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COMPARATIVE ANALYSIS OF STROMATOLITIC AND OTHER MICROBIAL KEROGENS BY PYROLYSIS-HYDROGENATION-GAS CHROMATOGRAPHY (PHGC)

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INTRODUCTION

The technique of pyrolysis-hydrogenation-gas chromatography (PHGC: McHugh *et al.*, 1976, 1978) provides a convenient means of analysing the carbon-skeleton structures of coals and coal-derived kerogens. Catalytic hydrogenation of the pyrolysate has the advantage of simplifying its composition prior to analysis by GC (or gas chromatography-mass spectrometry, GC-MS) without significantly diminishing the amount of structural information available in the resulting pyrogram. Alkenes and heteroatomic compounds are converted to the corresponding alkane or aromatic hydrocarbon. In the present study we extend the application of PHGC to kerogens of microbial origin, i.e., insoluble sedimentary organic matter derived from algae and bacteria.

The use of pyrolysis-gas chromatography (PGC) to study microbial kerogens is not new. Scott *et al.* (1970) pyrolysed finely-ground samples of early Precambrian (>3 Gyr B.P.) carbonaceous sedimentary rocks from the Swaziland System, South Africa, and identified hydrocarbons containing up to 20 carbon atoms. Onverwacht Group samples yielded mainly aromatic hydrocarbons whereas a sample from the younger Fig Tree Group gave mostly normal and branched aliphatic hydrocarbons (but cf. Philp, 1980). Kerogens isolated by acid digestion from three Precambrian cherts (including the Skillogalee Dolomite: Table 1) were analysed in a similar manner by Dungworth and Schwartz (1972). Stepwise PGC of 30 organic-rich Precambrian sediments by Leventhal *et al.* (1975) yielded CO_2, CO and low molecular-weight hydrocarbons (C_1-C_8). The H/C atomic ratios of these kerogens, where reported, are low (generally <0.30) and typical of high-rank organic matter. Analysis by vacuum pyrolysis-GC-MS of kerogen (thucolite) from the 2.6 Gyr old Witwatersrand Vaal Reef gold-uranium deposit, demonstrated its highly aromatic character which is attributable to prolonged exposure of the kerogen to ionising radiation (Nagy *et al.*, 1977; Zumberge *et al.*, 1978).

Algae were major precursors of the organic matter in coorongite, oil shales and boghead coals (Hutton *et al.*, 1980), and in the most prolific petroleum source rocks (Tissot and Welte, 1978). Previous pyrolytic studies of oil-shale kerogen from the Green River Formation (Table 1) include those by Scrima *et al.* (1974), Gallegos (1975), Leventhal (1976) and Larter *et al.* (1978, 1979). In boghead coals and oil shales, algal remains are preserved morphologically as either discrete chlorophycean bodies (*alginite A*) or thin films of lipid-enriched algal (probably cyanophycean) mat material (*alginite B*) (Hutton *et al.*, 1980). PGC analyses of alginite concentrates from torbanites have been reported by Larter *et al.* (1977, 1978) and Larter and Douglas (1978). The pyrogram of a Silurian marine shale containing abundant *Tasmanites* (Combaz, 1971) shows that, like other varieties of alginite A, tasmanite kerogen is rich in long-chain aliphatic moeities. Hydrogen-rich organic matter of this kind (original atomic H/C > 1.5: Fig. 1) has been classified as Type I kerogen by Tissot and Welte (1978). However, both forms of alginite also may contribute to the more heterogenous liptinitic Type II kerogen (Table 2), exemplified in this study by the Cretaceous Toolebuc Formation oil shale (Table 1).

McKirdy (1976) showed that the kerogen preserved in Proterozoic and Palaeozoic stromatolitic carbonates and cherts commonly is depleted in hydrogen and enriched in oxygen (Fig. 2) consistent with its probable derivation largely from cyanophyte mucilage (mucopolysaccharide). Such organic matter herein is designated Type III or IV kerogen (Table 2). PHGC analysis of selected stromatolitic kerogens (McKirdy, McHugh and Tardif, unpublished results) provides additional geochemical evidence for the previously reported chemotaxonomic similarity of two examples of the stromatolite form genus *Tungussia*. Pyrolysis in vacuo of kerogen from the 2.7 Gyr old Rupemba-Belingwe stromatolite (Sklarew and Nagy, 1979)

