

Figure 5: Plot of kerogen H/C atomic ratio against PHGC parameters benzene/ n -C₆, toluene/ n -C₇, and ethylbenzene + xylenes/ n -C₈. See Figure 4 for key.

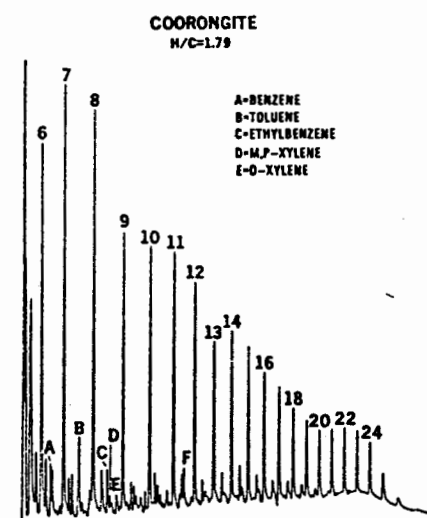


Figure 6: PHGC trace of coorongite (Recent). Peak F = n -pentylbenzene.

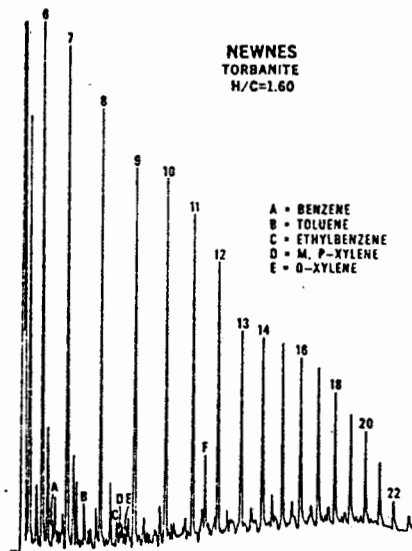


Figure 7: PHGC trace of Newnes torbanite (Permian).
Peak F = *n*-pentylbenzene.

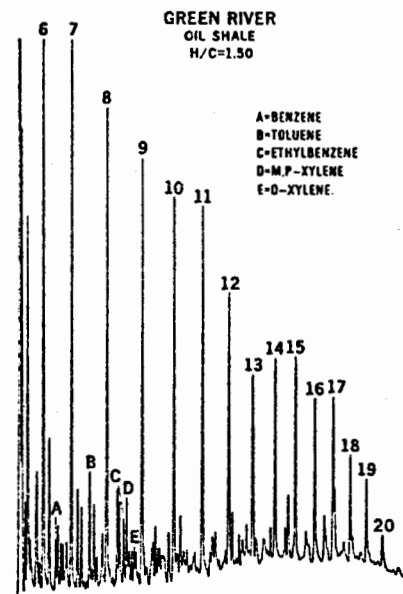


Figure 8: PHGC trace of Type I kerogen from Green
River Formation oil shale (Eocene).

