The source rock and petroleum geochemistry of the Early Jurassic Poolowanna Formation, Eromanga Basin

by

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The University of Adelaide

Dedicated to the memory of my sister

Nester Nyakato

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Abstract

Source rock evaluation based on Rock-Eval pyrolysis and organic petrography was undertaken on silty shales, carbonaceous shales and coal samples from the Early Jurassic fluviolacustrine Poolowanna Formation in oil fields located along the western edge of the Eromanga Basin, South Australia. Potential source rock lithofacies were delineated using gamma ray and sonic wireline logs. Their total organic carbon (TOC) values range from 1.5% in silty shales to 70% in coal facies. Maceral analysis data show that vitrinite (notably fluorescent desmocollinite) is the dominant maceral group (vitrinite≥liptinite>inertinite). The liptinites are mainly resinite and sporinite in the Poolowanna Trough . In the Patchawarra Trough, inertinite is the dominant maceral group (inertinite≥liptinite>vitrinite) and the liptinite group comprises mainly *Botryococcus*-like telalginite, indicative of lacustrine depositional environments. Generally the whole study area seems to have been subject to fluvial and paludal processes leading to a variety of sub-oxic to oxic terrestrial depositional environments, as illustrated by a wide range of vitrinite to inertinite ratios (V/I = 0.13–13.0). Low V/I ratios suggest either intense oxidation of autochthonous humic organic matter prior to burial, or a strong input of reworked allochthonous inertodetrinite. Both Rock-Eval and organic petrographic data indicate the presence of oil-prone Type II/III (or, more rarely, resinite-enriched Type II) kerogen. The maturity of source rock lithofacies range from early mature (R_o = 0.5–0.6%) in the Patchawarra Trough to mature (R_o = 0.9%) in the Poolowanna Trough.

In order to ascertain whether the potential source rocks of the Poolowanna Formation have actually contributed hydrocarbons to adjacent basin-edge reservoirs, fifteen representative rock samples and eighteen oils from five oil fields (Poolowanna, Tantanna, Sturt, Sturt East and Taloola) were selected for comparative isotopic and biomarker analysis. Three of these fields produce from stacked reservoirs which range in age from Cambrian (Mooracoochie Volcanics), through Permian (Patchawarra Fm), to Jurassic (Poolowanna Fm, Hutton Sst, Birkhead Fm and Namur Sst). All the oils appear to be early expulsion products (R_c = 0.5–0.8%). A primary higher plant input to both oils and source rocks is shown by the relative abundances of acyclic isoprenoids and *n*-alkanes (Pr/*n*-C_{17} versus Ph/*n*-C_{18}) and the presence of conifer resin-derived diterpenoid hydrocarbons. Intense microbial activity in the depositional environments of the source rocks is indicated by high hopane/sterane ratios and the presence of 2α-, 2β-, and 3β-methyl-17α(H), 21β(H)-hopanes in the C_{29}-C_{31} pseudohomologous series.

Pristane/phytane values and the relative concentrations of a suite of aromatic biomarkers characteristic of organic matter derived from the conifer family Araucariaceae (viz. 1,2,5-trimethylnaphthalene, 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene) allow recognition of four oil families: pre-Permian, Permian, Jurassic and mixed

Permian/Jurassic. The distinction of Jurassic from Permian and pre-Permian hydrocarbons is substantiated by cross plots of calculated reflectance (Rc) versus aromatic isotopic signature ($\delta^{13}C_{aro}$) and methylphenanthrene index (MPI) versus trimethylnaphthalene ratio (TNR-2). In these plots the Poolowanna source rocks coincide with most of the oils in Jurassic reservoirs. However, an unusually high abundance of 30-norhopane (C_{29}/C_{30} hopane ~1) was observed in the intra-Poolowanna shales and coals at Sturt, Sturt East and Tantanna, a feature seen in none of the oils. The Poolowanna-1 (Poolowanna) crude has a distinctively light isotopic signature, analogous to that of one of the waxy Jurassic source facies in Sturt Field. Sterane distributions are without exception ethylcholestane-dominant in both oils and source rock extracts.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institute and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

Meshack L. N. Kagya
21 March 1997

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Chapter 1

Introduction

1.1 Rationale

Recent additions to global oil and gas reserves have been discovered by the application of increasingly sophisticated petroleum exploration techniques. Petroleum geoscientists in their efforts to locate commercial accumulations of hydrocarbons, now ask specific questions concerning source rocks and their related crude oils. Major issues are the occurrence and distribution of source rocks in the basin, their potential to generate hydrocarbons, likely migration pathways of the expelled hydrocarbons and finally entrapment mechanisms. Moreover, knowledge of the geochemical composition of a petroleum sample provides insights on its source rock characteristics (e.g. lithology, depositional environment, thermal history, type of organic matter and age) and its post expulsion history, including the relative migration distance, and *in situ* alteration by water washing or biodegradation and thermal maturation.

In the Eromanga Basin of central Australia (Fig. 1.1), exploration for hydrocarbons commenced in the early 1900's but the first discoveries of gas and oil were not made until 1976 and 1977 respectively. The origin of the subsequently discovered hydrocarbons in this Mesozoic basin has been the subject of much discussion. Did they originate from within the Eromanga Basin or were they derived from underlying Palaeozoic basins? For instance, the oils which flowed from Early Jurassic reservoirs at Cuttapirrie-1 in the Patchawarra Trough and Poolowanna-1 in the Poolowanna Trough are reported to have shown features attributable to either Triassic (Barr and Youngs, 1981) or Early Jurassic source rocks (Thomas, 1982).

In order to solve this enigma the techniques of petroleum geochemistry were applied to the study of source rocks within the Early Jurassic Poolowanna Formation, in Poolowanna Trough where the first well (Poolowanna-1) to recover Jurassic oil was drilled; and in the south western Patchawarra Trough where there are several oilfields with multiple stacked reservoirs (Fig. 1.2). The oil bearing reservoirs in this part of the Patchawarra Trough include the Cambrian Mooracoochie Volcanics of the Warburton Basin; the Permian Patchawarra Formation of the Cooper Basin; and the Jurassic Poolowanna Formation, Hutton Sandstone, Birkhead Formation and Namur Sandstone of the Eromanga Basin.

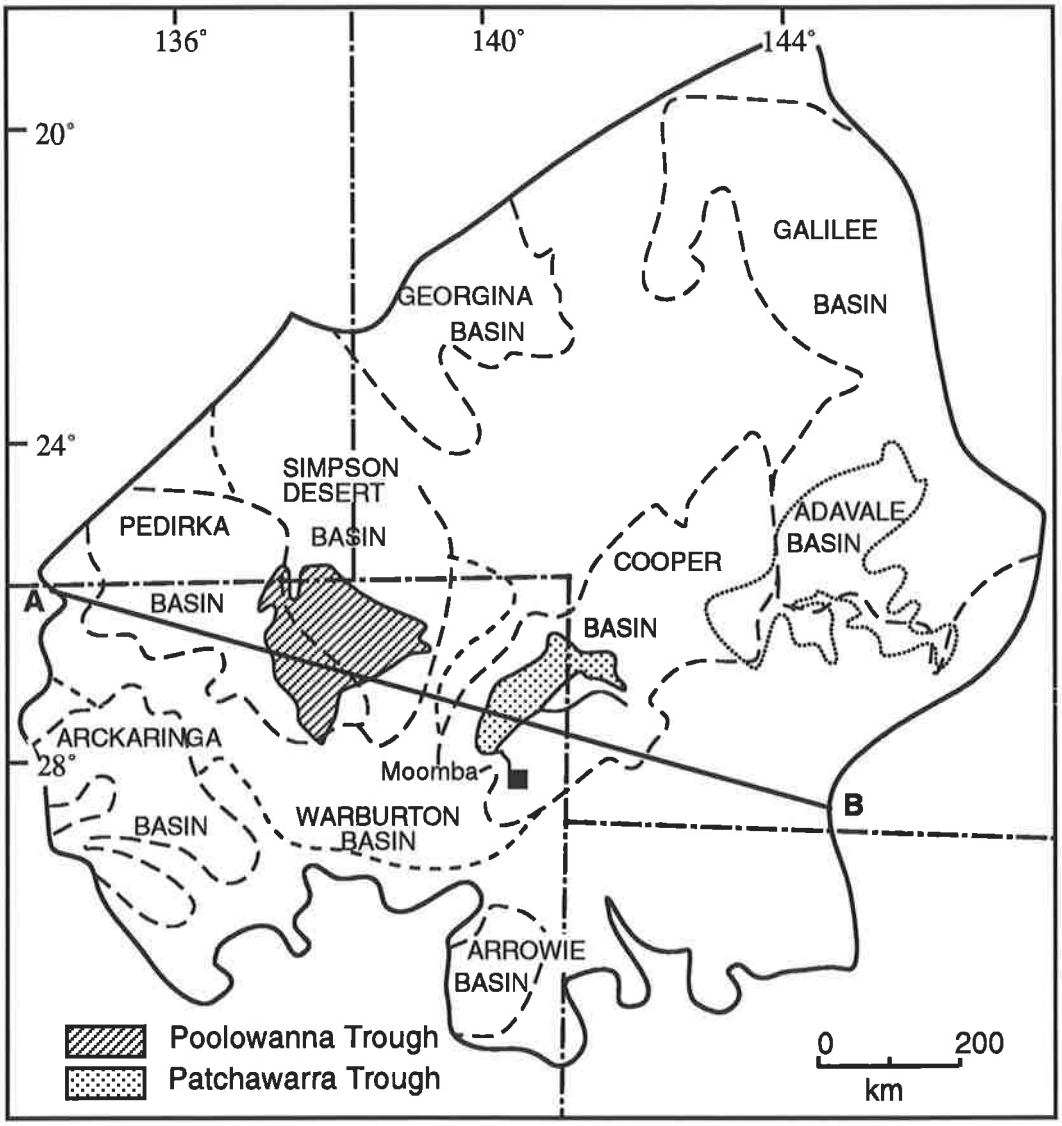


Figure 1. 1. The Eromanga Basin and its underlying basins. Cross section A-B is illustrated in Figure 1.6.

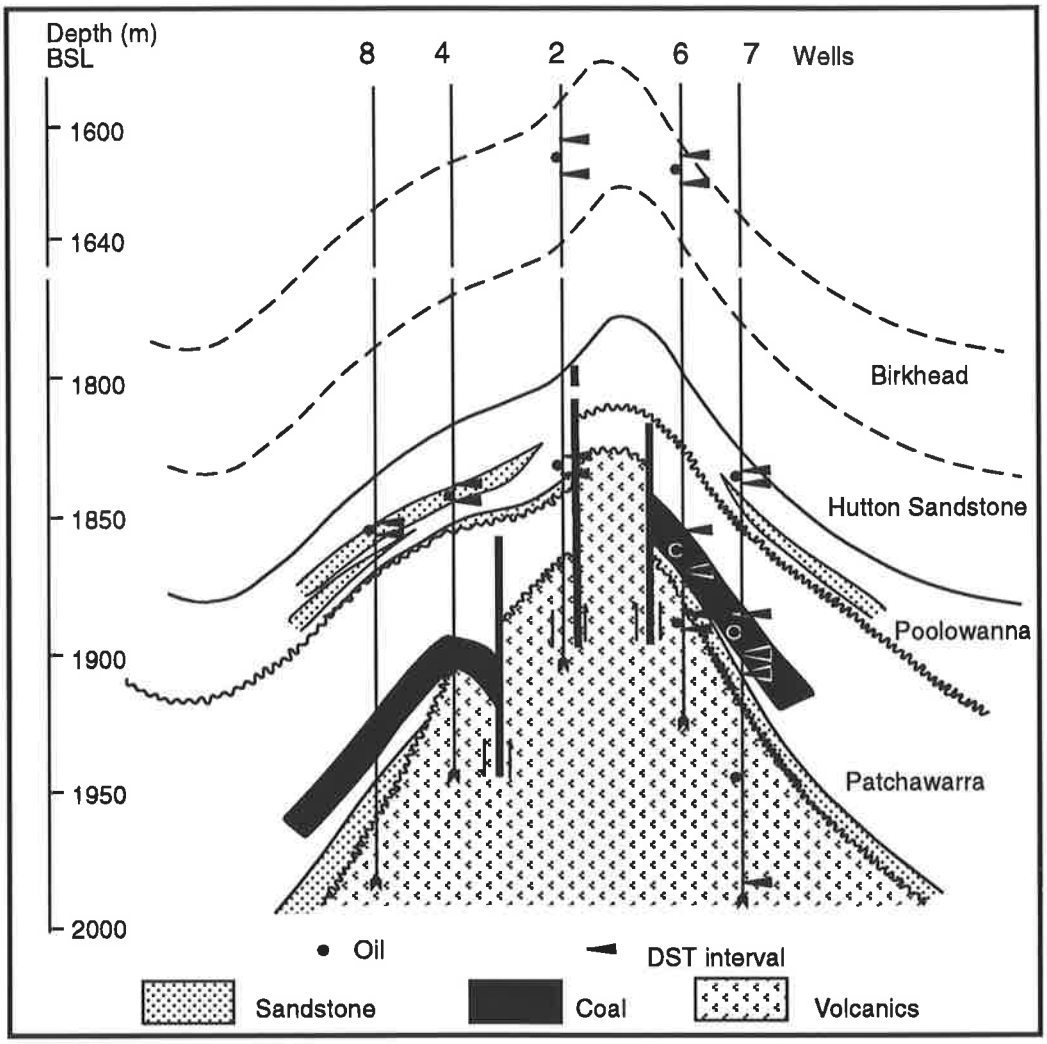


Figure 1.2a. Cross section of Sturt Field showing multiple stacked reservoirs (modified from Turner (1991)).

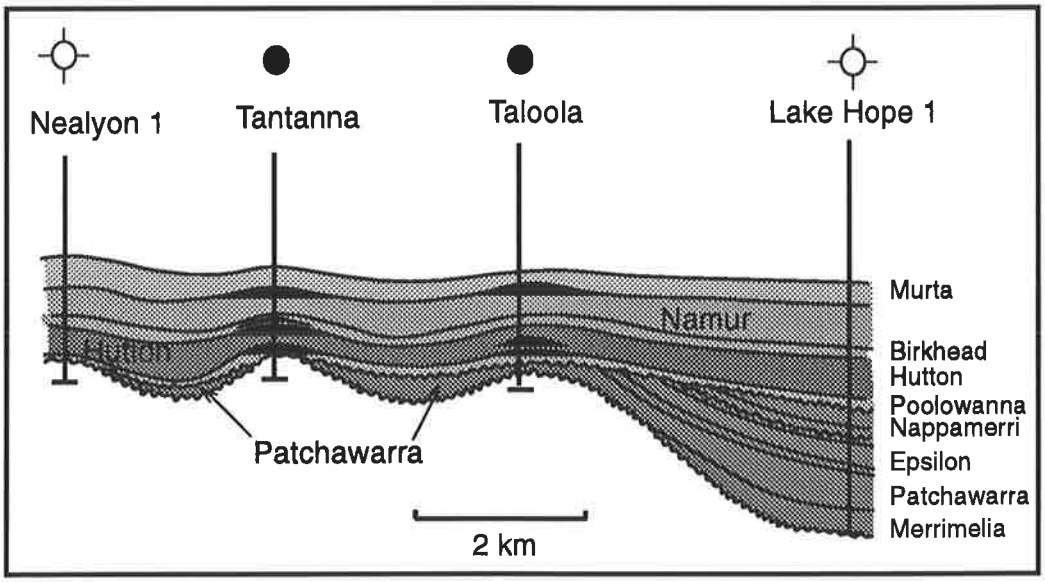


Figure 1.2b. Tantanna-Taloola cross section showing the occurrence of stacked Jurassic reservoirs (Heath *et al.*, 1989)

1.2 Objectives and scope of this work

The aims of this study are to establish the presence of source rocks in the Poolowanna Formation, to evaluate their hydrocarbon generative potential and to determine whether any of the generated hydrocarbons have been expelled as crude oil. Source rock evaluation was performed by employing the techniques of organic petrography; Rock-Eval pyrolysis; column chromatography of rock extracts; and gas chromatography, stable carbon isotope analysis and gas chromatography-mass spectrometry of saturated and aromatic hydrocarbons. Using these methods, the organic matter content, kerogen type, source rock richness, maturation levels, hydrocarbon yield and biomarker composition were determined. Source rock depositional environments were also reconstructed. Comparison of the source rock characteristics of the Poolowanna Formation in the Poolowanna and Patchawarra Troughs is of particular interest.

Specific geochemical characteristics (viz. saturated and aromatic hydrocarbon biomarkers and isotopic signatures) of oils from fields in which the Poolowanna Formation is one of the reservoir units were employed for oil-to-oil and oil-to-source correlations. The source affinity (precursor biota and depositional environment), maturation level and (where present) post-source alteration was determined for each oil in the expectation that it would enable differentiation of Jurassic-sourced oils from those which originated in older, underlying basins. In the same way, the possibility of the Poolowanna Formation itself being the source of some Eromanga Basin-reservoired oils was tested.

1.3 Study area and sampling locations

The part of Poolowanna Formation covered in this study is that which lies within the oil fields of the Poolowanna and southwestern Patchawarra Troughs on the western edge of Eromanga Basin (Fig. 1.3a). Rock and oil samples were obtained from the Poolowanna Field, located in the Pedirka Block, PELs 5 and 6 of South Australia, about 310 km northwest of Moomba; and from fields in the Lake Hope Block, PELs 5 and 6 of South Australia (Fig. 1.3b). The Patchawarra Trough fields include Tantanna, which is located about 62 km west of Moomba; Sturt/Sturt East, located about 60 km NW of Moomba (Sturt East is about 1.5 km east of Sturt); and Taloola located about 70 km WSW of Moomba.

The depth and thickness of drillhole sections of the Poolowanna Formation are shown in Table 1.1 where the intervals which are likely to be good source rocks because of their lithological composition (shale, siltstone and coal) are identified as potential source units. Intervals sampled for source-rock analysis, together with their lithology and mineralogy (for selected samples), are shown in Figure 1.4a-d and Table 1.2. The oil samples recovered from drill stem tests (DST) of Jurassic and underlying reservoirs in fields from the study area are shown in Table 1.3, along with their API gravities and pour points.

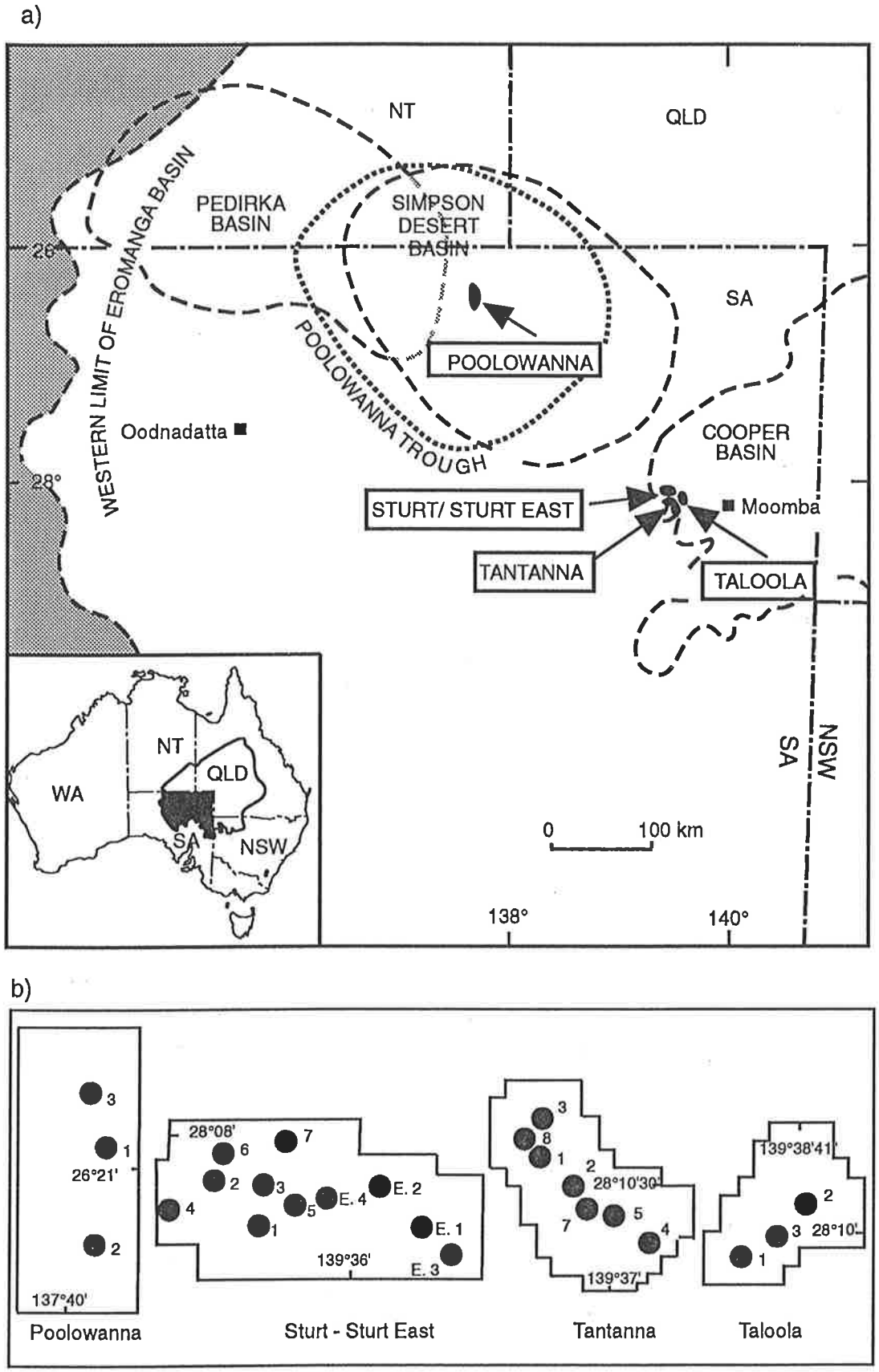


Figure 1.3 Study area showing a) oilfield locations and b) well locations in PELs 5 and 6

Table 1.1 Drillhole intersections of Poolowanna Formation in Poolowanna and Patchawarra Troughs

Well	Formation Interval	Thickness m	Potential Source Units*	Thickness m	Sample Type
Poolowanna 1	2387-2617	230	2387-2506	119	Cuttings
			2539-2563	25	"
Poolowanna 2	2395-2587	192	2395-2587	192	"
Poolowanna 3	2402-2604	202	2409-2416	7	"
			2425-2449	24	"
			2462-2464	2	"
			2507-2517	10	"
			2568-2565	4	"
Sturt 1	1868-1873	5	1868-1873	5	"
Sturt 2	1827-1866	39	1827-1831	4	"
			1838-1859	21	"
Sturt 3	1839-1864	25	1839-1844	5	"
			1844-1852	8	"
			1852-1864	12	"
Sturt 4	1846-1885	40	1846-1873	27	"
			1879-1884	5	"
Sturt 5	1819-1862	43	1819-1860	41	"
Sturt 6	1831-1867	36	1831-1840	9	"
			1848-1867	20	"
Sturt 7	1860-1880	20	1860-1871	12	"
			1876-1880	4	"
Sturt 8	1848-1884	37	1848-1875	27	"
			1876-1882	6	"
Sturt East 1	1819-1864	45	1819-1832	14	"
			1839-1847	9	"
Sturt East 2	1813-1851	38	1813-1823	10	"
			1828-1845	17	"
Sturt East 3	1833-1880	47	1833-1871	37	"
Sturt East 4	1816-1864	48	1816-1833	17	"
			1837-1855	18	"
			1857-1864	7	"
Tantanna 1	1788-1801	14	1788-1801	14	"
Tantanna 2	1788-1819	31	1788-1796	9	"
			1796-1810	14	Core
			1811-1811	1	"
Tantanna 3	1791-1814	23	1791-1809	18	Cuttings
Tantanna 4	1796-1818	22	1796-1818	22	"
Tantanna 5	1790-1816	26	1790-1808	18	"
Tantanna 6	1810-1832	22	1810-1825	14	"
Tantanna 7	1789-1818	29	1789-1808	18	"
			1801-1822	22	"
Tantanna 9	1788-1811	23	1788-1809	21	"
Tantanna 10	1788-1804	16	1788-1804	16	"
Tantanna 11	1786-1806	20	1786-1806	20	"
Tantanna 12	1797-1826	29	1797-1817	20	"

* Lithology mainly shale, siltstone and coal.

Table 1.2 Lithological and mineralogical composition of Poolowanna Formation samples selected for source rock analysis

Sample No.	Well	Depth (m)	Lithology	Gamma-ray API	Mineral assemblage (XRD) Quartz	Kaolinite	Illite	Gypsum
POL1-1	Poolowanna-1	2417	Silty shale + coal tr.	285	D	SD	M	-
POL1-2	Poolowanna-1	2423	Silty shale	285				
POL1-3	Poolowanna-1	2438	Silty shale + coal tr.	240-255	D	M	M	-
POL1-4	Poolowanna-1	2469	Silty shale + coal tr.	200-300				
POL1-5	Poolowanna-1	2499	Silty shale + coal tr.	240-320	D	M	M	-
POL1-6	Poolowanna-1	2545	Silty shale	200-300				
POL1-7	Poolowanna-1	2557	Silty shale + coal tr.	285-300				
POL2-8	Poolowanna-2	2496	Coaly siltstone	100-150	D	M	T	-
POL2-9	Poolowanna-2	2524	Coaly siltstone	140	D	M	T	T
POL2-10	Poolowanna-2	2542	Siltstone + coal tr.	130				
POL3-11	Poolowanna-3	2423	Siltstone + coal tr.	120-145				
POL3-12	Poolowanna-3	2438	Siltstone	140-160				
POL3-13	Poolowanna-3	2505	Silty shale	120-190	D	M	M	-
POL3-14	Poolowanna-3	2551	Coaly shale	100-140				
POL3-15	Poolowanna-3	2560	Silty shale	120-160				
TAN1-16	Tantanna-1	1795	Siltstone	170-180				
TAN2-17	Tantanna-2	1796	Siltstone	160				
TAN2-18	Tantanna-2	1799	Siltstone + coal tr.	190	D	SD	M	-
TAN2-19	Tantanna-2	1805	Siltstone	175				
TAN2-20	Tantanna-2	1811	Siltstone	150	D	SD	M	-
TAN3-21	Tantanna-3	1807	Coaly siltstone	160-170				
TAN4-22	Tantanna-4	1807	Coaly siltstone	160-170				
TAN4-23	Tantanna-4	1814	Siltstone + coal tr.	140-200	D	M	M	-
TAN5-24	Tantanna-5	1814	Siltstone + coal tr.	120-200				
TAN8-25	Tantanna-8	1823	Silty coal	nd	D	M	M	-
STU1-26	Sturt-1	1865	Siltstone + coal tr.	nd				
STU1-27	Sturt-1	1871	Coaly silty shale	nd	D	M	M	-

Table 1.2 (continued)

Sample No.	Well	Depth (m)	Lithology	Gamma-ray API	Mineral assemblage (XRD) Quartz	Kaolinite	Illite	Gypsum
STU2-28	Sturt-2	1829	Siltstone	160-180				
STU2-29	Sturt-2	1856	Silty shale	120-150				
STU4-30	Sturt-4	1859	Coaly silty shale	-180	D	M	M	-
STU4-31	Sturt-4	1881	Silty coal	120-160	D	M	T	-
STU3-32	Sturt-3	1859	Siltstone	nd				
STU3-33	Sturt-3	1862	Coaly siltstone	nd				
STU6-34	Sturt-6	1847	Coaly silty shale	nd				
STU6-35	Sturt-6	1865	Coal	nd	D	M	M	-
STU8-36	Sturt-8	1862	Coaly siltstone	120-160				
STE1-37	Sturt East-1	1835	Siltstone + Coal tr.	160-200				
STE1-38	Sturt East-1	1841	Silty shale	160-180	D	SD	M	-
STE1-39	Sturt East-1	1844	Siltstone	150-165				
STE2-40	Sturt East-2	1829	Silty shale	180				
STE3-41	Sturt East-3	1850	Siltstone	140-190				
STE3-42	Sturt East-3	1865	Siltstone	150-180				
STE4-43	Sturt East-4	1838	Siltstone	120-170				
STE4-44	Sturt East-4	1850	Silty coal	150				
STE4-45	Sturt East-4	1862	Coal	110-170	D	SD	M	-

D = Dominant
SD = Sub dominant
M = Minor
T = Trace

Figure 1.4a. Poolowanna Formation sample locations in the Poolowanna Field

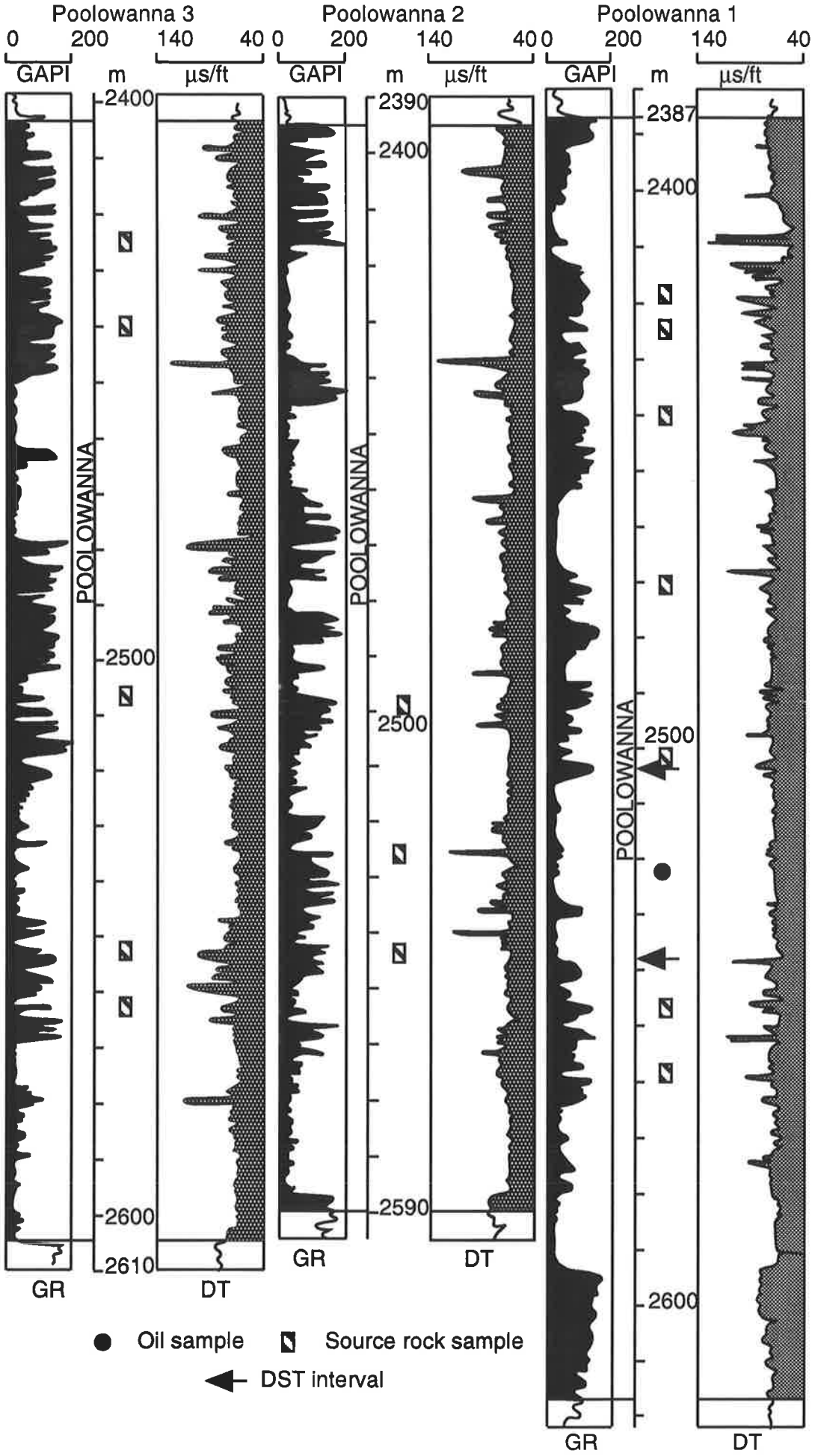


Figure 1.4b. Poolowanna Formation sample locations in the Tantanna Field

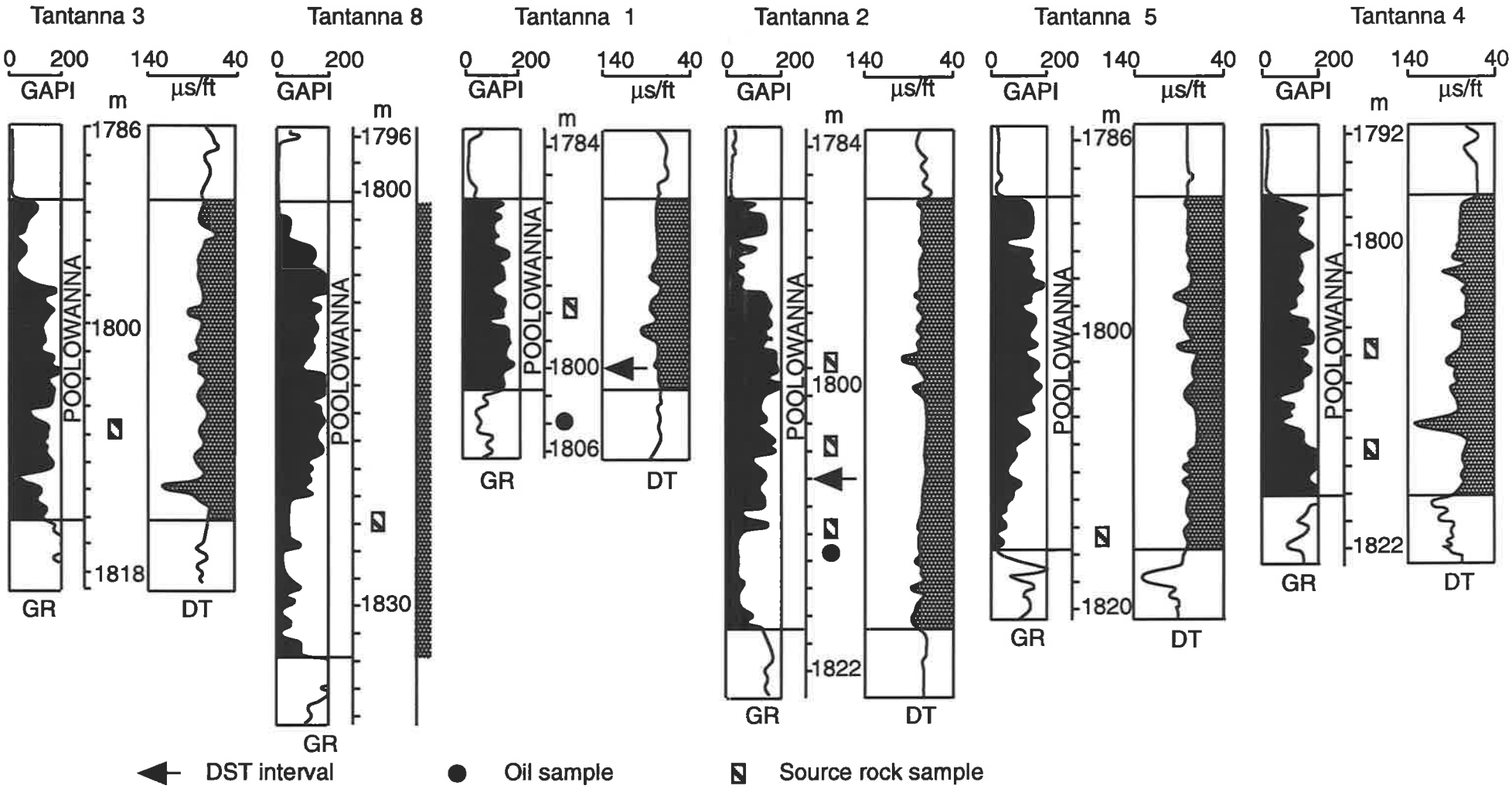


Figure 1.4c. Poolowanna Formation sample locations in the Sturt Field

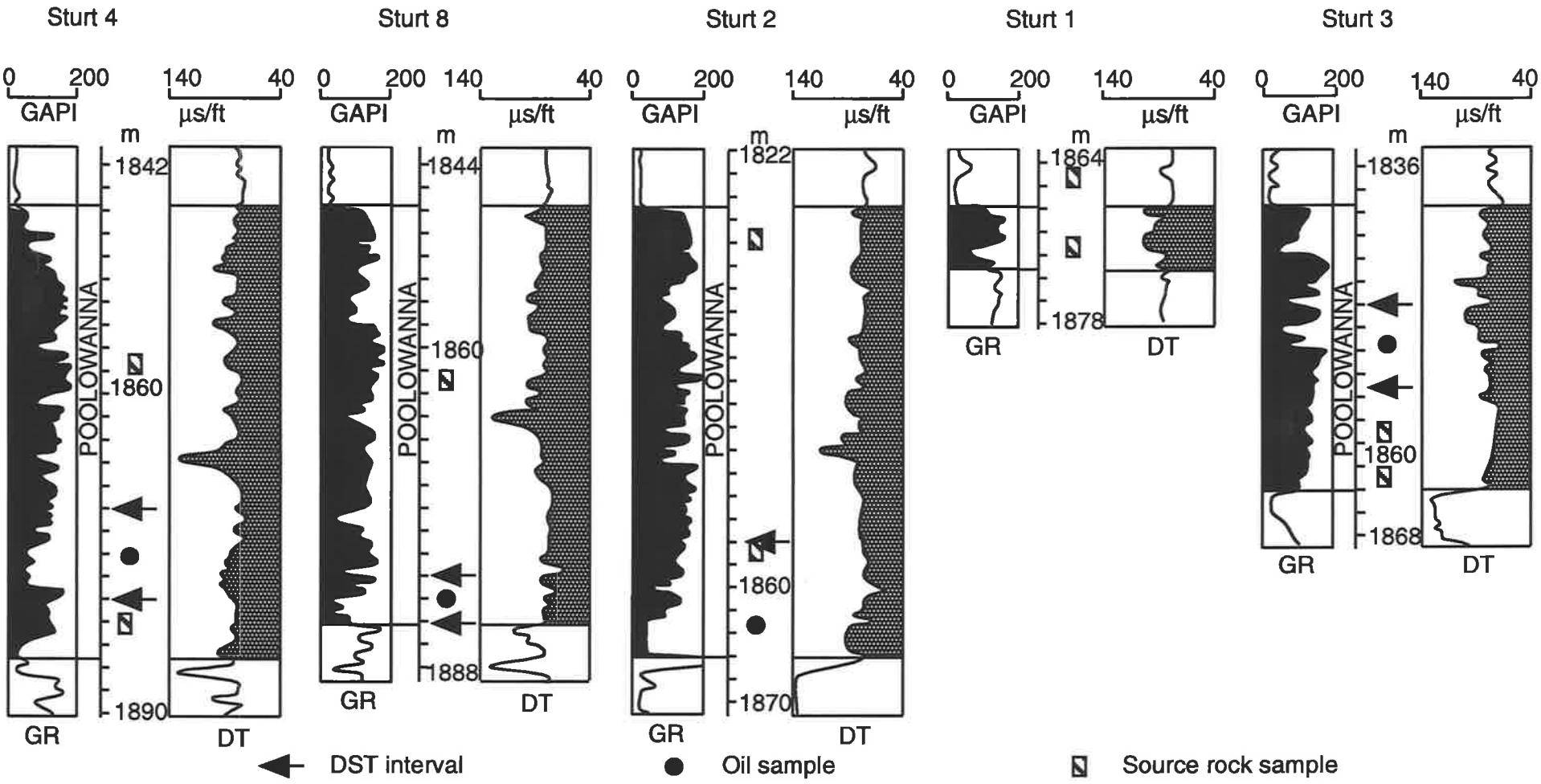


Figure 1.4d. Poolowanna Formation sample locations in the Sturt East Field.

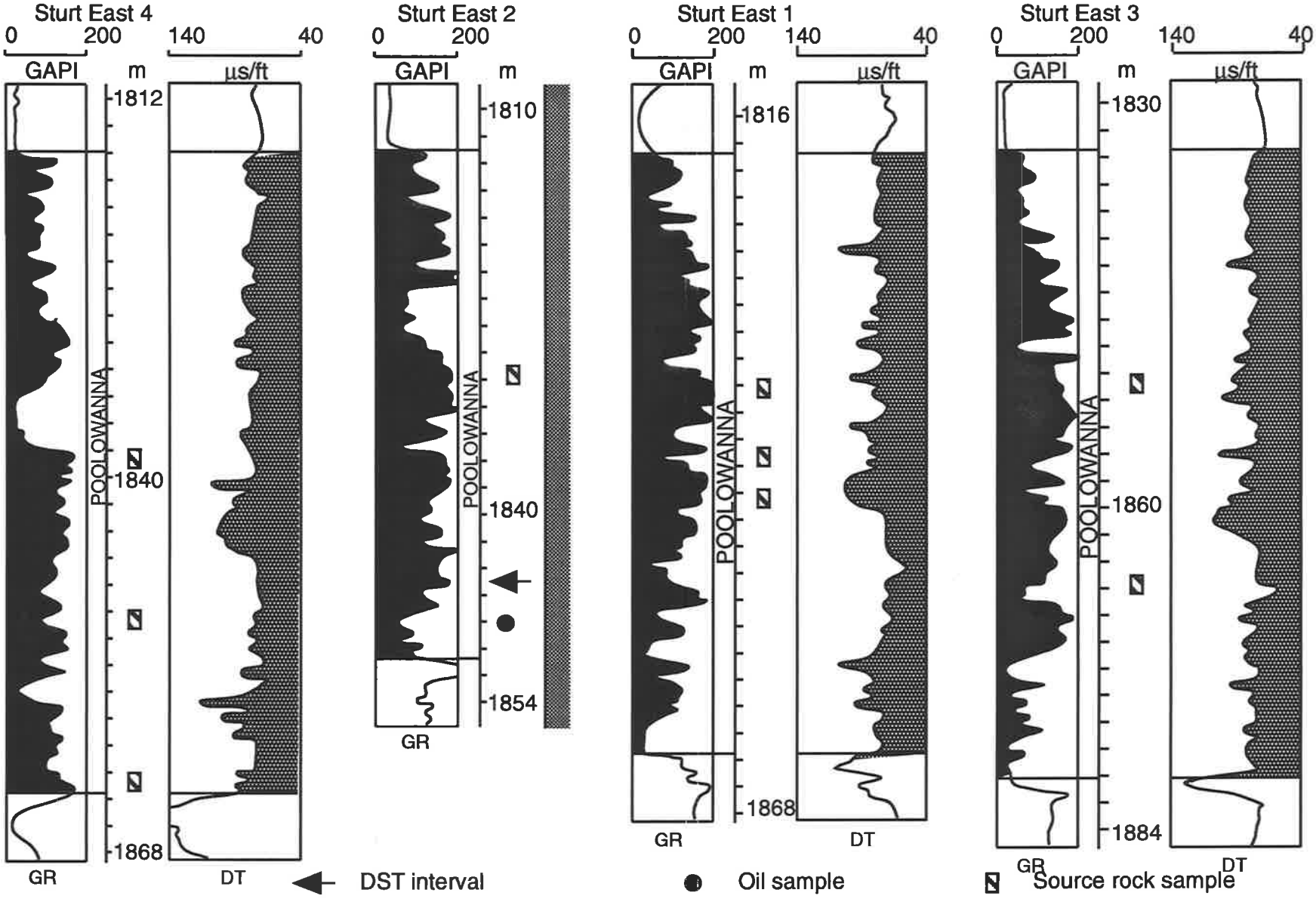


Table 1.3. Oils from selected drillholes in the Poolowanna and Patchawarra Troughs

Well	Reservoir	DST no.	Interval m	API gravity @60 °F	Pour point °C
Poolowanna 1	Poolowanna	2	2504-2538	36.9	41
Poolowanna 3	Poolowanna	1	2486-2509	-	-
Sturt 1	Birkhead	1	1652-1656	53.5	-
Sturt 2	Poolowanna	1	1856-1892	49.7	15
	Birkhead	3	1633-1645	45.1	17
Sturt 3	Birkhead	2	1653-1661	42.8	29
	Birkhead	1B	1654-1662	43.1	26
	Poolowanna	1A	1847-1856	48.9	17
Sturt 4	Poolowanna	1	1872-1880	48.9	17
	Poolowanna	2	1883-1892	48.8	17
Sturt 5	Poolowanna	1	1858-1868	49.6	17
Sturt 6	Birkhead	1	1883-1892	46.9	14
	Patchawarra	3	1884-1898	50.7	5
	Mooracoochie	5	1914-1919	53.0	-4
Sturt 7	Patchawarra	1	1923-1938	51.2	8
	Mooracoochie	2	1946-2021	47.4	2
	Poolowanna	3	1871-1876	49.2	17
	Poolowanna	4	1890-1894	47.8	20
	Poolowanna	5	1885-1889	49.5	14
Sturt 8	Poolowanna	1	1880-1884	48.8	20
Sturt East 1	Poolowanna	-	1854-1866	51.5	14
Sturt East 2	Poolowanna	1	1845-1899	51.3	20
Sturt East 4	Poolowanna	1	1852-1860	50.9	-
Taloola 1	McKinlay Mbr, Namur Sst	2	1392-1398	43.5	-
	Murta Mbr	3	1354-1384	48.8	-
Taloola 2	Poolowanna	1	1829-1836	53.0	2
	Hutton Sst.	2	1789-1793	46.5	20
	McKinlay Mbr, Namur Sst	3	1384-1397	44.5	20
Taloola 3	Namur Sst.	2	1403-1417	41.4	17
Tantanna 1	Poolowanna	1	1800-1815	50.1	<5
	Hutton	2	1635-1642	46.4	17
	Namur	3	1347-1359	48.3	2
Tantanna 2	Poolowanna	1	1809-1857	55.1	-7
Tantanna 3	Birkhead/Hutton	1	1625-1637	45.6	23
Tantanna 4	Hutton Sst.	1	1641-1647	45.7	23
Tantanna 5	Birkhead	1	1631-1639	45.6	23
Tantanna 8	Hutton Sst.	2	1639-1646	46.0	17
Tantanna 9	Hutton Sst.	4	1778-1782	48.1	-18
	McKinlay Mbr, Namur Sst	3	1361-1368	47.7	3
Tantanna 12	McKinlay Mbr, Namur Sst	1	1353-1362	47.8	3

1.4 Geological setting

The Eromanga Basin covers about 1,000,000 km^2 of central-eastern Australia, of which 360,000 km^2 lie in South Australia where it overlies the Permian Arckaringa and Pedirka Basins, the Permo-Triassic Cooper Basin and the Triassic Simpson Desert Basin (Fig. 1.1)

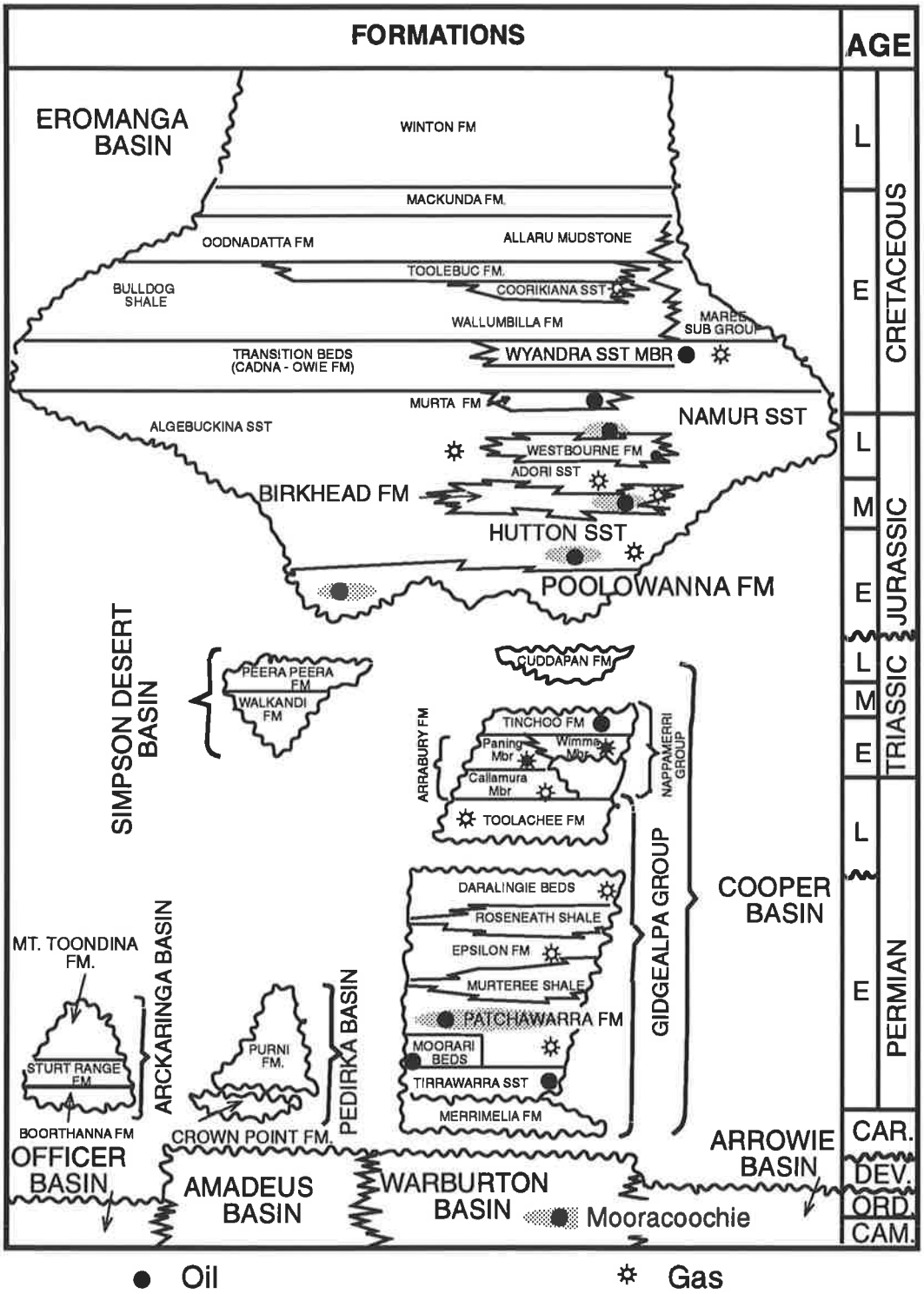


Figure 1.5 Generalised stratigraphy and significant hydrocarbon occurrences in the western Eromanga Basin region (after Kantsler *et al.*, 1986). Stiple indicates reservoir units from which oils were analysed in this study.

1.4.1 Stratigraphy and basin development

The generalised stratigraphy of the western Eromanga Basin and its intrabasins is illustrated in Figure 1.5. During the Cambro-Ordovician period, sedimentation took place in the Warburton, Arrowie, Amadeus and Georgina Basins (Gravestock, 1995). The clastics, redbeds, carbonates and volcanics which occur beneath the western Cooper Basin are of Early to Late Cambrian age, whereas the dark grey pyritic siltstone and sandstone attributed to the development of the Larapintine Sea, represent Ordovician sedimentation (Gatehouse, 1986). Low grade metamorphic rocks (argillites and arenites, probably of Silurian age), intruded by late Silurian and Devonian granite, underlie the Cooper Basin in southern Queensland (Green *et al.*, 1989).

Deposition in the Cooper and Pedirka Basins is reported to have been triggered by the decay of an Early Permian ice sheet which released an enormous volume of sediment. A non-marine to shallow marine, fluvio-lacustrine environment appears to have prevailed during this period giving rise to a typical Gondwana basin succession comprising basal diamictites overlain by non-marine and marine sediments (Gilby and Foster, 1988). The late Carboniferous to Early Permian record of the Pedirka Basin consists of a basal diamictite (Crown Point Formation) and the meandering fluvial deposits of the Purni Formation (Fig. 1.5).

The Cooper Basin is characterised by a major depocentre of Permo-Triassic age. It has a total sediment thickness of up to 2000 m, comprising cycles of fluvial sandstone, fluvio-deltaic coal measures, lacustrine shale and, in places, glacial sediments. This succession has been assigned to two groups. The first of these is the Gidgealpa Group of Late Carboniferous to Late Permian Age. At its base is the glacigenic Merrimelia Formation (Late Carboniferous). This unit is unconformably overlain by an Early Permian sequence consisting of the braided fluvio-deltaic and lacustrine Patchawarra Formation; the lacustrine Murtereee Shale; the fluvio-deltaic Epsilon Formation; the lacustrine Roseneath Shale; and fluvio-deltaic Daralingie Formation. Another major unconformity separates those Early Permian sediments from the Late Permian fluvio-deltaic Toolachee Formation. The second is the Late Permian to Early Triassic Nappamerri Group which consists of the nonmarine Arrabury and Tinchoo Formations. The Arrabury Formation contains the lacustrine, floodplain and meandering stream sediments of the Callamurra Member; and the braided fluvial channel and floodplain sediments of the Paning and the Wimma Sandstone Members. At the top the fluvio-lacustrine Tinchoo Formation conformably overlies the Arrabury Formation.

The Simpson Desert Basin is represented by two Triassic units, viz. the Walkandi and Peera Peera Formations. The Walkandi Formation is characterised by interbedded shale, siltstone and minor sandstone, deposited on floodplains and in shallow ephemeral lakes. The Peera Peera Formation conformably overlies the Walkandi Formation and consists of carbonaceous

shale, coal and thin sandstone interbeds, deposited in a fluvial environment. A slight but widespread compressional deformation, regional uplift and erosion at the end of the Late Triassic appears to have terminated deposition in the region.

The Eromanga Basin contains about 3000 m of Jurassic to Cretaceous sediments which were deposited in lacustrine, fluvial peat swamp and shallow marine environments. The lowermost unit is the Poolowanna Formation of South Australia (Moore, 1986) which is the time equivalent of the 'Basal Jurassic' unit of southern Queensland (Geological Survey of Queensland, 1985), the Windorah Formation of the eastern Eromanga region and the upper Precipice Sandstone and Evergreen Formation of the Surat Basin (Passmore and Burger, 1986).

Other Jurassic units of the Eromanga Basin include the Hutton Sandstone, Birkhead Formation, Adori Sandstone, Westbourne Formation, Namur Sandstone and Murta Formation. Collectively, these units are laterally equivalent to the Algebuckina Sandstone of the Poolowanna Trough (Nugent, 1969). Of these, the Birkhead Formation is characterised by interbeds of siltstone, coal and sandstone deposited in a flood-plain and lacustrine environment; the Westbourne Formation consists of fluvial and overbank siltstone and sandstone; and the Murta Formation comprises thinly interbedded lacustrine dark grey siltstone, shale, and sandstone.

The Early Cretaceous is marked by a transition to marine conditions as demonstrated in the Cadna-owie Formation by a sequence of interbedded sandstone, siltstone, claystone with minor limestone which reflects the non-marine (lacustrine) deposition in the lower part of the section and paralic conditions in the upper part (Moore and Pitt, 1984).

Sedimentology of Poolowanna Formation

In the Poolowanna Trough at Poolowanna-1, the Poolowanna Formation is characterised by up to 230 m of intercalated siltstone, sandstone and coal. Moore (1986) suggested a moderate to high energy (meandering or anastomosing-channel) fluvial environment on a moderate palaeoslope with limited flood plain sedimentation. A thin interval having marginal marine affinities was reported in Poolowanna-1 well where the Poolowanna type section was first defined (2387-2617 m: Wiltshire, 1978). The age of this type section is Early Jurassic. It consists of several stream channel-derived point bar facies of sand and shale. Thin overbank swamp-derived shale and coal units are also prevalent. The shales are medium to dark grey, silty and carbonaceous and coaly. The coals are black, shaly and bituminous. Individual seams are generally less than 0.5 m thick.

In southwestern Patchawarra Trough, the Poolowanna Formation unconformably overlies either pre-Permian basement or the Early Permian Patchawarra Formation. In the Tantanna

Field, its thickness ranges from 14 m in Tantanna-1 to 31m in Tantanna-2. These intervals generally consist of siltstone and sandstone with minor coal interbeds. The depositional environment seems to have varied from meandering or anastomosing fluvial to associated flood plain lacustrine, overbank and low energy swamp settings.
Fig. 1.5 Stratigraphy

In the Sturt and Sturt East Fields, the Poolowanna Formation unconformably overlies the Patchawarra Formation and ranges in thickness from 5m at Sturt-1 to 48m at Sturt East-4. It contains siltstone, coal and sandstone interbeds. In some intervals the siltstones are notably carbonaceous. Fluvio-lacustrine environments appear to have been prevalent, leading to interdistributary siltstone interbedded with minor distributory channel sands.

1.4.2 Structural setting

The structural setting of the southern Eromanga Basin is schematically illustrated in Figure 1.6. It forms a downwarp which appears to be controlled by the structure of several underlying Palaeozoic basins (Mott, 1952; Wiltshire, 1982). The Poolowanna, Patchawarra and Nappamerri Troughs, are three prominent depocentres (Armstrong and Barr, 1986).

Poolowanna Trough

The Poolowanna Trough is a large synclinal area which appears to be influenced by the structural settings of both the Pedirka and Simpson Desert Basins. Its broad structural low coincides with that of the underlying basins and is suggestive of a common depocentre. In the western part of the Trough, a structural setting similar to that of Cooper Basin has been suggested (Moore, 1986). Here, structural development in the Early Permian is marked by small horsts and grabens, suggesting a tensional tectonic regime. Erosion and a large time-break mark the separation of Permian, Pedirka Basin strata from the overlying Mesozoic strata. In the central and eastern part of the Trough, the Permian sediments are absent and there is very little sign of Permian or Mesozoic structural development. The main phase of structuring appears to have occurred in the mid-Tertiary. It was associated with epeirogenic movements which are verified by the presence of an elongate, anticlinal dome with strong fault control on the western margin. The main faults extend upwards from the basement into the Cretaceous Cadna-owie Formation, and possibly as far as the Toolebuc Formation (Moore and Pitt, 1984).

Patchawarra Trough

Deformation in this part of the Cooper Basin region has resulted in a group of anticlinal structures (Tantanna, Taloola, Sturt and Sturt East). All these structures are associated with pre-Permian palaeohighs and show evidence of continued growth from the Early Permian to the Tertiary, including co-axial closures and isopach thinning (Anonymous, 1988; Beech, 1989).

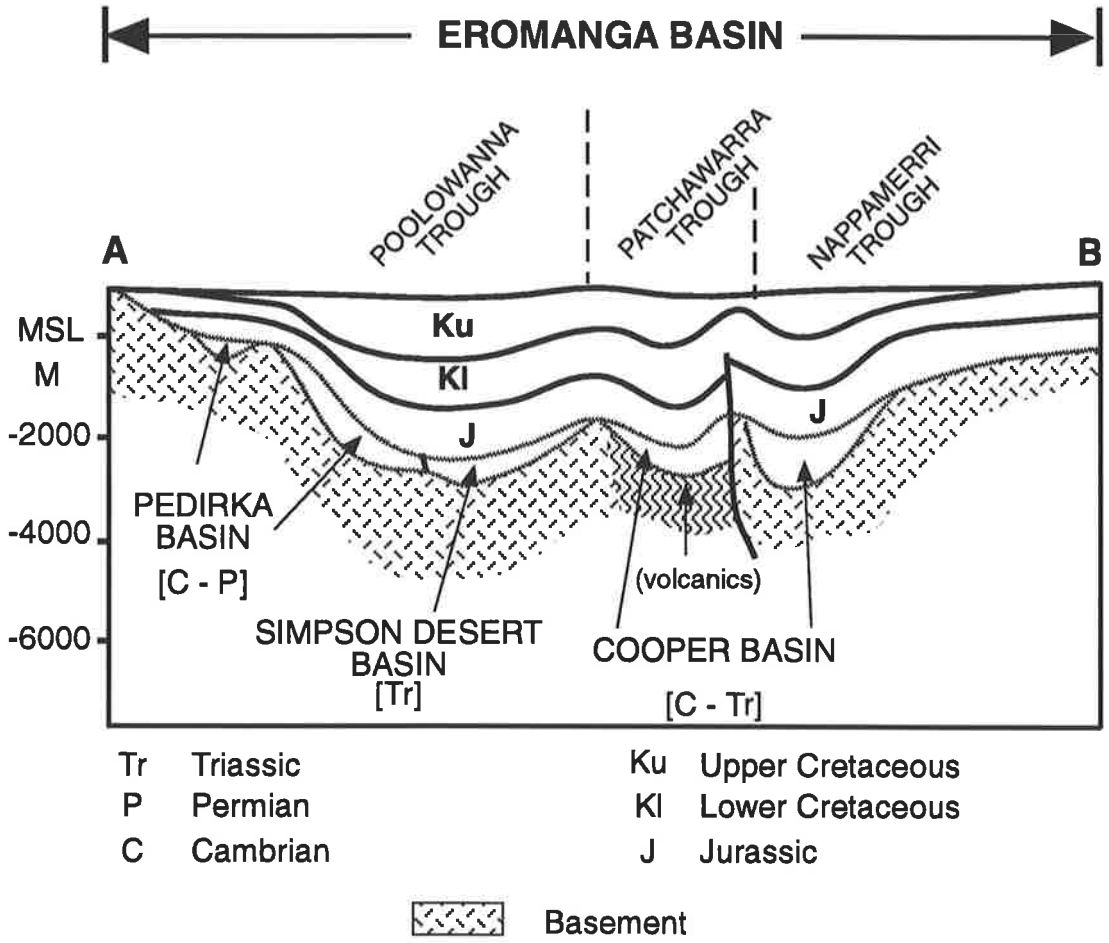


Figure 1.6 A generalised east-west cross-section showing the structural setting of Eromanga Basin and its underlying basins. For the location of section A-B see Figure 1.1.

An unconformable contact between the Patchawarra and Poolowanna Formations is present in most of these structures. Tectonic uplift and erosion appear to have been associated with the initiation of the Eromanga Basin in the Early Jurassic.

1.5 Previous organic geochemical work

This section gives an overview of the various organic geochemical assessments which have previously been made of the Cooper and Eromanga Basins. The geochemical characteristics of both source rock and oils are reviewed, including their maturation levels. Finally, the different opinions on the origin of oils encountered in various reservoirs, ranging in age from Palaeozoic to Mesozoic, are considered.

1.5.1 Source rock evaluation

As a result of studies of both the Cooper and Eromanga Basins carried out over the past sixteen years (e.g. McKirdy, 1981, 1982, 1983, 1984, 1985; Cook, 1982; Passmore and Boreham, 1982; Kantsler *et al.*, 1983; Smyth, 1983; Smyth *et al.*, 1984; Vincent *et al.*, 1985; Jenkins, 1987, 1989; Taylor *et al.*, 1988; Michaelsen and McKirdy, 1989; Powell *et al.*, 1989) several major potential source rocks for hydrocarbon generation have been identified. Potential source beds were recognised in the Patchawarra, Epsilon and Toolachee Formations of the Cooper Basin, and in the Poolowanna, Birkhead and Murta Formations of Eromanga Basin based on Rock-Eval pyrolysis, organic petrology and rock extract studies. These source rocks are of fair to good quality and their kerogens range from Type III to Type II/III in composition. Evolutionary changes in continental flora during the Early Jurassic are suggested to have led to a significant improvement in the hydrocarbon source potential of this area (Thomas, 1982).

Cooper Basin source rocks contain an average of 3.9% total organic carbon (TOC) and have an average hydrocarbon yield of 6.9 kg/t (Jenkins, 1989). In the intraformational fluvial and deltaic shales of the Toolachee and Patchawarra Formations TOC values range from 3 to 6% (Kantsler *et al.*, 1983; Smyth, 1983; Cook and Struckmeyer, 1986). Abundant inertinite-rich coals occur in the Patchawarra Formation of the Patchawarra Trough (Hunt, 1988) where Type III kerogen was identified in both coal and dispersed organic matter (DOM).

Better quality Type II/III kerogen with hydrogen index values up to 320 mg HC/g TOC was reported to be present in the Toolachee Formation of the Naccowlah Block, southwestern Queensland (Vincent *et al.*, 1985). These high HI values may be caused by bacterial degradation of terrigenous organic matter which is thought to improve the quality and oil generation potential of the source rock (Kantsler *et al.*, 1983). In PELs 5 and 6 and ATP 259P, the Toolachee Formation is reported to have an average TOC content of 7.2% and a hydrocarbon yield of 15.7 kg HC/t, whereas equivalent figures for the Patchawarra Formation are somewhat lower (3.0% TOC; 4.8 kg HC/t) (Jenkins, 1989).

Source rocks of Jurassic to Early Cretaceous age from the Eromanga Basin, have an average TOC content of 1.6%, and an average hydrocarbon yield of 4.3 kg/t (Jenkins, 1989). The Poolowanna Formation in the Poolowanna Trough, contains up to 15% TOC and Type II/III kerogen (Cook, 1982). The equivalent 'Basal Jurassic' unit in the northern area of the Cooper Basin has TOC values ranging from 0.5 to 2.0%, whereas in the Naccowlah Block TOC values range from 1 to 11% (Vincent *et al.,* 1985). Hydrogen index values ranging from 150 to 450 mg HC/g TOC appear to be quite common confirming the presence of Type II/III kerogen.

The Birkhead Formation in the northern Cooper Basin region has TOC values ranging from 2 to 4%, with a mean hydrocarbon generation potential of 41 kg/t in the non-coal facies (Scholefied, 1989). Coals in this area were found to be vitrinite-rich (>50%) and inertinite poor (<10%). Their liptinite fraction has a high content of sporinite and cutinite and lesser amount of resinite, suberinite and alginite. In the Naccowlah Block this unit is a good source rock with of this Type II/III kerogen TOC values up to 4.5% (Vincent *et al.*, 1985). The hydrogen-rich liptinite component HI value in the range 150-450 mg HC/g TOC, is thought to have been enhanced by aerobic bacterial decay of vitrinite (Powell, 1984). Throughout PELs 5 and 6 and ATP 259P, the Birkhead Formation is reported to have an overall average TOC value of 2.5% and a mean hydrocarbon yield of 10.8 kg/t, with a preponderance of vitrinite and liptinite contents varying from 10 to 70% of the DOM. The liptinite is mainly cutinite and sporinite, with minor resinite and alginite (Jenkins, 1989).

The Murta Member has somewhat lower TOC values ranging up to 3.1% and hydrogen indices in the range 100 to 350 mg HC/g TOC (Vincent *et al.*, 1985; Jenkins, 1989; Michaelsen and McKirdy, 1989). Its kerogen is of Type II/III composition. Potential hydrocarbon yields are typically in the range 2-8 kg/t. The DOM contains a high proportion of inertinite and liptinite. Sporinite and liptodetrinite are the most abundant liptinites although telalginite contents up to 26% have been recorded in some samples from the Murteree Horst (Michaelsen and McKirdy, 1989; Powell *et al.*, 1989).

1.5.2 Biomarkers in source rock extracts

Previous geochemical studies on source rock extracts have noted the similarities in conventional biomarker distributions (*n*-alkanes, acyclic isoprenoids, steranes and triterpanes) between the Cooper and Eromanga Basins (Vincent *et al.*, 1985). However, the existence of certain unique biomarkers in the Jurassic to Cretaceous sediments of the Eromanga Basin, which are absent or rarely found in the Permian sediments of Cooper Basin, has also been reported (Alexander *et al.*, 1988; Jenkins 1987, 1989).

The saturated hydrocarbon fractions of source rock extracts from the Eromanga Basin (Murta, and Birkhead Formations) and Cooper Basin (Toolachee and Patchawarra Formations) exhibit variable wax (n-C_{20+}) contents and high pristane to phytane ratios (pr/ph>3). High wax contents have been reported in the Westbourne and Birkhead Formations, whereas the Murta Formation saturates are non-waxy (Powell *et al.*, 1989; Gilby and Mortimore, 1989). Cooper Basin siltstones and shales have non-waxy n-alkane distributions, whereas the associated coals and carbonaceous shales tend to have waxy profiles (Jenkins, 1989).

Pristane to phytane ratios ranging from 3 to 9 have been recorded in the Murta Formation whereas the Birkhead Formation had ratios in the range 4 to 5 (Vincent *et al.*, 1985). The 'Basal Jurassic' has pristane to phytane ratios up to 5. Steranes and triterpanes were identified in almost all the aforementioned source rocks from the Cooper and Eromanga Basins (Jenkins, 1989). An average hopane to sterane ratio of 2.5 was reported from both basins, with occasional local variations indicating variable microbial influence on source rock input (McKirdy, 1984).

Alexander *et al.* (1988) identified a group of conifer-derived saturated and aromatic biomarkers in Eromanga Basin source rocks (Fig. 1.7). The saturated biomarkers include the bicyclic diterpanes 15,19-bisnorlabdane (C_{18}) and 19-norlabdane (C_{19}) and the tricyclic diterpane, 19-norisopimarane. The aromatic biomarkers include 1,2,5-trimethylnaphthalene, 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene. It was observed that both suites of saturated and aromatic biomarkers are derived from organic matter of *Agathis* resin origin, and are therefore natural products of araucariacean flora. The relative proportions of each suite and their molecular composition depend upon the depositional environment and maturation level of the host rock. In coaly and more mature sediments aromatic biomarkers are more abundant than saturated biomarkers. The Permian sediments of the Cooper Basin lack these biomarkers, thus providing a unique molecular signature for Permian source rocks and crude oils. However, a similar characteristic was also reported in certain 'Basal Jurassic' shales.

Two C_{27} demethylated triterpanes (25,28,30-trisnorhopane and 25,28,30-trisnormoretane: Katz and Elrod, 1983; Moldowan *et al.*, 1984) were found only in certain Late Jurassic and Early Cretaceous source rocks of the Eromanga Basin (viz. Namur, Murta) where they were always accompanied by 28,30-bisnorhopane and its corresponding moretane (Jenkins, 1989). However, these demethylated triterpanes were not detected in the Westbourne, Birkhead and Poolowanna Formations where 19-norisopimarane appeared to be abundant.

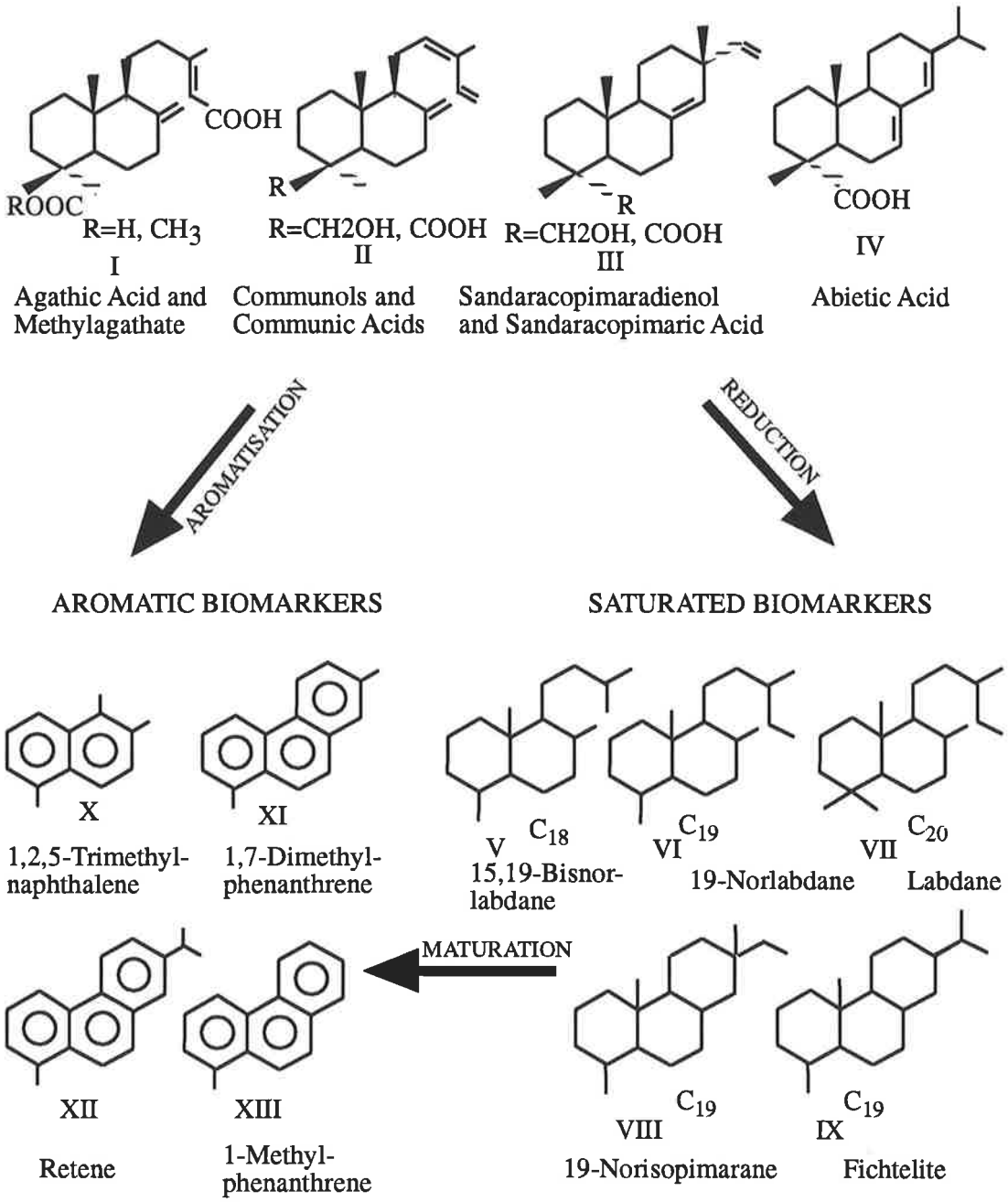


Figure 1.7 Relationships between saturated and aromatic biomarkers and their conifer resin precursors (after, Alexander *et al.*, 1988).

1.5.3 Source rock maturity

Source rock maturities have been reported as vitrinite reflectance measurements (Kantsler and Cook, 1979; Cook 1982; Kantsler *et al.*, 1982; Passmore and Boreham, 1982; Kantsler *et al.*, 1983) and in molecular parameters such as the methylphenanthrene index (MPI) (Alexander *et al.*, 1988; Michaelsen and McKirdy, 1989; Boreham *et al.*, 1988; Powell *et al.*, 1989; Tupper and Burckhardt, 1990); the dimethylnaphthalene ratio (DNR-1) and trimethylnaphthalene ratios (TNR-1 and TNR-2) (Alexander *et al.*, 1985; Radke *et al.*, 1986; Alexander *et al.*, 1988); and various triterpane and sterane isomer ratios (Mackenzie, 1984; Michaelsen and McKirdy, 1989; Powell *et al.*, 1989).

Vitrinite reflectance data show that source rocks in the Cooper and Eromanga Basins have overlapping maturities ranging from 0.5 to 1.0% Ro, and indicative of the onset to main stage of oil generation (Gilby and Mortimore, 1989; Powell *et al.*, 1989). However, at some localities in the Cooper Basin source rocks have Ro values up 4.0% which are overmature for oil generation and correspond to late-stage gas generation (Kantsler and Cook, 1979; Kantsler *et al.*, 1983 and Hunt *et al.*, 1989). However, immature source rocks occur on the flanks of both basins (Scholefield, 1989).

In the Poolowanna Trough, the Poolowanna Formation is at the early mature stage (Cook, 1982; Moore, 1986) with vitrinite reflectance varying from 0.7 to 0.9% Ro. In the central and southern Eromanga Basin, the maturity of this unit varied from 0.55 to 0.70% Ro (Kantsler *et al.*, 1982; Passmore and Boreham, 1982; Scholefield, 1989). Along the Naccowlah-Jackson trend and in the northern part of the basin, Vincent *et al.* (1985) reported maturities of 0.60-0.70% Ro, whereas in the central Nappamerri Trough area a maturity greater than 0.8% Ro was inferred for the Poolowanna Formation. In the northern Naccowlah Block the Birkhead Formation is early mature to mature (0.65-0.8% Ro) while the Murta Formation has an early oil generation maturity (0.45-0.6% Ro) shown from isoreflectance maps at the base of each formation (Vincent *et al.*, 1985). In the Nappacoongee-Murteree and Moomba Blocks a maturity range of 0.57-0.62% Ro was reported for the Murta Formations (Michaelsen and McKirdy, 1989; Powell et al., 1989).

Calculated vitrinite reflectance (Rc) determined from methylphenanthrene indices (MPI) (Radke and Welte, 1983; Boreham *et al.*, 1988), gave values ranging from 0.56 to 1.09% Rc for oil reservoired in both Cooper and Eromanga Basins (Tupper and Burckhardt, 1990). The Cooper Basin oils range from 0.65 to 1.09% Rc (mean value = 0.89% Rc) whereas the Eromanga Basin oils range from 0.56 to 1.09% Rc (mean value = 0.74% Rc).

Alexander *et al.* (1988) observed that for samples of Jurassic age such calculated vitrinite reflectance values are likely to be least reliable in the low maturity zone (Rc <0.7%) because of anomalously high concentrations of the araucariacean marker 1-methylphenanthrene. The

net result of this effect is for low maturity samples to have an artificially low Rc value. To overcome this problem, Alexander and coworkers developed several alternative maturity parameters based upon the abundance of other isomeric aromatic hydrocarbons including dimethylnaphthalenes and trimethylnaphthalenes. The first of these ratios (DNR-1) is defined as [2,6-DMN + 2,7-DMN]/1,5-DMN where DMN is dimethylnaphthalene (Alexander *et al.*, 1985). The second ratio (TNR-1) is defined as [2,3,6-TMN/[1,4,6-TMN + 1,3,5-TMN] where TMN is trimethylnaphthalene (Alexander *et al.*, 1985). A cross-plot of DNR-1 and TNR-1 for samples of different maturities shows an approximately linear relationship. Jurassic sediments from the Eromanga Basin have low maturity (TNR-1 <0.5; DNR-1 <5) to moderate maturity (TNR-1 ~0.8; DNR-1 ~6). Permian samples from the Cooper Basin have moderate to high maturity values.

The Murta Formation has been shown to be an effective early mature source rock as indicated by various saturated biomarker parameters (Michaelsen and McKirdy, 1989; Powell *et al.*, 1989). Its C_{32} hopane isomerisation ratio (22S/22S+22R) ranges between 52 and 61%, its moretane to hopane ratio varies from 0.10 to 0.13, and its sterane isomerisation ratio (20S/20S+20R) based on ethylcholestane (C_{29}) 5α,14α,17α epimers varies from 30 to 40%.

1.5.4 Characteristics of oils, gas liquids and associated gas

In the Cooper/ Eromanga region oils have been recovered over a wide stratigraphic range, extending from Cambrian (Mooracoochie Volcanics) to Lower Cretaceous (Coorikiana Sandstone). Two thirds of the established oil reserves occur within the Eromanga sequence. The largest fields are Jackson, with its Hutton, Westbourne, and Murta reservoirs; and Tirrawarra in which the Tirrawarra sandstone is the main reservoir (Vincent *et al.*, 1985; Heath *et al.*, 1989; Tupper and Burckhardt, 1990). Vertically stacked multiple hydrocarbon pools have been encountered in several fields (Passmore, 1989). One of these is illustrated in Figure 1.2.

API gravity of oils.

Eromanga reservoired oils typically have high API gravities (37 to 54°), with pour points ranging from less than -10°C to 40°C. Vincent *et al.* (1985) reported that Jurassic oils (Westbourne and Hutton) in the Jackson-Naccowlah area, are at the heavier end of the range (40 to 48°API), had high pour points (10 to 23°C) and are paraffinic and waxy; whereas Cretaceous oils (Murta, Namur) in the same area are lighter (47 to 54°API), have pour points <0 °C, and are paraffinic and non-waxy. Moore (1986) reported the recovery of heavy (37° API), waxy (pour point 41°C), paraffinic crude oil from the Poolowanna Formation in Poolowanna-1. The oils from Cooper Basin reservoirs are medium to light (30 to 60°API), paraffinic crudes with low to high wax contents (Hunt *et al.*, 1989).

Natural gas and gas liquids

Aspects of the composition of natural gas in the Cooper/Eromanga Basins have been discussed by Schwebel *et al.* (1980), Rigby and Smith (1981), Kantsler *et al.* (1983), Bodard *et al.* (1985), Cosgrove (1987) and McKirdy and Chivas (1992). Its content in oil ranges from about 50 SCF/BBL up to 16500 SCF/BBL. The wetness of this gas ranges from <1% in the Nappamerri Trough depocentre to 30% on the basin flanks (Schwebel *et al.*, 1980) and a value of 50% was noted in the oil associated gas in the Hutton Sandstone at Chookoo-1 (Vincent *et al.*, 1985). Gas wetness decreases with increasing burial depth, reflecting its increased maturity. The carbon isotopic composition ($\delta^{13}C$) of methane in this natural gas ranges from -43 to -28‰ (Rigby and Smith, 1981).

The carbon dioxide (CO_2) content of the Cooper/Eromanga gases is highly variable. Values ranging from 10 to 18% have been recorded. CO_2 content is a function of source rock maturity (Hunt, 1979; McKirdy, 1982). Moreover, CO_2 may play a key role in the primary migration of liquid hydrocarbons from source rocks containing hydrogen-poor terrestrial organic matter (McKirdy and Chivas, 1992). In the Patchawarra Trough, CO_2-rich gas (C_1/C_1-C_4 <0.85; $\delta^{13}C_{CO_2}$ = -12 to -11‰ appears to be associated with expulsion of paraffinic oil and condensate from the Permian coals and/or carbonaceous shales at maturation levels of 0.9-1.1% Rc. In the Nappamerri Trough, where (C_1/C_1-C_4> 0.85 and $\delta^{13}C_{CO_2}$ = -7 to 0 ‰, carbon dioxide is accompanied by aromatic condensate generated from very mature (1.2-1.5% Rc) Type III-IV kerogen. Powell *et al.* (1991) suggested that lower molecular weight hydrocarbons could have migrated with co-generated gas or carbon dioxide in a supercritical state during the main or late phase of oil generation to produce paraffinic condensate and light oils such as those of Cooper Basin type.

n-Alkane distributions of whole oils

From a lateral comparison of gas chromatograms of whole oils from within single formations, Kagya (1993) observed that most oils from Eromanga reservoirs are characterised by a broad unimodal *n*-alkane profile extending from C_6 to C_{27+}, with a maximum between C_8 and C_{13}. However, exceptions to this general pattern were noted in Nungeroo-1 (Namur), Gidgealpa-46 (Birkhead) and Kerinna-1 (Hutton) crudes where the *n*-alkane maximum occurs at higher carbon numbers (C_{19}-C_{23}). This feature may be a reflection of relative immaturity or removal of light ends by water washing (D. M. McKirdy, pers. comm., 1993). Oils from the Poolowanna Formation (Fig. 1.8), the subject of the present study, were found to exhibit three distinct *n*-alkane profiles: a) unimodal with maxima at C_{19-13}; b) weakly bimodal with maxima at C_{9-13} and C_{22}; and c) skewed unimodal with a maximum at C_{23}.

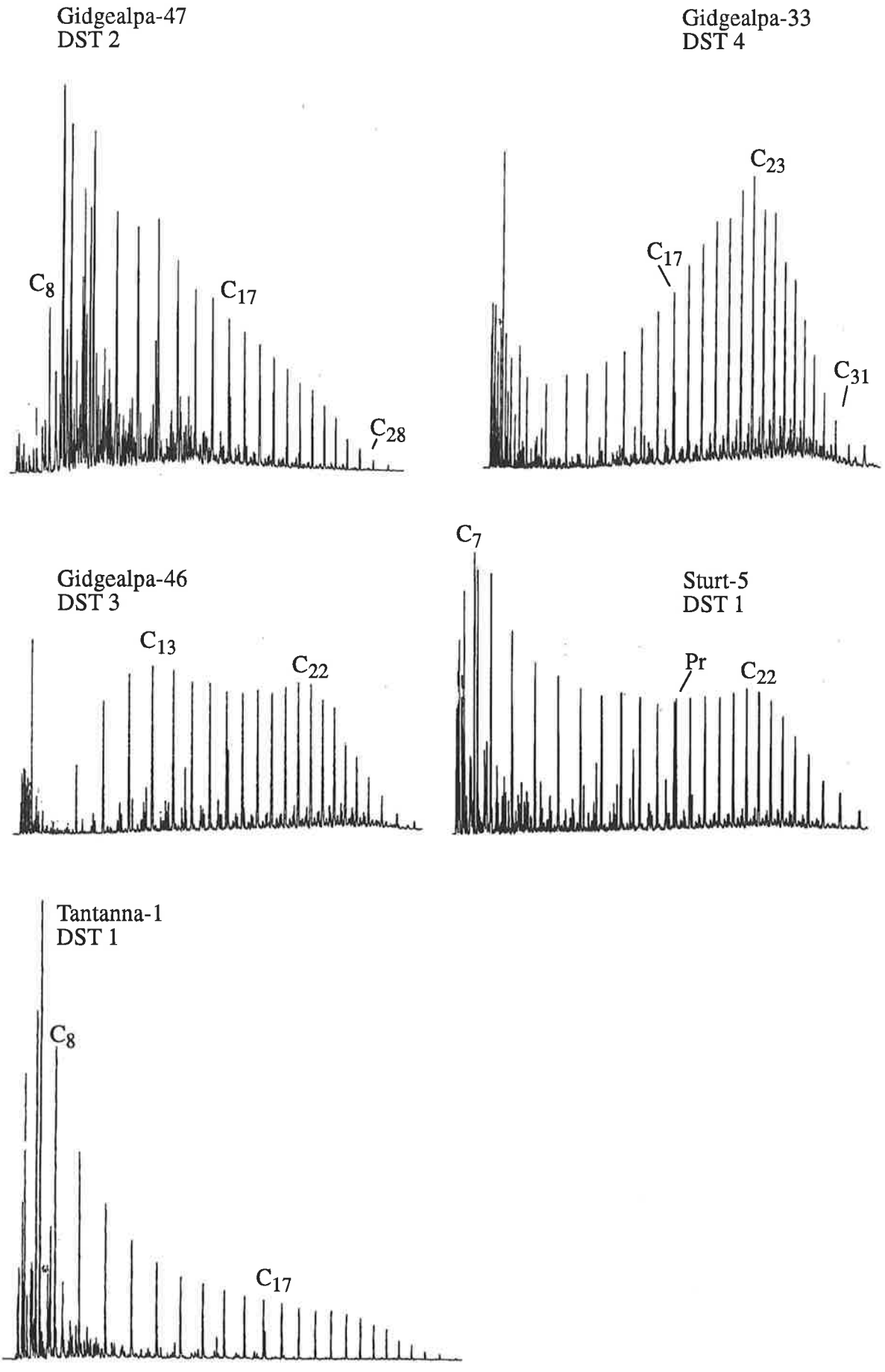


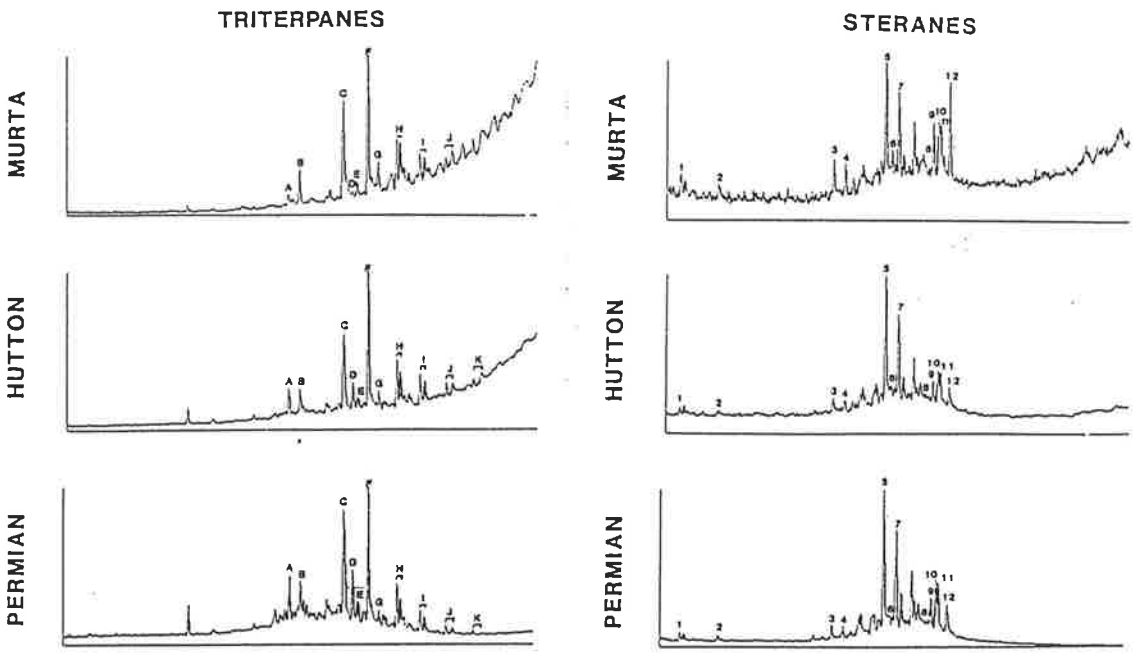
Figure 1.8 Variation of whole-oil alkane profiles of selected oils from the Poolowanna reservoirs in the Eromanga Basin.

Oils from Permian reservoirs (Tirrawarra, Patchawarra, Toolachee) are usually characterised by weakly bimodal C_6-C_{30+} *n*-alkane profiles with maxima at C_{8-10} and C_{19-23}. Such a profile is typical of fully mature non-marine crude oils derived from Type III kerogen (D. M. McKirdy, pers. comm., 1993). Exceptions to this rule for the Cooper Basin are the broad non-uniform profiles of the Gidgealpa-49 (Tirrawarra), Strzelecki-16 (Toolachee) and James-1 (Triassic) crudes.

Inspection of the oil GC traces assembled by Kagya (1993) showed that the weak *n*-alkane bimodality of the Permian oils could be traced upward into younger reservoirs in some fields (e.g. Gidgealpa). This could be due to vertical migration from Permian source rocks into younger Jurassic reservoirs. The above observations imply that different source rock facies in the Eromanga Basin were responsible for the oils found in its reservoirs. However, vertical migration of oil generated from Cooper Basin source rocks into younger formations cannot be ruled out. The Patchawarra and Tirrawarra oils can be singled out as having a specific source rock because of their unique *n*-alkane bimodality. High wax oils with *n*-alkane maxima in the C_{20+} range may be either relatively immature or water washed, or both.

Biomarkers

Steranes and triterpanes have been identified in oils from the Eromanga and Cooper Basins. Using their relative abundance and distribution, Vincent *et al.* (1985) were unable to reliably distinguish between oils of Permian, Jurassic and Cretaceous source affinity (see also Fig. 1.9). The saturated biomarkers 25,28,30-trisnorhopane and 19-norisopimarane identified in some Eromanga-reservoired oils were suggested by Jenkins (1989) to be diagnostic of their Jurassic source. The 19-norisopimarane marker was found in greatest abundance in crude oil pools from the northern region of ATP-259P at Cuddapan-1, Marengo-1 (Aquitaine Block) and Toby-1 (Wareena Block). A suite of aromatic biomarkers similar to that found in Jurassic source rock extracts (Alexander *et al.*, 1988; see also Fig. 1.7) was also identified in these oils, although a significant number of them did not conform to the DNR-1 versus TNR-1 relationship as shown by the sediment samples.



Key to triterpanes:

A	C_{27}	18α(H) 22, 29, 30-trisnorhopane (Ts)
B	C_{27}	17α(H) 22, 29, 30-trisnorhopane (Tm)
C	C_{29}	17α(H) 21β(H) norhopane
D	C_{30}	17α(H) diahopane
E	C_{29}	17β(H)21α(H) normoretane
F	C_{30}	17α(H) 21β(H) hopane
G	C_{30}	17β(H) 21α(H) moretane
H-K	C_{31}-C_{34}	17α(H) 21β(H) 22S(left) and 22R (right) homohopanes

Key to steranes:

1	C_{21}	sterane
2	C_{22}	sterane
3&4	C_{27}	20S and 20R diasteranes
5	C_{29}	20S diasterane
6	C_{27}	5α(H) 14α(H) 17α(H) 20R sterane
7	C_{29}	20R diasterane
8	C_{28}	5α(H) 14α(H) 17α(H) 20R sterane
9&12	C_{29}	5α(H) 14α(H) 17α(H) 20S and 20R steranes
10&11	C_{29}	5α(H) 14β(H) 17β(H) 20R and 20S steranes

Figure 1.9 Uniform sterane (m/z 217) and triterpane (m/z 191) signatures of Cretaceous, Jurassic and Permian oils in the Naccowlah Block, Cooper/Eromanga Basin (Vincent et al., 1985).

Oil maturity

A maturity range of 0.5-1.09% Rc, with a mean value of 0.74 %Rc was reported for a large suite of Eromanga-resevoired oils (Tupper and Burckhardt, 1990). The Murta-reservoired oils are of low maturity, analogous to the immature condensates described by Connan and Cassou (1980). Their Rc values vary from 0.54 to 0.61%, with the exception of those of the Merrimelia (Murta) oils which reflect a higher maturity (0.73-0.84% Rc). The corresponding C_{29} sterane isomerisation ratios (20S/20R = 0.53-0.82) and C_{30} moretane to hopane ratios (0.16-0.23) are likewise low (Michaelsen and McKirdy, 1989). The Jurassic oils are typicaly more mature than the Cretaceous oils. Michaelsen and McKirdy (1989) reported Rc values of 0.64-1.14%; C_{29} sterane 20S/20R ratios of 0.82-1.16; and moretane to hopane ratios in the range 0.09 to 0.17.

The maturity of oils reservoired in the Cooper Basin varies from 0.65 to 1.09 %Rc, with a mean value of 0.89% Rc, (Tupper and Burckhardt, 1990). Michaelsen and McKirdy (1989) reported C_{29} sterane (20S/20R) ratios ranging from 0.98 to 1.14 and moretane to hopane ratios of ~0.02 for these oils.

1.5.5 Origin of Cooper and Eromanga Basin oils

Differentiation of Cooper-derived oils from those which originated in the Eromanga appears to have been hampered by the gross chemical similarity of the oils and their source rocks. The source rocks in both basins are characterised by similar kerogen (Type II/III to III) and their maturity ranges overlap. Nevertheless, the Eromanga oils had previously been categorised as being largely of Jurassic or Early Cretaceous origin (Smyth and Saxby, 1981; Vincent *et al.*, 1985; Armstrong and Barr, 1986; Alexander *et al.*, 1988; Michaelsen and McKirdy, 1989; Powell *et al.*, 1989).

Based on their gasoline range (C_5-C_7) composition, the carbon isotopic signatures of their (C_{12+}) saturated and aromatic hydrocarbon fractions, and their pristane to phytane ratios, Vincent *et al.* (1985) and McKirdy (1985) categorised three separate oil families of different source affinity. The first category includes the Cretaceous oils which have higher pristane to phytane ratios than those of the Jurassic and Permian oils. The gasoline-range hydrocarbon data indicate a mixed to microbial source for their organic matter; and the isotopic data confirm that bacterial lipids were the predominant source of their hydrocarbons.

The second family is comprised of Jurassic oils which also had a bacterial contribution to their source material, except that in this case expulsion from the source rock occurred at higher maturity levels. As a result, generation of waxy hydrocarbons from leaf cuticles and spore coatings was achieved. Subsequently, the wax contents of many Jurassic oils were enhanced by removal of light ends through water washing in the reservoirs.

The third family consists of Permian oils and condensates, which may be distinguished from Jurassic oils on the basis of their gasoline range composition. They are clearly of higher plant origin, whereas the Jurassic oils are of mixed higher plant and microbial source.

Jenkins (1989), using the two biomarkers 25,28,30-trisnorhopane and 25,28,30-trisnormoretane, and Heath *et al.* (1989), using the general chemistry of the oil, suggested that a considerable proportion of the Eromanga-reservoired oils were derived from Cooper Basin source rocks. Although Jenkins (1989) employed the absence of specific biomarkers to indicate a Permian origin, his approach has to be applied with caution because in some of the potential Jurassic source rocks the said biomarkers were not identified.

Tupper and Burckhardt (1990) argued that, if the oil's maturity exceeds that of the local reservoir or source rock, a Cooper Basin source is implied. This argument, however, can also be true if the oil is derived from highly mature basal Jurassic source rocks in the Eromanga Basin. Vertical migration from Cooper source rocks into Eromanga reservoirs can only be confirmed if there exists a unique biomarker for Permian source rocks. Indications of long distance migration (either lateral or vertical) in the chemistry of an oil could just as easily be explained by migration within the Eromanga Basin sequence.

The source affinity approach discussed by Vincent *et al.* (1985) could be more confidently used to determine the origin of these crude oils if all the parameters (including those based on gasoline-range hydrocarbons) were applied to their respective source rocks. Cretaceous oils were shown to originate *in situ* but the low maturity of these source rocks casts doubt on their effective hydrocarbon generating potential.

As McKirdy (1982) and Kanstler *et al.* (1983) observed, and as later confirmed by Alexander *et al.* (1988), some of the oil in Jurassic and Cretaceous reservoirs was derived from within the Eromanga Basin and some may have had a Permian source. The Cooper Basin oils were of course derived largely from Permian source beds although some might have been derived from older sedimentary units. Oil expulsion from the Cooper Basin began in the Triassic with a significant phase of generation in the Jurassic to Late Cretaceous time interval (Kanstler *et al.*, 1983; Tupper and Burckhardt, 1990), whereas oil expulsion from potential Eromanga source rocks occurred during the early Late Cretaceous to Tertiary (Tupper and Burckhardt, 1990).

Chapter 2

Fundamentals of petroleum geochemistry

2.1 Background

Based on the observed associations of petroleum with organic-rich sedimentary rocks, and the presence of optically active compounds and biological markers in petroleum, it is obvious that the vast bulk of petroleum (oil and gas) is of organic origin. This concept has been proved by various methods such as oil-source rock correlation (Philippi, 1965) and experimental conversion of buried organic matter into petroleum (Hoering and Abelson, 1963). Marine and terrestrial lipids have been suggested to be the major source of petroleum (Silverman, 1965a). The great chemical similarity between lipid molecules and many petroleum hydrocarbons appears to corroborate this suggestion. The non-lipid part of bacteria and algae may also contribute to the formation of oil (Lijmbach, 1975).

Elaboration of this concept has been achieved by studies which embrace organic petrology and organic geochemistry. These studies have elucidated the, microscopic, visual and chemical composition of organic matter in unconsolidated sediments and rocks, and the changes induced in it by microbial activity and thermal alteration. The organic geochemistry of hydrocarbons in reservoirs is also investigated and compared to that of organic matter in source rocks.

2.2 Aspects of organic petrology relevant to petroleum genesis

It has been frequently observed that the regional distribution of oil and gas in a sedimentary basin is related to the rank of its coals (Teichmüller, 1971). The microscopic techniques which were initially applied in coal studies (van Krevelen, 1961) have been extended to cover the optical properties of sedimentary organic matter (Teichmüller, 1985). This type of study is possible because macerals, the smallest and relatively homogenous petrographic entities of coal (Stopes, 1935) are also present in the dispersed organic matter of sediments (Murchison, 1987). From the scrutiny of maceral types and assemblages, inferences can be made on land plant evolution in the geological record; depositional environments; transformation of vegetable matter into sedimentary organic matter and its maceral constituents and the eventual conversion of this organic matter to hydrocarbons.

2.2.1 Evolutionary trend of plants in the geological record: implications for fossil organic matter

The stratigraphic ranges of the major members of the plant kingdom are illustrated in Figure 2.1a. The *Thallophyta* (algae) is the oldest group which dominated the plant kingdom to the end of Silurian period when the *Pteridophyta* (fern-like plants) developed.

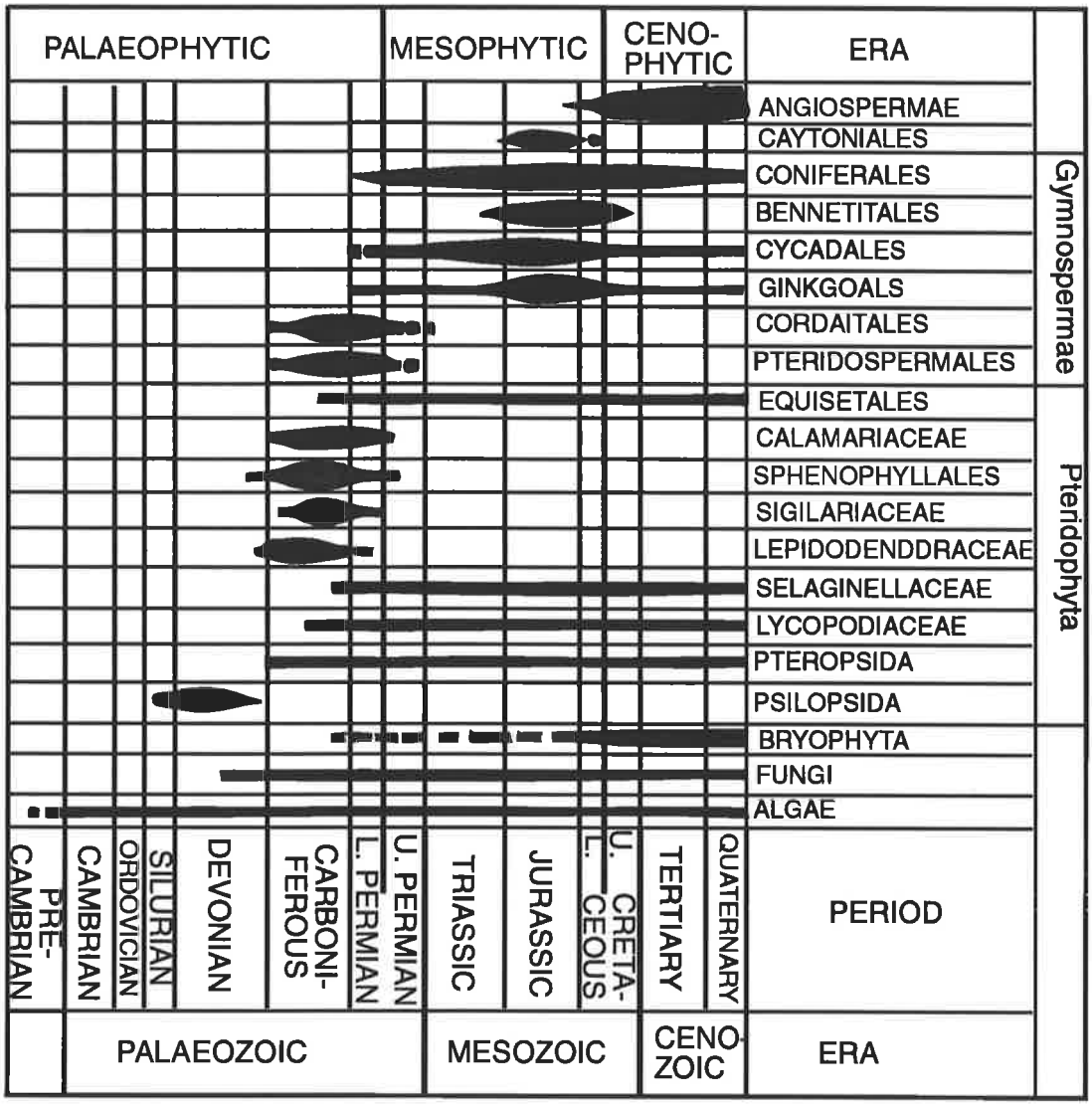


Figure 2.1a The stratigraphic ranges of major members of the plant kingdom showing the difference between plant- and animal- based eras (Diessel, 1992).

The Precambrian thucholite deposits of the Witwatersrand (Snyman, 1965) and the Ordovician kukersites (formed from *Gloeocapsomorpha prisca*) in Estonia (Foster *et al.*, 1989, 1990) are examples of early boghead coals or oil shales which formed from the remains of algae or cyanobacteria.

Oil shales continued to form after the advent of higher plants. Examples include the Eocene deposits of the Green River Formation in the western USA and the Tertiary deposits at Rundle and Julia Creek in Queensland, Australia (Diessel, 1992). Torbanites contain mainly the fossil green algae *Pila* and *Reinschia* which occur in many Permian boghead coals of Australia, South Africa and South America. Both *Pila* and *Reinschia* appear to be closely related to the extant genus *Botryococcus* (Stach, 1982) and are found in both fresh and brackish water. The species *Botryococcus braunii* is regarded as the source of coorongite, a Recent bituminous substance found near Salt Creek in South Australia. *Tasmanites* sp. is another fossil chlorophyte found in some marine oil shales (tasmanite). It is related to the extant genus *Pachysphaera*, and is known from Permian deposits in Tasmania and Cretaceous deposits in Alaska (Tissot and Welte, 1978).

Algal bodies show little differentiation, do not possess a vascular circulatory system and are therefore dependent on osmosis and the presence of water to sustain their life cycle. Apart from being diverse throughout the geological record, their presence indicates that the host rocks were deposited in sub-aquatic environments.

The first land plants, the Psilophyta (also called Psilopsida), appeared in the Early Devonian. They were descendants of the algae but are regarded as a separate group and assigned to a class of the pteridophytes (spore plants). They were the first plants to achieve the transition from water to land, having a simple vascular system and displaying cell differentiation. The early transitional forms lived half submerged in water and bore sporangia (spore capsules) at the tips of their leafless stems. Later fossil forms bear evidence of a more terrestrial habit and were well equipped for life in swampy environments. During the Carboniferous Period they gave rise to banded humic coals in the Northern Hemisphere. Ground water fluctuation seems to have affected their growth and diversity and consequently fewer economic coal seams were produced.

During the Permian Period, the effects of ground water fluctuation on peat formation are less evident. This time marked the appearance of arborescent vegetation which was dominated by seed plants. The arborescent gymnosperms were among the first plants to grow on relatively dry ground and therefore they are characterised by longer roots. The Permian flora had greater tolerance towards environmental change enabling them and their vegetational successors to continue accumulating peat where the Carboniferous flora would have ceased to do so. In addition to vitrinite-rich bright coals, Permian coal measures contain many dull

coals with high proportions of inertinite, which is commonly formed under relatively dry conditions.

The spore content of Carboniferous humic coals is higher than that of equivalent younger deposits which, from the Permian onward, were increasingly based on seed plants. However, it has been observed that reproduction of pteridophytes requires a moist environment and fresh water to fertilise the spores (Collinson and Scott, 1987; Phillips, 1979). Because of adverse conditions during the Carboniferous, fertilisation had a low success rate. The pteriodophyte flora overcame this problem by producing spores in large quantities in order to assure that reproduction was kept at high level. In some lacustrine environments, spores were so concentrated that they formed a special type of coal known as 'cannel' coal.

The Permian Period marks the end of the Palaeophytic and the beginning of Mesophytic Era (Fig. 2.1a), in which the gymnosperms (plants with naked seed) constituted the leading plant group. Like the psilophytes, which were the forerunners of most of the pteridophytes, the pteridosperm (seed ferns) constitute the link between spore-bearing ferns and seed plants. They reached their maximum development on the southern continents (Gondwana) during the late Carboniferous and Permian. They are responsible for the formation of rich coal deposits in Australia, South Africa, South America, India and Antarctica. One of their leading genera gives its name to the whole plant association, which is often referred as the Glossopteris flora (Gould, 1975; Gould and Shibaoka, 1980; Retallack, 1980). Other gymnosperms which were common in the Permian are the Cordaitales, the Coniferales and, toward the end of the period, the Cycadales. Post-Carboniferous coals therefore frequently have low spore contents but are rich in derivatives of plant resins and waxes (Diessel, 1992).

Figure 2.1b shows the stratigraphic distribution of conifer fossils in the Cooper and Eromanga Basins of Australia. Near the close of the Permian, the pteridosperms underwent an abrupt change with the introduction of the *Dicroidium* flora and an associated spore/pollen assemblage known as the *Falcisporites* microflora. The *Dicroidium* flora as a whole included only a low proportion of conifers, notably *Voltziopsis* and *Rissikia* (Gould, 1975; Gould and Shibaoka, 1980; Retallack, 1980; Townrow, 1969).

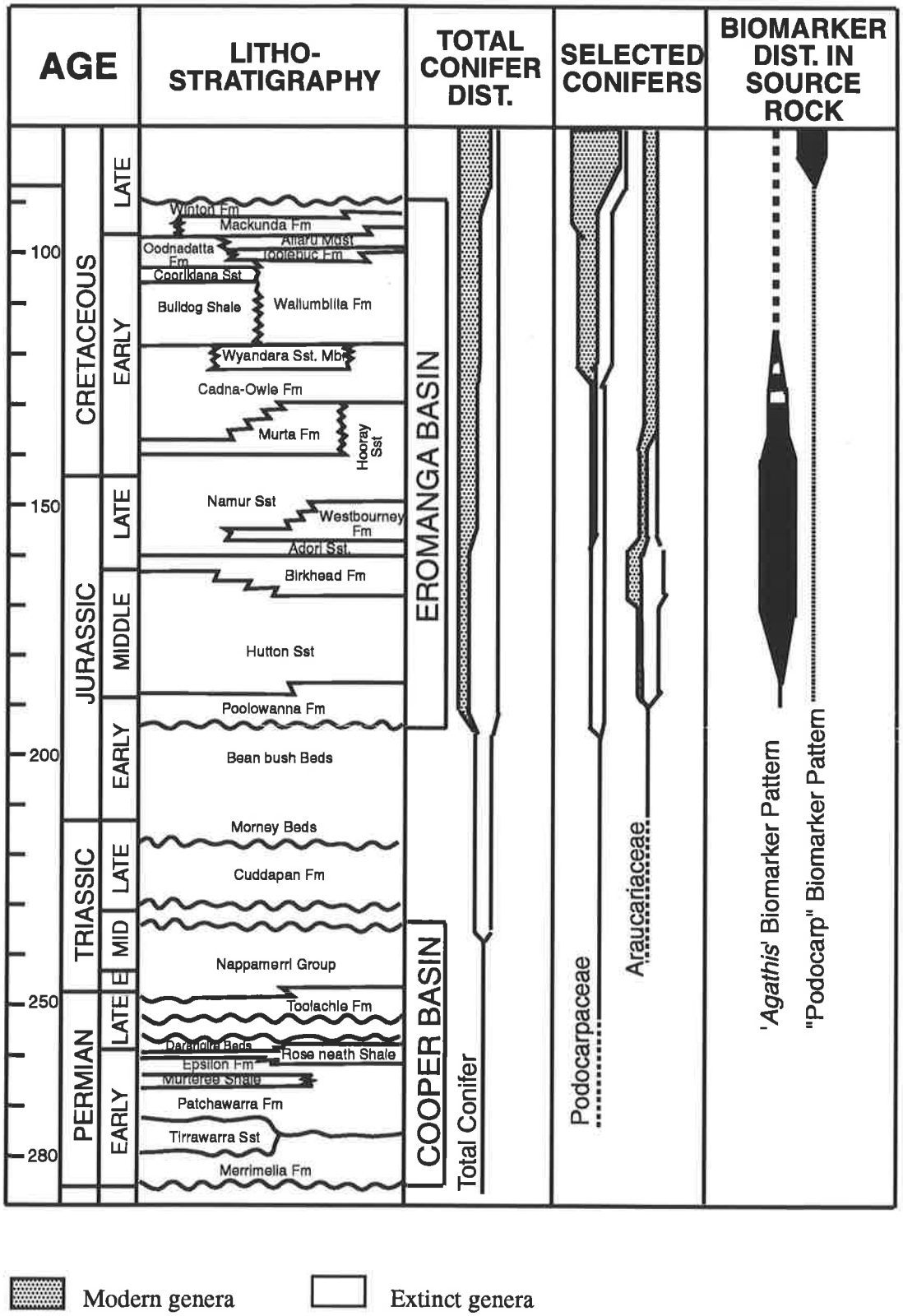


Figure 2.1b The stratigraphic distribution of selected plant genera in sediments of the Cooper and Eromanga Basin (modified after Alexander *et al.*, 1992).

