microbial mats. This is because of their dual requirements for light for energy and hydrogen sulfide as an electron donor for carbon fixation. The photosynthetic bacteria are sources of C_{40} aromatic carotenoids such as chlorobactene, okenone and isorenieratene. These carotenoids, among others, enable the efficient harvesting of light of different wavelengths and, thereby allow their hosts to make maximal use of the energy available at different depths in the water column. For example, isorenieratene is produced by the brown pigmented strains of the GSB living at 80-100m water depth whereas okenone is produced by the

PSB which require much higher light intensities and tend to live at depths as shallow as 20m. Chlorobactene and β-isorenieratene are formed by GSB living at intermediate depths. Strongly reducing conditions, along with H_2S, are required to saturate the double bonds of the hydrocarbon chain and thereby preserve these carotenoids as their carotane derivatives. These concepts provide a working model for the interpretation of oil carotenoid patterns as depicted in cartoon form in Figure 7.

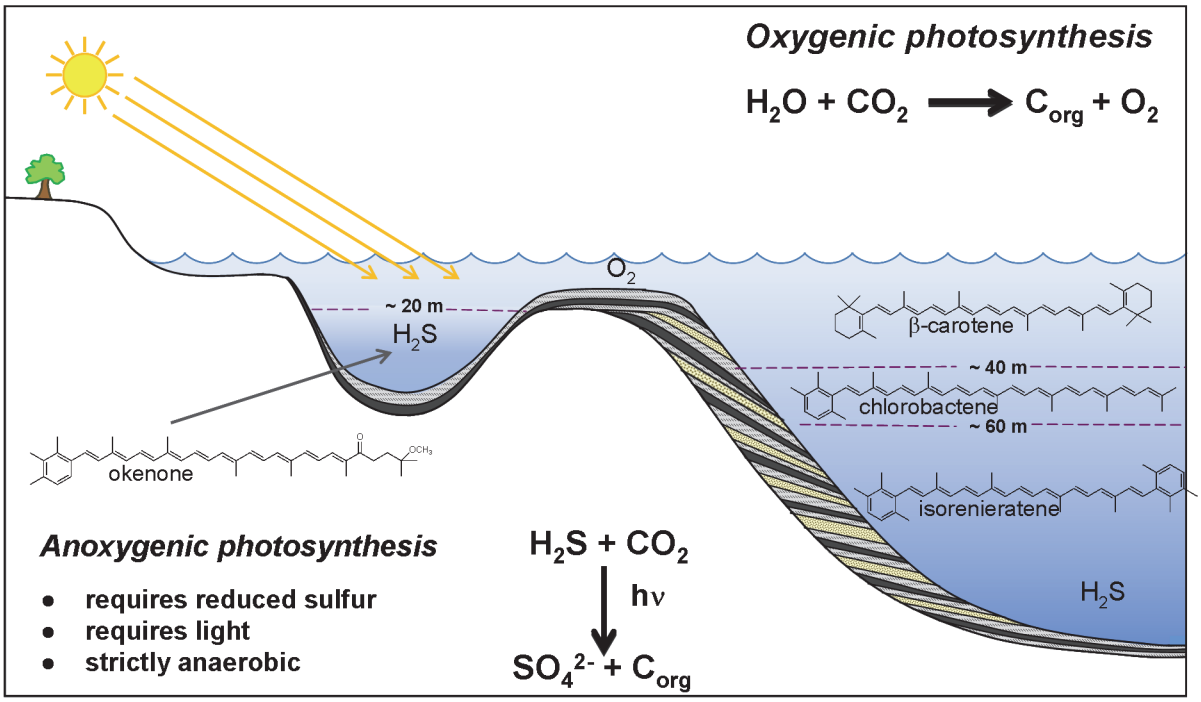

Figure 7. Cartoon depicting carotenoid pigments from algae & sulfur bacteria vs water column redox.

The following figures illustrate the application of carotenoid hydrocarbons to resource (and conventional) plays in multiple basins. In Figure 8, paleorenieratane is prominent in Paleozoic-sourced oils such as those generated from the Anadarko Basin Woodford source rock. As maturity progresses (as measured by vitrinite reflectance equivalent or %VREQ), β-carotane is the most stable and paleorenieratane appears more stable than isorenieratane.

