



Carotenoid-derived Hydrocarbons as a Geochemical Tool for Petroleum Exploration and Paleoreconstruction

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Summary

Here we report a comprehensive study of petroleum samples, and a suite of their corresponding source rocks, which were examined for the distributions and contents of C₄₀ carotenoid pigment derivatives. The sample set comprised oils and sedimentary sequences that ranged in age from Mesoproterozoic to the Paleogene and we used gas chromatography, coupled with tandem mass spectrometry, to look in detail at the biomarker distributions of both saturated and aromatic hydrocarbon fractions.

The anoxygenic green and purple sulfur bacteria (known as Chlorobi and Chromatiaceae, or GSB and PSB, respectively), the known sources of C₄₀ aromatic carotenoid hydrocarbons, are reportedly confined to the euxinic water columns of restricted, stratified marine basins or microbial mats. This is because of their dual requirements for light for energy and sulfide as an electron donor for carbon fixation. Thus, it came as a surprise to find that C₄₀ aromatic carotenoid-derived hydrocarbons were present in a majority of the petroleum systems studied here. From this we can deduce that the petroleum source rocks that sourced these oils must have been deposited under water columns with sufficiently restricted circulation to enable euxinic conditions to develop on a regular basis. In many cases we detected C₄₀ carotenoids, including okenane, renieratane, renierapurpane, and β-renierapurpane 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 source rock depositional systems.

Carotenoid-derived hydrocarbons are well-preserved, even in mature samples, and were prevalent in oils source from both marine carbonates and deep-water shales. Carotanes, derived from the β-carotene of oxygenic phototrophs (algae and cyanobacteria), were also present in all but the most mature oils in this study including oils from fresh and saline lacustrine petroleum systems where they were the main compounds identified. The secular distribution of C₄₀ diaromatic, monoaromatic, and saturated carotenoids also displayed unexpected trends that, together with sterane biomarkers of the saturated hydrocarbon fractions, afford tighter constraints on the geological ages of oils for which the source rocks are unknown. Overall, the carotenoid biomarker distributions of petroleum systems tend to be distinct so that, in combination with data on isotopes and other biomarkers, they allow oil-oil and oil-source correlations to be made with much greater fidelity.