

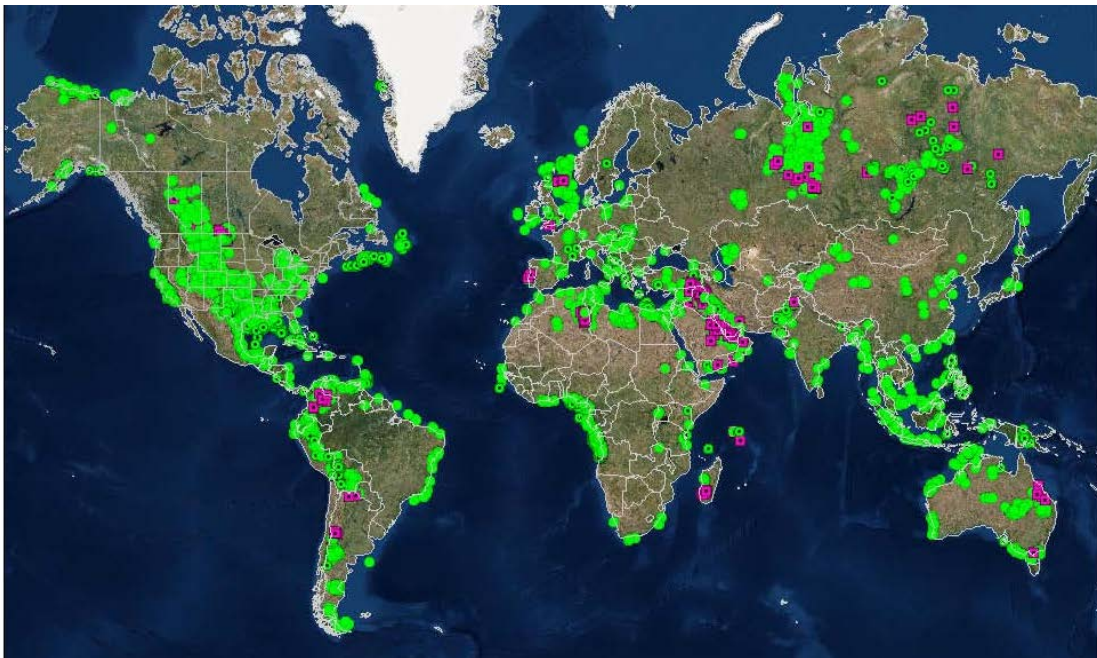
# Carotenoid-derived Biomarkers as Geochemical Tools for Petroleum Exploration and Paleoreconstruction

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**Summary:** This project is a study of diagnostic biomarker hydrocarbons derived from the pigments of algae and photosynthetic bacteria and their application as correlation tools in basins with complex oil-source rock relationships and for paleoenvironmental reconstruction. 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.

The cost to join this research consortium is US\$15,000 for the first five participants and US\$20,000 for participants 6-10. After 10 participants, the cost is US\$25,000. The project will commence after the commitment of at least three participants, and the duration of the project will be one year with a project update meeting in Houston after six months. A complete interpretive report and all data files constitute the deliverables.

**Samples:** The study is based on a comprehensive analysis of at least 100 oil samples from >50 petroleum systems that range in age from Neoproterozoic to the Paleogene. The oils represent all known source rock facies types from distal marine shales, marls, evaporites, shelfal carbonates as well as lacustrine shales and carbonates. Some representative source rock samples will also be included. Oil samples will be drawn from GeoMark's global collection of over 14,000 oils (Figure 1). Participants are not required to submit samples but can choose up to five oils each from either GeoMark's collection or from their own set of oils/source rocks.



