Geochimica et Cosmochimica Acta Vol. 51, pp. 2681–2697

0016-7037/87/$3.00 + .00

Hydrocarbon biomarkers from Ordovician sediments and the fossil alga *Gloeocapsomorpha prisca* Zalessky 1917

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(*Received February* 17, 1987; *accepted in revised form July* 10, 1987)

Abstract—Numerous Ordovician oils worldwide are known to show unusual and distinctive distributions of hydrocarbons which, it has been suggested, are derived from a "unique benthonic mat-forming non-photosynthetic prokaryotic organism", *Gloeocapsomorpha prisca* Zalessky 1917, which is the major contributor of organic matter. Organic matter-rich sediments from the Canning and Amadeus Basins of Australia, known to contain *G. prisca* fossils and to have the characteristic predominance of odd carbon number (C_{13}–C_{19}) *n*-alkanes, were investigated to determine other hydrocarbon distributions. Sediments from both basins contained abundant *n*-alkylcyclohexanes with odd carbon number predominance (C_{13}–C_{19}) and methyl-*n*-alkylcyclohexanes (C_{14}–C_{20}) which, in immature sediments, showed an even carbon number predominance. The isomer distribution of these latter compounds was determined by direct comparison with synthetic standards. The sediments from both basins also contained very similar distributions of steranes and pentacyclic triterpanes and the derived kerogens had a characteristically light carbon isotope signature.

Pyrolysis of a *G. prisca*-rich kerogen yielded a hydrocarbon mixture with a similar composition to the sediment extract, except that there was a marked increase in the relative abundance of pristane, phytane, alkylcyclohexanes, steranes and hopanes relative to *n*-alkanes. We argue on the basis of the geological, geochemical and palynological data that *G. prisca* was probably planktonic, photosynthetic and very possibly eukaryotic and that the striking character of Ordovician oils and sediments derive from bacterial and other diagenetic imprints superimposed on the primary signature of this organism.

INTRODUCTION

SEVERAL GROUPS OF WORKERS have commented on the rather unusual hydrocarbon distributions commonly encountered in Ordovician oils (*e.g.* POWELL and MCKIRDY, 1972; ILLICH and GRIZZLE, 1983; ALEXANDER *et al.*, 1984; REED *et al.*, 1986). MARTIN *et al.* (1963) first noted a significant odd over even predominance in the *n*-C_{11} to *n*-C_{19} alkane carbon number range in oils from Ordovician reservoirs which have experienced moderately high levels of maturity (equivalent vitrinite reflectance 0.65–1.25%). Subsequent work has shown that such Ordovician oils and organic matter-rich sediments are also characterised by a virtual absence of isoprenoids, particularly pristane and phytane, relative to *n*-alkanes (ZUMBERGE, 1983; ALEXANDER *et al.*, 1984; REED *et al.*, 1986; PALMER, 1986). *n*-Alkylcyclohexanes are generally abundant (FOWLER and DOUGLAS, 1984; REED *et al.*, 1986; RULLKÖTTER *et al.*, 1986) and show a similar odd over even predominance to the *n*-alkanes. FOWLER and DOUGLAS (1984) also tentatively identified abundant methyl-*n*-alkylcyclohexanes with "a carbon number distribution very similar to that of the *n*-alkanes".

ZUMBERGE (1983) found tricyclic terpanes in Ordovician oils from the Williston Basin as did ALEXANDER *et al.* (1984) in Canning Basin crude oils. A range of pentacyclic triterpanes have been identified in Ordovician samples including 17α(H),21β(H)-hopanes (FOWLER and DOUGLAS, 1984; ALEXANDER *et al.*, 1984) and their 3-methyl analogues (ALEXANDER *et al.*, 1984). REED *et al.* (1986) and JACKSON *et al.* (1984) reported very low abundances of hopanes in oils from North America and the Amadeus Basin, respectively. FOWLER (1984) detected no steranes in Ordovician oils from the Williston Basin and JACKSON *et al.* (1984) reported none from the Amadeus Basin. An Ordovician oil from the Canning Basin had a distribution of steranes typical of that observed in mature sedimentary rocks and crude oils and steranes were in low abundance relative to hopanes (ALEXANDER *et al.*, 1984). In one of the few studies of Ordovician sedimentary rocks FOWLER and DOUGLAS (1984) reported trace quantities of an immature distribution of steranes in the Guttenburg "oil rock" which also had an odd over even carbon number predominance of *n*-alkanes and abundant "algal bodies squashed parallel to the bedding plane and exhibiting a strong yellow-orange fluorescence". From their study of these algal bodies, FOSTER *et al.* (1986) considered that on morphological

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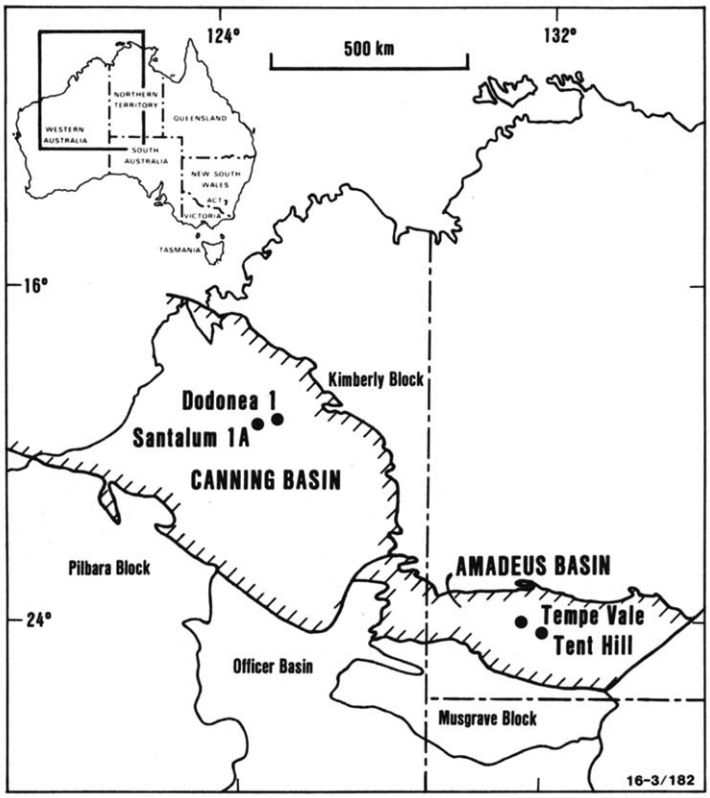

FIG. 1. Geographical location of the Canning and Amadeus Basins (after BROWN *et al.*, 1984).

criteria they belonged to *Gloeocapsomorpha prisca* Zalessky 1917.[1]

Gloeocapsomorpha prisca has been reported from Ordovician sequences from many parts of the world (*e.g.* ZALESSKY, 1917; EISENACK, 1958; MCGREGOR and CRAMER, 1971; COMBAZ and PENIGUEL, 1972; FOSTER *et al.*, 1986; REED *et al.*, 1986) and it is the principal organic source of hydrocarbons recovered from oil shales of the Baltic Basin, U.S.S.R. (see ZALESSKY, 1917; BAUKOV, 1958; PREIN, 1976). REED *et al.* (1986) have proposed a genetic relationship between *G. prisca* and the composition of certain North American oils. FOSTER *et al.* (1986) and MCKIRDY *et al.* (1986) have recognised the same relationship between organic extracts from the Ordovician of the Canning and Amadeus Basins, respectively. *G. prisca* is therefore an important hydrocarbon precursor.

HARRIS (1938), COOKSON (1953), TRAVERSE (1955) and TAPPAN (1980), amongst others, have either suggested or considered that, based on morphology, *Gloeocapsomorpha* is congeneric with the modern green alga *Botryococcus* Kuetzing 1849. This view, however, was not universally accepted (*e.g.* ADAMCZAK, 1963; BURNS, 1982) and on the basis of their respective, and distinctive, suites of biomarkers is not followed by the present authors. *G. prisca* is invariably recovered from sequences bearing marine megafossils and, following the original suggestion of ZALESSKY (1917), most authors have considered it to be of either algal or cyanobacterial affinity. Most recently, however, REED *et al.* (1986) proposed that *G. prisca* was a "non-photosynthetic, prokaryotic, benthonic and mat-forming, aerointolerant chemoautotroph". Their interpretation is based on biogeochemical evidence: namely the apparent low abundance of pristane and phytane and the low ratio of steranes to hopanes in extracts of sediments rich in *G. prisca*, and on sedimentological evidence: namely the occurrence of *G. prisca* in thin undisturbed laminae which discounted the probability that this organism lived in the water column.

This study was initiated to examine, in detail, hydrocarbon biomarker distributions from *G. prisca*-rich sediments, kerogens, and associated oils from the Canning and Amadeus Basins of Australia. With these data, we attempt to clarify the relationship between the oils and the apparent source rocks, particularly through examination of samples exhibiting a wide range of maturities, and to investigate the possible biological affin-

[1] *Note on nomenclature:* Although ZALESSKY (1917) suggested that the fossil forms were similar to the members of the modern *Gloeocapsa* Kuetzing, he assigned them to a new genus *Gloeocapsomorpha* (it is often mis-spelled *Gloeocapsamorpha*). Despite its wide usage, however, the nomenclatural status of *G. prisca* seems questionable. ZALESSKY (1917) did not designate a holotype or formally set out a description of either the genus or the type species; his treatment is more discursive than systematic and this may be in conflict with Art. 41 of the International Code of Botanical Nomenclature.

ities of *G. prisca*, through pyrolysis, and subsequent GC-MS analysis, of isolated microfossils.

DESCRIPTION OF THE SAMPLES

Our samples are from the Goldwyer Formation of the Canning Basin of Western Australia and the Horn Valley Siltstone of the Amadeus Basin of central Australia (Fig. 1). The Goldwyer Formation is a heterogeneous unit consisting of siltstones, sandstones, shales, limestones and dolostones (PURCELL, 1984). It is of late Early-Middle Ordovician age (late Arenig-Llanvirn, *ca.* 478 Ma). The sediments contain a diverse fauna including trilobites, nautiloids, brachiopods, molluscs, chitinozoans, conodonts, graptolites and a rich palynoflora of acritarchs (PLAYFORD and MARTIN, 1984). The Formation is considered to have been deposited in a relatively shallow, warm, epeiric sea covering an area about 500 km wide and 800 km long. The upper part of the Goldwyer Formation (Unit 4 of FOSTER *et al.*, 1986) consists of argillaceous carbonates with total organic carbon (T.O.C.) values ranging from 0.46 to 6.4% (FOSTER *et al.*, 1986). Abundant remains of the microfossil *Gloeocapsomorpha prisca* have been found in this interval and there is a strong correlation between the T.O.C. values and Rock-Eval hydrogen indices. Samples examined from this unit include five sediments and one oil from WMC Dodonea No. 1, a conventional oil well; and one sediment from the WMC Santalum No. 1A stratigraphic well. The Dodonea 299 oil is from a reservoir above the Dodonea sediment samples. Bulk organic geochemical parameters and molecular ratios for biomarkers are given in Tables 1 and 2, respectively.

