

# SOURCE ROCK DISTRIBUTION AND HYDROCARBON GEOCHEMISTRY

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**Chapter 8**

## INTRODUCTION

Although numerous commercial and non-commercial hydrocarbon discoveries have been made in the Cooper Basin and overlying Eromanga Basin, the origin of the oil has been the subject of considerable controversy with varied views over an exclusive Cooper Basin source versus a combined Cooper and Eromanga Basins source. However, there appears to be a growing tide, particularly over the last decade, in favour of a mixed source. Recent studies by Powell *et al.* (1989), Michaelsen and McKirdy (1996), Ryan (1996) and Alexander *et al.* (1996) have provided conclusive evidence for an Eromanga Basin hydrocarbon source in the southern Cooper Basin, South Australia.

This chapter draws on existing company and Departmental data accessed from the Rock-Eval pyrolysis module of the PEPS database, recent technical reports commissioned by PIRSA (Alexander *et al.*, 1996; Michaelsen *et al.*, 1995) and results from the National Geoscience Mapping Accord (NGMA) Cooper and Eromanga Basins Project. The data have been compiled to identify potential and probable hydrocarbon source rocks, summarise the biomarker geochemistry for oils and source rocks, and establish genetic relationships between potential source rocks and hydrocarbon accumulations.

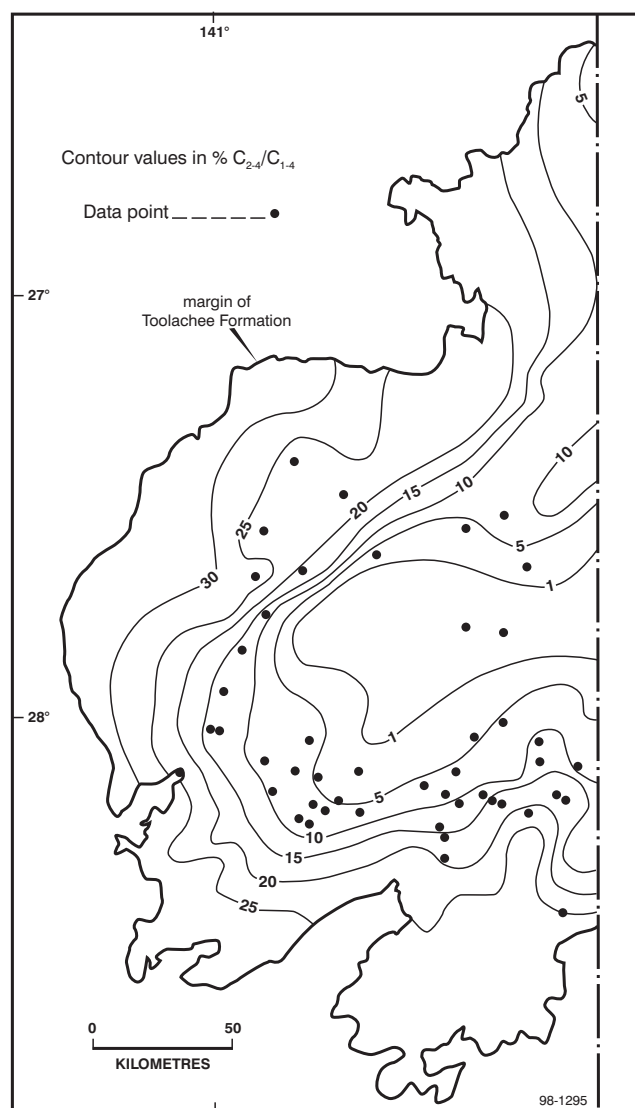
## BACKGROUND

### Cooper Basin

Numerous oil and gas fields in the Cooper Basin point to the Permian containing effective source rocks. Oil and condensate are typically medium to light (30–60° API) and paraffinic, with low to high wax contents. Most oil in Permian reservoirs contains significant dissolved gas and none shows any evidence of water washing (Hunt *et al.*, 1989). Gas composition is closely related to maturity with depth, with drier gas occurring towards basin depocentres (Figs 8.1, 8.2) although there is strong geological control on hydrocarbon composition (Hunt *et al.*, 1989). The Patchawarra Trough contains the bulk of the oil and wet gas reserves, consistent with local source rocks being in the 'oil window' while the Nappamerri Trough is overmature and contains mainly dry gas (Hunt *et al.*, 1989).

Permian source rocks have average total organic content (TOC) and S<sub>2</sub> pyrolysis yields of 3.9% and 6.9 kg of hydrocarbon per tonne, respectively (excluding coal). Locally, the Toolachee Formation is the richest source unit. The Patchawarra Formation is considered the other major source unit (Jenkins, 1989), especially the lower beds of

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**Fig. 8.1** Toolachee Formation gas wetness (after Hunt *et al.*, 1989, fig. 3).

shale and coal (Hunt *et al.*, 1989). The lacustrine Murteer and Roseneath Shales appear to have little source potential (Hunt *et al.*, 1989). Permian non-marine clastics are characterised by inertinitic dispersed organic matter (DOM) with liptinite and vitrinite totalling <25% of the organic matter. On the other hand, the coal units are low in liptinite and contain subequal amounts of inertinite and vitrinite (Smyth, 1983). Sub-microscopic alginite dispersed within the inertinitic matrix of some Patchawarra coal has been suggested as a novel source for oil (Taylor *et al.*, 1988).

Together, the petrographic and geochemical evidence support coal and associated DOM as the effective source

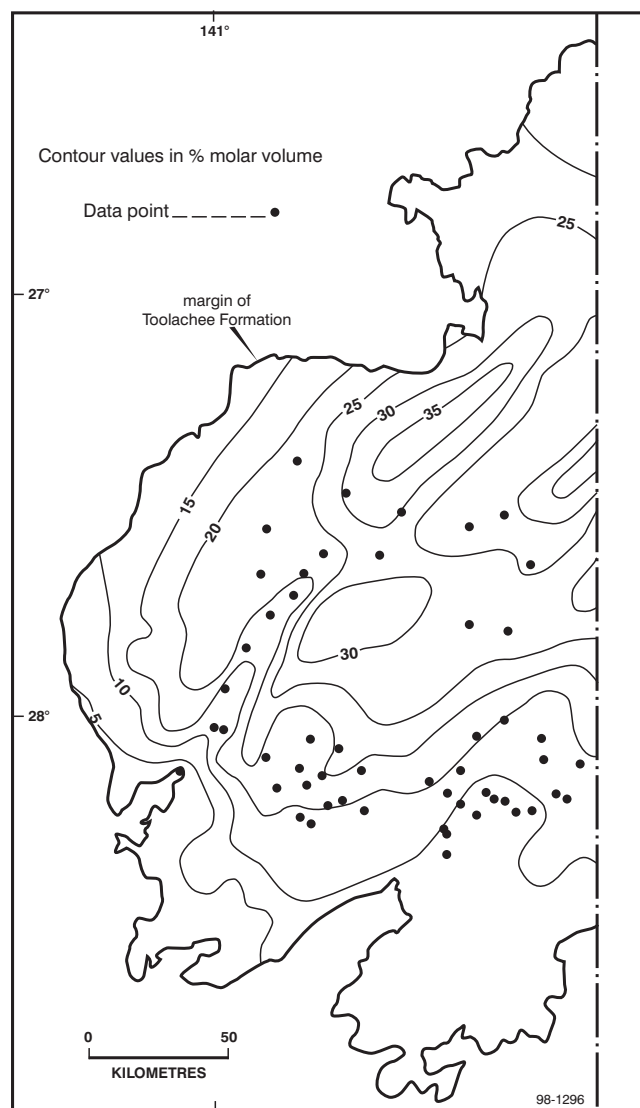


Fig. 8.2 Toolachee Formation CO<sub>2</sub> content (after Hunt *et al.*, 1989, fig. 4).

rocks capable of generating gas and minor oil, albeit in low yields (Hunt *et al.*, 1989). At maturity levels of 0.7–0.95% measured vitrinite reflectance ( $R_o$ ), initial generation from the richer facies led to partial filling of reservoirs with wet gas and oil. There is a sharp onset of significant hydrocarbon accumulation as the source reaches a maturity of 0.95%  $R_o$  (Hunt *et al.*, 1989). Faulting along anticlinal trends or basin margin pinchouts can provide migration paths for Cooper Basin-derived hydrocarbons into younger horizons (Heath *et al.*, 1989; Passmore, 1989).

## Eromanga Basin

The origin of oil in the Eromanga Basin has been attributed to a Cooper Basin source, an indigenous source or a mixture of both. Although it is recognised that Birkhead Formation and Murta Formation sources exist (Vincent *et al.*, 1985; Alexander *et al.*, 1988, 1992, 1996; Jenkins, 1989; Lowe-Young *et al.*, 1996; Powell *et al.*, 1989), there is still considerable debate as to their extent and relative contribution.

Potential source rocks of Jurassic and Early Cretaceous age contain Type II to Type III organic matter and have been shown to have maturities within the 'oil window' (onset of

oil generation between vitrinite reflectance of 0.65 and 0.7%; Kantsler *et al.*, 1983; Passmore and Boreham, 1982, 1986; Jenkins, 1989). Average TOC and pyrolysis yields are slightly lower for Eromanga Basin source rocks compared to Permian source rocks (Jenkins, 1989). However, the Birkhead Formation contains the most hydrogen-rich organic matter, has an average TOC of 2.5% and S<sub>2</sub> pyrolysis yield of 10.8 kg/t. Birkhead Formation coal is typically vitrinite rich (>50%) and inertinite poor (<10%), while the DOM is commonly more liptinitic and inertinitic (Smyth *et al.*, 1984). The Poolowanna Formation (formerly the 'basal Jurassic' unit in Queensland) shows fair to good source richness; the Westbourne Formation exhibits mainly fair source richness (Hawkins *et al.*, 1989).

Hydrocarbon extracts of Jurassic potential source rocks are paraffinic and waxy, similar to those from Permian sediments. This lack of distinction probably reflects only minor changes in organic facies and/or maturation histories (Gilby and Mortimore, 1989) or, alternatively, reflects oil contamination of Eromanga source rocks by migrating Permian hydrocarbons (Heath *et al.*, 1989). However, using age and source-specific Araucariacean conifer biomarkers, Alexander *et al.* (1988, 1992) proposed that Eromanga hydrocarbons can have both a combination from a local and Cooper Basin source or derive solely from the latter source. In addition, Jenkins (1989) suggested that the occurrence of 25,28,30-trisnorhopane, 25,28,30-trisnormoretane and 19-norisopimarane in an oil signifies an Eromanga source input. Using these criteria, a maximum Eromanga source contribution of 40% has been assigned to an individual pool (Jenkins, 1989) although an overall volumetric average of <20% can be attributable to an Eromanga source (Jenkins, 1989; Lowe-Young *et al.*, 1996).

But even this minor volumetric significance has been questioned by Tupper and Burckhardt (1990) since 19-norisopimarane occurs in Permian source rocks (Jenkins, 1989). Indeed, Heath *et al.* (1989) concluded a dominant Permian source for Jurassic oil and gas. Unlike Cooper Basin hydrocarbons, the Eromanga Basin petroleum in Jurassic reservoirs does not show regionally consistent trends in hydrocarbon type, composition and maturation. These differences have been interpreted to indicate variations in local source rock depositional environments (Vincent *et al.*, 1985; Alexander *et al.*, 1988; Powell *et al.*, 1989). The alternative model proposes that migration occurs beyond the edge of the Permian and Triassic seals and into the Eromanga aquifer system. Here, the physical and chemical properties of the Permian-sourced petroleum were significantly modified by pressure and temperature-induced migration fractionation and water washing (Heath *et al.*, 1989).