Upper Cretaceous-sourced oils from the open Western Interior Seaway (e.g., Niobrara) contain no isorenieratane and abundant 'after β' carotane isomer. Oils generated from the Lower Cretaceous Mowry shale, deposited during a restricted Western Interior Seaway, have abundant isorenieratane and a much smaller 'after β' isomer (Figure 9).

Carotenoid patterns for oils that are derived from marine source rocks deposited in increasingly restricted marine settings are shown in Figure 10. CN0266 is from an Upper Cretaceous marine shale in the Alberta Basin, FL0002 is from the Lower Cretaceous marine carbonate Sunniland Fm. and KW0003 is also a carbonate-sourced oil from the Upper Jurassic Burgan Raimula High.

Figure 10 shows good oil correlation between an oil produced from the younger Cardium reservoir compared to an oil produced from the Turonian Second White Specks source unit in the Alberta Basin.

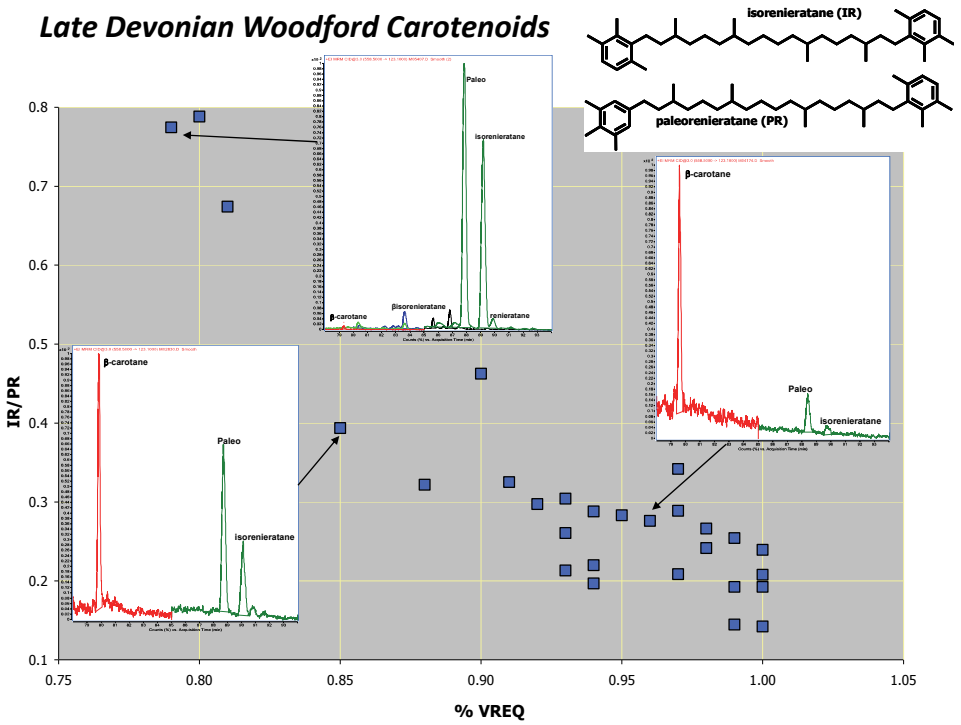

Figure 8. Paleorenieratane is prominent in Paleozoic-sourced oils such as those generated from the Anadarko Basin Woodford source rock. As maturity progresses, β-carotane is the most stable and paleorenieratane appears more stable than isorenieratane.