The Horn Valley Siltstone of the Amadeus Basin in central Australia is also a heterogeneous formation consisting of siltstones, marls and shelly limestones (WELLS *et al.*, 1970; GORTER, 1984; PREISS and FORBES, 1981). The diverse marine fauna and gross sedimentological characteristics of this unit suggest that depositional environments are comparable with those of the Goldwyer, although the Horn Valley Siltstone is older and of late Early Ordovician (Arenig) age. It seems likely that the two basins were connected during some part of the Ordovician. The organic carbon contents of the Horn Valley Siltstone are generally <0.5% but range to over 6% in some calcareous shales. The high T.O.C. values are associated with high abundances of algal organic matter (telalginite) observed by reflected light microscopy. These algal remains have been assigned as *G. prisca* (MCKIRDY *et al.*, 1986). Seven core samples of the organic matter-rich facies in the Horn Valley Siltstone from the Tent Hill No. 1 and Tempe Vale No. 1 stratigraphic holes were examined (Table 1). Data on Ordovician oils from the Amadeus Basin have been published previously (JACKSON *et al.*, 1984).

EXPERIMENTAL

Rock samples were washed briefly in dichloromethane and then ground to a fine powder in a disc mill. Bitumen was extracted from the samples using a mixture of chloroform and methanol (87:13) in a Soxhlet apparatus (72 h).

An aliquot of the bitumen (*ca.* 50–100 mg) was dissolved in dichloromethane:petroleum ether (1:1) and separated using a Sep-Pak Alumina N cartridge into an aliphatic + aromatic hydrocarbon and a resins + asphaltenes fraction (MeOH: $CHCl_3$, 1:1). Activated silica gel (150°C overnight, Merck 40, 70–230 mesh) was used to separate aliphatic from aromatic hydrocarbons by eluting with petroleum ether and dichloromethane:petroleum ether (1:1), respectively. Aliphatic fractions from the Amadeus Basin were further fractionated into normal and branched/cyclic hydrocarbons using 5 Å molecular sieves.

Gas chromatography (GC) was carried out on a Hewlett Packard 5790 A. The gas chromatograph was fitted with a fused silica capillary column (SGE, BP-1, cross-linked methyl silicone, 50 m × 0.33 mm i.d., 0.25 μm film thickness, hydrogen carrier gas) and on-column injector (SGE). Unless

Table 1a. Bulk parameters and Rock-Eval data for Amadeus Basin samples.

SAMPLE	WELL	DEPTH (m)	TOC[1]	S_1[2]	S_2[3]	PI[4]	HI[5]	Tmax[6]	Pr/n-C_{17}[7]	$\delta^{13}C$[8]
2342	Tent Hill 1	1122.2	0.45	0.21	0.48	0.30	107	433	<0.1	-31.2
2370	Tent Hill 1	1145.1	1.15	1.46	1.64	0.47	143	457	<0.1	-31.1
2375	Tent Hill 1	1157.6	2.74	4.14	4.67	0.47	170	455	<0.1	-32.1
2380	Tent Hill 1	1168.0	1.14	1.09	1.30	0.46	114	455	0.2	-29.5
2400	Tempe Vale 1	368.7	3.73	6.81	12.75	0.35	342	443	<0.1	-32.9
2419	Tempe Vale 1	407.6	4.09	7.01	12.15	0.37	297	448	<0.1	-33.6
2420	Tempe Vale 1	409.6	6.30	7.38	20.68	0.26	328	450	<0.1	-32.8

1. % total organic carbon 2. kg tonne^{-1} 3. kg tonne^{-1} 4. production index = S_1/S_1+S_2 5. hydrogen index = S_2/T.O.C. 6. °C 7. pristane/*n*-heptadecane GC peak areas 8. $\delta^{13}C$ of isolated kerogens

Table 1b. Bulk parameters and Rock-Eval data for Canning Basin samples.

SAMPLE	WELL	DEPTH (m)	% *G. prisca*	TOC[1]	S_1[2]	S_2[3]	PI[4]	HI[5]	Tmax[6]	Pr/n-C_{17}[7]	$\delta^{13}C$[8]
299	Dodonea 1	1519.0-1533.3	n.a.(oil)	n.a.	n.a.	n.a	n.a.	n.a.	n.a.	<0.1	
3205	Dodonea 1	1537.8	98	2.97	1.37	24.41	0.05	822	454	<0.1	-33.4
3206	Dodonea 1	1538.3	96	1.75	0.80	8.96	0.08	512	449	<0.1	-33.1
3241	Dodonea 1	1540.0	90	2.89	1.10	19.29	0.05	667	445	<0.1	-32.6
3207	Dodonea 1	1540.1	80	2.40	1.20	18.80	0.06	783	447	<0.1	-33.0
3242	Dodonea 1	1548.4	40	1.53	0.72	7.60	0.09	497	452	<0.1	-32.7
3208	Dodonea 1	1548.5	50	1.42	0.87	9.33	0.09	657	451	<0.1	-32.6
3050	Santalum 1A	470.0	95	6.40	0.50	52.96	0.01	828	433	0.25	-32.1

- not measured; n.a. not applicable; (1-8, see Table 1a).

Table 2a. Molecular ratios for biomarkers in Amadeus Basin samples.

SAMPLE	TRICYCLICS[1] $C_{26}/T_m + T_s$	HOPANES[2] T_m/T_s	HOPANES[3] % αβ C_{30}	HOPANES[4] 3-Me C_{31}/C_{30}	HOPANES[5] % 22 S C_{31}
2342					
2370					
2375	-	0.56	>95		58
2380	0.38	0.59	>95	0.05	60
2400	0.32	0.98	>95	0.10	55
2419		0.94	>95	0.07	57
2420	0.43	0.65	>95	0.02	60

- not measurable; (1-5, see Table 2b)

Table 2b. Molecular ratios for biomarkers in Canning Basin samples.

SAMPLE	TRICYCLICS[1] $C_{26}/T_m + T_s$	HOPANES[2] T_m/T_s	HOPANES[3] % αβ C_{30}	HOPANES[4] 3-Me C_{31}/C_{30}	HOPANES[5] % 22 S C_{31}	% DIASTERANES[6] C_{29}	STERANES[7] %C_{27}:C_{28}:C_{29}	STERANES[8] % 20S C_{29}	STERANES[9] % αββ C_{29}
299	0.42	1.28	>95	0.08	59	37	31 : 24 : 35	52	57
3205	0.22	2.00	>95	0.09	62	37	40 : 22 : 38	50	58
3206	0.16	2.33	94	0.10	58	39	33 : 34 : 33	37	53
3241	0.04	5.88	95	0.11	58	50	31 : 26 : 43	46	53
3207	0.05	4.00	95	0.10	58	36	*	50	59
3242	0.06	7.69	94	0.13	57	54	30 : 25 : 45	47	53
3208	0.06	5.26	92	0.11	59	42	35 : 28 : 37	50	49
3050	0.02	5.56	82	0.10	57	51	31 : 20 : 49	32	42

*C_{28} not measurable; See Appendices for explanation of peak lettering. 1. A/B+C 2. C/B 3. % (G/G+H)
4. Q/G 5. % (I/I+J) 6. % (e+f/e+f+o+p+q+r) 7. % (g+h+i+j) : (k+l+m+n) : (o+p+q+r)
8. % (o/o+r) 9. % (p+q/o+p+q+r)

stated otherwise the GC oven was programmed from 60°C to 280°C at 3°C/min and then held at 280°C for 60 min.

Gas chromatography-mass spectrometry (GC-MS) was performed on all samples on a VG7070E instrument controlled through a VG 11/250 data system. The gas chromatograph (HP 5790) was fitted with a fused silica capillary column (Hewlett Packard ULTRA, cross-linked methyl silicone, 50 m × 0.2 mm i.d., 0.33 μm film thickness, hydrogen carrier gas) and on-column injector (S.G.E. OCI-3). The source was operated at 70 eV and 250°C with the interface line and reentrant at 280°C. All samples were analysed using multiple reaction monitoring (MRM), whereby the B and E fields were simultaneously switched at a constant accelerating voltage of 6 kV. Up to 26 reactions were monitored in sequence with a sample time of *ca.* 80 ms per reaction, a settling time of *ca.* 20 ms per reaction and with a cycle time of *ca.* 2.6 s. Some samples were re-analysed using single-ion recording (SIR) and full scan recording (SCN) to confirm component identification.

Rock-Eval analyses of unextracted rock powders were obtained on a Rock-Eval II instrument. Total organic carbon measurements were carried out on a LECO Carbon Analyser.

A number of *n*-alkylcyclohexanes (C_{12}–C_{18}) and methyl *n*-alkylcyclohexanes (C_{13}–C_{19}) were synthesised *via* Grignard reactions from cyclohexanone or 2-, 3- or 4-methylcyclohexanone. For each methyl-*n*-alkylcyclohexane a mixture of two isomers was produced. Preparative gas chromatography (Varian 6000, 2 m, 20% SE 30 on Gaschrom Q., helium carrier gas) allowed the isolation of the individual stereoisomers of 2-, 3- and 4-methyl-*n*-hexylcyclohexane and 3-methyl-*n*-undecylcyclohexane in high purity (>90%). Analysis of each by ^{1}H and ^{13}C NMR (200 MHz) confirmed their structure as *cis*- and *trans*-isomers. It is known that diequatorially substituted dimethylcyclohexanes (*i.e. trans*-1,2-, *cis*-1,3- and *trans*-1,4-) elute before their axial/equatorial isomers on methylsilicone GC phases (HAYES and PITZER, 1982). Furthermore, it has been shown that the ^{13}C chemical shift of an axial methyl group in dimethylcyclohexanes has a lower value than when in the equatorial position (DALLING and GRANT, 1967). Based on additivity rules, this is also expected to be observed for higher homologues. Table 3 lists the calculated and observed chemical shifts for the ring methyl group in the six isomeric methyl-*n*-hexylcyclohexanes isolated by preparative GC. The methyl group was confirmed as being secondary by INEPT experiments performed on *cis*-3-methyl-*n*-undecylcyclohexane. It is assumed that the position of isomerisation for the synthesised standards is the same for each homologue due to the similar isomer ratios and elution orders. Coinjections of *cis*- and *trans*-2-, 3- and 4-methyl-*n*-nonylcyclohexane and *cis*- and *trans*-2-, 3- and 4-methyl-*n*-undecylcyclohexane were carried out on two GC phases (HP ULTRA, 50 m × 0.22 mm i.d., 0.33 μm film thickness and BP-10, 50 m × 0.22 mm i.d., 0.33 μm film thickness) with Santalum 3050.