The Triassic flora were dominated by the pteridosperm pollen *Falcisporites*. Microfossil observations have recorded the occurrence of a very low proportion of pinacean-like, podocarpacean-like and inaperturate pollen, which are thought to represent plants with araucariacean affinities. No megafloral remains of the Araucariaceae have been recorded in Australian Triassic sediments (Townrow, 1969). However, Alexander *et al.* (1988) noted some tentative evidence of sparse araucariacean forms in the Triassic of the Cooper Basin. Of the Triassic conifers, only the podocarp *Russikia* is related to a modern family (Townrow, 1969).

The beginning of Jurassic is marked by another floral change whereby, for the first time, conifers attained dominance over the pteridosperms and a low but significant proportion of araucariacean forms. The earliest Jurassic microfloral assemblages, such as those from the Poolowanna Formation, are strongly dominated by *Classopolis* (*Carollina*) pollen, believed to be derived from the Cheirolepidiaceae, an extinct conifer group. Cretaceous members of this family are allied to extant Cupressaceae (Miller, 1977), which are widely represented in Australian flora.

Araucariacean-like pollens assumed prominence and remained common throughout the Jurassic, and commonly are identified in Jurassic microfloras from the upper Poolowanna Formation to the Namur Sandstone (Alexander *et al.*, 1988). Megafloral remains of the Araucariaceae found in the Middle and Late Jurassic sediments are more closely allied to the genus *Araucaria* than to *Agathis* whose fossil record extends back only into the Tertiary (Stockey, 1982). Saccate pollen and a distinctive trisaccate pollen type (*Microcachryidites*), attributed to the podocarp *Microcachry* were also prominent. These bi- and trisaccate elements appear to have displaced the araucariacean forms.

The Cretaceous plant record is marked by the dominance of angiosperms which first appeared in Triassic Period. In spite of the preponderance of angiosperms, the gymnosperms remained important contributors to peat deposits. Their abundance in the resulting coals is related to their resinous wood which resists rapid aerobic decay (Diessel, 1992). The modern podocarpacean genera, *Dacrydium* and *Phyllocladus,* first appeared in the Cretaceous and together with *Podocarpus* gave rise to the distinctive the diterpane biomarkers, identified by Alexander *et al.* (1987) in oils and source rocks of the Gippsland Basin.

2.2.2 Macerals and maceral groups

Conventionally, macerals in brown coal are assigned to three groups: huminite, inertinite, and liptinite. In black (bituminous) coals the term huminite is replaced by vitrinite. The huminite-vitrinite group of macerals is derived from plant tissues which are humified to varying degrees prior to burial and anaerobic gelification. The inertinite group is derived from plant tissues, which are subjected to dehydration and oxidation before final burial. The

liptinite group comprises macerals which are derived from cuticular or other resistant vegetal matter rich in resinous and waxy substances.

The International Committee for Coal Petrology (1975) distinguishes between macerals and submacerals by reference to either their particular vegetal origin or their respective state of preservation. In addition, a unified brown/black coal maceral classification was adopted by Standards Association of Australia (1986), wherein three subgroups of tissue-derived macerals are recognised according to their state of humification prior to physico-chemical gelification (Table 2.1). The following discussion of macerals which make up the vitrinite , inertinite and liptinite groups draws heavily on the summary accounts of Stach *et al.* (1982) and Diessel (1992).

Table 2.1. Classification of macerals and maceral groups (Diessel, 1992).

Maceral Groups	Maceral Subgroups	Macerals
Vitrinite	Telovitrinite	Telinite, telocollinite
	Detrovitrinite	Desmocollinite, vitrodetrinite
	Gelovitrinite	Gelocollinite, corpocollinite
Inertinite	Telo-inertinite	Fusinite, semifusinite sclerotinite
	Detro-inertinite	Inertodetrinite, micrinite
	Gelo-inertinite	Macrinite
Liptinite	Primary liptinite	Resinite, cutinite, sporinite,alginite, suberinite, liptodetrinite
	Secondary liptinite	Exudatinite, fluorinite, bituminite

2.2.2.1 Vitrinite group

Huminite and vitrinite macerals are ubiquitous in humic coals. The terms 'huminite' and 'vitrinite' are applied to macerals which have followed the vitrinisation path of biochemical coalification (Fig. 2.2a). They are formed from wood, bark, root, leaf and other plant cell tissues which have been subjected to humification of varying intensity. Huminite eventually transforms into vitrinite at the beginning of the physico-chemical stage of coalification. This is accomplished by the polymerisation of biodegraded humic substances to form condensed aromatic and hydroaromatic ring structures connected by covalent cross-links (Allan and Larter, 1983). With increasing coalification, and at the expense of non-aromatic matter the cross-links become degraded and functional groups are lost leading to tighter packing of the aromatic clusters (Sakurovs *et al.*, 1989). Their increasing size and degree of crystallinity results in increased reflectance and bireflectance in high rank vitrinite (Mackowsky, 1951).

Humotelinite-telovitrinite

This subgroup is characterised by retention of cell tissue in various stages of preservation.

Woody and cortical cell tissues are thought to be the main progenitors of this subgroup. Under severe and prolonged conditions of degradation, the cell texture of lignin-rich wood will tend towards total breakdown. The rate of degradation of these tissues preservation will depend also on their botanical origin. For instance, wood tissues produced by gymnosperms are more resistant to mechanical, microbial and chemical degradation because of their high content of resins and tannins; whilst angiosperm wood is frequently badly degraded.

Macerals identifiable in brown coals are as shown in Figure 2.2a. *Textinite* is distinguished by its cell structural features which differ little from that of original wood. In some cases, the unaltered anisotropic cellulose and lignin with primary fluorescence are retained (Russell, 1984). It is equivalent to telinite of bituminous coal rank. Plant genera and species are readily identified from textinite tissue, whereas in telinite identification is possible only with difficulty.

Ulminite consists of two sub-macerals, namely *texto-ulminite* and *eu-ulminite*. It is distinguished by swelling and deformation of cell walls during a humification stage at which all cellulose and much of the lignin have been hydrolysed. *Texto-ulminite* is that type in which the cell lumens are still open whereas in *eu-ulminite* the cell walls are in contact with each other. This part of the cell tissue breakdown process takes place in the acrotelm (i.e. oxidation zone of the groundwater table). With increasing condensation under post-depositional anaerobic conditions both *textinite* and *texto-ulminite* transform into *eu-ulminite* due to impregnation of cell tissues by humic acids, resulting in closure of cell lumens. This gives rise to a homogenous surface when polished.

Eu-ulminite may form by either a syngenetic or an epigenetic pathway. The syngenetic pathway takes place in the acrotelm and involves the plastic deformation, collapse and diffusion of cell tissues during humification. Before closing of the cell lumens, they may be filled by colloids presumably generated from within the woody tissue. After polymerisation much of this material forms telocollinite or, alternatively semifusinite/macrinite if the hydrolysate is subjected to dehydration and oxidation before final burial in the catotelm (i.e. a reduction zone below the groundwater table where organic matter is preserved).

Epigenetic *eu-ulminite* is formed during diagenesis by successive impregnation of *textinite* and *texto-ulminite* and the filling of their cell lumens with fluid humic colloids. In the process the host tissue is metasomatically replaced by humic substances, which is often indicated by the loss of anisotropy and fluorescence from cellulose and lignin, respectively. The impregnating fluids may be generated from within the replaced tissue, but they could also represent migrating humic fluid hydrosols formed elsewhere in the deposit.

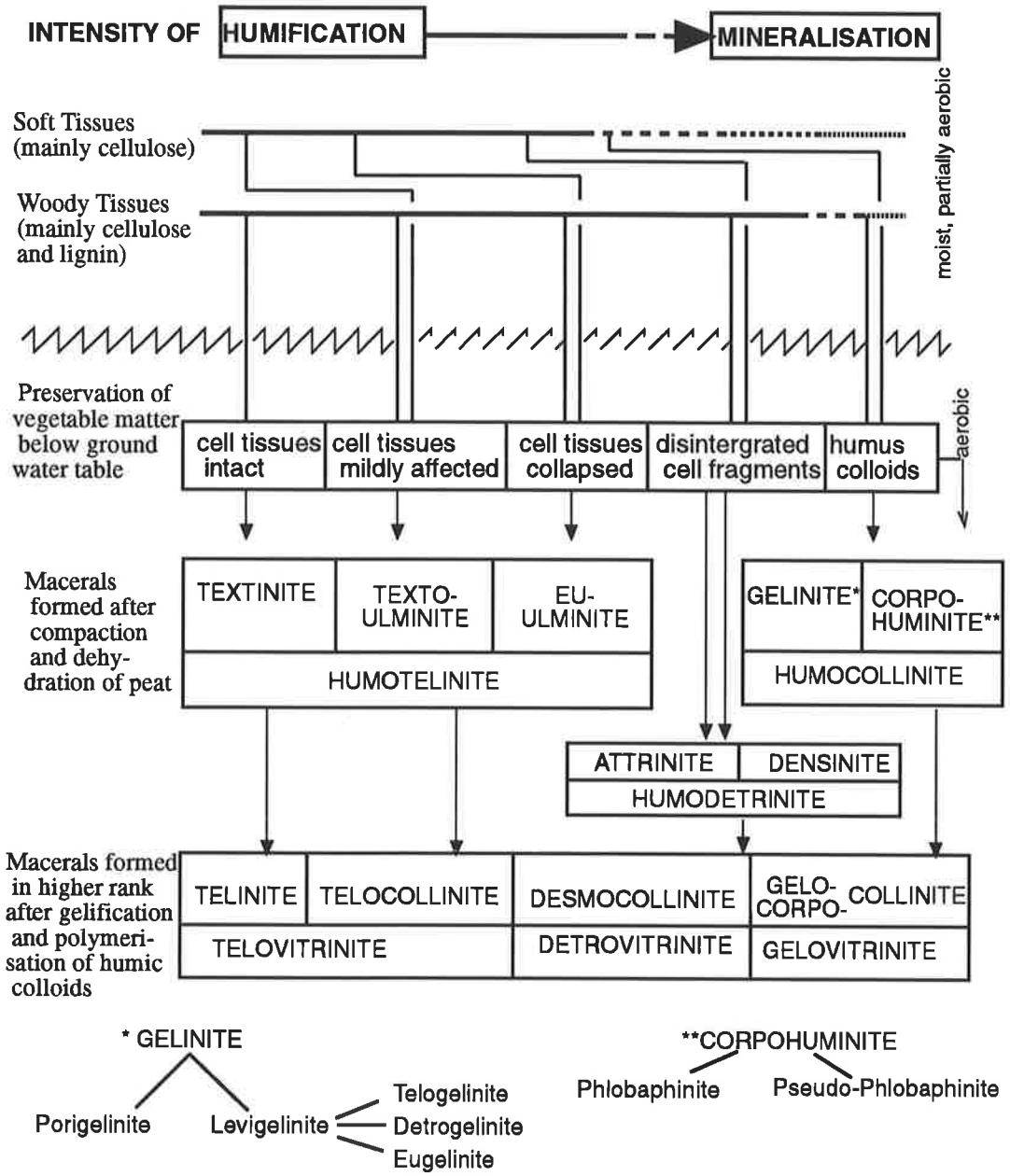


Figure 2.2a Schematic outline of the formation of the vitrinite group from tissued vegetable matter subjected to varying intensities of humification (modified after Diessel, 1992)

Post-depositional epigenetic gelification of cell tissue begins in the catotelm during the peat stage and, after polymerisation of the humus colloid, culminate in formation of telovitrinite, mainly in the form of telinite (Fig. 2.2a). The diagnostic feature of telovitrinite is that it is free from contamination by other macerals. All telovitrinite displays a reflectance 5% to 10% higher than that of its associated detrovitrinite which is subjected to a higher degree of cell destruction before final burial (Robert 1979).

Humodetrinite-detrovitrinite

Humodetrinite is a coagulated mixture of colloids and solids. Much of the material constituting humodetrinite and detrovitrinite is derived from non-woody cell tissues. Herbaceous plants are likely to be the main contributors to this subgroup because of their ready disintegration during humification. Prolonged humification, however, would affect trees and other wood producing plants in similar manner. The common brown coal macerals of this subgroup are *attrinite* and *densinite*.

Attrinite consists of loosely packed cell fragments and other plant debris, including liptinite and inertinite. The latter are discontinuous phases in humodetrinite. Epigenetic gelification of *attrinite* is common.

Densinite is a product of further humification and compaction of *attrinite*, in which the partially degraded cell fragments begin to lose their identity and merge with the surrounding colloidal matrix. It can be formed by either syngenetic or epigenetic processes of humification. The dense appearance of this maceral is caused by its high proportion of colloids.

Desmocollinite is the bituminous coal equivalent of *densinite,* where in vitrinitic ground-mass is the main constituent. In transmitted light microscopy of high volatile bituminous coal, the heterogeneous nature of this maceral is very recognisable, but without etching no differentiation can be made between colloidal continuous and attrital discontinuous phases. Liptinite and inertinite inclusions occur within the groundmass and are indicative of the total loss of coherent cell structure. A large portion of the enclosed liptinite debris consists of absorbed oils, resins and waxes and in most cases is too small to be resolved using white light microscopy. This disseminated liptinite has the effect of lowering the reflectance of desmocollinite.

Humocollinite-gelovitrinite

Humocollinite is a coalified humic colloid without any inclusions of remnant cell tissue. Although rare, it occurs sporadically in the form of *gelinite* and *corpohuminite* in brown coals. They occur as precipitates in cavities, cleats, and fissures of peat and are generated from a humic hydrosol (humic acid) during humification of decomposing vegetal matter.

Gelinite is further sub-grouped into two submacerals, *porigelinite* and *levigelinite*. Porigelinite has a granular texture presumably consisting of small droplets of humic colloids (Liu *et al.*, 1982) whereas levigelinite has a smooth and sometimes cloudy polished surface. Other submacerals in this subgroup are *detrogelinite, telogelinite* and *eu-gelinite*. They are normally distinguished on the basis of their increasing proportions of colloidal material (Diessel, 1992).

Gelocollinite is the black coal equivalent of gelinite. It occurs as infillings of cell lumens and gaps between cell walls in semifusinite. This colloidal humic matter commonly contains inclusions of cell fragments and other organic debris. The spheroidal and elliptical bodies of flocculated humic colloids contained in cell lumens of brown coal are known as *pseudo-phlobaphinite*. These are secondary infillings which resemble the *phlobaphinite*, a substance consisting of tannin and non-humic excretions like that in the cork cells of bark tissue. On disintegration of the cell tissue these corpohuminite bodies become isolated, forming the corpocollinite of black coal.

2.2.2.2 Inertinite group

The inertinite macerals have the same precursors as those of the vitrinite group. Many of these macerals pass through same stages of humification as vitrinite except that, before reaching a depositional base level below the groundwater table, they are subjected to a period of intensive desiccation and varying degrees of oxidation including partial burning of accumulated vegetal matter (Gould and Shibaoka, 1980). The fusinitisation pathway is as summarised in Figure 2.2b

Inertinites are characterised by high reflectance in incident light microscopy because of being rich in aromatic carbon. They are relatively brittle and hard and thus tend to develop a high polishing relief. The proportion of inertinite in humic coals varies over a wide range, but is frequently between 20 and 30%. Figures which deviate substantially either way from this average, occur in coals which have been formed under particular sets of environmental conditions. The inertinite group is divided into three subgroups according to the degree of cell tissue preservation.

Telo-inertinite

This subgroup comprises structured macerals in which gelification is either absent or minor. The most common members are pyrofusinite (or simply fusinite), semifusinite and sclerotinite. *Pyrofusinite* is fossil charcoal resulting from incomplete combustion of wood tissue. Of all the inertinites, it shows the highest degree of preservation of cell tissue, as well as the highest reflectance and polishing relief. It has a distinct yellow tinge in ordinary incident light, whereas it is opaque in transmitted light and does not fluoresce under UV illumination.

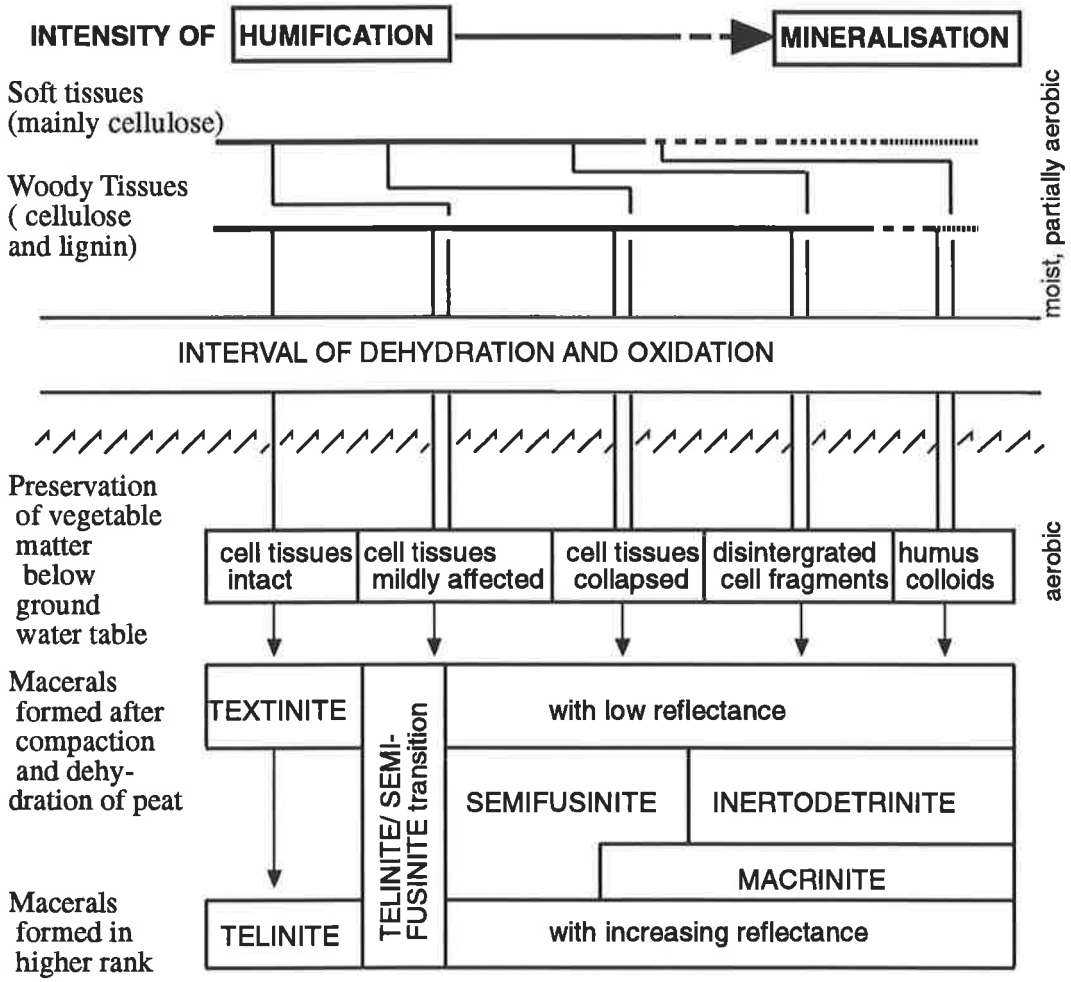


Figure 2.2b Schematic outline of the formation of macerals from tissued vegetable matter subjected to varying intensities of humification and drying before burial below the ground water table (Diessel, 1992)

The cell walls of pyrofusinite are rather thin, as suggested by Barghoorn (1949), only their resistant lignified portions survive combustion. In most cases pyrofusinite occurs as broken curved fragments, known as bogen (bow) structure, which are caused by either overburden or tectonic pressure. Its highly aromatic structure does not undergo further change during physical-chemical coalification.

Semifusinite is a product of either aerobic biodegradation during humification (Murchison et al., 1985) or oxidation and incomplete combustion of partially humified cell tissue. Unlike pyrofusinite, its cell walls are often swollen as a result of partial humification. Initially, it has a lower reflectance but this increases until anthracite rank is reached. Reflectance, hardness, degree of cell preservation, and other properties of semifusinite range between those of vitrinite and fusinite. Its characteristic colours in white incident light range from light grey to white. The darker varieties show brown translucence in transmitted light, and low reflecting varieties display long wave microfluorescence.

Depending on the degree of humification prior to oxidation, wood-derived semifusinite may also show poor cell preservation and occupy a transitional position to macrinite. Fusinite and semifusinite commonly occur as layers and lenses in which the cell cavities are either empty or may be filled with a wide range of substances including gelovitrinite, gelo-inertinite, resinous material and various minerals. Of the whole group, semifusinite is the most common. Its proportion varies but often accounts for more than 50% of all the inertinite in a coal seam.

Sclerotinite is a plant-specific inertinite comprising structured fungal remains, mainly in the form of spores (*corposclerotinite*) and to lesser extent, mycelium and hyphae (e.g. *plectenchyminite*). It is the hardest maceral and normally shows high polishing relief. Its reflectance is very high in bituminous coal but may be quite low in brown coals. Fusinite and sclerotinite are considerably less common and rarely make up more than a few percent.

Detro-inertinite

This subgroup consist of two macerals, *inertodetrinite* and *micrinite*. They both originate from fusinitised detrital plant fragments and are distinguished on the basis of their size. Inertodetrinite is a fragmented inertinite with the longest diameter ranging between 2 and 30 μm. Micrinite consists of the smallest inertinite grains and is commonly referred to as granular opaque matter by (Teichmüller, 1974a). Much micrinite forms at the sub-bituminous rank level from lipid rich material by a disproportional process which results in the formation of petroleum-like materials such as exsudatinite and bitumen, leaving behind micrinite as a residue (Teichmüller, 1974b).

The Australian Standard 2856 (Standard Association of Australia, 1986) regards all inertinites smaller than 2μm as micrinite. The proportion of inertodetrinite in coal varies quite considerably, but it is generally small. Carboniferous coals contain more micrinite than younger coals (average content is 3-6% but may be as high as 19%). The micrinite contents of Permian and the post-Carboniferous coals rarely exceed 3%.

Gelo-inertinite

Macerals of this subgroup are derived from plant material which was first biodegraded into humus colloids and subsequently dehydrated and oxidised (Stach and Alpern, 1966). The only defined representative maceral is *macrinite* which is subdivided into *corpomacrinite*, and *lammacrinite* (Diessel, 1992). In both transmitted and fluorescent light modes, macrinite covers not only a wide range of reflectance in relation to the associated vitrinite, but like semifusinite, there is an inverse relationship between reflectance and the intensities of translucency and fluorescence.

Corpomacrinite occurs as detrital angular to rounded bodies commonly associated with inertodetrinite. Its morphological appearance gives an impression of humic colloids which have undergone desiccation to residue angular bodies. Subsequent dispersal and redeposition converts the angular bodies to rounded forms. Lammacrinite occur as elongated bands or laminae. Diessel (1992) suggested that lammacrinite may represent dried humic groundmass, which would have formed desmocollinite had the peat not been exposed to oxidising conditions caused by a fall in the groundwater table.

2.2.2.3 Liptinite group

Macerals of the liptinite group are derived from specific plants or parts of plants. Under transmitted light they show a high degree of translucency at low rank, whereas they have a low reflectance in incident white light. Under a short wave (blue or UV light) irradiation they give strong fluorescence. When compared to other maceral groups, the liptinites are characterised by a high aliphatic contents (mainly long-chain alkanes); and higher hydrogen to carbon (H/C) atomic ratios. Their carbon content increases with increasing coalification, and thus at some stage they lose their distinctive optical and chemical properties. In low volatile bituminous and higher rank coals they become indistinguishable from vitrinite.

Liptinites are commonly subdivided into primary and secondary liptinite (Table 2.1). Primary liptinites are part of coalified plants, whereas secondary liptinites are a group of products derived from thermal condensation and dissociation reactions. Both categories occur in only relatively small proportions and rarely exceed 20% in most of humic coals, but they can be very concentrated in sapropelic coals (i.e. coals formed by subaquatic sedimentation of floating vegetation (algae) and allochthonous organic matter).

Primary liptinites

Macerals of this subgroup are as listed in Table 2.1 and their description is as follows:

Sporinite is the protective skin (exine) of spores and pollen grains. It is made up of sporopollenin which according to Shaw (1970) consists of oxidative polymers of carotenoid esters. Taylor and Liu (1987) suggested that the resistance to decay of sporinite is due to the high degree of molecular cross-linking in sporopollenin. Sporinite occurs in high concentrations in cannel coals and it is the most common primary liptinite maceral in humic coals and other carbonaceous sedimentary rocks. Because of compaction caused by overburden pressure, sporinite appears as small flattened lenses in sections normal to bedding.

Size and shape are the main features by which sporinite is normally distinguished. Large spores ranging in (flattened) diameter between several hundred micrometers and several millimetres are referred to as macro- or megaspores (hence *macro-* or *megasporinite*). Macrospores are the mostly female spores of heterosporous plants such as lycopods (Kosanke, 1969). Their exines are ornamented by various protrusions and small semi-detached spheroidal appendages which represent abortive spores. In polished sections of low rank coals their dark surface has reddish internal reflections and commonly also granular inclusions. They are relatively rare in Carboniferous coals and with the reduced contribution of pteridophytes to younger sediments it is most likely that macrosporinite will be even less common in post-Carboniferous coals. Smaller spores with diameters measuring less than a few tens of micrometers are referred to as *microsporinite*. These spores are derived from homosporous plants. Male microspores of heterosporous plant constitute the main liptinite maceral in some Carboniferous humic coals (up to 15%) and in some cannel coals (up to 80%: Diessel, 1992). The sporinite content of Permian coals in Australia averages only 3%. As a consequence of the advent of seed plants (gymnosperms and angiosperms), younger coals and carbonaceous sedimentary rocks contain an increasing proportions of pollen grains. The term for both microspores and pollen is *miospores* (Guennel, 1952).

Stach (1964) classified sporinites according to the thickness of their exine. The spores with an exine thickness less <2μm are referred to as tenuispores and those with exines >2μm thick as crassispores. The latter group has been subdivided further into torispores and densospores (Balme, 1952). Torispores are distinguished by their thick protective exines which form the outer wall of a sporangium (spore capsule). Densospores were first described by Thiessen *et al.* (1931) as dumbbell spores because of their characteristic shape. They occur in the late Devonian to Permian coals of the North Hemisphere.

Studies of its chemistry have shown that sporinite is not a major source for normal hydrocarbons. Liptinite-rich samples with abundant sporinite and liptodetrinite gave low yields of normal hydrocarbons, and those obtained were of lower molecular weight i.e. non-

waxy (Powell *et al.*, 1991). However, Kruge *et al.* (1991) noted that the pyrolysate of sporinite had a greater predominance of *n*-alkanes over branched and cyclic alkanes as compared to that of the parent coal; and it also showed a lesser predominance of polyaromatics over *n*-alkyl benzenes. Mild oxidation products of sporinite were also found to be significantly different, in that sporinite was less polycondensed than the parent coal. Allan and Larter (1983) reported the dominance of aliphatic, alkylated phenolic and alkylated aromatic components in the pyrolysates of both vitrinite and sporinite macerals, although sporinite of any given rank was found to have greater amounts of aliphatic material.

Cutinite under the microscope appears as straight or wavy lines either translucent in transmitted or dark in incident light, usually with palisade ridges on one side. It is formed from cuticles, the waxy cover on the epidermis of leaves and young shoots. Goodarzi (1984) and Bartram *et al.* (1987) suggested that some chitinous cuticles may have been derived from the epidermis of arthropods. Cuticles consist of cutin, a glycerine ester of fatty acids (Stach *et al.*, 1982) from which hydroxy and epoxy fatty acids can be derived by depolymerisation (Kolattukudy, 1976).

Cutinite resists biodegradation better than its associated mesophyl tissue which decompose rapidly, and as a result it sometimes appears to be densely packed. However, cutinite is not as resistant to biological and chemical attack as sporinite (Taylor and Liu, 1987). Cuticles concentrate mainly in shallow ponds, soon after detachment from the parent plant, without much transportation (Diessel, 1992). Cutinite is of relatively low abundance in most coals and rarely exceeds 2 or 3%.

Based on morphological its appearance, Littike (1985, as cited by Diessel, 1992) distinguished three types of cutinite in sections cut normal to bedding:

i) very long and thick cuticles exceeding 10μm in width;
ii) thin cuticles with a width of less than 1μm and a length of 100μm.; and
iii) a pair of thin cuticles enclosing a liptinitic 'middle lamella', possibly a vascular strand.

The thickness of cutinite seems to be influenced by the growth and depositional environment of the parent plant. This is because the thickness of the cuticle which protects the inner tissue of plant from drying, is related to the availability of water. It has been observed that plants of wet environments have thin cuticles, whereas those growing in comparatively dry areas are characterised by thick cuticles (Strasburger, 1983: as cited by Diessel, 1992).

In Australian coals and carbonaceous shale of Carboniferous to Tertiary age, the yield of high molecular weight *n*-alkanes upon pyrolysis correlates strongly with the content of cutinite plus liptodetrinite (Powell *et al.*, 1991).

Resinite is derived from the resins of vascular plants. It displays a wider range of optical properties than other liptinite macerals because of its varied origin and post-depositional history. It consists of high molecular weight (mainly) aliphatic compounds including resin acid, resin esters and terpenes (Selvig, 1945). Cunningham *et al.* (1983) noted that fossil resinite (amber) had been formed by photolytic polymerisation, upon exudation from the host tree.

In coal, resinite occurs either *in situ* in resin ducts and the cells of xylem, cortex, mesophyl and seeds (White, 1914; Selvig, 1945) or in dispersed form as lumps, nodules and rodlets (Kosanke and Harrison, 1957; Lyons *et al.*, 1984). Some concentrate as residuum after its host tissue has decayed. Substantial portion of resinous matter contained in vascular plants become absorbed by humus colloids during advanced humification, thus causing low reflectance readings in detrovitrinite.

Based on the pyrolysate results, Mukhopadhyay and Gormly (1984) reported that resinite begins to generate hydrocarbons at a very early stage of maturation and may not have much hydrocarbon potential left beyond a vitrinite reflectance of 0.8%. They also reported that different types of resin produce different classes of compound. Some resins contain both terpenoid compounds and *n*-alkanes whilst others (brown-fluorescent resinites) contain mainly *n*-alkanes. Most resins generate sesquiterpenoid compounds which on thermal maturation give rise to aromatic hydrocarbons.

Other types of resinite are derived from resin based primarily on polymers of labdatriene diterpenoid carboxylic acids, especially various isomers of communic acid, ozic acid and zanzibaric acid. Modern resins based on these compounds are produced, often in significant amounts by various plant taxa, including the Araucariaceae, Leguminosae and Cupressaceae (Anderson *et al.*, 1992). Others are derived from resins based on polycadinene structures (van Aarsen *et al.*, 1991). Analogous modern resins, sold commercially as 'dammar', are produced in large quantities by trees belonging to the taxon Dipterocarpaceae.

Resinites are sometimes differentiated according to their fluorescence characteristics and colour. The different fluorescence characteristics probably reflect differences in the nature and abundance of occluded materials, especially triterpenoids. Depositional and post-depositional oxidation may also play a role in determining the fluorescence characteristics.

Suberinite is the preserved suberin impregnated cell walls of the cork tissue. It is only known from Tertiary and few Mesozoic coals. Suberinite commonly occur concentrated into layers from 0.02 to 0.5mm thick. Under the microscope it displays an outline of its bearing cell tissues (i.e. rectangular, brick-like, or irregularly polygonal four- to six-sided shapes).

In cases such as biodegradation where the corpocollinite cell fillings disappear, it appears in schlierren form like resinite. In reflected light it is dark to medium grey in colour; green to red internal reflections, particularly, in the low rank (i.e. brown coal stage) and is unrecognizable beyond a vitrinite reflectance of about 0.8% Rm. It shows variable fluorescence intensties, ranging from greenish yellow to brown, with increasing rank. At higher rank (from 0.6% Rm) the fluorescence intensity becomes very weak. Suberinite is similar to cutinite in composition but the suberin is less strongly polymerized than the cutin and thus is more easily attacked. Suberin is considered to be a polymer containing aromatics and polyesters (Kolattukudy, 1980).

Alginite is attributable to small unicellular algae. Fossil alginites have been encountered in various geological settings, from the Ordovician kukersite of Estonia which is formed from the remains of a marine planktonic algal or cyanobacterial species *Gloeocapsomorpha prisca* (Downie, 1967; Foster *et al.*, 1989, 1990), to lacustrine deposits of the colonial green alga *Botryococcus braunii* (Robert, 1988). It is classified into two major types, *telalginite* and *lamalginite*, according to their microscopic morphology. Telalginite comprises intact structured bodies having spheroidal to flat lenticular shapes. In contrast, lamalginite occurs as thin anastomosing lamellae formed by algal mats inter-layered with mineral grains (Hutton *et al.*, 1980; Cook *et al.*, 1981).

The presence of *Botryococcus*-related telalginite in sediments invariably signifies lacustrine conditions and it does so irrespective of whether the sample consists of predominantly alginite (as in torbanite) or whether it contains only a few isolated algal bodies. The coexistence of a high proportion of inertinite and a small amount of alginite would be indicative of the allochthonous nature of inertinite. The amounts of alginite in humic coals are commonly small. They occur as fragments which have low resistance to biodegradation and their compounds are readily converted into material with the superficial appearance of humic matter of low fluorescence. In high rank coals and carbonaceous sedimentary rocks, alginite is characterised by brilliant yellow fluorescence. Under incident white light it appears dark grey with well defined spheroidal bodies.

Botryococcus braunii has in its outer cell walls a resistant aliphatic biopolymer that is a possible source of *n*-alkanes (Berkaloff *et al.*, 1983). On pyrolysis this biopolymer yields *n*-alkanes up to C_{31} and therefore appears to be a major building block for *Botryococcus*-derived Type I kerogen. Furthermore, McKirdy *et al.* (1986) noted that different clonal races of *Botryococcus* algae synthesize unsaturated hydrocarbons (C_{23}-C_{33}, *n*-alkenes and C_{34} botryococcenes) which are potential sources of long-chain *n*-alkanes and botryococcane found in certain freshwater sediments.

Secondary liptinites

These are liptinites formed during coalification as by-products of chemical dissociation of primary liptinites. They lack any distinctive morphology and some of them are characterised by intense fluorescence under blue/UV light. At the time of their formation they occupy mostly cell lumens and small fractures. This maceral subgroup includes fluorinite, bituminite and exsudatinite.

Fluorinite commonly occurs in leaves (phyllovitrinite surrounded by cutinite), and therefore its primary generation from essential oils or other liptinitic plant material as a decompositional product of lipid secretions is very probable (Teichmüller, 1974b; Robert, 1979). Under incident white light, it is dark with a low reflectance, whereas upon blue/UV light excitation it displays intense green to yellow fluorescence. It is normally observed only in low rank coals. Possibly because of its volatility, fluorinite disappears as early as the high volatile bituminous stage of coalification.

Bituminite is a decomposition product of algae, zooplankton and bacterial lipids. It commonly occurs as a groundmass for other macerals in sapropelic coals and other liptinite-rich coal types or as finely dispersed, streaky form ('schlieren': Teichmüller, 1974a,b) in bituminous coals and shales. Like exsudatinite, bituminite is normally recognized by lack of definite shape but differentiated from the latter by its autochthonous occurrence as 'schlieren' in bedding. Fine-grained micrinite in the high-volatile bituminous coal is regarded as a residual product of bituminite after petroleum-like substances are expelled during coalification (Spackman *et al.*, 1976). It has a higher reflectivity in high-volatile bituminous coal than does the associated sporinite and under UV light, it shows a weak initial fluorescence which increases strongly during irradiation.

Exsudatinite is a liquid derivative of liptinite produced by 'sweating' which first happens at the boundary between diagenesis and catagenesis during coalification (Teichmüller, 1974b). Thereafter it migrates into cleats and fissures. Exsudatinites are most frequently observed in sub-bituminous and high-volatile bituminous coals (Shibaoka, 1978). Their reflectivities and fluorescence properties vary strongly. However, strong yellow to orange fluorescence upon blue light excitation is very common.

2.2.3 Vitrinite reflectance

Reflectance is a measure of the ability of a macerals to reflect light from its polished surface. The variation of reflectance in coal macerals results from condensation reactions which systematically take place in the molecular structure during physico-chemical coalification. This process involves the alteration of small aromatic clusters (micelles) that are initially separated from each other by large volumes of intermicellar aliphatic and other non-aromatic material in which most of the hydrogen and oxygen are concentrated. As coalification

proceeds, fluids and gases are released by diffusion from these non-aromatic moeities. As the proportion of non-aromatic compounds decreases, there is an increase of aromaticity (f_a= aromatic C/total C) and consequently also an increase in reflectance. Aromaticity increases from approximately 0.56 in brown coal to 0.78 in medium-volatile bituminous coal and 0.95 in anthracite (Iyengar and Lahir, 1959).

Conventionally, vitrinite (particularly telocollinite) is used for the determination of coal rank by micro-reflectance; hence the term 'vitrinite reflectance'. Factors favouring the use of vitrinite for reflectance measurements include its ubiquity, homogeneity and ease with which a well-polished surface can be obtained. As condensation of the aromatic complexes is associated with an increasingly parallel orientation of their planar layers, the rise in reflectance is accompanied by the development of optical anisotropy. Therefore, reflectance measurements can be carried out in either polarised light or non-polarised light. In non-polarised light, R_m is the mean maximum reflectance (measured in oil immersion) and R_o is the mean random reflectance. The relationship between maximum and random reflectance can be expressed as $\% R_m = 1.106 R_o - 0.024$ (Neavel *et al.*, 1981). Diessel and McHugh (1986) suggested an alternative relationship for Australian coals: $\% R_m = 1.07 R_o - 0.01$.

2.3 Accumulation of organic matter and depositional environment

The current theory of the biogenic origin of oil suggests that plant and animal remains are degraded by micro-organisms, essentially leaving the more resistant biolipids as precursors for petroleum. The remains of the degrading microbes also, contribute significantly to this source material (Lijmbach, 1975).

The precursor organic matter accumulates in aquatic environments. There is an abundance of life in the upper layers of the water column where photosynthetic algae and bacteria fix CO_2 into organic matter. In the oxic zone, which in some environments extends down to the sediment-water interface, organic detritus including the remains of algae, bacteria and terrestrial organic matter is oxidised into CO_2 and H_2O by aerobic bacteria. This situation is typical of high-energy environments. Where the consumption of dissolved oxygen by aerobes exceeds the rate at which it is replenished (e.g. by current or wave action), anoxic conditions prevail immediately below the oxic zone. In the anoxic zone part of the remaining organic matter (mostly metabolic intermediates of aerobic degradation) is converted into CO_2 and H_2O by anaerobic bacteria such as nitrate-reducing, sulphate-reducing and methane-fermenting bacteria. In this way more of the organic matter is recycled. The microbially resistant organic detritus, such as pollen, spores, waxes and resins escape degradation.

In stagnant reducing environments (e.g. Black Sea, Lake Tanganyika) the boundary between the oxic and anoxic zones is higher up in the water column (Demaison and Moore, 1980). It has been observed that usually only small amounts of organic matter are finally deposited.

However, in conditions where photosynthetic activity is abnormally high because of enhanced nutrient supply considerable amounts of organic matter can accumulate. This occurs in areas of coastal up-welling. In such cases the oxic zone of the water-column is drastically attenuated as a result of heterotrophic bacteria consuming much of the dissolved oxygen. Consequently, anoxic conditions are established in the bottom waters where degradation of the sinking organic matter by anaerobic bacteria is slow and incomplete (Foree and McCarty, 1970; Otsuki and Hanya, 1972). In this way the original organic matter is reworked and converted into a biomass consisting of bacterial bodies mixed with the microbially resistant parts of the planktonic bodies and terrestrial organic matter supplied from elsewhere. Organic-rich sediments (3-20% TOC) can be deposited under these conditions.

2.4 Hydrocarbon source rocks

Source rocks are defined as sedimentary rocks which contain sufficient organic matter (kerogen) of suitable chemical composition to generate hydrocarbons. They are normally graded as either potential or effective sources according to their hydrocarbon generation status. An effective source rock is one which has generated and expelled oil or gas, whereas potential source rocks are those which have not yet generated significant amounts of hydrocarbon because of thermal immaturity.

The first step in identifying a hydrocarbon source rock is to determine its content of total organic carbon (TOC) and extractable organic matter (EOM) or bitumen. The second step is to determine the type of kerogen and the composition of the solvent-extractable hydrocarbons. Finally, the evolutionary stage or maturation level of the kerogen is determined.

2.4.1 Amount of organic matter

The lower limit of organic carbon in petroleum source rocks has been established to be 0.5% TOC (Ronov, 1958). However, some laboratories prefer to use 1% TOC as the cutoff value for detrital source rocks. A lower limit of 0.3% TOC for carbonate source rocks, has been proposed by Gehman (1962). These minimum values should be considered only as necessary threshold values, rather than as positive indications of source rock potential. Also, as a source criterion these values do not apply to rocks of very advanced maturity (metagenetic stage), where 0.3 or 0.5% TOC may merely indicate a residual amount of organic matter that initially was more than twice as high (Tissot and Welte, 1984). The values of 0.05 wt % (500 ppm) EOM and 300 ppm hydrocarbons are normally taken as lower limits for petroleum source rocks.

2.4.2 Kerogen types

After burial sedimented organic matter polymerises and condenses into a macromolecular material called kerogen (Forsman and Hunt, 1958). Kerogen is described as cyclic

polycondensed nuclei with alkyl side chains linked by heteroatoms such as S and O (Tissot *et al.*, 1974a); or as an organic constituent of sedimentary rocks that is soluble in neither aqueous alkaline solvents nor the common organic solvents (Tissot and Welte, 1984). It is commonly classified visually on the basis of its maceral group composition or chemically on the basis of its carbon (C), hydrogen (H) and oxygen (O) elemental composition. It is isolated from sediments by hydrofluoric and hydrochloric acid attack to remove the mineral matrix, or by density separation using heavy liquids. The amount and type of hydrocarbon products are determined by its biological precursors and the degree of preservation (Durand, 1980).

When the elemental ratios (H/C and O/C) are cross plotted on a van Krevelen diagram (Fig. 2.3a) they provide an immediate reference to the three main types of kerogen (viz. kerogen Type I, II and III: Fig. 2.3b). An approximate equivalence of various terms used in kerogen description are as summarised in Table 2.2.

Table 2.2. Various terms for kerogen description (Tissot and Welte, 1984).

Provenance	Terminologies			
Aquatic	Algal	Liptinite	Amorphous	Type I
	Amorphous			
	Herbaceous (fibrous)	Vitrinite	Humic	Type II
	Woody (plant structure)			Type III
Sub-aerial (terrestrial)	Coaly (angular to sub-angular fragments)	Inertinite		Residual

Due to the mixed nature of sedimentary organic matter, the Type I, II, and III pathways on the HI vs. OI plot are only generalised. Thermal maturation and early diagenetic oxidation of the organic matter also influence the position of sample on the HI vs. OI plot (Durand and Monin, 1980; Demaison and Bourgeois, 1984). For instance, coals of low maturity (R_o <0.6%) generate large amounts of carbon dioxide during pyrolysis; whereas at higher levels of maturity, proportionally more pyrolytic oxygen is released as carbon monoxide, which is not analysed by the Rock Eval pyrolyser and thus may give erroneously low OI values.

Table 2.3. Parameters relating to Rock-Eval pyrolysis (Espitalié et al., 1977, as cited by Murchison, 1987)

Parameter	Measurement
S_1	Quantity of hydrocarbons and related materials desorbed from rock sample during heating at 250°C for 5 min in helium – approximately equivalent to material extracted in solvent procedures
S_2	Quantity of hydrocarbons and related material produced during pyrolysis of kerogen and in volatile bitumens over the temperature range 250-550°C at 250°C min^{-1} in helium – approximately equivalent to thermal degradation of kerogen
S_3	Quantity of carbon dioxide produced during pyrolysis of sediment over the range 250-390°C
T_{max}	Temperature of maximum kerogen decomposition rate (maximum peak S_2 evolution) – relatable to the maturity of the sample
$S_1 + S_2$	Genetic potential
$S_1/(S_1 + S_2)$	Production index (PI)
S_2/TOC	Hydrogen index (HI)
S_3/TOC	Oxygen index (OI)

2.4.3 Maturation of organic matter

Maturation is a process of chemical change in sedimentary organic matter caused by the action of increasing temperature and pressure over geological time. The outcome of these changes is the production of oil and gas. The yield and composition of petroleum hydrocarbons depends on the type of organic matter. The extent of maturation is measured either indirectly from the resulting changes in fluorescence colour and reflectivity of the macerals; or directly by changes in the chemistry of the kerogen and associated soluble organic matter (bitumen). Maturation is generally subdivided into the following stages: immature, early mature, peak mature, late mature and post mature (Heroux *et al.*, 1979).

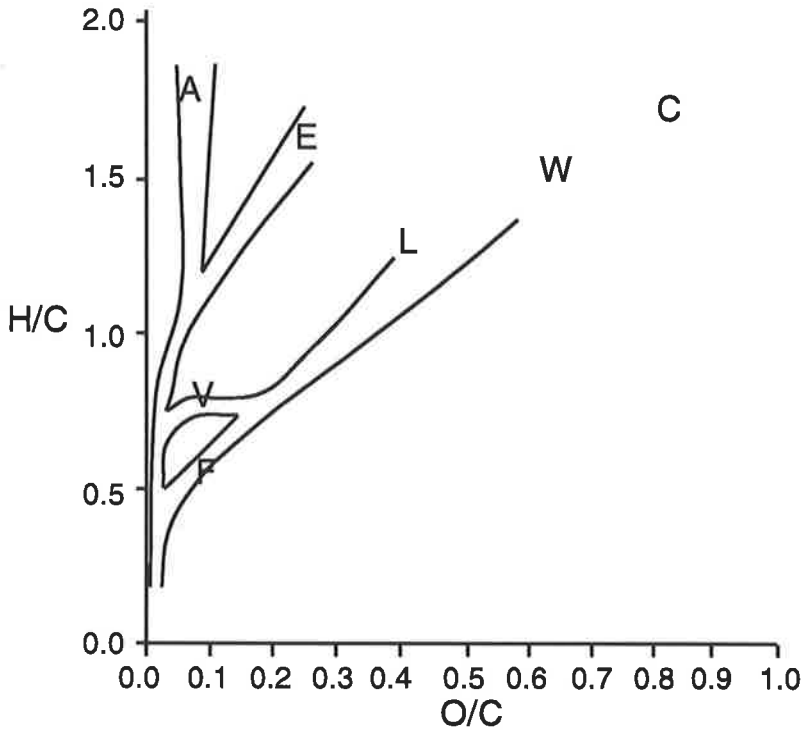


Figure 2.3a The atomic H/C versus O/C diagram of van Krevelen (1961) illustrating the convergence of maceral composition during the physicochemical stage of coalification.

(A= algal matter; C= cellulose; E= spore exines and other liptinite; F= inertinite; L= lignin; V= vitrinite; W= wood)

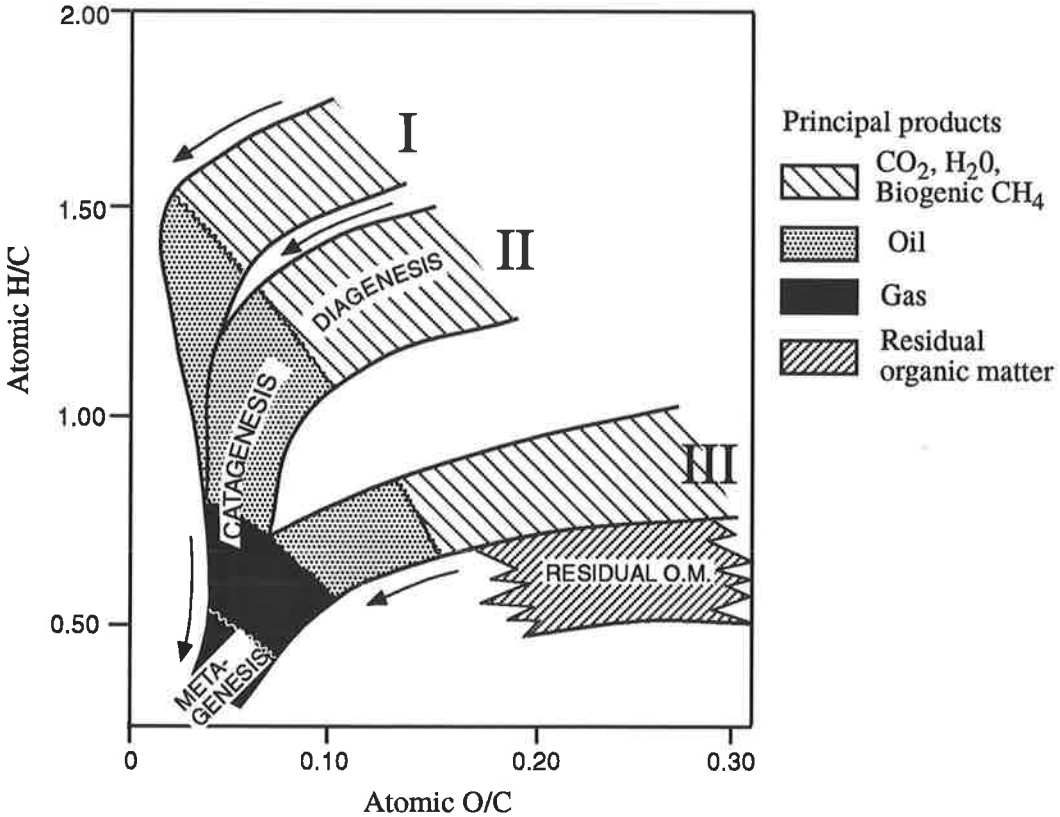


Figure 2.3b Generalized kerogen evolution and its principal products presented on van Krevelen's diagram (after Tissot and Welte, 1984).

2.4.3.1 *Maturation level based on vitrinite reflectance*

From the correlation of vitrinite reflectance with other maturation parameters of source rocks, and the occurrence of oil and gas fields, Tissot and Welte (1984) distinguished the following stages for organic matter maturation:

a) Diagenesis: characterised by vitrinite reflectance R_O <0.5 to 0.7%; immature source rock

b) Catagenesis: 0.5 to 0.7% < R_O < ca 1.3%; main zone of oil generation (oil window)

c) Catagenesis: ca 1.3% < R_O <2%; zone of wet gas and condensate generation

d) Metagenesis: R_O > 2% ; methane remains as the only hydrocarbon (dry gas zone).

The reflectance intervals shown above for the oil and gas zones are only approximate. There has been much discussion of this topic (see e.g. Dow, 1977; Heroux *et al.*, 1979; Alpern, 1980; Robert, 1980; Teichmüller, 1982).

2.4.3.2 *Maturation level based on pyrolysis parameters*

The Rock-Eval pyrolysis parameters; S_1/S_1+S_2 and T_{max} (Table 2.3), are sensitive to maturation trends (Peters, 1986). The continuous increase of S_1/S_1+S_2 with depth has regularly been observed in many wells. Therefore, in the absence of hydrocarbon migrating into the source rock, this ratio is considered to be an indicator of kerogen transformation or as commonly known as production index (PI: Tissot and Welte, 1984). In immature samples PI< 0.1, and in mature samples is between 0.1 and 0.4.

T_{max} is the temperature in °C at which the maximum kerogen pyrolysate (S_2) containing hydrocarbons and other compounds is produced. It also increases progressively with increasing depth thus qualifying as a maturation parameter. Unlike the production index, it is not affected by migration factors and a good correlation between these two parameters is quite common. It also correlate well with other maturation parameters such as vitrinite reflectance for Type III kerogen and humic coals. It is particularly valuable in the case of marine or lacustrine kerogen (Type I and II) where vitrinite is often scarce or absent.

Approximate T_{max} boundaries for oil generation are < 435°C (immature), 435 to 460°C (mature) and >460°C (postmature). However, the type of organic matter seems to influence T_{max} values during diagenesis and early catagenesis when values are generally higher in kerogen Types I and II (Tissot *et al.*, 1978). However some exceptions have been noted, where Type II kerogen do not always show higher T_{max} values than Type III kerogen of the same rank. T_{max} values are almost equivalent for the different kerogen types in the peak zone of oil generation and later in the gas zone (Peters, 1986).

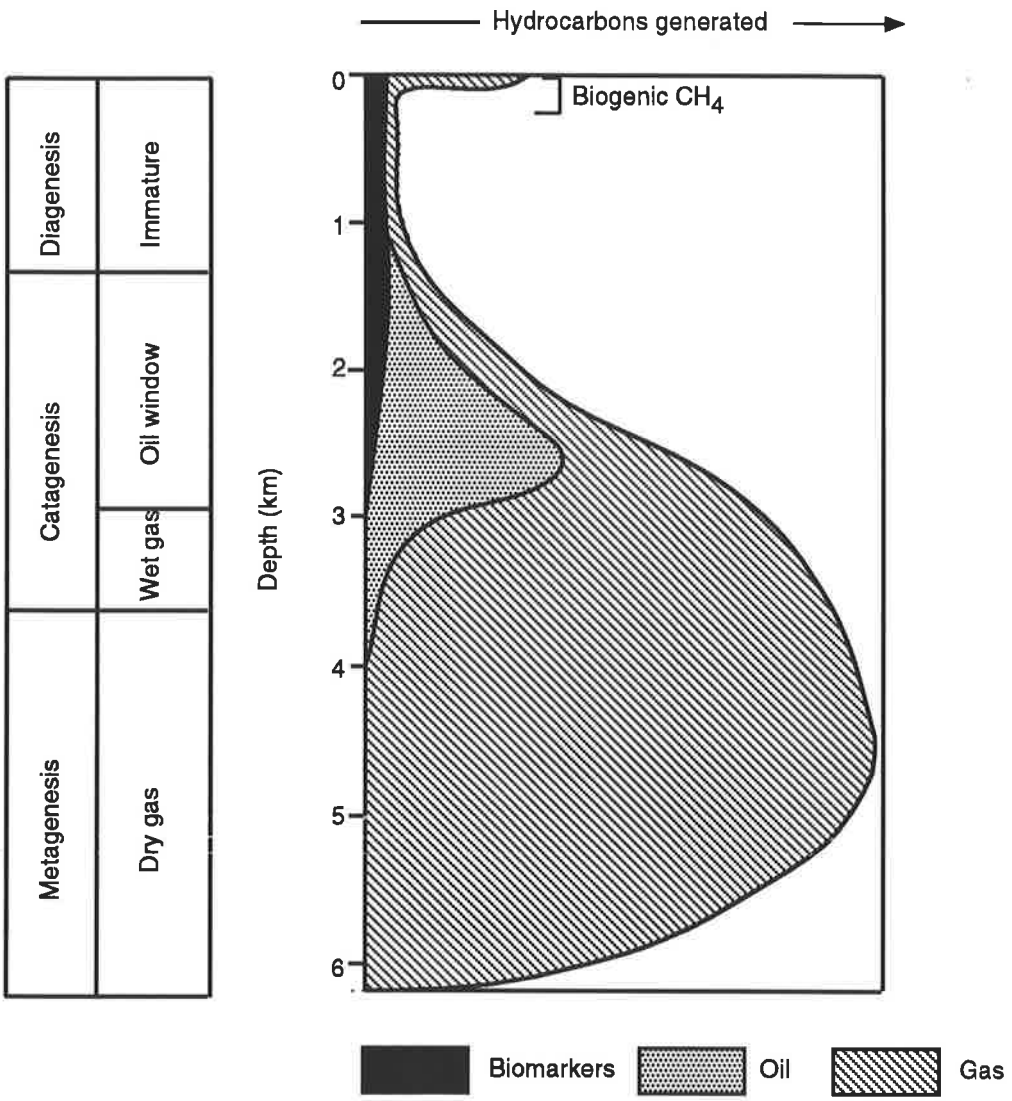


Figure 2.4 General scheme of hydrocarbon generation as a function of burial of the source rock (after Tissot *et al.*, 1974)

Recycled organic matter (OM) and altered samples appear to have elevated T_{max} values. If the total S_2 from the recycled OM greatly exceeds that from any accompanying primary OM, the T_{max} value can be much higher (40°C or more) than expected based on the actual maturity of the sediments. Normally, the T_{max} difference between recycled OM and mature or postmature OM is generally less than 5°C. Oxidised, highly mature, or Type IV kerogens usually show high T_{max} values or lack an S_2 peak (e.g. in siltstones and sandstones accessible to oxygenated ground water). This is because oxidation tends to remove hydrogen and add oxygen to the kerogen, thus resulting in depletion of S_1 and S_2 whilst enriching S_3 values. This S_3 enrichment results in erroneous OI signatures which give rise to ambiguous kerogen maturation pathways on the HI vs. OI cross plot. Therefore, in order to avoid such problems, a HI vs. T_{max} cross plot is used to differentiate maturation pathways rather than the conventional HI vs. OI plot (Espitalié et al., 1984).

2.4.3.3 *Chemical indicators of maturity based on bitumen*

The abundance and chemical composition of petroleum compounds (hydrocarbons, resins and asphaltenes) present is source rocks depends on the nature of the organic matter and its degree of thermal maturation. The abundance of bitumen may be expressed as bitumen ratio (EOM/TOC or HC+R+A/TOC), which is the ratio of the amount of soluble organic matter or bitumen extract in a source rock related to the total organic carbon. Likewise, the hydrocarbon ratio is the ratio of the sum of the saturate and aromatic fractions to the total organic carbon (HC/TOC). Both ratios are expressed as weight per cent (%) or mg/g TOC. The general trend of variation of these ratios with increasing thermal evolution have been reported from various case studies. Bitumen ratios are in the range 20-200 mg/g TOC and hydrocarbon ratios are in the range 10-150 mg/g TOC (Tissot and Welte, 1984).

Changes in kerogen type or geothermal gradient within the sequence may have an effect on the distribution and amount of bitumen, thus making it difficult to delineate regular trends of maturation and hydrocarbon generation. Short-range migration and minute accumulations within the source rock may also alter the amount of bitumen.

Further assessment of the maturity of the organic matter in source rocks may be carried out by using the detailed composition, rather than the abundance, of their hydrocarbons. These hydrocarbon compositional parameters (e.g biomarker isomer ratios) and their relation to maturation effects are discussed in later sections of this chapter.

2.4.4 Hydrocarbon generation

Several studies have shown that commercial oil accumulations are produced by thermal alteration of kerogen during burial of source rocks (Fig. 2.4). In recent sediments the hydrocarbon content is very low. Apart from bacterially formed methane (marsh gas) these hydrocarbons originate directly from the (micro) organisms incorporated in sediment.

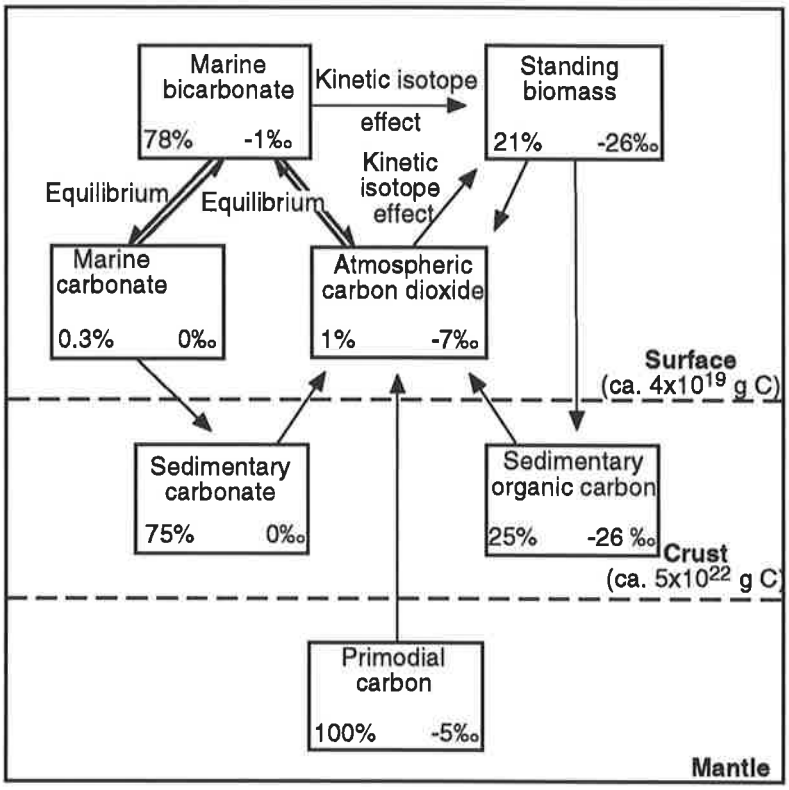


Figure 2.5 Approximate relative sizes of carbon reservoirs together with average $\delta\ ^{13}C$ values within the earth's surface, crust and mantle (Killops and Killops, 1993)

At shallow burial depths, decarboxylation and dehydration reactions remove CO_2 and chemically bound H_2O from the protokerogen. This stage of alteration is referred to as 'diagenesis' (Tissot and Welte, 1984). It is followed by a 'catagenesis' stage where the kerogen starts to generate new hydrocarbons, first gradually, then more rapidly, by thermal cracking. At this stage the main generation of petroleum occurs.

As the depth of burial of the source rock increases further, the 'metagenesis' stage is reached. Here cracking becomes so severe that the kerogen and any retained oils is broken down into light hydrocarbons and eventually into methane. At this stage more gas is generated and any unsaturated hydrocarbons formed become saturated by hydrogen derived from disproportionation reactions which lead to polyaromatic compounds and ultimately graphite.

Depending on the type of organic matter, some source rocks will generate oil and gas while others will generate mainly gas. A high kerogen H/C ratio or source rock HI is indicative of Type I kerogen, which normally produces oil at appropriate maturity. Type II kerogen produces mainly oil and some gas. Humic material with a low H/C ratio (i.e. Type III kerogen) is a source for gas and light oil or condensates.

2.5 Stable carbon isotope signature of rock extracts and crude oils

The ability of carbon to form chains and rings enables it to produce an immense variety of compounds, including hydrocarbons and their derivatives. It is therefore necessary to understand its mode of occurrence, and how it is first incorporated in living organisms, then into sedimentary organic matter and eventually into crude oils. One way of doing this is to examine its stable isotopic composition.

2.5.1 Occurrence and abundance of carbon

Carbon is a mixture of two stable isotopes ^{12}C and ^{13}C, whereas ^{14}C is a short lived radio-nuclide. The relative abundance of ^{12}C and ^{13}C in the earth are 98.894% and 1.106%, respectively. It is the twelfth most abundant element in the earth's crust and accounts for about 0.08% of the lithosphere, hydrosphere and atmosphere. The global distribution and abundance of various forms of carbon is summarised on Figure 2.5.

2.5.2 Living organisms and the carbon cycle

Photosynthesis is one of the primary mechanism by which carbon in the form of atmospheric carbon dioxide (CO_2) is taken up by growing plants. This process is normally represented by the following equation:

$$6CO_2 + 6H_2O \xrightarrow{\text{Sunlight/chlorophyll}} C_6H_{12}O_6 + 6O_2$$

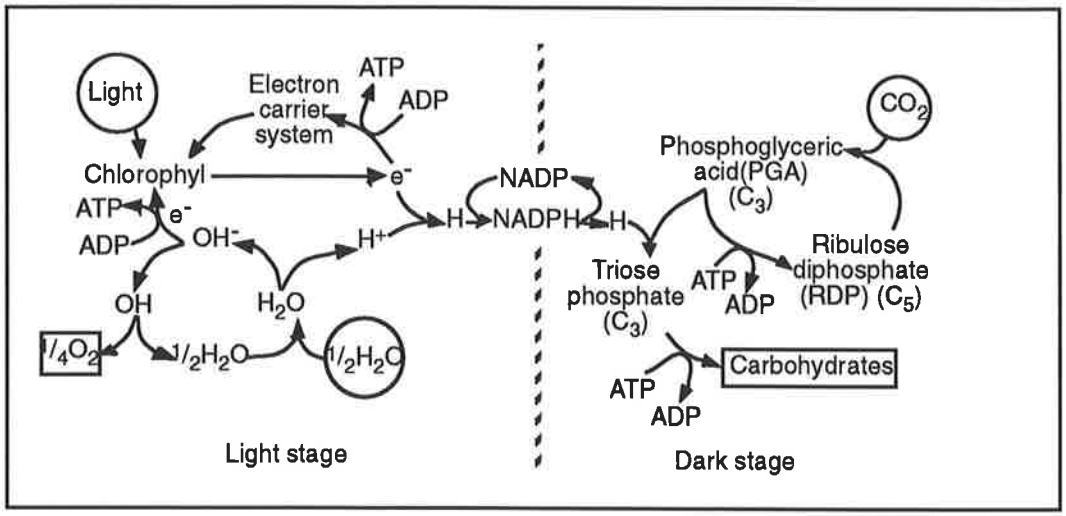


Figure 2.6a Summary of the chemical processes involved in oxygenic photosynthesis. Net inputs are shown in circles, products in rectangles. (ADP/ATP = adenosine di-/triphosphate: NADP/NADPH = nicotinamide adenine dinucleotide phosphate and its reduced form, respectively; Killops and Killops, 1993)

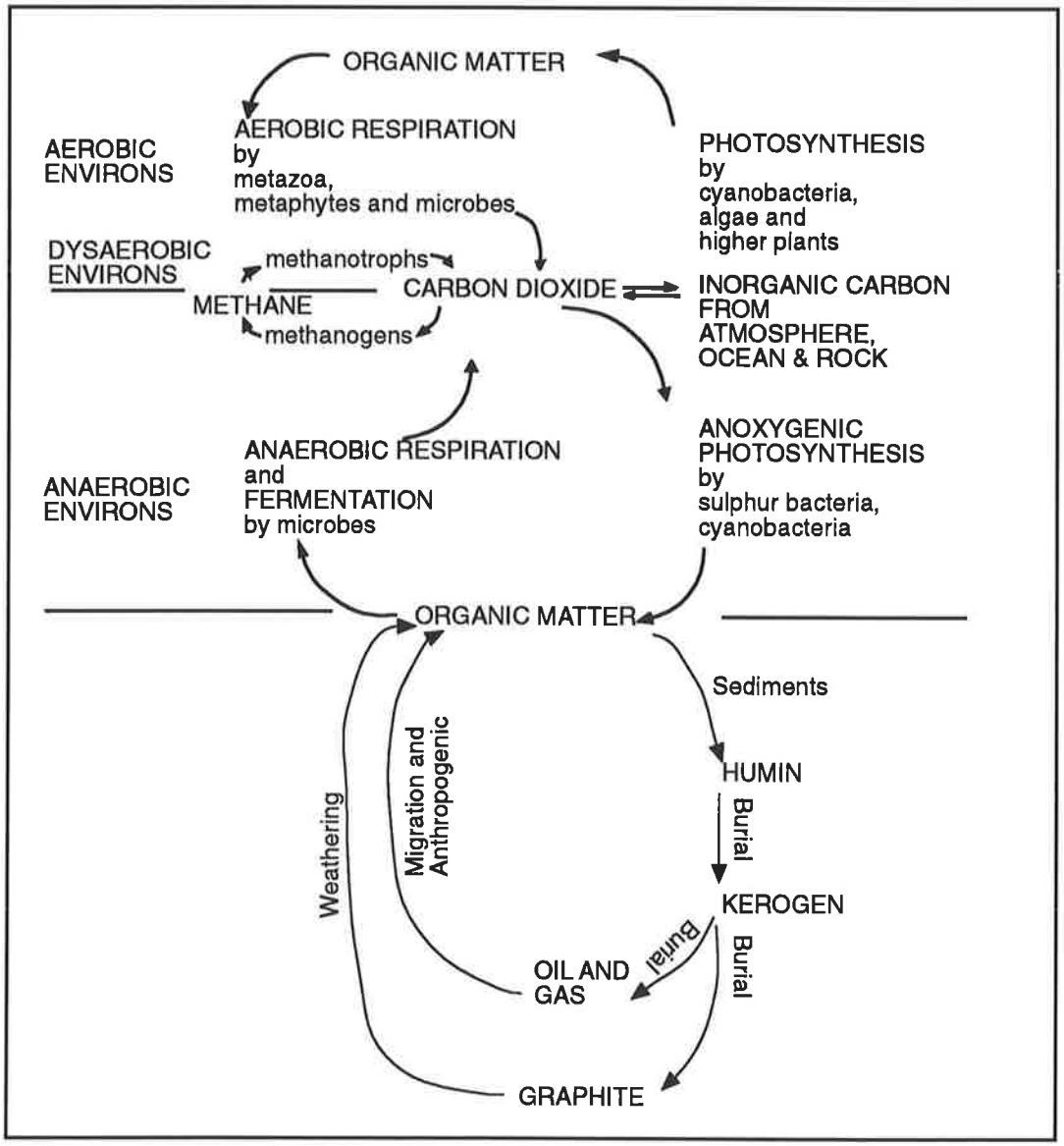


Figure 2.6b The carbon cycle and the interactions between its major participants (modified after Summons, 1993)

The photosynthetic process has two stages, one of which operates in the light and the other in the dark (Fig. 2.6a). In the first stage, light energy emitted by the sun is adsorbed by a green pigment, chlorophyll. This results in the formation of carbohydrate units by transfer of hydrogen atoms from water to carbon dioxide molecules and the liberation of oxygen from water molecules. Carbohydrates are used in the biosynthesis of other organic compounds and to provide an energy store for the performance of normal cell functions.

During the dark stage, various carbohydrates are synthesised through the assimilatory pathway known as the 'Calvin cycle'. Under this pathway carbon dioxide is first combined with a C_5 compound ribulose diphosphate (RDP), which then splits into two molecules of the C_3 compound phosphoglyceric acid (PGA). The PGA is used to synthesise further RDP while some of it is reduced by NADPH (nicotinamide adenine dinucleotide phosphate-H), utilising the energy supplied by the ATP/ADP system, to generate triose phosphate which consequently is converted to the glucose phosphate which is the source of various carbohydrates. All autotrophic carbon fixation, photosynthetic and chemosynthetic involve this cycle.

Most plants and cyanobacteria (blue-green algae) fix carbon using the Calvin or C_3 pathway. Those which use the Calvin cycle alone are termed C_3- plants to designate the involvement of PGA which contains three carbon atoms. Two additional biochemical pathways -the C_4 or Hatch-Slack pathway and the CAM (crassulacean acid metabolism) which fix CO_2 at night are used by smaller groups of plants. Under these processes the carbon dioxide fixed during the night is released again within the plant tissue during the day for incorporation via the Calvin cycle. This mechanism reduces photorespiration by closing stomatal pores during the day while maintaining essential supplies of CO_2. Two plant groups are named after their additional mechanisms, C_4-plants (tropical grasses, desert plants and salt marsh plants) and CAM-plants (succulents). Some photosynthetic anaerobic bacteria use H_2S as a source of hydrogen instead of water, and so liberate sulphur instead of oxygen. Other species, such as the purple non-sulphur bacteria (*Rhodospirillum*), use simple organic compounds as a source of hydrogen.

Chemosynthesis is another mechanism of incorporating carbon into organisms whereby energy stored in chemicals, mainly the reduced form of simple inorganic compounds, is utilised. This process is performed by some types of bacteria, most of which are obligate aerobes. These bacteria use an enzyme, dehydrogenase, to liberate energy and reducing power from chemical compounds such as H_2S. The necessary compounds for chemosynthesis are found in highest concentration in anoxic waters beneath areas of high productivity.

To summarise, carbon in the form of carbon dioxide, is continuosly cycled through plants, animals and sediments by the processes of respiration, photosynthesis, growth, decay and preservation in sediments. The organic carbon trapped in sedimentary rocks is involved in the generation of oil and gas, and some of it is liberated by weathering of outcropping rocks. Eventually, this carbon is returned, via the biosphere and the hydrosphere, back to the atmosphere (Fig. 2.6b).

2.5.3 Photosynthesis and carbon isotope fractionation

The ratio of ^{13}C to ^{12}C is measured by mass spectrometry after converting the carbon to carbon dioxide. The carbon isotopic composition of organic matter in a sample is normally given by δ values expressed as:

$$\delta^{13}C = \left(\frac{^{13}C/_{12}C \text{ in sample}}{^{13}C/_{12}C \text{ in standard}} - 1 \right) \times 1000$$

The units are per mil (‰) and the standard is usually PDB i.e. a belemnite from the Cretaceous Peedee Formation, USA (Craig, 1953). For PDB ^{12}C /^{13}C = 88.99 and its $\delta^{13}C$ value = 0‰ by definition. Therefore negative values for a sample indicate depletion in the heavier isotope compared with PDB.

The approximate relative sizes of carbon reservoirs (surface, crust and mantle) and their exchange pathways within each of the three main compartments is as illustrated in Figure 2.5. The isotopic signature for the earth as a whole has been assumed to be that inherited from the parent solar nebula as represented by the isotopic signature of the mantle ($\delta^{13}C$ ~ -5‰: Garrels *et al.*, 1975, Deines, 1980; Garrels and Lerman, 1984). All autotrophic processes favour incorporation of the lighter isotopes of carbon into live organic tissue. Consequently the isotopic signature of sedimentary organic matter is $\delta^{13}C$ ~ -26‰.

The isotopic lightness of biogenic substances results from isotope fractionation processes in the main assimilatory pathways and, to a lesser extent, in ensuing metabolic reactions. For example, the enzyme ribulose 1,5-bisphosphate carboxylase (RuBP carboxylase) is responsible for the primary fractionation of carbon isotopes in green plants, algae and most autotrophic bacteria (Fogel *et al.*, 1988; O'Leary, 1988). In most cases, the isotopic fractionation between photosynthetic carbon (δ ^{13}C ~ -27‰) and atmospheric or dissolved CO_2 (δ ^{13}C ~ -7‰) (Stuiver, 1978) is on average 20‰, a value 10‰ greater than that for the enzymatic fractionation alone (Fogel and Cifuentes, 1993).

Several models of isotope fractionation have been developed (Farquhar, 1980; Farquhar *et al.*, 1982; Guy *et al.*, 1986). These models assume that the amount of carbon isotope fractionation expressed in the tissues of plants is dependent on the ratio of the carbon dioxide

concentration inside the plant to that in the external environment. Therefore, when diffusion of CO_2 into the plant is a limiting process, the isotope fractionation of the plant decreases. Typically, the $\delta^{13}C$ values of the most plants (-20 to -30 ‰) show that both diffusion and carboxylation are limiting processes.

Plants that utilise the C_4 pathway for photosynthesis use an alternate enzyme, phosphoenol pyruvate carboxylase (PEP carboxylase), in the first steps of carbon dioxide fixation. The isotope effect associated with this enzyme (-2.2‰) is much smaller than that for RuBP carboxylase (O'Leary, 1988), such that C_4-plants have more positive isotopic compositions in the range -8 to -18‰ (Smith and Epstein, 1971; O'Leary, 1981; Deleens *et al.*, 1983). Figure 2.7a illustrates how the CO_2 fixed by PEP carboxylase is carried as part of a C_4 acid into the internal bundle sheath cells of vascular plants. Because the environment in the bundle sheath cell is an almost closed system, most of the CO_2 entering the cell is fixed back into organic matter. Thus little isotope fractionation by RuBP-carboxylase is expressed in the whole plant tissue (Farquhar, 1983; Fogel and Cifuentes, 1993).

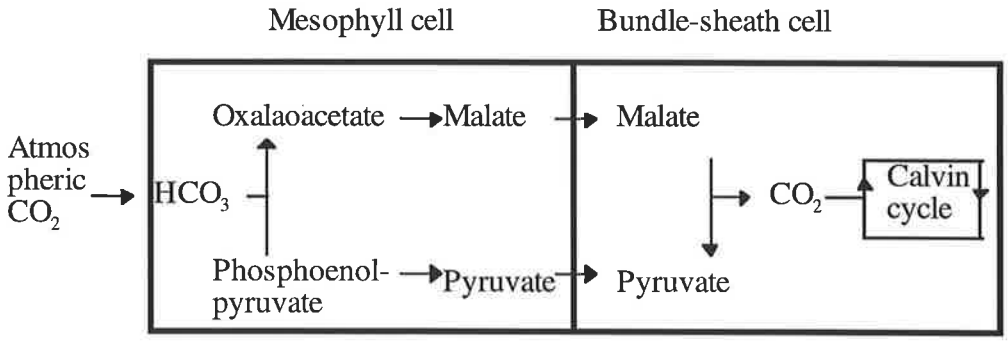


Figure 2.7a. Simplified diagram of CO_2 fixation in C_4 photosynthesis (Fogel and Cifuentes, 1993)

In aquatic environments the diffusion of CO_2 into the plant cell is often the limiting step (O'Leary, 1981; Raven *et al.*, 1987). This is due to the fact that CO_2 diffuses more slowly in water than in air. Consequently, most aquatic plants have some membrane-bound mechanism that actively transports dissolved inorganic carbon (DIC) into the photosynthesising cells (Lucas, 1983,). Studies have shown that when DIC (mostly CO_2 and HCO_3^-) concentration in aquatic environments is low the plants will turn on an HCO_3^- or CO_2 pump which will accumulate a higher concentration of DIC in the cell for photosynthesis (Fig. 2.7b). The exact mechanism of transport differs from organism to organism, but the final effect is the same. Despite living in CO_2-limiting environments, aquatic plants are able to carry on high rates of photosynthesis.

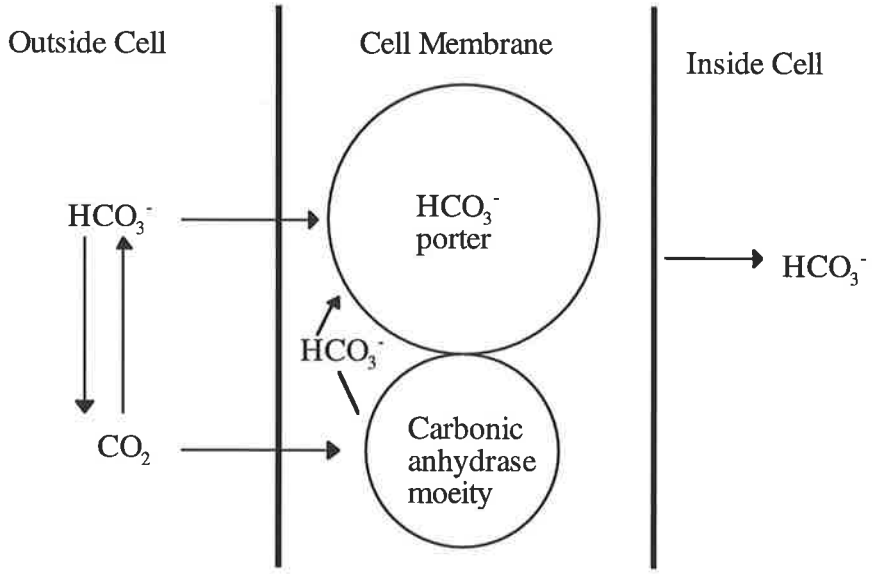


Figure 2.7b. Model for dissolved inorganic carbon transport (Fogel and Cifuentes, 1993)

Sharkey and Berry (1985) reported on the effects of a DIC-concentrating mechanism on the isotope composition of algae. When cells are growing in a high concentration of CO_2 (5%) the carbon isotope fractionations between cells and DIC are large and similar to those seen in terrestrial higher plants. In a low concentration of CO_2 (0.03%), however, the concentrating mechanism is activated whereby active transport of DIC into the cell results in large internal pool of substrate available for photosynthesis. Much of the accumulated CO_2 does not leave the cell before it is fixed by RuBP carboxylase. The model describing this fractionation is a modification of that developed for C_4 photosynthesis. Autotrophic organisms can be grouped according to their degree of isotopic fractionation, largely determined by the primary carboxylation step, as summarised by the Table 2.4 below.

Table 2.4: Isotopic composition of major autotrophs and methanogens (Schidlowski, 1988)

Organism	$\delta^{13}C$ ‰
Higher Plants	
C_3	-23 to -34
C_4	-6 to -23
CAM	-11 to -33
Algae	-8 to -35
Cyanobacteria	-3 to -27
Photosynthetic bacteria	
Green	-9 to -21
Purple	-29 to -36
Red	-19 to -28
Methanogenic bacteria	-6 to -41

2.5.3.1 Carbon isotopic fractionation in biosynthetic processes

Previous studies on biosynthesis have discovered that ^{13}C is not distributed uniformly among lipids and amino acids of photosynthetic and heterotrophic organisms (Abelson and Hoering, 1961). Lipids from the organisms studied were depleted in ^{13}C relative to total cellular carbon and relative to the glucose on which the organisms were grown, suggesting that isotope fractionation accompanying biosynthesis of lipids was a general phenomenon. In photosynthetic organisms, the carboxyl carbons of aspartate and glutamate were found to be highly ^{13}C-enriched compared to most of the other carbons of the amino acids. This difference was not observed in heterotrophically grown organisms (Abelson and Hoering, 1961; Monson and Hayes, 1982).

Different plant constituents such as carbohydrates, lignin, proteins and lipids have different carbon isotope compositions within the same plant (Deines, 1980; Benner *et al.*, 1987). Lipids are reported to be depleted in ^{13}C relative to carbohydrates (Park and Epstein, 1961). Depletion of total plant lipid relative to total leaf tissue of terrestrial C_3 plants averages 5 ± 2‰ (Deines, 1980). *n*-Alkanes are likely to provide an adequate guide to the $\delta^{13}C$ composition of homologous families of straight-chain lipids as they are closely related biosynthetically.

It is known that different species of plants synthesise differing proportions of the various *n*-alkane homologues (Harwood and Russell, 1984) and that such differences might be preserved in the sedimentary record (Cranwell *et al.*, 1987; Poynter *et al.*, 1989). However, no diagnostic features of *n*-alkane distributions were observed for a given metabolic grouping of plants. Thus Collister *et al.* (1994) suggested that *n*-alkane distributions from terrestrial plants cannot be used to distinguish between C_3, C_4 and CAM plants. However, because the $\delta^{13}C$ value of C_3, C_4 and CAM plants are known to be characteristic for each group (Smith and Epstein, 1971; Bender, 1971; Deines, 1980), the carbon isotopic compositions of individual *n*-alkanes and of total surface lipids from terrestrial plants are potentially useful in distinguishing between these metabolic groups.

2.5.3.2 Carbon isotope record in sediments

Carbon isotopic values of carbonate (+0.5 ± 2.5‰) and organic matter (-26 ± 7‰) appear to be fairly constant throughout the sedimentary record (Schidlowski, 1988). These values are similar to that of modern marine bicarbonate (-1‰) and the standing biomass (-26‰). Hence, consistent isotopic signal of autotrophic carbon fixation over at least 3500 Ma have been recorded, suggesting that photosynthesis has remained quantitatively the most important process of CO_2 assimilation and has undergone little evolution change.

Relatively constant isotopic signatures throughout the sedimentary rock record may imply

that a steady state in the balance between organic and carbonate carbon was reached at an early stage in the evolution of life (Schidlowski, 1988). This is verified, for instance, by the occurrence of stromatolites in the earliest sediments. These ancient stromatolites also signify that a high level of productivity was achieved by the cyanobacterial mats which built them. Such mats today can produce 8–12 g Corg /m^2d (Killops and Killops, 1993). It is also possible that photosynthesis has improved little in effectiveness and quantitative importance since the first microbial communities became established. The highly negative $\delta^{13}C$ values in Precambrian stromatolitic kerogens is thought to be related to the lack of an active transport system for DIC at that time (Sharkey and Berry, 1985; Raven and Sprent, 1989).

2.5.4 Carbon isotopic composition of hydrocarbon fractions of crude oils

As discussed above, in most cases of autotrophic and biosynthesis processes, the lighter carbon isotope ^{12}C appears to be more favoured to incorporate into live organic tissue than its ^{13}C counterpart thus influencing the isotopic signature preserved in sedimentary organic matter. Under diagenesis and catagenesis organic matter in form of kerogen is progressively transformed into hydrocarbons. It is therefore anticipated that the hydrocarbons generated would have isotopic signatures related to that of the parent kerogen. However, assuming that the lighter isotopic preference is carried over into the hydrocarbon generation process (^{12}C-^{12}C bonds are more labile than ^{13}C-^{12}C bonds) with increasing maturity, the hydrocarbons generated are likely to be somewhat more depleted in ^{13}C than its residual kerogen.

Stahl (1978) produced isotopic type curves based on the $\delta^{13}C$ values of the saturated, aromatic, NSO and asphaltene fractions of crude oils. He demonstrated that the ^{13}C content of a crude oil fraction increased with increasing polarity. Due to the structural and chemical similarities between asphaltene and kerogen, Yen (1972) suggested that the asphaltene fraction of an oil should have a $^{13}C/^{12}C$ ratio very similar to that of kerogen from which it was derived. The general trend in the isotopic composition of both source rock EOM and oil fractions is found to be: $\delta^{13}C_{kerogen} \geq \delta^{13}C_{asphalternes} \geq \delta^{13}C_{NSO} \geq \delta^{13}C_{aromatic} \geq \delta^{13}C_{saturates}$ (Galimov, 1973; Stahl, 1978).

The difference between the isotopic composition of the aromatic and saturated hydrocarbon fraction ranges up to 3.5‰ with the aromatic fraction being isotopically heavier. In very rare cases the aromatic fraction can be slightly lighter than the saturate fraction (Sofer, 1984). Fuex (1977) suggested that the causes for variations in the difference between these two fractions might be related to maturity effects, whereas Stahl (1977, 1979) suggested that the difference is related to the source of the oil. According to Fuex (1977), the C_{15+} saturate and aromatic hydrocarbon fractions of different oils or rock extracts can be analysed and compared isotopically. A positive correlation is usually established when the equivalent fractions of different oils differ by less than 1‰. Bacterial degradation, maturation and possibly migration effect on the oils, and minor inhomogeneities in the source material, are

possible limitations on this oil-oil and oil-source correlation technique.

Source: Sofer (1984) demonstrated that the isotopic difference between the saturated and aromatic hydrocarbon fractions (δ^{13}Caro - δ^{13}Csat, or $\Delta\delta_T$) exhibits a linear relationship which can differentiate oils of terrigenous source ($\Delta\delta_T = 0.12\delta^{13}Csat + 5.45$) and those of marine source ($\Delta\delta_T = 0.10\delta^{13}Csat + 3.75$). The source of the oil (i.e. marine or non-marine), the absolute isotopic value of the oil and, to a lesser extent, its maturity were suggested to be major factors which influence its $\Delta\delta_T$ value.

Maturation affects the whole oil (Fuex, 1977), such that with increasing maturity its $\delta^{13}C$ becomes more positive. Although, the C_{15+} fractions of saturate or aromatic fractions are much less sensitive to this maturity effect, Sofer (1984) noted that in a single family of oils maturation differences could cause, a shift of up to 2‰ in the saturate fraction which would result in a range of 0.2 to 0.25‰ in the value of $\Delta\delta_T$.

Biodegradation and *water washing* are other factors considered to affect the isotopic composition of crude oils. The extent of their effect depends on the isotopic composition of the compound classes removed from the oil. Typically, biodegradation results in a partial or total removal of *n*-alkanes, followed by removal of branched alkanes and some cycloalkanes and later on aromatics. Under water washing, soluble hydrocarbons are selectively extracted by meteoric water moving along the oil-water contact. Low molecular weight aromatic components (e.g. alkylbenzenes) are preferentially removed over less polar counterparts and saturated hydrocarbons (Tissot and Welte, 1978).

Migration: Silverman (1965b) noted that due to selective adsorption of polar components during migration, oils show an increase in paraffinity and a decrease in the NSO fraction in the direction of migration. Accordingly, a decrease in the $\delta^{13}C$ value of the total crude oil was observed and attributed to the apparent increase in the relative concentration of the ^{12}C-rich saturates fraction during migration. A wider spread of gasoline $\delta^{13}C$ values, attributed to the redistribution of low-and high-molecular components during migration of the oils through poorly permeable rocks, has been reported by Alekseyev *et al.* (1975). As the ratio of saturates to aromatics typically increases during migration because of the preferential removal of the more polar and water soluble aromatic compounds, Fuex (1977) suggested that whole-oil $\delta^{13}C$ values decrease slightly with migration as reflection of this change in chemical composition. Hence, selective removal of aromatic compounds which are commonly richer in ^{13}C than the saturates, results in a concurrent slight decrease in whole-oil $\delta^{13}C$.

2.5.5 Normal alkane distributions and carbon isotopic signatures

Normal alkanes (*n*-alkanes) are straight-chain hydrocarbons with the general formula

C_nH_{2n+2}. They are found in organic matter, oils and sediments where they may either be directly inherited from biological material or derived from other organic compounds such as esters, alcohols and fatty acids during early diagenesis. Their main sources are algae, bacteria and land plants. Therefore the relationship between *n*-alkanes in organisms and sediments is governed by the overlapping distributions of *n*-alkanes in different classes of organisms. They are normally eluted in the saturate fraction during column or liquid chromatography, where they appear to be dominant compounds. Their distribution and abundance, which in fact represent a mixing of materials from multiple sources, is usually demonstrated by their carbon number distribution as determined by gas chromatography.

Nevertheless, certain groups of organisms have apparently specific *n*-alkane distributions. For instance, the benthic marine algae have a characteristic *n*-alkane maximum at either C_{15} or C_{17} (Clark and Blumer, 1967). Non-marine algae and cyanobacteria have a characteristic C_{15}–C_{20} range with a maximum at C_{17} or C_{19} although some species have longer chains in the C_{21}–C_{37} range (Parker and Leo, 1965; Gelpi *et al.*,1970).

Photosynthetic bacteria are characterised by mid-chain length *n*-alkanes, i.e. C_{14}–C_{20}, whereas the non-photosynthetic bacteria synthesise longer chains (C_{20}-C_{27}: Oro *et al.*, 1967). The *n*-alkane distributions of cuticular waxes from vascular plants have a range of C_{23}–C_{35} with a maximum at C_{31} or C_{33} (Eglinton *et al.*, 1962; Eglinton and Hamilton, 1963). Fungal spores contain *n*-alkanes ranging from C_{14} to C_{37} although their abundances are generally low (Weete, 1976)

Collister *et al.* (1994) suggest that in multicomponent mixtures of *n*-alkanes the C_{16}–C_{19} range is likely to be dominated by algal sources; the C_{20}–C_{26} range by strong inputs from bacterial and aquatic plants; and the C_{27}–C_{31} range by terrestrial plant waxes. Further more, these workers found that the variation in the $\delta^{13}C$ content of individual extractable *n*-alkanes in the C_{16}–C_{29} range indicates a contribution from at least five distinct sources, namely cynobacterial (C_{16}–C_{18}) with the $\delta^{13}C$ value of -37‰; phytoplanktonic (C_{16}-C_{23}) with -32‰; chemoautrophic bacterial (C_{20}–C_{29}) with -38‰; phytoplanktonic or heterotrophic bacterial (C_{20}–C_{29}) with -30‰; and vascular plants (C_{23}–C_{29}) with -29‰.

2.6 Saturated hydrocarbon biomarkers

Geochemical studies on crude oils, recent sediments and ancient sedimentary rocks have revealed the occurrence of hydrocarbons with closely related molecular substances from a wide range of living organisms. The carbon skeleton of such molecules is preserved in such a way that it can be linked to some major structural types. It have been envisaged that they stem either directly from living organisms, without any chemical alteration, or indirectly with minor changes which occur mostly during diagenesis in young sediments. Tissot and Welte (1984) proposed the expression "geochemical fossil" to designate such compounds which

are also known as "chemical fossils" (Eglinton and Calvin, 1967; Blumer, 1973), "molecular fossils and biological markers" or simply "biomarkers" (Peters and Moldowan, 1993).

The main classes of alkanes which have been used as biomarkers include normal, iso- and anteiso-alkanes, acyclic isoprenoids and cyclic alkanes The saturated biomarker groups identified in this study are briefly discussed below.

2.6.1 Normal alkanes

Various sources of linear aliphatic chain compounds have already been discussed (section 2.5.5). The molecular preservation of their biochemical synthesis is evident from the distribution and relative abundance of homologues with even and odd numbers of carbon atoms. However, this feature is progressively erased by age or burial depth. A predominance of odd-carbon-numbered homologues among the higher molecular weight *n*-alkanes ($>C_{20}$) is rather common (Tissot *et al.*, 1977).

2.6.1.1 Odd-carbon-numbered *n*-alkanes of higher molecular weight (C_{25}–C_{33})

This group of *n*-alkanes is frequently reported in Recent siliciclastic sediments containing detrital organic material from plants. The relative abundance of molecules with odd and even numbers of carbon atoms is expressed by the Carbon Preference Index (CPI: Bray and Evans, 1961). A modified version of the original formula is as follows: CPI = $2(C_{23}+C_{25}+C_{27}+C_{29})/[C_{22}+2(C_{24}+C_{26}+C_{28})+C_{30}]$. CPI values between 2 to 5.5 are typical of young sediments (Bray and Evans, 1961; Meinschein, 1961; Kvennolden, 1962). Odd-carbon numbered *n*-alkanes may either be directly synthesised by plants or derived through an early diagenetic defunctionalization of even-carbon-numbered acids, alcohols or esters. Higher proportions of *n*-alkanes in the C_{25}–C_{33} range are normally found in continental organic matter. Marine planktonic matter preserved in carbonate sediments appears to be devoid of odd-carbon numbered predominance in the C_{20+} range (Koons *et al.*, 1965; Clark and Blumer, 1967; Powell and McKirdy, 1973a).

In ancient detrital sediments, the predominance of the original odd-carbon-numbered *n*-alkanes of higher molecular weight is preserved at relatively shallow burial depths where degradation of kerogen has not yet started, and where the hydrocarbon content remains low. This odd predominance therefore is encountered more in Lower Cretaceous and younger beds than in older rocks. Tissot and Welte (1984) suggested that this feature might be due to the greater thermal maturity of older rocks with higher plant input, or the increasing diversity and abundance of vascular plants following the development of angiosperms in the Early Cretaceous. A predominance of odd *n*-alkanes derived from higher plants is exhibited by oil shales (Robinson *et al.*, 1965), lignites and other low-rank coals (Leythaeuser and Welte, 1969; Brooks, 1970).

Most crude oils have CPI values around 1.0. This is because the high molecular weight *n*-alkanes inherited directly from terrestrial plants are diluted by hydrocarbons from kerogen degradation. Some oils, derived mainly or solely from terrestrial organic material which has been reworked by bacteria and other microbes, contain large amounts of high molecular weight *n*-alkanes with a moderate odd-carbon number predominance.

2.6.1.2 Odd-carbon-numbered *n*-alkanes of medium molecular weight (C_{15} and C_{17})

These may represent in some cases a direct heritage of the hydrocarbons and related fatty acids present in algae and cyanobacteria. The occurrence of odd- predominance in the C_{11}–C_{19} range was first noted by Martin *et al.* (1963) in several oils of lower Paleozoic age from the United States. This feature was subsequently found to be common in Ordovician oils and source rocks worldwide (e.g Jackson *et al.*, 1984; Jacobson *et al.*, 1988) and attributed to the benthonic alga or cyanobacterium, *Gleocapsomorpha prisca* (Foster *et al.*, 1989, 1990) which grew prolifically in shallow marine shelf or epeiric sea environments.

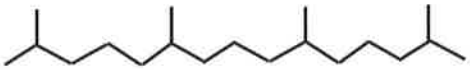
2.6.1.3 Even-carbon number predominance

Cases of even-carbon-number predominance among *n*-alkanes have been reported in carbonates or evaporite sediments and occasionally from crude oils (Welte and Waples, 1973; Albaiges and Torradas, 1974; Tissot *et al.*, 1974b; Douglas and Grantham, 1974). This particular type of distribution is usually associated with a high pristane/ phytane ratio. Welte and Waples (1973) suggested that, in very reducing environments, reduction of *n*-fatty acids and alcohols is prevalent over decarboxylation reactions, resulting in predominance of even over odd-carbon-numbered *n*-alkanes, CPI<1 and a predominance of phytane over pristane. In less reducing environments, decarboxylation results in a greater abundance of odd-numbered *n*-alkanes (CPI>1) and a predominance of pristane over phytane (Knoche *et al.*, 1968). An alternative interpretation of even *n*-alkane predominance was proposed by Shimoyama and Johns (1972) based on a study of the catalytic effects of montimorillonite and calcium carbonate on the degradation of *n*-fatty acids. They found that decarboxylation with loss of one carbon atom occurs when montmorillonite is the catalyst, and beta cleavage with loss of two carbon atoms when calcium carbonate is used. Therefore, an original even - carbon numbered fatty acid would generate mostly an odd *n*-alkane in shales and an even *n*-alkane in limestones.

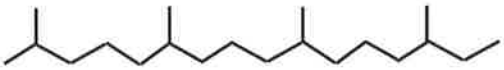
2.6.2 Acyclic isoprenoids (pristane and phytane)

Isoprenoids are among the compounds which are built from C_5 isoprene units. They are dominantly derived from plant and bacterial sources where they occur as hydrocarbons, alcohols esters such as in the phytyl side-chain of chlorophyll and glycerol ethers in bacterial membranes. Higher molecular-weight acyclic isoprenoids with carbon number up to C_{45} have been recorded in regular isoprenoids (Albaiges, 1980).

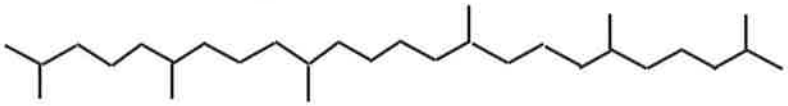
a. Regular and irregular isoprenoids



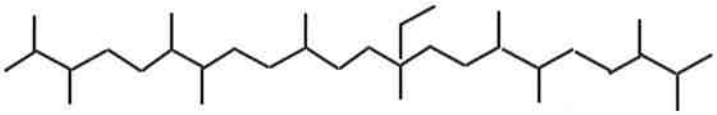
2,6,10,14-tetramethylpentadecane
Pristane (C_{19})



2,6,10,14-tetramethylhexadecane
Phytane (C_{20})

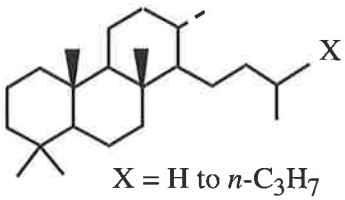


Squalane ($C_{30}H_{62}$)

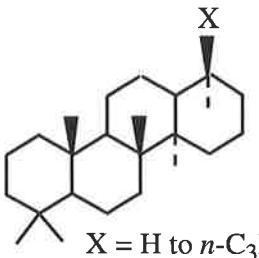


Botryococcane (C_{34})

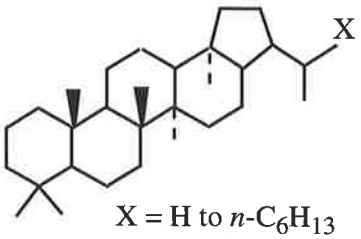
b. Terpanes



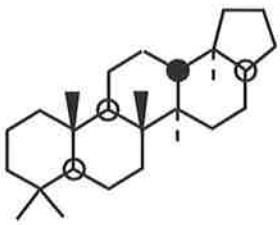
X = H to n-C_3H_7
Tricyclic (Cheilanthanes)



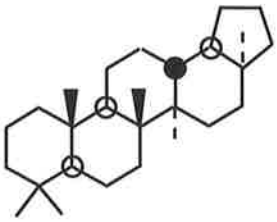
X = H to n-C_3H_7
Tetracyclic



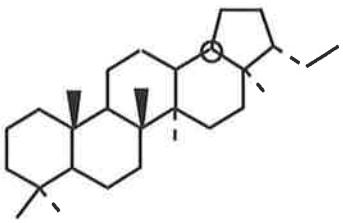
X = H to n-C_6H_{13}
Pentacyclic



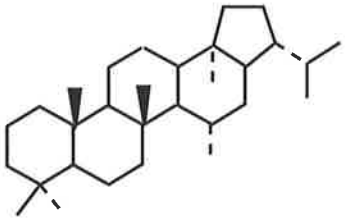
17α(H)-22,29,30-
Trisnorhopane (Tm)



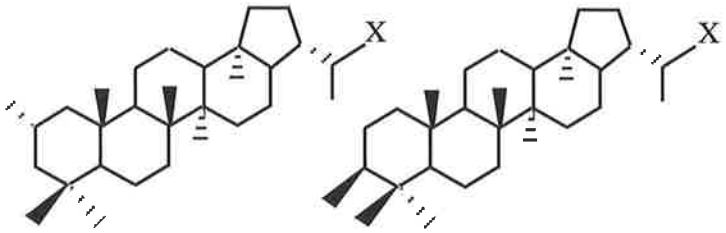
18α(H)-22,29,30-
Trisnorneohopane (Ts)



18α(H)-30-
Norneohopane (C_{29}Ts)

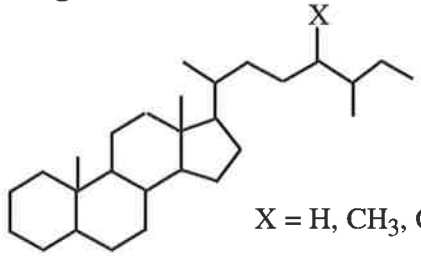


17α(H)-Diahopane
(C_{30}*)



X = n-alkyl side chain
2α-Methylhopane 3β-Methylhopane

c. Regular steranes



X = H, CH_3, C_2H_5

Figure 2.8 Structures of some saturated hydrocarbon biomarkers.

The most common isoprenoids are pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethyl-hexadecane) (Fig. 2.8a).

Isoprenoids with 20 or less carbon atoms are found in sediments where their direct introduction is possible through animals, particularly zooplankton, which feed on plants. Several saturated and unsaturated isoprenoid have been reported in zooplankton (Blumer and Thomas, 1965). Pristane (C_{19}), phytane (C_{20}), and smaller regular isoprenoids are primarily derived from the phytyl side chain of chlorophyll in phototrophic organism through reduction, oxidation and carboxylation processes (Tissot and Welte, 1984).

In very reducing environments, the ester linkage of the phytyl side chain is hydrolysed to yield phytol which is hydrogenated to dihydrophytol, followed by a subsequent reduction into phytane. In a normal oxygenated environment, the phytol is oxidised to phytenic acid, decarboxylated to pristene and then reduced to pristane. Welte and Waples (1973) and Powell and McKirdy (1973b) suggested that phytane or pristane may be predominant depending on the oxicity of the local depositional environment.

The archaebacterial lipids (from methanogens or halophiles) also appear to be a potential source for pristane and phytane, as well as the extended (C_{20+}) isoprenoids. These fossil molecules occur in kerogen and in the polar fraction of recent and ancient sediments and crude oils (Michaelis and Albrecht, 1979; Chappe *et al.*, 1979, 1980, 1982). Tocopherols, also known as vitamin E, are another possible source of pristane in ancient sediments and crude oils (Goosens *et al.*, 1984). Both flash pyrolysis and thermal degradation of α-tocopherols yield prist-1-ene as a major product. The organic moieties in the kerogens from which prist-1-ene is generated were previously shown by van Graas *et al.* (1981) to be similar to those yielding pristane under natural conditions. On the contrary the generation of phytane from this source appears to be less likely because α-cleavage next to the aromatic moiety is not favoured.

2.6.2.1 Acyclic isoprenoid to *n*-alkane ratios

Based on observations of the relative abundance of phytane and pristane in oils, it is mainly the total amount of pristane in the oils which fluctuates with the environment of deposition of the parent source rocks. Therefore Lijmbach (1975) came up with the idea of using a pristane/*n*-heptadecane ratio (pr/*n*-C_{17}) to characterise the depositional environment. The amount of pristane is related to that of *n*-C_{17} rather than another *n*-alkane in order to minimise the effect of differential evaporation.

By assuming that phytol is the precursor for both pristane and phytane, it follows that; in environments where bacterial activity is abundant, phytol is mineralised into CO_2 and H_2O and only small fraction is preserved as dihydrophytol. Accordingly, only small amounts of

phytane and pristane are yielded on catagenesis. This situation is likely to happen in environments of open water sedimentation, leading to low pristane/*n*-C_{17} alkane ratios (<0.5) in the resulting crude oils. Under peat swamp conditions, aerobic bacterial activity is normally reduced as a result of the combination of different factors such as low pH (<5), low oxygen content and the presence of toxic components like humic acids and phenols. Thus, under such environmental conditions, most of the phytol is converted microbiologically into phytanic acid, which accumulates, and subsequently is decarboxylated to pristane and CO_2 on thermal maturation. Therefore, oils from source rocks deposited under peat swamp conditions are relatively rich in pristane and poor in phytane, with pr/*n*-C_{17} >1.0. Source rocks deposited in environments with alternating swamp and open water conditions are likely to have intermediate pr/*n*-C_{17} ratios (i.e. 0.5 < pr/*n*-C_{17} < 1).

In a similar manner, the abundance of phytane may be related to that of *n*-octadecane (*n*-C_{18}). However, the ph/*n*-C_{18} ratio appears to be independent of the environment of deposition. Values in oils and mature source rocks are of the order of 0.1-0.5, whilst in moderately biodegraded oils and immature source rocks phytane is more abundant than *n*-C_{18} (i.e. ph/*n*-C_{18} generally >1).

Apart from the primary influence of source rocks depositional environment on the pr/*n*-C_{17} ratio, this ratio decreases sharply with increasing maturity. It reaches values below unity over the most of the oil window (Tissot *et al.*, 1977; Durand and Espitalié, 1973; Connan and Cassou, 1980). Hydrocarbon expulsion has also been reported to influence this ratio, whereby within source rock intervals of uniform kerogen type and maturity, the pr/*n*-C_{17} ratio increases with increasing degree of hydrocarbon drainage into the reservoir or carrier bed (McKenzie *et al.*, 1983; Leythaeuser *et al.*, 1984a).

2.6.3 Bicyclic sesquiterpanes

Bicyclic sesquiterpanes have frequently been reported in crude oils (Bendoraitis, 1974; Seifert and Moldowan, 1979; Philp *et al.*, 1981). Alexander *et al.* (1983) synthesised two of the bicyclic sesquiterpanes found to be widespread in Australian crude oils and identified them as 4β(H)-eudesmane and 8β(H)-drimane. Using synthesised standards and their mass spectra Noble (1986), identified several other bicyclic sesquiterpane structures (Fig. 2.9).

The carbon skeleton of 4β(H)-eudesmane has been related to eudesmanol which occurs only in higher plants (Philp, 1985) and higher plant terpenes (Peters and Moldowan, 1993) whereas drimanes have structural features and a widespread distribution similar to many biomarkers of prokaryotic origin (Alexander *et al.*, 1983; Volkman, 1988). Despite its terrestrial origin, 4β(H)-eudesmane is present in only very low amounts compared to the other sesquiterpanes in terrestrially derived Australian oils. In most cases drimane occur in higher abundance.

2.6.4 Diterpenoids

Diterpenoids are widely distributed in higher plants, particularly in resins (Thomas, 1969; Simoneit, 1977). Based on structural similarities, Alexander *et al.* (1987) classified the diterpanes most commonly found in crude oils and sediments into six families, viz: labdane, abietane, pimarane, beyerane, kaurane and phyllocladane (Fig. 2.10a). Their relative abundances in different plant types are shown in Table 2.5.

Table 2.5 Diterpenoid classification and abundance in plants (Alexander et al., 1987)

Plant Type	Bicyclic	Tricyclic		Tetracyclic		
	Labdane	Abietane	Pimarane[a]	Beyerane[b]	Kaurane	Phyllocladane
Angiosperm (flowering plants)	++	+	++	+	+++	-
Gymnosperm (mainly conifers)	++	++	+++	++	+++	++
Pteridophytes (ferns)	+	-	+	-	++	-
Bryophytes (mosses and liverworts)	+	-	+	-	++	-

a. pimaranes include isopimaranes and rimuanes; b. stachenes and hibaenes

+++ , widespread; ++ common; + infrequent; - rare or unreported.

2.6.4.1 Bicyclic diterpenoids

Bicyclic diterpenoids based on the labdane skeleton are common in southern conifers (*Araucariaceae*), particularly those of the genus *Agathis* (Thomas, 1969). However, labdane may also be derived from microbial sources (Dimmler *et al.*, 1984).

2.6.4.2 Tricyclic diterpenoids

Tricyclic diterpenoids of the pimarane type occur widely in conifers of the Pinaceae and Cupressaceae families (Gough, 1964); and are also represented in the southern conifer families Podocarpaceae (genus *Dacrydium*) and Araucariaceae (Thomas, 1969; Cambie *et al.*, 1971). They contain compounds such as isopimara-7,15-diene (Grant *et al.*, 1967) and rimuene (Salasoo, 1984), which can be readily reduced by subsurface processes to yield isopimarane and rimuane, respectively.