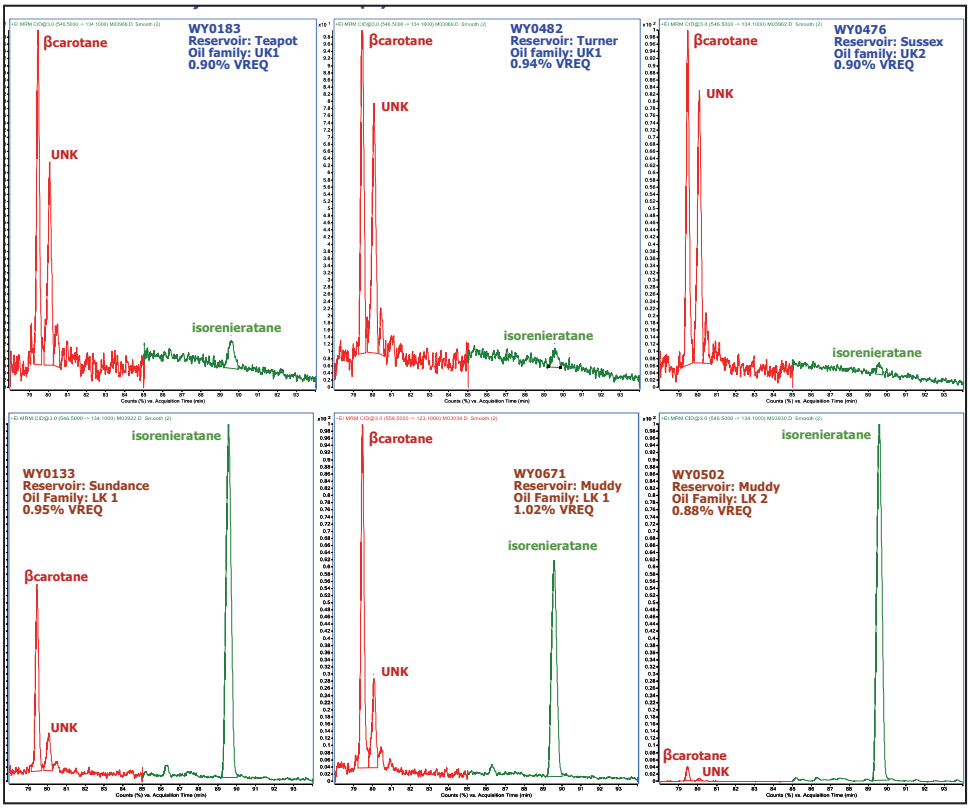

Figure 9. The secular distribution of C_{40} aromatic and saturated carotenoids also displayed unexpected trends. For example, a novel carotane isomer which elutes just after β-carotane (UNK, aka 'After β□) occurs primarily in oils generated from Cretaceous marine sources, with Upper Cretaceous-sourced oils (upper portion; Niobrara source rock) containing more of the isomer than Lower Cretaceous oils (lower portion; Mowry source rock).

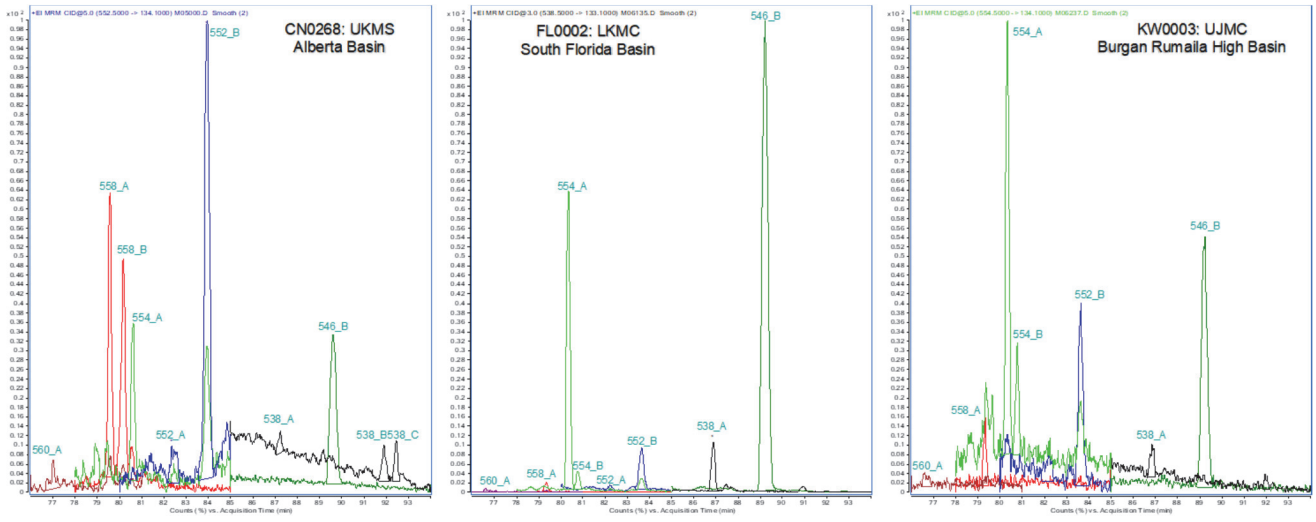

Figure 10. Carotenoid patterns for oils that are derived from marine source rocks deposited, left to right, in increasingly restricted marine settings. CN0266 is from an Upper Cretaceous marine shale in the Alberta Basin, FL0002 is from the Lower Cretaceous marine carbonate Sunniland Fm. and KW0003 is also a carbonate-sourced oil from the Upper Jurassic Burgan Raimula High. (Peak 558_A = β-carotane; Peak 554_A = clorobactane; Peak 552_B = β-isoreniertane; Peak 546_B = isorenieratane)