Oil in Cretaceous reservoirs is often geochemically distinct from that in Jurassic reservoirs. It is typically light (45° API), non-waxy, low sulphur, paraffinic crude (Vincent *et al.*, 1985) although waxy oil does occur (Michaelsen and McKirdy, 1989; Powell *et al.*, 1989). The Murta Formation oil is thought to be locally derived from Cretaceous source rocks (Vincent *et al.*, 1985; Michaelsen and McKirdy, 1989; Powell *et al.*, 1989). Pristane/phytane ratios (Pr/Ph = 5–9) are higher compared to those of greater reservoir age (Michaelsen and McKirdy, 1989). In addition, the Cretaceous oil shows lower levels of maturation based on

sterane isomers (Vincent *et al.*, 1985; Powell *et al.*, 1989; AGSO and GeoMark Research, in prep.) and their methylphenanthrene index (MPI-1) (Michaelsen and McKirdy, 1989; Powell *et al.*, 1989; Tupper and Burckhardt, 1990). Michaelsen and McKirdy (1989) and Powell *et al.* (1989) suggested that a major bacterial overprint of the original terrestrial organic matter has led to susceptibility to early generation of hydrocarbons. Although this may well be the case, kinetic studies on petroleum generation from potential Murta source rocks indicate that oil expulsion occurs at higher maturity levels (see Ch. 9). This discrepancy may be reconciled with the known source influence on the content of 1-methylphenanthrene (Alexander *et al.*, 1988, 1992) that will lower maturity estimates based on MPI-1. Furthermore, the results presented in Powell *et al.* (1989) show enough biomarker dissimilarities between Murta oil and the potential Murta source rocks to doubt whether a strong oil-to-source correlation has been demonstrated and the suggestion made by these authors, that migration effects could be an alternative explanation for the unusual chemistry of Murta oil, is explored further in this chapter.

Cretaceous accumulations which show reduced proportions of gasoline-range hydrocarbons ( $C_5$ – $C_{10}$ ) and low gas/oil ratios possibly reflect losses due to washing by meteoric waters, albeit to a less intense degree compared to Jurassic oil reservoirs (Vincent *et al.*, 1985; Michaelsen and McKirdy, 1989). The source for the Coorikiana Sandstone gas is less well studied, although a local Cretaceous source is highly likely (McKirdy *et al.*, 1986; Vincent *et al.*, 1985). Alternatively, an origin from an altered Permian-sourced petroleum has also been suggested for Cretaceous reservoired hydrocarbons (Heath *et al.*, 1989). The marine Cretaceous sequence contains good potential source rocks, but it is considered immature for hydrocarbon generation (Moore and Pitt, 1984). Clearly, more work needs to be done in order to distinguish local Eromanga Basin sourcing.

## SOURCE ROCK DISTRIBUTION

### Merrimelia Formation

Previous workers have concentrated on the source rock potential of DOM and coal of the Patchawarra and Toolachee Formations which represent the major source units and, to a lesser extent, the Epsilon and Daralingie Formations rather than focusing on the Merrimelia Formation and the Murteree and Roseneath Shales.

In the context of source quality and source richness of the Gidgealpa Group, shale of the Merrimelia Formation rates poorly. The formation is dominated by glaciogenic sandstone, siltstone and conglomerate with only minor amounts of mudstone, the last of which is organically lean. Thin, discontinuous coal lenses deposited as vegetated bar tops represent the best source rocks of the formation (hydrogen index (HI) average = 159; range 94–203). However, these units are infrequent and have little impact on the overall source quality.

Rock-Eval data from 13 wells (55 samples) are plotted in Figure 8.3 and selected Rock-Eval parameters for Cooper Basin shale and coal are summarised in Tables 8.1 and 8.2, respectively.

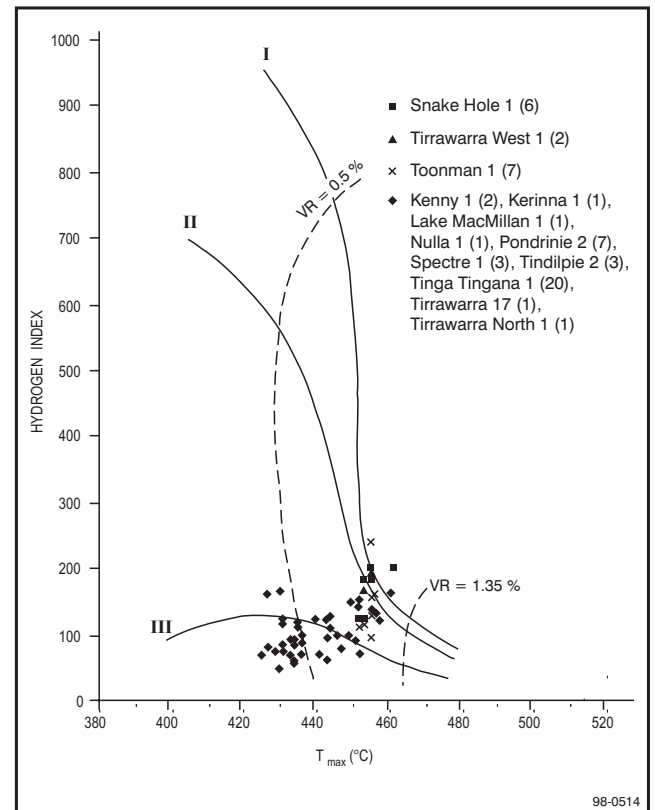


Fig. 8.3 HI versus  $T_{max}$  plot, Merrimelia Formation.

Source richness of Merrimelia Formation shale is generally very good (TOC average = 2.1) but ranges from poor to excellent (TOC = 0.03–9.9;  $S_1+S_2$  = 0.3–19 kg of hydrocarbon per tonne). Hydrogen indices are moderate (46–201) consistent with a Type III–IV gas-prone kerogen. Several wells have HI values >150, indicating potential for gas and minor light oil generation consistent with a Type II/III to III kerogen (Snake Hole 1, HI = 201; Tirrawarra West 1, HI = 163; Tinga Tingana 1, HI = 165).

### Patchawarra Formation

Coal and carbonaceous shale of the Patchawarra Formation represent the principal source rocks of the Cooper Basin, both in source richness and quality, and overall thickness. Patchawarra Formation total coal thickness is >60 m in the Weena Trough and up to 40 m in the Patchawarra Trough (see Fig. 6.6) in contrast to the Nappamerri Trough where total coal thickness rarely exceeds 10 m. Rock-Eval data are summarised in Tables 8.1 and 8.2, and plotted in Figure 8.4. Shale (<10% TOC) has the potential to generate oil (HI = 3–346;  $S_1+S_2$  = 0.04–36.6 kg hydrocarbon per tonne) and represents Type II/III kerogen, whilst carbonaceous shale and coal shale (10% < TOC < 30%) and coal (TOC > 30%) are capable of generating large quantities of oil ( $S_1+S_2$  = 2–182 kg hydrocarbon per tonne). In volumetric terms, the western Patchawarra Trough represents the most important kitchen where thick Patchawarra Formation shale and coal lie within the present-day oil window.

HI values >250 indicating good (Type II/III kerogen) to very good oil source potential (Type II kerogen) are found in Andree 2, Kurunda 1, Tibouchina 1, Snake Hole 1, Murteree 2, Gidgealpa 1 and Pondrinie 2 (Fig. 8.4).

**Table 8.1** Summary of Rock-Eval pyrolysis data for Cooper Basin shale, South Australia.

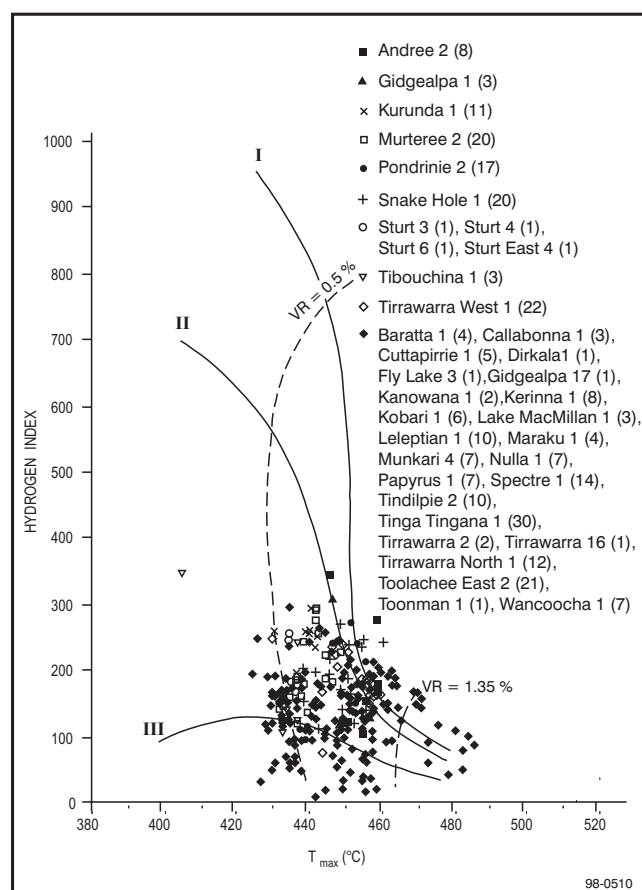
Unit	TOC (%)		Genetic potential		Hydrogen index (kg/t)		Oxygen index	
	average	range	average	range	average	range	average	range
Nappamerri Group	0.65	0.1–9.15	1.45	0.1–11.9	104	22–247	368	6–2509
Toolachee Formation	3.8	0.3–9.3	6.9	0.1–19.5	128	8–215	32	0–278
Daralingie Formation	5.3	2.1–9.0	12.7	1.6–24.4	157	66–245	20	0–82
Epsilon Formation	4.2	0.1–9.8	7.0	0.2–22.1	142	51–472	72	0–541
Murteree Shale	2.6	1.7–4.7	2.5	1.0–6.6	71	41–131	103	17–455
Patchawarra Formation	4.4	0.2–10.0	7.7	0.04–36.6	132	3–346	43	0–480
Merrimelia Formation	2.1	0.03–9.9	4.2	0.3–19	102	46–201	59	0–251

NB. Present-day Rock-Eval parameters are not corrected for maturity.

**Table 8.2** Summary of Rock-Eval pyrolysis data for Cooper Basin coal and coal-affected shale, South Australia.

Formation	TOC (%)		Genetic potential		Hydrogen index (kg/t)		Oxygen index	
	average	range	average	range	average	range	average	range
Nappamerri Group	13.6	10.7–16.4	25.9	21.3–30.5	175	175–175	10	4–15
Toolachee Formation	26.6	10.4–73.4	61.5	21.2–187	214	141–330	5	0–12
Daralingie Formation	13.1	11–15	30.3	19–40	206	151–268	4	0–8
Epsilon Formation	30.7	10.3–64.9	68.7	3.8–177.2	197	11–385	6	0–17
Patchawarra Formation	28.2	10–84.5	54	2–182	177	12–347	8	0–42
Merrimelia Formation	28.7	14.1–57.9	47.8	15.2–130.2	159	94–203	8	0–13

NB. Present-day Rock-Eval parameters are not corrected for maturity.