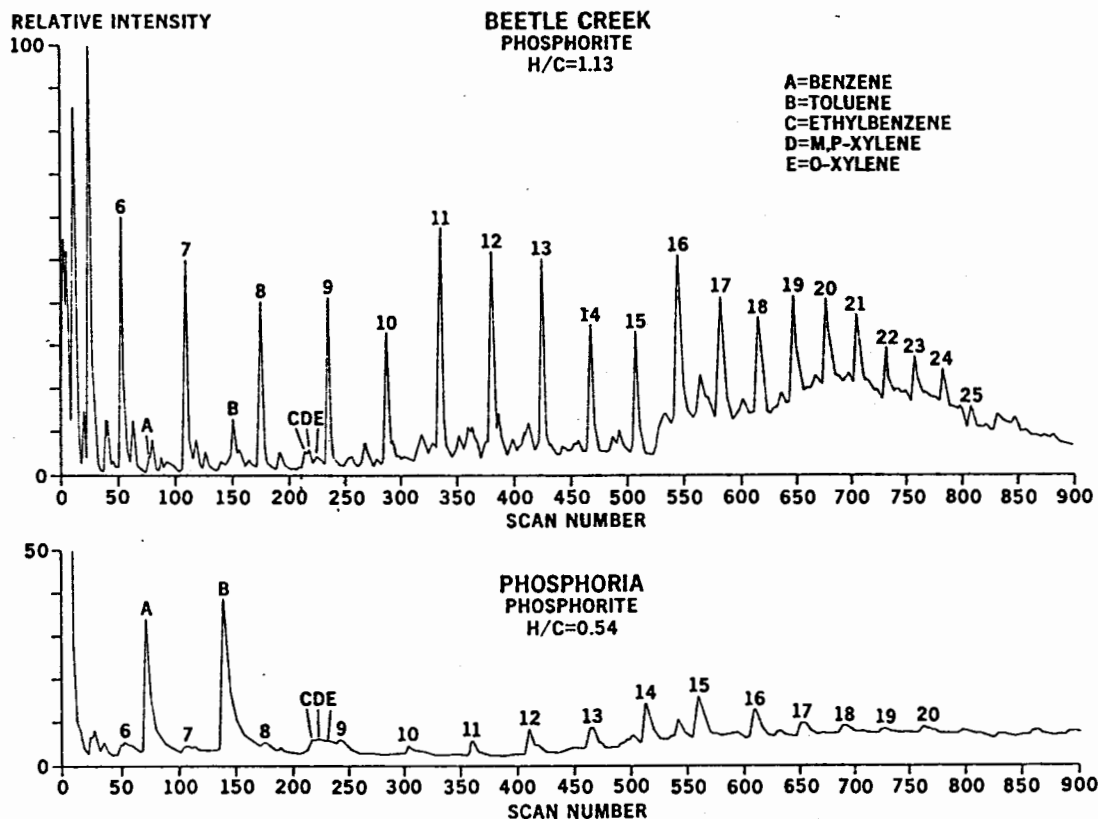


Figure 9: (a) PHGC trace of Type I kerogen from Beetle Creek Formation phosphorite (Cambrian).
(b) PHGC trace of secondary Type III kerogen from Phosphoria Formation (Meade Peak Member) phosphorite (Permian).

No systematic increase in aromaticity, as measured by the PHGC parameters percent simple aromatics in C_6 - C_{20} hydrocarbons, benzene/ n - C_6 , toluene/ n - C_7 and ethylbenzene + xylenes/ n - C_8 (Figs. 4, 5), is evident for Type I kerogen over the atomic H/C range 1.70-1.13 (corresponding to ca. 0.2-0.8% R_{max} equivalent vitrinite reflectance). Larter et al. (1978) noted a similar constancy of the *m*-xylene/ n - C_8 alkene ratio in alginite A pyrolysates over the same rank interval. It is noteworthy that even the appreciable humic, higher-plant contribution to the Joadja torbanite (vitrinite + inertinite = ca. 25% of total organic matter: A. J. Kantsler, personal communication) is not reflected in any of the above pyrolytic indices of aromaticity.

Comparison of the pyrograms of the medium rank (marginally mature) and high rank (mature) phosphorite kerogens shown in Fig. 9 throws light on the structural modification of an unusual variety of Type I microbial kerogen during the process of oil generation. Such kerogen, represented here by a sample from the Cambrian Beetle Creek Formation (Table 1), comprises a complex mixture of alginite B, acritarchs, and at least two vitrinite-like materials of which the major one has affinities with bituminite (A.J. Kantsler and A.C. Hutton, personal communication). By analogy with the genesis of micrinite from bituminite in high-volatile bituminous coals (Teichmuller, 1974), the Phosphoria kerogen may have formed via the rapid geochemical disproportionation of primary Type I organic matter similar to that preserved in the Beetle Creek phosphorite (or possibly a Type II kerogen),

resulting in liquid hydrocarbons (oil) and a secondary aromatic, oxygen-enriched kerogen. This would readily account for the appearance of its PHGC trace (Fig. 9b) which features toluene and benzene as major components, with residual amounts of *n*-alkanes up to C₂₀.