The electron impact (EI) mass spectra of representative synthetic standards of *n*-alkylcyclohexane and methyl-*n*-alkylcyclohexane are shown in Fig. 2. There is no major differ-

Table 3. NMR chemical shifts for isomeric methyl-*n*-hexylcyclohexanes.

ISOMER	Chemical Shift (ppm) CALCULATED[1]	OBSERVED	SUBSTITUENT[2]
cis-2-methyl-	12.0	13.8	ax./eq.
trans-2-methyl-	20.3	20.4	eq./eq.
cis-3-methyl-	23.1	23.1	eq./eq.
trans-3-methyl-	18.8	20.8	ax./eq.
cis-4-methyl-	18.8	20.3	eq./eq.
trans-4-methyl-	23.1	22.8	ax./eq.

1. On the basis of additivity rules for dimethylcyclohexanes
2. ax=axial, eq=equatorial alkyl substituents.

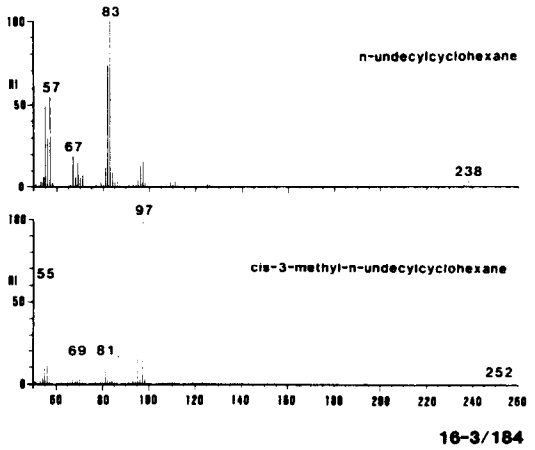

FIG. 2. Mass spectra of *n*-undecylcyclohexane and *cis*-3-methyl-*n*-undecylcyclohexane standards.

ence in the EI mass spectra of each of the six isomeric methyl-*n*-alkylcyclohexanes, although the position of the methyl group can be determined on the basis of minor differences in the abundance of *m/z* 96 which increases from 20% for the 2-methyl-isomers to 30% for the 3-methyl-isomers and to 40% for the 4-methyl-isomers. Furthermore, 2-methyl-*n*-alkylcyclohexanes are characterised by *m/z* 83 > *m/z* 81, as noted previously by RUSINOVA *et al.* (1980) from the examination of a more limited number of standards. Examination of the daughter ion spectra (constant B/E linked scanning for $M^{\ddagger}\rightarrow$ daughters) showed more marked differences. 4-Methyl isomers showed, apart from a major pair of ions at *m/z* 96/97, an abundant ion at $M^{\ddagger}$-29, 3-methyl isomers showed two abundant ions at $M^{\ddagger}$-15 and $M^{\ddagger}$-43, whereas 2-methyl isomers showed a series of $M^{\ddagger}$-alkyl ions all of similar abundance. A synthetic mixture of C_{13}–C_{19} methyl-*n*-alkylcyclohexanes was analysed by GC and GC-MS using full scan (SCN), single ion recording (SIR) and linked scanning (MRM) of $M^{\ddagger}\rightarrow$ *m/z* 97 to compare the response factors for each isomer using each of the techniques. Assuming GC presents the "correct" distribution of components, monitoring the total ion current in full scan GC-MS provided an almost identical distribution. SIR-GC-MS of *m/z* 97 (corresponding to the base peak in the mass spectra of the methyl-*n*-alkylcyclohexanes) showed a slight decrease in the measured relative abundance of the axial/equatorial isomers. MRM-GC-MS, while providing the greatest sensitivity, also showed the greatest differences including a decrease in the measured abundance of high molecular weight homologues (presumably due to their smaller molecular ions; RUSINOVA *et al.*, 1980) as well as the decrease in the abundance of axial/equatorial isomers observed in SIR-GC-MS.

Artificial thermal maturation experiments were performed using octadecanoic and octadecenoic acids on bentonite (1:9) and a mixture of six isomeric methyl-*n*-undecylcyclohexanes on bentonite in the presence and absence of sulphur as well as on palladium/carbon on alumina. Each was carried out in a sealed glass tube under vacuum at temperatures of 150°–250°C for periods of up to 20 days.

Approximately 25–50 mg aliquots of kerogen isolated from Soxhlet-extracted samples of 3050 from Santalum (predominantly *G. prisca*) and 2400 from Tempe Vale, were washed exhaustively with dichloromethane and pyrolysed in sealed glass tubes under vacuum at 250°C for between 24 and 48 h. The pyrolysates, which smelled strongly of sulphides, were extracted with dichloromethane and the saturates separated by liquid column chromatography (SiO_2, petroleum ether) from the rest of the extractable organic matter. Kerogen for $\delta^{13}C$ determination and pyrolysis was isolated using conventional, non-oxidising techniques: after crushing, any carbonate was removed using HCl; silicates and their subsequent products were removed by consecutive use of hot HF (40%) and HCl. Acidic reagents were washed from the residue using distilled water and the organic components concentrated using an aqueous solution of $ZnBr_2$ at a specific gravity of 2. Care had to be taken not to decant microfossils of *G. prisca* while washing out the respective acids, because many of the specimens float in aqueous solutions of specific gravity of 1. Kerogen isolates from Santalum 3050 were mounted in Zeiss Eukitt media, under No. 0 or 1 glass cover slips. They were examined using a conventional Zeiss Photomicroscope III with Zeiss Blue-Violet fluorescence attachment. Photomicrographs were taken using Kodak Ektachrome film, with a minimum exposure to Blue-Violet fluorescence of 10 min before photography (Fig. 3).

RESULTS

Bulk parameters

Rock-Eval and bulk geochemical parameters are listed in Table 1. The core from Tempe Vale No. 1 (Amadeus Basin) covered 66 m of the Horn Valley Siltstone. Samples were chosen for their high T.O.C. values and all show very good source potential. The Tent Hill No. 1 core included 71 m of Horn Valley Formation. Samples were chosen to show a range of T.O.C. values and all had lower source potential than those from Tempe Vale.

The Canning Basin samples were more oil-prone (higher Rock-Eval hydrogen indices) than those from the Amadeus Basin. Maturity increased progressively from Santalum 1A to Dodonea sediments to the Dodonea 299 oil.

Acyclic alkanes

Representative distributions of *n*-alkanes are shown in Fig. 4. These show a strong dominance of odd carbon number *n*-alkanes, especially from *n*-C_{14} to *n*-C_{20} and reduced *n*-alkane abundances above *n*-C_{20}. All Canning Basin samples show this as do most Amadeus Basin samples, apart from 2342 and 2380 which show typically mature distributions of *n*-alkanes with CPI values of *ca.* 1.0.

These unusual distributions appear to be related to the abundance of *G. prisca* in the kerogen, as those samples with high CPI values also show high *G. prisca* values.

Monomethyl branched alkanes were tentatively identified in the GC traces of all samples and confirmed

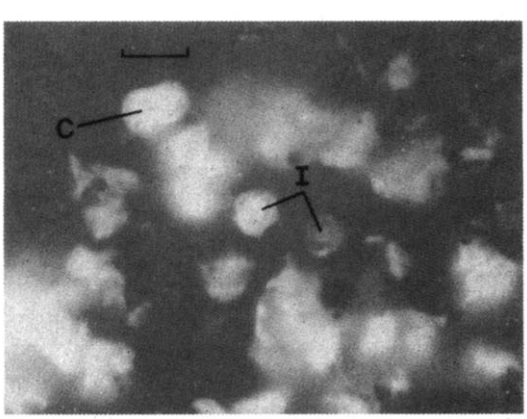

FIG. 3. Photomicrograph showing tetrad cocci; bar scale = 15 μm. i = individual, c = cluster.

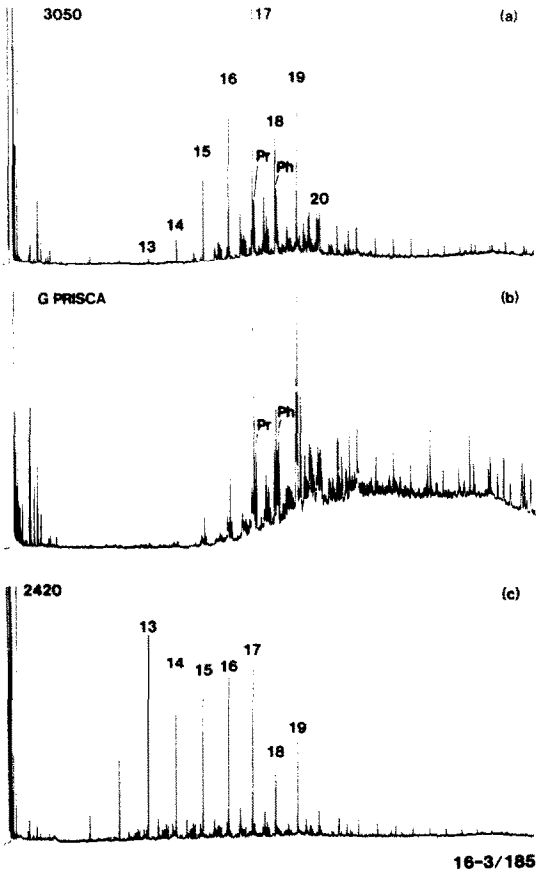

FIG. 4. GC traces of the saturated hydrocarbon fractions from: (a) Santalum 3050, (b) *G. prisca* pyrolysate, (c) Tempe Vale 2420.

in two samples (Tempe Vale 2420 and Santalum 3050) by MRM of $M^{\ddagger} \rightarrow$ ions corresponding to characteristic fragment ions in the mass spectra of each isomer (SUMMONS, 1987). They ranged in carbon number from C_{12} to at least C_{22}, maximising at C_{15}–C_{17}. There was no predominance of odd or even carbon numbers. In Tent Hill 2370, for example, methyl branched alkanes constituted 40% of all acyclic tetradecanes and a similar abundance was estimated for other carbon numbers. In general, *iso*-(2-methyl) and *anteiso*-(3-methyl) alkanes were slightly more pedominant than other isomers.

Isoprenoids

All the samples examined (apart from the pyrolysates) showed a very low abundance of pristane and phytane (Table 1) as previously reported for Amadeus Basin (JACKSON *et al.*, 1984) and Canning Basin (ALEXANDER *et al.*, 1984) crudes. Except for two sediments (Tent Hill 2380 and Santalum 3050) where they were abundant enough to be detected by GC, these compounds could only be detected using GC-MS (SIR). The least mature sample (Santalum 3050) showed the highest ratio of pristane/*n*-heptadecane (0.25).