**Fig. 8.4** HI versus  $T_{max}$  plot, Patchawarra Formation.

### Murteree Shale

Rock-Eval data from 10 wells (27 samples) are plotted in Figure 8.5 and summarised in Table 8.1. All samples plot within the Type III/IV kerogen envelope indicating a dry gas-prone source. TOC ranges from 1.7 to 4.7% (i.e. good to

very good), but genetic potential is poor to fair ( $S_1+S_2 = 1-6.6$  kg hydrocarbons per tonne), with the richest intersection occurring in Tindilpie 2.

Although these values point to poor source potential (observed HI = 41–131 kg hydrocarbon per tonne), initial HI values would be expected to be slightly higher although still gas prone.

There are no Rock-Eval data for Roseneath Shale sediments. Based on the same environment of deposition and stratigraphic relationship to the Murteree Shale, it is safe to conclude that it would share similar geochemical properties to this unit.

### Epsilon Formation

Rock-Eval data from 18 wells (50 samples) are plotted in Figure 8.6 and summarised in Tables 8.1 and 8.2. These data point to a Type II/III to Type II kerogen (i.e. good to very good oil source potential). HI values often exceed 250, with a carbonaceous shale sample from Andree 2 (HI = 472) and coally shale sample from Toonman 1 (HI = 385) having the greatest oil source potential. No organic petrology is available for either of these wells but presumably these samples would be exinite rich. Epsilon Formation shale demonstrates highly variable source richness (TOC = 0.1–9.8%;  $S_1+S_2 = 0.2-22.1$  kg hydrocarbon per tonne). Isolith maps of coal and mudrock percentage appear in Figures 6.24b and c, respectively.

### Daralingie Formation

Only 11 samples from four wells have been analysed for Rock-Eval pyrolysis (Fig. 8.7; Tables 8.1, 8.2). Such a small data set makes it difficult to predict basin-wide source richness and quality. Based on these wells, source richness of Daralingie Formation shale is moderate to very good (TOC = 2.1–9.0%;  $S_1+S_2 = 1.6-24.4$  kg hydrocarbon per tonne) and HI = 66–245 kg hydrocarbon per tonne,

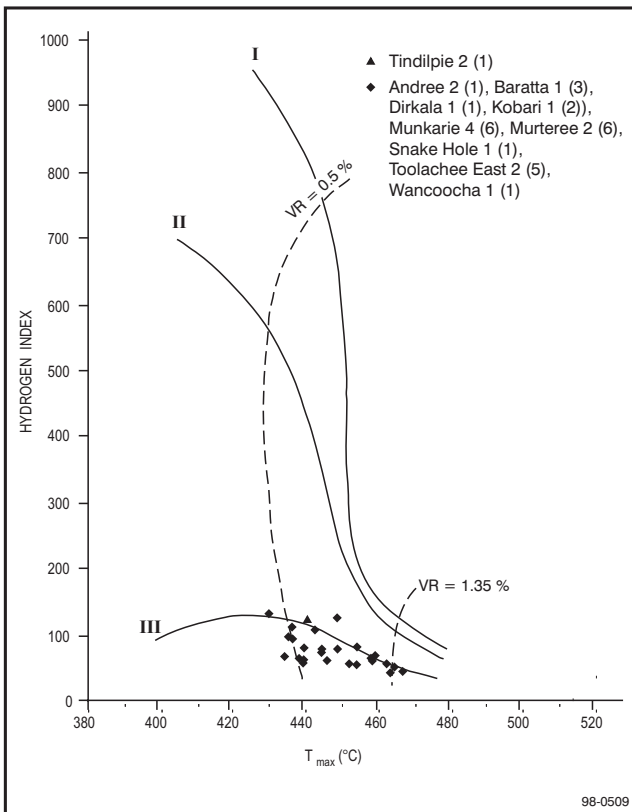


Fig. 8.5 HI versus  $T_{max}$  plot, Murteree Shale.

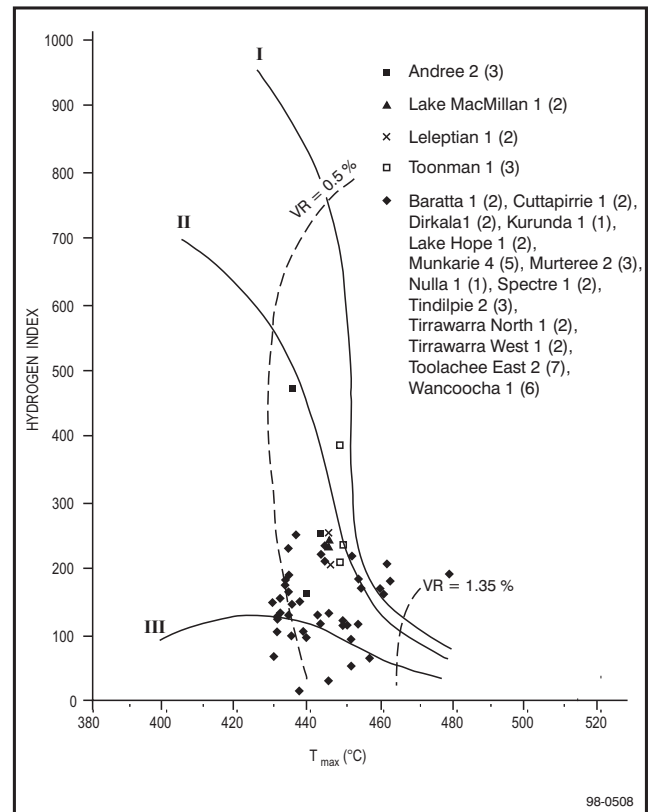


Fig. 8.6 HI versus  $T_{max}$  plot, Epsilon Formation.

indicating a moderately oil-prone source facies (Type II/III kerogen). Isolith maps of coal and mudrock percentage appear in Figures 6.26b and c, respectively.

### Toolachee Formation

Toolachee Formation coal and carbonaceous shale represent the second most important source rock unit of the Cooper Basin in terms of richness, quality and thickness. Combined Toolachee Formation coal reaches thicknesses >35 m in the northern Patchawarra Trough and 25 m in the Weena Trough, similar to regional coal thickness trends for the Patchawarra Formation. Isolith maps of coal and mudrock percentage appear in Figures 6.30b and c, respectively. Rock-Eval data from 22 wells (88 samples) are plotted in Figure 8.8 and summarised in Tables 8.1 and 8.2. They indicate a predominantly oil-prone source facies (Type II/III kerogen) with highly variable source richness (TOC = 0.3–9.3 for shale;  $S_1+S_2 = 0.1–19.5$  kg hydrocarbon per tonne). Source potential is also understandably variable given the large number of samples with HI values ranging from 8 to 330 kg hydrocarbon per tonne for the combined coal and shale data set. HI values >250 indicating good (Type II/III kerogen) to very good oil source potential (Type II kerogen) are found in Snake Hole 1, Toonman 1, Leleptian 1, Tirrawarra North 1 and Tirrawarra West 1.

In volumetric terms, the northern Patchawarra Trough represents the most important kitchen where thick Toolachee Formation shale and coal lie within the present-day oil window.

### Nappamerri Group

Thin, laterally discontinuous coal represents the best source rock of the Nappamerri Group whilst shale tends to

be organically lean. The oxidised humic-rich gas-prone nature of the kerogen is supported by Rock-Eval (Fig. 8.9; Tables 8.1, 8.2). Oxygen index (OI) for the shale averages 368 mg  $CO_2$  ( $S_3$ )/g TOC and range from 6 to 2509, whilst HI averages 104 kg hydrocarbon per tonne indicating an

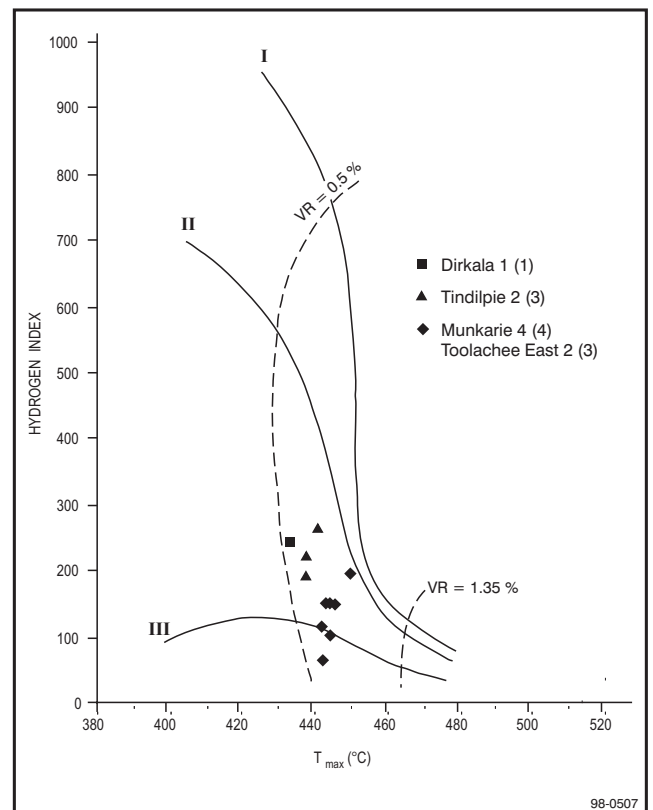


Fig. 8.7 HI versus  $T_{max}$  plot, Daralingie Formation.

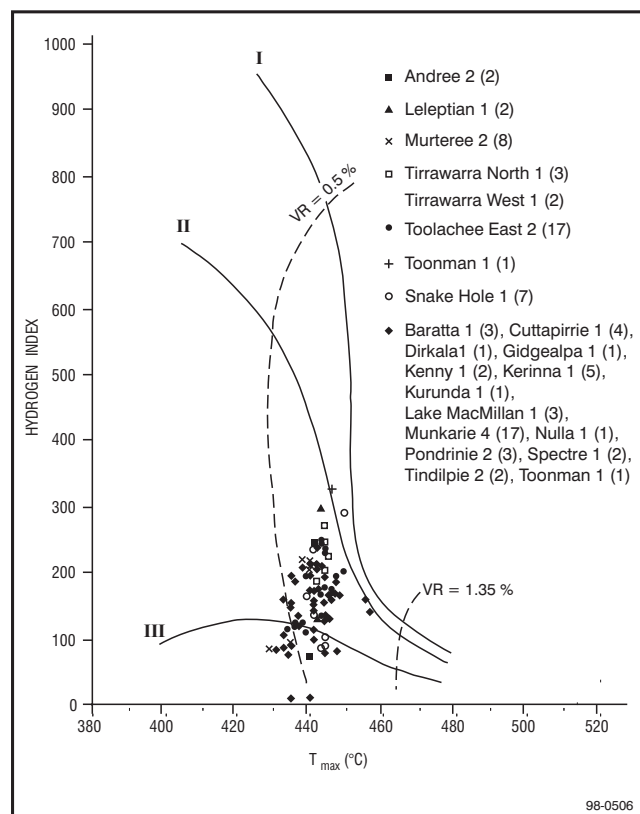


Fig. 8.8 HI versus  $T_{max}$  plot, Toolachee Formation.