2.6.4.3 Tetracyclic diterpenoids

The natural product precursors for the tetracyclic diterpenoids of the ent-beyerane, phyllocladane and ent-kauranes families are thought to be tetracyclic diterpenes which occur abundantly in the leaf resins of many conifer species (Hanson, 1968).

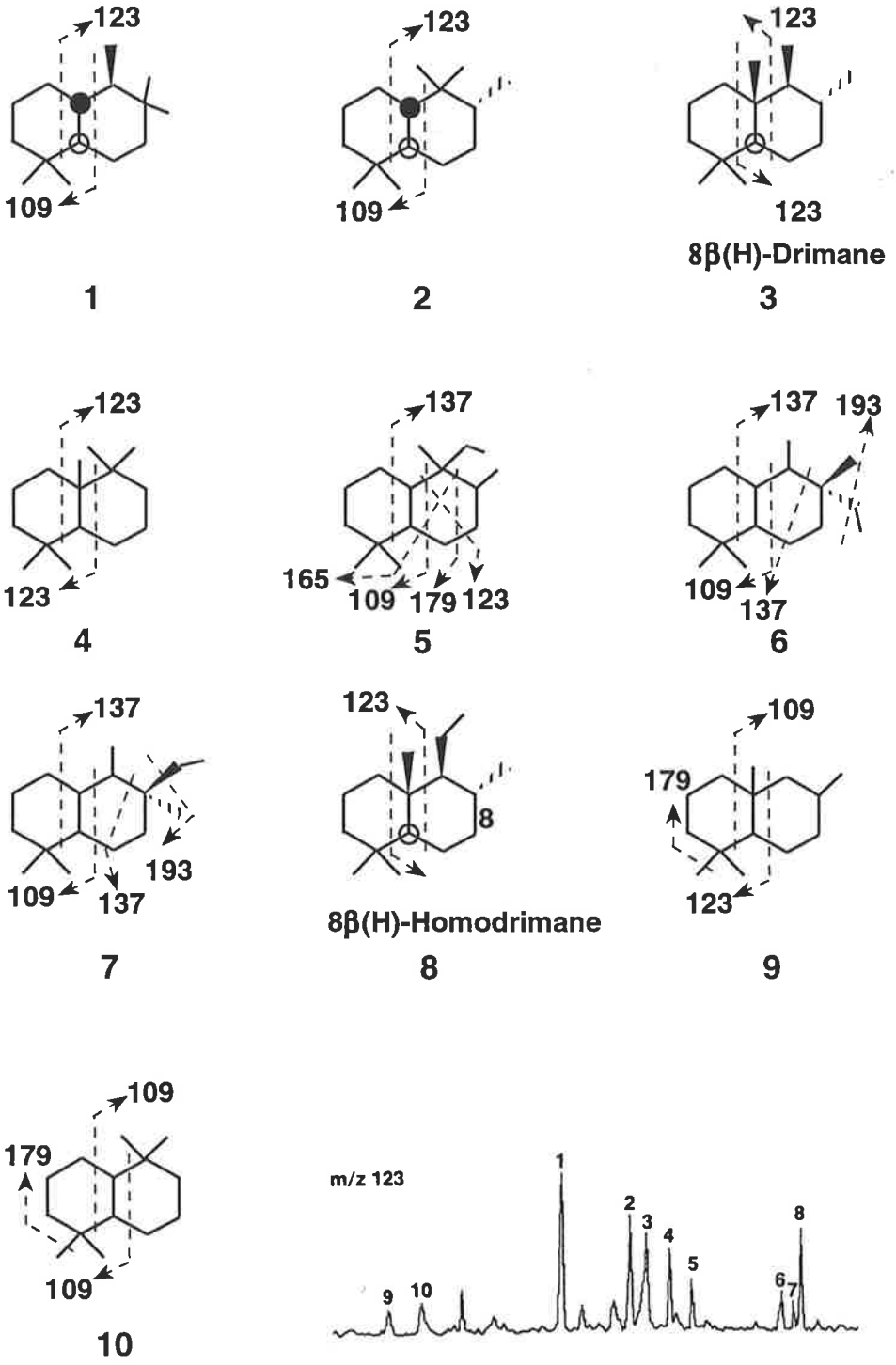


Figure 2.9 Bicyclic sesquiterpanes commonly identified in source rocks and oils (after Noble, 1986; Peters and Moldowan, 1993).

Compounds such as phyllocladene, kaurene and beyer-15-ene could be readily converted into saturated compounds by diagenetic reduction of their double bonds to produce phyllocladane, kaurane and beyerane respectively (Alexander *et al.*, 1987). The precursors of phyllocladane are widely found in conifers of the Podocarpaceae family, especially in the genera *Podocarpus*, *Phyllocladus* and *Dacrydium* (Aplin *et al.*, 1963; Cambie and Weston, 1968); whilst those of kaurane are abundant in many conifer species of the Araucariaceae, Podocarpaceae and Taxodiaceae families (Thomas, 1969). The precursors of beyerane are not as widely distributed as those of phyllocladane or kaurane, but are abundant in some species of the Cupressaceae, Podocarpaceae and Araucariaceae families (Carman and Sutherland, 1979).

Noble *et al.* (1985) observed that diagenetic reduction of phyllocladene and ent-kaurene produce mainly 16α(H)-phyllocladane and *ent*-16α(H)-kaurane, respectively. These compounds were identified in low rank coals where the concentration of 16α(H) compounds were reported to decrease relative to the thermodynamically more stable 16β(H) epimers with increasing coal rank.

Both the tricyclic and tetracyclic C_{19} petroleum diterpanes [4β(H)-19-norisopimarane and 17-nortetracyclane] are probably derived from C_{20} precursors (Alexander *et al.*, 1987). The C_{20} diterpenoid acids such as sandaracopimaric acid and isopimaric acid, which are constituents of conifer resins in particular, could readily decarboxylate in a manner analogous to the transformation of abietic acid to fichtelite in the subsurface (Streibl and Herout, 1969; Douglas and Grantham, 1974; Barrick and Hedges, 1981).

2.6.5 Tricyclic terpanes

A series of tricyclic terpanes [13β(H), 14α(H)-cheilanthanes: Fig. 2.8b] extending from C_{19} to C_{30} have been reported in ancient sediments and crude oils. (Seifert *et al.*, 1978; Aquino Neto *et al.*, 1982, 1983). Extended tricyclic terpanes up to C_{45} were reported in a Californian oil (Moldowan *et al.*, 1983). The structures of several homologues of the tricyclic terpanes have been proven by synthesis (Ekweozor and Strausz 1982; Heissler *et al.*, 1984; Sierra *et al.*, 1984).

Aquino Neto *et al.* (1982) identified three of several short chain tricyclic terpanes as C_{19}, and C_{20}. A C_{30} precursor was envisaged for this series, namely tricyclohexaprenol which is formed anaerobically from a universal cell constituent, hexaprenol. The saturated counterpart of hexaprenol has been reported in petroleum (Albaiges, 1981) and in the lipids of archaebacteria (Holzer *et al.*, 1979). The C_{23} member series was isolated by Ekweozor and Strausz (1982, 1983) from Athabascan Oil Sand bitumen. Tricyclic carboxylic acids (Cyr and Strausz, 1983) have also been suggested as possible precursors.

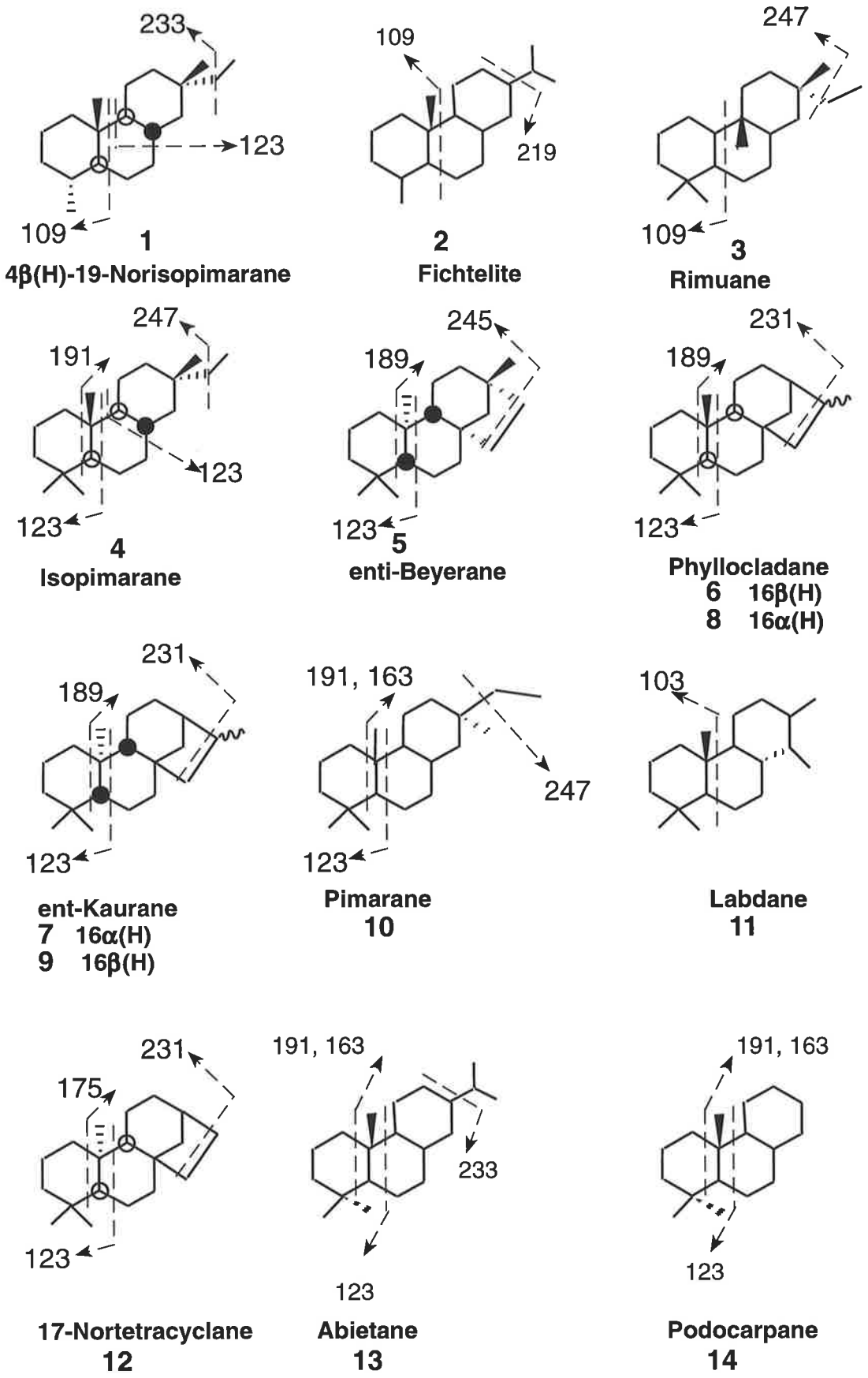


Figure 2.10a Bicyclic, tricyclic and tetracyclic diterpane structures identified in source rocks and crude oils, (after Noble, 1986; Peters and Moldowan, 1993)

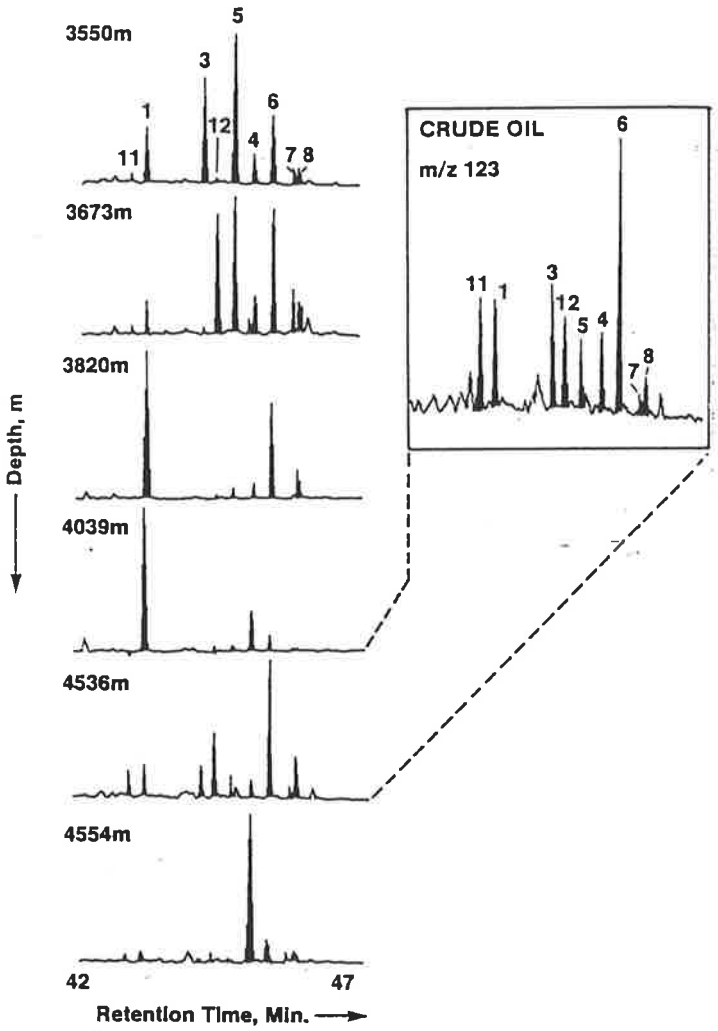


Figure 2.10b Bicyclic, tricyclic and tetracyclic diterpane peaks (in m/z 123 mass chromatograms) identified in source rocks and crude oils from the Gippsland Basin, Australia (after Noble, 1986; Peters and Moldowan, 1993); their corresponding structures are as shown in Figure 2.10a

The widespread occurrence of tricyclic terpanes, and the molecular properties of tricyclohexaprenol, suggest that they are derived from prokaryotic membranes (Ourisson *et al.*, 1982). A high concentration of tricyclic terpanes has also been reported in Tasmanite rock extracts, indicating a possible origin from the fossil marine alga *Tasmanites* sp. (Volkman *et al.*, 1989). Other evidence suggests a higher plant source for some C_{19} and C_{20} tricyclic terpanes. Thermal cleavage of the alkyl side chain in sester- and triterpanes was suggested to produce the C_{19}–C_{20} tricyclic terpanes (Zumberge, 1983). The C_{23} homologue is typically the most prominent tricyclic terpane (Connan *et al.*, 1980; Aquino Neto *et al.*, 1983; Sierra *et al.*, 1984). Oils and bitumens from carbonate rocks show low concentrations of tricyclic terpanes above C_{26} compared to those from other depositional environments where the C_{26}–C_{30} and C_{19}–C_{25} homologues are present in similar concentrations (Aquino Neto *et al.*, 1983).

2.6.6 Tetracyclic terpanes

C_{24}–C_{27} tetracyclic terpanes (Fig. 2.8b) have been identified (Aquino Neto *et al.*, 1983) and there is tentative evidence for homologues up to C_{35}. Tetracyclic terpanes are thought to be generated as result of thermal or microbial degradation of pentacyclic hopane (triterpane) or precursor hopanoids. An independent biosynthetic route to the tetracyclic terpanes may exist in bacteria (Peters and Moldowan, 1993).

High abundances of C_{24} tetracyclic terpane occur in both carbonate and evaporite source rocks and in related petroleums (Palacas *et al.*, 1984; Connan *et al.*; 1986; Connan and Dessort, 1987; Mann *et al.*, 1987; Clark and Philp, 1989). This compound has also been found in Australian oils and rock extracts generated from terrigenous organic matter (Philp and Gilbert, 1986).

2.6.7 Pentacyclic triterpanes

Pentacyclic triterpenoids are widely distributed among prokaryotes and higher plants such as ferns, but appear to be absent in algae. Bacterial and cyanobacteria appear to be the major sources for sedimentary hopanoids (Ourisson *et al.*, 1979, 1982). The C_{27}–C_{30} hopanes are derived from the C_{30} hopanoids diploptene and diplopterol found in nearly all prokaryotes; whereas the extended hopanes (C_{31}–C_{35}) are related to specific bacteriohopanepolyols, such as C_{35} bacteriohopanetetrol, found in bacteria (Ourisson *et al.*, 1979, 1982; Boon *et al.*, 1983; Rohmer *et al.*, 1992).

These naturally occurring hopanoid precursors generally have a 17β(H),21β(H) stereochemistry, with the R configuration at the C-22 position. Most of the hopanes found in recent sediments possess the same stereochemistry. Extended hopanes with the 17α(H),21β(H) stereochemistry (22R configuration) have also been found in lichens and fungi (Corbett and Heng, 1971) and in a number of peat samples (Taylor *et al.*, 1980; Quirk

et al., 1984). As thermal maturation increases a conversion to the thermodynamically more stable 17α(H),21β(H) configuration takes place, together with isomerisation at the C-22 position to give the 22S epimer.

A second series of hopanes, the moretanes, with a 17β(H),21α(H) stereochemistry, also starts to appear with increasing maturity. These may have either the 22R or 22S configuration in the C_{31} and higher homologues. At higher temperatures (i.e. during catagenesis) moretanes decrease rapidly relative to the 17α-hopanes (Seifert and Moldowan, 1980, 1981; Mackenzie *et al.*, 1980; ten Haven *et al.*, 1992). However, the moretane/hopane ratios in bitumens from hypersaline rocks are higher than those from adjacent non-saline sediments (Rullkötter and Marzi, 1988).

Two C_{27} hopanes, viz. 17α(H)-trisnorhopane (Tm or 17α(H)-22,29,30-trisnorhopane) and 18α(H)-trisnorneohopane (Ts or 18α(H)-22,29,30-trisnorneohopane) (Fig. 2.8b), are widespread in bitumens and crude oils. The behaviour of Tm appears to be similar to that of other regular hopanes, whereas Ts is likely to form via another diagenetic route (Pym *et al.*, 1975). During catagenesis Tm is less stable than Ts (Seifert and Moldowan, 1978; Kolaczkowska *et al.*, 1990).

The ratios Ts/Tm or Ts/Ts+Tm have used to indicate differences in source rock type and maturation level (Moldowan *et al.*, 1986; Hong *et al.*, 1986). The reliability of this ratio as a source maturity indicator is best when evaluating oils from a common source of consistent organic facies. The Ts/Ts+Tm ratio appears to be sensitive to clay-catalysed reactions. It is anomalously low in oils from carbonate source rocks compared to those generated from shales of similar maturity (McKirdy *et al.*, 1983, 1984; Rullkötter *et al.*, 1985; Price *et al.*, 1987).

C_{29}Ts is a C_{29} compound which elutes immediately after C_{29} 17α(H)-hopane in the m/z 191 fragmentogram. It has been identified as 18α(H)-30-norneohopane (Moldowan *et al.*, 1991); and its abundance is related to thermal maturity (Hughes *et al.*, 1985; Sofer *et al.*, 1986; Sofer, 1988; Cornford *et al.*, 1988; Riediger *et al.*, 1990). Peters and Moldowan (1993) described the detection of C_{29}Ts and another rearranged hopane 17α(H)-diahopane (C_{30}^{*}) in the m/z 191 fragmentogram of petroleum saturates fractions. An unidentified compound with the same retention index as C_{30}^{*} was previously reported by Volkman *et al.* (1983a) and Philp and Gilbert (1986). Both reports regarded this compound as a possible terrestrial marker because of its presence in coals and terrestrial-sourced oils. However, its bacterial origin has now been established (Peters and Moldowan, 1993). The structures of these rearranged hopanes are shown in Figure 2.8b.

Environmental conditions are thought to influence the abundance of C_{29}Ts and C_{30}^{*} such that the C_{30}^{*}/ C_{29}Ts ratios in oils can be used in the assessment of depositional environment of their source rocks. Therefore, Peters and Moldowan (1993) suggested that oils derived from shales deposited under oxic-suboxic conditions will show higher ratios than those derived from source rocks deposited under anoxic conditions. Nevertheless, it has been shown that 17α(H)-diahopanes are more stable than 18α(H)-neohopanes, which in turn are more stable than 17α(H)-hopanes (Moldowan *et al.*, 1991). Therefore, with increasing maturity the ratio of 17α(H)-diahopane to either 18α(H)-30-norneohopane or 17α(H)-hopane will also increase (Kolaczkowka *et al.*, 1990; Peters and Moldowan, 1993)

2.6.8 Methylhopanes

The most prominent series of these compounds to have been identified is the 2α-methyl-17α(H),21β(H)-hopanes (Summons and Jahnke, 1992). Each component in this series seems to elute near the corresponding 17α(H)-hopane with one less carbon. A second series is the 3β-methyl-17α(H),21β(H)-hopanes. These occur in lesser amounts and elute much later than the 2α-compounds. Both series comprise C_{28}–C_{36} pseudohomologues (Summons and Walter, 1990; Summons and Jahnke, 1992). The likely precursors for these hydrocarbons are 2β-methyldiplopterol and 3β-methylbacteriohopanepolyols found in methylotrophic bacteria (Bisseret *et al.*, 1985; Zundel and Rohmer, 1985). The structures of the 2α- and 3β-methylhopanes are shown in Figure 2.8b.

Another compound 2β-methyl-17α(H)-hopane was identified in significant concentrations in immature sediments. It is less abundant in sediments with intermediate maturities and absent in mature samples. This suggest that the common sedimentary 2α-methylhopanes are probably derived from less stable 2β-methyl biogenic precursors.

2.6.9 Steranes

Steranes (Fig. 2.8c) are formed by the reduction of sterols originally incorporated in sediments. They are widely distributed in both sediments and crude oils but not in living organisms. Their link to biota is through their precursors, sterols which are found in both free and bound forms in organisms. The carbon number distribution of regular (i.e. 4-desmethyl) sterols in young sediments has permitted, to a certain degree identification of the contributing organisms (Huang and Meinschein, 1979; Mackenzie, 1984; Moldowan *et al.*, 1985).

For instance, planktonic algae in general contain mostly C_{27} and C_{28} sterols, although diatoms contain approximately equal amounts of C_{27}, C_{28}, and C_{29} sterols (Volkman *et al.*, 1981). The zooplankton, of which crustaceans are a dominant class, often contain abundant C_{27} sterols.

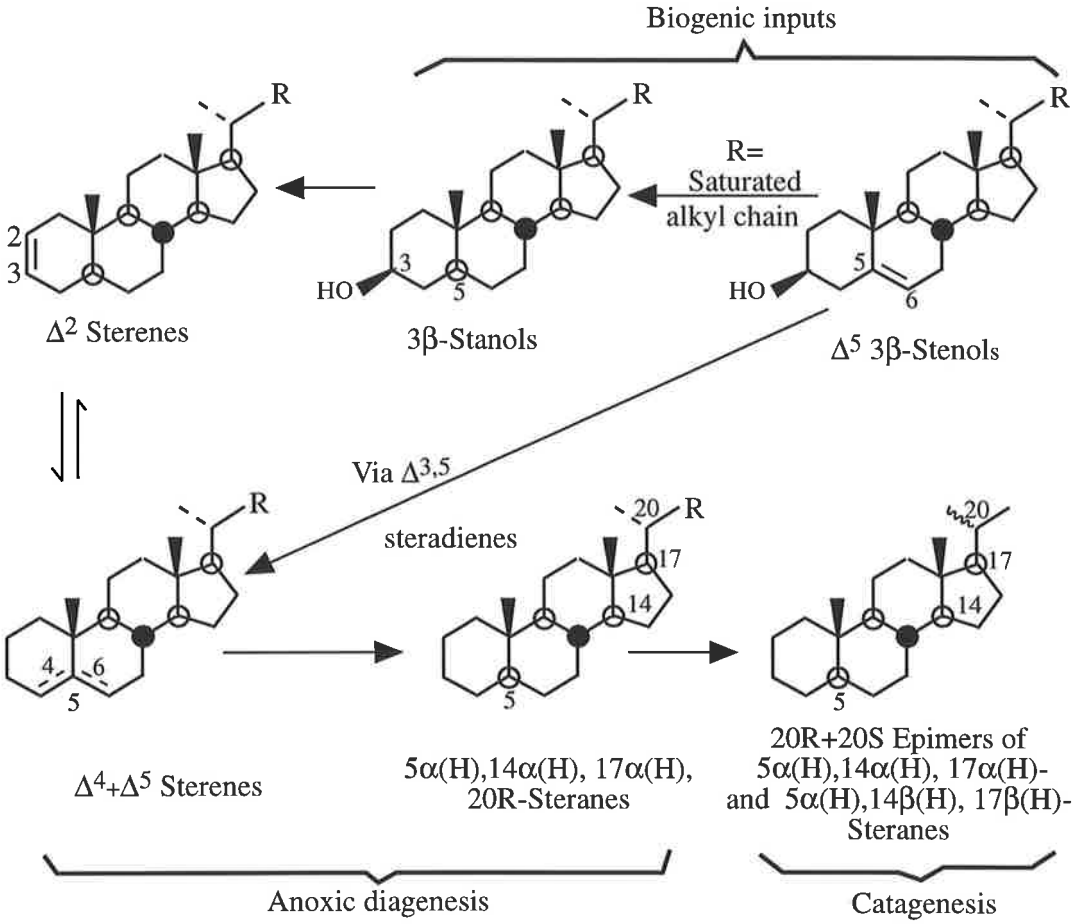


Figure 2.11 Transformation of sterols to steranes

In the higher plants the C_{29} compounds β-sitosterol [24α(H)-ethylcholest-5-en-3β-ol] and stigmasterol [24α(H)-ethylcholesta-5,22E-dien-3β-ol], are commonly dominant, although campesterol [24α(H)-methylcholest-5-en-3β-ol], a C_{28} sterol, is often abundant. The C_{27}–C_{29} sterols are also found in fungi where ergosterol, another C_{28}, compound often predominates.

Based on a study of recent marine and terrestrial sediments, Huang and Meinschein (1979) reported that the ratio of cholest-5-en-3β-ol to 24-ethylcholest-5-en-3β-ol is a source discriminator. This approach was extended by suggesting that the relative proportions of C_{27}, C_{28}, and C_{29} sterols in a ternary diagram, can be used to differentiate ecosystems. Accordingly, the relative abundances of cholestane (C_{27}), ergostane (C_{28}) and stigmastane (C_{29}) sterane homologues in oils and bitumen may be used in the same way.

The fate of sterols following the deposition and accumulation of organic matter is discussed by Mackenzie *et al.* (1982) and de Leeuw *et al.* (1989). The similarity of distributions in the supposed product and precursor compound classes, and inverse abundance trends in product-precursor pairs with increasing burial depth, make possible the identification of specific product-precursor relationships. Simulated diagenesis in the laboratory using isolated or synthesised individual compounds has also been used to confirm sterol transformations.

Conversion of sterols into steranes and other products appears to involve many diagenetic transformations (de Leeuw and Baas, 1986; Peakman and Maxwell, 1988). The subsequent transformations are summarised in Figure 2.11. The initial steps involve liberation of free sterols via hydrolysis of steryl esters, followed by reduction of free unsaturated sterols (stenols) to their saturated counterparts (stanols). These processes occur under anaerobic conditions in both sediments and particulate matter in the water column (Wakeham, 1989). The reduction process is then followed by dehydration of stanols to sterenes; like the preceding processes it is microbially mediated and takes place under anaerobic conditions. The conversion of sterenes to different products follows divergent reaction pathways of which the major products usually are steranes (Brassell, 1985). The reduction (hydrogenation) of sterenes to their fully saturated counterparts, steranes results mainly in a 5α(H) configuration.

In newly formed steranes the configuration at most of the chiral carbons appears to be unaffected by diagenetic reactions, and hence is that inherited from the original biogenic steroids. At the end of diagenesis, steranes therefore have predominantly the 5α(H),8β(H),9α(H),10β(CH_3),13β(CH_3),14α(H),17α (H) 20R configuration.

At a later stage during catagenesis or coalification, the isomerisation reactions involving chiral carbon atoms bearing a hydrogen atom occur. Mineral surfaces (e.g. clays) are

believed to play an important role in these processes. At a particular chiral centre (e.g. at C-14, C-17 and C-20) isomerisation converts the single biologically conferred configuration into an equilibrium mixture of two possible stereoisomers, 20R and 20S. Moreover, the flat configuration imposed by the 14α(H),17α(H) stereochemistry in the sterols is lost in favour of the thermodynamically more stable 14β(H),17β(H) form. Both laboratory experiments (Seifert and Moldowan, 1979) and theoretical calculations (van Graas *et al.*, 1982) have shown that isomerisation of the 5α(H),14α(H),17α(H) 20R configuration originated from biota results in increasing amounts of the other possible stereoisomers. The equilibrium ratio for αααR, αααS, αββR, and αββS is about 1:1:3:3.

Isomerisation ratios have therefore been used in thermal maturation assessments. For instance isomerisation at C-20 in the C_{29} 5α(H),14α(H),17α(H) steranes causes the 20S/(20S+20R) ratio to rise from 0 to about 0.5 with increasing maturity (Seifert and Moldowan, 1986). However, factors other than thermal maturity appear to have an influence on this ratio. These factors include facies effects; weathering (Clayton and King, 1987); and *in situ* oil biodegradation which can cause elevated ratios above 0.55 (Rullkötter and Wendisch, 1982; McKirdy *et al.*, 1983; Seifert *et al.*, 1984). Isomerisation at the C-14 and C-17 positions in the 20S and 20R of C_{29} regular steranes causes an increase in the αββ/(αββ+ααα) ratio from near zero values to about 0.7; equilibrium is inferred at 0.67 to 0.71 (Seifert and Moldowan, 1986). In contrast to the previous ratio, it appears to be independent of source facies and is slower to reach equilibrium than the latter, thus being effective at higher levels of maturity.

2.7 Aromatic biomarkers in source rocks and crude oils

Aromatic compounds are a particular type of unsaturated species containing one or more rings with conjugated (alternating) carbon-carbon double and single bonds which are delocalised to form an orbital ring current. The rings (single or condensed) may contain one or more short alkyl chains. The common six-member ring aromatics include: benzene (1-ring); naphthalene (2-rings); phenanthrene and anthracene (3-rings); and pyrene, benzanthracene and chrysene (4-rings). A second fundamental type consists of one five-member ring in addition to the six-member rings, e.g. fluorene (3-rings), benzofluorene and fluoranthene (4-rings).

The molecular formula of aromatic compounds is C_nH_{2n-p}, where p varies with the number of rings (e.g. benzene p = 6; naphthalene, p = 12; and phenanthrene, p = 18). The alkylated derivatives of these types comprise one to three additional carbon atoms and happen to be major components of crude oil. In accordance with the above formula, the naphthalene type, (C_nH_{2n-12}) will have a distribution which has its maximum at C_{12} or C_{13} (di- or tri-methylnaphthalene), and the phenanthrene type; (C_nH_{2n-18}), a maximum at C_{16} or C_{17} (di- or tri- methyl phenanthrene). When several structural types are possible as for molecules with

three or more aromatic rings, one of them is favoured in crude oils. Thus alkylanthracenes are present in small amounts and alkylphenanthrenes are largely predominant (Tissot and Welte, 1984)

Naphthenoaromatics are another type of aromatic compound found in crude oils. They consist of aromatic rings fused with naphthenic rings, either of which may contain alkyl substituents. These compounds are usually the major constituents of the high boiling fractions of petroleum. Naphthenoaromatics with one or two aromatic rings are more abundant than polyaromatics in paraffinic-naphthenic crude oils. Naphthenoaromatics are more abundant than pure aromatics in young or shallow, immature crude oils.

2.7.1 Formation and occurrence

2.7.1.1 Living organisms

Although possibly not of biogenic origin, trace amounts of naphthalene and a few methyl- and dimethylnapthalenes have been isolated from plant products. So far, no significant amount of hydrocarbons with more than two condensed aromatic rings are known from organisms that have grown in unpolluted environments. On the other hand, aromatic mono- and sesiquiterpenoids of biogenic origin are widely distributed in higher plants (Weiss and Edwards, 1980) (Fig. 2.12a). Structures I and III have been observed in a variety of plants and structure II has been isolated from essential oils (Carter *et al.*, 1939; Sorm *et al.*, 1951a,b).

Diterpenoid resin acids such as dehydroabietic acid (Harris, 1948; Fig.2.12b structure I) and podocarpic acid (Campbell and Todd, 1942; Fig.2.12b structure II) are among the most important monoaromatic compounds which occur in plants. Genetic relationships between diterpenoic acids in fresh kauri resins and various Recent and ancient fossil resins have been established (Thomas, 1969). Thus, the chemical structure of fossil kauri resins has been described as a polymerisation product of agathic acid, which is a bicyclic diterpenoid acid with two exocyclic double bonds (Brooks and Steven, 1967; Wilson *et al.*, 1984). Macrophyllic acid (Fig.2.12b structure III) from the heartwood of *Podocarpus macrophyllus* (Bocks *et al.*, 1963) is another example of the vast variety of hydroxy-substituted aromatics found in the plant kingdom.

2.7.1.2 Recent sediments

It is quite apparent that there are no significant concentrations of low molecular weight-aromatic hydrocarbons in unpolluted Recent sediments (Erdman, 1961). Thus low-molecular-weight aromatic hydrocarbons, which generally comprise a major proportion of crude oils, are not likely to be derived from early diagenetic processes. Instead, the polycyclic aromatic hydrocarbons (PAH) are widespread in both Recent and ancient sediments and in crude oils.

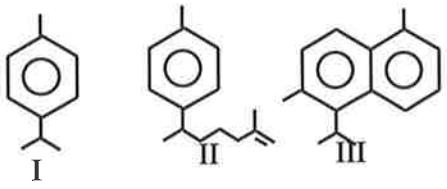
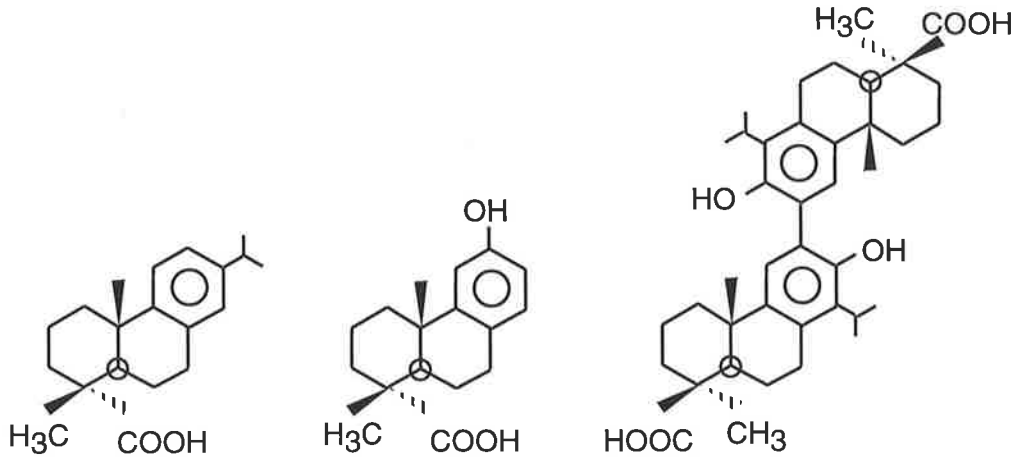


Figure 2.12a Benzenoid aromatic monoterpenoid (I) and sesquiterpenoid (II, III) hydrocarbons isolated from plants

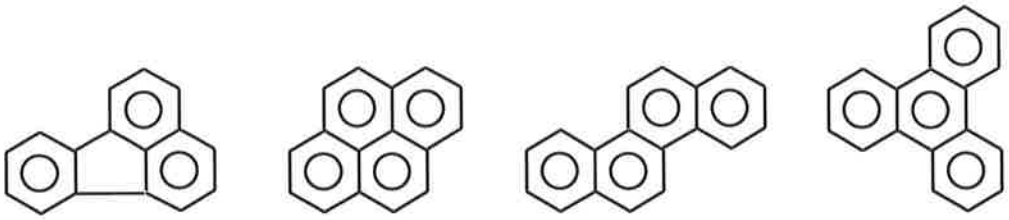


I Dehydroabietic acid

II Podocarpic acid

III Macrophyllic acid

Figure 2.12b Monoaromatic diterpenoid acids (I and II) frequently found in fresh resins and macrophyllic acid (III) showing bi-phenyl- and octahydrophenanthrene-type structural elements, isolated from terrestrial higher plants



I Fluoranthene

II Pyrene

III Chrysene

IV Triphenylene

Figure 2.12c Parent PAH which are more abundant than their respective alkyl-substituted derivatives in Recent marine sediments (Meinschein, 1959)

Studies have confirmed the predominance of unsubstituted PAH (Fig. 2.12c) in presumably unpolluted Recent sediments, whereas alkyl-substituted PAH prevail in ancient sediments (Blumer and Youngblood, 1975; Youngblood and Blumer, 1975). Nevertheless, the alkyl homologues of tri-, tetra-, and pentacyclic PAH display very little variation in Recent marine sediments. This constancy in PAH distribution possibly indicates that PAH and their alkyl derivatives have a common origin.

Natural fires are thought to be the major source of sedimentary PAH (Radke, 1987). PAH derived from incomplete combustion of plant material, when absorbed on soot particles retain their original distribution during long-range air transportation (Lunde and Bjøseth, 1977; Windsor and Hites, 1979). A lower methylphenanthrene/phenanthrene ratio than that typically measured in petroleum is considered to be indicative of anthropogenic combustion PAH (Blumer and Youngblood, 1975; Prahl and Carpenter, 1983). Hites *et al.* (1977) observed that in sediments deposted during human history, an upward increase in the total abundance of unsubstituted PAH, grossly parallels the calculated PAH production from anthropogenic combustion.

Parent PAH (Fig. 2.12c), such as fluoranthene (I), pyrene (II), chrysene (III) and triphenylene (IV), are more abundant than their respective alkyl-substituted derivatives in Recent marine sediments (Meinschein, 1959). This observation contrasts with the situation in crude oils where typically higher relative concentrations of alkyl-substituted PAH are evident. Thus, PAH from Recent sediments are not representative of sediments in general.

Many early studies aimed at detecting primary sources of PAH in Recent sediments were hampered by the unrecognised effects of erosion and successive resedimentation of sedimentary organic matter inputs from oil seeps; and anthropogenic pollution, by oil spills and the combustion products of fossil fuels. However, recent investigations of PAH in marine environments far from industrialised areas have revealed a background of pyrolytic-parent PAH, such as phenanthrene, fluoranthene, and pyrene (Tissier and Saliot, 1983), impliying that pyrolytic-like PAH were probably derived partly from natural combustion processes and partly from diagenesis.

Depth profiles of parent PAH in Recent sediment cores showed an exponential concentration decrease with depth, in situations where, during the past eighty years, sediments had received a continuous input of anthropogenic PAH. Deviating trends for individual PAH such as retene and perylene and for series of hydrochrysenes and hydropicenes, implies that these PAH are probably of biogenic origin (Wakeham *et al.*, 1980b; Tan and Heit, 1981).

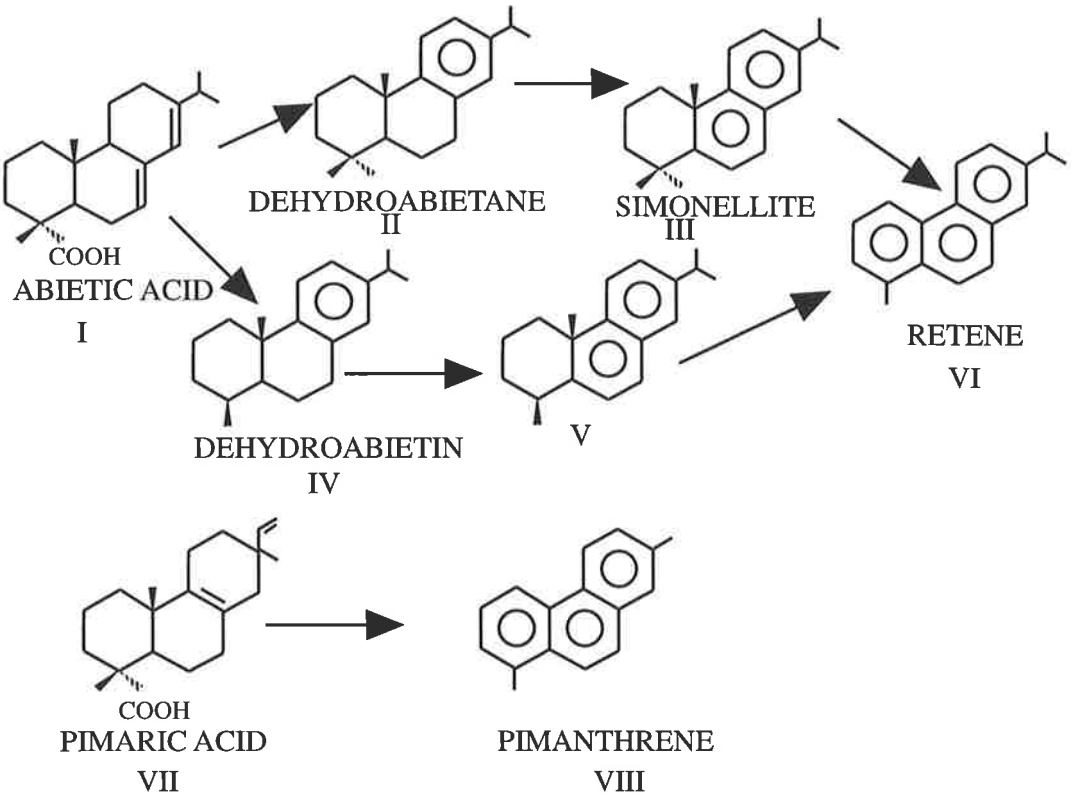


Figure 2.13 Suggested precursors and several intermediates in the *in situ* generation of retene (IV) and pimanthrene (VIII) (Wakeham et al., 1980b; Radke, 1987)

The occurrence of minor concentrations of retene, together with substantially higher concentrations of the structurally related compounds abietic acid, dehydroabiatic acid, methyldehydroabietane and dehydroabietane, in forest soil (Swan, 1965; LaFlamme and Hites, 1978) suggests that they are of biogenic origin.

Figure 2.13 illustrates the suggested precursors and intermediates in the *in situ* generation of retene (VI) and pimanthrene (1,7-dimethylphenanthrene: VIII) (Wakeham *et al.*, 1980b). Although abietic and pimaric acids are thought to be the respective precursors of retene and pimanthrene, other resin constituents belonging to the abietane-pimarane skeletal types (Thomas, 1969; Hanson, 1972) also could be sources by way of diagenetic rearrangement of their skeletons. It is also possible that retene may be contributed from the combustion of coniferous wood (Ramdahl, 1983).

2.7.1. Ancient sediments

Low-molecular-weight mono- and diaromatic hydrocarbons appear to be ubiquitous in ancient sedimentary rocks. Carotenoids, terpenoids and alkaloids have been suggested to be precursors for alkylbenzenes. Ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene), toluene, *m*-xylene and 2,6-dimethylnaphthalene were produced from thermal degradation of β-carotene (Day and Erdman, 1963; Ikan *et al.*, 1975). Minor quantities of 1-methyl-3-ethylbenzene and 1,6-dimethylnaphthalene, together with traces of 1,5-, 2,3-, and 2,7-dimethylnaphthalene, were produced from the pyrolysis of β-carotene in mesitylene at 150-170°C (Byers and Erdman, 1983).

Several high-molecular-weight aromatic hydrocarbons, including six types of PAH, were distinguished in soils sediments and sedimentary rocks by Hodgson *et al.* (1968). Some rare types of PAH have been identified in organic minerals. Pendletonite was shown to consist almost entirely of coronene (Murdoch and Geissman, 1967; Blumer, 1975) while curtisite and idrialite consist of chrysene and picene (Geissman *et al.*, 1967). A series of highly condensed aromatics, including alkyl homologues, sulphur- and nitrogen heterocycles with ring numbers ranging from four to seven were found in the latter minerals (Blumer, 1975). Although the primary sources of these PAH compounds remain unknown, their mineral accumulations were possibly derived from medium-temperature pyrolysis of sedimentary organic matter.

PAH have been observed in extracts of oil shales (Anders *et al.*, 1973) and coals (Hayatsu *et al.*, 1978; White and Lee, 1980; Radke *et al.*, 1982b), and in retort oils (Ingram *et al.*, 1983). These aromatic compounds, however, were found to be more difficult to correlate with natural precursors than is the case with saturated biomarker molecules. The occurrence of a substantial concentration of retene, along with fichtelite, in wood stumps sunk in peat (Skrigan, 1964) suggests that the PAH might have formed from unsaturated terpenoid

precursors by a disproportionation process involving intramolecular hydrogen transfer reactions among molecules of the same species (Eglinton, 1969). This view is supported by heating experiments, which show that under clay catalysis disproportionation may account for up to 50% aromatisation (Frenkel and Heller-Kallai, 1977). However, as noted by Radke (1987), in typical sedimentary conditions where other dehydrogenating agents besides the substrate itself will generally exist, such disproportionation reactions are not likely to be significant.

A stepwise aromatisation of saturated or partially unsaturated six-member rings in steroids and polycyclic terpenoids (Hussler *et al.*, 1981; Mackenzie *et al.*, 1981; Ludwig *et al.*, 1981) appears to be one means by which PAH are formed. For example, the persistence of at least one naphthenic ring per molecule during diagenesis and catagenesis provides an unambiguous link with known contemporary natural products such as hopanoids and steroids (e.g. Mackenzie, 1984)

2.7.1.4 Crude oils

Benzene and its alkylated homologues predominate in the low-molecular weight-aromatic hydrocarbon fraction of crude oils (boiling point up to 218°C: Smith, 1967) whilst methyl groups are the main substituents in C_8-C_{10} alkylbenzenes (Martin *et al.*, 1963). The abundance of methyl group substituents in alkylbenzenes has been considered to be a sign of their terpenoid origin (Mair, 1964). Terpenoids having similar structures, but unsaturated side chains, are known to occur in living organisms. For example, there is a possibile genetic relationship between limonene and *p*-cymene; and cadalene (1,6-dimethyl-4-isopropyl-naphthalene) may originate from cadinene. Farnesol has to be considered as another possible precursor of alkylbenzenes. High molecular weight alkylbenzenes have occasionally been identified in the gas chromatograms of monoaromatic petroleum fractions.

Examples of PAH compound types commonly found in crude oils are shown in Figure 2.14. Anthracene homologues are not normally major components, although a significant concentration have been encountered in certain oils (Carruthers, 1956). Phenanthrenes generally dominate over anthracene type compounds (Smith, 1967) and the phenanthrene/anthracene concentration ratio is about 50 (Grimmer and Böhnke, 1978). Variations in the concentrations of the prominent PAH in crude oils are suspected to be related to differences in the maturities of the oils (Grimmer and Böhnke, 1978).

2.7.2 Thermal maturation indicators based on aromatic hydrocarbons

Thermocatalytic reactions which occur in the source rock (or in the reservoir) during maturation are believed to be the cause of changes in the molecular composition of aromatic fractions of rock extracts and crude oils. Hydrogen transfer and cleavage of carbon-carbon single bonds are probably the major reaction types.

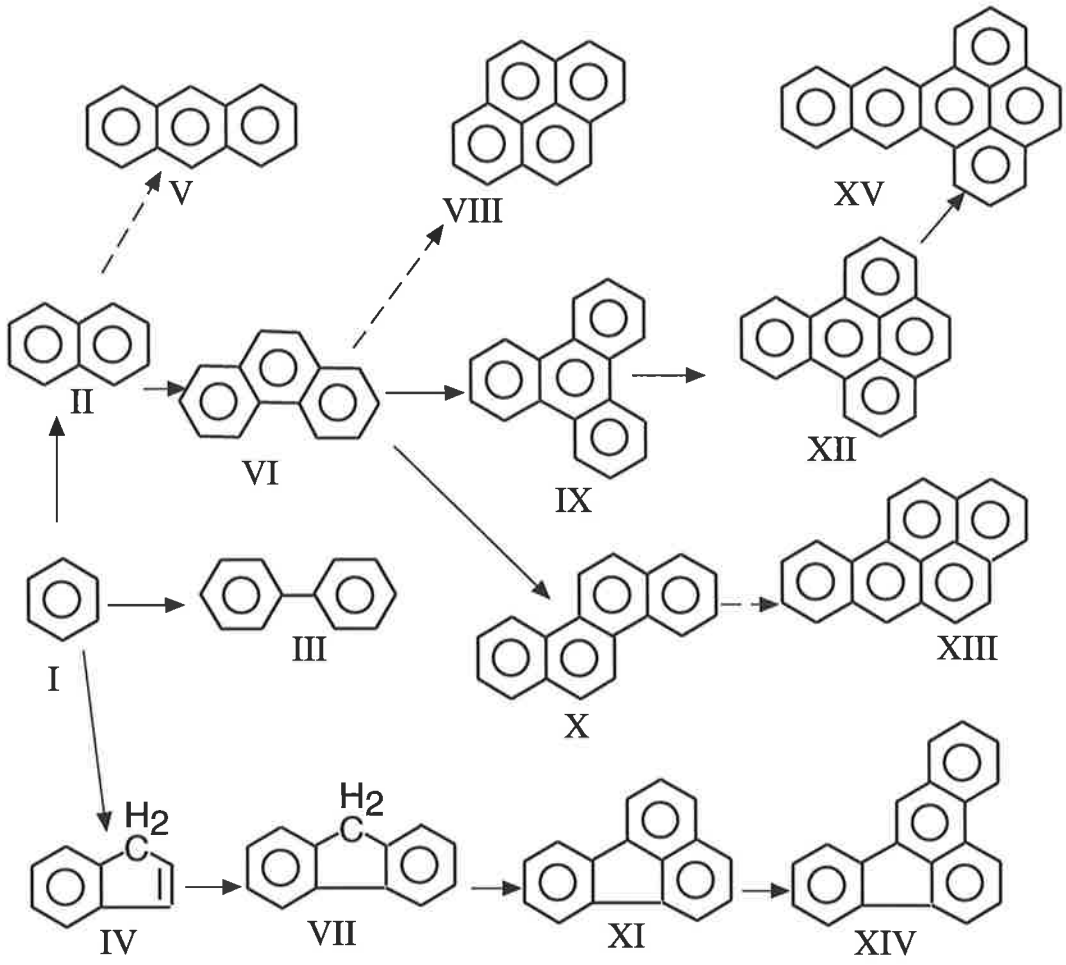


Figure 2.14 Aromatic compound types prevailing in crude oils and their structural relationship. Broken arrows point toward PAH types of minor importance (Grimmer and Bohnke, 1978; Radke, 1987).

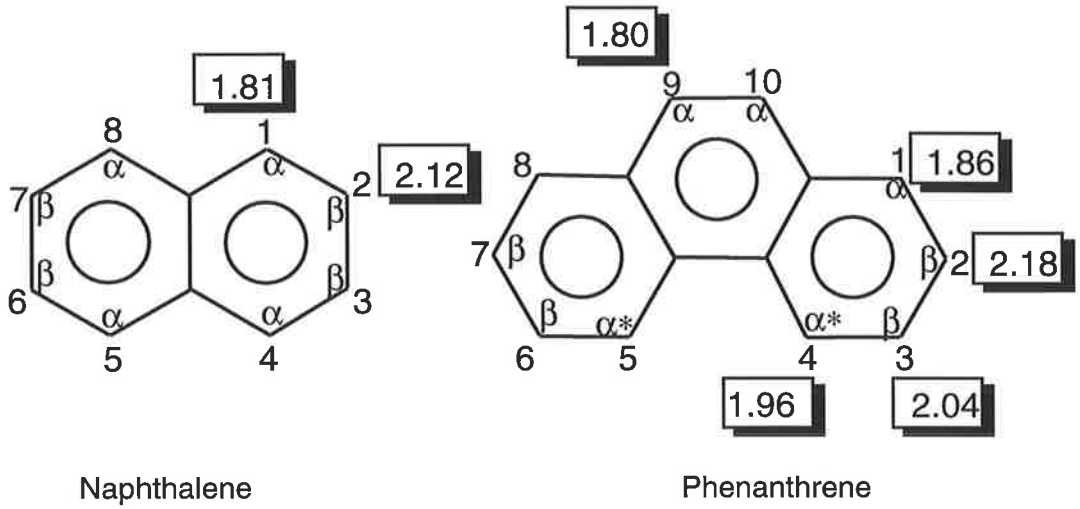


Figure 2.15 Dewar's reactivity numbers, Nr (bold figures) for naphthalene and phenanthrene (Dewar, 1952). Positions are designated by integer numbers. Sterically crowded positions where reactivity is lower than indicated by the Nr value are marked by asterisks (after Radke, 1987).

The net effect of those reactions is to produce, from a complex mixture of alkyl- and cycloalkylaromatics, an aromatic fraction that becomes increasingly depleted in hydrogen as thermal evolution proceeds, and a hydrogen-rich saturated hydrocarbon fraction (Alexander *et al.*, 1980). The following discussion draws heavily on Radke (1987).

Table 2.6. Maturity parameters based on aromatic hydrocarbons (after Radke, 1987)

Abbreviation	Name	Definition
DNR-1	Dimethylnaphthalene ratio	$\frac{\text{2,6-DMN+2,7-DMN}}{\text{1,5-DMN}}$
TNR-1	Trimethylnaphthalene ratio	$\frac{\text{2,3,6-TMN}}{\text{1,3,5-TMN+1,4,6-TMN}}$
TNR-2		$\frac{\text{1,3,7-TMN+2,3,6-TMN}}{\text{1,3,5-TMN+[1,3,6-TMN+1,4,6-TMN}}$
MPR-1	Methylphenanthrene to phenanthrene ratios	$\frac{\text{1-MP}}{\text{P}}$
MPR-2		$\frac{\text{2-MP}}{\text{P}}$
MPR-3		$\frac{\text{3-MP}}{\text{P}}$
MPR-9		$\frac{\text{9-MP}}{\text{P}}$
MPR		$\frac{\text{2-MP}}{\text{1-MP}}$
MPI-1	Methylphenanthrene index	$\frac{\text{1.5(2-MP+3-MP)}}{\text{P+1-MP+9-MP}}$
Rc-1	Calculated reflectance	0.60 MPI-1 + 0.40 (for % Rm <1.35) or -0.60 MPI-1 + 2.30 (for Rm ≥1.35%)

2.7.2.1 Methylphenanthrene index (MPI-1)

The methylphenanthrene index is based on the relative abundance of the four isomeric methylphenanthrenes (1-MP, 2-MP, 3-MP and 9-MP) and phenanthrene and shows a good correlation with measured vitrinite reflectance values (Ro) between 0.67 and 1.35% (Radke *et al.*, 1982a). The intensities of individual mono- and dimethylphenanthrenes relative to phenanthrene show a gradual change with depth, and are thus indicated to be sensitive to variation in thermal maturation. Apparent relationships between MPI and carbon-normalised

C_{15+} hydrocarbon yields are an indication that the generation of heavy hydrocarbons from Type III kerogen is accompanied by methyl-transfer reactions (Albrecht *et al.*, 1976).

Provided that phenanthrene has been involved in the methyl-transfer reactions taking place concomitant with hydrocarbon generation, then the coincident depth trends of 1- and 9-methylphenanthrene to phenanthrene ratios (MPR-1, MPR-9) may be explained on the basis of the very similar reactivities of the C-1- and C-9 positions (Fig. 2.15). Methylation may have involved also possible phenanthrene precursors, such as hydrophenanthrenes. A conversion of alkyldihydrophenanthrenes to alkylphenanthrenes with thermal evolution has been reported in the organic extracts of coal macerals (Allan and Larter, 1983).

As subsurface temperature increases, potential sources of methyl groups (e.g isoprenoid derived structural units in kerogen) will become more productive, hence resulting in the observed increase in various alkylphenanthrene/phenanthrene ratios until the maximum of C_{15+} hydrocarbon generation at 0.9% R_O. Beyond this point methyl-group sources presumably become more and more exhausted. The MPR-2 and MPR-3 values increase beyond 0.9-1.3% R_O. This behaviour was interpreted to result from steric-strain-induced reactions whereby methyl groups shift from α positions to sterically less crowded β positions. The approach to minimum values of all ratios beyond 1.3% R_O (i.e. the lower limit of the oil window), is believed to reflect a change in the predominant reaction type from methyl transfer to demethylation. The methylphenanthrene index overcomes some of the limitations observed in the aforementioned MPR ratios where there is either a trend reversal at the peak of oil generation or a low sensitivity.

2.7.2.2 Maturity assessment of crude oils and condensates

Based on calibrations of MPI-1 versus R_O, the R_C (calculated vitrinite reflectance) parameter for crude oil maturity was invented (Radke and Welte, 1983). MPI-1 values of the vast majority of the crude oils fall in the 0.35–1.00% range, corresponding to R_C values of 0.61–1.00%. Different oil types have tentatively been classified into maturity categories with respect to R_C value (Radke, 1987). Immature oils are those with R_C values <0.70%; whereas mature oils have values of 0.7-0.95%, and postmature oil values of >0.95%. From bulk oil parameters, such as API gravity and gross composition it is evident that thermal evolution of their respective source beds had probably not passed beyond R_O = 1.35% at the time the oils were released. Furthermore, the maturity of an oil is likely to be related to the kerogen type in the source rock from which it was generated. Tissot and Welte (1984) related the kerogen type to the composition of the crude oil it produces, thus inventing analogous oil types. Accordingly, different oil types may be distinguished based on their Rc values and bulk composition. It is usually assumed that the R_C value of a given oil will correspond to the R_O value of the source rock at the time of expulsion. This will be true provided that the original distribution of phenanthrene and its methyl homologues was retained during primary and secondary migration of the oil (Radke, 1987).

Type I oils belong to the paraffinic class and commonly have high wax and low sulphur contents. They are derived from Type I kerogen (sapropelic), which has a liptinite content >90%; hydrogen index > 650 mg HC/g TOC and oxygen index <25 mg CO2/g TOC; and H/C atomic ratio >1.5 and O/C atomic ratio <1.0. The liptinite precursors are largely freshwater algae and the biodegraded remains of terrestrial plants which, together with microbial biomass, were deposited in a eutrophic deep-water lacustrine palaeoenvironment. The R_C distribution of this oil type ranges from 0.57 to 0.71% with its mode at 0.65%.

Alkylphenanthrenes are virtually absent in the oils released from source rocks containing Type I kerogen because the major proportion of the kerogen is liptinitic with a structure known to be mainly aliphatic at the immature stage. Secondly, polycyclic aromatic structural units that are formed during catagenesis tend to remain incorporated in the three-dimensional kerogen network, and thus do not contribute significantly to oil formation. Therefore, the available alkylphenanthrenes are generated from a minor vitrinitic component of the kerogen and hence are similar to those of the soluble organic matter derived from immature Type III kerogen. Alternatively, they are picked up by the oil on its passage through adjacent Type III kerogen-containing strata.

Type I/II oils are aromatic-intermediate crudes which exhibit lower wax and higher sulphur contents than Type I oils. They are probably derived from a subtype of Type II kerogen, defined as Type IIB by Radke *et al.* (1986). The liptinite content of this kerogen is high, as is its as initial hydrogen index, whilst the oxygen index may have moderate values (up to 50 mg HC/ g TOC). It is composed almost entirely of biodegraded phyto- or zooplankton deposited in an anoxic shallow marine environment. The R_C distribution of its derived oils ranges from 0.66 to 0.81%, with the mode around R_C 0.75 ± 0.05%. The aforementioned R_C interval is in agreement with the generally accepted view that significant oil generation and expulsion from source rocks containing Type II kerogen occurs at 0.7-0.8% R_O. The presence of alkylphenanthrenes in Type II kerogen is attributed to amorphous liptinite (Radke *et al.*, 1986).

Type II/III oils are not grouped under any specific class defined by Tissot and Welte (1984). The oils are derived from mixtures of detrital Type II and III kerogens, with the former being predominant. Elevated liptinite contents are commonly observed along with elevated hydrogen index values in the range 100–300 mg HC/g TOC. Oxygen index values are very variable but generally greater than in the aforementioned types. The kerogen is commonly composed the remains of aquatic organisms and terrestrial plants deposited in moderately anoxic, lagoonal or deltaic environments. The R_C distribution of these oils ranges from 0.75–0.92%, with a mode at 0.82%.

Type III/II oils are also not grouped under the Tissot and Welte (1984) classification. These oils are presumably derived from a mixed Type II/III kerogen with a strong terrestrial organic matter input. Their R_C distribution has a mode at 0.90% and the maximum value at 1.02%. This mode, however, may correspond to a second maximum (Radke, 1987: Figure 19) of oil expulsion from the same Type II/III kerogen which have already released Type II/III oils.

2.7.2.3 Methylphenanthrene ratio (MPR)

The relationship between the 2- and 1-methylphenanthrene ratio (i.e. MPR = 2-MP/1-MP) and R_O is non-linear and unlike MPI-1 is not reversed at the base of the oil window. With R_O values ranging from 0.4–4.9%, MPR values increase exponentially up to R_O = 1.7% (Radke *et al.*, 1984b). The log MPR and R_O values are closely correlated in the 0.4–1.7 %Rm interval (Radke, 1987). Regression analysis of the data shows that the Rm value of 1.35% (floor of oil window) corresponds to an MPR value of 2.24.

Nevertheless, conflicting results were obtained for immature samples containing low quality kerogen in that their MPR values showed considerably higher maturities than those obtained from the MPI values. It was later revealed that these samples contained pyrolytic-like PAH distributions which are widespread in unpolluted Recent sediments (Tissier and Saliot, 1983). Such distributions are marked by the predominance of phenanthrene, fluoranthene and pyrene over their respective alkyl homologues. Thus, the relatively low MPI values in these sediments are caused by their high abundance of pyrolytic phenanthrene. As in Recent sediments, a background level of pyrolytic-like PAH exists in ancient sediments but here they are normally outweighed by PAH derived from catagenesis.

2.7.2.4 Methylnaphthalene homologues

Just as methyl-transfer reactions favour the most reactive α-position of phenanthrene and therefore control the distribution patterns of methylphenanthrene homologues in the initial stages of oil generation, so too the α-positions in naphthalene (Fig. 2.15) are favoured in the same type of reaction. This results in similar elevated relative abundances of the α-methyl isomers (2-MN), over the β-methyl isomer (1-MN). In high volatile bituminous coals, the ratios of the 2- to 1-methyl isomers of naphthalene (MNR) and of phenanthrene (MPR) exhibited very similar minimum values of 0.43 and 0.42, respectively, thus providing circumstantial evidence for a possible kinetic control of PAH distributions at lower rank stages (Radke *et al.*, 1984b).

The proposed shift of α-methyl groups to β-positions at elevated temperatures (Radke *et al.*, 1982b), coincides well with the observed increase of MNR values with rank. However, the relative increase of 2- over 1-methylnaphthalene does not necessarily mean a conversion of one compound to the other, as there could be other possible precursors. It has been argued

that α-substitution leads to the greater reactivity of the naphthalene homologues in general, which may be prompted to enter into other reactions (e.g. condensation) besides rearrangement (Madison and Roberts, 1958). Conversions of dimethylnaphthalenes with two α-methyl groups, (e.g. 1,4-, 1,5- and 1,8-DMN) are likely to be controlled by similar chemical principles. The abundance of kinetically more stable α,β- and ββ- DMN isomers increases with thermal maturation relative to those with two α-methyl groups.

***Dimethylnaphthalene ratios* (DNR)**

Several dimethylnaphthalene ratios have been developed (Radke *et al.*, 1982b; Alexander *et al.*, 1984, 1985) for the purpose of maturity assessment (Table 2.6). Most of the DNR's proposed by Alexander *et al.* (1985) rely on the decreasing abundance of 1,8-DMN, the least stable isomer, with increasing maturity. A rather good correlation between DNR-1 and R_o values has been observed (Radke *et al.*, 1982b).

***Trimethylnaphthalene ratios* (TNR)**

Two trimethylnaphthalene ratios (viz. TNR-1 and TNR-2: Table 2.6) were introduced by Alexander *et al.* (1985) and Radke *et al.* (1986), respectively. Both ratios have shown good correlation with %Rm values (Alexander *et al.*, 1985). Good correlations have also been found between TNR-2 and MPI-1 (Radke, 1987) and between TNR-1 and DNR-1 (Alexander *et al.*, 1988).

2.7.3 Alteration of crude oils in reservoirs

Biodegradation and water washing are two common processes which may alter the composition of the crude oil in the reservoir. The original aromatic distributions of crude oils are particularly susceptible to alteration. The distinction between altered and unaltered crude oils is commonly based on the solubility and resistance to biodegradation of aromatic compounds. Dibenzothiophene and methyldibenzothiophenes have greater solubility in water than phenanthrene and methylphenanthrene, respectively (Palmer, 1984). Thus, increases in the concentration of phenanthrenes relative to dibenzothiophenes with proximity to water-saturated reservoir zones have been attributed to water washing effects. Connan (1984) and Williams *et al.* (1986) noted the possibility of biodegradation of aromatic sulphur compounds. Therefore the low ratios of phenanthrenes to dibenzothiophenes could partly be due to biodegradation.

The selective losses of PAH components from the extractable organic matter of coal has also been attributed to water washing (Radke *et al.*, 1982b). A preferential depletion of components with relatively high solubilities in water, such as mono- and dimethylnaphthalenes and benzothiophenes, was reported in the organic extracts of coals samples derived from water-drained localities. The same samples seemed to be also depleted in phenanthrene, whilst the methylphenanthrene homologues apparently were not affected.

This tendency of preferential depletion of phenanthrenes is likely to be a cause of elevated MPI-1 values. An increase in PAH maturity parameters is also expected where α- and β-type isomers are involved. This is because the α-type isomers are more polar, presumably more soluble in water, and thus preferentially removed. As water washing affects the concentrations of C_1–C_3 naphthalenes more readily than those of phenanthrenes, comparisons between maturity indicators based on distributions of these compound types, such as TNR-2 and MPI-1 may also provide a clue to the effects of water washing (Radke, 1987).

As yet the possible effects of biodegradation on PAH maturity parameters appear to have not been investigated in much detail. However, it has been reported that biodegradation also results in preferential loss of individual alkylnaphthalene and alkylphenanthrene isomers (Volkman *et al.*, 1984; Williams *et al.*, 1986) which likewise would affect the respective maturity parameters.

Chapter 3

Analytical Methods

3.1 Introduction

The ability of the petroleum geochemist to answer geological and other queries which arise during an exploration program is entirely dependent on results of various geochemical analyses. Usually these analyses are carried out on rock cuttings, side wall cores, pieces of outcrop, formation waters drilling muds and fluid hydrocarbons (oil, condensate and gas). To meet the objectives of this study, rock cuttings and core samples of the Poolowanna Formation from selected wells in the Patchawarra and Poolowanna Troughs, and crude oils from adjacent reservoirs of the Eromanga and underlying Cooper and Warburton Basins were examined (Tables 1.1, 1.2 and 1.3). The analyses carried out are summarised in Figure 3.1.

3.2 Sample collection and preparation

Rock cuttings and cores were collected from the core library of the South Australian Department of Mines and Energy at Glenside, S.A. Sample selection was based on lithological and wire-line log data (Table 1.2) such that the well sections with relatively high gamma ray readings (>100 API units) were preferentially selected. A portion (ca 20 g) of the stored material (in most cases cuttings) from each of the targeted intervals was transferred into a pre-labelled polythene bag. Cutting samples which contained dry drilling mud were water washed and then air dried. Contaminants and cavings were removed with the aid of a binocular microscope, and core samples with visible residues from marker pens and mud cake were either brushed or scraped clean. The major portion of the sample was ground to a powder in a Seibtechnik ring mill. Samples of crude oils were provided by Santos Limited from their storage facility at Gillman. Most of analyses were carried out in the Organic Geochemistry Laboratory (OGL) of the Department of Geology and Geophysics at Adelaide University.

3.3 Screening analyses

Screening is a preliminary appraisal of samples which allows non-source rocks to be eliminated, and oils and source rocks to be grouped into families that can be submitted to more detailed analyses. Organic petrology, total organic carbon (TOC) determination and Rock-Eval pyrolysis are the main screening methods commonly used. During this study 45 rock cuttings and cores were screened. In addition, 24 oil samples were selected for preliminary analysis by using column and gas chromatography.

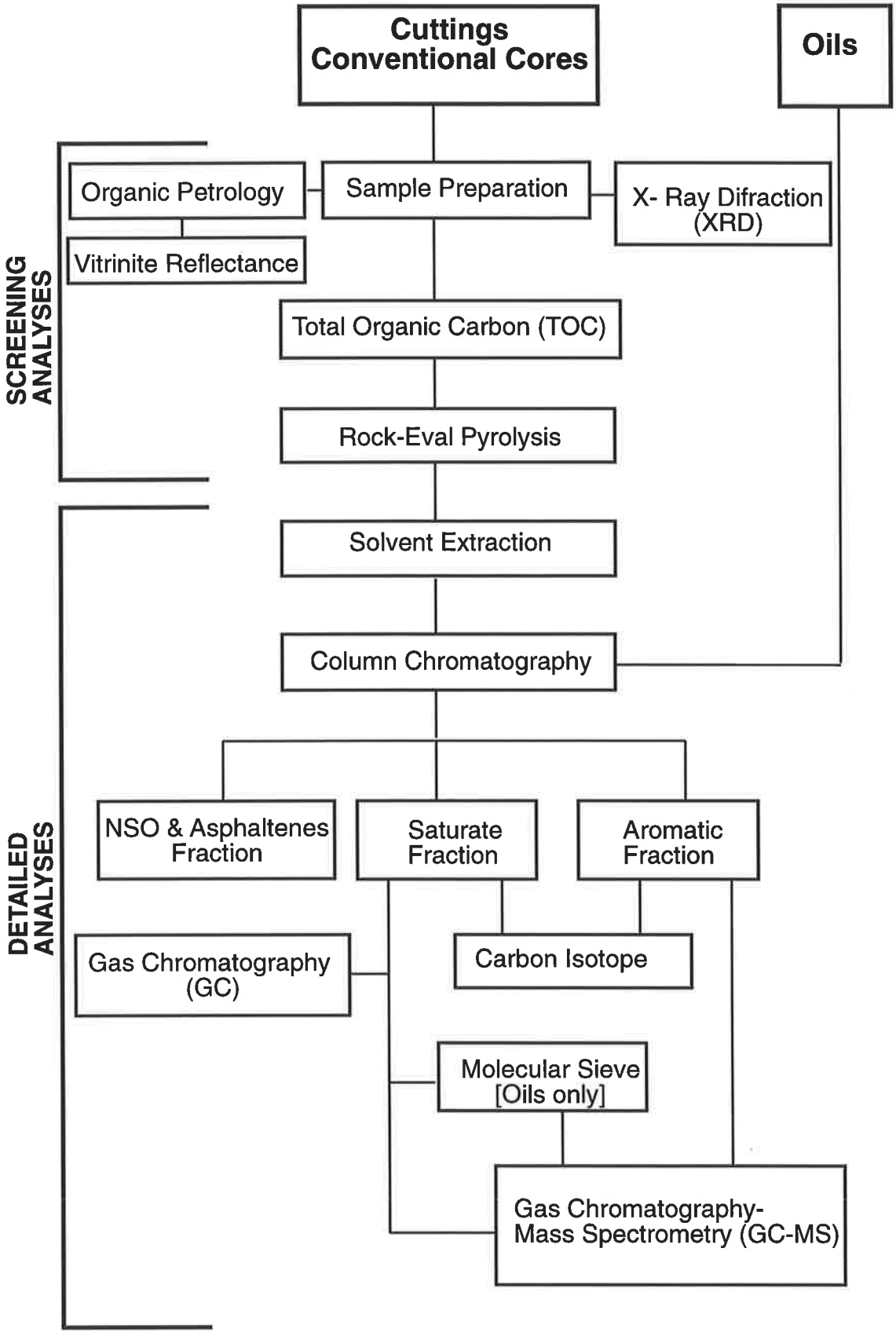


Figure 3.1 Flow diagram for source rock and petroleum geochemical analyses

3.3.1 Organic petrology

This is the microscopic study of coal and dispersed organic matter (DOM) using either transmitted or reflected white light and either UV or blue light irradiation. The properties of a given organic matter assemblage are determined by the proportions and identities of the petrographic components (macerals) present and their rank or degree of thermal evolution. In addition to the macerals, certain constituents of the mineral matter in coal and other sedimentary rocks may be determined.

The rock sample is prepared from either rock fragments (cuttings) or core pieces which are mounted in a block of cold setting resin and then ground and polished to give a flat surface. The polished block is examined under immersion oil using a reflected light microscope and the macerals are identified by their relative reflectance, colour, morphology and fluorescence characteristics. The proportion of each maceral is determined by the point-counting method.

3.3.1.1 Sample preparation

Either cuttings or core blocks were mounted in plastic moulds using a mix of araldite resin and a hardener. After removing excess air from the moulds, and curing the araldite in air at 40°C, the samples were first ground using carborundum paper and water (for coals) or ethanol (for shaly samples). Polishing of the samples with one micron diamond paste followed. The final polishing was carried out using either magnesium oxide and distilled water, and cleaning with distilled water or ethanol on Selvyt cloth; or by using quarter micron diamond paste and kerosene on Buehler micro cloth, and cleaning with ethanol on Selvyt cloth.

3.3.1.2 Optical microscopy

A Leitz Ortholux II Pol microscope was employed for this type of petrographic analysis. It was equipped with three light sources: white light for general observation and photography, stabilised white light for reflectance measurements, and blue light for fluorescence irradiation. A x10 ocular and a x50 oil immersion objective were routinely used, although in some cases the x32 and x120 objectives were also employed. For photography, a Wild Leitz camera and a x50 objective coupled with a x12.5 ocular was fitted to the microscope. When measuring vitrinite reflectance, a photomultiplier and a stabilised lamp source were fitted. The microscope on which the reflectance work was undertaken is housed at AMDEL Limited, Thebarton.

Maceral identification and quantification

Guidelines provided by the International Committee for Coal Petrology (1975) and the Standards Association of Australia (1986) were used to identify the maceral groups and their corresponding macerals under reflected white light and fluorescent blue light. Quantification of the macerals was achieved by employing a point counting device fitted to the microscope

stage. Counts were acquired by traversing the block and alternating the light modes on every move. At least 100 counts were made on every block. The relative abundance of each maceral was reported as percentage of the sum of all the macerals identified in the block. In addition the content of pyrite was reported as a percentage of the total macerals plus pyrite counts.

Vitrinite reflectance measurements

The reflectance at near normal incidence of vitrinite phytoclasts was measured under oil immersion using a photomultiplier. Before measuring the reflectance, the AMDEL microscope was first calibrated using two standards: synthetic spinel with a reflectance of 0.42% and synthetic yttrium aluminium garnet (YAG) with a reflectance of 0.92% at 546 nm wavelength. Calibrations were repeated after several measurements in order to maintain identical conditions for the standards and the mounted samples. At least 40 readings were taken from every sample depending on the abundance of vitrinite in the block. A mean random value (R_O) was obtained as the arithmetic average of the total number of readings from the sample.

3.3.2 Total organic carbon (TOC) analysis

TOC is a measure of the total organic carbon in a rock, usually expressed as weight percent. It is used as a fundamental parameter in source rock classification, along with kerogen type and maturity. For this study the TOC values were determined on ground cuttings and core samples by Geotechnical Services Pty Ltd, Western Australia. Carbonate minerals were first removed by acid digestion using hydrochloric acid (HCl) after which the sample was heated to 1700°C in a Leco Induction Furnace under an atmosphere of pure oxygen. The CO_2 produced was measured through an infrared detector, and processed by way of a standard calibration to give TOC values.

3.3.3 Rock-Eval pyrolysis

This method is based on the standard pyrolysis technique developed by Espitalié *et al.* (1977) for source rock characterisation and evaluation. It enables the bulk chemical composition of kerogen, and hence its hydrocarbon potential, to be determined. There are two automatic pyrolysis steps under which about 100 mg of ground sample is progressively heated in the pyrolysis oven to 550°C under an inert atmosphere of helium. The resulting pyrogram is shown in Figure 3.2.

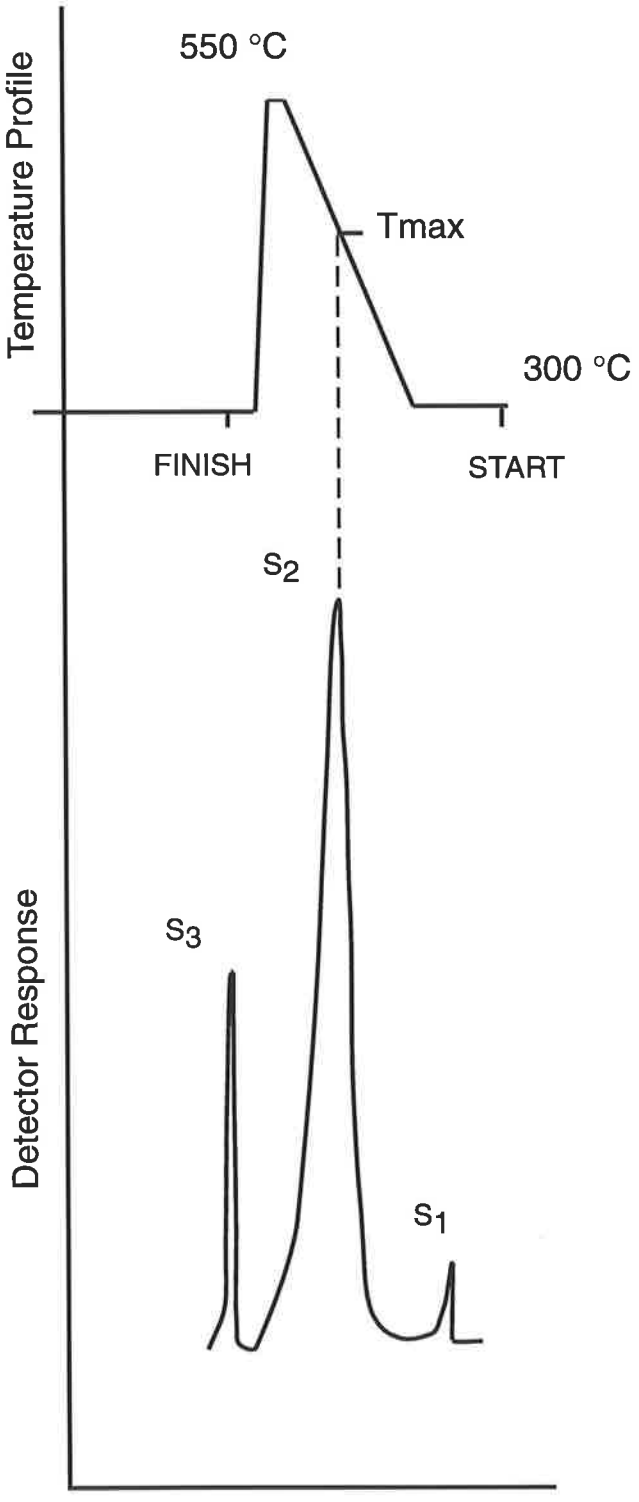


Figure 3.2 Schematic pyrogram of Rock-Eval pyrolysis

In the first step, hydrocarbons present in a free or adsorbed state (S_1) are volatilised at 300°C. The amount of these hydrocarbons is measured by a flame ionisation detector (FID). In a second step, the temperature is ramped from 300 to 500°C, whereupon hydrocarbons and hydrocarbon-like compounds (S_2) and oxygen-containing volatiles, i.e. carbon dioxide (S_3) and water, are generated as result of kerogen pyrolysis. The S_2 compounds are then measured through a FID, whilst S_3 is measured through a thermal conductivity detector. The measurement of S_3 is limited to a convenient temperature window (300–340°C) so that only the main stage of CO_2 generation from kerogen is included, and to avoid inorganic sources of CO_2. This analysis was also carried out by Geotechnical Services Pty Ltd. Only samples with TOC values >1.0% were analysed.

The various parameters measured, including T_{max} are: hydrogen index (HI), oxygen index (OI), production index (PI) and potential yield (S_1+S_2), are defined in Table 2.3.

3.4 Bitumen extraction

Bitumen or extractable organic matter (EOM) is removed from rock samples using organic solvents. Two extraction techniques are commonly employed, viz. ultrasonic and Soxhlet extraction. Ultrasonic extraction uses a cold solvent for short period of time, commonly an hour or less, whereas Soxhlet extraction involves refluxing, of hot solvent for 24 hours or more. The amount of extract may be used to determine the level of source rock maturation and in estimation of source rock potential yield (LeTran *et al.*, 1974; Philippi, 1974). Soxhlet extraction was employed during this study, as discussed below.

3.4.1 Soxhlet extraction

A pre-weighed portion of powdered rock (5-40 mg) was poured into a pre-extracted paper thimble and placed into the Soxhlet apparatus azeotropic mixture of dichloromethane (DCM) and methanol (93:7 v/v, 450 ml) was prepared and placed in a 500 ml round bottom flask. Pre-extracted anti-bumping granules and activated copper tunnings were added to the solvent flask which was later fitted to the Soxhlet extractor. Extraction was allowed to continue for at least 72 hours after which the extract solution was rotary evaporated until only 1–2 ml of solvent remained. The extract was then transferred into a pre-weighed vial and left to dry in air. When dry (i.e. the sample and the vial) were re-weighed and the weight of extractable organic matter (EOM) or bitumen obtained. All solvents (AR grade) were redistilled prior to use. The weight of extract is presented as % EOM or ppm EOM using the following formulae:

$$\%\,\text{EOM} = \frac{\text{Wt EOM}}{\text{Wt Sediment Extracted}} \times 100$$

$$\text{ppm EOM} = \frac{\text{Wt EOM (mg)}}{\text{Wt Sediment Extracted (kg)}}$$

3.5 Column chromatography

This form of liquid chromatography is the means by which bitumen (EOM) and crude oil are commonly separated into fractions of different polarity. Their separation is based on the "like-dissolves-like principle" whereby solvents most readily dissolve solutes of approximately the same polarity.

3.5.1 Sample and column preparation

Columns were prepared by packing 10 x 400 mm burettes with a slurry of activated silica gel (Kieselgel 40) in petroleum ether to about 4/5th full. The slurry was then topped up with 2–3 spatula of alumina (Merck 60, 70–230 mesh).

A small quantity (ca 50 mg) of each rock extract or oil sample was dissolved in DCM and then transferred onto dry activated alumina. The mixture of the sample and alumina was then left open to the air allowing the solvent to evaporate; occasionally the mixture was slightly heated to less than 40°C to facilitate solvent evaporation. Then, the dry adsorbed sample was gently poured onto the top of the column.

3.5.2 Chromatography of rock extracts and crude oils

Rock extracts and crude oil samples were separated into saturated hydrocarbons, aromatic hydrocarbons and NSO (nitrogen, sulphur, and oxygen-bearing compounds). The saturates fraction was eluted with 80 ml of petroleum ether and the eluate collected into a labelled 250 ml round bottom flask. When the last portion of the petroleum ether was still just covering the top of column packing, a mixture of petroleum ether and DCM (50:50 v/v, 80 ml) was added to elute the aromatic fraction. This formed a yellow band which was monitored down the column. As the yellow band of the eluate approached the base of the column, a new labelled round-bottom flask was put in place to collect the aromatic fraction. The NSO-compounds were eluted by adding mixture of DCM and methanol (35:65 v/v 80 ml). An additional 40 ml of methanol was added to obtain the entire polar fraction.

The excess solvent in the three eluted fractions was removed on a rotary evaporator. The fraction concentrates were then transferred to labelled, pre-weighed vials where they were dried in open air and then weighed. The weight of each fraction was used to calculate the percentage of each fraction in the rock in accordance with the following formulae:

$$\%\ \text{Fraction} = \frac{\text{Wt Fraction}}{\text{Wt of all Fractions}} \times 100$$

$$\text{ppm Fraction} = \frac{\text{Wt Fraction (mg)}}{\text{Wt Sediment Extracted (kg)}}$$

3.6 Stable carbon isotopic analysis

In this study carbon isotopic analyses were undertaken on the saturate hydrocarbon and aromatic hydrocarbon fractions from both rock extracts and crude oils. For $^{13}C/^{12}C$ determination, it is necessary to convert the carbon in the sample to CO_2.

3.6.1 Sample preparation

About 4 mg of the sample dissolved in dichloromethane was poured into a quartz tube and left in the open air until the solvent had evaporated. Cupric oxide (BDH, wire form, ~400 mg) was added to the quartz tube. The tube with sample was then evacuated and flame-sealed. To generate CO_2 from the sample, the tube was placed in a muffle furnace at room temperature, the temperature was raised to 900°C and maintained there for 6 hours.

3.6.2 Purification of CO_2 generated from the sample

The quartz reaction tube was allowed to cool to room temperature before it was attached to vacuum line via a tube cracker. When the tube was cracked the gases passed into the line where CO_2 and H_2O were condensed in a trap cooled by liquid nitrogen. H_2O was subsequently separated by freezing in trap cooled by ethanol at -80°C. Pure CO_2 was condensed in a glass tube which was flame sealed.

3.6.3 Isotope ratio measurement

The isotope ratio measurements were carried out by using a Micromass 602E Stable Isotope Mass Spectrometer (SIMS) fitted with Europa Scientific IRMS software for data collection and processing. Craig corrections (Craig, 1957) were applied. Results were given as $\delta^{13}C$ values relative to the PDB standard. The reference gas was calibrated against the international standard oil NBS-22, which has a $\delta^{13}C$ value of -29.61‰ relative to PDB. A precision of ± 0.02‰ was obtained for almost all samples.

3.7 Gas chromatography (GC)

During this study, capillary GC analysis was carried out on the saturate fractions from both rock extracts and crude oils using a Varian 3400 gas chromatograph. It was fitted with a 25 m x 0.22 mm i.d. fused silica capillary column (BP-1, 0.25 μm film thickness; SGE Australia).

Diluted samples (ca 1 mg/150 μl) in *n*-hexane were injected using a split /splitless injector, operating in split mode. About 1.0 μl of sample solution was injected. The carrier gas was hydrogen flowing at a linear velocity of 30 cm s^{-1}. Both the injector and the flame ionisation detector (FID) were maintained at a temperature of 300°C. The oven temperature was held at

40°C for 5 minutes and then programmed from 40 to 300°C at 4°C min^{-1} and then held at 300°C for 30 minutes.

The detector response data were acquired using a MacLab System comprising MacLab/4 hardware in conjunction with Chart software (Analog Digital Instruments, Sydney) connected to a Macintosh SE computer. Chromatographic data processing including determination of peak areas and heights were carried out using Peaks software (Analog Digital Instruments).

3.8 Molecular sieving

Molecular sieving was applied to the saturated hydrocarbon fraction of the crude oil samples. The purpose of this step was to remove the *n*-alkanes, which normally comprise a major proportion of the saturated hydrocarbon fraction of oils, and thereby concentrate the branched and cyclic alkanes for analysis by gas chromatography-mass spectrometry.

The silicalite filtration method of Flannigen *et al.* (1978) and West *et al.* (1990) was applied. Silicalite pellets were ground to powder using a pestle and mortar and then activated by oven-heating overnight at 500°C. Columns of silicalite were prepared by plugging a Pasteur pipette with a small piece of cotton wool and adding about 2 g of silicalite powder. A 2 mg sample of saturated fraction dissolved in *n*-hexane (ca. 2 ml) was poured onto the column and allowed to stand for 2 minutes before the column was eluted with at least three bed volumes of *n*-hexane into a pre-weighed vial. The silicalite plug was thoroughly washed with eluting solvent to avoid the retention of acyclic biomarkers. The eluate (non-adduct) was then dried in air and weighed ready for GC-MS analysis.

3.9 Gas chromatography-mass spectrometry (GC-MS)

GC-MS analyses were carried out on saturated and aromatic hydrocarbon fractions from both source rocks extracts and crude oils.

3.9.1 GC-MS of aromatic hydrocarbons

GC-MS analyses were undertaken at the Australian Wine Research Institute, Urrbrae, using a Varian 3400 gas chromatograph interfaced to a Finnigan TSQ 70 mass spectrometer. The gas chromatograph was fitted with a 60 m x 0.25 mm i.d. fused silica column (DB-1, 0.25 μm film thickness; J & W Scientific). Helium was the carrier gas with an inlet pressure of approximately 23.5 psi. The oven was programmed as follows: 50°C for 2 minutes, 50–120 °C at 8°C min^{-1}, 120–300°C at 4°C min^{-1}, and then held at 300°C for 35 minutes. The on-column injector was held at 50°C for 3 seconds, then ramped to 300°C at 180°C min^{-1} and held at 300°C for 5 minutes. Mass spectrometer operating parameters included an ionisation voltage of 70 eV and a filament current of 200 μA. The photomultiplier voltage was set at 1100 V.

Aromatic fraction samples dissolved in dichloromethane (CH_2Cl_2) were injected on-column. The mass spectrometer was programmed (multiple ion detection : MID) to monitor m/z 178 (phenanthrene), m/z 192 (methylphenanthrenes), m/z 206 (dimethylphenanthrenes), and m/z 219 (retene). The naphthalene, methylnaphthalenes, dimethylnaphthalenes and trimethylnaphthalenes were identified from their relative retention times on the reconstructed ion count (RIC) chromatogram. Quantitation was by measurements of peak heights.

3.9.2 GC-MS of saturated hydrocarbons

The GC-MS conditions for the saturates were identical to those used in the analysis of the aromatic hydrocarbons except that the photomultiplier voltage was set to 1800 V. The total saturates fractions from rock extracts and the branched/cyclic alkanes from crude oils were dissolved in *n*-hexane prior to injection. The multiple ion detection program was used to monitor m/z 123 and other associated fragmentograms for sesquiterpenoids, diterpenoids and triterpenoids; m/z 163, and m/z 177 for nor- and demethylated hopanes; m/z 191 for hopanes; and m/z 205 for methylhopanes. The fragmentograms m/z 217 and m/z 218 were monitored for regular steranes; m/z 231 for methylsteranes and m/z 259 for diasteranes.

3.10 XRD analyses

Powdered samples of source rocks from the Poolowanna Formation were prepared as smears for bulk mineralogical analysis by X-ray diffraction. Analysis took place on a modified Philips PW1050 X-ray diffractometer, using a Co-anode tube (operating at 50 kV, 30 mA) and a graphite monochromator. The divergence and receiving slits were 1° and 0.5°, respectively, and the scan rate was 2° min^{-1}. The scans were processed using the computer program XPLOT and the mineral phases quantified very approximately according to the following scale:

dominant	the mineral phase apparently most abundant
subdominant	the next most abundant phase(s) greater than about 20%
minor	mineral phases estimated to be between approximately 5 and 20%
trace	phases estimated to be less than about 5%

The XRD scans revealed no significant levels of carbonate minerals in any of the rock samples.

Chapter 4

Organic Petrography of the Poolowanna Formation

4.1 Introduction

Maceral distributions in coals and the dispersed organic matter (DOM) of associated clastic sediments – in particular the types of maceral present, their relative abundance and their fluorescence characteristics – are useful for qualitative assessment of their source rock potential.

The total amount of macerals (corrected for inertinite content: Horstman, 1994) gives a good estimate of source rock richness. The relative proportions of the maceral groups, (viz. vitrinite, liptinite or inertinite) give an indication of the kerogen type. Thus, a prediction of whether the source rock is oil or gas-prone can be made.

Particular macerals, or their morphological attributes, have been found to be characteristic of the depositional environment in which the precursor plants grew, or where the plant debris was deposited. Minerals, such as pyrite and certain clays, also may help identify the depositional environment.

In this chapter, the organic petrography of samples from selected wells in the Poolowanna and Patchawarra Troughs is discussed with a view to evaluating the source rock potential of the Poolowanna Formation.

4.2 Maceral group composition and distribution

The relative abundance of maceral groups is shown in Table 4.1 and individual macerals are illustrated in Plates 1–12. The distribution of maceral groups observed in the Poolowanna Formation of the Poolowanna and Patchawarra Troughs is summarised in Figure 4.1. The DOM is quite variable in composition whilst the coals are uniformly liptinite poor. The Poolowanna Trough DOM samples mostly plot near the centre of the ternary diagram whereas the Patchawarra Trough samples are more widely scattered, showing a possible difference in the organic inputs to these two depocentres.

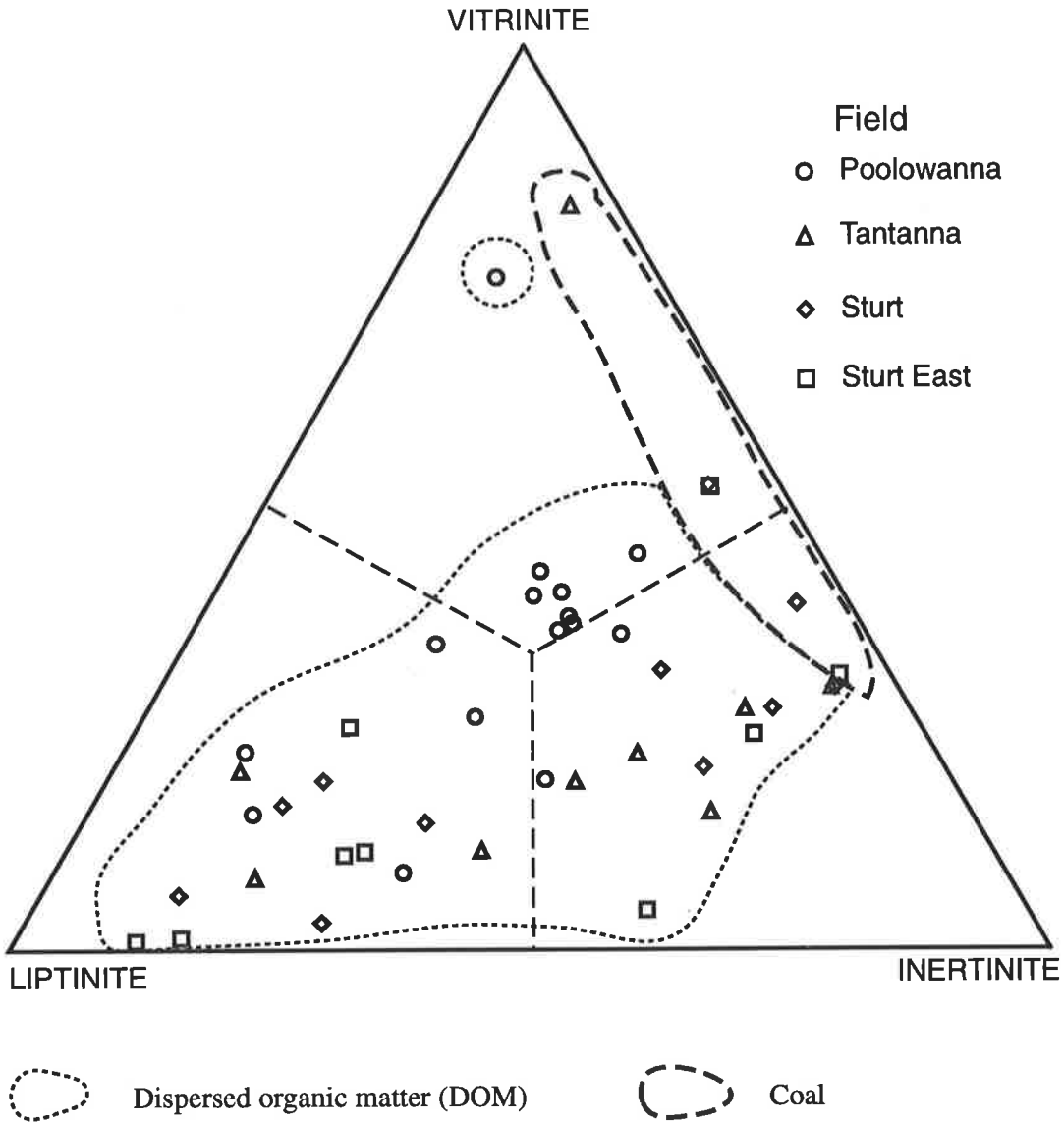


Figure 4.1 Distribution and relative abundance of maceral groups in the Poolowanna Formation

4.2.1 Vitrinite group

Macerals of the vitrinite group are quite common throughout the study area, on average amounting to 28% of the organic matter, but they are less abundant than both the liptinites (38%) and the inertinites (34%). In the case of the DOM, it is only in the Poolowanna Trough that vitrinite is generally more abundant than inertinite. A comparison between the two depocentres shows that the Poolowanna Formation has a higher content of vitrinite in the Poolowanna Trough than in the Patchawarra Trough.

4.2.1.1 Telovitrinite and detrovitrinite subgroups

Macerals of these subgroups appear to be ubiquitous and are represented by telocollinite and desmocollinite, respectively. Their relative abundances are shown in Table 4.1. Both macerals seem to be equally abundant in the two depocentres, although telocollinite appears to be more abundant in the Poolowanna Trough.

Examples of telocollinite are shown in the photomicrographs of Plates 1A, 2A, 6G and 10C. Desmocollinite is shown in Plates 1E, and 2G. Under blue light irradiation it occasionally fluoresces (Plate 1F). This fluorescence is possibly caused by disseminated liptinite macerals, such as resinite or bituminite.

4.2.1.2 Gelovitrinite subgroup

This subgroup is apparently very rare in the Poolowanna Formation. Macerals with close affinities to gelocollinite are illustrated in Plates 2C and 4A. In fluorescence mode they appear dark and are surrounded by resinite or fluorinite stringers forming cell-like structures. Alternatively these gelovitrinite-like macerals can be called coarse detrovitrinite.

4.2.2 Liptinite group

As summarised in Table 4.1 and shown in Figure 4.1, the liptinite group is more abundant in DOM facies than in coal facies where it is frequently associated with the inertinite group. It is commonly more abundant than either vitrinite or inertinite in both the Poolowanna Trough and the Patchawarra Trough. Unusually high abundances (80-87%) are observed in some samples from the Sturt and Sturt East Fields. The identity and relative abundance of individual primary and secondary liptinite macerals are as shown in Table 4.1.

Table 4.1 Relative abundance of maceral groups and their corresponding maceral contents

Sample no.	Well	Depth (m)	Vitrinite					Liptinite									Inertinite						
			Tc (%)	Dc. (%)	Cg (%)	Vd (%)	Total (%)	Sp (%)	Cu (%)	Re (%)	Ld (%)	Al (%)	Bi (%)	Ex (%)	Fl (%)	Total (%)	Fu (%)	Sf (%)	Id (%)	Ma (%)	Mi (%)	Sc (%)	Total (%)
POL1-1	Poolowanna-1	2417	18.3	24.2	-	-	42	9.2	6.6	1.3	9.2	0.6	0.8	-	-	28	7.6	13.9	8.2	-	p	-	30
POL1-2	Poolowanna-1	2423	49.6	25.2	-	-	75	2.6	p	2.6	4.3	5.2*	0.9	-	-	16	0.9	4.3	4.3	-	p	-	10
POL1-3	Poolowanna-1	2438	19.8	19.8	-	p	40	15.9	1.0	0.1	10.7	0.6	1.5	p	-	30	4.7	15.8	10.1	p	p	-	31
POL1-4	Poolowanna-1	2469	6.4	33.7	-	p	40	12.1	1.4	0.7	12.1	0.7	p	-	-	27	8.5	12.1	12.4	p	p	-	33
POL1-5	Poolowanna-1	2499	3.0	19.2	-	p	22	10.4	1.6	31.5	22.7	p	-	p	-	66	2.2	6.3	3.0	-	-	-	12
POL1-6	Poolowanna-1	2545	19.7	17.0	-	p	37	8.9	1.2	5.9	11.7	p	-	p	-	28	10.2	16.0	9.5	-	-	-	36
POL1-7	Poolowanna-1	2557	9.4	9.8	-	p	19	10.8	1.7	9.4	17.2	p	p	p	p	39	5.1	10.8	25.9	-	p	-	42
POL2-8	Poolowanna-2	2496	9.5	5.8	-	-	15	7.3	p	44.0	17.8	p	p	-	-	69	3.8	4.5	7.3	p	p	-	16
POL2-9	Poolowanna-2	2524	7.8	26.4	-	-	34	5.6	0.6	19.6	16.1	p	p	p	-	42	1.9	10.9	11.2	p	-	p	24
POL2-10	Poolowanna-2	2542	22.0	15.4	-	-	37	5.9	0.3	15.7	5.6	p	p	p	-	28	6.6	8.4	19.9	-	-	-	35
POL3-11	Poolowanna-3	2423	19.7	15.6	-	p	35	4.8	1.5	14.1	3.3	p	p	-	-	24	1.1	28.6	11.2	-	p	-	41
POL3-12	Poolowanna-3	2438	16.2	9.9	-	-	26	8.4	0.5	22.5	11.0	p	p	-	-	42	0.5	9.4	21.5	-	-	-	31
POL3-13	Poolowanna-3	2505	3.6	5.2	-	p	9	7.8	2.6	27.1	19.8	0.5	-	-	-	58	1.0	8.3	24.0	-	p	-	33
POL3-14	Poolowanna-3	2551	30.2	14.3	-	p	44	3.0	7.8	4.4	2.4	p	p	p	-	18	4.0	20.5	13.5	p	p	-	38
POL3-15	Poolowanna-3	2560	24.3	11.4	-	p	36	6.1	1.2	15.3	7.0	p	p	-	-	30	11.2	8.0	15.5	-	p	-	35
TAN1-16	Tantanna-1	1795	10.8	9.4	-	p	20	31.7	4.3	2.2	18.7	2.2	8.6	-	-	68	1.4	2.9	7.9	-	-	-	12
TAN2-17	Tantanna-2	1796	2.7	5.4	-	-	8	36.6	7.1	2.7	25.9	p	p	p	-	72	0.9	2.7	16.1	-	-	-	20
TAN2-18	Tantanna-2	1799	9.0	10.0	p	p	19	13.4	2.7	0.2	13.2	p	6.5	-	p	36	22.1	6.1	16.8	p	-	-	45
TAN2-19	Tantanna-2	1805			-	p	nd	-	-	-	p	-	-	-	-	nd	3.9	15.6	80.5	-	-	-	nd
TAN2-20	Tantanna-2	1811	3.6	7.7	-	p	11	14.0	5.9	8.6	17.1	p	3.6	-	p	49	8.1	13.1	18.5	-	-	-	40
TAN3-21	Tantanna-3	1807	11.5	15.3	-	p	27	7.1	0.9	0.9	7.1	p	p	p	-	16	7.4	38.3	11.5	p	p	-	57
TAN4-22	Tantanna-4	1807	14.0	15.3	-	p	29	3.5	0.2	0.5	1.6	p	0.6	-	-	6	20.6	38.3	5.3	-	p	-	64
TAN4-23	Tantanna-4	1814	9.3	12.7	-	p	22	15.0	1.4	0.0	9.1	1.4	1.7	-	-	29	16.7	7.9	24.6	-	-	-	49
TAN5-24	Tantanna-5	1814	8.0	7.3	-	p	15	12.3	0.9	2.1	7.0	1.6	1.1	-	-	25	27.5	14.6	17.6	-	-	-	60
TAN8-25	Tantanna-8	†1823	76.0	6.3	-	p	82	2.1	0.6	0.2	0.6	p	1.0	p	-	5	2.7	8.5	1.9	-	-	-	13
STU1-26	Sturt-1	1865	4.1	12.0	-	-	16	41.4	3.2	p	19.0	1.2	0.9	-	p	66	4.4	5.5	8.5	-	p	-	18
STU1-27	Sturt-1	1871	4.2	1.8	-	p	6	53.6	1.8	1.8	18.1	1.8	3.6	-	-	81	4.2	3.6	5.4	-	-	-	13

Table 4.1 (continued)

Sample no.	Well	Depth (m)	Vitrinite					Liptinite									Inertinite						
			Tc (%)	Dc. (%)	Cg (%)	Vd (%)	Total (%)	Sp (%)	Cu (%)	Re (%)	Ld (%)	Al (%)	Bi (%)	Ex (%)	Fl (%)	Total (%)	Fu (%)	Sf (%)	Id (%)	Ma (%)	Mi (%)	Sc (%)	Total (%)
STU2-28	Sturt-2	1829	10.4	8.3	-	p	19	16.7	10.4	8.3	16.7	p	8.3	-	p	60	4.2	p	16.7	-	-	-	21
STU2-29	Sturt-2	1856	3.2		-	p	3	33.3	p	6.3	27.0	p	1.6	-	p	68	p	p	28.6	-	-	-	29
STU4-30	Sturt-4	1859	12.1	8.3	-	p	20	13.7	1.1	1.8	4.5	0.3	1.6	-	p	23	27.4	22.2	7.0	-	-	-	57
STU4-31	Sturt-4	†1881	33.2	18.3	-	-	52	2.6	0.3	2.9	0.9	p	p	-	-	7	14.1	23.6	4.0	p	p	p	42
STU3-32	Sturt-3	1859	2.8	11.3	-	p	14	16.0	2.8	8.5	18.9	-	6.6	-	p	53	16.0	6.6	10.4	p	-	-	33
STU3-33	Sturt-3	1862	11.0	15.9	-	p	27	5.2	0.8	1.4	5.6	0.2	0.2	-	-	13	33.2	18.6	7.9	p	p	-	60
STU6-34	Sturt-6	1847	12.9	18.1	p	p	31	12.2	0.2	1.1	7.4	0.6	0.6	p	p	22	25.0	15.0	7.0	-	-	-	47
STU6-35	Sturt-6	†1865	18.7	19.7	p	p	38	1.9	p	1.5	1.9	-	p	-	p	5	28.1	24.7	3.6	p	-	p	56
STU8-36	Sturt-8	1862	10.0	19.2	p	p	29	3.3	0.1	0.8	1.9	p	0.1	p	p	6	37.7	23.6	3.3	-	-	-	65
STE1-37	Sturt East-1	1835	9.4	14.7	-	p	24	6.7	p	1.1	8.3	p	0.5	-	p	17	36.1	16.8	6.4	p	p	-	59
STE1-38	Sturt East-1	1841	-	1.2	p	p	1	58.1	0.5	1.0	24.5	3.2	-	-	p	87	5.1	1.7	4.7	-	-	p	12
STE1-39	Sturt East-1	1844	-	1.5	-	p	1	48.8	0.0	1.5	26.8	5.4	0.5	-	p	83	7.8	2.0	5.9	-	p	-	16
STE2-40	Sturt East-2	1829	5.8	4.8	-	-	11	38.2	1.2	1.2	19.4	1.8	0.9	-	-	63	12.1	6.1	8.5	-	-	-	27
STE3-41	Sturt East-3	1850	21.6	3.5	-	p	25	31.7	2.5	3.5	16.1	0.5	0.5	p	p	55	5.5	6.0	8.5	-	-	-	20
STE3-42	Sturt East-3	1865	2.3	2.3	-	p	5	12.0	4.6	3.4	14.9	p	1.7	-	p	37	33.1	10.9	14.9	-	-	-	59
STE4-43	Sturt East-4	1838	3.1	8.0	p	p	11	32.9	3.6	2.7	17.8	2.7	0.9	-	p	60	12.9	10.4	5.1	p	-	-	28
STE4-44	Sturt East-4	†1850	21.4	30.2	p	p	52	2.0	0.6	1.5	2.6	p	0.1	p	p	7	14.0	21.1	6.5	p	-	-	42
STE4-45	Sturt East-4	†1862	14.3	16.6	p	p	31	0.7	0.2	2.4	1.5	p	p	-	p	5	37.9	21.1	5.3	p	p	-	64

Tc=telocollinite; Dc=desmocollinite; Cg = Corpogelinite; Vd=vitrodetrinite; Sp=sporinite; Cu=cutinite; Re=resinite; Ld=liptodetrinite; Al=Alginite (telalginite, *lamalginite); Bi=bituminite; Ex=exsudatinite; Fl=Fluorinite; Fu=fusinite; Sf=semifusinite; Id=inertodetrinite; Mi=micrinite; Ma=macrinite; p = present

† = coal; remainder = DOM

4.2.2.1 Primary liptinites

Sporinite

Sporinite was the dominant liptinite in most samples. Its average relative abundance was 7.9% in the Poolowanna Trough) and 19.5% in the and Patchawarra Trough, with an overall average abundance of 13.7%. DOM in the Poolowanna Formation of the Sturt and Sturt East Fields contains an unusually high abundance of sporinite (up to 58.1% in Sturt East-1, 1841 m).

Different shapes and sizes of the spores were observed, possibly indicating contributions from various plant species. The common microsporinite (or tenuisporinite) in DOM occurs as miospores, as illustrated in Plates 3G-H and 9C-D. It is translucent in white light, and therefore can be identified only after blue light excitation. This miosporinite is likely to be contributed from pollens.

Macrosporinite (or crassisporinite) was identified in a couple of samples. Its characteristic feature is ornamentation of the exine by various protrusions (Plates 2G-H, and 3E-F). Some of this sporinite also appears translucent in DOM, but displays intense yellow fluorescence in blue light (Plate 9A-B). Sporangia related to *Torispores* (Balme, 1952) were identified in the Poolowanna Trough (Plate 2E-F) but rarely seen in any samples from the Patchawarra Trough. Megaspores were identified in some Sturt Field samples (Plate 7C-D). They show red internal reflections in white light. An unusual sporinite showing a fungal-like morphology was identified in DOM from the Tantanna Field. It is translucent in white light and fluoresces yellow in blue light excitation (Plate 3A-D). Sporinite with similar morphological features was identified in Sturt East (Plate 9G-H).

Resinite

Resinite appears to be quite common in the Poolowanna Formation. Average relative abundances of 14.3% and 2.5% were found for the Poolowanna and Patchawarra Troughs, respectively. An unusually high abundance was noted in several sections of the Poolowanna field. The highest values recorded were 44% in Poolowanna-2 and 31.5% in Poolowanna-1 (Table 4.1).

Rod-like shapes possibly representing resin ducts are noted in a sample from Poolowanna-1 (Plate 1C-D) and in the same section resins appear to fill the cell cavities of plant tissue (Plate 1G-H). In the latter case, the host telocollinite is impregnated with resinite thus showing a relatively weak fluorescence. Lumps of resinite, likely to be concentrated as residuum after the host woody tissue had decayed, are noted in DOM from the Sturt Field (Plates 5C-D; G-H). Isolated elliptical resin bodies and droplets with a strong orange fluorescence are evident in coal from Sturt East (Plate 10F).