Cyclohexanes

The major cyclic components in all the samples were shown to be cyclohexanes. One series (Fig. 5a), extending from C_{12} to C_{26} whose EI mass spectra all contained a major ion (base peak) at *m/z* 83, was identified as *n*-alkylcyclohexanes (I; Appendix 1) by coinjection of standards on GC-MS and by comparison of retention times and mass spectra with standards and previously published results (JOHNS *et al.*, 1966; RUBINSTEIN and STRAUSZ, 1979; FOWLER and DOUGLAS, 1984; REED *et al.*, 1986). As noted FOWLER and DOUGLAS (1984) and by REED *et al.* (1986) there is a marked similarity between the distributions of *n*-alkanes and *n*-alkylcyclohexanes as shown by comparison of the distributions of components in Fig. 5a and 5b.

Another series of components (Fig. 5c) extending from C_{13} to C_{27} with base peaks in their EI mass spectra at *m/z* 97 was identified as methyl-*n*-alkylcyclohexanes (II) by coinjection of standards on GC-MS and by comparison of retention times and mass spectra with standards. Figure 6 shows the resulting assignments of C_{16} and C_{18} components in the Santalum 3050 sample. In general, the *cis*-2-methyl-*n*-alkyl- and *cis*-3-methyl-*n*-alkylcyclohexanes are the most abundant isomers although there is significant variation between samples and between homologues in the same sample. The difference in retention times between *cis*- and *trans*-isomers decreases with increasing molecular weight resulting in co-elution of *trans*-2-methyl-*n*-alkylcyclohexane with *trans*-3-methyl-*n*-alkylcyclohexane for C_{18} (and greater) homologues. All six possible isomers were observed for each carbon number although the ratio of *cis*- to *trans*- components varied from sample to sample and from homologue to homologue. The methyl-*n*-alkylcyclohexanes show a similar carbon

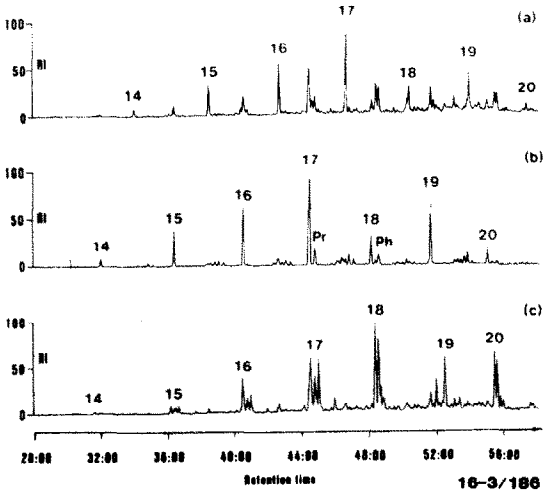

FIG. 5. Mass chromatograms from the GC-MS analysis of Santalum 3050 saturated hydrocarbons: (a) *m/z* 83 showing the distribution of *n*-alkylcyclohexanes, (b) *m/z* 85 showing the distribution of *n*-alkanes, (c) *m/z* 97 showing the distribution of methyl-*n*-alkylcyclohexanes.

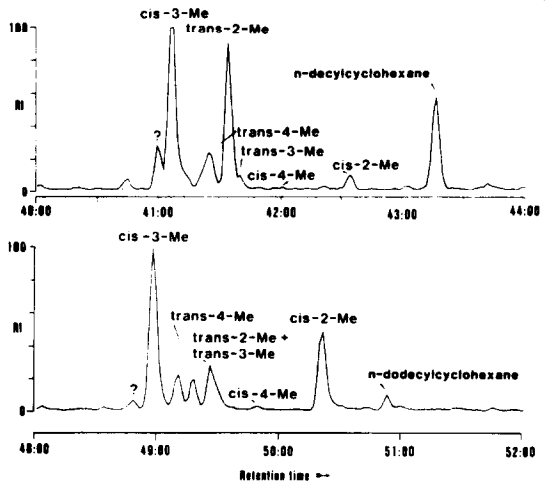

FIG. 6. MRM ($M^{+} \rightarrow m/z$ 97) chromatograms from Santalum 3050 showing the distribution of methyl-*n*-nonyl- and methyl-*n*-undecylcyclohexanes. Peak assignments confirmed by coinjection of standards.

number distribution as the *n*-alkanes in some samples although displaced upward by one carbon number. This can best be seen by comparison of Figs. 5b and 5c for Santalum 3050. However, the carbon number dominance seen in the Santalum sample is not seen in all. It is suggested that, as the Santalum 3050 sample is the least mature (see below), it shows this predominance of certain carbon numbers best. With increasing maturity the predominance in the cyclohexane homologues appears to become less significant, as is known to occur in *n*-alkanes (*e.g.* TISSOT and WELTE, 1984).

Methyl-*n*-alkylcyclohexanes were formed by heating oleic and stearic acids on bentonite. Similar results were obtained for both acids although the yields of products in the case of the unsaturated acid were far lower. In summary, the initial low temperature products from stearic acid were methyl and ethyl esters. At higher temperatures cyclisation of the acids/esters produced mainly *cis*-2-methyl-*n*-undecylcyclohexane (C_{18}) as well as *n*-alkanes (C_{17} and C_{19} predominant) and *n*-alkylcyclohexanes (C_{17} predominant). At the later stage cracking and addition reactions occurred to produce an homologous series of *n*-alkanes, *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes ranging from C_{12} to C_{30} with no predominance of any single carbon number. The 2-methyl-*n*-alkylcyclohexanes were, however, still far more abundant than the 3- and 4-methyl isomers.

In an attempt to confirm the relative thermodynamic stabilities of the synthesised methyl-*n*-alkylcyclohexanes, a mixture of all six isomeric methyl-*n*-undecylcyclohexanes (containing approximately equal abundances of all isomers) was heated in a sealed glass tube under conditions known to produce isomerisation in isoprenoid alkanes and steranes (ABBOTT *et al.*, 1985). No change in the relative abundance of the isomers was observable under the time/temperature conditions used. However, the use of 5% palladium on carbon in the presence of alumina (*cf.* BARBIER *et al.*, 1980) caused a marked change in their distribution. In addition to significant amounts of dehydrogenation products (methyl-*n*-undecylbenzenes), isomerisation of the cyclohexanes also occurred to produce three major isomers in approximately equal abundance (*trans*-2-methyl-, *cis*-3-methyl- and *trans*-4-methyl-) comprising 90% of all C_{18} cyclohexanes. Although the conditions used probably do not mimic those taking place in sedimentary rocks, they do confirm the order of the calculated thermodynamic stabilities (Table 4). No methyl group migration appeared to be occurring. The fact that no isomerisation occurred (or occurred at a much slower rate) on a clay mineral in the presence of sulphur is probably a reflection of the differing activation energy and pre-exponential factor governing the rate of isomerisation of cyclohexanes than those for the isomerisation of pristane, for example.

Tricyclic terpanes

In samples from the Amadeus Basin tricyclic terpanes (III) were only present in trace quantities, thus precluding any measurement of molecular ratios. In sediment samples from the Canning Basin they were also present in low abundance, but in keeping with the overall higher abundance of biological markers in the Canning in contrast to the Amadeus Basin samples, it was possible to calculate ratios of the relative quantities of C_{26} tricyclics to both C_{27} hopanes. These values (Table 2) showed a marked change from 0.04 to 0.22 over a very narrow depth range (2.2 m). The oil reservoired at the top of the bore hole possesses the highest value of this parameter, suggesting perhaps that the shallower sediments have been stained to some extent by this oil during migration. No evidence for staining is observed in the Rock-Eval results. However, maturity- or source-related trends in the distributions of hydrocarbon biomarkers over such a narrow depth range are even more unlikely. No change in lithology over this range is evident.

Table 4. Enthalpies of formation for isomeric methyl-*n*-undecylcyclohexanes.

ISOMER	ΔH_f (kJ mol^{-1})
cis-2-methyl-	-275.22
trans-2-methyl-	-283.05
cis-3-methyl-	-287.82
trans-3-methyl-	-279.62
cis-4-methyl-	-279.70
trans-4-methyl-	-287.65

Based on ΔH_f for dimethylcyclohexanes in the ideal gas state at 298.15 K and assuming -20 kJ mol^{-1} increments for each -CH_2- group (WEAST,1978).

Steranes

All samples apart from Santalum 3050 contained a high abundance of C_{19}–C_{22} steranes (IV, R = H to *i*-C_3H_7) (Fig. 7) far in excess of the C_{27}–C_{29} steranes (Appendix 2, *e.g.*, V, R = H, CH_3, C_2H_5). However, the complexity of the mixture and lack of standards made it impossible to draw any conclusions from the distributions of these compounds.

The samples from the Amadeus Basin (Tent Hill, in particular) showed very low abundances of C_{27}–C_{29} steranes which could only be detected (in MRM) by severely overloading the GC column. As a consequence the resolution of individual sterane isomers decreased markedly. It was felt that due to the poor resolution and low signal/noise level, molecular ratios would be subject to too many variations to allow any meaningful comparison. They are therefore not listed in Table 2a. Nevertheless, some general observations could be made on the distributions. In particular, diasteranes (*e.g.* VII) were more abundant than the corresponding regular steranes and C_{27} homologues were slightly more abundant than C_{28} or C_{29} ones. Also the distributions are similar to those found in thermally mature sedimentary rocks, with the 20*R* and 20*S* C_{29} 5α(H),14β(H),17(H) (VI, R = C_2H_5 unresolved) isomers visibly more abundant than the 5α(H),14α(H),17α(H) isomers (V, R = C_2H_5).

In contrast to the Amadeus Basin sediments, the Canning Basin samples contained steranes in sufficient abundance for molecular ratios to be calculated (Table 2b). Figure 8 shows the distribution of C_{27}–C_{29} steranes in Tempe Vale 2420 and Santalum 3050. The relative abundance of C_{27}:C_{28}:C_{29} steranes showed some variation from sample to sample. In fact, three repeat analyses of Dodonea 299 gave *ca.* 7% variation in the percentage abundances of C_{29} steranes.

There was a slight predominance of C_{29} components in most Dodonea samples. Since Ordovician sediments predate the radiation of vascular plants (STEWART, 1983) this predominance cannot be ascribed to an input from land plant C_{29} sterols. Instead an algal/cyanobacterial input of C_{29} precursors is more likely (MATSUMOTO *et al.*, 1982; BOON *et al.*, 1983; VOLKMAN, 1986). The single sample from the Santalum borehole also showed a marked predominance of non-rearranged C_{29} steranes.