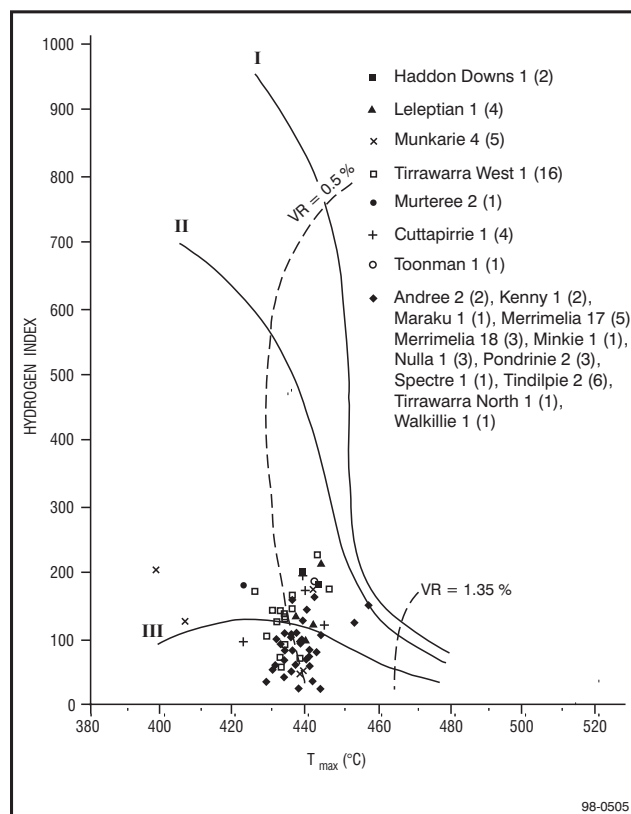


Fig. 8.9 HI versus  $T_{max}$  plot, Nappamerri Group.

oxidised Type III/IV kerogen. Wells with HI values >150 include Haddon Downs 1, Leleptian 1, Toonman 1, Cuttappirrie 1, Tirrawarra West 1 and Munkarie 4.

## PETROLEUM GEOCHEMISTRY

The following synopsis of the petroleum geochemistry of the Cooper Basin is drawn from the NGMA Cooper and Eromanga Basins Project which is due for completion in September 1999, and draws on a regionally significant data set of parameters based on bulk chemistry, gas chromatography, gas chromatography-mass spectrometry, and *n*-alkane isotope profiles of oils and condensates. The outcome of this analysis is to better understand the active source rocks of the Cooper and Eromanga Basins, and provide a reassessment of their relative contributions to oil occurrences in these basins. It was considered imperative that this product-based analysis not only address factors associated with primary source and maturity controls, as traditionally has been the case, but to understand the influence of secondary alteration processes such as migration fractionation, water washing and biodegradation on oil chemistry. Additional factors such as contamination during secondary migration and multiple charge histories may have compounded to influence oil composition. The latter two are the subjects of a separate study currently underway by the Universities of Adelaide and Cologne (Germany).

## BULK CHEMISTRY

Appendix 2 lists the API gravity and  $<C_{15}$  fraction of the whole oil. As expected, the cross-plot of the two parameters shows a positive linear relationship (Fig. 8.10), but the large 'scatter' suggests that the relationship between oil

composition and API gravity is rather complex. The API gravities range from 35 to 55, representing a medium to light oil-condensate. At the low end of the API range,  $<C_{15}$  fractions range from 0 to 15%, while up to 90% of the  $<C_{15}$  fraction is able to be lost on standing from the high API gravity light oils. In the Cooper and Eromanga Basins, it is common for vertically stacked oil reservoirs to show a progression from low API gravity oils in the deeper reservoirs to the highest API gravity oil-condensate in the shallowest reservoir (Heath *et al.*, 1989).

## SOURCE CONTROL

### Light hydrocarbons

Mango (1990) suggested that petroleum formation is mainly controlled by catalytic reactions mediated by transition metals (Mango *et al.*, 1994) and not, as traditionally believed, by thermal cracking processes (Tissot and Welte, 1984). Mango (1990) supported his views with genetic relationships between various light hydrocarbon components.

Figure 8.11a shows a strong correlation between the branched hydrocarbons 2,3- and 2,4-dimethylpentane. There is very little relationship with reservoir position and the major control is associated with the bulk parameters (Fig. 8.10) in which the oils biased towards the lower molecular weight fractions have the higher weight percent of each of the two  $C_7$  compounds in Figure 8.11a. Furthermore, there is no clear distinction between oil from the different reservoirs using the source-related parameters P3 and P2+N2 (Fig. 8.11b). This suggests that oils from the Eromanga and Cooper Basins are from a similar source or that, if there are multiple sources, secondary alteration

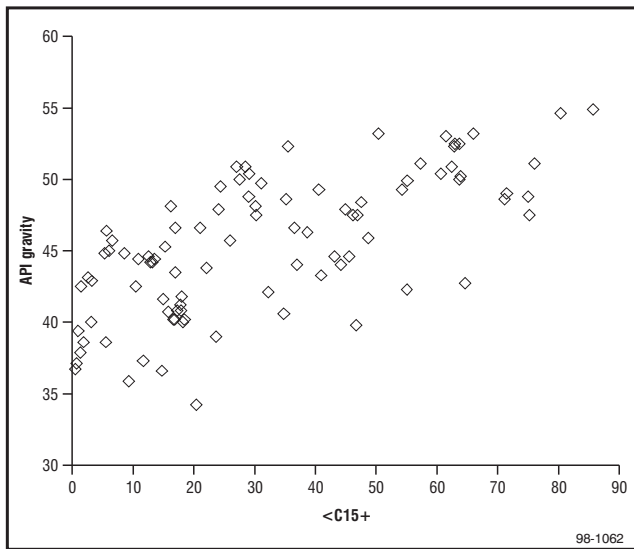


Fig. 8.10 Plot of API gravity versus  $\langle C_{15}$ .

processes are sufficiently strong to overprint the source signature.

### *n*-Alkanes and isoprenoids

Gas chromatograms of representative whole oils are shown in Figure 8.12. Appendix 2 lists a range of parameters derived from quantisation of individual compounds from the gas chromatographic traces. For the vertically stacked reservoirs (Fig. 8.12), the variation in API gravity is readily reconciled at the molecular level. Since *n*-alkanes are the major class of compounds of the oil, they can be considered representative of oil as a whole. Waxy *n*-alkanes, maximising between *n*-C<sub>21</sub> and *n*-C<sub>23</sub>, dominate the *n*-alkane profile of the deepest oil and progressively give way to lower molecular weight homologues higher in the succession. This variability is further illustrated in the ternary diagram of the relative proportion of *n*-C<sub>11</sub>, *n*-C<sub>17</sub> and *n*-C<sub>23</sub> together with colour-filled contours defining the composition limits of oil from the main reservoirs (Fig. 8.13). Light oil within the Cooper and Eromanga Basins ranges up to 90% *n*-C<sub>11</sub> whereas up to 70% *n*-C<sub>23</sub> is characteristic of the low API gravity oil. The composition of Cooper Basin oil (representatives from Merrimelia Formation to Nappamerri Group) shows two end-member groupings. One group is dominated by light hydrocarbons (*n*-C<sub>11</sub> dominant) while the other group is the high wax oil (*n*-C<sub>23</sub> dominant). Compared to this latter group, Eromanga Basin oil shows slightly lower *n*-C<sub>23</sub> content. The highest *n*-C<sub>17</sub> content is encountered in oil from the younger reservoirs (Murta, Wyandra and Cadna-owie). A secondary group of light oil is also encountered in the Murta Formation. Namur Sandstone oil shows a similar range of *n*-alkane compositions to the Murta oil, while oil lower in the section (Westbourne to Poolowanna) show a much narrower range of *n*-C<sub>17</sub> content, with the variability distributed between *n*-C<sub>11</sub> and *n*-C<sub>23</sub>.

All oil accumulations have Pr/Ph >3, indicative of a predominantly non-marine source from terrestrial organic matter (Fig. 8.14). Furthermore, the progressive change from waxy to light oil has been interpreted to indicate an increased contribution of bacterial or algal source inputs to the lighter oil (Powell *et al.*, 1989). An alternative

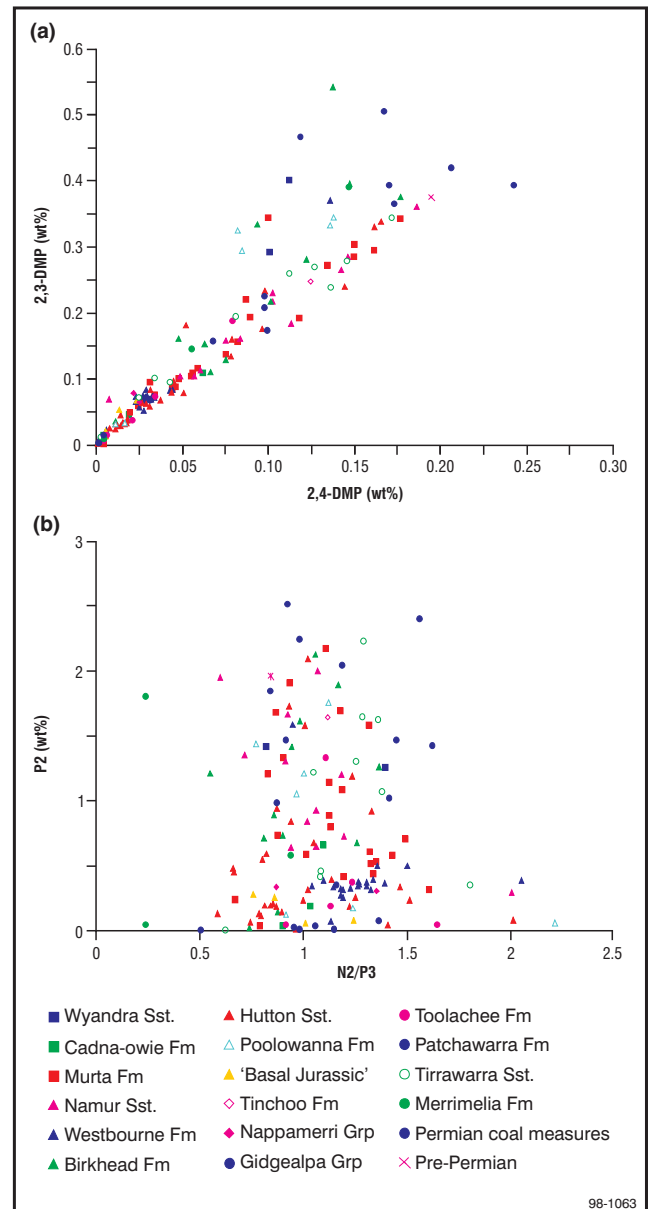


Fig. 8.11 Mango plot of (a) 2,3- versus 2,4-dimethylpentane (DMP), (b) source parameter ( $P2 = 2- + 3\text{-methylhexane}$ ;  $N2 = 1,1- + 1\text{-cis-}3 + 1\text{-trans-}3\text{-dimethylcyclopentane}$ ;  $P3 = 2,2- + 2,3- + 2,4- + 3,3\text{-DMP}$ ).

interpretation is that the original source input, although dominantly from terrestrial organic matter, has been masked by secondary alteration processes (see below).