Cutinite

Cutinite also appears to be ubiquitous throughout the Poolowanna Formation although it is somewhat less abundant than the aforementioned liptinite macerals. Its average abundance is 2.2% in both troughs. Most of the identified cutinites are thick and long (Plates 2C-D and 4A-B). A thick cutinite, possibly deformed by syngenetic pyrite as shown in Plate 10A-B. Its compressed cell structures, display a strong orange to brown yellow fluorescence which is probably enhanced by fluorinite excretion as result of compaction.

Cutinites of medium thickness (Plate 6G-H) and an unusually long, irregularly compacted leaf cutinite (Plate 7A-B) were identified in DOM from the Sturt field. Thin cutinites are rare. In the Poolowanna Trough they are associated with lamalginite (Plates 1F and 2B); and in the Sturt Field they occur as isolated stringers (Plate 6A-B).

Alginite

The abundance of alginite is very low compared to the other liptinite macerals. It has an average abundance of 1.5% in the Poolowanna Trough and 1.7% in the Patchawarra Trough. *Lamalginite* appears to be very rare and was only identified in the Poolowanna Trough. A relative abundance of 5.2% (Table 4.1) was recorded in silty shale from Poolowanna-1. The general morphological features of lamalginite are illustrated in Plates 1F and 2B.

Telalginite is quite common, particularly in the Patchawarra Trough. It is very abundant in Sturt East Field (maximum value = 5.4% at Sturt East-1, 1844 m: Table 4.1). Most of it is similar in form to the fossil alga *Pila* (Plate 4B). Another type (Plate 8B) strongly resembles colonies of *Botryococcus braunii.* In reflected white light most telalginites are identified by their brownish colour with rust-red internal reflections, and their irregular to oval-shaped bodies. In blue light excitation they give a characteristic yellow to orange fluorescence. In some parts of the Poolowanna Formation they occur in association with inertodetrinite (Plates 4C-E and 9-E) whereas in other areas they occur as isolated phyterals (Plates 7E and 8A, C and E). Occasionally they are associated with pyrite and fusinite (Plates 4G and 7G).

4.2.2.2 Secondary liptinites

Bituminite

Bituminite in most cases appears to be disseminated in desmocollinite, to which it imparts a brownish fluorescence under blue light excitation (Plate 6G-H). It is quite widespread, having an average relative abundance of 1.0% in the Poolowanna Trough and 2.3% in the Patchawarra Trough (Table 4.1). It occurs as groundmass for other macerals in some samples (Plates 3G-H and 10E-F).

Fluorinite and exsudatinite

Fluorinite and exsudatinite are the least abundant liptinites. They appear in various forms and shapes. Exsudatinite occurs in cracks or fissures particularly in coarse detrovitrinite surrounded by cutinite (Plates 2C-D and 4A-B). It also occurs as yellow fluorescent rings surrounding coarse inertodetrinite (Plate 5C-D). Fluorinite occurs in association with telocollinite as either layers (Plates 1A-B and 6C-D) or globules which fluoresce an intense green or yellow under blue light excitation (Plate 5E-F). In silty shales it may also appear as scattered through the mineral matrix globules (Plate 6A-B and E-F). Sturt Field appears to have the highest abundance of fluorinite.

4.2.3 Inertinite group

As a proportion of the kerogen preserved within the Poolowanna Formations, inertinite appear to be more common than vitrinite, having an average abundance of 34.4% (Table 4.1). It is also overall more abundant in the Patchawarra Trough (38.9%) than in the Poolowanna Trough (29.8%). This maceral group consists of almost equal amounts of semifusinite and inertodetrinite (12.9% and 12.8%, respectively) while fusinite is the least abundant of the three macerals (Table 4.1). Inertinite relative abundances >50% were recorded in samples from Tantanna, Sturt and Sturt East (Fig. 4.1).

4.2.3.1 Telo-inertinite subgroup

Fusinite

Fusinite is widespread with a higher relative abundance in the Patchawarra Trough (16.2%) than in the Poolowanna Trough (4.6%). The highest volume recorded in the Poolowanna Trough is 11.2% (Poolowanna-3, 2560 m) while in the Patchawarra Trough the highest value is 37.9% (Sturt East-4, 1862 m). This is a strong indication of contrasting depositional conditions between these two troughs.

It commonly occurs in association with the vitrinite and liptinite maceral groups (Plates 5A, 6C and 10C). In some carbonaceous shale facies, it occurs as a monomaceralic layer bounded by liptinite macerals, e.g. miosporinite in a bituminite groundmass (Plates 9C-D and 4A-B) and telalginite (Plate 4G-H).

Semifusinite

Semifusinite is similarly widely distributed. It has an overall abundance of 12.9% (Table 4.1). In the Poolowanna Trough, semifusinite is more abundant than fusinite (11.9%) and less abundant than inertodetrinite. In Patchawarra Trough, it is less abundant than fusinite but slightly more abundant than inertodetrinite.

Semifusinite is identified by its swollen cell walls, a result of humification, and a lower reflectance than that of coexisting fusinite. The characteristic colours in incident light range from light grey to white. Like fusinite it commonly occurs in the form of layers (Plates 2A, 6C and 10C) and lenses in which the cell cavities are either empty or filled with a wide range of substances including gelovitrinite, gelo-inertinite, resinite and various minerals.

Sclerotinite

Sclerotinite is very rare in this part of the Poolowanna Formation. It was sparsely identified in Poolowanna-2 and in a some Sturt and Sturt East field samples (Table 4.1).

4.2.3.2 Detro-inertinite subgroup

Inertodetrinite and micrinite

Detro-inertinite is equally distributed between the two depocentres with an average abundance of 13.2% in the Poolowanna Trough and 12.3% in the Patchawarra Trough. Inertodetrinite comprises inertinite fragments with a diameter between 30 and 2 μm. It occurs in association with liptinite macerals. The inertinite phytoclasts may have the same orientation as the bounding liptinite (Plates 1C-D; and 9E-F) or be randomly dispersed (Plates 4E and 6G). Micrinite is much smaller than inertodetrinite and is referred to as granular inertinite. It commonly occurs as DOM in clastic sediments (Plates 6E, 8C and 9A), or as granular masses in the desmocollinite layers of coals (Plate 5C) and bituminite groundmass (Plate 6E).

4.2.3.3 Gelo-inertinite subgroup

Macrinite

Macrinite was identified in relatively few samples. No significant counts were recorded, and it is therefore denoted by letter 'p' in Table 4.1. An example of macrinite is illustrated in Plate 7G. This is a sort of corpomacrinite which probably resulted from desiccation or oxidation of a resinite body.

4.2.4 Microlithotypes

A microlithotype denotes the form in which organic matter as macerals appears under the microscope in a manner analogous to the description of coal bands in hand specimen (i.e. lithotypes). Under ICCP conventions a microlithotype can only be recorded as such if, on a polished surface perpendicular to the bedding plane, it has a width of at least 50 microns or covers a minimum area of 50 x 50 μm. Also, a minimum quantity of 5% is required for the maceral to be incorporated in the microlithotype. Microlithotypes are subdivided into three groups, viz. monomaceral, bimaceral and trimaceral.

Table 4.2 Maceral association and pyrite contents

Organic facies*	Sample no.	Well	Depth (m)	Bimaceral abundances (%) V+L	I+L	V+I	Characteristic maceral association*	Pyrite (%)
L > I, V (vitrinertoliptite)	POL2-8	Poolowanna-2	2496	84	85	31	Vitrinertoresite	1.97
	POL2-9	Poolowanna-2	2524	76	66	58	"	2.13
	POL1-5	Poolowanna-1	2499	88	78	34	"	4.45
	POL3-12	Poolowanna-3	2438	69	74	58	"	0.52
	POL3-13	Poolowanna-3	2505	67	91	42	"	7.25
	TAN1-16	Tantanna-1	1795	88	80	32	Vitrinertosporite	nd
	TAN2-17	Tantanna-2	1796	80	92	28	"	nd
	TAN2-20	Tantanna-2	1811	60	89	51	"	nd
	STU1-26	Sturt-1	1865	82	84	34	"	nd
	STU1-27	Sturt-1	1871	87	94	19	"	1.78
	STU2-28	Sturt-2	1829	79	81	40	"	2.04
	STU2-29	Sturt-2	1856	71	97	32	"	8.70
	STU3-32	Sturt-3	1859	67	86	47	Vitrinertoliptodetrite	5.36
	STE1-38	Sturt East-1	1841	88	99	13	Sporodurite	1.45
	STE1-39	Sturt East-1	1844	84	99	17	"	0.49
	STE2-40	Sturt East-2	1829	73	89	37	Vitrinertosporite	0.90
	STE3-41	Sturt East-3	1850	80	75	45	"	1.00
	STE4-43	Sturt East-4	1838	72	89	40	"	0.66
V > I, L (duroclarite)	POL1-1	Poolowanna-1	2417	70	58	72	Duro-sporoclarite	0.48
	POL1-2	Poolowanna-1	2423	90	25	84	"	6.50
	POL1-3	Poolowanna-1	2438	69	60	70	"	0.24
	POL1-4	Poolowanna-1	2469	67	60	73	"	2.42
	POL1-6	Poolowanna-1	2545	64	63	72	Duro-liptodetroclarite	nd
	POL2-10	Poolowanna-2	2542	65	63	72	Duro-resinoclarite	0.69

Table 4.2 (continued)

Organic facies*	Sample no.	Well	Depth (m)	Bimaceral abundances (%) V+L	I+L	V+I	Characteristic maceral association*	Pyrite (%)
V > I, L (duroclarite)	POL3-14	Poolowanna-3	2551	62	56	82	Duro-cutinoclarite	0.13
	POL3-15	Poolowanna-3	2560	65	64	70	Duro-resinoclarite	p
	STU4-31	Sturt-4	1881	58	48	93	Duro-resinoclarite	0.11
	STE4-44	Sturt East-4	1850	58	48	93	Duro-liptodetroclarite	0.93
	TAN8-25	Tantanna-8	1823	87	18	95	Vitrinertite	nd
I > V, L (clarodurite)	POL1-7	Poolowanna-1	2557	58	81	61	Claro-liptodetrodurite	nd
	POL3-11	Poolowanna-3	2423	59	65	76	Claro-resinodurite	nd
	TAN2-18	Tantanna-2	1799	55	81	64	Claro-sporodurite	p
	TAN3-21	Tantanna-3	1807	43	73	84	"	nd
	TAN4-22	Tantanna-4	1807	36	71	94	"	nd
	TAN4-23	Tantanna-4	1814	51	78	71	"	nd
	TAN5-24	Tantanna-5	1814	40	85	75	"	nd
	STU4-30	Sturt-4	1859	43	80	77	"	0.16
	STU3-33	Sturt-3	1862	40	73	87	Claro-liptodetrodurite	0.73
	STU6-34	Sturt-6	1847	53	69	78	Claro-sporodurite	0.37
	STU6-35	Sturt-6	1865	44	62	95	"	nd
	STU8-36	Sturt-8	1862	35	71	94	"	nd
	STE1-37	Sturt East-1	1835	41	76	83	Claro-liptodetrodurite	0.27
	STE3-42	Sturt East-3	1865	41	95	63	"	0.57
	STE4-45	Sturt East-4	1862	36	69	95	Vitrinertite	nd

*Described using microlithotype nomenclature of Stach *et al.* (1982)

Monomaceral microlithotypes are characterised by not less than 95% content of a given maceral group. They include *vitrites* which contain not less than 95% vitrinite and not more than 5% of liptinite and/or inertinite; *liptites* containing more than 95% liptinite (e.g. sporite, resite, liptodetrite, cutite and algite); and *inertites* containing more than 95% inertinite (e.g. fusite, semifusite and inertodetrite).

Bimaceral microlithotypes include:

(a) clarite, which contains vitrinite and liptinite that together account for more than 95%, and each comprise more than 5% of the whole;

(b) vitrinertite, which contains at least 95% vitrinite and inertinite; and

(c) durite, which contains at least 95% liptinite and inertinite.

Durite may contain up to 5% of vitrinite which in many cases is present in the form of vitrodetrinite.

Trimaceral microlithotypes are the only ones in which all three maceral groups are present to extent of more than 5%. They are subdivided into:

(a) duroclarite, in which vitrinite is more abundant than liptinite and inertinite;

(b) clarodurite, in which the proportion of inertinite is greater than that of vitrinite plus liptinite; and

(c) vitrinertoliptite (Marchioni, 1976), in which liptinite is predominant.

In these trimacerites the specific origin of the liptinite can be emphasized by adding the liptinite maceral type, to the description. For example, a 'duro-sporoclarite' is a trimacerite in which vitrinite exceeds the inertinite content whilst sporinite is the main liptinite.

Microlithotypes in the Poolowanna Formation can be visually identified from photomicrographs in Plates 1-11 (magnification = x 625 and x 400 for Plate 7C-D). Based on these magnifications the field of view for each photomicrograph is ca. 136 μm x 197 μm, and ca 213 μm x 308 μm for Plate 7C-D.

A combination of two maceral groups or bimaceral association (Table 4.2) was obtained by adding together their relative abundances as determined from point counting (Table 4.1). The combination of inertinite and liptinite seem to be most abundant with an average value of 71.8%, followed by vitrinite and liptinite (65.7%), and vitrinite and inertinite (62.4%). The combination showing the highest mean value in the Poolowanna Trough is that of vitrinite and liptinite (70.2%), whereas in the Patchawarra Trough it is that of inertinite and liptinite (77.6%).

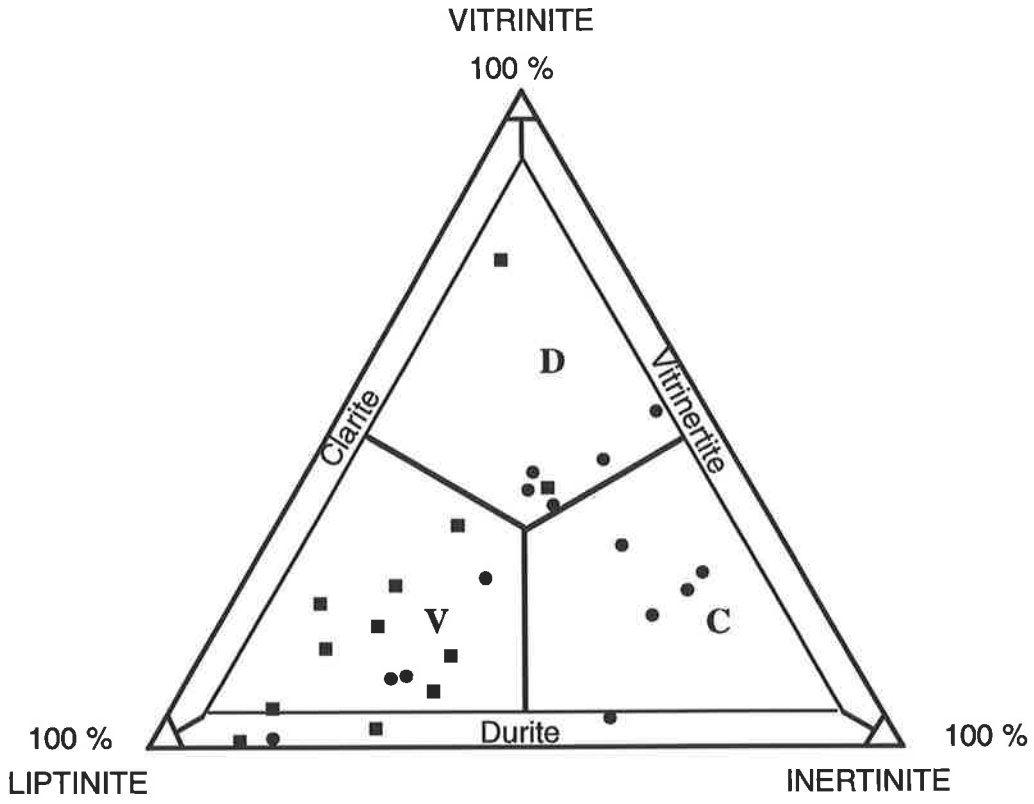


Figure 4.2 Maceral group abundance for some DOM of the Poolowanna Formation, replotted to illustrate its relationship to microlithotype compositions and pyrite abundance.

Based on the position of the DOM samples in the maceral group ternary diagram (Fig. 4.1), most can be assigned to one of the three types of trimacerite (viz. vitrinertoliptite, duroclarite and clarodurite: Table 4.2, Fig. 4.2). This trimacerite nomenclature was used informally to identify three major source rock facies in the Poolowanna Formation. Most of the coals plot as the bimacerite vitrinertite.

4.2.4.1 Vitrinertoliptite facies

This facies is represented differently in each trough. In the Poolowanna Trough the diagnostic liptinite is resinite (hence vitrinertoresite) whereas in the Patchawarra Trough it is largely sporinite (vitrinertosporite). These two features highlight the marked contrast between these two troughs which can be attributed to differences in organic input and depositional conditions.

4.2.4.2 Duroclarite facies

In the Poolowanna Trough this facies is strongly represented at Poolowanna-1 where it may be described as duro-sporoclarite. In other wells, viz. Poolowanna-2 and -3, the resinite influence is again significant giving rise to a duro-resinoclarite facies. This facies is poorly developed in the Patchawarra Trough (Table 4.2). A sample in the Tantanna Field (Tantanna-8, 1823 m), has a similar composition but is best described as the bimacerite vitrinertite. The sample from Sturt-4 (1881 m) has a duro-resinoclarite maceral association, whereas in Sturt East-4 the equivalent association is duro-liptodetroclarite.

4.2.4.3 Clarodurite facies

This facies is largely confined to the Patchawarra Trough where it occurs in the form of claro-sporodurite and in a few cases claro-liptodetrodurite. However, among those samples showing the clarodurite maceral association, a sample from Sturt East-4 (1862 m) actually plots in the vitrinertite domain. Only two Poolowanna Trough derived samples may be assigned to the clarodurite facies. One of the sample is classified as claro-liptodetrodurite and the other as claro-resinodurite.

In summary, the source rock facies of the Poolowanna Trough can be characterised by the vitrinertoresite and duro-sporoclarite maceral associations, whereas in the Patchawarra Trough the source rocks have vitrinertosporite and claro-sporodurite signatures. The Poolowanna Trough source facies are strongly influenced by resinite and vitrinite, whereas in the Patchawarra Trough there is a strong inertinite and sporinite association.

4.2.5 Microlithotypes and mineral association

The inorganic matter contained in coals and phytoclasts of dispersed organic matter occurs mainly in the form of mineral inclusions. Depending on their origin, three groups of inorganic constituents can be realised. The first group is made up of phytogenic minerals

derived from inorganic matter contained in the coal-forming plants; for example, dispersed opal (opaline phytolith) and fine crystalline quartz (David *et al.*, 1984). The second group comprises all minerals which were washed into the coal swamp as detrital fragments. The third group consists of inorganic matter precipitated from pore or surface water (Ward, 1986). The minerals resulting from the second and third groups are referred to as adventitious (Francis, 1961). However, a clear distinction between the inherent and adventitious groups of minerals is not always possible. Commonly, both types of mineral matter occur together. Although the list of minerals found in coal and carbonaceous sediments is long, only pyrite and to some extent clay and carbonate minerals are commonly identified.

4.2.5.1 Pyrite

Under the microscope, pyrite is easily identified by its very high reflectance and its yellow to bronze colour in ordinary white light. It occurs in several forms, including granules to small nodules in vitrinite (Plates 1C and G) and as precipitated concretions infilling cell cavities (Plate 1C). Large syngenetic nodules in clastic rocks (Plates 7E and 9E) that deform the adjacent laminae are also common. Framboids in clastic sediments (Plate 8C) and carbopyrite (Plate 11C-D) are examples of this feature.

The abundance of pyrite relative to the sum of the associated macerals was determined by point counting. The general abundance and distribution of pyrite is as shown in Tables 4.2 and 4.3 and Figure 4.2. The highest values recorded were 7.25% in the silty shale from the Poolowanna Trough and 8.70% in the silty shale at Sturt-2 (1856 m) in the Patchawarra Trough. Generally, the vitrinertoliptite facies appears to contain the most pyrite, except for a few vitrinertosporite samples from Tantanna, Sturt and Sturt East which appear to have very low to low pyrite contents.

The duroclarite facies typically has a low to moderate pyrite content, whereas the clarodurite facies is the least pyritic. It is very interesting to note that the Poolowanna Formation in the Tantanna Field is devoid of pyrite, regardless of its organic facies.

4.2.5.2 Clay and carbonate minerals

The occurrence of clay minerals in the organic matter of these samples is generally as finely dispersed inclusions in vitrinite, causing the vitrinite to show a very weak fluorescence in blue light excitation (Plate 5A-B and C-D). A greyish spherical body filling a cell cavity (Plate 8G-H), with internal reflections in white light and brown fluorescence when irradiated with blue light, is possibly another example of clay minerals. Other greyish fillings in fusinite cell lumens, with very weak yellowish fluorescence in blue light (e.g. Plate 9C-D), were frequently observed. A huge illite-like aggregate bounded by vitrinite, with brownish internal reflections and fibrous orange yellow fluorescence in blue light irradiation (Plate

11A-B) was noted in one sample (Poolowanna-3, 2560 m). It is tentatively identified as carbargillite. Other examples of carbonate minerals seem to be very rare, with only one questionable occurrence shown in Plate 11E-F. It displays possible cleavage and is characterised by a brownish grey colour in white light with a strong yellow fluorescence in blue light irradiation.

4.3 Botanical attributes of macerals and depositional environments

The botanical affinities of certain macerals are evident from the preserved structure of the coalified plant remains from which they originate. Examples of macerals whose botanical origin is recognisable are telocollinite and fusinite which occur as coalified cell walls, and most of the liptinite group macerals. Desmocollinite and macrinite are examples of macerals whose botanical origins are hardly recognisable because of their high degree of degradation. It should also be noted that, for many macerals, the place of burial does not necessarily coincide with the place of origin. The presence of only a few maceral components would therefore not be sufficient to define the type of environment that the coal and/or DOM originated in. However, when present in large quantities, the environmental significance of a maceral increases considerably. Conversely, the presence of *telalginite*, whether in small or large amounts, indicates the aqueous conditions (lacustrine or marine) in which the host rock was deposited.

4.3.1 Vitrinite group

As mentioned earlier the vitrinite group macerals originate from humic substances chiefly the lignin and cellulose of plant cell walls. Tannins also participate in the formation of vitrinites, especially corpovitrinite. Since humic compounds are present wherever vascular plants grow, automatically the presence of vitrinite macerals indicates the contribution of such plants to the preserved organic matter.

The maceral types of this group are largely related to certain parts of higher plants. For example, much of the telovitrinite in Euro-American Carboniferous coals originates from the barks of the Lycophyta and the wood of Gymnosperms and Cycadophytes (Stach *et al.*, 1982). Telovitrinites which are bounded by cutinite are derived from leaves or green twigs. Desmocollinite is derived mainly from the cellulose of soft tissues; and the cellulose and liginin of disintegrated cell fragments from woody tissues.

The depositional conditions favourable to the preservation of the vitrinite group are also those which favour the transformation of lignin and cellulose into humic acid. Aerobic microbiological activity in a weak acid medium is conducive to such transformations (Stach *et al.*, 1982). Further, conversion of vegetable matter to vitrinite group macerals continues below the ground water table. Under conditions of total absence of atmospheric or dissolved oxygen the vegetable matter is subject to further physical and chemical degradation by

anaerobic bacteria. Under these anoxic conditions, the precursors of vitrinite group macerals (i.e. humotelinite, humodetrinite and humocollinite) are subject to compaction and dehydration followed by gelification and polymerisation, to eventually form the vitrinite macerals of bituminous coals.

The relative abundance of vitrinite macerals in a sample is therefore a measure of the relative input of organic matter from vascular plants under first oxic then anoxic conditions. As shown in Table 4.1, the Poolowanna Trough depocentre of the Poolowanna Formation appears to have been the site of a higher vascular plant influx and more anoxic conditions than was the case in the Patchawarra Trough. Several coals from Tantanna (Tantanna-8, 1823 m), Sturt (Sturt-4, 1881 m) and Sturt East (Sturt East-4, 1850 m) have similar maceral group abundances and, by inference, depositional settings to those of the Poolowanna Trough carbonaceous shales.

4.3.2 Inertinite group

As reported previously, many macerals of the inertinite group have the same precursors as vitrinite group macerals. Therefore their botanical attributes are related to vascular plants. However, this group undergoes a different transformation history in which the humified plant material suffers a period of intense desiccation and oxidation before final burial. Therefore the occurrence of abundant inertinite gives an impression of organic matter contribution from vascular plant remains which have undergone severe oxidation.

As already mentioned the presence of inertinite will not necessarily mean oxic conditions at the site of burial. The inertinite may have been brought in from somewhere else. Different types of inertinite may sometimes indicate the fusinitisation pathway taken by its precursors. For instance, most of fusinites consist of fossil charcoal (the most common type), resulting from incomplete combustion. Semifusinite is a product of either aerobic biodegradation during humification, or oxidation and incomplete combustion of partially humified cell tissue. However, an accurate identification of the various modes of origin is difficult in most cases because they commonly overlap and rarely proceed in isolation. Important indicators include the degree of cell preservation which is a measure of the relative effects of humification and associated biodegradation; and reflectance, which increases with the amount of oxidation and/or extent of combustion that the maceral has been subjected to. Wood-derived inertinite typically displays better preserved plant cells than leaf-derived semifusinite.

Depending on the degree of humification prior to oxidation, wood-derived semifusinite also shows poor cell preservation and occupies a transitional position between fusinite and macrinite. The combustion of dehydrated peat will, on resumption of peat accumulation, result in a discrete band of charcoal which will form a fusinite-rich layer. This may explain

the layering features shown in Plates 4G and 9C.

Inertodetrinite consists of remnants of plant tissue, mainly in the form of cell fragments of fusinite and semifusinite. Sometimes it may result from charcoal formed from burning vegetation (forest fires), which is then dispersed by wind or water as relatively small fragments.

As shown in Table 4.1, the abundance of inertinite in the Patchawarra Trough is greater than that in the Poolowanna Trough, indicating different degrees of oxic conditions in the two depocentres. While the Poolowanna Trough samples contain of more semifusinite and inertodetrinite than fusinite, the Patchawarra Trough samples consistently display more fusinite than other inertinite macerals. On the basis this observation suboxic aquatic conditions may be inferred for the Poolowanna Trough whereas the Patchawarra depocentre appears to have been subject to dry episodes leading to prolonged exposure oxic conditions. However, the predominance of inertodetrinite in the Tantanna area is an indication of a major contribution from herbaceous plants.

The inferred oxic conditions are confirmed by high inertinite to vitrinite ratios (I/V: Table 4.3). It is suggested that I/V values less than unity indicate the prevalence of anoxic conditions whereas values greater than unity may indicate suboxic to oxic conditions. Most of the Poolowanna Field samples have values less than 1 whereas the Patchawarra Trough samples have values greater than 1, verifying the previously noted contrast in depositional conditions for the Poolowanna Formation between the two areas. A couple of samples from the Sturt East field have anomalously high I/V ratios (9–13) an indication of strongly oxic conditions and hence the possible influx of allochthonous inertinite.

As a point of interest, the duroclarite facies has I/V values of less than unity, whereas the clarodurite facies has values >1. The vitrinertoliptite facies has mixed values but the majority are >1, thus showing a strong association between liptinite and inertinite.

4.3.3 Liptinite group

While the other macerals can be derived from a range of plant tissues, the liptinite macerals are plant-specific components related to particular fossil plants or parts thereof. The presence of individual liptinites is therefore of considerable botanical and palaeoenvironmental significance. They include the waxy protective cover (cuticle) of leaves and young shoots; the resistant skins (exines) of spores and pollens; and plant resins and waxes. The morphological features of these macerals, and the presence of alginites, may sometimes allow the palaeoenvironment of the parent plant(s) to be determined.

Among the liptinite macerals, sporinites are nearly ubiquitous in Mesozoic sediments. Their

occurrence is associated with the existence of the spore-bearing plants (pteridophytes) which reproduce either heterosporously (e.g. lycopods) or homosporously (e.g. pteropods) (Collinson and Scott, 1987). Both require a moist environment and free water in order to fertilise the spores. Pollens on the other hand are produced by seed-bearing plants (gymnosperms). These plants may survive in wetlands by having shallow roots, or in dry ground by having deep roots. Therefore, the high abundance of sporinite, particularly in the Patchawarra Trough samples signifies the prevalence of wetland environments for extended periods. This situation is well illustrated by Plate 9C-D. In this figure, the fusinite layer represents dry conditions which alternated with wet conditions represented by two layers of sporinite. Telalginite is also present and this supports the existence of an aqueous depositional environment.

The morphological features of sporinite also have implications for the kinds of plant and the type of the environment in which they grew. For instance, thin-walled tenuispores (particularly in the form of lycospores) are characteristic of wet, arborescent lycopod swamps (Smith and Butterworth, 1967). High abundances of lycospores are reported in coals with high vitrinite/inertinite ratios in close proximity to palaeochannels (Harvey and Dillon, 1985). Phillips *et al.* (1985) noted that high vitrinite/inertinite ratios are consistent with maximum preservation of biomass in continuously wet terrains where water covers the ground for long periods. A similar observation may be made for the Poolowanna Trough where tenuisporinite is more abundant than crassisporinite. The vitrinite to inertinite ratio was generally greater than 1 for the Poolowanna organic facies in this area (Table 4.3).

Crassisporinite, particularly densosporinite, is derived from herbaceous lycopods (Phillips and Pepper, 1984). These sporinites frequently co-exist with inertinite in durite, and thus their presence signifies relatively dry peat forming conditions (Fulton, 1987). This type of sporinite is quite common in the Patchawarra Trough, further emphasising that dry conditions prevailed in this area. Van Wijhe and Bless (1974) considered the densosporinite facies to be indicative of a strand-plain.

Further information on the palaeoclimate in which fossil plants grew is provided by their cutinite. The plants of wet environments are characterised by thin cuticles whereas those growing in comparatively dry climates (i.e. xenophytic plants) possess relatively thick cuticles. The cutinite in the Poolowanna Formation from both troughs has a thickness between 1.6 and 9.6 μm. This thickness range indicates growth conditions that extend from subaqueous to dry.

The contribution of organic matter from vascular plants is further demonstrated by the presence of resinite, of which terpenoid resin acids are major precursors (Alexander *et al.*, 1988). Cunningham *et al.* (1983) concluded that fossil resinite had been formed by

photolytic polymerisation of resin acids (e.g. agathic acid) after their exudation from the host tree. The form of resinite encountered in Poolowanna Trough appears to be different from that in the Patchawarra Trough, thus suggesting that different types of vascular plants grew in these two areas during the early Jurassic.

Freshwater lacustrine or lagoonal settings are indicated by the presence of structured alginite, referred to as telalginite. The telalginite that occurs in the Poolowanna Formation is of the *Pila* type which is related to *Botryococcus braunii*, an extant lacustrine colonial alga (Robert, 1988). It has been found floating as jelly-like masses on the surface of stagnant water near Salt Creek in South Australia where it is referred to as coorongite (Diessel, 1992).

The Poolowanna Formation in the Patchawarra Trough appears to contain a relatively high amount of telalginite, particularly in the Sturt East area. Occasionally, it occurs together with inertinite, indicating that the inertinite is allochthonous. This telalginite is hardly ever seen in samples from the Poolowanna Trough. Lamalginite, which occurs as thin anastomosing lamellae formed by algal mats is noted in some samples (Plate 2A-B). This also indicates an aqueous, probably lacustrine environment.

4.3.4 Microlithotypes

The microlithotypes of coal and dispersed organic matter (DOM) have been attributed to different environmental settings by various authors (e.g. Hacquebard *et al.*, 1967; Teichmüller, 1982; Diessel, 1992). Among other microlithotypes, vitrite is generally considered to be derived from woody tissues like stems, branches and roots and is indicative of a forest swamp environment. Clarite is usually characterised according to its content of liptinite. Liptinite-poor clarite originates from strongly decomposed plant litter (wood, bark, etc.) in a forest moor environment; whilst liptinite-rich clarites originate from reeds and non-arborescent vegetation which decompose readily, resulting in concentration of the more resistant liptinite. Durite is usually characterised by its content of sporinite. Thus, sporinite-rich durites are generally considered to be subaquatic ooze deposits (e.g. Poolowanna Formation samples at 1841 m and 1844 m in Sturt East-1), whereas spore-poor durites are considered to represent deposition above the water table where extensive oxidation (and bush fires) have occurred. Only two samples from the analysed section of the Poolowanna Formation show a bimaceral association characteristic of the latter setting.

As discussed earlier, almost all the Poolowanna Formation samples can be characterised in terms of diagnostic trimaceral assemblage (Table 4.3).

Table 4.3 Depositional environments of Poolowanna Formation source rock facies

Organic facies	Well	Depth (m)	Characteristic maceral association	Predominant Maceral Vitrinite	Inertinite	Al (%)	Pyrite (%)	Inertinite / Vitrinite	Depositional environment
L> I, V	Poolowanna-2	2496	Vitrinertoresite	Telocollinite	Inertodetrinite	p	1.97	1.02	
(vitrinertoliptite)	Poolowanna-2	2524	"	Desmocollinite	"	p	2.13	0.70	Arborescent wet forest
	Poolowanna-1	2499	"	"	Semifusinite	p	4.45	0.52	swamps
	Poolowanna-3	2438	"	Telocollinite	Inertodetrinite	p	0.52	1.20	
	Poolowanna-3	2505	"	Desmocollinite	"	0.5	7.25	3.76	
	Tantanna-1	1795	Vitrinertosporite	Telocollinite	"	2.2	nd	0.61	
	Tantanna-2	1796	"	Desmocollinite	"	p	nd	2.44	
	Tantanna-2	1811	"	"	"	p	nd	3.52	Herbaceous wet swamps
	Sturt-1	1865	"	"	"	1.2	nd	1.15	
	Sturt-1	1871	"	Telocollinite	"	1.8	1.78	2.20	
	Sturt-2	1829	"	"	"	p	2.04	1.11	
	Sturt-2	1856	"	"	"	p	8.70	9.00	
	Sturt-3	1859	Vitrinertoliptodetrite	Desmocollinite	Fusinite	nd	5.36	2.33	
	Sturt East-1	1841	Sporodurite	"	"	3.2	1.45	9.40	Lacustrine with occasional
	Sturt East-1	1844	"	"	"	5.4	0.49	10.67	drying episodes
	Sturt East-2	1829	Vitrinertosporite	Telocollinite	"	1.8	0.90	2.51	(sub aquatic)
	Sturt East-3	1850	"	"	Inertodetrinite	0.5	1.00	0.80	
	Sturt East-4	1838	"	Desmocollinite	Fusinite	2.7	0.66	2.56	
V > I, L	Poolowanna-1	2417	Duro-sporoclarite	Desmocollinite	Semifusinite	0.6	0.48	0.70	
(duroclarite)	Poolowanna-1	2423	"	Telocollinite	"	5.2	6.50	0.13	
	Poolowanna-1	2438	"	Tel/Descollinite	"	0.6	0.24	0.77	
	Poolowanna-1	2469	"	Desmocollinite	Inertodetrinite	0.7	2.42	0.82	Limnotelmatic
	Poolowanna-1	2545	Duro-liptodetroclarite	Telocollinite	Semifusinite	p	nd	0.97	

Table 4.3 (continued)

Organic facies	Well	Depth (m)	Characteristic maceral association	Predominant Maceral Vitrinite	Inertinite	Al (%)	Pyrite (%)	Inertinite / Vitrinite	Depositional environment
V > I, L (duroclarite)	Poolowanna-2	2542	Duro-resinoclarite	"	Inertodetrinite	p	0.69	0.93	
	Poolowanna-3	2551	Duro-cutinoclarite	"	Semifusinite	p	0.13	0.86	
	Poolowanna-3	2560	Duro-resinoclarite	"	Inertodetrinite	p	p	0.97	
	Sturt-4	1881	Duro-resinoclarite	"	"	p	0.11	0.81	
	Sturt East-4	1850	Duro-liptodetroclarite	Desmocollinite	"	p	0.93	0.81	
	Tantanna-8	1823	Vitrinertite	"	Semifusinite	p	nd	0.16	
I > V, L (clarodurite)	Poolowanna-1	2557	Claro-liptodetrodurite	Desmocollinite	Inertodetrinite	p	nd	2.18	
	Poolowanna-3	2423	Claro-resinodurite	Telocollinite	Semifusinite	p	nd	1.16	
	Tantanna-2	1799	Claro-sporodurite	Desmocollinite	Fusinite	p	p	2.36	Terrestrial
	Tantanna-3	1807	"	"	Semifusinite	p	nd	2.13	(low water table)
	Tantanna-4	1807	"	"	"	p	nd	2.19	
	Tantanna-4	1814	"	"	Inertodetrinite	1.4	nd	2.23	
	Tantanna-5	1814	"	Telocollinite	Fusinite	1.6	nd	3.90	
	Sturt-4	1859	"	"	"	0.3	0.16	2.77	
	Sturt-3	1862	Claro-liptodetrodurite	Desmocollinite	"	0.2	0.73	2.22	Lacustrine
	Sturt-6	1847	Claro-sporodurite	Telocollinite	"	0.6	0.37	1.51	
	Sturt-6	1865	"	Desmocollinite	"	nd	nd	1.47	
	Sturt-8	1862	"	"	"	p	nd	2.21	
	Sturt East-1	1835	Claro-liptodetrodurite	"	"	p	0.27	2.47	Terrestrial
	Sturt East-3	1865	"	Tel/Descollinite	"	p	0.57	12.88	(low water table)
	Sturt East-4	1862	Vitrinertite	Desmocollinite	"	p	nd	2.08	

The duroclarite association is produced by reed-like herbaceous vegetation such as those found in the topogenous marshlands and around the edge of treed swamps, whereas the duro-sporoclarite association normally forms in the telmatic zone which is situated in environments periodically inundated by water (Diessel, 1992). This type of environment could perhaps explain the type of Poolowanna source rock facies deposited in the Poolowanna Trough at Poolowanna-1. The accumulation of organic matter in continuously wet forest swamps with a consistently high groundwater table in the Poolowanna Trough is further emphasized by the presence of duro-cutinoclarite in association with vitrinite-rich clarite, Poolowanna-3 (2551 m). This setting is best described as limnotelmatic. As in the terrestrial (low water table) zones, this facies is characterised by arborescent vegetation with or without herbaceous undergrowth. Duro-resinoclarite is formed in a similar environmental setting. Vitrinertoresite is possibly also from a similar setting in which resin-producing plants were common. The liptinite-rich vitrinertoliptite facies, typical of the Poolowanna Trough at Poolowanna-2 and -3 and the Patchawarra Trough is generally considered subaquatic.

The clarodurite association generally accumulates in areas of low water table and thus under conditions of increased oxidation. The high abundance of fusinite in the clarite matrix indicates the terrestrial zone which is affected by periods of dryness. This facies is characterised by both arborescent vegetation and a low ground water level. Such an environment may be similar to the one in which some of Poolowanna Formation source rock facies, particularly those from the Sturt and Sturt East Fields, were deposited. Carbargillite and other dispersed organic matter typically associated with the clarodurite facies occurs beyond the fringe of rooted vegetation and is indicative of lakes and ponds which collect detritus blown or washed in from other parts of the swamp. Indigenous algal-derived microlithotypes, such as algite, algoclarite, vitrinertoalgite and duroalgoclarite are also associated with clarodurite. Allochthonous inertodetrinite forms the bulk of the inertinite component. Lacustrine conditions are indicated for this facies. In the Patchawarra Trough this facies is clearly developed in the Sturt and Sturt East Fields, whereas in the Tantanna Field there is less contribution from algal organic matter.

4.3.5 Origin and significance of pyrite

Pyrite is an iron sulphide that commonly occurs in coals and in association with DOM in clastic rocks. It occurs as small individual crystals; nodules; framboids (small crystals usually less than 2 μm in diameter, which form spheroidal clusters, rarely exceeding 30 μm) and concretions; as well as infilling the cell lumens of semifusinite or fusinite (Section 4.2.5.1). In general, coals or clastic sediments deposited in paralic settings (hydrologically connected to the sea) are richer in pyrite than those in limmic (lake) basins.

In marine or brackish-water environments, pyrite forms from the reaction of sulphide with

iron, either directly or via a monosulphide precursor (Goldhaber and Kaplan, 1974). Iron is supplied to the sediments in detrital minerals and as iron oxide coating on grains, mainly in the ferric form. In order for the bacterial reduction of sulphate to sulphide to take place, anoxic conditions must prevail since the sulphate-reducing bacteria are obligate anaerobes. In addition, organic matter is also a prerequisite as it is the material on which the bacterial heterotrophs feed (Harrison and Thode, 1958; Demaison and Moore, 1980).

The reactions involved are summarised as follows (Fisher and Hudson, 1987):

1. $SO_4^{2-} + 2CH_2O \longrightarrow 2HCO_3^- + H_2S$ (bacterial sulphate reduction; the organic matter is represented by carbohydrate)
2. $3H_2S + 2\ FeO{\cdot}OH \longrightarrow 2FeS + S^o + 4H_2O$ (bacterially-produced sulphide reacting with hydrated iron oxide, goethite, to form an iron monosulphide, mackinawite),
3. $FeS + S^o \longrightarrow FeS_2$ (conversion of mackinawite to pyrite)

The last reaction may proceed via an intermediate greigite (Fe_3S_4) phase from which the characteristic framboidal texture results (Sweeney and Kaplan, 1973).

The formation of greigite from mackinawite is an oxidation reaction, in which every fourth sulphur oxidised to S^o. This suggests that the formation of framboids requires conditions which are not totally reducing (Hudson, 1982; Fisher and Hudson, 1987). In fact, pyrite generally forms within reducing microenvironments in oxic sediments, for example, disused burrows, faecal pellets and enclosed voids such as foram tests or ammonite chambers (Kaplan *et al.*, 1963).

Based on reaction kinetics, FeS_2 can only form in peats and organic muds by bacterial activity because there is insufficient energy for a purely chemical reduction of sulphate to disulphides. Therefore, as a prerequisite for the formation of FeS_2 in this environment, there needs be a supply of both sulphur and iron. Sulphur originates from protein (largely bacterial) or is carried in as sulphate ions by streams and/or sea water. On the other hand iron is present wherever silicate minerals weather, or where ground water carries ferrous or ferric ions in solution (Stach, 1982).

The relative abundance of pyrite in Poolowanna Formation microlithotypes is as shown in Table 4.3. It appears to be most abundant in the vitrinertoliptite facies of both the Poolowanna and Patchawarra Troughs except in the Tantanna field where it is apparently rare or absent. The high abundance of pyrite in this facies may indicates strongly anoxic condition together with a good supply of both sulphate and iron.

An adequate supply of sulphate is a feature of coastal flood plains where major inundations

could and be linked to influxes of brackish water, banked-up by long-tides and storm waves. Syngenetic pyrite is occasionally found in the shaly coal facies of the Poolowanna Trough (Plate 1C-D) where it can also be related to a concomitant increase in pH in the tide-affected marginal portions of the swamp (Anderson, 1976, as cited by Diessel, 1992). Similar but dispersed syngenetic pyrite is observed in the fluvio-lacustrine, silty shale facies (Plates 8C-D and 9E-F). The absence or rare abundance of pyrite in the Tantanna area is possibly due to scarcity of sulphate and/or highly oxic conditions in which sulphate-reducing bacteria could not thrive.

The duroclarite facies has relatively moderate abundances of pyrite, with values ranging from 0.1 to 6.5%. Once again, this facies in the Tantanna Field appears to be almost devoid of pyrite. The concentration of pyrite here is similar to that of the vitrinertoliptite facies; except that the syngenetic pyrite appears to be framboidal (Plate 11C-D), indicating the lowering of dissolved O_2 to anoxic or suboxic levels. The lower pyrite concentrations may also indicate the preference of sulphate-reducing bacteria for a particular type of organic substrate.

The clarodurite facies is shown to have the lowest pyrite contents ranging from nil to 0.6%. As in the other organic facies, the Tantanna samples contain rare or no pyrite. The lack or absence of pyrite in this facies may be attributed to the persistence of oxic conditions. This conclusion is strongly supported by inertinite/vitrinite ratios >1.0. The presence of alginite in this facies, indicates perennial aqueous conditions which probably lacked a sulphate source (e.g. a raised bog). Such settings are reported to suppress bacterial activity (Diessel, 1992). Alternatively, as argued above, inertinite may be an unsuitable organic substrate for sulphate reducers.

4.4 Thermal maturity assessment based on maceral optical characteristics

Thermal evolution of source rocks is shown by various changes in the physical and chemical properties of organic matter caused by thermal and other diagenetic factors. As mentioned previously, coalification and petroleum genesis depend on the same diagenetic factors (temperature and time), in a such way that each stage of petroleum maturation can be matched with a particular rank stage of coal, as measured by vitrinite reflectance. Other optical changes, such as the colour variation of sporinite in transmitted light (thermal alteration index: Jones and Edison, 1979) and vitrinite aromaticity (*f*a) are occasionally used.

4.4.1 Vitrinite reflectance

The mean random vitrinite reflectance (% R_o) of Poolowanna Formation source rocks was measured as described in Chapter 3. The maximum reflectance (% R_m) was determined by applying the relationship % R_m = 1.07 R_o - 0.01 suggested by Diessel and McHugh (1986) for Australian coals (Table 4.4). The thermal maturation levels are shown to vary from 0.5% R_o (0.53% R_m) to 0.85% R_o (0.9% R_m) indicating that the source rocks in question range

from immature/early mature to mature for hydrocarbon generation.

Table 4.4 Source rock maturation parameters of the Poolowanna Formation based on vitrinite reflectance

Sample no.	Well	Depth (m)	Ro (%)	Std	Rm*. (%)	*f*a **
POL1-1	Poolowanna-1	2417	0.75	0.06	0.79	0.76
POL1-3	Poolowanna-1	2438	0.82	0.07	0.87	0.79
POL1-5	Poolowanna-1	2499	0.79	0.09	0.84	0.77
POL1-7	Poolowanna-1	2557	0.85	0.17	0.90	0.80
POL2-8	Poolowanna-2	2496	0.71	0.05	0.75	0.75
POL2-9	Poolowanna-2	2524	0.72	0.05	0.76	0.75
POL2-10	Poolowanna-2	2542	0.74	0.06	0.78	0.76
POL3-11	Poolowanna-3	2423	0.76	0.09	0.80	0.76
POL3-12	Poolowanna-3	2438	0.72	0.05	0.76	0.75
POL3-13	Poolowanna-3	2505	0.79	0.13	0.84	0.77
POL3-15	Poolowanna-3	2560	0.85	0.16	0.90	0.80
TAN1-16	Tantanna-1	1795	0.67	0.04	0.71	0.73
TAN2-17	Tantanna-2	1796	0.63	0.06	0.66	0.71
TAN2-18	Tantanna-2	1799	0.67	0.03	0.71	0.73
TAN2-20	Tantanna-2	1811	0.6	0.07	0.63	0.70
TAN3-21	Tantanna-3	1807	0.62	0.07	0.65	0.71
TAN4-22	Tantanna-4	1807	0.75	0.07	0.79	0.76
TAN5-24	Tantanna-5	1814	0.66	0.07	0.70	0.73
TAN8-25	Tantanna-8	1823	0.58	0.05	0.61	0.69
STU1-26	Sturt-1	1865	0.59	0.1	0.62	0.70
STU1-27	Sturt-1	1871	0.57	0.06	0.60	0.69
STU2-28	Sturt-2	1829	0.62	0.06	0.65	0.71
STU4-30	Sturt-4	1859	0.64	0.05	0.67	0.72
STU4-31	Sturt-4	1881	0.57	0.07	0.60	0.69
STU3-33	Sturt-3	1862	0.64	0.04	0.67	0.72
STU6-35	Sturt-6	1865	0.66	0.05	0.70	0.73
STU8-36	Sturt-8	1862	0.59	0.05	0.62	0.70
STE1-37	Sturt East-1	1835	0.66	0.05	0.70	0.73
STE1-38	Sturt East-1	1841	0.58	0.1	0.61	0.69
STE1-39	Sturt East-1	1844	0.57	0.07	0.60	0.69
STE2-40	Sturt East-2	1829	0.69	0.06	0.73	0.74
STE3-41	Sturt East-3	1850	0.5	0.04	0.53	0.65
STE3-42	Sturt East-3	1865	0.6	0.05	0.63	0.70
STE4-43	Sturt East-4	1838	0.64	0.07	0.67	0.72
STE4-45	Sturt East-4	1862	0.56	0.04	0.59	0.68

* R_m = 1.07 $\%R_o$-0.01 (Diessel and McHugh, 1986)
** *f*a = Aromatic C/total C

Std = Standard deviation; nd = not determined

Vitrinite aromaticity values (*f*a) were calculated from the following expression:

$f\text{a} = 0.34 + 0.78x - 0.3x^2 + 0.05x^3$; where x stands for the mean maximum vitrinite reflectance in oil immersion (Davis, 1978).

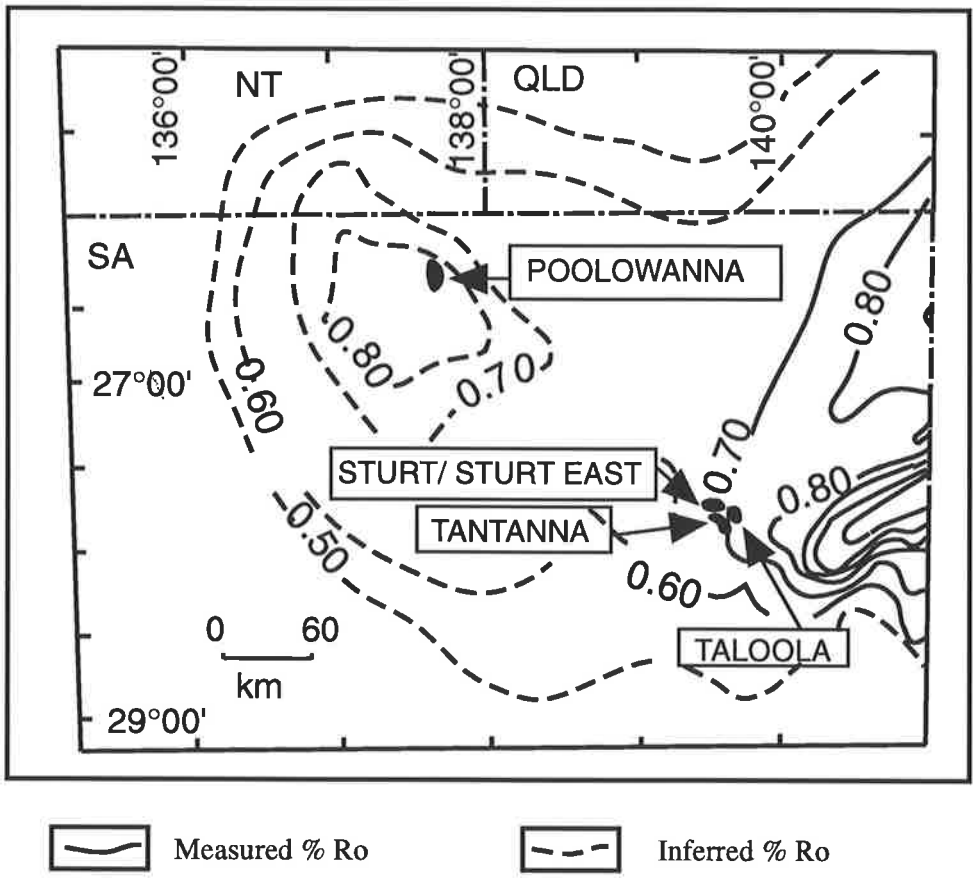


Figure 4.3 Vitrinite reflectance (% Ro) at top Poolowanna Formation level

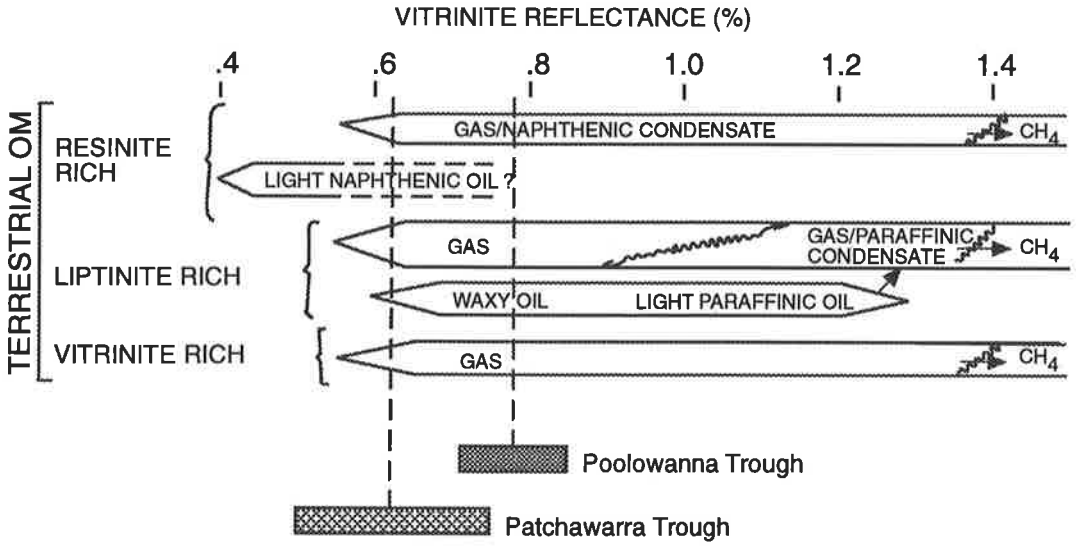


Figure 4.4 Relationship between organic matter type, expected hydrocarbon product and thermal maturity for the Poolowanna Formation (based on diagram from from Powell and Snowdown, 1983)

The Poolowanna Trough samples have values ranging from 0.71% R_o (0.75% R_m) at 2496 m in Poolowanna-2 to 0.85% R_o (0.90% R_m) at 2560 m in Poolowanna-3, and are thus indicated to be within the oil window. A discrepancy is noted in the trend of reflectance with increasing depth whereby some samples at relatively shallow depth have a higher reflectance than those below. Coincidentally, those samples showing an unexpectedly low reflectance are those with relatively high contents of resinite (e.g. at 2499–2496 m and 2524 m in Poolowanna-1 and 2542 m in Poolowanna-2).

In the Patchawarra Trough, the Poolowanna Formation of the Tantanna Field has values ranging from 0.58% R_o (0.61% R_m) at 1823 m in Tantanna-8 to 0.75 % R_o (0.79% R_m) at 1807 m in Tantanna-4, placing it at early mature to mature stage (or onset) of oil generation. Here again, there is almost no consistent pattern of reflectance variation with depth and this is likely to be due to the diversity of organic facies. The formation in the Sturt Field is less mature than in the Tantanna field, with values ranging from 0.57% Ro (0.60% Romax) at 1881 m in Sturt-4 to 0.66% R_o (0.73% R_m) at 1865 m in Sturt-6. The onset of oil generation has been also reached here although again the vitrinite reflectance data behaves inconsistently with depth. In the Sturt East Field, vitrinite reflectance varies from 0.5% R_o (0.53% R_m) at 1850 m in Sturt East-3 to 0.69% R_o (0.73% R_m) at 1829 m in Sturt East-2. The same thermal maturation level as in the neighbouring field is indicated. The regional variation of thermal maturity at the top of Poolowanna Formation is illustrated in Figure 4.3.

As shown in Table 4.4, the *f*a values for the Poolowanna Trough range from 0.75 to 0.80, which is equivalent to high-volatile bituminous to medium-volatile bituminous rank. The Patchawarra Trough samples have somewhat lower values ranging from 0.65 to 0.76 which are equivalent to high-volatile bituminous rank. Like the vitrinite reflectance data, these aromaticity values show that the Poolowanna Formation in the Poolowanna Trough is within the oil window, whereas in the Patchawarra Trough it is at the onset of oil generation.

4.5 Hydrocarbon generative potential

The presence of organic matter suitable for hydrocarbon generation has certainly been verified by the nature and abundance of the macerals in these samples of the Poolowanna Formation. Although not quantitatively determined, the high relative abundance of both vitrinite and liptinite as a proportion of the DOM shows that the Poolowanna Formation is rich in oil-prone organic matter (Fig. 4.4). It can therefore be categorised as good source rock with a potential to generate liquid hydrocarbons. Moreover, its maturity implies that it has been an effective source rock.

4.5.1 Type of organic matter

The maceral groups are related to kerogen types as illustrated in Table 2.2. Algal liptinites deposited in aquatic environments give rise to kerogens which range from Type I to Type II

in composition. Woody-herbaceous organic matter varies from Type II kerogen comprising mainly cutinite, resinite suberinite and/or sporinite ± bituminite and desmocollinite to Type III kerogen in which woody plant structures (mainly telocollinite) are still visible, and from Type III kerogen rich in vitrinite and inertinite (mainly semifusinite) to Type IV kerogen which comprises highly oxidised inertinite.

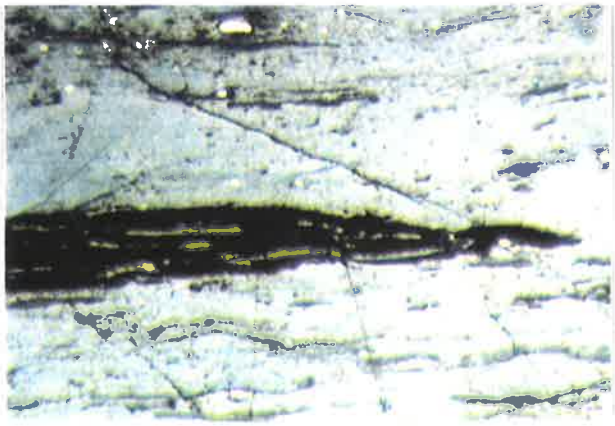
In the Poolowanna Trough the average maceral abundances show that vitrinite ≤ liptinite > inertinite, whereas in the Patchawarra Trough their average relative abundance is vitrinite < liptinite ≤ inertinite It can therefore be suggested that the Poolowanna Trough source rocks contain Type II/III kerogen whilst those in the Patchawarra Trough contain mostly Type III/II kerogen. The characteristic Type I macerals in the Poolowanna Trough are resinite and/or lamalginite, whilst in the Patchawarra Trough it is *Botryococcus*-like telalginite.

4.5.2 Hydrocarbon generation

Hydrocarbon generation from potential source rocks commences at various maturation levels depending on the type of kerogen. Powell and Snowdon (1983) suggested a composite hydrocarbon generation model for various kerogen types derived from marine and terrestrial derived organic matter. A similar approach may be applied to the Poolowanna Formation source rocks as shown in Figure 4.4. Their status for hydrocarbon generation is first defined by their maturation levels, as obtained from vitrinite reflectance data. Next, their maceral assemblages suggest that their organic matter is entirely of terrestrial origin, although a minor marine influence is evident in some cases.

Relatively high resinite contents in the Poolowanna Trough impart the potential for early generation of light naphthenic oil. Because of the considerable abundance of other liptinites, the Poolowanna Formation here is probably at the peak of waxy oil generation. The high content of vitrinite suggests that the early stage of gas generation may have been reached. It is therefore concluded that carbonaceous shales in the Poolowanna Trough are effective sources for waxy oil and minor gas. The maturation level of the Poolowanna Formation in the Patchawarra Trough indicates that it is at the early stage of both oil and gas generation, except where there is a significant resinite content. However, as shown from the maturity map (Fig. 4.3), this formation in the deeper parts of the trough may be at peak generation for waxy paraffinic oil or perhaps even within the light paraffinic oil window.
Plate 1

PLATE 1



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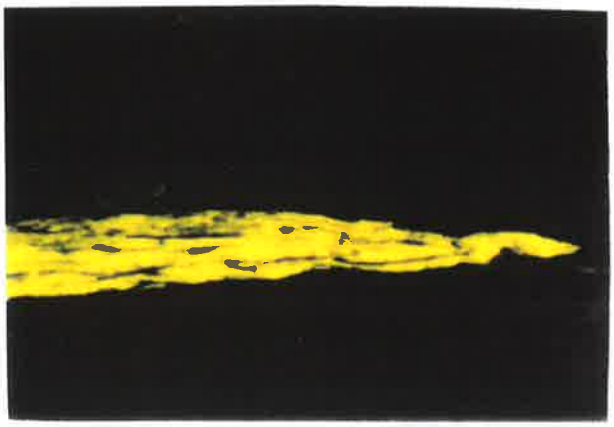

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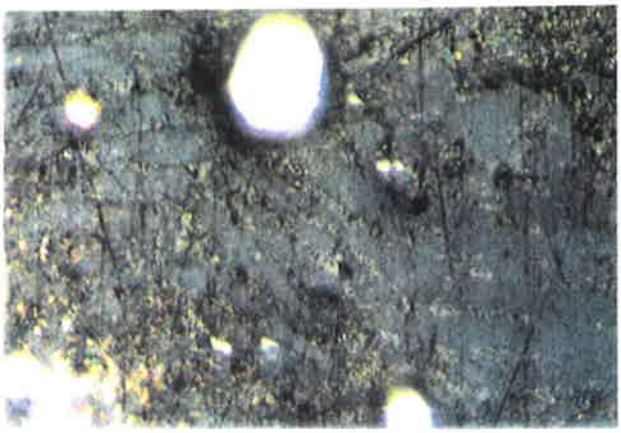
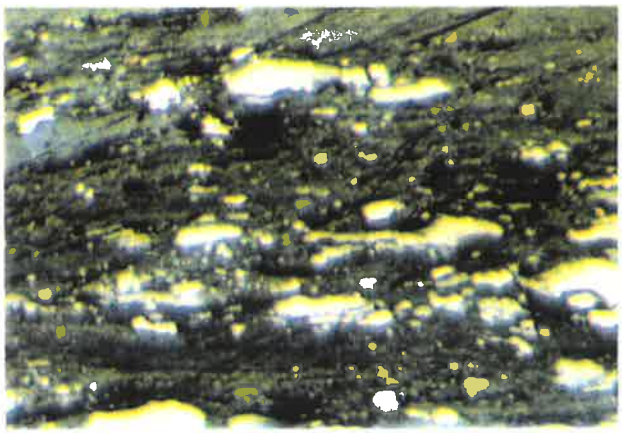


C

D



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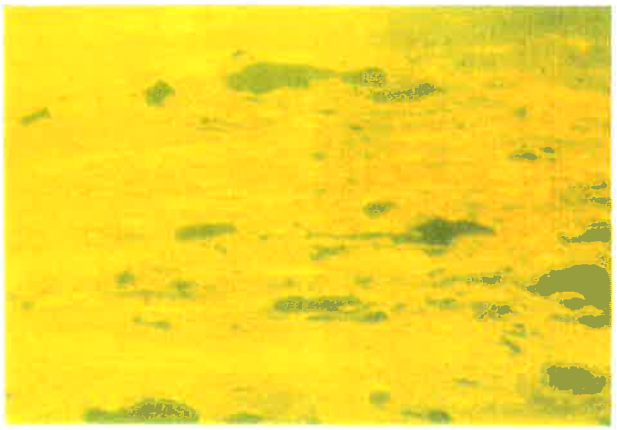

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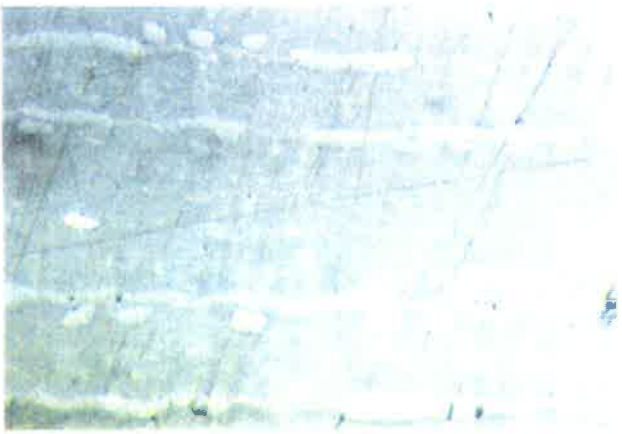


G

H

PLATE 1

A: Well: Poolowanna-1
Depth: 2417 m
Microlithotype: Clarite
R_O: 0.75%
Field of view: 136 μm x 197 μm
Description: Vitrinite (telocollinite); resinite/fluorinite, minor inertodetrinite

B: As in A, blue light excitation; fluorinite showing strong fluorescence.

C: Well: Poolowanna-1
Depth: 2499 m
Microlithotype: Monomacerite (DOM in silty shales)
R_O: 0.79%
Field of view: 136 μm x 197 μm
Description: Rod-like resinite and pyrite nodules and concretions

D: As in C, blue light excitation; resinite shows dull yellow fluorescence.

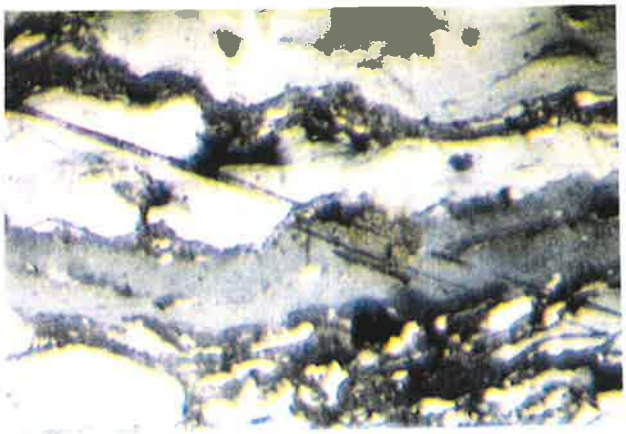
E: Well: Poolowanna-2
Depth: 2542 m
Microlithotype: Trimacerite
R_O: 0.74%
Field of view: 136 μm x 197 μm
Description: Desmocollinite, coarse inertodetrinite and liptodetrinite

F: As in E, blue light excitation; fluorescing vitrinite; lamalginite and bituminite.

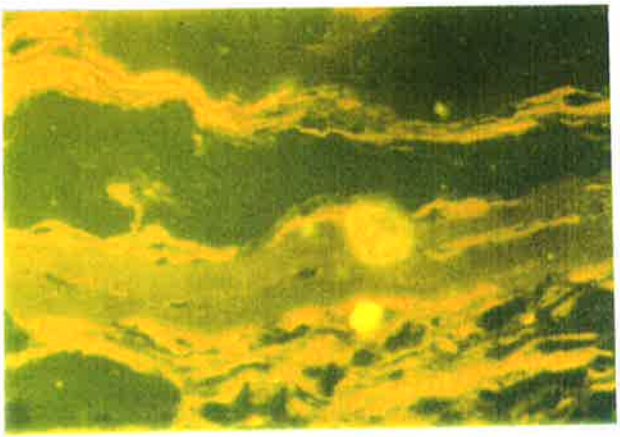
G: Well: Poolowanna-1
Depth: 2499 m
Microlithotype: Trimacerite
R_O: 0.79%
Field of view: 136 μm x 197 μm
Description: Resinite in cell cavities (telocollinite); semifusinite band and pyrite nodules.

H: As in G, blue light excitation; dull orange resinite fluorescence.

PLATE 2



A



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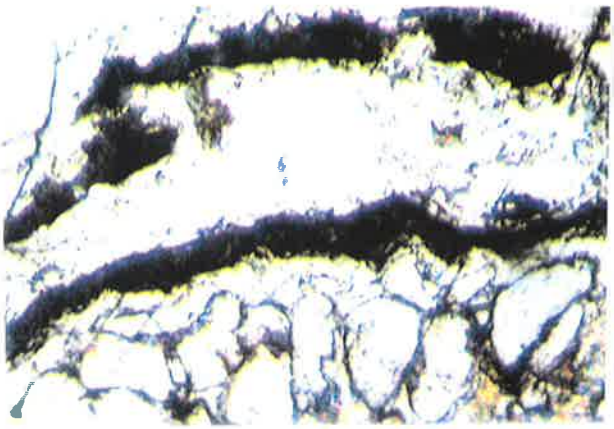

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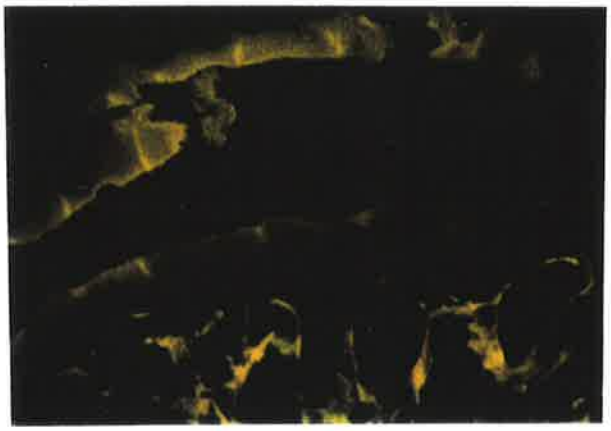

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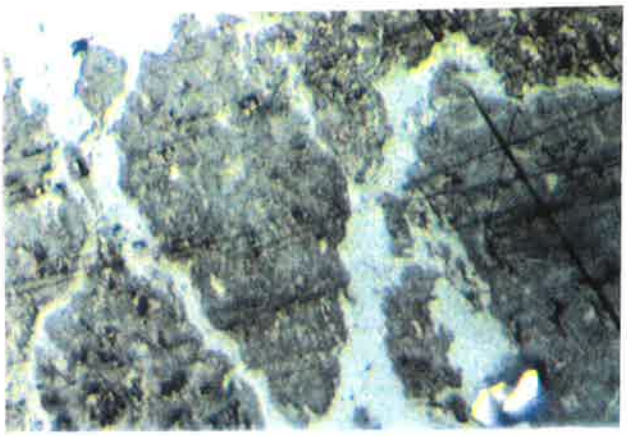

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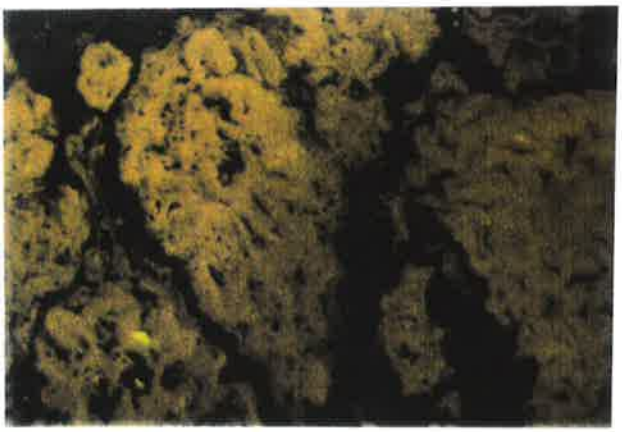

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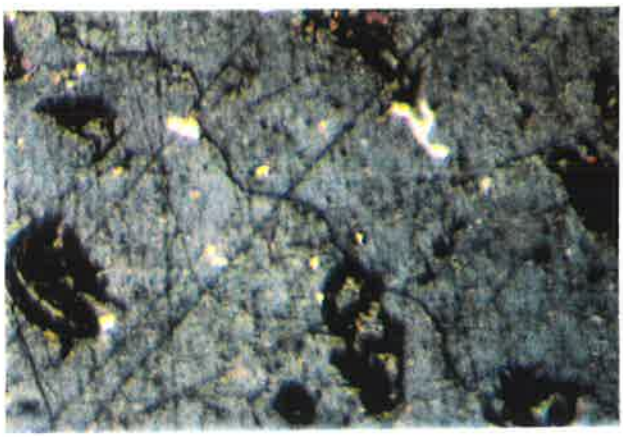

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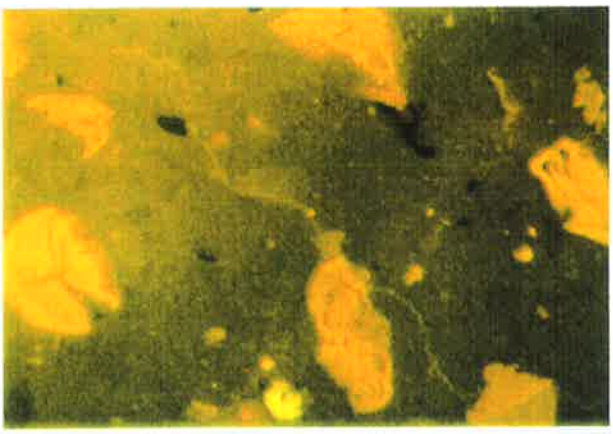


H

PLATE 2

A: Well: Poolowanna-2
Depth: 2542 m
Microlithotype: Trimacerite
R_O: 0.74%
Field of view: 136 μm x 197 μm
Description: Layers of inertinite (fusinite, semifusinite and inertodetrinite); vitrinite (telocollinite); and a round brownish yellow haze (bituminite ?)

B: As in A, blue light excitation; alginite (lamalginite); fluorescing vitrinite; round yellowish fluorescing ?bituminite.

C: Well: Poolowanna-1
Depth: 2417 m
Microlithotype: Trimacerite
R_O: 0.75%
Field of view: 136 μm x 197 μm
Description: Bands of vitrinite (coarse detrovitrinite); inertinite (semifusinite) and liptinite (cutinite, ca 9.6 μm thick).

D: As in C, blue light excitation; thick cutinite, resinite and/or fluorinite stringers.

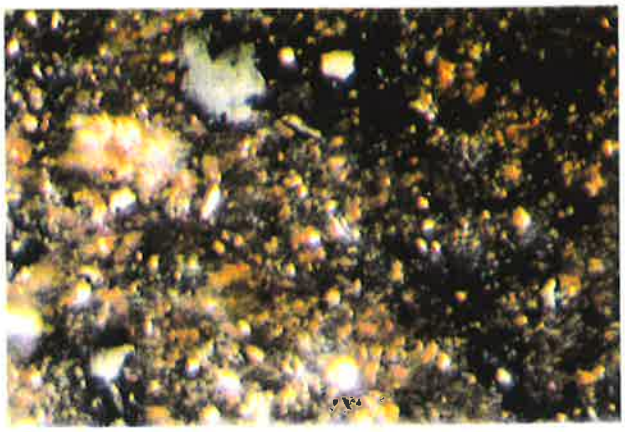
E: Well: Poolowanna-2
Depth: 2496 m
Microlithotype: Bimacerite (Clarite)
R_O: 0.71%
Field of view: 136 μm x 197 μm
Description: Sporangia (sporinite) separated by vitrinite bands; pyrite concretion.

F: As in E, blue light excitation; brownish yellow fluorescence of sporangia.

G: Well: Poolowanna-3
Depth: 2560 m
Microlithotype: Bimacerite (Clarite)
R_O: 0.85%
Field of view: 136 μm x 197 μm
Description: Vitrinite (desmocollinite); liptinite (different forms of macro-sporinite)

H: As in G; blue light excitation; sporinite exhibiting a near perfect preservation of the entire spore and its inner contents; fluorescing vitrinite and alginite.

PLATE 3



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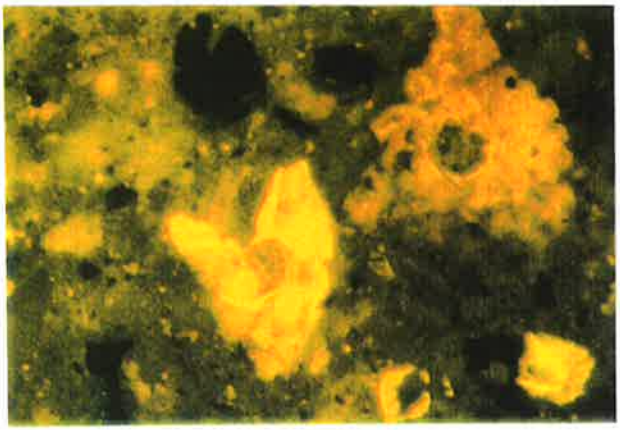

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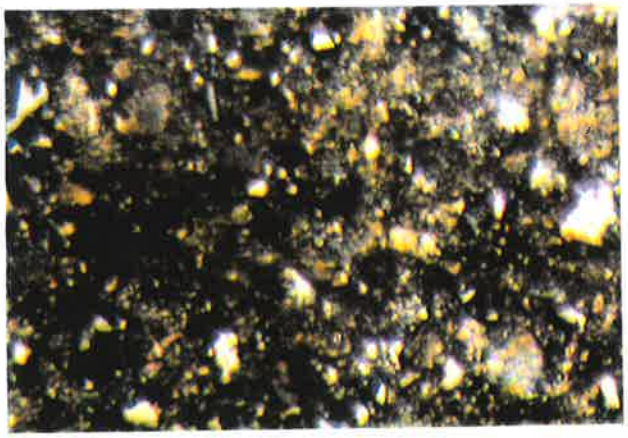

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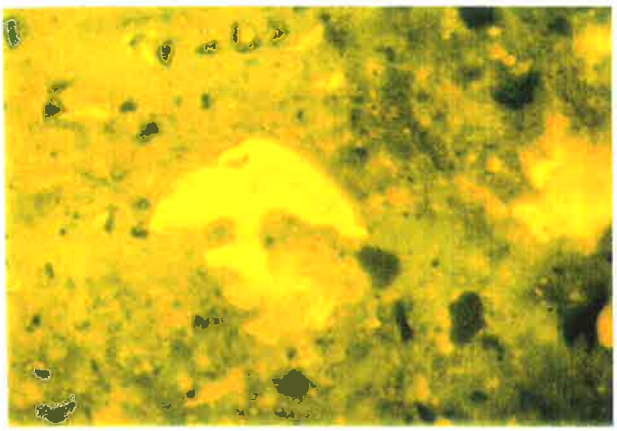

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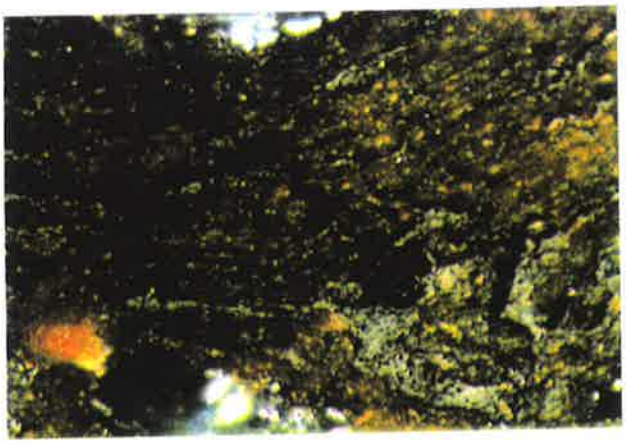

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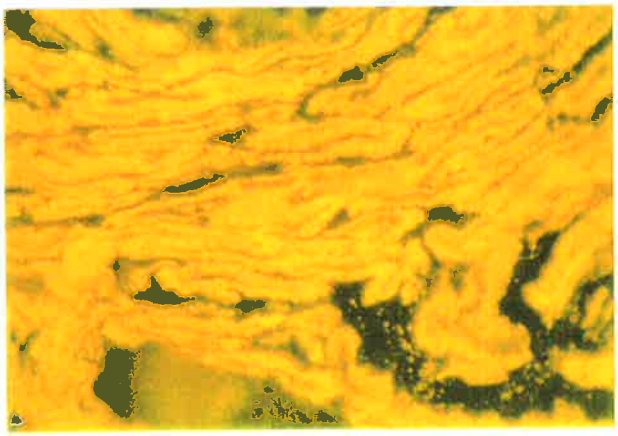

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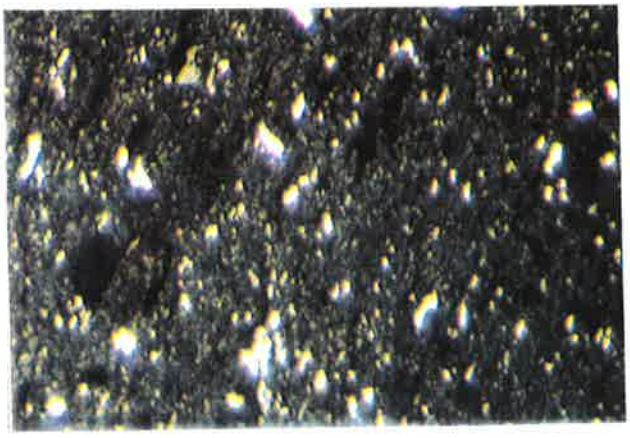

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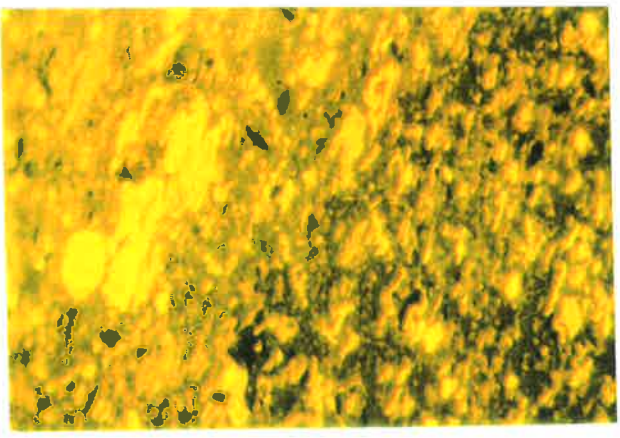


H

PLATE 3

A: Well: Tantanna-3
Depth: 1807 m
Microlithotype: Monomacerite
R_O: 0.62%
Field of view: 136 μm x 197 μm
Description: Dispersed organic matter (DOM) liptinite (bituminite, ?sporinite appears translucent brown).

B: As in A, blue light excitation; bituminite, yellowish groundmass; ?sporinite, yellow to orange fluorescence.

C: Well: Tantanna-1
Depth: 1795 m
Microlithotype: Monomacerite
R_O: 0.67%
Field of view: 136 μm x 197 μm
Description: DOM; bituminite, brownish translucent liptinite

D: As in C, blue light excitation; yellow ?sporinite; brownish orange bituminite and liptodetrinite.

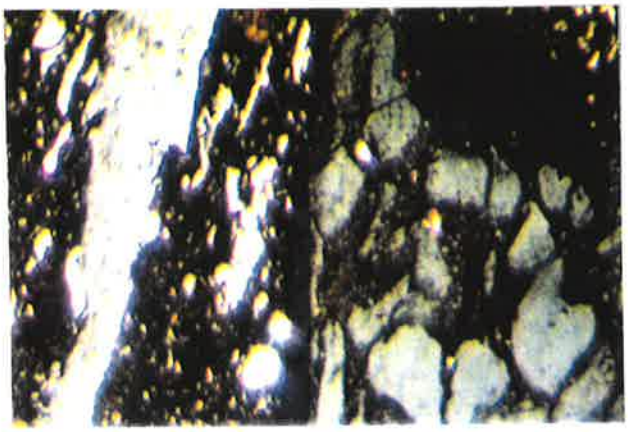
E: Well: Tantanna-8
Depth: 1823 m
Microlithotype: Monomacerite
R_O: 0.58%
Field of view: 136 μm x 197 μm
Description: Sporangium, reddish brown with partial internal reflection; desmocollinite.

F: As in E, blue light excitation; yellow ornamented sporangium

G: Well: Tantanna-2
Depth: 1799
Microlithotype: Trimacerite
R_O: 0.67%
Field of view: 136 μm x 197 μm
Description: Fine-grained vitrodetrinite; inertodetrinite and alginite

H: As in G, blue light excitation; miosporinite, telalginite and bituminite

PLATE 4



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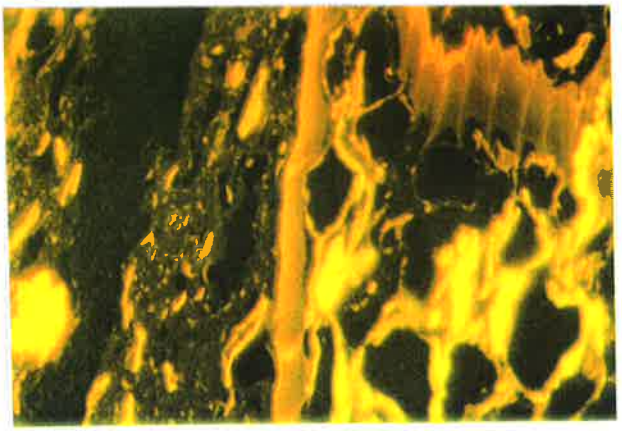

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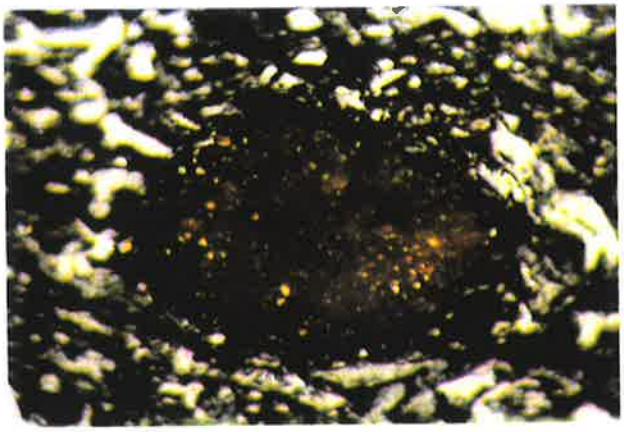
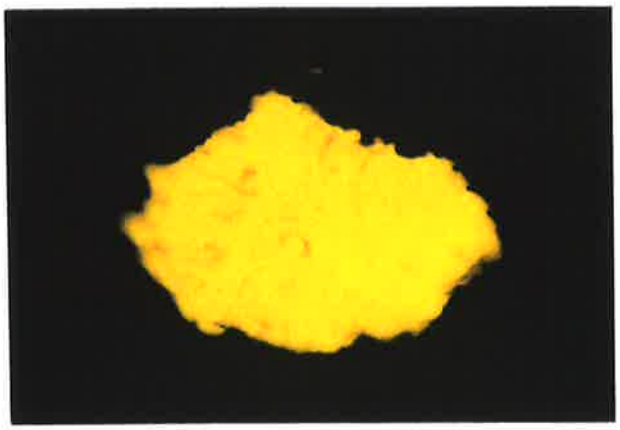


C



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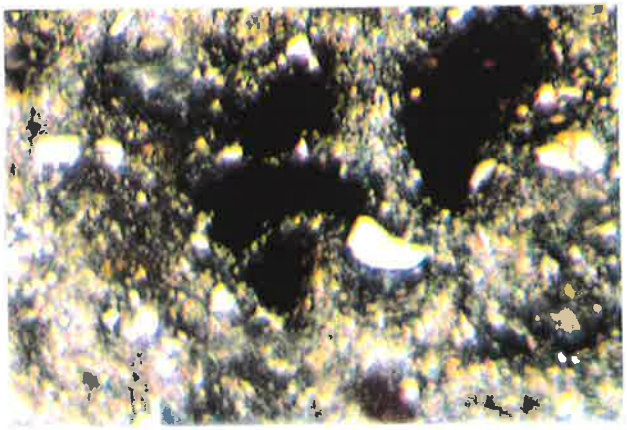

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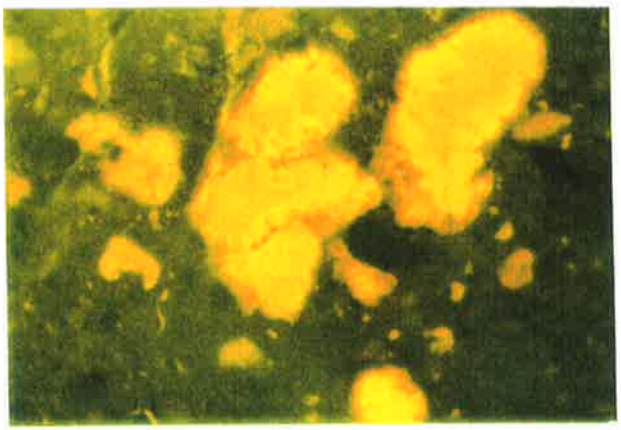
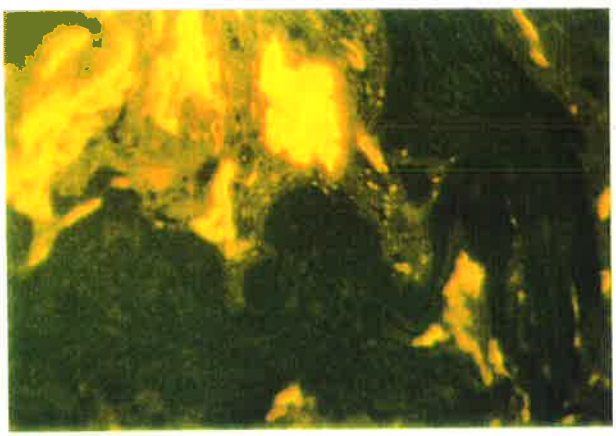


F

G



H

PLATE 4

A: Well: Tantanna-2
Depth: 1799 m
Microlithotype: Trimacerite
R_O: 0.67%
Field of view: 136 μm x 197 μm
Description: DOM; vitrinite (coarse vitrodetrinite); inertinite (fusinite and inertodetrinite); liptinite (telalginite, cutinite and bituminite) and pyrite.

B: As in A, blue light excitation; liptinite-rich, resinite, fluorinite/exsudatinite; cutinite ca 9.6 μm

C: Well: Tantanna-4
Depth: 1814 m
Microlithotype: Bimacerite (durite)
R_O: 0.66%
Field of view: 136 μm x 197 μm
Description: Liptinite (*Pila* alginite brownish and translucent); inertinite (inertodetrinite)

D: As in C, blue light excitation; the *Botryococcus*-like telalginite (*Pila* colonies) are shown by strong orange yellow fluorescence.

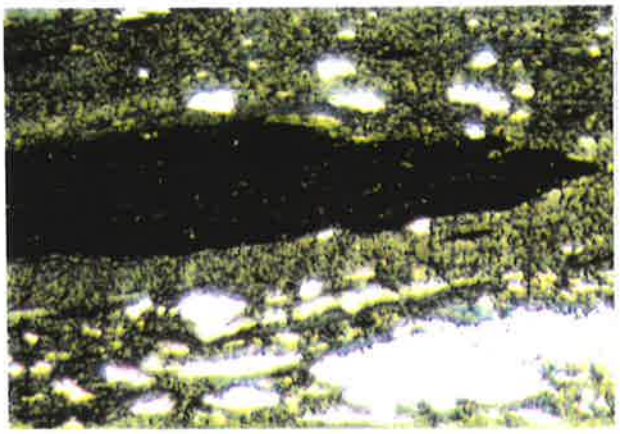
E: Well: Tantanna-3
Depth: 1807 m
Microlithotype: monomacerite
R_O: 0.62%
Field of view: 136 μm x 197 μm
Description: Telalginite (brownish with internal reflections) in association with minor inertodetrinite dispersed in siltshale.

F: As in E, blue light excitation; orange fluorescence of telalginite.

G: Well: Tantanna-2
Depth: 1799 m
Microlithotype: Bimacerite
R_O: 0.67%
Field of view: 136 μm x 197 μm
Description: Inertinite (deformed fusinite and semifusinite) dispersed in shale together with; liptinite (telalginite, dark brown bodies; and bituminite, brownish groundmass)

H: As in G, blue light excitation; telalginite (orange fluorescence); bituminite (dull brownish yellow fluorescent groundmass); sporinites and liptodetrinite.

PLATE 5



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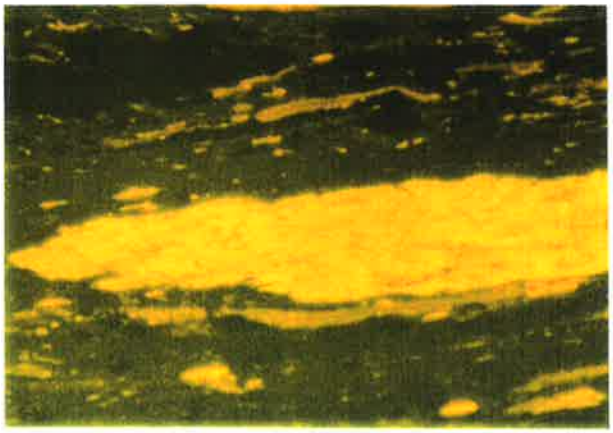

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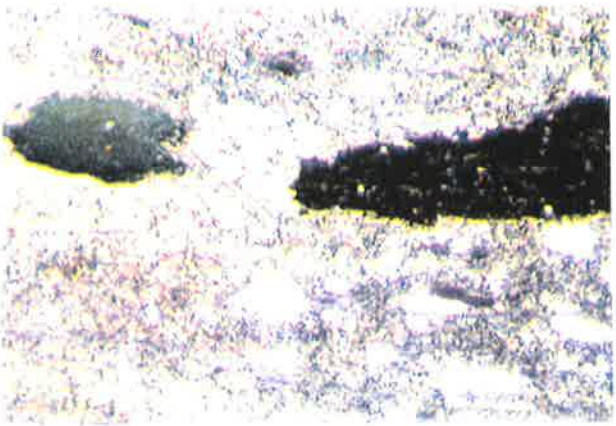

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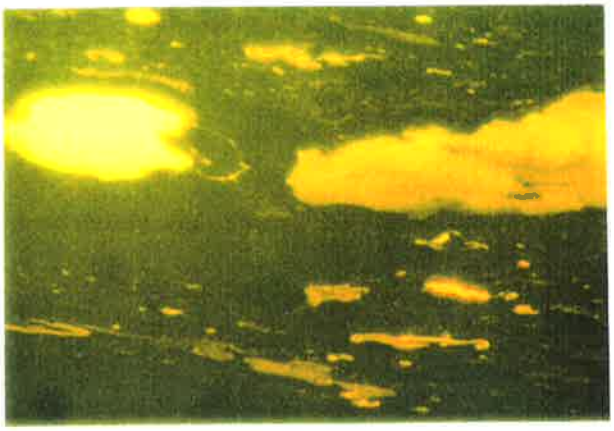

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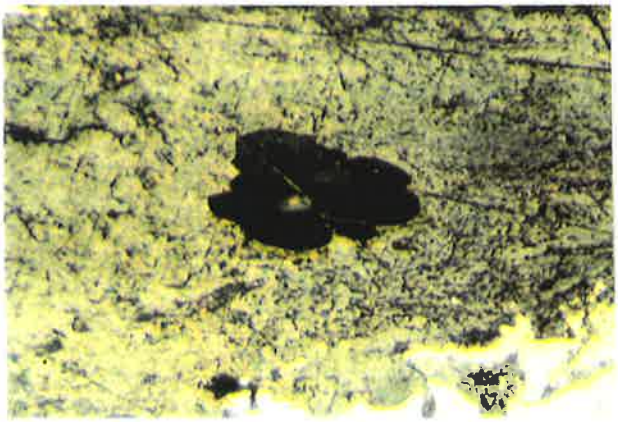

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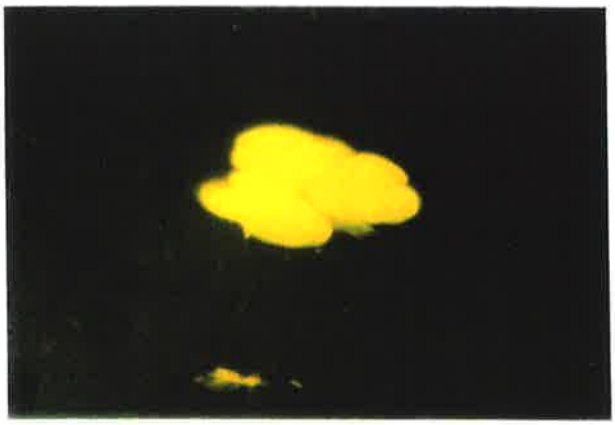
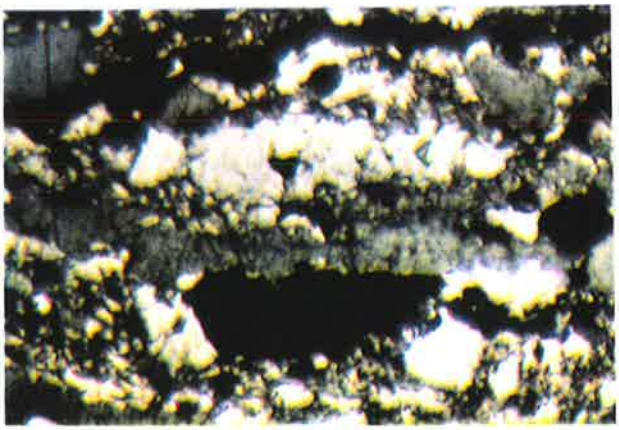
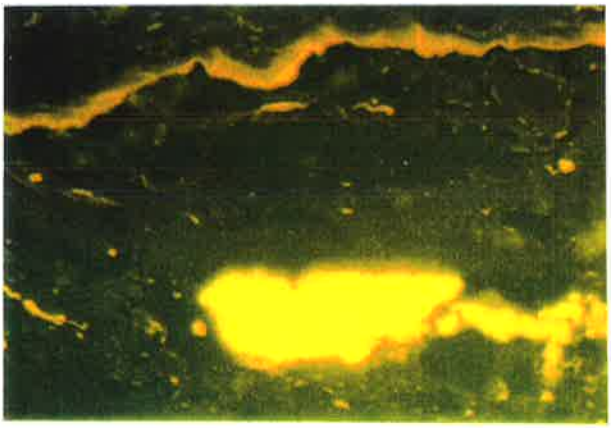


F



G



H

PLATE 5

A: Well: Sturt-1
Depth: 1865 m
Microlithotype: Trimacerite
Ro: 0.59%
Field of view: 136 μm x 197 μm
Description: A layer of fluorinite (dark elongated lens) in desmocollinite, liptodetrinite, inertodetrinite and fusinite.

B: As in A, blue light excitation; strong yellow fluorescence of fluorinite; fluorescing liptodetrinite, miosporinite (tenuisporinite); and desmocollinite.

C: Well: Sturt-8
Depth: 1862 m
Microlithotype: Trimacerite
R_O: 0.59%
Field of view: 136 μm x 197 μm
Description: Resinite bodies (dark) in association with desmocollinite, semifusinite, micrinite and liptodetrinite.

D: As in C, blue light excitation; strong yellow fluorescence of resinite, miosporinites and stringers of exsudatinite and fluorinite (strong orange-yellow fluorescence)

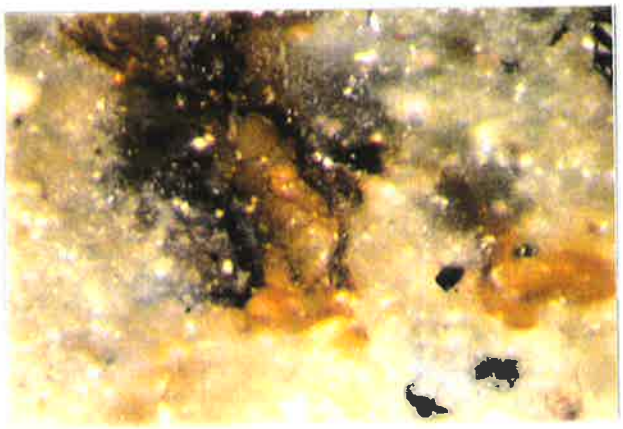
E: Well: Sturt-6
Depth: 1847
Microlithotype: Trimacerite
R_O: not determined
Field of view: 136 μm x 197 μm
Description: Resinite and/ or fluorinite (dark) globules in telocollinite interlayered with fusinite (displaying bogen structure)

F: As in E, blue light excitation; strong green yellow fluorescence of fluorinite

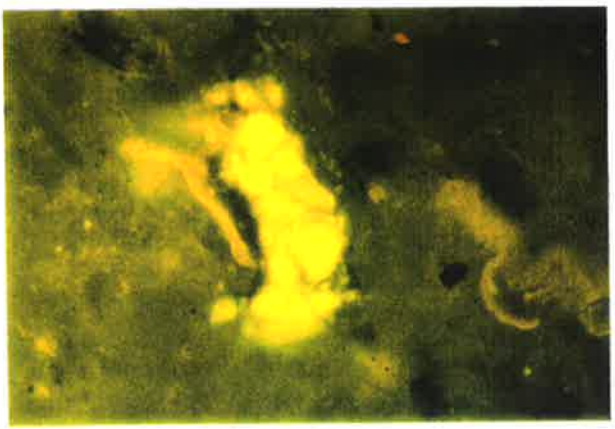
G: Well: Tantanna-4
Depth: 1807 m
Microlithotype: Trimacerite
R_O: 0.75%
Field of view: 136 μm x 197 μm
Description: Layers of telocollinite, semifusinite and dark brown telalginite bodies, in association with inertodetrinite.

H: As in G, blue light excitation; showing fluorescence of cutinite and liptodetrinite.

PLATE 6



A



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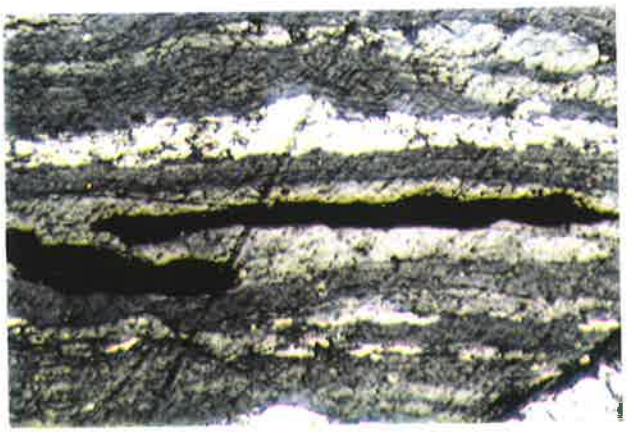

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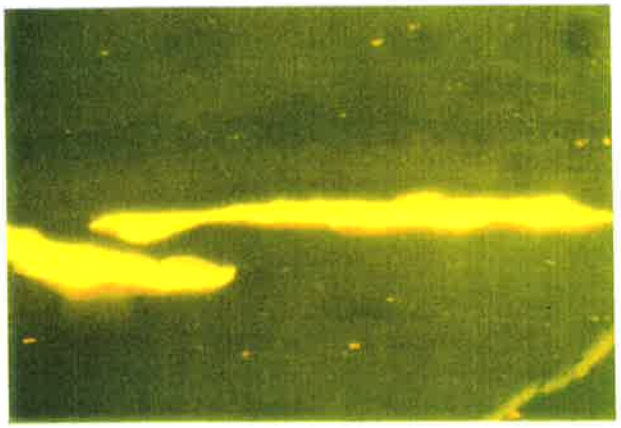
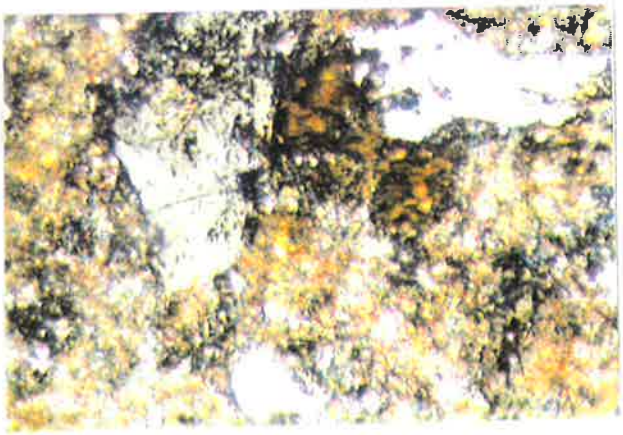
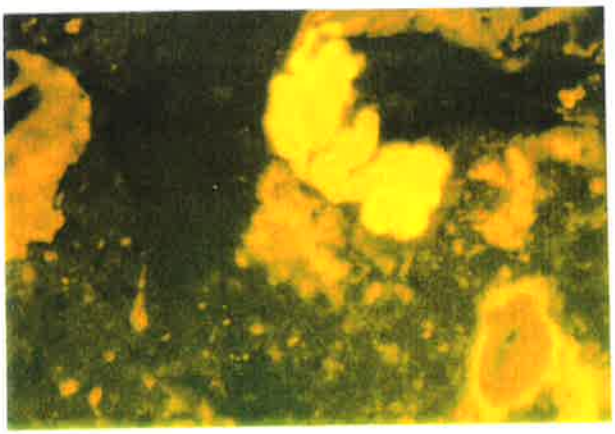


D



E



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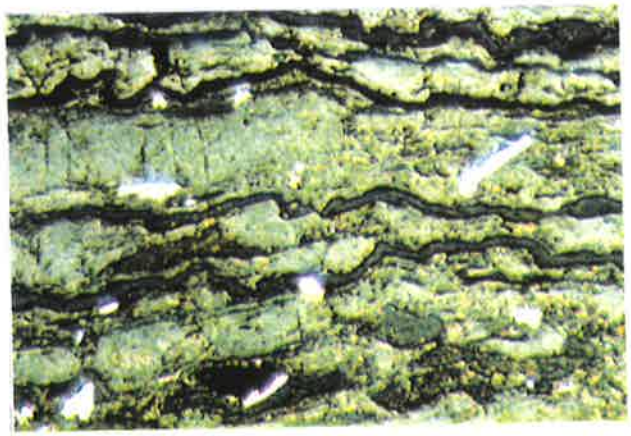

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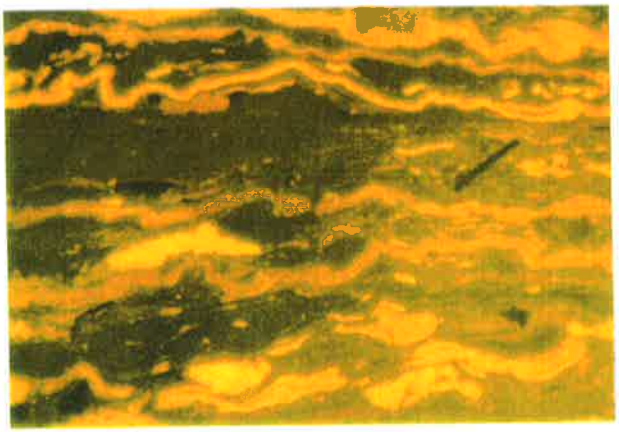


H

PLATE 6

A: Well: Sturt-3
Depth: 1859 m
Microlithotype: Monomacerite
R_O: not determined
Field of view: 136 μm x 197 μm
Description: Spherical brownish fluorinite, translucent brown cutinite and sparse vitrodetrinite in siltstone.

B: As in A, blue light excitation; strong green fluorescence of fluorinite globules; cutinite stringer showing yellowish orange fluorescence.

C: Well: Sturt-4
Depth: 1859 m
Microlithotype: Trimacerite
R_O: 0.64%
Field of view: 136 μm x 197 μm
Description: Alternating bands of vitrinite (desmocollinite and telocollinite); inertinite (semifusinite and fusinite) and liptinite (fluorinite - dark layer)

D: As in C, blue light excitation; strong greenish-yellow fluorescence of fluorinite; weak greenish-brown bituminite in desmocollinite; and liptodetrinite specs.

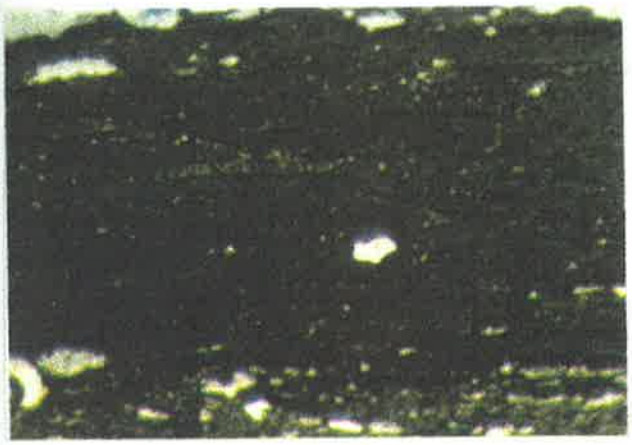
E: Well: Sturt-6
Depth: 1865 m
Microlithotype: Trimacerite
R_O: 0.66%
Field of view: 136 μm x 197 μm
Description: DOM; coarse vitrodetrinite and inertodetrinite; translucent liptodetrinite and light brown resinite in silty shale.

F: As in E, blue light excitation; strong yellow fluorescing globules of fluorinite; light brownish yellow cutinite; resinite body with zonal structures.

G: Well: Sturt-4
Depth: 1881 m
Microlithotype: Bimacerite
R_O: 0.57%
Field of view: 136 μm x 197 μm
Description: Alternating bands of thin cutinite (1.6–3.2 μm thick) and desmocollinite associated with miosporinite, telalginite and liptodetrinite; and a band of telocollinite and inertodetrinite.

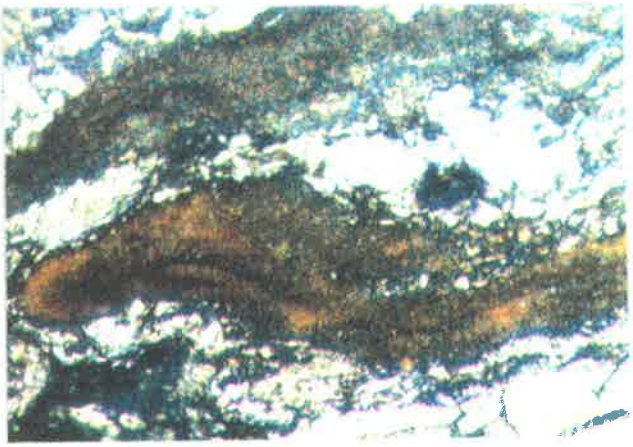
H: As in G, blue light excitation; fluorescing desmocollinite and other liptinite macerals.