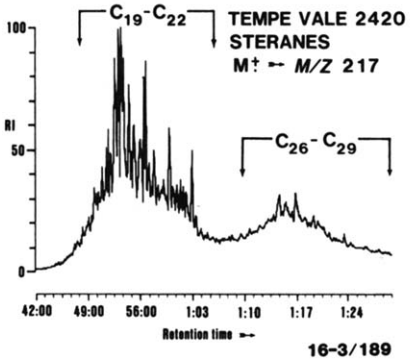

FIG. 7. Summed MRM ($M^+ \rightarrow m/z$ 217) chromatograms from Tempe Vale 2420 showing the distribution of C_{19}–C_{22} and C_{26}–C_{29} steranes.

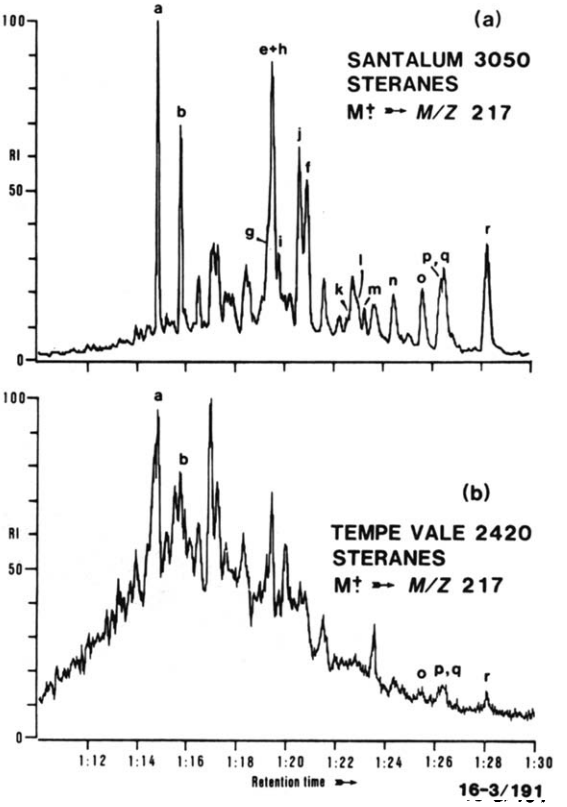

FIG. 8. Summed MRM ($M^+ \rightarrow m/z$ 217) chromatograms showing the distribution of C_{27}–C_{29} steranes from: (a) Santalum 3050, (b) Tempe Vale 2420.

All Dodonea samples appear to be of equal maturity as shown by conodont colour alteration indices (CAI) over this interval (CAI 1.0–1.5; S. T. WATSON, pers. commun.) and as would be expected from their relative stratigraphic position. But despite this there are significant but random differences in molecular ratios between samples (Table 2b). The relative amounts of diasteranes seemed to increase with increasing burial depth, though this occurs over such a small depth range that it cannot be related to maturity. Lithological differences could cause changes in the abundance of diasteranes, but none were observed. The abundance of the thermodynamically more stable 5α(H),14β(H), 17β(H)-steranes is consistently high, as is the ratio of 20*S* to 20*R* 5α(H),14α(H),17α(H)-steranes (*cf.* MACKENZIE *et al.*, 1980). The Santalum sediment is only marginally mature as the sterane isomerisation ratios have not yet reached their thermodynamic end-points.

Hopanes

Figure 9 shows the summed MRM chromatograms for the reactions of C_{27}, C_{29}–C_{31} hopane molecular ions → m/z 191 in representative samples from the

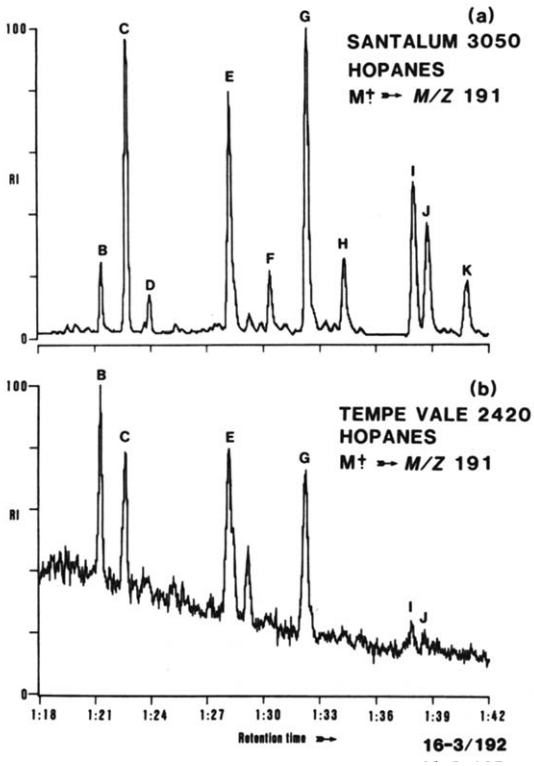

FIG. 9. Summed MRM ($M^{+\cdot} \rightarrow m/z$ 191) chromatograms showing the distribution of C_{27} and C_{29}–C_{31} hopanes from: (a) Santalum 3050, (b) Tempe Vale 2420.

Amadeus and Canning Basins. Molecular parameters based on these compounds are listed in Tables 2a and 2b. The usual range of 17α(H),21β(H)-hopanes (Appendix 3; *e.g.*, VIII, R = *i*-C_3H_7) derived from prokaryotic organisms (OURISSON *et al.*, 1979) are present in all samples (except 2342 and 2370), although their abundance varies from high in Santalum 3050 to trace amounts in the Amadeus Basin sediments. In all cases they were more abundant than the steranes (data not shown). Putative 3-methylhopanes (*e.g.* X) were also detected in low abundance in most samples (Table 2) as reported previously by ALEXANDER *et al.* (1984) for a Canning Basin oil. A second unidentified series of methylhopanes eluting after the 3-methylhopanes were in fact more abundant. They appear to be methylated in the A or B ring from their mass spectra and showed a similar distribution of carbon numbers as the 3-methylhopanes. They may be structurally related to the recently identified 2β-methylhopanoids found in certain microorganisms by BISSERET *et al.* (1985). They were evident in all Canning Basin samples, but could only be detected in trace amounts in Tempe Vale sediments from the Amadeus Basin.

Maturity parameters for the Dodonea samples showed no variation in the isomerisation at C-22 in C_{31} 17α(H),21β(H)-hopane (VIII, R = *s*-C_4H_9) nor in the abundance of moretanes (17β(H),21(H)-hopanes (*e.g.* IX). But T_m/T_s (IX, R = H/XIII) ratios, which are known to decrease with increasing burial depth (*e.g.* SEIFERT and MOLDOWAN, 1978), showed the reverse trend herein over a narrow depth range. This is interpreted as a result of staining of the shallower samples by the Dodonea 299 oil which has a low value for this ratio.

The relative proportion of C_{27} hopanes increases with depth which is the trend usually observed (*e.g.* SPIRO *et al.*, 1984) and ascribed to maturation effects. Such a trend is unlikely to be the result of maturity differences here because the separation of the shallowest and deepest Dodonea sample is only 10 m. The abundance of C_{31} hopanes also increases with depth. In light of the proposed explanation for variation in T_m/T_s ratios (see above), it seems staining of the shallower samples by the Dodonea 299 oil also would explain these variations, as this oil contains the lowest proportion of C_{27}/C_{29} hopanes and C_{31}/C_{29} hopanes. Santalum 3050 possesses a far less mature distribution of hopanes which is evident by the significant amounts of moretanes present in the sample (*e.g.* MACKENZIE *et al.*, 1980). No 25-Norhopanes (*e.g.* XIV were observed in any sample but trace amounts of 28,30-bisnorhopane (XV) were present in many samples (confirmed by coinjection of a North Sea oil which contained this hopane, *cf.* GRANTHAM *et al.*, 1980).

Pyrolysis of G. prisca

The results from the 48 hour pyrolysis of *G. prisca* are essentially identical to those from the shorter time (24 h) although more cracking of carbon-carbon bonds had apparently occurred leading to more low molecular weight *n*-alkanes, a decrease in their odd over even predominance and an increase in C_{18} methyl-*n*-undecylcyclohexanes over other carbon numbers. Not unexpectedly, the 24 hour pyrolysis (*cf.* Fig. 4 and 10) showed a similar distribution of saturated hydrocarbons to that in the Santalum 3050 sample. *n*-Alkanes were present, maximising at C_{17} with a significant odd over even carbon number predominance and much reduced abundance of C_{20+} homologues. Similarly, *n*-alkylcyclohexanes also maximised at C_{17} and exhibited an odd over even carbon number predominance. The C_{18} members of the homologous series of methyl-*n*-alkylcyclohexanes were by far the most abundant with *cis*-2-methyl-*n*-undecylcyclohexane predominant. A predominance of even over odd carbon numbers in the range C_{16}–C_{20} was also evident (compare Fig. 5c and 10c). These compounds are readily seen in the GC trace.

Pristane and phytane were present in significant quantities (Fig. 4b) which is in marked contrast to their absence in the pyrolysates of Ordovician kerogens reported by REED *et al.* (1986) and their low abundance in the hydrous pyrolysates of FOWLER *et al.* (1986). Hopanes and steranes in the pyrolysates also exhibited similar distributions to those in the extractable organic matter from Santalum 3050 but there were minor differences. The steranes (Fig. 11a) were much less mature in the pyrolysates with 20*S*/*R* ratios of *ca.* 19% and a

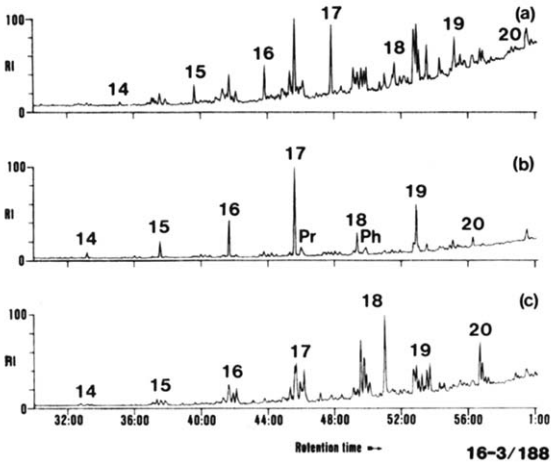

FIG. 10. Mass chromatograms from the GC-MS analysis of the *G. prisca* pyrolysate: (a) *m/z* 83 showing the distribution of *n*-alkylcyclohexanes, (b) *m/z* 85 Chromatogram showing the distribution of *n*-alkanes, (c) *m/z* 97 Chromatogram showing the distribution of methyl-*n*-alkylcyclohexanes.

low abundance (27%) of C_{29} 5α(H),14β(H),17β(H) relative to 5α(H),14α(H),17α(H)-isomers. C_{27} components were slightly more abundant than C_{29} components and diasteranes predominated over regular steranes. Hopanes showed similar immature distributions with abundant moretanes (%C_{30} 17α(H),21β(H)-hopanes = 72%) and trace amounts of 18α(H)-trisnorneohopane. Hopanes (Fig. 11b) were far more abundant than steranes. 3-Methylhopanes and the unidentified series of ring A or B-methylated hopanes observed in 3050 were also present in the pyrolysate (Figure 11c).