Type II Kerogen

Petrologically, Type II microbial kerogens consist of bituminite and liptodetrinite (e.g. McMinn Formation, Horn Valley Silstone: Table I) or, more commonly, a mixture of lipid-rich (Type I) and humic (Type III) organic matter (e.g. Toolebuc Formation oil shale, Tertiary limestones: Table I). Accordingly, on a van Krevelen diagram, they occupy an intermediate position which overlaps the liptinite coalification pathway (Fig. 1).

H/C values of the Type II kerogens analysed in this study extend over the range 1.29-0.75 (Table I). The 'mixed' Type II kerogens are those to which land plant residues have contributed and in Figs. 4 and 5 they stand out as being more aromatic in composition than Type I and other Type II kerogens of similar H/C value. The PHGC trace of the Toolebuc 'mixed' Type II kerogen (Fig. 10) illustrates this enhanced concentration of aromatic hydrocarbons relative to *n*-alkanes. Also apparent are probable pristane and phytane (pr > ph), and a moderate odd/even predominance in the C₁₀-C₂₀ *n*-alkanes.

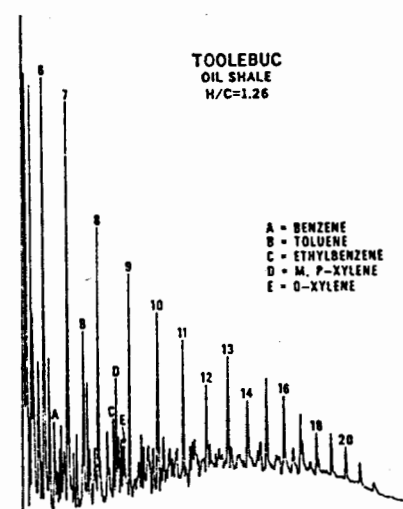


Figure 10: PHGC trace of Type II kerogen from Toolebuc Formation oil shale (Cretaceous).

Pyrolysates of Type II (bituminite, liptodetrinite) kerogens, with decreasing H/C atomic ratio, show a slight decrease in the proportion and chain-length of *n*-alkanes (Fig. 4) but otherwise differ little in aromaticity from Type I kerogens (Figs. 4, 5).

Type III Kerogen

Microbial organic matter of this kind (Table 2) is either a heteropolycondensate of algal humic substances or, as previously discussed, a by-product of the generation of oil from certain lipid-rich kerogens. The former, primary Type III kerogen, has a similar elemental composition to vitrinite (Fig. 1) and is exemplified by the humic organic matter in some

subtidal stromatolites (Fig. 2); whereas the latter is somewhat more depleted in hydrogen (cf. macrinite pathway, Fig. 1). The more aromatic composition of both primary and secondary Type III kerogens (relative to Types I and II) is reflected in their H/C values (0.83-0.54, Table 1) and PHGC parameters (Figs. 4,5). In the pyrolysates of half the samples analysed the C₁₀₊ n-alkanes display an odd carbon-number predominance. The significance of this feature is discussed below.

Type IV Kerogen

The majority of the stromatolite kerogens isolated by McKirdy (1976) have a hydrogen-poor composition analogous to that of the coal maceral fusinite (Fig. 2, Table 2). The H/C atomic ratios of these and other Type IV kerogens selected for PHGC analysis fall within the range 0.54-0.28 (Table 1). Stromatolitic kerogens with H/C values \leq ca. 0.25 appear to be of higher rank and are here described as subgraphitic (Table 1).

Comparison of the PHGC traces of stromatolitic and non-stromatolitic Type IV kerogens reveals that the former are considerably more aliphatic in character than the latter, although both contain more aromatic hydrocarbons than do pyrograms of Type III kerogens (Figs. 4,5). The aliphaticity of volatile carbon in the stromatolitic kerogens is illustrated by Fig. 11, and is still evident, although much less pronounced, in sub-graphitic samples (Fig. 12).

It should be emphasised that for Type IV kerogens the volatile carbon analysed by PHGC constitutes a very small proportion (ca. 20% or less) of the total organic carbon and, therefore, is far less representative of the carbon skeleton of the kerogen structure than are the pyrolysates of other kerogen types. PHGC of Type IV kerogens provides information on relatively minor structural moieties bonded to the periphery of what presumably is a highly condensed aromatic 'nucleus', itself largely inaccessible to pyrolytic analysis.