PLATE 7

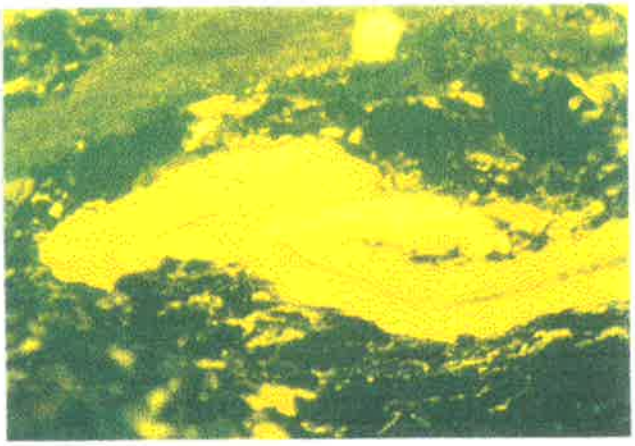


A

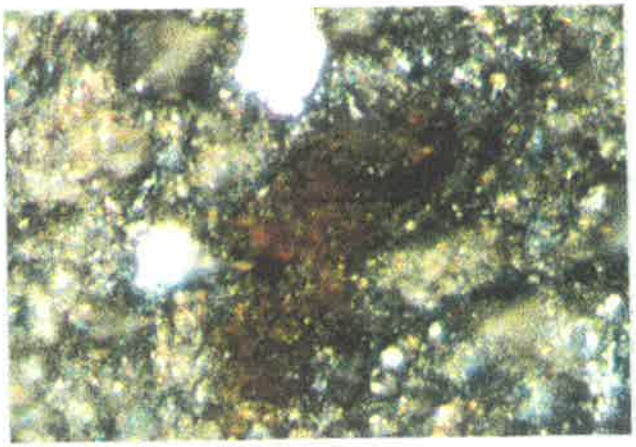
B



C



D



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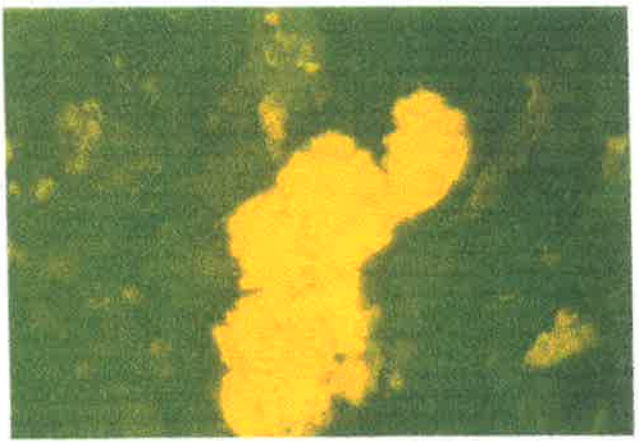
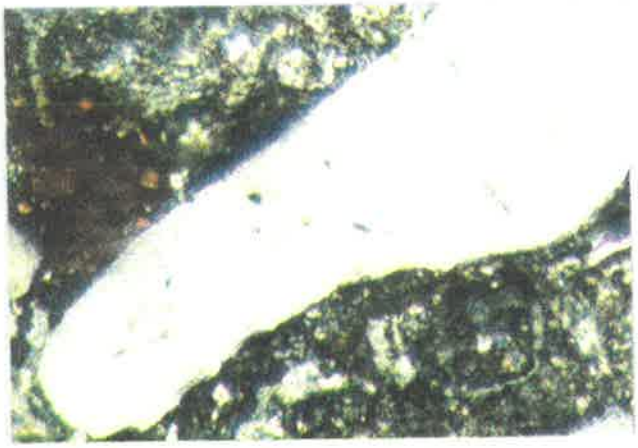


F



G

H

PLATE 7

A: Well: Sturt-1
Depth: 1865 m
Microlithotype: Monomacerite (liptite)
R_O: 0.59%
Field of view: 136 μm x 197 μm
Description: Cutinite-rich liptite (leaf cuticles closely compacted) and sparse inertodetrinite.

B: As in A, blue light excitation; yellow fluorescing cutinite band.

C: Well: Sturt-1
Depth: 1865 m
Microlithotype: Bimacerite (durite)
R_O: 0.59%
Field of view: 213 μm x 308 μm
Description: Mega-sporinite, brownish spongy texture indicative of oxidation; in association with fusinite.

D: As in C, blue light excitation; yellow fluorescing mega-sporinite and liptodetrinite.

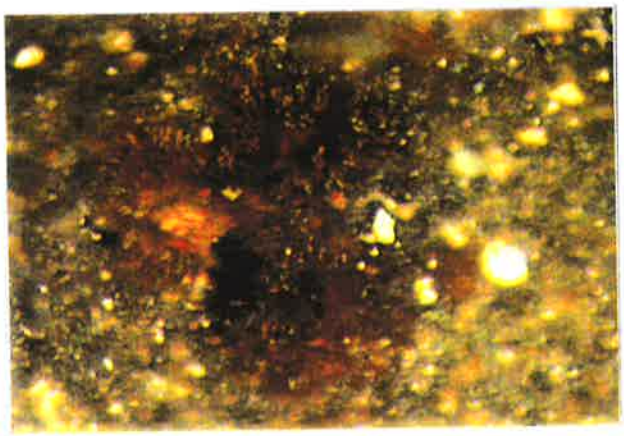
E: Well: Sturt-4
Depth: 1859 m
Microlithotype: Monomacerite
R_O: not determined
Field of view: 136 μm x 197 μm
Description: DOM; telalginite (reddish-brown internal reflection) associated with pyrite concretions in silty shale.

F: As in E, blue light excitation; strong orange fluorescence of *Pila* colonies

G: Well: Sturt-3
Depth: 1862 m
Microlithotype: Bimacerite (durite)
R_O: 0.64%
Field of view: 136 μm x 197 μm
Description: Telalginite in association with macrinite (likely transformed from resinite) and inertodetrinite in carbonaceous shales.

H: As in G, blue light excitation; strong orange yellow fluorescence of *Pila* colonies and liptodetrinite.

PLATE 8



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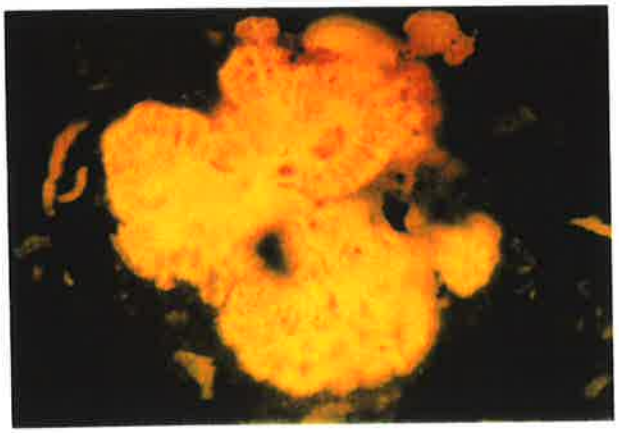

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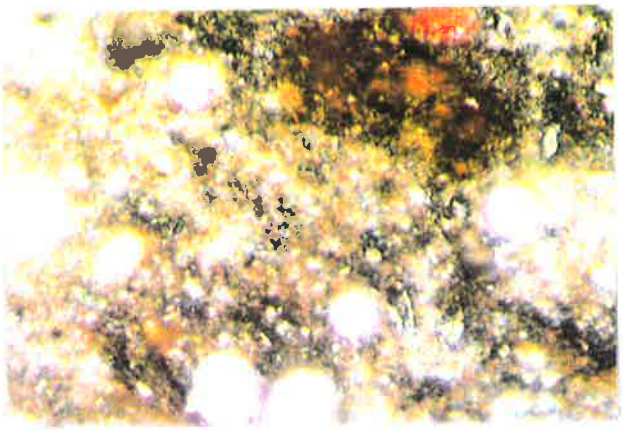

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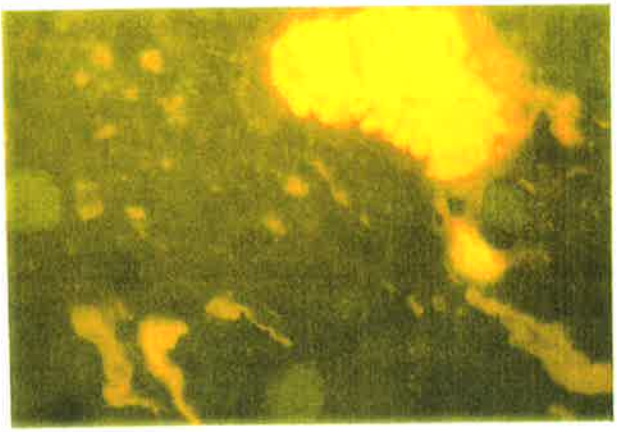

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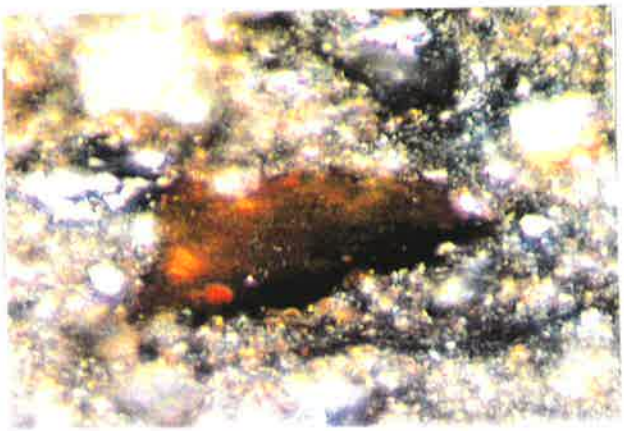

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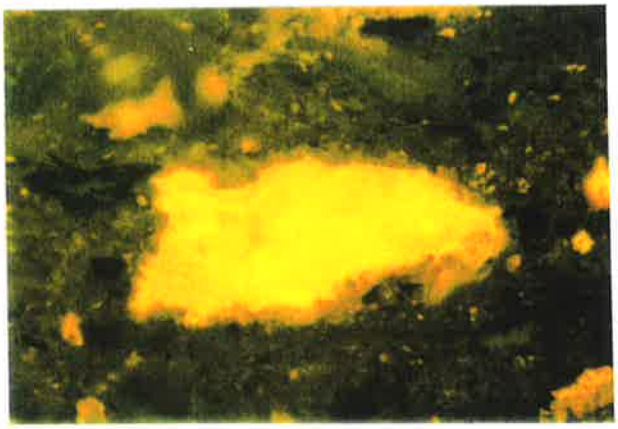

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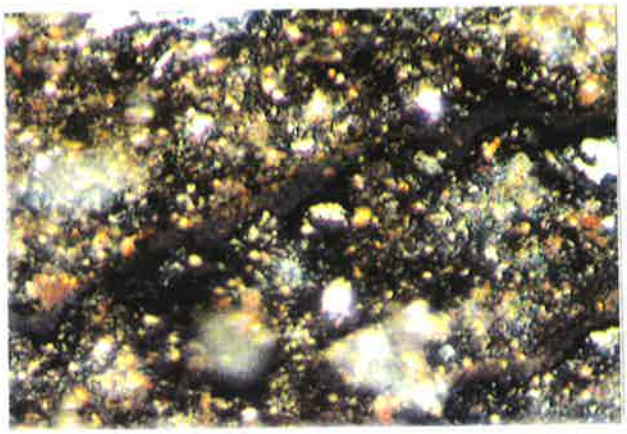

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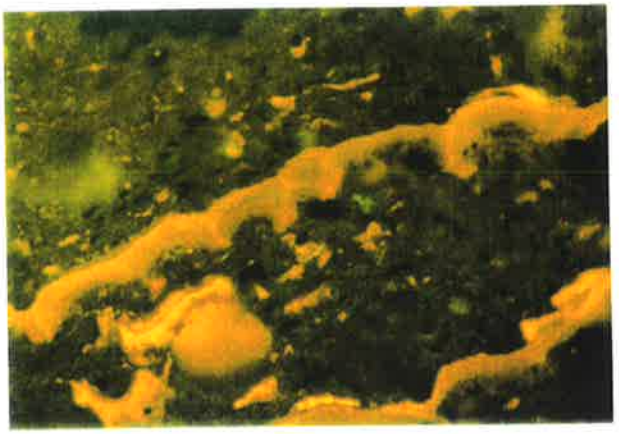


H

PLATE 8

A: Well: Sturt East-4
Depth: 1838 m
Microlithotype: Bimacerite (durite)
R_O: 0.64%
Field of view: 136 μm x 197 μm
Description: *Botryococcus*-like telalginite (*Pila*) and sparse inertodetrinite.

B: As in A, blue light excitation; *Pila* colonies (strong orange fluorescence).

C: Well: Sturt East-1
Depth: 1841 m
Microlithotype: Monomacerite
R_O 0.58%
Field of view: 136 μm x 197 μm
Description: DOM; telalginite in association with pyrite framboids in shales; sparse inertodetrinite and liptodetrinite.

D: As in C, blue light excitation; telalginite and dull orange fluorescing sporinite and liptodetrinite.

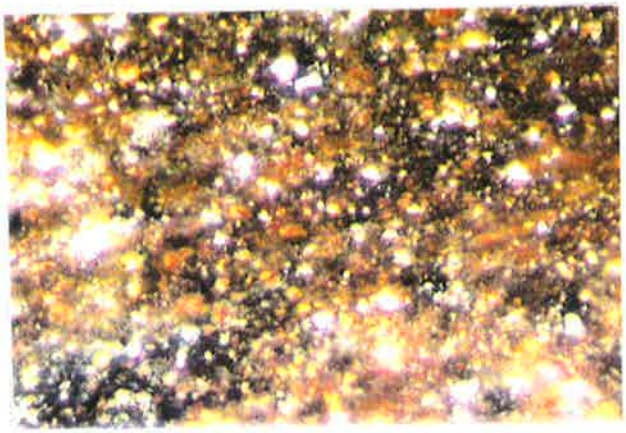
E: Well: Sturt East 3
Depth: 1850 m
Microlithotype: Monomacerite
R_O: 0.50%
Field of view: 136 μm x 197 μm
Description: DOM; telalginite (brownish red) in association with sparse inertodetrinite and vitrodetrinite in silty shale.

F: As in E, blue light excitation; deformed telalginite in association with liptodetrinite.

G: Well: Sturt East-3
Depth: 1850 m
Microlithotype: Bimacerite
R_O: 0.50%
Field of view: 136 μm x 197 μm
Description: DOM; thick cutinite (ca 9.6 μm) and inertodetrinite in silty shales.

H: As in G, blue light excitation; brownish-orange fluorescence of cutinite showing cuticular edges; associated with brownish spherical resinite and liptodetrinite.

PLATE 9



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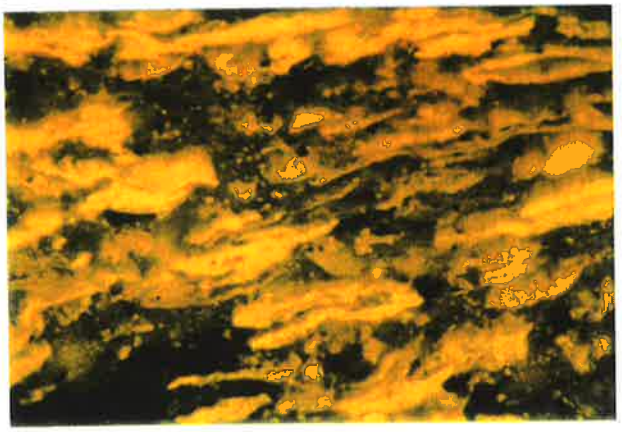

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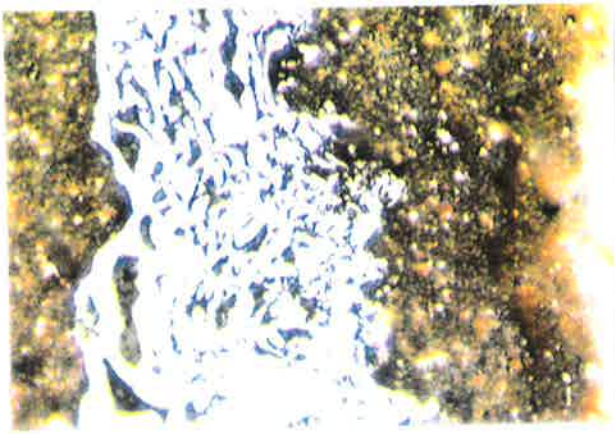
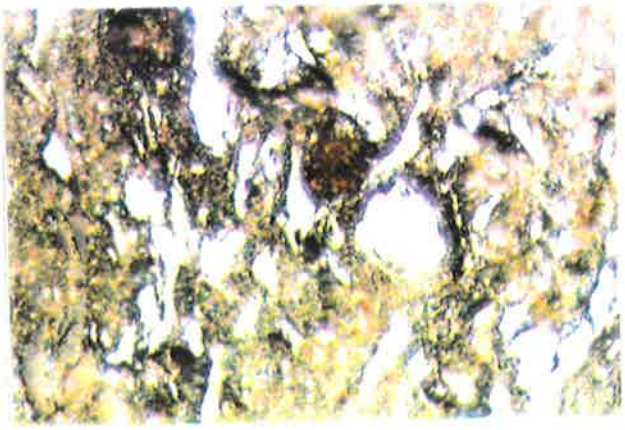


C

D



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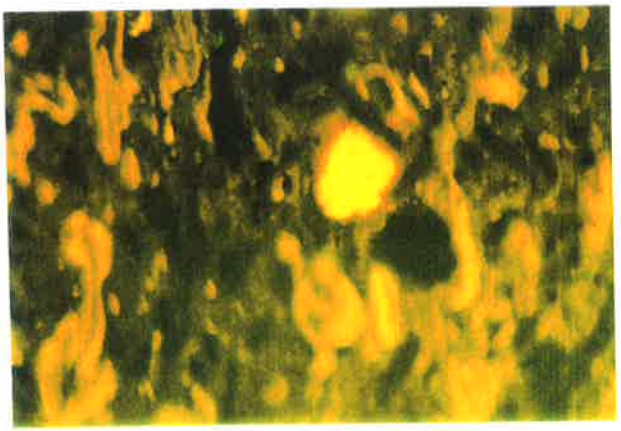
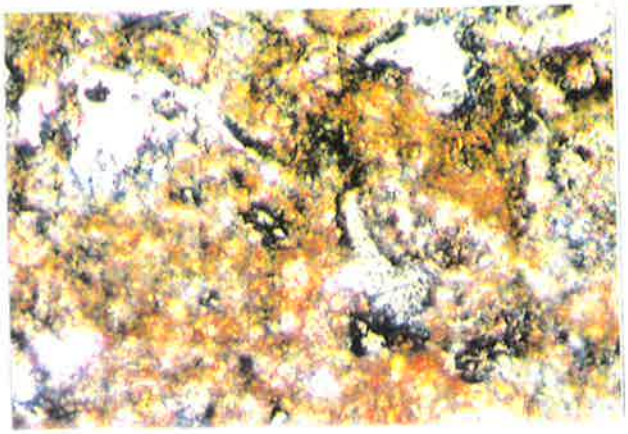
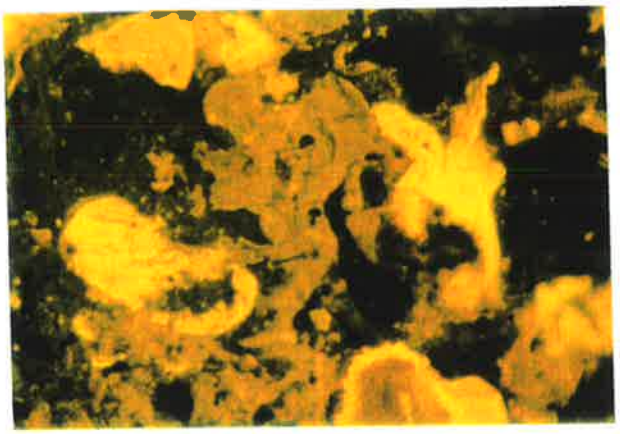


F



G



H

PLATE 9

A: Well: Sturt East-1
Depth: 1835 m
Microlithotype: Trimacerite
R_O: 0.66%
Field of view: 136 μm x 197 μm
Description: DOM; brownish translucent liptinite associated with fine inertodetrinite, vitrodetrinite and pyrite nodules in silty shale.

B: As in A, blue light excitation; abundant orange yellow fluorescing microsporinite (crassisporinite) or miosporinite and bituminite.

C: Well: Sturt East-1
Depth: 1841 m
Microlithotype: Monomacerite
R_O: 0.58%
Field of view: 136 μm x 197 μm
Description: DOM; layers of translucent liptinite and fusinite (deformed cell structures), overlain by sandstone layer.

D: As in C, blue light excitation; liptodetrinite and miosporinite associated with telalginite in bituminite groundmass.

E: Well: Sturt East-1
Depth: 1844 m
Microlithotype: Trimacerite
R_O: 0.57%
Field of view: 136 μm x 197 μm
Description: DOM; inertodetrinite, vitrodetrinite, telalginite (brownish), liptodetrinite, sporinite and other translucent liptinite; and pyrite concretions in carbonaceous silty shale.

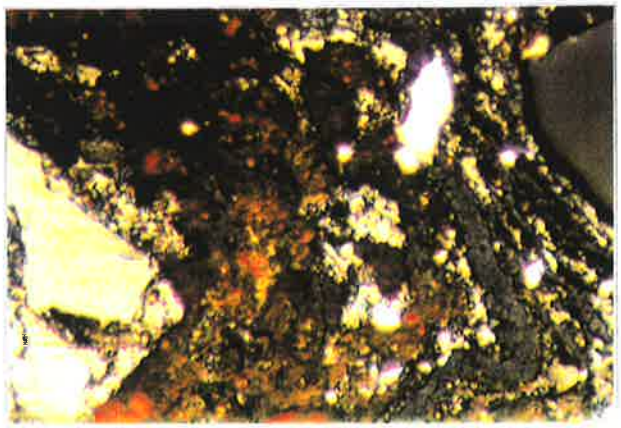
F: As in E, blue light excitation; strong orange yellow fluorescence of telalginite; brownish orange sporinite (crassisporinite) and liptodetrinite.

G: Well: Sturt East-2
Depth: 1829 m
Microlithotype: Trimacerite (liptinite most abundant)
R_O: 0.69%
Field of view: 136 μm x 197 μm
Description: Brownish translucent liptinite in association with coarse detrovitrinite and inertodetrinite; and sparse pyrite nodules.

H: As in G, blue light excitation; abundant sporinite (crassisporinite), fluorescing brown

to orange yellow.

PLATE 10



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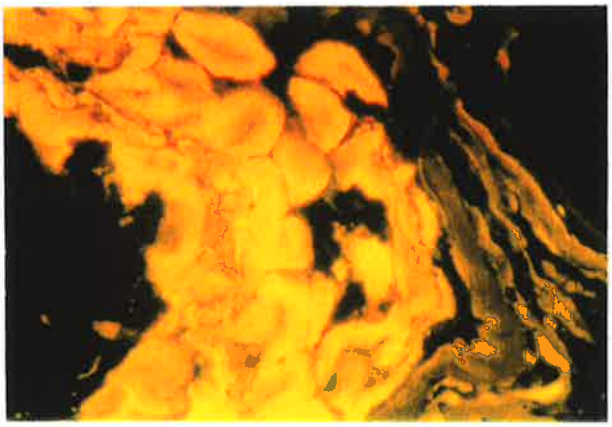

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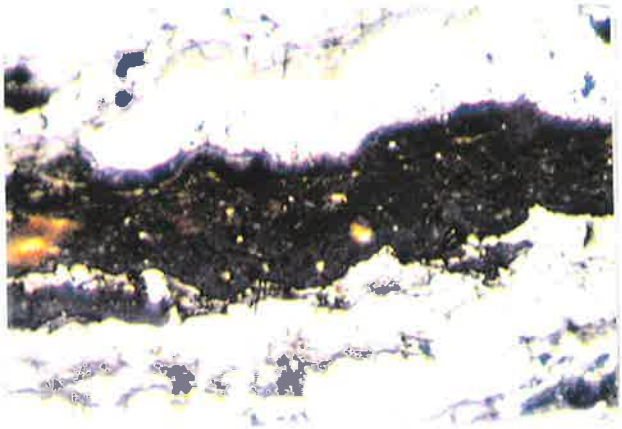

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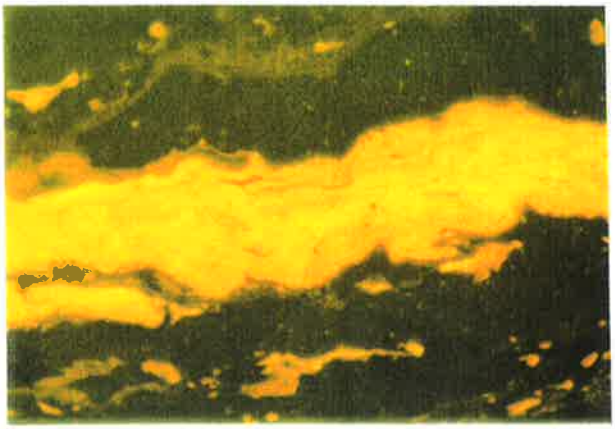
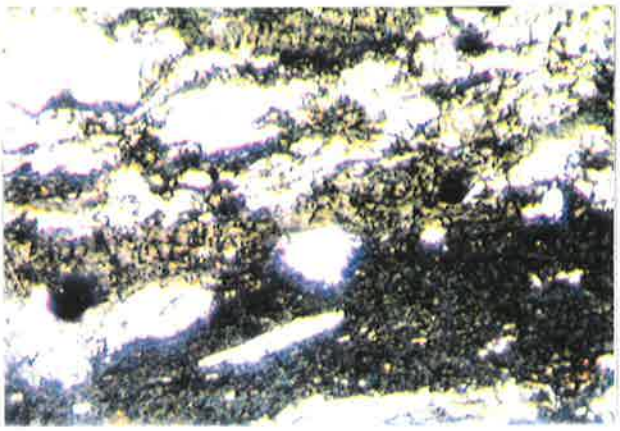


D



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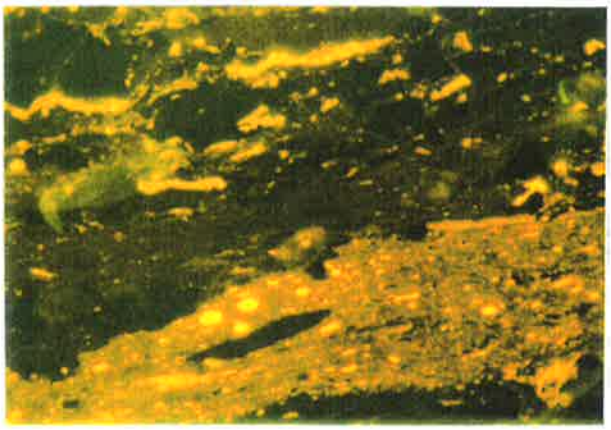
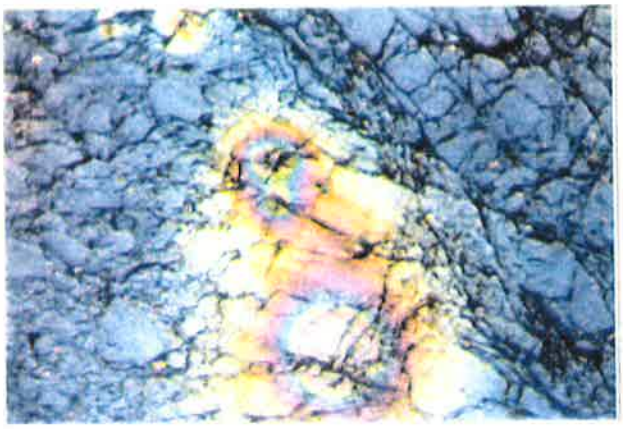


F



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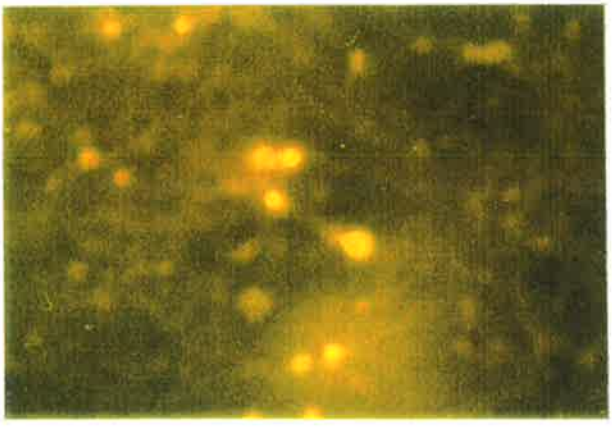


H

PLATE 10

A: Well: Sturt East-3
Depth: 1865 m
Microlithotype: Bimacerite (durite)
R_O: 0.60%
Field of view: 136 μm x 197 μm
Description: Oblique to bedding section through a thick (ca 10 μm) cutinite, in association with fusinite, micrinite, sparse vitrodetrinite and some pyrite nodules.

B: As in A, blue light excitation; orange to brown fluorescence of cutinite, showing compressed cell structures and possibly orange fluorescence of fluorinite excretion (in the middle).

C: Well: Sturt East-4
Depth: 1862 m
Microlithotype: Trimacerite
R_O: 0.56%
Field of view: 136 μm x 197 μm
Description: Bands of semifusinite, fusinites and desmocollinite, telocollinite and liptinite.

D: As in C, blue light excitation; orange yellow fluorescence of sporinite clusters in band (?sporangia).

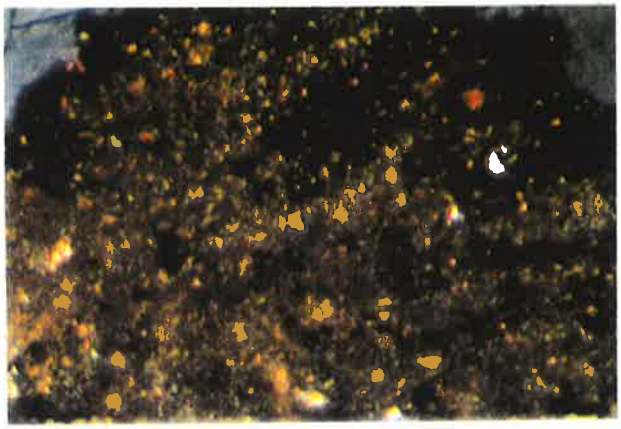
E: Well: Sturt East-4
Depth: 1862 m
Microlithotype: Trimacerite
R_O: 0.56%
Field of view: 136 μm x 197 μm
Description: Inertinite (inertodetrinite and micrinite); desmocollinite and bituminite bands in coal.

F: As in E, blue light excitation; brown fluorescing bituminite band containing micro-elliptical shaped resinite/fluorinite (orange fluorescent); abundant liptodetrinite; micro-sporinite and dull-brown fluorescing desmocollinite. Exsudatinite or fluorinite stringers and droplets fluorescing orange are around the coarse inertodetrinite.

G: Well: Sturt East-4
Depth: 1852 m
Microlithotype: Monomaceral (vitrite)
R_O: not determined
Field of view: 136 μm x 197 μm
Description: Oil haze in vitrodetrinite

H: As in G, blue light excitation; greenish yellow fluorescing oil specs.

PLATE 11



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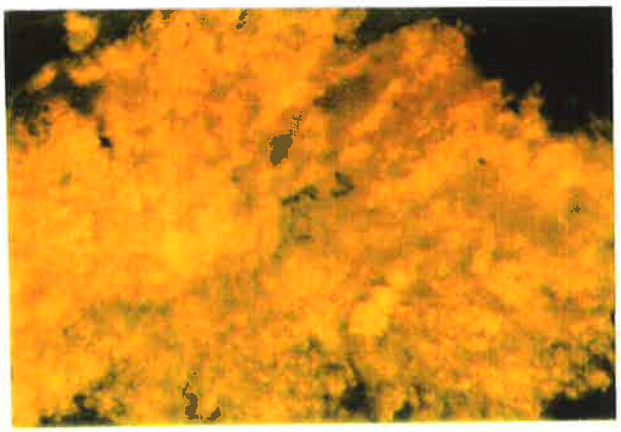

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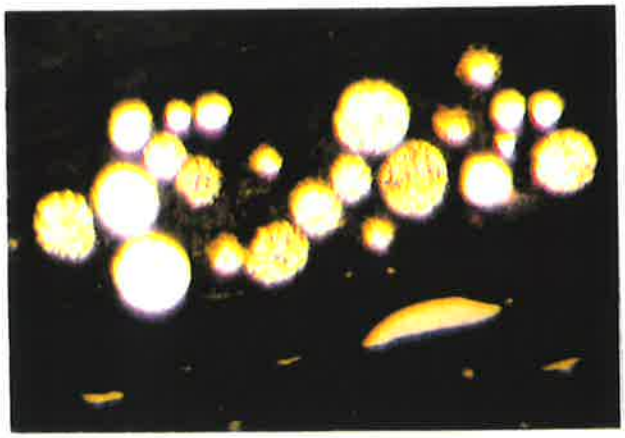

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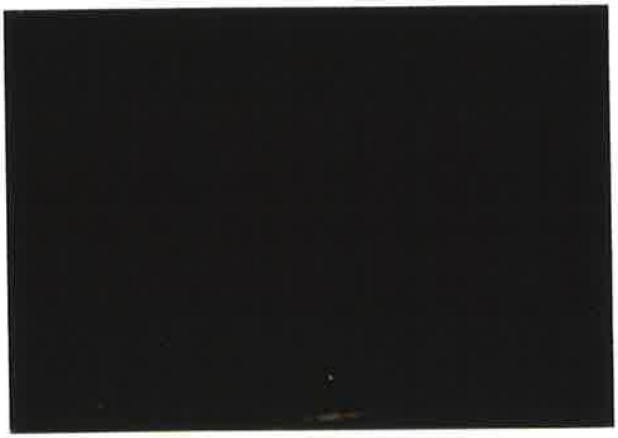
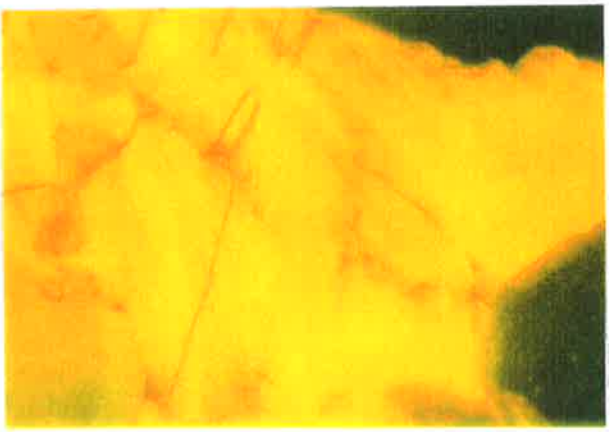


D

E



F

G

H

PLATE 11

A: Well: Poolowanna-3
Depth: 2560 m
Microlithotype: ?Carbargillite
R_O: 0.85%
Field of view: 136 μm x 197 μm
Description: Clay mineral (?illite) or amorphous organic matter, dark brown to translucent, bounded by tellocollinite.

B: As in A, blue light excitation; massive fibrous body with yellowish fluorescence.

C: Well: Poolowanna-3
Depth: 2551
Microlithotype: Carbopyrite
R_O: not determined
Field of view: 136 μm x 197 μm
Description: Pyrite framboids (spherical concretions of fine crystallite); in desmocollinite band.

D: As in C, blue light excitation; deformation orientation of sporinite (dull orange fluorescence), indicates syngenetic formation of pyrite.

E: Well: Sturt-4
Depth: 1881 m
Microlithotype:
R_O: not determined
Field of view: 136 μm x 197 μm
Description: ?Carbonate mineral bounded by quartz grain.

F: As in E, blue light excitation.

Chapter 5

Hydrocarbon source rock identification and evaluation

5.1 Introduction

Source rocks are defined as sedimentary rocks which contain sufficient organic matter of suitable chemical composition to generate hydrocarbons. The term 'source rock' is applied irrespective of whether the organic matter is mature or not. The presence of kerogen is a prerequisite for an active or potential source rock. The term 'potential source rock' is used to describe the organic-rich rocks which have not yet generated significant amounts of hydrocarbon due to immaturity. Active or effective source rocks are those which have generated and expelled the hydrocarbons.

Petroleum source rocks are normally recognised by determining their total organic carbon (TOC) and extractable organic matter (EOM) or bitumen contents. A second step in source rock identification is the determination of the type of kerogen and the composition of the solvent extractable hydrocarbons and non-hydrocarbons. The final step is the determination of the evolutionary stage of the kerogen, a concept commonly referred to as source rock thermal maturation. In this case it has been determined by vitrinite reflectance (Section 3.3.1.2) and by chemical indicators based on bitumen and Rock-Eval pyrolysis parameters. A combination of data derived from these methods allows the evaluation of the hydrocarbon-generative potential of the source rock and prediction of whether it is gas or oil-prone.

5.2 Amount of organic matter

The TOC content of the Poolowanna Formation is as shown in Table 5.1. For the 45 samples analysed, TOC values range from 1.0% in silty shale at Tantanna to 68.1% in coal at Sturt East. Both these localities are in the Patchawarra Trough. The Poolowanna Trough samples show intermediate values, between 5 and 10% TOC in shales and silty shales and between 10 and 49% TOC in carbonaceous shales. Given their present thermal maturation levels (Section 4.4.1), it is clear that these rocks can be classified as petroleum source rocks with good to excellent richness (see also Fig. 5.8).

5.3 Type of organic matter

The type of organic matter is usually determined by a combination of optical and physicochemical methods. With optical microscopy different types of contributing macerals can be identified and quantified (Chapter 4). The primary physicochemical method used in this study was Rock-Eval pyrolysis.

Table 5.1 Rock-Eval pyrolysis data and expected hydrocarbon product for the Poolowanna Formation

Sample No.	Well	Depth (m)	T_{max} °C	S_1 mgHC/ g rock	S_2 mgHC/ g rock	S_3 mgHC/ g rock	S_1+S_2 mgHC/ g rock	S_2/S_3	PI	TOC %	HI mgHC/ g TOC	OI mgHC/ g TOC	Hydrocarbon Product
POL3-12	Poolowanna-3	2438	444	1.4	13.7	0.4	15.1	31.1	0.09	7.3	188	6	
POL1-2	Poolowanna-1	2423	441	1.4	9.6	0.4	11.0	24.7	0.12	5.1	190	8	Gas
POL1-4	Poolowanna-1	2469	447	5.3	22.5	1.1	27.9	21.2	0.19	11.8	191	9	
POL3-11	Poolowanna-3	2423	447	3.9	41.2	1.2	45.1	33.8	0.09	18.3	225	7	
POL3-13	Poolowanna-3	2505	441	1.6	12.4	0.4	14.0	28.7	0.12	5.4	227	8	
POL1-1	Poolowanna-1	2417	447	3.7	38.3	1.1	41.9	33.9	0.09	16.3	235	7	
POL1-3	Poolowanna-1	2438	447	7.4	46.3	1.5	53.7	30.3	0.14	19.5	237	8	
POL1-6	Poolowanna-1	2545	448	4.6	38.5	1.1	43.1	35.9	0.11	15.4	250	7	Gas and Oil
POL1-7	Poolowanna-1	2557	449	3.5	29.3	0.8	32.8	38.1	0.11	11.2	262	7	
POL2-10	Poolowanna-2	2542	451	4.7	52.8	1.0	57.5	55.0	0.08	19.8	266	5	
POL3-15	Poolowanna-3	2560	450	4.4	44.3	0.9	48.7	50.3	0.09	16.3	272	5	
POL3-14	Poolowanna-3	2551	451	11.2	96.6	2.0	107.8	48.1	0.10	33.5	288	6	
POL1-5	Poolowanna-1	2499	442	6.4	65.2	1.9	71.6	34.1	0.09	20.7	315	9	
POL2-9	Poolowanna-2	2524	452	8.7	106.4	1.5	115.1	71.0	0.08	30.7	347	5	Oil
POL2-8	Poolowanna-2	2496	449	13.5	146.3	2.5	159.8	59.2	0.08	42.1	348	6	
TAN2-17	Tantanna-2	1796	nd	nd	nd	nd	nd	nd	nd	1.0	nd	nd	nd
TAN2-19	Tantanna-2	1805	nd	nd	nd	nd	nd	nd	nd	1.2	nd	nd	nd
TAN4-23	Tantanna-4	1814	439	2.8	20.5	1.3	23.3	16.3	0.12	14.4	142	9	
TAN3-21	Tantanna-3	1807	436	5.9	34.4	1.3	40.4	26.1	0.15	23.5	146	6	Gas
TAN4-22	Tantanna-4	1807	437	8.7	53.7	2.5	62.4	21.3	0.14	35.4	152	7	
TAN5-24	Tantanna-5	1814	437	6.8	60.1	3.0	66.9	20.4	0.1	34.5	174	9	
TAN2-20	Tantanna-2	1811	432	1.3	8.4	0.3	9.6	32.1	0.13	3.9	212	7	
TAN8-25	Tantanna-8	1823	430	15.6	138.7	3.8	154.2	36.2	0.1	51.0	272	8	Gas and Oil
TAN2-18	Tantanna-2	1799	439	3.6	53.5	1.6	57.1	34.5	0.06	18.1	296	9	
TAN1-16	Tantanna-1	1795	435	0.6	8.5	0.4	9.1	24.2	0.07	2.8	299	12	
STU2-29	Sturt-2	1856	432	0.1	1.1	0.8	1.2	1.4	0.08	1.4	76	55	Gas

Table 5.1 (continued)

Sample No.	Well	Depth (m)	T_{max} °C	S_1 mgHC/ g rock	S_2 mgHC/ g rock	S_3 mgHC/ g rock	S_1+S_2 mgHC/ g rock	S_2/S_3	PI	TOC %	HI mgHC/ g TOC	OI mgHC/ g TOC	Hydrocarbon Product
STU3-32	Sturt-3	1859	440	0.3	1.4	5.9	1.6	0.2	0.16	1.6	88	380	
STU2-28	Sturt-2	1829	436	0.1	3.5	0.8	3.6	4.5	0.04	2.1	165	36	
STU3-33	Sturt-3	1862	437	7.6	60.8	2.8	68.4	22.0	0.11	36.1	168	8	Gas
STU4-30	Sturt-4	1859	435	2.1	37.5	1.5	39.6	25.7	0.05	21.4	175	7	
STU6-35	Sturt-6	1865	436	12.2	111.7	4.2	123.9	26.8	0.1	61.4	182	7	
STU6-34	Sturt-6	1847	435	2.2	43.6	1.8	45.8	24.2	0.05	22.1	197	8	
STU8-36	Sturt-8	1862	434	2.8	66.3	3.5	69.1	19.0	0.04	33.4	199	10	
STU1-26	Sturt-1	1865	436	0.9	23.9	1.1	24.8	21.9	0.04	10.4	230	10	
STU1-27	Sturt-1	1871	436	0.8	28.0	1.0	28.8	27.2	0.03	11.7	239	9	Gas and Oil
STU4-31	Sturt-4	1881	435	15.6	132.8	4.0	148.4	32.9	0.1	51.9	256	8	
STE3-42	Sturt East-3	1865	431	0.8	5.1	1.2	5.8	4.2	0.13	5.4	93	23	
STE4-45	Sturt East-4	1862	437	5.1	115.4	4.9	120.6	23.8	0.04	68.1	170	7	Gas
STE1-37	Sturt East-1	1835	434	2.2	47.4	2.1	49.6	22.3	0.04	24.9	190	9	
STE2-40	Sturt East-2	1829	436	1.5	31.4	1.7	32.9	18.6	0.04	15.6	201	11	
STE3-41	Sturt East-3	1850	433	0.6	18.0	0.8	18.6	22.8	0.03	7.9	229	10	
STE1-39	Sturt East-1	1844	432	0.7	12.4	1.1	13.1	11.1	0.05	5.3	234	21	
STE4-44	Sturt East-4	1850	435	14.8	137.9	4.0	152.7	34.5	0.1	56.4	245	7	Gas and Oil
STE4-43	Sturt East-4	1838	437	1.3	36.4	1.3	37.7	29.1	0.03	14.2	256	9	
STE1-38	Sturt East-1	1841	438	0.9	22.0	0.9	22.9	23.4	0.04	7.8	283	12	

(Abbreviations are defined as in Table 2.3)

5.3.1 Type of organic matter under optical microscopy

Several approaches were used to determine the relative contribution of maceral groups to the organic matter preserved in the Poolowanna Formation. Figures 5.1a and b show an increase of TOC from silty shales to coals wherein the high TOC values are a result of contributions from mainly vitrinite and inertinite. It has already been shown that the general relationship among maceral groups in this formation is vitrinite < liptinite ≤ inertinite in the Patchawarra Trough, and vitrinite ≥ liptinite ≥ inertinite in the Poolowanna Trough. The trend of increasing liptinite with decreasing TOC (Fig. 5.1b) suggests the presence of Type I or Type II kerogen in the shale and silty shale lithofacies. This is clearly not the case (see Fig. 5.2b). Hence, the liptinite in organically leaner parts of the Poolowanna Formation must be partially oxidised, presumably during transportation to its site of burial (McKirdy *et al.*, 1986b). The high proportion of better preserved liptinite in the DOM of the organically richer shales accounts for the Type II/III composition of their kerogen (Fig. 5.2b).

5.3.2 Pyrolytic categorisation of source rock

Rock-Eval pyrolysis provides two parameters, the hydrogen index (HI) and oxygen index (OI), which may be used as a tool for determining kerogen types in source rocks (Section 2.4.2). These indices are independent of the amount of organic matter and they are strongly related to the elemental composition of kerogen. As mentioned earlier, these indices correlate well with the atomic H/C and O/C ratios, respectively. Thus, they may be plotted in a manner analogous to the normal van Krevelen diagram (Fig. 2.3a).

A cross plot of HI versus OI for the Poolowanna Formation source rocks is shown in Figure 5.2a. It appears from this diagram that samples from the Poolowanna Trough and some from the Patchawarra Trough lie to the left of the Type I evolution pathway. These samples are characterised by very low oxygen index values which seem to be an analytical artefact. The only clearly indicated categorisation is that between kerogen Types II and III for a couple of samples from the Patchawarra Trough. Obviously this plot does not resolve the kerogen types adequately. Instead a plot of HI versus T_{max} (Espitalié *et al.*, 1984) was used for kerogen classification (Figure 5.2b). It is clear from this figure that most of the Poolowanna Trough source rock facies contain Type II/III kerogen, although an apparent Type I kerogen may be presented in samples which have a high resinite content (Table 4.1). The Patchawarra Trough samples plot mostly in the Type III/II zone.

5.3.2.1 Relationship of HI to maceral group content

A comparison of HI and maceral group content was carried out by plotting the HI values against the relative abundance of the maceral groups. The purpose of this comparison was to examine whether there exists a relationship between these two parameters as they are both related to the gross chemical composition of the organic matter. The trends that emerge from this exercise are shown in Figure 5.3a-c.

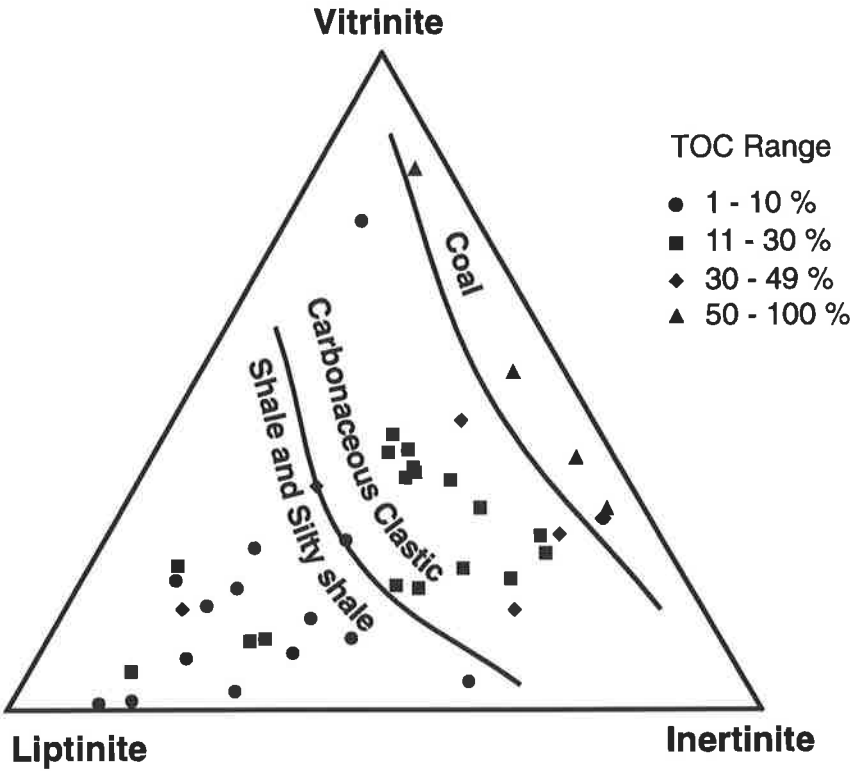


Figure 5.1a Relation of maceral groups to lithofacies and TOC content

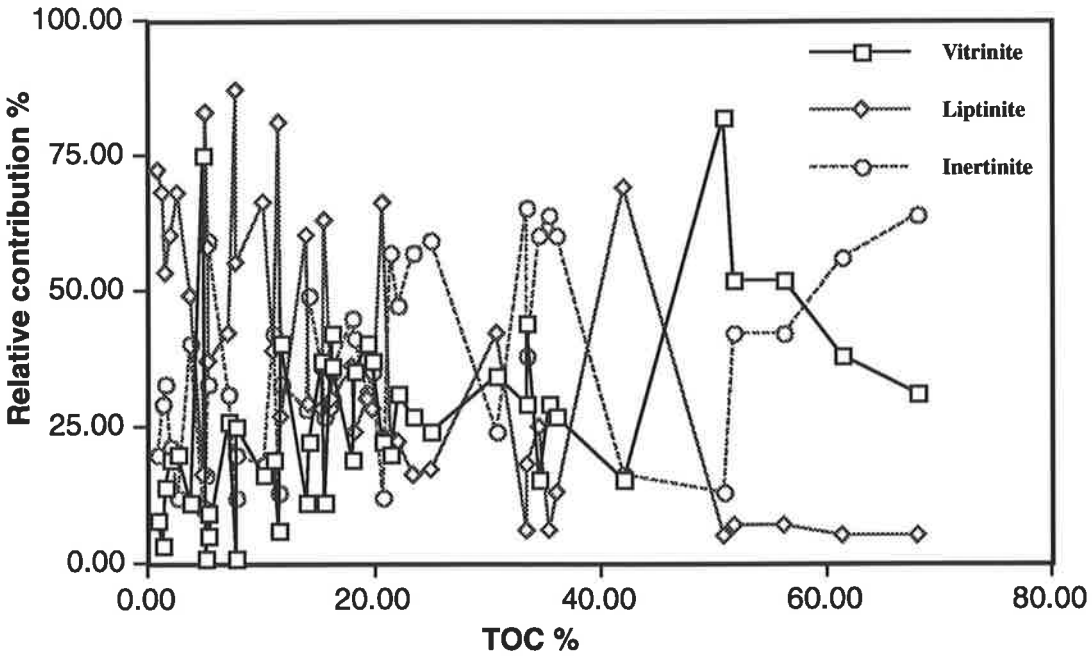


Figure 5.1b Relative contribution of maceral groups to organic content

Liptinite

The cross plot of liptinite versus HI (Fig. 5.3a) reveals a weak positive correlation between these two variables. The Poolowanna Trough samples show a positive linear relationship with a regression coefficient (r) of 0.52. The Tantanna and Sturt East data have regression coefficients of 0.48 and 0.46, respectively, whereas a negative correlation is observed in the Sturt data (r = -0.23). These variations indicate different organic matter inputs to the Poolowanna Formation in these fields. A negative correlation possibly shows that the hydrogen in those samples is rarely contributed from liptinite or alternatively is released from liptinite finally disseminated in other maceral groups (e.g. bituminite and resinite in vitrinite, or fluorinite in inertinite which were not accounted for in point counting). Another possible explanation for the lack of a strong positive correlation between liptinite and HI is that it is due to oxidation effects or the presence of reworked liptinite.

Vitrinite

Again, there is only a weak positive correlation between vitrinite and HI (Fig. 5.3b). A negative correlation is observed for data from the Poolowanna field where the highest HI values (>300 mg HC/g TOC) are recorded. This may imply that the vitrinite content in this area does not significantly contribute to the measured HI values. The Tantanna data display a weak positive correlation (r = 0.25) whereas in the Sturt data a somewhat stronger positive correlation (r = 0.5) is observed, implying some contribution by vitrinite to the HI values. The lack of a correlation in the Sturt East data is a possible indication of a mixed hydrogen contribution from all the maceral groups.

Inertinite

A negative correlation between inertinite content and HI is shown for all the fields giving an overall trend with a regression coefficient of -0.49 (Fig. 5.3c). This indicates that inertinite makes no contribution to the measured HI values.

5.3.3 Bitumen characteristics as indicators of organic matter type

The yield and bulk composition of the extractable organic matter in the suite of Poolowanna Formation samples analysed in this study are summarised in Table 5.2. The relative abundance of the saturated and aromatic hydrocarbons and NSO compounds are illustrated in a ternary diagram (Fig. 5.4). In this diagram, samples from the Poolowanna Trough appear to plot close to each other, indicating a similar or common precursor organic matter type. The Tantanna Field samples are somewhat more scattered, and those from Sturt and Sturt East are the least uniform in composition. Generally, the Patchawarra Trough samples are shown to be enriched in NSO components relative to those from the Poolowanna Trough. This may indicate differences in source input to the two troughs, although it is also partly due to the lower maturity of the Poolowanna Formation in the Patchawarra Trough fields.

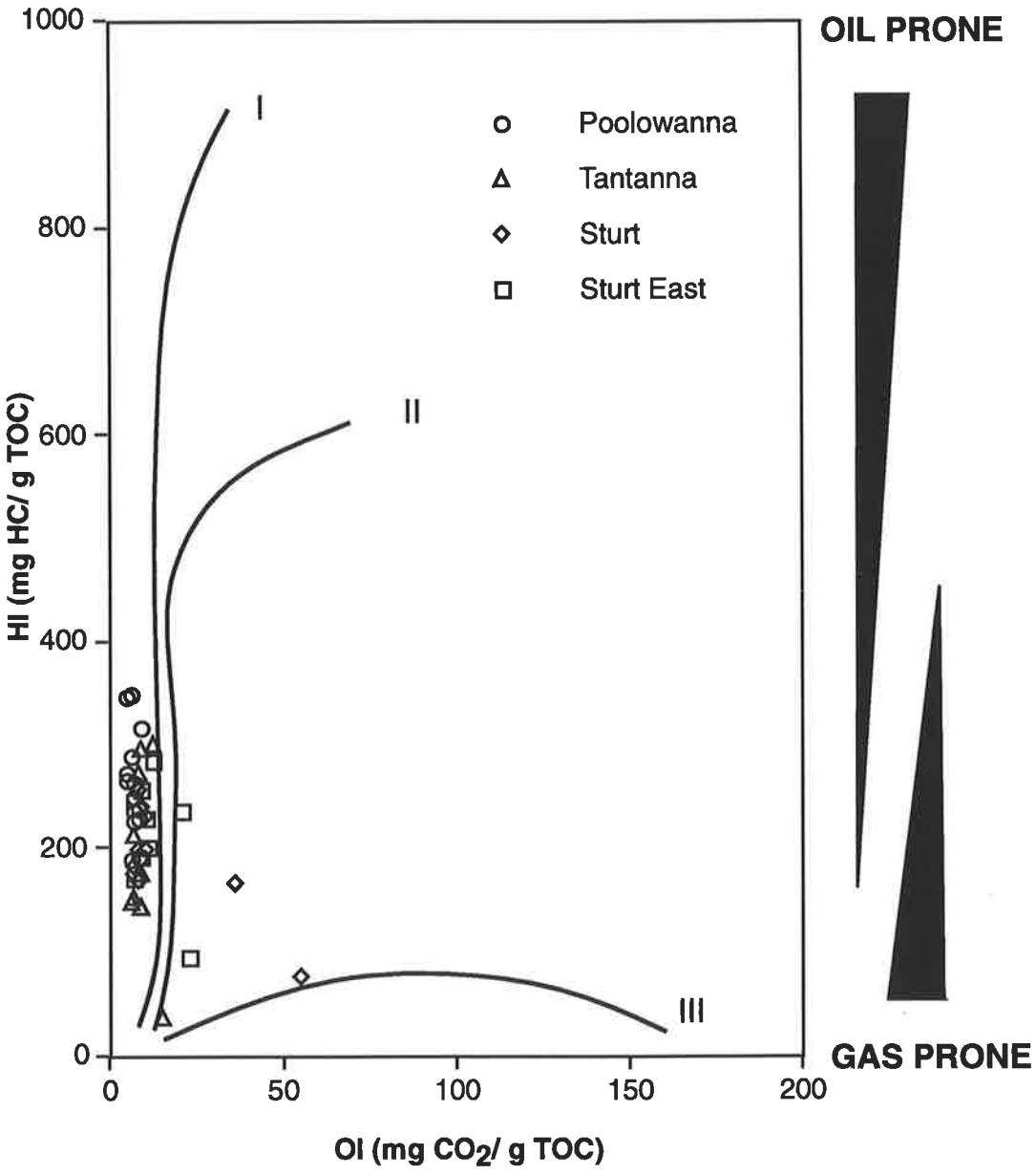


Figure 5.2a Kerogen classification based on hydrogen and oxygen indices

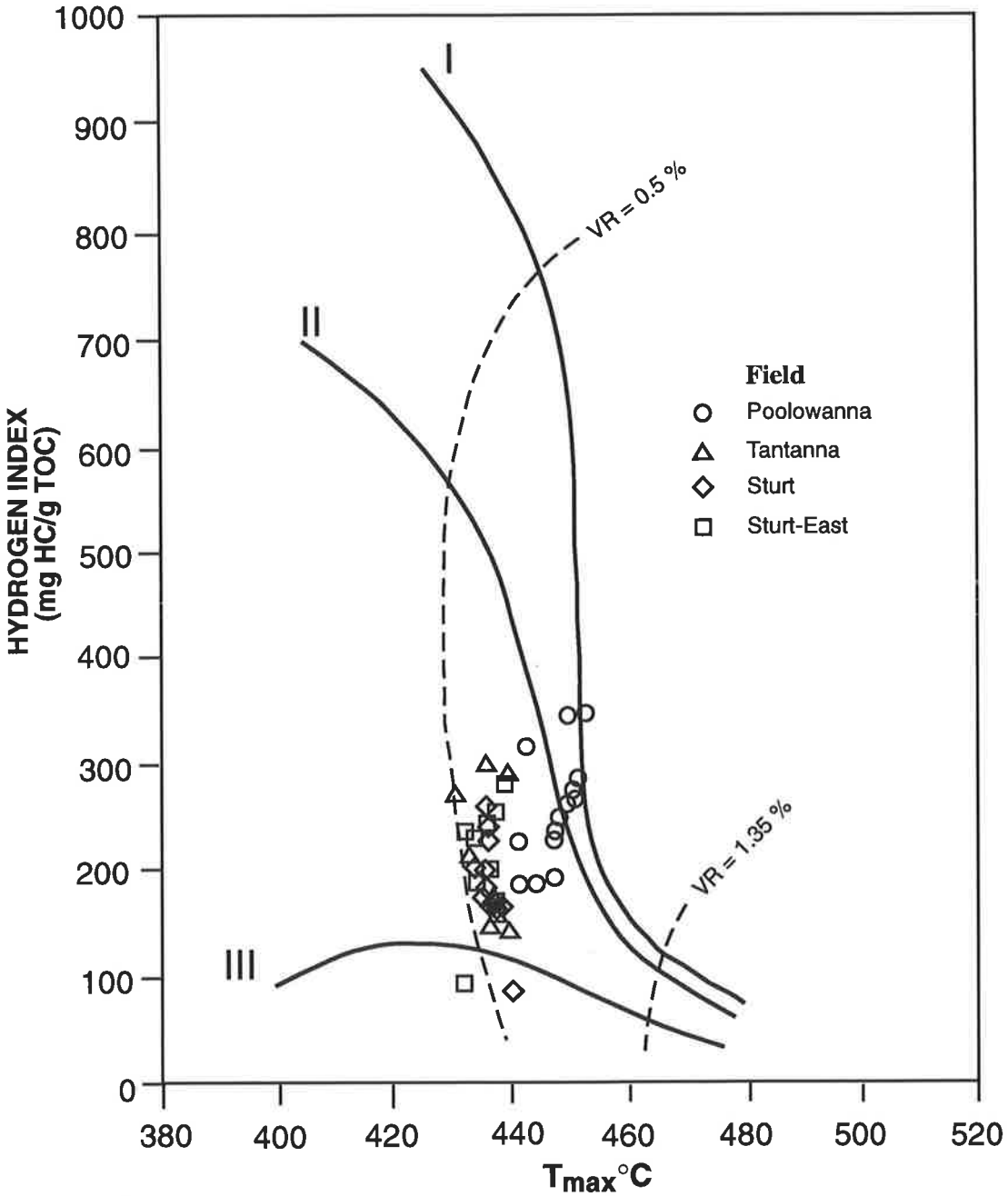


Figure 5.2b Kerogen classification based on hydrogen index and T_{max}

Saturated hydrocarbons as a function of the total EOM range from 7% in silty coals from Tantanna and Sturt East to 35% in coal from Sturt. Across all the fields saturates comprise an average of 15% of the EOM. Aromatic hydrocarbons range from 23% in coal from Sturt-6 to 37% in silty shale from Poolowanna-1. It is noted that where the liptinite (sporinite) content is relatively high the aromatic content is relatively low. Poolowanna Trough extracts tend to have larger aromatic fractions (average 34%) of EOM than do those from fields, in the Patchawarra Trough. Almost all samples have aromatic to saturate ratios (A/S) greater than unity, except one coal sample from Sturt-6 which has a value of 0.65. This sample appears to be unusual as most coals have higher A/S values than do non-coal lithologies of the same rank or maturity. Coincidently, another coal sample (Sturt-4, 1881 m) has a relatively low A/S value (1.22) and thus is likely to be of higher maturity than indicated by its vitrinite reflectance (0.57% R_O), or contain migrated hydrocarbons rich in saturates. Liptinite-rich silty shales from Sturt East-1 (1841 and 1844 m) and Tantanna-2 (1799 m) also have relatively low A/S ratios (1.09–1.3).

The macromolecular structure of Type III kerogen comprises condensed polyaromatic units and oxygenated functional groups, with minor aliphatic chains (Tissot and Welte, 1984). Aromatic and naphthenic rings are common in Type II kerogen, whereas Type I kerogen consist of cross-linked aliphatic chains and a few aromatic nuclei.
Therefore the high NSO contents (average = 53%), and generally high aromatic to saturate ratios of the Poolowanna source rock extracts appear to be typical of mixed Type II/III kerogen.

A comparison of hydrocarbon yield (i.e. the sum of saturate and aromatic fraction: Table 5.2) and maceral group abundance (Table 4.1) shows that where vitrinite content is relatively low the hydrocarbon yield is also low (< 5000 ppm). Liptinite is the highest contributing maceral in these samples. This situation might be explained by an oxidation event, whereby resistant liptinites survived while the vitrinite and the contained hydrocarbons were readily oxidised. In samples with intermediate hydrocarbon yields (5,000 to 10,000 ppm), there is an increase in vitrinite content. However, inertinite abundance increases more noticeably than both vitrinite and liptinite. It is well known that inertinite does not contain significant amounts of extractable hydrocarbons. The observed increase in these samples is probably due to disseminated liptinite (Chapter 4).

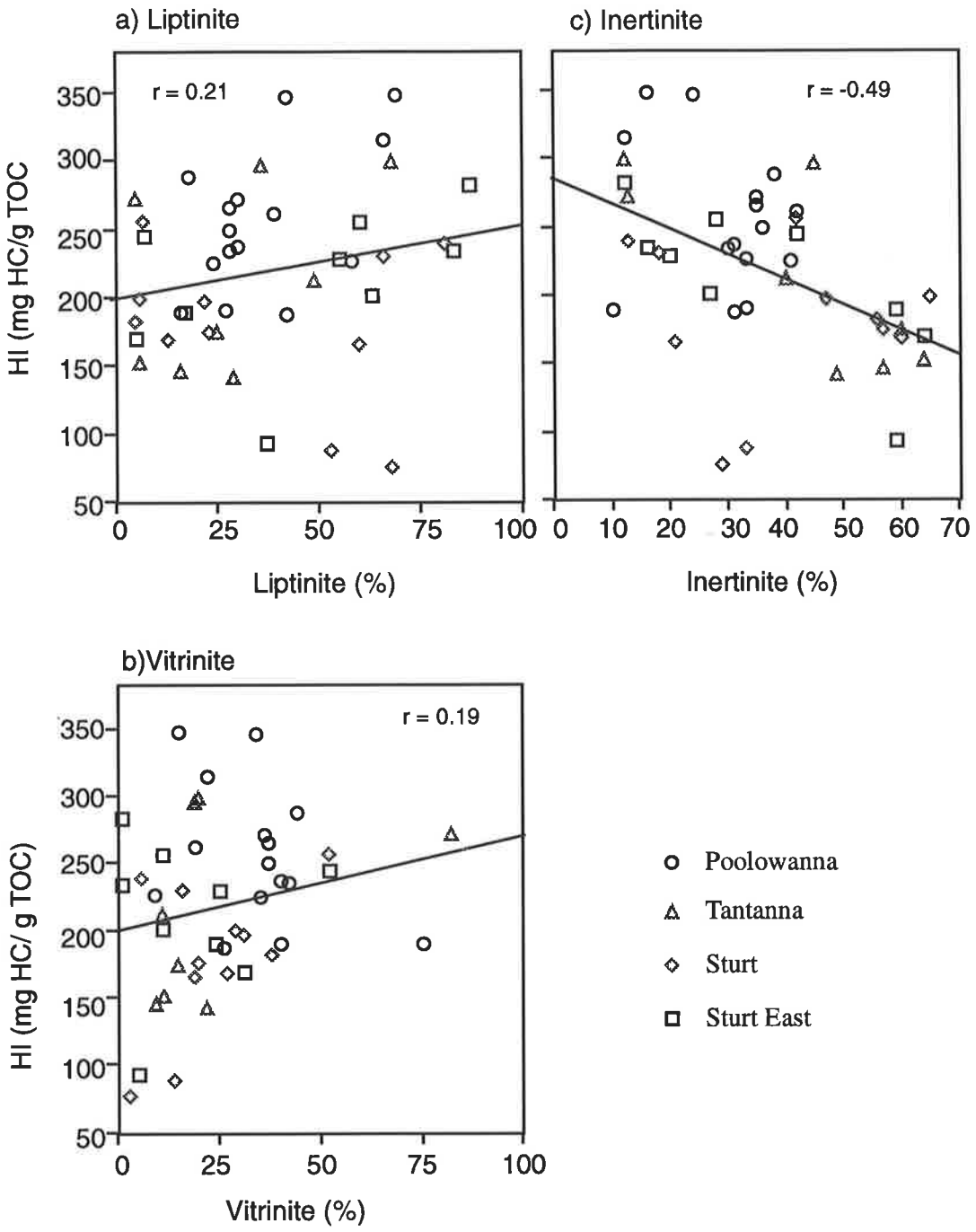


Figure 5.3 Influence of maceral groups on hydrogen index values. The regression line in each panel is that for the whole sample population.

Table 5.2 Rock extract yield and composition data for the Poolowanna Formation

Sample No.	Depth (m)	EOM (ppm)	Saturates (ppm)	Aromatics (ppm)	NSO (ppm)	Saturates (%)	Aromatics (%)	NSO* (%)	mgEOM gTOC	mgSat gTOC	mgAro gTOC	mgHC gTOC	Aromatic Saturate
POL1-1	2417	15693	1674	4318	7785	12	31	57	96	10	26	37	2.58
POL1-3	2438	23410	3799	5301	9444	20	29	51	120	19	27	47	1.40
POL1-4	2469	15765	3143	4428	5767	24	33	43	134	27	38	64	1.41
POL1-5	2499	29518	2514	8291	11326	11	37	51	143	12	40	52	3.30
POL1-6	2545	18731	1638	4265	6330	13	35	52	122	11	28	38	2.60
POL1-7	2557	12242	1623	3155	4207	18	35	47	109	14	28	43	1.94
POL2-8	2496	62390	3297	12097	23635	8	31	61	148	8	29	37	3.67
POL2-9	2524	40835	4183	8877	12448	16	35	49	133	14	29	43	2.12
POL2-10	2542	23363	2342	5460	10388	13	30	57	118	12	28	39	2.33
POL3-11	2423	19767	2028	4632	6753	15	35	50	108	11	25	36	2.28
POL3-12	2438	6915	452	1520	2427	10	35	55	95	6	21	27	3.36
POL3-13	2505	8186	853	1664	2233	18	35	47	150	16	31	46	1.95
POL3-14	2551	38299	4436	10570	13258	16	37	47	114	13	32	45	2.38
POL3-15	2560	18374	1396	4761	6671	11	37	52	113	9	29	38	3.41
TAN2-18	1799	8018	1762	1868	2550	29	30	41	44	10	10	20	1.06
TAN2-20	1811	7653	459	1368	2919	10	29	62	194	12	35	46	2.98
TAN3-21	1807	16771	1367	3783	6127	12	34	54	71	6	16	22	2.77
TAN4-22	1807	19875	2216	5474	7048	15	37	48	56	6	15	22	2.47
TAN4-23	1814	16999	1065	4090	7713	8	32	60	118	7	28	36	3.84
TAN5-24	1814	29556	3074	8152	11067	14	37	50	86	9	24	33	2.65
TAN8-25	1823	37555	1784	7816	15682	7	31	62	74	3	15	19	4.38
STU1-27	1871	9175	714	1715	3888	11	27	62	78	6	15	21	2.40
STU4-30	1859	12373	1400	2895	4676	16	32	52	58	7	14	20	2.07
STU4-31	1881	38585	5916	7241	13455	22	27	51	74	11	14	25	1.22
STU3-33	1862	18367	2433	3306	6823	19	26	54	51	7	9	16	1.36
STU6-34	1847	14127	931	2922	5193	10	32	57	64	4	13	17	3.14
STU6-35	1865	28770	7491	4862	9223	35	23	43	47	12	8	20	0.65
STU8-36	1862	19620	1834	4659	6165	14	37	49	59	5	14	19	2.54

Table 5.2 (continued)

Sample No.	Depth (m)	EOM (ppm)	Saturates (ppm)	Aromatics (ppm)	NSO (ppm)	Saturates (%)	Aromatics (%)	NSO* (%)	mgEOM / gTOC	mgSat / gTOC	mgAro / gTOC	mgHC / gTOC	Aromatic / Saturate
STE1-37	1835	15950	1203	3352	6515	11	30	59	64	5	13	18	2.79
STE1-38	1841	4256	682	767	1602	22	25	53	55	9	10	19	1.12
STE1-39	1844	3818	443	575	1250	20	25	55	72	8	11	19	1.30
STE2-40	1829	10182	907	1839	3703	14	29	57	65	6	12	18	2.03
STE3-41	1850	5903	612	1166	2333	15	28	57	75	8	15	23	1.90
STE4-43	1838	10135	888	2006	3682	14	31	56	71	6	14	20	2.26
STE4-44	1850	42761	3490	7953	18041	12	27	61	76	6	14	20	2.28
STE4-45	1862	26083	1284	5874	10815	7	33	60	38	2	9	11	4.58

* NSO = polar compounds eluted from the column during liquid chromatography. The balance of the non-hydrocarbon fraction of the EOM (mainly asphaltenes) was retained on the column

5.4 Source rock maturity

5.4.1 Maturation indicators based on pyrolysis data

Maturity parameters derived from Rock-Eval pyrolysis data include the transformation ratio $S_1/(S_1+S_2)$ (also known as production index, PI) and T_{max} (°C).Their values for the Poolowanna Formation are shown in Table 5.2. PI in the Poolowanna Trough samples does not show a consistent increase with depth. Its values range from 0.08 at 2500 m in Poolowanna-2 to 0.19 at 2469 m in Poolowanna-1. In the Patchawarra Trough, the PI values range from 0.06 at 1799 m in Tantanna-2 to 0.15 at 1807 m in Tantanna-3 (Tantanna Field); and from 0.03 at 1871 m in Sturt-1 to 0.11 at 1862 m in Sturt-3 (Sturt Field). The Sturt East Field has an almost similar range to that of its neighbouring field (PI = 0.03-0.1). The observed inconsistency of PI value with depth may indicate variable responses from different types of organic matter (i.e. it may in part be facies dependent). As far as maturity is concerned this range of PI values indicates an early mature to mature source rock and shows that the Poolowanna Trough source rock facies are more mature than those in the Patchawarra Trough.

T_{max} values range from 441°C at 2423 m in Poolowanna-1 to 452°C at 2524 m in Poolowanna-2. These values are significantly higher than those in the Patchawarra Trough fields (T_{max} = 430–440°C). It is clearly shown in Figure 5.2b that the Poolowanna Formation in the Poolowanna Trough is at a more advanced stage of maturation than it is where sampled in the Patchawarra Trough.

5.4.2 Maturity indicators based on bitumen

Maturity parameters based on bitumen and its components include the ratio of total hydrocarbons (i.e. the sum of the saturated and aromatic hydrocarbon fractions) to the total organic carbon content. The values of this ratio are summarised in Table 5.2. In order to compare this parameter with a known maturity measurement, the hydrocarbon yield versus vitrinite reflectance cross-plot was constructed (Fig. 5.5). Hydrocarbon yield appears to correlate well with vitrinite reflectance by showing a regression coefficient of 0.7. It is also clearly evident from this diagram that the Poolowanna Trough section has reached the peak of oil generation whereas the Patchawarra Trough sections are still at the early mature to mature stage.

Several samples plot off trend in the early mature zone. The cause of this inconsistency is either variation in kerogen type or contamination by migrated bitumen. For instance, the coaly siltstone facies at 1811 m in Tantanna-2 has an anomalously high hydrocarbon yield while not yet fully mature. A possible explanation is either that it contains migrated hydrocarbons or its recorded vitrinite reflectance is too low as a result of bitumen or resinite dissemination in the vitrinite. The PI value (0.13) of this sample reasonably indicates early

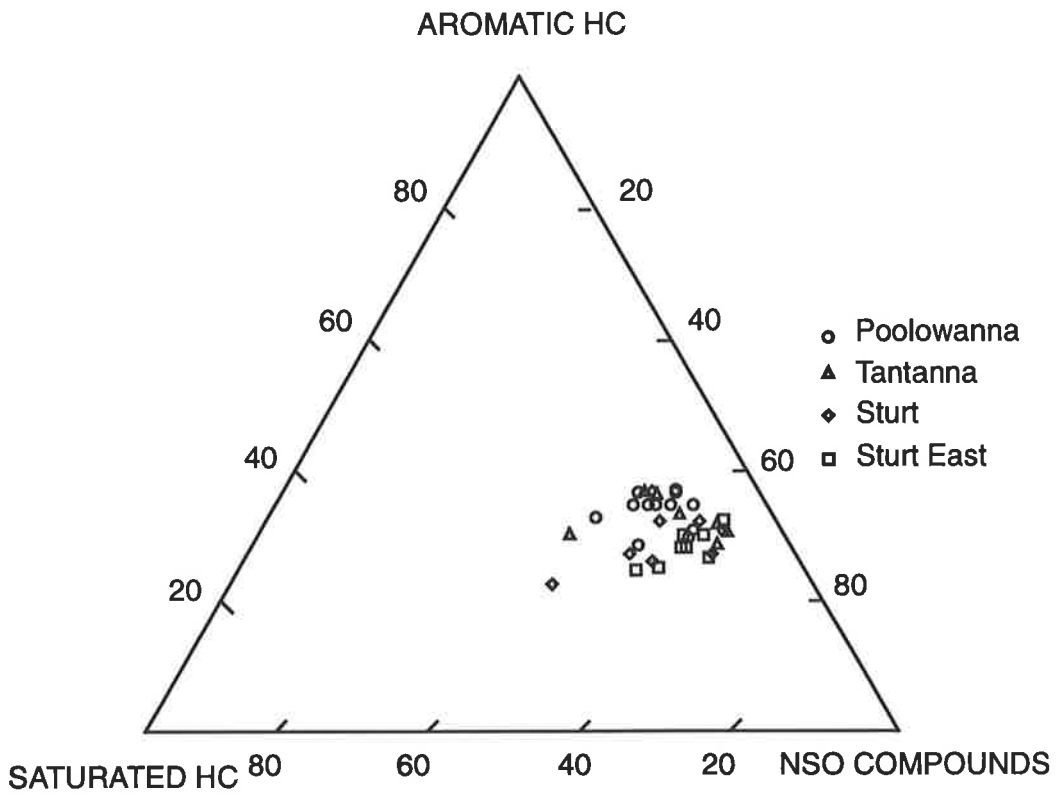


Figure 5.4 Gross composition of Poolowanna Formation source rock extracts as demonstrated by the relative abundance of their hydrocarbon fractions (saturate and aromatic) and NSO compounds. The latter fraction does not include asphaltenes.

hydrocarbon generation without contamination by migrated hydrocarbons. Therefore, early hydrocarbon generation from labile resinite (Powell and Snowdon, 1983) may possibly be the cause of its high hydrocarbon yield.

The relationship between kerogen type, extractable hydrocarbon yield and maturity was checked by plotting the hydrocarbon yield against hydrogen index (Fig. 5.6). Here, three categories of positive correlation were identified based on maturity zones. Zone I represents the 0.50–0.69% Ro maturity range. Two trends were observed in this zone. The first trend shows a wide spread of HI values with little or no variation in hydrocarbon yield (ca. 20 mg HC/g TOC). This suggests that, regardless of the type (or quality) of the kerogen, it has not acquired a level of maturity suitable for hydrocarbon generation. Most of the samples from Sturt East and Sturt and a few from Tantanna, belong to this category. A second subordinate trend is marked by an increase of HI with hydrocarbon yield. Such a trend may indicate that at this relatively low maturity level, at least one kerogen type is able to generate hydrocarbons. Most of the Tantanna samples plot within this trend which indicates that they contain a kerogen type capable of hydrocarbon generation at early maturity. A similar but stronger trend is noted in the 0.70–0.79% R_O maturity zone. All but one of the samples in this zone are from the Poolowanna Trough, reflecting hydrocarbon generation from its resinite-rich organic matter.

The peak maturity zone (0.80–0.89% R_O) is characterised by an apparently negative correlation between HI and hydrocarbon yield for three samples from the Poolowanna Trough. This is possibly due to the fact that their resinite-rich kerogen is now beyond the peak of its hydrocarbon generation (Figs. 4.4 and 5.5). An anomalously high hydrocarbon yield (64 mg HC/g TOC) corresponding to a HI value of 191 mg HC/g TOC is noted in a sample from Poolowanna-1 (2469 m); such a high yield possibly reflects minor staining by migrated hydrocarbons.

5.5 Quantitative evaluation of hydrocarbon generative potential

The geochemical parameters used in the evaluation of hydrocarbon generative potential include Rock-Eval $S_1 + S_2$ (Table 5.1); and the total extractable hydrocarbon yield (Table 5.2).

The $S_1 + S_2$ values of the Poolowanna Formation in the Poolowanna Trough range from 11 mg HC/g in silty shale (Poolowanna-1, 2423 m) to 160 mg HC/g in shaly coal (Poolowanna-2, 2496 m). Very good to excellent generative potential is indicated. In the Patchawarra Trough, the values at Tantanna range from 9 mg HC/g in shale (Tantanna-1, 1795 m) to 154 mg HC/g in coal (Tantanna-8, 1823 m) and indicate good to excellent hydrocarbon generative potential.

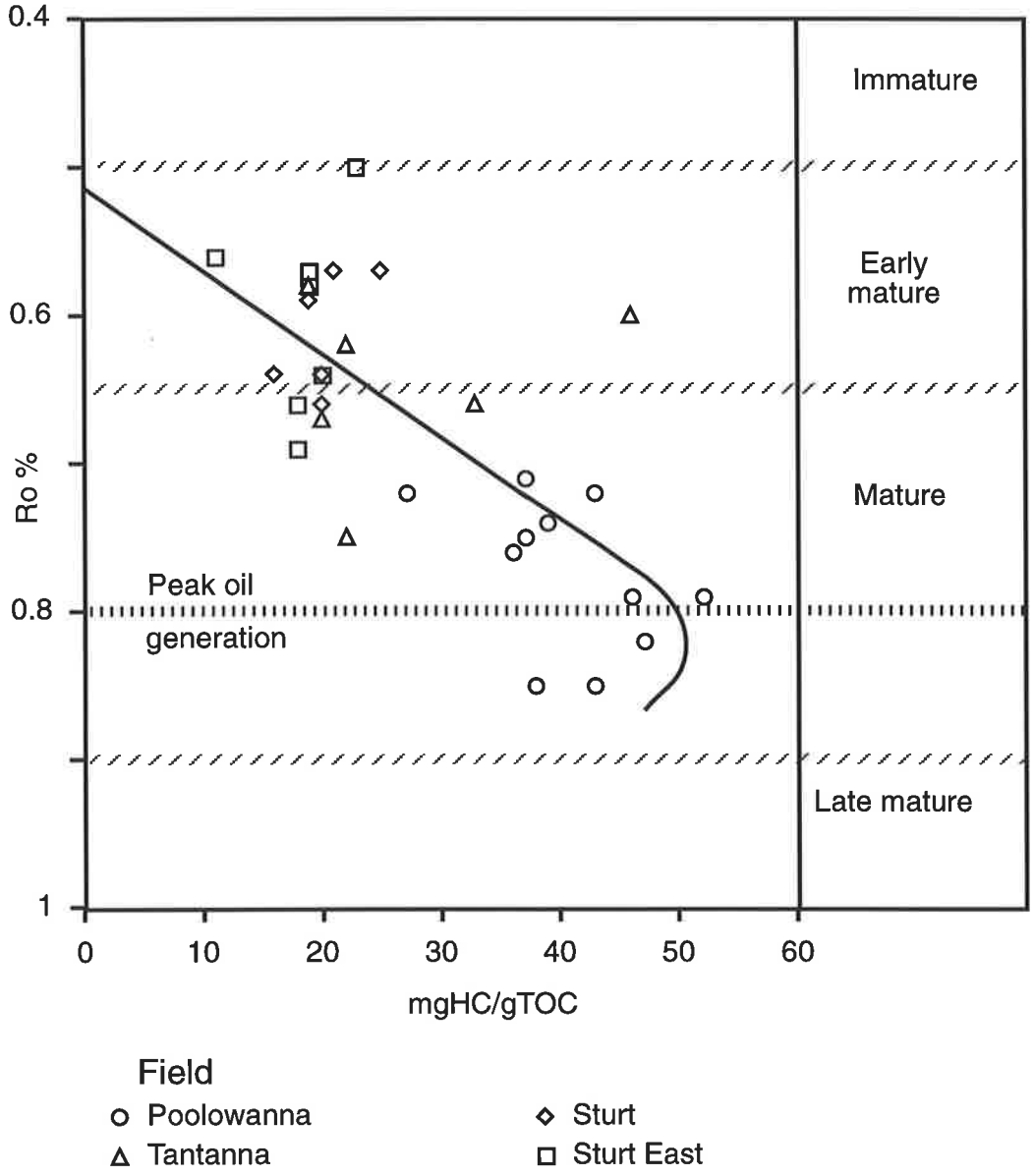


Figure 5.5 Hydrocarbon yield as a function of source rock maturity

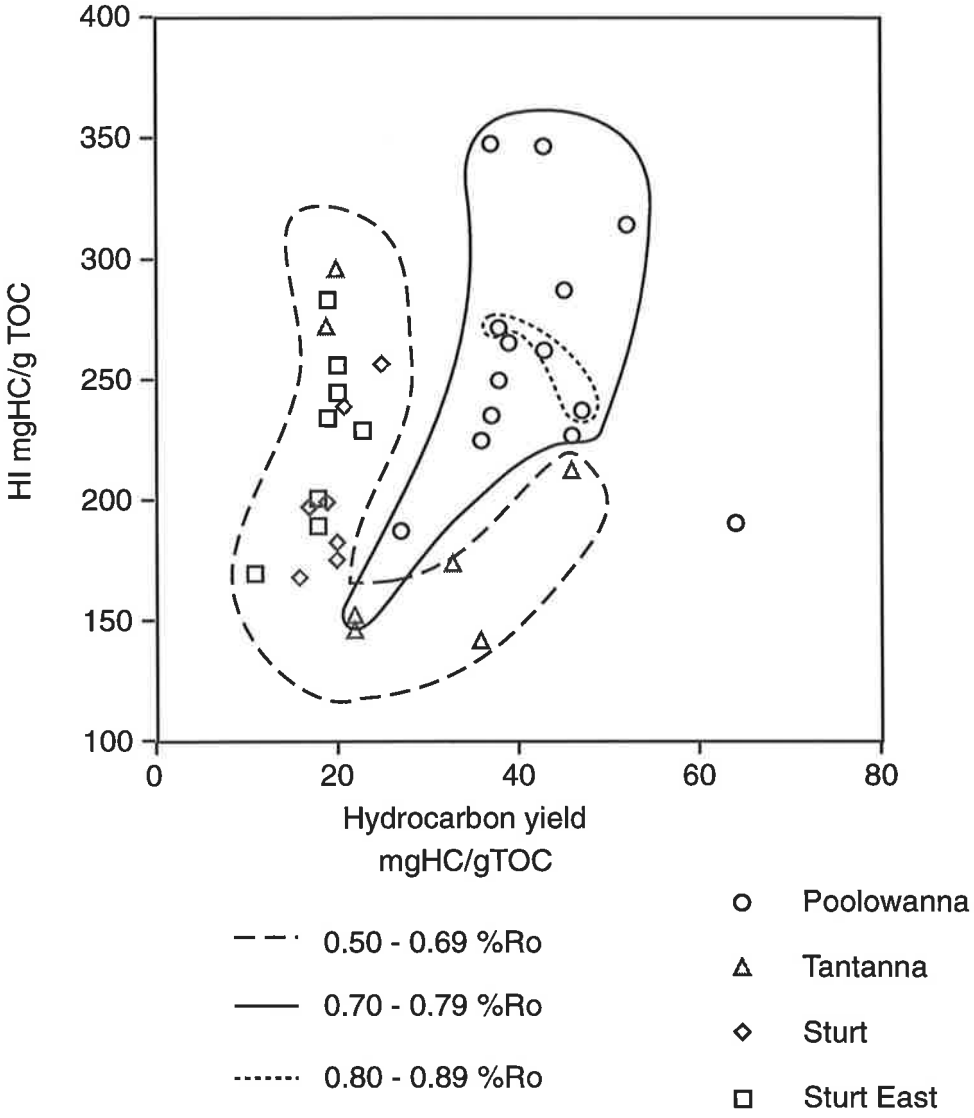


Figure 5.6 Influence of kerogen type and maturity on the yield of extractable hydrocarbons

A good to very good generative potential is demonstrated in the Sturt field where the S_1+ S_2 values range from 4 mg HC/g in siltstone (Sturt-2, 1823 m) to 148 mg HC/g in coal (Sturt-4 1881 m). At Sturt East the values range from 6 mg HC/g in siltstone (Sturt East-3, 1865 m) to 153 mg HC/g in silty coal (Sturt East-4, 1850 m). It should be noted that in both troughs the highest values were recorded in the coal facies.

Like the S_1+ S_2 parameter, the extractable hydrocarbon yield (ppm) has values that indicate very good to excellent generative potential. The Poolowanna Trough samples have values in the range 1972-15394 ppm whilst those of Patchawarra Trough have ranges of 1827–11226 ppm at Tantanna; 2429–13157 ppm at Sturt and 1018–11443 ppm at Sturt East. In both troughs the highest hydrocarbon yields are those of the coal or shaly coal facies. The outcome of this assessment is that the coal facies of the Poolowanna Formation is capable of generating oil.

5.5.1 Influence of maceral content on source rock generative potential

The possible influence of maceral type on source rock genetic potential was examined by plotting the relative abundance of the maceral groups against the genetic potential (S_1+S_2). The general outcome is as shown in Figures 5.7a, b and c. With the exception of the Poolowanna Trough samples, liptinite shows a negative correlation with genetic potential (Fig. 5.7a).

This is contrary to the expected scenario of liptinites being hydrocarbon-rich phytoclasts. A likely explanation for this outcome is that the most abundant liptinite maceral in the Patchawarra Trough, sporinite, does not yield significant quantities of long-chain hydrocarbons upon pyrolysis (Powell *et al.*, 1991). The positive correlation displayed by the Poolowanna Trough samples is probably related to their high abundance of resinite.

Similarly, a positive correlation is shown for vitrinite (Fig. 5.7b). In the Tantanna and Sturt East Fields a strong contribution from vitrinite is demonstrated by positive correlations with a regression coefficient of 0.88. An even stronger correlation (r = 0.92) is recorded in Sturt field. The influence of inertinite is shown to vary between these fields (Fig. 5.7c). While an apparent negative regression is displayed for the Poolowanna and Tantanna Fields a positive regression is shown at Sturt and Sturt East. The positive correlation is likely due to disseminated liptinite (fluorinite and resinite).

These observations are consistent with the presence of Type II/III kerogen in the Poolowanna Trough and Type III/II kerogen in the Patchawarra Trough.

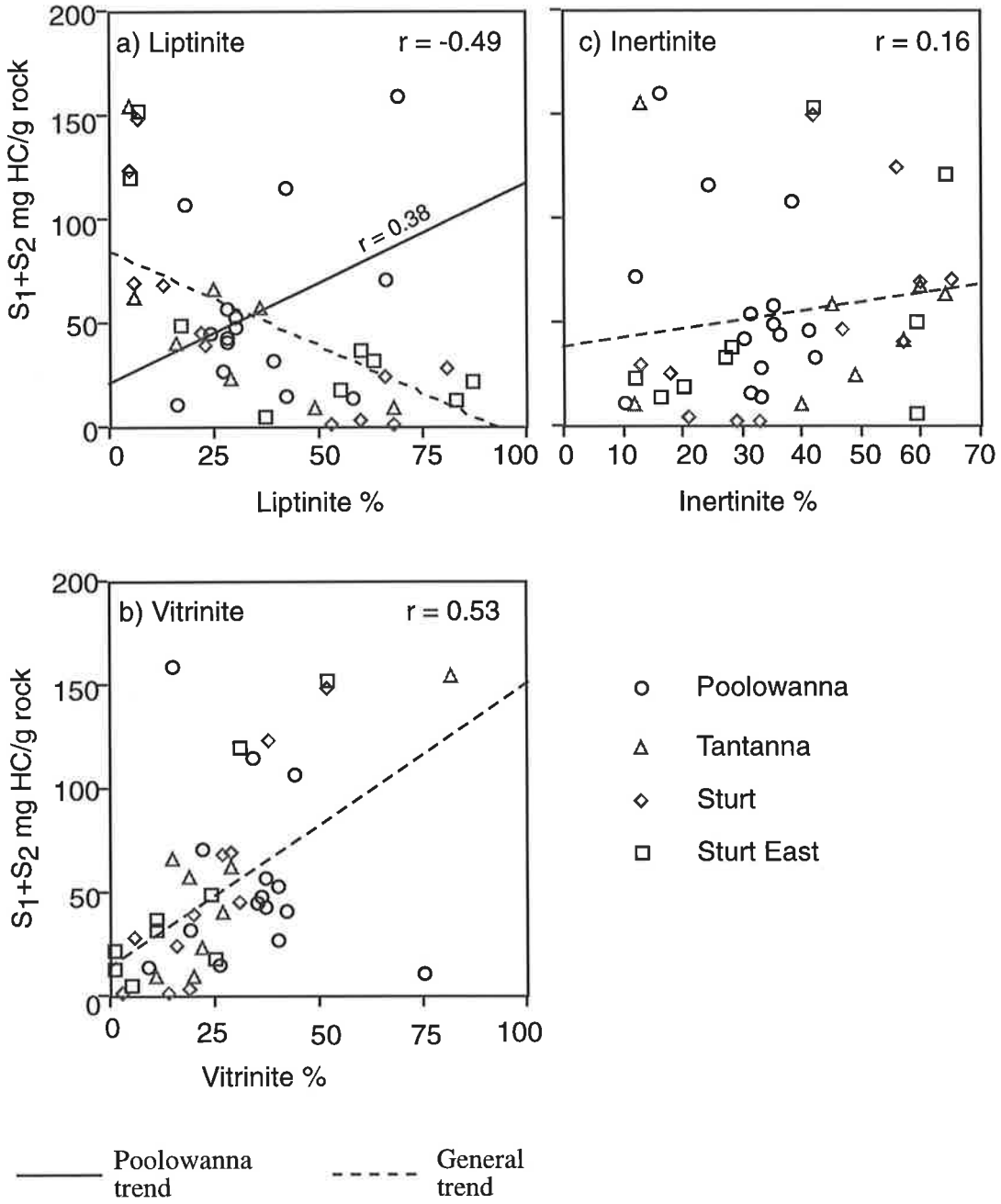


Figure 5.7 Influence of maceral content on source rock generative potential

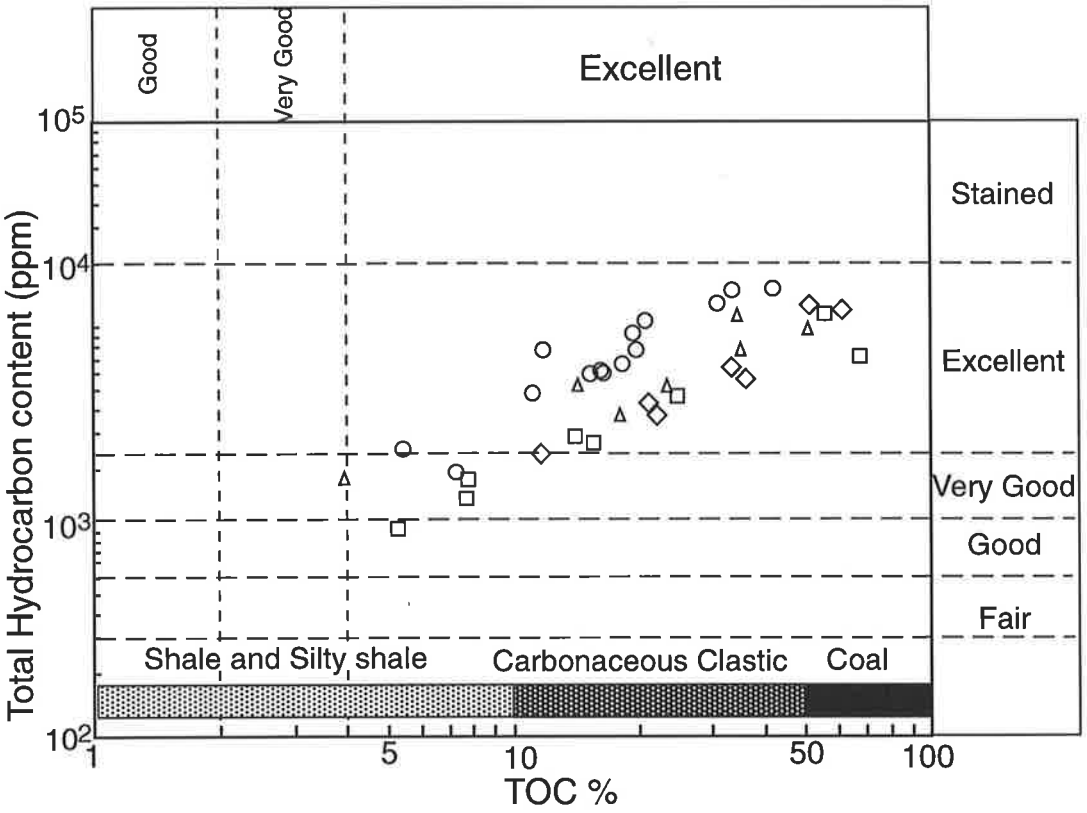


Figure 5.8 Source rock richness based on organic carbon content and hydrocarbon yield

5.5.2 Source rock richness and types of hydrocarbon generated

The categories of source rock richness are illustrated in Figure 5.8. Both TOC and total hydrocarbon yield are employed to categorise the source rock richness which in turn is related to the genetic potential (S_1+S_2). Excellent source rock richness is indicated for most of the samples, particularly those of the carbonaceous clastic and coal facies. The shale and silty shale facies have good to very good source richness for hydrocarbons.

In every category the Poolowanna Trough samples appear to have higher hydrocarbon yields than those in Patchawarra Trough. This is because the Poolowanna Formation in the Poolowanna Trough is thermally more mature than the sections in the Patchawarra Trough. A comparison of the Patchawarra Trough sections shows that the Poolowanna Formation is more mature at Tantanna than in the other fields. As mentioned earlier, hydrocarbon yield increases with maturation level. Oil staining of these rock samples is not indicated.

The type of hydrocarbon (either gas or oil or both) anticipated to be generated from potential source rocks is normally assessed using the Rock-Eval parameters, hydrogen index and S_2/S_3, and kerogen atomic H/C ratios (Espitalié *et al.*, 1977; Peters, 1986). The atomic H/C ratios are obtained from elemental analysis (not carried out in this study). The Rock-Eval data and the anticipated type of hydrocarbon product are shown in Table 5.1. Almost all the S_2/S_3 values are >10, and indicative of oil-prone source rocks. Hydrogen index values forecast the existence of gas, gas and oil and rarely oil-prone source rocks (Table 5.1).

The oil-prone source rock facies is developed in the middle section (2499–2524 m) of the Poolowanna Formation in the Poolowanna Trough. The gas and oil-prone source rock facies occurs in the lower section and happens to be the most predominant, whereas the gas-prone facies is confined to the upper part of the formation.

In Patchawarra Trough, only the gas and oil-prone facies and the gas-prone facies were identified. In the Tantanna Field silty shales and coals of the upper (1795–1807 m) and lower (1811–1832) parts of the section are oil and gas-prone whilst the gas-prone facies is the carbonaceous clastic middle section (1807–1814 m). At Sturt, the gas-prone facies appears to be predominant and is identified in the carbonaceous clastics and coals of the upper section (1829–1865 m) of the formation, whereas the carbonaceous clastics and coals of the lower section (1865–1881 m) are gas and oil-prone. In the Sturt East Field, the gas and oil-prone facies appears to be the most predominant. It occurs in the upper section (1829–1850 m) with an occasional, gas-prone interval. The lower section (1862-1865 m) is a gas prone facies.

Chapter 6

Carbon isotopic signatures of source rocks and associated crude oils

6.1 Introduction

It is well established that autotrophic biosynthetic processes like photosynthesis favour the lighter isotope (^{12}C) over the heavier isotope (^{13}C) during the incorporation of carbon into live organic tissue (Section 2.5.1). Accordingly, this ^{13}C-depleted isotopic signature is preserved in sedimentary organic matter (Cranwell *et al.*, 1987; Poynter *et al.*, 1989). During the diagenesis and catagenesis of kerogen, this isotopic signature is passed on, to the generated hydrocarbons which therefore contain isotopic clues to their source materials.

As mentioned in Section 2.5.2, the general trend of $^{13}C/^{12}C$ ratios across the compositional spectrum from kerogen to saturated hydrocarbons is as follows $\delta^{13}C$ kerogen $\geq$ $\delta^{13}C$ asphaltenes $\geq$ $\delta^{13}C$ NSO compounds $\geq$ $\delta^{13}C$ aromatics $\geq$ $\delta^{13}C$ saturates (Yen, 1972; Fuex, 1977; Stahl, 1978). In this chapter the isotopic characteristics of the aromatic and saturated hydrocarbon fractions of both oils and source rocks are highlighted with respect to their implications for source affinity, depositional environment and maturation.

6.2 Carbon isotopic composition of saturated and aromatic hydrocarbons in source rocks and oils

The saturates fraction of a crude oil or a rock extract contains normal, branched, and cyclic alkanes. Its relative concentration in oils and extracts appears to increase with increasing maturity. For the samples examined in this study, saturates comprise 20–30% of the extracts and 30–80% of the crude oils (Tables 5.2 and 6.1). The bulk carbon isotopic signature of the saturated hydrocarbon fraction is the mean of the individual $\delta^{13}C$ values of its constituent normal, branched and cyclic alkanes. Thermal maturity, microbial activity, depositional environment and possibly migration will also have some influence on this signature.

Likewise the aromatic fraction is generally made up of low to medium-molecular-weight aromatic hydrocarbons. The quantity and type of these aromatic compounds in a rock extract or crude oil are determined by both maturity level and the type of source organic matter.

Aromatic hydrocarbons appear to be prevalent in humic organic matter and highly mature oils and source rock bitumens. As mentioned in Section 2.7.3., the low-molecular-weight compounds may be preferentially removed from oils by water-washing.

Table 6.1 Bulk composition of crude oils from the Poolowanna and Patchawarra Troughs

Sample No.	Well	Formation	DST No.	Depth (m)	Saturates (%)	Aromatics (%)	NSO (%)	Asphaltenes* (%)	Aromatics / Saturates
P1	Poolowanna-1	Poolowanna	2	2504-2538	68.5	7.4	2.7	21.5	0.11
T2	Tantanna-1	Poolowanna	1	1800-1814	47.6	4.7	2.6	45.1	0.10
T3	Tantanna-1	Hutton	2	1635-1642	23.5	3.0	2.5	71.0	0.13
T4	Tantanna-1	Birkhead/Hutton	3	1347-1359	17.8	2.4	3.3	76.4	0.14
T5	Tantanna-2	Poolowanna	1	1808-1856	63.8	5.2	2.8	28.3	0.08
T6	Tantanna-2	Hutton	2	-	76.5	3.4	3.2	16.9	0.04
S9	Sturt-2	Poolowanna	1	1856-1892	75.6	8.5	2.3	13.6	0.11
S11	Sturt-3	Poolowanna	1A	1848-1855	79.1	6.9	1.1	12.9	0.09
S12	Sturt-3	Birkhead	1B	1654-1662	93.0	6.3	2.2	1.4	0.07
S13	Sturt-4	Poolowanna	1	1872-1880	87.0	8.2	1.0	3.8	0.09
S14	Sturt-4	Poolowanna	2	1883-1892	84.9	7.8	1.0	6.3	0.09
S15	Sturt-5	Poolowanna	1	1858-1866	75.8	7.5	1.4	15.2	0.10
S16	Sturt-6	Mooracoochie	5	1914-1919	64.7	13.8	3.9	17.6	0.21
S17	Sturt-6	Patchawarra	3	1884-1898	62.3	13.8	1.7	22.2	0.22
S18	Sturt-6	Birkhead	1	1883-1892	69.3	6.6	2.7	21.5	0.09
S19	Sturt-7	Patchawarra	1	1923-1938	65.5	11.4	4.1	19.0	0.17
S20	Sturt-7	Mooracoochie	2	1946-2021	63.5	11.6	3.7	21.1	0.18
S21	Sturt-7	Poolowanna	3	1871-1876	77.5	6.2	3.2	13.2	0.08
S22	Sturt-7	Poolowanna	5	1885-1889	81.1	7.9	1.4	9.7	0.10
S23	Sturt-8	Poolowanna	1	1880-1884	87.2	8.1	1.5	3.2	0.09
SE24	Sturt East-2	Poolowanna	1	1845-1899	77.4	9.2	0.8	12.6	0.12
TAL25	Taloola-2	Poolowanna	1	1829-1836	64.1	12.1	3.9	19.9	0.19
TAL26	Taloola-2	Hutton	2	1789-1793	64.7	11.8	3.2	20.3	0.18
TAL27	Taloola-2	Namur	3	1384-1397	74.4	7.1	3.3	15.1	0.10

* Values > 10% are considered unreliable. In these cases, the asphaltenes fraction is probably contaminated by waxy alkanes inadvertently precipitated during the isolation procedure.

Hence, as for the saturates fraction, the carbon isotopic signature of the aromatic fraction is the average of the isotopic signatures of its constituent compounds, but may be modified by various fractionation and disproportionation processes.

As shown by their *stable carbon isotope type-curves* (Galimov, 1973; Stahl, 1978; Chung *et al.*, 1981), oils and rock extracts (bitumens) display a general enrichment in ^{13}C for fractions of increasing polarity and boiling point. Peters and Moldowan (1993) point out that the whole oil or bitumen generally shows an isotopic composition between that of its saturates and aromatics fractions because of mass balance considerations. The bulk carbon isotopic signatures of these two hydrocarbon fractions in source rocks from the Poolowanna Formation and a suite of oils from adjacent reservoirs are summarised in Table 6.2a, b.

Table 6.2a Carbon isotopic composition of saturated and aromatic hydrocarbon fractions of selected source rock extracts from the Poolowanna Formation.

Sample No.	Well	Depth (m)	$\delta^{13}C$ PDB‰ Saturate	$\delta^{13}C$ PDB‰ Aromatic	$\delta^{13}C_{sat}$ / $\delta^{13}C_{aro}$	$\delta^{13}C_{aro-sat}$ (‰)	CV
POL1-1	Poolowanna-1	2417	-26.26	-24.97	1.05	1.29	-0.64
POL1-3	Poolowanna-1	2438	-26.18	-24.63	1.06	1.55	-0.09
POL1-4	Poolowanna-1	2469	-26.78	-24.43	1.10	2.34	1.85
POL1-5	Poolowanna-1	2499	-26.12	-24.53	1.07	1.60	0.00
POL1-7	Poolowanna-1	2557	-26.57	-24.39	1.09	2.19	1.44
POL2-9	Poolowanna-2	2524	-27.52	-25.10	1.10	2.42	2.25
POL3-13	Poolowanna-3	2505	-27.34	-24.57	1.11	2.78	2.99
POL3-15	Poolowanna-3	2560	-25.55	-24.09	1.06	1.46	-0.48
TAN2-18	Tantanna-2	1799	-27.50	-25.62	1.07	1.88	1.05
TAN2-20	Tantanna-2	1811	-25.16	-24.75	1.02	0.41	-2.94
TAN3-21	Tantanna-3	1807	-26.23	-24.70	1.06	1.53	-0.13
TAN4-22	Tantanna-4	1807	-26.37	-24.86	1.06	1.51	-0.13
TAN5-24	Tantanna-5	1814	-26.89	-25.36	1.06	1.53	0.07
STU1-27	Sturt-1	1871	-28.56	-25.44	1.12	3.12	4.14
STU4-30	Sturt-4	1859	-26.13	-25.14	1.04	1.00	-1.34
STU4-31	Sturt-4	1881	-25.99	-24.89	1.04	1.10	-1.15
STU6-35	Sturt-6	1865	-26.03	-25.20	1.03	0.84	-1.72
STE1-38	Sturt East-1	1841	-29.11	-26.54	1.10	2.57	3.07
STE1-39	Sturt East-1	1844	-28.45	-26.73	1.06	1.72	0.99
STE4-44	Sturt East-4	1850	-26.34	-24.88	1.06	1.47	-0.22
STE4-45	Sturt East-4	1862	-26.34	-24.96	1.06	1.38	-0.42

Canonical variable (CV) = $-2.53\ \delta^{13}C_{sat} + 2.22\ \delta^{13}C_{aro} - 11.65$ (Sofer, 1984).

Table 6.2b. Carbon isotopic composition of saturated and aromatic hydrocarbon fractions of selected oil samples from the Poolowanna Formation and adjacent reservoirs in the western Eromanga Basin.

Sample No.	Well	Formation	DST No.	Depth (m)	$\delta^{13}C$ PDB ‰		$\frac{\delta^{13}C_{sat}}{\delta^{13}C_{aro}}$	$\delta^{13}C_{aro-sat}$ (‰)	CV
					Saturate	Aromatic			
P1	Poolowanna-1	Poolowanna	2	2504-2538	-29.66	-26.06	1.14	3.60	5.53
T2	Tantanna-1	Poolowanna	1	1800-1814	-26.36	-24.84	1.06	1.52	-0.11
T3	Tantanna-1	Hutton	2	1635-1642	-26.84	-25.01	1.07	1.83	0.73
T4	Tantanna-1	Birkhead/Hutton	3	1347-1359	-26.79	-25.22	1.06	1.58	0.15
T5	Tantanna-2	Poolowanna	1	1808-1856	-26.35	-24.88	1.06	1.47	-0.22
T6	Tantanna-2	Hutton	2	-	-26.79	-25.37	1.06	1.43	-0.18
S9	Sturt-2	Poolowanna	1	1856-1892	-26.26	-24.95	1.05	1.31	-0.59
S11	Sturt-3	Poolowanna	1A	1848-1855	-26.17	-25.08	1.04	1.09	-1.12
S12	Sturt-3	Birkhead	1B	1654-1662	-25.97	-24.98	1.04	0.99	-1.41
S13	Sturt-4	Poolowanna	1	1872-1880	-26.20	-25.03	1.05	1.17	-0.94
S14	Sturt-4	Poolowanna	2	1883-1892	-26.18	-25.00	1.05	1.18	-0.92
S15	Sturt-5	Poolowanna	1	1858-1866	-26.30	-24.98	1.05	1.32	-0.56
S16	Sturt-6	Mooracoochie	6	1914-1919	-26.51	-24.59	1.08	1.93	0.85
S17	Sturt-6	Patchawarra	3	1884-1898	-26.49	-24.63	1.08	1.86	0.69
S18	Sturt-6	Birkhead	1	1883-1892	-26.04	-24.96	1.04	1.08	-1.17
S19	Sturt-7	Patchawarra	1	1923-1938	-26.42	-24.54	1.08	1.88	0.71
S20	Sturt-7	Mooracoochie	2	1946-2021	-26.26	-25.10	1.05	1.16	-0.94
S21	Sturt-7	Poolowanna	3	1871-1876	-26.19	-24.86	1.05	1.33	-0.58
S22	Sturt-7	Poolowanna	5	1885-1889	-26.27	-24.78	1.06	1.49	-0.20
S23	Sturt-8	Poolowanna	1	1880-1884	-26.11	-24.92	1.05	1.20	-0.90
SE24	Sturt East-2	Poolowanna	1	1845-1899	-26.23	-24.83	1.06	1.40	-0.41
TAL25	Taloola-2	Poolowanna	1	1829-1836	-26.45	-25.08	1.05	1.38	-0.40
TAL26	Taloola-2	Hutton	2	1789-1793	-26.49	-25.17	1.05	1.32	-0.51
TAL27	Taloola-2	Namur	3	1384-1397	-26.99	-25.32	1.07	1.67	0.43

Canonical variable (CV) = -2.53 δ^{13}Csat + 2.22 δ^{13}Caro - 11.65 (Sofer, 1984).

6.2.1 Saturates in source rock extracts

The isotopic composition of saturated hydrocarbons in source rock extracts of the Poolowanna Formation in the Patchawarra Trough range from -29.1‰ at Sturt East-1 (1841 m) to -25.2‰ at Tantanna-2 (1811 m). In the Poolowanna Trough, values ranging from -25.6‰ at Poolowanna-3 (2560 m) to -27.5‰ at Poolowanna-2 (2524 m) were recorded (Table 6.2a). Almost all fields have a similar average saturate composition of about -26.9‰, with the exception of Sturt East which shows a slightly lighter composition (average = -27.6‰).

The range of isotopic variation within the fields is 1.9‰ at Poolowanna; 2.3‰ at Tantanna; 2.6‰ at Sturt; and 2.8‰ at Sturt East. These variations imply that the organic input is more heterogenous in the Patchawarra Trough than in the Poolowanna Trough.