Pyrolysis of a sample of kerogen from Tempe Vale 2400 was also carried out. *n*-Alkanes with a significant odd over even carbon number predominance dominated the distribution of hydrocarbons. However, unlike the *G. prisca* pyrolysate, they showed a maximum at *n*-C_{19} and also extended above *n*-C_{20} in significant quantities. Pristane and phytane, in addition to high relative abundances of alkylcyclohexanes, were also observed.

DISCUSSION

Rock-Eval analysis of the sedimentary rocks from both the Amadeus and Canning Basins confirmed that most have good to very good source potential as indicated by T.O.C. values and S1 + S2 values. Maturity estimates from Rock-Eval data are usually derived from Tmax values and production indices. However, the latter parameter is subject to variation depending on the type of organic matter present in the sample and FOSTER *et al.* (1986) have presented data which demonstrate that, for Canning Basin sediments, Tmax values are directly related to the algal content rather than maturity. Nevertheless, because of the uniform organic matter in the sample set, production index values permit the ranking of the samples in the following order of increasing maturity:

Santalum < Dodonea < Tempe Vale < Tent Hill.

Thus, within the data set, samples from Unit 4 of the Goldwyer Formation (Santalum or Dodonea) are less mature than those from the Amadeus Basin.

There was a distinct similarity between the distribution of *n*-alkanes in Santalum 3050, the Dodonea 299 oil, the Dodonea sediments and in the *G. prisca* pyrolysate. In particular, there was a strong odd carbon number preference in the range C_{15}–C_{19} and a very much reduced abundance of C_{20+} *n*-alkanes. This characteristic pattern has been observed before in Ordovician oils by numerous authors (*e.g.* REED *et al.*, 1986) including those from the Amadeus Basin (JACKSON *et al.*, 1984) and indicates the *G. prisca* was the major source for the Dodonea oil.

n-Alkylcyclohexanes have long been recognised as significant components of the hydrocarbon fraction of

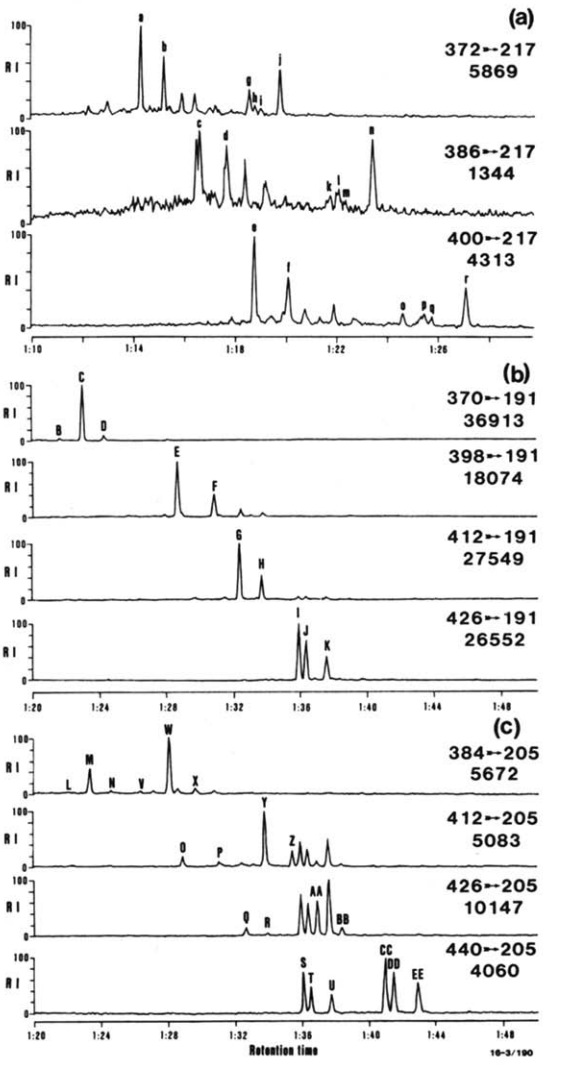

FIG. 11. MRM mass chromatograms from the GC-MS analysis of the *G. prisca* pyrolysate: (a) ($M^+ \rightarrow m/z$ 217) showing the distribution of C_{27}, C_{28} and C_{29} steranes, (b) ($M^+ \rightarrow m/z$ 191) showing the distribution of C_{27} and C_{29}–C_{31} hopanes, (c) ($M^+ \rightarrow m/z$ 205) showing the distribution of C_{28} and C_{30}–C_{32} methylhopanes.

sedimentary rocks and petroleums. The earliest reports in the literature were generalised mass spectrometric studies which reported a series of compounds with a general formula of C_nH_{2n} in petroleum. In later work (*e.g.* JOHNS *et al.*, 1966) synthetic standards were available for mass spectrometric comparison and this permitted the identification of a series of *n*-alkylcylohexanes (I) which are characterised by an abundant ion at *m/z* 83 (corresponding to $C_6H_{11}^+$). More recent work using gas chromatography-mass spectrometry has confirmed earlier results and extended the carbon number range of homologues and the age of geological samples in which they have been found. Not only have they been reported in Proterozoic oils and sediments (*e.g.* MacArthur Basin, 1.4×10^9 years, JACKSON *et al.*, 1986), but are also present in contemporary algal mats (R. ALEXANDER, pers. commun.) and Holocene sediments. There are few examples of biological markers which are so widespread and this indicates that they probably came from ubiquitous precursors in a wide range of organisms. The synthesis of the C_{12}–C_{18} members of this series was repeated herein and the occurrence of the C_{15} and C_{17} members confirmed by coinjection with Santalum 3050 sediment on two different GC phases. The presence of the other homologues was determined by comparison of mass spectra and retention times.

Apart from the monosubstituted series of cyclohexanes, a second series (characterised by *m/z* 97) has also been observed and attributed to methyl-*n*-alkylcyclohexanes (II, *e.g.* RUBINSTEIN and STRAUSZ, 1979). FOWLER and DOUGLAS (1984) have inferred the presence of three isomers for each carbon number in the series; however, no synthetic standards were used to determine the structure of these isomeric cyclohexanes. The synthesis of the C_{13}–C_{19} members of this series was carried out, thus allowing the complete isomer characterisation of this major series of biological markers for the first time. The synthetic approach employed (see Experimental) produced a pair of isomers for each of the 2-, 3-, and 4-methyl-*n*-alkylcyclohexanes. In the case of the C_{13} members, each pair of stereoisomers was separated by preparative GC and the individual compounds characterised by ^{13}C NMR. This permitted the identification of these pairs of compounds as *cis*- and *trans*-isomers of 2-, 3-, and 4-methyl-*n*-hexylcyclohexane.

From Table 4 the thermodynamic stability of methyl-*n*-undecylcyclohexanes, and in theory, all methyl-*n*-alkylcyclohexanes, is as follows:

cis-3-Me > *trans*-4-Me > *trans*-2-Me > *cis*-4-Me > *trans*-3-Me > *cis*-2-Me.

cis-3-Methyl-*n*-undecylcyclohexane is indeed the major isomer in Santalum 3050, however, *trans*-4-methyl-*n*-undecylcyclohexane which is estimated to be of similar stability is in low relative abundance and *cis*-2-methyl-*n*-undecylcyclohexane, which should be the least stable isomer, was often quite abundant. In fact, in a sediment from the mature Cambrian Chandler Formation of the Amadeus Basin it is the major observed isomer (HOFFMANN, POWELL and SUMMONS, unpublished results). Neither was there any apparent trend between the immature Santalum sample and the more mature sediments from the Canning and Amadeus Basins. Clearly, factors other than relative thermodynamic stabilities, such as the abundance of precursors, are equally important in determining the final distribution of isomeric cyclohexanes in sedimentary rocks. In this context, it is interesting to note that the results of the thermal maturation experiments of methyl-*n*-undecylcyclohexanes on palladium/carbon on alumina showed that isomerisation to produce the thermodynamically most stable isomers can be brought about in the laboratory and therefore may also occur in geological samples which have been subjected to high levels of maturity. Further work is currently in progress to determine whether a parameter based on this isomerisation is of value in assessing the maturity of sedimentary organic matter.

The thermal maturation experiments of RUBINSTEIN and STRAUSZ (1979) which involved heating oleic and stearic acids on bentonite, were repeated using a wider range of temperatures in an attempt to determine possible pathways for the formation of alkylcyclohexanes in sediments. Considering their early diagenetic occurrence, there would appear to be two routes for the formation of these compounds: either from the cyclisation of a suitable precursor or from the defunctionalisation of a cyclic precursor. There are only isolated reports of functionalised cyclohexanes in nature. ω-Cyclohexylalkanoic acids (XVI) are known, but their occurrence (only two carbon numbers) is at present restricted to a species of thermoacidophilic bacteria (*Bacillus acidocaldarius*, DE ROSA *et al.*, 1971) and to a non-thermoacidophile (*Curtobacterium pusillum*, SUZUKI *et al.*, 1981). In addition, ethenylcyclohexane has been reported in algae (WHELAN *et al.*, 1982). It is unlikely that these isolated examples could fully account for the geological diversity of the alkylcyclohexanes. On the other hand, it is known that triunsaturated *n*-alkanoic acids can undergo cyclisation after moderate heating to form ω-cyclohexenyl alkenoic acids (XVII, *e.g.* AWL *et al.*, 1986). Furthermore, under more vigorous conditions (300°C, 168 h.) both alkanoic and alkenoic acids, which occur widely in eukaryotes, prokaryotes and recent sediments, have been converted to a complex mixture of hydrocarbons including methyl-*n*-alkylcyclohexanes and *n*-alkylcyclohexanes (RUBINSTEIN and STRAUSZ, 1979). Repeating this work under milder conditions we found that the C_{18} acid produced predominantly *n*-C_{17} alkane, C_{17} *n*-alkylcyclohexane and C_{18} *cis*-2-methyl-*n*-alkylcyclohexane. Periods of longer heating produced a wider range of carbon numbers; however, the C_{18} *cis*- and *trans*-2-methyl-*n*-alkylcyclohexanes were by far the most abundant of the six possible isomers. These preliminary results suggest that *n*-alkanoic acids mainly give rise to the 2-methyl-series. The 3- and 4-methyl-series may

arise from the cyclisation of *iso*- and *anteiso*-acids, respectively; however, these acids were not available to confirm this suggestion. An alternative explanation is that acids bound in kerogen produce different distributions to the heating of free acids. Bound alkanoic acids are known to be present in recent sediments (CRANWELL, 1981), asphaltenes and resins (EKWEOZOR and STRAUSZ, 1983) and the mineral matter associated with oil sands (CYR and STRAUSZ, 1984).