### Biomarkers

The recognition of selective enrichment in saturated and aromatic hydrocarbons related to conifer-derived input has implied an effective Eromanga Basin source (Alexander *et al.*, 1988, 1992; Jenkins, 1989). Furthermore, this approach has enabled a semi-quantitative analysis of the proportion of Eromanga and Cooper source contribution to an oil (Jenkins, 1989). Consistent with the model, Figure 8.15 shows a clear distinction between oil reservoired in the Cooper Basin and that reservoired in the Eromanga Basin. The latter oil is characterised by enhanced relative enrichments in 1-methylphenanthrene, 1,7-dimethylphenanthrene, retene and 1,2,5-trimethylphenanthrene.

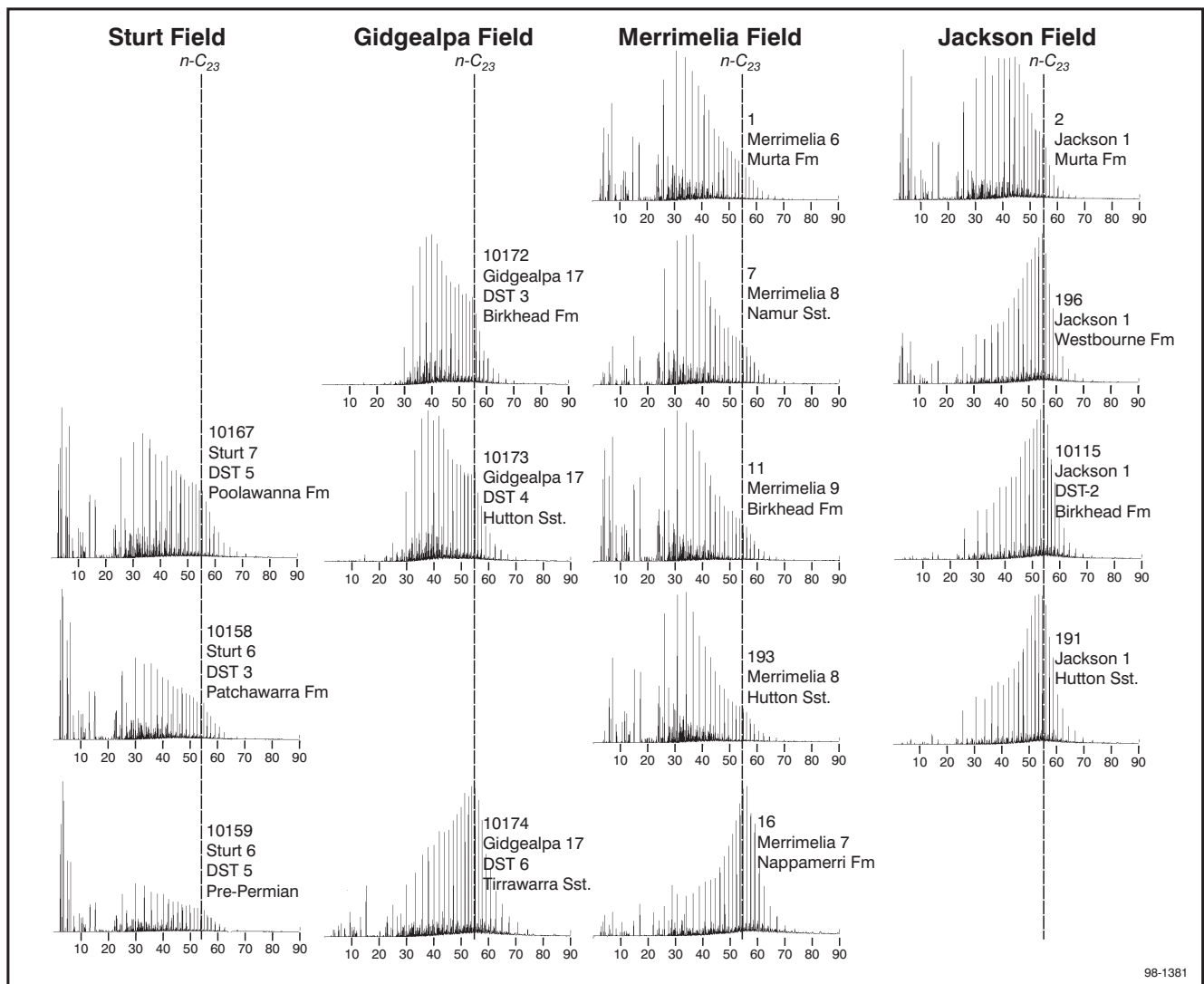


Fig. 8.12 Gas chromatograms for vertically stacked reservoirs from selected oil fields, Cooper and Eromanga Basins.

Moorari 4 shows the highest relative content of these components (Fig. 8.15) and is considered to be representative of an oil sourced predominantly from the Eromanga Basin (Alexander *et al.*, 1996). Considering its low maturity based on high Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub>, and carbon preference index >>1 (Appendix 2), a local source from the Birkhead Formation is implied. Oil from stacked reservoirs in the Gidgealpa and Merrimelia Fields clearly show a compositional distinction between Cooper and Eromanga reservoirs. It could also be argued that the Eromanga Basin oil from these two reservoirs has a contribution from a Cooper Basin source since the Birkhead signature of this oil is not as strong as that shown in Moorari 4 (Fig. 8.15). This is consistent with the recent study by Boulton *et al.* (1998) where, using a greater range in biomarkers, the two Gidgealpa 17 oils from the Birkhead Formation and Hutton Sandstone have been attributed to a local Eromanga Basin source. It also agrees with a multi-component statistical analysis based on bulk carbon isotopes and saturated biomarkers (AGSO and GeoMark Research, in prep.; oil included in that study is shown in Appendix 2) where Cooper Basin oil at Gidgealpa and Merrimelia showed a low correlation with oil higher in the section in the Eromanga Basin. Thus, for these two oil

fields, a classical oil–oil correlation study based on biomarker and bulk carbon isotopes has implicated two main active petroleum systems (source–reservoir),

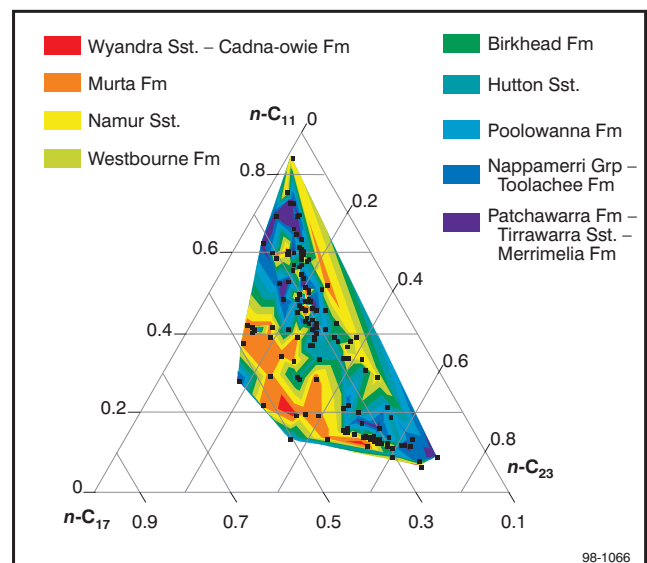


Fig. 8.13 Ternary diagram of relative proportions of n-C<sub>11</sub>, n-C<sub>17</sub> and n-C<sub>23</sub> in Cooper–Eromanga whole oil.

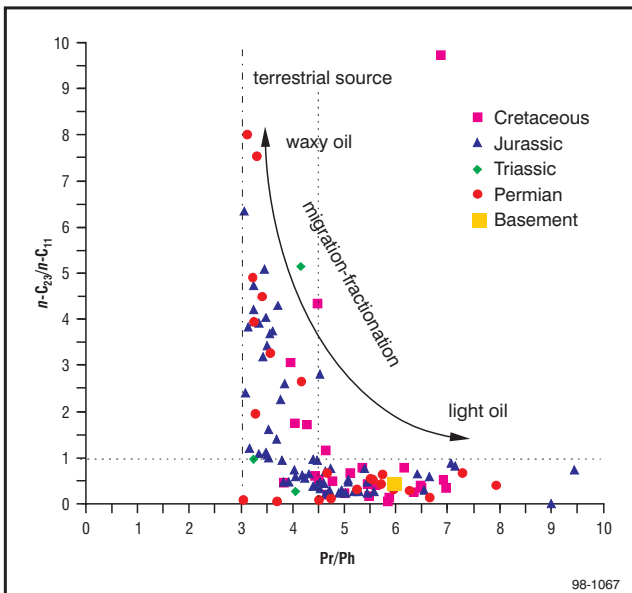


Fig. 8.14 Plot of  $n\text{-C}_{23}/n\text{-C}_{11}$  versus  $Pr/Ph$  for Cooper–Eromanga oil.

Cooper–Cooper and Eromanga–Eromanga, with latter showing variable contributions from a Cooper–Eromanga petroleum system.

### *n*-Alkane isotope profiles

Unquestionably, the biomarkers are information-rich and are an indispensable and valid component of any serious attempt in oil–oil and oil–source correlations leading to the identification of active petroleum systems (AGSO and GeoMark Research, 1996; Boreham *et al.*, 1997). However, it is debatable that quantitative analysis can be achieved by relying solely on those ‘classical’ sterane and triterpane biomarkers which are biased towards the higher molecular weight components. For example, Alexander *et al.* (1996) recently recognised that some oil in the Eromanga Basin is a composite produced by mixing of a light Permian oil with a waxy Eromanga oil of differing maturities. In this case, analysis of biomarkers would not do justice to the contribution of the former oil considering its much lower biomarker content. A similarly biased interpretation would exist for migration contamination where a light Permian oil migrates through Eromanga strata inherently enriched in biomarkers.

On the other hand, the *n*-alkanes represent the major structurally-related class of compounds in an unaltered oil. Their individual carbon isotopes have given new insights into the origins of Australian oil (Boreham and de Boer, 1998; Boreham *et al.*, 1995; Edwards *et al.*, 1997; Murray *et al.*, 1994; Summons *et al.*, 1995).