It is worth noting that samples with the highest liptinite contents have lighter isotopic signatures, e.g. a resinite-rich sample from Poolowanna-2, (2524 m) has a $\delta^{13}C$ value of -27.5‰; and sporinite-rich samples from Sturt East-1 (1841 and 1844 m) have values of -29.1‰ and -28.4‰, respectively. The more mature samples of the Poolowanna Trough show slightly more positive signatures within a narrow range than do early mature ones from the Patchawarra Trough.

6.2.2 Saturates in crude oils

The saturated hydrocarbons of the oils have $\delta^{13}C$ values ranging from -29.7‰ at Poolowanna-1 (DST 2, Poolowanna) to -26.0‰ at Sturt-6 (DST 1, Birkhead) with an average value of -26.5‰ (Table 6. 2b). Although from reservoirs of different ages, almost all the oils have very similar isotopic signatures. The waxy Poolowanna-1 oil (Fig. 6.2) is an exception ($\delta^{13}C_{sat}$ = -29.7‰). Its lighter isotopic signature reflects its derivation from a distinctly different source rock facies.

The Poolowanna-reservoired oils have an average $\delta\ ^{13}C_{sat}$ value of -26.5‰, and a range of 3.6‰. When the Poolowanna-1, DST 2 sample is excluded from the suite because of its anomalously negative signature, the isotopic variation is reduced to 0.3‰. The corresponding average $\delta^{13}C_{sat}$ values (and variation) for the oils in other Eromanga reservoirs are as follows: Namur, -27.0‰; Birkhead, -26.3 (0.8)‰; and Hutton, -26.7 (0.1)‰. The two oils from Patchawarra (Permian) reservoirs have almost identical $\delta^{13}C_{sat}$ values of -26.5 and -26.4‰ whilst those from the Mooracoochie Volcanics (Cambrian) have values of -26.3 and -26.5‰. With the exception of the Poolowanna-1 crude all oils in Jurassic reservoirs have isotopic signatures similar to those of the oils in Permian and Pre-Permian-reservoirs. This implies a common origin, or generation from source rocks with similar organic matter inputs. Mixing of oils as a result of migration may also be a cause of similar isotopic signatures.

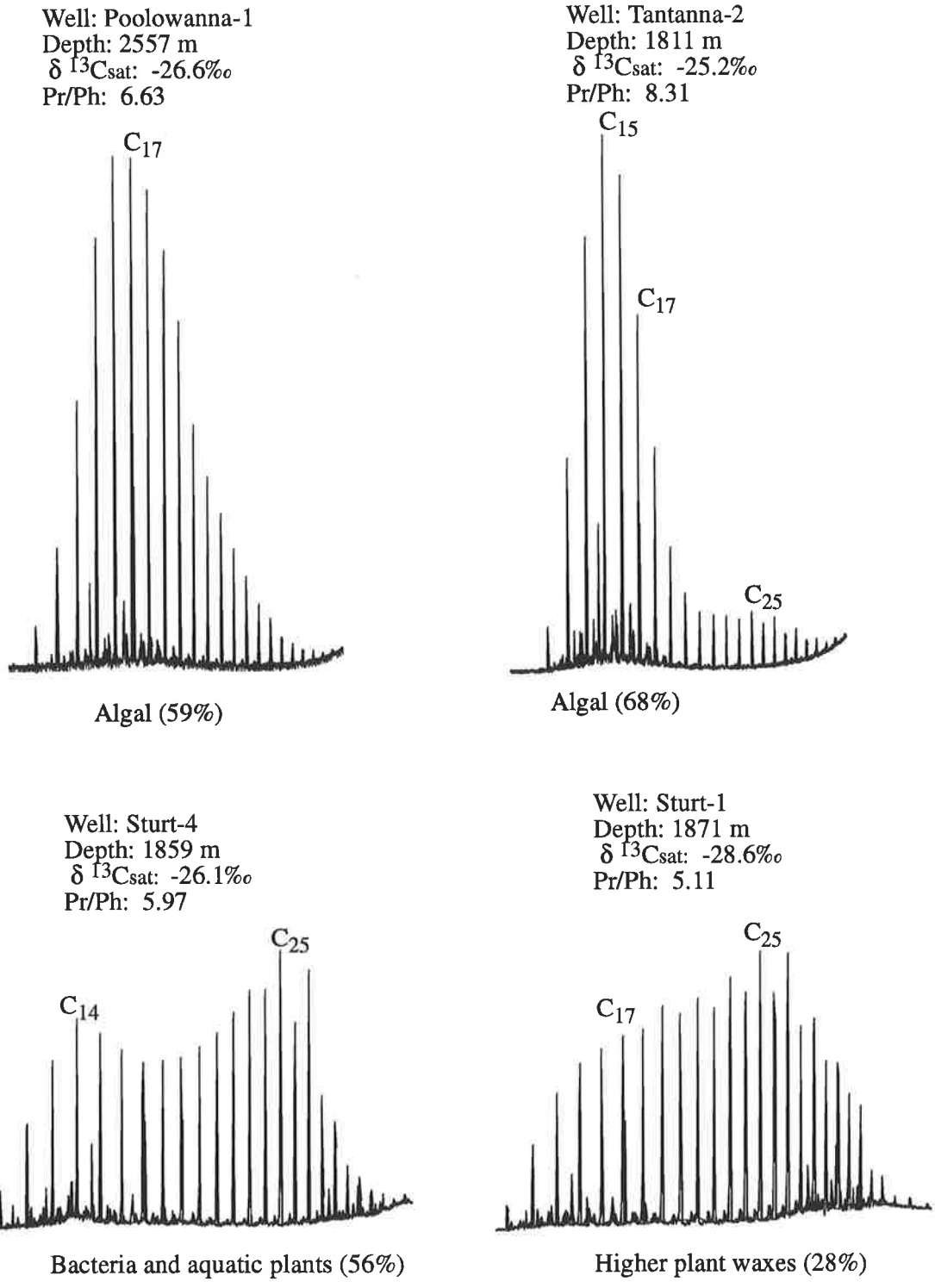
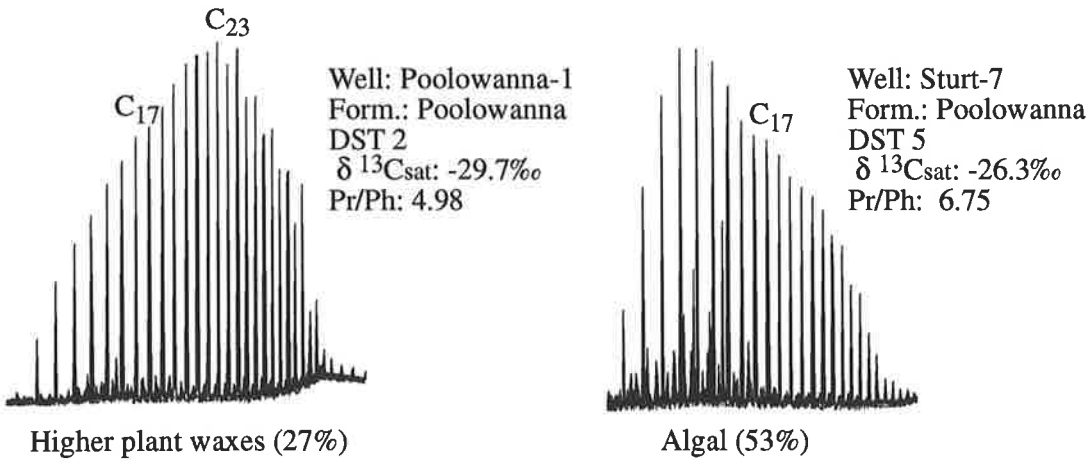


Figure 6.1 Influence of different precursor biota on the *n*-alkane profiles of source rocks from the Poolowanna Formation. Interpretation based on diagnostic carbon number ranges from Collister *et al.* (1994).



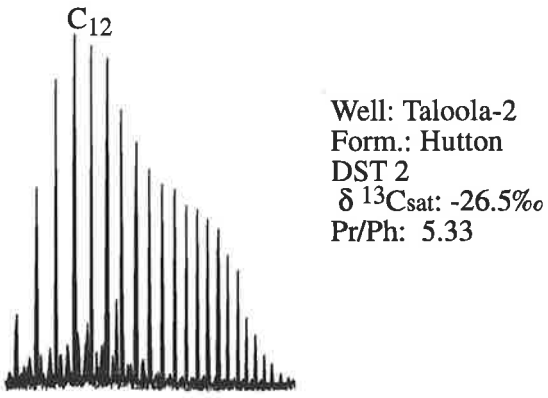


Figure 6.2 Source affinity of selected Eromanga Basin oils as indicated by their *n*-alkane profiles

Oils from multiple stacked reservoirs in the same field show a very narrow range of isotopic variation. For instance, in Tantanna-1 there are three stacked oil pools of which the Poolowanna has a $\delta^{13}C_{sat}$ value of -26.4‰, while both the Hutton and Birkhead pools have values of -26.8‰. In Tantanna-2, the Poolowanna and Hutton oil pools differ by 0.5‰, and in Sturt-3, the Poolowanna and Birkhead oils differ by only 0.2‰. In Sturt-6, the Patchawarra and Cambrian oils have the same value which is 0.5‰ lighter than that of the Birkhead oil. In Sturt-7 the variation between the Patchawarra and Poolowanna oils is 0.2‰, whereas in Taloola-2 the Namur oil is lighter than both the Poolowanna and Hutton crudes by 0.5‰. Therefore either the bulk isotopic signatures of the saturated hydrocarbons are incapable of differentiating Jurassic from Permian and Cambrian oils, or the oils have common source.

6.2.3 Aromatics in source rock extracts

The isotopic composition of the aromatic fraction (δ^{13}Caro) in source rock extracts ranges from -24.1‰ at Poolowanna-3 (2560 m) to -26.7‰ at Sturt East-1 (1841m), thus showing a significant variation of 2.6‰. The $\delta^{13}C_{aro}$ values in the Poolowanna Trough are more positive than those in Patchawarra Trough. The variation of isotopic signature (2.0‰) observed in the Patchawarra Trough (2.0‰) is wider than that of the Poolowanna Trough (1‰) suggesting a more heterogenous organic matter input to the former depocentre. Their average $\delta^{13}C_{aro}$ values (-24.6‰ in the Poolowanna Trough and 25.3‰ in the Patchawarra Trough) further emphasise the difference between the organic facies of these two troughs. For the fields in the Patchawarra Trough, the average $\delta^{13}C_{aro}$ values (and variation) are as follows: Sturt East, -25.8 (1.6)‰; Sturt, -25.2 (0.5)‰; and Tantanna, -25.1 (0.9)‰.

The overall average $\delta^{13}C_{aro}$ value for the entire Poolowanna Formation is -25.0‰. As is the case for the saturated hydrocarbons, the 2.6‰ variation may indicate the heterogeneity of source input and possibly maturity differences between the Poolowanna and Patchawarra Troughs. The indicated source input heterogeneity supports the observations based on maceral group distributions, which showed the samples to be very diverse especially in the Patchawarra Trough (Section 4.2: Fig. 4.1).

6.2.4 Aromatics in crude oils

The $\delta^{13}C_{aro}$ signatures of the oils range from -26.1‰ at Poolowanna (Poolowanna-1, Poolowanna) to -24.5‰ at Sturt (Sturt-7, Patchawarra), giving a variation of 1.6‰. It is observed that the Cambrian (Mooracoochie) and Permian (Patchawarra) oils are heavier than those in younger reservoirs. Within the multiple reservoirs of the same field, the isotopic variations range between 0.4 and 0.6‰. These are too small to indicate significant genetic differences among these oils.

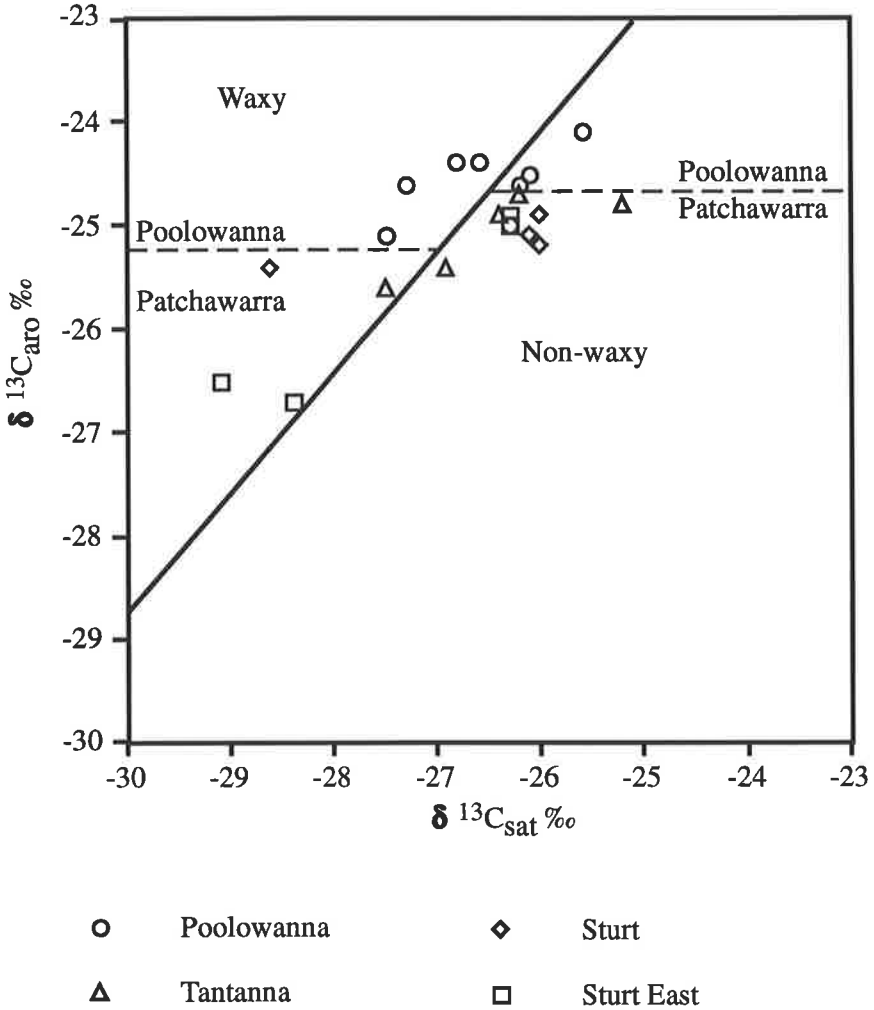
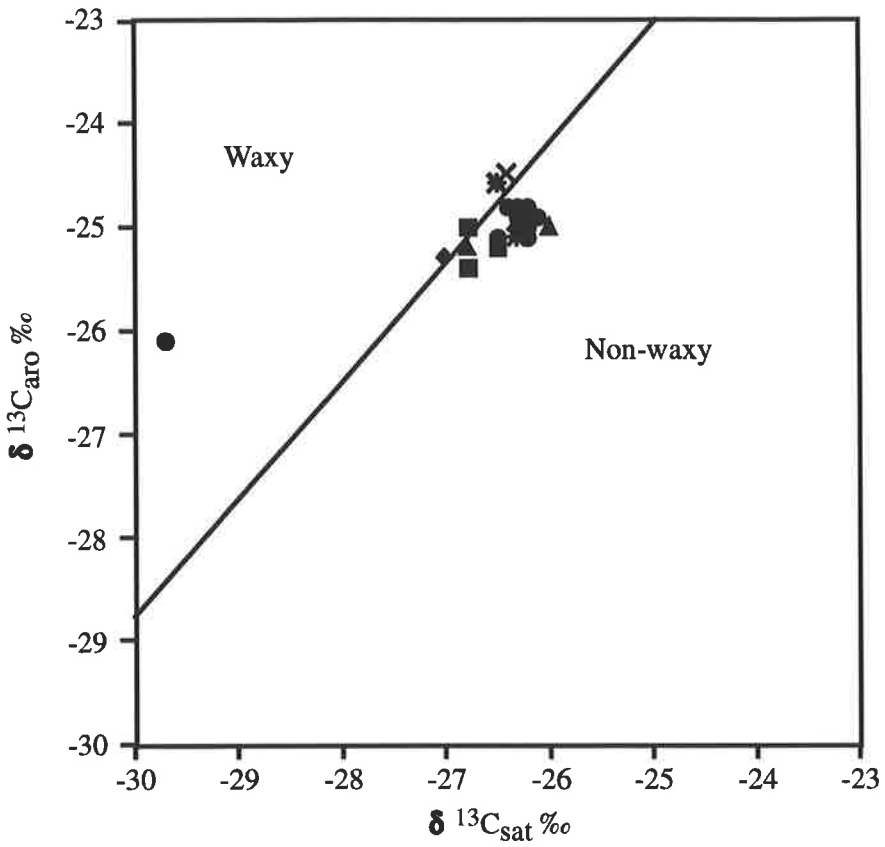


Figure 6.3a Waxy and non-waxy character of Poolowanna Formation source rock extracts as demonstrated by carbon isotopic composition of saturated and aromatic hydrocarbons. The oblique line separating the waxy and non-waxy extracts corresponds to CV = 0.47 (after Sofer, 1984).



Jurassic

◆ Namur

▲ Birkhead

■ Hutton

● Poolowanna

Permian and Cambrian

✕ Patchawarra

✱ Mooracoochie

Figure 6.3b Isotopic composition of saturated and aromatic hydrocarbon fractions of oils from Jurassic and non- Jurassic reservoirs

6.2.5 Relationship between isotopic composition of saturated and aromatic hydrocarbons

Several parameters which are commonly used to express the relationship between the carbon isotopic signatures of the saturated and aromatic hydrocarbon fractions are presented in Table 6.2a, b. Of these, $\delta^{13}C_{aro\text{-}sat}$ describes the isotopic difference between the two fractions. The $\delta^{13}C_{sat}/\delta^{13}C_{aro}$ ratio and the canonical variable (CV) have been used to differentiate marine and non-marine crude oils (Sofer, 1984).

It is noted that the isotopic difference between the saturated and aromatic fractions of source rocks in the Poolowanna Formation ranges from 0.4‰ at Tantanna-2 (1811 m) to 3.1‰ at Sturt-1 (1871 m) with an average value of 1.7‰. This shows that the aromatic fractions are always isotopically heavier than the saturates. The exact cause of this relationship is not known; but it is most likely related to the fact that the organic precursors of the aromatic compounds are formed via processes that result in less discrimination against the heavier ^{13}C isotope.

It should also be noted that the $\delta^{13}C_{aro\text{-}sat}$ values of the source rock extracts increase as the saturates become more waxy (based on GC *n*-alkane profiles). This is illustrated by comparing the *n*-alkane profiles of the Tantanna-2 (1811 m) extract (non-waxy; $\delta^{13}C_{aro\text{-}sat}$ = 0.4 ‰) with that of the Sturt-1 (1871 m) extract (waxy; $\delta^{13}C_{aro\text{-}sat}$ = 3.1‰: Fig. 6.1). This tells us that the waxy C_{23+} *n*-alkanes are isotopically lighter than the lower molecular weight alkanes. The difference between the $\delta^{13}C_{sat}$ values of these two samples is 3.4‰; and only 0.6‰ in the case of $\delta^{13}C_{aro}$ values. Clearly, the isotopic composition of the saturates fraction is less constant than that of the aromatic fraction.

The $\delta^{13}C_{aro\text{-}sat}$ values of the oils range from 0.99‰ in the Sturt-3 (DST 1B, Birkhead) crude to 3.60‰ in the Poolowanna-1 (DST 2, Poolowanna) sample, with an average of 1.5‰. Not suprisingly Poolowanna-1 oil is very waxy (Fig. 6.2). This oil might have been generated from a source rock with characteristics similar to that at Sturt -1 (1871 m).

Other possible causes of large isotopic differences between the saturated and aromatic hydrocarbon fractions of crude oils are fractionation processes attributable to water washing and migration (Fuex, 1972; Alekseyev *et al.*, 1975).

The $\delta^{13}C_{sat}$ to $\delta^{13}C_{aro}$ ratio does not show much variation in either oils or source rocks. It varies between 1.02 and 1.12 in source rocks and between 1.04 and 1.14 in oils. As for the $\delta^{13}C_{aro\text{-}sat}$ parameter, the waxy samples have the highest values and non-waxy samples the lowest. Because the wax content is routinely attributed to land plant precursors, the observed isotopic signature in waxy source rock and oil samples also may be confidently assigned to organic matter inputs of higher plant origin.

The relationship between the isotopic compositions of these saturated and aromatic fractions was further evaluated by applying the canonical variable (CV) method devised by Sofer (1984). Values for Poolowanna Formation source rocks range from -2.94 in siltstone at Tantanna-2 (1811 m) to 4.14 in carbonaceous clastic at Sturt-1 (1871 m). No systematic differences were observed between the Patchawarra and Poolowanna Troughs (Fig. 6.3a). Waxy and non-waxy source rocks occur in both troughs. In each source rock category, the samples from the Poolowanna Trough tend to be isotopically heavier, as is discussed below.

According to Sofer (1984), CV values less than 0.47 are indicative of strong marine influence. Whether the non-waxy source rocks (CV < 0.47) in this study (Table 6.2a, Fig. 6.3a) have any marine affinity is questionable because no other marine features have been reported for the Poolowanna Formation in the Patchawarra Trough. However, some marine influence has been recorded elsewhere in the Poolowanna Trough (Wiltshire, 1978). McKirdy *et al.* (1986b) attribute CV values in the non-waxy range to algal and bacterial precursors, not necessary of marine origin.

The CV values of the oils range from -1.41 (Sturt-3, Birkhead) to 5.53, (Poolowanna-1, Poolowanna). Almost all the Jurassic oils have values much less than 0.47 and are thus indicated to have an algal or bacterial affinity. The Poolowanna-1, (Poolowanna) and Tantanna-1, (Hutton) have CV values of 5.53 and 0.73 respectively, thus signifying their strong terrigenous affinity. All the Permian oils and one of the two Cambrian (Mooracoochie) oils also have CV values much greater than 0.47 and are obviously derived mainly from terrigenous plant material.

These results show that the Jurassic-reservoired oils have a different origin from those in Permian and Cambrian reservoirs. Regardless of source affinity two families of oils and source rocks are recognised based on their CV values (greater or less than 0.47). Both oil families could have originated from Poolowanna Formation source rocks, as discussed in more detail below.

Cross-plots of saturate isotopic signature ($\delta^{13}C_{sat}$) versus aromatic isotopic signature ($\delta^{13}C_{aro}$) have been used to discriminate waxy from non-waxy oils and to distinguish non-marine from marine source affinities (Sofer, 1984; McKirdy *et al.*, 1986). The distribution of Poolowanna Formation source rock isotopic signatures in the Poolowanna and Patchawarra Troughs is shown in Figure 6.3a, and that of the Jurassic, Permian and Cambrian oils is illustrated in Figure 6.3b. With the exception of the Poolowanna-1 (Poolowanna) outlier, the oils are isotopically more homogeneous than are the rock extracts.

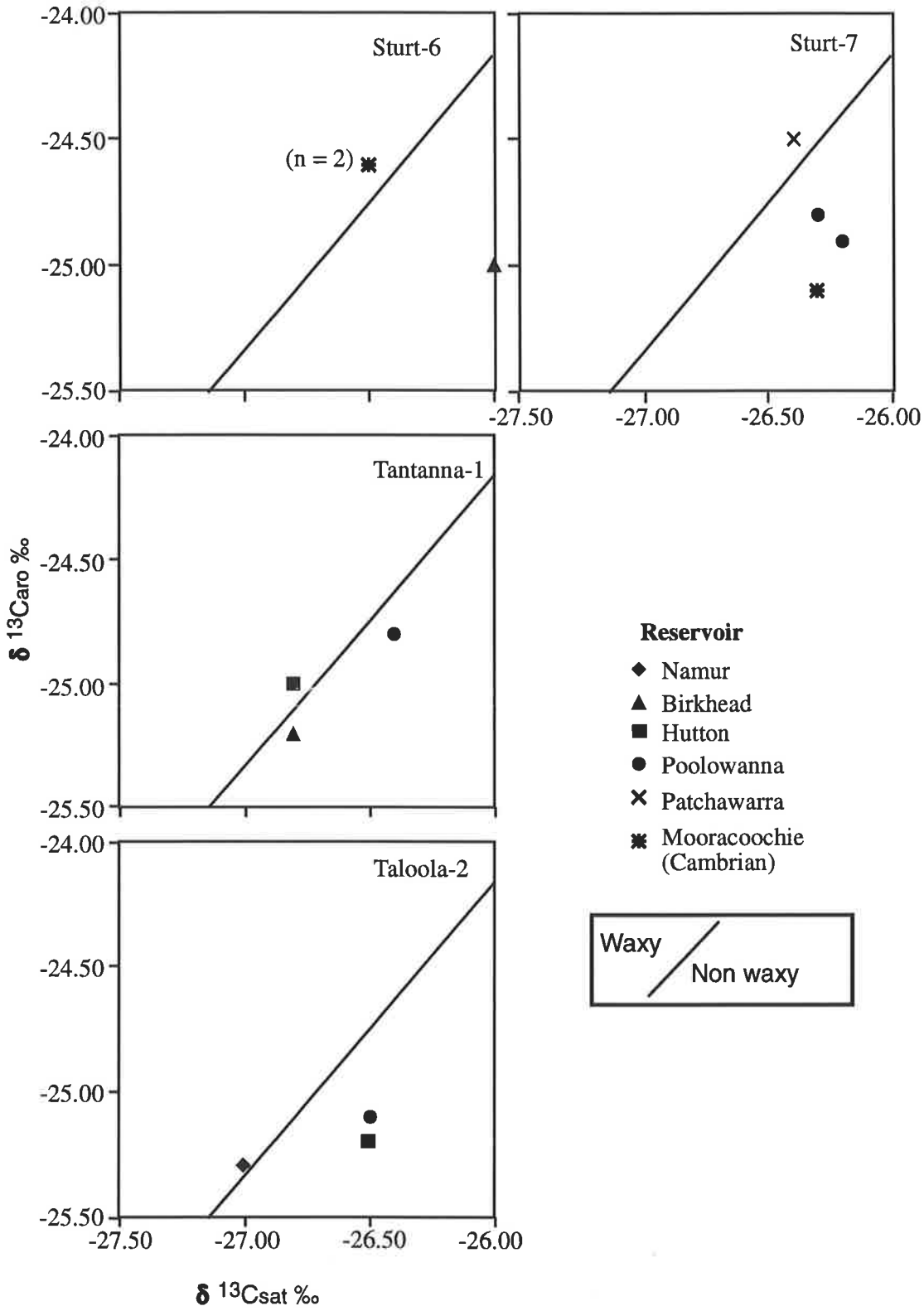


Figure 6.4. Comparison of the isotopic signatures of oils in selected stacked reservoirs

Both waxy and non-waxy organic inputs appear to characterise the Poolowanna Formation source rock facies of the study area. In the waxy zone (non-marine) the Poolowanna Trough samples plot as isotopically more positive than the Patchawarra Trough samples. A Similar separation is observed in the non-waxy (marine) zone (Fig. 6.3a). This offset towards more positive (i.e. heavier) values is most likely to be caused by the greater maturity of the Poolowanna Trough samples.

The distinction between Jurassic oils and those from Permian and Cambrian reservoirs is quite subtle, as shown in Figure 6.3b. With the exception of one Cambrian (Mooracoochie) sample, the Permian and pre-Permian oils plot in the waxy zone, which is in agreement with their terrestrial plant affinity. Most of the Jurassic oils have a non-waxy, bacterial signature. The Poolowanna-1 (Poolowanna) crude, which happens to have a very strong waxy signature, is an obvious exception. Here, land plant lipids clearly outweigh the bacterial input to the rock.

On the basis of the isotopic evidence, the Poolowanna source rocks are possible sources for the Eromanga-reservoired oils. Generally, the non-waxy source rock facies appear to have played a more important role in the generation of these oils than the waxy facies. The waxy Poolowanna-1 (Poolowanna) oil is likely to have been generated by a local waxy organic facies with characteristics similar to those of carbonaceous silty shale at Sturt-1 (1871 m). Its position in the cross-plot, apart from organic matter input, might have been influenced by water washing (Sofer, 1984).

6.2.6 Isotopic signatures of oils in stacked reservoirs

The isotopic signatures of oils in stacked reservoirs at four different well localities are illustrated in Figure 6.4.

Sturt-6 The waxy Patchawarra (Permian) and Mooracoochie (Cambrian) oils plot in the same spot indicating their common origin, probably from an intra-Permian source. The non-waxy Birkhead oil is well separated and thus of different origin (probably Jurassic).

Sturt-7 Here the Permian (Patchawarra) oil plots in the waxy zone, whilst the Cambrian (Mooracoochie) and the Jurassic (Poolowanna) oils plot in the non-waxy zone. In this case the Mooracoochie oil plots together with the Poolowanna oils and is likely to be derived from a similar non-waxy Jurassic source.

Tantanna-1 These three oils are of similar origin, and plot close to the line (CV = 0.47) which separates waxy from non-waxy crudes. On balance, they are probably of Jurassic origin. However, it is not possible to determine from their isotopic composition alone whether the source is the Poolowanna or the Birkhead Formation.

Table 6.3a Gas chromatographic data on saturated hydrocarbon fractions of rock extracts, Poolowanna Formation.

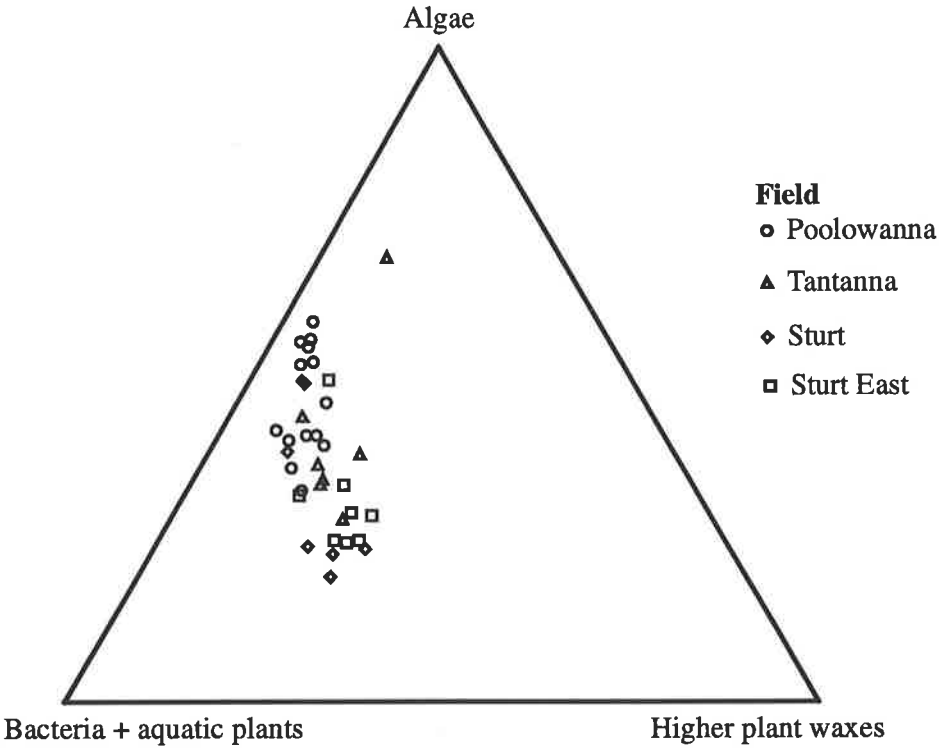
Sample No.	Depth (m)	Carbon Range	nCmax	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI	OEP			C_{16}-C_{19}	C_{20}-C_{26}	C_{27}-C_{31}
								i=16	i=22	i=26	Algal %	Bacterial %	Plant waxes %
POL1-1	2417	nC_{12}-nC_{34}	C_{15}	6.56	0.40	0.07	1.16	1.02	1.02	1.12	41	46	13
POL1-3	2438	nC_{12}-nC_{34}	C_{19}	4.11	0.56	0.12	1.08	0.99	0.96	1.04	52	43	6
POL1-4	2469	nC_{12}-nC_{32}	C_{19}	4.12	0.64	0.14	1.02	1.01	0.99	1.04	55	41	4
POL1-5	2499	nC_{12}-nC_{33}	C_{18}	4.88	0.50	0.10	1.21	0.99	1.08	1.09	52	41	7
POL1-6	2545	nC_{12}-nC_{34}	C_{16}	5.94	0.45	0.08	1.19	1.00	1.04	1.05	56	39	5
POL1-7	2557	nC_{12}-nC_{32}	C_{17}	6.63	0.35	0.06	1.10	0.99	1.02	1.11	59	38	4
POL2-8	2496	nC_{14}-nC_{36}	C_{15}	3.23	0.16	0.05	1.10	0.97	1.03	1.09	41	48	11
POL2-9	2524	nC_{12}-nC_{37}	C_{16}	3.26	0.23	0.08	1.09	0.99	1.02	1.02	46	42	12
POL2-10	2542	nC_{11}-nC_{32}	C_{15}	3.81	0.15	0.04	1.16	0.99	1.02	1.14	54	40	5
POL3-11	2423	nC_{12}-nC_{35}	C_{18}	5.25	0.25	0.04	1.16	0.96	1.02	1.12	33	52	15
POL3-12	2438	nC_{12}-nC_{35}	C_{15}	4.09	0.45	0.11	1.39	0.99	1.28	1.07	36	52	12
POL3-13	2505	nC_{12}-nC_{37}	C_{16}	4.29	0.39	0.10	1.14	1.02	1.10	1.06	39	46	15
POL3-14	2551	nC_{11}-nC_{34}	C_{15}	3.87	0.17	0.04	1.15	0.97	1.07	1.08	42	51	7
POL3-15	2560	nC_{11}-nC_{35}	C_{16}	3.86	0.18	0.05	1.13	0.97	1.04	1.09	40	50	10
TAN2-18	1799	nC_{11}-nC_{37}	$C_{14,23}$	7.63	0.56	0.08	1.25	1.03	1.11	1.24	28	49	23
TAN2-20	1811	nC_{12}-nC_{33}	C_{15}	8.31	0.40	0.08	1.37	1.00	1.09	1.32	68	23	9
TAN3-21	1807	nC_{11}-nC_{32}	C_{14}	5.40	0.47	0.09	1.26	0.99	1.07	1.27	44	46	10
TAN4-22	1807	nC_{11}-nC_{33}	$C_{13,25}$	2.29	0.37	0.18	1.27	0.98	1.07	1.31	34	49	17
TAN4-23	1814	nC_{12}-nC_{33}	C_{14}	5.85	0.97	0.16	1.12	0.95	1.10	1.33	37	48	16
TAN5-24	1814	nC_{11}-nC_{32}	$C_{13,23}$	7.48	1.04	0.15	1.14	1.00	1.10	1.18	34	49	17
TAN8-25	1823	nC_{10}-nC_{35}	C_{13}	7.34	0.96	0.14	1.26	0.97	1.08	1.26	38	41	20
STU1-27	1871	nC_{12}-nC_{37}	C25	5.11	0.55	0.10	1.23	1.04	1.14	1.22	23	48	28
STU4-30	1859	nC_{11}-nC_{37}	$C_{14,25}$	5.97	0.63	0.10	1.38	0.97	1.12	1.41	24	56	21
STU4-31	1881	nC_{10}-nC_{34}	C_{13}	6.87	0.74	0.12	1.19	0.99	1.05	1.21	49	44	7
STU3-33	1862	nC_{10}-nC_{32}	C_{13}	7.32	0.58	0.09	1.09	1.01	1.07	1.16	49	44	8
STU6-34	1847	nC_{10}-nC_{37}	$C_{14,25}$	4.52	0.45	0.09	1.31	0.98	1.09	1.30	23	53	24
STU6-35	1865	nC_{10}-nC_{32}	C_{14}	6.79	0.86	0.13	1.16	1.00	1.09	1.15	38	51	10
STU8-36	1862	nC_{10}-nC_{37}	$C_{15,25}$	4.82	0.47	0.09	1.39	0.98	1.13	1.42	19	55	26

Table 6.3a (continued)

Sample No.	Depth (m)	Carbon Range	nCmax	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	CPI	OEP			C_{16}-C_{19}	C_{20}-C_{26}	C_{27}-C_{31}
								i=16	i=22	i=26	Algal %	Bacterial %	Plant waxes %
STE1-37	1835	nC_{11}-nC_{35}	$C_{15,25}$	6.04	0.76	0.13	1.28	0.99	1.10	1.32	25	52	23
STE1-38	1841	nC_{12}-nC_{38}	$C_{15,27}$	7.25	0.52	0.08	1.26	1.01	1.12	1.25	29	45	26
STE1-39	1844	nC_{12}-nC_{37}	C_{15}	5.38	0.80	0.16	1.35	0.99	1.29	1.23	34	46	20
STE2-40	1829	nC_{12}-nC_{37}	$C_{17,25}$	3.61	0.62	0.17	1.27	1.01	1.11	1.27	29	47	24
STE3-41	1850	nC_{11}-nC_{37}	$C_{16,25}$	6.02	0.73	0.12	1.31	0.99	1.14	1.30	25	50	25
STE4-43	1838	nC_{11}-nC_{37}	$C_{16,25}$	5.81	0.62	0.10	1.23	0.97	1.12	1.24	25	49	26
STE4-44	1850	nC_{9}-nC_{32}	C_{12}	8.28	0.69	0.10	1.02	0.98	1.08	1.24	50	40	10
STE4-45	1862	nC_{10}-nC_{33}	$C_{14,23}$	8.44	1.85	0.21	1.18	0.99	1.08	1.33	32	53	15

$$CPI = \frac{1}{2}\left[\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right]$$

$$OEP = \left[\frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}}\right]^{(-1)^{i-1}}$$



Key:	C no. range
Algae	16 - 19
Bacteria and aquatic plants	20 - 26
Higher plant waxes	27 - 31*

* Certain freshwater algae (e.g. Botryococcus) may also contribute to this range

Figure 6.5a Source rock affinity to organic matter inputs based on *n*-alkane distributions, Poolowanna Formation

Taloola-2 Like in Tantanna-1, these three oils have very similar carbon isotopic signatures for both the saturated and aromatic hydrocarbon fractions. It is probable that they are of the same origin. Their source rock is almost certainly of Jurassic rather than Permian age (i.e. Birkhead and/or Poolowanna).

The above observations suggest that the oils from Jurassic reservoirs have a different origin from that of the Permian oils. One of the Mooracoochie oils (Sturt-6) is of Permian origin, and the other (Sturt-7) is clearly of Jurassic origin.

6.3 Relationship of *n*-alkane distribution to source biota and saturate $\delta^{13}C$ signature

6.3.1 Organic matter inputs based on *n*-alkane distribution

Because the composition of various homologous series of straight-chain lipids are biosynthetically closely related to *n*-alkanes (Deines, 1980), carbon number distributions of *n*-alkanes in sediments have been used to broadly infer the types of precursor organisms. Furthermore, different species of plants are reported to synthesise differing proportions of various *n*-alkane homologues (Gelpi *et al.*, 1970; McKirdy *et al.*, 1986a). Due to the mixed nature of the biota contributing organic matter to sediments, certain *n*-alkane ranges can be used to infer only the dominant contributing organism(s). As suggested by Collister *et al.* (1994), the C_{16}-C_{19} range is likely to be dominated by algae; C_{20}–C_{26} by bacteria and aquatic plants; and C_{27}–C_{31} by (waxy) higher plants.

The relative abundance of these three diagenetic-alkane groups for the Poolowanna Formation source rock extracts are presented in Table 6.3a, and for the crude oils in Table 6.3b. The resulting implications for the major organic matter inputs to the source rock are illustrated by a ternary diagram (Fig. 6.5a). The corresponding diagram for the oils (Fig. 6.5b) demonstrates their source affinity.

A strong contribution of organic matter to the Poolowanna Formation by algae, bacteria and aquatic plants is indicated for the Poolowanna Trough. Here, the relative abundance of the algal input ranges from 33% at 2423 m in Poolowanna-3 to 59% at 2557 m in Poolowanna-1. An algal presence would also account for the lamalginite noted in this area (Chapter 4). The Patchawarra Trough samples are characterised by a stronger input from bacteria and aquatic plants: 23–49 % at Tantanna; 44–53% at Sturt East. However, an anomalously high algal contribution (68%) is also noted in Tantanna (Tantanna-2, 1811 m).

Table 6.3b Gas chromatographic data on saturated hydrocarbon fractions of crude oils from the Poolowanna and Patchawarra Troughs

Sample No.	Well	Formation	DST No.	Depth (m)	Carbon Range	n-Cmax	Pr / Ph	Pr / n-C_{17}	Ph / n-C_{18}	CPI	OEP i=16	OEP i=22	OEP i=26	C_{16}-C_{19} Algal %	C_{20}-C_{26} Bacterial %	C_{27}-C_{31} Plant Wax %
P1	Poolowanna-1	Poolowanna	2	2504-2538	nC_9-nC_{39}	C_{23}	4.98	0.21	0.04	1.17	0.99	1.06	1.08	24	50	27
T2	Tantanna-1	Poolowanna	1	1800-1814	nC_9-nC_{31}	C_{12}	6.03	0.36	0.07	1.29	1.00	1.07	1.28	46	48	7
T3	Tantanna-1	Hutton	2	1635-1642	nC_9-nC_{31}	C_{13}	7.23	0.61	0.09	1.32	1.01	1.10	1.21	42	50	8
T4	Tantanna-1	Birkhead/Hutton	3	1347-1359	nC_{10}-nC_{29}	C_{14}	8.88	0.90	0.11	1.48	1.00	1.13	1.34	49	47	5
T5	Tantanna-2	Poolowanna	1	1808-1856	nC_9-nC_{34}	C_{12}	2.29	0.41	0.19	1.02	1.01	1.05	1.09	42	50	8
T6	Tantanna-2	Hutton	2	-	nC_9-nC_{30}	C_{12}	6.10	0.62	0.11	1.32	1.00	1.13	1.22	45	49	6
S9	Sturt-2	Poolowanna	1	1856-1892	nC_9-nC_{33}	C_{13}	7.59	0.81	0.13	1.19	0.86	0.88	0.92	41	51	8
S11	Sturt-3	Poolowanna	1A	1848-1855	nC_9-nC_{35}	C_{14}	5.42	0.97	0.18	1.22	0.80	1.05	1.18	53	38	9
S12	Sturt-3	Birkhead	1B	1654-1662	nC_{10}-nC_{33}	C_{11-14}	6.88	0.94	0.14	1.18	1.02	1.03	1.11	38	51	11
S13	Sturt-4	Poolowanna	1	1872-1880	nC_{10}-nC_{33}	C_{14}	6.97	0.84	0.12	1.21	1.01	1.03	1.17	41	50	9
S14	Sturt-4	Poolowanna	2	1883-1892	nC_{10}-nC_{33}	C_{14}	6.69	0.87	0.13	1.15	0.98	1.02	1.07	40	50	10
S15	Sturt-5	Poolowanna	1	1858-1866	nC_{10}-nC_{36}	C_{13}	5.38	0.97	0.18	1.14	1.02	1.01	1.13	36	50	14
S16	Sturt-6	Mooracoochie	6	1914-1919	nC_{10}-nC_{34}	C_{13}	6.01	0.79	0.14	1.18	1.01	1.04	1.06	40	50	10
S17	Sturt-6	Patchawarra	3	1884-1898	nC_{10}-nC_{31}	C_{13}	6.31	0.72	0.12	1.22	0.99	1.03	1.17	45	48	8
S18	Sturt-6	Birkhead	1	1883-1892	nC_{10}-nC_{32}	C_{12}	6.79	1.06	0.16	1.19	0.98	1.04	1.15	44	48	8
S19	Sturt-7	Patchawarra	1	1923-1938	nC_{10}-nC_{34}	C_{13}	5.71	0.74	0.13	1.15	0.99	1.06	1.08	39	50	11
S20	Sturt-7	Mooracoochie	2	1946-2021	nC_{10}-nC_{32}	C_{14}	6.80	0.73	0.11	1.20	0.99	1.07	1.26	44	47	9
S21	Sturt-7	Poolowanna	3	1871-1876	nC_9-nC_{35}	C_{13}	6.75	0.87	0.14	1.11	1.02	1.04	1.11	39	50	12
S22	Sturt-7	Poolowanna	5	1885-1889	nC_9-nC_{34}	C_{13}	6.75	0.85	0.13	1.17	0.73	1.06	1.12	53	39	9
S23	Sturt-8	Poolowanna	1	1880-1884	nC_9-nC_{34}	C_{14}, C_{19}	7.21	0.86	0.12	1.11	1.00	1.02	1.04	39	51	10
SE24	Sturt East-2	Poolowanna	1	1845-1899	nC_9-nC_{34}	C_{12}	7.55	0.85	0.11	1.18	0.99	1.03	1.08	41	49	10
TAL25	Taloola-2	Poolowanna	1	1829-1836	nC_9-nC_{34}	C_{12}	5.01	0.35	0.07	1.19	1.00	1.07	1.14	41	50	9
TAL26	Taloola-2	Hutton	2	1789-1793	nC_9-nC_{31}	C_{12}	5.33	0.33	0.06	1.24	1.01	3.05	1.02	34	61	5
TAL27	Taloola-2	Namur	3	1384-1397	nC_9-nC_{33}	C_{12}	7.40	0.73	0.10	1.25	1.00	1.07	1.19	40	52	9

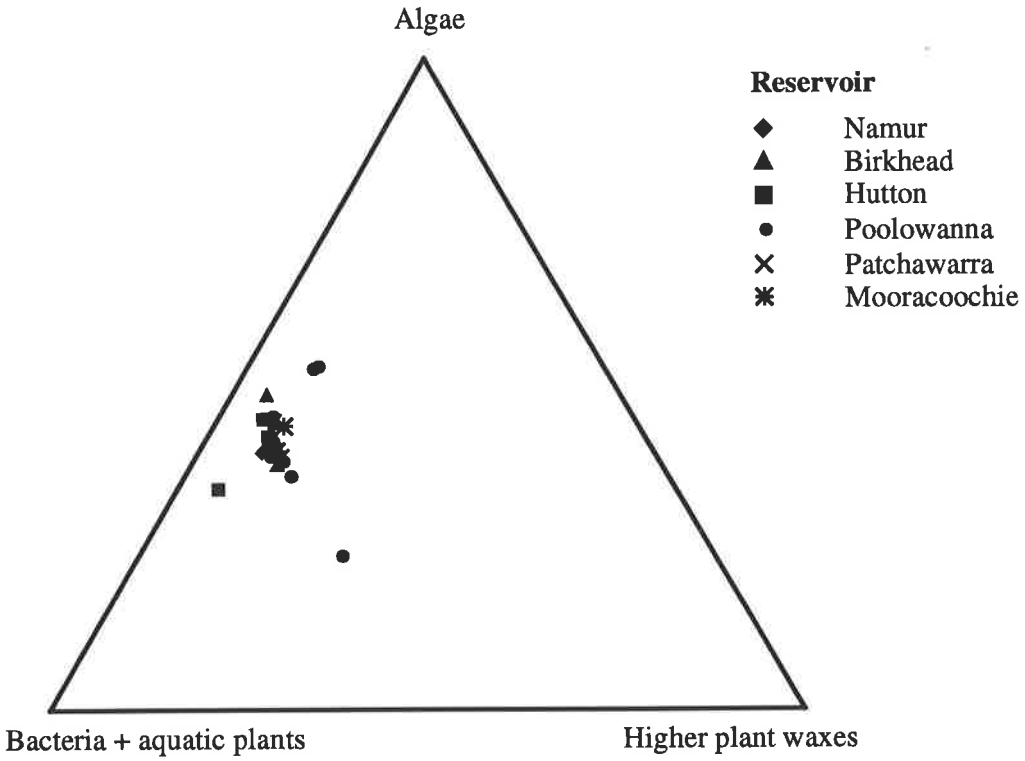


Figure 6.5b Oil source affinity based on *n*-alkane distributions, Poolowanna and Patchawarra Troughs. Key as for Figure 6.5a.

The contribution of higher plant waxes is shown to be relatively lean in all fields. However, there is an apparent trend of increasing higher plant input from Poolowanna to Sturt East (Fig. 6.5a). The presence of telalginite, especially *Botryococcus*-like alginite, in samples from the Patchawarra Trough (Chapter 4), would tend to enhance this trend.

A strong affinity with algal, bacterial and aquatic plant precursors is inferred for almost all the oils based on their *n*-alkane group distributions (Fig. 6.5b). The highest algal input (53%) is recorded in the Poolowanna-reservoired oils from Sturt-3 and Sturt-7 whereas the highest bacterial and aquatic plant contribution (61%) is recorded in the Hutton oil from Taloola-2. The higher plant wax contribution is relatively low in all the analysed oils.

The highest value of 27% is recorded in the Poolowanna-1 (Poolowanna) oil whilst the rest of the oils have values ranging from 5% to 14%.

The inferred source affinity of oils plotted in Figure 6.5b is remarkably uniform. Of all the reservoir units sampled, the Poolowanna Formation and, and to a lesser extent, the Hutton Sandstone display the greatest variability in oil source affinity. This is attributable to ranging degrees of *in situ* alteration of the oils in the latter reservoirs by water washing.

Finally, the *n*-alkane-based compositional fields of the source rocks (Fig. 6.5a) and the crude oils (Fig. 6.5b) overlap. Thus, this method cannot be used to distinguish oils of Jurassic and Permian origin.

6.3.2 Assignment of saturates isotopic signature to source biota contribution as derived from *n*-alkane distribution

It is assumed that since the specified *n*-alkane ranges are likely to be dominated by the nominated biota, the saturates isotopic signature is likely to reflect the combined contributions of such source biota (Collister *et al.*, 1994). The above assumption is tested by plots of $\delta^{13}C_{sat}$ versus the relative abundances of precursor biota (algae; bacteria and aquatic plants; and higher plant waxes) for source rocks and oils (Figs. 6.6 and 6.7).

6.3.2.1 Influence of source biota on $\delta^{13}C_{sat}$ in source rock extract

The cross-plot of $\delta^{13}C_{sat}$ versus relative algal input displays a weak positive correlation with a regression coefficient of 0.54 (Fig. 6.6). Isotopically heavy signatures are associated with increased algal inputs. The bacterial and aquatic plant input is shown to have a weak negative correlation with $\delta^{13}C_{sat}$. The higher plant waxes exhibit a moderately strong negative correlation with $\delta^{13}C_{sat}$ ($r = -0.71$) indicating that the terrestrial organic input tends to drive isotopic signature of the saturated fraction to lighter values.

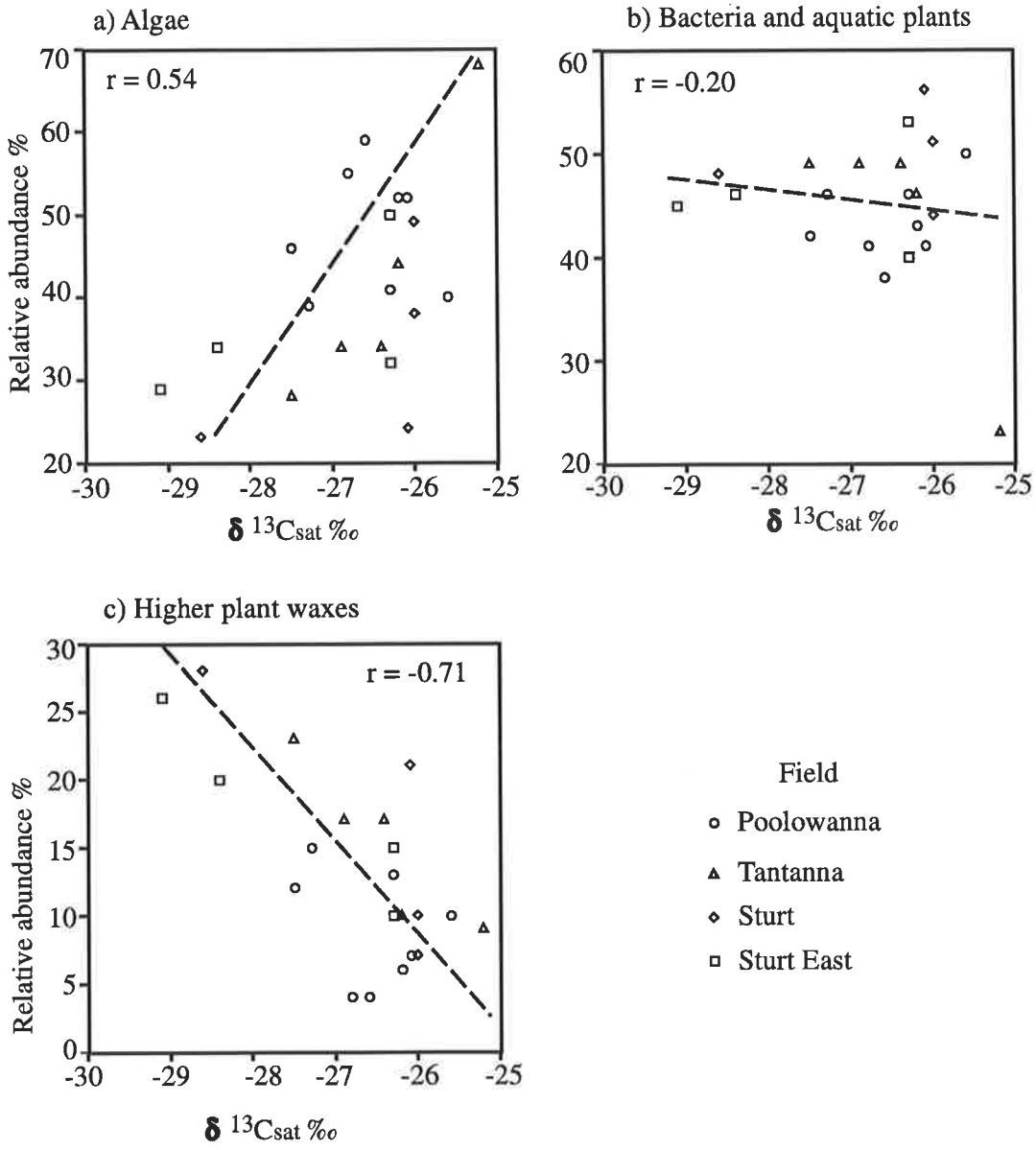


Figure 6.6 Relationship between source biota and saturates isotopic signature in Poolowanna Formation extracts

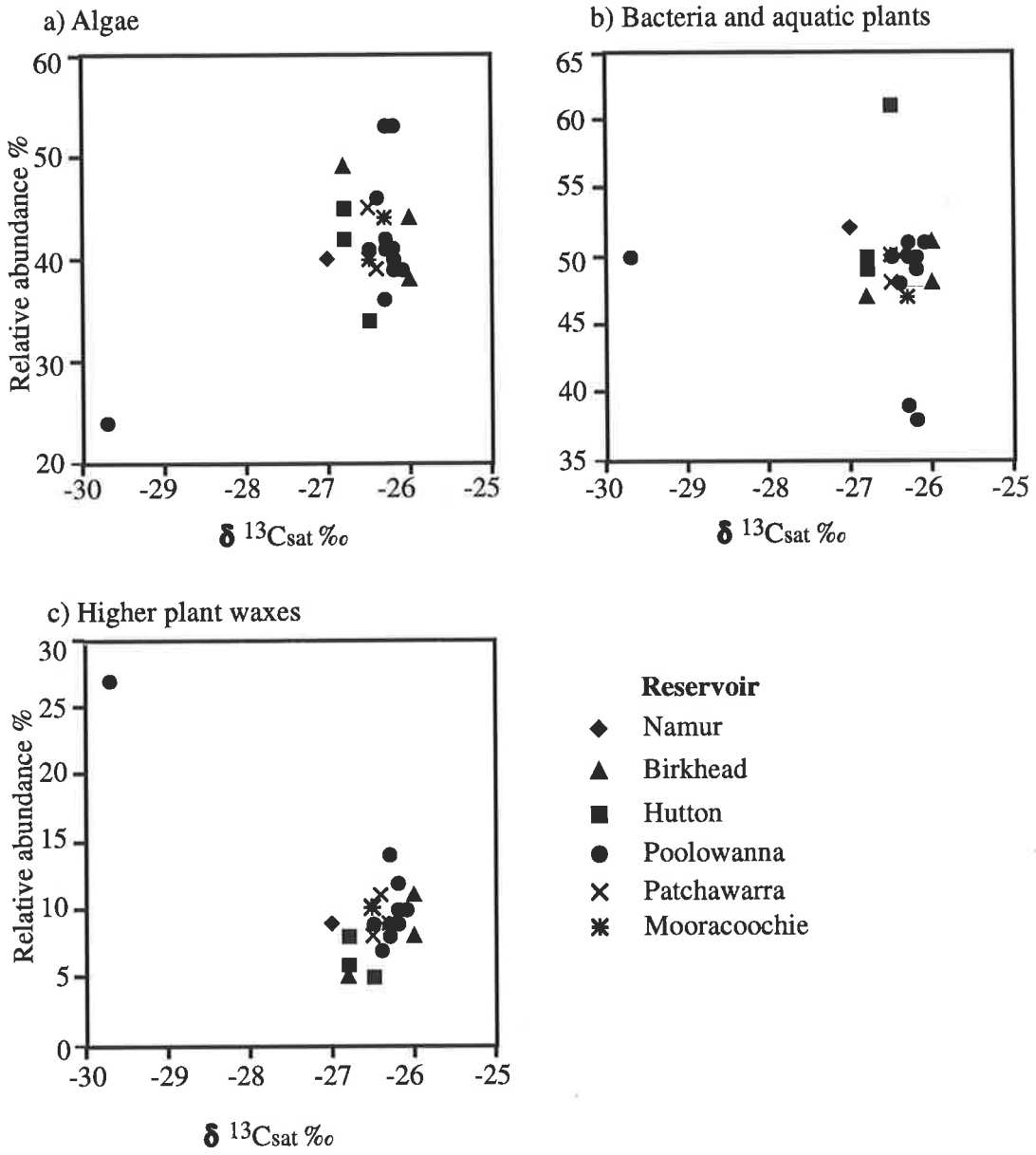


Figure 6.7 Relationships of saturates isotopic signature to the inferred source affinity of crude oils in the Poolowanna and Patchawarra Troughs

From the above illustrations, it can be deduced that the saturates isotopic signature, of the Poolowanna Formation in the Poolowanna Trough is related to a freshwater algal input whereas in the case of the Sturt and Sturt East samples higher plants exert a major influence. The bacterial influence is relatively minor.

It is concluded that the isotopically lighter signatures of the saturates fraction result from a progressive increase of the higher plant wax input, whereas the isotopically heavier signatures coincide with strong algal inputs. These two observations agree with the interpretation of the CV data.

6.3.2.2 Influence of source biota on $\delta^{13}C_{sat}$ in oils

The influence of the source biota on the $\delta^{13}C$ signature of the saturates fraction of the oils is shown in Figure 6.7. As is evident in the Poolowanna Formation rock extracts, the observed isotopic signature is little influenced by the bacterial and aquatic plant input. The anomalously negative signature of the Poolowanna-1 (Poolowanna) oil is attributable mainly to the higher plant wax input. The heavier $\delta^{13}C_{sat}$ values of the remainder of the oils, is due to their greater algal inputs. Figure 6.7 illustrates again the very uniform isotopic composition of the Patchawarra Trough oils.

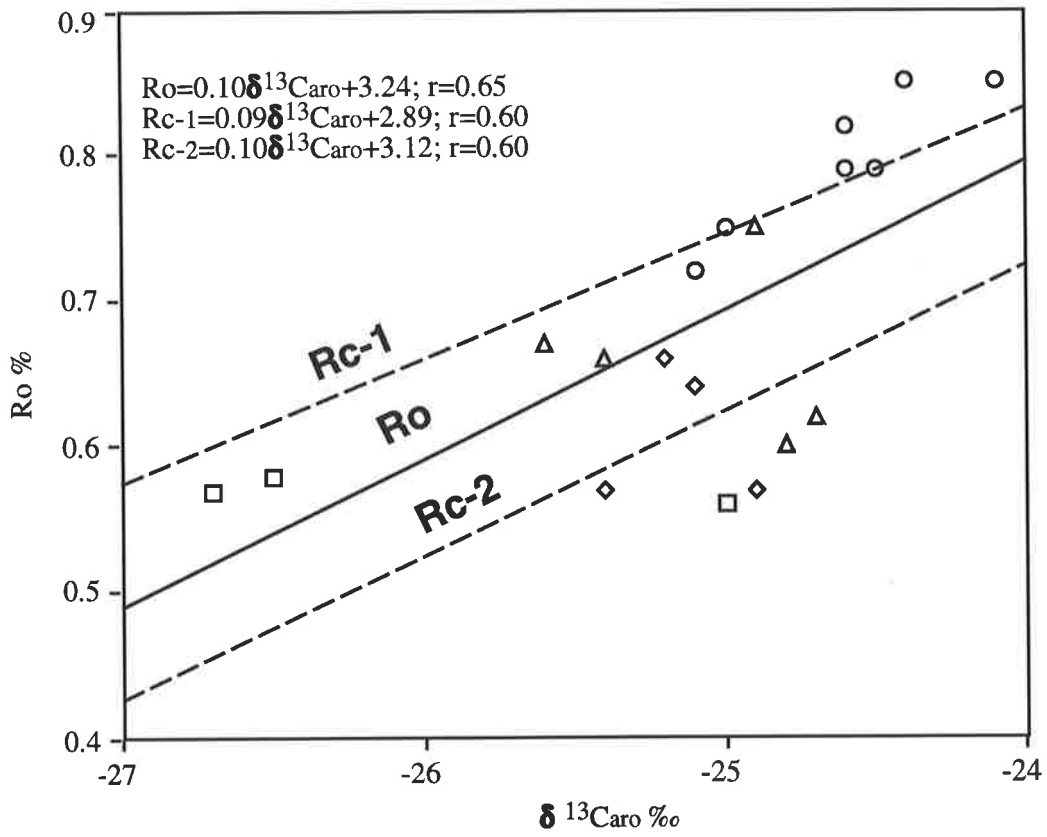
6.4 Variation of $\delta^{13}C_{sat}$ signature with maturation

The $\delta^{13}C$ signature of the whole oil was reported by Fuex (1977) to become more positive with increasing maturity. The effect of maturation on the C_{15+} saturates or aromatic fractions however, was expected to be much less than that shown by the whole oil.

In this study, the maturation effect was examined by comparing the $\delta^{13}C$ signatures of the saturated and aromatic hydrocarbon fractions with measured vitrinite reflectance (R_O) in the case of source rocks and calculated vitrinite reflectance (R_C-1 and R_C-2)in the case of oils and source rocks. R_C-1 is the calculated reflectance proposed by Radke and Welte (1983) and R_C-2 is the one suggested by Boreham *et al.* (1988).

Cross-plots of the $\delta^{13}C_{aro}$ signatures versus R_O and R_C are shown in Figure 6.8. The $\delta^{13}C_{sat}$ of the rock extracts showed only a weak positive correlation with maturity, yielding regression coefficients of 0.59 for R_C-1; 0.60 for R_C-2 and 0.33 for R_O. In contrast, no such correlation was observed in the oils. This suggests that the effect of maturation on the $\delta^{13}C$ signature of the saturates is slight to non-existent.

The $\delta^{13}C$ signature of the aromatic fraction of the Poolowanna rock extracts showed positive correlations with maturity ($r = 0.65$ for R_O and 0.61 for both R_C-1 and R_C-2). The general trend for the whole Poolowanna source rock population is illustrated in Figure 6.8a.



Ro = Measured vitrinite reflectance
Rc-1 = 0.60 MPI + 0.40 (Radke and Welte, 1983)
Rc-2 = 0.7 MPI + 0.22 (Boreham et al., 1988)

Figure 6.8a Variation of aromatic δ ^{13}C signature with maturity (Ro, Rc-1 and Rc-2) in source rocks

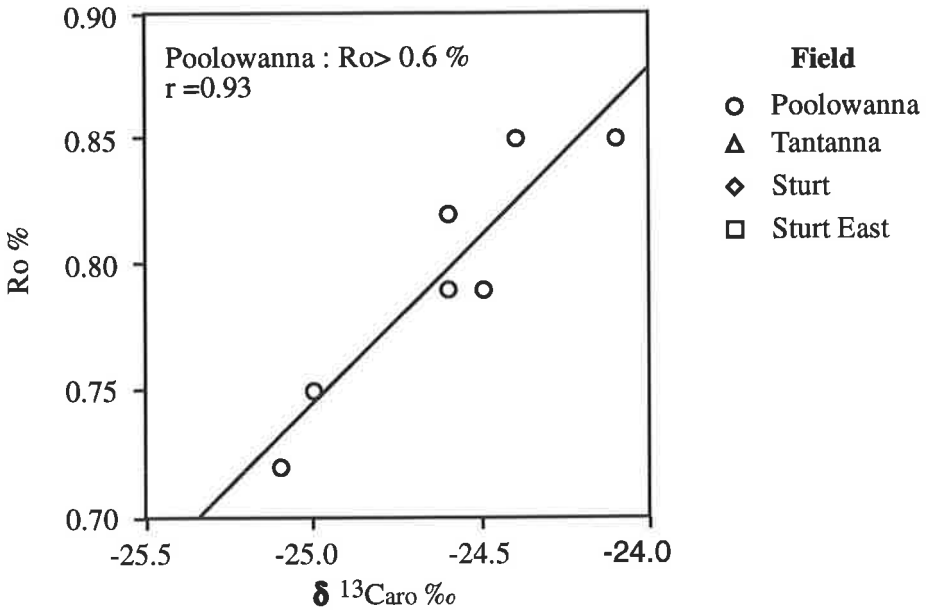


Figure 6.8b Variation of aromatic δ ^{13}C signature with maturity (Ro) in Poolowanna Trough source rock

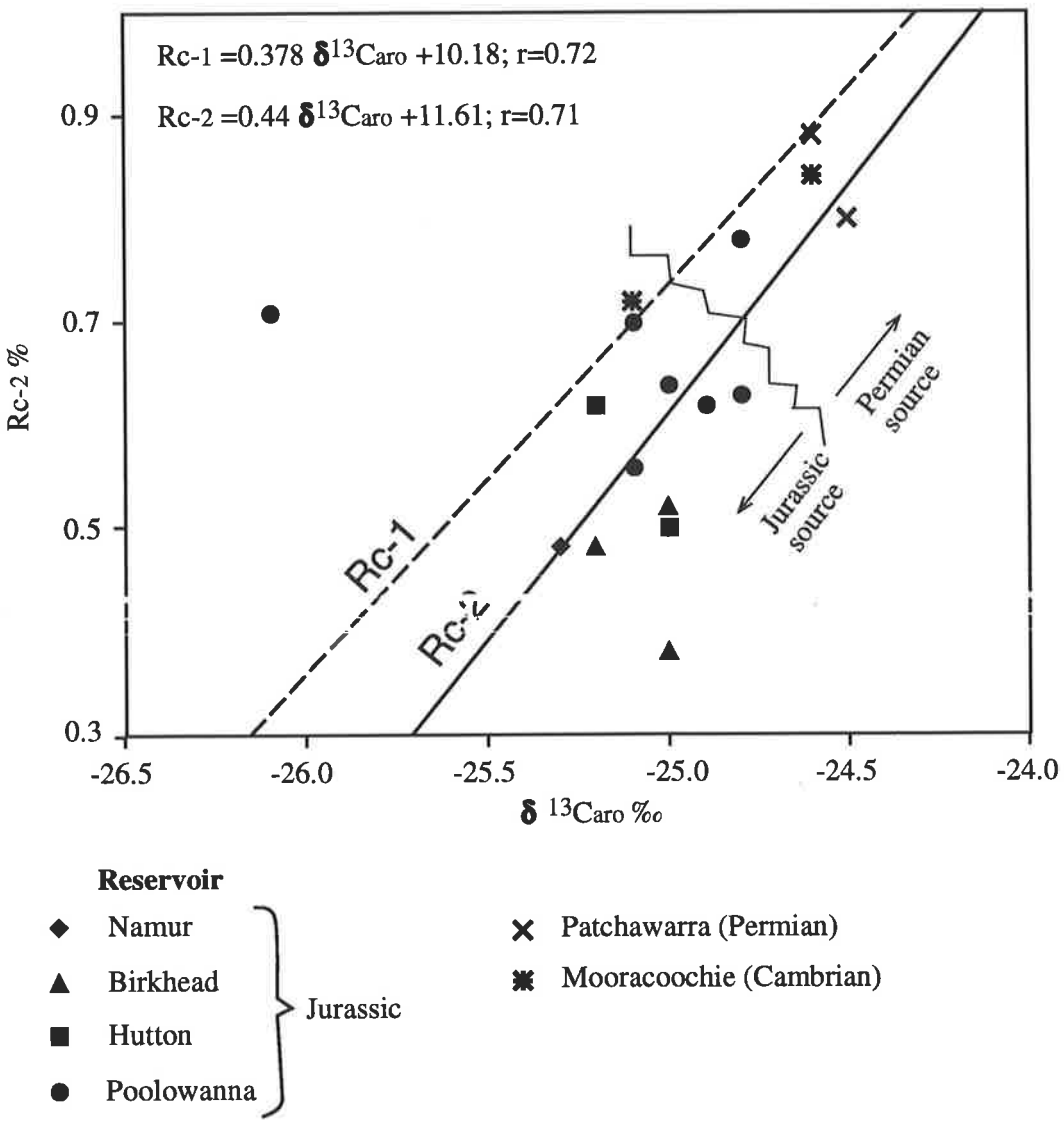


Figure 6.8c Variation of aromatic isotopic signature with oil maturity based on calculated reflectances (Rc-1 and Rc-2)

Once again it is shown that the source rock in the Poolowanna Field is more mature than those in neighbouring fields of the Patchawarra Trough. A very strong positive correlation (r = 0.93) was observed when the mature Poolowanna Trough samples were plotted alone (Fig. 6.8b). This observation suggests that at high maturation levels (>0.6% R_O), the $\delta^{13}C$ signature of aromatic fraction become more positive with increasing maturation, particularly in similar lithological facies.

The total suite of oil aromatic fractions also showed a positive correlation with maturity (r = 0.34 for both R_C-1 and R_C-2). Because of the extreme $\delta^{13}C_{aro}$ value (-26.1‰) of the Poolowanna-1 oil, this sample was excluded for the purposes of correlation (Fuex, 1977). After its exclusion, a stronger positive correlation resulted (r = 0.72 for R_C-1, and 0.71 for R_C-2). In both cases, it is shown that there is an apparent positive increase of $\delta^{13}C$ signature of aromatic fraction with increasing maturity. A more pronounced positive correlation is also observed in the case of calculated reflectance values >0.6% R_C (Fig. 6.8c).

It is clearly shown by Figure 6.8c that the Permian and Cambrian oils are isotopically more positive and thus more mature than the overlying Jurassic oils. It can also be deduced from this figure that the Tantanna-1 (Poolowanna) oil originated from a Cooper Basin source rock. The Jurassic oils from Birkhead Formation, Namur Sandstone and Hutton Sandstone and the rest of those from the Poolowanna Formation, are shown to be quite separated from those in Patchawarra Formation and Mooracoochie Volcanics because of their lower maturity. The Sturt-7 (Mooracoochie) oil plots in the same maturity domain as the bulk of the Jurassic oils. However, biomarker evidence (Chapter 7) suggests that it may not be of Jurassic origin.

Chapter 7

Characterisation of source rocks and oils based on saturated hydrocarbon biomarkers

7.1 Introduction

Saturated hydrocarbon biomarkers are part of the suite of molecular fossils derived from once living organisms. The group of molecular fossils dealt with in this chapter are normally encountered in source rock extracts (bitumen) and oils and include a range of acyclic normal alkanes, acyclic isoprenoids, and cyclic alkanes (viz. sesquiterpanes, triterpanes and steranes).

The relative distribution and abundance of these biomarker alkanes is used to identify the type of biota (algae, bacteria and land plants) which contributed organic matter to the source rocks. In the case of oils, the biomarkers help determine their source affinity by providing information on the organic facies and depositional environment of the source rock. Source rock and oil maturity assessment is also possible using biomarkers (Peters and Moldowan, 1993). Oils can then be grouped into families of the same source and maturity and each family be correlated with a potential source rock.

7.2 Biomarker distribution in source rocks and oils

The biomarker distributions in source rocks and oils are presented as relative abundances or as ratios to other biomarker compounds identified in the sample. This section describes the general characterisation of Poolowanna Formation source rocks and associated oils in terms of their source biota, depositional environment and maturity for several locations in the Poolowanna and Patchawarra Troughs.

7.2.1 Alkane distributions in source rocks

The *n*-alkane profiles and the related alkane parameters of the source rocks are summarised in Table 6.3a. Their carbon number ranges vary between C_{10} and C_{38}. The sample with the highest carbon number is from the Patchawarra Trough (Sturt East-1, 1841 m). Most of the profiles are unimodal having a maximum (*n*-C_{max}) between C_{13} and C_{27}. Bimodal profiles are displayed by a couple of Patchawarra Trough samples. Such bimodality is apparently absent or poorly displayed in the Poolowanna Trough samples. The bimodalities commonly observed include $C_{14, 23}$, $C_{13, 25}$ and $C_{15, 25}$ (usually indicators of contributions from algal and bacterial biota); and $C_{15, 27}$ (an indicator of inputs from both algae and higher plants). The anomalous abundance of C_{25} is noted in some samples (e.g. Sturt East-1, 1844 m: Fig. 7.1).

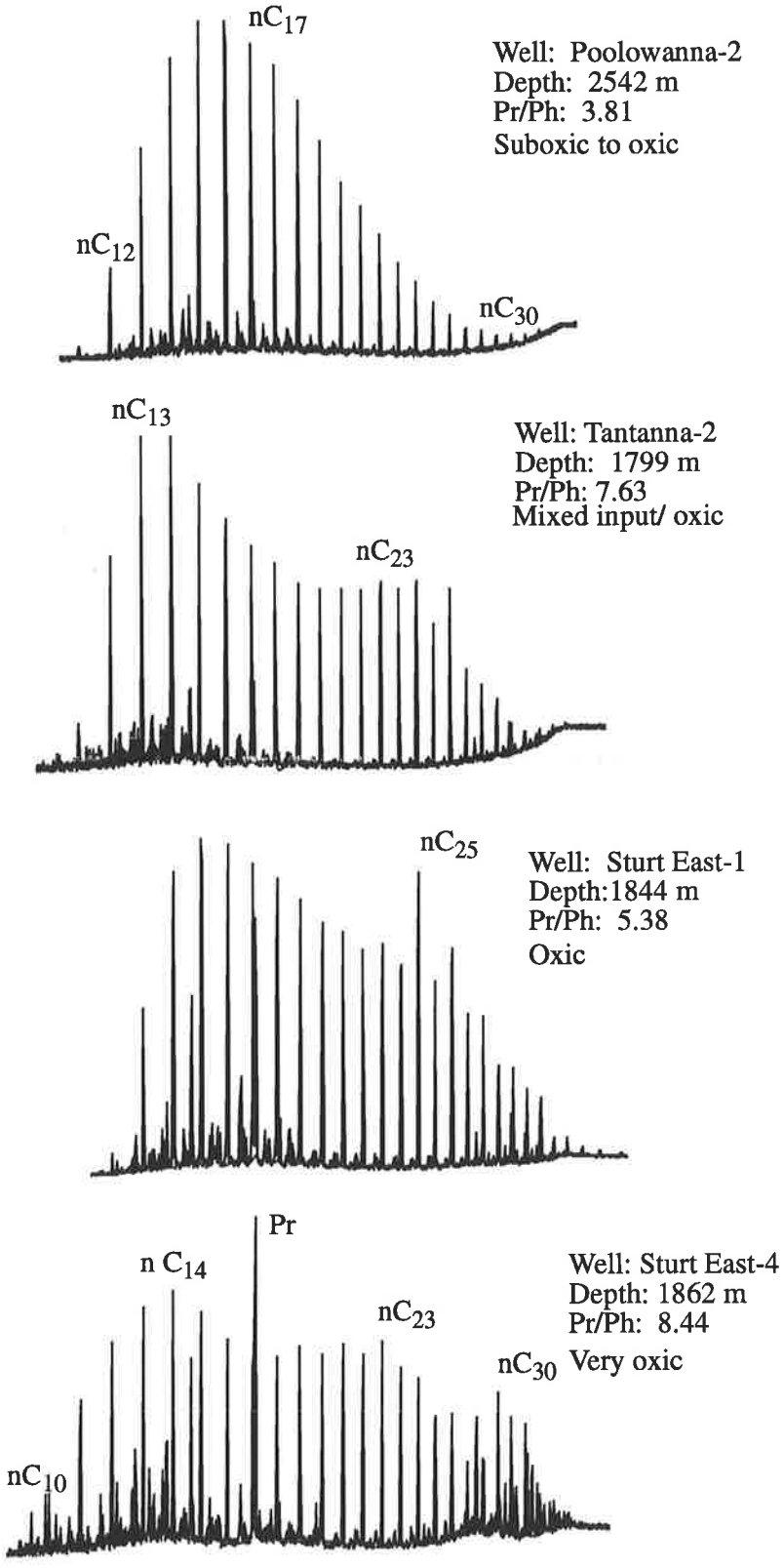


Figure 7.1 Gas chromatograms of alkanes in Poolowanna Formation source rock facies: implications for source biota and depositional environment

This feature is possibly caused by an unusual mix of bacteria, aquatic plants and higher plants.

The regular isoprenoids, pristane (C_{19}) and phytane (C_{20}), are clearly identified (Fig. 7.1). Pristane is commonly predominant over phytane. The pristane to phytane ratio (pr/ph) ranges from 2.29 in coaly siltstone (Tantanna-4, 1807 m) to 8.44 in coal (Sturt East-4, 1862 m). The average pr/ph value for the Poolowanna Trough is 4.56 and that for the Patchawarra Trough is 6.21, implying differences in depositional environment and/or organic matter input between these troughs. An anomalously high pristane peak is noted in the Sturt East-4 (1862 m) coal sample (Fig. 7.1). Such an abundance may indicate more than one source for the pristane (Goosens *et al.*, 1984), although another explanation is more likely (see below).

Pristane to *n*-heptadecane ratios (pr/*n*-C_{17}) vary from 0.15 in a Poolowanna Trough siltstone (Poolowanna-2, 2542 m) to 1.85 in the coals of the Patchawarra Trough (Sturt East-4, 1862 m). The average value for pr/*n*-C_{17} in the Poolowanna Trough is 0.35, whereas that in Patchawarra Trough is 0.71. According to the criteria suggested by Lijmbach (1975), the Poolowanna Trough source rock facies appear to have been deposited in relatively open water environments with abundant bacterial activity, whereas the Patchawarra Trough source rock facies were deposited in environments with alternating peat swamp and open water conditions. This observation supports the organic petrographic data which shows inertinite (inertodetrinite) occurring in association with liptinite (telalginite) (Chapter 4). The high value observed at 1862 m in Sturt East-4 (pr/*n*-C_{17} >1.0) clearly indicates the persistence of peat-swamp conditions in that area.

Phytane to *n*-octadecane ratios (ph/*n*-C_{18}) vary from 0.04 in the Poolowanna Field to 0.21 in Sturt East Field. The relative lower values shown in the Poolowanna Trough are probably indicative of the higher maturity of the Poolowanna Formation in this area. However, it is possible that this ratio also might have been influenced by depositional conditions.

Carbon preference index (CPI) and odd-even predominance (OEP) trends are as shown in Table 6.3a. The CPI values in both the Poolowanna and Patchawarra Troughs are very similar with average values of 1.14 and 1.24, respectively. These values normally are indicative of mature source rocks (Bray and Evans, 1961). As was noted from the vitrinite reflectance data, the Patchawarra Trough samples are somewhat less mature, and this would account for their slightly higher CPI values.

The OEP $\left[\frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}}\right]^{(-1)^{i+1}}$ values, centred at i=16, i=22 and i=26 (Scalan and Smith, 1970) show only very slight differences between the two troughs.

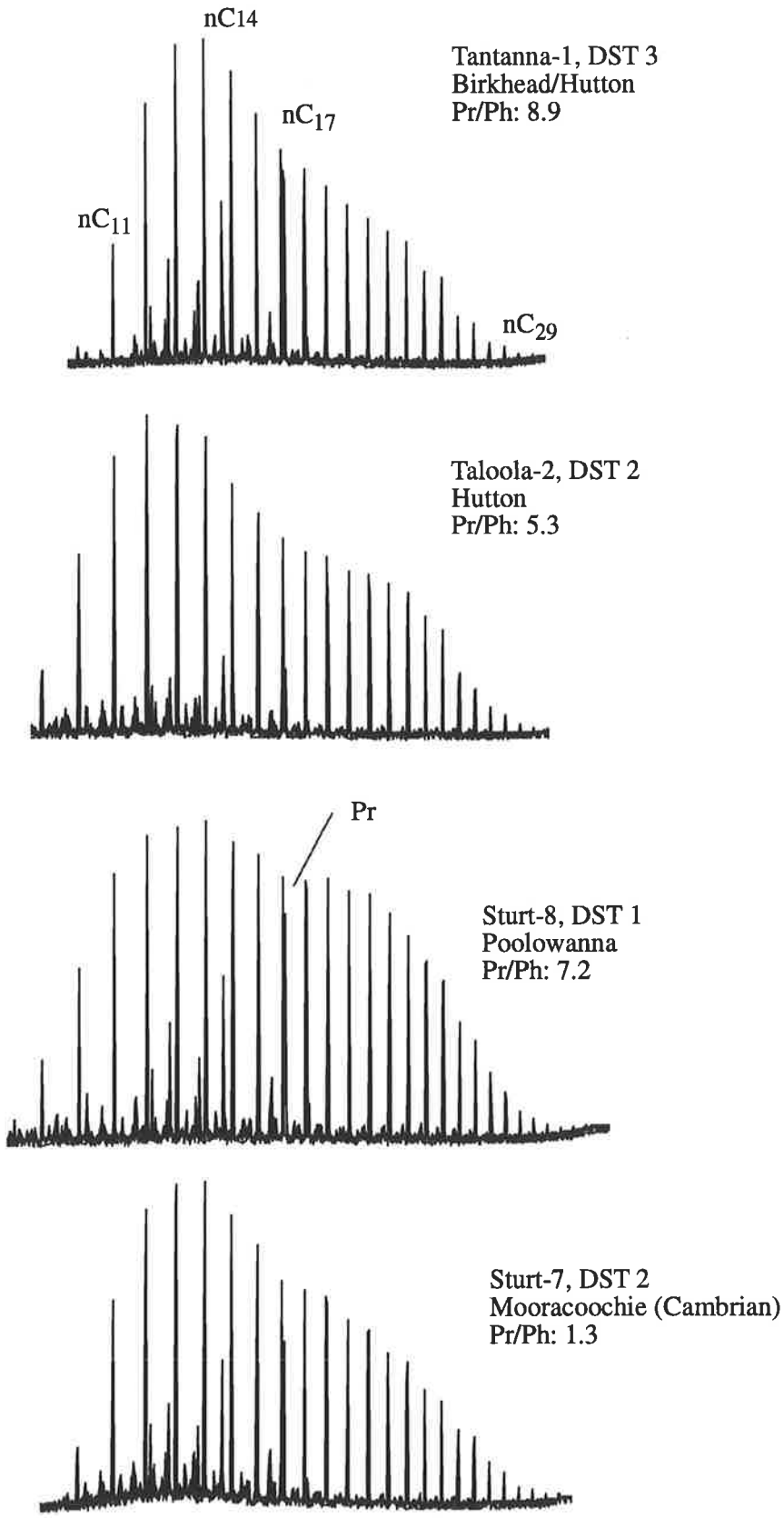


Figure 7.2a Gas chromatograms of alkanes in selected oils from Jurassic and non -Jurassic reservoirs in the Patchawarra Trough

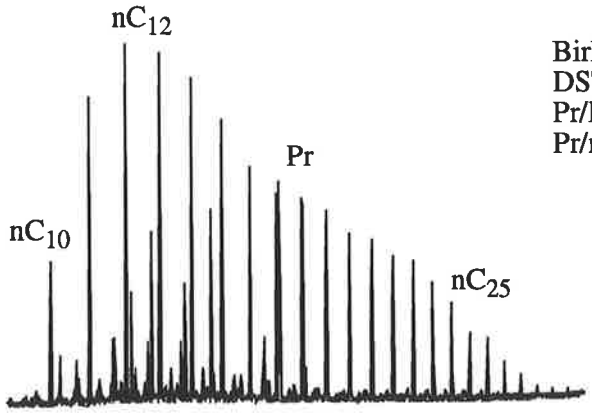
The average OEP values for the Poolowanna Trough are 0.99, 1.04 and 1.08, respectively; and for the Patchawarra Trough they are 0.99, 1.10 and 1.27 (Table 6.3a). As pointed out previously, the samples from the former depocentre are slightly more mature than the latter; and this is entirely consistent with values shown in the Patchawarra Trough source rocks.

A tentative quantification of source biota inputs, based on the relative abundance of three *n*-alkane groups (Collister *et al.*, 1994: Fig. 6.5a), shows that the Poolowanna Trough on average is characterised by almost equal contributions from algae (46%), and bacteria (45%), and lesser contribution from higher plant waxes (9%). The Patchawarra Trough is characterised by high average contributions from bacteria and aquatic plants (47%), followed by algae (34%) and higher plant waxes (18%). Although both areas have low contributions from higher plant waxes, the input to the Poolowanna Trough is half that to the Patchawarra Trough. The higher algal input to the Poolowanna Trough is possibly of the lamalginite type (Chapter 4).

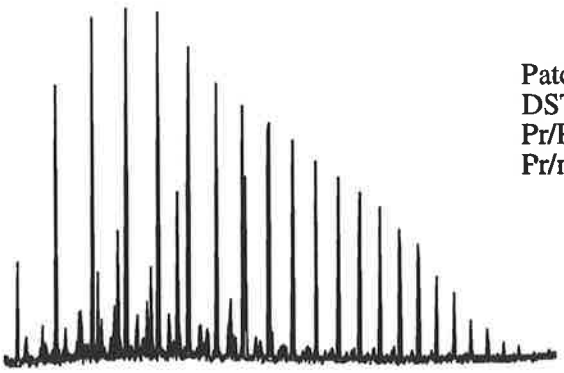
7.2.2 Alkane distributions in crude oils

The alkane distributions of the crude oils are summarised in Table 6.3b. Representative alkane chromatograms are illustrated in Figure 7.2. Their *n*-alkane profiles have carbon number ranges between C_9 and C_{39}, with *n*-C_{max} between C_{12} and C_{23}. An apparent bimodal profile with maxima at C_{14} and C_{19} is evident in the Sturt-8 (Poolowanna) oil. Quite a number of the oils have *n*-C_{max} between C_{12} to C_{14}. Although primarily controlled by source biota these maxima are likely to be modified by cracking of medium molecular weight *n*-alkanes (C_{15}–C_{17}). Such thermal effects are only likely to be significant in the more mature (i.e. Permian) oils. The unique Poolowanna-1 (Poolowanna) oil (Fig. 6.2) has the carbon range up to *n*-C_{39} and a peak at *n*-C_{23}, thus signifying strong bacterial and land plant inputs. In all the oil samples analysed in this study no clear distinction can be made between Jurassic and Permian/pre-Permian oils on the basis of their *n*-alkane profiles.

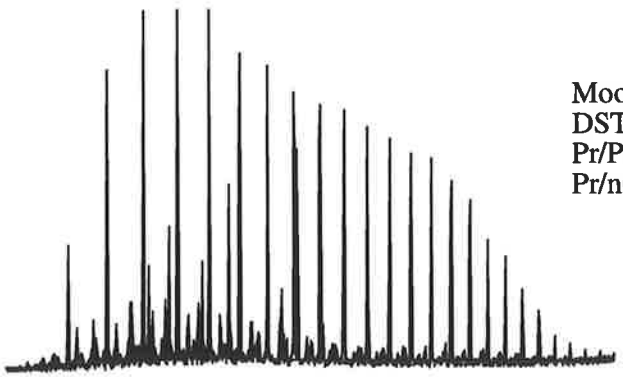
The pristane to phytane ratios of all but two of the oils range from 4.98 in the Poolowanna-1 (Poolowanna) sample to 8.88 in the Tantanna-1 (Birkhead/Hutton) crude suggesting that their source rocks were deposited in peat-swamp conditions. The two exceptions are the Tantanna-2 (Poolowanna) and Sturt-7 (Mooracoochie) oils with pr/ph values of 2.29 and 1.25, respectively (Table 6.3b). The latter oil may be of pre-Permian (possibly Cambrian) origin (see below), whereas the former sample could be a mixture of the pre-Permian and Jurassic oils.



Birkhead - Jurassic
DST 1
Pr/Ph: 6.8
Pr/nC_{17}: 1.06



Patchawarra - Permian
DST 3
Pr/Ph: 6.3
Pr/nC_{17}: 0.72



Mooracoochie- Cambrian
DST 6
Pr/Ph: 6.0
Pr/nC_{17}: 0.79

Figure 7.2b Gas chromatograms of alkanes in oils from stacked reservoirs at Sturt-6, Patchawarra Trough

The average pr/ph ratio of 4.56 in the Poolowanna Trough source rocks almost coincides with that of the Poolowanna Trough oil (4.98) whereas the average pr/ph ratio value 6.21 for the Patchawarra Trough source rocks falls well within the observed range of oil values in this trough. This is one piece of evidence that some of the oils in these troughs were generated from Poolowanna Formation source rocks.

The pr/*n*-C_{17} values vary from 0.21 in the Poolowanna Trough oil (Poolowanna-1, DST 2; Fig. 6.2) to a maximum of 1.06 in the Patchawarra Trough oils (Sturt-6, DST 1; Fig. 7.2b). A value of 0.21 is indicative of a source rock deposited in an environment of open water sedimentation. This value falls within the observed range of source rock values in the Poolowanna Trough (0.15–0.64). Values between 0.5 and 1.0 are indicative of source rocks deposited in environment with alternating swamp and open water conditions. Most of the Poolowanna Formation source rocks in the Patchawarra Trough have pr/*n*-C_{17} values in this range. The high value (pr/*n*-C_{17} = 1.06) shown by the Sturt-6 (Birkhead) oil indicates that this oil was derived from a source rock deposited under peat-swamp conditions. It can be correlated to the Sturt East-4 source rock sample (1862 m) which has a pr/*n*-C_{17} value of 1.85 (Fig. 7.1). It is also noted that the Permian and Cambrian oils have Pr/*n*-C_{17} values between 0.72 and 0.79 whilst most of the Patchawarra Trough Jurassic oils have values >0.80.

The Ph/*n*-C_{18} values range from 0.04 in the Poolowanna-1 oil to 0.19 in the Patchawarra Trough oils with the one exception of the Sturt-7 (Mooracoochie) oil which has a value of 0.60. Once again there is good agreement between the oils and Poolowanna Formation source rocks in the two troughs. The source of the Sturt-7 (Mooracoochie) crude is likely to be quite different from those of the Jurassic and Permian oils and the other Cambrian oil.

The CPI values of the oils range from 1.02 in the Tantanna-2 (Poolowanna) oil to 1.48 in the Tantanna-1 (Birkhead/Hutton) oil This spread of values reflects a range of affinities and maturities (see below). The OEP values ≈1 indicate mature oils. A high OEP value (3.05) centred at i=22 in the Taloola-2 (Hutton) oil supports the previously suggested indication of a high bacterial contribution to the source organic matter (Fig. 6.2). An even-carbon-number predominance (OEP <1) is shown by the Sturt-2 (Poolowanna) oil. This might be suggestive of an unusual source rock facies.

A tentative quantification of source biota based on the relative abundance of certain ranges of *n*-alkanes (Fig. 6.5b) suggests that most of the alkanes are derived from bacterial and algal organic precursors. The contribution of land plants is shown to be very low. However, these data need to be treated cautiously because oil *n*-alkane profiles are also influenced by their maturation level and by the possibility of oil cracking in the reservoir.

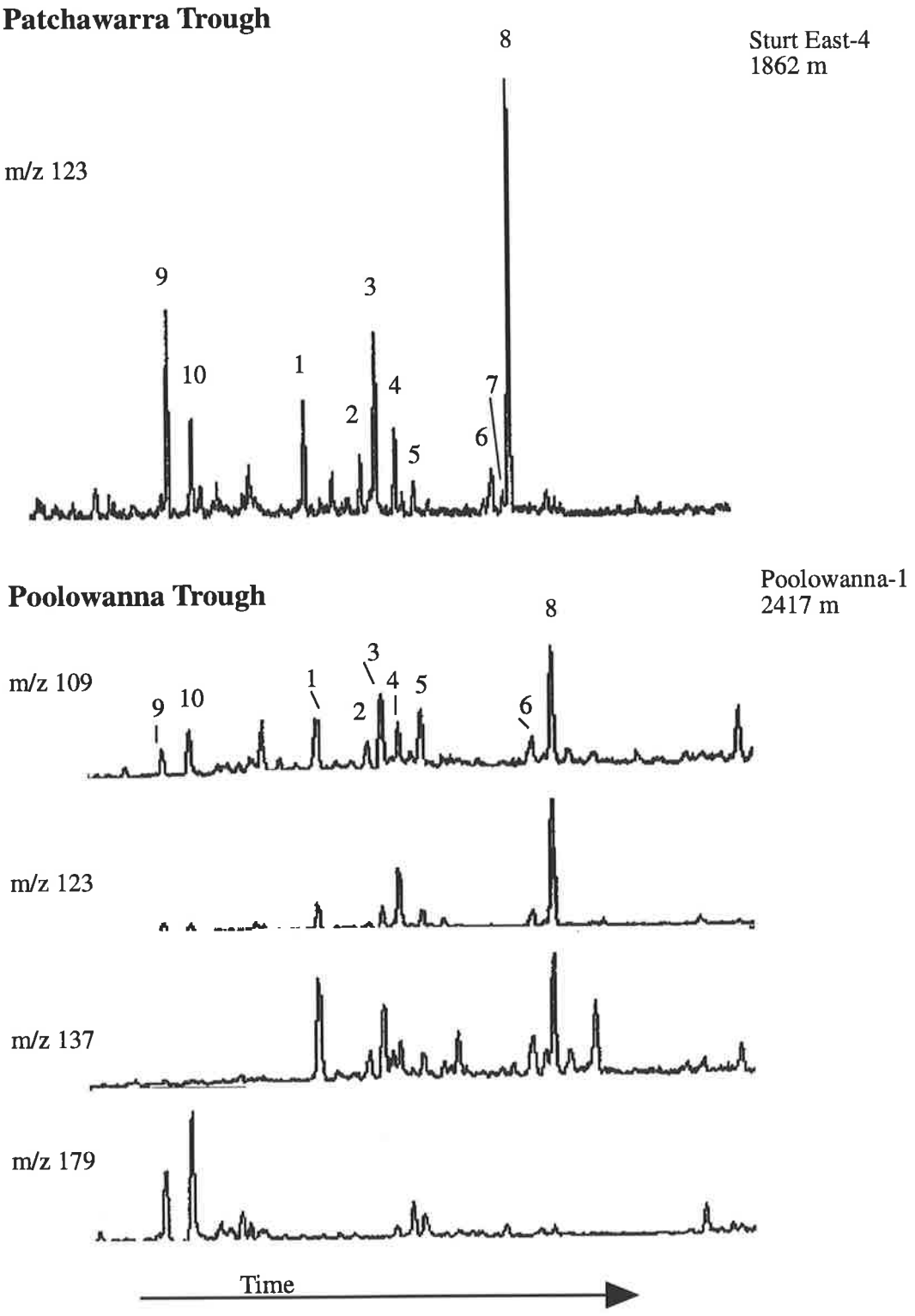


Figure 7.3a Mass fragmentograms showing the bicyclic sesquiterpane distributions in selected Poolowanna Formation source rocks

Table 7.1a Distribution of bicyclic sesquiterpanes (m/z 123) in selected rock extracts, Poolowanna Formation

Sample No.	Well	Depth m	9 C_{14} %	10 C_{14} %	1 C_{15} %	2 C_{15} %	3 C_{15} %	4 C_{15} %	5 C_{15} %	6 C_{16} %	7 C_{16} %	8 C_{16} %	HDr(8) Dr(3)	Hopane* Bi-Sesq.***	Steranes** Bi-Sesq.***
POL1-1	Poolowanna-1	2417	3.65	3.65	10.22	7.30	19.71	4.38	2.92	5.11	1.46	41.61	2.11	0.27	0.08
POL1-3	Poolowanna-1	2438	3.77	2.83	7.55	3.77	15.09	3.77	1.89	5.66	1.89	53.77	3.56	0.26	0.08
POL1-5	Poolowanna-1	2499	4.04	2.02	8.08	4.04	12.12	7.07	0.00	6.06	0.00	56.57	4.67	0.10	0.28
POL2-9	Poolowanna-2	2524	2.84	2.27	17.05	10.23	17.05	7.39	4.55	4.55	1.70	32.39	1.90	0.25	0.18
POL3-13	Poolowanna-3	2505	1.89	2.83	9.43	5.66	11.32	3.77	0.94	7.55	2.83	53.77	4.75	0.25	0.16
TAN2-18	Tantanna-2	1799	7.87	3.15	6.30	3.94	15.75	6.30	3.15	4.72	1.57	47.24	3.00	0.74	0.32
TAN2-20	Tantanna-2	1811	0.00	0.00	5.66	5.66	15.09	8.49	2.83	7.55	3.77	50.94	3.58	2.10	0.47
TAN3-21	Tantanna-3	1807	2.38	1.59	9.52	4.76	15.87	11.11	3.17	7.14	0.00	44.44	2.80	0.39	0.16
TAN8-25	Tantanna-8	1823†	6.74	6.74	12.36	5.62	15.73	11.24	2.25	4.49	3.37	31.46	2.00	0.28	0.26
STU1-27	Sturt-1	1871	3.06	1.02	4.08	3.06	10.20	6.12	3.06	7.14	3.06	59.18	5.30	1.16	0.42
STU4-30	Sturt-4	1859	8.77	2.63	6.14	4.39	12.28	5.26	1.75	4.39	1.75	52.63	4.29	1.64	0.37
STU4-31	Sturt-4	1881†	8.26	5.50	12.84	7.80	20.64	8.26	4.13	4.59	2.75	25.23	1.22	0.26	0.12
STU6-35	Sturt-6	1865†	9.03	5.16	7.74	5.81	19.35	7.74	1.29	5.16	1.29	37.42	1.43	0.76	0.27
STE1-38	Sturt East-1	1841	4.30	1.72	6.02	5.16	13.77	6.88	4.30	6.02	0.17	51.64	3.75	5.99	0.81
STE4-45	Sturt East-4	1862†	15.52	6.90	10.34	5.17	13.79	6.90	2.87	3.45	1.72	33.33	2.42	0.16	0.38

* $C_{30}\alpha\beta$ hopane ** Σ C_{27}-C_{29} steranes *** Σ Bicyclic sesquiterpanes

1-10 refer to peak assignments in Figure 7.3; peak 3 = 8β(H)-drimane; peak 8 = 8β(H)-homodrimane

† coaly facies

7.2.3 Bicyclic sesquiterpanes in source rocks

The distribution of bicyclic sesquiterpenoids in the Poolowanna Formation source facies is summarised in Table 7.1a and illustrated by the mass fragmentograms of two samples in Figure 7.3a. The structures of the important mass spectral fragments of these compounds are illustrated in Figure 2.9. The most abundant compound in this group of terpanes appear to be 8β(H)-homodrimane (peak 8) with an average relatively abundance of 48% in the Poolowanna Trough and 43% in the Patchawarra Trough. 8β(H)-Drimane (peak 3) has an average relative abundance of 15% in both areas. The C_{14} bicyclic compounds (peaks 9 and 10) are on average more abundant in the Patchawarra Trough (10%) than in the Poolowanna Trough (3%). The C_{15} bicyclic compounds (peaks 1–5) have an average relative abundance of 39% in both troughs. The C_{16} bicyclic compounds are therefore more abundant in the Poolowanna Trough (58%) than in the Patchawarra Trough (51%) . The variations in C_{14}–C_{16} bicyclic alkane carbon number distribution seem to show no logical relationship to the previously described difference in maturity of the Poolowanna Formation between the two troughs.

The 14α(H)-hopane ($C_{30}\alpha\beta$) to bicyclic sesquiterpane ratio (hopane/bi-sesq.: Table 7.1a) varies between 0.10 (Poolowanna-1, 2499 m) and 0.27 (Poolowanna-1, 2417 m) with an average value of 0.23 in the Poolowanna Trough. A wider range of values from 0.26 (Sturt-4, 1881 m) to 5.99 (Sturt East-1, 1841 m), gives an average of 1.62 for the Patchawarra Trough. This contrast is significant and reflects differences in the type or intensity of bacterial reworking of organic matter between the two areas. According to Alexander *et al.* (1983), bicyclic sesquiterpanes of the drimane series could arise from microbial degradation of triterpanes like hopanes. The fact that higher proportions of drimanes are found in the Poolowanna Trough, where the Poolowanna Formation is richer in resinite (Chapter 4) suggests that bacterial decay of resin-derived diterpanes may be an alternative source of such sesquiterpanes.

The ratio of C_{27}–C_{29} steranes to bicyclic sesquiterpanes (sterane/bi-sesq.: Table 7.1a) has a range of 0.08-0.28 (average = 0.16) in the Poolowanna Trough source rocks, and a range of 0.16-0.81 (average = 0.36) in the Patchawarra Trough. Once again, the higher relative abundance of bicyclic sesquiterpanes in the rocks from the Poolowanna Trough is consistent with more intense bacterial reworking of detrital organic matter here than in the Patchawarra Trough. However, the Patchawarra Trough coal facies (Tantanna-8, 1823 m; Sturt-4, 1881 m; Sturt-6, 1865 m) show values similar to those of the carbonaceous shales in the Poolowanna Trough.

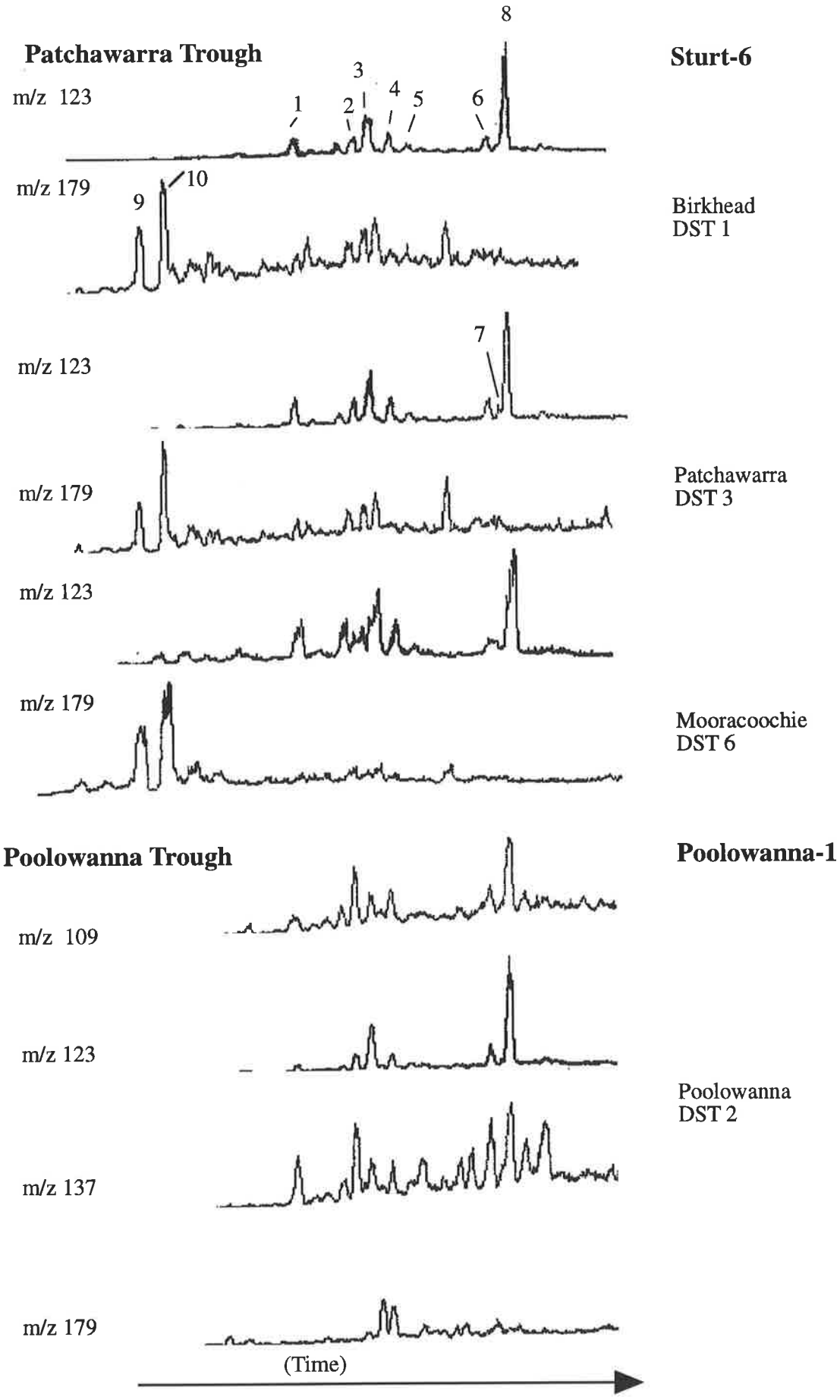


Figure 7.3b Mass fragmentograms showing the distribution of bicyclic sesquiterpanes in selected crude oils

Table 7.1b Distribution of bicyclic sesquiterpanes m/z 123 in crude oils from the Poolowanna and Patchawarra Troughs

Sample no.	Well	Dst no.	Depth m	Formation	9 C_{14} %	10 C_{14} %	1 C_{15} %	2 C_{15} %	3 C_{15} %	4 C_{15} %	5 C_{15} %	6 C_{16} %	7 C_{16} %	8 C_{16} %	HDr (8) / Dr (3)	Hopane / Bi-Sesq.	Steranes / Bi-Sesq.
P1	Poolowanna-1	2	2504-2538	Poolowanna	0.0	0.0	3.7	7.4	20.4	7.4	0.9	9.3	0.9	50.0	2.45	1.51	0.59
T2	Tantanna-1	1	1800-1814	Poolowanna	2.3	4.0	17.1	9.1	15.4	10.3	2.3	6.3	1.7	31.4	2.04	0.16	0.07
T3	Tantanna-1	2	1635-1642	Hutton	1.7	0.8	9.2	3.4	16.8	12.6	3.4	5.0	0.0	47.1	2.80	0.26	0.20
T4	Tantanna-1	3	1347-1359	Birkhead/Hutton	0.0	0.0	7.9	5.9	11.9	7.9	2.0	7.9	1.0	55.4	4.66	0.45	0.33
S11	Sturt-3	1A	1848-1855	Poolowanna	0.0	0.0	7.8	6.2	23.3	7.8	2.3	7.8	2.3	42.6	1.83	1.70	0.94
S12	Sturt-3	1B	1654-1662	Birkhead	3.0	2.3	10.5	7.5	18.0	9.0	2.3	4.5	2.3	40.6	2.26	0.59	0.23
S13	Sturt-4	1	1872-1880	Poolowanna	2.8	2.8	9.2	5.7	22.7	8.5	4.3	6.4	0.0	37.6	1.66	0.64	0.35
S16	Sturt-6	6	1914-1919	Mooracoochie	3.7	4.3	12.3	8.0	20.4	11.1	2.5	4.9	0.0	32.7	1.60	0.38	0.22
S17	Sturt-6	3	1884-1898	Patchawarra	0.7	1.4	10.1	8.0	18.8	8.7	2.2	7.2	4.3	38.4	2.04	0.71	0.36
S18	Sturt-6	1	1883-1892	Birkhead	1.8	2.7	7.1	6.2	15.9	8.0	2.7	6.2	1.8	47.8	3.00	0.48	0.27
S19	Sturt-7	1	1923-1938	Patchawarra	2.8	3.5	11.1	8.3	19.4	8.3	4.9	5.6	0.0	36.1	1.86	0.73	0.29
S20	Sturt-7	2	1946-2021	Mooracoochie	1.2	2.4	12.1	10.3	24.2	7.3	3.6	4.8	3.6	30.3	1.25	0.75	0.32
S21	Sturt-7	3	1871-1876	Poolowanna	2.6	4.0	11.9	7.9	17.2	9.3	4.0	6.6	1.3	35.1	2.04	0.36	0.22
S23	Sturt-8	1	1880-1884	Poolowanna	0.0	0.0	7.9	7.9	19.3	8.8	3.5	7.0	0.0	45.6	2.36	3.46	0.75
SE24	Sturt East-2	1	1845-1899	Poolowanna	1.9	2.5	8.7	6.8	19.9	17.4	2.5	5.6	1.2	33.5	1.68	0.39	0.20
TL25	Taloola-2	1	1829-1836	Poolowanna	1.7	1.7	10.0	6.7	15.0	8.3	4.2	7.5	0.0	45.0	3.00	0.44	0.23
TL26	Taloola-2	2	1789-1793	Hutton	2.1	2.1	12.8	8.5	15.6	9.9	4.3	6.4	0.0	38.3	2.46	0.30	0.19
TL27	Taloola-2	3	1384-1397	Namur	1.7	1.7	10.2	6.8	13.6	6.8	1.7	7.6	3.4	46.6	3.43	1.20	0.31

Key: as for Table 7.1a

7.2.4 Bicyclic sesquiterpanes in oils

The distribution of bicyclic sesquiterpanes in crude oils is as shown in Table 7.1b and the mass fragmentograms of selected samples in Figure 7.3b. As in the source rock extracts the 8β(H)-homodrimane (peak 8) is the most abundant compound with an average relative abundance of 41%. In the Permian and Cambrian oils its relative abundance is 30–38%. The next most abundant compound is 8β(H)-drimane (peak 3, 18%) followed by the other C_{15} compounds. The C_{14} compounds (peaks 9 and 10) are least abundant.