TABLE 1

SAMPLES ANALYSED BY PHGC

Formation or Deposit	Basin and Location[a]	Sediment Type	Age	Kerogen			
				C % d.a.f.[b]	H/C atomic	O/C atomic	Type[d]
Coorongite	Murray, S.A.	algal peat	Recent	72.7	1.79	0.16	I
Green River	Piceance Creek, CO.	oil shale	Eocene	76.9	1.50	0.10[c]	I
Illawarra Coal Measures	Sydney, N.S.W.	torbanite	Permian				
- Newnes				83.9	1.60	0.03	I
- Joadja				82.1	1.33	0.06	I
Beetle Creek	Georgina, Q.	phosphorite	Cambrian	80.9	1.13	0.05	I
Un-named	Browse, W.A.	limestone	Eocene	61.2	1.29	0.29	II
Hibernia Beds	Browse, W.A.	limestone	Miocene	72.0	1.27	0.16	II
Toolebuc	Eromanga, Q.	oil shale	Cretaceous	68.6	1.26	0.14[c]	II
Horn Valley Siltstone	Amadeus, N.T.	shale	Ordovician	64.3	1.10		II
Horn Valley Siltstone	Amadeus, N.T.	shale	Ordovician	85.8	0.75	0.06	II
McMinn	McArthur, N.T.	shale	Proterozoic	73.6	1.17	0.13	II
McMinn	McArthur, N.T.	shale	Proterozoic	81.2	0.86	0.06	II
Phosphoria	Cordilleran, WY.	phosphorite	Permian	68.7	0.54	0.18	III
Stairway Sandstone	Amadeus, N.T.	shale	Ordovician	66.7	0.83	0.28	III
Pacoota Sandstone	Amadeus, N.T.	shale	Ordovician	70.7	0.63	0.23	III
Jay Creek Limestone	Amadeus, N.T.	siltstone	Cambrian	71.6	0.71	0.23[c]	III
Pertatataka	Amadeus, N.T.	shale	Proterozoic	78.0	0.66	0.15[c]	III
McMinn	McArthur, N.T.	shale	Proterozoic	81.9	0.65	0.08	III
McMinn	McArthur, N.T.	shale	Proterozoic	81.4	0.59	0.10[c]	III
McMinn	McArthur, N.T.	shale	Proterozoic	83.4	0.54	0.09[c]	III
Cavan Limestone	Taemas Platform, N.S.W.	stromatolite	Devonian	81.2	0.54	0.12[c]	IV
Wonoka	Adelaide Geosyncline, S.A.	stromatolite	Proterozoic	77.9	0.47	0.09[c]	IV
Skillogalee Dolomite	Adelaide Geosyncline, S.A.	stromatolite	Proterozoic	75.3	0.33	0.20[c]	IV
Skillogalee Dolomite	Adelaide Geosyncline, S.A.	cryptalgal chert	Proterozoic	85.2	0.31	0.08	IV
Bitter Springs	Amadeus, N.T.	dolomite	Proterozoic		0.28		IV
Bitter Springs	Amadeus, N.T.	gypsiferous dol.	Proterozoic		0.46		IV
McMinn	McArthur, N.T.	shale	Proterozoic	86.6	0.36	0.06	IV
Cavan Limestone	Taemas Platform, N.S.W.	stromatolite	Devonian	88.2	0.26	0.06	s/g
Tapley Hill	Adelaide Geosyncline, S.A.	stromatolite	Proterozoic	84.0	0.24	0.07	s/g
Skillogalee Dolomite	Adelaide Geosyncline, S.A.	cryptalgal chert	Proterozoic	92.2	0.19		s/g
Skillogalee Dolomite	Adelaide Geosyncline, S.A.	stromatolite	Proterozoic	90.9	0.10	0.03	s/g

[a] Details of sample localities are given in McKirdy (1977). [b] d.a.f. = dry, ash-free.

[c] C_{10+} *n*-alkanes in PHGC trace display significant odd carbon-number predominance. [d] s/g = subgraphitic.

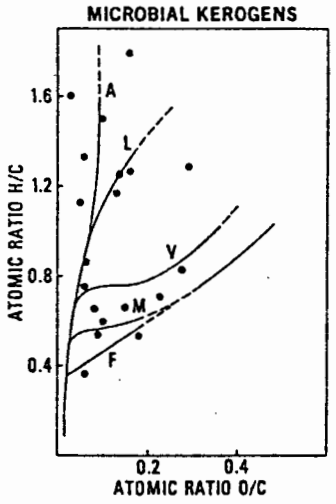

Figure 1: Van Krevelen diagram showing elemental composition of selected microbial kerogens. Lines are coalification tracks of coal macerals: A = alginite, L = liptinite (exinite), V = vitrinite, M = macrinite, F = fusinite.