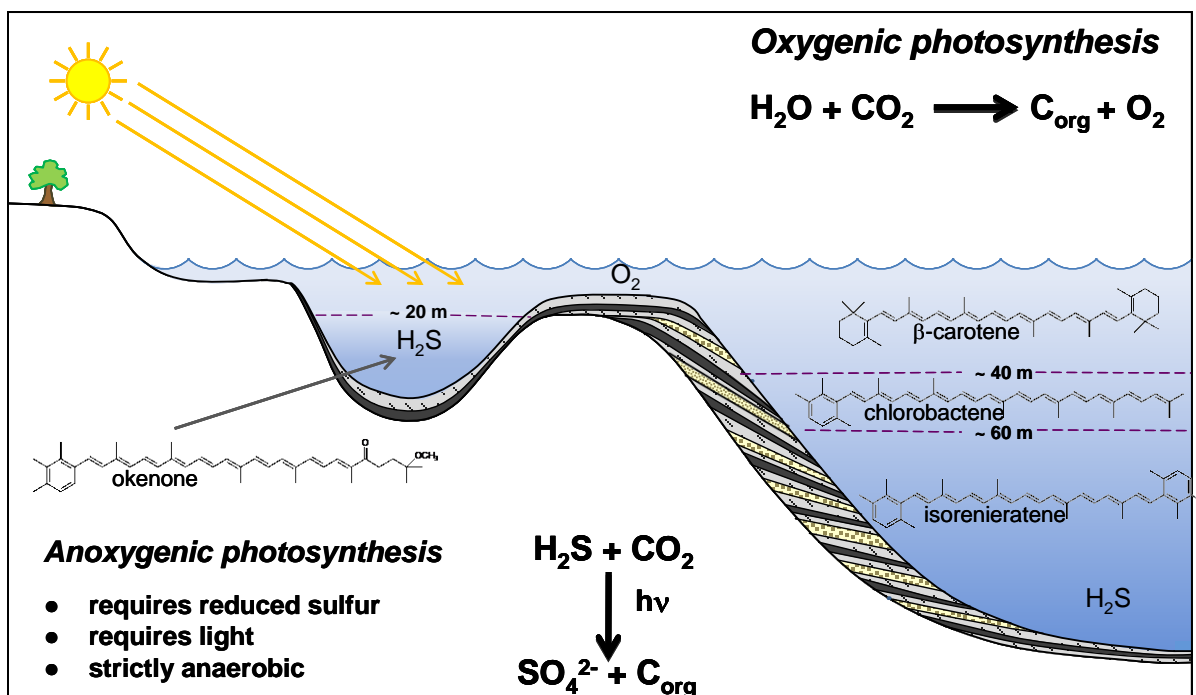
**Figure 1:** Map of distribution of crude oils (green dots; GeoMark's RFDbase.com)

**Rationale:** 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 study we focus on the carotenoid pigments which are relatively more stable than the chlorophylls.

Eukaryotic algae and cyanobacteria use carotenes ( $\beta$ - and  $\gamma$ - mainly) and lycopene as their primary carotenoid pigments that are preserved as the saturated hydrocarbons  $\beta$ -carotane,  $\gamma$ -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  $\beta$ -isorenieratene are formed by GSB living at intermediate depths. Strongly reducing conditions 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 2.

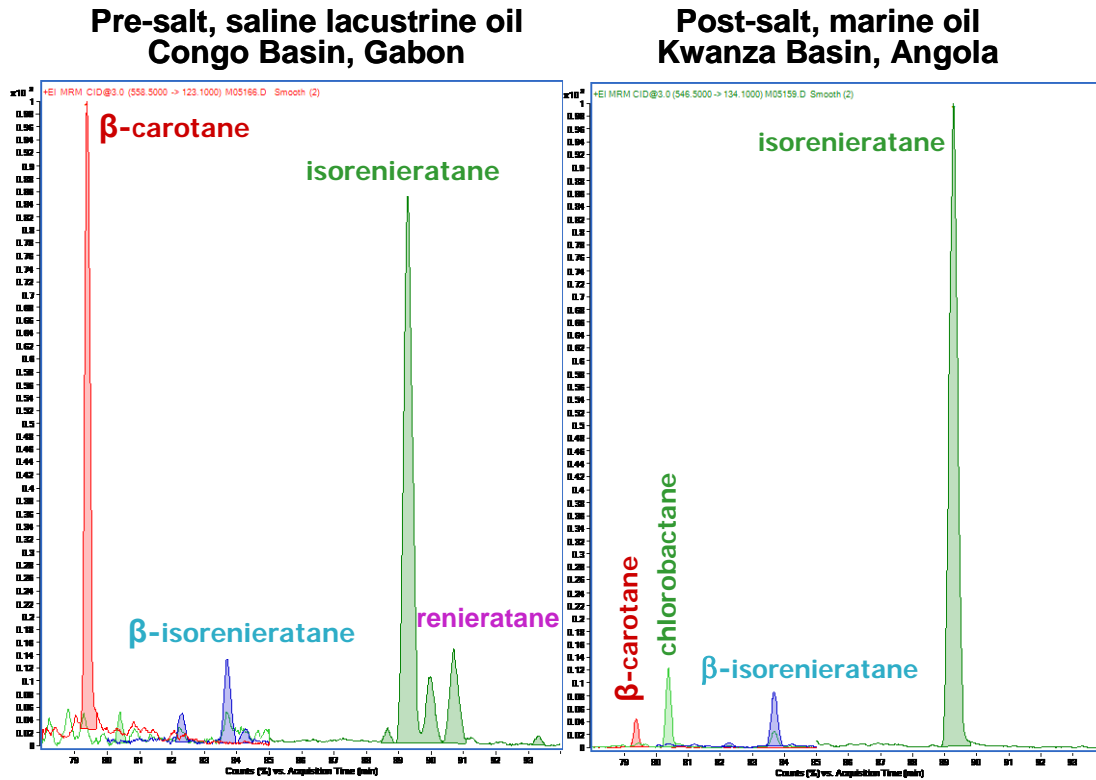
In a preliminary survey, we found that intact  $C_{40}$  carotenoid-derived hydrocarbons were present in a majority of the oils examined. In some cases we only observed the saturated carotane hydrocarbons produced by algae and cyanobacteria. However, a great many of the oils contained the  $C_{40}$  aromatic carotenoids of GSB and PSB and, from this, we can deduce that the source rocks from which these oils originated must have been deposited under water columns that had sufficiently restricted circulation to enable euxinic conditions to develop on a regular basis. In many cases we detected  $C_{40}$  carotenoids that are thought to be specific to the purple sulfur bacteria. This implies that the shallow sunlit surface ocean (<24 m) became sulfidic more frequently in the geologic past than was previously thought or that benthic microbial mats were a common feature of these source rock depositional systems.



