DITERPANE DISTRIBUTIONS IN OILS IN RELATION TO SOURCE AGE AND DEPOSITIONAL ENVIRONMENT

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Introduction

Gymnosperms dominated the terrestrial vegetation until the rise of the angiosperms, and their distinctive diterpane distributions, which include tetracyclanes and tricyclanes, have been traced back to the Early Carboniferous (Disnar & Harouna 1994). Tetracyclanes are reported to dominate over tricyclanes in Devonian and Carboniferous coals, whereas tricyclanes predominate in Mesozoic and Tertiary oils/rocks (Peters et al. 2005). Phyllocladane (Phyl) is, at most, of low abundance in Devonian samples, but is generally a major component in Carboniferous and Permian samples. Fleck et al. (2001) has proposed that more open water conditions, favouring pteridophytes and bryophytes, yield more isopimarane (iPim) and kaurane (Kau). Paul & Dutta (2015) concluded that iPim and abietane (Ab) are produced by all conifer families (e.g. araucaria, podocarps, cypress and pine), whereas Bey and Phyl precursors are found in cypress, podocarps and araucaria, but have not been reported in pines.

The most reliable gymnosperm indications are provided by abundant tetracyclanes Bey, Phyl and Kau (Peters et al. 2005). These compounds are synthesized by the gibberellin pathway, which is important in reproduction and growth in fungi and bacteria, as well as plants. Tricyclanes such as rimuane (Rim), pimarane (Pim), rosane (Ros) and iPim have been found in oils from pre-Silurian marine sources, indicating that microbial sources are possible. This poster presents examples of distributions likely to be encountered in oils representing various source ages and depositional environments, attempts to establish the identity of erstwhile higher-plant markers in pre-Silurian oils and illustrates some chromatographic problems associated with identifications based on m/z 123 mass chromatograms.

Results

Common features of the diterpane retention time region of oils from carbonate/evaporate settings are abundant C_{20} cheilanthane (20/3) and an unknown tricyclane (Z). Also present are variable, often abundant, Pim and 8β-methyl-13α-ethylpodocarpane (13α20/3; Wang & Simoneit 1995). Samples from Ordovician and younger sources can also contain traces of Rim, Ros, iPim and Ab, and sometimes also Bey and atisane isomers (aka atirisane, Ati1 & Ati2).

In oils from distal marine shales, tricyclanes are again more abundant than tetracyclanes, although diterpanes abundances are relatively low. From the Ordovician onwards variable amounts of Pim, 13α20/3, Z and 20/3 are observed. Occasional traces of Rim, Ros and iPim may be seen from the Early Jurassic. Among tetracyclanes, traces of Bey, Ati1/βKau and Ati2 can be present. The frequent dominance of Ati and Bey in oils with high diasterane content has been attributed to acid/clay catalyzed kaurene rearrangement (Peters et al. 2005).

Higher plant contributions to oils from proximal marine and lacustrine settings can be highly variable. In the most obvious coal mire samples, tetracyclanes are typically dominant, whereas transitional and paralic facies can produce oils with diterpane distributions similar to distal marine shales, as can Tertiary lacustrine sources. Diterpanes can be impoverished in oils from Palaeozoic proximal marine settings when compared to Cretaceous-Tertiary counterparts.

The relative retention times of the tricyclanes and tetracyclanes can vary depending upon GC conditions. For example, a small change in temperature programme rate can cause the Ros/Bey pair to switch positions, so it is inappropriate to monitor only m/z 123 during SIR analyses.

Conclusions

The medical applications of diterpanes has resulted in studies of DNA sequencing in bacteria related to diterpane synthases, providing some insight into potential sources prior to the appearance of higher plants (Smanski et al. 2012). Among the bacterial groups found to contain diterpane synthases are many types of soil bacteria (actinomycetes, streptomycetes, Nocardia and Rhizobium) and some non-S bacteria (Chloroflexus and Rhodospirillum). These bacteria can produce kaurene, pimara-9(11),15-diene and atiserene, so the likely geological end products are Kau, Ati and Pim, which are among the most common diterpanes in the oils from carbonates/evaporites and marine shales.

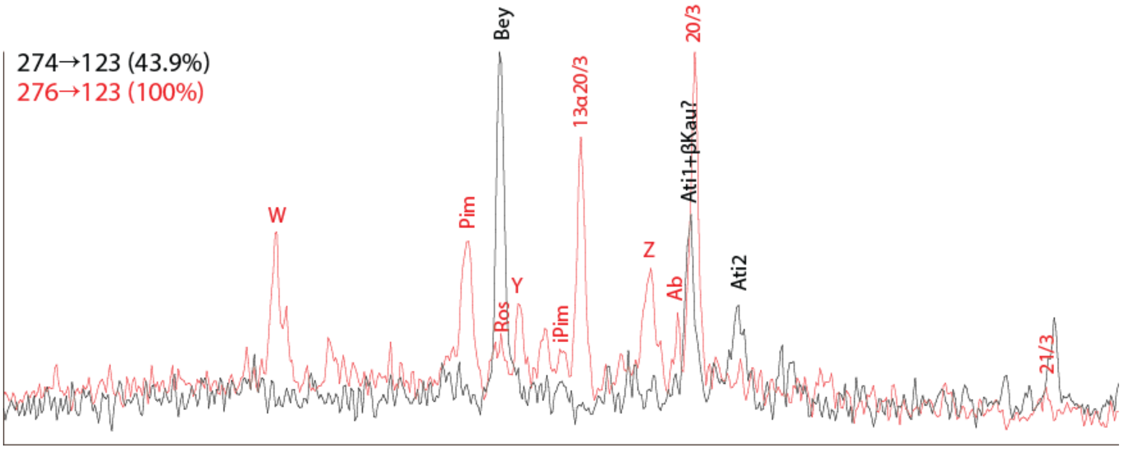

Figure 1. Diterpanes in Ordovician marine shale (W–Z unknowns).

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