Assuming that the bicyclic sesquiterpanes of the drimane series arise from microbial degradation of triterpanes (Alexander *et al.*, 1983), the hopane to bicyclic sesquiterpane ratio in the Poolowanna and Patchawarra Trough oils may be used to compare the extent of this process in the organic matter of their respective source rocks. The values of the ratio range from 0.16 in the Tantanna-1 (Poolowanna) oil to 3.46 in the Sturt-8 (Poolowanna) oil (Table 7.1b). The Permian and Cambrian oils show a relatively narrow range of values (0.38–0.75) compared to that in the Jurassic oils (0.16–3.46) of the Patchawarra Trough. The Poolowanna-1 (Poolowanna) oil in the Poolowanna Trough has a relatively high value of 1.51. Such high values (>1) probably indicate less intense bacterial reworking of the oil-source organic matter. With the exception of the Sturt-8 (Poolowanna), Sturt-3 (Poolowanna) and Taloola-2 (Namur) oils, the Patchawarra Trough oils appear to have been derived from source rocks deposited in environments which favoured pervasive bacterial degradation of pre-existing prokaryotic and higher plant triterpenoids. The oils with very low values (e.g. Tantanna-1, Poolowanna, 0.16; and Tanatanna-1, Hutton, 0.26) originated from source beds in which the microbial degradation of triterpanes was extreme.

The sterane to bicyclic sesquiterpane ratio values range from 0.07 in the Tantanna-1 (Poolowanna) oil to 0.94 in the Sturt-3 (Poolowanna) oil. This range show that the contribution of microbially reworked triterpenoids is greater than that of eukaryotic sterols. Once again, the source rocks of some of the Poolowanna oils (Poolowanna-1, Sturt-3 and Sturt-8: Table 7.1b) appear to have been subjected to a different type or lesser intensity of microbial degradation whereas, at the other extreme, the Tantanna-1 (Poolowanna) oil records evidence of very strong bacterial reworking.

7.2.5 Tetracyclic terpane in source rocks

The C_{24} tetracyclic terpane (Fig. 2.8) was identified in source rock extracts from both the Poolowanna and Patchawarra Troughs on the basis of its relative retention time in the m/z 191 fragmentogram (Fig. 7.4a-c). Its abundance relative to that of 17α(H)-hopane is shown in Table 7.2a. The C_{24} tetra/C_{30}αβ values range from 0.05 to 0.43 (average = 0.25) in the Poolowanna Trough.

Table 7.2a Terpane ratios (m/z 191) in selected rock extracts, Poolowanna Formation

Sample	Well	Depth (m)	$\frac{C_{27}\ Ts}{(Ts+Tm)}$	$\frac{C_{29}Ts}{C_{29}+C_{29}Ts}$	$\frac{C_{30}*}{C_{29}Ts}$	$\frac{Ts}{C_{30}\alpha\beta}$	$\frac{C_{31}\alpha\beta\ 22S}{22S+22R}$	$\frac{C_{32}\alpha\beta\ 22S}{22S+22R}$	$\frac{C_{29}\ \beta\alpha}{\alpha\beta}$	$\frac{C_{30}\ \beta\alpha}{\alpha\beta}$	$\frac{C_{24}tetra}{C_{30}\alpha\beta}$	$\frac{C_{30}hop}{C_{29}hop}$
POL1-1	Poolowanna-1	2417	0.16	0.18	1.33	0.11	0.57	0.59	0.21	0.19	0.20	1.72
POL1-3	Poolowanna-1	2438	0.19	0.17	1.41	0.09	0.58	0.53	0.20	0.15	0.24	2.17
POL1-5	Poolowanna-1	2499	0.30	0.17	1.29	0.20	0.54	0.57	0.13	0.16	0.05	1.18
POL2-9	Poolowanna-2	2524	0.52	0.41	1.16	0.39	0.51	0.52	0.21	0.17	0.34	1.85
POL3-13	Poolowanna-3	2505	0.32	0.20	2.43	0.21	0.59	0.58	0.21	0.19	0.43	1.43
TAN2-18	Tantanna-2	1799	0.08	0.13	0.75	0.06	0.63	0.48	0.25	0.24	0.18	1.52
TAN2-20	Tantanna-2	1811	0.16	0.15	0.56	0.13	0.64	0.67	0.22	0.30	0.20	1.07
TAN3-21	Tantanna-3	1807	0.08	0.13	0.42	0.07	0.57	0.59	0.20	0.29	0.15	1.08
TAN8-25	Tantanna-8	1823†	0.11	nd	nd	0.09	0.59	0.58	0.15	0.23	0.16	0.76
STU1-27	Sturt-1	1871	0.10	nd	nd	0.07	0.54	0.53	0.24	0.31	0.14	0.97
STU4-30	Sturt-4	1859	0.05	nd	nd	0.05	0.61	0.57	0.26	0.39	0.17	0.83
STU4-31	Sturt-4	1881†	0.06	nd	nd	0.06	0.59	0.59	0.29	0.45	0.12	1.05
STU6-35	Sturt-6	1865†	0.06	nd	nd	0.06	0.58	0.58	0.24	0.37	0.17	1.16
STE1-38	Sturt East-1	1841	0.13	0.11	0.67	0.09	0.65	0.58	0.25	0.31	0.10	1.10
STE4-45	Sturt East-4	1862†	0.03	nd	nd	0.03	0.59	0.58	0.36	0.46	0.13	1.17

† coaly facies

The Patchawarra Trough samples have more consistent values, in the range 0.1–0.2 (average = 0.15). This compound is a member of the 17,21-secohopane series which is thought to be derived from the thermal or microbial rupture of the E-ring in hopanes (Peters and Moldowan, 1993). Similar low abundances of this compound have been found in Australian non-marine crude oils (Philp and Gilbert, 1986). Its slightly higher average abundance in the Poolowanna Trough is consistent with the previous observation that the Poolowanna Formation here is more mature than in the Patchawarra Trough.

7.2.6 Tetracyclic terpane in crude oils

The abundance of the C_{24} tetracyclic terpane in the oils is indicated in Table 7.2b. The range of C_{24} tetra/$C_{30}\alpha\beta$ values are similar to those shown by the source rock facies (see also Fig. 7.4). There is no significant difference between the Cambrian and Permian oils and those in Jurassic reservoirs. This observation suggests that the C_{24} tetracyclic terpane in these oils is derived through microbial degradation rather than thermal alteration of pentacyclic hopanes or their precursor hopanoids.

7.2.7 Pentacyclic triterpanes in source rocks and oils

The relative abundance and distribution of pentacyclic triterpanes identified in the Poolowanna Formation source rock facies (Fig. 7.4a, b) are expressed as various molecular ratios in Table 7.2a. The range of C_{27}–C_{33+} pentacyclic triterpane homologues includes hopanes, moretanes and rearranged hopanes. The C_{27} hopanes, 17α(H)-22,29,30-trisnorhopane (Tm) and 18α(H)-22,29,30-trisnorneohopane (Ts), were identified in all samples. Their relative abundance is expressed as the Ts/Ts+Tm ratio.

In the Poolowanna Trough, this ratio increases from 0.16 at 2417 m in Poolowanna-1 to 0.52 at 2524 m in Poolowanna-2. This trend appears to be consistent with increasing thermal maturation, although this ratio may also be affected by organic facies variation (McKirdy *et al.*, 1983, 1984). In the Patchawarra Trough, this ratio increases from 0.03 at 1862 m in Sturt East-4 to 0.16 at 1811 m in Tantanna-2 whereby an increase of the ratio with increasing maturity is apparently demonstrated. However, the coaly facies tends to have lower values than the shaly facies (Fig. 7.4b). Comparison of the Poolowanna Formation in these two troughs shows that the shaly facies in Poolowanna Trough is more mature, and thus characterised by higher Ts/Ts+Tm ratios, than the early mature shales in the Patchawarra Trough.

The Poolowanna Trough oil (Poolowanna-1, DST 2: Table 7.2b) has the Ts/Ts+Tm value of 0.44 . This value is within the range indicated for the Poolowanna Formation source rocks in this area (0.16–0.52), consistent with a local origin for this oil.

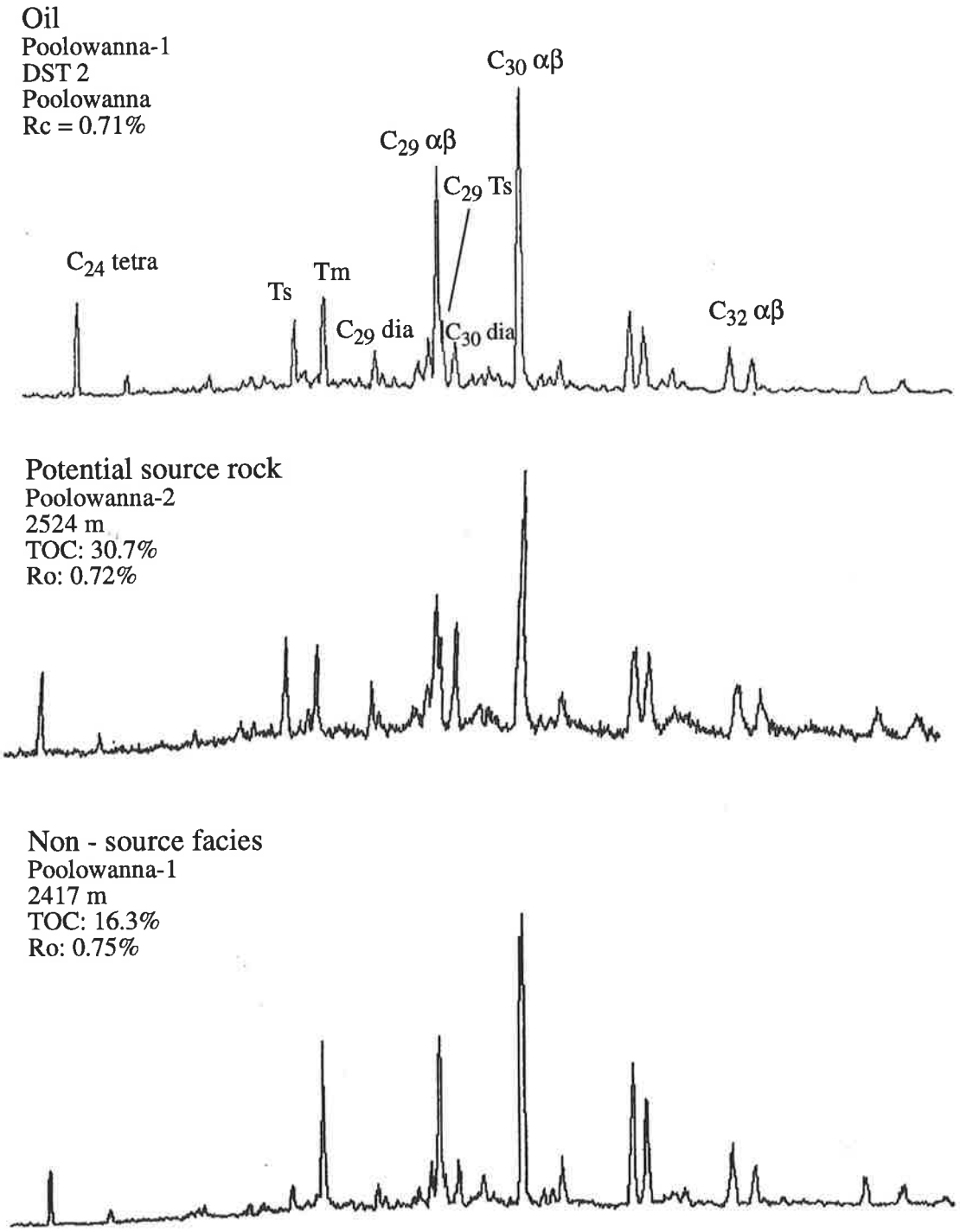
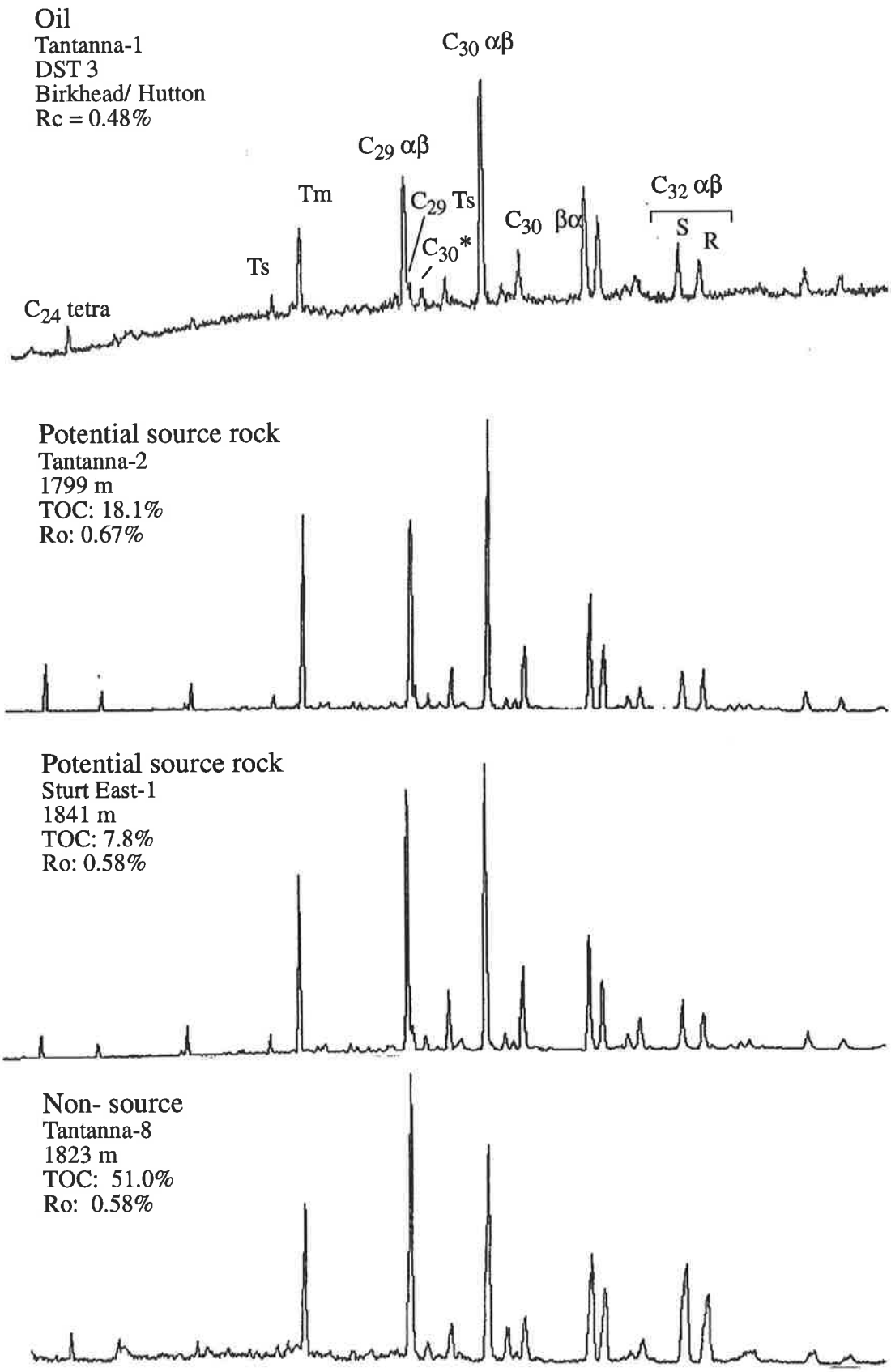


Figure 7. 4a Triterpane m/z 191 signatures of the Poolowanna oil and selected Poolowanna source and non-source facies in the Poolowanna Trough



C_{30}* = diahopane

Figure 7. 4b Comparison of triterpane m/z 191 signatures of a Jurassic oil and selected source and non-source facies of Poolowanna Formation, Patchawarra Trough

In the Patchawarra Trough, the Jurassic oils have values ranging from 0.19 (Sturt-East-2, DST 1) to 0.33 (Taloola-2, DST 1). These values are somewhat higher than those shown by the Poolowanna source rock facies, an indication that the oils are unlikely to have originated from these sections of the Poolowanna Formation sampled. However, these values may be influenced by factors other than thermal maturation. The Permian and pre-Permian oils have values similar to those of the Jurassic oils, suggesting either shaly source rocks of equivalent organic facies and maturity or coaly source rocks of higher maturity.

The rearranged C_{29} hopane, 18α(H)-30-norneohopane (C_{29}Ts: Fig. 2.8) was identified in all the rock samples from the Poolowanna Trough but it is absent from the coal facies of the Patchawarra Trough. Its abundance relative to C_{29}17α(H)-hopane (C_{29}αβ) is expressed using the ratio $C_{29}Ts/C_{29}\alpha\beta+C_{29}Ts$. In the Poolowanna Trough, the values of this ratio fall in the range 0.17-0.41 and apparently increase with thermal maturity. Like Ts [18α(H)-trisnorneohopane], its relative abundance is highest at 2524m in Poolowanna-2, being influenced by both maturity and also the oxicity of the depositional environment (Peters and Moldowan, 1993).

Again, the Poolowanna Trough oil (Poolowanna-1, DST 2) has the highest $C_{29}Ts/C_{29}\alpha\beta+C_{29}Ts$ value (0.25: Table 7.2b). The Jurassic oils in Patchawarra Trough have values ranging from 0.12, Sturt 3 (Birkhead) to 0.19 Tantanna-1, (Birkhead/Hutton). A similar range is observed for the Cambrian (Mooracoochie) and Permian oils. Therefore, this parameter appear not to be suitable for distinguishing between Jurassic and Permian/pre-Permian oils.

Another rearranged hopane, 17α(H)-diahopane(C_{30}*: Fig. 2.8) was identified in the source rock extracts and crude oils. Its abundance relative to C_{29}Ts is shown in Table 7.2a. The Poolowanna Trough rock samples have higher values (1.16–2.43) than those from the Patchawarra Trough (0.42–0.75). Both maturity and depositional environment have been suggested to influence the C_{30}*/C_{29}Ts ratio (Kolaczkowska *et al.*, 1990; Peters and Moldowan, 1993). Thus, this parameter confirms that the Poolowanna Trough source rock facies are relatively more mature than those in Patchawarra Trough, but also hints at possible differences in their depositional environments.

The oil in the Poolowanna Trough has higher C_{30}*/C_{29}Ts value (0.72) than do the Patchawarra Trough oils (0.82-1.33), without any clear distinction between Jurassic and Permian/pre-Permian oils.

Table 7.2b Terpane ratios (m/z 191) in crude oils from the Poolowanna and Patchawarra Troughs

Sample	Well	Dst no.	Depth m	Formation	$\frac{C_{27}Ts}{(Ts+Tm)}$	$\frac{C_{29}Ts}{C_{29}+C_{29}Ts}$	$\frac{C_{30}*}{C_{29}Ts}$	$\frac{Ts}{C_{30}\alpha\beta}$	$\frac{C_{31}\alpha\beta\ 22S}{22S+22R}$	$\frac{C_{32}\alpha\beta\ 22S}{22S+22R}$	$\frac{C_{29}\ \beta\alpha}{\alpha\beta}$	$\frac{C_{30}\ \beta\alpha}{\alpha\beta}$	$\frac{C_{24}tetra}{C_{30}\alpha\beta}$	$\frac{C_{30}hop}{C_{29}hop}$
P1	Poolowanna-1	2	2504-2538	Poolowanna	0.44	0.25	0.72	0.25	0.55	0.56	0.09	0.12	0.32	1.35
T2	Tantanna-1	1	1800-1814	Poolowanna	0.32	0.17	1.18	0.16	0.54	0.51	0.14	0.15	0.18	1.66
T3	Tantanna-1	2	1635-1642	Hutton	0.32	0.17	1.00	0.17	0.62	0.60	0.12	0.15	0.25	1.52
T4	Tantanna-1	3	1347-1359	Birk/Hutton	0.27	0.19	0.82	0.13	0.57	0.58	0.27	0.26	0.14	1.70
S11	Sturt-3	1A	1848-1855	Poolowanna	0.20	0.16	0.90	0.12	0.57	0.56	0.22	0.24	0.15	1.44
S12	Sturt-3	1B	1654-1662	Birkhead	0.25	0.12	1.33	0.13	0.53	0.60	0.20	0.12	0.19	1.52
S13	'Sturt-4	1	1872-1880	Poolowanna	0.23	nd	nd	0.12	0.59	0.61	0.18	0.17	0.16	1.55
S16	Sturt-6	6	1914-1919	Mooracoochie	0.26	nd	nd	0.15	0.59	0.61	0.11	0.15	0.22	1.49
S17	Sturt-6	3	1884-1898	Patchawarra	0.31	0.15	1.20	0.16	0.58	0.59	0.13	0.18	0.18	1.67
S18	Sturt-6	1	1883-1892	Birkhead	0.24	0.13	0.96	0.16	0.58	0.55	0.15	0.20	0.26	1.19
S19	Sturt-7	1	1923-1938	Patchawarra	0.20	nd	nd	0.14	0.58	0.59	0.19	0.18	0.16	1.59
S20	Sturt-7	2	1946-2021	Mooracoochie	0.22	0.14	0.80	0.13	0.59	0.60	0.22	0.26	0.17	1.48
S21	Sturt-7	3	1871-1876	Poolowanna	0.21	0.13	1.50	0.13	0.58	0.54	0.21	0.20	0.18	1.64
S23	Sturt-8	1	1880-1884	Poolowanna	0.21	nd	nd	0.09	0.59	0.57	0.24	0.22	0.10	1.98
SE24	Sturt East 2	1	1845-1899	Poolowanna	0.19	0.15	1.08	0.10	0.59	0.61	0.16	0.21	0.22	1.46
TL25	Taloola-2	1	1829-1836	Poolowanna	0.33	0.18	1.25	0.14	0.61	0.60	0.12	0.16	0.20	1.70
TL26	Taloola-2	2	1789-1793	Hutton	0.31	0.18	1.19	0.14	0.62	0.59	0.14	0.19	0.17	1.58
TL27	Taloola-2	3	1384-1397	Namur	0.32	0.18	1.04	0.12	0.60	0.54	0.15	0.18	0.11	1.63

High ratio values (i.e. high C_{30}*), apart from being indicative of terrestrial organic matter, have also been suggested to be related to bacterial hopanoid precursors that have undergone oxidation in the D-ring and rearrangement by clay-mediated acidic catalysis (Peters and Moldowan, 1993).

A series of hopanes with the 17β(H),21α(H) stereochemistry (i.e. moretanes) were identified in both source rock extracts and crude oils. Their concentrations relative to their corresponding C_{29}αβ- and C_{30}αβ-hopanes are shown in Table 7.2a for source rock extracts and Table 7.2b for oils. Whilst there is no significant variation of the C_{29}βα/αβ ratio in the source rock extracts, appreciable variation is shown by C_{30}βα/αβ. The latter ratio in the Poolowanna Trough source rock facies has values of 0.15-0.19 whereas in the Patchawarra Trough the values are in the range 0.23–0.46. During catagenesis the moretanes decrease rapidly in relation to the αβ-hopanes (ten Haven *et al.*, 1992). Therefore, the lower moretane/hopane ratios of the Poolowanna Formation in the Poolowanna Trough are further evidence of its more advanced level of catagenesis.

The moretane/hopane (C_{30}βα/αβ) for the oils have a range of 0.12–0.26. Assuming that these values are close to those of their source rocks at the time of expulsion, it appears that the Poolowanna Formation source rocks are most likely the source for the Poolowanna-1 oil. Also, in the Patchawarra Trough, the Poolowanna Formation source rocks analysed seem to be not quite mature enough to generate the oils found in this trough. The Sturt-7 (Mooracoochie) oil and Tantanna-1 (Birkhead/Hutton) (with the C_{30}βα/αβ value of 0.26) appear to have been generated at an earlier maturity stage than the other Permian and Pre-Permian oils.

The concentration of norhopane (C_{29}αβ) relative to hopane (C_{30}αβ) is as shown in Table 7.2a and b. In source rocks and crude oils it is quite common for the C_{30}/C_{29}αβ ratio to have a value >1 (Philp, 1985). This characteristic is demonstrated by the Poolowanna Formation rock extracts in the Poolowanna Trough which have C_{30}/C_{29}αβ values in the range 1.18-2.17 (average = 1.67). The unusual phenomenon of C_{30}/C_{29}αβ <1 is shown by a couple of samples in the Patchawarra Trough (Table 7.2a, Fig. 7.4b). Furthermore, with the exception of the sample from 1799 m in Tantanna-2, other all the samples have values <1.2. The cause of this enhanced C_{29}αβ abundance is not quite clear. Possibly, it is due to microbial reworking of the terrestrial organic matter input to this Early Jurassic fluvial-lacustrine depositional environment.

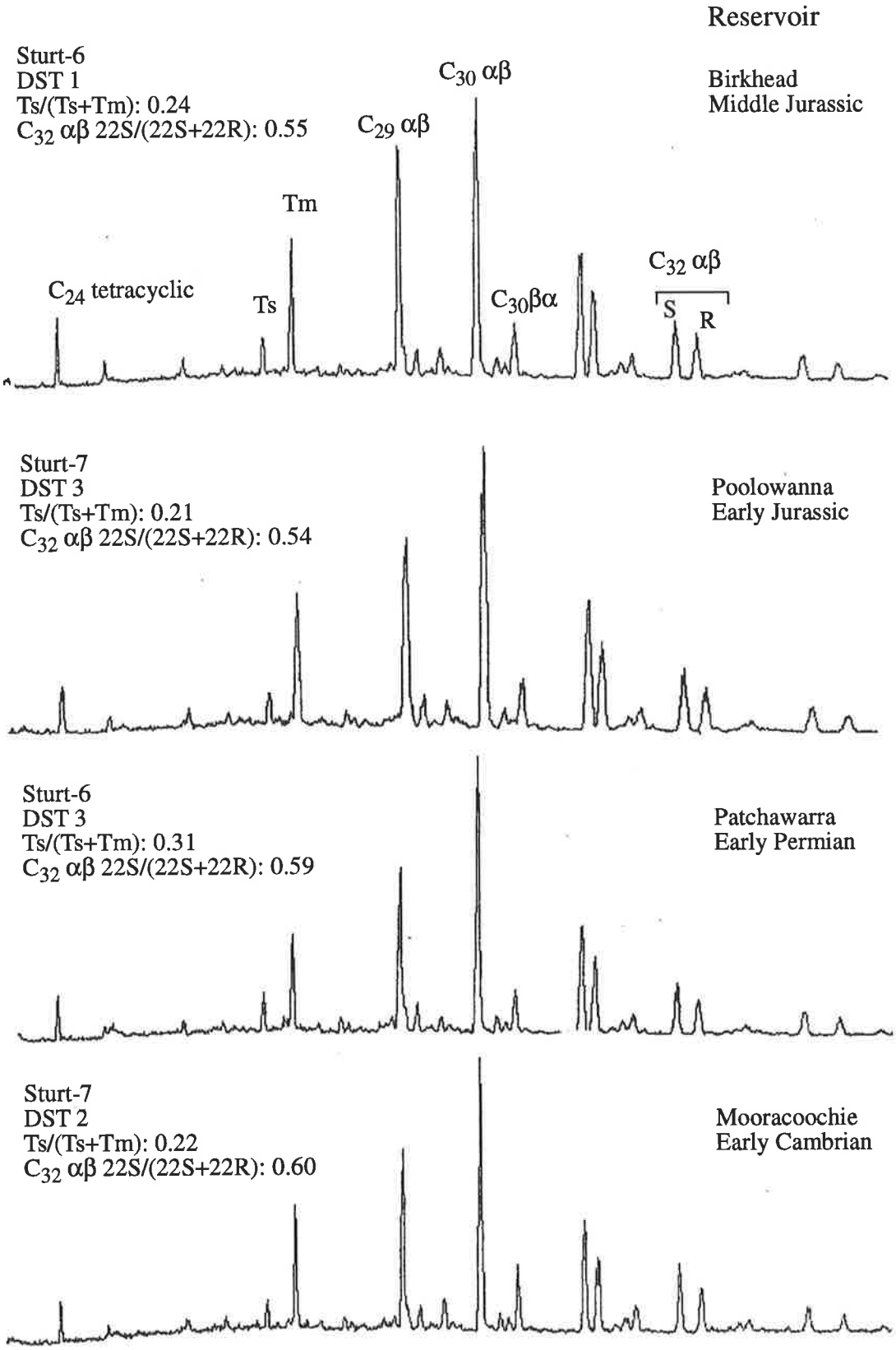


Figure 7. 4c Triterpane m/z 191 signatures of oils in stacked reservoirs of the Sturt field, Patchawarra Trough

Table 7.3a Distribution of methylhopanes (m/z 205) in selected rock extracts, Poolowanna Formation.

Sample No.	Well	Depth (m)	C_{29}				C_{30}					C_{31}					
			2β %	2α %	3β %	3β/2α	2β %	2α %	3β* %	2α (βα) %	3β/2α	2α %	3β %	m %	k %	3β/2α	k/m
POL1-1	Poolowanna-1	2417	3.8	9.8	8.4	0.85	7.7	12.9	7.1	0.0	0.55	21.3	9.2	11.1	8.8	0.43	0.79
POL1-3	Poolowanna-1	2438	0.0	9.3	11.7	1.26	9.7	12.5	7.3	0.0	0.59	18.6	8.6	12.3	9.9	0.47	0.81
POL1-5	Poolowanna-1	2499	0.0	0.0	10.1	nd	11.6	13.1	10.1	0.0	0.77	19.1	10.8	15.8	9.5	0.57	0.60
POL2-9	Poolowanna-2	2524	0.0	0.0	26.9	nd	0.0	18.6	0.0	0.0	0.00	20.8	10.5	11.6	11.6	0.51	1.00
POL3-13	Poolowanna-3	2505	4.7	8.5	17.1	2.00	0.0	15.5	7.0	0.0	0.45	19.4	8.5	11.6	7.8	0.44	0.67
TAN2-18	Tantanna-2	1799	4.8	15.3	6.3	0.41	14.4	18.1	9.2	3.5	0.51	19.7	8.7	0.0	0.0	0.44	nd
TAN2-20	Tantanna-2	1811	0.0	14.4	7.2	0.50	0.0	16.7	11.7	13.5	0.70	24.3	12.2	0.0	0.0	0.50	nd
TAN3-21	Tantanna-3	1807	0.0	13.3	10.2	0.77	0.0	24.0	14.6	3.3	0.61	25.4	9.2	0.0	0.0	0.36	nd
TAN8-25	Tantanna-8	1823†	6.4	11.5	7.0	0.61	0.0	25.5	8.3	7.3	0.33	24.2	3.2	3.5	3.2	0.13	0.91
STU1-27	Sturt-1	1871	6.3	11.3	9.9	0.88	0.0	22.5	10.6	4.9	0.47	26.1	8.5	0.0	0.0	0.32	nd
STU4-30	Sturt-4	1859	6.0	17.5	11.1	0.63	0.0	20.3	12.4	5.1	0.61	18.3	9.4	0.0	0.0	0.51	nd
STU4-31	Sturt-4	1881†	5.1	18.2	6.5	0.36	0.0	18.5	9.5	4.0	0.51	29.8	6.5	0.7	1.1	0.22	1.50
STU6-35	Sturt-6	1865†	5.5	19.9	6.2	0.31	0.0	15.8	8.2	4.1	0.52	34.7	5.5	0.0	0.0	0.16	nd
STE1-38	Sturt East-1	1841	5.3	9.1	7.6	0.84	15.0	13.8	10.6	4.1	0.77	23.5	10.9	0.0	0.0	0.46	nd
STE4-45	Sturt East-4	1862†	4.8	19.4	7.7	0.40	8.7	15.5	11.0	5.5	0.71	20.3	7.1	0.0	0.0	0.35	nd

Key: m and k are unidentified C_{31} methylhopanes

2α (βα) is a C_{30} 2α-methylmoretane

† coaly facies

The $C_{30}/C_{29}\alpha\beta$ values for the oils vary from 1.35 in the Poolowanna-1 (Poolowanna) crude to 1.98 in the Sturt-8 (Poolowanna) oil of Patchawarra Trough. By comparing these oil ratios to those of the source rock extracts, most of the Poolowanna Formation extracts from the Patchawarra Trough can be shown to be non-sources; and most of those from the Poolowanna Trough to be potential sources. Only the Sturt-6 (Birkhead) oil, (with a value of 1.19) could be generated from a local Poolowanna Formation source rock facies. A general overview of the m/z 191 mass fragmentograms of the oils from the Sturt field look very similar (Fig. 7.4c). However, closer inspection of their various terpane ratios reveal subtle differences that show these oils in multiple stacked reservoirs of the same field do not have a common origin.

7.2.8 Methylhopane distributions in source rock extracts

The 2α-, 2β-, and 3β-methyl-17α(H),21β(H)-hopane series have been identified using m/z 205 mass fragmentograms (Summons and Jahnke, 1992; Michaelsen *et al.*, 1995). The relative abundances of the different isomers at each carbon number in the Poolowanna Formation source rocks are shown in Table 7.3a and Figure 7.5a. The 2β-series is represented by the C_{29} and C_{30} compounds. The C_{29} compound appears to be very common in the Patchawarra Trough but was identified in only two samples from the Poolowanna Trough. The C_{30} compound was identified in the lower maturity zone or near the top of the formation in Poolowanna-1. The C_{31} member of this series is apparently absent.

The (C_{29}-C_{31}) 2α-compounds appear to be ubiquitous. The 2α-isomer is the most abundant of the C_{31} methylhopanes, with a relative concentration of 18.6–21.3% in the Poolowanna Trough and 18.3–34.7% in the Patchawarra Trough. The 2α-isomer is also the most abundant of the C_{29} and C_{30} methylhopanes, except in the Poolowanna Trough. A C_{30} 2α-methylmoretane was tentatively identified in the Poolowanna Formation from the Patchawarra Trough, but not in the more mature samples from the Poolowanna Trough.

The C_{29}-C_{31} 3β-methylyhopanes were also identified and no significant variation in their distribution was noted between the two troughs. The 3β/2α ratio is <1 in all cases except for the C_{29} compounds in two samples from the Poolowanna Trough. This may be partly due to increasing maturity, although this ratio is also influenced by organic facies. The C_{31} 3β/2α ratio is relatively low (0.13–0.22) in the coal facies of the Patchawarra Trough.

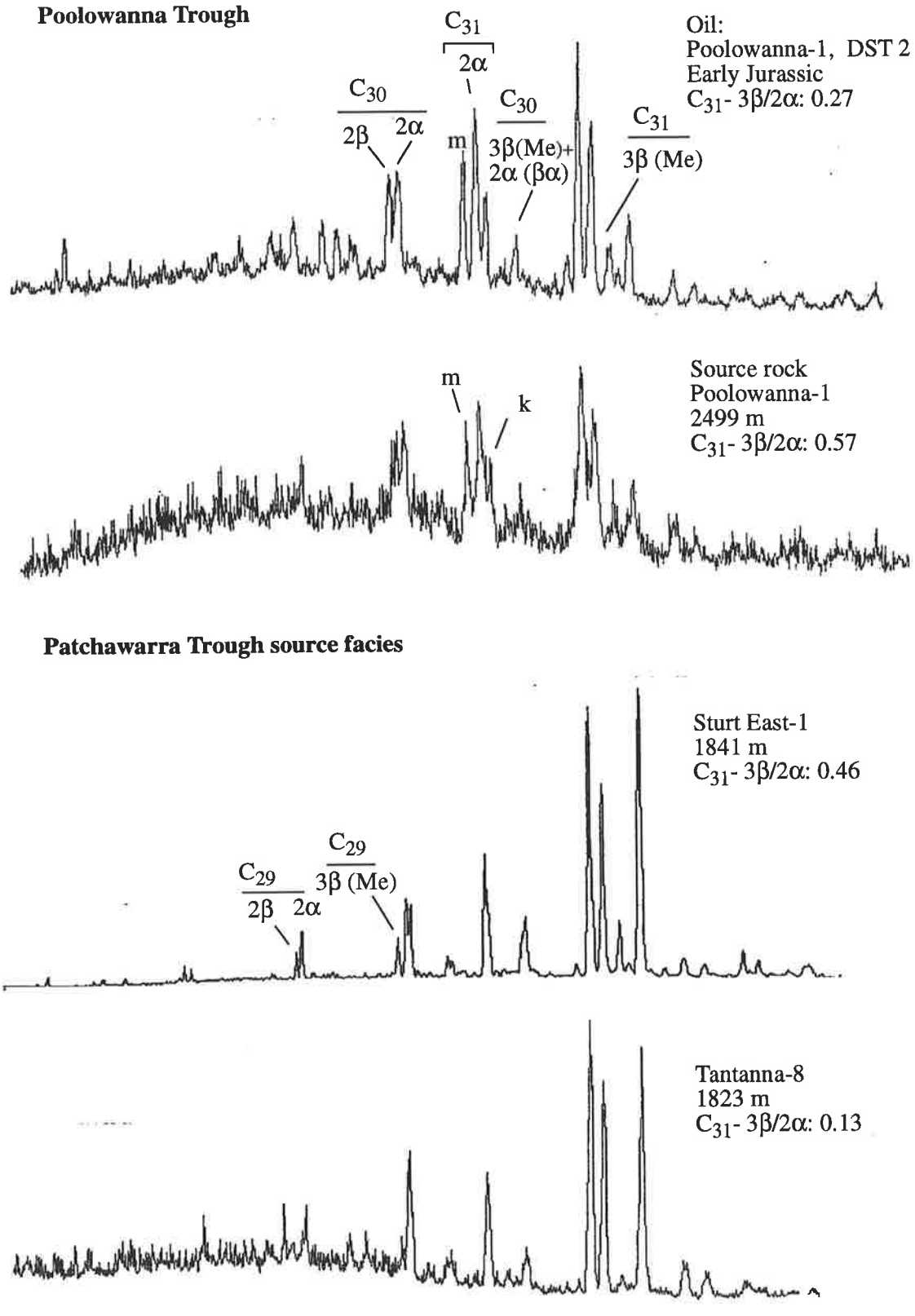


Figure 7. 5a Methylhopane m/z 205 signatures of the Poolowanna Trough oil and selected Poolowanna Formation source facies

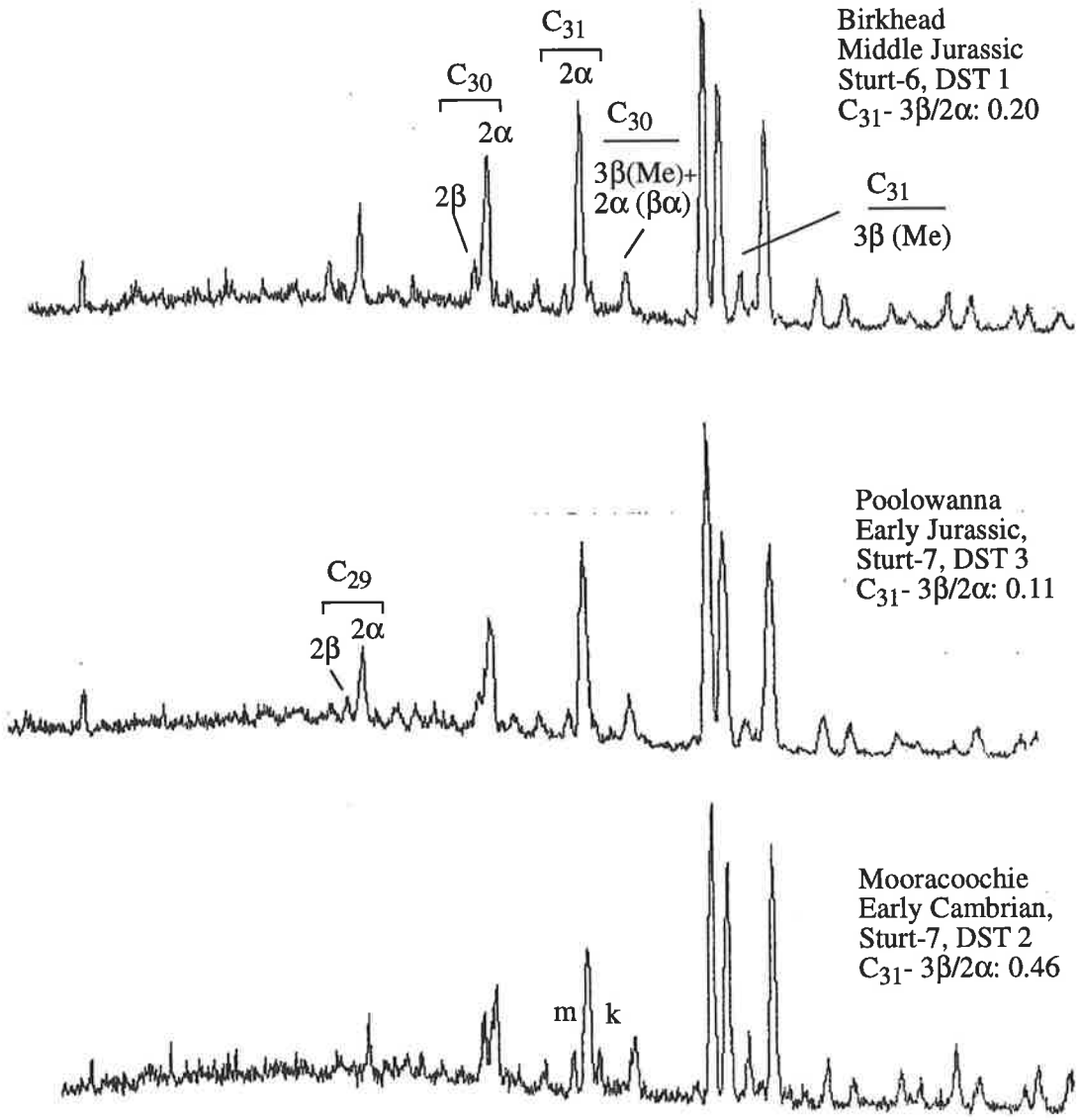


Figure 7. 5b Methylhopane m/z 205 signatures of oils in stacked reservoirs of the Sturt Field, Patchawarra Trough

Table 7.3b Distribution of methylhopanes (m/z 205) in crude oils from the Poolowanna and Patchawarra Troughs

Sample No.	Well	Formation	DST	C_{29}			C_{30}				C_{31}					
				2α %	3β %	3β/2α	2α %	3β %	2α(βα) %	3β/2α	2α %	3β %	m %	k %	3β/2α	k/m
P1	Poolowanna-1	Poolowanna	2	7.6	13.4	1.76	14.0	6.6	0.0	0.47	23.1	6.2	17.4	11.6	0.27	0.67
T2	Tantanna-1	Poolowanna	1	10.0	6.2	0.62	17.2	6.9	0.0	0.40	37.8	7.6	8.9	5.5	0.20	0.62
T3	Tantanna-1	Hutton	2	11.1	5.2	0.47	21.5	5.2	3.1	0.24	36.3	3.7	7.1	6.8	0.10	0.96
T4	Tantanna-1	Birkhead/Hutton	3	7.6	9.0	1.19	21.0	7.1	0.0	0.34	32.9	7.6	7.6	7.1	0.23	0.94
S11	Sturt-3	Poolowanna	1A	10.3	8.5	0.83	20.5	9.4	0.0	0.46	31.6	8.5	3.4	7.7	0.27	2.25
S12	Sturt-3	Birkhead	1B	10.7	8.3	0.78	22.0	9.2	3.6	0.42	29.4	5.6	6.2	5.0	0.19	0.81
S13	Sturt-4	Poolowanna	1	12.9	5.7	0.44	16.8	7.9	5.4	0.47	33.6	5.4	6.4	6.1	0.16	0.94
S16	Sturt-6	Mooracoochie	6	10.7	6.1	0.57	16.1	6.9	0.0	0.43	41.4	5.4	6.9	6.5	0.13	0.94
S17	Sturt-6	Patchawarra	3	14.7	7.3	0.50	19.8	7.3	0.0	0.37	32.6	7.3	6.6	4.4	0.22	0.67
S18	Sturt-6	Birkhead	1	14.6	6.5	0.44	21.7	6.0	4.3	0.28	32.0	6.5	4.3	4.1	0.20	0.94
S19	Sturt-7	Patchawarra	1	14.7	8.3	0.56	18.7	9.8	0.0	0.52	29.4	7.4	6.7	4.9	0.25	0.73
S20	Sturt-7	Mooracoochie	2	9.9	11.8	1.19	15.5	9.3	5.3	0.60	24.1	11.1	6.8	6.2	0.46	0.91
S21	Sturt-7	Poolowanna	3	12.9	7.1	0.55	20.0	7.7	4.5	0.39	34.8	3.9	5.2	3.9	0.11	0.75
S23	Sturt-8	Poolowanna	1	11.8	4.6	0.39	20.2	8.4	3.8	0.42	35.5	6.1	5.0	4.6	0.17	0.92
SE24	Sturt East-4	Poolowanna	1	13.0	6.8	0.52	19.2	7.4	3.1	0.39	35.9	5.9	5.0	3.7	0.16	0.75
TAL25	Taloola-2	Poolowanna	1	10.0	3.6	0.36	17.9	7.1	3.6	0.40	43.2	5.7	5.0	3.9	0.13	0.79
TAL26	Taloola-2	Hutton	2	10.6	6.3	0.60	18.0	7.0	3.5	0.39	38.7	5.3	6.3	4.2	0.14	0.67
TAL27	Taloola-2	Namur	3	8.4	6.7	0.80	20.2	9.1	4.0	0.45	34.0	6.7	6.1	4.7	0.20	0.78

Key: as for Table 7.3a

Two unidentified C_{31} methylhopanes were noted in the m/z 205 chromatograms (Fig. 7.5). One compound (m) elutes just before and the other (k) just after the C_{31} 2α-methylhopane. These compounds are quite common in the Poolowanna Trough, but very rare in the Patchawarra Trough where they occur only in two coal samples. The k/m ratio ranges from 0.60 to 1.00 in the Poolowanna Trough and 0.91 and 1.5 in the Patchawarra Trough.

7.2.9 Methylhopane distributions in crude oils

The composition and relative abundance of the C_{29}–C_{31} pseudohomologous series of methylhopanes identified in the crude oils are shown in Table 7.3b. As in the source rocks, the 2α- and 3β- methylhopanes are very common. However, the 2β-compounds were rarely detected. Again, the 2α-compound is usually more abundant than the 3β-compound, its prominence being shown by 3β/2α ratios <1. Only three oil samples, including the Poolowanna-1 (Poolowanna) oil, have C_{29} 3β/2α values >1. This ratio appears to decrease with increasing carbon number. The C_{31}methylhopanes have low 3β/2α values which range from 0.10 in the Tantanna-1 (Hutton) oil to 0.46 in the Sturt-7 (Mooracoochie) oil. The 3β-compounds seem to be of lower concentration in the oils than in the source rock extracts. Different values of this ratio may reflect variations in the bacterial input to the source rock.

The unidentified C_{31} methylhopanes (peaks k and m) noted in some of the source rock extracts are surprisingly present in all the oil samples. The k/m ratio varies from 0.62 in the Tantanna-1 (DST 1) to 2.25 in the Sturt-3 (DST 1A) oil, both from Poolowanna reservoirs. However, no consistency is evident in this ratio. Nevertheless, the presence of these compounds may be applied in oil-source correlation. The source rocks containing these compounds are most likely to have generated these oils. As indicated by other parameters, most of the Poolowanna Trough source rock facies identified in this study are likely to be effective sources of Jurassic oil (see below).

7.2.10 Sterane distributions in source rock extracts

Cholestane (C_{27}), methycholestane (C_{28}) and ethylcholestane (C_{29}) were identified in the Poolowanna Formation rock extracts using the m/z 217 (Fig. 7.6) and m/z 218 mass fragmentograms. Their relative abundance and isomeric distributions are summarised in Table 7.4a. Ethylcholestane (or stigmastane) is the dominant homologue with a relative abundance range of 52–63% in the Poolowanna Trough and 47–66% in the Patchawarra Trough. Methylcholestane (or ergostane) (19–29%) and cholestane (10–32%) are less abundant.

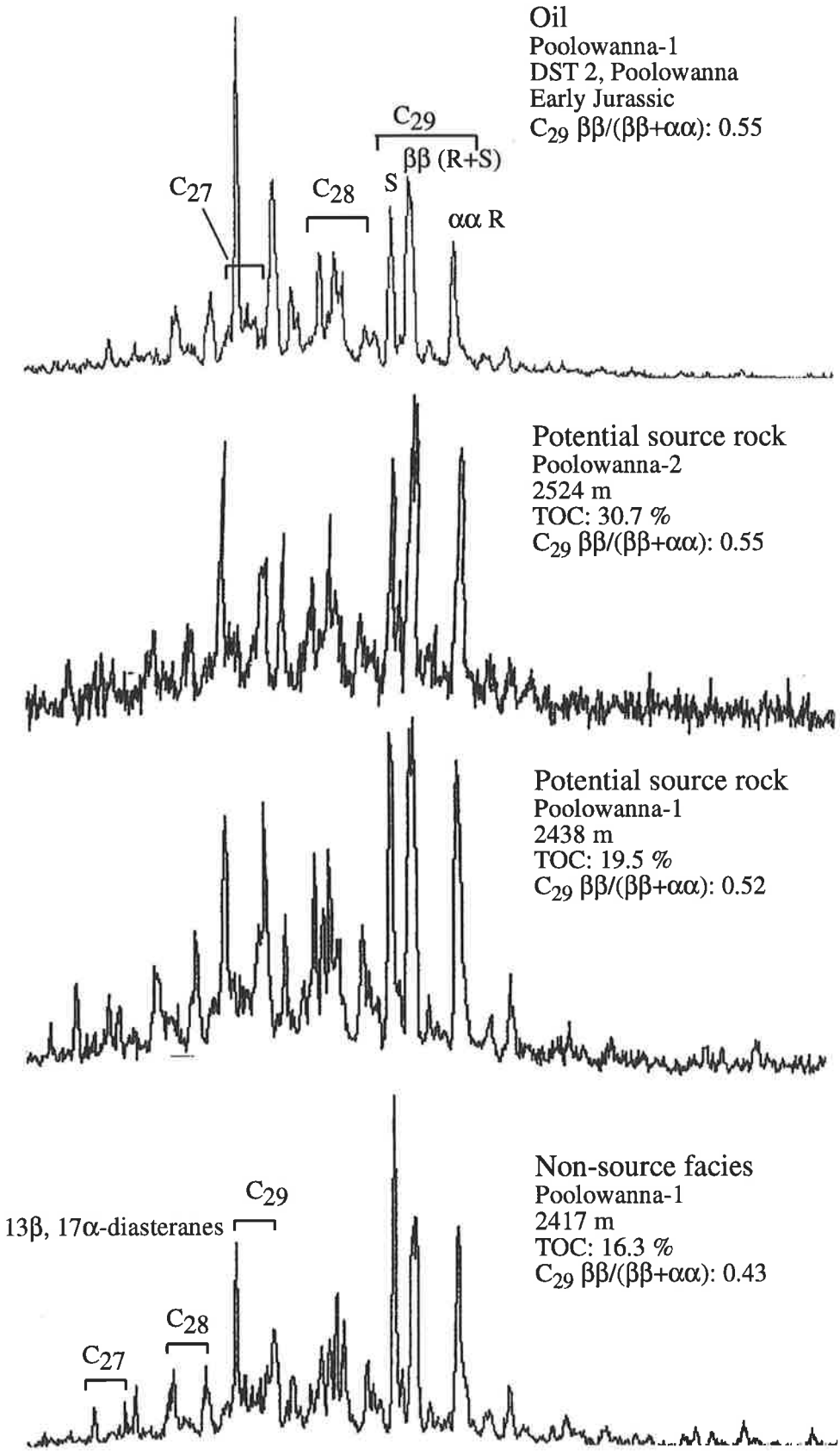


Figure 7. 6a Sterane m/z 217 signatures of the Poolwanna oil and selected source and non-source facies in the Poolowanna Trough

Table 7.4a Relative distribution of steranes and C_{29} isomerisation ratios in Poolowanna Formation source rocks

Sample no.	Well	Depth (m)	C_{27} (%)	C_{28} (%)	C_{29} (%)	C_{29} $\frac{\beta\beta}{\beta\beta+\alpha\alpha}$	C_{29} $\frac{20S}{20S+20R}$	C_{29} $\frac{5\alpha\ (20S)}{5\alpha(20R)}$	C_{29} $\frac{14\beta,17\beta(20R)}{5\alpha(20R)}$	C_{29} $\frac{\beta\alpha\ (20R)}{\alpha\alpha(20R)}$	$\frac{\text{Sterane}}{\text{Hopane}}$
POL1-1	Poolowanna-1	2417	13	24	63	0.43	0.58	1.59*	0.94	0.38	0.18
POL1-3	Poolowanna-1	2438	14	28	57	0.52	0.51	1.09	1.10	0.75	0.18
POL1-5	Poolowanna-1	2499	16	24	60	0.56	0.50	0.77	0.99	0.78	1.70
POL2-9	Poolowanna-2	2524	17	23	60	0.55	0.49	0.96	1.20	0.50	0.44
POL3-13	Poolowanna-3	2505	24	24	52	0.48	0.51	0.88	0.79	0.59	0.34
TAN2-18	Tantanna-2	1799	18	25	56	0.36	0.48	0.81	0.46	0.51	0.07
TAN2-20	Tantanna-2	1811	nd	nd	nd	0.43	0.48	0.77	0.61	1.52	0.13
TAN3-21	Tantanna-3	1807	21	25	54	0.33	0.49	0.77	0.34	0.40	0.21
TAN8-25	Tantanna-8	1823†	32	20	48	0.39	0.50	0.97	0.61	0.89	0.45
STU1-27	Sturt-1	1871	28	26	47	0.37	0.51	0.76	0.37	0.58	0.17
STU4-30	Sturt-4	1859	15	24	61	0.33	0.50	0.88	0.41	0.28	0.14
STU4-31	Sturt-4	1881†	10	24	66	0.40	0.56	1.16	0.59	0.70	0.31
STU6-35	Sturt-6	1865†	24	19	57	0.34	0.50	0.96	0.50	0.53	0.21
STE1-38	Sturt East-1	1841	23	29	48	0.34	0.51	0.85	0.39	0.57	0.07
STE4-45	Sturt East-4	1862†	12	23	65	0.33	0.48	0.74	0.37	0.36	0.25

† coaly facies

$$\frac{\text{Sterane}}{\text{Hopane}} = \frac{\sum C_{29}\ \text{sterane}}{C_{30}\ \alpha\beta\text{-hopane}}$$

$$\frac{\beta\alpha\ (20R)}{\alpha\alpha\ (20R)} = C_{29}\ \frac{\text{Diasterane}}{\text{sterane}}$$

* Anomalously high (artefact of quantitation procedure)

The various isomer ratios of 24-ethylcholestane are given in Table 7.4a. These three ratios were in order to assess the influence of source rock facies on sterane isomerisation. Isomerisation at the C-14 and C-17 positions of the C_{29} sterane, represented by the 14β(H),17β(H)/(αββ+ααα) ratio, has values ranging from 0.43 to 0.56 in the Poolowanna Trough. An increase of the ratio with depth was noted in Poolowanna-1, reflecting the previously noted increase in thermal maturity. In the Patchawarra Trough, values range from 0.33 to 0.43. The rocks are indicated to be less mature than those in the Poolowanna Trough. This ratio seems to be independent of the TOC content of the source rock (Fig. 7.7).

Isomerisation at C-20 in the C_{29} 5α(H),14α(H),17α(H) sterane is measured by the 20S/(20S+20R) ratio which varies from 0.49 to 0.58 in the Poolowanna Trough. In contrast to the previous isomerisation ratio, it decreases with increasing depth in Poolowanna-1. Such a decrease with increasing thermal maturity is quite unusual but has been reported elsewhere (Peters *et al.*, 1990; Marzi and Rullkötter, 1992). This ratio has similar values (0.48–0.56) in samples from the Patchawarra Trough. It is unlikely that this ratio is influenced by organic facies. As seen from Figure 7.7, it remains remarkably constant with increasing TOC.

The 5α,14α,17α(20S)/5α,14α,17α(20R) ratio, as expected appears to behave in a similar fashion to 20S/(20S + 20R). The unusually high value (1.59) for the Poolowanna-1 (2417 m) sample may be an artefact of the quantitation procedure (based on peak height: see Fig. 7.6a). This ratio appears to decrease with increasing TOC in the coal facies, although this trend may be mainly due to the lower maturity of the Sturt East-4 coal (TOC = 68.1%).

The αββ(20R)/ααα(20R) ratio varies from 0.79 to 1.20 in the Poolowanna Trough and from 0.34 to 0.61 in the Patchawarra Trough, highlighting in a similar fashion to the αββ/ββ+ααα ratio the lower maturity of the latter samples.

The ratio of diasteranes to regular steranes in source rocks is known to be affected by lithofacies, oxicity of the depositional environment and thermal maturity (Peters and Moldowan, 1993). In this study the C_{29}βα (20R)/ααα (20R) (i.e. diasterane/sterane) ratio was determined for the Poolowanna Formation source rock facies in the Poolowanna and Patchawarra Troughs (Table 7.4a). For silty shales at Poolowanna-1 the values of this ratio increase from 0.38 at 2417 m to 0.78 at 2499 m. This trend is attributable mainly (but not entirely: see below) to increasing maturity.

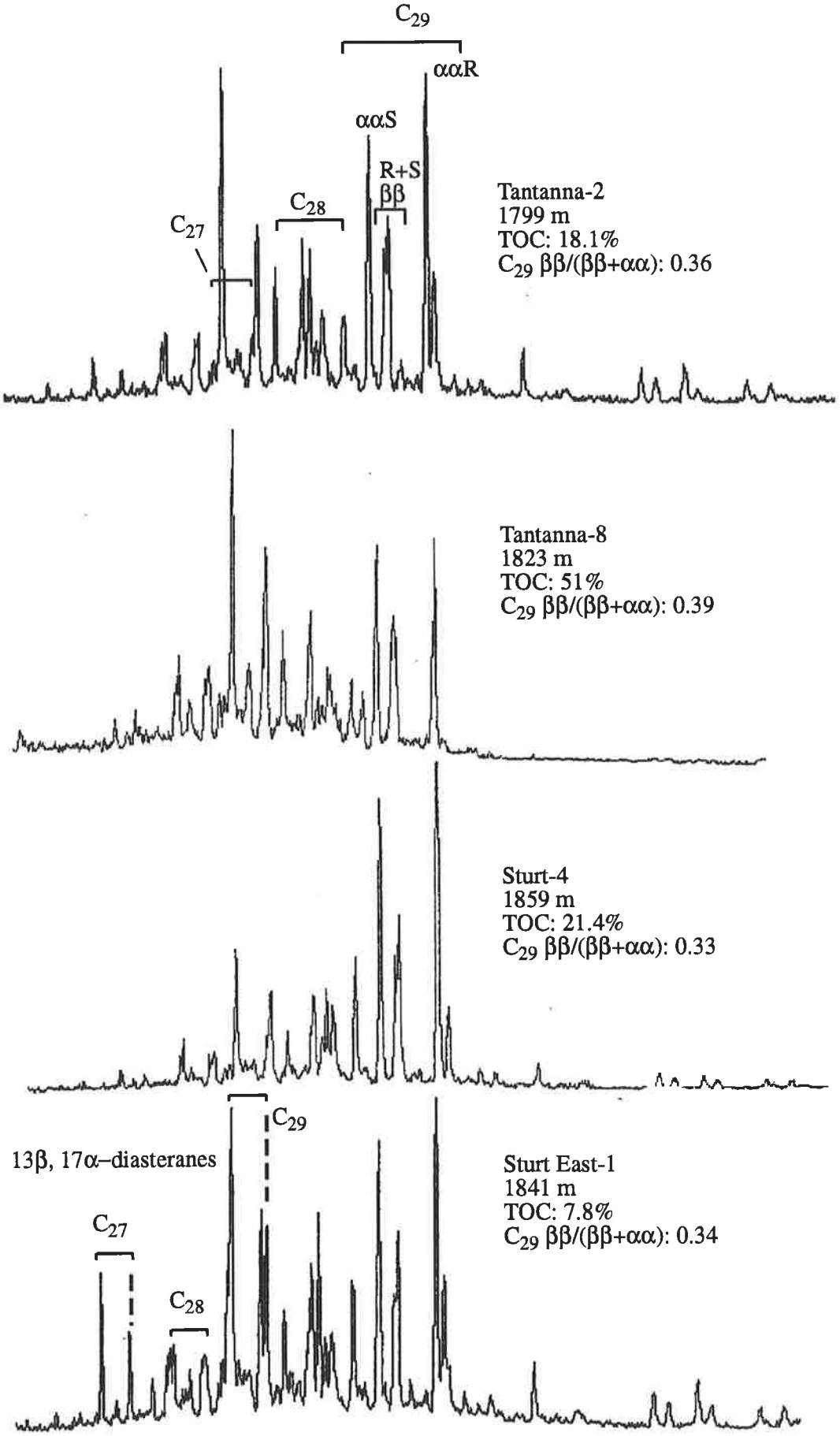


Figure 7. 6b Sterane m/z 217 signatures of potential source facies in the Poolowanna Formation, Patchawarra Trough

A wider range of values, from 0.28 in carbonaceous shale (Sturt-4, 1859 m) to 1.52 in siltstone (Tantanna-2, 1811 m), is observed in the Patchawarra Trough. Since there is very little difference in maturity between these samples, this wider range presumably reflects variation in their lithological character and depositional setting.

As reported by McKirdy *et al.* (1983) and Rullkötter *et al.* (1985) low diasterane/sterane values are indicative of anoxic, clay-poor depositional conditions. Thus, the anomalously high value (1.52) in the Tantanna-2 (1811 m) sample may signify a higher clay content. The same argument may be applied to the less mature Poolowanna-1 (2417 m) sample in the Poolowanna Trough which has a much lower value than other samples in that trough. Its low value may also partly reflect less oxic conditions in the upper part of the formation. The coals are also characterised by a wide range of diasterane/sterane values (0.36–0.89). Like other samples from the Patchawarra Trough, the coals do not differ very much in maturity, and therefore the variation in their diasterane/sterane ratio reflects the different surface catalytic properties of their kerogen matrix and/or differences in their mineral matter content. The influx of mineral matter, including clays, may explain the higher diasterane content of the Tantanna-8 (1823 m) coal. This is consistent with its relatively low TOC content (50.1%: Table 5.1). In both the Poolowanna and Patchawarra depocentres, the Poolowanna Formation source rocks are indicated by such variations to be of paludal to fluvial-lacustrine origin.

The abundance of steranes relative to hopanes was evaluated using the ΣC_{29} sterane/$C_{30}\alpha\beta$-hopane ratio. This ratio is used to compare the input of eukaryotic biota (i.e. algae and higher plants) to that of prokaryotic organisms (bacteria). In the Poolowanna Formation from the Poolowanna Trough the values are mostly in the range 0.18–0.44, indicating high bacterial inputs. The unusually high ratio (1.7) observed at 2499 m in Poolowanna-1 may indicate diminished bacterial reworking of the higher plant contribution to its preserved organic matter.

In samples from the Patchawarra Trough the sterane/hopane values range from 0.07 to 0.45. Coaly facies are shown to have relatively high values, consistent with their high terrestrial organic matter contents. Very low values (0.07) shown by the Tantanna-2 (1799 m) and Sturt East-1 (1841 m) shales indicate higher pH and stronger microbial activity in their sub-aquatic depositional environments. The strong bacterial influence indicated by this parameter supports earlier observations based on the *n*-alkane distributions of these samples (Table 6.3a).

7.2.11 Sterane distributions in crude oils

The distribution and relative abundances of the steranes in the oils are shown in Table 7.4b.

Table 7.4b Relative distribution of steranes and C_{29} isomerisation ratios of oils in the Poolowanna and Patchawarra Troughs

Sample no.	Well	Depth (m)	DST no.	Formation	C_{27} (%)	C_{28} (%)	C_{29} (%)	C_{29} $\frac{\beta\beta}{\beta\beta+\alpha\alpha}$	C_{29} $\frac{20S}{20S+20R}$	C_{29} $\frac{5\alpha\ (20S)}{5\alpha(20R)}$	C_{29} $\frac{14\beta,17\beta(20R)}{5\alpha(20R)}$	C_{29} $\frac{\beta\alpha(20R)}{\alpha\alpha(20R)}$	$\frac{\text{Sterane}}{\text{Hopane}}$
P1	Poolowanna-1	2504-2538	2	Poolowanna	21	26	53	0.55	0.50	1.24	1.49	1.31	0.39
T2	Tantanna-1	1800-1814	1	Poolowanna	32	27	40	0.59	0.53	1.09	1.36	2.50	0.18
T3	Tantanna-1	1635-1642	2	Hutton	36	26	37	0.56	0.48	1.00	1.35	2.55	0.29
T4	Tantanna-1	1347-1359	3	Birkhead/Hutton	29	28	42	0.49	0.47	0.87	0.93	1.50	0.30
S11	Sturt-3	1848-1855	1A	Poolowanna	24	28	48	0.50	0.50	0.83	0.80	1.13	0.27
S12	Sturt-3	1654-1662	1B	Birkhead	28	27	46	0.54	0.49	0.96	1.18	1.48	0.18
S13	Sturt-4	1872-1880	1	Poolowanna	26	26	48	0.54	0.46	0.85	1.14	1.26	0.26
S16	Sturt-6	1914-1919	6	Mooracoochie	29	25	46	0.57	0.48	0.78	1.14	1.28	0.27
S17	Sturt-6	1884-1898	3	Patchawarra	30	25	45	0.55	0.50	1.16	1.36	1.68	0.23
S18	Sturt-6	1883-1892	1	Birkhead	27	26	47	0.59	0.47	0.85	1.36	1.38	0.26
S19	Sturt-7	1923-1938	1	Patchawarra	27	25	48	0.56	0.47	0.99	1.36	1.49	0.19
S20	Sturt-7	1946-2021	2	Mooracoochie	27	24	49	0.51	0.49	0.86	0.92	1.06	0.21
S21	Sturt-7	1871-1876	3	Poolowanna	36	21	44	0.61	0.48	0.86	1.44	1.69	0.26
S23	Sturt-8	1880-1884	1	Poolowanna	26	23	51	0.57	0.44	0.81	1.35	1.19	0.21
SE24	Sturt East-2	1845-1899	1	Poolowanna	30	24	46	0.52	0.51	0.85	0.88	1.38	0.24
TL25	Taloola-2	1829-1836	1	Poolowanna	33	27	40	0.57	0.48	1.04	1.48	2.09	0.21
TL26	Taloola-2	1789-1793	2	Hutton	33	28	40	0.56	0.49	1.00	1.36	1.77	0.25
TL27	Taloola-2	1384-1397	3	Namur	28	27	44	0.58	0.50	0.92	1.27	2.15	0.26

Key: as for Table 7.4a

As in the source rock extracts, the C_{29} homologue is the most abundant sterane, ranging from 37% in the Tantanna-1 (Hutton) oil to 53% in the Poolowanna-1 (Poolowanna) sample. The C_{27} sterane appears to be second in abundance (average = 29%), whereas the C_{28} sterane is the least abundant (average = 26%). However, the C_{27} steranes are subject to interference by co-eluting C_{29} diasteranes (Fig. 7.6).

The αββ/(αββ+ααα) isomerisation ratio ranges from 0.49 in the Tantanna-1 (Birkhead/Hutton) oil to 0.61 in the Sturt-7 (Poolowanna) sample. There is no marked difference between the Poolowanna and Patchawarra Trough oils or between Jurassic, Permian and Cambrian oils. Comparing the oil values with those of the rock extracts shows that only the Poolowanna Trough source rocks are capable of generating oils of this maturity.

The 20S/20S+20R isomerisation ratio has values ranging from 0.44 in the Sturt-8 (Poolowanna) oil to 0.53 in the Tantanna-1 (Poolowanna) sample. Like the previous isomerisation ratio, it does not differ much among these oils. For instance, in oils from stacked reservoirs at any one location the difference in this parameter is between 0.01 and 0.06. Thus, the implication is that these oils in stacked reservoirs have roughly equal maturation levels. However, the average 20S/20S+20R values in the Poolowanna Trough (0.52) and Patchawarra Trough (0.50) source rocks are slightly higher than those of the adjacent oils.

The diasterane/sterane values in the Poolowanna and Patchawarra Trough oils (Table 7.4b) suggest highly mature oils (Peters *et al.*, 1990). They range from 1.06 in the Sturt-7 (Mooracoochie) oil to 2.55 in the Tantanna-1 (Hutton) oil. This is in contrast to the Poolowanna source rock extracts which in all but one case have values <1 (Table 7.4a). The higher values in the oils may be attributed to a geochromatographic effect during primary migration. Peters *et al.* (1990) reported increased diasterane/sterane ratios in expelled oils, compared to the source rock bitumen, during hydrous pyrolysis experiments.

Oils from Permian and Cambrian reservoirs tend to have lower diasterane/sterane ratios (1.06–1.68; average = 1.38) than those from Jurassic reservoirs (1.13–2.55; average = 1.70) in the Patchawarra Trough. Given that the Permian and Cambrian oils are more mature than the Jurassic reservoired oils (Chapter 6), it can be asserted that the source rocks for most of the Jurassic oils were richer in clays than those of the former oils. The Poolowanna-1 (Poolowanna) oil from the Poolowanna Trough has a diasterane/sterane ratio of 1.31 which places it in the clay-poor source affinity category.

Hopanes appear to be more abundant than steranes in all but two of the oils. This is shown by sterane/hopane ratios mostly in the range 0.03–0.39 (Table 7.4b).

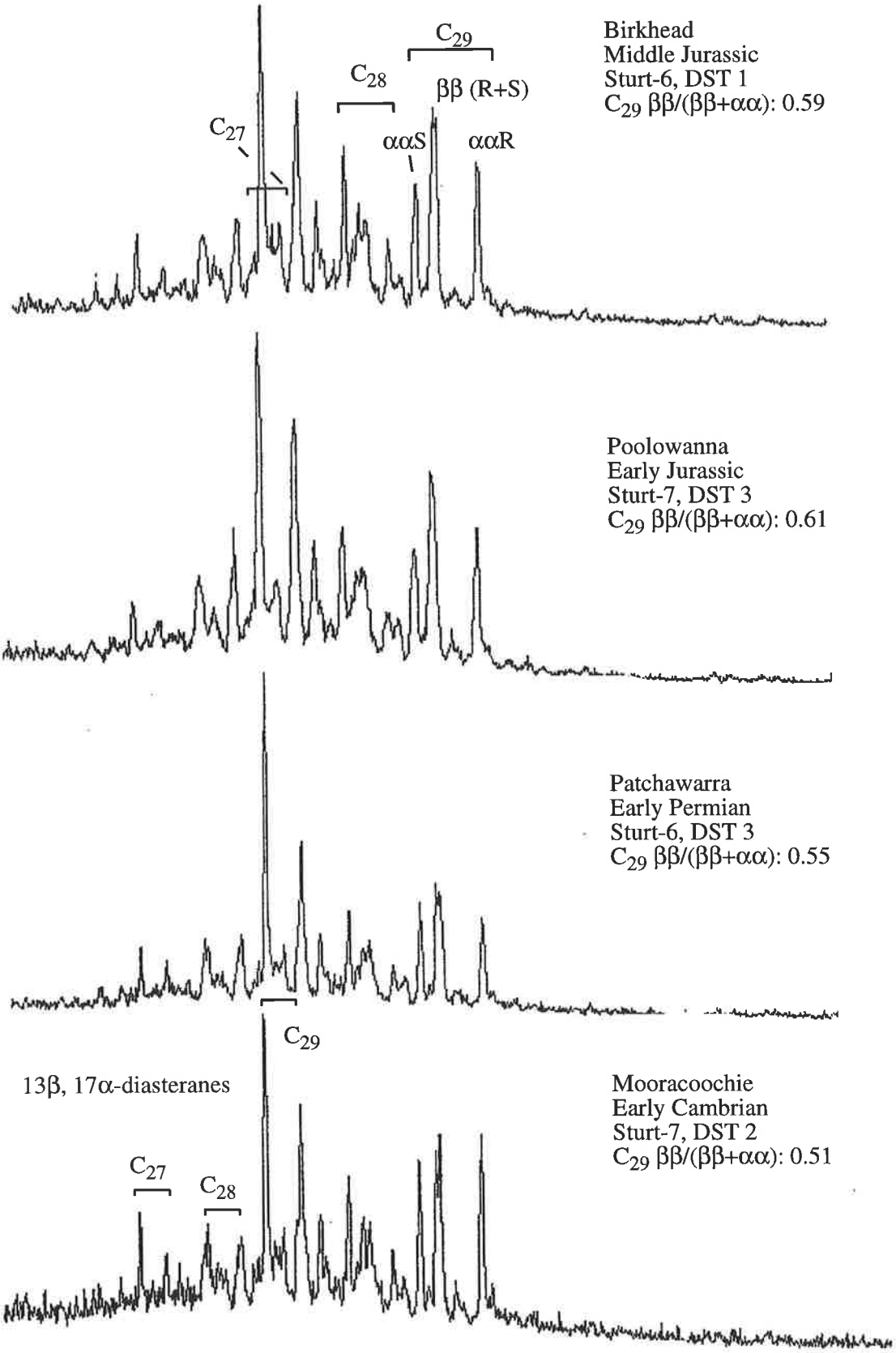


Figure 7. 6c Sterane m/z 217 signatures of oils in stacked reservoirs of the Sturt Field, Patchawarra Trough

From this ratio the Taloola-2 (Namur) and Tantanna-1 (Birkhead/Hutton) oils appear to have the strongest contribution from bacterial lipids. The Tantanna-1 (Hutton) and Sturt-8 (Poolowanna) oils show anomalously high sterane/hopane values indicative of minimal bacterial reworking of the organic matter in their respective source rocks.

7.3 Implications of biomarkers for source biota and depositional environments

7.3.1 Acyclic biomarkers in Poolowanna Formation source rocks

7.3.1.1 n-Alkanes

As discussed previously (Sections 6.3 and 7.2.1) the *n*-alkane profiles of source rock extracts represent multi-component mixtures from different source biota. Normal alkanes between C_{15} and C_{19} are the most prevalent and are usually assigned to algae deposited in either marine or in this case lacustrine environments. A strong bacterial contribution is also indicated by the abundance of *n*-alkanes in the C_{20}–C_{26} range, whereas land plant inputs show up in the C_{27}–C_{31} range (Table 6.3a).

CPI and OEP values are used not only as maturity indicators but also for organic matter input verification. High CPI values (above 1.5) always signify immature source rocks. Low CPI values, however, do not necessarily mean higher maturity. They can also imply a lack of C_{23+} *n*-alkanes stemming from terrestrial inputs. The Poolowanna Formation source rocks have CPI values between 1.02 and 1.39, which is indicative of them being mature or instead having strong inputs of planktonic algae and/or bacteria that dilute the higher land plant contribution.

The bimodal profiles, comprising both medium and high molecular weight *n*-alkanes in the Patchawarra Trough rock extracts imply contributions from a wider range of biota. A maximum at *n*-C_{25} is frequently shown in the higher molecular weight range of the bimodal profiles (Fig. 6.1 and 7.1). According to CPI, measured vitrinite reflectance and other data, it seems that most of the bimodal and unimodal profiles with a maximum at *n*-C_{25} may indicate bacterial rather than higher land plant influence. Coincidentally, such samples (Fig. 6.1) also show strong contributions from bacteria based on the relative abundance of *n*-alkanes, in the C_{20}–C_{26} range.

A lacustrine algal contribution is indicated by a prominent *n*-C_{23} peak. This observation is supported by the occurrence of *Botryococcus*-like telalginite (Chapter 4) in the Poolowanna Formation from the Patchawarra Trough. Higher land plant contribution is positively indicated by the *n*-C_{27} peak in Sturt East where the land plant input are substantiated by high content of sporinite macerals (Chapter 4). The diversity of *n*-C_{max} peaks and unimodal and

bimodal profiles indicates a fluvial depositional setting wherein various types of organic matter are inter-mixed.

7.3.1.2 Pristane and phytane

The most likely origin of pristane and phytane is from either photoantotrophic organisms, or the lipids of the archaebacteria (Section 2.6.2). Where the photoantotrophic organic matter is the source, phytane is formed under reducing conditions whereas pristane is formed under oxidising conditions (Welte and Waples, 1973). Assuming there are no other sources for these biomarkers, pristane/phytane ratios may give clues to the depositional conditions. Low values (pr/ph <1) imply a reducing or anoxic setting, whereas high values (pr/ph >1) imply oxidising or oxic conditions. Peters and Moldowan (1993) have suggested that for samples within the oil-generative window, high pr/ph ratios (>3) indicate terrestrial organic matter deposited under oxic conditions.

Terrestrial organic matter deposited under suboxic to oxic conditions is therefore inferred for the Poolowanna Formation source rock since its pr/ph ratios are >2. The source rocks in the Patchawarra Trough seem to have experienced a wider range of oxicity (pr/ph = 2.3 to 8.4) than those in Poolowanna Trough (pr/ph =3.2 to 6.6). A strong terrestrial organic matter input is further demonstrated in the plot of pr/*n*-C_{17} versus ph/*n*-C_{18} (Fig. 7.8). The Poolowanna Trough source rocks are shown to have been deposited in less oxidising conditions and to be of higher maturity than those in the Patchawarra Trough. However, since there is a possibility of a strong bacterial contribution (as previously indicated by other parameters), the pr/ph ratios in this case are likely to be influenced by pristane derived from bacterial lipids (Volkman and Maxwell, 1986).

7.3.2 Cyclic biomarkers in Poolowanna Formation source rocks

7.3.2.1 *Terpanes*

Several homologous series of terpanes including bicyclic (drimane), tricyclic, tetracyclic and pentacyclic compounds found in source rocks and crude oil are believed to originate from bacterial membrane lipids (Ourisson *et al.*, 1982; Alexander *et al.*, 1983; Volkman, 1988). The presence of these compounds in the Poolowanna Formation source rocks is discussed in previous sections of this chapter. Though not very specific, their presence is indicative of bacterial inputs. The heterogeneity of depositional conditions between source rocks of the Poolowanna Trough and those of the Patchawarra Trough is well illustrated by non-uniform αβ-hopane/bicyclic sesquiterpane ratios (Table 7.1a). The variation in depositional conditions is further demonstrated by the unusually low C_{30}/C_{29} hopane ratios (≤1) in some sections, and by the absence of the unidentified methylhopanes peaks (k and m) in the Patchawarra Trough source rocks.

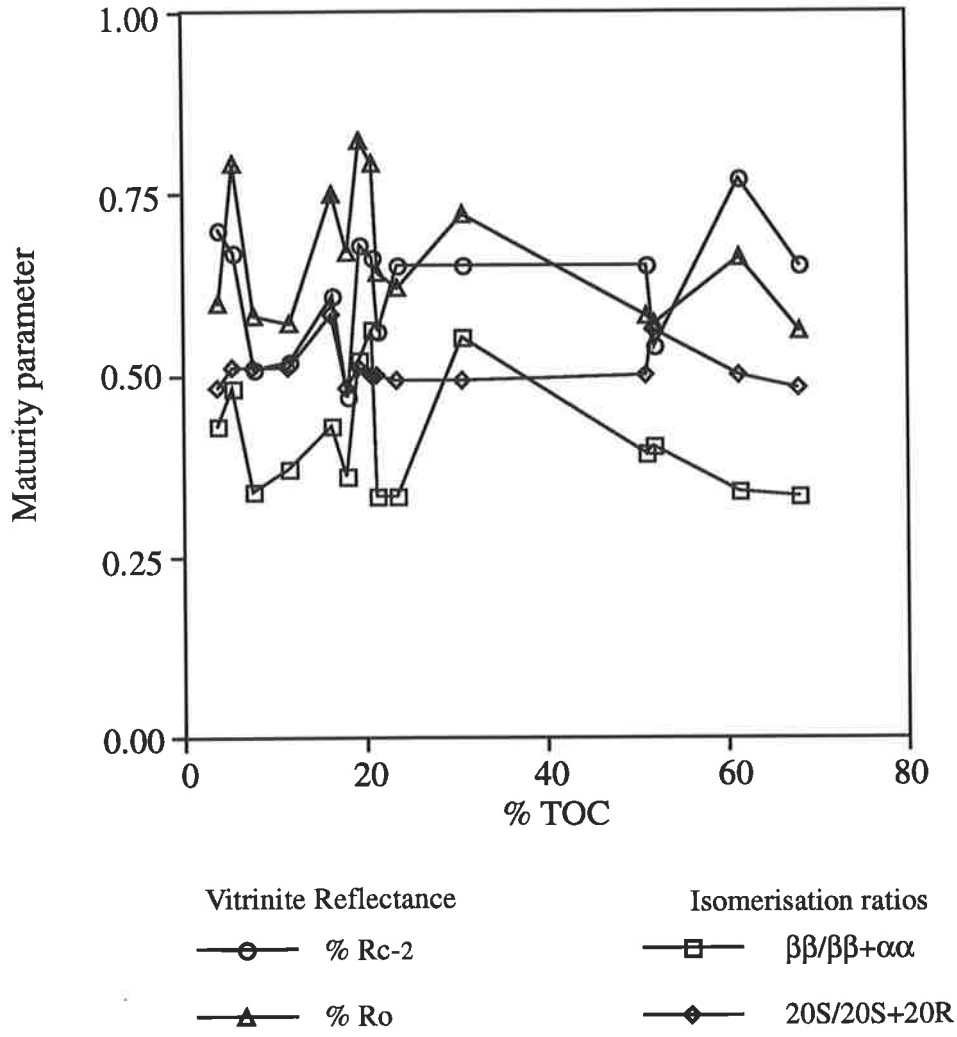


Figure 7.7 Comparison of C_{29} sterane isomerisation ratios with non-biomarker maturity parameters, and their relationship to organic facies based on TOC

7.3.2.2 *Steranes*

The presence of steranes in the source rocks reflects inputs of eukaryotic organisms mainly higher plants and algae. Therefore, the abundance of steranes relative to hopanes indirectly reflects the proportional inputs of eukaryotic and prokaryotic organisms. The C_{29} sterane/C_{30} hopane ratios (Table 7.4a) show that the input of prokaryotic organic matter was predominant over that of eukaryotic origin. A similar conclusion is suggested by the steranes/drimane ratios (Table 7.1a)

The relative abundance of C_{27}, C_{28} and C_{29} steranes plotted in a ternary diagram (Huang and Meinschein, 1979) was used to categorise different depositional environments and the type of contributing organisms. A mixed depositional regime of lacustrine and terrestrial environments appears to have been prevalent during the deposition of the Poolowanna Formation source rocks (Fig. 7.9). Neither zooplankton nor phytoplankton are indicated to be significant contributors to the source biota, but an enhanced contribution by higher plants is shown for coals from the Sturt and Sturt East Fields. Otherwise a mixed non-marine depositional environment (i.e. lacustrine to meandering fluvial and paludal) is indicated.

7.3.3 Oil source affinity based on acyclic biomarkers

7.3.3.1 n-Alkanes

The *n*-alkane range in the crude oils suggests a strong contribution from terrestrial organic matter precursors, particularly cuticular and leaf waxes which are known to have a carbon range number up to *n*-C_{35} or *n*-C_{37} with a maximum between *n*-C_{27} and *n*-C_{33} (Eglinton *et al.*, 1962). However, the credibility of a strong terrestrial input is doubtful due to the lack of maxima in the higher plant range. Most of these oils have a maximum between *n*-C_{12} and *n*-C_{14}. It is likely that the original maxima have been altered by migration processes or thermal cracking. There is no evidence of microbial activity (i.e. biodegradation) within the reservoirs of the Poolowanna and Patchawarra Troughs. Nevertheless, terrestrial and bacterial inputs are implicated in Poolowanna Trough oil by its *n*-alkane range of C_9–C_{39} and maximum at C_{23}.

The CPI values of the oils (0.79–1.25) appear to be within the normal range for mature source rocks and oils. Values >1.1 possibly signify terrestrial plant inputs to the source rock of the oil. No significant differences are evident between the Jurassic, Permian and Cambrian oils as far as their CPI and *n*-alkane ranges are concerned. Therefore these parameters can not be used positively to identify oil source affinity in the study area, although the bacterial affinity of the oils is clearly indicated by their high relative abundance of C_{20}–C_{26} *n*-alkanes.

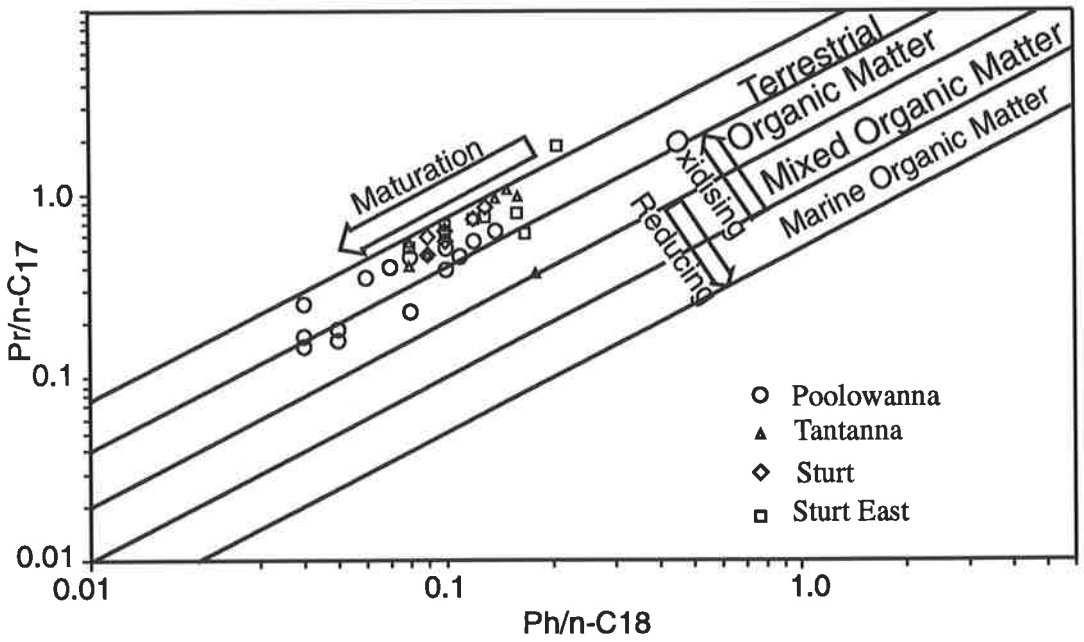


Figure 7.8 Source rock characterisation based on isoprenoid to *n*-alkane ratios, Poolowanna Formation

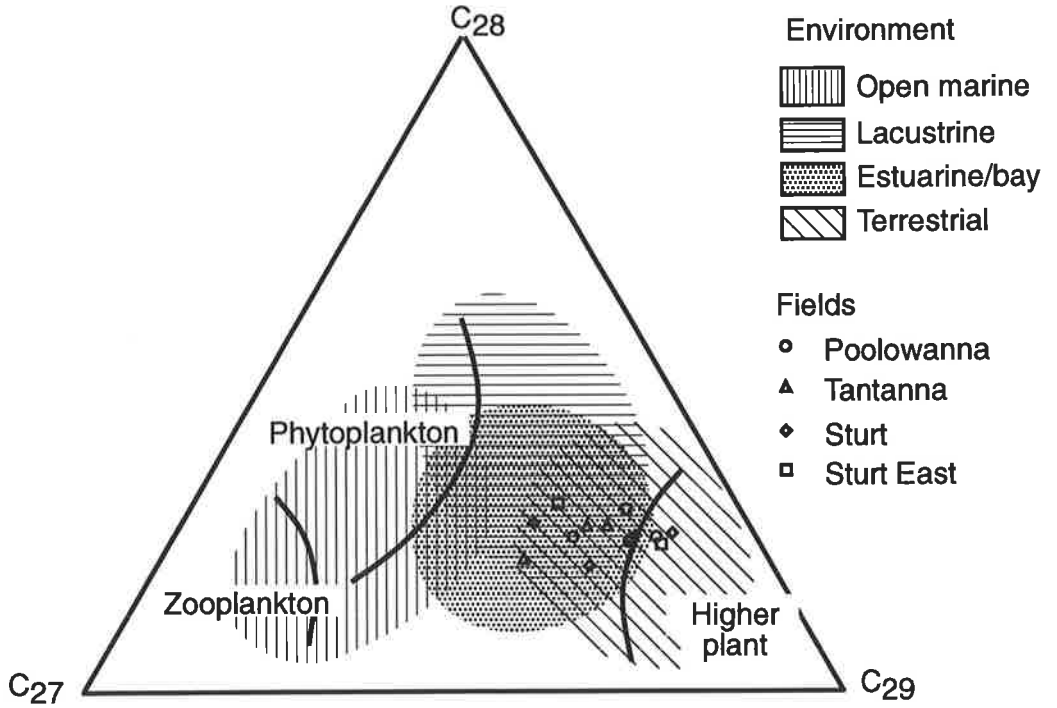


Figure 7.9 Source biota and depositional environments of Poolowanna Formation source rocks based on regular steranes. Ternary plot modified from Huang and Meinschein (1979)

7.3.3.2 *Pristane and Phytane*

Oxic depositional environments for source rocks of all but one of the studied oils are indicated by their pristane to phytane ratios (2.3–8.9). A significantly less oxidising source rock environment is indicated for the Tantanna-2 (Poolowanna) oil in which pr/ph = 2.3. The cross-plot of pr/*n*-C_{17} versus ph/*n*-C_{18}, (Fig. 7.10) shows that most of the oils were derived from terrestrial organic matter deposited under sub-oxic to highly oxic conditions. The obvious exception is the Mooracoochie oil from Sturt-7. It is of anoxic, marine algal source affinity and plots well away from the other oils in Figure 10.

7.3.4 Oil source affinity based on cyclic biomarkers

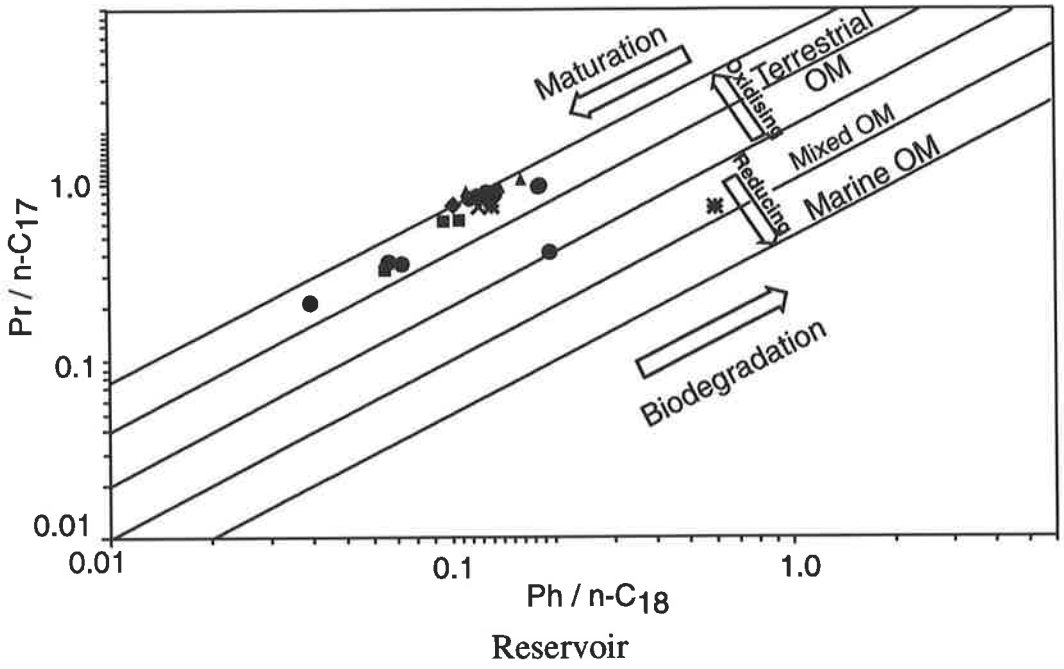
7.3.4.1 *Terpanes*

Bacterial inputs to the oils are demonstrated by a number of terpanes series. The drimanes are quite abundant in many oils. The hopane ($C_{30}\alpha\beta$) to bicyclic sesquiterpane ratio has values ranging from 0.16 to 3.46 (Table 7.1b) indicating large differences in the types of bacterial input. Different values may indicate different biota or depositional conditions. Based on this ratio it can be seen in several fields that the oils in multiple stacked reservoirs do not have common source (Table 7.1b). For instance, in Tantanna-1 well, the Poolowanna oil has a very much higher abundance of bicyclic sesquiterpanes than the Birkhead/Hutton oil; and the Namur oil seems to have a very different source from the rest of the oils in Taloola-2. The Sturt-7 (Mooracoochie) sample is unique among this collection of oils because its source rock appears to have been deposited under highly reducing conditions (pr/ph = 1.2)

Another type of bacterial contribution is indicated by the presence of the methylhopanes. These are related to the 2β-methyldiplopterol and 3β-methylbacteriohopanepolyols found in methylotrophic bacteria (Bisseret *et al.*, 1985; Zundel and Rohmer, 1985). The unidentified compounds k and m observed in the Poolowanna Trough source rocks are also found in almost all the oils, thus suggesting that the oil sources are similar to some of the Poolowanna Trough source rocks (Fig. 7.5b). The C_{29} sterane/C_{30} hopane ratios (Table 7.4b) show persistently higher contributions from prokaryotic organisms than eukaryotic organisms. Only two oils, viz. Tantanna-1 (Hutton) and Sturt-8 (Poolowanna), show a relatively high contribution from eukaryotic organisms (i.e. algae and higher plants).

7.3.4.2 *Steranes*

A derivation from source rocks deposited in terrestrial, lacustrine or estuarine environments is indicated by the relative abundances of C_{27}, C_{28} and C_{29} steranes in the oils (Fig. 7.11). None of major biota (higher plant, zooplankton and phytoplankton) is indicated to be dominant.



Reservoir

- ◆ Namur
- ▲ Birkhead
- ■ Hutton
- ● Poolowanna
- × Patchawarra (Permian)
- ✱ Mooracoochie Volcanics (Cambrian)

Figure 7.10 Oil source affinity, maturity and biodegradation based on isoprenoid to *n*-alkane ratios, Poolowanna and Patchawarra Troughs.

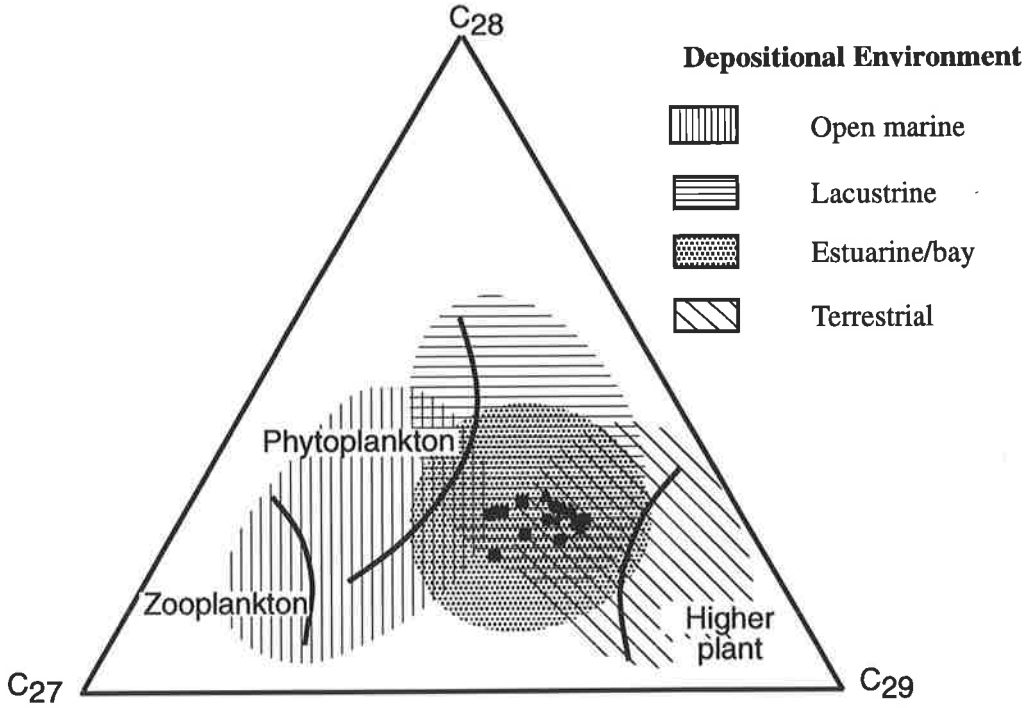


Figure 7.11 Oil source affinity based on the distribution of regular steranes, Poolowanna and Patchawarra Troughs. Ternary plot modified from Huang and Meinschein (1979). (Key as in Figure 7.10)

However, a mixture of higher plants and phytoplankton are the most likely eukaryotic precursors. It is interesting that the Sturt-7 (Mooracoochie) marine oil plots within the compositional field of other non-marine oils.

7.4 Biomarker maturity parameters

The heat-driven reactions which convert sedimentary organic matter into petroleum (Section 2.4.3) appear to have consistent implications for the molecular and isomeric structures of the saturated hydrocarbons found in source rocks and in oils. In the case of the *n*-alkanes, such reactions result in generation of large amounts of additional *n*-alkanes which consistently dilute the inherited biogenic odd or even-carbon-number preferences. Molecular transformations involving isomerisation at cyclic and acyclic chiral centres in steranes and triterpanes also reflect the extent of heat-driven reactions in sedimentary organic matter.

7.4.1 Source rock maturity based on acyclic biomarker parameters

In the acyclic *n*-alkanes, CPI (or OEP) is normally used as a maturity parameter especially when there is an obvious odd over even predominance in the C_{25}–C_{33} range resulting from higher plant waxes. CPI values are initially >1.0 but tend towards a value of 1.0 with increasing maturity. The CPI values of the source rocks in both the Poolowanna and Patchawarra Troughs range from 1.02 to 1.39, and are therefore indicated to be at the early mature level. The OEP values at *n*-C_{26} (for the plant wax input) range from 1.02 to 1.14 in the Poolowanna Trough and from 1.15 to 1.33 in the Patchawarra Trough, thus more clearly indicating a lower level of maturity in the latter area.

Pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios decrease with increasing maturity as more *n*-paraffins are generated from kerogen by cracking (Tissot *et al.*, 1971). It appears from Figure 7.8 that the Poolowanna source rock facies in the Poolowanna Trough are more mature than those in the Patchawarra Trough.

7.4.2 Source rock maturity based on cyclic biomarker parameters

7.4.2.1 Terpanes

The thermal maturity applications of the triterpane biomarkers are based on the fact that the biologically produced hopane precursors carry a 22R configuration which is gradually converted to a mixture of 22R and 22S diastereomers. Thus, under normal circumstances, the proportions of 22R to 22S in the C_{31} to C_{35} homologues will give a relative thermal maturity of the source rock.

The 22S/(22S+22R) ratios for the C_{31} and C_{32} 17α-homohopanes derived from the Poolowanna Formation source rock extracts are shown in Table 7.2a. Values in the Poolowanna and Patchawarra Troughs are in the range 0.51–0.59 and 0.54–0.65,

respectively for the C_{31} hopanes (both with an average value of 0.56 that is indicative of the early mature stage). However, since the equilibrium value of 22S/(22S+22R) is 0.60, the indicated maturity level is under estimated, particularly for the Poolowanna Trough source rocks which are indicated by vitrinite reflectance data to be mature. On the other hand, the maturity indicated for the Poolowanna Formation in the Patchawarra Trough agrees with vitrinite reflectance data.

Other terpane-derived parameters, such as the ratio of 17β(H),21α(H)-moretanes to the corresponding C_{29} and C_{30} 17α(H),21β(H) hopanes and Ts/(Ts+Tm) and Ts/17α(H)-hopane ratios (Table 7.2a) confirm that the source rocks from the Poolowanna Trough are more mature than those in the Patchawarra Trough.

7.4.2.2 Steranes

Thermally driven reactions undergone by steranes include equilibration between the biological epimer 20R and the geological epimer 20S 5α(H),14α(H),17α(H) (Section 2.6.9) which is expressed in the 20S/(20S+20R) ratio. Isomerisation at C-20 in the C_{29} 5α(H),14α(H),17α(H)-sterane causes this ratio to rise from 0 to about 0.5 with increasing maturity (Seifert and Moldowan, 1986). The source rocks in the Poolowanna Trough have values ranging from 0.49 to 0.58 (Table 7.4a), which are very similar to those of the Patchawarra Trough source rocks (0.48–0.56). These values are indicative of early mature to mature source rocks.

Isomerisation at the C-14 and C-17 positions in the 20S and 20R C_{29} sterane, causes an increase in the αββ/(αββ+ααα) ratio from near-zero values in immature sediments to about 0.7 which is equivalent to peak oil generation. The Poolowanna Formation source rocks in the Poolowanna Trough have values ranging from 0.43 to 0.56 (Table 7.4a) and are thus indicated to be within the oil window. In the Patchawarra Trough, the source rocks have values ranging from 0.33 to 0.43 and are thus again shown to be less mature than those in Poolowanna Trough.

Lithological effects on isomerisation are apparently demonstrated in the αββ(20R)/ααα(20R) versus ααα(20S)/ααα(20R) cross-plot (Fig. 7.12), adapted from the biomarker migration index (BMAI) plot of Seifert and Moldowan (1981). In this diagram the first order kinetic conversion curve is translated to fit the present sample distribution. It is noted from this figure that samples from different lithological facies have different maturation pathways.

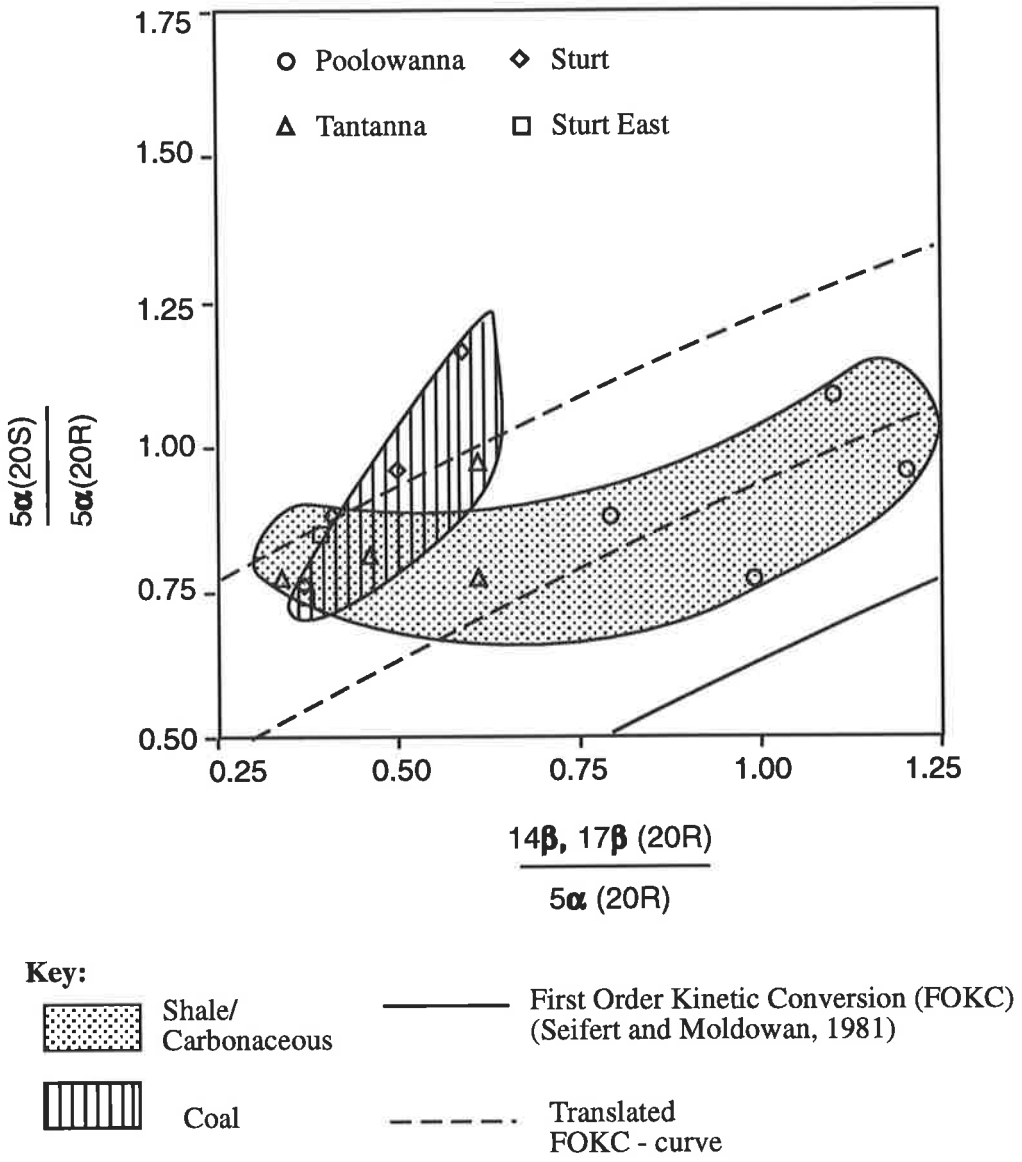


Figure 7.12 Maturation pathways in Poolowanna Formation source rock lithofacies as demonstrated by sterane isomerisation ratios

The shaly-carbonaceous clastic source rocks from the Poolowanna Trough plot along a separate trend from that of the coaly Patchawarra Trough samples. This has important implications for oil - source correlations (see Section 7.4.4).

7.4.3 Oil maturity based on acyclic biomarkers

The thermal maturity of an oil reflects the maturity at which it was generated and expelled from its source rock. However, other factors such as microbial degradation, oil mixing and thermal cracking in the reservoir may alter the original biomarker maturity signature. Therefore, techniques used on the source rock extracts should be applied to the oils with caution.

The pr/*n*-C_{17} and ph/*n*-C_{18} values of most of the oils (Fig. 7.10) overlap those of the Poolowanna Formation source rocks (Fig. 7.8). Suggesting that they are of similar maturity. The one exception is the marine oil from the Mooracoochie Volcanics in Sturt-7. This oil appears to be appreciably less mature than the other oils, although its isoprenoid/*n*-alkane ratios may have been enhanced by an early phase of biodegradation when the Cambrian reservoir was invaded by meteoric water.

7.4.4 Oil maturity based on cyclic biomarkers

The thermal maturation parameters based on terpane isomer ratios are as shown in Table 7.2b. The 22S/(22S+22R) ratios of the C_{31} and C_{32} 17α(H)-homohopanes have values ranging from 0.53 to 0.61 for Jurassic oils, and from 0.58 to 0.61 for Permian and Cambrian oils. These data indicate that the oils in this region were generated from early mature to mature source rocks. In the Sturt Field, on the basis of these epimer ratios, the oils from Jurassic reservoirs appear to be less mature than those from the Permian and Cambrian reservoirs (Fig. 7.4c). In this and other fields which contain stacked reservoirs, the oils in the older reservoirs are more mature, except in Tantanna-1 where the Poolowanna oil has the lowest maturity. This observation shows that oils in the stacked reservoirs are generated from different sources.

The C_{29} moretane/hopane ratios have values ranging from 0.09 to 0.24 for Jurassic oils and from 0.11 to 0.22 for Permian and Cambrian oils. The corresponding ranges for the C_{30} isomers are 0.12 to 0.26 and 0.15 to 0.26, respectively. Generally in stacked reservoirs, oils from the younger reservoirs have higher values than those from older reservoirs (e.g. at Sturt-6 and Taloola-2). Thus, the latter oils are indicated to be more mature than the former. Ts/Ts+Tm values appear to be too inconsistent to be employed for maturation assessment. This inconsistency is attributed to variations in organic facies.