Figure 8.16 shows the *n*-alkane isotope profile for stacked reservoirs in Gidgealpa and Merrimelia oil fields together with oil from the Birkhead reservoir at Bookabourdie 8 and Moorari 4. For the Merrimelia and Gidgealpa crudes, the pronounced negative slope to the *n*-alkane isotope profile is consistent with an origin from a predominantly land plant source (Murray *et al.*, 1994). At Gidgealpa, the different slope and a wider isotopic range for the Patchawarra crude compared to the identical isotopic composition for the *n*-alkanes in Birkhead and Hutton oil

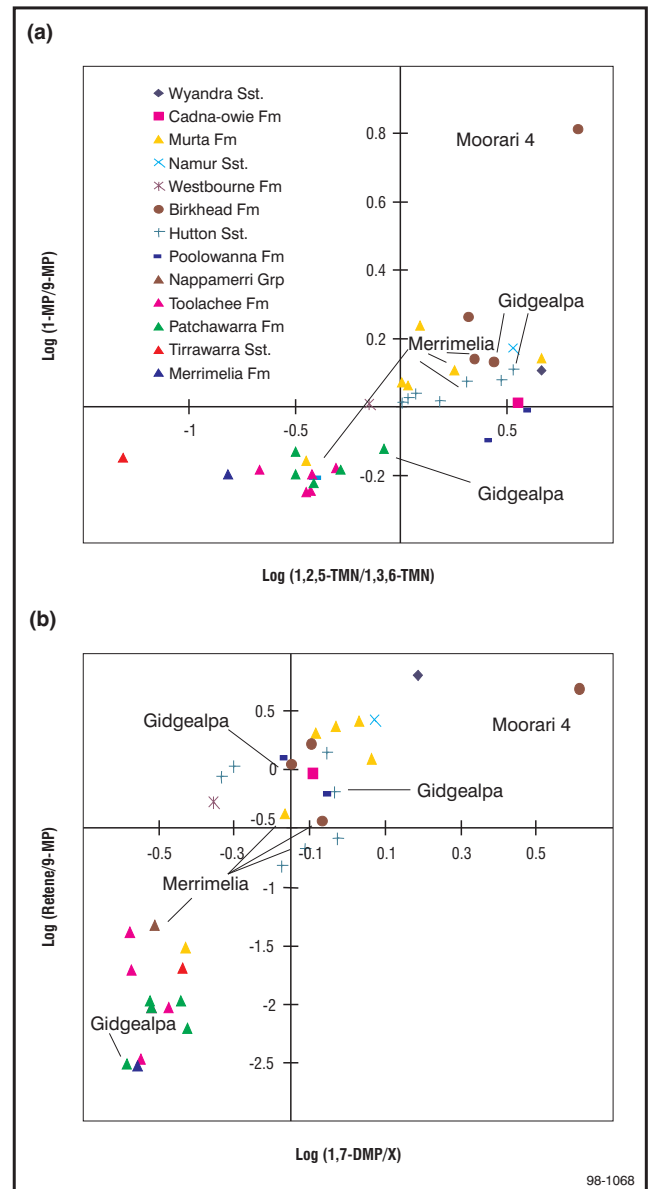


Fig. 8.15 Source indicators based on ratios of selected aromatic hydrocarbons (after Alexander *et al.*, 1988). MP = methylphenanthrene, TMN = trimethylnaphthalene, DMP = dimethylphenanthrene and X = group of other DMP isomers.

suggests a different source rock for oil from the Cooper and Eromanga Basin, in agreement with biomarker evidence (AGSO and GeoMark Research, in prep.).

A structural cross-section of the Gidgealpa Field (after Boulton *et al.*, 1998) shows possible migration pathways and source contributions to the oil accumulations (Fig. 8.17). The dissimilar *n*-alkane profiles between Patchawarra oil at Gidgealpa 17 (Fig. 8.16) and Gidgealpa 2 (not shown) indicates different source kitchens and migration pathways. On the other hand, the identical isotopic composition for Merrimelia Field oil implies a common origin (from a Permian source) for both the Cooper and Eromanga accumulations. However, a minor Eromanga source input is implied from the biomarker evidence (Fig. 8.15). Figure 8.18 shows a cross-section of the Merrimelia Field with

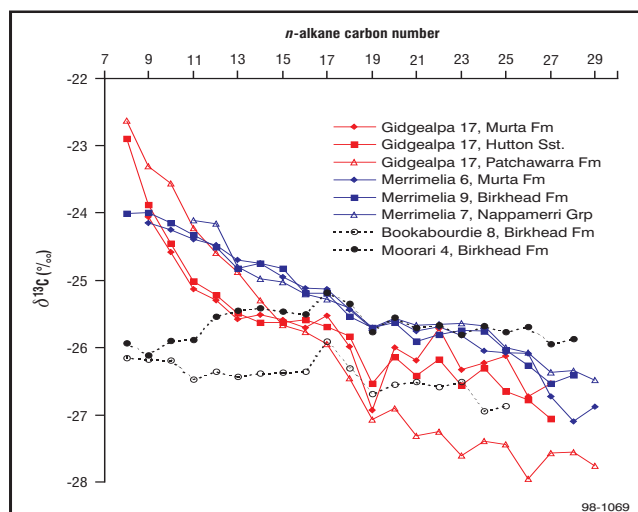


Fig. 8.16 n-Alkane isotope plot of carbon number versus carbon isotopic composition.

migration from Permian source rocks responsible for the major charge to the Eromanga Basin oil accumulations.

Birkhead Formation oil in Moorari 4 and Bookabourdie 8 shows a different isotopic profile to Birkhead Formation oil at Gidgealpa and Merrimelia. The former have a carbon isotope composition that remains reasonably constant over the range  $n-C_8$  to  $n-C_{29}$ . This isotopically ‘flat’ profile is considered a characteristic of an oil generated locally from the Birkhead Formation and establishes the existence of oil accumulations primarily from this source. The two wells are notably within the region of thickest Birkhead Formation (Paton, 1986). The isotopic difference of up to 1‰ between the  $n$ -alkanes in the Moorari and Bookabourdie oil suggests that isotopic variations of this magnitude are due to slight changes in organic facies. Indeed, Paton (1986) has shown considerable lateral variations in the coal swamp to lacustrine environments for unit 2 (highest source potential) of the Birkhead Formation.

The isotopic variability between and within formations can be readily seen in the carbon isotopic composition of the organic matter from potential source rocks (Fig. 8.19). Here, an isotopic difference of up to 3‰ occurs in organic matter from rocks of the same formation. Furthermore, the range in isotopic composition of organic matter in the Eromanga Basin (average =  $-24.7‰$ ;  $sd = 1.4‰$ ;  $n = 18$ ) is similar to that in the Cooper Basin (average =  $-24.0‰$ ;  $sd = 1.5‰$ ;  $n = 13$ ). In Moorari 4 and Bookabourdie 8, there is no clear source distinction between Late and Early Permian source rocks based on bulk carbon isotopes. Furthermore, organic matter from the Cretaceous Murta Formation and the Permian of the Cooper Basin appears to be isotopically indistinguishable. Although this may suggest that bulk isotopes offer little source differentiation, the regional isotopic variability in the Murta Formation is much less than that for any of the other formations. For the latter, organic matter in the Jackson Field of South-West Queensland is slightly lighter isotopically than in the same formations in the Merrimelia area of South Australia.

For reservoirs where multiple charging from Permian and Jurassic sources is suspected (Alexander *et al.*, 1988,

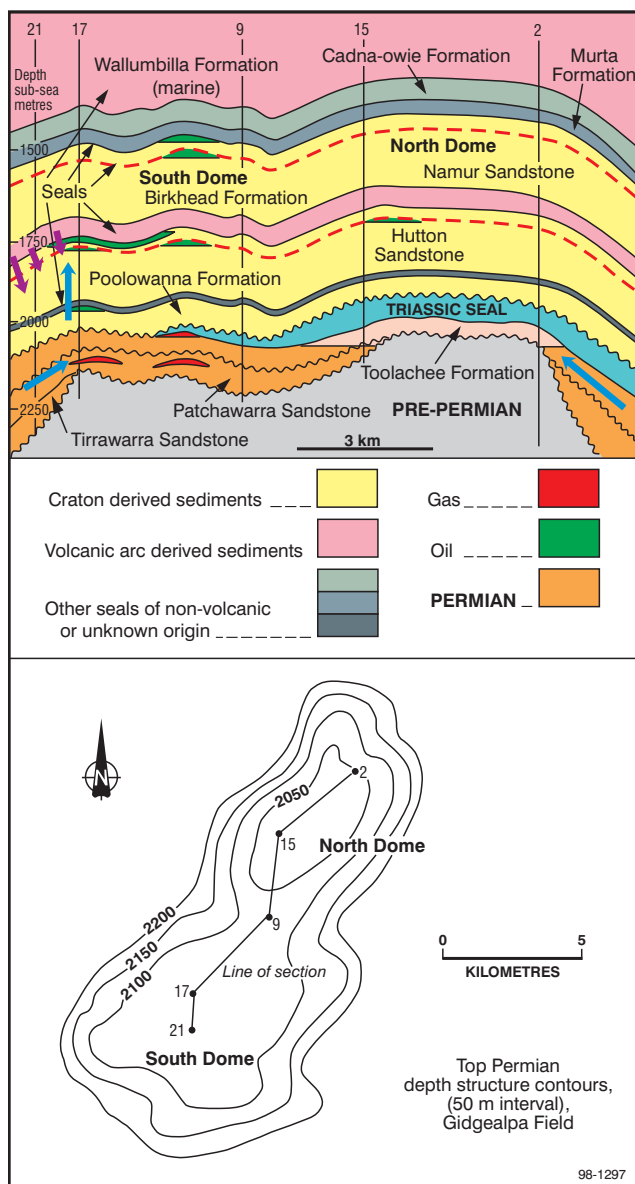
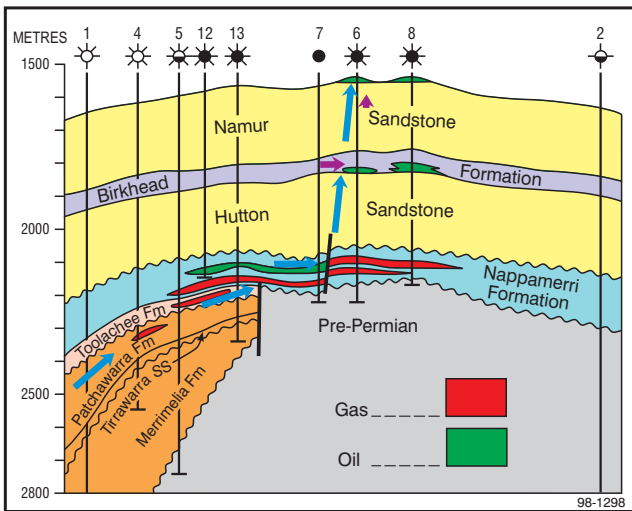


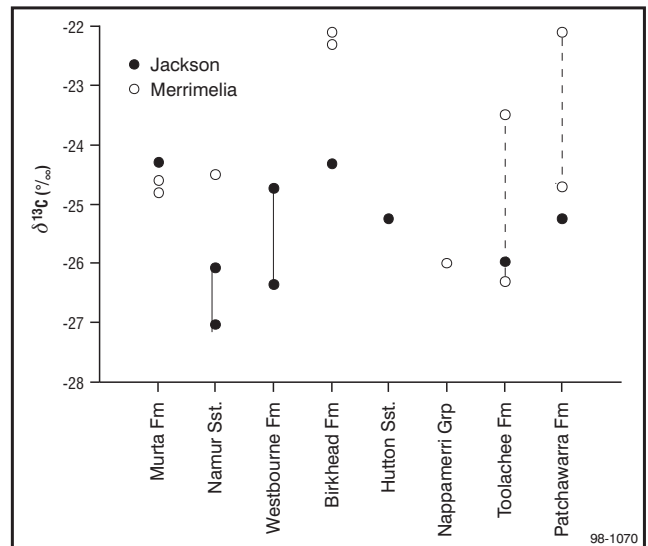
Fig. 8.17 Cross-section of Gidgealpa Field showing oil and gas accumulations and migration pathways from Cooper (blue arrows) and Eromanga (purple arrows) sources (after Boulton *et al.*, 1998, fig. 14).

1992; Jenkins, 1989; Heath *et al.*, 1989), a measure of the  $n$ -alkane ‘isotopic gradient’ may provide an estimate of the degree of mixing.