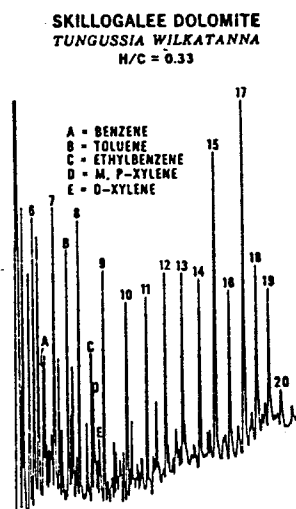


Figure 11: PHGC trace of Type IV kerogen from the stromatolite *Tungussia wilkatanna*, Skillogalee Dolomite (Late Proterozoic).

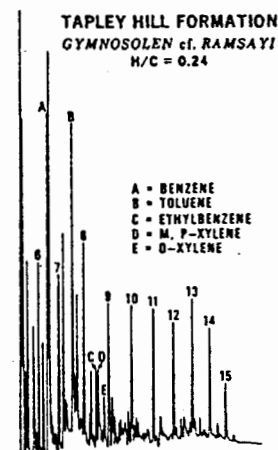


Figure 12: PHGC trace of (?) subgraphitic kerogen from the stromatolite *Gymnosolen cf. ramsayi*, Tapley Hill Formation (Late Proterozoic).

A predominance (which may be quite striking, as in Fig. 11) of odd carbon-numbered homologues in the C_{10} - C_{20} *n*-alkanes of many Type IV and Type III kerogen pyrolysates (Table 1) provides a clue to the origin of the straight-chain aliphatic component of this otherwise highly aromatic organic matter. A similar odd/even predominance has been noted in the *n*-alkane profiles of pre-Devonian oils and their source-rock extracts (McKirdy and Kantsler, 1978). Evidence from degradation studies of algal and bacterial cultures (Lijmbach, 1975; Philp and Calvin, 1976) suggests that, in both cases, this feature may be attributable to the cell-wall lipids of bacteria.

Rank Versus Type

PHGC traces of low to medium-rank kerogens ($H/C > 0.80$) show that the principal effect of early maturation is a steady decrease in the proportion and chain-length of the C_6+ *n*-alkanes. The relative abundance in the pyrolysate of simple aromatic hydrocarbons (viz. benzene, toluene, ethylbenzene and the xylenes) increases significantly with decreasing H/C atomic ratio only at values less than 0.80. This may indicate a primary compositional difference between hydrogen-rich (Types I and II) and hydrogen-poor (Types III and IV) kerogens, or a major discontinuity in the structural evolution of microbial kerogen during catagenesis. Notable exceptions to the general pattern of maturation are Type IV stromatolitic kerogens which contain anomalously aliphatic volatile carbon.

Notwithstanding the arguments of Larter *et al.* (1978) against the use of benzene in any pyrolytic index of aromaticity, for the experimental conditions employed in this study, the ratio benzene/*n*- C_6 appears to be just as valid a measure of aromaticity as indicators based on other aromatic species such as toluene and the xylenes.

SUMMARY AND CONCLUSIONS

PHGC is an effective tool for the structural analysis of microbial kerogens which possess 'carbon skeletons' ranging from hydrogen-rich, highly aliphatic to hydrogen-poor, aromatic in character. Clearly, algal and bacterial precursors do not give rise only to aliphatic kerogens.

Oil generation from certain aliphatic (Type I and II) microbial kerogens may involve their rapid disproportionation into liquid hydrocarbons and a residual humic (secondary Type III) kerogen possibly analogous in composition and mode of origin to micrinite in bituminous

coals.

Stromatolitic Type IV kerogens contain small amounts of volatile carbon that is anomalously aliphatic for organic matter so deficient in hydrogen. The aliphatic component of these and other primary humic kerogens (Type III and IV) commonly is 'fingerprinted' by odd/even predominance in the C₁₀₊ n-alkanes and may be a biological marker of bacterial cell-wall lipids.

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