Information regarding source type can sometimes be obtained from the relative abundance of steranes (MEINSHEIN and HUANG, 1981; VOLKMAN, 1986). The few samples from the Amadeus Basin that showed measurable amounts of steranes all showed C_{27} steranes predominant, whereas those from the Canning Basin showed a wide variation from approximately equal amounts of C_{27} and C_{29} steranes up to a predominance of C_{29} components. Algae possess a wide range of desmethylsterols (C_{26}–C_{29}); thus, it is usually difficult to derive any detailed information on the specific type of algae contributing to sedimentary organic matter. However, it can be stated that the presence of significant amounts of steranes is a strong indication that eukaryotes must have been major contributors. In this regard it is significant that the pyrolysates of *G. prisca*-rich kerogens contained abundant steranes with similar amounts of C_{27} and C_{29} components and reduced amounts of C_{28} components. Although some cyanobacteria reportedly synthesise sterols (*e.g.* ROHMER *et al.*, 1984; DE SOUZA and NES, 1968), they are mainly C_{29}, and hence a eukaryotic input is more consistent with the C_{27}–C_{29} distribution observed here.

Sedimentary hopanes are known to be derived from functionalised hopanoids in bacteria (OURISSON *et al.*, 1979), so their presence in these samples is not unexpected. Hopanes in the Horn Valley sediments showed a common distribution dominated by approximately equal abundances of C_{27}, C_{29} and C_{30} 17α(H),21β(H)-hopanes and lower amounts of extended hopanes. The Canning Basin samples showed quite variable distributions, but these are interpreted to be the result of staining by the Dodonea 299 oil. If Dodonea 3208 is assumed to be non-impregnated and representative of the upper unit of the Goldwyer Formation it would appear that the 299 oil was not sourced by this unit, based solely on the different hopane distributions, although the genetic relationship is clear when other biological marker distributions (Table 2b) are considered. 3-Methylhopanes are thought to be markers for certain bacteria as their functionalised precursors have been identified in such organisms (ROHMER and OURISSON, 1976). The additional series of methylhopanes has not been reported in sediments before. They were identified in Santalum 3050 in high abundance relative to the regular series of 17α(H),21(H)-hopanes and eluted after the putative 3-methylhopane series on methylsilicone fluid GC phase. They may be products from the diagenesis of the 2β-methylhopanoids found by OURISSON and co-workers (ROHMER *et al.*, 1984; BISSERET *et al.*, 1985) in *Methylobacteria* and *Nostoc* sp. The examination of a range of Ordovician samples from another stratigraphic hole in the Canning Basin (R. E. SUMMONS, unpublished results) suggests that these compounds are not derived from the lipids of *G. prisca*, since they are often quite abundant in samples with only minor apparent *G. prisca* content.

Pristane and phytane are believed to be derived primarily from the phytol moiety in chlorophyll, although pristane occurs as the free hydrocarbon in algae (CLARK and BLUMER, 1967) and can be derived from tocopherol (GOOSSENS *et al.*, 1984) and phytane can be produced from archaebacterial lipids (HAHN, 1982). REED *et al.* (1986) have interpreted the very low abundance of isoprenoid alkanes in Ordovician sediments and oils as an indication that *G. prisca* was a non-photosynthetic microorganism (or one which lacked chlorophyll with a phytyl side chain). We, however, prefer the alternative explanation that the low abundance of pristane and phytane is due to the overwhelming abundance of *n*-alkanes (and alkylcyclohexanes) which mask all other biological markers. This is supported by the higher abundance of pristane (and phytane, steranes and hopanes) in Santalum 3050 and in the 250°C pyrolysates of *G. prisca*-rich kerogen from this sample. The organic matter in Santalum 3050 is significantly less mature than all other samples and the generation of alkanes from kerogen has probably not proceeded far enough to dominate the distribution of hydrocarbons. Further support for this suggestion comes from the pyrolysis of *G. prisca*-rich kerogen at higher temperatures (300°C; data not shown). This produced a distribution of hydrocarbons similar to Fig. 4b; dominated by *n*-alkanes with only trace amounts of pristane and phytane. As far as we are aware, this apparent "swamping" of biomarkers has not been observed before to the extent seen in these Ordovician sediments. This is also circumstantial evidence for *G. prisca* being a lipid-rich organism.

To our knowledge, the isolation, pyrolysis and subsequent detailed biomarker analysis of a kerogen preparation overwhelmingly dominated by a single organism has not been carried out before. Kerogen isolated from Santalum 3050 was pyrolysed under vacuum and the resulting hydrocarbons analysed by GC-MS. The kerogen from Santalum 3050 comprised predominantly *Gloeocapsomorpha prisca* (>95%). Minor components include rare spinose acritarchs (see PLAYFORD and MARTIN, 1984) and, within the "ground mass" of *G. prisca*, coccoid bodies whose distinctive tetrad arrangement suggest that they might be of bacterial origin (Fig. 3). The occurrence of these coccoid bodies was only evident after fluorescence microscopy. It is noteworthy that ZALESSKY (1971) also reported that in some colonies from Estonia "one can observe at a magnification of about 1700× brownish spots distributed either in groups, or in lines. If these are not micrococci, living within the mucus of the algae, then their nature remains unclear". As discussed below, the distinctive biomarker chemistry of the *G. prisca*-bearing kerogen is also consistent with contributions from

a bacterial source. As can be seen from Fig. 4, there is a great similarity between the extractable organic matter from Santalum 3050 and the pyrolysate. The *n*-alkanes in the pyrolysate showed a marked odd over even carbon number predominance and the methyl-*n*-alkylcyclohexanes are sufficiently abundant to be clearly visible on the GC trace. The abundance of pristane, steranes and hopanes relative to *n*-alkanes was higher in the pyrolysate providing further evidence that these biomarkers are present in these sediments, but are masked by the large excess of *n*-alkanes as opposed to the suggestion of REED *et al.* (1986) that they are not there at all. The fact that the biomarker distributions in pyrolysates of *G. prisca* ae similar to the extractable organic matter from the Amadeus and Canning Basin sediments and oils provides unambiguous confirmation of the genetic relationship proposed by REED *et al.* (1986). This was not entirely evident from the pyrograms of Ordovician kerogens reported by these authors, but may be in part due to the different pyrolysis technique *i.e.* sealed tube pyrolysis in this study *versus* pyrolysis-GC in that of REED *et al.* (1986). Presumably these differences are also the result of varying contributions of other organic matter present in the kerogen in addition to *G. prisca* (*cf.* the results of the pyrolysis of Tempe Vale kerogen). The presence of rearranged biomarkers (*e.g.* 18α(H)-trisnorneohopane and diasteranes) in these pyrolysates is at first sight rather unexpected as these types of compounds have previously been reported only in hydrous pyrolysates of sedimentary rocks (RULLKÖTTER *et al.*, 1984). However, the isolation procedure used to prepare the algal specimens did involve aqueous work-up and these specimens were not dried thoroughly before pyrolysis. It is therefore probable that there was adequate water present during the pyrolysis to allow the formation of these biomarkers to take place.

The fact that pristane and phytane are present in significant abundance in the pyrolysates (pristane/*n*-heptadecane = 0.35) suggests that *G. prisca* was a phototroph. Furthermore, the uniformly light carbon isotope signatures of *G. prisca*-rich kerogens ($\delta^{13}C$: −29 to −34‰) is indicative of maximum discrimination against ^{13}C and consistent with (but not diagnostic of) photosynthetic carbon assimilation where the carbon source is not limiting. It is also consistent with selective preservation of the lipid components of biota which are themselves depleted in ^{13}C relative to the whole biomass (DENIRO and EPSTEIN, 1977). REED *et al.* (1986) have suggested, however, that *G. prisca* was a "non-photosynthetic, prokaryotic, benthonic and mat-forming, aerointolerant chemoautotroph". Their suggestion relied in part on the apparent absence of pristane and phytane in their pyrolysates, but as shown here, this is not the case. Moreover, considering the geographical distribution and thickness of *G. prisca*-bearing rocks (*e.g.* kukersite deposits of the Baltic Basin which cover an area of 50 000 km^2 and attain thicknesses of 2.5 to 3 m; BAUKOV, 1958; and in the Canning Basin, evidence of *G. prisca* occurs over approximately two thirds of the onshore area of 430 000 km^2 and in parts, contains cumulative thicknesses of *G. prisca*-rich layers of 1 m; FOSTER *et al.*, 1986), it is unlikely that a chemotroph could produce, globally in intracratonic basins, such an abundance of organic matter without a defined source of reducing power. Moreover, evidence for a benthonic, mat-forming habit which is based on the presence of thin, discontinuous laminae preserved in cores can be equivocal. This is because of the general problem that there are few diagnostic features which can be used to demonstrate the presence of former stratiform benthic mats. Thus, it can be difficult to distinguish between laminae resulting from benthic communities and those derived from pelagic fallout.

Whether or not *G. prisca* is a planktonic or benthic organism was first discussed by ZALESSKY (1917). Zalessky proposed two scenarios (pp. 14–16, translation) for the deposition of kukersite:

(i) "The alga forming kukersite lived freely swimming in water and covered its surface in a known period, just as in the present epoch various species of *Microcystis* and other representatives . . . cover the surface of the lakes like a carpet during a bloom in their waters. After this period, which coincides with the summer warm, the whole mass of this living carpet gradually settles to the bottom where it continues to live and grow, significantly increasing in volume until such times as the mat of algae of the following year covers it and creates such conditions under which the life of the algae is cut short as a result of a deficiency of oxygen and light."

(ii) Based on the morphological features of *G. prisca* "which recall modern representatives of *Gloeocapsa* which cover most moist rocks on the shore with a mucous mat", it was proposed that wave action might remove the thick mats from adjacent rocks and the particles would settle out on the bottom. It was therefore a question "simply whether a bed of rock up to three feet thick can form in this way, bearing in mind that it has been compressed up to three times from its original thickness. It seems . . . possible to admit this only in the case in which continuous and strong wave action at the shoreline and rapid compensation of the algae on the shore by means of growth . . . takes place". Consequently individual beds of kukersite could be ". . . the result of a large storm or a whole series of successive stormy days, or even a stormy period in the year".