Figure 8.20 plots the isotopic difference between average isotopic composition over selected carbon number ranges between  $n-C_{10}$  and  $n-C_{25}$  for oil from Murta to Merrimelia Formations. Accumulations sourced from the Jurassic Birkhead Formation show the least isotopic differences. For the Gidgealpa 17 stacked reservoirs, a calculation based on the average isotopic difference in the range  $n-C_{10}$  to  $n-C_{20}$  of  $-1.7‰$  for a Cooper-sourced oil and an average of  $0.08‰$  for a Birkhead-sourced oil (Fig. 8.20) leads to 35:65 mixing of Permian and Jurassic sources (Fig. 8.17) in the Birkhead and Hutton oils (average isotopic difference of  $-0.54‰$ ). In this case a lower than 25% Birkhead-source contribution would not have been resolvable considering the  $0.5‰$  analytical error.



**Fig. 8.18** Cross-section of Merrimelia Field showing oil and gas accumulations and migration pathways from Cooper (blue arrows) and Eromanga (purple arrows) sources (after Bowering and Harrison, 1986, fig 6).

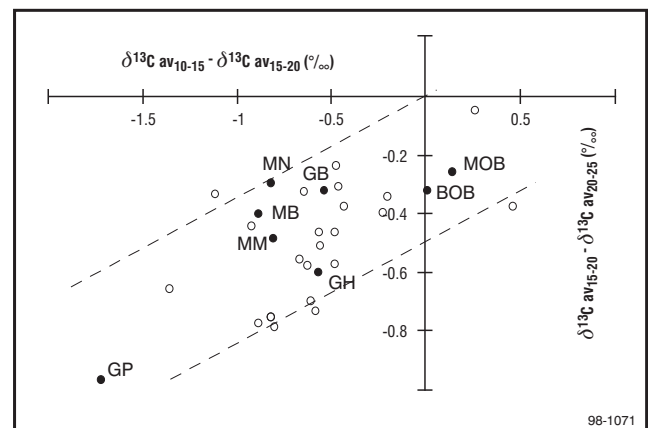


**Fig. 8.19** Carbon isotopic composition of organic matter from sedimentary rocks in the Jackson and Merrimelia wells. Data represent maximum and minimum values.

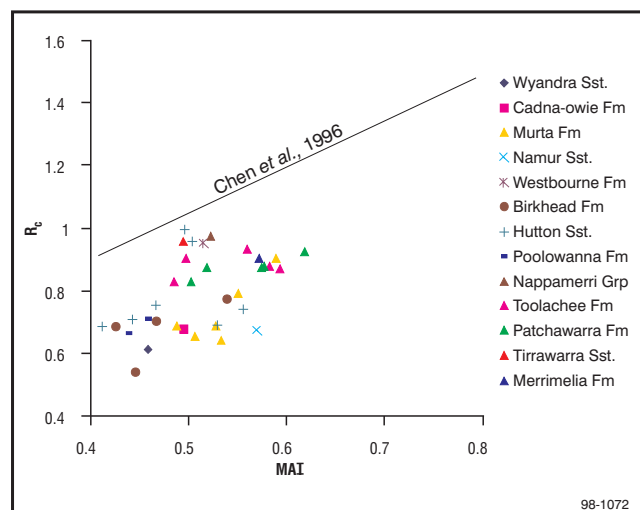
### MATURITY CONTROL

Almost every biomarker parameter is affected to varying degrees, by both source and maturity. Thus, the specificity expressed in the aromatic source parameters (Fig. 8.15) is diluted with increasing maturity and becomes unrecognisable past the main oil window. Similarly, the most commonly used aromatic maturity parameter (MPI-1) and the derived calculated vitrinite reflectance ( $R_c$ ; Radke and Welte, 1983) are source dependent for Eromanga Basin sediments by virtue of the presence of 1-methylphenanthrene in their formulae. The  $R_c$  values of the oil samples (in Fig. 8.15) are plotted in Figure 8.21 and are in the range  $0.5\% < R_c < 1.0\%$ . Oil higher in the section in the Eromanga Basin has, on average, the lowest  $R_c$ , as has been previously recognised (Alexander *et al.*, 1988; Michaelsen and McKirdy, 1989; Powell *et al.*, 1989; Tupper and Burckhardt, 1990). This  $R_c$  distribution, attributed primarily to maturity, has subsequently been used to infer migration directions from maturity gradients (Tupper and Burckhardt, 1990). An independent measure of maturity based on the highly stable, low molecular weight diamondoid structure (Chen *et al.*, 1996; methyl adamantane index (MAI) = 1-methyl adamantane/(1-methyl adamantane + 2-methyl adamantane) has proven useful in identifying maturity effects at the high maturity end (past peak oil generation; Chen *et al.*, 1996, 1998; Boreham *et al.*, 1997; Boreham and de Boer, 1998) where most hopane and sterane-based maturity parameters are ineffective. Figure 8.21 plots MAI versus  $R_c$  (based on MPI-1). The two parameters show a weak positive correlation although the oil has a higher extrapolated maturity range based on MAI ( $0.9\% < R_c < 1.2\%$ ) compared to that based on  $R_c$  ( $0.5\% < R_c < 1.0\%$ ). Despite the limited use of the MAI parameter, and uncertainties concerning its source dependency (cf. source dependency of MPI-1; Boreham *et al.*, 1988), the similar range in MAI for the Murta and Cooper oil compared to lower  $R_c$  for Murta oil may implicate a mixed origin with a high and low maturity fraction in the Murta oil.

Maturity effects are also evident in the *n*-alkane profiles. The Cooper oil from Merrimelia, Moorari and Strzelecki wells shows *n*-alkane isotope profiles with parallel negative slopes (Fig. 8.22), characteristic of oil derived from coal and associated terrestrial source rocks (Murray *et al.*, 1994). On the other hand, the Kanowana oil shows a much flatter *n*-alkane profile. Such a profile is similar to that displayed by Birkhead oil (Fig. 8.16) and is also typical of oil derived from marine source rocks (Murray *et al.*, 1994). Marine sediments are known to be present in the underlying Ordovician to Cambrian Warburton Basin (Sun, 1997), and fault-controlled migration from a deep source may be a possibility. Flat *n*-alkane profiles are characteristic of organic matter in sediments of similar age in the Officer and Amadeus Basins, but the *n*-alkanes are isotopically light (i.e.



**Fig. 8.20** Plot of carbon isotope difference between the average of ( $\delta^{13}C$  n-C<sub>10</sub> to  $\delta^{13}C$  n-C<sub>15</sub>) and the average of ( $\delta^{13}C$  n-C<sub>15</sub> to  $\delta^{13}C$  n-C<sub>20</sub>) versus the carbon isotope difference between the average of ( $\delta^{13}C$  n-C<sub>15</sub> to  $\delta^{13}C$  n-C<sub>20</sub>) and the average of ( $\delta^{13}C$  n-C<sub>20</sub> to  $\delta^{13}C$  n-C<sub>25</sub>). Oils: MM = Merrimelia 6, Murta Formation; MB = Merrimelia 9, Birkhead Formation; MN = Merrimelia 7, Nappamerri Group; GB = Gidgealpa 17, Birkhead Formation; GH = Gidgealpa 17, Hutton Sandstone; GP = Gidgealpa 17, Patchawarra Formation; MOB = Moorari 4, Birkhead Formation; BOB = Bookabourdie 8, Birkhead Formation.



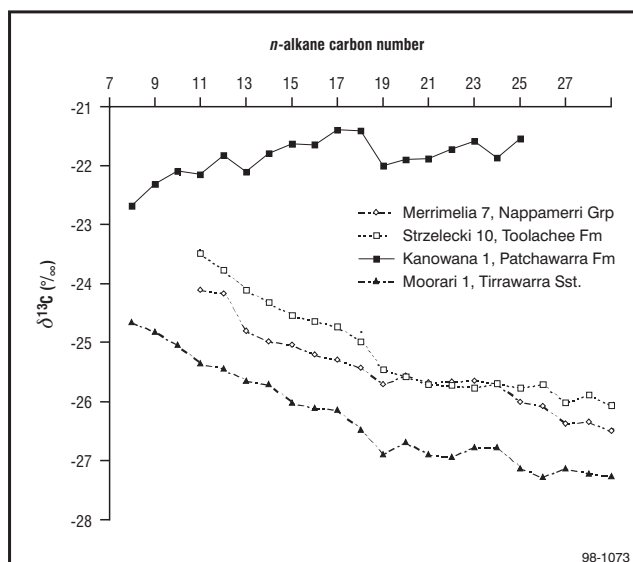
**Fig. 8.21** MAI versus  $R_c$  plot (based on MPI-1 of Radke and Welte, 1983). The line of Chen et al. (1996) is the best-fit straight line for an effective vitrinite reflectance based on MAI.

depleted in  $^{13}\text{C}$ ) with  $\delta^{13}\text{C}$  mainly between  $-28$  and  $-32\text{‰}$  (Logan *et al.*, 1997), outside the range shown for any oil from the Cooper and Eromanga Basins. The isotopically heavy  $n$ -alkanes in Kanowana light oil–condensate are more likely to be high temperature products of secondary cracking reactions and the overall profile is predominantly maturity influenced.

## SECONDARY ALTERATION

### Migration fractionation

Migration fractionation (Curiale and Bromley, 1996) or evaporative fractionation (Thompson, 1987 1988) is one mechanism that can account for some of the systematic changes in composition for stratigraphically and spatially constrained oil reservoirs in the Cooper and Eromanga Basins. As upward-migrating petroleum experiences decreasing pressure, oil expands and higher molecular weight components become less soluble. Finally, as the fluid passes through the bubble point pressure, it separates into gas and oil-rich phases. Furthermore, ineffective oil seals in the deeper reservoirs can allow preferential leakage of low molecular components. In all of these processes a less mobile fluid (residual oil) becomes enriched in higher molecular components. Ultimately, in stacked reservoirs, low API gravity crude resides at the base and high API gravity light oil at the top of reservoirs (Fig. 8.12). However, there are many stacked reservoirs that do not show significant compositional differences (Fig. 8.12). This may be a function of multiple sourcing but could also reflect a phase with high gas–oil ratio (GOR) that does not undergo phase separation. For the latter, oil dissolved in gas could be an effective phase for lateral migration within the Cooper and Eromanga Basins and extending well past the Permian edge in Eromanga Basin reservoirs. Gas loss along the migration pathway will reduce the ability of the migrating phase to retain dissolved oil. Thus, an initial waxy oil leg devoid of low molecular weight hydrocarbons will be exsolved, becoming progressively enriched in light hydrocarbons with increasing migration distance from its



**Fig. 8.22**  $n$ -Alkane isotope plot of carbon number versus carbon isotopic composition.

source. Thus, the initial GOR will be critical in determining compositional variability along a migration fairway.

It would be naive to propose migration fractionation as the sole process operating in the Cooper and Eromanga Basins without considering the primary controls of source and maturity. As stated above, all oil shows Pr/Ph  $>3$ , attesting to terrestrial origin. However, Pr/Ph also shows a regular trend with  $n\text{-C}_{23}/n\text{-C}_{11}$  (Fig. 8.14), a parameter associated with the waxy to light oil character. Thus, oil with Pr/Ph  $>4.5$  and  $n\text{-C}_{23}/n\text{-C}_{11} <1$  may have experienced secondary alteration by migration fractionation. Indeed, Ph, being of higher molecular weight than Pr, will be preferentially retained in the heavier residual oil. These effects have previously been recognised in South East Asian oil, again from terrestrial sources (Curiale and Bromley, 1996).