**Figure 2:** A depiction of where in the water column and under what conditions carotenoids form. Low-light-adapted brown pigmented green sulfur bacteria, also known as chlorobi, which require sulfide and sunlight live as deep as 80-100 m in the water column and produce isorenieratene. High-light-adapted chlorobi live within 40 m of the surface indicating a shallower oxycline. Cyanobacteria and algae producing  $\beta$ -carotene don't tolerate sulfide and live in oxygenated surface waters. Purple sulfur bacteria, which also require sulfide need more intense sunlight than chlorobi and tend to live in very restricted water bodies which can support an oxycline as low as 20m.

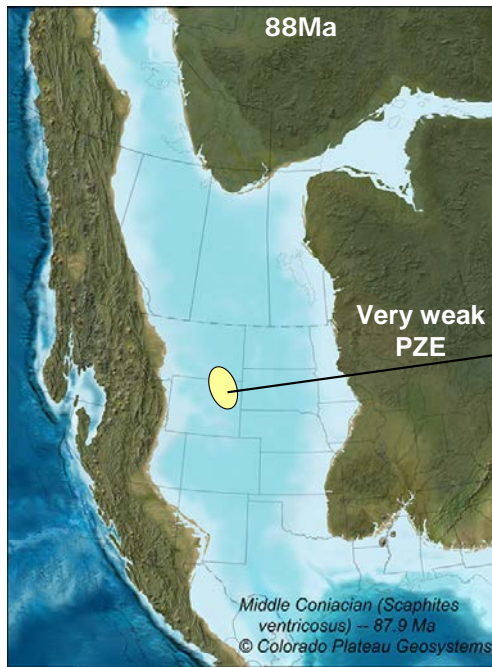
Carotenoid-derived hydrocarbons tend to be well preserved, even in mature samples, and were prevalent in oils sourced from both marine carbonates, deep-water shales and lacustrine sediments (Figures 3, 4, and 5). The secular distribution of  $C_{40}$  aromatic and saturated carotenoids also displayed unexpected trends. For example, a novel carotane isomer which elutes just after  $\beta$ -carotane (After  $\beta$ ) occurs primarily in oils generated from Cretaceous marine sources, with Upper Cretaceous-sourced oils (Figure 4) containing more of the isomer than Lower Cretaceous oils (Figure 5).

Overall, the carotenoid biomarker distributions of petroleum systems tend to be distinct so that, in combination with data on isotopes and the commonly used sterane and hopane biomarkers, they allow oil-oil and oil-source correlations to be made with much greater fidelity.



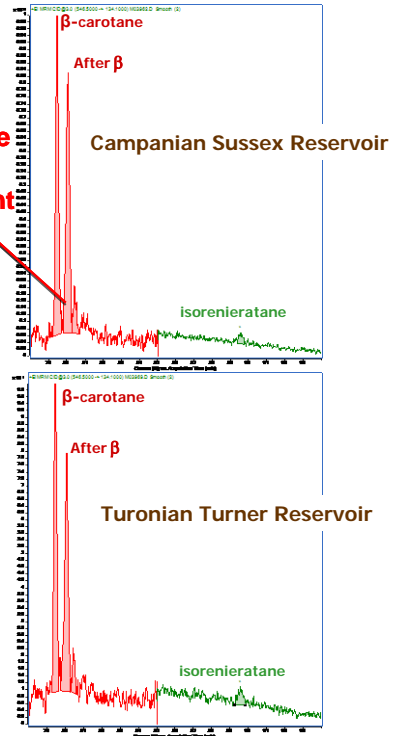
**Figure 3:** Contrasting carotenoid patterns in two oils from the South Atlantic. Biomarkers identify the Gabon oil as ‘saline lacustrine’ while the oil from Angola is typed as coming from a marine shale. PZE (photoc zone euxinia) is evident in both samples including the presence of chlorobactane.