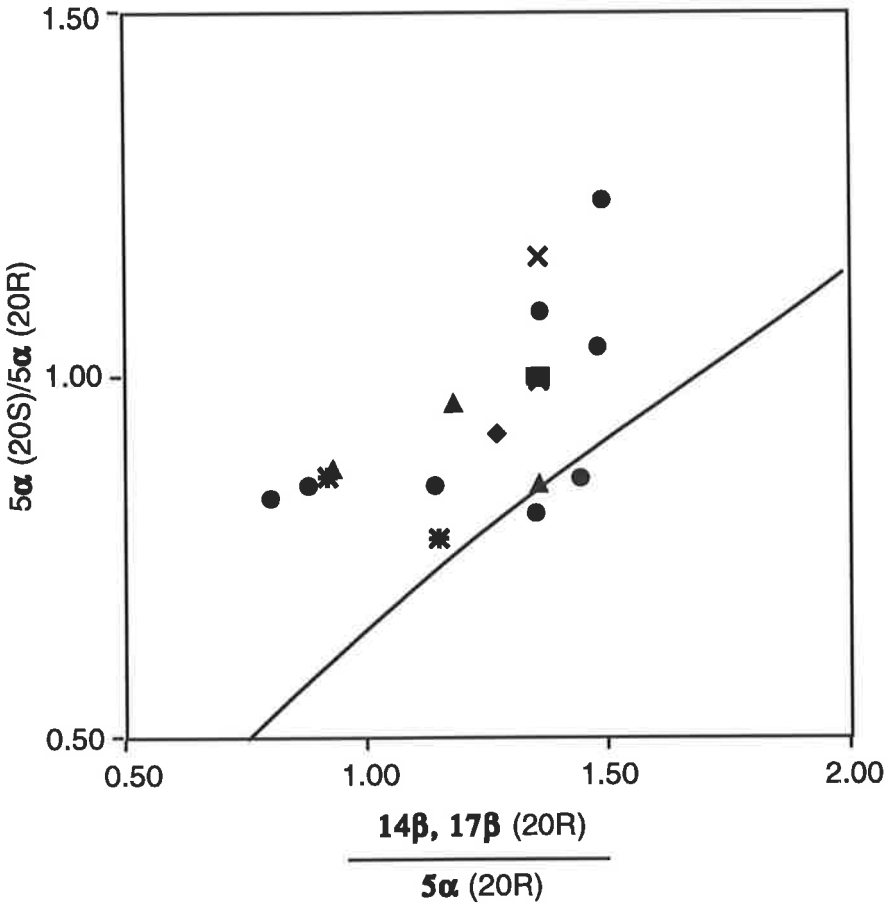


Figure 7.13a Oil maturity based on C_{29} sterane isomerisation ratios

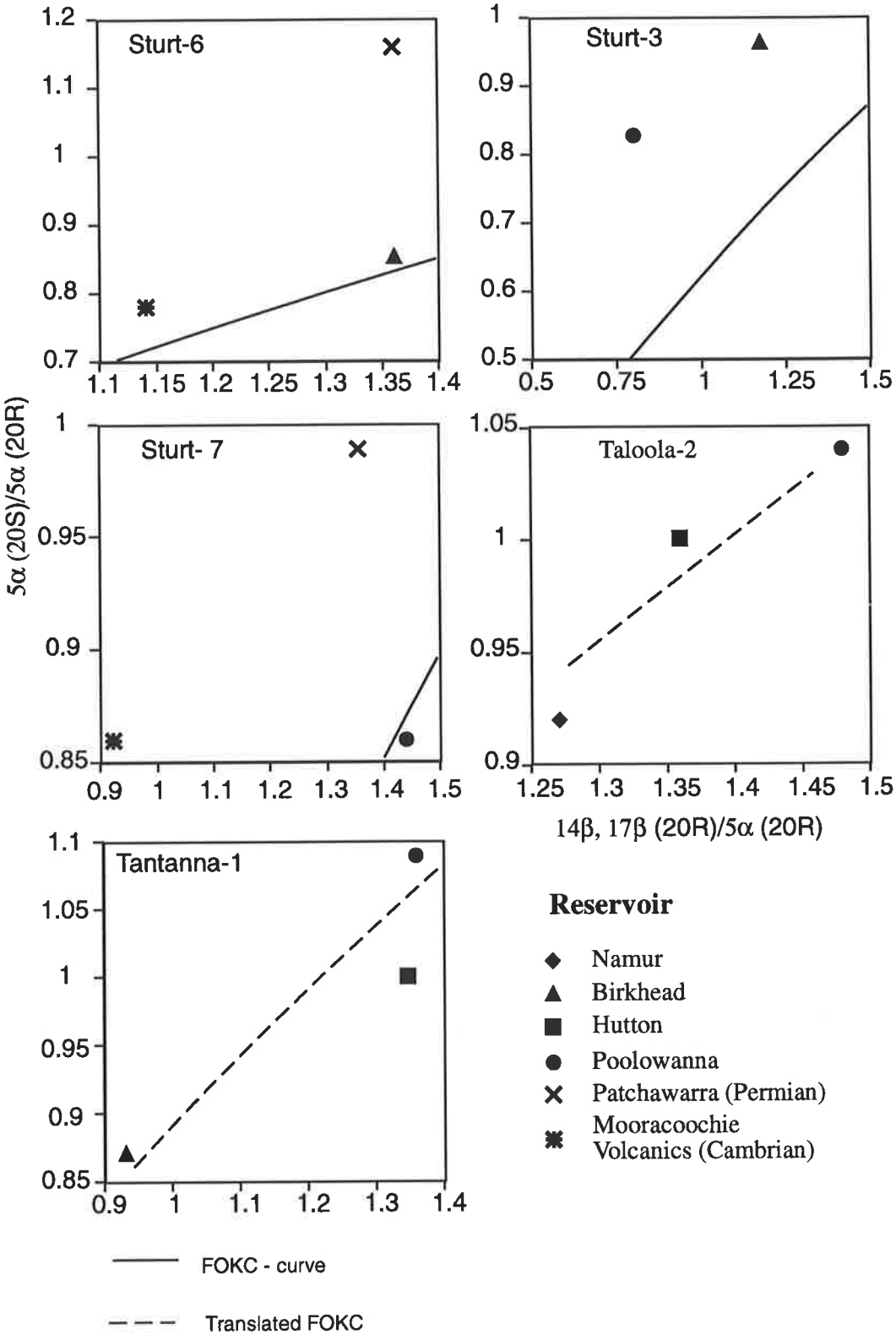


Figure 7.13b Maturity differences in oils from stacked reservoirs based on C_{29} sterane isomerisation ratios and the FOKC curve (Seifert and Moldowan, 1981).

The oils are indicated to be early mature to mature oils by their C_{29} sterane 20S/(20S+20R) and αββ/αββ+ααα isomerisation ratios. The 20S/(20S+20R) values for Jurassic oils range from 0.44 to 0.51; for Permian oils from 0.47 to 0.51; and for Cambrian oils from 0.48 to 0.49. The corresponding αββ/αββ+ααα ratios are 0.49 to 0.61 for Jurassic oils; 0.55 to 0.56 for Permian oils; and 0.51 to 0.57 for Cambrian oils. These sterane maturity parameters fail to support the impression of significantly lower maturity indicated for the Sturt-7 (Mooracoochie) oil by its isoprenoid/n-alkane ratios (Figs. 7.10 and 7.13a). However, they do show that in the Patchawarra Trough the Permian oils are more mature than the Cambrian oils and most of the Jurassic oils.

In the cross-plot of αββ(20R)/ααα(20R) versus ααα(20S)/ααα(20R) (Fig. 13a) most of the oils plot above the FOKC curve, almost in the same position as that of the non-coaly Poolowanna Formation source rocks (Fig. 7.12). This indicates that the Poolowanna Formation carbonaceous clastic source rock facies have a similar maturity pathway to that of the Jurassic oils. A comparison of the oils within the stacked reservoirs (Fig. 7.13b) shows that the Jurassic oils in Sturt-3, Taloola-2 and Tantanna-1 are likely to be generated from a common source, in that they plot along the same maturation trend.

In Sturt-6, the Mooracoochie and Birkhead oils plot close to the FOKC line (and thus may have the common origin); but are clearly different from the Patchawarra oil. In Sturt-7, however, the Mooracoochie, Patchawarra and Poolowanna oils all plot on different maturation trends and are genetically unrelated. Finally, comparison of Figures 7.12 and 7.13 reveals that none of the oils originated from the coal facies of the Poolowanna Formation.

Chapter 8

Aromatic hydrocarbon distributions in source rocks and crude oils

8.1 Introduction

Aromatic compounds are major constituents of crude oils and source rock extracts (Radke, 1987). These compounds include aromatic hydrocarbons of the benzene, naphthalene, phenanthrene and anthracene, pyrene, benzanthracene and chrysene type (Section 2.7); naphthenoaromatic hydrocarbons; and aromatic sulphur compounds, of which benzothiophene derivatives are the most common.

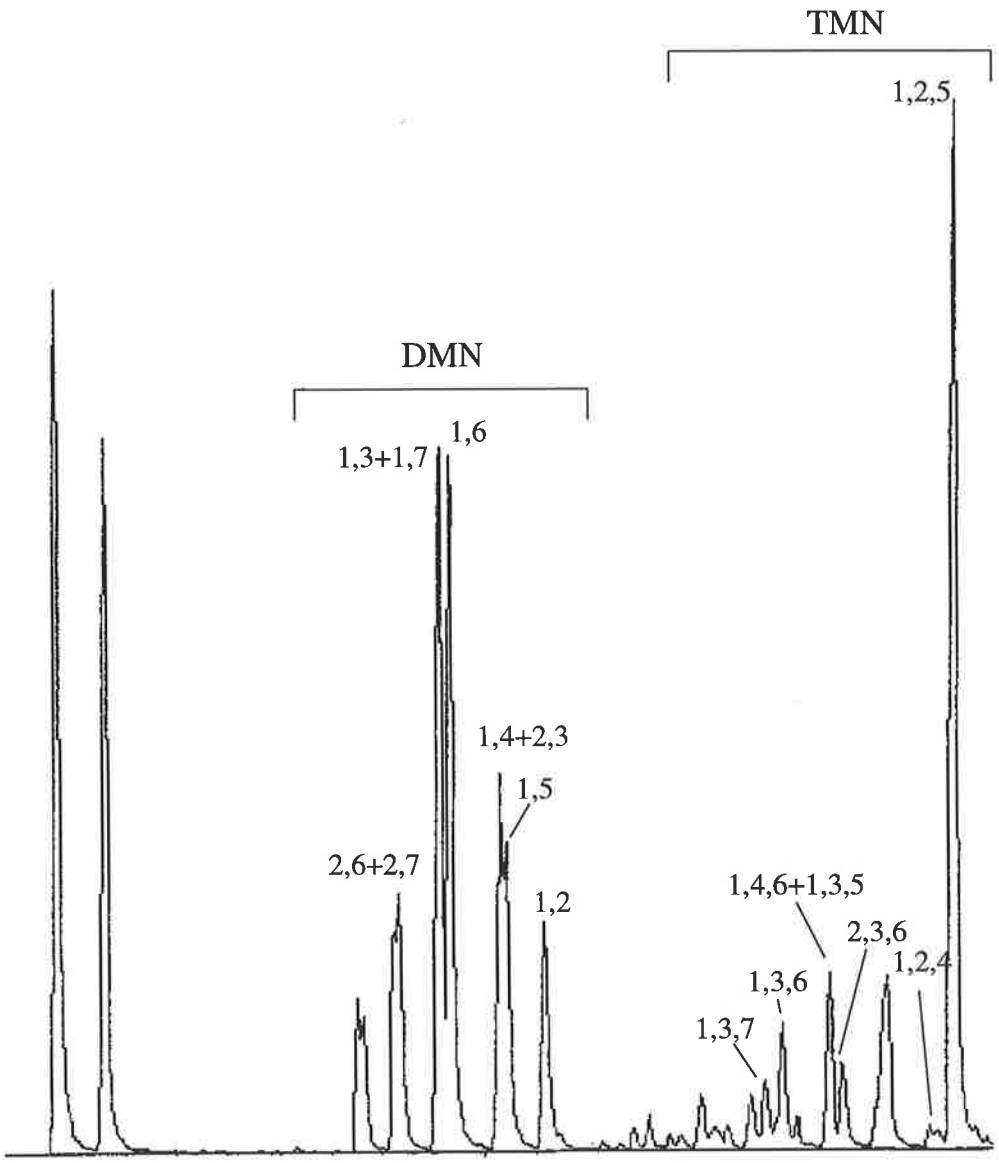
Their use as biomarkers has been based on their structural similarities to certain naturally occurring biogenic compounds, as first noticed by Mair and Martinez-Pico (1962). As an example, laboratory experiments by Ruzicka and Hosking (1930) showed that aromatisation of the bicyclic resin acids and alcohols produced agathalene (1,2,5-trimethylnaphthalene) whereas the tricyclic components gave rise to pimanthrene (1,7-dimethylphenanthrene) and retene (Fig. 1.7). The presence of polycyclic aromatic hydrocarbons (PAH) in petroleum are thought to be products of complex transformations of naphthenic and olefinic biological precursors, because they are not synthesised in significant quantities by living organisms (Grimmer and Düvel, 1970; Grimmer *et al.*, 1972; Hase and Hites, 1976).

A suite of aromatic hydrocarbons including the di- and trimethylnaphthalenes; phenanthrene the methylphenanthrenes and dimethylphenanthrenes; retene; anthracene and a methyl-anthracene were identified in the rock extracts and oil samples of the study area (Fig. 8.1a, b). They are commonly employed to assess the maturation level of both source rock extracts and oils; and in the case of oils may also provide information on their source affinity (Alexander *et al.*, 1988). They are used in this study to evaluate the maturity of source rocks and oils in the Poolowanna Formation, and to establish the genetic relationships of these oils and those in adjacent reservoirs.

8.2 Aromatic hydrocarbon fraction of source rock bitumens and oils

8.2.1 Aromatic fraction of source rock extracts

The relative abundance of the total aromatic fraction in source rock extracts of the Poolowanna Formation is as shown in Table 5.2 and illustrated in Figure 5.4.



DMN = Dimethylnaphthalene

TMN = Trimethylnaphthalene

Figure 8.1a RIC chromatogram of di- and trimethylnaphthalenes in a representative rock extract of the Poolowanna Formation

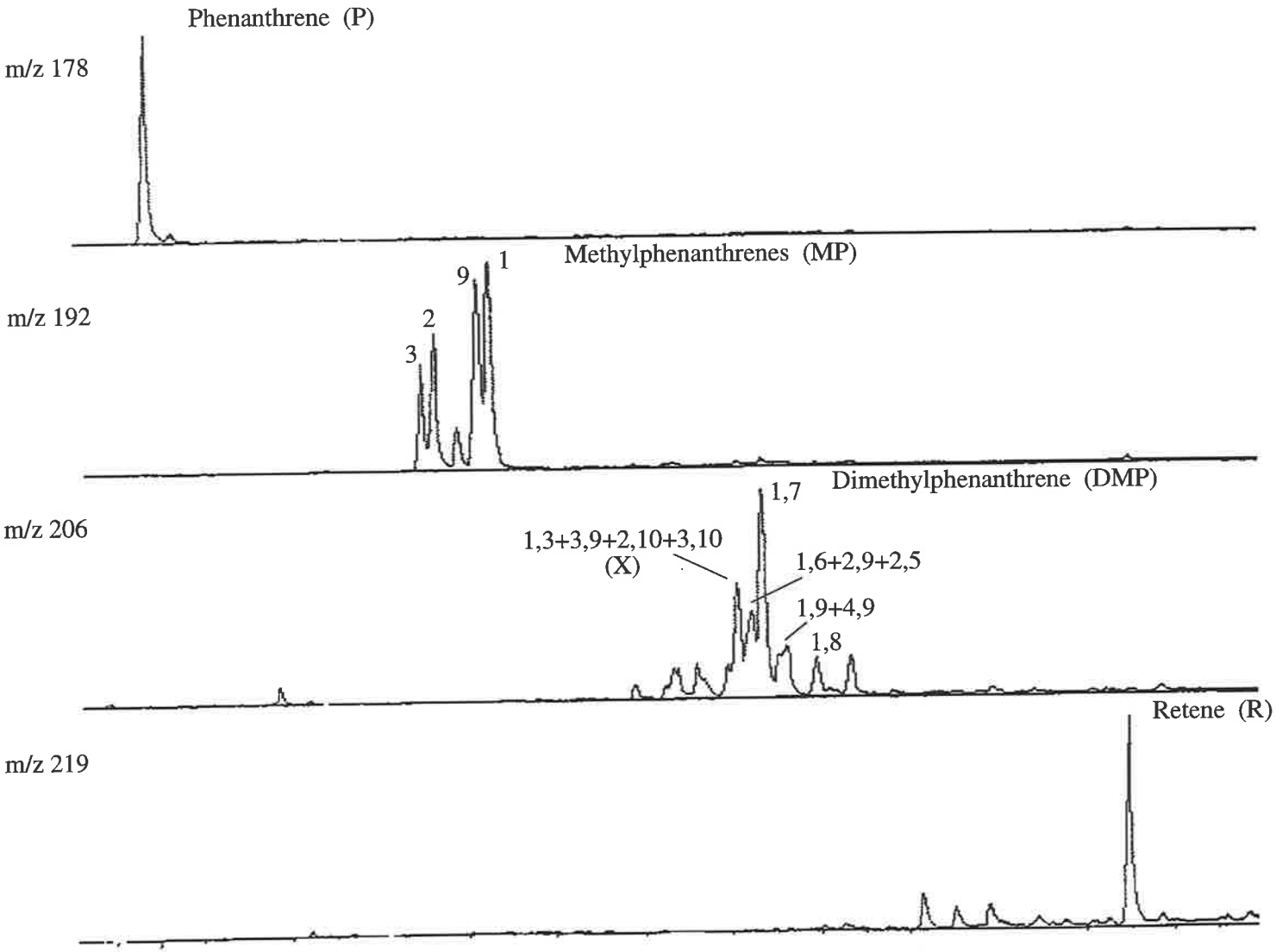


Figure 8.1b Mass fragmentograms of phenanthrenes and retene in a representative rock extracts of the Poolowanna Formation

Values range from 23% in coals at Sturt-6 to 37% in carbonaceous shale at Poolowanna-1. Extracts from the Poolowanna field have the highest average aromatics content (34%) followed by Tantanna (33%); Sturt (29%) and Sturt East (28%). The higher values in the Poolowanna Trough are likely to be due to differences in organic matter type (e.g. a higher vitrinite content in the DOM and the maturity of the Poolowanna Formation being higher here than in the Patchawarra Trough.

8.2.2 Aromatic fraction of crude oils

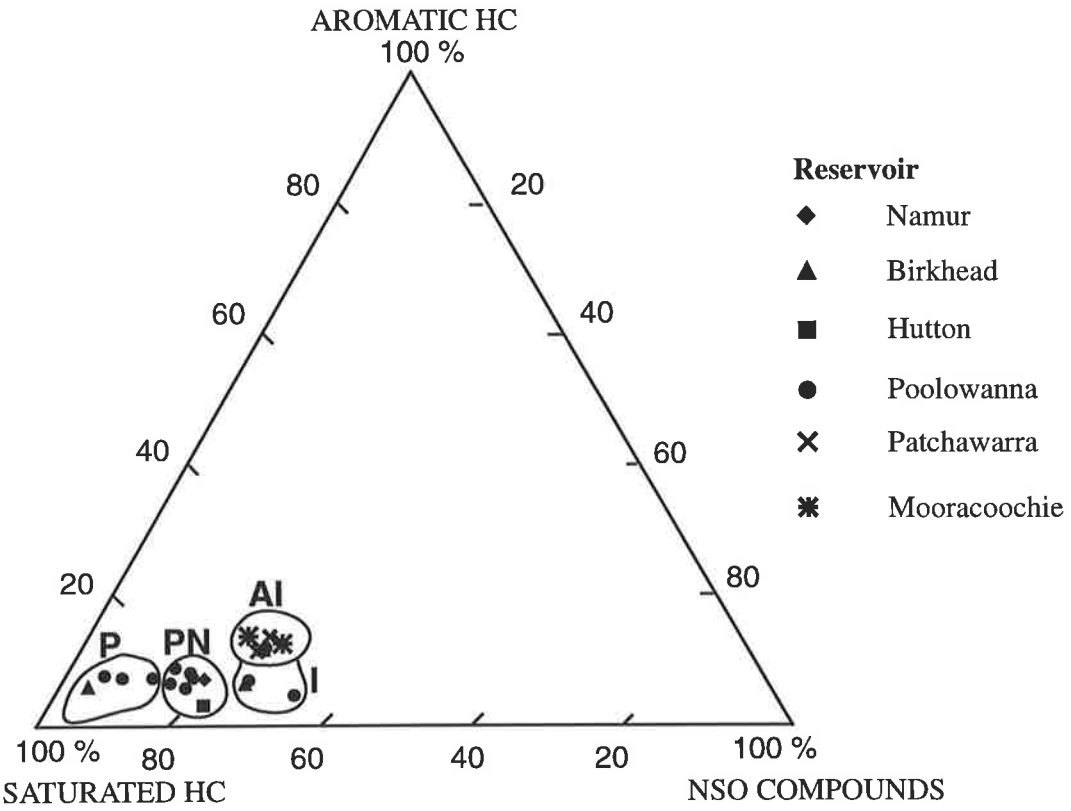
Comparison of comparing the gross chemical composition of the crude oils (Fig. 8.2) and the source rock bitumens (Fig. 5.4) reveals that the oils are depleted in aromatic hydrocarbon and NSO compounds, and enriched in saturated hydrocarbons, relative to the bitumens. This phenomenon has been observed elsewhere and attributed to fractionation effects during primary migration (Bray and Evans, 1965; Tissot and Pelet, 1971; Tissot and Welte, 1984; Leythaeuser *et al.*, 1984a). The reasons for such behaviour are that the aromatic hydrocarbons and NSO compounds, being more polar than the saturated hydrocarbons, interact more strongly with kerogen and mineral matrix of the source rock, and are therefore less easily expelled during the migration process.

8.3 Distribution of aromatic biomarkers in source rock extracts and crude oils

Various molecular parameters based on the di- and triaromatic biomarkers identified in source rock extracts of the Poolowanna Formation and crude oils from Poolowanna and Patchawarra Troughs are presented in Table 8.1. The relative abundance of the aromatic hydrocarbons in question was determined from their RIC traces or mass fragmentograms (Fig. 8.1a,b). These parameters provide information on the organic input, and in some cases depositional environment of the source rocks; the source affinity of the oils; and the thermal maturity of the source rocks and the oils.

8.3.1 Conifer-related biomarkers in the Poolowanna Formation

A group of four aromatic biomarkers, viz. 1,2,5-trimethylnaphthalene, 1,7-dimethylphenanthrene, 1-methylphenanthrene and retene (Fig. 1.7), can be related to the natural product precursors in the resins of modern Araucariaceae (Ruzicka and Hosking, 1930; Thomas, 1969). Such conifers of the kauri pine group assumed prominence for the first time in the Early to Middle Jurassic (Miller, 1977, 1982; Stewart, 1983). Therefore high concentrations of these compounds in Jurassic and Cretaceous source rock extracts may signify the input of araucarian organic matter. However, sources other than resins from the Araucariaceae have been reported. For example, 1,2,5-trimethylnaphthalene can be derived from pentacyclic triterpenoids (Strachan *et al.*, 1988) and retene from phyllocladane (Alexander *et al.*, 1987).



Oil Classification

P	Paraffinic
PN	Paraffinic-naphthenic
AI	Aromatic - Intermediate (aromatic HC > 10%)
I	Intermediate (aromatic HC<10%)

Figure 8.2 Gross composition of saturated hydrocarbons, aromatic hydrocarbons and NSO compounds in Jurassic, Permian and Cambrian oils (after, Tissot and Welte, 1984)

Moreover, upon maturation the 1,2,5-TMN compound reacts to give 1,3,6-TMN and other isomeric trimethylnaphthalenes (Strachan *et al.*, 1988). Therefore, the ratio 1,2,5-TMN/1,3,6-TMN (Table 8.1a) is dependent upon both source and maturity.

In the Poolowanna Trough 1,2,5-TMN/1,3,6-TMN values range from 0.81 at 2505 m, in Poolowanna-3 to 3.04 at 2417 m, in Poolowanna-1. The present maturation level of this section, is 0.72–0.82% R_O. A strong araucarian resin input is clearly indicated at the top of the Poolowanna Formation and decreases towards the base of the unit (Fig. 8.3a). In the Patchawarra Trough the values range from 0.21 at 1881 m in Sturt-4 to 12.5 at 1841 m in Sturt East-1. Here, a strong araucarian signature is again evident near the top of the Poolowanna Formation in the Tantanna (Fig. 8.3b) and Sturt/Sturt East Fields (Fig. 8.3c). It appears that in both the Patchawarra and Poolowanna Troughs a dominant Araucariaecean flora became established near the end of the deposition of the Poolowanna Formation. In early Poolowanna time, the major conifer group was the Cheirolepidiaceae (Alexander *et al.*, 1988).

Another araucarian marker, 1-methylphenanthrene (1-MP), is derived from abietic acid and sandarocopimaric acid-type natural products (Fig. 1.7). It has also been suggested to form during catagenesis by methyl-transfer reactions which favour the most reactive α-positions of phenanthrene (Albrecht *et al.*, 1976; Allan and Larter, 1983). Radke *et al.* (1986) suggested that the thermal stability of 9-methylphenanthrene (9-MP) is similar to that of 1-MP because in both the methyl group occupies an α-position in the phenanthrene molecule (Fig. 2.15). Therefore the ratio 1-MP/9-MP should be largely independent of thermal evolution. Rather, as suggested by Alexander *et al.* (1988), the 1-MP/9-MP values >1 are likely to indicate strong organic matter inputs from Araucariaecean flora. Such high values are therefore another marker for terrestrial organic matter of Middle Jurassic to Middle Cretaceous age.

The 1-MP/9-MP ratio ranges from 0.93 to 1.24 in the Poolowanna Trough samples, and from 0.83 to 1.43 in the Patchawarra Trough. Samples with 1-MP/9-MP values less than unity come from low in the Poolowanna Formation where the Araucariaceae were not yet a major part of the local flora. As in the case of the 1,2,5-TMN/1,3,6-TMN ratio, strong Araucariacean inputs are indicated near the top of the Poolowanna Formation in both troughs.

Table 8.1a Aromatic maturity and source-related biomarker parameters of source rock extracts, Poolowanna Formation

Sample	Well	Depth (m)	DNR-1	TNR-1	TNR-2	1,2,5-TMN / 1,3,6-TMN	MPI	Rc-1 (%)	Rc-2 (%)	1-MP / 9-MP	1,7-DMP / X	Retene / 9-MP	A+MA / P
POL1-1	Poolowanna-1	2417	2.16	0.74	0.65	3.04	0.55	0.73	0.61	1.24	1.91	0.11	0.03
POL1-3	Poolowanna-1	2438	3.20	0.96	0.82	1.55	0.65	0.79	0.68	0.93	0.89	0.02	0.06
POL1-5	Poolowanna-1	2499	3.35	0.96	0.71	0.84	0.63	0.78	0.66	1.01	1.02	0.05	0.00
POL2-9	Poolowanna-2	2524	2.60	0.77	0.75	1.24	0.61	0.76	0.65	1.20	1.26	0.03	0.00
POL3-13	Poolowanna-3	2505	3.85	1.00	0.80	0.81	0.65	0.79	0.67	0.98	0.82	0.02	0.00
TAN2-18	Tantanna-2	1799	1.65	0.68	0.75	7.41	0.36	0.61	0.47	1.43	3.41	0.32	0.08
TAN2-20	Tantanna-2	1811	nd	0.97	0.86	1.09	0.68	0.81	0.70	0.83	0.72	0.16	0.07
TAN3-21	Tantanna-3	1807	3.93	0.98	0.83	1.22	0.61	0.77	0.65	0.96	1.10	0.15	0.14
TAN8-25	Tantanna-8	1823	3.67	0.97	0.89	1.34	0.61	0.77	0.65	1.16	0.95	0.29	0.15
STU1-27	Sturt-1	1871	1.55	0.47	0.49	8.70	0.43	0.66	0.52	1.09	1.79	0.31	0.14
STU4-30	Sturt-4	1859	1.16	0.78	0.70	9.74	0.49	0.69	0.56	1.21	2.83	0.21	0.19
STU4-31	Sturt-4	1881	3.77	0.85	0.81	2.07	0.45	0.67	0.54	1.11	1.00	0.55	0.15
STU6-35	Sturt-6	1865	nd	1.00	0.85	2.68	0.79	0.87	0.77	1.22	1.03	0.04	0.42
STE1-38	Sturt East-1	1841	1.30	0.49	0.57	12.50	0.41	0.65	0.51	0.96	1.54	0.35	0.15
STE4-45	Sturt East-4	1862	nd	0.94	0.83	3.75	0.61	0.77	0.65	1.09	1.24	0.05	0.45

See Table 2.6 and 8.1c for key to parameters.
nd = not determined

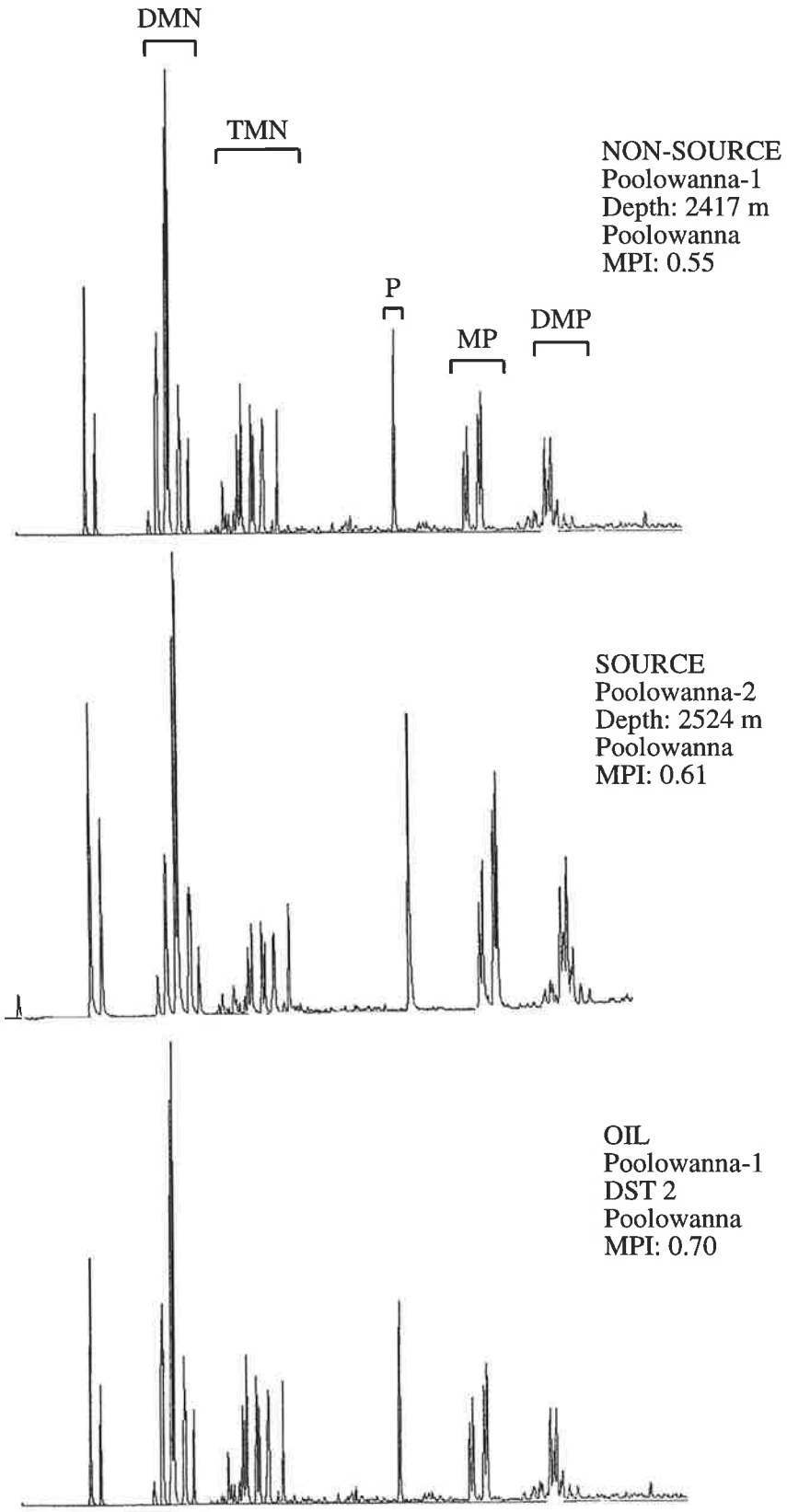


Figure 8.3a Comparison of aromatic hydrocarbons (RIC chromatograms) in source rock facies and oil from the Poolowanna Formation in the Poolowanna field, Poolowanna Trough

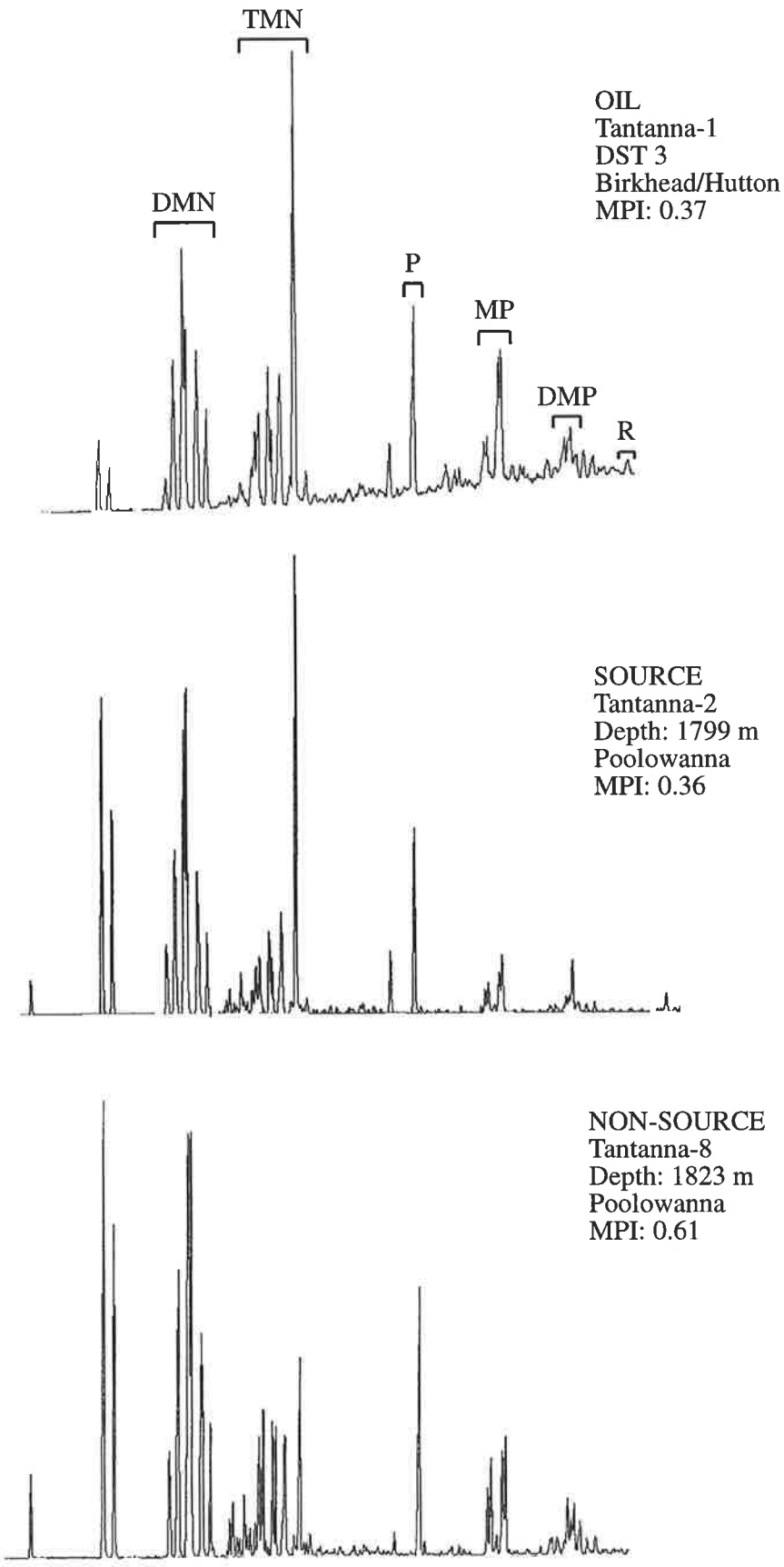


Figure 8.3b Comparison of aromatic hydrocarbon distributions (RIC chromatograms) in source rock facies (Poolowanna Formation) and oil in the Tantanna field, Patchawarra Trough.

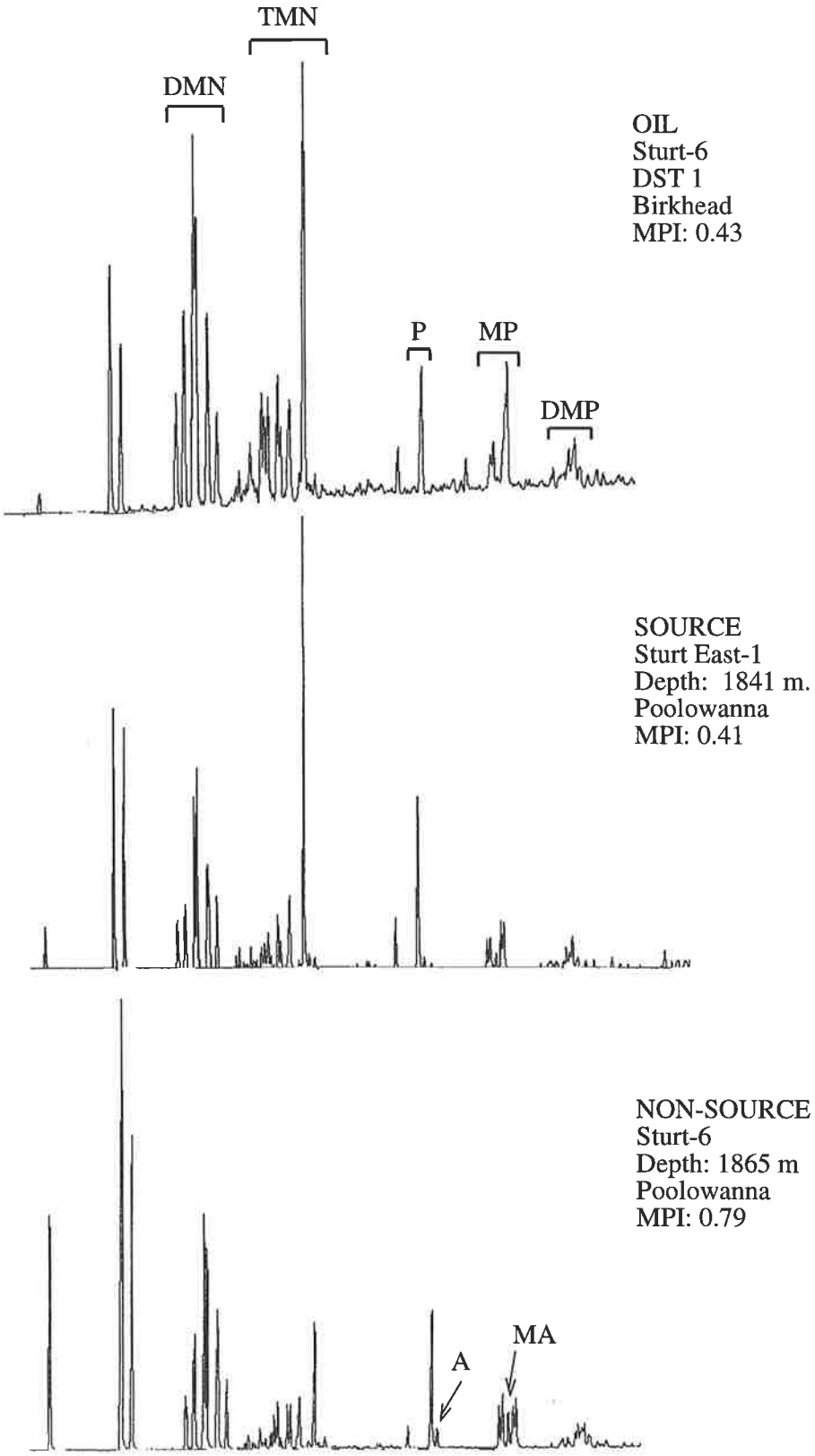


Figure 8.3c Comparison of aromatic hydrocarbon distributions (RIC chromatograms) in source rock facies (Poolowanna Formation) and oils in the Sturt and Surt East fields Patchawarra Trough.

The effectiveness of these two parameters was assessed using a log-log cross-plot (Fig. 8.4). It is apparent from this plot that two thirds of the samples analysed (all from the upper part of the Poolowanna Formation) have biomarker signatures characteristic of an Araucariacean flora. Those samples plotting just within the Permian zone are from low in the formation and predate this flora. As a result of this study, 1,2,5-TMN/1,3,6-TMN values <1.8 and 1-MP/9-MP value >1 are taken to indicate samples lacking a significant input from Araucariacean flora (Alexander *et al.*, 1988). Therefore strong Araucariacean inputs are demonstrated for the samples plotting in quadrant III of Figure 8.4.

Minor concentrations of retene occur in association with substantially higher concentrations of the structurally related abietic acid (Simoneit, 1977), dehydroabietic acid, methyldehydroabietate and dehydroabietane in forest soil (Swan, 1965; LaFlamme and Hites, 1978). Therefore, its major precursors were suggested to be natural products of the Araucariaceae flora, (Wakeham *et al.*, 1980b) (Fig. 2.13). However, sources other than abietic acid have been reported in resin constituents belonging to the pimarane skeletal type (Thomas, 1969; Hanson, 1972). Another potential source of retene in sediments is the combustion of coniferous wood (Ramdahl, 1983).

The retene/9-MP ratio is another molecular indicator of the relative input to the Poolowanna Formation by Araucariacean flora provided that the main source of retene is the abietic acid (Alexander *et al.*, 1988). The ratio has values ranging from 0.02 to 0.11 in the Poolowanna Trough samples, and from 0.04 to 0.55 in those from the Patchawarra Trough (Table 8.1a). The, higher abundance of retene in the latter samples is possibly related to higher inputs of araucarian plant remains in the Patchawarra Trough than in Poolowanna Trough.

Once again, the highest values of an araucarian marker are shown near the top of the Poolowanna Formation in the Poolowanna and Tantanna fields, whereas the lowest values occur near the base of the unit in Sturt-6 (1865 m) and Sturt East-4 (1862 m). However, the highest retene/9-MP value of 0.55 is shown by the deepest sample (Sturt-4,1881 m) in Sturt field. In this case the enhancement of retene is probably not related to Araucariacean resin input.

Pimanthrene (1,7-dimethylphenanthrene) is thought to be derived from pimaric acid (Wakeham *et al.*, 1980b). As in the case of abietic acid versus retene, the pimaric acid of kauri pine resin may not be an unequivocal precursor of pimanthrene because many other resin constituents are known to belong to the pimarane skeletal type. The presence of these compounds, however, may signify the contribution of organic matter from Araucariacean flora.

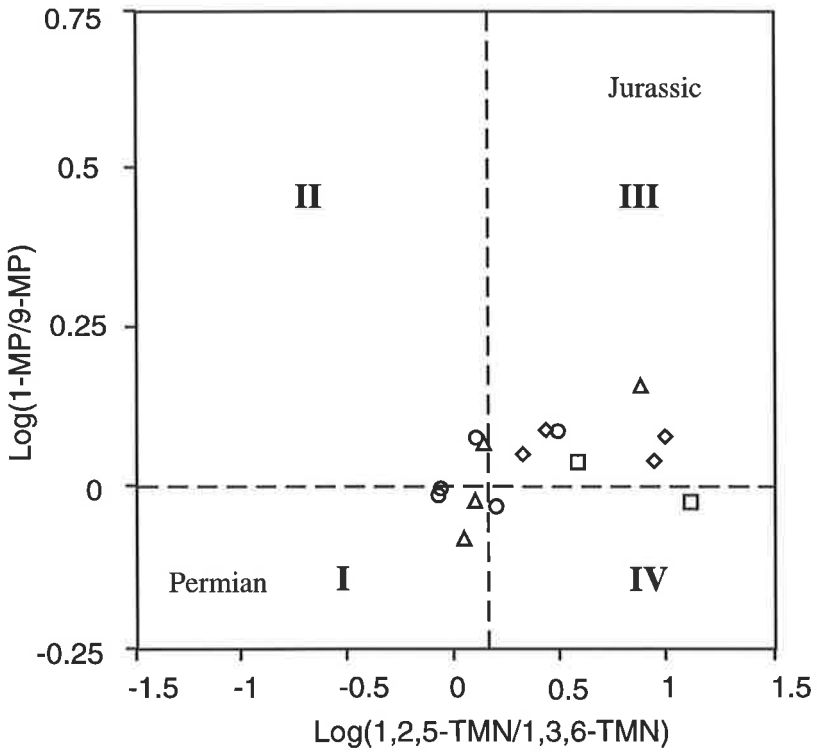


Figure 8.4 Aromatic biomarker signatures of Poolowanna Formation source rocks based on isomeric methylphenanthrenes and trimethylnaphthalenes

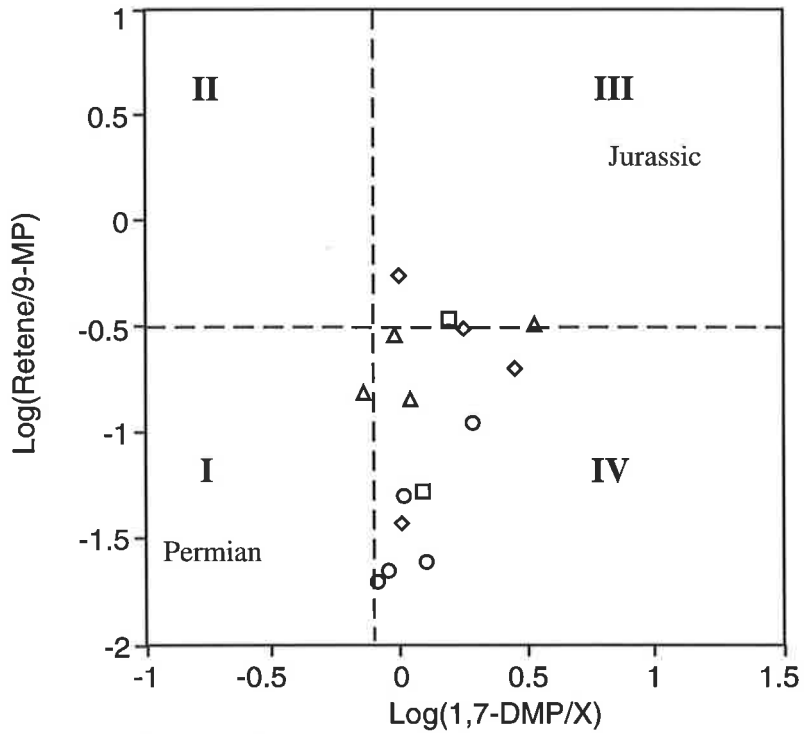


Figure 8.5 Aromatic biomarker signatures of Poolowanna Formation source rocks based on retene, and isomeric dimethylyphenanthrenes (Key as for Fig. 8.4)

The peak labelled 'X' (Fig. 8.1b) in the mass fragmentograms of alkylphenanthrene homologues represents an unresolved mixture of 1,3-, 3,9-, 2,10- and 3,10-dimethylphenanthrene isomers (Radke *et al.*, 1986) which are thought to be products of thermal maturation. Therefore, the 1,7-DMP/X ratio may also be used to determine the relative input from Araucariacean flora (Alexander *et al.*, 1988).

Like the preceding parameters, the 1,7-DMP/X ratio shows its highest values near the top of the Poolowanna Formation and relatively low values near the base of the unit (Table 8.1a). The values range from 0.82 at 2505 m, in Poolowanna-3 to 1.91 at 2417 m in Poolowanna-1 in the Poolowanna Trough; and from 0.72 at 1811 m in Tantanna-2 to 3.41 at 1799 m in the same well in the Patchawarra Trough. This parameter happens to be most consistent in the Patchawarra Trough where, in every well, the values decrease with increasing depth, hence signifying the relative increase of Araucariacean-related organic matter up section in the Poolowanna Formation.

In the log-log cross-plot of the retene and 1,7-DMP-based biomarker parameters (Fig. 8.5) most of the samples plot in quadrant IV. Only one sample plots in the Permian zone and several Patchawarra Trough samples plot in the Jurassic zone designated by Alexander *et al.* (1988). It is apparent from Figures 8.4 and 8.5 that the Poolowanna Formation occupies a transitional zone between the Permian and Jurassic compositional fields (quadrants I and III, respectively). Only those samples from the upper part of the formation (i.e. of early Middle Jurassic age and deposited after the first appearance of the Araucarian flora) display the characteristic Jurassic biomarker signatures.

8.3.2 Oil source affinity

The aromatic biomarker parameters of the oils are given in Table 7.2b and their source affinity is illustrated in Figures 8.6 and 8.7. The values of 1,2,5-TMN/1,3,6-TMN range from 0.07 in the Sturt-6 (Patchawarra) oil to 10.0 in the Tantanna-1 (Hutton) oil. The Permian and Cambrian oils have values <1, therefore indicating that their source rock had insignificant Araucariacean organic matter input. Most of the Jurassic (Eromanga Basin) oils have values >1, indicating strong inputs of Araucariacean flora to their respective source rocks. The low value (0.83) shown by the Poolowanna-1 (Poolowanna) oil is consistent with its derivation from a source rock in the lower Poolowanna Formation as discussed in the previous section.

Table 8.1b Aromatic maturity and source-related biomarker parameters of oils from the Poolowanna and Patchawarra Troughs

Sample No.	Well	FORMATION	DST No.	Depth (m)	DNR-1	TNR-1	TNR-2	1,2,5-TMN / 1,3,6-TMN	MPI	Rc-1	Rc-2	1-MP / 9-MP	1,7-DMP / X	Retene / 9-MP	A+MA / P
P1	Poolowanna-1	Poolowanna	2	2504-2538	4.10	0.75	0.70	0.83	0.70	0.82	0.71	1.20	1.02	0.09	0.00
T2	Tantanna-1	Poolowanna	1	1800-1814	nd	1.05	0.93	1.03	0.81	0.88	0.78	0.82	0.65	0.38	0.08
T3	Tantanna-1	Hutton	2	1635-1642	nd	0.71	0.80	10.00	0.41	0.64	0.50	1.49	1.01	3.94	0.02
T4	Tantanna-1	Birkhead/Hutton	3	1347-1359	nd	0.52	0.63	5.06	0.37	0.62	0.48	1.08	1.20	2.76	0.04
S11	Sturt-3	Poolowanna	1A	1848-1855	1.84	0.48	0.62	4.64	0.48	0.69	0.56	1.15	1.11	1.04	0.18
S12	Sturt-3	Birkhead	1B	1654-1662	2.06	0.22	0.37	9.00	0.23	0.54	0.38	5.00	2.86	5.43	0.08
S13	Sturt-4	Poolowanna	1	1872-1880	nd	0.59	0.69	1.91	0.60	0.76	0.64	0.99	0.87	0.62	0.15
S16	Sturt-6	Mooracoochie	5	1914-1919	nd	0.84	0.86	1.26	0.88	0.93	0.84	0.78	0.51	0.54	0.07
S17	Sturt-6	Patchawarra	3	1884-1898	nd	0.89	0.91	0.07	0.94	0.96	0.88	0.84	0.53	1.20	0.04
S18	Sturt-6	Birkhead	1	1883-1892	nd	0.59	0.69	4.33	0.43	0.66	0.52	1.58	13.20	1.13	0.05
S19	Sturt-7	Patchawarra	1	1923-1938	nd	0.74	0.87	0.92	0.83	0.90	0.80	0.79	0.49	0.20	0.04
S20	Sturt-7	Mooracoochie	2	1946-2021	nd	0.51	0.65	0.78	0.71	0.83	0.72	0.66	0.39	0.31	0.06
S21	Sturt-7	Poolowanna	3	1871-1876	nd	0.64	0.69	2.35	0.57	0.74	0.62	1.22	0.79	0.93	0.09
S23	Sturt-8	Poolowanna	1	1880-1884	1.21	0.59	0.70	2.00	0.57	0.74	0.62	0.99	0.87	1.88	0.23
SE24	Sturt East-2	Poolowanna	1	1845-1899	3.20	0.71	0.78	1.75	0.58	0.75	0.63	1.45	0.99	0.95	0.21
TAL25	Taloola-2	Poolowanna	1	1829-1836	nd	0.62	0.77	1.17	0.68	0.81	0.70	1.10	0.75	0.60	0.16
TAL26	Taloola-2	Hutton	2	1789-1793	nd	0.60	0.73	1.95	0.57	0.74	0.62	1.13	0.67	0.65	0.21
TAL27	Taloola-2	Namur	3	1384-1397	nd	0.52	0.61	4.23	0.37	0.62	0.48	1.45	1.30	2.56	0.04

See Table 2.6 and 8.1c for key to parameters
nd = not determined

The 1-MP/9-MP values range from 0.66 in the Sturt-7 (Mooracoochie) oil to 5.0 in Sturt-3 (Birkhead) oil. The Permian oils appear to lack any significant Araucariacean input (1-MP/9-MP = 0.66-0.84), whereas most of the Jurassic oils are indicated to have an Araucariacean source affinity which ranges from weak in the Tantanna-1 (Birkhead/Hutton) oil (1-MP/9-MP = 1.08) to very strong in the Sturt-3 (Birkhead) crude (1-MP/9-MP = 5). The Tantanna-1 (Poolowanna) crude is the only oil from a Jurassic reservoir with a 1-MP/9-MP value <1 . This indicate either that it is of mixed Permian and Jurassic origin, or that it was derived entirely from the lower Poolowanna Formation source facies. The distinction between oils of Permian and Jurassic origin is clearly illustrated in Figure 8.6. All the Permian and Cambrian-reservoired oils plot in quadrant I; while most of the Jurassic oils plot in quadrant III. Oils of possible mixed source affinity plot in the borderline region between these two quadrants. These oils are all from Poolowanna reservoirs, making it more likely that they originated from source beds of late Early Jurassic age in the lower Poolowanna Formation.

The 1,7-DMP/X values range from 0.39 in the Sturt-7 (Mooracoochie) to 13.2 in the Sturt-6 (Birkhead) crude. It is again demonstrated that the Permian and Cambrian oils are characterised by low values (0.39–0.51) and are therefore genetically unrelated to the Araucariaceae. Most of the Jurassic oils have 1,7-DMP/X values >1, but quite a number from Poolowanna reservoirs and the Taloola-2 (Hutton) oil show values <1. These low values may indicate either a mixed oil charge from adjacent Permian and Jurassic source rocks, or just derivation from, pre-Araucariacean Jurassic source rocks.

The retene/9-MP values of the oils range from 0.20 in the Sturt-7 (Patchawarra) crude to 5.43 in the Sturt-3 (Birkhead) sample. The Permian and Cambrian oils appear to have values at the low end of the range, with the exception of the Sturt-6 (Patchawarra) crude which has a value of 1.20. This enhanced value may be due to a local alternative source of retene, possibly phyllocladane. It is significant that this oil is the most mature sample analysed (MPI = 0.94: Table 8.1b) It is also shown that most of the Jurassic oils show values >0.3, consistent with the lower limit of the Jurassic zone in Figure 8.7. In this cross-plot the Jurassic oils are more poorly discriminated from Permian and Cambrian oils than in Figure 8.6; and the Poolowanna oils once again tend to plot in between those in the Permian and younger Jurassic reservoirs.

8.3.3 Comparison of oils in stacked reservoirs

The contrasting source affinities of oils in the wells containing stacked reservoirs are illustrated by the log-log cross-plot of the 1-MP/9-MP and 1,2,5-TMN/1,3,6-TMN ratios (Fig. 8.8).

Table 8.1c Abbreviations of aromatic compounds and definitions of aromatic maturity parameters (also see Table 2.6)

Abbreviation	Name	Definition
TMN	Trimethylnaphthalene	
P	Phenanthrene	
A	Anthracene	
MA	Methylanthracene	
MP	Methylphenanthrene	
DMP	Dimethylphenanthrene	
X	1,3-DMP + 3,9-DMP + 2,10-DMP + 3,10-DMP	
MPI	$\frac{1.5[2\text{-MP} + 3\text{-MP}]}{P + 1\text{-MP} + 9\text{-MP}}$	
R_c-1	Calculated reflectance	0.60 MPI + 0.40 (for R_o <1.35%)
R_c-2	Calculated reflectance	0.7 MPI + 0.22 (for R_o <1.7%)

It is apparent shown from this plot that oils from different reservoirs within the same well have different biomarker signatures, an indication of them not having a common source or origin. On the other hand, oils from the same reservoir unit in different wells display similar molecular signatures (Table 8.2).

Tantanna-1 Oils from the Poolowanna, Hutton and Birkhead reservoirs (Fig. 8.9a) are represented in this well. The Poolowanna oil plots in the Permian zone and is quite different from the Hutton and Birkhead/Hutton oils which are clearly of Jurassic origin. In the well correlation diagram for this field (Fig. 1.4b) it can be seen that the Poolowanna oil was recovered from near the base of Poolowanna Formation. Therefore it is almost certain that this oil has migrated from an underlying Permian source particularly in view of its relatively high maturity (MPI = 0.81). The other oils were generated from Jurassic source rocks, most likely from within the upper Poolowanna Formation (Fig. 8.3b).

Table 8.2 Source-dependent biomarker signatures in oils from the Sturt Field, Patchawarra Trough

Reservoir	Pr/Ph	1,2,5-TMN / 1,3,6-TMN	1-MP / 9-MP	Well
Birkhead	6.9	9.0	5.0	Sturt-3
	6.8	4.3	1.6	Sturt-6
Poolowanna	5.4	4.6	1.2	Sturt-3
	6.8	2.4	1.2	Sturt-7
Patchawarra	6.3	0.1	0.8	Sturt-6
	5.7	0.9	0.8	Sturt-7
Mooracoochie	6.0	1.3	0.8	Sturt-6
	1.3	0.8	0.7	Sturt-7
Jurassic source (Alexander *et al.*, 1988)		>1.5	>1.0	

Sturt-3 The oils recovered from the Birkhead and Poolowanna reservoirs in this well both plot in the Jurassic zone of Figure 8.8. Although they are both of Jurassic origin it is obvious that they have different sources. Because the Birkhead oil has a much higher 1-MP/9-MP value its source had a much stronger Araucariacean input than that of the Poolowanna oil. Hence it is likely that the Birkhead crude was generated from a local Birkhead source rock whereas the Poolowanna oil originated from the upper Poolowanna source facies.

Sturt-6 This well produced oils from reservoirs in the Birkhead and Patchawarra Formations and the Mooracoochie Volcanics (Fig. 8.9b). The Birkhead oil is well separated from the Permian and Cambrian oils in Fig. 8.8 and has a molecular signature similar to that of an upper Poolowanna Formation source rock (Fig. 8.3c). At the same time the Patchawarra oil appears to differ from the Cambrian oil by having a much lower 1,2,5-TMN/1,3,6-TMN value, indicating their origin two different Permian source facies.

Sturt-7 Oils occur in Cambrian (Mooracoochie), Permian (Patchawarra) and Jurassic (Poolowanna) reservoirs in this well. The Permian and Cambrian oils are well separated from the Jurassic oil in Figure 8.8 and, hence are indicated to be of different origin. The Cambrian oil in this case is also distinguished by its very low pr/ph value (Table 8.2) and is clearly not of Permian higher plant origin. A Cambrian marine algal source affinity seems likely (Fig. 7.10).

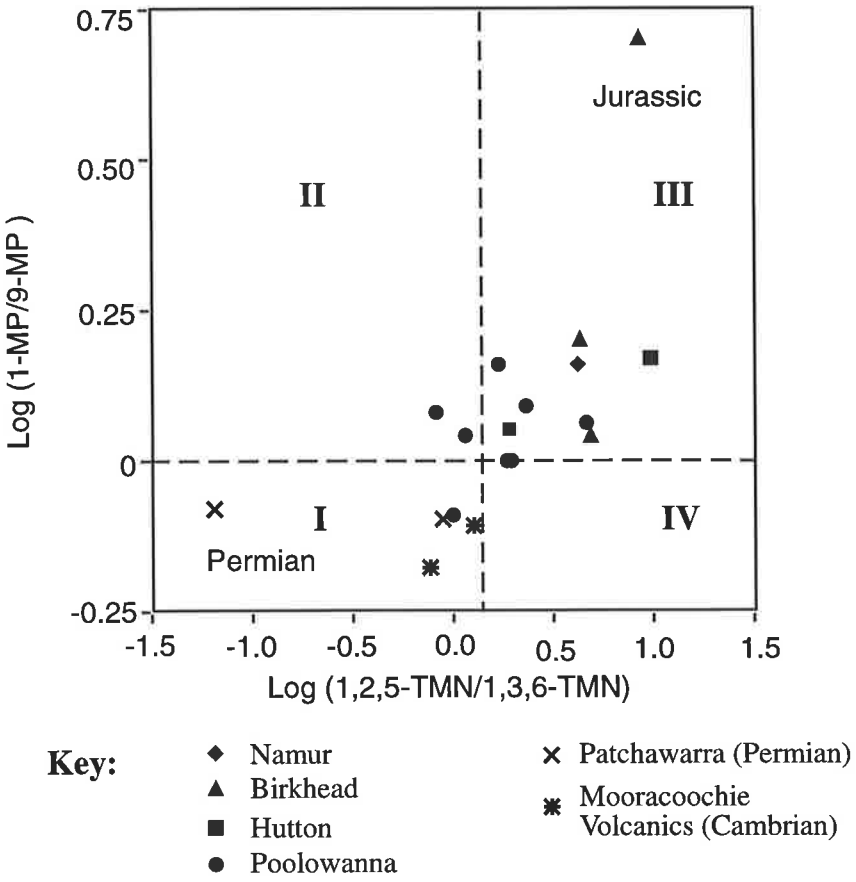


Figure 8.6 Oil source affinity based on isomeric methylphenanthrenes and trimethylnaphthalenes

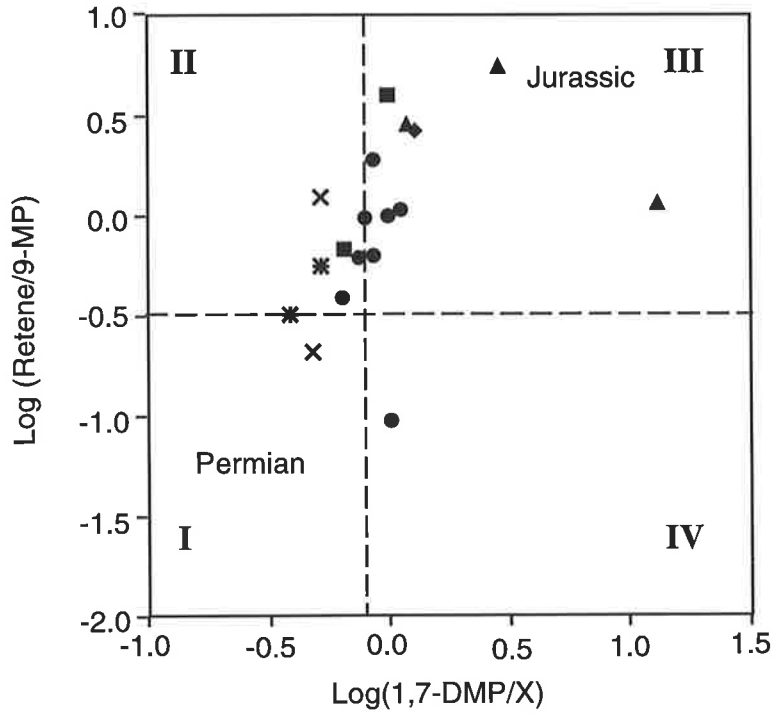
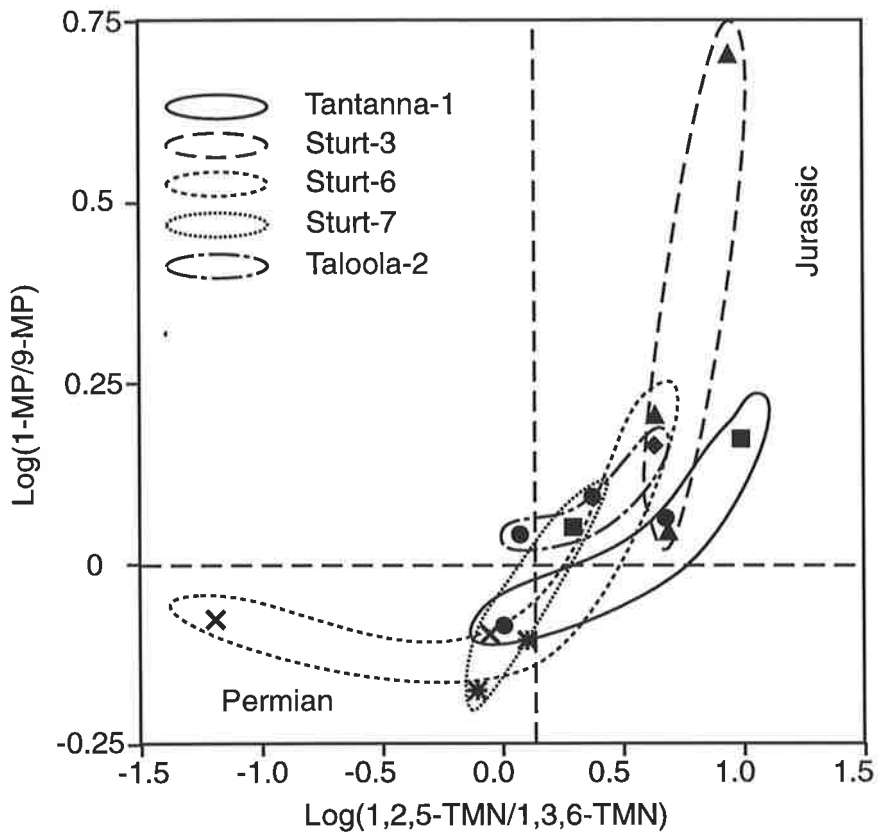


Figure 8.7 Oil source affinity based on retene and isomeric dimethylphenanthrenes (Key as in Fig. 8.6)



Reservoir

- Namur
- Birkhead
- Hutton
- Poolowanna

} Jurassic

- Patchawarra (Permian)
- Mooracoochie Volcanics (Cambrian)

Figure 8.8 Source affinity of oils in the stacked reservoirs of five wells in the Sturt, Tantanna and Taloola fields

Taloola-2 This well flowed oils from the Namur, Hutton and Poolowanna reservoirs. Here, the Poolowanna oil plots between the Permian and Jurassic quadrants of Figure 8.8 and, therefore is likely to be of mixed Permian/Jurassic origin, or to have been sourced from the lower Poolowanna Formation. The Hutton and Namur oils are indicated to be of Jurassic source affinity.

8.4 Source rock and oil maturity based on aromatic molecular parameters

Aromatic molecular parameters used in the determination of source rock and crude oil maturity include MPI (Radke and Welte, 1983), DNR-1 (Radke *et al.*, 1982b), TNR-1 (Alexander *et al.*, 1985) and TNR-2 (Radke *et al.*, 1986). Their behaviour with respect to thermal evolution is discussed in Section 2.7.2.

8.4.1 Source rock maturity assessment

The parameters % R_C-1 and % R_C-2 (Table 8.1a) denote calculated vitrinite reflectance based on the respective calibrations of MPI by Radke and Welte (1983) and Boreham *et al* (1988) (Table 8.1c). In the case of the Poolowanna Formation, the R_C-1 values overall appear to be somewhat higher than measured reflectance, whereas the R_C-2 values are slightly lower (Fig. 6.8a).

In the Poolowanna Trough, there is good agreement between the R_C-1 values of the Poolowanna Formation (0.73–0.79%) and corresponding measured reflectance values (R_O = 0.75–0.79 %). However, in the Patchawarra Trough, it is the R_C-2 values (in the range 0.47-0.77%) that more closely match the measured vitrinite reflectance (R_O = 0.57–0.67%). This suggests that no single calibration of MPI is appropriate for both the Poolowanna Trough and the Patchawarra Trough. Possibly there are significant differences in the burial and thermal histories of the Poolowanna Formation between these two depocentres.

The DNR-1 values range from 1.16 at 1859 m in Sturt-4 to 3.85 at 2505 m in Poolowanna-3 (Table 8.1a). These values correspond to measured vitrinite reflectances of 0.64% and 0.79% R_O, thus showing a good correlation between these two parameters. However, samples, from 1807 m in Tantanna-3, 1823 m in Tantanna-8, and 1881 m in Sturt-4, with measured vitrinite reflectance values of 0.62%, 0.58% and 0.57%, have DNR-1 values of 3.93, 3.67 and 3.77, respectively. In this case the dimethylnaphthalene ratios indicate a higher maturity than that derived from vitrinite reflectance. Coincidentally, these samples happen to be of the silty coal and coal facies (Table 1.2), and therefore this ratio may be influenced by the type of organic matter or its depositional environment. Even so, DNR-1 appears to be a reliable maturity parameter for the Poolowanna sequence in Sturt-4 (Fig. 8. 10). Generally the Poolowanna Trough source rocks seem to be characterised by DNR-1 values >2, whereas in the Patchawarra Trough the values extend over a wider range (1.3–3.93) and are likely not to be related only to maturity.

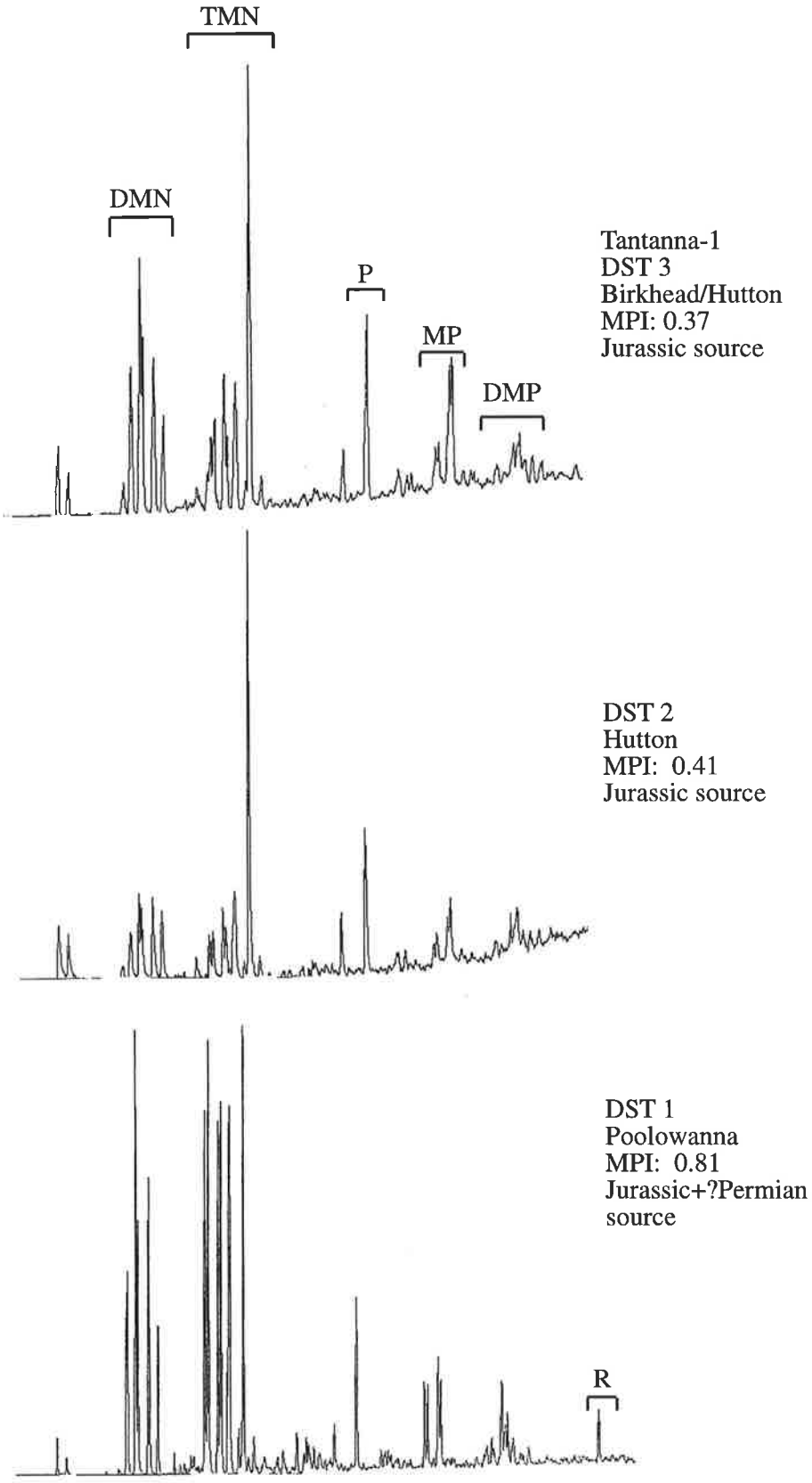


Figure 8.9a Comparison of oils in stacked reservoirs at Tantanna-1 based on their aromatic RIC chromatograms

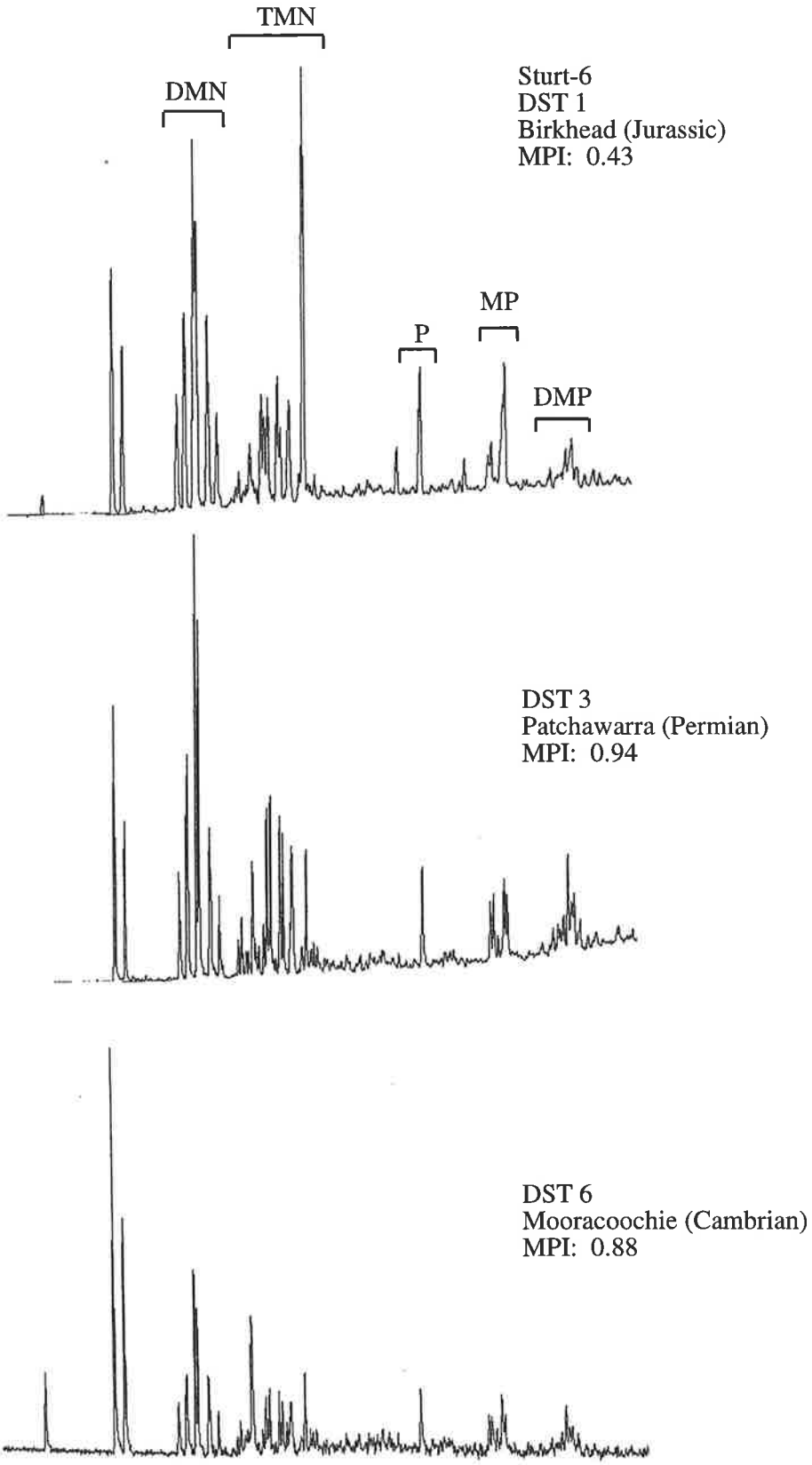


Figure 8.9b Differentiation of Jurassic from non-Jurassic oils in stacked reservoirs at Stur-6 based on their aromatic RIC chromatograms

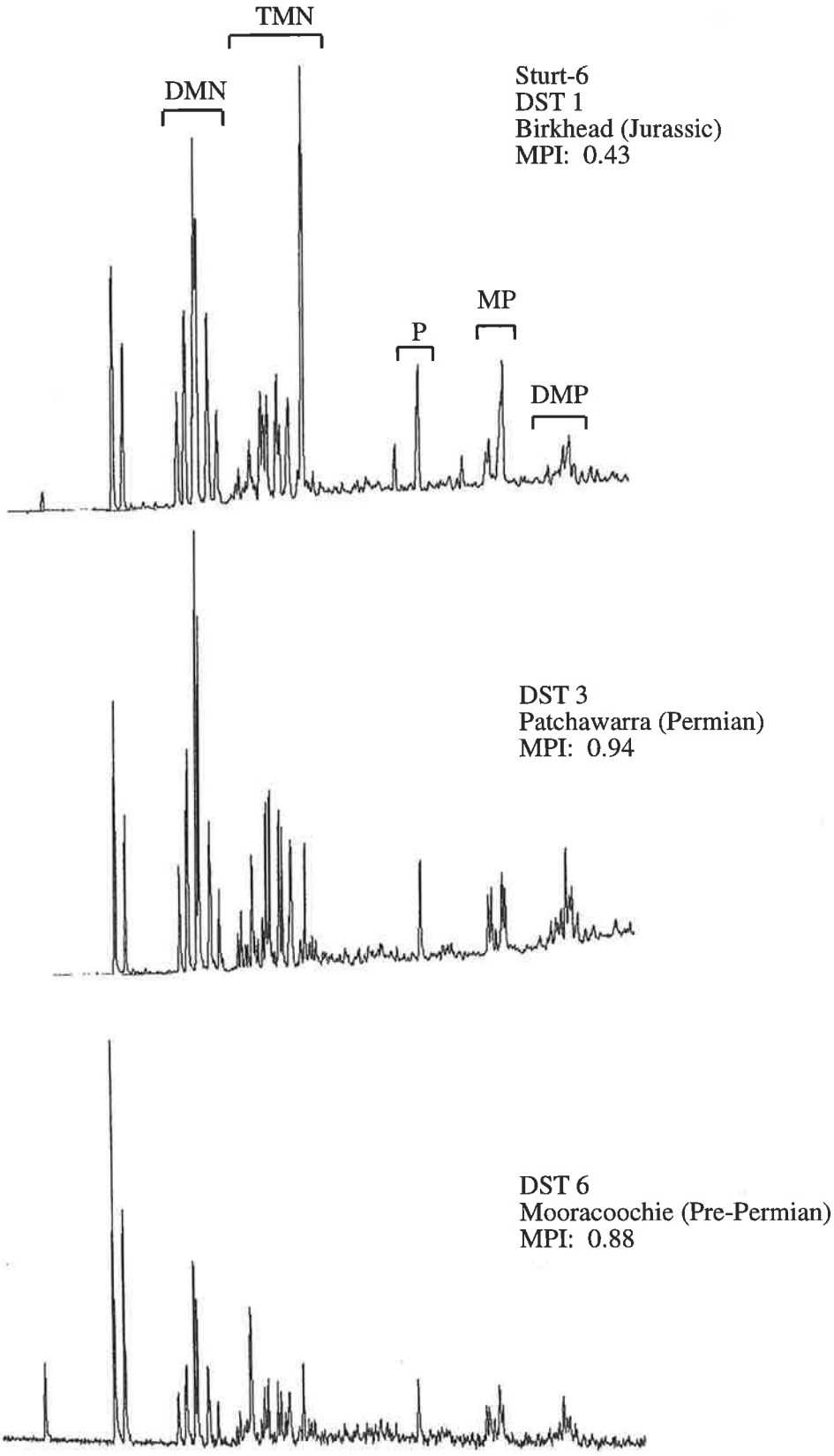


Figure 8.9c. Differentiation of Jurassic from non-Jurassic oils based on aromatic biomarkers in the stacked Sturt-6 oil reservoirs

The TNR-1 values range from 0.47 at 1871 m in Sturt-1 to 1.00 at 2505 m in Poolowanna-3 (Table 8.1a). Like DNR-1, this parameter show some correlation with Ro but also seems to be influenced by organic facies.

This is verified by early mature coal samples at 1865 m in Sturt-6, 1881 m in Sturt-4, 1823 m in Tantanna-8, 1807 m in Tantanna-3 and 1862 m in Sturt East-4 which have TNR-1 values between 0.85 and 1.00 while their corresponding R_O is between 0.57 and 0.66%. On the other hand the Poolowanna Trough carbonaceous shales show a rather good correlation between TNR-1 and R_O values. Both DNR-1 and TNR-1 appear to correlate well as illustrated by Figure 8.9. Some of the coal samples plot in the mature zone although they are of relatively low maturity according to their measured vitrinite reflectance. Either the measured vitrinite reflectance was suppressed by bituminite dissemination in vitrinite, in which case DNR-1 and TNR-1 are the more reliable maturity indicators, or the elevated values of the aromatic parameters are due to differences in organic input and/or depositional conditions.

8.4.2 Oil maturity assessment

The molecular maturity parameters based on the aromatic hydrocarbon fraction of the crude oils are shown in Table 8.1b. The MPI values of the analysed samples fall in the range 0.23–0.94, corresponding to R_C-2 values of 0.38–0.88%. Assuming that these oils are generated from source rocks with a similar kerogen type, (Section 2.7.2.1), it is clear that the oils in Permian and Cambrian reservoirs are more mature (R_C-2 = 0.72–0.88%) than those in Jurassic reservoirs (0.48–0.71%). An exception is the Tantanna-1 (Poolowanna) oil which has an R_C-2 value of 0.78%. It is very likely that this oil is of Permian origin (see also Fig. 8.13).

Recognising that the R_C values of oils correspond to the maturity of their source beds at the time of expulsion, the observed Rc values may reflect the type of kerogen responsible for oil generation. This is because different kerogens expel oils at different maturation levels. As explained by Radke (1987), the oils with R_C values ranging from 0.5 to 0.7% are paraffinic, commonly waxy, and have low sulphur contents. They are derived from liptinite-rich lacustrine Type I kerogen and thus are known as Type I oils. However, Radke (1987) also points out that these oils are strikingly similar to the bitumen in source rocks containing immature Type III kerogen. Non-marine oils with R_C values in the range 0.75–0.9% were assigned to either the Type II/III or Type III/II category. In the present study most of the oils in Jurassic reservoirs of the Eromanga Basin were generated by Jurassic source rocks containing early mature to mature Type II/III kerogen. The Tantanna-1 (Poolowanna) oil, and those oils in Permian and Cambrian reservoirs, are indicated to be generated from more mature Type II/III or Type III/II kerogens (Table 8.3).

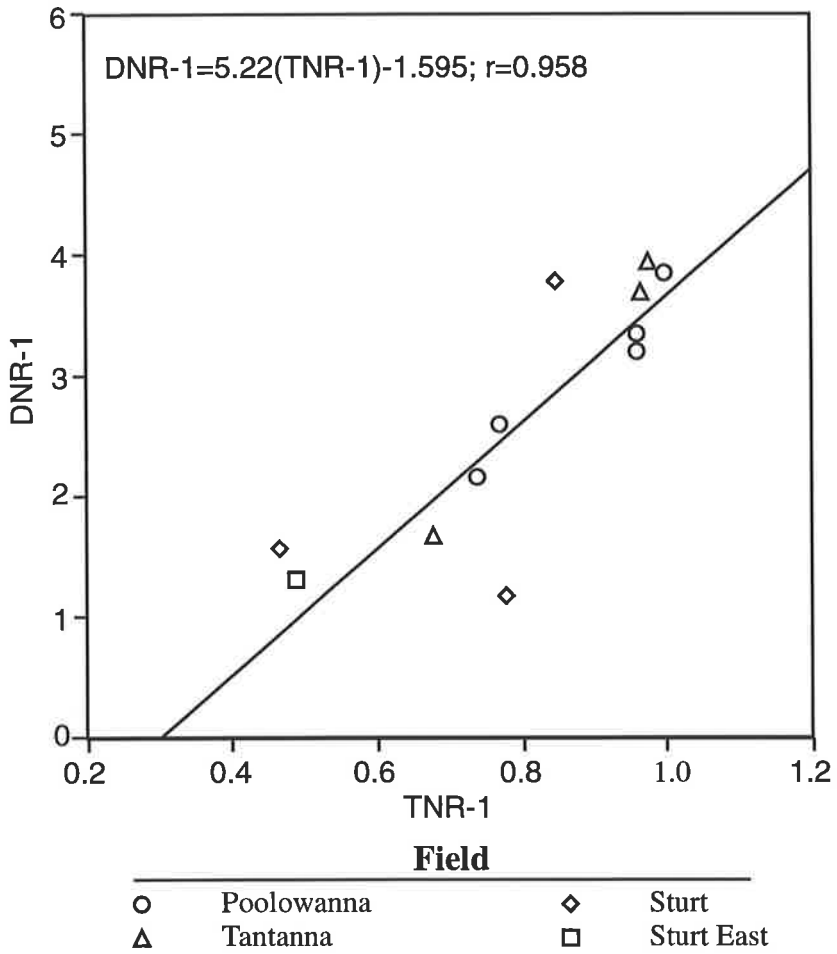


Figure 8.10 Relationship between the dimethylnaphthalene ratio (DNR-1) and the trimethylnaphthalene ratio (TNR-1) in source rocks of the Poolowanna Formation

The Poolowanna-1 (Poolowanna) oil, while almost certainly derived from a local lower Poolowanna source facies, is the most mature of indigenous Jurassic crudes (R_C-1 = 0.82%). R_C-1 is the preferred measure of this oil's maturity because R_C-1 gives a better correlation with measured vitrinite reflectance (R_O) in the source rocks of the Poolowanna Trough (see Section 8.4.1).

Table 8.3 Oil families based on aromatic maturity and source affinity parameters

Rc %	Reservoir[1]	Well	DST	Kerogen type	Possible source(s)[2]
< 0.55	Birkhead	Sturt-3	1B	Resinite-rich	1
	Namur	Taloola-2	3	Type II/I	1
	Birkhead/Hutton	Tantanna-1	3		1
	Hutton	Tantanna-1	2		1, 2
	Birkhead	Sturt-6	1		1
0.56 - 0.64	Poolowanna	Sturt-3	1A	Early mature	2
	Hutton	Taloola-2	2	Type II/III	1, 2
	Poolowanna	Sturt-7	3		2
	Poolowanna	Sturt-8	1		3
	Poolowanna	Sturt East-2	1		3
	Poolowanna	Sturt-4	1		3
0.70 - 0.72	Poolowanna	Taloola-2	1	Type II/III	3, 4
	Mooracoochie	Sturt-7	2		5
0.78 - 0.88	Poolowanna	Tantanna-1		Type III/II	4
	Patchawarra	Sturt-7	1		4
	Poolowanna	Poolowanna-1	2		3
	Mooracoochie	Sturt-6	5		4
	Patchawarra	Sturt-6	3		4

1. Oils listed in order of increasing maturity (R_C-2; except for Poolowanna-1, DST 2 where R_C-1 value used).
2. Identified by age, as follows: 1 = Middle Jurassic (Birkhead); 2 = Middle Jurassic (upper Poolowanna); 3 = Early Jurassic (lower Poolowanna); 4 = Permian; 5 = Cambrian

Some oils particularly those in the Namur and Birkhead reservoirs, have very low R_C-2 values (<0.55%), which are possibly not a reliable indication of their true maturity. Thus the observed R_C-2 values in this low range are probably due to enrichment of 1-methyl-phenanthrene in the expelled oil. Anomalously high 1-MP/9-MP ratios have been found in other Birkhead-derived oils and source rocks (D. M. McKirdy, pers. comm., 1997).

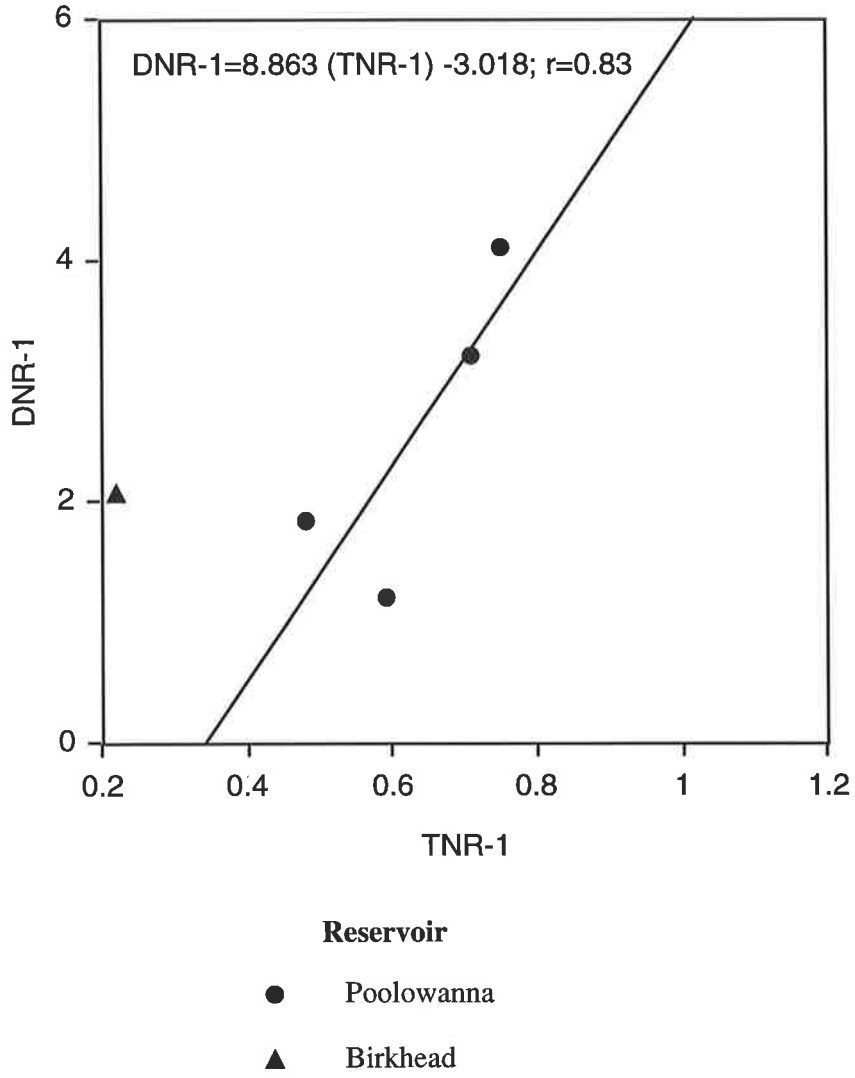


Figure 8.11 Relationship between the dimethylnaphthalene ratio (DNR-1) and the trimethylnaphthalene ratio (TNR-1) in oils from the Poolowanna and Patchawarra Troughs

The only available DNR-1 values for the oils range between 1.21 and 4.10 (Table 8.16). In most samples the 1,5-dimethylnaphthalene peak (Fig. 8.1a) was not resolved. The TNR-1 values range from 0.22 in the Sturt-3 (Birkhead) oil to 1.05 in the Tantanna-1 (Poolowanna) oil. Most of the Permian and Cambrian oils have values ranging from 0.74 to 0.89. The Sturt-7 (Mooracoochie) oil, with a DNR-1 value of 0.51, is an obvious exception, possibly because of the different organic matter (marine algal) and depositional environment (anoxic to suboxic) of its source rock. The high TNR-1 value of 1.05 in the Tantanna-1 (Poolowanna) oil is consistent with its Permian origin, whilst the values of the other Jurassic oils show them to be less mature than the Permian and Cambrian oils. The DNR-1 versus TNR-1 cross-plot (Fig. 8.11) reveals a good correlation between these two parameters. In this diagram the Sturt-3 (Birkhead) oil plots well away from the regression line, although the reason for this is not obvious.

8.5 Oil-source correlation based on aromatic maturity parameters

The relative concentrations of different aromatic compounds in crude oils can be affected by either bacterial biodegradation or water washing (Section 2.7.3). Compounds with relatively high solubilities in water, such as mono-methylnaphthalenes, dimethylnaphthalenes, phenanthrenes and benzothiophenes are preferentially depleted by water washing (Radke *et al.*, 1982b). In contrast, the methylphenanthrene homologues are apparently not affected, and thus may become concentrated relative to phenanthrene, giving rise to elevated MPI values. Mono-, di- and trimethylnaphthalenes are even more depleted by water washing than are the phenanthrenes, with the more polar α-isomers being more soluble and hence preferentially removed (Radke, 1987). Thus, maturity parameters such as TNR-2 (Table 8.1c) are likely to be affected in the same way as MPI. Both increase with water washing, TNR-2 more so than MPI. The relationship between these two maturation parameters in source rock extracts and oils may be used to recognise such alteration effects (Radke, 1987), and to compare the aromatic signatures of source rocks and oils for correlation purposes.

The relationship between the MPI and TNR-2 parameters for the Poolowanna source rock extracts is illustrated in Figure 8.12. Many samples including the coals, plot well to the left of the trend line (taken from Radke, 1987, fig. 25). Most of these off-trend samples are from the Patchawarra Trough. The Poolowanna Trough samples seem to define a trend of increasing maturity, whereas the Patchawarra Trough samples are more scattered. This sort of distribution is analogous to that observed for the maceral group distribution (Fig. 4.1). Therefore the relationship between these two ratios may well reflect variations in organic facies. So far no other geochemical evidence has indicated significant secondary alteration in these samples. Thus, their distribution in this plot is most likely related to maturation and primary organic matter type.

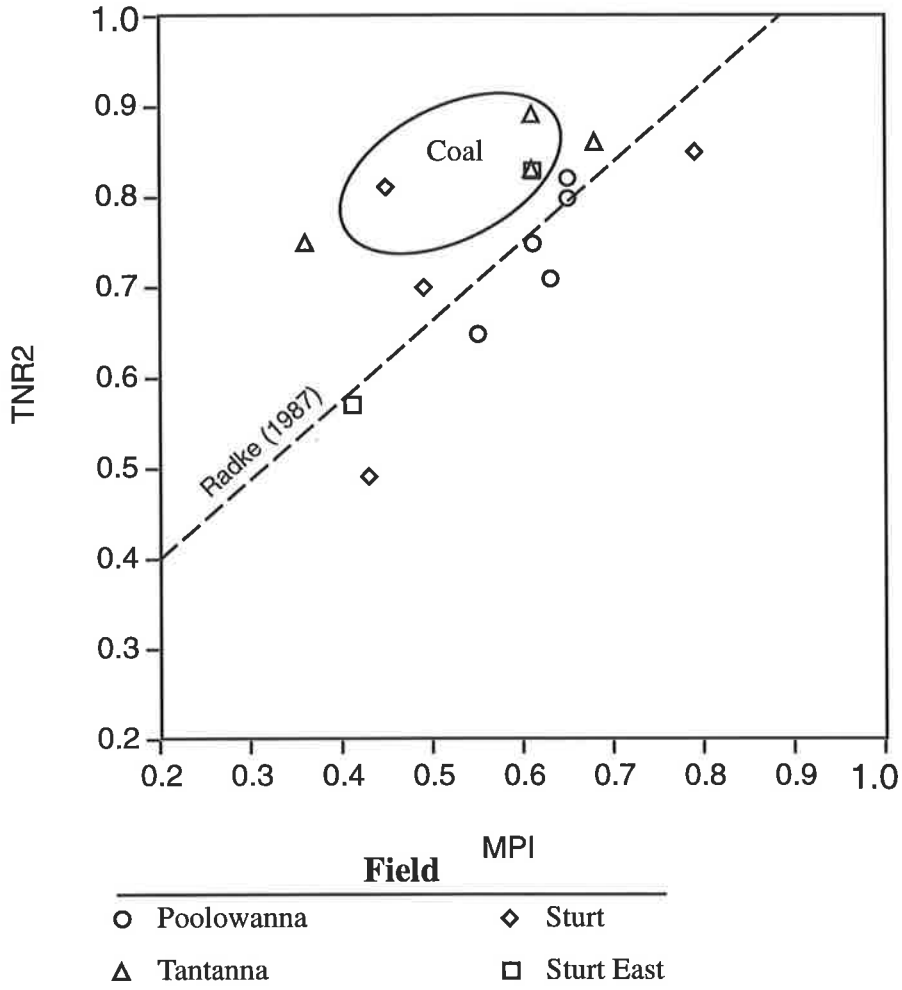


Figure 8.12 Relationship between the trimethylnaphthalene ratio (TNR-2) and the methylphenanthrene index, (MPI) in source rock facies of the Poolowanna Formation

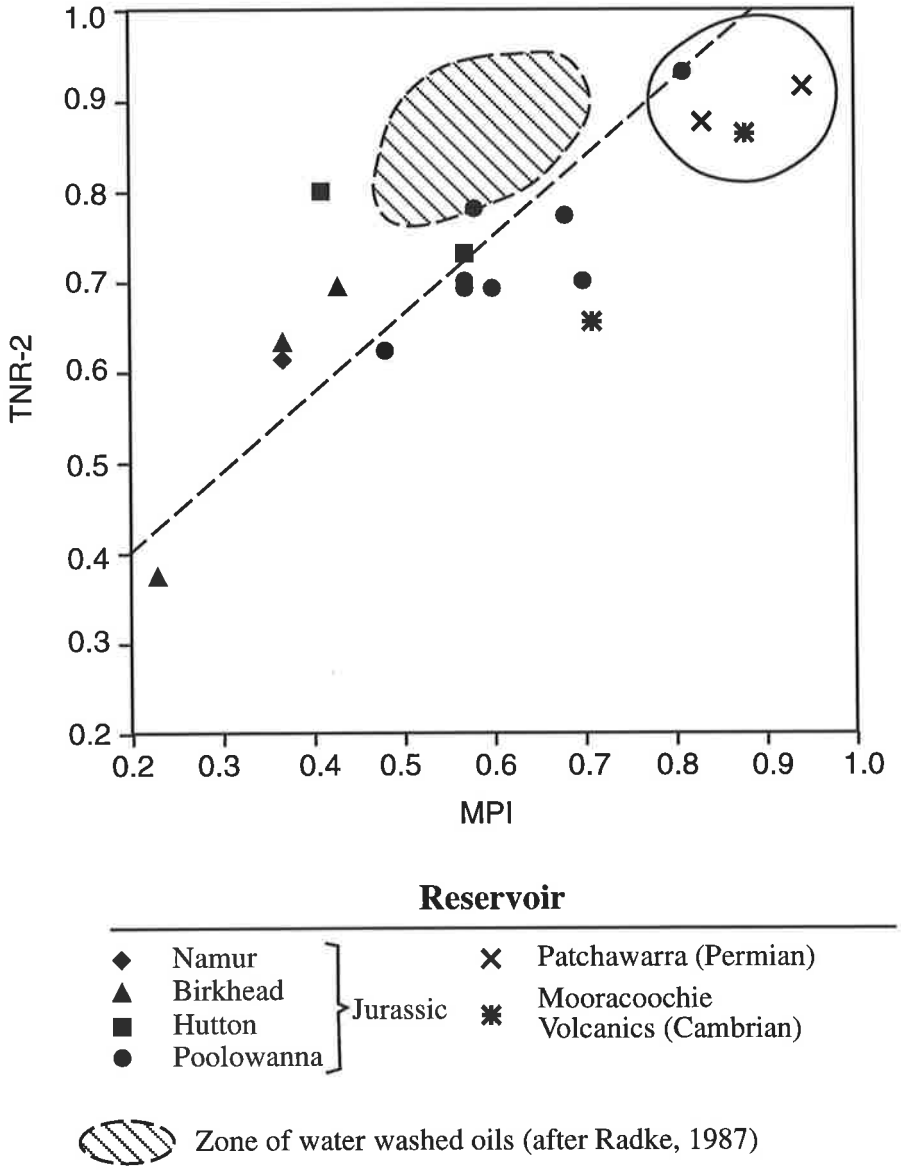


Figure 8.13 Differentiation of Jurassic oils from Permian-sourced oils (circled) based on the aromatic maturity parameters, TNR-2 and MPI

The relationship between MPI and TNR-2 in the oils is shown in Figure 8.13. As far as alteration is concerned, only four samples (one from the Hutton two from Birkhead and one from the Namur reservoirs) plot off-trend, possibly in the zone of water-washed oils. However, all four of these oils have 1-MP/9-MP ratios >1, suggesting araucarian-related input of 1-methylphenanthrene to their source rocks which thereby depresses their MPI values. The Tantanna-1 (Poolowanna) oil plots together with the Permian-sourced oils, thus confirming that it originated from a Permian source rock.

A comparison of the cross-plots for the source rocks (Fig. 8.12) and the oils (Fig. 8.13) suggests that many of the oils from Jurassic reservoirs could have originated from source rocks of the same organic facies and maturity as exist within the Poolowanna Formation on the southwest margin of the Patchawarra Trough.

The oils from the Mooracoochie Volcanics in Sturt-7, the Patchawarra Formation in Sturt-6 and Sturt-7, and the Poolowanna Formation in Tantanna-1 have all been assigned a Permian origin on the basis of isotopic and biomarker evidence. It is therefore significant that they plot quite separately from the Jurassic and Cambrian-sourced oils in Figure 8.13. Neither does the position of these Permian and Cambrian oils on the plot coincide with any of the Poolowanna Formation source extracts.

Chapter 9

Summary and conclusions

The Poolowanna Formation in both the Poolowanna Trough and the southwestern Patchawarra Trough is characterised by good source rock facies. Total organic carbon (TOC) values range from 1.5% in silty shales to 70% in coals. The dispersed organic matter is commonly enriched in liptinite, and the amount of extractable hydrocarbons (1018–15384 ppm) is evidence of very good to excellent source richness.

Maturity data based on both non-biomarker and biomarker parameters show that these source rocks are at the early mature to mature stages of hydrocarbon generation from terrestrial organic matter. Vitrinite reflectance values of 0.5–0.9% R_O and calculated reflectance values of 0.47– 0.77% R_C are consistent with homohopane (C_{32}: 22S/22S+22R) and sterane (C_{29}: 20S/20S+20R) epimerisation ratios of 0.48-0.67 and 0.48-0.58, respectively. However, only in the Poolowanna Trough is the Poolowanna Formation undoubtedly mature enough (R_O >0.7%) to be an *effective* source rock.

The hydrocarbon genetic potential of these Poolowanna source rocks, as determined by Rock-Eval pyrolysis, is very good in the Poolowanna Trough (S_1+S_2 = 11–160 mg HC/g rock) and fair to very good in the Patchawarra Trough (4–154 mg HC/g rock). The quality of the preserved organic matter, as represented by hydrogen index (HI) values, is somewhat better in the Poolowanna Trough (188–348 mg HC/g TOC) than in the Patchawarra Trough (93–296 mg HC/g TOC). The higher total extractable hydrocarbons yields (i.e. saturates and aromatics) in the Poolowanna Trough (27–64 mg HC/g TOC; cf. 11–46 mg HC/g TOC in the Patchawarra Trough) reflect the differences in source quality and maturity between the two depocentres.

Oil and gas-prone Type II/III kerogen is the major variety of organic matter preserved in the Poolowanna Formation, as indicated by the relative abundance of the vitrinite, liptinite and inertinite maceral groups, and verified on the HI versus T_{max} cross-plot. The actual range of kerogen compositions is from Type I/II to Type II/III in the Poolowanna Trough; and from Type II/III to Type III in the Patchawarra Trough. The presence of significant amounts of resinite, which may be assigned to kerogen Type I, implies the possibility of generating oil at early maturity in the Poolowanna Trough. The best example of this resinite-rich facies is the 2496–2524 m interval in Poolowanna-1 and 2 which has highest recorded HI values (315-348 mg HC/g TOC). Both resinite and *Botryococcus*-like telalginite impart a Type I character to the kerogen but their influence is obscured by the inertinite and thus not easily recognised by Rock-Eval pyrolysis (i.e. in the HI vs OI and HI vs T_{max} cross-plots).

This Type II/III kerogen is attributed to the mixed inputs of organic matter from higher plants, non-marine algae and bacteria found in terrestrial to lacustrine depositional environments. The land plant input is indicated by very high pristane to phytane ratios (>3) in conjunction with C_{29}-dominant sterane and diasterane distributions in some cases, and the carbon isotopic signatures of the saturated and aromatic hydrocarbon fractions. The algal input is represented by the presence of *Botryococcus*-like telalginite, which in turn is a reliable indicator of lacustrine depositional conditions. The non-waxy affinity shown by the carbon isotopic signatures may be related to aquatic plants and non-marine bacteria. The bacterial input or influence is demonstrated by high hopane to sterane ratios (>2), and the presence of C_{14}–C_{16} drimanes and C_{29}–C_{31} 2α- and 3β-methylhopanes. The *n*-alkane distributions and the isotopic signature of the saturated hydrocarbon fractions give the impression that algae, bacteria and aquatic plants contributed more organic matter to the Poolowanna Formation than did land plants.

Oxic to sub-oxic depositional conditions appear to have prevailed during the accumulation of the organic matter. The oxic conditions are strongly indicated by the aforementioned pristane/phytane values and a notable predominance of inertinite over vitrinite (i.e. I/V >1) in most samples. The anomalously high I/V ratios, in the Patchawarra Trough are related to deposition of recycled vitrinite and inertinite rather than primary oxidation effects. Sub-oxic conditions are indicated where pyrite is present and where vitrinite is significantly more abundant than inertinite (I/V <1). Acyclic isoprenoid to *n*-alkane ratios (i.e. pr/*n*-C_{17} versus ph/*n*-C_{18}) confirm that oxidising conditions were more prevalent than reducing ones.

The first appearance of a new Jurassic flora, the Araucariaceae, midway through the deposition of the Poolowanna Formation led to a major change in the biomarker signature of its coals and carbonaceous shales. The resin acids of these conifers contributed a novel suite of aromatic hydrocarbons to the upper part of the formation, viz. 1,2,5-trimethylnaphthalene, 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene. Elevated concentrations of these biomarkers (particularly 1,2,5-TMN and 1-MP) are displayed towards the top of the Poolowanna Formation, more so in the Patchawarra Trough where limnic peat swamps were better developed.

There are important differences between the two depocentres of the Poolowanna Formation as far as its source rock potential is concerned. The primary differences relate to its depositional environment, which in the Poolowanna Trough was predominantly telmatic with arborescent wet forest swamps while in the Patchawarra Trough it was mainly fluvio-lacustrine with herbaceous limnic swamps. In both the waxy and non-waxy source facies of the Poolowanna Formation the carbon isotopic signature of the aromatic hydrocarbon fraction is heavier in the Poolowanna Trough than in the Patchawarra Trough. This isotopic difference is largely due to the greater maturity of the Poolowanna Trough source rock

facies.

Most of the oils from Jurassic, Permian and Cambrian reservoirs in the study area seem to be generated from source rocks that were deposited in oxic to sub-oxic terrestrial swamp and lacustrine environments. They include oils of both waxy and non-waxy source affinity as illustrated by their *n*-alkane profiles and the carbon isotopic signatures of their aromatic and saturated hydrocarbons. Algae, bacteria and aquatic plants appear to be the main sources of these hydrocarbons while the land plant input is significant only in the waxy oils. The major contribution of prokaryotic organisms (bacteria) to the parent source rocks is emphasised by the high hopane to sterane ratios (>2.5) of the oils. In the Patchawarra Trough, the two Permian oils together with the out-of-place Tantanna-1 (Poolowanna) and Sturt-6 (Mooracoochie) crudes have MPI-derived maturities (R_C = 0.8–0.9%) which indicate that they were derived from mature source rocks containing Type III/II kerogen, presumably in the Early Permian Patchawarra Formation. Less mature Type II/I and Type II/III kerogen of Early to Middle Jurassic age are the likely sources of the Jurassic oils (R_C = 0.5–0.75%). The Sturt-7 (Mooracoochie) oil is of suboxic, algal source affinity and probably originated from an unidentified Cambrian marine mudstone containing Type II/III kerogen in the underlying Warburton Basin. In the Poolowanna Trough, the waxy Poolowanna-1 (Poolowanna) crude has an unusually light carbon isotopic signature which in part reflects its alteration by water washing. It is the most mature of the Jurassic oils analysed in this study (R_C = 0.82%) and was probably generated locally from Type II/III kerogen in the lower Poolowanna Formation.

The oils in the Permian and Cambrian reservoirs of the Patchawarra Trough appear to be generated from source rocks of higher maturity than those in the Jurassic reservoirs. The Namur Sandstone and Birkhead Formation oils are clearly related to early mature source rocks. The present maturity range of the local Poolowanna Formation source rocks, corresponds rather well to that of the oils in adjacent reservoirs of the Poolowanna Formation, Hutton Sandstone, Birkhead Formation and Namur Sandstone. Thus, on the grounds of both kerogen type and maturity, the Poolowanna Formation is a possible source of these oils. The evidence which supports this argument includes the cross-plot of measured and calculated vitrinite reflectance versus carbon isotopic signature of the aromatic hydrocarbons; and that of trimethylnaphthalene ratio (TNR-2) versus methylphenanthrene index (MPI). In both plots, most of the Jurassic oils are separated from those in the Permian and Cambrian reservoirs and closely match the Poolowanna Formation source rocks. The one Jurassic-reservoired oil which plots together with the Permian ones has a Permian aromatic biomarker signature. Finally on the sterane isomerisation diagram [i.e. $\alpha\alpha\alpha$(20S)/$\alpha\alpha\alpha$(20R) versus $\alpha\beta\beta$(20R)/$\alpha\alpha\alpha$(20R)] the Jurassic oils plot along the maturation pathway delineated by the Poolowanna Formation source rock facies.

A clear distinction between the Jurassic and Permian/Cambrian oils in the Patchawarra Trough can be made using the previously described Araucariacean markers particularly 1,2,5-trimethylnaphthalene and 1-methylphenanthrene. Again, all but one of the oils recovered from Jurassic reservoirs have unambiguous Middle Jurassic aromatic biomarker signatures, and therefore must have originated from source rocks in either the upper Poolowanna Formation or the Birkhead Formation. In the Poolowanna Trough, the mass fragmentograms of triterpanes (m/z 191), methylhopanes (m/z 205) and steranes (m/z 217) of source rock facies in the lower Poolowanna Formation correlate well with those of the Poolowanna-1 (Poolowanna) oil.

Oils of mixed Permian and Jurassic origins are difficult to distinguish from those which originated within the Early Jurassic source rock facies of lower Poolowanna Formation. One such example may be the Taloola-2 (Poolowanna) oil which has a transitional aromatic biomarker signature and a maturity (R_C = 0.70%) at the high end of the range for bona fide Jurassic oils. On the other hand the Tantanna-1 (Poolowanna) and Sturt-6 (Mooracoochie) oils are clearly of Permian origin by virtue of their lack of Araucariacean resin biomarkers and their relatively high maturity (R_C = 0.78–0.84%).

Generally, most of the oils in Jurassic reservoirs of the Patchawarra Trough appear to have been generated from within the Eromanga Basin, and probably from the Poolowanna Formation. The presence of significant amounts of resinite and resinous vitrinite imparts the potential for early generation of the immature oils (Rc ~ 0.5%) found in the Hutton, Birkhead and Namur reservoirs of the Tantanna and Taloola fields, although these oils could also have originated from a local Birkhead source rock. Those oils which lack Jurassic biomarkers may have been generated solely from source rock facies in the lower half of the Poolowanna Formation which was deposited prior to the emergence of the Araucariacean conifers.

Finally, it needs to be pointed out that the only source rock samples analysed in this study came from the crest of anticlinal structures on the southwest margin of the Patchawarra Trough. The effective Poolowanna oil kitchen may be located further to the northeast in a deeper part of the basin, e.g. near Lake Hope-1 (Fig. 1.2b).

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