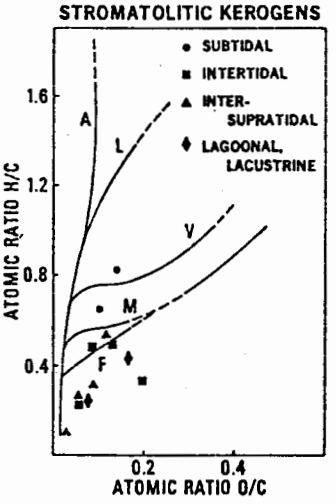

Figure 2: Van Krevelen diagram showing elemental composition of stromatolitic kerogens. See Fig. 1 for key.

yielded, among other compounds, 2, 5-dimethylfuran, 2-methylfuran, and C_9-C_{20} *n*-alkanes. These products were interpreted respectively as remnants of biological carbohydrates and fatty acids. Furan was identified in the pyrolysates of two other Precambrian stromatolitic kerogens analysed by the same technique (Nagy *et al.*, 1977).

Previous pyrolytic investigations of microbial kerogens may be categorised, according to their principal aim, as follows:

TABLE 2

POSSIBLE ORIGIN AND MACERAL EQUIVALENTS OF THE PRINCIPAL TYPES OF MICROBIAL KEROGEN (MODIFIED FROM McKIRDY, 1977)

Kerogen Type [a]	Maceral Group	Equivalent Individual Macerals	Source
Type I	Liptinite	alginite A	Lipid-rich eukaryotic algae, e.g. *Reinschia*, *Tasmanites*, *Gloecapsomorpha*
		alginite B	Bloom and mat-forming blue-green algae
Type II[b]	Liptinite	bituminite	Partially degraded (i.e. sapropelised) algae and zooplankton; bacterial lipids
		liptodetrinite	Acritarchs
Type III	Huminite	humodetrinite detrogelinite	Biochemically humidified and gelified algal cellulose; Maillard condensation of algal amino acids and carbohydrates
		dopplerite	Calcium humate formed from algal humic acids in carbonate-depositing environments
	Vitrinite	desmocollinite	Geochemically gelified algal huminite incorporating some bacterial lipids; e.g. sub-tidal stromatolites
	(Inertinite)[c]	rank micrinite	Coalification residue of alginite B and/or bituminite
Type IV	Inertinite	degradofusinite	Partially oxidised algal cellulose and sheath mucilage; bacterial pectic tissue (cell walls); e.g. inter-supratidal stromatolites

[a] As defined by H/C and O/C atomic ratios, or H/C and %C d.a.f. where incomplete elemental analysis precluded determination of oxygen content.

[b] Alternatively, a mixture of lipid-rich (Type I) and humic (Type III) organic matter,

[c] Although micrinite has been traditionally classified as a member of the inertinite group, it "is neither inert nor especially carbon-rich, since it contains relatively large amounts of hydrogen and volatile matter" (Teichmuller, 1975, p. 228).

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1. characterisation of algal/bacterial organic matter using 'finger-print' pyrograms;
2. identification of specific 'biological marker' compounds in the pyrolysate; or
3. monitoring of the structural evolution of specific kerogen types during diagenesis and catagenesis.

The present study is based on earlier work (McKirdy, 1977) which showed that microbial kerogens are surprisingly diverse in composition (Figs. 1, 2; Table 2). PHGC was employed to investigate further this hitherto poorly documented compositional diversity and, in particular, its dependence on (i) the dominant precursor material (lipid, protein or carbohydrate) and (ii) the degree of thermal alteration (i.e., rank) of the kerogen.

SAMPLES AND METHODS

The 31 kerogens analysed in this study (Table 1) include eight from stromatolitic sediments and range in age from mid-Proterozoic (ca. 1.4 Gyr B.P.) to Recent. For many samples, microbial affinity was established simply on the basis of their pre-Devonian age. In the case of kerogens isolated from younger sediments, some of which were deposited in lacustrine or paralic environments, recognition of their source as predominantly microbial depended on micropalaeontological and other organic geochemical evidence.

Finely-ground sediments were extracted in Soxhlet apparatus for at least 48 h with a mixture of benzene and methanol (3:2) before isolation of the kerogen using the method of Powell *et al.* (1975). For coorongite and the two torbanites, PHGC analyses were performed on material which had not been extracted with solvent. The kerogen concentrates were analysed for C, H, N, S and ash by the Australian Microanalytical Service, Melbourne. Oxygen was determined by difference.

The basic apparatus and experimental parameters for PHGC analysis have been described by McHugh *et al.* (1976). For the present work, the equipment and operating conditions were modified as shown in Fig. 3. Upon completion of the pyrolysis, the cold trap was quickly removed from the end of the hydrogenator and placed (via Swagelok fittings) in the oven of the gas chromtograph between the injection port and SCOT column. Rapid heating of the trap by direct applicatibn of a low-voltage current volatilised the hydrogenated pyrolysis products and facilitated their flushing on to the column. The oven door was then closed and the chromatograph temperature-programmed from 50-300° at 10° min^{-1}, with a final heating time of 10 min. Major peaks in the C_4-C_{20} range of the resulting chromatogram were identified by comparison with a reference PHGC trace of the Greta coal. In this trace, obtained under the same experimental conditions, the major component peaks had been characterised by mass spectrometry. PHGC traces of the two phosphorite kerogens were obtained with a Finnegan 1015D GC-MS system, incorporating a 20 m x 0.5 mm i.d. glass SCOT column (stationary liquid phase SE-30), and interfaced to a Finnegan 6000 data system.