**Coniacian/Santonian Niobrara Sourced Oils  
Powder River Basin**

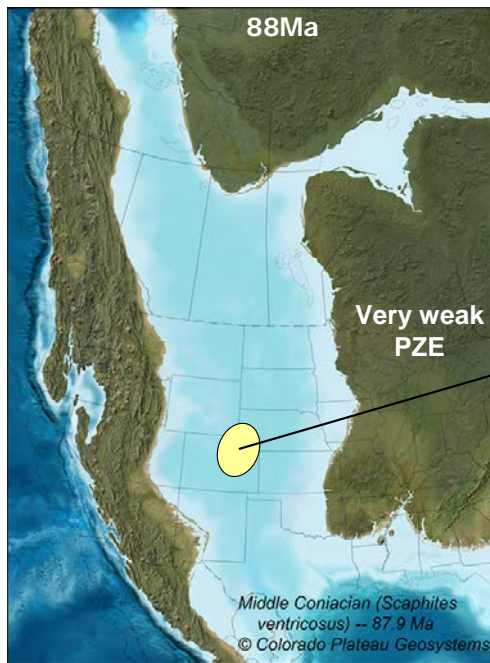


Paleogeography after Ron Blakey NAU Geology

**Novel  
carotane  
isomer  
abundant**

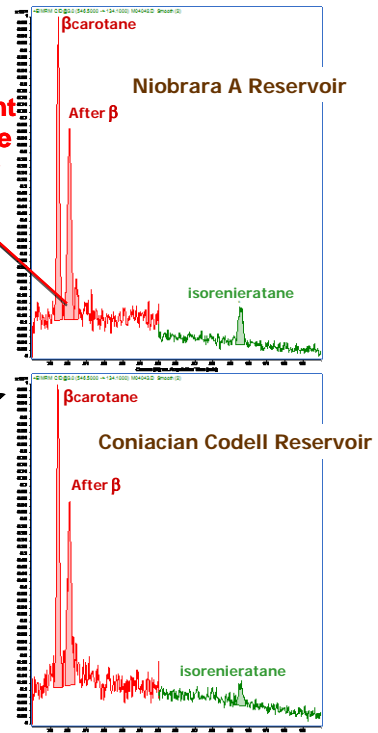


**Coniacian/Santonian Niobrara Sourced Oils  
Denver Basin**



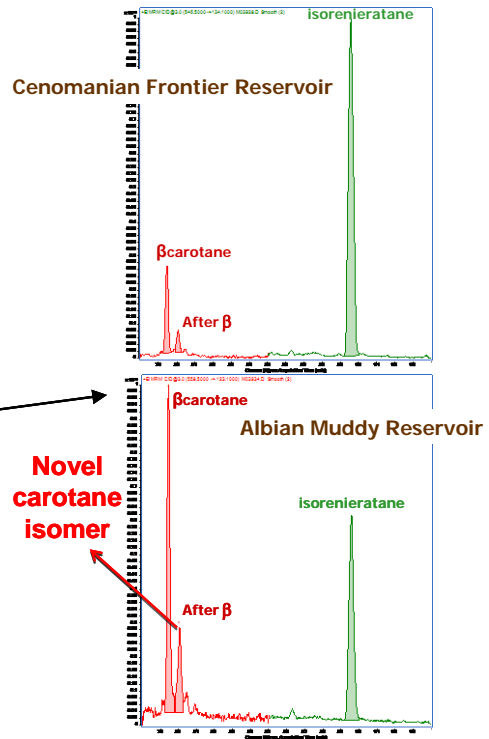
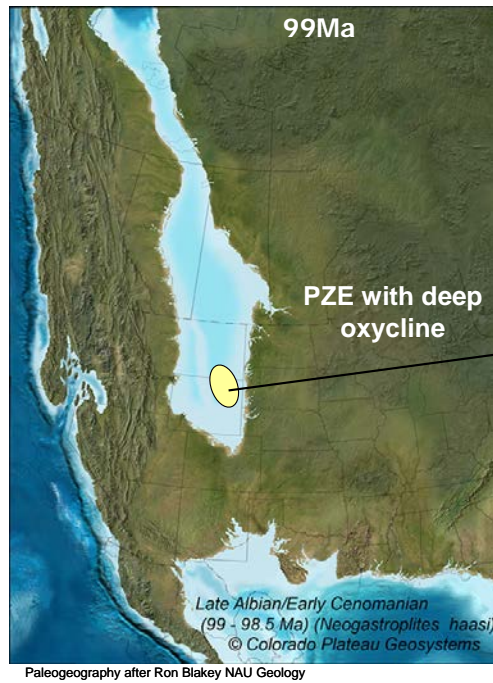
Paleogeography after Ron Blakey NAU Geology