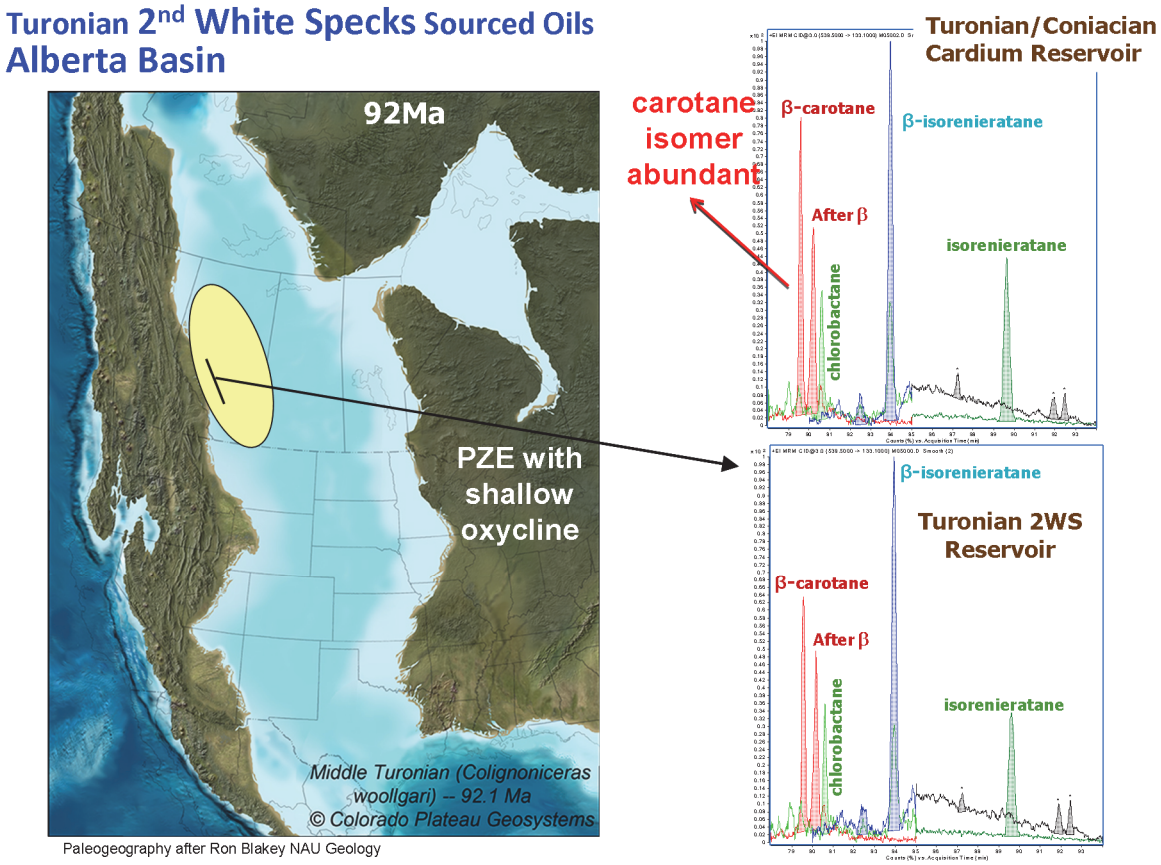

Figure 11: During more restricted Western Interior Seaway times, such as Lower Cretaceous Mowry source rock deposition, isorenieratane is abundant (persistent PZE conditions) with a relatively low After β component. Upper Cretaceous 2nd White Specks sourced oils have chorobactane, reflecting shallow water PZE, with deposition near the western margin.

Conclusions

As illustrated for multiple petroleum systems, both compound specific carbon isotope (CSIA) and carotenoid hydrocarbon analyses provide new insights into resource plays using novel and relatively rapid analytical methods. Additionally, expanded isotopic data and carotenoid biomarker distributions of petroleum systems tend to be distinct so that, in combination with commonly used sterane and hopane biomarkers, allow oil-oil and oil-source correlations to be made with much greater fidelity.

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