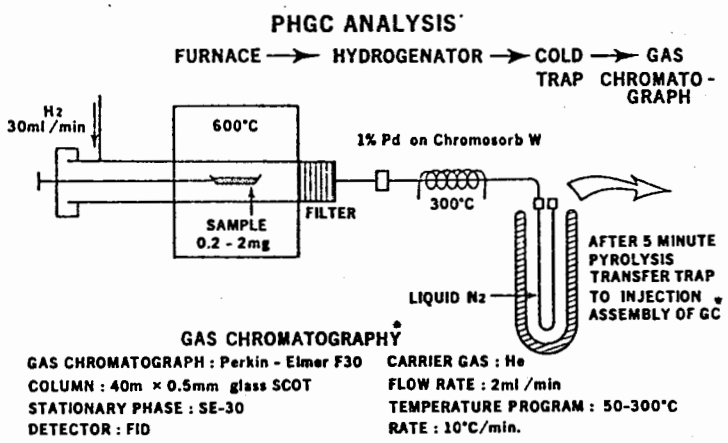

Figure 3: Schematic diagram of PHGC equipment and operating conditions.

RESULTS AND DISCUSSION

Microanalytical and PHGC data on examples of the four principal types of microbial kerogen (Table 2) are presented in Table 1 and Figs. 4 and 5. The spread in H/C values (1.79 - 0.10) reflects differences in both genetic type and thermal maturity. Kerogen maturation levels range from unaltered (early diagenesis) to subgraphitic (anchizone of metamorphism).

Type I Kerogen

This hydrogen-rich organic matter plots along the coalification track of alginite on a van Krevelen diagram (Fig. 1) and is characterised by PHGC traces in which *n*-alkanes are by far the dominant components (Figs. 6-8, 9a). Simple aromatic compounds (viz. benzene, toluene, ethylbenzene and the xylenes) occur in very low concentrations relative to aliphatic moeities (Figs. 4, 5) although the fact that aromatics are present at all in low to medium rank lipid-rich kerogens is significant. An homologous series of C_7-C_{19} *n*-alkylbenzenes (and the corresponding *n*-alkylcyclohexanes) was identified in the hydrogenated pyrolysates of coorongite and the torbanites (alginite A). Larter *et al.* (1978) found that the *n*-alkylbenzene homology in the 600° pyrolysate of a torbanite kerogen extended up to C_{31} and differed significantly from those of sporinite (Type II kerogen) and vitrinite (Type III kerogen).

Kerogen from the Green River Formation oil shale comprises predominantly alginite B. Inspection of its PHGC trace (Fig. 8) reveals the presence of peaks with the same Kovats retention indices on SE-30 as pristane (1710) and phytane (1814) (relative concentration pr>ph), in contrast to their apparent absence in alginite A-derived kerogens (Figs. 6, 7). This observation accords with the findings of Larter *et al.* (1979) who, however, reported only the C_{19} isoprenoid (as prist-1-ene) in the 600° pyrolysate of Green River kerogen.

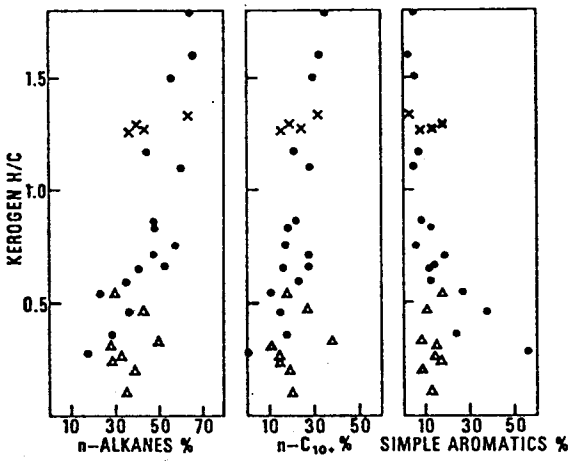

Figure 4: Plot of kerogen H/C atomic ratio against PHGC parameters % *n*-alkanes, % *n*-C_{10+}, and % simple aromatics. Percentage based on all peaks in range *n*-C_6 to *n*-C_{20}. • = microbial (non-stromatolitic) kerogen; x = microbial kerogen with significant land-plant component; Δ = stromatolitic kerogen. Data from phosphorite kerogens are not included.