**abundant  
carotane  
isomer**

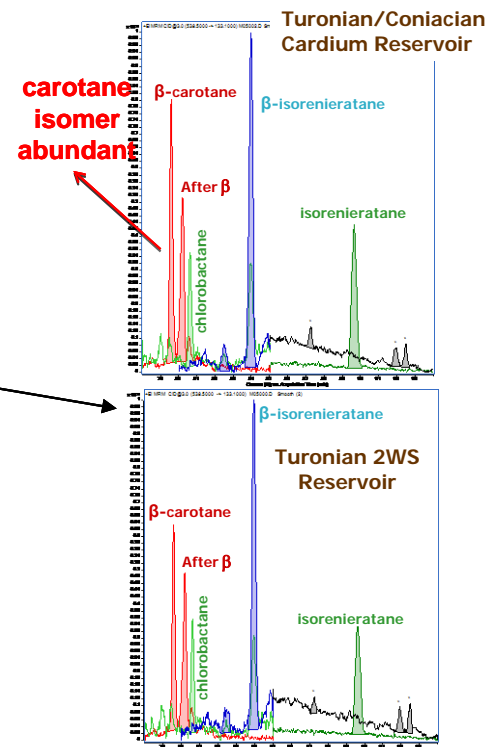
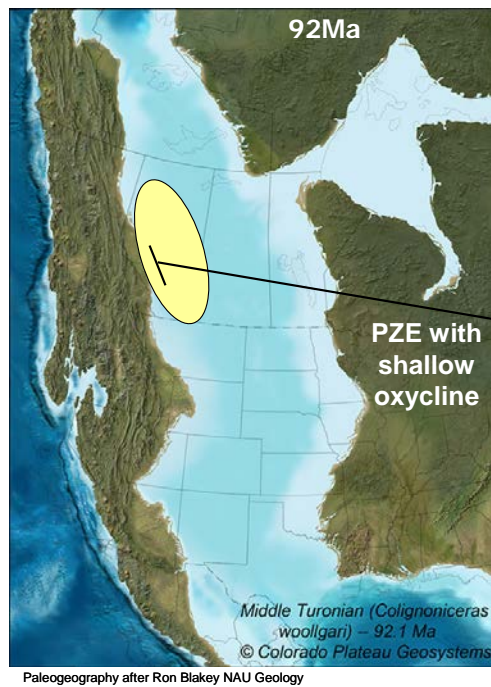


**Figure 4:** The novel 'After  $\beta$ ' carotane isomer is higher relative to  $\beta$ -carotane in oils from Upper Cretaceous source rocks than Lower Cretaceous oils. Only traces of isorenieratane are present in oils from the Niobrara suggesting more open water depositional conditions with little photic zone euxinia (PZE).

## Albian/Cenomanian Mowry Sourced Oils Powder River Basin



## Turonian 2<sup>nd</sup> White Specks Sourced Oils Alberta Basin



**Figure 5:** During more restricted WIS times, such as Lower Cretaceous Mowry source rock deposition, isorenieratane is abundant (persistent PZE conditions) with a relatively low After  $\beta$  component. Upper Cretaceous 2<sup>nd</sup> White Specks sourced oils have chlorobactane, reflecting shallow water PZE, with deposition near the western margin.

**Methods:** We have developed an analytical method that is simple and allows all carotenoids, steranes and hopanes to be measured in a single run. Whole oils or sedimentary bitumens are flooded with pentane to precipitate the asphaltenes. The resulting total hydrocarbon fractions are spiked with standards and injected on 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.

**References:**

French, K.L., Rocher, D., Zumberge, J.E. and Summons, R.E., 2015. Assessing the distribution of sedimentary C40 carotenoids through time. *Geobiology* 13, 139–151. [DOI: 10.1111/gbi.12126].

Summons, R.E. *et al.*, 2017. Carotenoid-derived biomarkers as geochemical tools for petroleum exploration and paleoreconstruction. AAPG Annual Meeting, Houston TX., Abstracts with programs.

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