### Water washing and biodegradation

The  $\text{C}_6\text{--C}_7$  light hydrocarbons are greatly influenced by secondary alteration processes (Thompson, 1987, 1988). For example, compared to the parent oil, the toluene/ $n$ -heptane ratio has been shown in field (Thompson, 1987) and laboratory studies (Carpentier *et al.*, 1996) to increase in the residual heavy oil and decrease in light oil (dissolved in the gas phase) through the process of migration fractionation. However, Heath *et al.* (1989) interpreted the higher toluene/ $n$ -heptane in Cooper Basin oil compared to oil in the Eromanga Basin as indicating greater water washing of the latter. This behaviour is also evident in the much larger data set (Fig. 8.23; Appendix 2). The strong positive linear relationship between toluene/ $n$ -heptane and  $n$ -heptane/methylcyclohexane (Fig. 8.24) is further evidence that water washing is the dominant factor operating on the light hydrocarbons. The trend is what would be predicted from laboratory experiments (Lafargue and Barker, 1988). There the rate of loss of light hydrocarbons from oil exposed to water washing is in the order toluene  $>$  heptane  $>$  methylcyclohexane. Again, oil from the Cooper Basin is the least affected by water washing (Heath *et al.*, 1989; Hunt, 1989) and this may suggest shorter

migration distances, being closer to the Permian source rocks.

Dibenzothiophene (DBT) is another compound that has been suggested to be highly affected by water washing (Lafargue and Barker, 1988). Phenanthrene (P) and 1,3,6,7-tetramethylnaphthalene (1,3,6,7-TeMN) are two ubiquitous compounds in crude oil and both have similar chromatographic behaviour. Water solubilities are in the order  $DBT > P > 1,3,6,7\text{-TeMN}$  (Alexander *et al.*, 1996). Indeed, a plot of  $P/1,3,6,7\text{-TeMN}$  versus  $DBT/1,3,6,7\text{-TeMN}$  (Fig. 8.25) shows a good linear correlation. However, there is no clear distinction between oil from the Cooper and Eromanga Basins, suggesting that other factors (e.g. source) have an increased influence relative to the light hydrocarbons.

The unusual oil in Figure 8.14 with  $Pr/Ph = 6.85$  and  $n\text{-}C_{23}/n\text{-}C_{11} = 9.74$  is from Cuddapan 1 (45 km north of the Permian edge in Queensland). This oil is interpreted to be severely water washed with  $C_6\text{-}C_7$  light hydrocarbons being completely lost, with the alteration effects extending past  $n\text{-}C_{11}$ . Based on  $Pr/Ph$ , the original Cuddapan oil was relatively light (Fig. 8.14).

In-reservoir alteration by biodegradation is of little importance in the Cooper and Eromanga Basins although biodegradation is a major alteration process in the adjacent Bowen and Surat Basins. The reason for the absence for biodegradation in the Cooper and Eromanga Basins is unclear since reservoirs in most regions have access to nutrient-rich connate water. However, levels of dissolved oxygen observed in the aquifer waters of the Eromanga Basin may be too low (R. Habermehl, AGSO, pers. comm., 1998) to support intense aerobic biodegradation. Furthermore, temperature of the Eromanga reservoirs is generally  $>80\text{-}90^\circ\text{C}$ , which is above the threshold for sustainable bacterial growth.

### Migration contamination

The concept of migration contamination has been largely ignored. However, it has been previously identified in the

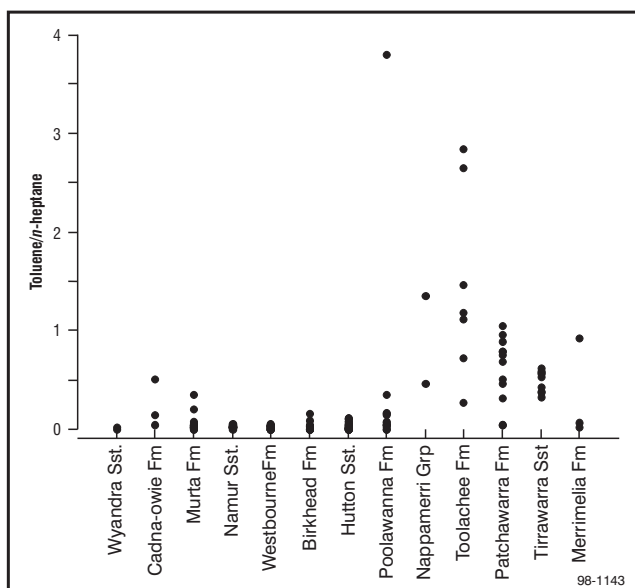


Fig. 8.23 Plot of toluene/n-heptane in whole oils grouped within their reservoir units.

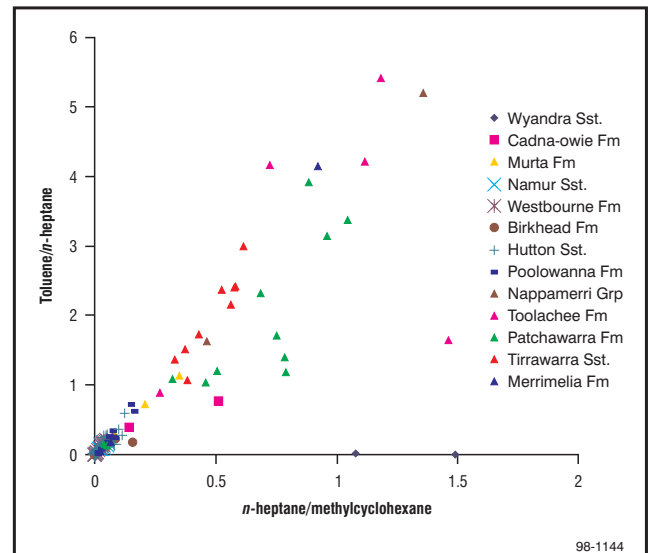


Fig. 8.24 Plot of toluene/n-heptane versus n-heptane/methylcyclohexane.

Gippsland Basin (Philp and Gilbert, 1982) and recently recognised in Birkhead oil at Gidgealpa 17 (Boult *et al.*, 1998). In principle, migration contamination is an end-member in the continuum of mixing of different oils. However, the term attracts a degree of uncertainty and can obviously be misused to ‘cover’ shortfalls in geochemical interpretations. Following expulsion from the effective source rock, the mobile oil phase finds its way through the permeable migration pathway to the reservoir. Thus, between source and reservoir there exists the possibility that the mobile oil phase can be supplemented with ‘soluble’ organics either from contact with DOM or through mixing with other mobile hydrocarbons from different effective sources at various stratigraphic levels before it reaches the trap.

All oil reservoir in the Eromanga Basin has enhanced levels of conifer-derived biomarkers compared to Cooper Basin oil (Fig. 8.15). For the Merrimelia Field stacked accumulations, this is despite a Cooper origin for the  $n$ -alkanes. Here the reliance on aromatic biomarkers would lead to a disproportionately higher level of Eromanga oil contribution than is considered the case. Studies of oil accumulations in the Bowen and Surat Basins have shown that they are predominantly from Permian source rocks and there is no contribution from Jurassic sources (Boreham,

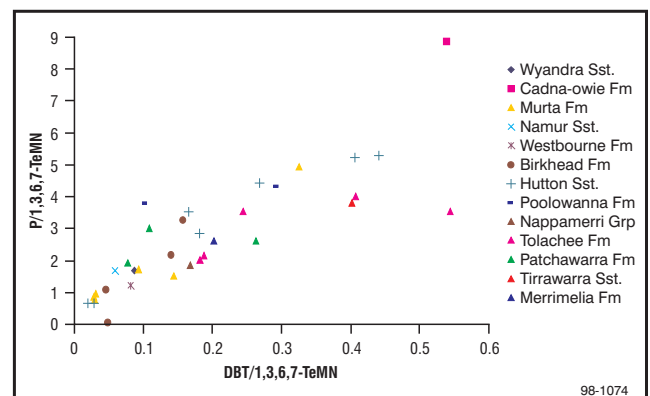


Fig. 8.25 Cross-plot of the ratio of DBT to 1,3,6,7-TeMN versus the ratio of P to 1,3,6,7-TeMN.

1995). The difference between the Surat and the Eromanga Basins is that the main Jurassic source rocks (Walloon Coal Measures in the Surat Basin, and the Birkhead Formation in the Eromanga Basin) are immature in the former but marginally mature to mature in the latter. Furthermore, oil in the Surat Basin is effectively trapped before it can come into contact with Walloon Formation sediments containing conifer-derived biomarkers (Boreham, 1994). Migration contamination of upward-migrating oil should be seriously considered when mobile hydrocarbons are expelled from Jurassic and Cretaceous source rocks, and these hydrocarbons remain pervasive throughout the Eromanga Basin succession in varying concentrations.

## SUMMARY

Both Cooper and Eromanga Basin source rocks have contributed to oil accumulations in the region. Each oil accumulation needs to be considered on its merits with respect to the extent of 'mixing' from Permian and Mesozoic sources. The ultimate 'mix' will be biased by those chemical parameters that are used since different classes of compounds respond differently to source, maturity and secondary alteration processes. *n*-Alkane isotope profiles provide a means for quantitatively assessing contributions from Cooper and Eromanga Basin sources. However, minor contributions (volumetrically <25%) from either source are difficult to access through *n*-alkane isotope profiles and other more sensitive geochemical tools are required (e.g. biomarkers).

The Cooper Basin contains both light oil–condensate and waxy oil with depleted light hydrocarbon contents. The source of the oil is Permian coal and associated terrestrial organic matter. The oil is characterised by low saturated biomarker contents, lack of conifer-derived biomarkers and an *n*-alkane isotope profile that becomes isotopically lighter with increasing carbon number.

The Eromanga Basin oil accumulations with a Birkhead source appear to be confined to the area of mature and thickest Birkhead Formation in the vicinity of Moorari and Bookabourdie Fields. This oil is characterised by high conifer-derived biomarkers (Moorari 4) and *n*-alkane isotope profiles that are 'flat' (where the isotopic composition of individual *n*-alkanes does not change significantly with carbon number).

Gas chromatographic fingerprints and parameters derived for Jurassic oil are only marginally distinguishable from Cretaceous and Cooper Basin oil. The Jurassic oil has a much narrower range of bulk compositions. The Moorari 4 oil, being the least mature, can be used to define the maturity threshold (0.65%  $R_o$  for a local source) below which no expulsion of oil can occur. Birkhead Formation oil at Gidgealpa and Merrimelia would be considered to have an Eromanga Basin source content based on biomarker evidence. However, *n*-alkane isotope data only support a strong local source contribution at Gidgealpa, whereas the Birkhead oil in the Merrimelia Field is dominantly sourced from the Cooper Basin.

A local source to the Murta Formation oil accumulation may have been overestimated since secondary alteration processes have been undervalued in previous studies. Murta oil in the Merrimelia Field in South Australia and some other accumulations in Queensland (e.g. Jackson Field) have

biomarker characteristics that set them apart from oil lower in the succession, but their *n*-alkane profiles match all others in the stacked reservoirs.