CAROTENOIDS AS CORRELATION TOOLS AND ENVIRONMENT- AND AGE-SENSITIVE BIOMARKERS IN OILS

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Introduction

The C_{12}-C_{21} aryl isoprenoids, degradation products derived from the aromatic C_{40} carotenoid precursors of green and purple sulfur bacteria, have been recognized and utilized as biomarkers for photic zone euxinia (PZE) in source rock depositional environments. However, their distributions can be very complex and suffer from multiple interferences that limit their wide use as correlation and interpretive tools. More recent work has shown that simpler and more consistent patterns for the intact saturated and aromatic C_{40} carotenoids can be readily acquired by GC-QQQ-MS. These compounds are even preserved in mature samples and show trends that are diagnostic for source rock environments (French et al., 2015). In this study we analysed ~150 petroleum samples that could be confidently affiliated with source rocks of known age and paleoenvironmental setting. Following asphaltene precipitation, dilution and addition of internal standards, the maltene fractions were analysed with the QQQ configured to detect conventional sterane, triterpane and tricyclic biomarkers together with the C_{40} carotenoids in a single GCMS run.

Results and Discussion

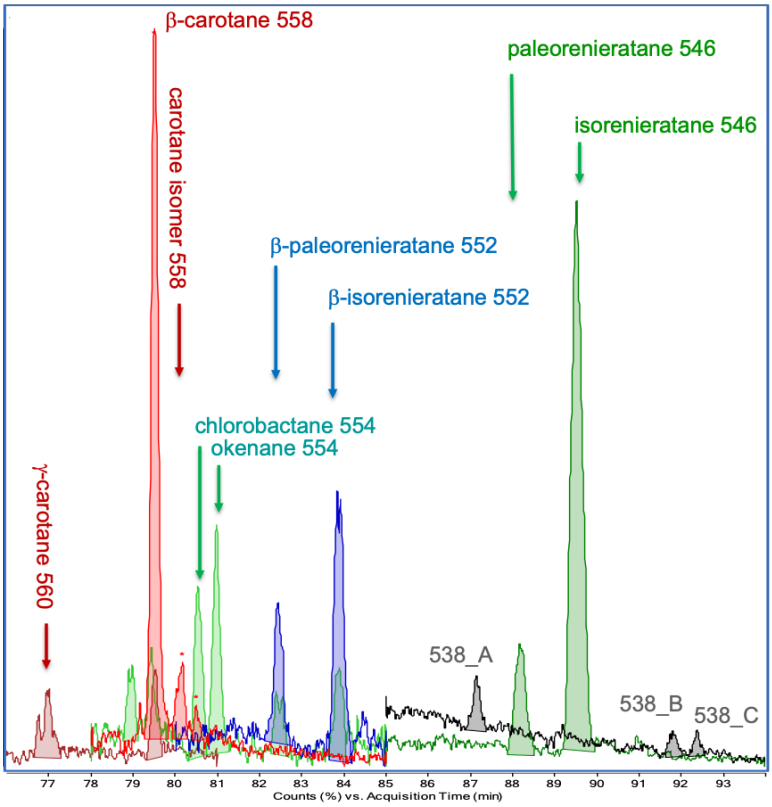

Figure showing the carotenoid distribution in a composite oil to illustrate the array of compounds that can be detected and quantified using GC-QQQ-MS.

We found that C_{40} carotenoid derivatives are widely distributed in crude oil samples across geological time and in all types of paleoenvironmental settings. In fact, very few samples in our study set were devoid of detectable carotenoids. The exceptions to this observation were oils from some distal marine shales and non-marine samples with significant contributions of organic matter from vascular plants. Another primary control on their absolute abundances was found to be thermal maturity with progressive loss of the aromatic carotenoids at vitrinite reflectance equivalent values above 1.1% Ro.

The presence of saturated and aromatic carotenoids, minimally isorenieratene along with carotene, in most of the samples analysed implies that green sulfur bacteria (GSB) were present, at least episodically, in most environments where petroleum source rocks were being deposited. This is rather surprising since, as far as we can determine, there are no regions of the open oceans of today where the oxygen minimum zones are sufficiently shallow and sulfidic to support significant populations of GSB. As expected, paleorenieratane predominated over isorenieratane in a significant proportion of the early Paleozoic oils in our study set (French et al., 2015; Hartgers et al., 1994; Koopmans et al., 1996; Requejo et al., 1992) and its presence was notable in many other oils extending from the Neoproterozoic to the early Jurassic.

The monoaromatic carotenoids chlorobactane and okenane were generally much lower in abundance and more sparsely distributed. From the few exceptions to this observation, it appears that they are largely confined to samples derived from highly restricted or shallow evaporitic settings, both marine and non-marine. This observation adds weight to the hypothesis that microbial mats, as opposed to planktonic communities, (French et al., 2015) could be their primary source.

Overall, the C_{40} 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. They have greater utility than aryl isoprenoids since the C_{40} precursors and their primary diagenetic products provide better constraints on biological sources paleoenvironmental settings.

References

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