FOSTER *et al.* (1986) discussed this last scenario, although they inferred that ZALESSKY (1917) had considered a freshwater habitat for the alga. That was incorrect; ZALESSKY (1917) made it clear that in his opinion "the marine origin [of the kukersite] was beyond doubt".

FOSTER *et al.* (1986) commented on the presence of skeletal-oolitic grainstones in the Goldwyer Formation of the Canning Basin and suggested that deposition occurred in a warm, shallow, epeiric sea. Climatic conditions were most likely humid, as there is little anhydrite within the section. Where anhydrite does occur, in a shallowing sequence immediately overlying the Goldwyer, it does not exhibit the textures indicative of arid, sabkha environments. Although dealing with assemblages of *G. prisca* of apparently Silurian age, CRAMER and DIEZ DE CRAMER (1972) recognised a *G. prisca* palynofacies which they suggested was located within a latitudinal belt around "10

to 20 degrees from the [Silurian] palaeoequator". FOSTER *et al.* (1986) showed a similar palaeogeographic distribution of proven and probable Ordovician occurrences of *G. prisca*. They noted, however, that the distribution of *G. prisca* sequences through time might be attributable to either continent migration through the equatorial belt or migration of climatic events through time.

The characteristics of the oils, sediments and fossil pyrolysates all demonstrate that *G. prisca* was a lipid-rich organism. The abundant odd carbon number *n*-alkanes and, to a lesser extent, alkylcyclohexanes and the even carbon number methyl-*n*-alkylcyclohexanes are derived from even carbon number fatty acids present in this organism (although a minor input of free *n*-alkanes is also possible). To account for the distribution of the major C_{13}–C_{19} acyclic and C_{14}–C_{20} cyclic alkanes in these samples, fatty acids with carbon numbers C_{14}–C_{20} must have been abundant in the lipid of *G. prisca*. Cyanobacteria are not known to either produce abundant lipid or synthesise fatty acids with carbon numbers greater than C_{18} (OREN *et al.*, 1985). Although cyanobacteria often produce significant amounts of free hydrocarbons (WEETE, 1976; C_{17} and Me-C_{17}) their distribution does not resemble those of the Ordovician sediments. Eukaryotic algae, on the other hand, often contain abundant lipid and produce fatty acids $\geq C_{20}$. Additional evidence for the suggestion that *G. prisca* was a eukaryote comes from the size of the fossil cells and the relative abundance of steranes in immature sediments and pyrolysates. There are only a few cases where *de novo* biosynthesis of sterols has been demonstrated in prokaryotes (*e.g.* ROHMER *et al.*, 1984). Although some modern coccoid cyanobacteria resemble *G. prisca* in size and apparent morphology (*e.g. Gloeocapsa* and *Entophysalis*) unicells of colonial habit (10–40 μm) are just as likely to be eukaryotic algae (*e.g. Botryococcus*).

Thus, the Ordovician sediments and oil examined in this study are suggested to have characteristics dominated by the fatty acid composition, pristane, phytane and steroids of the dominant phototroph with an additional component of hydrocarbons added by bacteria during early diagenesis.

CONCLUSIONS

This study has confirmed previous reports that Ordovician sediments and oils possess unusual hydrocarbon profiles which are related to the abundance of *Gloeocapsomorpha prisca*. Characteristics observed were:

1. low abundance of biological marker compounds in general.
2. high abundance and significant odd over even carbon number predominance of *n*-C_{13} to C_{19} alkanes.
3. low abundance of isoprenoids and *n*-C_{20+} alkanes.
4. significant amounts of monomethyl branched alkanes, *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes.

The structure of a series of methyl-*n*-alkylcyclohexanes has been confirmed by the synthesis of standards. Further tentative evidence for the origin of alkylcyclohexanes from alkanoic acids was obtained from artificial maturation experiments.

The pyrolysis of kerogen composed mainly of fossil cells of *Gloeocapsomorpha prisca* indicated that *G. prisca* was a lipid-rich organism contaning abundant fatty acids and steroids and a chlorophyll containing phytol. Together with the light ^{13}C values these factors indicate that *G. prisca* was probably planktonic and phototrophic, and possibly a eukaryotic alga, widely distributed in the marine environment during the Ordovician.

Acknowledgements—We would like to thank P. Fletcher, V. Grey and Z. Horvath for technical assistance. We are particularly grateful to R. Capon, Australian National University, for NMR analyses and to Western Mining Corporation Ltd. and Pancontinental Petroleum Ltd. for providing core samples. M. R. Walter contributed many valuable ideas and comments during the course of the work. This paper is published with the permission of the Director of the Bureau of Mineral Resources, Geology and Geophysics; Western Mining Corporation Ltd. and its Canning Basin JV partners Poseidon Oil Ltd. and Australian Hydrocarbons NL; and Pancontinental Petroleum Ltd. The Baas Becking Geobiological Laboratory is jointly funded by BMR, CSIRO and AMIRA.

Editorial handling: J. Rullkötter

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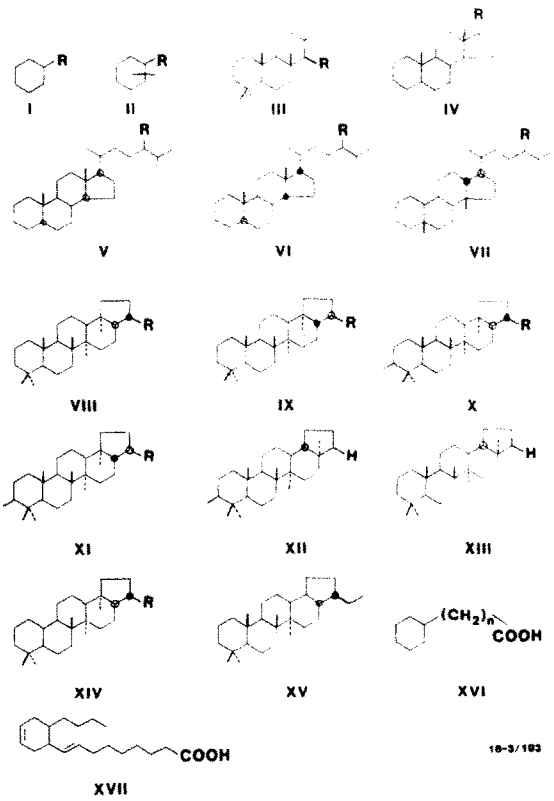
APPENDIX 1



APPENDIX 2
STERANE IDENTIFICATION AND STRUCTURES

Peak	Compound	Structure
a	13β(H)17α(H)-diacholestane (20*S*)	VII, *R*=H
b	13β(H)17α(H)-diacholestane (20*R*)	VII, *R*=H
c	13β(H)17α(H)-24-methyl-diacholestane (20*S*)	VII, *R*=CH_3
d	13β(H)17α(H)-24-methyl-diacholestane (20*R*)	VII, *R*=CH_3
e	13β(H)17α(H)-24-ethyldia-cholestane (20*S*)	VII, *R*=C_2H_5
f	13β(H)17α(H)-24-ethyldia-cholestane (20*R*)	VII, *R*=C_2H_5
g	5α(H)14α(H)17α(H)-cholestane (20*S*)	V, *R*=H
h	5α(H)14β(H)17β(H)-cholestane (20*R*)	VI, *R*=H
i	5α(H)14β(H)17β(H)-cholestane (20*S*)	VI, *R*=H
j	5α(H)14α(H)17α(H)-cholestane (20*R*)	V, *R*=H
k	5α(H)14α(H)17α(H)-24-methyl-cholestane (20*S*)	V, *R*=CH_3
l	5α(H)14β(H)17β(H)-24-methyl-cholestane (20*R*)	VI, *R*=CH_3
m	5α(H)14β(H)17β(H)-24-methyl-cholestane (20*S*)	VI, *R*=CH_3
n	5α(H)14α(H)17α(H)-24-methyl-cholestane (20*R*)	V, *R*=CH_3
o	5α(H)14α(H)17α(H)-24-ethyl-cholestane (20*S*)	V, *R*=C_2H_5
p	5α(H)14β(H)17β(H)-24-ethyl-cholestane (20*R*)	VI, *R*=C_2H_5
q	5α(H)14β(H)17β(H)-24-ethyl-cholestane (20*S*)	VI, *R*=C_2H_5
r	5α(H)14α(H)17α(H)-24-ethyl-cholestane (20*R*)	V, *R*=C_2H_5

APPENDIX 3
TERPANE IDENTIFICATION AND STRUCTURES (3-METHYLHOPANE IDENTIFICATIONS ARE TENTATIVE)

Peak	Compound	Structure
A	C_{26} tricyclic terpane	III
B	18α(H)-trisnorneohopane	XIII
C	17α(H)-trisnorhopane	VIII, R=H
D	17β(H)-trisnorhopane	IX, R=H
E	17α(H)21β(H)-norhopane	VIII, R=C_2H_5
F	17β(H)21α(H)-norhopane	IX, R=C_2H_5
G	17α(H)21β(H)-hopane	VIII, R=i-C_3H_7
H	17β(H)21α(H)-hopane	IX, R=i-C_3H_7
I	17α(H)21β(H)-homohopane (22S)	VIII, R=s-C_4H_9
J	17α(H)21β(H)-homohopane (22R)	VIII, R=s-C_4H_9
K	17β(H)21α(H)-homohopane (22S + R)	IX, R=s-C_4H_9
L	18α(H)-3-methyltrisnorneohopane	XII
M	17α(H)-3-methyltrisnorhopane	X, R=H
N	17β(H)-3-methyltrisnorhopane	XI, R=H
O	17α(H)21β(H)-3-methyl-norhopane	X, R=C_2H_5
P	17β(H)21α(H)-3-methyl-norhopane	XI, R=C_2H_5
Q	17α(H)21β(H)-3-methylhopane	X, R=i-C_3H_7
R	17β(H)21α(H)-3-methylhopane	XI, R=i-C_3H_7
S	17α(H)21β(H)-3-methyl-homohopane (22S)	X, R=s-C_4H_9
T	17α(H)21β(H)-3-methyl-homohopane (22R)	X, R=s-C_4H_9
U	17β(H)21α(H)-3-methyl-homohopane (22S + R)	XI, R=s-C_4H_9
V	18α(H)-methyltrisnorneohopane	—
W	17α(H)-methyltrisnorhopane	—
X	17β(H)-methyltrisnorhopane	—
Y	17α(H)21β(H)-methylnorhopane	—
Z	17β(H)21α(H)-methylnorhopane	—
AA	17α(H)21β(H)-methylhopane	—
BB	17β(H)21α(H)-methylhopane	—
CC	17α(H)21β(H)-methyl-homohopane (22S)	—
DD	17α(H)21β(H)-methyl-homohopane (22R)	—
EE	17β(H)21α(H)-methyl-homohopane (22S + R)	—